Advances in Carbohydrate Chemistry and Biochemistry

Volume 59

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Editor
DEREK HORTON
The American University
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PREFACE

Many recent volumes in this series have been strongly oriented toward biochemical or medicinal chemical aspects. This current volume focuses on basic chemical aspects of mono- and oligo-saccharides, and on polysaccharide technology. de Lederkremer and Gallo-Rodriguez (Buenos Aires) provide a comprehensive survey of those monosaccharides (excluding amino and deoxy sugars) that are found in natural products, in a treatment that greatly extends a 1972 treatment of this subject by Schaffer. The chapter by Garegg (Stockholm) presents a broad overview of the chemistry of glycosides, dealing with their synthesis, structure, and properties. It places particular emphasis on the ongoing challenge of glycoside synthesis as it applies to complex oligosaccharide targets, and it features much of the author's own considerable contribution to this area.

The inositols and their derivatives can be regarded as monosaccharide sugars in which the ring oxygen atom has been replaced by carbon, and they may thus be named as carba sugars. The inososes derived by their oxidation react with hydrazines in transformations that are often of considerable complexity, thus resembling the behavior of sugars. The hydrazine derivatives of sugars have been surveyed in detail in this Series by El Khadem in Volume 20 and again in conjunction with Fatiadi in Volume 55. In this volume El Khadem and Fatiadi (Washington, DC) complement this aspect with a comprehensive account of the hydrazine derivatives of carba sugars.

The technology of polymeric carbohydrates is strongly oriented to the most abundant examples, namely starch and cellulose. Tomasik (Cracow) and Schilling (University Center, Michigan), in their wide-ranging article on chemical derivatization of starch, present an extensive compilation of the literature on potentially useful products formed by esterification, etherification, oxidation, and other reactions with starch. Much of the literature cited comes from patent sources, not subject to the conventional refereeing procedures in effect for journal articles, and so the reader needs to judge appropriately the validity of some of the claims made for product structure and practical application.

The life and work of Edward J. Hehre, a pioneer in our knowledge of the mechanism of action of glycosylase enzymes, is the subject of the article by Brewer (New York). It is noted with regret the passing on February 23, 2004, of Aleskander Zamojski, who contributed in Volume 40 an article on the synthesis of sugars from noncarbohydrate sources, and on July 31, 2004, of Jacques van Boom (Leiden), who made important contributions to carbohydrate synthesis and to glycobiology.

With this volume we thank two members of the Board of Advisors, Roy L. Whistler and Bengt Lindberg, for their long service to the series, and welcome Geert-Jan Boons and Serge Pérez to the Board.

DEREK HORTON

Washington, DC
September 2004

Edward J. Heber

ADVANCES IN CARBOHYDRATE CHEMISTRY AND BIOCHEMISTRY, VOL. 59

EDWARD JAMES HEHRE

1912–2002

The field of carbohydrate enzymology lost a major contributor with the passing of Professor Edward J. Hehre, Emeritus Professor and founding chairman of the Department of Microbiology and Immunology, Albert Einstein College of Medicine, New York. Dr. Hehre worked in the field of carbohydrate enzymology, biology and immunochemistry for over 60 years. His early work led to the discovery of glycosyltransferases (see ref. 1), and his subsequent work provided new insights into their scope and mechanisms.[2] These latter studies included the mobilization of glycosyl residues in glycosyl transfer reactions (glycosyl fluorides as substrates), demonstrations of the catalytic flexibility of the functional groups in glycosylases, and the use of prochiral enolic substrates to establish the role of protein structure in determining the stereochemical outcome of carbohydrase-catalyzed reactions. His overall contributions form a cohesive body of basic observations which have altered and advanced our understanding of the catalytic scope and mechanisms of glycosylases. His 98 publications range from his early seminal observations (1941–1943) on the enzymatic synthesis of dextran from sucrose,[1] to the use of X-ray crystallography to examine the active sites of glycosylases.[2] Professor Hehre's awards included the Samuel H. Golding Professorship of Microbiology (1964–1978); John Simon Guggenheim Fellowship (1964–1965); John Polachek Fellowship (1970–1971); N.I.H. (Fogarty) Senior International Research Fellowship (1998); Honorary Symposia by the Division of Carbohydrate Chemistry, American Chemical Society (1990 and 1997); and the Melville L. Wolfrom Award, Division of Carbohydrate Chemistry, American Chemical Society (2002).

Ed was born in 1912, the only child of Edward Hehre and Antonietta di Gaetano, native New Yorkers of German and Italian heritage respectively. He grew up happily in a family fostering compassion and good demeanor that comprised mother, father, and maternal grandparents living together in the grandparents' modest

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home in the Bronx, New York. Ed did well at the local public grammar and junior high schools, and came to love mathematics and science (at this school he built an early one-tube long-functioning radio, part-by-soldered part; and enjoyed classic music and the clean lines of mechanical drawing and lettering). When Ed's father's successful management of a small self-constructed boat shop and dock on Clauson Point on Long Island Sound had expanded it to a highly productive luxury motor yacht-building plant, he built the family a new home in Pelham Manor, a village just north of the Bronx. Here, Ed received an excellent education, particularly in mathematics, physics, and chemistry, and also became a fairly fast sprinter on the track team.

At Cornell University, Ed's in-depth progress in the sciences brought early admission to its Medical College, where he gained the M.D. degree and thereafter, an appointment on the College's preclinical faculty. Also, in 1938 he was married to his long-waiting childhood sweetheart, Florence D. Baker. From their union were born Edward J. Hehre, Jr., 1940; Elizabeth J. Hehre, 1942; and Warren J. Hehre, 1945.

At Cornell Medical College, from 1938 to 1956, Ed taught (with two other faculty) a comprehensive annual course in Microbiology and Immunology for classes of 60+ medical students, with special emphasis on specific uses of these sciences to prevent, diagnose, and treat infectious diseases. Research in immunochemistry also was begun in 1938, but an initial study unexpectedly led to the curious finding that nearly all samples of reagent and food-grade sucrose carry an impurity reactive with type 2 pneumococcus antiserum. By 1940, the impurity was identified (with J. Y. Sugg) as dextran, a glucose polymer produced by *Leuconostoc mesenteroides* bacteria growing on field-cut sugar cane. Dextran produced by some strains grown in media containing sucrose reacted strongly with antisera to types 2, 12, and 20 pneumococcus; that of other strains reacted strongly only with types 2 and 20 antisera. These serological properties of dextrans would enable Ed to envision and carry out productive studies in several different areas.

The most important of these studies by far were those which brought Ed permanently into the field of enzymic polysaccharide synthesis. Between 1941 and 1946 he reported evidence for the *in vitro* synthesis of dextran from sucrose. Serological tests were critical in identifying dextran (at minute levels) as the product was increasingly being formed in sterile enzyme–sucrose mixtures; also in showing that no dextran was formed when sucrose was replaced by other sugars or α-D-glucopyranosyl phosphate. This was the first polysaccharide synthesis clearly shown not to require the latter compound. Until then, it was generally believed that

a sugar derivative of the 1-phospate ester-type would be required as a substrate for polysaccharide formation. Ed's work on dextransucrase, which refuted this belief, was soon confirmed and recognized as a contribution of major importance. His 1948–1949 discovery of the *Neisseria* enzyme amylosucrase (and especially the evidence that it converts sucrose into an amylopectin-like polysaccharide without involving phosphate) directly opposed Carl Cori's confident claim that all glycogen and starch in Nature arise from glucose 1-phospate by phosphorylase action. Ed's amylosucrase and dextransucrase studies would continue to be cited by others, even after 50 years.

In 1951 he made a second, farther-reaching, contribution to carbohydrate enzymology in the course of a first complete review of what was known concerning the process of enzymic polysaccharide synthesis. Here, Ed introduced the term "glycosyl" for the group most likely to be transferred by saccharide-forming enzymes, and further proposed that such enzymes be called "transglycosylases" rather than the then accepted term, "transglycosidases," so as to provide the appropriate name for the chemical change effected in their reactions [by whatever catalytic mechanism(s)]. Despite some investigators' doubts about whether all saccharide syntheses proceed by transglycosylation, members of the IUPAC Enzyme Commission preparing a new system of enzyme nomenclature recommended the creation of a class of glycosyltransferases (transglycosylases). Transglycosylase terminology came into general use by the late 1950s and ever since has effectively served to articulate in a chemically meaningfully way the huge array of newly discovered complex saccharide syntheses from nucleotide sugar diphosphates, revealing the astonishing commonality of their synthetic processes.

Ed's use of serological tests at Cornell for detecting dextran also led to significant new findings in other areas; thus, the identification of dextran as the predominant polysaccharide formed in sucrose-cultures of streptococci from the blood of subacute endocarditis patients brought awareness of the existence of a new *Streptococcus* variety (var. DS., now *S. sanguis*) as an important agent of the disease (1946). This streptococcus variety was also found in the throats of healthy persons (1948). Much later, J. Carlsson (1965) demonstrated that such streptococci rapidly produce dental plaque in subjects fed a high-sucrose diet, while others showed that they preferentially colonize teeth and contribute to the formation of dental caries.

In addition, semi-quantitative serological tests led to the discovery of one *Streptococcus* DS endocarditis strain (No. 50) that produces a unique mini-sized dextran—apparently only about 5% of the size of all other known natural dextrans or roughly similar to that of partly hydrolyzed dextrans used to treat patients in

shock (1952). Detailed structural and molecular-weight distribution studies of this unique dextran, (reported jointly with Drs. F. R. Senti and N. N. Hellman of the U.S. Department of Agriculture's Northern Laboratory, NRRL, in 1956) confirmed its overall similarity to a clinical-sized dextran.

At this time Ed left Cornell for the Albert Einstein College of Medicine to assume the post of Professor and Chairman of the Department of Microbiology and Immunology he would establish at this newly opened medical school. The reason was primarily financial—his earnings at Cornell had not sufficed to support his family; also, the saving of two precious hours each day because of a much shorter commuting time was a factor; finally, the opportunity to work with a Dean and a group of Chairmen obviously dedicated to ensuring the development of a top-rank medical school was an exciting prospect. Ed created and presented a course in microbiology and immunology for classes of medical students that was designed to be an introduction to infectious diseases; for the first ten years, each class's performance on National Board examinations in these subjects ranked within the top ten in the country. Ed's experimental research was put on hold for several years as he deferred setting up a laboratory or seeking research associates. He believed that teaching medical students was an irrevocable social responsibility and, in all, he taught for more that 60 years. He retired as departmental Chairman in 1978 after serving 22 years, and was appointed Professor Emeritus at that time.

After Ed's move to Einstein in 1956, a joint U.S. patent in the public interests was filed (together with H. M. Tsuchiya and N. N. Hellman) on the practical production of the *Streptococcus* DS-50 dextran. Pilot plant production was undertaken at NRRL; clean-up and bottling were carried out as a service by the Cutter Corp.; and a successful clinical trial of the dextran for treatment of patients in shock was conducted by Dr. W. Metcalf of Einstein's Department of Surgery. Ed presented a final report to the National Research Council in 1962. In the end, despite the discovery of a simpler way to manufacture a product of great potential military usefulness, dextran in general would be replaced by blood and plasma as agents of plasma volume expansion in shock patients.

Ed became a collaborator in an extensive program at the U.S. Department of Agriculture's Northern Laboratory (NRRL) directed at physicochemically and otherwise characterizing the dextrans produced by a wide variety of bacteria. Ed's aim was to learn whether the serological specificity of a dextran could be correlated with its structure. He examined, using standardized protocols, more that 100 dextrans from 96 different microorganisms. These were supplied by Dr. Allene Jeanes of the NRRL together with analyses of their structures based on periodate oxidation. At a 1960 meeting of an International Colloquium sponsored by the

French Centre National de la Recherche Scientifique, in Gif sur Yvette, France, Ed presented the final analysis of the data obtained at Cornell, demonstrating the clear correspondence between the degree of type 2 and 20 reactivity of dextrans and the extent of formic acid release on periodate oxidation—indicative of their (1→6)-linked glucose content. Clear correspondence was also found between the degree of reactivity with type 12 pneumococcus antibody and the proportion of (1→2)-glucose, and later by methylation studies carried out in several laboratories.

At the same meeting in Gif, Ed presented a further far-reaching general proposal: to redefine the term "transglycosylases" as catalysis of glycosyl/proton interchange in order to provide an overall expression of what chemical change is effected in all reactions catalyzed by carbohydrases, whether transferases or glycosidases. This expression was illustrated by a compact stoichiometric equation,

$$\text{glycosyl-X} + \text{H-X}' \leftrightarrows \text{glycosyl-X}' + \text{H-X}.$$

This expression was the first to emphasize the functionality of the glycosyl group in enzymic reactions. It predicted something that, until then, had not been appreciated: namely, that a compound need have only the ability to bind appropriately at an active site, and to yield a glycosyl group in exchange for a proton, in order to serve as a substrate. Biochemists took little notice of this suggestion, but experiments in 1959 (with Drs. G. Okada and D. S. Genghof) on the reversals of hydrolysis catalyzed by beta amylase and glucoamylase from β-maltose and glucose, respectively, demonstrated the synthesis of maltosaccharides by these "inverting" amylases, proving that the glycosyl moiety is mobilized in each case.

By 1973 much evidence existed to show the validity of the concept of glycosyl–proton interchange. At an American Chemical Society Symposium (and published in a special volume), Ed and his associates proposed that "glycosylation" represents the paradigm of all carbohydrase actions. Among the effects of this proposal was the attention to, the relief of, a long-standing sinistral relationship between classic carbohydrate chemistry and carbohydrate enzymology. The general organic chemical concept of nucleophilic displacement in enzymic reaction mechanisms indicated the correctness of the glycosylation hypothesis. Its validity was clearly shown by an extensive series of studies in Ed's laboratory (in collaboration with C. F. Brewer and a succession of mainly Japanese research associates). Glycosyl (but nonglycosidic) compounds, such as glycosyl fluorides of both α and β configurations), as well as glycols having a double bond between carbon atoms 1 and 2, were shown to be substrates convertible by glycosylases to products of the same configuration as formed from "normal" glycosidic substrates. These results showed for the first time that the catalytic groups of glycosylases are

functionally flexible, and also that product configuration is determined by structural features of the enzyme protein that limit the orientation of acceptor cosubstrates to the reaction center.

In a recent (1999) analysis of the X-ray three-dimensional structures reported for various well known glycosylases (reviewed in ref. 2), Ed found evidence both for the catalytic group flexibility and topological control of product configurations. With the recent appearance of the first reports of crystal structures for enzymes that synthesize biologically critical complex glycoproteins and glycolipids from nucleotide sugars, the opportunity arises to learn if the foregoing conclusions extend to them. The development of potent new drugs for the alleviation of disease will be enhanced by knowing what enzyme features control the formation of specific complex saccharides; and that will help ensure the inexpensive large-scale enzymic syntheses of such saccharides for medical use.

In spite of the vast contributions of the glycosyl transfer concept to modern biochemistry in the past 50 years, the history of the development of the concept has been lacking. At career's end, Ed wrote a detailed account of its evolution in an article in *Carbohydrate Research*.[3]

Among his outside interests, Ed enjoyed paleontology, spending many weekend and longer trips "fossil hunting" with his sons, and he was an avid stamp collector, having nearly complete collections for both the U.S. and Japan. He was a "Japanophile," enjoying many visits to that country and hosting Japanese research associates. He made serious attempts to learn to read and write Japanese. Ed enjoyed excellent health for most of his life, except for the last year, where both old age and cancer took their toll, but even then he still read or worked 5–10 hours/day, had dreams of work to come, and valiantly travelled to national meetings to present research papers.

Professor Hehre died on August 6, 2002 at his home in Bronxville, New York. He is survived by his wife, Florence, and his daughter and two sons.

C. Fred Brewer

Acknowledgments

A large portion of this manuscript is autobiographical having been written by Professor Hehre before his death. The author (C. F. B.) thanks the Department of Microbiology and Immunology, Albert Einstein College of Medicine, for help in preparing this manuscript.

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NATURALLY OCCURRING MONOSACCHARIDES: PROPERTIES AND SYNTHESIS

By Rosa M. de Lederkremer and Carola Gallo-Rodriguez

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I. Introduction

This article deals with the naturally occurring monosaccharides (including 6-deoxy sugars) and its layout follows that employed by Schaffer in an earlier comprehensive survey of monosaccharides.[1] The sugars are grouped according to the number of carbon atoms and are classified as aldoses or ketoses in each group. The reader is referred to Schaffer's article for details of melting points, specific rotations, and characterizing derivatives of those monosaccharides known in 1972. The present article records information on the many more individual sugars that have been found in natural sources during the past three decades, and also cites the chromatographic techniques that have aided in their identification.

In addition, the use of monosaccharides as chiral synthons and of enzymes for carbohydrate synthesis are included.

Monosaccharides are constituents of such widely abundant biomolecules as starch, cellulose, pectin and chitin. They are units of the sugar chains of glycoproteins and other important glycoconjugates in bacteria and in eukaryotic

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cells, and are also key components of DNA and RNA. Moreover, monosaccharides are useful chiral precursors for the synthesis of various natural products and drugs. Their low cost, abundance, and availability in large commercial quantities are key advantages for their use as raw materials. Some of the reviews that have appeared in this area are listed.[2–4]

The common monosaccharides are linear polyhydroxyaldehydes or linear polyhydroxy-2-ketones having one hydroxyl group on each non-carbonyl carbon atom, and they exist in multiple stereoisomeric and cyclic tautomeric forms.

The chain length of most natural monosaccharides currently known ranges from 3 to 9 carbon atoms. Of those monosaccharides that occur in Nature, this chapter deals only with aldoses and ketoses having an unbranched carbon chain, and with 6-deoxy-hexoses and -heptoses. Naturally occurring amino sugars and branched-chain sugars are excluded, as are other deoxy sugars. Enzymes that catalyze reactions leading to some of the sugars found in Nature are also capable of effecting similar reactions *in vitro*, as well as with substrates not normally available to these enzymes.[5,6]

Prior to the advent of modern methods for separation and identification, the only sugars known to occur in botanic materials as free monosaccharides were two aldoses (D-glucose and L-arabinose) and four ketoses (D-fructose, L-sorbose, D-*manno*-heptulose, and sedoheptulose). Now, however, chromatographic techniques applied to extracts of plants have revealed traces of other free aldoses, already known to occur commonly in glycosidic combination, for instance, D-xylose, the hexoses D-galactose and D-mannose, and also various higher-carbon sugars. As regards the occurrence of free sugars in animals, D-glucose is a normal constituent of blood, lymph, and other body fluids. The blood of the newborn has been found to contain D-fructose; this ketose is also found in semen.

II. Naturally Occurring Monosaccharides

1. Preparation and Isolation

The preferred source materials for preparation of monosaccharides are the homopolysaccharides built of repeated residues of a single sugar. A more-complex natural product may be used if the desired monosaccharide can be selectively liberated by hydrolysis, or if other sugars present in the hydrolyzate can be conveniently eliminated, for example, by fermentation. Alternatively, a more-complex

source may provide at least a limited amount of a desired monosaccharide through use of newer chromatographic methods for separation.

In the isolation of unsubstituted monosaccharides, care must be taken to prevent their being altered or decomposed, for example, as a result of excessive heating during concentration, or by keeping them in the presence of even a small proportion of alkali, which can effect profound changes in free sugars. Often, an effective procedure includes the preparation of a crystalline derivative from which the pure sugar can be regenerated. Ultimately, however, isolation and purification requires crystallization, preferably of the free sugar itself. Most of the known sugars have been crystallized, and crystallization of new preparations of them usually proceed without difficulty, although frequently this is facilitated by nucleating with a few crystals of the desired product. Impurities may impede crystallization; and even small proportions of ionic contaminants can interfere; ion-exchange treatments are commonly employed to remove last traces of such contaminants.

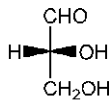
2. Properties and Identification

Sugars are commonly identified by comparison of their infrared or nuclear magnetic resonance spectra[7] with those of known sugars, or by comparisons based on chromatographic methods. The methods most widely used for the identification of monosaccharides are gas-liquid chromatography (GLC) and high-pressure anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). With the GLC approach, a derivatization step is required to produce volatile compounds. Trimethylsilylation may result in more than one peak for a monosaccharide as each tautomer gives a separate per(trimethylsilyl) ether.[8] Analysis of monosaccharides as alditol acetates involves reduction and acetylation, but results in the formation of a single derivative per monosaccharide.[9] GLC requires approximately 1 μg of monosaccharide for the identification. With the HPAEC-PAD system it is possible to identify free monosaccharides, in a range of sensitivity of about 50 pmol, using alkaline aqueous solutions as eluent.[10] None of these procedures allow assignment of enantiomeric identity for which polarimetric data is required, or special procedures involving derivatization using an independent chiral standard.

A table which includes physical properties and a characteristic derivative for each natural sugar can be found in the article by Schaffer.[1]

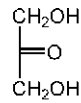
3. The Monosaccharides

a. Trioses.—



D-glyceraldehyde

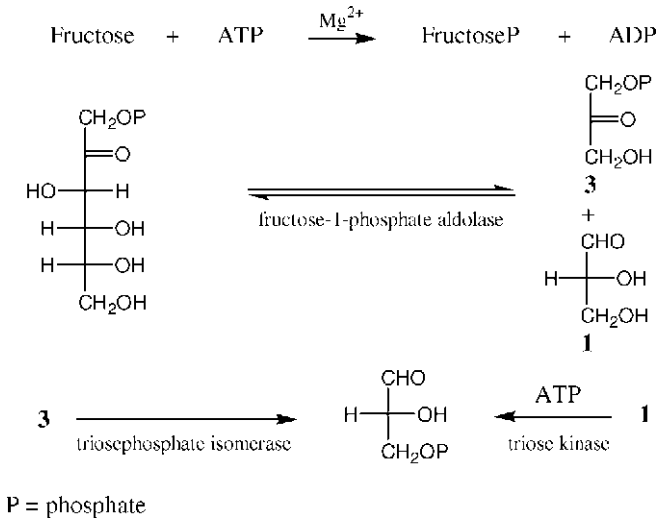
1



1,3-dihydroxy-2-propanone

2

Occurrence. D-Glyceraldehyde (**1**) and dihydroxyacetone phosphate (**3**) are biological products of the retro-aldol reaction of fructose and enter the glycolytic pathway as glyceraldehyde 3-phosphate (Scheme 1).[11]



SCHEME 1.

A review on the physiological importance of trioses and related substances has appeared.[12]

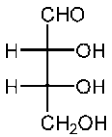
Preparation. Fischer and Baer employed the glycol cleavage of 1,2:5,6-di-*O*-isopropylidene-D-mannitol, followed by acid hydrolysis, to provide D-glyceraldehyde.[13] A most convenient preparation is that of Perlin,[14] who oxidized D-fructose with a limited proportion of lead tetraacetate, and hydrolyzed the resulting derivative. D-Glyceraldehyde 3-phosphate has been synthesized.[15]

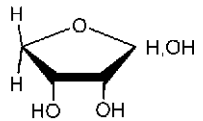
DL-Glyceraldehyde, known, in contrast to the optically active forms, as a crystalline material (dimer, mp 142°), has been resolved by condensation with (*dextro*)-α-(2-hydroxy-1-naphthyl)benzylamine.[16]

The oxidation of glycerol in the presence of *Acetobacter xylinum* gives the ketotriose **2**, which can be separated as its insoluble sodium hydrogensulfite addition compound, and then, recovered on acidification. The dimer, mp 82°, is obtained on crystallization from ethanol but, on standing, higher-melting products are deposited from the mother liquor.[17] The 1-phosphate has been synthesized.[18]

b. Aldotetroses.—

D-Erythrose





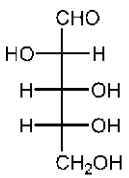
D-erythrofuranose

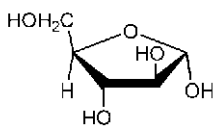
4

Occurrence and preparation. The tetrose (**4**) participates as D-erythrose 4-phosphate in the pentose phosphate pathway of carbohydrate metabolism.[11] D-Erythrose can be prepared using a method of degradation from the pentose, D-arabinose,[19] or from D-glucose.[20] Synthesis of the 4-phosphate has been reported.[21]

c. Aldopentoses.—

D-Arabinose





α-D-arabinofuranose

5

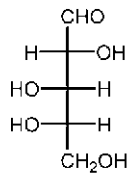
Occurrence. D-Arabinose (**5**) is not encountered frequently but, as its furanose tautomer is a constituent of important glycoconjugates and polysaccharides. For

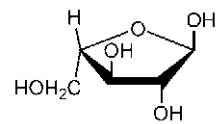
instance, D-arabinofuranose is part of a lipoarabinomannan and an arabinogalactan necessary for the survival of *Mycobacterium tuberculosis*, the causative agent of tuberculosis.[22] A polysaccharide composed of Gal*f* and Ara*f* is also present in other mycobacteria.[23]

α-D-Arabinofuranose has been also detected in lipopolysaccharides from Gram-negative bacteria. In some serogroups of *Stenotrophomonas maltophilia*, an opportunist pathogen, it is present as branching units of the O-specific side chain polymers.[24]

Preparation. D-Arabinose, having the same configuration of the lower three carbon atoms as D-glucose, is conveniently prepared from this abundant sugar, as well as from D-mannose.[25]

L-Arabinose





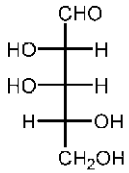
α-L-arabinofuranose

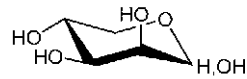
6

Occurrence. L-Arabinose (**6**) occurs free in the heartwood of many coniferous trees. In the combined state, it is very widely distributed in plant products, being found mainly in arabinogalactans, as a component of pectins[26] or linked to proteins forming glycoproteins.[27] L-Arabinose is mainly present as readily hydrolyzed α-L-arabinofuranose residues. In hemicelluloses feruloyl and *p*-coumaroyl arabinoxylans have been characterized.[28] An arabinogalactan heavily substituted by complex arabinofuranan branches has been isolated from the leaves of *Nerium indicum*.[29] In bacterial polysaccharides, L-arabinose was found in the β-furanose form. Thus, a polysaccharide isolated from an enteritis-associated strain of *Campylobacter jejuni* is composed of a trisaccharide repeating-unit containing β-L-Ara*f*.[30]

Preparation. Gum from mesquite (*Prosopis juliflora*), a plant common in the southwestern United States, and also cherry gum, are good natural sources of L-arabinose. Mesquite gum consists of L-arabinose, D-galactose, and 4-*O*-methyl-D-glucuronic acid residues in combination, and cherry gum has, in addition, some D-xylose and D-mannose residues. By controlled hydrolysis, most of the pentose is removed without hydrolyzing the other constituents to any great extent. The L-arabinose is then partially purified by dialysis[31] or ion-exchange procedures[32] and crystallized from methyl or ethyl alcohol.

D-Lyxose





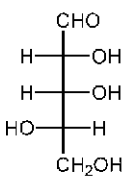
D-lyxopyranose

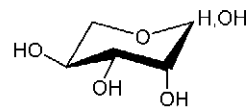
7

Occurrence. D-Lyxose (**7**), a rare sugar, has been detected in glycolipids from *Mycobacterium phlei*. The pentose is substituted by an acyl group at position 2 and in some instances, at both positions 2 and 4. It is difficult to distinguish D-lyxose from D-arabinose, and thus, a wider distribution in Mycobaterium should be examined.[33]

Preparation. D-Lyxose is conveniently prepared from D-galactono-1,4-lactone by the Ruff degradation method.[34]

L-Lyxose





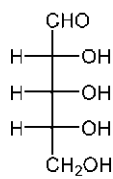
L-lyxopyranose

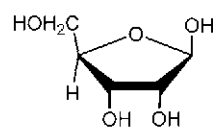
8

Occurrence. L-Lyxose (**8**) is rare in Nature. It has been identified among the products of hydrolysis of the antibiotic curamycin, in flambamycin, an antibiotic from *Streptomyces hygroscopicus* and in other members of this family of related antibiotics, such as avilamycin and the everninomycin.[35]

Preparation. L-Lyxose may be prepared from L-galactono-1,4-lactone by the Ruff degradation method.[36]

D-Ribose





β-D-ribofuranose

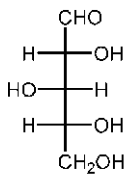
9

Occurrence. D-Ribose (**9**) and 2-deoxy-D-*erythro*-pentose ("2-deoxy-D-ribose") are the carbohydrate constituents of nucleic acids, which are found in all cells. D-Ribose is also a constituent of several coenzymes. In these natural products, the sugar occurs in the β-furanose form.

D-Ribose is known as a component of the lipo- and capsular polysaccharides from many Gram-negative bacteria, where it is found as a β-furanosyl unit.[37] It is found as terminal α-D-Rib*f* substituents in some serotypes of the O-antigen of lipopolysaccharides (LPS) from *Stenotrophomonas maltophilia*.[38] Also as α-furanosyl residues, ribose is part of the extracellular polysaccharides of cyanobacteria.[39]

Preparation. The best methods for laboratory preparation involve the stepwise hydrolysis of yeast nucleic acid.[40] The original procedure of Levene and Clark, which requires the action of ammonia at elevated temperatures and pressures, has been greatly improved by Phelps, who used magnesium oxide as the degradative agent. A mixture of nucleosides is obtained and then further hydrolyzed by a mineral acid to produce D-ribose.[41] Ribose may be obtained by the enzymic hydrolysis of yeast nucleic acid.[42] The chemistry of D-ribose has been reviewed.[43]

D-Xylose



β-D-xylopyranose

10

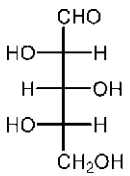
Occurrence. D-Xylose (**10**) is present in widely abundant polysaccharides of plant tissues. Xylan is the main carbohydrate found in the hemicellulosic fraction, and accounts for one third of all renewable organic carbon available on earth. The structure and composition of xylans are variable, from linear β-(1→4)-linked xylose chains to highly branched heteropolysaccharides. The branches may involve short oligosaccharides, usually of L-arabinofuranosyl units. Xyloglucans are also important hemicellulose polysaccharides consisting of a backbone of (1→4)-β-D-glucopyranosyl residues heavily substituted with α-D-Xyl*p*. Other monosaccharides may also be present.[44]

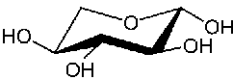
D-Xylose was found in *N*-glycosylic chains in glycoproteins of plants[45] and pollens.[46] Free xylose, together with other sugars and alditols, has been also detected in some plants, for instance in aqueous extracts of Pichi tops.[47]

Preparation. The presence of xylose polysaccharides in many important agricultural wastes has stimulated interest in its preparation and uses. Corncobs and bagasse are good sources of the sugar. Acid hydrolysis is cheap and simple.[48] Enzymic hydrolysis is slower but proceeds under conditions that exclude the formation of toxic by-products. Crystalline D-xylose can be obtained in good yields (~30%) from beechwood xylan by using a crude xylanolytic system of *Aspergillus niger* N° 14.[49]

A review of xylanases has appeared.[50] Reduction of D-xylose affords xylitol, which is used as a dietary sugar substitute.[51]

L-Xylose





β-L-xylopyranose

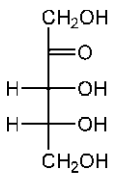
11

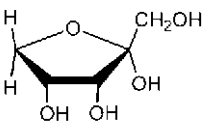
Occurrence. β-L-Xylose (**11**) occurs as a terminal sugar, branching on an L-rhamnan, in the O-chain polysaccharide of the lipopolysaccharide of *Xanthomonas campestris* pv. *begoniae* GSPB 525.[52]

Preparation. L-Xylose has been prepared by periodate oxidation of 2,4-*O*-benzylidene-D-glucitol followed by acid hydrolysis of the benzylidene group.[53]

d. Ketopentoses.—

D-*erythro*-2-Pentulose





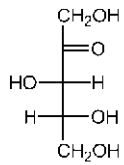
α-D-*erythro*-pentulofuranose

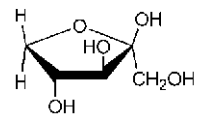
12

The D-2-pentuloses, D-*erythro*-2-pentulose (D-ribulose, **12**) and D-*threo*-2-pentulose (D-xylulose, **13**) are able to cyclize as 2-pentulofuranoses. The 2-ketopentoses are important metabolic intermediates in glycolysis.[11]

Preparation. D-*erythro*-2-Pentulose (**12**) has been synthesized from D-arabinose by isomerization with pyridine, followed by isolation as the crystalline (*o*-nitrophenyl)hydrazone.[54] Enzymic synthesis provides D-*erythro*-2-pentulose by oxidation of ribitol with NAD-dependent ribitol dehydrogenase[55] or from D-arabinitol with D-arabinitol dehydrogenase.[56]

D-*threo*-Pentulose





β-D-*threo*-pentulofuranose

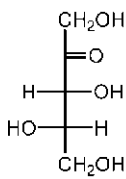
13

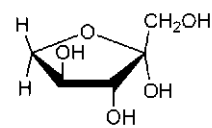
Occurrence. D-*threo*-Pentulose 5-phosphate (D-xylulose 5-phosphate) is an intermediate in the metabolism of xylose in bacteria, and is also formed from D-*erythro*-pentulose 5-phosphate in the presence of an epimerase.[57] D-*threo*-Pentulose has been found in a lipopolysaccharide from *Pseudomonas diminuta*, from which it was obtained after hydrolysis by mild acetic acid as used to release lipid A.[58] It was also found in the LPS of a *Yersinia enterocolitica* serologic variant.[59]

Preparation. D-*threo*-Pentulose may be synthesized by isomerization of D-xylose in hot pyridine. Better yields are obtained by the oxidation of D-arabinitol employing *Acetobacter xylinum*.[60]

D-*threo*-Pentulose was obtained from D-xylose in 82% yield by enzymic conversion, using xylose isomerase.[61]

L-*threo*-Pentulose





β-L-*threo*-pentulofuranose

14

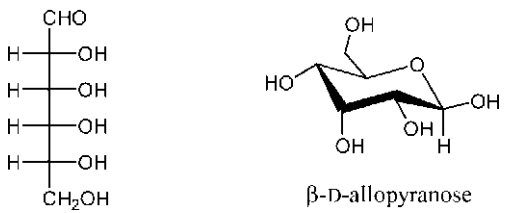
Occurrence. The ketopentose **14** (L-xylulose) is found in the urine of many cases of pentosuria.[62] It was also detected in the serum of adult-onset diabetics.[63] Essential pentosuria is the result of a partial deficiency of L-xylulose reductase.[64]

L-Xylulose is a constituent of the lipopolysaccharide from *Yersinia enterocolitica* serovar O:10,[65] from which it was obtained by mild acid hydrolysis and purification by paper chromatography.

Preparation. L-Xylulose has been synthesized by boiling L-xylose with pyridine, removing unchanged L-xylose by crystallization, and isolating the L-*threo*-pentulose as the (*p*-bromophenyl)hydrazone.[66] Both enantiomers of xylulose were produced biologically by the oxidation of the corresponding alditol. A *Klebsiella pneumoniae* mutant was constructed for the oxidation of D-arabinitol to D-xylulose, and a *Erwinia uredovora* mutant was used for the oxidation of xylitol to L-xylulose. Cell suspensions of either mutant oxidized ~60% of the pentitol to the ketopentose, which was excreted into the medium. The ketopentoses are readily purified from the remaining pentitol by hydroxyl affinity chromatography.[67]

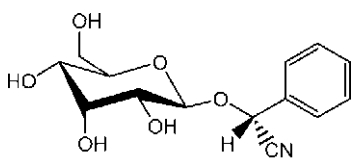
e. Aldohexoses.—

D-Allose



15

Occurrence. Several reports on the occurrence of D-allose (**15**) in natural glycosides have appeared during recent decades. A rare class of benzylic β-D-glycosides having D-allose as the only sugar constituent have been isolated from leaves of the edible passion-fruit plant *Passiflora edulis*. The glycoside **16** is the first known cyanogenic glycoside containing a sugar other than D-glucose attached to the cyanohydrin center.[68]



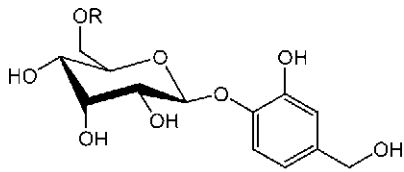
16

Other known examples of natural β-D-allopyranosides include an iridoid glycoside, together with its several acetylated derivatives,[69] an alloside of phenylethanol,[70] and caffeoyl phenylethanoid allosides.[71]

The leaves of *Protea rubropilosa* Beard contain D-allose in the form of the 6-cinnamate (rubropilosin, **17**) and the 6-benzoate (pilorubrosin, **18**) of 2-hydroxy-4-hydroxymethylphenyl β-D-allopyranoside.[72]

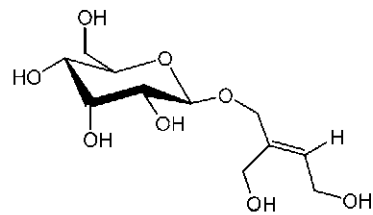
A number of flavonoid allosides[73] and terpenoid allosides[74] have been characterized.

The major soluble carbohydrate in the leaves of *Cardiomanes reniforme* is the β-allopyranoside **19** for which the name cardiomanol was proposed.[75] More examples can be found in Ref. 68.



17 R= PhCH=CHCO

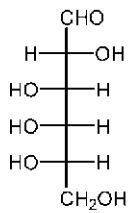
18 R= Bz

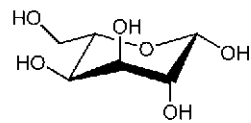


19

Preparation. D-Allose was obtained by alkaline followed by acid hydrolysis of the phenolic β-D-allopyranoside esters (**17** and **18**) purified from leaves of *Protea rubropilosa*. The sugar was obtained crystalline and identified with an authentic sample prepared from D-ribose by the cyanohydrin reaction.[76a] A more-convenient preparation involves an oxidation-reduction sequence with 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, followed by acid hydrolysis. [76b]

L-Altrose





β-L-altropyranose

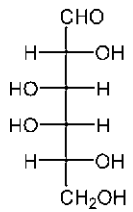
20

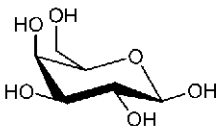
Occurrence. L-Altrose (**20**) was found for the first time in Nature in the extracellular capsular polysaccharide from *Butyrivibrio fibrisolvens* strain CF3.[77]

Further structural studies of this material have been reported.[78] In strain 49 and X6C61, this hexose is replaced by the C-5 epimer, α-D-Gal*p*. L-Altrose was purified by preparative paper chromatography after hydrolysis of the polymer, and the L-configuration was confirmed by its optical rotation. L-Altrose is transformed into 1,6-anhydroaltrose on treatment with aqueous acid; the acid catalyzed equilibrium is reached when the latter compound constitutes 60–65% of the total carbohydrate in solution. Apparently, the enantiomeric D-altrose has not been found in Nature.

Preparation. L-Altrose can be prepared by the Kiliani synthesis, starting from L-ribose.[79] More recently, an efficient synthesis of L-altrose starting from glucose has been reported.[80]

D-Galactose





β-D-galactopyranose

21

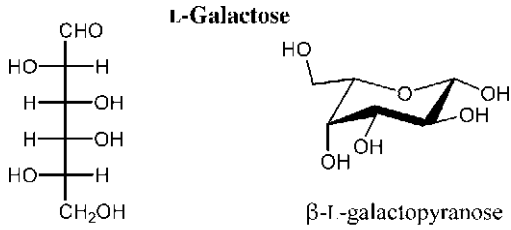
Occurrence. D-Galactose (**21**) is a constituent of several oligosaccharides, notably lactose, melibiose, and raffinose. Polysaccharides that yield D-galactose on hydrolysis include agar, gum arabic, mesquite gum, western larch gum, and many other plant gums and mucilages. Polysaccharides composed of alternating units of β-D-galactose and 3,6-anhydro-α-galactose are commonly found in red seaweeds.[81] In agars, the 3,6-anhydrogalactose units belong to the L series, whereas in carrageenans they are in the D form. D-Galactose occurs glycosidically combined with *myo*-inositol in sugar beets[82] and with glycerol in certain algae.[83] Crystalline D-galactose has been observed in ivy berries. Traces of the free sugar have been detected in fruits. In tomato fruits a large increase in free galactose was detected during ripening.[84]

D-Galactose is one of the few sugars, other than D-glucose, that is found distributed to any great extent in the animal kingdom. In combination with D-glucose, as the disaccharide lactose, it is an important constituent of the milk of mammals. D-Galactose is a common constituent of glycoproteins, as part of the complex-type N-glycans and of the O-glycans of mucins.[85] D-Galactose is found in the neutral and acid glycolipids of mammals.[86] This monosaccharide is present only in the pyranose form in the mammalian oligosaccharides. However,

D-galactose may be found as the furanose in microorganisms, some of these being important pathogens like *Trypanosoma cruzi* and *Mycobacterium tuberculosis*.[87]

Preparation. The method most frequently used involves the hydrolysis of lactose by acids, and fractional crystallization of the D-galactose liberated. A modification of the method entails removal of the D-glucose by fermentation with yeasts, and crystallization of the D-galactose remaining. Water-soluble gums extractable from the western or eastern larch also serve as sources of the sugar.[88]

The crystalline sugar is usually encountered as α-D-galactopyranose, although the β-D anomer is obtained by crystallization from cold, alcoholic solution. D-Galactose and D-glucose differ only in the configuration of C-4, and this difference is accompanied by a greater tendency of D-galactose to give furanose derivatives. Considerable proportions of furanose isomers are formed when the sugar is acylated directly. Combined or free D-galactose can be determined enzymatically with galactose oxidase, which oxidizes D-galactose at C-6 to D-*galacto*-hexodialdo-1,5-pyranose and hydrogen peroxide in the presence of oxygen. The hydrogen peroxide is determined colorimetrically.[89]



22

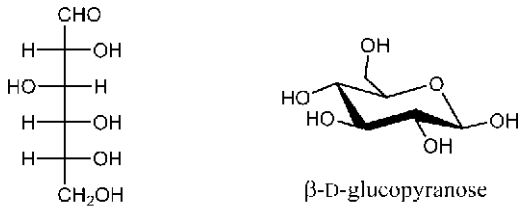
Occurrence. L-Galactose (**22**) is present together with D-galactose in high molecular weight snail galactans.[90] L-Galactose has also been detected in seaweeds of the genus *Porphyridium*.[91] It is a constituent of agars, carrageenan, other algal polysaccharides, and flaxseed gum.

The assignment of absolute configuration has been established by separation of the two enantiomers by gas chromatography of the acetylated glycosides of the chiral alcohol (+)-octanol[92] or the trimethylsilylated(−)-2-butyl glycosides.[93]

An enzymic method which uses NAD-dependent L-fucose dehydrogenase can be used, in the absence of L-fucose to oxidize L-galactose liberated by hydrolysis of the polysaccharide.[94]

Preparation. L-Galactose can be prepared by acid hydrolysis of agar or flaxseed gum. Since D-galactose is also present, it is removed by fermentation using D-galactose-adapted yeasts.[95]

D-Glucose



23

Occurrence. D-Glucose (**23**), in free or combined form, is not only the most common of the sugars but also is probably the most abundant organic compound. It occurs free in blood, cerebrospinal fluid, fruits, honey, lymph, plant juices, and urine, and is a major component of many oligosaccharides and D-glucosides, including sucrose. The most abundant polysaccharides, cellulose, starch, and glycogen are glucans.

Preparation. D-Glucose (often called dextrose commercially, because of its dextrorotation) is manufactured on a large scale by acid hydrolysis of starch, usually potato starch in Europe and corn starch in the United States.[96]

By using microwave irradiation, a suspension of starch (10%) in dilute hydrochloric acid (0.5 M) is completely hydrolyzed to glucose within 5 min without the formation of colored byproducts. The same suspension of starch heated at 100 °C in sealed tubes was hydrolyzed to glucose after 60 min, but some retrograded starch still remained suspended in the solution. If the retrograded starch is isolated, resuspended in dilute hydrochloric acid and irradiated, it is completetly hydrolyzed after 5 min.[97] In the presence of metal halides, complete hydrolysis was achieved in 2–3 min.[98]

D-Glucose can also be obtained by enzymic conversion of starch or cellulose. Two separate enzymic processes, liquefaction and saccharification, are generally used in the production of D-glucose from starch. The liquefaction process solubilizes the molecules in the starch granules and decreases the viscosity of the starch. In the saccharification step, the liquefied starch is further hydrolyzed to D-glucose by the action of glucoamylase. The majority of starches used for the manufacture of D-glucose contain up to 80% amylopectin.[99]

During liquefaction, the starch is solubilized by heating and partially hydrolyzed with a thermostable alpha amylase from *Bacillus licheniformis* or from other sources. The endo-acting alpha amylases are able to bypass the α-(1→6)-D-glucosidic linkages at the branch points in amylopectin but are not capable of hydrolyzing them. The oligosaccharides formed can be branched or linear. The

branch points act as a barrier during saccharification by glucoamylases, which hydrolyze (1→6) linkages at a low rate. The saccharification reaction can be improved by incorporating a specific debranching enzyme, such as pullulanase or isoamylase, into the system. The glucoamylase requirement is decreased because this enzyme has only to hydrolyze the α-(1→4)-D-glucosidic linkages.

By using both enzymes in combination, the yield of crystalline D-glucose is increased.[100] The use of cellulosic wastes for the production of glucose is of commercial interest, and in consequence much research work has been done on the characterization of cellulases. In particular, the cellulase system of the fungus *T. ressei* has the full complement of enzymes required to degrade crystalline cellulose. This and other fungal extracellular cellulases are commercially available.[101]

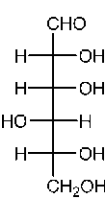
Below 50 °C, α-D-glucopyranose monohydrate is the stable crystalline phase, but above 50 °C, the anhydrous form is obtained. At higher temperatures, β-D-glucose is more stable.

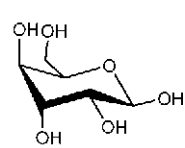
β-D-Glucose has proved of some technical interest because of its initial solubility. It has been prepared[102] by dissolution in hot pyridine and crystallization at 0 °C. The accompanying molecule of pyridine is removed at 105 °C. The β-D anomer is also prepared[103] by crystallization from hot acetic acid and recrystallization from water and alcohol. At temperatures above 115 °C, β-D-glucose is the stable form in contact with a saturated aqueous solution. β-D-Glucose may be prepared by seeding a concentrated D-glucose solution at 100 °C with β-D-glucose and evaporating it at this temperature to a solid mass.[104]

The commercial material known as glucose syrup is made by autoclaving aqueous starch suspensions with acid. It usually has a reducing power in the range of 40–45% of the same weight of D-glucose; the concentration of solid material lies in the range of 78–85%.

The industrial, non-food utilization of glucose includes its oxidation to D-gluconic acid, a chelating agent, its reduction to D-glucitol ("sorbitol") used for the production of vitamin C, and its glycosidation with long-chain alcohols to provide surfactants, which are produced at about 40,000 tons per year.[105]

D-Gulose



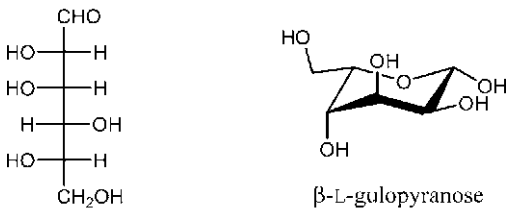


β-D-gulopyranose

Occurrence. D-Gulose (**24**) was found as a terminal sugar in the capsular polysaccharide of *Caulobacter crescentus*.[106] In a low amount, this rare sugar is found in the cell wall of the green alga *Tetraselmis striata* Butcher.[107] D-Gulose has been identified in the cardiac glycoside antiarigenin isolated from the cytotoxic bark extract of *Lophopetalum toxicum*.[108] Minor amounts of gulose were found in the glycoprotein of the green alga *Volvox carteri*[109] and in a glycolipid secreted during the infective cycle of *Chlamidia trachomatis*.[110]

Preparation. D-Gulose may be obtained as a pure syrup by the Kiliani synthesis from D-xylose.[111] Crystalline α-D-gulose.$CaCl_2$.H_2O was obtained upon evaporating *in vacuo* an aqueous solution of D-gulose containing about two molecular equivalents of calcium chloride.[112]

L-Gulose



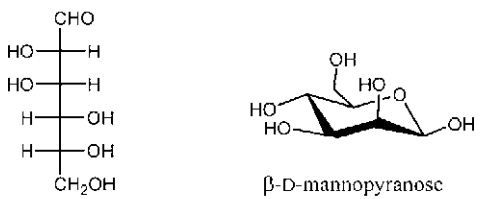
β-L-gulopyranose

25

Occurrence. L-Gulose (**25**) has been rarely found in Nature. α-L-Gulopyranose is a component of the antitumor glycopeptide, bleomycin, produced by a *Streptomyces*.[113] β-Linked L-gulose is the only monosaccharide present in the main polar lipid of the archaeobacterial species *Thermoplasma acidophilum* and *T. volcanicum*.[114] In a later paper[115] gulose was identified in other neutral glycolipids isolated from *T. acidophilum* but the enantiomeric configuration was not established.

Preparation. L-Gulose was prepared by the Sowden and Fischer method from 2,4-*O*-benzylidene-L-xylose, which can be conveniently prepared from 2,4-*O*-benzylidene-D-glucitol.[116]

D-Mannose



β-D-mannopyranose

26

Occurrence. There are many polysaccharides that yield D-mannose on hydrolysis. For preparative purposes, the most important source is the seed of the tagua palm *Phytelephas macrocarpa*, also known as vegetable ivory.[117] Salep mucilage from tubers of Orchidaceae, the seed of *Phoenix canariensis*, and white spruce hemicellulose are rich enough sources of D-mannose that they have been used for the preparation of this sugar. Konjac flour, which is commonly available in Japan from *Amorphophallus konjac*, provides another source of this hexose.[118]

A D-mannan was obtained from the kernel of the African doum palm (*Hyphaene thebaica*).[119] α-D-Mannans having glucose as a minor component have been isolated from the lichen *Tornabenia intricata*.[120]

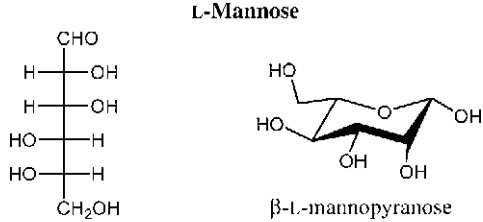
β-(1→4)-Linked D-mannose is the backbone of a major group of cell storage-polysaccharides in seeds. Galactomannans with different amounts of terminal α-galactose residues are typical of legume seeds.[121]

D-Mannose is also part of the core of N-glycans in glycoproteins and major component in the high-mannose oligosaccharides of glycoproteins.[85] The latter type of sugar chain is typical of yeast glycoproteins.[122] In addition, short *O*-linked oligosaccharides of mannose have been identified in yeast.[123] Oligomannoside-type glycans, not linked to protein have been described.[124]

Preparation. Shavings obtained from the ivory nut (*Phytelephas macrocarpa*) are considered the best source for the preparation of **26**. Alternatively, shavings obtained from doum-palm kernel may be used.[125] The shavings are hydrolyzed with mineral acid, and, by fractionation with alcohols D-mannose is separated from other substances and crystallized directly from the alcoholic solution.

Both anomers of the pyranose sugar are known, and either may be obtained from aqueous solution by adding nucleating crystals of the desired form to a supersaturated solution. In laboratories where the α-D anomer had been obtained, it became difficult to obtain the more soluble β-D form. β-D-Mannose can be obtained only by very careful exclusion of the seed of the α-D-anomer.[126]

L-Mannose



β-L-mannopyranose

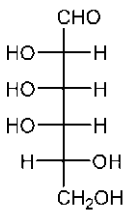
27

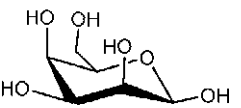
Occurrence. L-Mannose (**27**) is not as common as the D enantiomer. It has been described in steroid glycosides[127] and in some polysaccharides. The extracellular

polysaccharide elaborated by *Pseudomonas* ATCC 31544 is composed of a pentasaccharide repeating-unit with the unusual feature that one of the sugar residues may be L-rhamnose or L-mannose.[128] An extracellular polysaccharide from *Alcaligenes* species which gives highly viscous aqueous solutions has as its repeating unit a tetrasaccharide branched with a single L-rhamnose or L-mannose.[129]

Preparation. L-Mannose can be prepared by chain elongation methods, starting from L-arabinose. Both L-glucose and L-mannose are obtained. The nitromethane synthesis leads to a mixture of the nitroalditols that are separated by fractional crystallization and converted individually into the L-monosaccharides.[130]

D-Talose





β-D-talopyranose

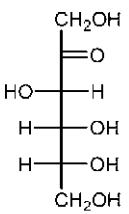
28

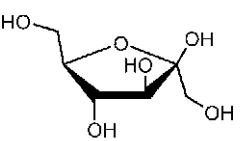
Occurrence. D-Talose is obtained on hydrolysis of the antibiotic hygromycin B, which is produced by *Streptomyces hygroscopicus*.[131,132] The configuration of the sugar is β-pyranosic in this compound as well as in the antibiotic Destomycin A.

Preparation. D-Talose was first prepared by reduction of D-talono-1,4-lactone obtained by epimerization of D-galactonic acid.[133] The sugar is also obtained by oxidation of D-galactal,[134] or by configurational-inversion procedures from derivatives of D-mannose or D-galactose.[135]

f. Ketohexoses.—Two ketohexoses are accessible in large quantities and are inexpensive: D-fructose and L-sorbose.

D-Fructose





β-D-fructofuranose

29

Occurrence. D-Fructose (**29**) is found, usually accompanied by sucrose, in uncombined form in fruit juices and honey. Apples and tomatoes are said to contain particularly large proportions of the sugar. When combined in natural products, the sugar is always found as the furanose. Sucrose consists of D-fructose and D-glucose residues in glycosidic union.[136]

Inulin and "oligofructose" are fructans extracted commercially from chicory root and are present in a wide range of plants, including common vegetables and fruits.[137] The fructose units are joined to each other by β-(2→1) links and glucose residues may be linked to the end of the chain by an α-(1→2) linkage, as in sucrose. Inulin is a polydisperse oligosaccharide having degree of polymerization of DP 2–60. The fructans possess many of the physiologic properties of dietary fiber.[138] Digestion of inulin by a *Bacillum circulans*-derived fructosyltransferase leads to linear and cyclic oligosaccharides.[139]

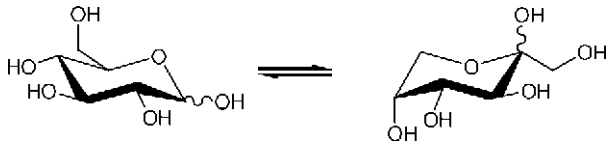
Fructose has also been found in the capsular polysaccharides of strains of *Haemophilus influenza*. The ketose is present as β-D-fructofuranosyl residues in the repeating units.[140]

Preparation. The abundance and wide distribution of D-fructose in natural products, its sweetness, and its poor crystallizing properties have stimulated considerable experimental work on methods of preparation. Most methods for isolation of the sugar depend on the formation of a difficultly soluble calcium "levulate" or "fructosate."

The best source of D-fructose for large-scale purposes is probably the "inversion" of sucrose by acids or invertase. The separation of the ketose from the concomitant D-glucose may then be accomplished by direct crystallization, by removal of the D-glucose after oxidation with bromine to D-gluconic acid (the ketose is not affected), or by precipitation of the calcium "fructosate." Hydrolysis of the natural inulins already mentioned may also serve for the preparation of D-fructose, which may be isolated from the hydrolyzate by precipitation of the lime complex.[141] D-Fructose is fermented by yeast.

Most tests have shown D-fructose to be the sweetest of the sugars, although the actual ratios between the various sugars depend to a considerable extent on the taster and on the methods and conditions adopted for the comparison. Compared to a sweetness value for sucrose of 100, that for D-fructose has been reported as varying from 103 to 173. The alleged relative sweetnesses of some sugars and other organic compounds can be found in Ref. 1.

D-Glucose (D-xylo) isomerases are large-scale industrial products employed for the multi-ton conversion of D-glucose into high-fructose corn syrup (Scheme 2).[142]



SCHEME 2.

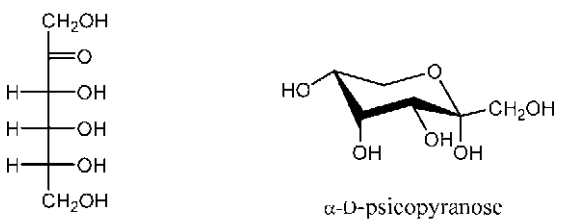
D-Glucose isomerases are exceptionally stable enzymes and the industrial processes are conducted around 60 °C. A study on the structural requirements of substrates and mechanistic features has been recently reported.[143]

Fructose contributes useful physical and functional attributes in food and beverage applications, including sweetness, flavor enhancement, humectancy, freezing-point depression, and osmotic stability.[144]

A review of new developments for the non-food utilization of D-fructose as organic raw material for the chemical industry has appeared.[105]

In aqueous solution, the equilibrium composition of fructose as determined by ^{13}C NMR spectroscopy is β-pyranose:β-furanose:α-furanose:α-pyranose in about 6:3:1:trace ratio.[145] Other compositions in different solvents and temperatures have been reported.[146] D-Fructose crystallizes in the β-pyranoid form.

D-Psicose



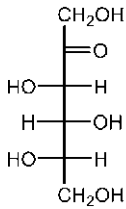
α-D-psicopyranose

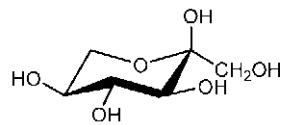
30

Occurrence. D-Psicose (D-*ribo*-hexulose, **30**) is produced in the hydrolysis of the antibiotic psicofuranine.[147,148] Although the sugar was initially isolated only as the phenylosazone, its identity was proved by synthesis of psicofuranine from tetra-*O*-acetyl-D-psicosyl chloride. The ketose also occurs in *Itea* plants, from which it has been isolated as the diisopropylidene acetal.[149]

Preparation. Isomerization of D-allose in anhydrous pyridine gives syrupy D-psicose, which may be isolated as the crystalline 1,2:3,4-diisopropylidene acetal.[150] D-Psicose is not fermentable by yeast. A review of the chemistry of D-psicose has appeared.[151]

L-Sorbose





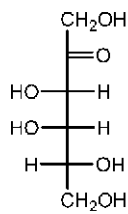
α-L-sorbopyranose

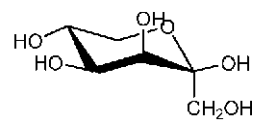
31

Occurrence. L-Sorbose (L-*xylo*-hexulose, **31**), the 5-epimer of D-fructose, has been found in the enzymic hydrolyzate of a pectin from the skin of the passion fruit (*Passiflora edulis*).[152]

Preparation. L-Sorbose is the most readily available L sugar, produced from D-glucitol as an intermediate in the vitamin C synthesis.[153] Fermentations with *Acetobacter suboxidans* produce over 90% of L-sorbose. The ketose is obtained crystalline. In solution, the α-pyranoid tautomeric form is highly favored (87–98%).[146] The chemistry of L-sorbose has been reviewed.[151]

D-Tagatose





β-D-tagatopyranose

32

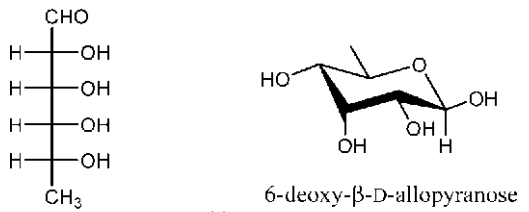
Occurrence. D-Tagatose (D-*lyxo*-hexulose, **32**) has been found only as a hydrolytic product from a gum exudate of the tropical tree *Sterculia setigera*.[154] A biological role of its 1-phosphate and 1,6-bisphosphate has been described in biotransformations of D-galactose in several microorganisms.[155]

Preparation. D-Tagatose is a bulking sweetener that can be economically used as a sugar substitute. Large-scale production of D-tagatose from D-galactose, using an immobilized L-arabinose isomerase has been described.[156] Enzyme extracts of *Escherichia coli* with the plasmid harboring the L-arabinose isomerase gene converted galactose into tagatose in 96.4% yield.[157]

A chemical route is afforded by isomerization of D-galactose in alkaline medium[158] or with *N,N′*-dicyclohexylcarbodiimide.[159] The chemistry of D-tagatose has been reviewed.[151]

g. 6-Deoxyaldohexoses.—

6-Deoxy-D-allose

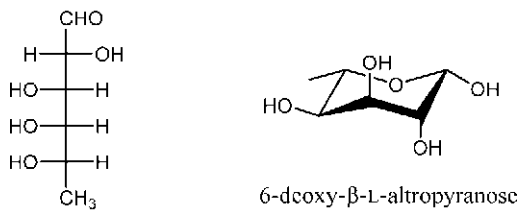


33

Occurrence. The sugar is found in cardiac glycosides[160] obtained, for example, from *Gomphocarpus fruticosus*,[161] *Digitalis canariensis* var. *isabelliana*,[162] and the Phillipinean plant *Lophopetalum toxicum*.[108]

Preparation. 6-Deoxy-D-allose may be obtained through the series of configurational inversions that occur on treatment of methyl 2,3-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-L-rhamnofuranoside with sodium methoxide.[163]

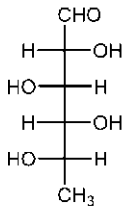
6-Deoxy-L-altrose

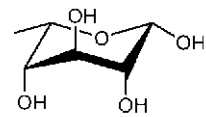


34

Occurrence and preparation. 6-Deoxy-L-altrose (**34**) is a monosaccharide occurring rarely in Nature. 6-Deoxy-L-altropyranose forms homopolysaccharide O-chains in LPSs of some *Yersinia enterocolitica* serovars.[164] 6-Deoxy-L-altrofuranose is one of the constituent monosaccharides of an O-specific polysaccharide of *Y. pseudotuberculosis* serovar VB[165] and was also found in a polysaccharide from *Campylobacter jejuni* 176.83 (serotype O:41) that contains only furanose sugars.[30] A homopolymer of 6-deoxy-L-altrofuranose has been found in the LPS of *Pectinatus frisingensis*,[166] which is in turn the source for the isolation of this sugar.

6-Deoxy-L-idose





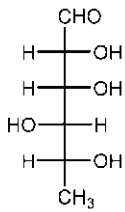
6-deoxy-β-L-idopyranose

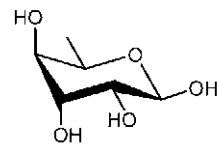
35

Occurrence. 6-Deoxy-L-idose (**35**) was reported to be a constituent of some diterpene glycosides isolated from *Aster spathulifolius* maxim.[167]

Preparation. A short synthesis of 6-deoxy-L-idose from 1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose has been recently described.[168]

6-Deoxy-D-gulose





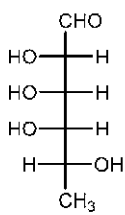
6-deoxy-β-D-gulopyranose

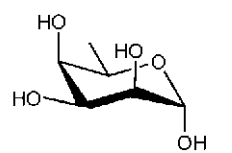
36

Occurrence. 6-Deoxy-D-gulose (**36**) occurs in steroidal glycosides,[160] for example, from the sap of the upas tree, *Antiaris toxicaria*,[169] from the wallflower, *Cheiranthus cheiri*,[170] and from *Digitalis canariensis* var. *isabelliana*.[162] It has also been described in the lipopolysaccharide O-antigen of *Yersinia enterocolitica* serotype O:8.[171]

Preparation. 6-Deoxy-D-gulose was originally prepared by the cyanohydrin synthesis from 5-deoxy-D-xylose. A simple preparation of 6-deoxy-D-gulose from D-gulono-1,4-lactone has been described.[172]

6-Deoxy-D-talose





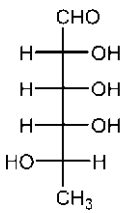
6-deoxy-α-D-talopyranose

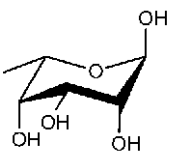
37

Occurrence. A homopolysaccharide of 6-deoxy-D-talose (6-deoxy-α-D-talan) was obtained by extraction with 2-propanol from the Gram-negative bacterium *Burkholderia plantarii*, the causing agent of rice seedling blight.[173] Recently, an O-antigenic polysaccharide with the repeating unit 3)-Glc-(1→3)-6-d-Tal-(1→, was reported in *B. pseudomallei*, although its D or L configuration was not then established.[174]

Interestingly, 6-deoxy-D-talan is a specific antigen of *Actinobacillus actinomycetemcomitans* serotype a,[175] whereas serotype c consists of 6-deoxy-L-talan with a disaccharide repeating unit.[176] The absolute configurations were established by comparing the corresponding D(+)-2-glycoside acetates, as well as from the values of their optical rotation.[175] Although 6-deoxy-hexoses have been often reported as constituents of microbial polysaccharides, polysaccharides composed solely of one type of 6-deoxyhexose are rare. *A. actinomycetemcomitans* is isolated from patients having dental illness. As those from *B. plantarii*, these homopolysaccharides were biologically active.

6-Deoxy-L-talose





6-deoxy-α-L-talopyranose

38

Occurrence. 6-Deoxy-L-talose (**38**) was first isolated from the cardiac glycoside sarmentoside A.[177] Other cardiac glycosides isolated from several plants contain 6-deoxy-L-talose.[160]

The exopolysaccharide of *Burkholderia caribensis* strain MWAP 71 contains 6-deoxy-L-talose.[178] Other strains of *Burkholderia pseudomallei* incorporate 6-deoxytalose, as a polymer with D-glucose but its configuration has not been established.[174]

6-Deoxy-L-talose is also present in the glycan moiety of lipopolysaccharides (LPS) of several bacteria. For example, **38** was recently characterized in the trisaccharide repeating unit of the lipopolysaccharides isolated from *Rhizobium leguminosarum*, in which it was attached as a side chain, α-(1→2)-linked to rhamnosyl residues.[179]

The carbohydrate O-specific side-chain moiety of the lipopolysaccharide (LPS) of a member of the *Enterobacteriaceae* family, *Yokenella regensburgei*,

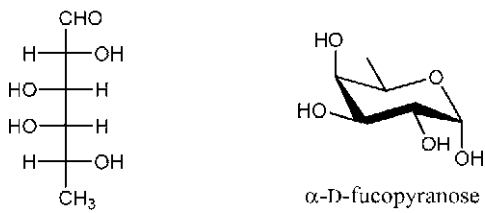
showed the presence of 6-deoxy-L-talose in the basic trisaccharide repeating unit −3)-α-D-Fuc*p*NAc-(1→2)-L-α-D-Hep*p*-(1→3)-6-deoxy-α-L-Tal*p*-(1→.[180] High resolution magic-angle spinning NMR showed for the first time that the O-specific polysaccharide observed on the surface of the bacteria has the same structure as in the isolated LPS.

Other examples of the presence of this sugar are the LPSs from *Rhizobium loti*, which contain mainly 6-deoxytalose with small amounts of the 2-*O*-methyl derivative.[181] The O-specific polysaccharide chain of *Proteus penneri* LPS also contains 6-deoxy-L-talose, together with another rarely occurring sugar, 2,3-diacetamido-2,3,6-trideoxy-L-mannose.[182]

The O45, O25-related, and O66 antigens from the LPSs of *Escherichia coli*, contain 6-deoxy-L-talose.[183] Other examples are the LPSs of *Pseudomonas fluorescens*[184] and *Stenotrophomonas maltophilia*.[185] 6-Deoxy-L-talose is found also in some glycopeptidolipid (GPL) antigens. For instance, the *Mycobacterium avium* serocomplex has a pentasaccharide hapten containing this sugar.[186] These antigenic GPLs are highly characteristic surface components with unusual sugar constituents.

Preparation. 6-Deoxy-L-talose was prepared by a method described by Collins and Overend.[187] The yield has been improved by a method which involves inversion of configuration at C-4 of a derivative of methyl α-L-rhamnopyranoside.[188] Other similar strategies have been described.[189]

D-Fucose



α-D-fucopyranose

39

Occurrence. D-Fucose (**39**, 6-deoxy-D-galactose) is rather uncommon in Nature. It was found in the hydrolytic products of cardiac glycosides.[160] The roots of certain South and Central American plants (*Convolvulaceae*), gives resins of a glycosidic nature: Jalap resin (convolvulin) and Scammonium or Tampico jalap (jalapin) are obtained from *Tubera jalapae* and *Ipomoea orizabensis*, respectively.[190] This sugar is also present in a sulfated steroidal glycoside of the starfish *Dermasterias imbricata*.[191]

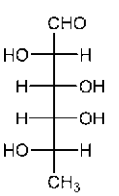
D-Fucose, in the furanose or pyranose form, has been identified in bacteria. *Actinobacillus actinomycetemcomitans* strains, of all serotypes, commonly produce polysaccharide antigens consisting of 6-deoxyhexoses. In fact, the serotype b-specific polysaccharide antigen from *A. actinomycetemcomitans* Y4 consists of the following disaccharide repeating-unit –3)-α-D-Fuc*p*(1→2)-α-L-Rha*p*-(1→.[192] On the other hand, serotype a consists solely of 6-deoxy-D-talose and serotype c is a polysaccharide of the L enantiomer.[175]

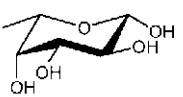
The minor fraction of a neutral polysaccharide obtained from *Campylobacter jejuni*, which causes enteritis in humans, having only the furanose structure of the sugar units, contains α-D-Fuc*f*. In the major fraction, the fucose is replaced by its 5-epimer, 6-deoxy-β-L-altrofuranose.[30] Also, the extracellular polysaccharide produced by *Caulobacter crescentus* contains D-fucose.[193] The antigenic polysaccharide produced by *Eubacterium saburreum* strain T19, is composed of D-*glycero*-D-*galacto*-heptose in the backbone structure and a D-fucofuranosyl disaccharide as a branch group, thus defining a new chemotype for this bacterium.[194] Another polysaccharide has been reported in strain L452, having α-D-fucofuranosyl terminal groups.[195]

D-Fucose has also been found in lipopolysaccharides. The O-specific polysaccharide chain of mild smooth-type LPS of *Pectinatus cerevisiiphilus* incorporates a disaccharide consisting of D-glucose and D-fucose with the following structure: −2)-β-D-Fuc*f*-(1→2)-α-D-Glc*p*-(1→.[166] The O-antigen isolated from the LPS of *Stenotrophomonas maltophilia* serogroup O3,[196] as well as that from the O19 serotype[197] contains α-D-Fuc*p*. D-Fucose is also present in the O-antigen of the LPS from *Burkholderia (Pseudomonas) cepacia* serotype E.[198] A fucorhamnan with α-Fuc*p* units constitutes the LPS of *Burkholderia vietnamiensis*.[199] The side chain of *Erwinia amylovora* LPS also contains D-fucose.[200]

Preparation. D-Fucose is obtained from glycosides found in various species of *Convolvulaceae*.[190] It has been synthesized by several methods, all based in deoxygenation at C-6 of D-galactose. A review on the chemistry and biochemistry of D- and L-fucose has been published.[201]

L-Fucose





β-L-fucopyranose

40

Occurrence. L-Fucose (6-deoxy-L-galactose) is widespread in seaweeds (*Fucus*) in which it occurs as the polysaccharide fucan (fucoidan). Fucoidans have not been found in other algae or plants. They are highly sulfated polysaccharides displaying various biological activities (anticoagulant, antiviral, antifertilizing, and antitumoral). The relationship of structure with anticoagulant activity of low molecular weight fucans obtained by partial acid hydrolysis has been studied.[202] Sulfated fucose, as a branching component of the glycosaminoglycan from the body wall of the sea cucumber *Stichopus japonicus* has been decribed.[203]

L-Fucose is a constituent of polysaccharides isolated from gum tragacanth, frog spawn, and the jelly coat of sea urchin eggs.

L-Fucose is the terminal monosaccharide found in α linkage in several biologically important oligosaccharide side-chains of glycolipids and glycoproteins. Fucoglycosphingolipids were isolated from erythrocytes and intestinal cells, many from human tumors. Multiple fucose residues branching a carbohydrate core may be present.[204]

L-Fucose may be present in O- and N-glycosylic chains of glycoproteins.[85] Polylactosamine chains in O- or N-linked glycans of glycoproteins, or in glycosphingolipids, may be modified by attachment of fucose residues, giving rise to blood-group determinants.[205]

Although L-fucose can be found internally linked in polysaccharides from plant and algae, it is usually found as a terminal modification in mammalian glycans. However, fucose residues may be internally linked to serine or threonine in a glycoprotein.[206]

Oligosaccharides of mammalian milk contain α-L-fucosyl residues. In particular, the oligosaccharides in human milk play a protective role against infectious agents.[207]

The external localization of the fucopyranosyl groups makes them labile to exo-L-fucosidases that are present in most higher organisms.

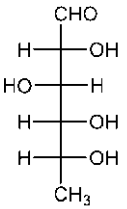
A genetic disorder involving a deficiency of α-L-fucosidase leads to accumulation of fucosylglycoconjugates in tissues and body fluids.[201]

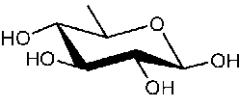
L-Fucose is also found in bacterial glycoconjugates, for instance in the lipopolysaccharide of the gastric pathogen *Helicobacter pylori*.[208]

Preparation. L-Fucose can be prepared by acid hydrolysis of seaweeds of the *Fucus* genus, preferably *Fucus vesiculosus*, which are initially washed with cold dilute hydrochloric acid to solubilize inorganic salts, and soluble alditols, and sugars.[209]

A synthesis of L-fucose starting from methyl α-L-rhamnopyranoside has been described.[188]

D-Quinovose





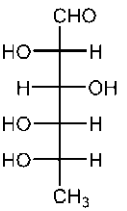
β-D-quinovopyranose

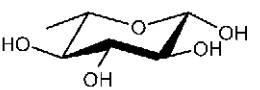
41

Occurrence. D-Quinovose (6-deoxy-D-glucose, **41**) occurs in several glycosides, such as quinovin (chinovin) in the bark of many species of Chinchona, from which it is extracted along with the quinine alkaloids.[210] The sugar also occurs as a glycoside of digitoxigenin.[162] β-D-Quinovose was found in triterpenoid saponins from *Acacia victoriae* which induce apoptosis.[211] β-D-Quinovose and α-L-rhamnose in 3:1 ratio are present as a tetrasaccharide in the glycoside calonyctin A, a plant-growth regulator isolated from leaves of *Calonyction aculeatum* L. House.[212] The majority of triterpene glycosides from sea cucumbers have quinovose in the oligosaccharide chain.[213]

Preparation. Quinovose may be synthesized by reduction of the 6-*O*-*p*-tolylsulfonyl group in a conveniently substituted glucose derivative.[214] The sugar crystallizes from ethyl acetate.

L-Quinovose



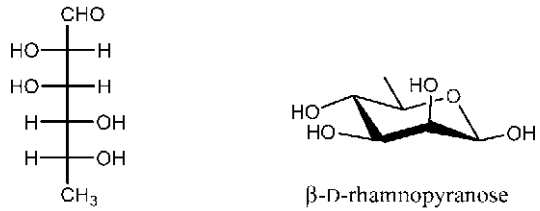


β-L-quinovopyranose

42

Occurrence. L-Quinovose (6-deoxy-L-glucose, **42**) is a rare sugar found as its phenazine ester in a marine actinomycete.[215] It was also tentatively identified in a lipopolysaccharide of *Legionella feeleii*.[216]

D-Rhamnose

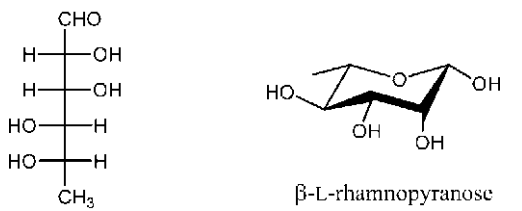


43

Occurrence. D-Rhamnose (6-deoxy-D-mannose, **43**) is not as common as the L enatiomer in Nature. It has been found in the O-antigen chain of lipopolysaccharides (LPS) of Gram-negative bacteria, sometimes together with L-rhamnose as in the LPS of some strains of *Helicobacter pylori*.[217] A linear α-D-rhamnan with a trisaccharide repeating-unit is present in the O-antigen of some strains of *Stenotrophomonas malthophilia*, and *Pseudomonas* and *Burkholderia* species.[218] The O-specific polysaccharide chain of a serotype of *Campylobacter fetus* contains D-rhamnose and 3-*O*-methyl-D-rhamnose (D-acofriose) in 24:1 ratio.[219] In the O-antigen of the enterobacterium *Citrobacter freundii* α-D-mannose and β-D-rhamnose are present in 1:2 ratio.[220]

Preparation. D-Rhamnose is synthetized from 6-*p*-toluenesulfonic esters of D-mannose by reductive displacement of the sulfonyloxy groups.[221]

L-Rhamnose



44

Occurrence. L-Rhamnose (6-deoxy-L-mannose, **44**) is a constituent of many glycosides, which provide its best source. It is a component of polysaccharides or glycoconjugates in plants and microorganisms. In seed cell-walls, the monosaccharide is present in pectin as a rhamnogalacturan having a backbone of GalA-Rha disaccharide repeating-units.[222] A glycoconjugate, in which the polysaccharide constitutes 94.5% and is dominated by 36% of L-rhamnose was isolated from the corm of the saffron plant.[223]

L-Rhamnose is the main monosaccharide in the polysaccharide produced by *Bradyrhizobium* species within soybean nodules.[224] An acidic polysaccharide from

the leaves of *Malva sylvestris* contains L-rhamnose and D-galacturonic acid as major components.[225]

In algae, an example is found in the sulfated polysaccharide spirulan, isolated from the blue-green alga *Spirulina platensis*, composed of two types of disaccharide repeating-units, *O*-rhamnosyl-acofriose (3-*O*-methylrhamnose) and *O*-hexosyluronic-rhamnose.[226]

Rhamnosides are mainly found in plant heteroglycans. For instance L-rhamnose is found in saponins[227] from the bark of the Quillaja tree. Glycosides isolated from lichens may contain L-rhamnose.[228]

In bacteria, L-rhamnose may be found linked α and β in the same oligosaccharide chain, for instance in the capsular polysaccharide of *Streptococcus pneumoniae*[229] and in the secreted polysaccharide of *S. thermophilus*.[230] In Gram-negative bacteria, L-rhamnose is present in the O-antigen of lipopolysaccharides; some recent examples are cited.[231] A rhamnan and fucorhamnan are present in the lipopolysaccharide of *Burkholderia vietnamiensis*.[199]

Both D-and L-rhamnose may be present in the same oligosaccharide, as reported for the glycopeptidolipids of *Mycobacterium avium*.[232] The surface antigens of all serovars examined present the inner disaccharide α-L-rhamnopyranosyl(1→2)-6-deoxy-α-L-talopyranose. L-Rhamnose is also part of the highly immunogenic phenolic glycolipids from *Mycobacterium*.[233]

Rhamnose has been described as a component of glycoproteins isolated from plants and microorganisms. A glycan chain of the surface-layer glycoprotein of *Bacillus stearothermophilus* is composed of only L-rhamnopyranosyl residues in α and β linkages.[234] A novel asparaginyl-rhamnose linkage was described for this glycoprotein.[235] Rhamnosyl residues are present in cell-surface glycoproteins of *Trypanosoma cruzi*.[236]

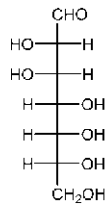
Preparation. "Lemon flavin," a khaki dyestuff obtained from the bark of an oak species (*Quercus tinctoria* Mich.), provides an excellent source of the sugar. The main constituent of the lemon flavin is the rhamnoside quercitrin, which after hydrolysis, yields the aglycon (quercetin) and L-rhamnose. The lemon flavin is hydrolyzed in boiling dilute acid, and after neutralization of the solution and treatment with a considerable proportion of decolorizing carbon, the sugar crystallizes from the evaporated solution.[237]

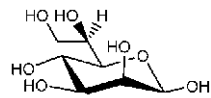
h. Higher-Carbon Sugars.—Higher-carbon sugars (aldoses and glyculoses) and alditols have been isolated from higher plants. Avocado is a good source of this class of sugars, mostly identified in the laboratory of Richtmyer.[238] In addition, aldoheptoses are components of the lipopolysaccharides of Gram negative bacteria.[239]

Methods for the synthesis of higher sugars generally involve chain-ascent procedures from lower aldoses.

(i) ***Aldoheptoses.—***

D-*glycero*-D-*manno*-Heptose

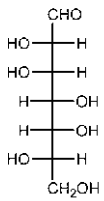


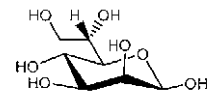


D-*glycero*-β-D-*manno*-heptopyranose

45

L-*glycero*-D-*manno*-Heptose



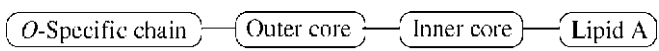


L-*glycero*-β-D-*manno*-heptopyranose

46

Heptoses are typical constituents of lipopolysaccharides (LPS), in most cases occurring in the core region in the L-*glycero*-D-*manno* or D-*glycero*-D-*manno* configuration.[239] However, a few other heptoses have been identified in the O-antigen polysaccharide of LPS, and these examples are discussed next.

The LPS (endotoxin), which is a characteristic component of the outer membrane of Gram-negative bacteria, contains in the inner core (Scheme 3) two or three units of a heptose, generally L-glycero-D-*manno*-heptose (**46**).



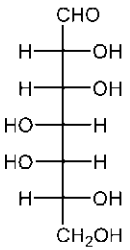
Gram-negative bacteria LPS

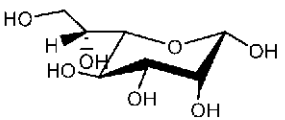
SCHEME 3.

Some recent reports on the presence of L-*glycero*-D-*manno*-heptose (**46**) include the LPS of *Pseudomonas syringae* pv. atrofaciens IMV 948[240] and the LPS of nontypeable *Haemophilus influenzae* strain 486.[241] The LPS of *Helicobacter pylori* contains, in the inner core, both L-*glycero*-D-*manno*-heptose (LD-Hep) and D-*glycero*-D-*manno*-heptose (DD-Hep, **45**).[242]

In some strains of *H. pylori*, an oligosaccharide made up of D-*glycero*-D-*manno*-heptose units intervenes between the O-chain and the LPS core.[243] Also both heptoses, LD-Hep and DD-Hep, are present in the LPS of *Yersinia enterocolitica* serotype O:8.[244] The absolute configuration of the two heptose constituents can be determined by the chiral glycoside procedure.[92] Only small amounts of these heptoses are available from natural sources. Convenient synthesis of L- and D-*glycero*-D-*manno*-heptose have been reported.[245]

D-*glycero*-L-*manno*-Heptose



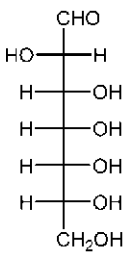


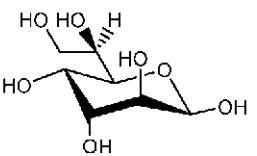
D-*glycero*-β-L-*manno*-heptopyranose

47

Occurrence and preparation. The major heptose of the LPS of *Vibrio cholera* Inaba 569B was proved to be D-*glycero*-L-*manno*-heptose (**47**), by isolating the sugar through repeated purification on paper chromatography, and was confirmed by comparison with an authentic sample (synthesized *via* condensation of nitromethane with D-galactose).[246]

D-*glycero*-D-*altro*-Heptose





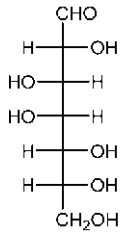
D-*glycero*-β-D-altro-heptopyranose

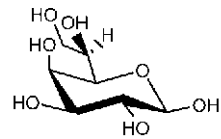
48

Occurrence. This rare heptose (**48**) has been found in O-chains of lipopolysaccharides of *Campylobacter jejuni* serotypes O-23 and O-36 as the α-pyranose, together with a related heptose, 6-deoxy-D-*altro*-heptose, as major constituent. The relative configuration at C-6 of the heptose was established by GLC of the corresponding D-*glycero*-D-*altro*-heptitol heptaacetate derivative and by

comparison with an authentic sample. The DD configuration was established, rather than LL, by taking into account the close relationship between this heptose and 6-deoxy-D-*altro*-heptose, and remains to be confirmed.[247]

D-*glycero*-D-*galacto*-Heptose





D-*glycero*-β-D-*galacto*-heptopyranose

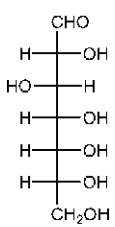
49

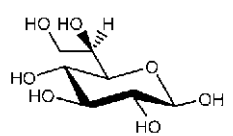
Occurrence. D-*glycero*-D-*galacto*-Heptose (**49**) was found among a number of higher-carbon sugars in the ripe avocado (Californian calavo, Hass variety), from where it was obtained by column chromatography.[248]

Compound **49** has been identified as a component of the Gram-negative bacterium *Chromobacterium violaceum*,[249] and unusually, in both α and β-pyranosyl form[250] in the O-specific polysaccharide of the LPS.

Antigenic polysaccharides from the Gram-positive microorganism, *Eubacterium saburreum*, contain unusual structural features, for example D-*glycero*-D-*galacto*-heptose, as a main constituent. The antigen from strain L44 is a homopolysaccharide composed of (1→6)-linked D-*glycero*-D-*galacto*-heptopyranosyl residues.[251] The antigens from strains L49, O2, and 29 also contain D-*glycero*-β-D-*galacto*-heptopyranosyl residues, and in addition, 6-deoxy-α-D-*altro*-heptofuranosyl groups.[252–254] Strains T27, T17, and T18 possess a homoglycan composed of the sugar **49**, but in this case both, β-heptopyranose and α-heptofuranose are present.[255] Strain T19 contains D-*glycero*-β-D-*galacto*-heptopyranosyl units as the backbone and a D-fucofuranosyl disaccharide in α configuration as branch groups.[194]

D-*glycero*-D-*gluco*-Heptose



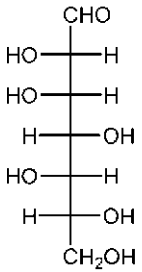


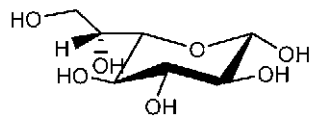
D-*glycero*-β-D-*gluco*-heptopyranose

50

Occurrence and preparation. Begbie and Richtmyer have shown that the dried root of the primose (*Primula officinalis* Jacq.) contains the heptose **50** among a number of other sugars. It was purified by column chromatography from aqueous extracts of the root.[256]

D-*glycero*-L-*gluco*-Heptose



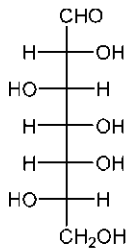


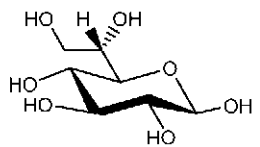
D-*glycero*-β-L-*gluco*-heptopyranose

51

Occurrence and preparation. Heptose **51** was isolated from the LPS of *Vibrio cholera* Inaba 569 B as a minor heptose by purification on paper chromatography and identified by comparison with an authentic synthetic sample.[246]

L-*glycero*-D-*gluco*-Heptose





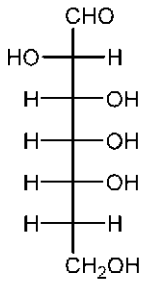
L-*glycero*-β-D-*gluco*-heptopyranose

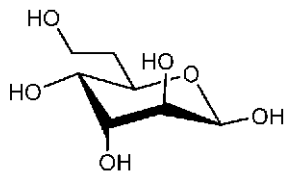
52

Occurrence and preparation. L-*glycero*-D-*gluco*-Heptose (**52**) is the major heptose present in the LPS, O-antigen polysaccharide, and core polysaccharide of *Vibrio cholera* Ogawa G-2102, together with small proportions of L-*glycero*-D-*manno*-heptose. The heptose was shown to be identical to an authentic sample (synthesized *via* condensation of L-galactose with nitromethane) and was isolated in pure state.[257]

(ii) *6-Deoxyaldoheptoses.*—

6-Deoxy-D-*altro*-heptose



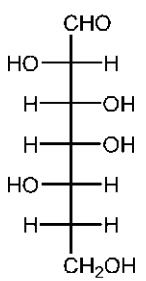


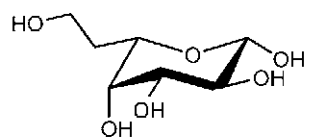
6-deoxy-β-D-*altro*-heptopyranose

53

Occurrence. 6-Deoxyheptoses have been found as components of antigenic polysaccharides produced by bacteria. Thus, 6-deoxy-D-*altro*-heptose (**53**) was identified in a polysaccharide from the nonsporing, Gram-positive *Eubacterium saburreum* that inhabits the oral cavity.[252] The strains L49, O2, S29, T21, and T110 contain this sugar, which characterizes chemotype II.[194] 6-Deoxy-β-D-*altro*-heptose occurs as the pyranose form in the associated extracellular polysaccharide from *Campylobacter jejuni* O:23 and O:36 (which causes enteritis in humans),[247] in contrast to *C. jejuni* O:41 LPS, where this sugar is present only in the furanosyl form. In fact, the latter polysaccharide only contains furanosyl residues.[30] On the other hand, α-linked rather than β-linked 6-deoxy-D-*altro*-heptofuranose occurs in capsular polysaccharide from *Eubacterium saburreum*.[253] Recently, a homopolymer of a 6-deoxyheptose was purified from *Burkholderia pseudomallei*.[174]

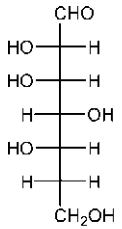
6-Deoxy-L-*galacto*-heptose and 6-deoxy-L-*gulo*-heptose

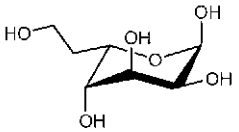




6-deoxy-β-L-*galacto*-heptopyranose

54





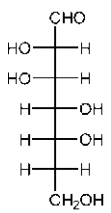
6-deoxy-α-L-*gulo*-heptopyranose

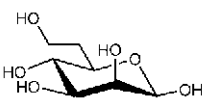
55

Occurrence. As already described, strains of *Campylobacter* are remarkable in their capacity to synthesize unique heptose- and 6-deoxyheptose-containing oligosaccharides. *Campylobacter lari* presents a tetraglycosyl phosphate polymer with 6-deoxy-L-*galacto*-heptose (**54**) as a constituent in both pyranose and furanose ring-forms. The presence of this sugar was established by comparison to 6-deoxy-L-*galacto*-heptose, and the L-enantiomeric configuration was substantiated through formation of chiral glycosides.[258]

The tetraglycosyl phosphate repeating-unit polymer of the extracellular polysaccharide of *Campylobacter lari* strain ATCC 3521 contains 6-deoxy-L-*gulo*-heptose (**55**) in α-pyranosyl form. The identity of this constituent was established by comparison with synthetic 6-deoxy-L-*gulo*-heptose, with substantiation of the L-enantiomeric configuration through formation of chiral glycosides.[259]

6-Deoxy-D-*manno*-heptose



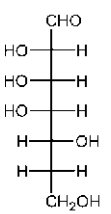


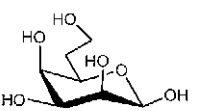
6-deoxy-β-D-*manno*-heptopyranose

56

Occurrence. 6-Deoxy-D-*manno*-heptose (**56**) is a component of the lipopolysaccharides isolated from *Yersinia pseudotuberculosis* type IIA[260] and from *Pseudomonas pseudomallei*.[261]

6-Deoxy- D-*talo*-heptose





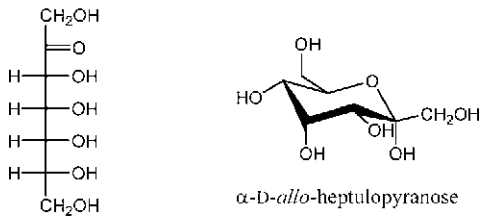
6-deoxy-β-D-*talo*-heptopyranose

57

Occurrence and preparation. As already described, *Campylobacter* species produce components containing unusual heptoses and deoxyheptoses. In fact, the LPS-associated, water-soluble antigenic polysaccharide of *C. coli* serotype O:30 contains the unique 6-deoxy-D-*talo*-heptose (**57**). This sugar was shown to be the D enantiomer by comparison of the 2(*S*)-butyl glycoside acetates of the natural sugar with those of the chemically synthesized 6-deoxy-D-*talo*-heptose. The configuration of this sugar is β-pyranose, in a teichoic acid-like structure.[262]

(iii) *Ketoheptoses.—*

D-*allo*-Heptulose

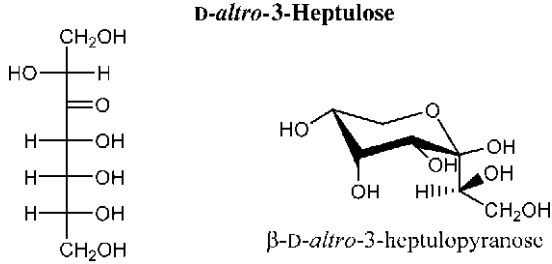


α-D-*allo*-heptulopyranose

58

Occurrence and preparation. In its first known natural occurrence, Begbie and Richtmyer[256] isolated this heptulose **58** from *Primula officinalis* Jacq. (see under D-*glycero*-D-*gluco*-heptose). The ketose is obtained by alkaline isomerization of D-*glycero*-D-*allo*- and D-*glycero*-D-*altro*-heptose[263] and of D-*manno*-3-heptulose.[264] 1,3-Dihydroxy-2-propanone adds to D-erythrose in an alkaline medium to give D-*allo*-heptulose toghether with D-*altro*- and D-*gluco*-heptulose.[264] An *allo*-heptulose, probably of the D series, has been isolated from the avocado.[265]

D-*altro*-3-Heptulose



β-D-*altro*-3-heptulopyranose

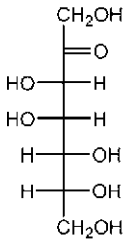
59

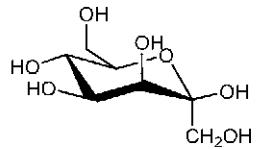
Occurrence and preparation. D-*altro*-3-Heptulose (coriose) is the first clearly characterized 3-heptulose found in a natural product. This 3-heptulose was obtained from chromatographed extracts of the roots of *Primula officinalis* Jacq[256] (see under D-*glycero*-D-*gluco*-heptose), and it has also been isolated from the leaves

and stem of *Coriana japonica*.[266] D-*altro*-3-Heptulose is prepared by isomerization of sedoheptulose in pyridine,[256] or from 2,4-*O*-ethylidene-D-erythrose by an aldol reaction.[266]

X-Ray crystallographic studies have shown that the sugar crystallizes as the α-furanose.[267]

D-*manno*-Heptulose



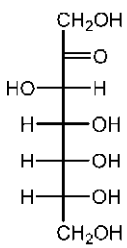


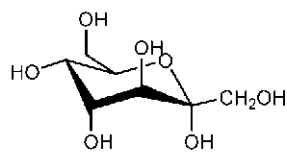
β-D-*manno*-heptulopyranose

60

Occurrence and preparation. LaForge reported the first isolation of a naturally occurring higher sugar, D-*manno*-heptulose (**60**), from the avocado (*Persea gratissima* Gaertn.).[268] Avocado varieties differ greatly in their content of the heptulose; yields vary from 0.1 to 5%, based on the weight of wet pulp.[269] The purified extract of the avocado first gives crystalline perseitol. On nucleating, the mother liquor deposits the heptulose.[268,269] Compound **60** together with other higher sugars, has been also isolated from Pichi tops, the dried herbage of *Fabiana umbricata* Ruiz & Pav.[47] and from *Cannabis sativa L.*[270] The occurrence and preparation of D-*manno*-heptulose has been reviewed.[271] Isomerization of D-*glycero*-D-*galacto*-heptose in alkali gives synthetic D-*manno*-heptulose plus D-*gluco*-heptulose; but, in pyridine, only D-*manno*-heptulose is allegedly obtained.[272]

D-*altro*-Heptulose (sedoheptulose)





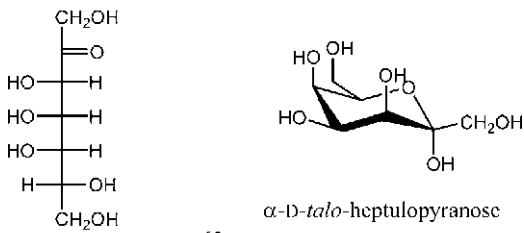
α-D-*altro*-heptulopyranose

61

Occurrence. Although sedoheptulose (**61**) is universal in the plant kingdom, it is normally encountered in the form of its monophosphate and bisphosphate esters, in the pentose phosphate cycles. Free sedoheptulose has been identified in *Cannabis sativa L.*[270] and in vascular plants, mostly of the Crassulaceae.[273] It was also detected in ethanolic extracts from the brown seaweed *Desmarestia aculeata*.[274] Of special interest is the occurrence of high concentrations of free sedoheptulose (up to 18% of the dry weight) together with volemitol (D-*glycero*-D-*manno*-heptitol) in *Primula* leaves.[275] It was shown that volemitol is biosynthesized from sedoheptulose by a NADPH-dependent sedoheptulose reductase. On the other hand, in the brown alga *Pelvetia canaliculata* volemitol was synthesized from sedoheptulose 7-phosphate by the action of an NADH-dependent reductase *via* volemitol 1-phosphate.[276]

Preparation. The sugar is extracted by water from ground *Sedum* leaves and stems, and the extracts are evaporated to a thick syrup. The sedoheptulose is extracted by alcohol, which is then removed by evaporation. An aqueous solution of the syrup is purified with basic lead acetate. After removal of the excess of lead by precipitation with hydrogen sulfide, a solution of the crude sugar is obtained.[277] It is usually isolated as the readily crystallized anhydride, sedoheptulosan monohydrate, whose structure is 2,7-anhydro-β-D-*altro*-heptulopyranose monohydrate.[278] Sedoheptulosan is formed by treating the sugar with acid. The proportion of this anhydride varies from 84.5 to 91%, according to the temperature employed to attain equilibrium.[279] Sedoheptulose has been prepared by the stereospecific condensation of D-ribose with hydroxypyruvic acid, catalyzed by a transketolase from spinach leaves.[280]

D-*talo*-Heptulose



α-D-*talo*-heptulopyranose

62

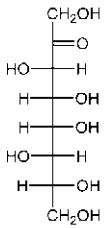
Occurrence and preparation. The sugars present in the ripe avocado (Calavo, Fuerte variety) were first studied chromatographically by Charlson and Richtmyer, who obtained as one of the fractions a syrupy product having properties strongly suggestive of D-*talo*-heptulose.[281] The avocado extract (deionized, freed of gums, and fermented with yeast) gave perseitol, *myo*-inositol, and D-*erythro*-D-*galacto*-octitol (the first octitol discovered in Nature). Aldoses in the mother liquor were removed by bromine oxidation, and the remaining sugars were chromatographed

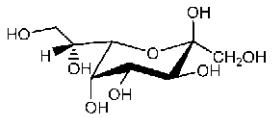
on cellulose columns. In the fraction containing D-*talo*-heptulose, which could not be induced to crystallize, both D-fructose and D-*manno*-heptulose were detected.[265] Another fraction gave D-*glycero*-D-*manno*-octulose.

Oxidation of D-*glycero*-D-*altro*-heptitol by *Acetobacter suboxydans* gives D-*talo*-heptulose, which has been crystallized.[263]

(iv) ***Ketooctoses.—***

D-*glycero*-L-*galacto*-Octulose





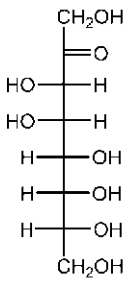
D-*glycero*-α-L-*galacto*-octulopyranose

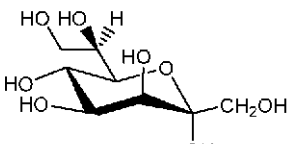
63

Occurrence and preparation. In the first report of its occurrence,[248] D-*glycero*-L-*galacto*-octulose (**63**) was obtained from the pulp of ripe avocados (Calavo, Hass variety) by extraction and chromatography (see under D-*glycero*-D-*galacto*-heptose). The octulose was also isolated from the dried roots of *Primula officinalis* Jacq.

Chromatography has shown the octulose to be present in several genera of Crassulaceae.[282] The following octuloses have been shown to accumulate when the leaves of red clover (*Trifolium pratense*) were allowed to imbibe solutions of the pentoses and hexoses as indicated: D-*glycero*-L-*galacto*-octulose (D-xylose or D-gulose), L-*glycero*-L-*galacto*-octulose (L-arabinose or L-mannose), and D-*glycero*-D-*altro*-octulose (D-ribose or D-allose).[283]

D-*glycero*-D-*manno*-Octulose





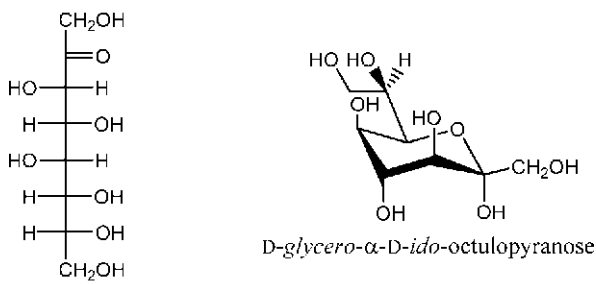
D-*glycero*-α-D-*manno*-octulopyranose

64

Occurrence and preparation. D-*glycero*-D-*manno*-Octulose (**64**) is the first naturally occurring octulose to have been isolated.[281] Charlson and Richtmyer obtained this ketose by chromatography of extracts of the ripe avocado (Calavo, Fuerte variety; see under D-*talo*-heptulose), and also from extracts of *Sedum spectabile*. For preparation of the octulose from *Sedum*, fermented extracts were heated in acid, and sedoheptulosan monohydrate crystallized. The mother liquor was freed from aldoses by oxidation with bromine, and the unoxidized products were fractionated by cellulose-column chromatography. D-Mannitol, *myo*-inositol, additional sedoheptulosan, D-*glycero*-D-*gluco*-heptitol (β-sedoheptitol), and D-*glycero*-D-*manno*-octulose were isolated. The octulose is also present in *Primula officinalis* Jacq[256] (see under D-*glycero*-D-*gluco*-heptose) and in Pichi tops[47] (see under D-*manno*-heptulose). The octulose was isolated as a syrup and charaterized as its phenylosazone and phenylosotriazole. D-*glycero*-D-*manno*-Octulose, together with heptuloses, has been identified in *Cannabis sativa* L.[270]

The formation of octuloses from pentoses in plants has been demonstrated.[283,284] Incubation of D-ribose, D-fructose 1,6-diphosphate, and aldolase, followed by phosphatase treatment gave D-*glycero*-D-*altro*-octulose (**65**) as the main product and D-*glycero*-D-*manno*-octulose (**64**). The yield of **65** was 10% of that for **64**.[285] Apparently, **65** has not been found in plants.

D-*glycero*-D-*ido*-2-Octulose

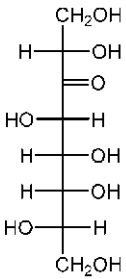


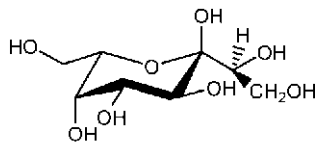
D-*glycero*-α-D-*ido*-octulopyranose

66

Occurrence. D-*glycero*-D-*ido*-2-Octulose (**66**) constitutes the dominant carbohydrate in the fully hydrated leaves of the resurrection plant *Craterostigma plantagineum*, from where it has been extracted.[286] The structure was confirmed by NMR analysis of the tri-*O*-isopropylidene derivative.[287] Resurrection plants have the unique ability to be able to survive up to almost complete dehydration and then be rehydrated in a biologically functional state.[288] Upon dehydration there is a conversion of 2-octulose into sucrose. The 2-octulose **66** appears to be used as a storage carbohydrate in the leaves, and is mobilized at night.[289]

L-*glycero*-D-*gluco*-3-Octulose





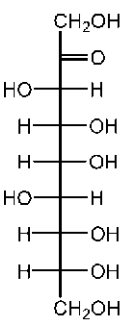
L-*glycero*-α-D-*gluco*-3-octulopyranose

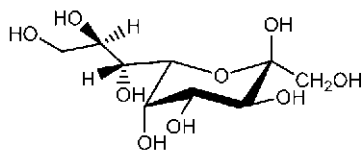
67

Occurrence. L-*glycero*-D-*gluco*-3-Octulose (**67**), the first naturally occuring 3-octulose, was identified as the main constituent of aqueous extracts from *Laurus nobilis* leaves and buds.[290]

(v) *Ketononoses.*—

D-*erythro*-L-*galacto*-Nonulose



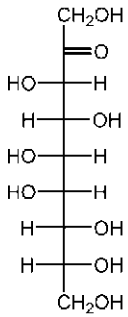


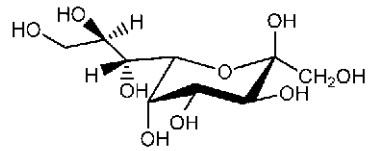
D-*erythro*-α-L-*galacto*-nonulopyranose

68

Occurrence and preparation. D-*erythro*-L-*galacto*-Nonulose (**68**) is obtained as a hygroscopic syrup in very low yield by chromatography of extracts of the avocado[282] (*Persea gratissima* Gaertn., family Lauraceae; see under D-*glycero*-D-*galacto*-heptose) and from dried roots of *Primula officinalis* Jacq[256] (see under D-*glycero*-D-*gluco*-heptose). It is also present in several genera of the Crassulaceae, including *Sedum*.[282] Sephton and Richtmyer prepared the nonulose by using Sowden's 2-nitroethanol procedure and the diazomethane synthesis.

D-*erythro*-L-*gluco*-Nonulose



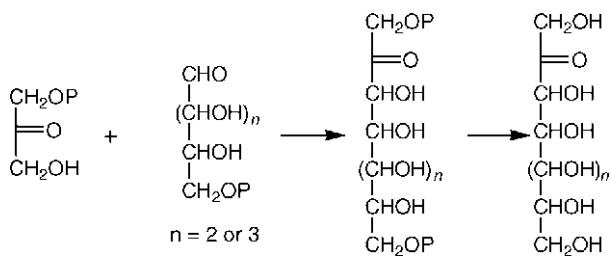


D-*erythro*-α-L-*gluco*-nonulopyranose

69

Occurrence and preparation. This nonulose was obtained from the ripe avocado (Calavo, Hass variety) by extraction and cellulose chromatography (see under D-*glycero*-D-*galacto*-heptose). It is also present in *Sedum*.[282] Dried roots of *Primula officinalis* Jacq. provide another source of the nonulose[256] (see under D-*glycero*-D-*gluco*-heptose). The synthetic nonulose was prepared by the diazomethane method.[291,292]

Enzymatic coupling of sugar phosphates by aldolase has been use to prepare octuloses and nonuloses (Scheme 4).[293]



SCHEME 4.

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ADVANCES IN CARBOHYDRATE CHEMISTRY AND BIOCHEMISTRY, VOL. 59

SYNTHESIS AND REACTIONS OF GLYCOSIDES

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A comprehensive survey of the subject of glycosides in 1972 by Overend[1] contains much information of permanent value on their reactivity, especially on the kinetics of their hydrolysis in acid and alkaline media, and these aspects are not repeated here. Methods for synthesis of glycosides have undergone dramatic improvements and developments during the past three decades, and form a major focus of the present article.

I. Introduction, Definitions

In an *O*-glycoside, the hydroxyl group of a cyclic hemiacetal is replaced by an alkyloxy, or aryloxy group. In a corresponding thioglycoside, the hydroxyl group of the cyclic hemiacetal is replaced by an alkylthio or arylthio group. Replacement of the same hydroxyl group by an alkyl- or aryl-amino function yields a glycosylamine, while replacement of the hydroxyl by an alkyl or aryl group leads to an alkyl or aryl *C*-glycosylic compound. The last two classes of compounds are not discussed in this article.

The ring size in a glycoside may be five-membered, giving rise to a furanoside, six-membered to give a pyranoside, or (rarely) seven-membered to give a septanoside. In aldosides, derived from aldoses, it is carbon 1 that is involved in ring formation, while in ketosides, derived from 2-ketoses, carbon 2 assumes this role. The non-carbohydrate part of a glycoside may be referred to as the aglycone, and the carbohydrate portion as the glycone.

The prefixes α-D- (β-L-) and β-D- (α-L-) define the aglycone as being above or below the ring structure as depicted in Fig. 1.

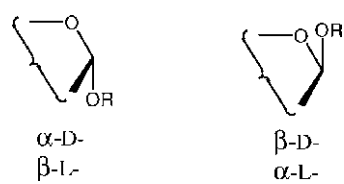


Fig. 1. Anomeric relationships.

This article treats exclusively those reactions and structural considerations pertaining to the anomeric center of glycosides. Obviously the presence of functionality at each of the other carbons implies rich opportunities for chemical transformations, but these are outside the scope of the present chapter.

II. Methods for Synthesis. *O*-Glycosides

Considerable progress has been made in stereocontrolled synthesis of the glycosidic bond since Overend's article.[1] This is due to the importance of glycosides as natural products, and especially because of their significance as the link between monosaccharide units in oligosaccharide structures of biological importance. Thus oligosaccharides, usually in the form of conjugates with lipids or proteins, appear to occur ubiquitously on cell surfaces, where they play a decisive rôle in a wide range of cell-recognition processes.

1. Nature of the Leaving Group at C-1

Standard leaving groups used in glycosidation reactions are acyl (such as acetyl, benzoyl), halogeno, phosphate, acetamido, trichloroacetamido, alkylthio and variants thereof, seleno groups, and recently also telluro groups. Methods for obtaining O-5–C-1 oxocarbenium glycosylating intermediates from such compounds are illustrated in the following sections.

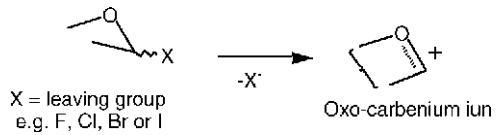
2. Mechanistic Considerations

Several mechanistic opportunities are available for designing the chemical synthesis of glycosides. The most important of these are enumerated here. Each one is then discussed in more detail. Practically all methods depend on creating some type of carbocationic centre at C-1, which can then react with a nucleophilic hydroxyl compound to give a glycoside. It is also possible to proceed through anionic intermediates. Probably, the majority of glycosylation reactions proceed via a preequilibrium to an ionic intermediate which then proceeds via a transition state to the product. These intermediates are considered next.

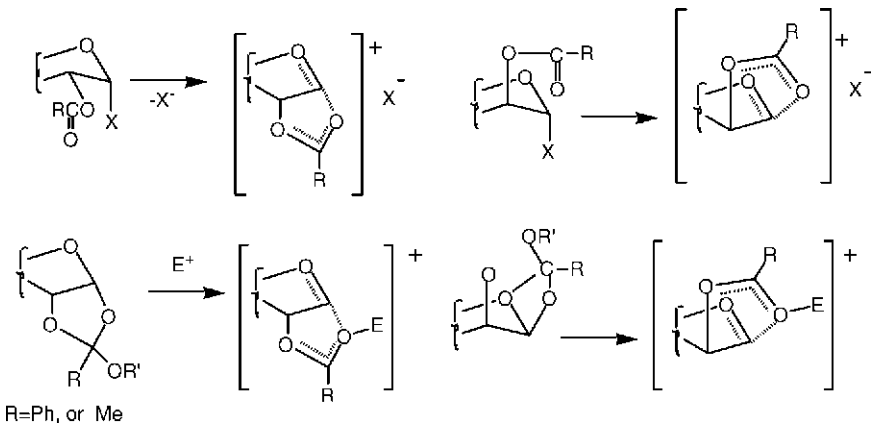
3. Via Glycosyl Oxocarbenium Ion Intermediates

These may be created by having a suitable leaving group attached to C-1. Its removal produces a carbenium ion whose extent of delocalization depends on whether the substituent at C-2 is a participating or non-participating one.

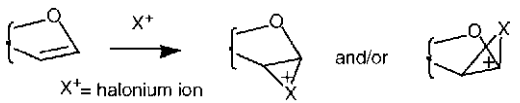
Non-participating 2-substituent:

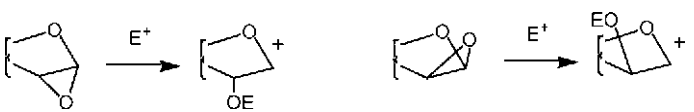


Participating 2-substituent (as from a glycosyl halide or a 1,2-orthoester):



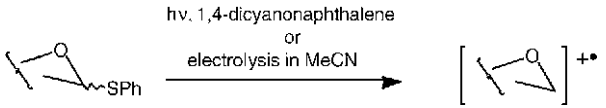
Via 1,2-Anhydro Sugars ("Brigl's Anhydrides"):





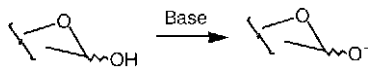
4. Via Carbocation Radicals

These may be generated photochemically or electrochemically:[2,3]



5. Via Glycosyloxy Anion Intermediates

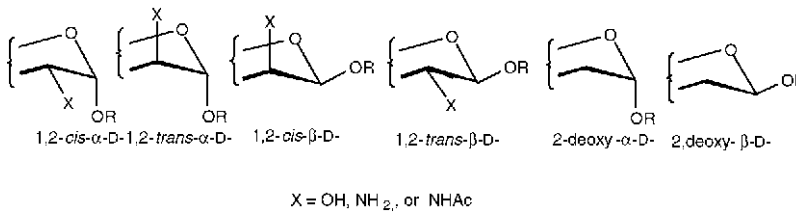
These may be generated by deprotonation of an unsubstituted anomeric hydroxyl group.



6. Stereochemical Considerations, α or β, Relative Configuration at C-1–C-2

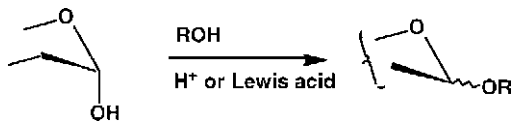
In glycoside synthesis, the relative configuration in the product of glycosylation of the two functional groups in the 1- and 2-positions is of paramount importance. This is because a *trans*-relationship between these permits steric control in the transition state, leading to the product by means of neighboring-group participation. Another most important factor is the anomeric effect, which may be used to advantage in the synthesis of 1,2-*cis*-α-D-(β-L)-glycopyranosides. 1,2-*cis*-β-D-(α-L)-Glycosidation (as in β-D-mannopyranosides) constitutes a problem, since here there is no assistance from either 2-participation or from the anomeric effect. Similar problems surface in the synthesis of 2-deoxyglycosides. The various configurations, each giving rise to its own particular problem, are illustrated for the D series in the following scheme.

These various situations and current solutions to the various problems are discussed in the following sections. First of all, the two classical methods are presented.

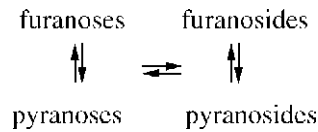


7. Fischer Glycosidation

An aldose or ketose is simply treated in solution in the presence of an acid (protonic or Lewis) with the appropriate alcohol.[4]



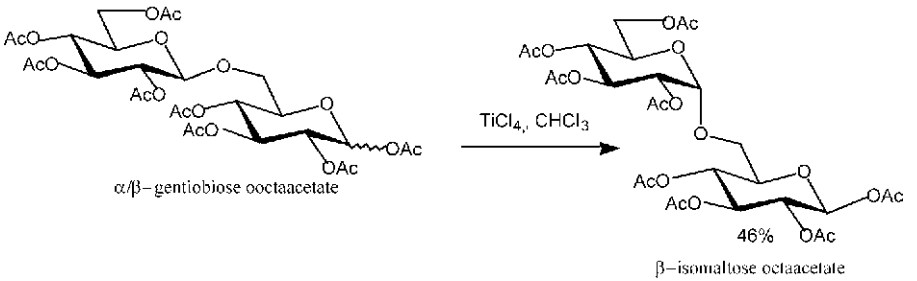
This produces a mixture of α- and β-furanosides and pyranosides. Analysis of the progress of methanolysis has shown that competing equilibria are set up between:



most probably proceeding via open-chain intermediates, α,β anomerizations, and oxocarbenium ions. Furanosides are first formed and the equilibrium subsequently changes towards pyranosides.[5] Chromatography is often required to isolate pure anomers from such reaction mixtures.

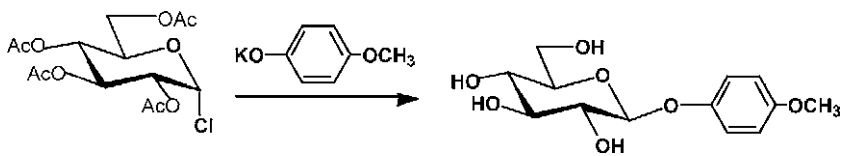
Glycosides Via Anomerization.—From the foregoing it follows that a single glycoside having the α or β configuration at C-1 may be equilibrated to a mutarotated mixture, from which another, desired anomer may be isolated. An early example of exploitation of this principle is a preparation of β-isomaltose octaacetate, an α-linked disaccharide, from the (β-linked) gentiobiose octaacetate. Since α-glycosides are generally of lower energy than β-glycosides (anomeric effect),

the method generally is most suitable for obtaining the former anomer from equilibrium mixtures.[6]



8. Michael and Koenigs–Knorr Glycosidation

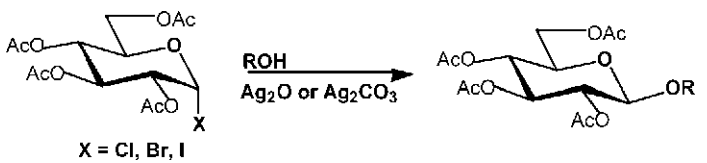
In the first successful synthesis of a 1,2-*trans* glycoside, 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl chloride was treated with the potassium salt of a phenol. Under the conditions used, deacylation occurred.



The presence of a participating acetyl group at O-2 in the pyranoside ensures production of the 1,2-*trans* glycoside.[7]

Although this is a convenient method for the preparation of aryl glycosides, it does not work so well for the synthesis of the corresponding alkyl ones.

In an extension of this method, Koenigs and Knorr subsequently reported that reaction between acylated glycosyl halides (bromides, chlorides, or iodides) with alcohols, in the presence of silver promoters (oxide or carbonate) furnished 1,2-*trans* alkyl glycosides.

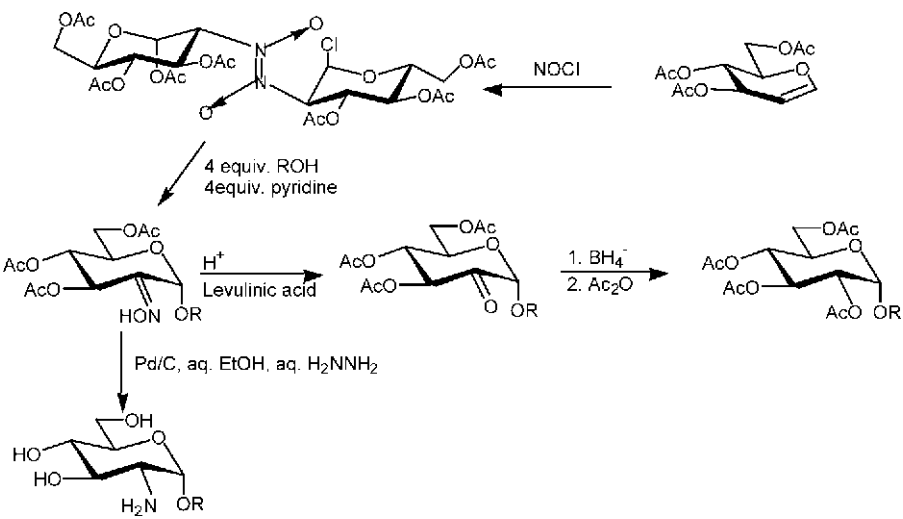


Again, the stereochemistry at C-1 is ensured by participation from the 2-position. This reaction has been most extensively reviewed.[1,8–14] An obvious disadvantage is that water is a product. This can be circumvented by using a drying agent in the reaction mixture.

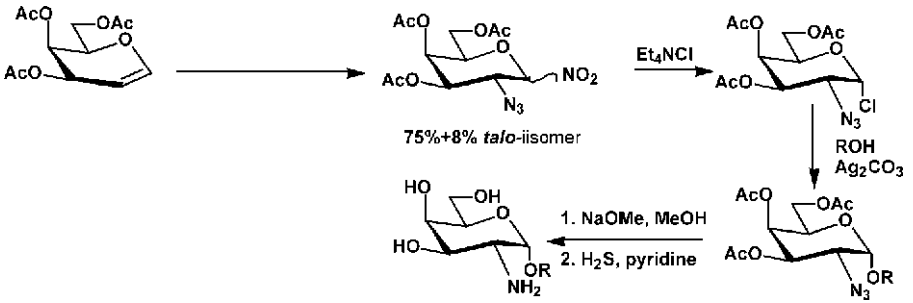
An important modification was introduced by Helferich and coworkers, consisting in using mercury salts, particularly mercury(II) cyanide or a mixture of mercury(II) cyanide and mercury(II) bromide as promoters.[15–17] Mercury(II) promoters tend to give good yields, but even in the presence of acetyl substituents at O-2, the steric outcome, α or β, is often unpredictable.

9. Modern Methods for 1,2-*cis*-α-D-(β-L)-Glycosidation

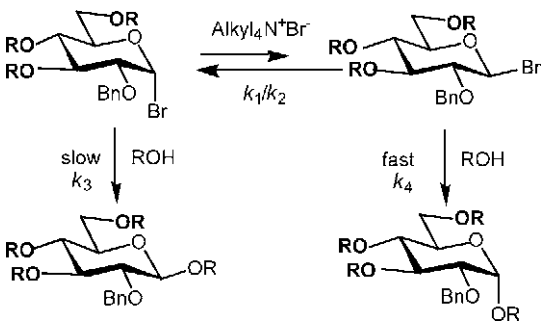
The presence of a non-participating group in the 2-position in an otherwise protected glycosyl halide will, in the presence of a mercury or silver promoter (silver triflate generally being the most efficient), give rise to an anomeric mixture from which a 1,2-*cis*-α-D-(β-L)-glycoside may be isolated. usually by means of chromatography. This approach was improved by the use of glycals, which via nitrosyl chloride adducts give the *cis* orientation at C-1 and C-2. The methodology can also be used for the synthesis of 1,2-*cis*-α-D-(β-L)–2-amino-2-deoxyglycosides.[18–22] The dimeric nitrosyl chloride adducts can also be used in a highly stereoselective synthesis of 2-amino-2-deoxy glucopyranosides.[23]



2-Amino-2-deoxy glycopyranosides may also be obtained by azidonitration of glycals using ceric ammonium nitrate:[24]



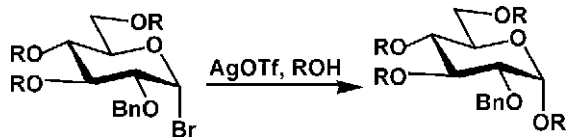
The nitrosyl chloride route to α-D-glycosides having the 1,2 *cis*-configuration has largely been superseded by the *halide assistance* glycosylation method[25] shown in the following scheme:



Provided that k_1 and $k_2 > k_4 > k_3$, the reaction produces an α-glycoside. Originally, the hydrogen bromide formed in the reaction was removed using non-nucleophilic bases. Later on it was found that the molecular sieves used to remove water from the reaction mixture also absorbed the HBr.[26]

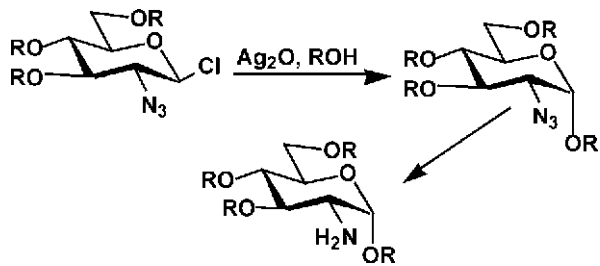
Kinetic studies have shown that the reaction proceeds via a bimolecular transition state.[27]

A disadvantage of this procedure is that it requires long reaction times, and also needs relatively reactive glycosyl acceptors. In such situations, the use of silver triflate as promoter and a glycosyl donor having a benzyl group in the 2-position of the glycosyl donor has been proved to be useful.[12,28]

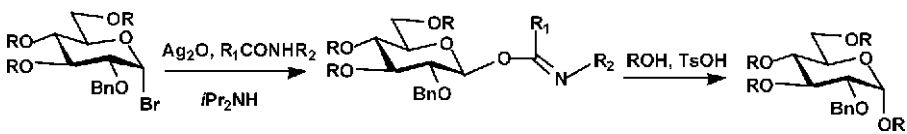


These transformations are less stereoselective than the foregoing halide-assisted reaction, but this selectivity appears to increase with diminshing reactivity of the glycosyl acceptor. Also, the reaction is more stereoselective in producing an α-D-glycoside in the galactose (and fucose) than in the *gluco* series. This has been ascribed to steric hindrance in the galactose (fucose) donors to nucleophilic attack by the glycosyl acceptor from above the pyranosyl ring, because of steric hindrance from the axial substituent at C-4 in the donor.

An extension of this methodology into synthesis of 2-amino-2-deoxy-α-D-glycosides was the introduction of the non-participating azido group at C-2 of the glycosyl donor. This has proved to be most useful in the synthesis of oligosaccharides.[29–32]



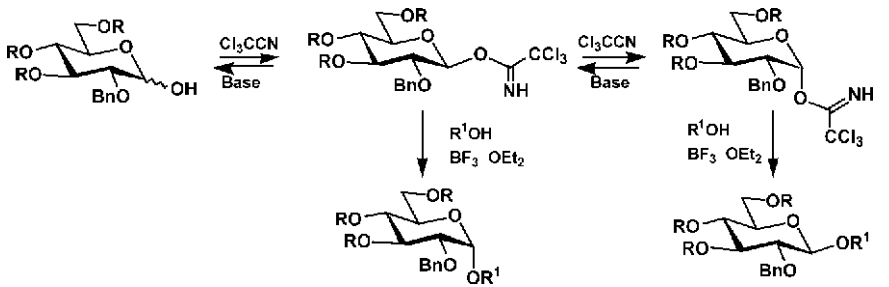
In contrast to these glycosylations, which proceed essentially through cationic intermediates on their way to transition states, the *imidate* glycosylation method is thought to go directly from imidates to glycosides via bimolecular transition-states.



A glycosyl bromide having a non-participating 2-substituent is first transformed into an imidate by reaction with, for instance, acetonitrile, promoted by silver

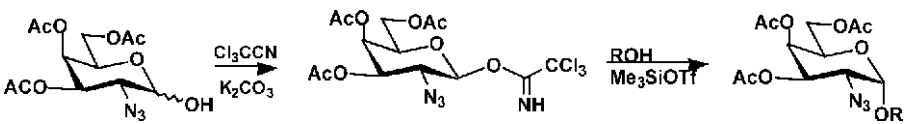
oxide in the presence of diisopropylamine. The imidate thus formed is allowed to react with an alcohol (glycosyl acceptor) in the presence of *p*-toluenesulfonic acid, producing a glycoside of inverted configuration relative to that of the imidate. Yields and stereoselectivity are close to or somewhat greater than those obtained in the halide-assisted reaction.[33,34]

A further development along these lines was the subsequent introduction of the *trichloroacetimidate* glycosylation method for the synthesis of both α- and β-glycosides.



A pyranose, having a benzyl group in the 2-position, is transformed into a β-trichloroacetimidate under kinetic control. If the reaction mixture is allowed to equilibrate, the α-trichloroacetimidate predominates in the equilibrium mixture. Reaction with an alcohol (glycosyl acceptor) then proceeds stereoselectively with inversion, leading to α- or β-glycosides, depending on the configuration at the anomeric center of the imidate. This procedure has developed into a major method in glycosylation reactions, particularly in oligosaccharide synthesis.[35]

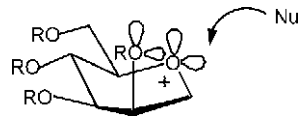
Trichloroacetimidates may alo be used for the synthesis of 2-amino-2-deoxy-α-D-glycopyranosides particularly in the galactose series.[36]



10. Modern Methods for 1,2-*cis*-β-D-(α-L)-Glycosidation

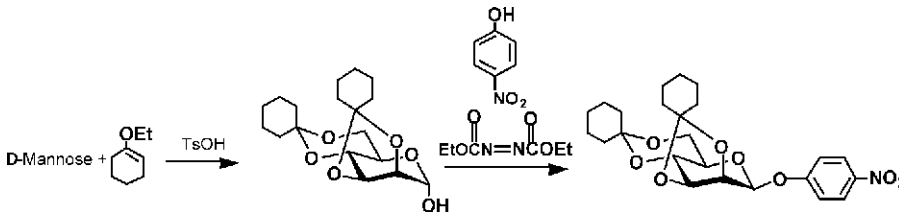
In the synthesis of glycosides having the 1,2-*cis* relative configuration, as in β-D-mannopyranosides, a participating group in the 2 position would direct the

aglycon residue to the α-anomeric position. The halide-assisted procedure would, by virtue of the anomeric effect, direct the aglycon to the same anomeric position. Also, a nucleophile incoming from the β side would encounter an electronegative vicinal oxygen atom in the 2-position, as well as a vicinal electronegative O-5 (or O-4 in furanosides) in the ring. This has been termed the Δ2 effect. All of this taken together migitates agains the formation of a 1,2-*cis*-β-D-(α-L)-glycoside.



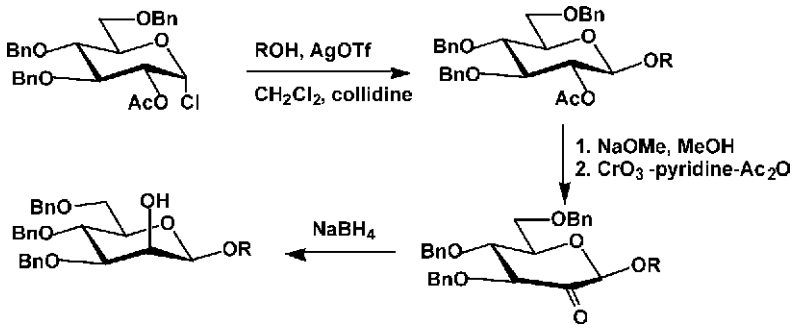
Approach of a Nucleophile From the β Side of a D-Mannopyranosyl Carbenium Ion.

Various solutions to the problem have been suggested. In a straightforward synthesis of aryl β-D-mannopyranosides, 2,3:4,6-di-*O*-cyclohexylidene-α-D-mannopyranose was treated with diethyl azodicarboxylate, triphenylphosphine, and a phenol in toluene (Mitsunobu reaction conditions) to give, after hydrolytic removal of the two cyclohexylidene groups, the β-mannosides in good yield.[37]

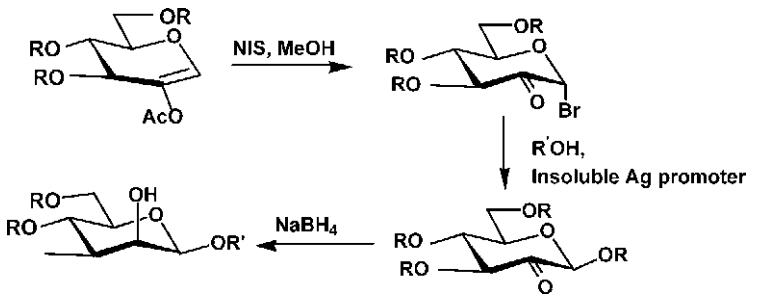


Much lower stereoselectivity was observed with aliphatic alcohols, since for these, the presence of a Lewis acid is necessary for glycosylation to proceed.

Many proposals have been made for syntheses of general applicability for β-D-mannopyranosides, especially in oligosaccharide synthesis. One such scheme is shown here. A stereocontrolled synthesis is performed of a β-D-glucopyranoside having an arrangement of protecting groups that allows O-2 to be selectively deprotected. The acyloxy group at C-2 also ensures high β-selectivity in the glycosylation step, through participation at C-1 of the carbenium-ion intermediate. Inversion at the 2-position by oxidation followed by reduction then gives a β-D-mannopyranoside:[38–40]



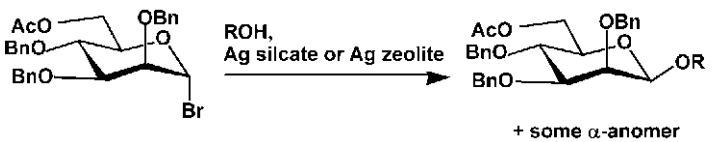
Another route, which also proceeds via a 2-oxo-β-D-pyranoside, starts from a 2-acetoxyglycal:[41,42]



The insoluble promoter can be either silver silicate[43] or silver zeolite.[44]

These two routes are reliable, but obviously lengthy, and a number of other proposals starting from D-mannose precursors are shown next.

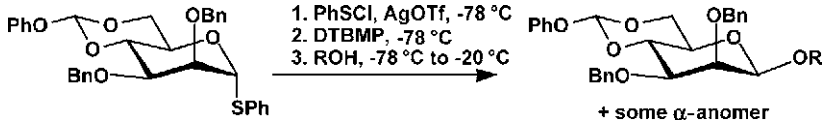
Insoluble promoters may also be used in *direct* synthesis of β-D-mannosides from mannosyl halides:



The most successful insoluble silver promoters used thus far in this context have been silver silicate[43] and silver zeolite.[44] Other insoluble promoters described, earlier starting from α-mannosyl bromides carrying non-participating substituents at O-2 are: silver oxide,[45–47] silver oxide and silver perchlorate,[48] silver salicylate,[49] and silver carbonate.[50] The point of using an *insoluble* promoter together with an

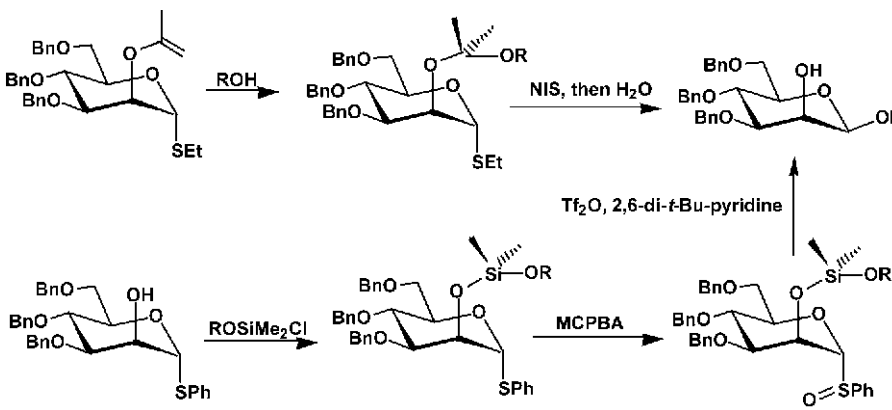
α-mannosyl halide is that complexation of the insoluble promoter with an α-halide leads to nucleophilic attack from the β side more rapidly than anomerization to a β-mannosyl halide–silver complex, leading to an α-mannoside.

Glycosidation with *apparent* S_N2 type stereochemistry is achieved by reacting a phenyl 1-thio-α-D-mannopyranoside, carrying a non-participating 2-substituent, with phenylsulfenyl triflate in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) at −78 °C to first give an α-triflate, presumably via a a carbenium ion. Upon adding the glycosyl acceptor, the triflate then undergoes favored attack of the nucleophile from the β side, producing a β-D-mannopyranoside.[51a]



Originally, β-D-mannopyranosides were produced, also via α-triflates, by first treating the corresponding mannopyranosyl phenyl sulfoxide at −78 °C and then adding the glycosyl acceptor with triflic anhydride in the presence of DTBMP. One disadvantage of this method was the oxidation step from the phenyl 1-thiomannoside to the sulfoxide.[51b,52] The use of 1-thioglycosides and sulfoxides in glycosylation reactions is discussed separately later.

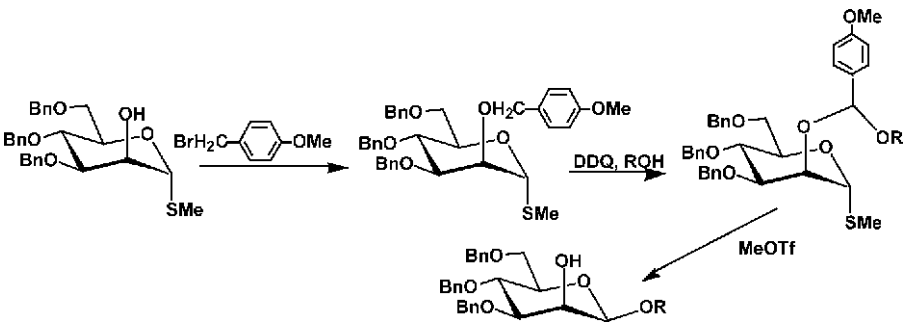
Yet another approach to the synthesis of β-D-mannopyranosides is the use of *tethered* glycosylation, also known as *intramolecular aglycon delivery*. Two such approaches are shown next:



In the first synthesis,[53] the 2-propenyl ether is made from the corresponding acetate using Tebbe's reagent.[54] Reaction with a hydroxyl compound gives a mixed

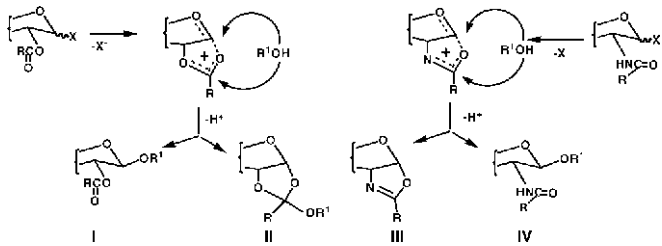
acetal which, upon activation at the anomeric center with *N*-iodosuccinimide gives an intermediate carbenium ion. This, because of the tether, can undergo attack only from the β side. In the second synthesis,[55] a silicon tether is used. The hydroxyl compound (ROH) is converted into a chlorodimethylsilyl ether by reaction with butyllithium and dichlorodimethylsilane. The phenylthio group is then oxidized with *m*-chloroperoxybenzoic acid to the corresponding sulfoxide, which is then activated with triflic acid. Again the only possible anomeric attack is from the β side.

In a third variant on this theme, methyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside is converted into a *p*-methoxybenzyl acetal by first etherifying the 2-OH group with *p*-methoxybenzyl bromide and then treating the resulting *p*-methoxybenzyl ether with a hydroxyl compound in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Activation of the methylthio anomeric center with methyl triflate then produces the β-D-mannopyranoside as the only possible glycoside, again because of the acceptor being tethered to the β side of the mannopyranoside.[56]



11. Modern Methods for 1,2-*trans*-α-D-(β-L)-Glycosidation

This configuration concerns chiefly the mannose and rhamnose series. Most glycosidations to give this stereochemistry at C-1 and C-2 depend on steric control by neighboring-group participation from the C-2 substituent and are chiefly further developments of the classical Koenigs–Knorr reaction. The glycosidation methods and some mechanistic consideration are quite similar to those for 1,2-*trans*-β-D-(β-L) glycosidations. These are discussed in Section II.12.

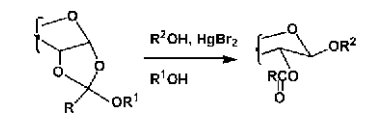


12. Modern Methods for 1,2-*trans*-β-D-(α-L)-Glycosidation

a. Orthoesters and Oxazolines.—Glycosylations using glycosyl halides having a participating acyloxy group in the 2-position proceed via a dioxolenium or dioxazolium cation. These are able to react with an alcohol to produce either a 1,2-*trans* glycoside (I or IV), an orthoester (II), or an oxazoline (III) as shown here.

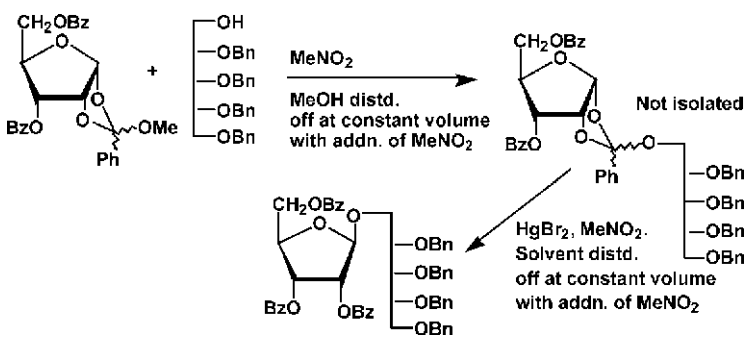
This knowledge led to the development of the orthoester and oxazoline methods for producing 1,2-*trans* glycosides.

In the *orthoester* method, a simple orthoester is condensed with a nonvolatile alcohol in the presence of mercury(II) bromide to yield a 1,2-*trans*-linked glycoside:[57]



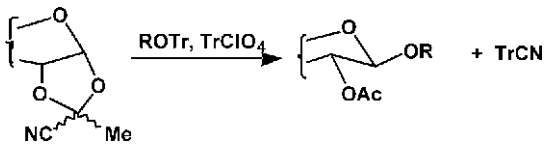
R = Me, Ph. R^1 = Me, Et, *t*-Bu. R^2 = carbohydrate moiety

An example is shown here:[58]

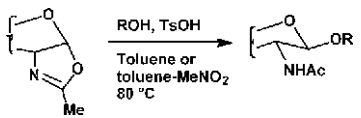


However, it was later shown that a more rapid route to 1,2-*trans*-linked furanosides is possible from 1,2-*trans* acetates with an alcohol, using promotion by trimethylsilyl triflate.[59,60]

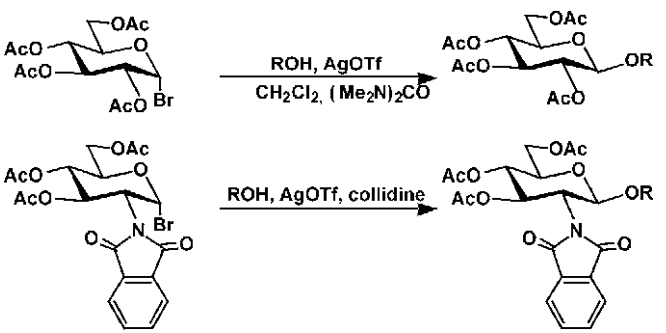
A further development of the orthoester method is the condensation of a cyanoorthoester with a trityl ether. A disadvantage of this method is having to prepare the cyanoorthoester before the glycosidation.



In the *oxazoline* method, an oxazoline is treated with an alcohol in the presence of *p*-toluenesulfonic acid at 80 °C to produce a 2-acetamido-2-deoxyglycoside.[61]



b. Silver Triflate-Promoted Glycosylations.—For glycosylations performed in the presence of an acyl or phthalimido group at the 2-position of a glycosyl halide, the most commonly used promoter is silver triflate.[62–64] These glycosylation methods have been of considerable importance for the development of oligosaccharide synthesis.



A disadvantage of the phthaloyl group for *N*-protection and neighboring-group participation is the harsh procedure required for its conversion into an amino group, namely, by heating with hydrazine hydrate or ethylenediamine. This shortcoming may be overcome by the use of 4,5-dichlorophthaloyl as the *N*-protecting group. Conversion into an amino group is achieved by treatment with ethylenediamine in an alcoholic solvent under milder conditions than those used for the phthaloyl group. The 4,5-dichlorophthaloyl group is stable under normal *O*-deacetylation conditions.[65] Tetrachlorophthaloyl has been proposed for the same purpose. It is, however, more labile under deacetylation conditions.[66,67]

The amount of base used in these reactions is critical. In studies of the effect of added collidine in the first of the two foregoing reactions (acyl at O-2), it was found that the presence of more than 1 mol/mol collidine:alcohol promoted the formation of orthoesters rather than glycosides. Benzoylated, rather than acetylated glycosyl bromides tended to give better yields and more β-stereoselectivity than did the corresponding acetylated ones. Provided that an adequate amount of molecular sieves were present in the reaction mixture, the addition of a base such as collidine was often unnecessary. This observation indicated that orthoesters are intermediates in these reactions and that, at least in some of these them, weakly acidic conditions are required in order to obtain high yields of β-glycosides.[68]

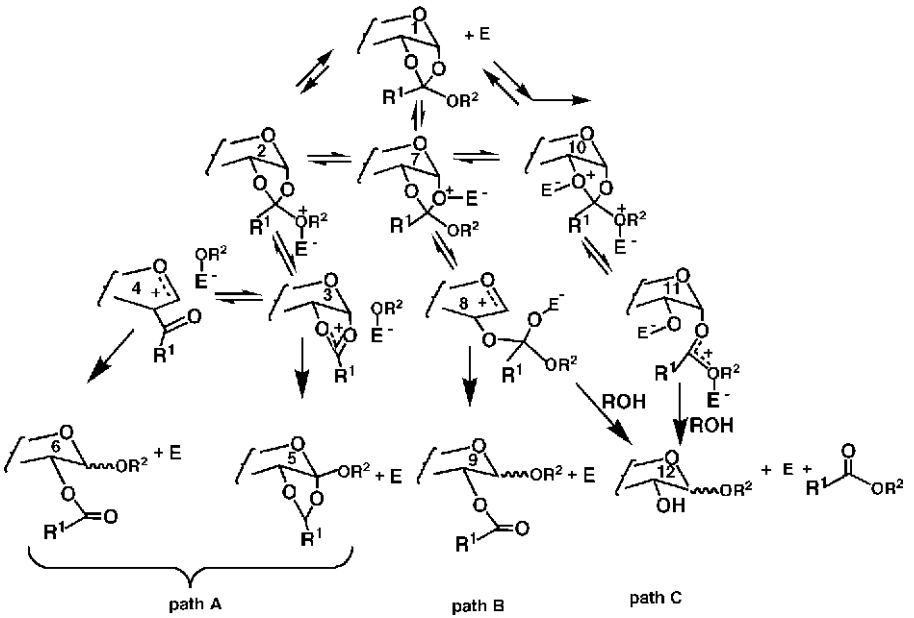
These observations subsequently led to studies on Koenigs–Knorr-type glycosylations employing promotion by mercury salts and silver triflate. The studies were based on product composition rather than on kinetics.[69]

The glycosyl halides used were 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide, and 3,4,6-tri-*O*-acetyl-2-*O*-benzoyl-α-D-glucopyranosyl bromide. The alcohols used were mono-. di-, and tri-chloroethanol, and the promoters were $Hg(CN)_2$, 1:1 $Hg(CN)_2$–$HgBr_2$, and AgOTf. The product compositions obtained were rationalized by the following scheme which shows the possible consequences of attack of the electrophile on each of the three oxygen atoms of the intermediate orthoester. The products on the bottom line were observed, in varied proportions in the various experiments, along also (in some experiments) with (1→2)-linked disaccharides arising from products having free 2-OH groups.

In the mercuric ion-promoted reactions, decreasing electron density on the oxygen atom of the alcohol gave an increase in the proportion of α-glucosides and a decreased rate of formation of β-glucosides.

The rate-determining step in path A is probably the rearrangement of the ion pair 3 to the β-glucoside. Path B probably unimportant.

Path C is only important in those instances where compounds having 2-OH free are used and products from them (disaccharides) are formed.



The silver triflate-promoted reactions demonstrate the importance of the type of acid produced. There is a much weaker trend towards the α-glucosides with increased chloro substitution on the alcohol (decreasing its nucleophilicity), probably due to an increased rate of rearrangement of ion pair 3 into glucoside 5 by the strong acid.

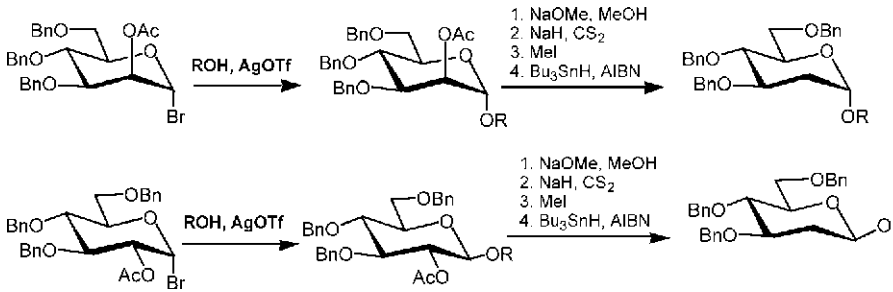
Glucosides having 2-OH free (12) and products from them were not observed when using 3,4,6-tri-*O*-acetyl-2-*O*-benzoyl-α-D-glucopyranosyl bromide as the glycosylating agent. This behavior was rationalized in terms of increased stabilization, on account of R^1 being phenyl rather than methyl in cyclic cation 3, as compared to the open forms 4, 8, and 11.

From a preparative point of view, silver triflate promotion, and the use of glycosyl halides having a benzoyl group at O-2, with dichloromethane alone or in admixture with toluene, is recommended.

13. 2-Deoxyglycosides

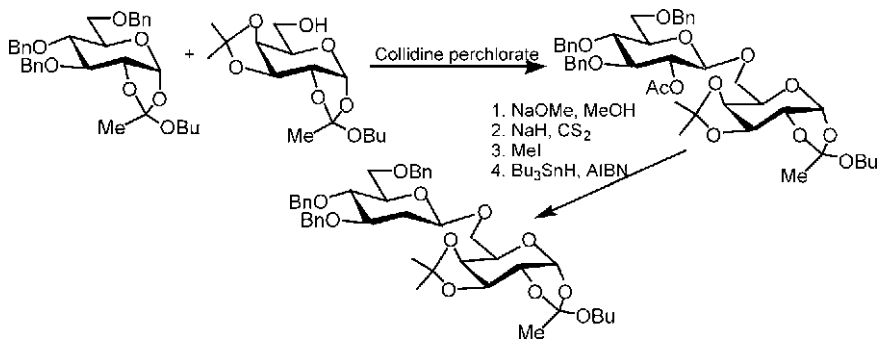
A general review has been given by C. H. Marzabadi and R. W. Franck.[70]

a. From Glycosides Having O-2 Substituents.—One inherent difficulty in the synthesis of 2-deoxyglycosides is that the absence of a participating substituent at C-2 means that there is no directing effect from a 2-substituent on the stereochemistry of nucleophilic attack on an intermediate O-5–C-1 oxocarbenium ion. This can be circumvented by having a directing O-2 substituent which subsequently is subjected to regiospecific deoxygenation, as exemplified here:

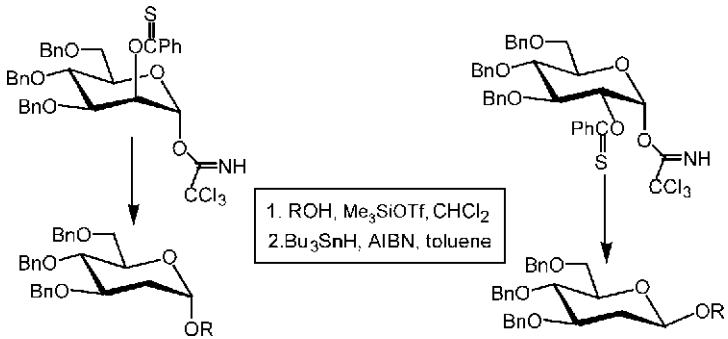


Thus glycosylation with a 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-manno- or gluco-pyranosyl bromide leads to 1,2-*trans*-α-D-mannopyranosides and 1,2-*trans*-β-D-glucopyranosides, respectively, with acetoxy functions at C-2. Deoxygenation at this position by deacetylation, followed by xanthation and reduction with tributyltin(IV) hydride in the presence of azoisobutyronitrile (Barton–McCombie procedure) will give 2-deoxyglycosides with the α-D-(β-L-) and β-D- (α-L-) configurations respectively.[71]

Similar results are obtained starting from 1,2-orthoesters:[72]



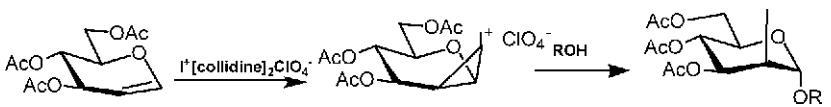
A 2-*O*-thiobenzoyl group in pyranosides has found similar use:[73]



The 1,2-anhydro sugar (Brigl's anhydride) approach, developed by Danishefsky and coworkers (see Section V) also lends itself to the deoxygenation procedures of α- and β-pyranosides having a single free OH group at C-2 and the remaining positions suitably protected.

Another difficulty in making 2-deoxyglycosides is that acidic conditions may cause hydrolysis or anomerization, as these glycosides are much more susceptible to such conditions than are the correponding pyranosides having an oxygen or nitrogen function at C-2.

b. 2-Deoxy-α-D-(β-L-)-glycosides From glycals.—In 1965, Lemieux and Morgan found that an acetylated glycal can be converted into an intermediate iodononium ion, which by reaction with an alcohol is converted into a 2-deoxy-2-iodoglycoside.[74]



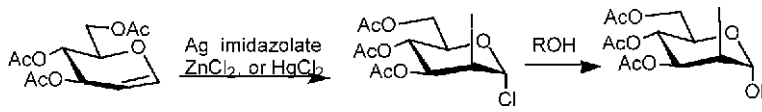
[For safety reasons it is probably advisable to substitute their iodonium(collidine)$_2$ perchlorate, which is a potential explosive, with the corresponding triflate, which is made in the same manner as the perchlorate)].

The 2-deoxy-2-iodonium glycoside may then be reduced to a 2-deoxyglycoside by standard procedures.[75,76]

Subsequent development of the use of glycals to obtain the intermediate iodonium cation include the following:

The use of *N*-bromosuccinimide and *N*-iodosuccinimide in order to obtain the intermediate 2-bromo and 2-iodo compounds.[77–79]

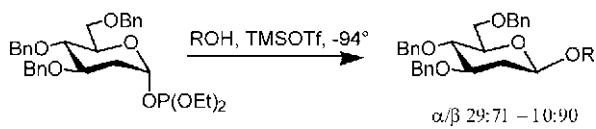
The use of silver imidazolate and zinc chloride[(or mercury(II) chloride] together with iodine, and then adding the alcohol in a one-pot procedure, which affords the 2-deoxy-2-iodoglucosides.[80]



c. 2-Deoxy-β-D-(α-L-)-glycosides.—Stereospecific synthesis of these 2-deoxyglycosides has long been a most difficult problem because the cationic 2-deoxy intermediates tend to give α-D- (β-L-)-glycosides preferentially. Chromatographic separations are consequently required to obtain the β-D-(α-L-) anomers, often in only modest yield. On the other hand, glycosidation of 2-deoxy-3,4,6-tetra-*O*-acylglycosyl halides with an alcohol under promotion by silver silicate or by silver zeolite, proceeds via a bimolecular transition-state. The resultant predominant anomeric inversion leads to better yields of β-D-(α-L-)–2-deoxy glycosides.[81–84]

A later approach to this problem has been shown already (II.13.a).[73]

A preponderance of β-D-(α-L-)-glycosides has been reported from the α-D-phosphite shown here:

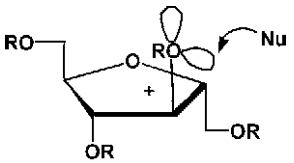


Other 1-phosphites have been shown to give varying α,β ratios.[70]

14. β-D-Fructofuranosides

β-D-Fructofuranosides occur abundantly in Nature. They occur in plants, examples include inulin, levan, and sucrose, and also in bacterial cell-walls and capsules such as those of species of *Streptococcus, Haemophilus, and Yersinia*.[85]

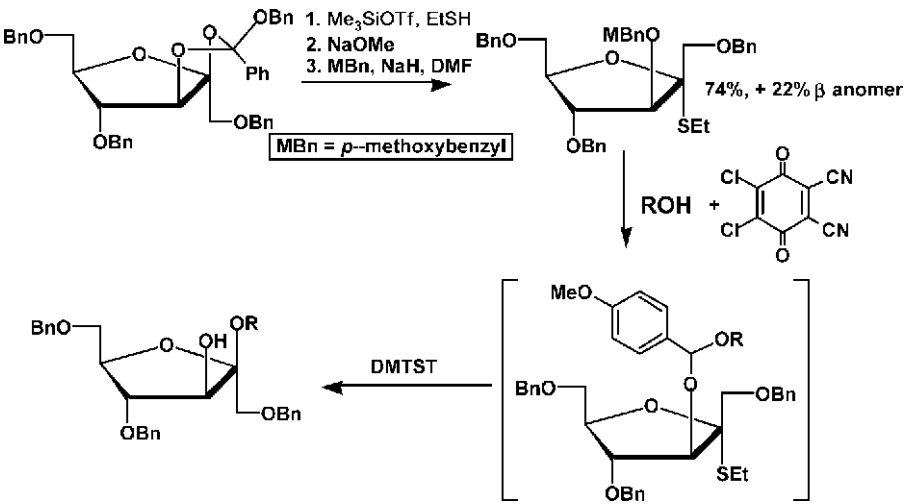
Unfortunately, synthesis of their glycosides presents the same type of problem as that in the synthesis of β-mannosides, namely difficulty of approach of a nucleophile from the β side:



Attempts to overcome this obstacle have included the use of ethyl 1,3,4,6-tetra-*O*-benzyl-2-thio-D-fructofuranoside as the glycosyl donor, and use of thiophilic promoters. Predictably, α,β mixtures were obtained, with the α anomers predominating.

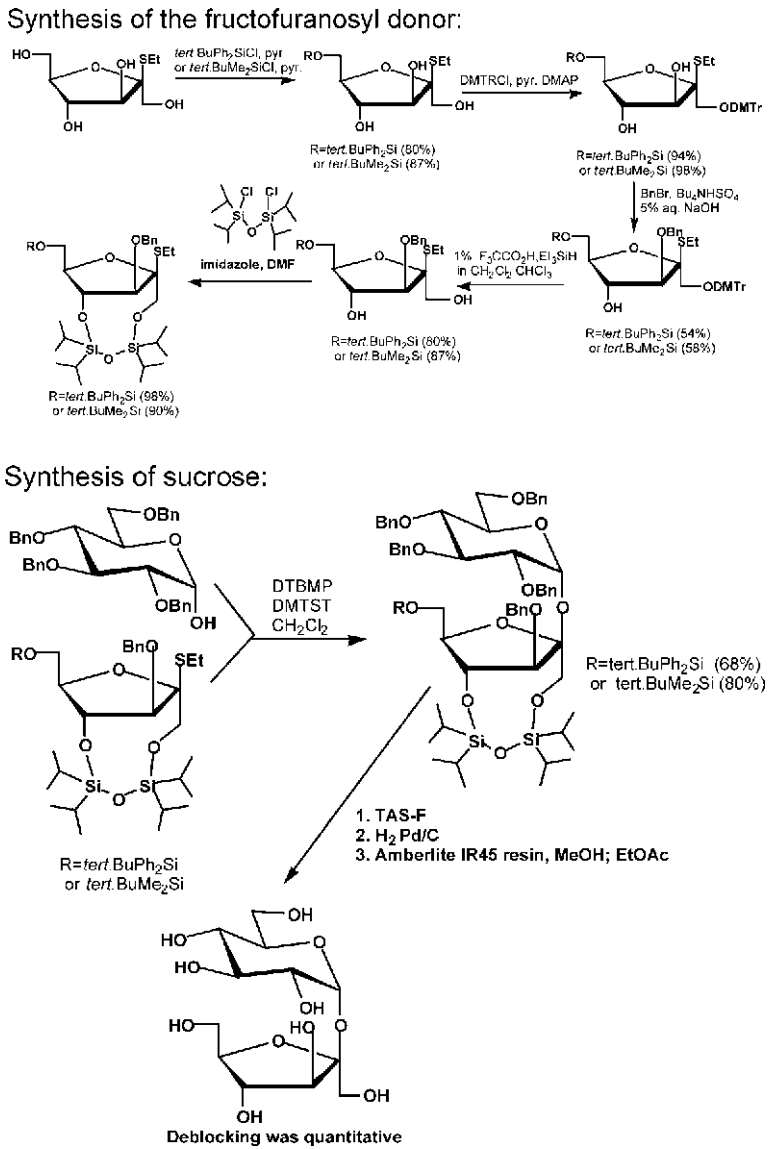
In contrast, the corresponding 1,3,4,6-tetra-*O*-benzoyl-2-thio-D-fructofuranoside produced exclusively the α anomers, demonstrating that there is no difficulty in producing α-D-fructofuranosides as long as the fructosyl donor has a participating 3-*O*-substituent.[86a]

Recourse has therefore been taken to adopt the strategy successfully used for β-mannosides, employing intramolecular aglycon delivery, namely, using a tether that forces the nucleophile to approach the oxocarbenium intermediate from the β side:[86b]



The alcohols used were ethanol, methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside, and 4-nitrophenylethyl 2-azido-2-deoxy-4,6-*O*-benzylidene-α-D-mannopyranoside. A range of promoters were tried: dimethyl(methylthio)-sulfonium triflate, methyl triflate, iodonium dicollidine perchlorate, and iodonium dicollidine triflate. Yields were in the 30–70% range.

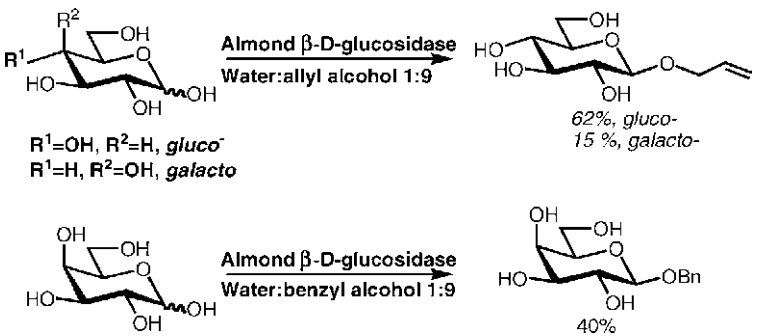
Subsequently another method was developed for forcing the nucleophile to approach the anomeric center of a fructose oxocarbenium ion from the β side, namely to block the furanoside with bridging substituents so as to make α approach impossible. The method is illustrated here in a benchmark synthesis of sucrose:[87]



15. Enzymatic Methods

Two main alternatives are available for enzymatic synthesis of glycosidic bonds. These are (a) use of glycosidases that in concentrated solutions of an appropriate mono- or oligo-saccharide produce reversion products, or transglycosidases that transfer one glycosyl unit to another with minimal hydrolysis occurring, or (b) the use of glycosyltransferases that effect transfer of a carbohydrate moiety from an appropriate nucleotide sugar to a suitable acceptor. The following discussion focuses on the enzymatic glycosylation as applied to synthesis of di- and oligosaccharides.[88,89]

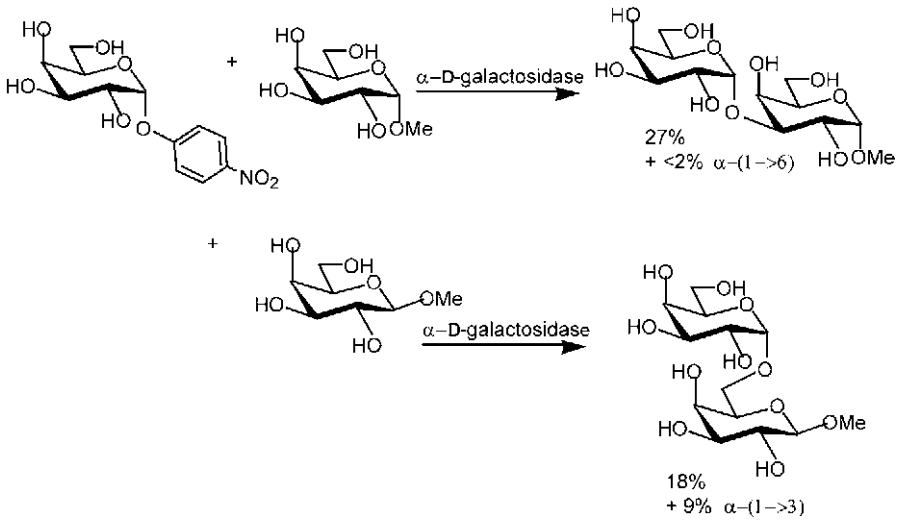
a. Use of Glycosidases.—Glycosidases.are hydrolytic enzymes that transfer either a glycosyl group or an oligosaccharyl group to water. Those transferring a glycosyl group are termed exo-enzymes and hydrolyze one unit at a time from the non-reducing end of an oligo- or poly-saccharide. The second type, termed endo-enzymes, cleave elsewhere in the oligosaccharide chain and transfer an oligosaccharyl group to water. These reactions are reversible so that, under thermodynamic control and using limited quantities of water, the transfer may instead be onto a carbohydrate or another alcohol.[90]



However, the thermodynamic (equilibrium approach) generally does not provide yields in excess of 15%.

Glycosidases may also be used in kinetically controlled glycosylations. These reactions depend on trapping by a glycosyl acceptor of a reactive intermediate. Suitable donors for such glycosylations include aryl glycosides, glycosyl fluorides

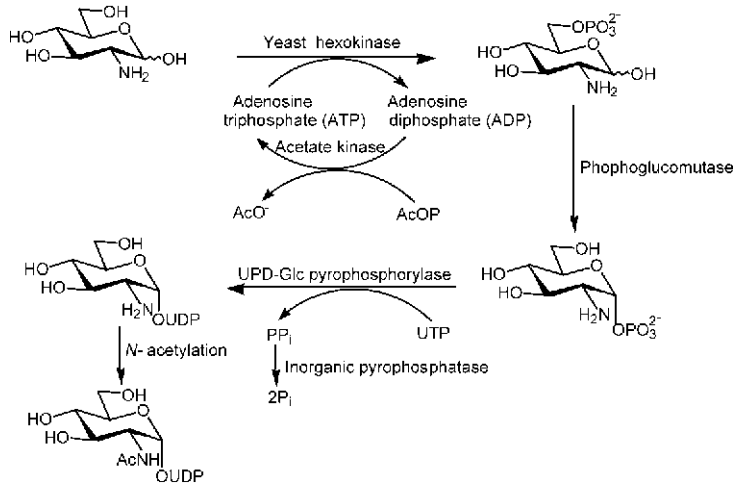
and di- or oligo-saccharides. Yields are normally between 20 and 40%. The following is a typical example.[91]



Thus, although these transfers generally produce (1→6) linkages, control of selectivity can be achieved by selection of the appropriate combination of donor and acceptor.[92,93]

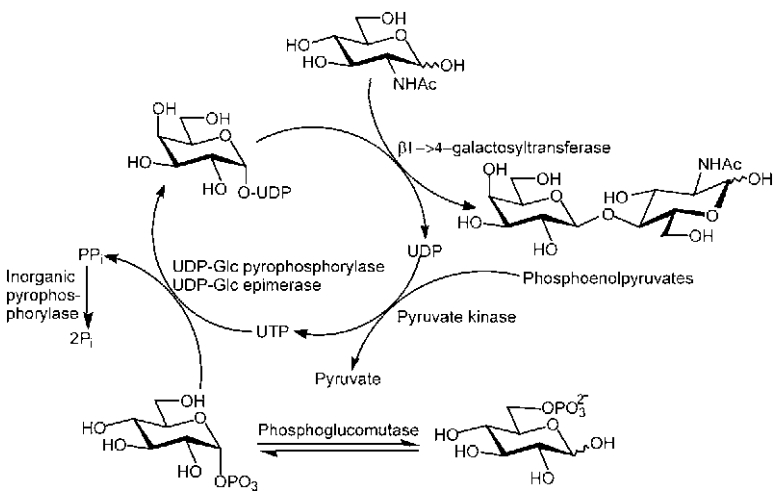
b. Use of Glycosyltransferases.—In the biosynthesis of oligosaccharides there are two groups of enzymes, those of the non-Leloir and those of the Leloir pathways.[94] In the Leloir biosynthetic pathways the glycosyltransferases utilize eight main nucleoside sugar mono- and di-phosphates, namely UDP-D-Gal, UPD-D-GalNAc, UDP-D-Glc, UDP-D-GlcNAc, GDP-D-Man, GDP-L-Fuc, UDP-D-GlcA, and CMP-NeuAc. Other monosaccharides present in Nature include arabinose, xylose, and various deoxy sugars, including 3-deoxy-D-*manno*-octulosonic acid. The enzymes involved in the biosynthesis of polysaccharides containing these monomers have, however, not been much exploited for enzymatic synthesis.

Both chemical and enzymatic syntheses have been reported of nucleoside sugar phosphates.[88] An enzymatic synthesis of UDP-D-GlcNAc is shown next:[95]

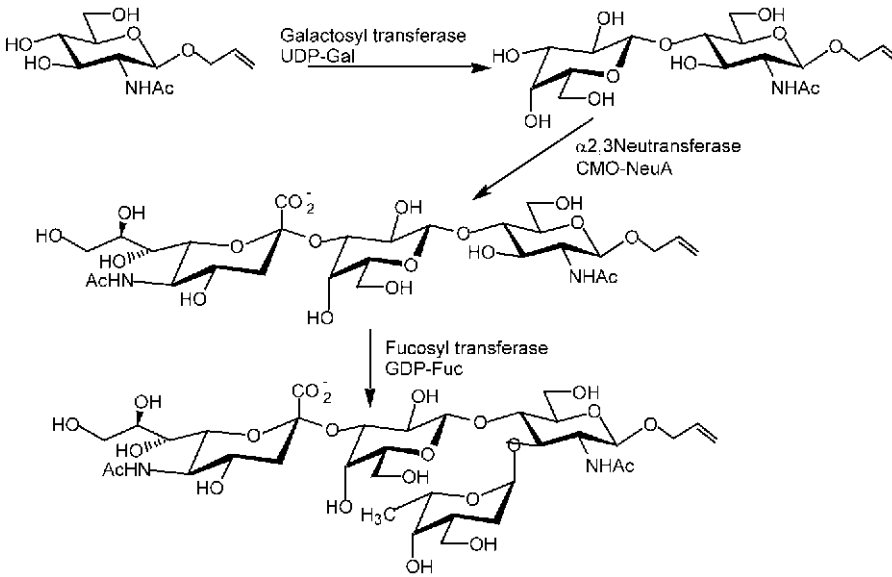


The driving force in the step producing UDP-GlcNH_2 is provided by inorganic pyrophosphatase.

The high cost of sugar nucleotides and also product inhibition by released nucleotide mono- and di-phosphates have brought forth the concept of regeneration *in situ* of the sugar nucleotide otherwise spent. An early example is the enzymatic synthesis synthesis of *N*-acetyllactosamine.[96]



Interaction between the glycoprotein E-selectin (expressed on the surface of endothelial cells) and the sialyl Lewis^x ligand structures on the surface of neutrophils is a major event in inflammation, infection, and metastasis. Both chemical and enzymatic syntheses have been described for the synthesis of the sialyl Lewis^x structure. A summary of the general strategy used in chemoenzymatic synthesis is shown here. Extensive *in situ* regenerations of the sugar nucleotides are not shown in the scheme.[97]



III. 1-Thioglycosides

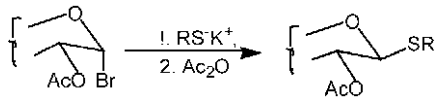
Replacement of the exocyclic anomeric oxygen atom in a glycoside by sulfur or selenium produces the corresponding 1-thio- or a 1-seleno-glycoside. Certain 1-thioglycosides occur in Nature and others are important as glycosidase inhibitors.[98–100]

A major use for 1-thio- and 1-seleno-glycosides is in the synthesis of O-linked glycosides and oligosaccharides.[101]

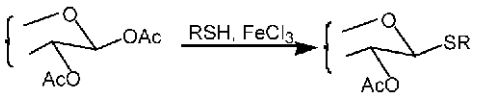
1. Preparation

a. Reaction of Acylated Glycosyl Halides with Thiolate Anion.—Reaction of an acylated glycosyl halide with a thiolate anion produces a 1-thioglycoside,

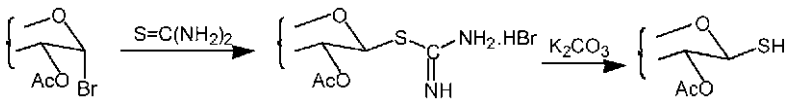
normally having the 1,2-*trans* configuration. On account of the alkaline conditions used, reacetylation of the product is usually required.[102–110]



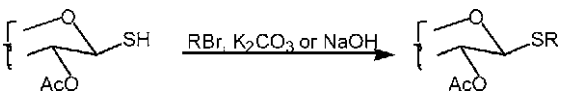
b. Reaction of Acylated Aldoses with Thiols in the Presence of Lewis Acids.—In the presence of Lewis acids, fully acetylated pyranoses react with thiols. Participation by the 2-substituent makes the 1,2-*trans* acetates react faster than that the 1,2-*cis* ones, and the 1,2-*trans* configuration predominates in the products. Instead of thiols as such, stannyl or trimethylsilyl deriatives may be used.[111–120]



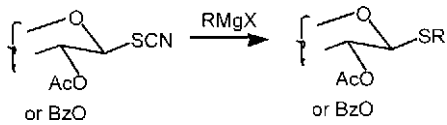
c. Reaction of Acylated Glycosyl Halides with Thiourea Intermediates. Reaction of 1-Thioaldoses with Alkyl Bromides or Alkyl Iodides.—Treatment of an acylated glycosyl halide with thiourea produces a pseudothiouronium salt, which upon hydrolysis with aqueous potassium carbonate yields an acylated 1-thioglycopyranose having the 1,2-*trans* configuration.[103]



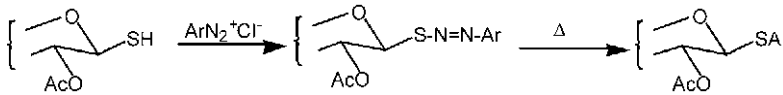
Reaction of the tetra-*O*-acetyl-1-thiopyranose with an alkyl bromide or iodide yields an alkyl-1-thioglycoside. This method is particularly useful when the appropriate thiol is not available.[121,122]



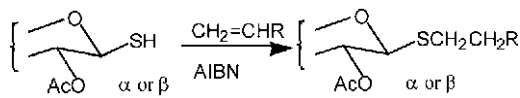
d. Reaction of Glycosyl Thiocyanates with Grignard Reagents.—Reaction of acetylated glycopyranosyl halides with potassium thiocyanate produces the corresponding 1-thiocyanates.[121] Reaction of these at −40 °C with Grignard reagents affords 1-thioglycosides.[123]



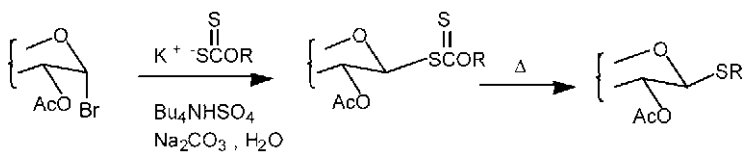
e. Reaction of 1-Thioaldoses with Aryldiazonium Salts.—Acylated aryl 1-thioglycosides may be obtained by reaction of, for example, 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose with an aryldiazonium salt, and then decomposing the intermediate diazonium compound by thermal treatment.[121,124]



f. Radical Addition of 1-Thioaldoses to Alkenes.—Reaction of acetylated 1-thioaldoses with alkenes in the presence of azobis(isobutyronitrile) (AIBN) produces acylated 1-thioglycosides.[125]

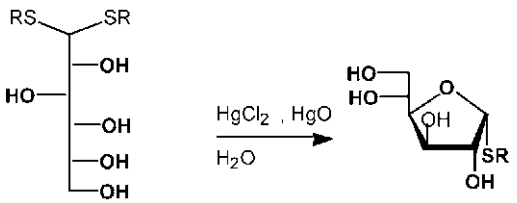


g. Decomposition of Glycosyl Xanthates.—Treatment of glycopyranosyl halides with a potassium alkylxanthate,[121,126] either in solution or under phase-transfer conditions,[127] or treatment of 2,3,4,6-tetra-*O*-benzylglycopyranoses with *p*-toluenesulfonyl chloride and potassium alkylxanthates under phase-transfer conditions[128] produces 1-dithiocarbonates (xanthates), which are readily decomposed to 1-thioglycosides by thermal treatment in a melt.



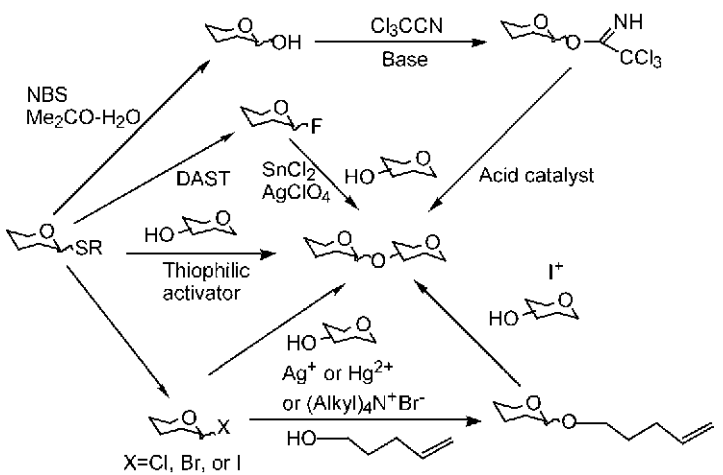
h. Partial Hydrolysis of Dithioacetals.—Partial desulfurization of dithioacetals by mercury(II) salts is useful for obtaining 1-thioglycosides having the

1,2-*cis* configuration not normally obtained by the foregoing methods, and also, as it involves thermodynamic ring-closure, for the preparation of furanosidic thioglycosides.[103,129]



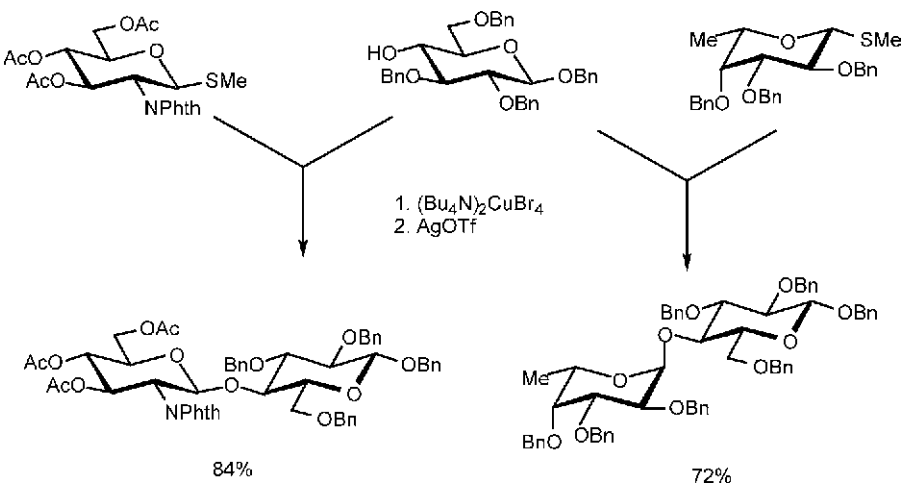
2. Reactions

a. 1-Thioglycosides as Glycosyl Donors.—1-Thioglycosides are exceptionally versatile donors in glycosylation reactions. They can be converted directly into *O*-glycosides by reaction with hydroxylic compounds in the presence of a thiophilic promoter. Furthermore, they can readily be converted into other glycosyl donors, such as glycosyl chlorides, bromides, iodides or fluorides, trichloroacetimidates, or pentenyl glycosides. This allows considerable flexibility, as in the construction of oligosaccharides and glycoconjugates.The various possibilities are sketched here.

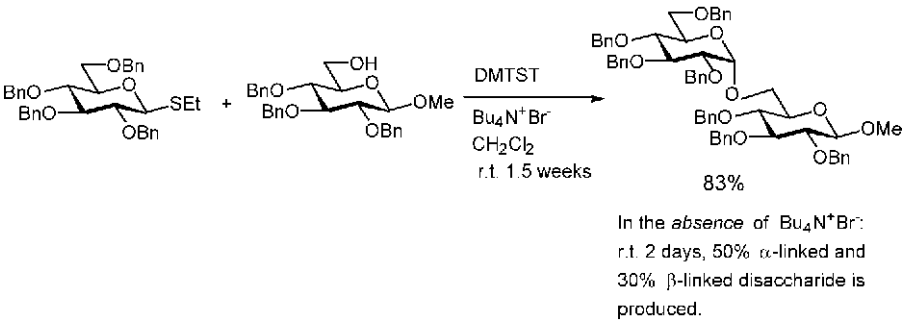


Under *direct* activation by thiophilic promoters, 1-thioglycosides react with hydroxylic compounds to gives glycosides. Several other possibilities are available. Thus 1-thioglycosides may be converted into glycosyl bromides, chlorides, or (transient) iodides. These may then serve as glycosyl donors by activation with Ag^{+}, Hg^{2+}, or a tetraalkylammonium bromide (Section II). They may also be converted into 4-pentenyl glycosides by use of these same promoters; the pentenyl glycosides may in turn be activated by iodonium ion to become glycosyl promoters in glycosidation reactions. Other alternatives include the conversion of thioglycosides into glycosyl fluorides, and use of these latter as glycosyl donors. Finally, 1-thioglycosides may be converted into compounds having 1-OH free. These may then be converted into imidates or trichloroimidates to produce yet another glycosyl donor. In oligosaccharide chemistry this gives a wide spectrum of possibilities for synthesis.

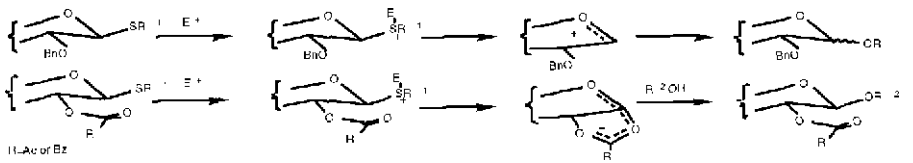
b. *In situ* Generation of Glycosyl Halides From 1-Thioglycosides.—In the presence of a hydroxylic compound and silver triflate as promoter, the reaction of a thioglycoside with $(Bu_4N)_2CuBr_4$ converts it *in situ* into a glycosyl bromide, which then produces a glycoside.[130]



Similarly, reaction of a thioglycoside with a hydroxylic compound in the presence of an excess of a tetraalkylammonium bromide and the thiophilic promoter dimethyl(methylthio)sulfonium triflate (DMTST) proceeds with high stereoselectivity.[131–133]



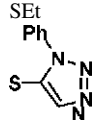
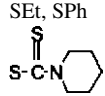
c. Direct Use of 1-Thioglycosides as Glycosyl Donors Using Thiophilic Activators.—The general course of glycosylation with benzylated or acylated 1-thioglycosides is shown in the following scheme.



The *direct* use of 1-thioglycosides as donors in glycosylation reaction was pioneered by Ferrier and coworkers.[134] They reported that phenyl 1-thio-β-D-glucopyranosides in the presence of mercuric acetate could be solvolyzed in methanol or reacted with other hydroxylic compounds to give glycosides in useful yields. These observations sparked the discovery of a range of promoters. These included $Cu(OTf)_2$,[135] $Hg(OBz)_2$,[136] $Hg(NO_3)_2$,[137] $Pd(ClO_4)_2$,[138,139] *N*-bromosuccinimide (NBS),[140] PhHgOTf,[141] and $HgCl_2$.[142] However, these various promoters did not give the consistently high yields desirable for oligosaccharide synthesis.

This situation was substantially improved by Lönn's demonstration that methyl triflate was a most useful direct promoter for glycosylations using 1-thioglycosides.[143–146] 1-Thioglycosides having a participating substituent at O-2 gave the expected 1,2-*trans* glycosides, whereas those with a non-participating O-2 substituent gave anomeric mixtures. However in reactions conducted in diethyl ether, α-glycosidic products predominated. These observations led in turn to the discovery of several high-yielding thiophilic promoters, as shown in Table I.

TABLE I
Thiophilic Activators

Activator	SR^1	Main Author(s)
MeOTf	SMe, SEt, SPh	Lönn[143–146]
DMTST	SMe, SEt, SPh	Fugedi and Garegg[132]
$NOBF_4$	SMe	Pozsgay, Jennings[147,148]
MeSOTf, MeSBr	SMe,SEt, SPh	Dasgupta, Garegg[149]
$TrClO_4$ (cat)	SCN, (ROTr acceptor)	Kochetkov *et al.*[150]
PhSeOTf	SMe	Ogawa *et al.*[151]
MeI	SPy	Reddy *et al.*[152]
NIS-TfOH	SMe, SEt, SPh	van Boom *et al.*[153] Konradsson *et al.*[154]
IDCP	SEt	Veeneman, van Boom *et al.*[155]
AgOTf		Tsuboyama *et al.*[156]
TBPA	SEt, SPh	Sinaÿ *et al.*[157]
DMTST or AgOTf or Sn Cl_4 or $FeCl_3$		Fügedi *et al.*[158]

Tris(4-bromophenyl)ammonium hexachloroantimonate (TBPA) is unique among the promoters in that its cation is a radical, and it produces radical-cation sulfonium intermediates in glycosylation reactions.

d. 1-Thioglycosides as Glycosyl Acceptors in Glycosylation Reactions.— Since cationic activation is necessary for a 1-thioglycoside to become a glycosyl donor, it follows that, if it contains a free hydroxyl group, it may also act as a glycosyl acceptor, provided that the actual glycosyl donor is activated by some other means. Thus, a 1-thioglycoside having a free hydroxyl group can undergo silver triflate-, or tin(II)chloride–silver perchlorate-promoted glycosylation with a glycosyl bromide, chloride or trichloroacetimidate, as well as glycosylation with phenyl 1-selenoglycosides in the presence of potassium or silver carbonate as activator.[159–162]

e. 1-Thioglycosides in Protecting-Group Sequences.—Since cationic activation is necessary for reaction at the anomeric center of 1-thioglycosides, a wide range of protecting-group manipulations is possible at other positions in the pyranosidic (or furanosidic) ring. The reactions include esterification, deesterification, acetalation, hydrolysis of acetals (under conditions not affecting

the anomeric center) phase-transfer alkylations and esterifications,[163] and reductive opening of benzylidene acetals. Following such manipulations they may then chemoselectively be activated to become glycosyl donors.

IV. 1-Sulfoxides, 1-Sulfones, and 1-Telluroglycosides in Glycosylation Reactions

Glycosyl sulfoxides are generally made by oxidation of the corresponding 1-thioglycosides. They are activated to become glycosyl donors by catalytic amounts of triflic anhydride at low temperature. Since 1-thioglycosides are not activated under these conditions, this means that, if they are suitably protected with only a single hydroxyl group remaining free (or several hydroxyl groups if more than one is to be glycosylated), 1-thioglycosides can act as glycosyl acceptors. Since in turn, 1-thioglycosides can correspondingly act as glycosyl acceptors in glycosylation with glycosyl halides and (for instance) silver triflate as promoter, this opens useful possibilities in oligosaccharide synthesis. Glycosyl sulfoxides have found use in several oligosaccharide syntheses, including solid-phase synthesis.[164–166]

Further oxidation of 1-thioglycosides leads to glycosyl sulfones. These have been reported to be activable by magnesium bromide etherate in the presence of sodium hydrogencarbonate.[167]

It has been shown that glycosyl 2-pyridyl sulfones react with alcohols using samarium triflate as promoter to permit the synthesis of di- and tri-saccharides containing both furanoside and pyranoside residues. Again, 1-thioglycosides are not activated under these conditions, making possible their use as glycosyl acceptors. Also, benzylated sulfones are activated more rapidly than their benzoylated counterparts. The sulfones are inert to activation with *N*-iodosuccinimide and triflate promoters. This opens up possibilities for selective oligosaccharide syntheses.[168]

1-Selenoglycosides are prepared by methods analogous to those for 1-thioglycosides.[169,170] They are activable by the same promoters as those used for 1-thioglycosides. A particularly useful one is silver triflate, in the presence of potassium carbonate. 1-Selenoglycosides can be thus activated in the presence of 1-thioglycosides having a free hydroxyl group to produce *O*-glycosidic bonds. They can also, if they have a free hydroxyl group, function as glycosyl acceptors by using glycosyl bromides in the presence of silver triflate as promoter along with collidine, and also with glycosyl trichloroacetimidates in the presence of triethylsilyl triflate as promoter.[171]

1-Telluroglycosides are obtainable by treatment of acylated α-glycopyranosyl bromides with diaryltellurides in the presence of sodium borohydride. Good to excellent yields are obtained of aryl 1-telluro-β-glycosides having acetyl, benzoyl, or benzyl at the 2,3,4-positions, and acetyl at the 6-position.[172]

Electrochemical oxidation of telluroglycosides in the presence of primary or secondary alcohols results in *O*-glycosylation.[173]

Activation of 1-telluroglycosides with *N*-bromosuccinimide in the presence of an alcohol gives good yields of glycosides. Selectivity in the formation of α- or β-glycosides is readily achieved by appropriate choice of solvent and protecting groups (participating or nonparticipating O-substituents in the 2-position).[174]

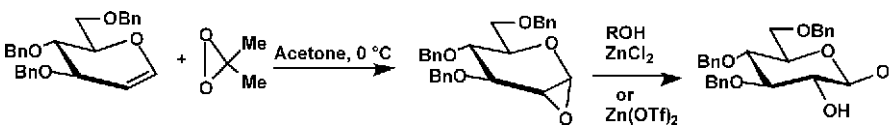
Strong preferential activation of 1-telluroglycosides is possible in the presence of of the corresponding 1-selenoglycoside by using *N*-iodosuccinimide as promoter. This further extends the possibilities for selective glycosylation reactions in oligosaccharide synthesis.[175]

Glycosyl fluorides, which have many applications in chemical and biomedical studies, are obtainable by treatment of both 1-seleno- and 1-telluro-glycosides with diethylaminosulfur trifluoride (DAST).[176]

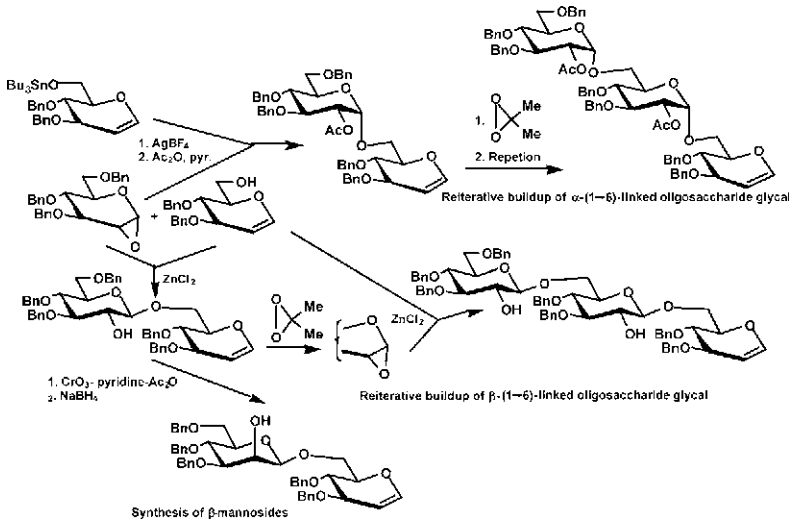
V. 1,2-Anhydro Sugars in Glycoside Synthesis

1,2-Anhydro sugars were first obtained by multistep synthesis, the first report of such a derivatives being by Brigl.[177] Their potential as glycosyl donors was subsequently explored in disaccharide synthesis, but at that stage they did not enjoy widespread use.[178–181]

However, the demonstration that 1,2-anhydro sugars are readily obtained from glycals by treatment with dimethyldioxirane led to a renaissance of their use in glycoside synthesis and, indeed, in solution-phase and solid-phase oligosaccharide synthesis.[182]



The following scheme outlines some of the possibilities using glycals and anhydro sugars in oligosaccharide synthesis.[182]



Thus activation by tributyltin leads to a fortuitous α-glycosidation, whereas activation by zinc chloride leads to the normal β-glycosidation. Taking advantage of the 2-hydroxyl group produced from the 1,2-anhydro sugar opens up a route to β-mannopyranosides.

VI. Glycosidations on a Solid Phase

The subject of oligosaccharide synthesis on a solid phase has recently been reviewed.[183]

This topic is discussed from the point of view of oligosaccharides synthesis. Solid-phase synthesis is well established in the oligonucleotide and oligopeptide fields. Its obvious advantage over solution-phase methodology is the avoidance of chromatographic purification along the synthesis route, and also the potential for using an excess of monomer added on at each step, since the excess unreacted monomer can be washed off the polymeric material after each step. However, the development of corresponding techniques for oligosaccharide synthesis has been much slower. Some of the reasons for this are:

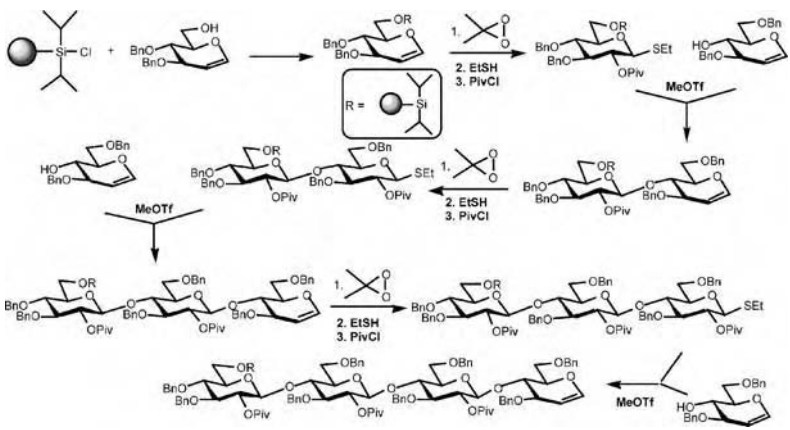
(a) Oligosaccharide epitopes rarely contain more than 10 monosaccharide residues, whereas oligonucleotide and oligopeptides involved in their respective biointeractions tend to have much longer chains. The need for solid-phase methods thus are more obvious for the latter two types than for oligosaccharides.

(b) In oligosaccharide synthesis there is the added problem of a requirement for stereospecificity (α- or β-glycosylation). One single wrong anomeric configuration in the oligosaccharide chain is likely to render the oligomer biologically irrelevant.

(c) The necessary protecting-group sequences in oligosaccharide synthesis tend to be more complex than in oligonucleotide and oligopeptide synthesis.

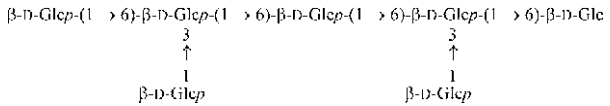
Despite these considerations, there has been substantial progress in recent years in the synthesis of oligosaccharides on a solid phase. Since the central issue here is glycosidation, this topic is the current focus. An obvious decision at the outset is the mode of linkage of the saccharide oligomer to the solid phase, either attachment at the anomeric center, or attachment to the polymer through one of the other positions. This question is illustrated in the following two examples.

In the first illustration, the polymer is attached to the 6-position at the nonreducing end of the oligosaccharide to be formed. The work describes a long sought-for solution to a highly anomer-selective solid-phase synthesis of β-(1→4)-linked oligosaccharides.[184] In the first step, 3,4-di-*O*-benzyl-D-glucal was attached through O-6 to a silyl polystyrene resin. Iterative conversion of the glycal double bond into a 1,2-anhydride, followed by a two-step conversion of this oxirane into an ethyl 2-*O*-pivaloyl-1-thioglucopyranoside, and methyl triflate-promoted glycosylation by the latter as donor with 3,6-di-*O*-benzyl-D-glucal led to a rapid synthesis of the β-(1→4)-linked D-*gluco* tetrasaccharide shown. The overall yield from the starting polymer-linked glucal was 20%.

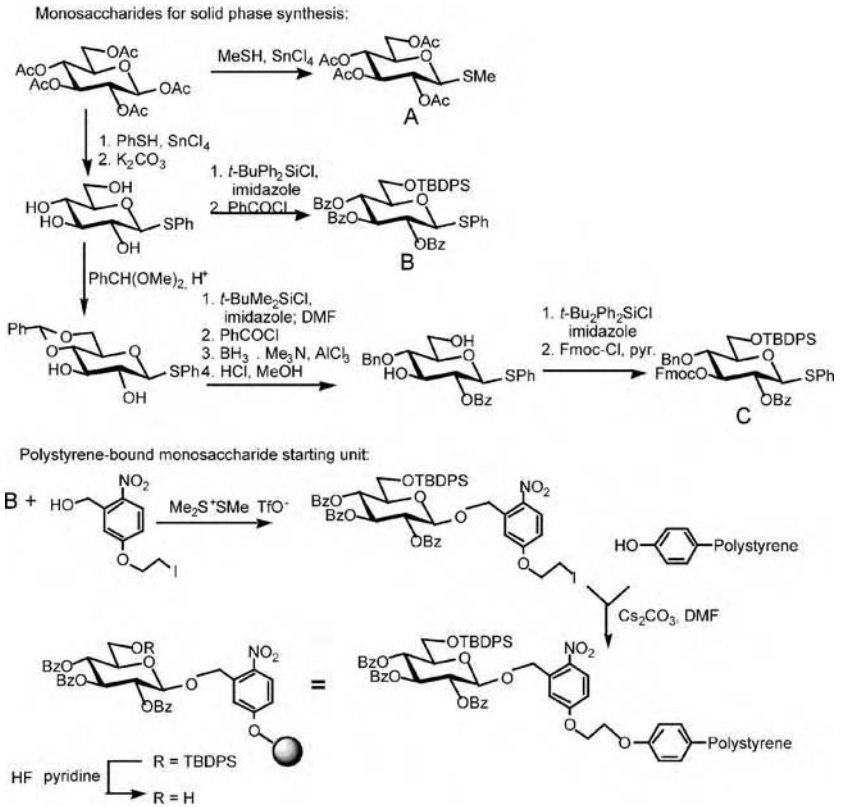


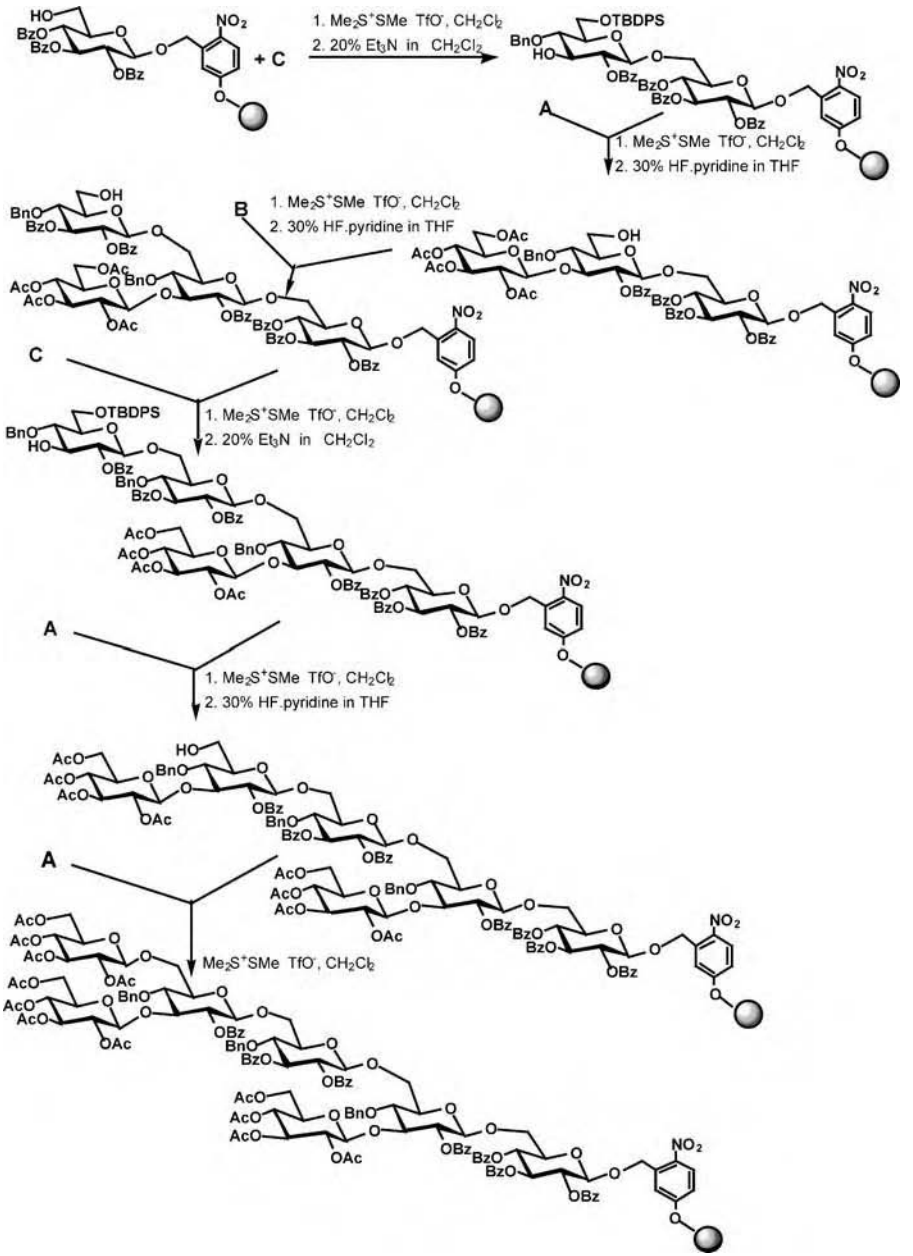
The second example is a solid-phase synthesis of a heptasaccharide phytoalexin elicitor. Here, attachment of the polymer was to the reducing end of the oligosaccharide. The structure was chosen as an example for the development of

solid-phase synthesis.[191] Infection of the soybean plant with the mold *Phytopthora megasperma* triggers a defense in the plant. Recognition is associated with a glucan structure in the mycelium and the minimal structural unit for this is five β-(1→6)-linked D-glucopyranose units carrying two single β-(1→3)-linked D-glucopyranosyl branch units. Several liquid-phase syntheses of this heptasaccharide have been published,[185–189] as well as an early solid-phase synthesis.[190]



A seven-step synthesis, from the starting materials A–C and the polystyrene-bound starting monomer unit proceeded in 20% yield. Each step involved condensation and chemospecific deprotection at a single position.[191]




1. Me2S+SMe TfO-, CH2Cl2
2. 20% Et3N in CH2Cl2
+ C
A
1. Me2S+SMe TfO-, CH2Cl2
2. 30% HF.pyridine in THF
B
1. Me2S+SMe TfO-, CH2Cl2
2. 30% HF.pyridine in THF
C
1. Me2S+SMe TfO-, CH2Cl2
2. 20% Et3N in CH2Cl2
A
1. Me2S+SMe TfO-, CH2Cl2
2. 30% HF.pyridine in THF
A
Me2S+SMe TfO-, CH2Cl2

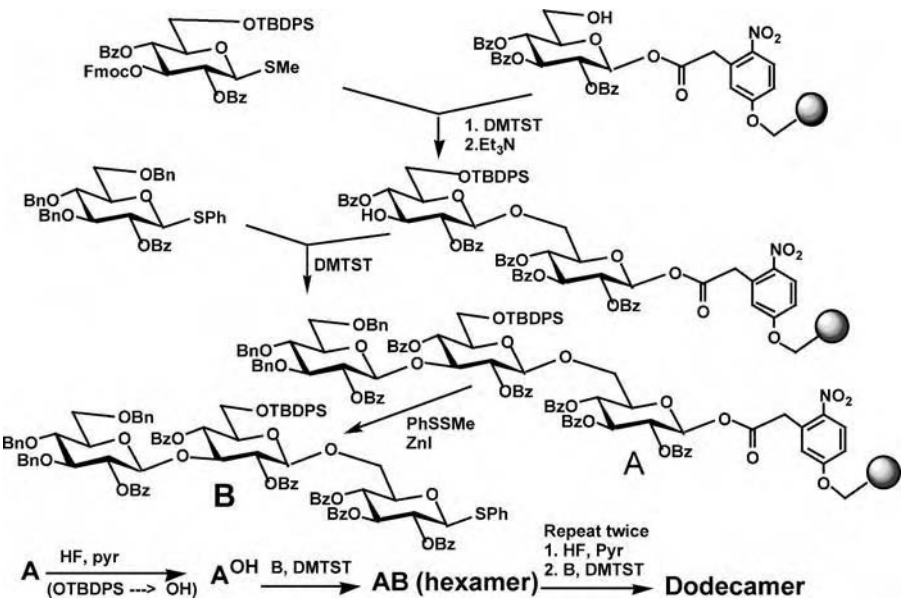
The fully protected heptasaccharide was finally removed, photochemically in tetrahydrofuran, from the solid support, deacylated with sodium methoxide in tetrahydrofuran–methanol, and finally debenzylated by hydrogenolysis with Pd/C in methanol to yield the deprotected target heptasaccharide.[191]

The foregoing synhesis was followed up in the next year by a solid-phase synthesis of a dodecamer having the *Phytophtora megasperma* elicitor structure.[192]

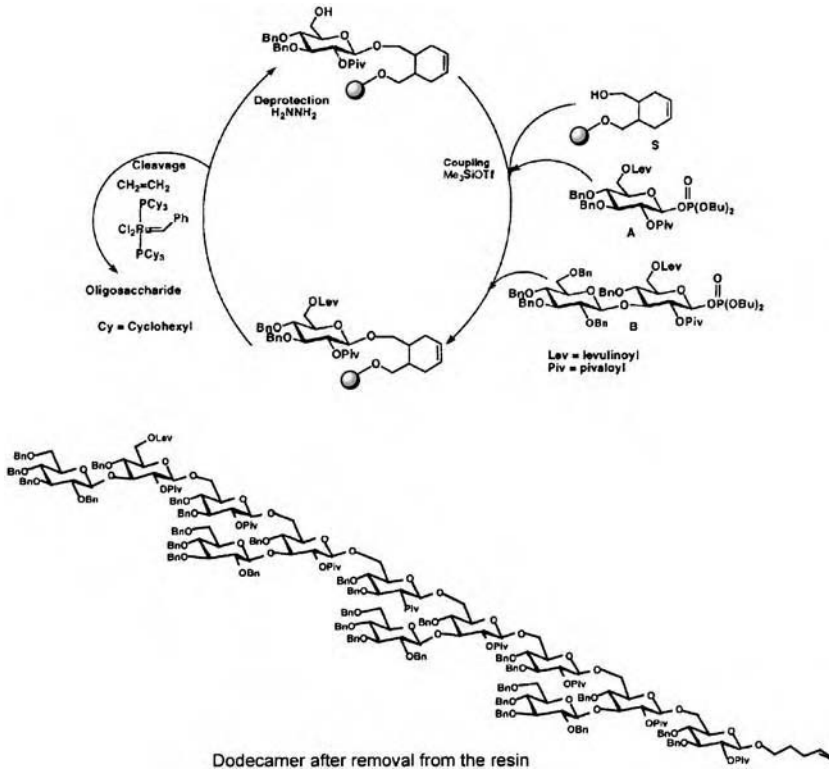
β-D-Glc-[β-D-Glc-(1→6)-β-D-Glc-]$_2$(1→6)-β-D-Glc-(1→6)-β-D-Glc-(1→6)-β-D-Glc
3 3 3
↑ ↑ ↑
1 1 1
β-D-Glc β-D-Glc β-D-Glc

The end-point of the synthesis was the fully protected dodecasccharide, detached photochemically from the solid phase.

For this synthesis a photolabile link-up to a Merrifield-type resin was used. The following summarizes the synthesis, which elegantly combines the advantages of solid-phase synthesis with that of iterative block synthesis:



The next logical step in the exploitations of solid-phase synthesis is automation on machines. This is illustrated by work carried out by Seeberger and coworkers.[193] Their approach is again well demonstrated by synthesis of the dodecameric *Phytophthora megasperma* phytoalexin elicitor structure. The machine used was a modified peptide synthesizer. The solid phase was an octenediol-functionalized, 1% crosslinked polystyrene. In order to achieve steric control in the glycosylation reactions the participating 2-*O*-pivaloyl substituent was used. As a temporary 6-*O*-substituent, the levulinoyl group was used, as it is readily removable by treatment with hydrazine. Persistent O-protecting groups, removed only at the end of the synthesis, were benzyl groups. The leaving group at C-1 in the glycosylations was a β-dibutylphosphate group, activable by treatment with trimethylsilyl triflate at –15 °C. Only two saccharide building blocks were used, a β-D-glucopyranosyl phosphate, and a β-laminarabiosyl phosphate. The synthesis, including removal from the resin, is illustrated here:



The machine synthesis ran as follows. In the first cycle, the resin was condensed with A and the levulinoyl group was removed. The product was then condensed with B, and the levulinoyl group was removed from the trimer. This was then condensed with A, and the levulinoyl group was removed to give a tetramer. Continued alternate couplings with B and then A, and ending with condensation with B in the same manner ultimately produced a dodecamer which was removed from the resin, and deprotected to the dodecamer glycoside. This synthesis most probably constitutes a major milestone in the machine synthesis of oligosaccharides.

VII. Structure at the Anomeric Center: Anomeric Effects

1. Determination of Anomeric Configuration

a. Optical Rotation.—An important attribute of carbohydrates is that, being chiral, they are capable of rotating the plane of polarization of light. In glycosides, discrimination between the α- and β-anomeric configurations is readily made by measurement of optical rotation. Hudson's isorotation rule: "the names should be so selected that for all sugars which are genetically related to D-glucose the subtraction of the rotation of the β-form from that of the α-form gives a positive difference, and for all sugars which are genetically related to L-glucose a negative difference." The rule presupposes that contribution to the optical rotation from the remaining chiral centers in each of a pair of α- and β-glycosides are not appreciably different. The rule is normally taken to mean that, in an α,β pair of the D series, the more dextrorotatory anomer is assigned the α configuration, and conversely in the L series the α anomer is the more levorotatory.[194] Exceptions to this rule are rare, but complete reversal is possible when certain aryl substituents are present at C-2.[194a]

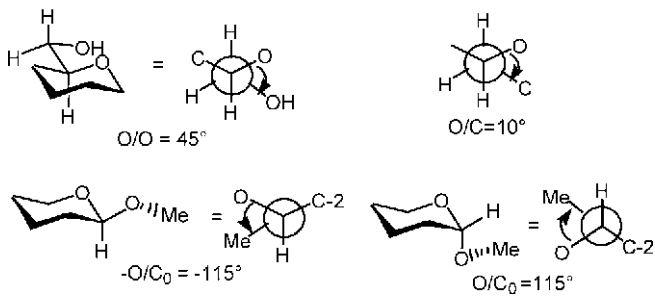
Hudson's isorotation rule was subsequently expanded by Whiffen, who suggested a set of empirical rules based on additive contributions to the molecular rotation based on contributions along each asymmetrically substituted bond. He established six structural parameters and assigned to each of these a numerical value, making possible an estimation of the molecular rotation in aqueous solution of the various pyranoses.[195]

These entirely empirical rules were later elaborated by Brewster,[196] and subsequently refined substantially by Lemieux and Martin.[197]

For pyranoid sugars, the Whiffen–Brewster rules were reduced to four rotational parameters. These are based on pairwise *gauche* relationships between carbon

atoms, oxygen atoms, and between carbon and oxygen atoms, and whether these are bridged by C–C or O–C bonds. Numerical values, based on simple model compounds, were assigned to these parameters. An additional parameter taken into account was the favored conformation of methyl glycosides (anomeric effects, see later in this section) and also to conformation around the C-5–C-6 bond in hexopyranosides. The various molecular rotatory contributions are illustrated in the accompanying scheme. Molecular rotation is defined as:

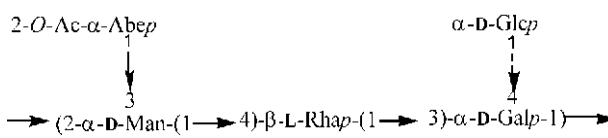
$$[M]_D = \frac{[\alpha]_D \times \text{Mol. wt}}{100}$$



Reasonable correlations between the calculated and observed molecular rotation were observed. For example, the molecular rotation for a 6-deoxy-β-D-mannopyranoside was calculated to be −195°, according to −2O/O + O/C − O/C_0. The value reported in the literature is −170°.

b. Circular Dichroism.—This method determines the difference in absorption between right and left circularly polarized light. In glycosides having a chromophore at C-2, a distinction can be made between the α and β configuration. An example is the following:

The repeating unit of the O-specific polysaccharide side-chains of the *Salmonella typhimurium* antigenic outer bacterial cell wall is as follows:



There remained some uncertainty concerning the anomeric configuration of the 2-*O*-acetyl-3,6-dideoxy-D-*xylo*-hexosyl (2-*O*-abequosyl) residues. Since these

fortunately carried a 2-*O*-acetyl group adjacent to the anomeric center, confirmation of the anomeric configuration was achieved by synthesizing methyl 2-*O*-acetyl-α- and β-abequosides, determining their opposite circular dichroism spectra, and comparing these to that of the lipopolysaccharide.[198]

c. Enzymatic Methods.—Since glycoside hydrolases are stereospecific and the required analysis can be carried out on a miniscule amount of substance, the use of appropriate exo-hydrolases, whenever available, may be especially useful for the determination of anomeric configuration. The only limitation of the method is the purity of the enzymes, which must be carefully established.[199]

d. Nuclear Magnetic Resonance.—In two landmark papers, it was shown first in 1958 that, in acetylated pyranoses, "*. . . an equatorial hydrogen atom comes into resonance at a lower field than does a chemically similar axial one*." In the following year the same authors published a finding that was to change organic chemistry totally: "*. . . anti-periplanar, vicinal hydrogen atoms are coupled 2–3 times more strongly than are the corresponding syn-clinical ones.*" The foundation for the subsequent spectacular success of NMR in carbohydrate chemistry was thus laid.[200,201]

The subject of NMR in relation to determination of anomeric configuration has been summarized by Bundle and Lemieux,[202] and the much wider subject of the use of NMR generally in carbohydrate chemistry has been reviewed by Duus, Gottfriedsen, and Bock.[203]

Normally, for unsubstituted and non-alkenic glycosyl groups, the anomeric proton gives a signal at lower field than the other ones. Exceptions have been found for oligosaccharides having crowded structures. Similarly, the foregoing observation concerning axial vs. equatorial ^{1}H shifts has exceptions. These are general rules and they should be corroborated by spin decouplings, 2-dimensional methods, and by observations of nuclear Overhauser (NOE) effects whenever doubt arises.

The second classical parameter is the coupling constant. Vicinal couplings between *axial* H-1 and H-2 in a pyranose ring are normally 8–9 Hz, whereas the corresponding coupling for *equatorial* H-1 and H-2 is usually less than 2 Hz. The vicinal couplings for axial–equatorial or equatorial–axial protons are usually about 4 Hz. The ^{13}C chemical shifts for anomeric carbons show a similar dependence on α or β configuration as do the anomeric ^{1}H shifts. More important is the fact that anomeric ^{13}C–^{1}H couplings strongly depend on the anomeric geometry. Thus an α anomer has $^{1}J_{C1,H1}$ ~160 Hz, whereas that for a β anomer is ~170 Hz. This relation is, of course, independent of D or L enantiomeric identity. Unfortunately, a corresponding correlation is not observed for furanose structures.

2. The Anomeric Effects

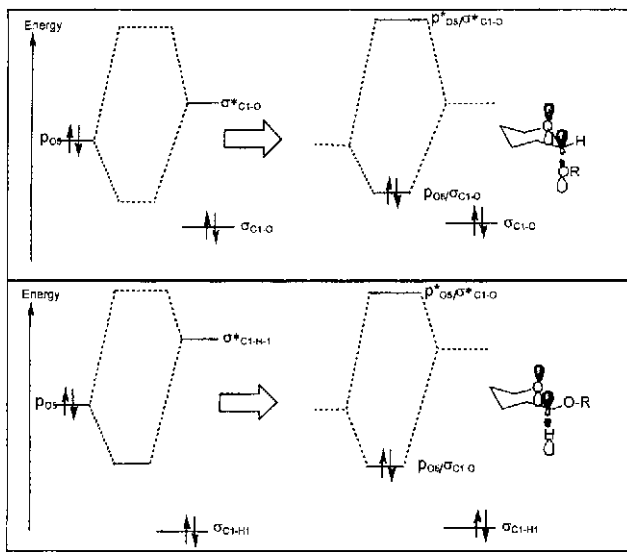
On the subject of conformational effects, Nikolay S. Zefirov has stated:

> ". . . To date, many conformational effects have been proposed, all of which have had some kind of experimental 'verification.' Many of them have special names, e.g. '*gauche*,' '*rabbit-ears*,' '*hockey-sticks*' '*anomeric*' effects . . .. Such development of conformational analysis has led to a paradoxial situation: the abundance of "effects" permits us to explain everything, but to predict close to nothing!"[204] Possibly this subject should be approached with some caution.

In cyclohexanol, the hydroxyl group exists mainly in equatorial orientation, however in 2-hydroxytetrahydropyran it is mainly axial. This preference for a polar group adjacent to the ring oxygen has been termed the *anomeric effect*.[205,206]

One "explanation" often advanced for the phenomenon is an unfavorable dipolar interaction for the β anomer between the two electron pairs on the ring oxygen atom with the polar C–O bond at the anomeric position. Unfavorable dipolar interactions, however, do not fit well with the preference for the *gauche* orientation of two highly polar groups, such as F or OR, in 1,2-disubstituted ethanes.[207,208]

A more satifying model is provided by molecular orbital theory. This is presented in the following cartoon:[209]

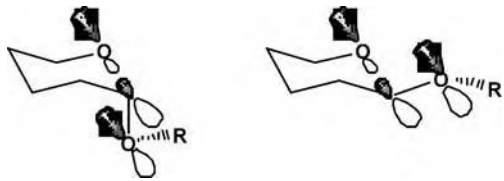


When the exocyclic C–O bond is axial, its orbital overlaps well with the *p*-type orbital on the ring oxygen atom. When the exocyclic C–O bond is equatorial it is the anomeric C–H bond instead that overlaps well with the *p*-orbital of the ring oxygen atom.

The C–O σ* (antibonding) orbital for the α anomer is of lower energy than the corresponding axial C–H orbital for the β anomer. The overlap of the lone-pair *p*-orbital is therefore more efficient in the α anomer than in the β anomer.

This factor, and the exo-anomeric effect, discussed next, have profound consequences for the favored orientation of glycosidic bonds, and indeed on the conformation of oligo- and poly-saccharides.

Consider now the conformation around the *exocyclic oxygen* atom in a glycoside. It also has lone pairs of electrons, one pair of which may be delocalized in similar fashion to the foregoing, by creating a new orbital with lower energy than a *p*-orbital by orbital mixing between an oxygen *p*-orbital and the antibonding orbital of the C-1−O-5 (σ*-bond) in the pyranose ring. This is illustrated diagrammatically here. Only one of the two free electron-pair orbitals, the overlapping *p*-type, is shown. This effect has been termed the exo-anomeric effect.[210]



In a pyranose ring, an electronegative, polar C-1 substituent tends to take up the axial disposition. If, instead the C-1 substituent carries a *positive charge*, as in glycosylpyridinium derivatives, it tends to show a preference for the *equatorial* position. This has been termed the *reverse* anomeric effect.[211]

This behavior could possibly be rationalized in ways similar to those already presented. However, the C-1 substituent in the glucopyranosylpyridinium structure is quite bulky, and the equatorial prefence could be merely steric. To eliminate this possibility, recourse was taken to glycosylimidazoles, since protonation at the distant nitrogen atom would not be expected to increase the steric bulk around the anomeric C–N bond. Nevertheless *N*-protonation or *N*-methylation appeared to shift the anomeric preference toward the equatorial orientation. However, the "reverse anomeric effect" has become a subject for serious doubts. Thus, for example, an NMR titration method applicable to a mixture of α and β anomers in glycosylimidazoles revealed that $\Delta\Delta G$ β → α is almost always

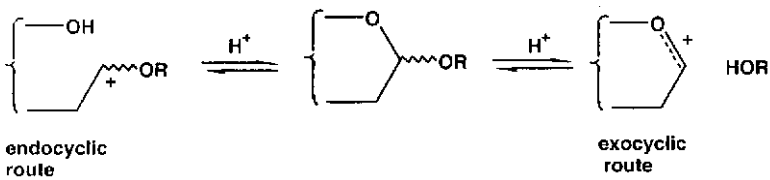
negative.[212] It therefore seems likely that the original observations pertaining to the glycopyranosylpyridinium structure have a steric origin.

VIII. Reactions at the Anomeric Center

1. Anomerization

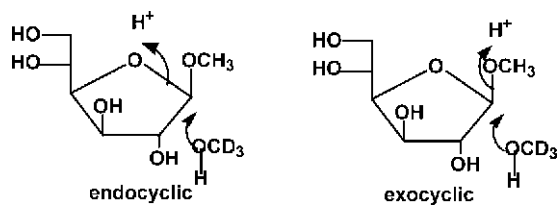
The subject of anomerization of glycosides was briefly discussed in Section II.1. Because of the anomeric effect (Section VII), α-glycosides are generally more stable than the β-glycosides, and anomerization of a β-glycoside in the presence of acid tends to produce an equilibrium mixture in which the α anomer predominates.

The mechanism of anomerization has been studied, with special attention to the question as to whether the initial protonation (or Lewis acid attack) is on the endocyclic or exocyclic oxygen atom. The bulk of the evidence favors the latter in most instances.



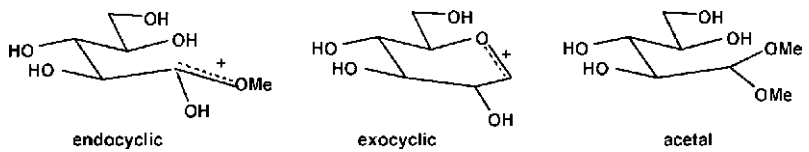
This subject up until 1969 has been extensively reviewed by B. Capon.[213]

a. Furanosides.—In work before 1969, the rate constants for the anomerization of methyl furanosides in methanol were studied for the four D-pentoses, and for D-glucose. Tracer experiments with methyl β-D-glucofuranoside in ^{14}C-labeled methanol showed that incorporation of the label occurred. When the anomerization was conducted in CD_3OD, all α-furanosidic products contained CD_3O. Thus the main reaction route involved exchange with the solvent. This, and the observed negative entropy of activation was taken to indicate one of the following two routes.



In later studies, trapping experiments of the intermediate oxocarbenium or other cation were performed using 4-methylmorpholine–borane. The methyl furanosides investigated, which when necessary carried a methyl group in the 5-position in order to avoid isomerization to pyranosides, produced 1-*O*-methylalditols, indicating protonation at O-5, followed by endocyclic ring-cleavage. Methyl 2-deoxy-5-*O*-methyl-α-D-*arabino*-hexofuranosides, however, gave a mixture of 2-deoxy-1,5-di-*O*-methyl-D-*arabino*-hexitol and 1,4-anhydro-2-deoxy-5-*O*-methyl-D-*arabino*-hexitol, demonstrating the operation of both of these routes. Similar results indicating the operation of both routes were obtained with methyl fructosides and 1-deoxyfructosides.[214]

b. Pyranosides.—Anomerization of pyranosides is the final step in the Fischer glycoside synthesis (Section II.7). Again, rate studies have been performed for the four D-pentoses, and for D-glucose. In contrast to the furanosides, the entropy of activation is positive. The following intermediates were considered:



The "endocyclic" and "acetal" intermediates were excluded since experiments conducted in CD_3OD showed that anomerization was accompanied by >98% exchange of the methoxyl group and solvent. Stereospecific formation of a glycopyranosidic product from the acetal was excluded by the fact that acidic treatment of it produced only furanosides, which were converted only slowly into pyranosides. The "exocyclic" intermediate was considered to be the most likely one.[213]

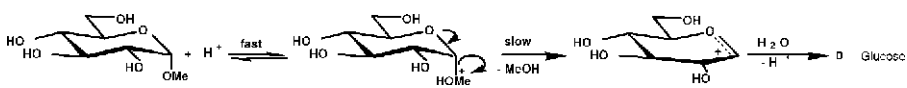
Trapping experiments as for the furanosides, using 4-methylmorpholine–borane were also performed with pyranosides. The pyranosides used were methyl 4-*O*-methyl-α-D-glucopyranoside and its 2-deoxy analog. With the first of these, the experiment was unsuccessful. The reducing agent decomposed and only anomerization was observed. Hovever, with the more reactive methyl 2-deoxy-4-*O*-methyl-α-D-*arabino*-hexopyranoside, both 1,5-anhydro-2-deoxy-4-*O*-methyl-D-*arabino*-hexitol and 2-deoxy-1,4-di-*O*-methyl-D-*arabino*-hexitol were formed in addition to anomerized starting material (α,β 9:1). This result indicates anomerization via both endo- and exo-routes.[214]

2. Acidic Hydrolysis

Hydrolysis of acetals by acid is considered to proceed normally via the *A*1 mechanism. Electron release in the aldehyde facilitates reaction, the ρ value being −3.5, indicating stabilization of a cationic intermediate. The solvent isotope-effect $k\ H_2O/kD_2O$ is approximately 2.6, which indicates that the acidic property of the solvent is more important than its nucleophilicity. The entropy of activation is positive, 5–20 $K^{-1}\ mol^{-1}$. Glycopyranosides fit into this generalization, but the acidic hydrolysis of the corresponding furanosides shows negative entropies of activation, indicating a difference in mechanism.

A key mechanistic question is the position of bond fission, the glycosyl–oxygen bond or the oxygen–aglycone one. This was settled by conducting the hydrolysis in ^{18}O enriched water, and it was shown that the normal cleavage is of the glycosyl–oxygen bond, unless there is special stabilization of the aglycone carbocation.

Another question is whether the rate-determining step involves endocyclic cleavage, namely cleavage of the C-1−O-5 bond, or the C-1–Oaglycone one. The observation of an oxygen isotope-effect for for the methoxyl group in the acidic hydrolysis of methyl glycopyranosides has shown that the rate-determining step is exocyclic cleavage. The following mechanism was therefore advanced.[213]



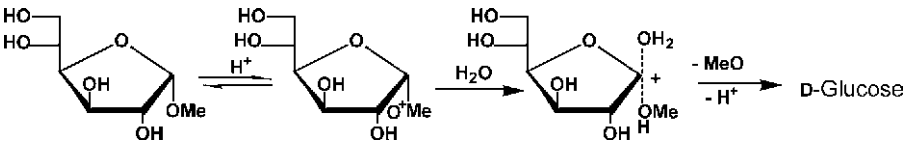
It seems reasonable to assume that this is the normal route for acidic hydrolysis of pyranosides. Exceptions include the hydrolyis of *tert*-butyl β-D-glucopyranoside, which is cleaved at the oxygen–*tert*-butyl bond.[215]

Another exception is the hydrolysis of isopropenyl glucopyranosides, where the α anomer is hydrolyzed 4 times faster than the β anomer, contrary to the expectation from the anomeric effect, that the β anomer should be hydrolyzed the faster, the behavior normally observed for α,β-pairs of pyranosides. The reason for the anomalous behavior of the 2-propenyl glycosides is that cleavage occurs between O-1 and the 2-propenyl group.[216]

In contrast to the pyranosides, acidic hydrolysis of furanosides is generally considered to follow the *A*2 mechanism.[213]

Volumes of activation have been determined for the acid-catalyzed hydrolysis of 19 glycosides, both furanosidic and pyranosidic, and were found to parallel closely the trend in entropies of activation, positive for pyranosides and negative

for furanosides. Thus whereas the ΔV for pyranosides is 10–17, that for the corresponding furanosides was -2 to $-10\,\mathrm{cal\,K^{-1}\,mol^{-1}}$.[217] The following mechanism agrees with these findings:

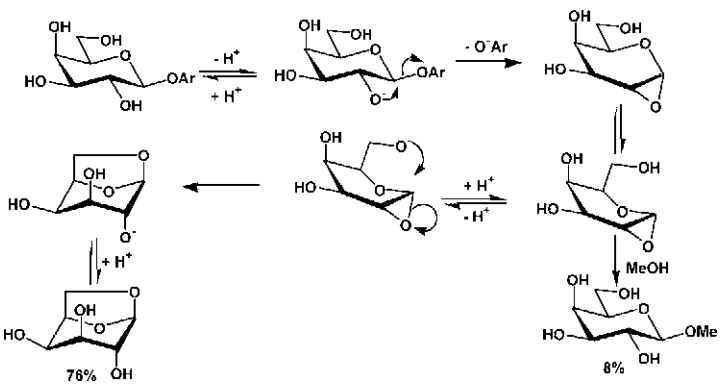


3. Basic Hydrolysis

Alkaline cleavage of glycosidic bonds depends on the leaving-group ability of the aglycone and upon participation by alkoxy groups in the furanose or pyranose ring arising from treatment with alkali. The subject has been reviewed by Capon.[213]

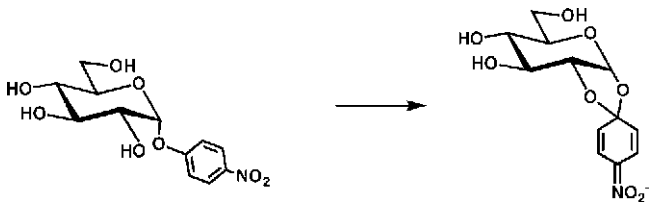
Thus phenolic glycosides are cleaved much more rapidly than are alkyl glycosides. Participation from 2-*O*- and 6-*O*-alkoxy groups play an important rôle. Methyl β-D-glucopyranoside in 2.5 molar aqueous sodium hydroxide at 170 °C undergoes alkaline cleavage, accompanied by further decomposition.[218]

Rate studies of alkaline cleavage of various phenyl D-glucopyranoside with various substituents in the aromatic ring show a clear dependence on the presence of electron-withdrawing substituents, and particularly on the presence of a 1,2-*trans* configuration at O-1 and O-2. Cleavage is greatly retarded by methylation at O-2.[213] These results are in agreement with the following mechanism, shown here for treatment of aryl β-D-galactopyranosides upon treatment with sodium methoxide in methanol.



By contrast, phenyl α-D-mannopyranoside under the same conditions gives only methyl α-D-mannopyranoside. It was suggested that neighboring group participation from the 2-oxygen atom produces 1,2-anhydro-D-mannopyranose, which then reacts with methoxide ion to give the methyl mannoside.[219]

A somewhat different mechanism involving participation from the 2-oxyanion has been proposed from the observation that *p*-nitrophenyl α-D-glucopyranoside is cleaved 105 times faster than the corresponding phenyl glucopyranoside in 3.9 molar aqueous KOH at 60 °C, suggesting initial nucleophilic attack by O-2 on the aryl group.



The aryl group of the intermediate Meisenheimer complex then migrates to O-2 and from there to O-3, after which breakdown to saccharinic acids occurs.[220]

4. Reductive Hydrolysis

In structural studies of oligo- and poly-saccharides, and of glycoconjugates, partial or complete hydrolysis are standard procedures. Unfortunately, some sugars, such as 3,6-anhydrogalactose, 3-deoxyaldulosonic acids, and dideoxy sugars are degraded under normal conditions of acidic hydrolysis. Hydrolysis under conditions wherein the free sugar upon release is rapidly reduced to the corresponding alditol is therefore a useful objective. However, standard reducing agents such as sodium borohydride decompose under the normal conditions for acidic hydrolysis. A solution to this problem is the use of sodium dicyanoborohydride, or 4-methylmorpholine–borane in 0.5 M aqueous trifluoroacetic acid (TFA). Thus, the former of the two reducing agents in TFA at 100 °C for 1 h transformed methyl 3,6-didoxy-D-*xylo*-hexopyranoside into a 1:1 mixture of the corresponding alditol and 1,4-anhydroalditol. Agarose, on treatment with 0.5 M trifluoroacetic acid and 4-methylmorpholine–borane at 60 °C for 15 h underwent transformation of all of the 3,6-anhydro-L-galactose to the corresponding alditol, but no products from the galactose residues were formed.[221]

In a useful variant of the classical methylation procedure for linkage analysis in the structural determination of oligo- and poly-sacccharides, the fully methylated oligomer is treated with triethylsilane and boron trifluoride etherate or triethylsilane and trimethylsilyl trifluoromethanesulfonate. This procedure produces partially methylated anhydroalditols. These are acetylated and analyzed by GLC-MS.[222,223] This "reductive-cleavage method" makes possible simultaneous determination of identity, ratio, linkage position, and especially the ring size for each monosaccharide component.

5. Hydrogenolysis

In early work it was reported that benzyl ethers of sugars can be cleaved by hydrogenolysis with sodium amalgam or by catalytic hydrogenolysis using platinum metals in acetic acid.[224] This also applies to anomeric benzyl glycosides. Acetic acid is still the recommended solvent, but the customary catalyst is palladium on carbon.[225]

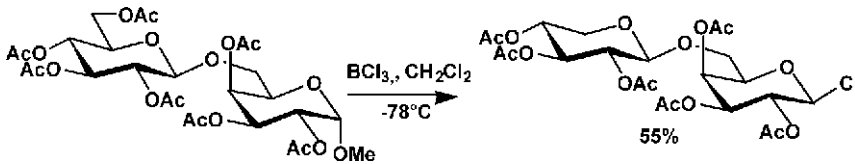
Subsequent developments include transfer hydrogenolysis, as with Pd-C in the presence of ammonium formate as the hydrogen donor, in methanol. This procedure allows regioselective hydrogenolysis at the anomeric center of fully benzylated benzyl glycosides. Perbenzylated glycopyranoses having the *arabino, galacto*, and *gluco* configurations were thus obtained, and also those of lactose and maltose.[226]

6. Transformation Into Glycosyl Chlorides

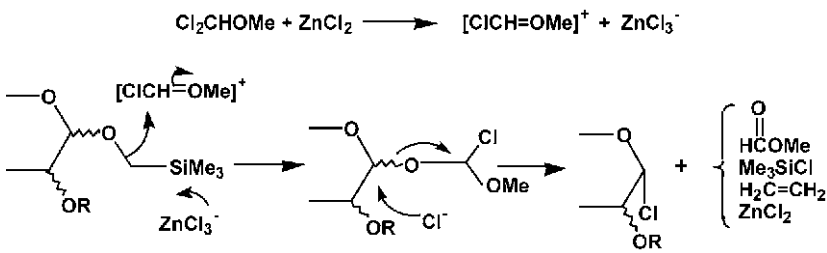
In the synthesis of oligosaccharides it sometimes is necessary to protect temporarily the anomeric position of a fragment while either building up an oligosaccharide block or while performing protecting-group sequences. When this is completed, the next problem is to activate the anomeric center to become a glycosyl donor. In this connection, a methyl group at the glycosidic position is extremely stable during a range of manipulations, as is also the 2-(trimethylsilyl)ethyl group.[227]

Several routes have been described for the conversion of methyl glycosides into glycosyl bromides or iodides, but they require elevated temperatures incompatible with the presence of interglycosidic bonds. However, methyl glycosides readily

react with boron trichloride in dichloromethane to produce the corresponding glycosyl chlorides. The reaction is compatible with the presence of *O*-acetyl and *O*-benzyl groups.[228]



A 2-(trimethylsilyl)ethyl glycoside is convertible into a glycosyl chloride by treatment with 1,1-dichloromethyl methyl ether in the presence of zinc(II) chloride, tin(IV) chloride, or iron(III) chloride. Normally an α-chloro sugar is the product. If a β-chloro product is formed first (kinetic product) by participation from a 2-*O*-substituent, this is rapidly equilibrated into the thermodynamically more stable α product (anomeric effect, Section VI). The transformation is compatible with acetyl, benzoyl, and benzyl protecting groups and most importantly, also with the presence of inter-residue glycosidic bonds.[229,230]



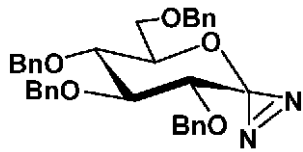
7. Photolysis

Photolytic cleavage at the anomeric center of glycosides as an analytical or preparative tool does not have a very extensive literature. It has, however, been found useful in the solid-phase synthesis of oligosaccharides. Thus the synthesis by Nicolaou and coworkers of the phytoelicitor heptasaccharide of *Phytophthora megasperma* (Section V) depends on detachment of the protected heptasaccharide from the support by photolytic cleavage of a 4-nitrophenoxy link to the polystyrene polymer.

Photochemical cleavage in the presence of 1,4-dicyanonapthalene of aryl 1-thio-β-D-glucopyranosides produces glycosylthio radical-cation intermediates, which then split to give an oxocarbenium ion. However, the process is not compatible with the presence of *O*-benzyl groups and has not found general use in glycoside synthesis.[2]

Electro-oxidative generation of oxycarbenium ions from 1-thioglycosides also proceed via glycosylthio radical-cations to produce oxocarbenium ions. These react with alcohols to give glycosides. In contrast to the foregoing photochemical process, the electro-oxidative procedure is compatible with the presence of benzyl groups, and is therefore potentially more useful.[3]

Thermal or photolytic treatment of the diazirine illustrated here in the presence of a range of alcohols [MeOH, EtOH, Me_2CHOH, Me_3COH, F_3CCH_2OH, and $(F_3C)_2C(Me)OH$] produces the correponding glycosides. The diastereoselectivity varies with the acidity of the alcohol, the nature of the solvent, and the reaction temperature.[231]



Photoinduced activation by electron transfer between aromatic compounds and the phenylselenyl group of selenoglycosides generates glycosyl cations that react with various alcohols to give *O*-glycosides.[232]

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ADVANCES IN CARBOHYDRATE CHEMISTRY AND BIOCHEMISTRY, VOL. 59

HYDRAZINE DERIVATIVES OF CARBA SUGARS AND RELATED COMPOUNDS

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I. Importance of Carba Sugars[1–11]

Carba sugars are carbocyclic analogs of monosaccharides in which the ring-oxygen atom has been replaced by a methylene group. They were first synthesized by McCasland and coworkers,[12] who called them "pseudo-sugars," but they

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were later renamed "carba sugars."* They are now grouped as a subclass of the larger family of cyclitols, which counts among its members several biologically and pharmacologically important compounds, such as inositols, conduritols, cyclophellitols, mannostatins, validamine, and aristermycin. Carba sugars have received considerable attention due to the close similarity between their structures and those of carbohydrates, which imparts upon several carba sugars the ability to inhibit such enzymes as glycosidases[13–26] and the growth of bacteria[27,28] (as for example by carba-α-D-galactopyranose). Most carba sugars are also resistant to enzymatic and acid hydrolysis, in contrast to sugars, because they lack the hemiacetal function of the latter.

Certain aminocyclopolyols (amino-polyhydroxycyclohexanes) have long been known as constituents of several broad-spectrum antibiotics, such as streptomycin, gentamicin, and tobramycin, which interfere with translational fidelity during protein synthesis. More recently amino-cyclopentanepolyols have been recognized as important glycosidase inhibitors. Examples of such compounds are, mannostatin A and cyclopentylamine (both of which are potent α-D-mannoside inhibitors), allosamidine (a chitinase inhibitor), and trehazolin and its aglycon, trehalamine (α,α-trehalase inhibitors).[29–45]

Carbocyclic nucleoside analogues have also attracted considerable attention because of their antiviral and antitumor activities. Of particular interest are cyclohexenyl nucleosides, whose conformation resembles that of natural nucleosides. They can hybridize with nucleic acids and may therefore hold promise as components of antisense oligonucleotides.[46–52]

Related to carba sugars are the imino sugars, which have attracted considerable attention because many members of this group act as enzyme inhibitors, while others show anticancer and/or anti HIV activity.[53–78]

The chemistry of carba sugars is quite similar to that of cyclitols; both groups lack the latent carbonyl groups of their saccharide counterparts, and therefore fail to exhibit many of the characteristic properties of monosaccharides. Thus carba sugars and cyclitols do not form hydrazones or osazones, nor do they mutarotate, or reduce heavy-metal salts in base, in contrast to their oxidation products, the inososes.

* IUPAC-IUBMB "Nomenclature of Carbohydrates,"*Adv. Carbohydr. Chem. Biochem.*, 52 (1997) 43–177; see also Nomenclature of Cyclitols, *Eur. J. Biochem.,* 57 (1975) 1–7.

II. Synthesis of Carba Sugars and Cyclitols

Interest in carba sugars has resulted in the development of a plethora of synthetic approaches that were used to prepare all 16 racemic carba-hexopyranoses as well as their enantiopure α and β forms. For example, the potential use of carba-fructopyranose as an artificial sweetener led to the synthesis of racemic, and later to enantiomerically pure, 6-carba-β-D-fructopyranose.[79–88] Several carba sugars have been synthesized from such naturally occurring cyclohexanol derivatives as quinic acid (1,3,4,5-tetrahydroxycyclohexanecarboxylic acid)[89–96] and quebrachitol (2-*O*-methyl-*chiro*-inositol),[97–107] as well as from cyclic and acyclic saccharides.[108–123] Cyclization of acyclic carbohydrate intermediates was achieved via free radicals generated by halogens or by other means.[124,125] Other carba sugars have been prepared by using a variety of metal catalysts,[126–145] by alkene ring-closing metathesis reactions, and by ring opening of oxabicyclic alkenes,[146–155] as well as by addition, or cycloaddition, of dienes via Diels–Alder-type reactions.[156–163] Finally some carba sugars have been prepared by microbial oxidation of benzene derivatives, for example, (+)-pinitol (which possesses hypoglycemic activity),[164–172] was produced from halobenzenes by oxidation using such microorganisms as *Pseudomonas putida*.[164–172] Recently, more complex carba sugars have been synthesized, for example carba disaccharides,[173–185] certain of which inhibit resistance-causing enzymes in bacteria, and carba nucleotides that are capable of inhibiting key enzymes.[186–193]

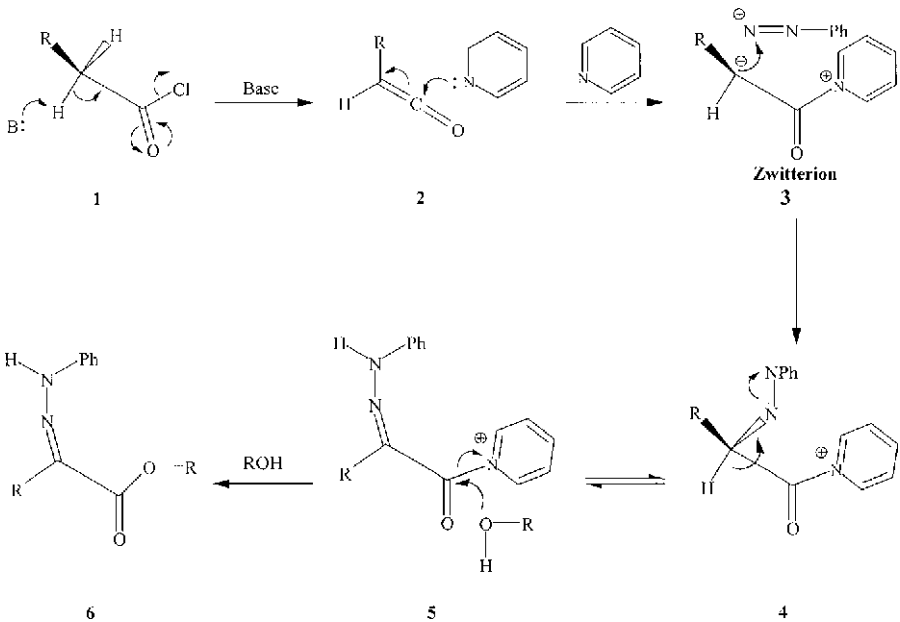
III. Ketohydrazones and α-Hydrazono Esters of Cycloalkanones

1. General

Carba sugars and cyclitols do not form hydrazones, but their oxidation products, the inososes and ketocyclitols, readily react with hydrazines to form hydrazones. Many inososes prepared as intermediates during the synthesis of the carba sugars mentioned in the previous section, or synthesized as target compounds, were purified by conversion into phenylhydrazones. For example, 2,4,6/3,5-pentahydroxycyclohexanone (*myo*-inosose-2), was purified by crystallization of its phenylhydrazone, which was then treated with benzaldehyde or with a sulfonic acid type cation-exchange resin to regenerate the pure inosose.[194–198] Other phenylhydrazones were prepared from the hydroxycyclohexanones,

hydroxycyclopentanones, or hydroxycyclobutanones and used as synthons of natural heterocycles or as model compounds in the study of their absorption spectra.

In addition to forming hydrazones by adding nucleophilic hydrazines to the carbonyl carbon of inososes, it is possible to reverse the polarity of the reaction and prepare hydrazones by reacting electrophilic diazonium salts with the active methylene groups of ketenes or 1,3-diones.[199–205] It was recently shown that α-hydrazono esters may be prepared in a one-step reaction by simply adding diazonium salts to acyl halides (**1**) dissolved in pyridine. The reaction starts with the formation of a ketene (**2**), which exists as a zwitterion (**3**) in basic media. Coupling the electrophilic phenyldiazonium salt to this zwitterion affords a phenylazo derivative (**4**), which tautomerizes to the more stable phenylhydrazono form (**5**), and treatment of the reaction mixture with ethanol yields an α-hydrazono ester (**6**), (see Scheme 1).[204] Alternatively, addition of water yields an α-hydrazono acid, and by addition of hydrazine, a hydrazonohydrazide. A number of analogous ketene reactions have been carried out with acid chlorides obtained from steroids and were found to give consistently high yields of the α-hydrazono products.[204] This



SCHEME 1. Formation of α-hydrazono esters by reacting arenediazonium salts with the active methylene group of acyl chlorides.[204]

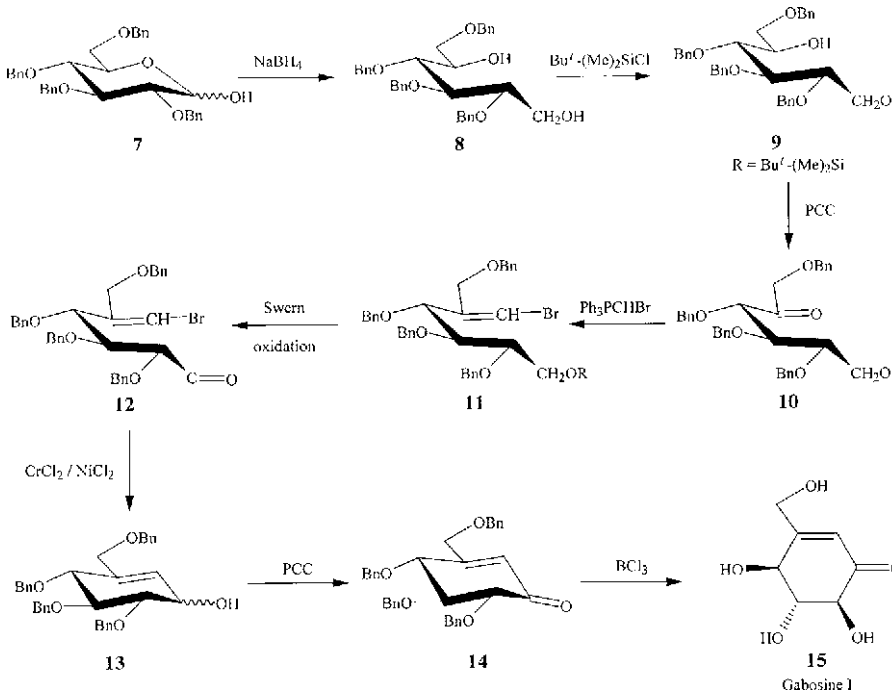
method holds great promise for the synthesis of α-hydrazono esters of carba sugars and of analogous reactions with such acyclic sugar derivatives as 2-deoxyaldonic acid chlorides. Finally, the reaction of diazonium salts with the active methylene group of β-diketones and diesters is well established, it was used in the formation of cyclohexane-1,2,3-trione 2-phenylhydrazone from cyclohexane-1,3-dione and benzenediazonium chloride.[199–205]

Discussed in the following sections are the syntheses of hydroxycyclohexanones, hydroxycyclopentanones, hydroxycyclobutanones, and their hydrazones.

2. Hydroxycyclohexanones (Inososes) and Their Hydrazones

a. Hydroxycyclohexanones and Their Monohydrazones.—Among the naturally occurring cyclohexanones are several carba sugars that exhibit interesting biological properties.[206–220] For example some gabosines inhibit enzymes, while others possess antibacterial properties (for example gabosine C), and at least one (gabosine E) inhibits cholesterol biosynthesis.[219,220] The most widely used procedure for the synthesis of inososes was introduced by Ferrier and coworkers. They and others succeeded in converting 6-deoxy-5-enopyranosides into enantiomerically pure inososes and deoxyinososes by a mercury salt-mediated ring transformation[206–209] (a Ferrier reaction is depicted in Scheme 14). Many inososes have been prepared chemically by oxidation of inositols, quinic acid, and D-glucopyranose and D-ribofuranose derivatives,[217–224] while others were obtained biochemically by bacterial oxidation of inositols.[225,226] An example of the chemical synthesis of a ketonic carba sugar derivative is the conversion of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**7**) into gabosine I (**15**), as outlined in Scheme 2. The reaction starts with borohydride reduction to form 2,3,4,6-tetra-*O*-benzyl-D-glucitol (**8**), followed by 1-silylation (giving **9**) and oxidation with pyridinium chlorochromate (PCC) to form an L-sorbose derivative (**10**), which is then subjected to a Wittig reaction that yields exclusively the *Z* isomer of a vinyl bromide (**11**). A Swern oxidation then yields aldehyde **12**, which is cyclized to **13** with $CrCl_2/NiCl_2$ and then oxidized by PCC to form tetra-*O*-benzylgabosine I (**14**), which is finally deprotected to give the desired gabosine I (**15**).[220]

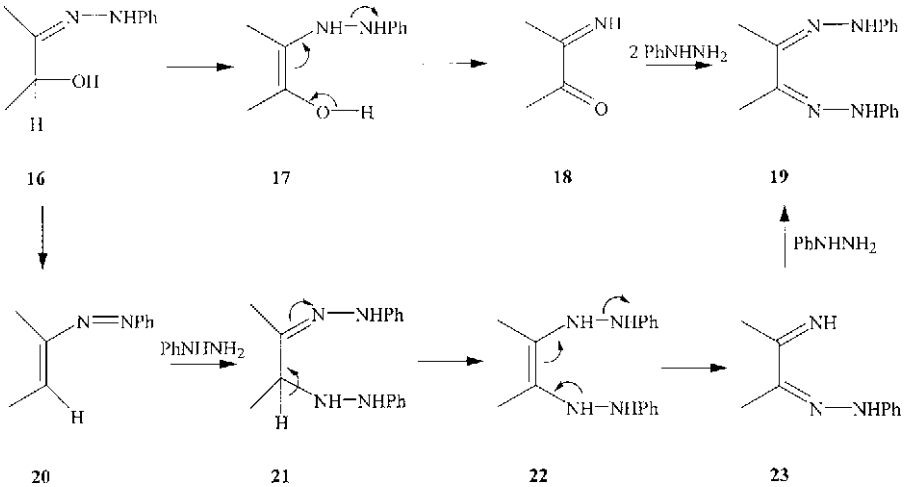
b. Formation of Inosose 1,2-Bis(phenylhydrazones).—Inosose phenylhydrazones, such as *myo*-inosose-2 phenylhydrazone, are converted with difficulty into bis(phenylhydrazones); for this reason, many cyclitol osazones have been prepared



SCHEME 2. Synthesis of gabosine I from tetra-*O*-benzyl-D-glucopyranose.[220]

directly from cyclic 1,2-diketones.[217,227–234] Investigation of the rate of formation of cycloalkane-1,2-dione bis(phenylhydrazones) (**19**) from 2-hydroxycycloalkanone phenylhydrazones (**16**) revealed that the azoalkene **20**, formed by 1,4 elimination, rather than **17** and **18**, was a key intermediate in these reactions proceeding via **21**, **22**, and **23**. Other studies have confirmed the formation of intermediate azoalkenes similar to **20** during the conversion of α-acetoxycyclohexanone, and of α-substituted oxo-steroids into the corresponding bis(phenylhydrazones) **19** (Scheme 3).[229,230]

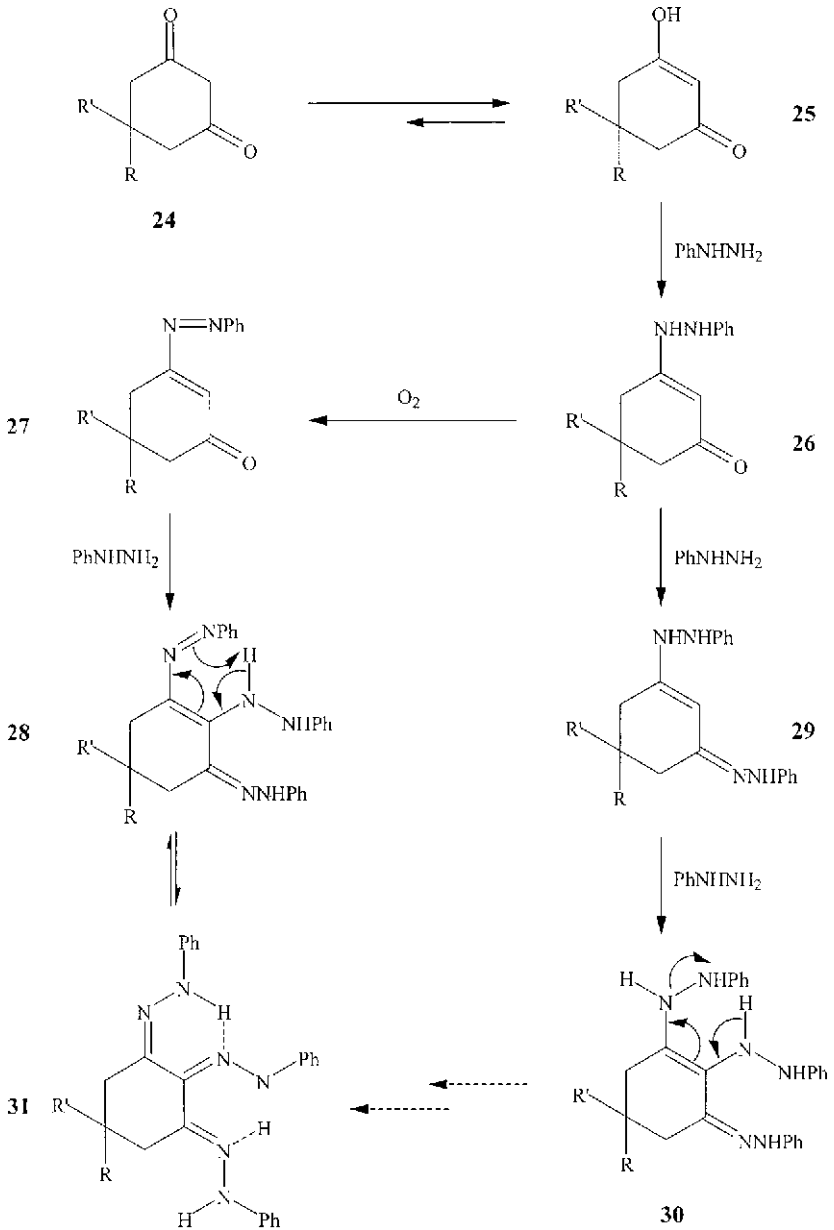
c. Conversion of Cyclohexane 1,3-Dione into Bis- and Tris-(phenylhydrazones).—Reaction of the tautomeric forms of cyclohexane-1,3-dione derivatives (**24, 25**) with phenylhydrazine yields the cyclohexane 1,3-dione 1,3-bis(phenylhydrazones) (**29**) and cyclohexanetrione tris(phenylhydrazones), shown in the chelated form **31**. The reaction proceeds by an ionic mechanism, such as that shown in Scheme 4.[235–238] It involves oxidation of the phenylhydrazinocyclohexenone **26** by air to give a phenylazocyclohexenone (**27**), which upon nucleophilic



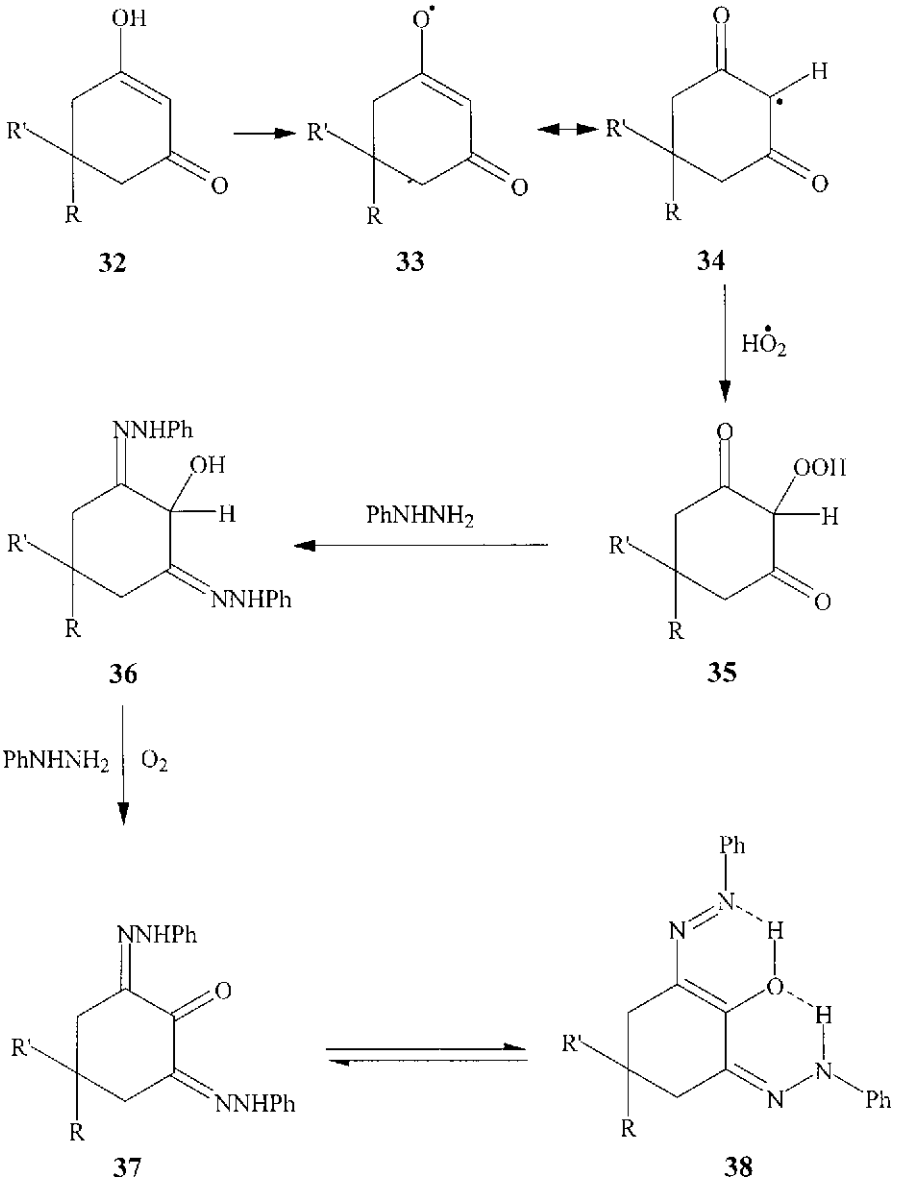
SCHEME 3. Formation of inosose 1,2-bis(phenylhydrazones).[229,230]

addition of phenylhydrazine, affords a phenylazophenylhydrazinocyclohexenone phenylhydrazone (**28**), which tautomerizes to the tris(phenylhydrazone) **31**. Alternatively, the cyclohexenone phenylhydrazine (**26**) reacts with phenylhydrazine to affords first a hydrazinocyclohexenone phenylhydrazone (**29**) and then a bis(phenylhydrazino)cyclohexenone phenylhydrazone (**30**). This is an analogue of a key intermediate in Weygand's mechanism,[11] which undergoes oxidation by heterolytic fission of the N–N bond of a bishydrazine residue to form aniline, and an imino group. The latter reacts with another phenylhydrazine molecule to afford the isolated cyclohexanetrione tris(phenylhydrazone) **31**. The formation of this compound by an ionic mechanism is supported by the fact that, upon treatment with phenylhydrazine and acetic acid, intermediates **26**, **27**, and **30** all give the same tris(phenylhydrazone) **31**, without formation of any paramagnetic species.[239–241]

d. Cyclohexane 2-Oxo-1,3-bis(phenylhydrazone).—Unlike the previous cyclohexanetrione 1,2,3-tris(phenylhydrazones), the formation of cyclohexanetrione bis(phenylhydrazones) **37** and **38** from 1,3-cyclohexanediones (**32**, **33**, and **34**) involves a free-radical peroxidation to form **35**. Condensation with phenylhydrazine yields a 2-hydroxy-1,3-bis(phenylhydrazone) **36**, which is oxidized to the cyclohexanetrione bis(phenylhydrazones) **37** and **38**. The formation of free radicals was established by electron spin resonance (ESR) studies of solutions containing the cyclohexane-1,3-dione and phenylhydrazine, which revealed



SCHEME 4. Formation of 1,2,3-tris(phenylhydrazones) by an ionic mechanism.[235–241]



SCHEME 5. Formation of cyclohexane-1,2,3-trione 1,3-bis(phenylhydrazone) by a free-radical mechanism.[235–241]

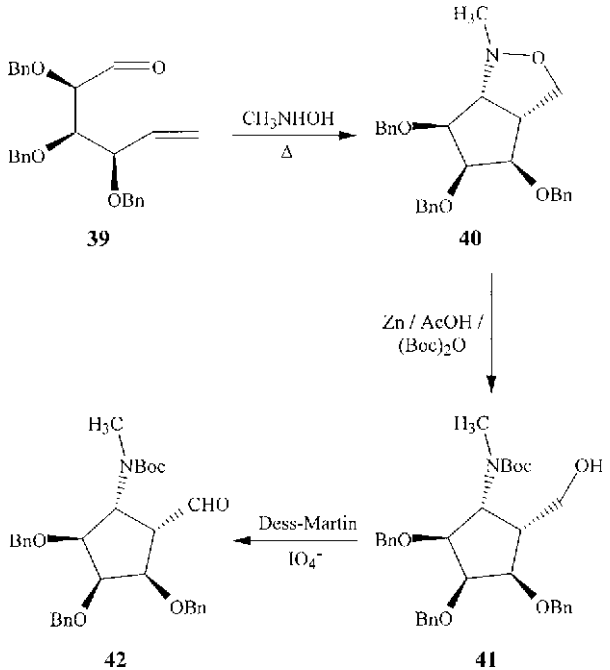
the presence of a paramagnetic species, identified as a phenylazo radical (Scheme 5).[235–238]

Free-radical and photo-oxygenation reactions of compounds containing C=N groups, such as hydrazones, are not uncommon, for example, the N–H groups of hydrazones react with oxygen to give C-hydroperoxy-azo adducts, and *N,N*-dimethylhydrazones having C–H bonds react with singlet oxygen ($^1O_2$) to give ketones.[242–252]

3. Hydrazones of Cyclopentyl Carboxaldehydes and Hydroxycyclopentanones

It was already mentioned that naturally occurring aminocyclopentitols occur in several antibiotics and others are glycosidase inhibitors.[13–26,29–45] The synthesis of these compounds was found to be more challenging than that of their six-membered ring counterparts, because of the close proximity of the functionalities and chiral centers. In spite of this, useful syntheses have been devised for their preparation; these include, (a) subjecting ω-halo-α,β-unsaturated esters, derived from a carbohydrate, to radical cyclization reactions mediated by samarium iodide (SmI_2); (b) aldol condensations; and (c) 1,3-dipolar cycloadditions.[253,254] Cyclopentyl carboxaldehydes and hydroxycyclopentanones capable of forming hydrazones have been prepared as intermediates in the synthesis of aminocyclopentitols, or as the desired products themselves. An example of the first type is the synthesis of a cyclopentyl carboxaldehyde derivative (**42**) needed as a precursor to an α-mannosidase inhibitor. It was prepared from a 2,3,4-tribenzyloxy-5-penteneal (**39**), which was treated with *N*-methylhydroxylamine and the resulting oxazolidine (**40**), reduced and *N*-blocked with a *tert*-butoxycarbonyl (Boc) group to form a 2,3,4-tribenzyloxy-2-hydroxymethylcyclopentylamine derivative **41**. This was readily oxidized to the desired cyclopentanecarboxaldehyde derivative **42** (Scheme 6).[255]

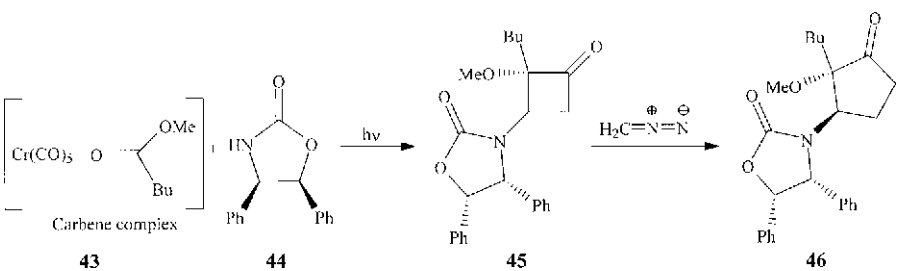
Hydroxycyclopentanones and hydroxycyclohexanones are both accessible by ring expansion of such strained rings as are present in cyclobutanone and cyclobutenedione. Two examples of such ring expansions are given (see Schemes 7 and 9); the first, to a cyclopentanone, is mediated by diazomethane, and the second to a cyclohexadienedione (a benzoquinone) with an alkynyllithium (see Scheme 9). In the first example, a chromium carbene complex **43** was combined with a chiral racemic aryloxazolidinone (**44**) to produce the cyclobutanone **45**,



SCHEME 6. Synthesis of a cyclopentylcarboxaldehyde capable of forming a hydrazone.[255]

which was then treated with diazomethane to afford the desired substituted methoxycyclopentanone **46**.[256]

The polyhydrazones of cyclopentane-1,3-diones and -1,2,3-triones, like their cyclohexane counterparts, are accessible from 1,3-diones. For example, cyclopentane- 1,3-dione yields cyclopentane-1,2,3-trione 3-phenylhydrazone

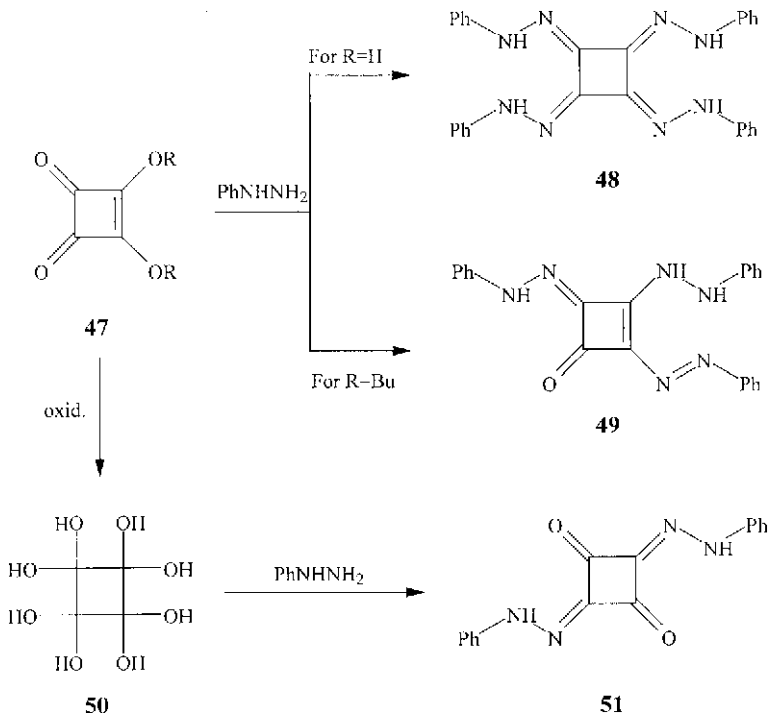


SCHEME 7. Synthesis of a methoxycyclopentanone by ring expansion of a cyclobutanone with diazomethane.[256]

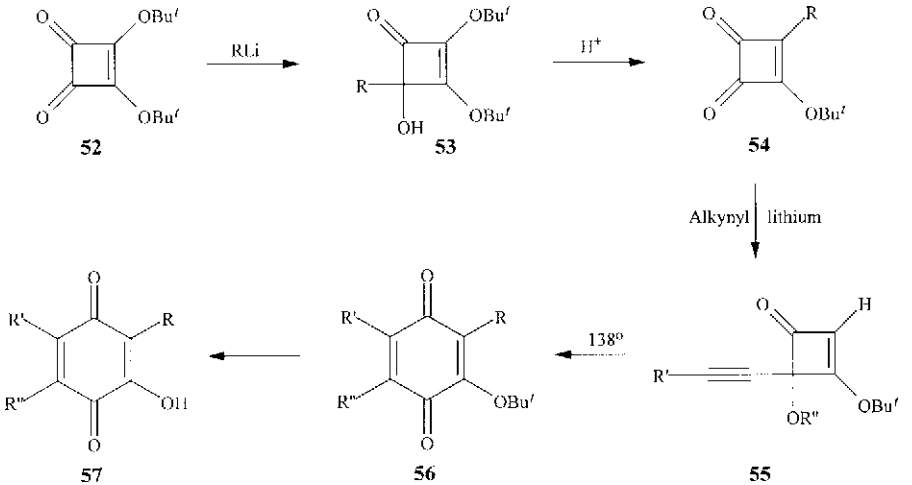
by treatment with benzenediazonium chloride, and 1,2-bis- and 1,2,3-tris-(phenylhydrazones) by treatment with phenylhydrazine.

4. Hydrazones of Cyclobutanones and Squaric Acid[257–263]

Cyclobutane polyhydrazones are accessible from the commercially available squaric acid (**47**, R = H). The latter, when treated with phenylhydrazine yields a tetrakis(phenylhydrazones) (**48**), and its butyl ester (**47**, R = Bu) yields the tris(phenylhydrazone) **49**. When squaric acid is oxidized by bromine to cyclobutanetetraone (shown in the tetrahydrated form **50**) and treated with phenylhydrazine, it yields the 1,3-bis(phenylhydrazone) **51**. The tetrakis- and the bis-(phenylhydrazones) exist in the all-hydrazone forms, whereas the tris(phenylhydrazone) exists in the azoenehydrazine form **49** (see Scheme 8).[257–261]



SCHEME 8. Synthesis of squaric acid phenylhydrazones.[258–260]



SCHEME 9. Ring expansion of acetylene-substituted squaric acid esters and formation of substituted cyclohexadienediones.[264]

Treatment of di-*tert*-butylsquarate (**52**) with an alkyllithium gives **53**, which yields upon acidification, an alkyl *tert*-butylcyclobutenedione (**54**). Reaction with an alkynyllithium introduces an acetylene group in the ring giving **55** and, if desired, a new R′ substituent. Pyrolysis causes expansion of the strained four-membered ring and yields a cyclohexadienedione (**56**) having the newly introduced substituent R′ in the ring. Hydrolysis of the ester group affords the desired substituted 2-hydroxy-1,4-benzoquinone **57**, having the selected R, R′ and R″ groups (see Scheme 9).[264]

IV. STRUCTURE AND CHELATION OF CYCLOALKANE HYDRAZONES

The structure of inosose mono(phenylhydrazones) is quite similar to that of acyclic saccharide hydrazones; neither possess chelated rings and both exist in the Schiff-base form. Cyclization to hydrazino forms, a common process among many saccharide hydrazones, has not been observed in inosose hydrazones, probably because the resulting bicyclic compounds would be unduly strained or rigid.

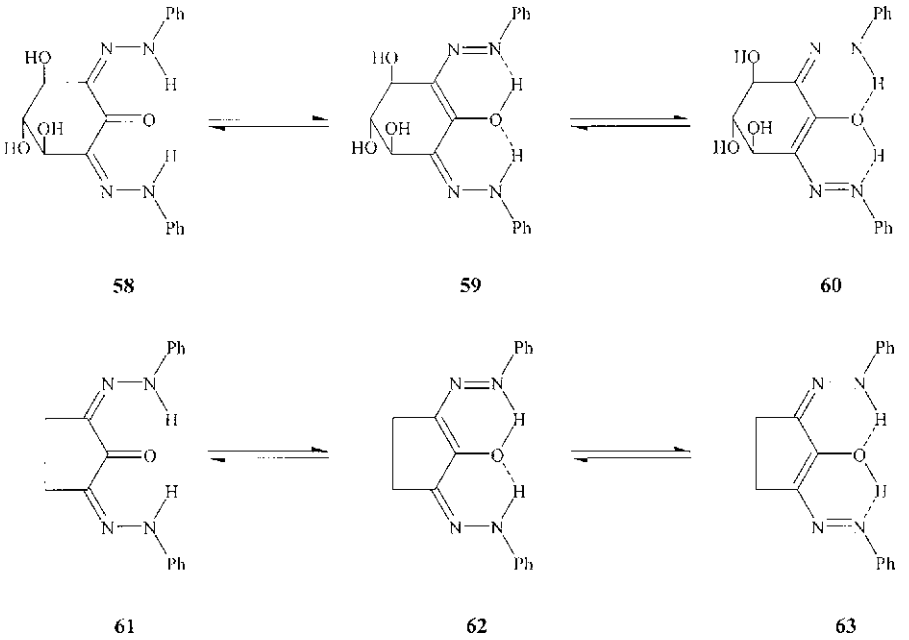
1. Chelated Structures of Bis(phenylhydrazones)

The structure of inosose bis(phenylhydrazones) resembles that of saccharide osazones in that the bishydrazone residues in both are chelated; that is, bridged by an imino group (the other NH group is unchelated).

2. Chelated Structures of 2-Oxo-1,3-bis(phenylhydrazones)

Reactions of cyclic and acyclic 1,2,3-triones with phenylhydrazine give rise to mono- and bis-(phenylhydrazones). The central carbonyl group of a vicinal tricarbonyl system is electron-deficient and highly electrophilic,[255] which is why treatment with an aryldiazonium ion affords 2-phenylhydrazones. The structure of such bis(phenylhydrazones) as cyclopentane-1,2,3-trione 1,3-bis(phenylhydrazone), dehydroascorbic acid 2,3-bis(phenylhydrazone), and cyclobutanetetraone 1,3-bis(phenylhydrazone) has been studied by UV, IR, ^{1}H-, ^{13}C-, and ^{15}N-NMR spectroscopy.[265–268] Quantum-mechanical calculations to predict the most stable tautomeric forms of some 1,2- and 1,3-bis(phenylhydrazones) revealed that the chelated bis(hydrazone) structure was usually more stable than the azoene-hydrazine structure.[269–271] This does not mean that such structures do not exist, for example cyclobutanetetraone 1,2,3-tris(phenylhydrazone) exists in a stable phenylazoene-hydrazine structure (see **49** Scheme 8).[257–263]

In contrast to saccharide mono- and bis-(phenylhydrazones) and inosose mono(phenylhydrazones), which are isolated in one form only, cyclohexanetrione bis(phenylhydrazones) that possess an oxo group adjacent to a phenylhydrazone residue exist in more than one form. Several 2-oxo-1,3-bis(phenylhydrazones) exist in two tautomeric forms, one yellow and one red.[269–271] When freshly prepared, 2-oxo-1,3-bis(phenylhydrazones) are usually yellow, but they become dark red on being kept or on heating. The yellow forms possess bis(phenylhydrazone) structures, such as **58** and **61**, and the red ones exist as tautomeric pairs of enolic phenylhydrazono-phenylazo structures (**59, 60**) and (**62, 63**). The deep-red color of 2-oxo-1,3-bis(phenylhydrazones), and the strong $\pi \rightarrow \pi^*$ absorptions suggest that they have conjugated phenylhydrazono-phenylazo groups, similar to the diphenylformazans of sugars.[11,13–26] The latter were studied by ^{15}N-NMR spectroscopy using ^{15}N-labelled formazans, which confirmed the formazan ring structure. The marked similarity in the absorption spectra of the 2-oxo-1,3-bis(phenylhydrazones) and of formazans clearly supports the phenylhydrazono-enol-phenylazo structures

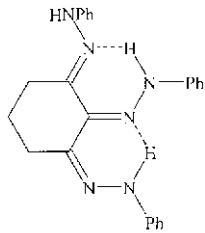


SCHEME 10. Chelated forms of trihydroxycyclohexanetrione bis(phenylhydrazone) and cyclopentanetrione bis(phenylhydrazone).[270,271]

assigned to these compounds. This was confirmed by ^{1}H-NMR studies, which revealed the presence of both chelated and non-chelated imino protons in the spectra of the tautomeric forms **58–60** and **61–63**.[270,271] It seems that interconversion of the tautomers occurs in polar solvents, and that structure **58** is preponderant in the solid state or in nonpolar solvents.[270,271] Quantum-mechanical calculation (HMO) of the bonding energies of various tautomers indicates that the most stable tautomeric structure is the bis(phenylhydrazone) (**58** and **61**) (Scheme 10).[242–246]

3. Chelated Structure of Tris(phenylhydrazones)

Vicinal tris(phenylhydrazones) of cyclitols, as with 2-oxo-1,3-bis(phenylhydrazones), possess two chelated-ring structures. The NMR spectra of 1,2,3-tris(phenylhydrazono)cyclohexane (**64**), 1,2,3-tris(phenylhydrazono)



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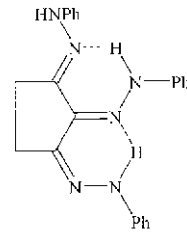

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SCHEME 11. Chelated structures of cyclohexane- and cyclopentane-1.2.3-trione tris (phenylhydrazones).[270,271]

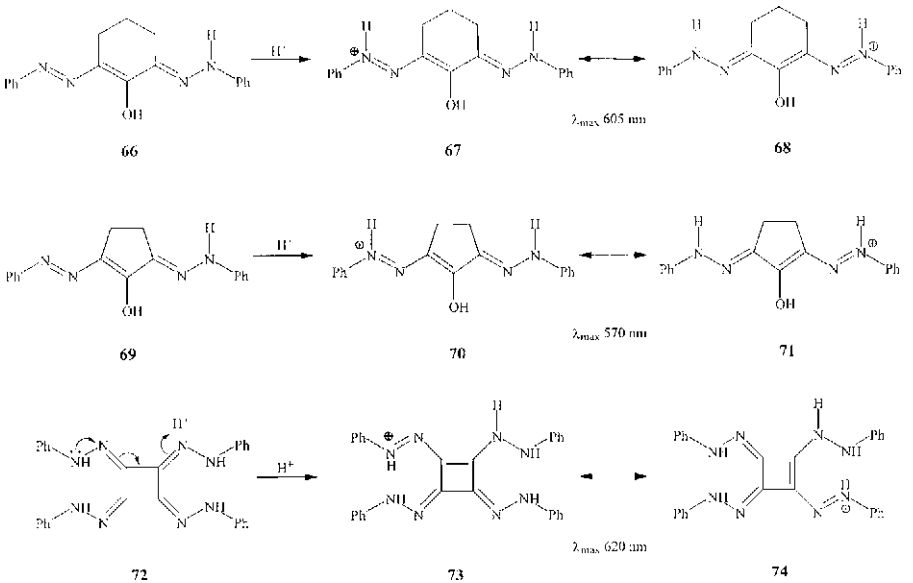
cyclopentane (**65**), and other vicinal tris(phenylhydrazono)cyclohexanes all confirm the presence of two chelated rings (Scheme 11).[270,271]

V. REACTIONS OF CYCLOALKANE PHENYLHYDRAZONES

1. Action of Acids and Bases

a. Formation of Resonance-Stabilized Anions.—Protonation of 2-oxo-1,3-bis(phenyl-hydrazones), of diphenylformazans, and of 1,2-bis(phenylazo)ethene turns these red colored compounds into purple or blue, whereas cyclitol phenylosazones and bis(phenylhydrazones) do not undergo such changes.[271] For example, addition of perchloric acid to a solution of 2-oxo-1,3-bis(phenylhydrazono)cyclohexene (**66**) and 2-oxo-1,3-bis(phenylhydrazono)-cyclopentene (**69**) gives rise to protonated, resonance-stabilized, blue-colored cations **67** and **68**, and **70** and **71**, respectively.[270,271] The polyphenylhydrazones of cyclobutanetetraone, such as the tetrakis-, tris-, and bis-(phenylhydrazones), also change color when acidified.[257–261] For example the red cyclobutanetetraone tetrakis(phenylhydrazone) (**72**) turns deep blue on acidification due to the formation of resonance-stablized cations (**73** and **74**), which possess a more-extended conjugation system than the neutral compound **72** becuse the phenyl rings in their resonance hybrid are in conjugation with the azoenehydrazine system. The groups needed to form such extended resonance-stabilized hybrids include phenylazo groups linked through double bonds to phenylimines, or to phenylhydrazone groups.[259–261]

Bis- and tris-phenylhydrazones that possess keto groups exhibit hypsochromic shifts in basic media, because they readily tautomerize to enolates, which are



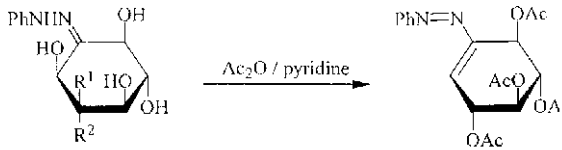
SCHEME 12. Structure of 2-oxo-1,3-bis(phenylhydrazono)-cyclohexene, -cyclopentene, and squaric acid tetrakis(phenylhydrazone) in neutral and acid media.[258–261,270,271]

stronger acids. These enolates possess weaker chromophores than the starting keto forms (a C=C group can only undergo $\pi \rightarrow \pi^*$ transitions, whereas a C=O groups can undergo $\pi \rightarrow \pi^*$, as well as $n \rightarrow \pi^*$ transitions) (Scheme 12).[258–261]

b. Formation of Stable Free Radicals.—Unlike saccharide hydrazones, which decompose in basic media and exhibit the three-line ESR patterns characteristic of nitroxide radicals, the more stable free radicals of inosose phenylhydrazones and their esters are clearly revealed in ESR spectra. For example, 2,4,5,6/3-pentahydroxycyclohexanone phenylhydrazone pentapropanoate (DL-*epi*-inosose-2 phenylhydrazone pentapropanoate), shows a 30-line spectrum.[272]

2. Elimination Reactions (Formation of Phenylazo-cycloalkenes)

Elimination reactions, similar to those observed when saccharide phenylhydrazones are treated with base during acetylation, have been observed with some, but not all, inosose phenylhydrazones. Thus, treatment of



75: R^1–H; R^2–OH

77: R^1=OH; R^2=H

78: R^1 OAc; R^2–H

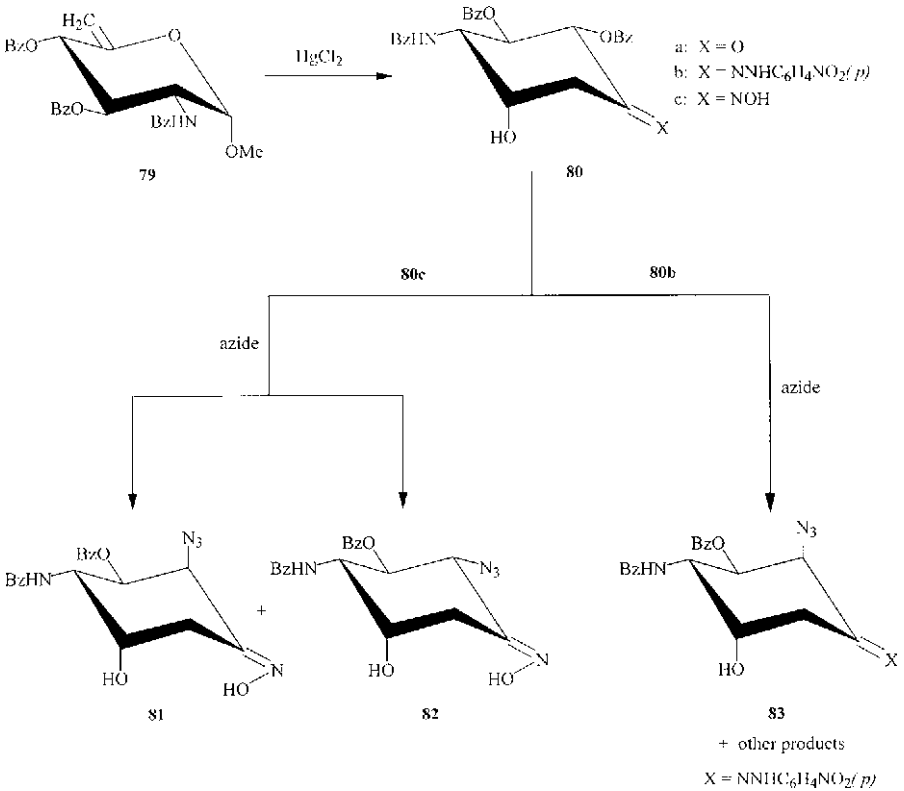
76

SCHEME 13. Formation of phenylazocycloalkenes.[272]

2,4,6/3,5-pentahydroxycylohexanone phenylhydrazone (*myo*-inosose-2 phenylhydrazone, **75**) with acetic anhydride and pyridine yields a pale-yellow elimination product, namely 6-phenylazo-5-cyclohexene DL-*ido*-1,2,3,4-tetrol tetraacetate (**76**). In contrast, a similar treatment of 2,4,5,6/3-pentahydroxycyclohexanone phenylhydrazone (DL-*epi*-inosose-2 phenylhydrazone) (**77**) yields a pentaacetate **78**, without elimination. Treatment of both inosose phenylhydrazones with propanoic anhydride and pyridine gives pentapropanoates, without elimination (Scheme 13).[272]

3. Nucleophilic Substitution

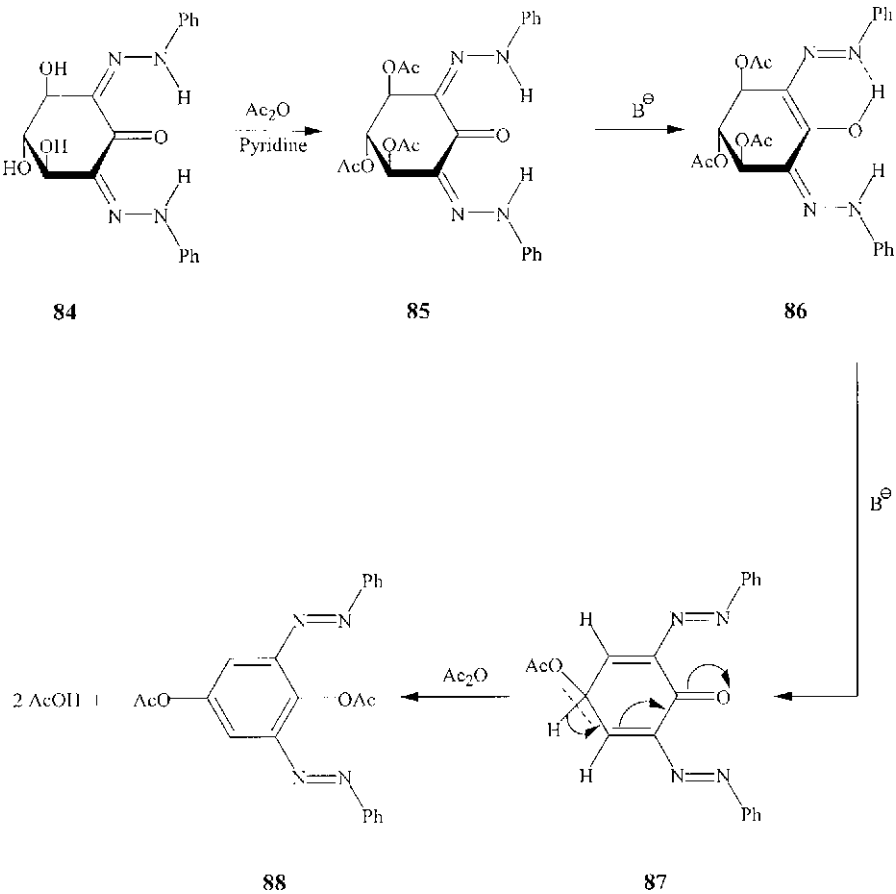
When a leaving group, present in the α position relative to a hydrazone residue, undergoes elimination such as the one just described, the resulting phenylazocycloalkene may undergo addition of a nucleophile, such as an azido group, in the same position.[273–275] For example, when [2L-(2,4,5/3)-4-benzamido-2,3-dibenzoyloxy-5-hydroxycyclohexanone, **80a**], prepared from alkene **79** via a Ferrier transformation, is treated with *p*-nitrophenylhydrazine it gives a *p*-nitrophenylhydrazone (**80b**), which upon treatment with sodium azide affords azide **83**. An analogous product is obtained from the corresponding oxime (**80c**), by treatment with tetrabutylammonium azide (see Scheme 14).[275–279] The product in this case is a mixture of the epimers of 2-azido-4-benzamido-3-benzoyloxy-5-hydroxycyclohexanone (*E*)-oxime (**81** and **82**). Here, the hydroximino group shows[274] an activating effect similar to that of the arylhydrazone group, affording a nitroso-cycloakene intermediate. Removal of the oxime or hydrazone groups from derivatives **81, 82**, or **83** to fom the azidoinososes can be achieved by use of a cation-exchange resin or by acid hydrolysis.[194–198]



SCHEME 14. Nucleophilic substitution.[275]

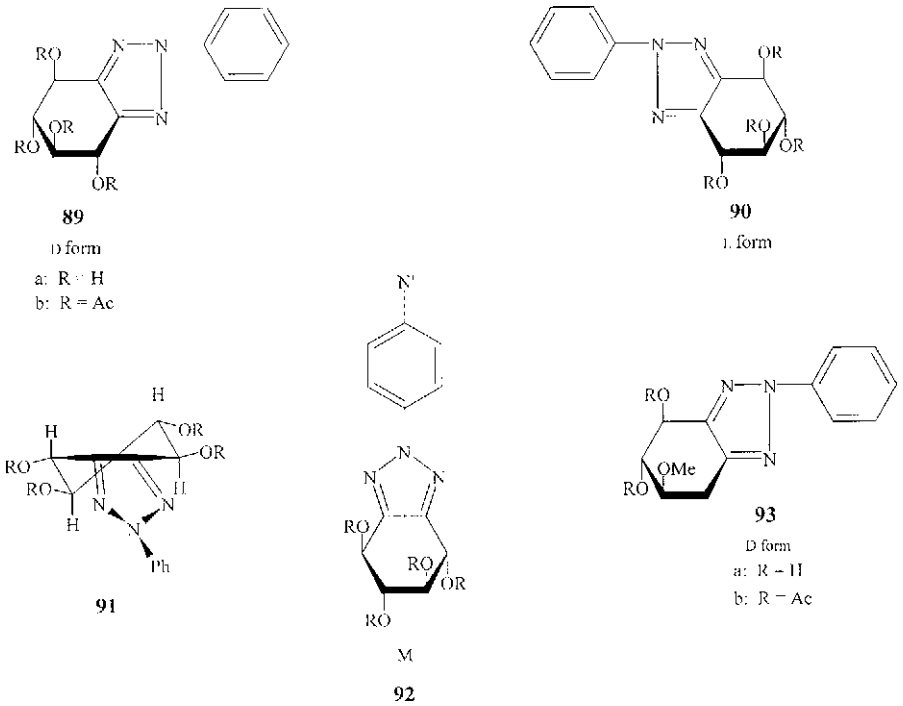
4. Aromatization

a. Aromatization of the Cyclohexane Ring.—The base-catalyzed acetylation of **75** in Scheme 13 is accompanied by elimination to give an arylazocyclohexene derivative (**76**).[272] However, the thermodynamically less stable 4,6/5-trihydroxy-1,3-bis(phenylhydrazono)cyclohexanone (**84**), shown in Scheme 15, upon similar treatment undergoes complete aromatization to give a substituted benzene **88**.[280–284] The formation of **88** from **84** probably proceeds via an ionic pathway that involves: (*i*) acetylation of the hydroxyl groups to give **85**, (*ii*) ionization of the imino hydrogen atom and enolization of the keto group to **86** and; (*iii*) sequential cleavage of the acetoxy group to give **87**, and (*iv*) aromatization with acetic anhydride to give product **88**.



SCHEME 15. Aromatization of the cyclohexane ring.[280–285]

b. Aromatization of the Bis(hydrazone) Residues: Formation of Phenylosotriazoles.—A number of cyclitol phenylosotriazoles has been prepared from the corresponding bis(phenylhydrazones). For example, 1D- (**89**), 1L-chiro- (**90**), and DL-inositol phenylosotriazoles have been prepared from the corresponding inosose phenylosazones[217–224] by using mercuric acetate as the oxidant.[285] Some cyclitol phenylosotriazoles possess symmetrical structures, as indicated by the simplicity of their proton-decoupled ^{13}C-NMR spectra.[285] Thus, the ^{1}H-NMR spectra of inositol phenylosotriazoles and their esters reveal the presence of a simple, two-fold axis of symmetry with the ring protons

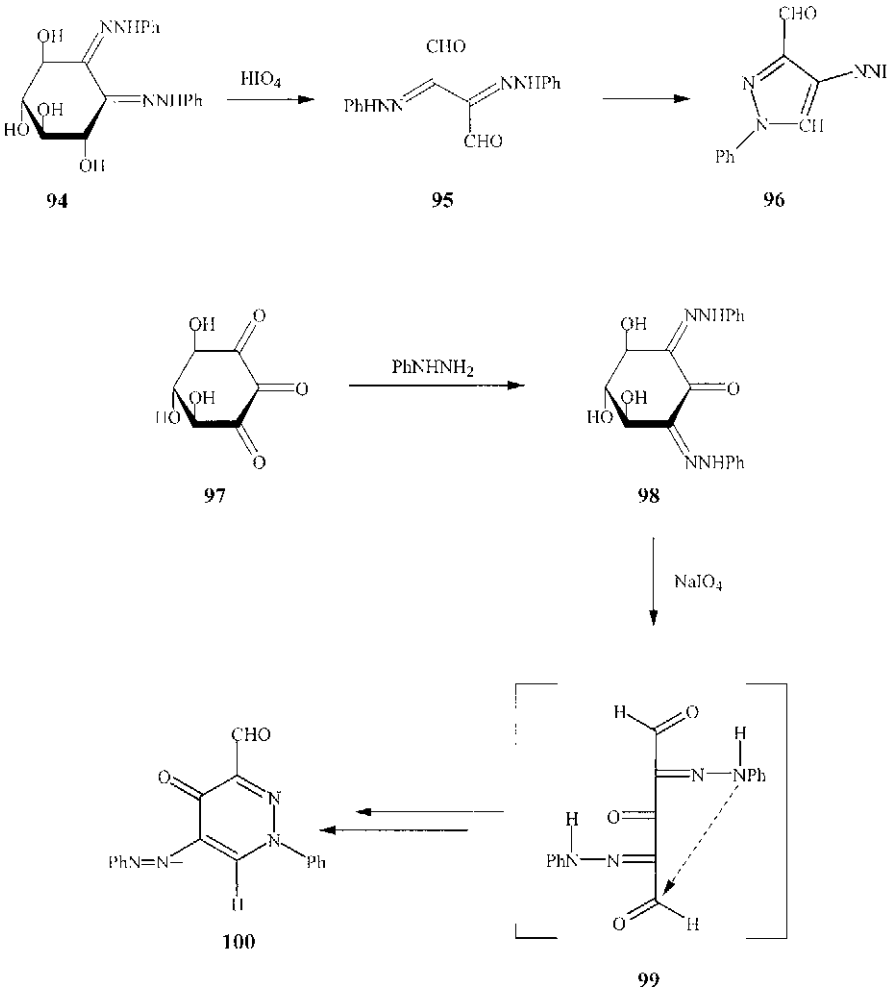


SCHEME 16. Aromatization of hydrazone residues; formation of phenylosotriazoles.[285]

symmetrically arranged about a midpoint (see **92**), affording an example of four-nucleus AA′BB′ systems. On the other hand, the NMR spectra of the substituted inositol phenylosotriazole from (+)-quercitol (1D-1,3,4/2,5-cyclohexanepentol) (**93**a) or its acetate (**93**b), which are not symmetric, show the ring proton signals as part of an ABX system.[285] In solution, the favored conformation for the osotriazole tetraisobutanoate is $^{5}H_{4}$, as depicted in structure **91**. A small coupling-constant for H-3/H-6 is attributed to the influence of the neighboring, planar osotriazole ring, and is consistent with a half-chair conformation (Scheme 16).[285]

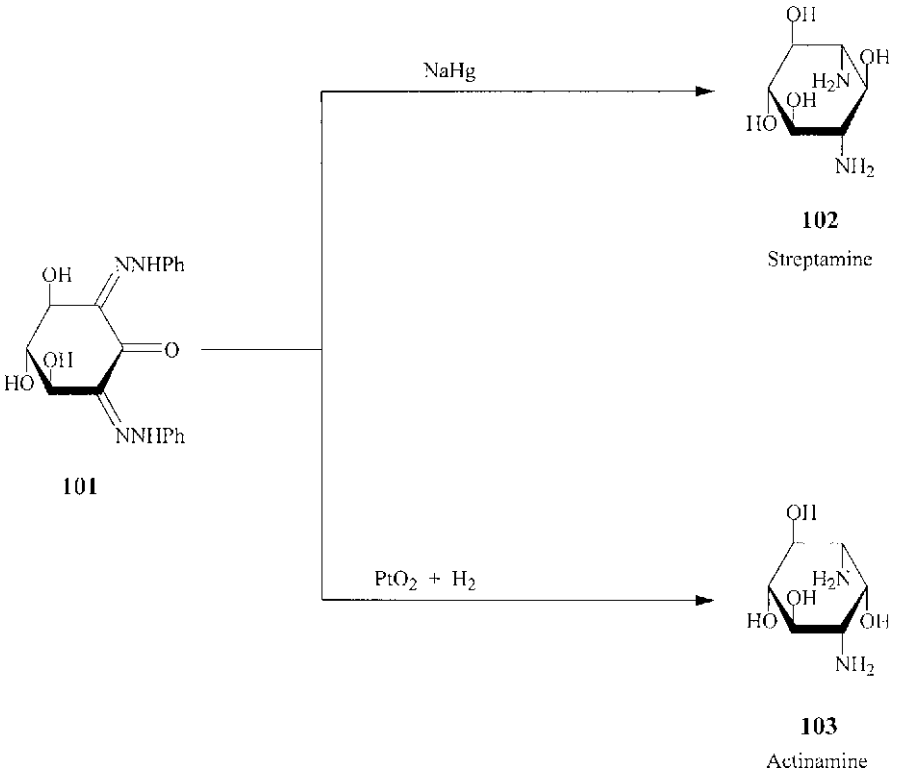
5. Oxidation and Reduction

Magasanik and Chargaff[286,287] have shown that cyclitol osazones, for example, 1D-*chiro*-inositol phenylosazone (**94**), consume the expected amount of periodate



SCHEME 17. Periodate oxidation of inositol bis(phenylhydrazones).[286–288]

(three moles), but that the product, namely, 2,3-bis(phenylhydrazono)butanedial (**95**), cyclizes to give a pyrazole (**96**). The periodic acid oxidation of cyclitol phenylhydrazones proceeds similarly,[286,287] as in the treatment of the 2-oxo-1,3-bis(phenylhydrazone) **98**,[288] with sodium periodate, which yields 3-oxo-2,4-bis(phenylhydrazono)pentanedial (**99**), and which is directly converted into



SCHEME 18. Reduction of inositol bis(phenylhydrazones).[289,298]

the hemiacetal of 4-oxo-1-phenyl-5-(phenylazo)-3-pyrazinecarboxaldehyde (**100**) (Scheme 17).[288]

Reduction of the oxobis(hydrazone) **101** provides access to biologically important derivatives. Thus, reduction with sodium amalgam gives streptamine (**102**),[289] a degradation product of streptomycin; whereas catalytic hydrogenation over platinum affords the antibiotic actinamine (**103**).[289] The formation of this 1,3-diamine, having two amino groups equatorial instead of axial, is uncommon during hydrogenation of inosose or hexulose phenylhydrazones.[290–292] This may be due to **101** existing mainly in the phenylhydrazono-phenylazo form[247–252] instead of the bis(phenylhydrazone) form,[270,271] or to the phenyl group playing a directing role during catalytic hydrogenation (Scheme 18).[289–298]

VI. Conclusions

Because of the unusually large amount of research on carba sugars and aminocyclitols published in the past decade and the high quality of some of this work, the present authors had difficulty discussing this topic within the confines of the space provided, and they were obliged to treat some novel synthetic methods quite tersely. Despite these limitations, they have endeavored to examine the subject as a whole and explain the reasons for the similarities and differences between the properties of the hydrazine derivatives of carba sugars and those of normal sugars, and to show how these influence the way the different groups behave. For example, the mechanism of formation of inosose hydrazones has been more extensively studied by ESR spectroscopy than the mechanism of formation of saccharide hydrazones, because inosose hydrazone radicals are stable and can be detected in basic media by this method, whereas the (less stable) saccharide hydrazones decompose and show only spectra of their degradation products (nitroxide radicals). As a result, ESR studies were able to reveal in the carba systems some unique free radical pathways that were either absent or not observed with their normal sugar counterparts.

In recent years, serious attempts have been made to offer plausible mechanisms for all reactions; so that when a mechanism was not be found in the literature, a "plausible mechanism" was offered based on an analogous reaction. For example, many of the reaction mechanisms of carba sugar hydrazones were based on the analogous reactions of saccharide hydrazones, and some of these were in turn modeled on benzaldehyde hydrazone reactions. Similarly, some reactions of bishydrazones are modeled on the analogous reactions of hydrazones. In many cases the mechanisms offered explained why certain isomers are formed and not others. For example, protonation of the most basic nitrogen of a chelated osazone, namely the aliphatic imine of the C-2 hydrazone, explains why the C-2 hydrazone is eliminated during acid hydrolysis to form the glycosulose 1-phenylhydrazone.

The ready availability of some sugars and inososes renders their hydrazones ideal enantiomerically pure synthons to consider in the preparation of other chiral natural products. An example of such an application is the synthesis of imino sugars by reduction of hydrazones. These imino sugars, together with the carba sugars discussed here in greater detail, continue to attracted the interest of many researchers in the medicinal chemistry field seeking compounds endowed with useful biochemical, or biological properties, such as enzyme inhibitors[55,56,59–62] and antibacterial[27,28,74] or antiviral[50,58] agents.

Among the many reaction products obtained from hydrazones and osazones that offer promise to synthetic chemists are the carbenes generated from azirines and sulfonylhydrazono-1,5-lactones by irradiation.[299,300]

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ADVANCES IN CARBOHYDRATE CHEMISTRY AND BIOCHEMISTRY, VOL. 59

CHEMICAL MODIFICATION OF STARCH

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I. Introduction

The chemical reactivity of starch is first of all controlled by the reactivity of its glucose residues. Normal amylose contains a single terminal 1-OH group on the

reducing end and one 4-OH on the nonreducing end of the macromolecule. Thus, there are in each glucose residue of amylose two secondary hydroxyl groups, at C-2 and C-3, as well as one primary hydroxyl group (at C-6). In amylopectin, each (1→6) branch decreases the number of primary hydroxylic groups by one and simultaneously increases the number of secondary hydroxyl groups at C-4 by one. The reactivity of the hydroxyl groups depends on electronic and conformational factors, including their steric availability for reagents and/or the possibility of competing β-elimination. Figure 1 shows the results of *ab initio* calculations of the order of decreasing preference for the α- and β-glucopyranose C-5–C-6 rotamers of D-glucopyranose-$^4C_1$ in the gaseous state.[1] Protonation at O-6 of these rotamers **1–6** (Fig. 1) seems to be electronically favored. AM1 molecular-orbital calculations performed for the D-glucopyranose conformers[2] indicated decreases in OH group acidity in the following order: 3-OH > 2-OH > 6-OH.

All available hydroxyl groups of amylose and amylopectin potentially exhibit reactivity specific for alcohols, that is, they can be oxidized and reduced, they may participate in the formation of hydrogen bonds, and their hydrogen atoms are susceptible to H–D isotope exchange. These groups may form salts and participate in the formation of ethers and esters. The latter may be formed with inorganic as well as organic acids, including such acyl derivatives as halides, anhydrides, and so on.

The single reducing terminal hemicaetal group in each molecule of amylose (as well as amylopectin) reacts in a manner specific to aldehydes and their hemiacetals, with the anomeric C-1 carbon atom being the reaction site. Thus, these polysaccharides can be either reduced or oxidized at this position, and also form derivatives with NH_2–X-type compounds (that is, with hydrazine, phenylhydrazine, hydroxylamine, semicarbazide, and thiosemicarbazide). The pyranose ring oxygen atom of the reducing-terminal glucose group exhibits reactivity typical for its involvement in a hemiacetal, and is susceptible to protonation, generating the 5-OH group of the open-chain saccharide. Mutarotation may consequently take place in this sole position. The full acetal character of the α-(1→4) and α-(1→6) glycosidic bonds obviates similar reactivity of the remaining glucose units, unless these glycosidic bonds are split.

Glycosidic bonds exhibit reactivity typical for the acetalic C–O–C bonds, that is, they undergo cleavage on protonation. Under acidic conditions this cleavage is rather statistical and the terminal glycosidic bonds are slightly favored over those within the chains. Such glycosidic bond-splitting (starch hydrolysis) increases the number of free 1-OH, 4-OH, and 6-OH groups, and leads ultimately to D-glucose.

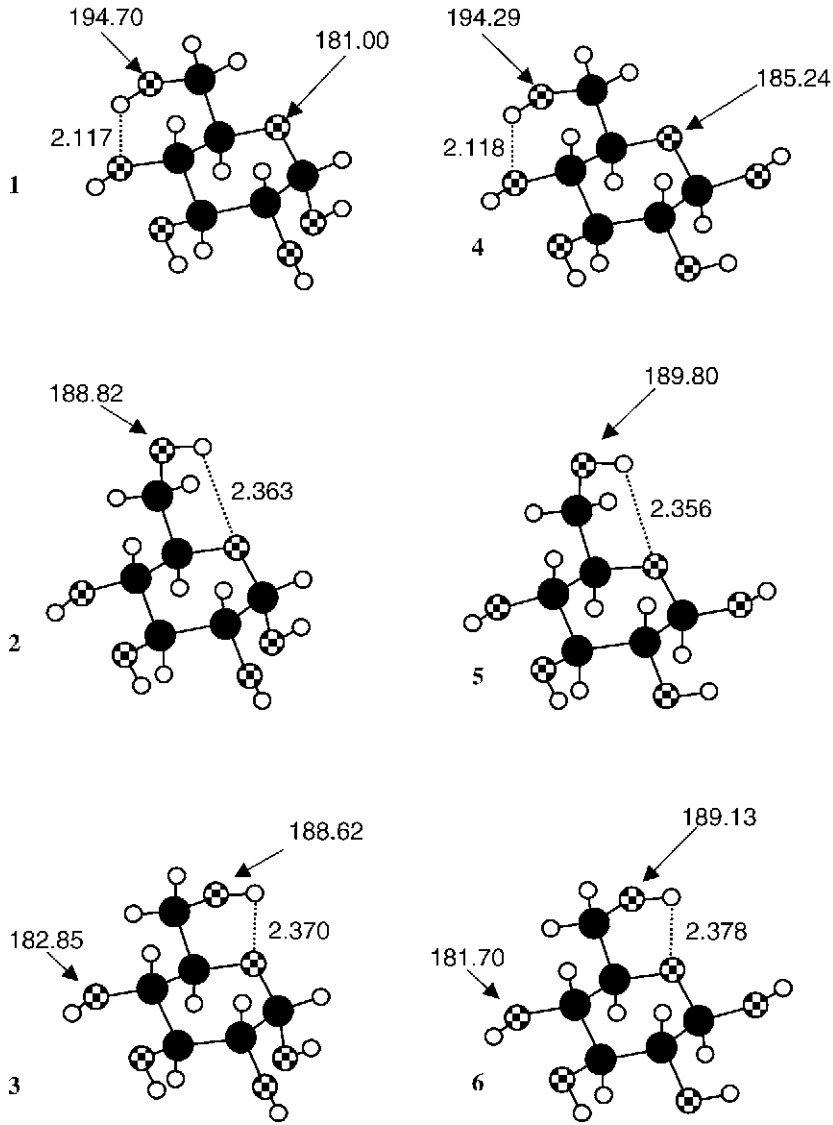


FIG. 1. Gas phase basicities of C-5–C-6 rotamers of α (left) and β (right)-D-glucose calculated by the HF/6-31G* method.[1] Hydrogen-bond distances are in Ångstrom units.

Periodates cause oxidative cleavage of the C-2–C-3 bond of glucose derivatives to give "dialdehydes."* The same reaction occurs in starch, giving "starch dialdehyde." Because of its polymeric structure, the reactions of starch show some other specific features beyond those resulting purely from the reactivity of the glucose units. The macrostructure of starch has also an impact on its reactivity. Inter- and intramolecular hydrogen-bond interactions decrease the solubility of the material and limit the accesibility of potential reaction sites to the reagents used. Entanglement[3] of amylose and amylopectin chains may also be a factor. These circumstances do not change the reactivity of starch in the qualitative sense, but may have serious quantitative impact. Hence, the selection of the reagents and reaction conditions require special consideration.

The limited solubility of starch and its modified products may affect the reversibility of many reactions. This may explain several, apparently unusual, reactions reported in starch chemistry. There are, for example, reports of starch esterification with sodium hydrogenphosphates, acylation of starch with acyl amides (which is equivalent to the transformation of an amide into an ester), and the formation of alkali-metal "starchates" upon treatment of starch with alkali (a reaction which fails for simple alcohols). A specific property of starch is its ability to form surface sorption and helical inclusion-complexes with many inorganic and organic guest molecules.[4]

The granular character of native starch also impacts on the reactivity of starch. Depending on the penetrating ability of the reagent, the reaction of starch proceeds either on the granule surface or in its interior. Moreover, the capillaries between granules, together with the polar character of the granule surface, make starch a fairly good, porous sorbent. Many reagents undergo inclusion in the capillaries, forming starch capillary complexes.

II. H–D–T Isotope Exchange and Labeled Starches

Hydrogen atoms of the hydroxyl groups of starch are accessible to deuterium oxide, and therefore, isotope exchange proceeds readily,[5] although not always completely.[6,7] Almost total exchangeability of the hydroxyl group hydrogen atoms by deuterium was found to be independent of the crystallographic pattern of

*Generally hydrated and internally cyclized.

starch and whether the molecules assumed helical or retrograded structures, but involvement of hydrogen bonds in the inhibition of exchange cannot be excluded. Penetration of the solvent carrying deuterium into starch seems to be an essential factor.[8] Thus, water and methanol completely exchanged deuterium, whereas ethanol caused only partial exchange. Plants that accumulate deuterium do so mainly via their starch content.[9]

Several properties of starch depend on intra- and inter-molecular hydrogen bonds. Therefore, it is to be expected that hydrogen–deuterium–tritium exchange will significantly modify the physical behavior of this molecule. Indeed, gels formed in heavy water exhibit a lower viscosity as a result of the higher density of the micelles.[10] Specific hydrodynamic volumes of starch micelles are also lower in heavy water than in water, which means that the bonds formed by deuterium are stronger than hydrogen bonds. It has been reported that the rate of formation of a deuterated starch complex with the I_5^- anion was higher than with non-deuterated starch.[11] The equilibrium constant for the H–D exchange in the OH hydrogen atoms is expressed as:

$$K = \{[AD_{n/n}][H_2O]\}\{[AH_{n/n}][HDO]\}^{-1} \quad (1)$$

where n is the number of OH groups in the molecule ($n = 0.8$ and 0.6 at 50 and 100 °C, respectively). The exchange is exothermic. Comparable studies performed with mono- and di-saccharides revealed that starch is hydrated in a manner similar to maltose rather than fructose.[12] Tritiation of starch by tritium-labeled water was also successful.[13] The incorporated tritium was found mainly in the outer sphere of the granules, and in this region tritium resided mainly in the non-reducing ends of the amylose molecules. This means that starch molecules are organized in the granules in such a manner that the nonreducing ends of each molecule are exposed at the granule surface.[14] Exchange of the hydrogen atoms in the hydroxyl groups of amylopectin was exhaustive.[15] Bombardment of starch with tritium resulted in 51% incorporation of that isotope in non-labile, similarly treated carbon-bound form. Negligible amounts of tritium were observed on C-3 and C-2, whereas in α-D-glucose there was no isotope on C-2, but some was observed on C-5.[16]

Labeling starch with the ^{14}C isotope of carbon at the anomeric position of the reducing terminal D-glucose unit was achieved by treatment with labeled cyanide followed by alkaline hydrolysis of the resulting cyanohydrin.[17] Labeled maltose could be prepared from such labeled starch.[18] In addition, starches modified by substitution might be labeled in the substituent being introduced, as shown by Kratz and Kaufmann,[19] who prepared starch acetylsalicylate with ^{14}C in the acetylsalicylate moiety.

III. Behavior of Starch Under Basic Conditions

The behavior of starch with base depends first of all on the type of base, its concentration, and on either the presence or absence of oxygen, as well as on the temperature and time of the reaction. Earlier reports[20] used the term "hydrolysis" to describe the reaction of starch with bases as well as with various acids and hydrolyzing salts, but the term "degradation" is more appropriate to describe the reaction of starch under basic conditions.[21]

Ammonia, one of the most frequently used bases, sorbs onto amylose regardless of the temperature, or whether it is in gaseous or liquid state. Temperature below 0 °C favors sorption on both the helix exterior and interior, whereas at 10 °C, sorption occurred only on the exterior surface.[22] It might thus be concluded that, under normal reaction conditions at room temperature and above, ammonia is a poorly penetrating reagent. Gaseous ammonia inhibited the dextrinization of starch upon roasting. Nitrogen compounds of low molecular weight were formed, presumably urea and carboxylic acid ammonium salts. In addition, residual amounts of nitrogen remained in starch after roasting for 6 h at 220 °C.[23–25] Aqueous solution of ammonia (ammonium hydroxide, being a weak base) as well as liquid ammonia in methanol, caused swelling of starch granules, their disruption, and gel formation.[26–28] Starch degraded in ammonia then combined with fatty material produce materials having "cream-like" properties.[29] The use of ammonium hydrogencarbonate provided porous, swollen starch.[30]

Diluted aqueous alkali (0.1–0.4%) at room temperature caused swelling of starch granules and also the liberation of proteins and lipids present therein. Because swelling occurs also with alkali in chlorinated hydrocarbons[31] it could be a convenient way to remove these non-carbohydrate components from starch[32,33] and a method of starch activation prior to derivatization.[34] More concentrated alkali solutions gelatinized starch.[35] It was also reported that starch gelatinization is retarded by hydroxyl anions, especially in the presence of salts, and that the gelation temperature increases with anion concentration.[36] Starch gelatinization by the action of diluted, 0.3–1% alkali, 15–25% sodium sulfate, and aqueous ammonia at room temperature was patented.[37] Prolonged action of 15–25% aqueous NaOH gave, after neutralization, a liquid starch solution useful for the starching of linen.[38] Treatment of starch with alkali in the presence of pentanols and aromatic amines gave a product that swelled in cold water.[39] Concentrated alkali formed well-defined isolable complexes with starch.[40–45] Such complexes have been proposed as flocculants for heavy metal salts.[46,47] Products of the treatment of starch with various metal hydroxides, for instance, these of zinc, magnesium, and aluminum were used as

materials for the sizing of paper.[48] Studies of the effect of various metal hydroxides upon starch degradation are lacking. However, there are some comparative studies on the effects of alkali metal hydroxides upon the course of starch xanthation.[49] An essential difference was noted between the effect of lithium and sodium hydroxides on one hand, and potassium, rubidium, and cesium hydroxides on the other. The latter three hydroxides behaved similarly in that they facilitated xanthation and also increased the degree of substitution as the hydroxide concentration increased. Neither lithium nor sodium hydroxide provided such effective xanthation. Increased concentrations of lithium and sodium hydroxides inhibited this reaction. These observations may be attributed to several overlapping effects. The penetrating effect of hydroxides into interior of the starch granule could be one critical factor. This penetrating effect is perturbed by hydration of ions and the consequent change in solution viscosity, which affects the transport properties of the solution. Larger cations decrease the solution viscosity of aqueous solutions.[50] Rheological studies[51] demonstrated that there is a network structure in KOH–starch solutions, and that these solutions may be treated as linear viscoelastic fluids.

The alkaline degradation of starch under anaerobic conditions is a slow process that increases with the concentration of alkali.[52,53] Part of the starch undergoes degradation with diluted aqueous alkali, whereas other parts are resistant, even to concentrated alkali solutions. It has been reported that these proportions may be changed by treatment of starch with acids, heat, or by grinding.[54,55] Moreover, viscosity measurements[51] indicate that the rate of the process is faster during the initial stages. These findings suggest that starch undergoes selective degradation, and that these reaction sites are hindered inside the starch matrix. The degradation of starch is considered to progress from the reducing end of the macromolecular chains, and the degradation products that were identified strongly supported this interpretation. The reducing-terminal glucose units, even in branched structures, are split off, indicating that not only amylose but also amylopectin is alkali labile. Nevertheless it has been widely accepted that only the amylose component is alkali labile, and that amylopectin is almost completely stable under alkaline conditions.[56] This may be true in terms of the amount of carboxylic acids produced from both polysaccharides. However, considerations in terms of molecular-weight stability suggest that amylopectin is more prone to degradation by alkali than is amylose.[52]

Various carboxylic acids (formic, acetic, glycolic, lactic, 2-hydroxybutanoic, 2-hydroxy-2-methylpropanoic, and 2-hydroxypentanoic acids) were isolated from alkali-degraded starch. They constituted 41–46% of the weight of the starting material.[57,58] The reaction first involves the Lobry de Bruyn–Alberda van Ekenstein rearrangement (**7** into **8**) and then proceeds according to generally accepted

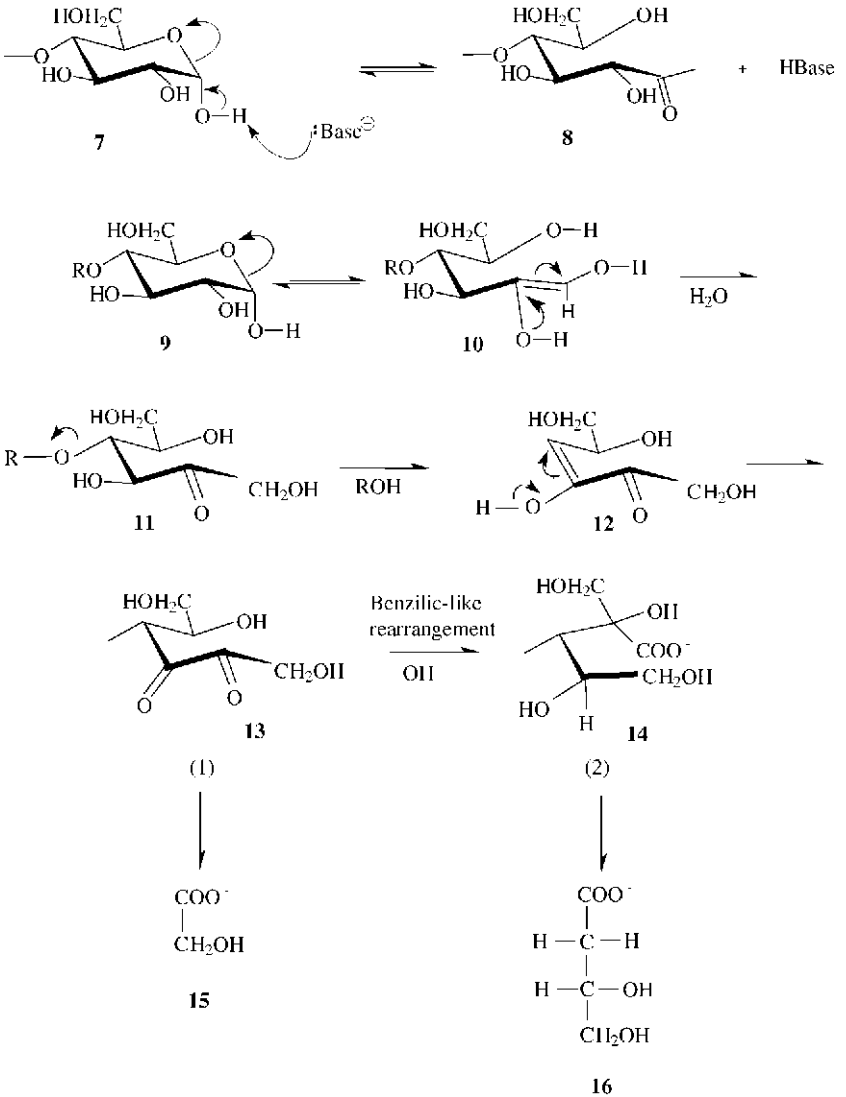


FIG. 2. Alkaline degradation of starch.

β-elimination process to produce carboxylic acids in consecutive steps (**9** into **10**) (see Fig. 2), step **13** → **14** being an example of the benzil–benzylic acid rearrangement. Concurrently, a glucose unit at the reducing end may undergo β-elimination

with loss of the hydroxyl group at C-3. This alternative reaction is responsible for the alkaline stability of this fragment of the starch because α,β-isosaccharinic acid (**14**) is not formed in this pathway.[59,60] Calcium hydroxide favors formation of **14**, whereas sodium hydroxide causes splitting of the carbon chain of glucose, which initiates a sequence of reactions leading to the formation of lower acids (**15** and **16**).[61] This observation provides an additional argument for the dependence of the reaction on the acting base. It was reported that the reaction under anaerobic conditions was unimolecular, with activation energy, $\Delta H = 110.79$ kJ/mole.

In air, the reaction retains its unimolecular character, but it proceeds faster[62] and accelerated by phosphate and acetate ions.[63] The degradation just described is further assisted by oxidation. The combined activation energy, ΔH, reached 242.67 kJ/mole. According to Hollo and coworkers,[52] amylopectin decomposed faster than amylose. Within the temperature range of 180–300 °C, the reaction followed second-order kinetics, and the activation energy was 165.27 kJ/mole. The parameters of the process, as well the as products and their yields, were very similar for starch and cellulose, but starch reacted more slowly.[57] Starch can also be degraded by treatment with hydrolyzing salts formed from strong bases and weak acids, this is, sodium carbonate, sodium hydrogencarbonate, sodium borate, hydrogenphosphates[64,65], alumina blended with sodium oxide.[66] Terminal glucose units were also attacked by other nucleophiles whose nucleophilicity was not the sole, essential factor; also important was their ambident (dipolar) character and size.[67]

The index of alkali liability is one of the properties that characterizes a starch sample. This index is related to the proportion of amylose to amylopectin in the granules.[68] In view of the characteristic behavior of amylose in alkaline solutions, it is not surprising that this estimation requires a rigorously oxygen-free atmosphere. In order to avoid the effects of the compactness of the granule structure, the material must be gelatinized on vigorous boiling in water. The effect of the degree of polymerization of the polysaccharide may be a significant factor, because polysaccharides decomposed faster than dextrins and oligosaccharides.[53] Muruyama[69] proposed the use of light-scattering amylography instead of estimations of carboxylic acid production as a better approach for analyzing alkali liability.

Starch derivatives may also undergo hydrolysis and degradation under alkaline conditions. The hydrolysis of the nitriles, amides, and esters resulting from the reaction of starch with corresponding vinyl monomers is obvious. Considerable attention has been paid to the alkaline degradation of "starch dialdehyde." It depolymerized readily supposedly as a result of β-elimination at C-5, although such a questionable *cis*-elimination should not be facile).[70]

Alkaline conditions degraded starch dialdehyde to glycolic acid, DL-$CH_2(OH)CH_2CH(OH)CO_2H$, and formic acid. The latter was the predominant product. Moreover, there were products of the Cannizzaro rearrangement plus carbon dioxide.[70] The degree of depolymerization could be controlled by pH and temperature.[71] Glucuronic acid could be prepared by alkaline degradation of starch dialdehyde.[72]

Former reviews of the subject appeared in 1958[73] and 1967.[18]

IV. Behavior of Starch in Acidic Conditions

1. Reactivity and Applications: Introduction

Starch, being a polyacetal, is naturally sensitive to protonic acids, which readily catalyze its hydrolysis. Even very small amounts of weak organic acids, residing in the form of inclusion complexes within the amylose helix, produce visible decreases in the viscosity of starch gels.[74] Potato starch, which has some phosphate ester groups as metal salts, can be decationized to produce the so-called hydrogen starch.[75,76] Although this acidic group occurs on only one of every 30–200 glucose units, it is sufficient to make this starch unstable during storage.[71–79]

Kirchhoff's historical discovery of starch saccharification by acids[80] opened what became the most practically utilized method of starch modification before the advent of enzymic methods. The original Kirchhoff paper described the formation of D-glucose from starch as the result of total acid hydrolysis of this biopolymer. Later it was shown that the acid hydrolysis of starch could be stopped at various stages, giving a variety of products termed dextrins. These findings significantly increased interest in acid-catalyzed modifications of starch. Notable among the many early contributions was that of Lintner,[81] who designed a frequently utilized method of starch dextrinization by its treatment with 2.2 M hydrochloric acid for 15 days at 35 °C. The product of such treatment was the subject of later structural studies.[82] Clark[83] reported the so-called lintnerized starch, which is a water-soluble mixture of starch, "erythrodextrins," and small proportions of lower oligosaccharides. The parameters of lintnerization depend on the starch variety. Usually, 5% hydrochloric acid is suitable for such processing.[84] For example, increasing the temperature to 140–160 °C decreased the hydrolysis time by 15–40 min, even when the acid concentration was lower.[85] Other methods of hydrolysis have been reported for

TABLE I
Catalytic Activity of Some Acids Related to That of Hydrochloric Acid[88]

Acid	Catalytic Activity
Hydrochloric	1.000
Hydriodic	0.977
Hydrobromic	0.928
Sulfuric	0.511
Nitric	0.228
Phosphoric	0.114
Formic	0.071
Acetic	0.048

the production of soluble starch, dextrins, maltose, glucose, and partly hydrolyzed products for various applications.[86] Slightly hydrolyzed starch has a low viscosity and good gel-forming ability. More-extended hydrolysis has been used to produce adhesives (see, for instance, Hao Jingguo[87]). Finally, oligo- and mono-saccharides are achieved with further extended hydrolysis.

Prior to the discovery that the catalytic activity of hydronium ions in starch hydrolysis depends on their chemical activity and not on the pK_a of the proton donor, several inorganic and organic acids as well as hydrolyzing salts were tested. Hydrochloric acid has always proven to be the most effective catalyst (Table I).

2. Survey of Hydrolyzing Acids

a. Water.—Water is the simplest, although not the most convenient, hydrolyzing agent. Although neutral water at 25 °C has pH 7, at elevated temperatures the dissociation of water increases, and the pH decreases to 6.8 at 100 °C. This acidity is sufficient to produce water-soluble starch, and even to cause hydrolysis of starch to glucose, particularly when elevated temperatures are combined with elevated pressure[89] and also under conditions of extrusion cooking.[90], It was reported that heating aqueous starch slurries in a microwave oven also resulted in rapid saccharification[91] or at least dextrinization.[92] Another method of starch hydrolysis involves the use of acid ion-exchangers, although the rate of hydrolysis is lower than with the use of comparable soluble acids. Nevertheless, glucose can be produced by such a process.[93–96]

b. Hydrochloric Acid.—Hydrolysis with hydrochloric acid has received the most attention. The quality of the final products depends on several factors. Different possible pathways may exist for penetration of the acid into the interior of the starch granule, a factor that is especially crucial when gaseous hydrochloride is used. An induction period in the hydrolysis is typically observed.[97] The optimum concentration of acid and optimum methods for its neutralization can be determined potentiometrically.[98] The use of cold, concentrated hydrochloric acid to produce glucose gave product contaminated with 6% of isomaltose.[99] Full saccharification of starch was completed within 50 hours. The use of under pressure with 32% hydrochloric acid under pressure[100] and a concentrated azeotrope were also patented.[101] Another process of hydrolysis was described in which concentrated acid was deposited on an inert mineral sorbent, which was then blended and heated with starch or cereals.[102] In a similar process, acidified starch was mixed with steam,[103] and the latter method was utilized for further fermentation to alcohol.[104] Increase in both the hydrolysis temperature and the acid concentration decreased the reducibility of the products, that is, they evoked side reactions and that the reaction is first order.[105] Concentrated hydrochloric acid caused a sharp drop in the molecular weight of the products and a moderate decrease of the specific rotation, whereas dilute hydrochloric acid, even when hot, decreased the molecular weight only slowly and significantly accelerated changes in specific rotation (the latter resulting from mutarotation of the maltose and glucose formed).[106] Conditions specially for hydrolysis of waxy starches have also been reported.[107] Hydrochloric acid has also been used in hydrolyzing crosslinked starches.[108]

In an early patent,[109] dilute hydrochloric acid was applied to a starch suspension in order to remove impurities by partial hydrolysis and subsequently to produce dextrins by drying the residue in the presence of this acid. Maltose could be produced using 1% and even 0.02% hydrochloric acid at 55 °C.[110–112] In another patent, a liquid spray of diluted acid and starch was projected into a heated chamber.[113] More-dilute acids either left some dextrins or did not change starch granules within 4 days (hydrochloric acid of d_{15} 1.049). The use of dry hydrogen chloride on starch powder was suitable for dextrin production but unsuitable for the preparation of soluble starch.[114] Soluble starch was conveniently prepared within 1–1.5 h by the action of dilute hydrochloric acid and steam[115] or with 9–10% hydrochloric acid at low temperature.[116] The reaction proceeds faster when starch is hydrolyzed in the form of a paste.[117] Another approach entailed the use of dilute hydrochloric acid with heating in a closed vessel using a low overpressure,[118,119] and also in the presence of 4-ethoxyphenyl carbamate.[120] After thorough studies on the hydrolysis of corn starch, the use of 0.040–0.045 M hydrochloric acid in the amount of 0.75% per 18%

starch suspension was proposed.[121] The reaction required a pressure of 3040 hPa for 25 min. For potato starch, 0.5 M acid in a 40% starch suspension for 3 h at 50 °C has been established as optimal conditions.[122] For the preparation of organic acids, including formic and levulinic acids, pyrolysis of starch with 20% hydrochloric acid has been proposed; humic substances were, however, also formed.[123]

In most procedures the acid is neutralized when hydrolysis has reached a desired stage. An electrolytic process for the removal of acid has been reported.[124] It was found that isostatic processing of starch was faster with starch acidified with hydrochloric acid.[125–127] Pre-hydrolysis of starch for further hydrolysis with milder hydrolyzing agents, such as sulfur dioxide, might also be of some benefit.[128,129]

A more-recent development in starch hydrolysis by hydrochloric acid involves processing in alcohol suspensions.[130] For example, the use of 0.36% hydrochloric acid gave products of hydrolysis and alcoholysis within 1 h at 65 °C. The yield of glycosides decreased with the molecular weight of the alcohol. In methanol, it reached 50% but decreased to 6% with 1-butanol. The effects of the acid and alcohol concentration were different between amylopectin and amylose depolymerization. However, the limiting degree of polymerization of the resulting dextrins increased with the acid concentration and decreased with the molecular weight of the alcohols.[131] More information on this topic is presented in Section V.

Dry hydrogen chloride can be used at low temperatures under pressure,[132,133] and also in the presence of such organic liquids as benzine (light petroleum).[134] Dry hydrogen chloride can also be applied on moist starch.[135] In order to obtain a product free of paste and lumps, the starch should be impregnated with dry hydrogen chloride and dehydrated in vacuum followed by heating at 155 °C.[136] Hydrolysis of starch was also carried out by heating in the presence of anhydrous glucose.[137]

Hydrobromic and hydriodic acid have also been used to hydrolyze starch.[20,138] Hydrobromic acid seems to be particularly useful in the production of levulinic acid,[139] and both acids have been used for demethylation (and depolymerization) of methylated starch.[140]

The hydrolytic ability of hydrochloric acid may be affected by salts present in the reaction mixture. The effect may be based on salting out of the hydrolysis products from the reaction mixture. For instance, magnesium and ammonium sulfates showed such an effect.[117] Zinc and cadmium cations, as well as acetate and sulfate anions, decreased the hydrolysis rate with 0.1 M hydrochloric acid, whereas calcium, strontium, and barium ions exerted no effect.[141] Neither copper metal, stainless steel, tin, nor sulfur dioxide impeded the hydrolysis with a solution of 0.03–0.05 M hydrochloric acid.[142] There is a report[143] that traces of metal salts affect the rate of hydrolysis but there are also contradicting findings[144,145] that

metal salts [with the possible exclusion of chromium(III) salts] have no effect on the rate. These discrepancies seem to result from the ratio of salts and acid applied. Other reports indicate that acid hydrolysis is catalyzed by thorium and zirconium ions.[146,147] The addition of molybdenum compounds had measurable effects on the composition of the starch hydrolyzate,[148] and zinc and tin(II) chlorides decreased the reversion of glucose in the hydrolyzate.[149]

c. Other Hydrohalic Acids.—Hydrogen fluoride has not been used to a great extent because of its corrosive properties and low hydrolytic rate (one seventeenth of that of hydrochloric acid).[150] The use of anhydrous hydrogen fluoride was more promising, although its use on a laboratory scale required silver crucibles.[151] Soluble starch ("amylan") was obtained in 85% yield within 30 min at 20 °C. A low degree of hydrolysis was achieved with either liquid or gaseous hydrogen fluoride performed at low temperature, and with subsequent treatment with other acids.[152]

d. Sulfuric Acid.—The hydrolytic converting power of sulfuric acid is only about 56% of that of hydrochloric acid,[153] but despite this the acid has been used extensively by researchers and technologists involved in starch saccharification. The acid concentration is recommended to be within the range of 0.25–0.5%, and either on a steam bath[154] or under pressurized steam heating at 140–155 °C.[155] Another patent[156] recommends the use of 32.2% acid at 160–210 °C providing a 9.3% yield of glucose.[157–160] The concentration of sulfuric acid should not exceed 0.5 M if the destructive effects of sulfuric acid are to be minimized during hydrolysis.[161,162] As compared to hydrochloric acid, sulfuric acid produced more humic substances and less levulinic and formic acids.[123] In contrast to hydrochloric acid, the hydrolysis of starch by sulfuric acid is not accompanied by a change in the specific rotation of the reaction mixture, suggesting that it does not promote isomerization of the product sugars.[106] Sulfuric acid, however, disintegrates starch to a considerable extent. Specific "amylodextrins" obtained from cornstarch hydrolyzed with 16% sulfuric acid (Naegeli dextrins) appear to result from splitting of the amylopectin component.[163] Splitting of the side chains of the amylopectin component proceeds with lower activation energy than the splitting of the main chain.[164] Ultrasonication was reported to increase the rate of hydrolysis,[165] and first-order reaction with respect to starch and hydrogen ion concentrations was observed.

e. Nitric Acid.—Nitric acid is commonly used as a nitrating and oxidizing agent, and this limits its hydrolytic action when applied at 0.25 M concentration. Glucose was produced at 100 °C in a unimolecular process, and the reaction

time was inversely proportional to the acid concentration.[166,167] However, "white dextrins" could be obtained within 20–45 min using concentrated (*d* 1.4) nitric acid in a drying drum.[168]

f. Phosphoric Acid.—There are only a few studies on the hydrolyzing ability of phosphoric acid. Thus, 85% acid produced soluble starch at room temperature.[169] The soluble starch retained its ability for blue staining with iodine. Upon heating, the reaction progressed with the formation of dextrins, and after dilution of the acid with ethanol, the starch was modified to a soluble product. Further studies confirmed the effectiveness of phosphoric acid as a dextrinizing agent but not a saccharifying agent.[170] In order to hydrolyze starch, phosphoric acid must penetrate the starch granules, and this process is promoted by high acid concentrations. On the other hand, the rate of hydrolysis rate increases in diluted acid because of increase in its dissociation.[171]

g. Other Inorganic Acids.—Weaker inorganic acids require elevated pressure, at least. For example, sulfurous acid-modified starch in a closed vessel at 100–105 °C.[172] Optimum conditions for such hydrolysis were established as 165 °C for 15 min in the presence of 0.2–0.4% sulfur dioxide.[173] Still more drastic conditions were required to effect hydrolysis of starch with carbonic acid.[174] Thus, at 156–216 °C and 70,000 hPa, glucose was formed, and the rate of hydrolysis was linear with respect to time.[175] Boric acid effected hydrolysis of starch to give 97.7% of water-soluble dextrins having relatively high viscosity when mixed at 4% by weight in aqueous solutions at ∼100 °C. Increased temperature and additions of hydrogen chloride caused more extensive degradation. *O*-Hydroxyethyl starch has also been hydrolyzed with boric acid.[176]

h. Organic Acids.—There was a significant amount of interest in hydrolysis of starch with organic acids during the first part of the twentieth century. However, this approach was almost completely abandoned because the processes were slow, as could be predicted from the data in Table I. The processes were also accompanied by simple esterification. Formic and acetic acid saccharified starch at approximately the same rates, and these rates were proportional to the acid concentration.[177] However, it was reported that boiling acetic acid with starch produced a mixture of starch acetates having up to three acetyl groups per glucose residue.[178,179] Monocarboxylic acids lower than heptanoic (capric) acid could liquefy starch fairly effectively,[180] and the hydrolysis rate of starch with dicarboxylic (dioic) acids was

also high.[181] The latter authors reported that hydrolysis with malonic acid was faster than with than oxalic acid, and hydroxycarboxylic acids were even more effective. Lactic acid exhibited a higher rate than tartaric, malonic, and oxalic acids.[182] Hydrolysis with oxalic acid gave a mixture of mono-, di-, and tri-saccharides, but not their esters.[183] Modification of starch by heating with aliphatic acids in organic solvents was also patented.[184] When starch was heated under pressure with 0.1 M oxalic acid, isomaltose was isolated as the major product.[185] Liquefied starch was also available by heating a slurry with oxalic acid under 2000–4000 kPa, a process that was used as a pretreatment during enzymic saccharification of starch.[186] However, heating starch to 185 °C with anhydrous oxalic acid caused decomposition into water, carbon dioxide, and formic acid, and the latter became esterified with starch hydroxyl groups.[187] The esterification of formic acid with starch was also confirmed in other reports.[188,189] and it was found to be monoesterification of the glucose units. The instability of starch in the presence of ascorbic, "arabinoascorbic," and dihydroxymaleic acids was studied[190,191] from the point of view of food texturization.

The acid hydrolysis of starch dialdehyde produced high yields of D-erythrose and glyoxal, provided that the hydrolyzed solutions were diluted.[192] Mild degradation (partial hydrolysis) of starch dialdehyde occurred on cation-exchange resins,[193] making it readily soluble in ethanol, ethylene glycol, pyridine, and dimethylamine. 3,4,6-Tri-*O*-acetyl-1,2-*O*-ethylene-β-D-glucopyranose and 3,5,6-tri-*O*-acetyl-1,2-*O*-ethylene-α-D-glucofuranose were characterized[194] as the products of the acid hydrolysis of *O*-(2-hydroxyethyl)starch.

3. Reaction Mechanism

Several early papers reported that acid catalyzed hydrolysis of starch is a unimolecular process resembling the hydrolysis of simple glycosides, and leads to glucose as the sole, acid-stable product.[166,195,196] Later reports confirmed these observations, despite the further discovery[197] that hydrolysis is accompanied by reversion (that is, repolymerization of the primary hydrolysis products and their decomposition, both reactions depending on the reaction time, temperature, concentration, and pH).[198–200]

The hydrolysis pathway according to Bunton and coworkers (Fig. 3) starts with a fast, reversible protonation at either the pyranose ring oxygen (**17**) atom and/or the oxygen atoms of the glycosidic bonds (**19**).[201] This step is followed by slow

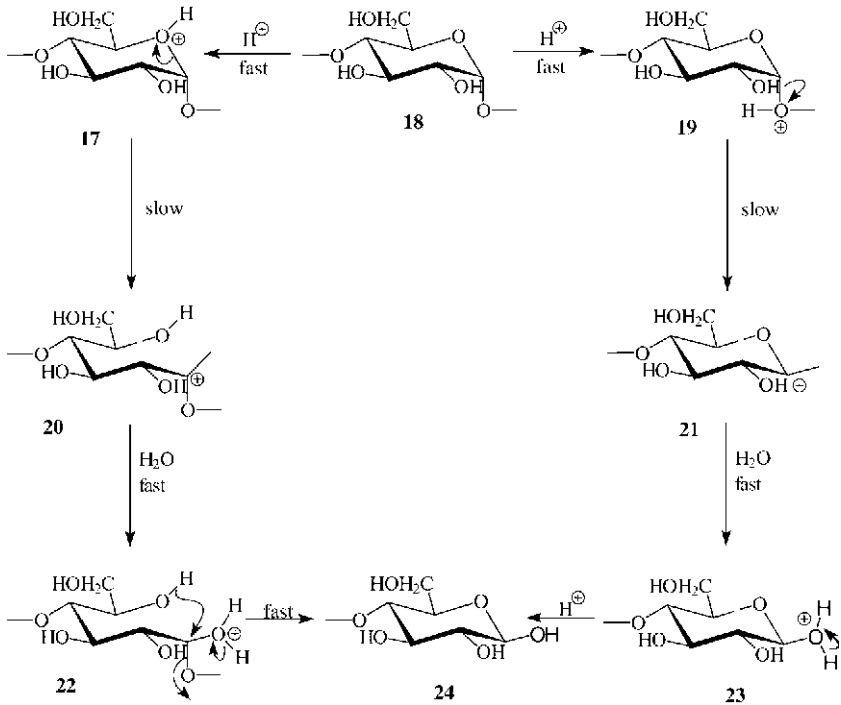


FIG. 3. Proton-catalyzed hydrolysis of starch.[211]

breakage of the respective C–O bond. The resulting carbocations (**20** and/or **21**) rapidly accept a water molecule from the solution (**20** into **22**) and/or (**21** into **23**). This scheme was postulated[202] already early in the twentieth century. The dominance of one or the other of these pathways has not been rigorously proven, despite several studies.[202–210] It is likely that both mechanisms operate in parallel, and that the particular reaction conditions give priority to one of them.[211]

Starch is gradually saccharified, and its liquefaction results in the initial formation of amylodextrin paste that still develops a strong blue stain with iodine.[212] Subsequently, it turns into a complex of "dextrin" and maltose, the so-called maltodextrin. However, this stage is preceded still by the slow penetration of acid into starch granules,[212] a critical factor that may differentiate the hydrolyzing ability of various acids. Electron microscopy of acid-attacked starch granules showed that lamellae in the starch granules were preferably attacked by acid.[213] The rate constants for transformation of the dextrin into maltose and maltose into glucose in the

presence of either 0.1 M hydrochloric acid or 0.5 M sulfuric acid appeared to be nearly the same.[153] The linear, isokinetic relationship was described as follows:

$$\log k = 0.0552t - 7.442 \quad (2)$$

The rate of the formation of reducing sugars was also given by the following relationship:

$$\log k = 0.0552t - 7.693 \quad (3)$$

In these expressions, t is the reaction time. These differences may be interpreted in terms of the data in Table I. However, some changes of the rate constant for starch hydrolysis depended on the concentration of the same hydrochloric acid.[214]

Comparative studies[215] on the acid hydrolysis of inulin, sucrose, and starch revealed that starch was degraded 618 times more slowly than the two carbohydrates containing furanoside rings. This result nicely illustrates the effects of the chemical and physical structure of starch on its hydrolysis. There are also several reports[216,217] documenting the effects of the starch variety on its hydrolytic affinity. A number of confusing results[212,218,219] on the dominant role of either amylose or amylopectin in acidic hydrolysis have been reported and these appear to be related either to differences in the starch variety or to various samples of the same starch.

It was reported in some papers[212,218,220] that amylopectin depolymerized relatively fast as compared with amylose. These results contradicted some findings on the higher stability of the α-D-(1→6) glycosidic bond.[221–223] These results are not consistent with the evidence that, in disaccharides, α-D-(1→4) bonds undergo acid hydrolysis more readily than α-(1→6).[224] It was observed[212] that amorphous regions of granules (in which is there definitely less ordering of intra- and inter-molecular hydrogen-bond interactions) accepted the catalyzing acid first. In contrast, crystalline regions (that is, regions containing more intermolecular hydrogen-bonds) hydrolyze much more slowly. This is consistent with the observation that hydrolysis increases the crystallinity of the starch granule.[225] Hence, it was also concluded that crystalline regions contain mainly amylose and that amorphous regions contain mainly amylopectin. The amylodextrins commonly produced appeared to be a complex of amylose and the hydrolysis products of amylopectin.[218] These results may be attributable to the availability of the positions of potential attack by hydronium ions. In the case of large, entangled, and aggregated molecules of starch, a significant proportion of these reaction sites could be hidden or at least partly hindered. In the contrast to these interpretations there are reports[226,227] showing that molecular structure seems to have has no effect on the

rate of hydrolysis. Moreover, the first-order reaction parameter for the hydrolysis of starch with 0.5 M sulfuric acid[226] agreed fairly well with the parameters for the hydrolysis of starch with hydrochloric acid.[228] To complicate the matter further, in the early sixties, it was shown that hydrolysis is a more complex processs than was formerly accepted. Dilute solutions of sweet potato starch react according to a pseudo-first-order process, whereas at higher concentrations the process turns into a second-order reaction. The rate constant is dependent on the acid concentration but not on the kind of acid, and the temperature effect followed approximately the Arrhenius law.[229] Recently[230] a newer model of the kinetics of starch hydrolysis was proposed.

Additional information on the behavior of starch in acidic conditions can be found in several other references.[231–237]

V. Alcoholysis and Phenolysis

These reactions involve transacetalation of starch with alcohols and phenols, respectively, and are acid-catalyzed much like the common hemiacetalation and acetalation. It was reported that a trace of water in the reaction mixture is useful,[238–240] although dry starch and dry methanol also react, provided that elevated temperatures and elevated pressures are applied.[241,242] The reactions are equivalent to starch hydrolysis, and α-D-glucopyranosides, accompanied by a lesser proportion of β-D-glucopyranosides, are formed. Methanolysis is the reaction studied most commonly. Reactions are typically 10 h at reflux with 1% of hydrochloric acid added, and yields are between 80 and 96%. Other acid catalysts tested include 4-toluic acid. Rapid heating of the reagents in a pressure vessel to 165 °C followed by cooling after 10 min, is a process that can be run continuously.[243] The product contained 48% methyl α-D-, 25% methyl β-D-glucopyranoside, and 13.5% of both methyl α- and β-maltosides.[244,245] Among other alcohols investigated, glycerol elicited particular interest. In the absence of a catalytic amount of H_3PO_4, it was reported that the temperature required was ∼180 °C, which is still below the dehydration temperature (estimated at 210 °C).[246,247] In contrast, the reaction proceeded satisfactorily at 130 °C when using a catalytic amount of H_3PO_4. The reaction with ethylene glycol required 24 h of heating at 180 °C. Phenol and benzyl alcohol reacted similarly. A method of *in situ* gelatinization wherein starch, water, and glycerol were blended was proposed.[248] It was reported that the results of glycerolysis depend on the starch variety. Among three varieties, potato, wheat,

and rice, the first reacts the most readily, and the last with the most difficulty.[249] Kinetic studies carried out on acid catalyzed methanolysis of V and B amylose[250] revealed that they are first-order reactions with activation energies of 83.60 and 92.05 J/mole, respectively. Such alcoholysis is usually performed with alcohols no higher than butanol. The route to the higher alkyl α-D-glucopyranosides may involve the transacetalation of lower alkyl derivatives with higher alcohols.[251]

It was reported that the reaction of starch with phenol in the presence of a Lewis acid such as $AlCl_3$ resulted in resins of controlled melt viscosity.[252] Probably, the product results from the hydrolysis of starch to glucose with conbversion of the latter into 5-(hydroxymethyl)-2-furaldehyde, which subsequently condensed with phenol.[253] The reaction of starch with phenol without any catalyst required temperatures between 200 and 260 °C, and the resultant resinous product was then hardened by condensation with formaldehyde.[254] Mastication of either glycerol or phenol with starch and water was said not to involve alcoholysis, but instead results in the formation of polymeric products.[255] Reactions with gossypol[256,257] and propylene glycol[258] that were performed in the presence of a basic catalyst were in fact polymerization reactions and not alcoholyses.

Alcoholysis (and phenolysis) of starch provides α-D-glucopyranosides of practical utility. The methyl derivative is useful for making polyethers for rigid polyurethane foams and surfactants.[251] Allyl glucoside was designed as a polyol initiator for making polyethers and it offers several possibilities for modification, for example, by addition of halogen atoms to the double bond. Foams made from these materials were flame-resistant. Other alkyl pyranosides have found use as polyol initiators in polymerization of unsaturated ethers and as biodegradable surfactants and emulsifiers. Glycol polyols have been evaluated for the use in conventional and urethane alkyd resins.

VI. Reduction

In contrast to the vast range of studies on starch oxidation, reduction of starch has evoked only limited interest and has been mainly devoted to catalytic hydrogenation of starch to alditols. The latter, although less sweet than sucrose, are widely used as sweeteners for diabetics, as they undergo metabolism without insulin. In the food industry they are used for sweetening some beverages, for instance, liqueurs, and for maintaining the moist character of some foodstuffs. Hydrogenated starch hydrolyzates are accepted as safe ingredients for food.[259]

In most reports and patents, reduction with hydrogen on nickel catalysts is described. Early reports described the manufacture of hexitols from starch and also from mono- and di-saccharides and dextrins. These saccharides were hydrogenated over Ni and Ni-Fe catalysts at 1.5×10^8 Pa. Hexitols were formed at temperatures between 130 and 200 °C whereas the products formed between 250 and 300 °C were glycerol and propylene glycol. The Ni-Fe catalyst was more effective for the high-temperature reaction.[260] A similar Ni-Fe catalyst that was used on silica gel at 240–250 °C and at 3×10^7 Pa to produce, on hydrogenation, 2-propanol, propylene glycol, ethylene glycol, DL-erythronolactone, and glycerol.[261] A more economical process entailed hydrolysis of starch to starch (glucose) syrup prior to hydrogenation.[262,263] Hydrogenation of such monosaccharides as D-glucose and D-fructose over Raney nickel at 50 °C and atmospheric pressure at pH 9–9.5 yielded D-glucitol.[264] The hydrogenation of starch could be performed under hydrolytic conditions. The nickel catalyst deposited on diatomaceous earth was more successful than nickel sulfate.[265–267] The addition of such co-catalysts as ammonium, magnesium, calcium, and tin(II) chlorides, and sulfates, was also recommended. Such a process at 10^8 Pa and 200 °C was claimed to give a 100% yield of D-glucitol. Similar reaction conditions (170 °C, 2×10^8 Pa) were patented by Natta and Beati,[268] who claimed a 99.6% yield of D-glucitol after reacting starch for a period of only 3 h. Similar results were achieved[269] after modifying the nickel catalyst and performing the reaction in an acidic medium. Other nickel catalysts were subsequently patented for making polyalcohols from starch, for example, a catalyst containing Ni combined with nickel phosphate (12–45%) and ferrous sulfate.[270] D-Glucitol was produced in 94.5% yield by running the process on a starch hydrolyzate at 160–180 °C and around 10^9 Pa. The use of Ru/C or Ru/SiO_2 catalysts, which produced 70–80% yields of polyalcohols in an acidic medium at 156–160 °C and 7×10^7 Pa has also been proposed.[271] Starch dialdehyde has also been hydrogenated in such process yielding erythritol and ethylene glycol when the process was performed out under pressure over Raney nickel catalyst.[272,273] A hydrocracking technology for the manufacture of glycols from carbohydrates in a fixed, trickle-bed reactor has been reported.[274] Reduction of oxidized amylopectin with sodium borohydride was said to give a high yield of glucuronic acid.[275] Acidic degradation of the reduction products gave mannuronic acid and either alluronic or altruronic acid.[276] Borohydride-reduced products could also be esterified by chlorosulfonic acid in formamide.[277] Polarographic reduction studies of starch dialdehyde in an alkaline medium on a mercury cathode have also been described.[278]

VII. Oxidation

1. Introduction

Numerous oxidation methods exist, and they all break down to starch to various extents.[279] Oxidants may be arranged in the following ascending order of their action upon starch: $I_2 < FeCl_3 < Na_2S_2O_8 < NaBO_3 < K_2Cr_2O_7 < H_2O_2 < Na_2O_2 < 1\%H_2O_2 + 1\%\ FeCl_3 < NaOCl < KMnO_4 <$ chloramine $< 0.5\%\ NaClO_2 + 1\%\ NaOH < HNO_3$.[280] These results are based on measurements of the yield of starch oxidized in 1% solutions with the various oxidants, in addition to measurements of the specific viscosity, the molecular weight calculated by the Staudinger equation, and the reaction with KI_5. The degradation is generally insignificant as compared with degradation caused by sulfuric acid, sodium hydroxide, pancreatic enzymes, and amylases taken in comparable concentrations.[281] Total decomposition of starch into carbon dioxide and water can be effected under utraviolet irradiation, and is also promoted by metal oxide sensitizers.[282] Other methods yield several products, such as poly(glucuronic) acid and/or starch hydrolysis products, and mono- and di-carboxylic acids. In the literature, reaction products are often characterized only with respect to their intended applications, and little attention is frequently paid to the structure. However, the properties of an oxidation product always depend on the reaction conditions, and on the oxidant applied; the starch origin is usually much less important.

2. Survey of Oxidants

a. Nitric Acid and Nitrogen Oxides.—A discussion of starch oxidation methods may begin with the use of diluted nitric acid, which did not yield an oxidized starch, but hydrolyzed it to dextrin[283] and glucose.[166] These authors and many others[284–287] recognized that organic mono-carboxylic and di-carboxylic acid (mainly oxalic acid) were among the reaction products. When the oxidation was carried out in either carbon tetrachloride or in chloroform, D-glucoronic acid was the major product.[288,289] Oxidation in aqueous solution, afforded D-glucuronic acid and D-glucurono-1,4-lactone in 50 and 13% yields, respectively.[290] The combined use of nitric acid and nitrogen dioxide[291,292] was also proposed. Such a combination may contain diluted nitric acid. The use of nitrogen dioxide as the sole oxidant

resulted in mild oxidation of starch without pronounced degradation.[293] Nitrogen dioxide also oxidizes starch in the solid state. By this method D-glucuronic acid[294] and a "tricarboxystarch" could be prepared.[295] Amylose is oxidized more readily than amylopectin.[294] Oxidation in carbon tetrachloride, led to "polyanhydroglucuronic acids."[296–299] Oxidative degradation of starch by ultraviolet irradiation in the presence of nitrites has also been described, but the degradation products were not characterized.[300] The products of starch oxidation by nitric acid are independent of the starch origin, although the course of the oxidation and the accompanying processes (for instance, hydrolysis and esterification) do depend on the starch origin.[167]

b. Hydrogen Peroxide.—Diluted hydrogen peroxide does not oxidize starch,[301–307] even when used in conjunction with ferric,[308] and ferrous salts,[309–312] and iron metal.[313] However, when starch was pasted in the presence of hydrogen peroxide (0.7%) and copper sulfate catalyst, resulting pastes had significantly modified viscosity, particularly at elevated temperatures.[314] At higher concentrations, hydrogen peroxide behaves as an oxidant. Amylopectin, is rapidly depolymerized in the range of pH from 7 to 12.5 followed by rapid oxidation of lower fragments. Probably the oxidation proceeds on the reducing ends of chains.[315] The reaction products included polygalacturonic acids[316–318] and mixtures of carboxylic acids such as formic, oxalic, glycolic, D-erythronic acid, gluconic and glucuronic acid, acetaldehyde.[315,319] Other products included dextrin and maltose,[301] large amount of D-glucose,[315] showing that oxidation is accompanied by hydrolysis, and CO_2.[315] The action of this oxidant is stimulated by light,[320] permanganates,[321] cupric salts[312] or tungstate,[312,322] chloramine-B,[323] and sulfur dioxide (which exposed the granule interior to penetration by oxidant and prevented the product from fermentation.[324] With copper(II) or tungstate, under either acidic or alkaline conditions, production of carbonyl compounds preponderated (6.6 carbonyl groups per 100 glucose residues) over formation of carboxylic compounds (up to 1.4 carboxyl groups per 100 glucose residues). The overall yields were 90 and 99% in the alkaline and acidic reactions, respectively.[312] Free radicals also stimulate the reaction, for instance, those from ascorbic acid[325] as well as such hydrolytic agents as hydrochloric acid,[326] and aluminium trichloride.[327] Use of sodium peroxide and other peroxy salts gave results similar to those with hydrogen peroxide.[328,329]

c. Ozone.—The oxidation of starch led to either carbonyl compounds[330–332] or dicarboxylic acids, when ozone was used in cooperation with silver(I) oxide and/or

cobalt(II) acetate.[333] Ozone cleaved C-2–C-3 as well as the C-1–C-4 bonds, while Ru(III) compounds increased the ozonation selectivity with respect to C-2–C-3 bond cleavage.[334] The consecutive use of ozone followed by potassium permanganate has been patented.[335]

d. Metal Salts.—Inorganic salts and oxides are common chemical oxidants and have been used for oxidation of starch. Among them, potassium permanganate is the most frequently used, providing carbonyl and carboxyl products. This oxidant can be used either in acidic or alkaline media.[336–345] Slightly acidic conditions and a low degree of oxidation are beneficial from the point of view of promoting gelling capacity.[346]

Among known chromium oxidants, chromium(VI) oxide in acidic media has been employed for oxidation of starch leading to carboxylic acids, aldoses, and ketoses. It was also observed that amylose is oxidized more readily than amylopectin.[347–349] Potassium dichromate in sulfuric acid was also reported as an effective oxidant.[350] These studies also revealed that susceptibility to oxidation is dependent upon the starch variety. It is possible that this variability is related to the susceptibility of the given starch to hydrolysis. Oxidation with dichromate in 0.5 M nitric acid was also described.[351] Dichromate can decompose starch totally to carbon dioxide and water, a procedure applicable quantitatively for determining starch concentrations as low as 250 ppm.[352] Quantitative analysis of starch and other saccharides in sewage that was based on a similar approach.[353] Other metal salts used in oxidation of starch include K_2FeO_4, which selectively oxidizes the 6-CH_2OH group to the aldehydo group,[354] lead(IV) acetate,[355,356] which gives "starch dialdehyde," and mecury(II) chloride with borax.[357]

Starch acts as reducing agent for U(VI) compounds leading to U(IV) compounds,[358] a reaction that may proceed on the surface of granules.[359] When uranyl salts were autoclaved at 100–230 °C with starch, nitric acid, and some inorganic salts and oxides the reduction to uranium doxide was completed within 35 min.[360,361]

e. Non-metal Inorganic Compounds.—A report[362] describing oxidation of starch by means of phosphates involved peroxydiphosphate salts, and it gave gels of low viscosity. The structure of the oxidation product remains unknown. The application of sulfuric oxidants has evoked little interest in the field of starch chemistry; they degrade amylose hydrolytically to higher dextrins prior to degrading amylopectin.[363] Sodium peroxysulfate has been used for the oxidative removal of

starch size on cotton cloth.[364] Dimethyl sulfoxide also oxidizes starch; and oxidation of the glucose units is largely non-selective but possibly favors the 2-OH group.[365] Nevertheless, dimethyl sulfoxide is frequently used as a so-called "unreactive" solvent for starch.

f. Halides and Their Compounds.—Oxidation of starch with halogens (chlorine, bromine, and iodine) is the most commonly used method of starch processing for food technology. The simplest oxidation method involves aqueous solutions of chlorine.[366–368] The results are pH dependent. For example, at pH 4.0–4.2, the total yield of the oxidation products reached 95%, but it dropped to 78% at pH 5.5. Approximately 76% of the resulting product was water-soluble. This fraction contained carbonyl and the carboxylic groups, with a preponderance of carbonyl groups. Approximately 65–80% of the carbonyl groups were present as aldehydo groups, and only 9% were in the form of the keto groups at the 2-position of the glucose units.[369] Contradictory results were also reported,[370] where D-gluconic acid was the major product, accompanied by D-glucuronic acid. The C-2 and C-3 positions of the D-glucose units were not attacked by the oxidant. These units were attacked at the anomeric carbon atom, causing starch hydrolysis.[371] When oxidation was accompanied by ultraviolet irradiation, a product was formed containing 25% carbonyl groups.[372] This reaction was favored at low (0.5) pH value. (Colorimetric determination of the carbonyl group is possible by the reaction with 2,3,5-triphenyltetrazolium chloride, which reacts to give red triphenylformazan[373]). Textile sizes have been produced by oxidation of starch with either $NaClO_2$ or ClO_2.[374] According to earlier reports,[375] ClO_2 does not attack starch. Instead, it removes nitrogen-containing impurities and abstracts the phosphoric acid ester moieties in potato starch. Carboxylated starch[376] as well as starch dialdehyde[377] were claimed as the products. The aldehyde groups could be selectively oxidized with chlorous acid ($HClO_2$) or alkaline hypoiodite (IO^-).[378] Chlorous acid did not oxidize starch, whereas perchloric acid ($HClO_4$) did. The latter oxidized only the secondary hydroxyl groups (at C-2 and C-3). Other authors[379] reported that oxidation produced a variety of products, among them glucaric, glucuronic, gluconic, and oxalic acids. Hydrolysis to glucose accompanied this reaction. Chloramine vigorously oxidizes starch to form soluble starch suitable for sizing applications.[380] In addition, sodium chlorite oxidizes starch to carbonyl and carboxyl derivatives, an oxidation stimulated by thiourea[381] and bromine.[382] Joint use of hypochlorite and ammonium dichromate was also reported.[383]

The use of hypochlorous acid (HClO) in alkaline solutions has evoked great interest and widespread application. In contrast with the oxidation in acidic

solution, this oxidant attacks the D-glucose residues between C-2 and C-3.[384,385] As in acidic media, uronic acids are produced, although in conjunction with carbonyl compounds, the amount of which are controlled by pH.[316,386–409] D-Glucono-1,4-lactone, glycolic, and D-erythronic acids were also identified in the reaction mixture.[384] A textile size has been produced by directly oxidizing starch on textile fibers using NaOCl in a dry process.[410] The use of calcium hypochlorite has also been evaluated.[338,392,411] There was no preference in the oxidation between amylose and amylopectin.[412] The oxidation kinetics of various starches in the pH range from 7.5 to 11.0 was similar.[413] Oxidation of starch with di- or tetra-chloroglycouril (1*H*,7*H*-4,8-dihydro-2,6-dihydroxyimidazo[3,4-*b*]imidazole) produced excellent films.[414] Material that increases in viscosity on storage could be obtained.[415] This effect can be minimized if a neutral pH is maintained on oxidation and when the oxidized product is preserved with sulfurous acid (H_2SO_3). Acetylation of the oxidized product (up to 10% of the hydroxyl groups) also improves the stability.

The use of bromine in alkaline media resulted in the formation of uronic acids.[416,417] Oxidation to some non-uronic acid products, (carbonyl compounds) accompanied the major oxidation pathway.[418–420] The 2,2,6,6-tetramethyl-1-piperidinyloxy-mediated oxidation by hypobromite was highly selective for the 6-OH groups of the glucose residues.[421] Potassium bromate ($HBrO_3$) was also used.[338] The kinetics of oxidation with bromine at pH 6–8 has been studied.[422] It was observed that oxidation decreases the heat and temperature of gelation as the oxidation proceeds. Simultaneously, the molecular weight of starch and the viscosity of its aqueous solutions decreased. Subsequent reduction of the oxidation products increased the viscosity. Microscopic observations revealed that the starch granularity vanished at a low level of oxidation.[423]

Iodine compounds have received considerable attention because of their unique oxidative properties. The use of hypoiodite was considered of little value.[424] Salts of periodic acid have usually been employed, and they produce the classic "starch dialdehyde" through oxidative C-2–C-3 bond-cleavage.[425,426] The reaction appears to proceed in both strong[427] and weak acid solutions.[428–431] As well as in neutral[432–434] and alkaline solutions.[435–437] *N,N*-Dimethylformamide inhibits this starch oxidation.[438] Fleche[439] optimized the conditions of oxidation with the use of HIO_4. Net consumption of the oxidant can be decreased by its electrolytic regeneration *in situ*.[440–444] Dialdehyde yields of up to 30–40% are relatively easy to achieve, but higher yields become a challenge.[445–448] Interestingly the water solubility of starch dialdehydes is not proportional to the degree of oxidation.[449] A product oxidized to approximately 20% was reported as being the most soluble, because its

structure is the most disordered. Higher degrees of oxidation facilitate intramolecular acetal bonding causing crosslinking.[450] This effect might, however, be a result of aggregation.[451] Ultracentrifuge molecular weight determinations suggested that the oxidized starch retained its original, stiff, and helical conformation.[452] Mejzler and coworkers[453] discussed the theory of periodate oxidation. The content of aldehyde groups in such oxidized starches may be determined by colorimetric titration with alcoholic solutions of *p*-nitrophenylhydrazine at 445 nm.[454] Complementary determinations based on either the consumption of sodium borohydride in reduction of the aldehyde group or the condensation of the aldehyde groups with semicarbazide were proposed.[455,456] Determinations in alkaline media are not recommended, because of the alkali lability of starch dialdehyde, which generates additional aldehyde groups.[457] For analytical purposes, it has been recommended that starch dialdehyde should be transformed into oxime derivatives.[458] An alternative method proposed by the same group of authors[459] is based on the formation of either 2,4-dinitrophenylhydrazones or 4-nitrophenylhydrazones, followed by iodometric titration of excess of reagent. Infrared (KBr)-spectrophotometric determination of oxidized starch has been reported,[460] but such starch should be separated from other starchy material. Differential thermal analysis of starch dialdehyde has been conducted.[449] γ-Irradiation of starch dialdehyde produced free radicals similar to those produced from D-glucose.[461]

Oxidation of starch with periodates (IO_4^-), with simultaneous electrochemical recovery of the oxidant, can be considered as a semi-electrosynthesis. Electrooxidation of starch caused only subtle changes as reflected by the rheological properties of starch gels.[462] Small changes resulted from the lack of sufficient concentration of supporting electrolyte in the electrochemical bath. Nevertheless, this method might be suitable for making starch sufficiently anionic for complexation with protein at the anode of an electrolytic cell.[463] Increasing the concentration of the supporting electrolyte resulted in extensive transformation of starch into mono- and di-carboxylic acids.[464] Starch pretreatment with acids, followed by oxidation with sodium iodate in order to produce erythritol and D-erythronolactone, was reported.[465]

g. Catalytic Air Oxidation.—Atmospheric oxygen is the cheapest oxidant. Passing a stream of oxygen by aqueous starch suspensions containing 1% of KCl resulted in cleavage of amylose and amylopectin and oxidation at positions C-2 and C-6 as well as C-3, that is, it did not proceed selectively.[466] Tapioca starch was air-oxidized in a 3% suspension of hydrochloric acid at 48 °C.[467] Sunlight acts cooperatively with air in starch oxidation, and such sensitizers as

zinc oxide might be employed.[468–470] Air oxidation over Ce(III) hydroxide or Fe(II) hydroxide caused total decomposition of starch to carbon dioxide and water.[471,472] However, oxidation in alkaline media (pH 9) over metal catalysts of the 11(1B) transition group (copper and/or silver) did not cause such deep decomposition, and some thickeners for ink, coatings, and detergent builders were obtained by this process.[473] The metal ions should preferably be chelated. Silver in combination with either sodium or ammonium peroxysulfate caused oxidation to carbonyl products rather than to carboxylic acids, although peroxysulfate alone also catalyzed the oxidation.[474] Carbon-supported Pd/Bi and Pd/Pb catalysts have also been used in the preparation of polyhydroxypolycarboxylic acids.[475]

There is a report in the literature describing the air oxidation of corn starch over a vanadium(V) catalyst.[476] The authors claimed oxidation of starch to carboxyl and carbonyl compounds, with a preference for the latter. The oxidation products gave more viscous gels than unprocessed starch. In such reactions, the penetration of air might be strongly dependent on the specific structure of the starch granules. Indeed, the oxidation of potato starch gave less viscous gels,[477] suggesting that the degree of oxidation of potato starch under the same reaction conditions was higher. Oxidation initially increased the viscosity rapidly, with subsequent decrease in viscosity as the degree of oxidation increased.[478] However, the behavior of starches on oxidation, expressed as the viscosity of their gels, is specific for different starch varieties.[479] Carboxylic and carbonyl groups contribute in building up the viscosity to approximately the same extent. The air oxidation of starch to carboxylic starch using Cu, Cr, Co, Ni, Fe, V, Mn, and Ti salts in alkaline media has been patented,[480] with a specific example of oxidation using a Cu(II) salt at 80 °C for 2 h. Starch was also oxidized with oxygen in supercritical CO_2.[481]

Kinetic,[412] microscopic,[482,483] and structural X-ray studies[484] suggested that the amorphous regions of starch granules are attacked first by the oxidant, and that the excess subsequently consumes the crystalline material, however, according to other authors[477] the granule surface is attacked first.

Oxidation products from starch are also available indirectly. For example, Horton and coworkers[485–487] prepared 6-aldehydo amylose and starch derivatives by photolysis of 6-azido-6-deoxy derivatives. The oxidation pattern of starches can be determined by hydrolysis of the reaction product and subsequent identification of the components of such hydrolyzates as their trimethylsilyl derivatives.[488]

Carboxylic groups in oxidized starches have been analyzed with silver(I) nitrophenolate or copper(II) acetate.[489] A colorimetric method based on the affinity of Methylene Blue for the carboxylic group in oxidized starch is also known.[490] Determination of the carboxylic and carbonyl groups can be performed

separately.[347] Carboxyl groups may either be titrated with aqueous alkali or estimated via ion exchange with calcium acetate or sodium bromide.

A quantitative method of estimating the carbonyl groups is based on their reaction with hydroxylamine[491] and sodium cyanide.[492] The ketone carbonyl was determined by condensation of the oxidation product with hydrogen cyanide. After hydrolysis, the condensation product cyclized in the presence of hydriodic acid to 2-methyl-4-hydroxyhexanoic acid lactone, which was separately determined. This approach showed that 17% of the carbonyl groups were present at C-2, and approximately 33% of the total number of carbonyl groups existed as aldehyde groups on the glucose units, presumably located at C-6. Both types of carbonyl groups could be determined simultaneously by their reduction with potassium ferricyanide and by photometric determination of the excess reagent.[493]

3. Oxidation of Starch Derivatives

Oxidation of various starch derivatives has generally been performed empirically to control the functional properties of products, and in general, the structures of such products have not been characterized.

O-(Hydroxypropyl)starch oxidized at approximately pH 11 using either sodium hypochlorite or chlorine gives products of low viscosity, high clarity, and improved film-forming properties.[494,495] The same oxidant applied to epichlorohydrin-crosslinked corn starch provided a product having a stable, hot-paste viscosity.[496] Oxidation with NaOCl[497] and $NaClO_2$[498] also gave products of stable viscosity.[499] The degree of crosslinking of the oxidized material is a critical factor.[500] Products having 1–5% of the D-glucose residues bearing dicarboxylic component were more viscous than more-oxidized products. In addition, electrolytes decreased the viscosity, increased the gel time, diminished the rate of viscosity increase, and improved the stability.[499] *O*-(Carboxymethyl)starch was oxidized with potassium peroxysulfate, and the aldehydo groups that were formed in the reaction underwent conversion into carboxylic groups on drying the product.[501] *O*-(Carboxymethyl)starch grafted with acrylamide was more difficult to oxidize. Polysaccharides dicarboxymethylated with sodium halomalonates gave wood-like composites after oxidation with sodium hypochlorite.[502]

Oxidation of starch xanthate by either hydrogen peroxide[503] or sodium hypochlorite[504] gives the "xanthide."[503] Patents[505,506] have described the oxidation of cyanoethylstarch with 30% hydrogen peroxide at pH 8.5 and with hypochlorite

in an alkaline medium,[507] the products exhibit good pasting properties and better aqueous dispersibility. The products from starch formates and 2-cyanoethyl esters, upon oxidation with periodate, retained these ester in the products.[508] The oxidation of starch blended with polyformaldehyde by 65% nitric acid has been patented.[509] Probably, the acid first catalyzes the formation of hemiacetals, which are then oxidized, but structural characteristics of the product were not given. Starch dialdehyde was further oxidized with $HClO_2$ to generate "dicarboxylic starches."[510–513] The oxidation of starch dialdehyde with hydrogen peroxide increased the stability of dispersions.[514–516] In fact, the dispersibility of starch dialdehyde could be significantly improved by heating a mixture of hypochlorite-oxidized starch with starch dialdehyde having a 90–98% degree of oxidation, followed by adjustment to pH 4.3 and spray drying.[517] The oxidation of starch dialdehyde with sodium hypochlorite and hydrogen peroxide was recommended[518] as the most economically sound procedure, and such starch carboxylates were reported to have superior metal-ion binding properties. Paper coatings having improved wet-rub resistance resulted from oxidation of quaternary ammonium starches by sodium hypochlorite.[519] Hydrogen peroxide with either hydrobromic acid or bromine caused selective oxidation of terminal glucose units of starch and its hydrolysis products.[520] Oxidation of starch with hydrogen peroxide in the presence of iron(II) sulfate can be carried out simultaneously with crosslinking of acrylamide.[521] Similarly, NaOCl oxidation and phosphorylation of starch was performed simultaneously to produce a cold water-insoluble coating for lithography.[522] Oxidation of starch crosslinked with $POCl_3$ was also patented.[523] A batch condensation–oxidation reaction was applied to a mixture of starch and protein, and the mixture was oxidized with hypochlorite, hydrogen peroxide, or peroxysulfates upon extrusion cooking.[524]

4. Reactions of Starch Dialdehyde

Mercaptolysis of starch dialdehyde occurs upon reaction with thiolacetic acid.[525] It is possible that acetalation and crosslinking are involved in making a size consisting of starch dialdehyde, starch, and boric acid.[526]

Sodium hydrogensulfite reacts with starch dialdehyde in a 1:1 ratio.[527,528] Despite the fact that aldehydes react with hydrogensulfites, these compounds are described as adducts. Sodium sulfite degrades starch dialdehyde and the glyoxal liberated forms tetrahydrobenzoquinone.[529]

Etherification of starch dialdehyde is possible. The reaction of starch dialdehyde with propylene oxide and other etherification reactions were described.[530] Esterification of starch dialdehyde with carboxylic anhydrides stabilizes the viscosity and adhesiveness of starch dialdehyde.[531] This adhesive is additionally blended with urea.

Esterification of starch dialdehyde with chlorosulfonic acid in formamide gave a sulfate ester that could be transformed into an amide and methyl ester.[532–536] The classical method of sulfonation, namely, by the action of sulfur trioxide in pyridine, is also applicable.[537,538] Hemiacetals of starch dialdehyde result upon treatment with suitable alcohols in the presence of an acidic catalyst. In acetic media amides condensed with the carbonyl groups. Acetylation of starch dialdehyde with acetic anhydride is an obvious reaction. Esters with hexanedioic (adipic) acid were also prepared.[537] Starch dialdehyde undergoes etherification with monochloroacetic acid in an alkaline medium.[538]

Starch dialdehyde also reacts with carbanions. For instance, reaction with nitromethane produces a nitro compound that after reduction with iron(II) hydroxide in ammonia afforded an aminated product.[539] Molded articles from starch dialdehyde and elemental sulfur were also patented.[540]

5. Applications of Oxidized Starches

Applications of oxidized starches have been reviewed.[442,541–543]

Earlier applications of oxidized starches involved preparation of wood veneer glue,[462] a joint cement consisting of cement mixed with gelatinized oxidized starch and asbestos,[544] gypsum board,[545] and textile dressings and sizes.[297,329,342,374,396,406,501,546–550] Oxidized starches can be components of phosphate-free detergents.[551] Oxidized starches are also used in food texturization because of the smoothness and rigidity of their gels. This application typically utilizes either hypochlorite-oxidized starch[387,396,552,553] or ozone-oxidized starch,[341] but also potassium permanganate-oxidized starches plus hydrochloric acid can be used.[554] Oxidized starches can partly replace agaroids in jellies, but in excess they negatively influence the taste of foodstuffs.[555] The starch variety is critical in such applications. Oxidized potato starch provided better stability of gels, whereas corn starch gave higher elasticity.[556] The quality of bread could be improved by the use of either $KMnO_4$- or $KBrO_3$-oxidized cassava starch.[552,557] Although the use of starch dialdehyde in foodstuffs is illegal, its effect on the nutritional value

of proteins,[558] and rheology of casein and carrageenan supplemented by starch[559] have been studied. The effect of starch dialdehyde on the nutritional value of proteins was found to be negligible, but the availability of certain amino acids could be changed by its inclusion.[558,560] Limitations to the use of starch dialdehyde in foodstuff modifications and supplements may result from its crosslinking of polypetide chains and globulin.[561]

Adhesives, sizes, and coatings for paper are perhaps the largest applications for oxidized starches.[562] Simple oxidized starches were first used for this purpose,[316,327,362,367,396,399,406,516,517,563–567] and blends of oxidized starch with inorganic salts were also reported.[568] These oxidized starches were subjected to further modifications, for instance, by esterification with boric acid,[569] acetylation with acetic anhydride,[570] and hydroxypropylation.[571] Starch dialdehyde itself increased the wet tensile strength of paper by 250%,[572] upon acetalation with glyoxal.[573] It was also used to make paper sheets for thermal recording[574] and in photolithography.[575] Co-crosslinking of starch with poly(vinyl alcohol) and formaldehyde produced a material resistant to boiling water and having a good capability to absorb dyes.[576] Starch dialdehyde acetals,[577,578] hydrazones,[579] oximes, hydrogensulfite compounds,[528] and condensation products with *N,N*-diallylmelamine were all proposed as additives increasing the wet and dry strength of paper.[435] Studies were also conducted on condensates of oxidized starches with amines[580] and alkylammonium salts.[581,582] Paper-coating products have been made by several modifications. Such metal salts as a chromium(III) chloride, zirconium(IV) chloride, zirconium(IV) oxychloride or zirconium(IV) ammonium carbonate,[383] and aluminium hydroxide together with titanium(IV) oxide were proposed to decrease the solubility of oxidized starch.[583] Oxidized starch added to cellophane decreased its hydrophobic properties and dimensional stability during exposure to humidity.[584]

Several copolymers and condensates of oxidized starches with polymers have been developed. For example, products of starch dialdehyde condensation with acrylamide were prepared for further copolymerization with various monomers to form resins for coatings, molding powders,[585] and materials for immobilization of enzymes, for instance, alpha amylase.[586] Hypochlorite-oxidized starches were also reacted with acrylonitrile.[507,521] Hypochlorite-oxidized starches were allowed to react with allylated starch dialdehyde,[587] polycondensates of ammonia–dimethylamine–epichlorohydrin,[588] polycondensates of starch dialdehyde with melamine,[589] urea[433,541,590] capable of precipitation of tannin[591], carboxyamides,[411] urea and formaldehyde,[592] proteins,[524,593,594] poly(vinyl alcohol),[595] alkylammonium salts,[519,596] alkoxyalkylamines,[597]

polyamide–epichlorohydrin resins,[598] and propylene oxide.[599] Such products could be used as adhesives for labels and corrugated paper.[600] Phosphated oxidized starches are recommended as coatings for lithography.[522] Further applications involved thickening[601] and backing of photographic film.[297] Thin films were prepared from starch dialdehyde and partially hydrolyzed poly(vinyl acetate),[589] starch dialdehyde and *O*-(carboxymethyl)cellulose,[602] starch dialdehyde and ethylene–vinyl alcohol copolymers,[603] as well as starch oxidized with di- or tetrachloro-glycouril (2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione).[414] The acidic properties of oxidized starches were utilized in trapping metal ions,[295,322,518,521,604] and heavy metal salts of oxidized starches have been suggested as dye mordants.[297] When cerium nitrate was added to oxidized starch supported on silica gel, an oxidation catalyst was produced. Its applicability was tested for air oxidation of hydroquinone to 1,4-benzoquinone.[605] Starch oxidized with CrO_3 containing a chromium(III) compound was effective after alkalization as a corrosion inhibitor in cooling units.[348] An additive for drilling muds was prepared using starch oxidized jointly with chromic and nitric acid.[351] Oxidized starches have also been used as binders. For example, they were used to bind particles of artificial fertilizers.[333,606] Other applications for oxidized starches include detergent builders,[333,400,502,513,607] scale-preventing agents,[608] and microencapsulating agents for aromas.[609] Oxidized cationic starches were also used as flocculating and dewatering agents of municipal sludge.[610,611]

A wide variety of medical applications have been proposed for oxidized starches and their derivatives.[612] For example, oxidized starch was proposed as a powder that could decrease gauze adherence to wounds.[296] Several thiosemicarbazones were reported as tuberculostatic against infected mice.[613,614] On the other hand, thiosemicarbazones of starch dialdehyde significantly accelerated *Mycobacterium tuberculosis in vitro*, and therefore were proposed as reagents for the taxonomy of this disease.[615,616] Antitumor activity both *in vitro* against HeLa cells and against solid, transplantable sarcoma 180 in mice was recognized.[617] Starch dialdehyde of 40–100% oxidation can be temperature- and compression-molded, provided it contains 22–32% of moisture prior to processing.[431] Supposedly biodegradable shapes could be made, although a progressive loss of susceptibility of starch dialdehyde to beta amylase was noted. Starch dialdehyde can be condensed with isoniazid and amithiozone, and the condensation products showed tuberculostatic acitivity.[618]

Polysulfates of oxidized starches, being heparin-like compounds, show blood anticoagulant activity. Their activity increases with the number of sulfate residues, and the 6-carboxyl groups decreased the toxicity of the compound.[533–536,619] Complexes of these anticoagulants with pepsin had no proteolytic activity.[620,621] Methyl

esters of polysulfates of oxidized starches exhibited anticoagulant properties, and they also reduced blood cholesterol.[532] Heparin-like activity was also shown by polyaminopolysulftaes of oxidized starches.[535,536] Starch dialdehyde was shown to be a convenient carrier for some biologically active compounds, for instance, the enzyme papain.[622] Oxidized starches were evaluated as pharmaceutical tablet excipients, showing similar drug release properties as gelatin.[623,624] Polycondensates of starch dialdehyde with proteins may immobilize enzymes by binding them covalently.[625] The ability of amides and amines to bind to starch dialdehyde was utilized in the removal of uremic waste metabolites from human organisms.[626] The use of carboxystarch polymers as a component of toothpaste and mouthwashes was also reported.[514] These additives did not stain teeth, and they inhibited plaque formation. Feeding nephrectomized rats (200 mg/day) with oxystarch significantly prolonged their life.[627] This result may be attributed to an increase of the nitrogen fecal excretion. However, urea does not bind directly to starch dialdehyde.[628]

Oxidized starches having carboxylic groups are able to capture various metal ions. For example, derivatives with bound components were reported as ion carriers.[538,601] Calcium derivatives[629] were proposed for treating hypocalcemia.[630] Oxidized starches can also carry radionuclides for use in immunoradiometric assays.[631,632] The viscosity of starch dialdehyde solutions can be readily increased by the addition of gelatin.[633,634] Crosslinking of gelatin by starch dialdehyde has been described.[635] Another possibility results from the fact that starch dialdehyde readily adsorbs various cations. The adsorption order of is as follows: $Ca^{2+} > Mg^{2+} > Na^{+}$. Acetate anions adsorb better than chloride anions. Because the adsorption increases the viscosity of aqueous starch dialdehyde solutions, this phenomenon can be utilized for practical applications. The order of the effect of cations on the viscosity is as follows: Na > K > Mg> Ca.[636] Starch dialdehyde is able to coordinate other metal ions, for instance calcium and chromium(III) cations.[637] Starch dialdehyde is a stronger sequestering agent than pectins.[638]

VIII. Metal Starchates

Native starch, being a polyalcohol, may form polyalcoholates—starchates—retaining metal cations bound to the hydroxyl groups of glucose residues. Native potato starch, being a polyphosphate in its amylopectin portion, has ion exchange properties and is capable of binding metal ions to C_6H_2–OPO_3^{2-} moieties. Several metal derivatives of potato starch are described in the literature, and have been

reviewed.[639] The same author also described the iron(III) derivative of starch. The most common method of preparation entails metathetical reactions of alkali metal salts of amylopectin phosphates with water soluble salts of a given metal. Metal atoms bound to the C_6H_2–OPO_3^{2-} moiety affect gelatinization properties of these starches.[640]

Other starch varieties chemically bind metal atoms only to the hydroxyl groups, in the same manner as alcoholates. Alkali metal starchates were obtained for the first time by the use of either metal amides in liquid ammonia[641] or metals in liquid amines.[642] These methods were subsequently used by others.[643] Sodium 2-starchate could be prepared by refluxing an alcohol solution of NaOH and dry starch.[644] The reaction of dry starch with controlled amount of NaOH in 1-butanol provided either monosodium 2-starchate or disodium 2,3-starchate.[645,646] However, complexes of NaOH with starch were also characterized.[37,38] Thallation of starch could be performed with thallous hydroxide.[647]

Sodium starchates were then converted into 2,3-dicupric and 2,3-diarsenous starchates by reaction with the corresponding metal chlorides.[645] Chloride ions remaining associated with metal atoms to satisfy their valence could be replaced by other groups. Among them, HCO_3 and CNS provided higher stability. Similarly, mono- and di-potassium starchates could be obtained from KOH in 1-butanol. It was reported that trisodium 2,3,6-, tripotassium 2,3,6-, and dipotassium-2,3-monosodium-6-starchates could be prepared by reacting dimetal starchates and corresponding metal amides in liquid ammonia.[645] Lithium starchates[648] are also readily alkylated and acylated.

Alkali metal alkoxides have also been used as sources of the metal.[649,650] The result is similar to the reaction with metal hydroxides, this is, metal 2,3,6-tristarchates are formed, but in a single step. Thallation,[647] titanation,[651] and lanthanation[652] was reported with corresponding metal alkoxides. The reactions were carried out either in ethanol (thallation) or in toluene suspensions (titanation and lanthanation), and the results were dependent on the reagent ratio. Titanation and lanthanation resulted in intra- and inter-molecular crosslinking of the starch. Lanthanation was possible either on reflux in a toluene reagent suspension or during microwave heating of dry reagent mixture gave pure products. The structure of lanthanum starchates depended on the mode of heating. Alumination of starch was achieved with an alkali metal aluminate.[653]

If metal halides are sufficiently reactive (this is, readily hydrolyzable), the preparation of relevant metal starchates may be simpler. Aluminum starchate was produced by vigorous stirring of dry anhydrous aluminum chloride and starch[654] but the reaction with $AlCl_3$ as well as $AsCl_3$ in a benzene suspension was also reported.[655]

Tin(IV) starchate was prepared by reacting an aqueous starch slurry with $SnCl_4$ at pH 4.[656] Production of tin derivatives by reacting starch with trialkyltin chloride in dimethyl sulfoxide has been described,[657] Bactericides were produced[658] by reacting amylose with tin organics having the general formula R_2SnCl_2. Reactions of starch with $TiCl_4$[94] and $SbCl_5$[659] proceeded violently and produced hydrogen chloride, which formed a black, amylose–hydrogen chloride complex. However, $FeCl_3$ did not react in this manner, and only the starch–$FeCl_3$ complex could be formed. Ferric starchate was prepared by stirring a starch gel with reduced iron powder for 3 days. It was reported that up to 10 wt.% of iron could be incorporated into starch and Fe^{3+} was bound prefreably via the CH_2OH group, with additional coordination to other sterically available lone electron pairs of the oxygen atoms.[660]

Reactions with potassium pyroantimonate[661] and bismuth hydroxide nitrate oxide[662] proceeded smoothly. Signaigo[663] produced a starch–titanium compound by curing starch with either titanium sulfate or hydrous titanium(IV) oxide at 130–135 °C under moderate pressure. The Grignard reagents react with starch in a manner typical for alcohols,[664] thus, EtMgBr in diethyl ether produced the starch monobromomagnesyl etherate, St-OMgBr·Et_2O. Oxidized starch was reacted with sodium stannate.[665]

It was reported that metallation of starch did not change its thermal properties to any significant extent.[647,651,655] but also there is report that an increases in thermal resistance of starch can be afforded by derivatizing such starches with metal atoms.[666] In every case the reaction products were less susceptible to hydrolysis as compared with unreacted metal salts.

Aluminium starchates were suggested as potential dermatological and gastric system antiulcer aids[655] as well as products useful for manufacturing of gypsum board.[654] Arsenous starchate was suggested as molding agent[645] and as a poison for rodents.[655] Cupric starchate was also used for molding applications.[645] Thallous starchate was also prepared as a poison for rodents.[647] Titanium starchates were prepared as additives for corrugated paperboard and plywood[663] as well as a heterogenous catalyst.[651] Propylene is readily grafted onto aluminum and titanium starchates,[667] and polyvinyl alcohol has been grafted onto hydroxypropyl starch titanated with titanium(IV) isopropoxide.[668]

A separate group of metal starchates comprises metal salts of starches carrying carboxyl, xanthate, sulfate, phosphate, and similar groups. Oxidized, carboxyalkylated, sulfated, xanthated, and phosphorylated starches readily form corresponding salts by methatetical reactions between the sodium salts of the aforementioned derivatives and other water-soluble, metal salts. There are several patents on the formation of these salts for ion exchangers and the removal of

heavy metal contaminants from water. It was reported that the sodium salt of *O*-di(carboxymethyl)starch acts as a calcium sequestrant.[669] Carboxystarch has also been used for this purpose.[604] *cis*-Platinum derivatives of starch were tested against leukemia tumors in mice ands found more effective and less toxic than *cis*-platin.[670] Starch glycolate was also reported as a heavy metal collector,[671] and there have been several reports on the use of xanthates as heavy metal collectors[672–676] and as flocculants for metal oxides and hydroxides.[677] Related salts were recommended as a wood adhesive and also as binders in the textile, paper, and paint industries, for example, *O*-(carboxymethyl)starch aluminate prepared by a treatment of *O*-(carboxymethyl)starch with alum in the presence of calcium hydroxide.[678] *O*-(carboxymethylstarch aluminates have been patented as antiulcer preparations,[679] and aluminum–bismuth starch sulfates were designed[680] for the same purpose. The low solubility of certain metal salts promotes sedimentation of starch derivatives from aqueous solutions, as shown[681] in the case of starch phosphate sedimented in the form of a zinc salt. Bivalent metal ions can act as crosslinkers for such compounds, as demonstrated by the application of the following compounds in paper manufacturing: starch xanthate,[682] an oxidized starch titanium derivative,[683] and an oxidized starch zirconium derivative.[684] Crosslinking of starch xanthate was also utilized in latex processing.[685]

IX. Etherification

1. Syntheses and Properties of Starch Ethers

a. Alkylation with Alkyl and Aralkyl Halides and Sulfates.—The hydroxyl groups of the glucose residues in starch exhibit reactivity typical for alcohols, and undergo conversion into ethers. Methyl and ethyl ethers were first studied, using typical methylating and ethylating agents such as alkyl sulfates and[686–695] activated starch can be methylated in 4% aqueous NaOH. Ethers are also produced by blending starch with alkyl halide in the presence of such dessicating agents as $CaCl_2$.[696] Starch can be methylated with methyl iodide in the presence of BaO within 24 h at 30 °C in dimethyl sulfoxide.[697] Methylation with dimethyl sulfate in dimethyl sulfoxide with added alkali required 25 h at room temperature under nitrogen.[698] The product was fractionated in acetone and diethyl ether. The infrared spectra of the reaction products revealed little absorption at 3400–600 cm^{-1} indicating a high degree of methylation, and low absorption at 1736 cm^{-1} revealed that oxidation

had not occurred. Diluents and metal salt catalysts may be used in alkylation.[692,699] Methylation of starch in a mixture of methanol, ethylene glycol, and alkali has been described.[700] Methylation of starch may be conveniently effected by portionwise addition of diazomethane to starch suspended in absolute ether.[701,702] Further modifications of the etherification involve alkylation of metal starchates [for instance, sodium, copper(II), or barium]. They are used for etherification with more complicated alkylating reagents. For instance, production of tricarboxystarches by reacting metal starchates with carboxylic acids during freeze-drying was reported.[703] Their salts are obtainable by heating starch with metal hydroxides in 1-butanol.[644,645] Another etherification method involves rapid heating of starch above its gelatinization temperature while being pressed into thin layers.[704]

The products are then dissolved in aqueous alkali and alkylated at 40–50 °C for 30 min. Higher alkyl halides react with starch in aqueous alkali,[705] but the use of high pressure is recommended.[706] It is beneficial to soak starch in alkali prior to alkylation, arylation, or aralkylation. The use of ammonium hydroxide instead of NaOH for this purpose has been patented.[707] The amount of alkali can be decreased when starch used for alkylation is precipitated from 33% aqueous chloral solution.[708]

In an industrial process, vapors of alkylating agents reacted either with semi-moist starch under pressure without any alkali added[709–711] or under diminished pressure on starch soaked with aqueous NaOH. Alkali starch is allowed to react with carbon dioxide[712,713] or is steeped in aqueous NaOH and alkylated under pressure.[714] Industrial scale methylation, ethylation, and propylation of starch in carbon tetrachloride in the presence of 8.5 M NaOH has been described.[715] Ungelatinized products that were soluble in cold water were produced only upon careful adjustment of the alkali concentration.[716] Methylation of starch may retain the granular structure of the product, although the alkylation was uniform throughout the granule interior.[717] The addition of sodium phosphate inhibits gelatinization of starch granules,[718] and has been used in preparation of granular di- and tri-*O*-methylstarches,[719] including mixed alkyl, alkylallyl, and other ethers.[720,721]

Chlorotriphenylmethane generally etherifies only one of three hydroxyl groups of the glucose residues in starch, in contrast to cellulose, where all three hydroxyl groups may undergo tritylation.[722] The starch trityl ether is very sensitive to cleavage, even in aqueous solutions. Benzylation of starch gives mainly dibenzyl ethers,[723–727] whose degree of substitution can be analyzed by proton NMR and UV spectroscopy.[728] Benzylation in the presence of methylsulfinylmethyl carbanion gave the tribenzyl ether in 86% yield.[729] The progress of benzylation can be controlled by regulating the rate of consumption of the benzylating agent with an

alkali catalyst. The addition of sodium chloride or sodium sulfate inhibited starch gelatinization.[730,731] The rate of benzylation is linearly proportional to the amount of hydroxyl ions absorbed by starch.[732] The substitution pattern in benzyl starches has been determined by GLC–MS.[733] Di-*O*-benzylstarch has resinous properties.[734]

The degree of alkylation is obviously controlled by the concentration of alkylating agent. A product of low DS can subsequently react to give a product of high degree of substitution.[658] It is beneficial to add the alkylating agent in small portions after previous portions of the reagent have been consumed.

Thorough studies[735] suggest that dimethylation occures only at the 2-and 3-OH groups, whereas trimethylation involves 2-, 3-, and 6-OH groups Two to three treatments are usually sufficient for the reaction to be completed.[736] When methylation with methyl iodide was carried out in liquid ammonia, the addition of sodium metal led to mono-, di-, and tri-methylation. A product having a DS of 0.34 was a 6:2:1 mixture of mono-, di-, and tri-*O*-methylstarch. Similarly, a product having a DS of 0.90 was a 3:2:1 mixture of mono-, di-, and tri-*O*-methylstarch. The ratios of 2- and 6-monosubstitution were 3:2 and 1:1 for products having DS values of 0.34 and 0.90, respectively, and 3-substitution was stated not to occur at all.[737,738] It was reported that slightly more than monomethylation occurred, in contrast to alkylation with alkyl halides and alkyl sulfates in alkali.[739] The degree of substitution and molar substitution of ethyl starch ether can be eveluated by HPLC.[740]

Fully alkylated starches are insoluble in water but are soluble in many polar nonaqueous and nonpolar solvents. Starch alkylated to a lower extent retains its water solubility but is also soluble in alcohols and chloroform. The solutions have a micellar character.[741] Decrease in the softening points of alkyl starch ethers as the length of the alkyl chains increased is observed.[706] The solubility of etherified starches depends also on which etherifying agent is applied.

Alkylated starch can be fragmented by acetolysis into water soluble tri- and tetrasaccharides.[742] Formic acid, together with a small amount of acetyl chloride, may be used instead.[743] Alkyl α-D-glucosides can be prepared by treating starch with hydrogen chloride a solution of hydrochloride in a simple alcohol.[744]

The chemistry of starch ethers has progressed with the use of a greater variety of alkylating agents, for instance, ethylene oxide,[745] chloroacetic acid, epichlorohydrin, vinyl monomers, and other alkylating agents.[746]

b. Alkylation with Alkenyl Halides.—In the preparation of monoallyl starch with allyl bromide, the nature of the starch variety influenced the reaction yield and the properties of the product.[747] Corn starch gave a higher yield of reaction product. Monoallyl potato starch shrank at 160–165 °C and decomposed at approximately

260–270 °C, whereas the corn starch derivative only turned brown at this temperature. Further allylation led to diallyl ethers.[748–752] For this purpose, an acetone solution of starch acetate in a 50% solution of NaOH containing allyl bromide was boiled or heated in an autoclave at 80 °C. These procedures were then improved by using either butanone and KOH[753] or 1,4-dioxane and NaOH.[754] Di-*O*-allylstarch is a soft, gummy product that is soluble in most of organic solvents except for aliphatic hydrocarbons. This solubility is lost after exposure of diallyl starch to air.[748] It can also be hardened by the addition Co(II) octanoate or Co(II) naphthenate.[755]

A process for determination of the allyl groups by addition of bromine was described.[756] Allyl starch of DS 3 was also reported,[757] and another procedure for determination of the allyl groups is based on the addition of mercury(II) acetate to the double bonds.[758]

Etherification with cyanuric chloride provides insoluble products.[759] Ethers from dichlorocyanuric acid or its salts produce a smooth paste that is stable for 4 weeks.[760]

c. Alkylation with Halocarboxylic Acids.—Early patents on carboxyalkyl starches[761,762] described the reaction of halo fatty acids with starch in aqueous alkali. This procedure was subsequently improved by the addition of organic solvents to the reaction mixtures. *O*-(Carboxymethyl)starch was readily produced by stirring starch for 20 h in alcohol or acetone with 35–40% aqueous NaOH, followed by 20 h of treatment with chloroacetic acid at 30–40 °C.[763] Several minor modifications of this procedure has been reported that involved changes of reagent proportions, solvent, and reaction temperature.[764–803] Other modifications entail the use of pressure[765,804,805] and extrusion at elevated temperatures.[806] Newer preparations[807] involve the partial replacement of water by ethanol. The following order of solvents affect the DS of the product: water < acetone < methanol < DMF < cyclohexane < 2-propanol.[800] Activation of starch by irradiation of the reaction mixture was also proposed.[808] The reaction proceeds readily, but a decrease of the molecular weight was noted. Water-soluble carboxymethylstarch, as its alkali metal salt, readily precipitates after the addition of silicates.[809] The viscosity of aqueous solutions of carboxymethylstarch strongly depends on the DS as well as the electrolyte present. The effect of electrolyte upon the viscosity depends, again, on the solute DS.[810] It was reported that the adhesive properties of the final product can be modified by exposure to a stream of chlorine at the dextrinization temperature.[811] Methods of preparing this derivative from industrial waste have also been reported.[812] Chloroacetates can react with (alkoxycarbonylmethyl)starch.[491] Higher halogenated fatty acids also reacted with starch to give the corresponding carboxyalkyl ethers.[813] Di- and tri-chloroacetic acids also react with starch, giving

carboxydi- and carboxytri-chloromethyl starches.[814,815] Chloroacetic acid reacting with starch in conjunction with bis(hydroxymethyl)urea affords a product of unusually high viscosity.[816]

O-(Carboxyhydroxyalkyl)starch derivatives have been prepared from chlorohydroxyalkanoic acid and starch in alkali,[817] and starch reacted with isatic acid anhydride gave carboxyphenyl starch.[818] *O*-(Carboxymethyl)starch can be determined[819] by paper elution analysis with perchloric acid. The same authors reported a procedure for determining the molecular weight.[820] When *O*-(carboxymethyl)starch was benzylated, partial decarboxymethylation occurred.[821,822] The thixotropic properties of *O*-(carboxymethyl)starch solutions were studied.[823] Carboxymethylated starch forms cold-water swellable granules,[824] which are biodegradable.[825]

Reaction of sodium *O*-(carboxymethyl)starch with epichlorohydrin catalyst introduced epoxide groups into starch.[826] The opposite sequence of reactions, namely epoxidation of starch followed by carboxymethylation was also carried out[827–829] in order to produce an absorbent material. Rheological studies of swelling and crosslinking were performed on carboxymethyl starch, which was used as a gel thickener.[830] Similar rheological behavior was found for carboxymethylstarch prior to crosslinking. Reactions with alkylene oxides were performed at elevated pressure in either alkaline or in acidic media, and they produced poly(oxyalkylene) ether-grafted starches with enhanced viscosity and adhesiveness.[831,832] A reaction of starch with sodium chloroacetate in alkali and simultaneous crosslinking with sodium metaphosphate has also been described.[833] Cationic–anionic starches were produced by reacting it with 2,3-dihalocarboxylic acids (2 parts) and with secondary amines (1 part). The resulting product was used for carboxyaminoalkylation of starch.[834,835] Etherification of starch with simultaneous crosslinking was described[836] using 2,5-dimethoxytetrahydrofuran. The product slowly hydrolyzed in water, producing succinaldehyde.

Starch ethers having amino groups in the side chain are produced by alkylation with either ω-chloroalkylamines or alkylamino-substituted alkylenes.

d. Alkylation with Acetylene and Vinyl Monomers.—Starch reacts with acetylene to produce vinyl starch. This process requires a pressure of 2410–5170 kPa[837] A sequence of catalytic hydrogenation, methanolysis, and chromatography indicated the 2-position of the glucose units to undergo preferential vinylation.[838] The vinylation with acetylene proceeded more readily when the reaction was performed under microwave irradition in flowing acetylene and in the

presence of a hydrogen peroxide catalyst.[94] On average every 40th glucose unit was vinylated, and the product was readily water-soluble. In contrast to acetylene, ethylene caused depolymerization of starch.[839]

Treatment of starch with acrylonitrile in alkali afforded *O*-(2-cyanoethyl)starch.[840–849] A degree of substitution as high as 3 was reached.[850] The first-order rate constant decreased during the early stages of etherification and subsequently reached a steady state, reflecting differences in the reactivity of primary and secondary hydroxyl groups. For the primary hydroxyl groups, the activation energy was 53.14 kJ/mole, the activation enthalpy was 51.5 kJ/mole, the activation entropy was −102.5 J/deg/mole, the rate constant was 1.38 L/mole/min at 20 °C, and the equilibrium constant was 79.4 mole/L. Corresponding values for secondary hydroxyl groups were 3.6, 2.9, −61.2, 9.05×10^{2}, and 31.0×10^{-2}, respectively.[851] The addition of sodium sulfate is beneficial for cyanoethylation.[852] There is a patent for the oxidation of *O*-(cyanoethyl)starch with 30% H_2O_2 at pH 8.5.[505]

O-(Carboxyethyl)starch is also obtainable by treatment of starch with acrylonitrile in 10% aqueous NaOH solution at temperatures no higher than 60 °C,[852–854] and hydrolysis of the nitrile group can be stopped at the carbamoylethyl group stage.[855] The apparent viscosity of cyanoethyl starch decreased upon storage, whereas the shear rate significantly increases.[856] This behavior is opposite to that of alkali-treated starch.

O-(Cyanoethyl)starch, crosslinked with epichlorohydrin and then hydrolyzed to a carbamoylethyl intermediate and then oxidized with hydrogen peroxide, gives *O*-(carboxyethyl) starch.[857] Reaction of starch with acrylamide can give the carbamoylethylated product directly.[858,859] The second-order rate constant was invariable until a DS of 0.33 was reached, suggesting that only the primary OH group of the glucose unit was involved. In 0.235 M NaOH at 25 °C, the rate constant was 12.5×10^{-4} L/mole/min, the activation energy was 67.8 kJ/mole, the activation enthalpy was 65.3 kJ/mole, the activation entropy was −78.2 J/deg/mole, and the equilibrium constant was 2.47 mole/L. Crosslinking resulted upon treatment of carbamoylethyl ethers with sodium hypochlorite.[860,861] The use of *N*-methylacrylamide afforded *O*-(2-*N*-methylcarbamoylethyl)starch.[862] A reaction with glycidyl methacrylate has also been patented.[863] As with acrylonitrile, other vinyl monomers can also etherify starch. For example, vinyl acetate readily reacts with starch and oxidized starch in an aqueous slurry in the presence of sodium carbonate.[864] An alkaline solution is required for etherification of starch with acrylic acid.[865] Such reactions have also been carried out with long-chain alkylketenes.[866,867] Carbamoyl starches were condensed with various azo dyes bearing an active chlorine atom capable of substitution

with the amino group of the carbamoyl moiety.[868,869] Alkali catalyzed etherification with 2-(acrylamido)-2-methylpropansulfonic acid was performed[870] to obtain products having the general structure $ROCH_2CH_2CINHCMe_2CH_2SO_3OH$, where R is starch and the sulfonic moiety bears various metal cations (Li, Na, K, Mg, or Ca).

e. Alkylation with Alkylene Oxides.—Etherification of starch by alkylene oxides can occur without addition of alkali.[711] The reaction is catalyzed by tertiary amines, which form quaternary compounds with an alkylating agent or quaternary ammonium salts.[871] A food additive from *O*-(hydroxyalkyl)starch has been designed[872] which was produced using disodium hydrogen phosphate (1–1.5%) as a catalyst. Ethylene oxide-modified starch was prepared in granular form by pressure heating air dried starch containing ~10% of moisture.[873,874] The reaction rate increased with temperature and the concentration of absorbed ethylene oxide. The reaction rate was also exponentially dependent on the mositure content in the starch granules.[875] Newer procedures recommend treatment of starch in alkaline suspensions with alkylene oxides and either alcohol,[876–888] 50% aqueous NaOH,[889–892] or pyridine.[893–895] Alkylene oxides of complicated structures provide novel opportunities for starch modifications.[896] Critical parameters that minimize production of glycols and polyglycols, resulting from addition of water to alkylene oxides and polymerization without participation of starch include minimizing the water content in the reaction mixture, reducing the temperature to below 50 °C, and also maintaining the alkali concentration below 50%.[897] The granular character of the product is retained if the reaction is performed in an alkaline slurry containing sodium chloride or sodium sulfate.[898–901] The alkali concentration in aqueous slurry can be decreased to 2%, provided that CaO is added as the catalyst.[902,903] The alkali concentration could be lowered to 0.25% when dry starch was blended with NaOH powder and aged for 3 days. Granular *O*-(hydroxyethyl)starch can be readily gelatinized.[904]

Hydroxyethylation increases the water-binding capacity of the product in relation to that of untreated starch.[905] A procedure involving a low degree of overpressure was also reported.[906] Films from high-amylose corn-, normal corn-, and waxy corn-starch were produced.[907] High-amylose corn starch produced the strongest films, however, they were less transparent than those made from the other varieties. Another process is decribed in which aqueous KOH and ethylene oxide are introduced into a fluidized bed reactor.[908] 2-Chloroethanol in alkali was also reacted.[909] Improved methods of preparing *O*-(hydroxyethyl)starch for cryogenic protection applications were reported.[910–913]

Gas–liquid chromatography of hydrolyzates indicated that commercial samples had a degree of substitution ranging from 0.65 to 1.03.[914] Substitution at O-6 results from the reaction of starch with ethylene oxide in 1,4-dioxane in the presence of alkali,[915] whereas other procedures gave 2,6 disubstitution in ratios between 0.1 and 2.[916] Studies carried out on commercial *O*-(hydroxyethyl)starch of DS 0.1 showed that glucose units had 84% of the substituents at O-2,[917,918] with the remaining hydroxyethyl groups being situated almost exclusively at O-6. Only traces of etherification at O-3 took place. These findings were generally confirmed by gas–liquid chromatography of *O*-(hydroxyethyl)starch hydrolyzates[919–921] and by ^{13}C NMR spectroscopy.[922,923] The degree of branching is about 0.3.[924] Hydroxypropylation occurs first in the amorphous regions of starch granules, and the *O*-bound side chains are flexible. Therefore, these products may be considered as internal plasticizing resins.[925] Results of this reaction depend on the reaction conditions and involve diffusion of the reagent into the granule interior.[926,927] The water-binding capacity of modified maize starch varies nonlinearly with DS for DS values in the range of 0–0.27. The water-binding capacity decreases to a minimum at a DS of 0.07 (0.39 g of water/g of unmodified starch) and then increases to 0.45 g/g.[928] Hydroxypropylation decreases the gelation temperature of starch, but crosslinking with epichlorohydrin enhances it.[929]

The reaction of starch with propylene oxide in alkali forms *O*-(2-hydroxypropyl)starch.[892,930–938] A granular derivative can be prepared by impregnating starch with acetic acid prior to its alkali treatment with and reaction propylene oxide.[939] Etherification at O-3 and O-2 occurs at approximately the same rate, and the reaction at O-6 is slightly less favorable.[933] However, etherification at O-2 has priority.[940]

Hydroxyethylation on extrusion is also possible.[941] It was reported that enzymic hydrolysis of both 2- and 6-*O*-(hydroxyethyl)starch with alpha amylase decreased with increasing DS. The product having 2-substitution was more resistant to that enzyme than a 6-substituted product.[942] The reaction of ethylene oxide with starch is accompanied by concurent hydrolysis of ethylene oxide to ethylene glycol.[943]

Extended studies on starch etherification with C_2 to C_5 aliphatic alkylene oxides in alkaline slurries have been performed.[944,945] This reaction was subsequently re-examined for hydroxypropylation.[946] No significant effects were observed as a result of using added hydrogen peroxide, benzoyl peroxide, azodiisobutyronitrile, or $K_2S_2O_8$.[945] In all instances, including those studied without such additives, led to water- and alcohol-soluble thermoplastic materials. Further improvements involved etherification in either acetone or butanone in the presence of aqueous NaOH. Ethylene oxide was introduced incrementally.[947] Etherification of starch

sulfate gave products of DS of 0.22–0.44 that were insoluble in cold water.[948] A continous production of *O*-(hydroxypropyl)starch in a static mixer reactor has been described.[949] It was also reported that etherification with styrene epoxide produced starch 1-hydroxy-2-phenylethyl ether.[944,950,951] No grafting occurred when the reaction was performed using potassium starchate in dimethyl sulfoxide.[952] Reaction conditions providing ungelatinized, unswollen, cold-water soluble hydroxypropyl starch apply also to other etherified starches.[953,954] Diepoxides crosslink starch.[955–957] The viscosity of the product depends on the reaction pH. At neutral pH, the reaction gives a product of lower viscosity than that obtained in acidic or alkaline media. Starch etherification with 1-dialkylaminooxiranes required use of elevated pressures.[958] Kinetic studies on the alkali-catalyzed hydroxypropylation of potato starch in aqueous slurries revealed that there are four parallel processes,[959] catalyzed and uncatalyzed hydroxypropylations of starch as well as catalyzed and uncatalyzed hydrolyses of propylene oxide. All reactions were first order with respect to both reactants. The viscosity was further increased by reacting hydroxyalkyl starch with esters of D-glucitol with higher fatty acids crosslinked with poly(oxyethylene) chains.[960]

The reaction of starch with epichlorohydrin involves the oxirane function, and chlorine remains in the ether side-chain. A high starch-to-water ratio favors crosslinking.[961,962] When crosslinking does not occur, epichlorohydrin reacts monofunctionally, attacking only one of the 2-, 3-, and 6-OH groups of the glucose units.[963] *O*-(Hydroxyethyl)starch results when the reaction is performed in pyridine.[964] *O*-(2,3-Epoxypropyl)starch was detected when the reaction was performed using sodium hydride in dimethyl sulfoxide.[965] Crosslinking occurred by reaction in the vapor phase[966] as well as in an emulsion of NaOH and $NaBH_4$ in paraffin oil.[967] Several authors reported that crosslinking generally proceeds readily.[968–971] The degree of swelling of crosslinked starch varied regularly with the degree of crosslinking.[972,973] Gelatinization of such products is controlled by the entropy of melting.[974] An alternative method for producing hydroxyethylstarch involves ethylene carbonate in dimethyl sulfoxide in the presence of sodium hydride; etherification favors the 3- and 6-OH groups. The reaction is facile and appears to give better yields than with the use of ethylene oxide.[975] Other alkylene carbonates were also reacted with starch under nitrogen in the presence of tetralkylammonium halides.[976] O-(Hydroxypropyl) starches are produced when the corresponding chloropropanols react with starch. Chromatographic analysis for chlorohydrins in the products is possible with a precision of 1–5 μg.[977] Hydroxypropylated starch crosslinked by epichlorohydrin is described as a food thickener[978–982] and a wound secretion absorbent.[983] The reactions are catalyzed

by trisodium phosphate.[978] Starch polyether methacrylates have been produced by treating starch with methacrylic anhydride in pyridine.[984]

f. Alkylation with Polyols.—Polyhydroxy ethers were formed by treating starch with such polyols as D-glucitol in the presence of Lewis acids, for instance, BF_3 etherate.[985] Chlorodiols, for example, 3-chloro-1,2-propanediol, also react with starch to form such ethers. This reaction has been carried out in the presence of disodium tetraborate.[986] Hydroxymethyloxirane was also utilized for this purpose.[987–990]

2. Applications of Starch Ethers

Applications for starch ethers include adhesives for paper and cardboard,[712,991–994] paper coatings,[995] food coatings,[996] additives to beverages,[714] films, threads, dressings, sizings,[711,783,997–1001] absorbents,[1002–1004] viscosity reducing agents for coal slurries,[1005] carriers for proteins and drugs,[1006,1007] additives for plastic shaping[1008,1009] and emulsion paints,[1010] and protective colloids.[1011,1012] Such ethers retain their ability to gelatinize. They can be applied in combinations with starch esters,[1013] reactive thermosetting resins, and acrylic resins.[1014] It was reported that such ethers can be added to suspensions to enhance filtration[1015] and to improve the turbidity of mill-effluents in pulp processing.[1016] Ungelatinized products were obtained when starch was alkylated with simultaneous crosslinking by the use of either dihaloalkanes or epichlorohydrin. They form smooth, slightly cohesive pastes that are useful in salad dressings, puddings, pies, textile printing gums,[1017–1019] edible thickeners, and emulsifiers.[1020] When blended with rock wool and asbestos mineral-fiber, thermal insulation plates were obtained.[1021]

Diallylstarch was suggested as film-former, as it slowly "dries" in air.[753,1022] It was also suggested as a protective and decorative coating for wood, glass, and metals. Allyl starch constitutes a thermosetting polymer. Its use as a printing ink was suggested.[1023] Allyl starch can be vulcanized with sulfur.[748,1024] Allyl starch can be polymerized in solutions using catalysts and/or oxidants.[1025] Such homopolymerization, at least in the early stages, has an intramolecular character and depends on the size of the polymerizing molecules. This process is accompanied by some degradation.[1026] The addition of dichromates has been used to form photosensitive allylstarch coatings.[1027]

Allylstarch can be blended with lower alkyl itaconates in the ratio from 2:1 to 10:1 and then copolymerized with a variety of coating materials to enhance coating plasticity, drying, and hardening.[1028] Allylstarch can be polymerized into insoluble products using either sulfur chloride or disulfur dichloride.[1029] The reaction product of allylstarch with propylene oxide was utilized as a dispersant for petroleum emulsions.[1030] Novel resinous materials have been obtained from adducts of unsaturated esters of dienophilic dioic acids and cyclic polyenic hydrocarbons with mono- and di-allyl starch.[1031]

Benzyl and/or allyl starch were combined with methyl acrylate, methyl methacrylate, styrene, or vinyl acetate, to develop resins having good tensile strength, high softening temperatures, reduced tackiness, and increased hardness and flexibility.[1032] Benzylstarch exhibited foaming properties.[1033] Allylstarch was copolymerized with styrene at 25 °C until the viscosity reached 3 Stokes. Films were made of this product for use as lacquer coatings.[1034] *O*-(Cyanoethyl)starch of high DS was used as a selective sorbent for hydrocarbons.[850] Lower DS products of (cyanoethyl)starch were used as flocculants of clays and muds.[1035] Products of DS of 0.1–1.0 gelatinized in a slurry at pH of 9.5–11 when heated to 100 °C.[1036] *O*-(Cyanoethyl)starch was also used for separation by flotation of copper and iron from lead and molybdenum.[1037] *O*-(Cyanoethyl)starch was also patented as a component of drilling muds,[1038] as coating adhesive, and also for paper sizing.[1039–1041] *O*-(Cyanoethyl)starch in combination with polyacrylonitrile and/or its copolymers produced dyeable fibers.[1042–1044] These fibers could be made antistatic by the addition of halides or nitrates of Cu(I), Ca, Sn(IV), Zn, Al, Cr(III), Mn(II), Fe(III), or Ni(II).[1045] Good dyeability of fibers was achieved when cyanoethylstarch was oxidized with periodic acid, followed by condensation with amines.[1046] Because (cyanoethyl)starch forms an amorphous glassy matrix with a glass transition $>50\,^{\circ}C$, it could be used as a layer in dry recording devices.[1047] *O*-(Carbamoylethyl)starch was proposed as a dye paste.[1048]

O-(Carboxymethyl)starch salts serve as soap substitutes and detergent components.[1049–1055] They are also recommended as adjuvants in pharmaceutical preparations[775,1056–1068] as they supposedly hydrolyze readily to glucose by saliva.[1059] A hydrogel of (carboxymethyl)starch and cysteine was used for the slow release of drugs.[1060] Improved stability resulted when the hydrogel was prepared with poly(vinyl alcohol).[1061–1063] This enabled production of paper sizing,[1064,1065] a coating for silver emulsion films,[1066] and as filling material for the anode compartment of small-size alkaline batteries.[1067,1068] In the latter application, the electrical storing and discharge characteristics were improved. Swelling films

were obtained by using a blend of (carboxymethyl)starch and chitosan dissolved in formic acid.[1069] *O*-(Carboxymethyl)starch chelates various metal ions,[1070] and it could be spun as a multivalent metal salt to produce fibers of up to 2.3 g/denier.[1071] Potassium salts of (carboxymethyl)starch are proposed as a component of drilling muds.[1072] *O*-(Carboxyalkyl)starches are generally water-soluble, and their aqueous solutions are very viscous even at 0.66% concentration.[762] In combination with other polymers, carboxyalkyl starches are used as remoistenable adhesives[1073] and absorbents.[1074,1075] They are also used as a textile sizes,[996,1076] thickeners,[1077–1079] detergent builders,[1080] curing agent in epichlorohydrin–starch copolymers, in dextrin-containing adhesives[1081] and styrene–butadiene resin (SBR) latex,[1082] and as a printing paste.[1083,1084] In combination with poly(vinyl alcohol) and poly(methylacrylate), it has also been used as a fabric size.[1085]

An absorbent was produced by reacting starch with bis(acrylamide)acetic acid, followed by treatment with chloroacetic acid.[1086] *O*-(Carboxyalkyl)starches were reported to improve the oxygen balance in wastes produced by the textile industry,[1087,1088] and have also been used to improve the water retention of cement slurries.[1089] It was reported that carboxymethylstarch is useful in paper screening when used together with alum, methyl starch, and invert soap,[1090] and has also been proposed for a binding agent in combination with alum and calcium hydroxide.[678] A wood adhesive has also been produced with maleated polybutadiene.[1091,1092] The viscosity of sodium (carboxymethyl)starch increases with increasing DS,[1093] and these solutions readily coagulate hydrophobic suspensions.[1094] They have also been used as a soil carriers in detergents.[1095]

O,O-(Dicarboxymethyl)starch diesters, prepared from starch and diethylchloromalonate in alkali, are useful as a component of detergent compositions.[1096,1097] *O*-(Carboxymethyl)starch can be blended with carboxymethylcellulose to prevent the formation of an intractable mass[1098] used in printing textiles with direct, acid, vat, disperse, naphthol and Rapidogen dyes.[1099,1100] When reacted with acrylonitrile in alkali and then blended with viscose, an absorbent useful in pads and tampons was obtained.[1101] This blend improves the functional properties of gluten for manufacturing meat-paste foods.[1102] Solutions of sodium carboxymethylstarch are hydrolyzed to reducing sugars by human saliva.[1059] Carboxymethylation can be performed on crosslinked starches, as in the reaction of chloroacetic acid with starch crosslinked with glycerol dichlorohydrin, and cold-swelling products are obtained. Crosslinking of (carboxymethyl)starch has also been patented as a method for preparing novel ion exchangers[1103] and absorbents.[1104] Oxirane, 1,2,3,4-diepoxybutane, 3-propiolactone, 1,2-epoxy-3-propanol, and

bis(hydroxymethyl)urea have also been used instead of chloroacetic acid.[1033] *O*-(Carboxymethyl) piperidinostarch was a component of a rustproofing coating composition.[1105]

Starch crosslinked with epichlorohydrin was proposed as a talc substitute,[1106–1108] as an adhesive for corrugated cardboard,[1109] and as artificial silkworm feed.[1110] A sorbent for electrophoresis was prepared when hydrolyzed starch was crosslinked with epichlorohydrin.[1111] The same material can also be used as a wound shield.[1112] Crosslinking does not necessarily result from use of a bifunctional, crosslinking agent. For example, when epichlorohydrin is used together with alkali metal sulfite below 20 °C, only slightly crosslinked ethers are formed. These reaction products easily gelatinize and do not retrograde.[1113] More-highly crosslinked products do not gelatinize, even in boiling water.[1114] Weakly crosslinked polymers were used to produce a network for intravascularly administered compounds.[1115,1116] The same material was proposed for use in the purification of alpha amylase by affinity chromatography.[1117,1118] A polymer of epichlorohydrin–starch and polyethylene glycol ether to which poly(vinylalcohol)[1119] or guar gum[1119] were added were used as dry-cell battery fillings.[1120] A copolymer of epichlorohydrin-treated starch with polyacrylate is used as a filling material for anode compartments in zinc alkaline batteries,[1121] and product for the same application is obtained by simple crosslinking of starch with epichlorohydrin.[1122] Hydroxyethyl- and hydroxypropyl-starch crosslinked with epichlorohydrin are used as thickners in food production.[1123–1125] *O*-(Hydroxypropyl)starch with glycerol triacetate was proposed as a component of a nonaerated pudding composition.[1126]

O-(Carboxymethyl)starch causes diarrhea in experimental rats, and this effect increases with the DS of the product. *O*-(Carboxymethyl)amylose is more laxative than *O*-(carboxymethyl)amylopectin.[1127] Despite this result, (carboxymethyl)starch has been proposed as a texture and taste improver for ice cream.[1128,1129] Aluminum salts of this material have been patented as antiulcer preparations.[679] A syrup conatining *O*-(carboxymethyl)starch the treatment of respiratory ailments was patented.[797] Glyceryl starch was reported as a component of protective ointments.[1130]

O-(Hydroxyethyl)starch appears to be one of the most intriguing starch modifications. Its applications involve suspending components for dermatological lotions,[1131] suspending media for phothosensitive silver halides,[1132–1134] a ZnO electroconductive layer in electrographic devices,[1135] a desensitizer of lithographic printing plates,[1136] a component of paper coatings[1137–1139] and a sizing component for glass fibers,[1140,1141] textiles,[1142] and yarns.[1143] Plastics from

butadiene–styrene–rubber (BSR) latexes and (hydroxyethyl)starch have been patented.[1144] (Hydroxyethyl)starch was used as an antifoaming component in antifreeze media.[1145] In blends with either calcium or sodium chlorides, it helps reduce water loss from evaporation.[1146] It was reported that hydroxethylstarch binds calcium ions better than unprocessed starch, however, the binding decreases as the concentration of calcium ions increases.[1147] Because (hydroxyethyl)starch is more stable than gelatin, it has been proposed as a capsule shell.[1148] (Hydroxyethyl)starch having dialkylamino substituents in the hydroxyethyl chain were proposed for the production of dyeable fibers.[958] In combination with urea, (hydroxyethyl)starch is used as a size for hydrophobic synthetic yarns.[1149] In combination with alkylaminopropylamines[1150] or acetylated starch and poly(vinylalcohol), (hydroxyethyl)starch is used as a corrosion inhibitor[1151] and a microgel precursor[1152] When added to wood pulp, (hydroxyethyl)starch decreased the amount of surface lint on paper.[1153] (Hydroxyethyl)starch films were reported to show negligible transmission of oxygen.[1154] Blends of *O*-(hydroxyethyl)starch and *O*-(hydroxyethyl)cellulose were effective thickeners for textile printing[1155] and developing pastes for motion-picture films, X-ray films and photographic paper.[1156] It was reported that (hydroxyethyl)starch should have a DS of approximately 0.03 when used as a food thickener and in foodstuff coatings.[1157] Such foodstuffs are freeze–thaw stable.[1123,1124,1158–1160] In conjuction with carrageenan, (hydroxyethyl)starch stabilizes milk–starch systems.[1161] Starch-derived ethylene glycol and glycerol glycosides reacted with alkylene oxides and were tested as biodegradable detergents[1162–1164] and components of polyurethane foams.[1165] (Hydroxyethyl)starch accelerated disintegration of tablets prepared by direct compression.[1166] It can also be used as a drug carrier.[1167] Water-resistant, short-tack adhesives were formed by blending (hydroxyethyl)starch with formaldehyde–urea copolymers and polyethylene glycol dodecanoate.[1168] (Hydroxyethyl)starch is utilized in rapidly dissolving pharmaceutical tablets.[1169] A glue is obtained when (hydroxyethyl)starch is blended with maleic anhydride–styrene copolymer.[1170] Blends of (hydroxyethyl)starch with vinyl polymers were used as biodegradable materials by extrusion and pressing.[1144,1171,1172] Blends with borax, urea, and ethylene glycol constituted an aerosol for ironing garments.[1173] (Hydroxyethyl)starch is also a potential soil stabilizer.[1174] Alkylation of (hydroxyethyl)starch provided a biodegradable surfactants.[1175]

(Hydroxyethyl)starch has been extensively studied as a blood expander, sometimes in partially hydrolyzed form.[1176] It was reported that the bleeding volume index of (hydroxyethyl)starch was similar to that of whole blood.[1177,1178] Subsequent experiments showed a prolonged bleeding time after infusing (hydroxyethyl)starch

into dogs.[1178–1181] (Hydroxyethyl)starch maintained arterial hematocrit values at approximately 50% of prehemorrhage levels in dogs. The ratios of fibrinogen-to-total-plasma-protein decreased by 10% after infusion of (hydroxyethyl)starch. Red and white blood cells agglutinated.[1179] No specific deleterious effects on fibrynolysis were observed.[1182] The pH of blood remained unchanged after infusion of (hydroxyethyl)starch.[1183,1184] Negligible changes in arterial gases were observed in dogs.[1184] Further studies on dogs and other experimental animals showed that (hydroxyethyl)starch is an effective plasma expander.[911,1185–1199] Experiments on human volunteers have also been reported.[1200] (Hydroxyethyl)starch is inert in the central nervous system[1201] and is readily eliminated from storage sites in tissues.[1202] In rabbits it temporarily increased the red cell count but had no effect on the leukocyte phagocytic activity in mice.[1203,1204] A suitable derivative for this purpose should have a DS of 0.83–0.93, an intrinsic viscosity of 13–27, and an average molecular weight between 106,000 and 320,000.[1155] However, a product of DS between 0.43 and 0.55 and an average molecular weight of 216,000 was superior.[1190] Measurements of the viscosity, the osmotic pressure, and light scattering were carried out on such starches by Sakamoto and coworkers,[1205] who also standardized the method for characterization of (hydroxyethyl)starch for clinical purposes.[1206] It was shown that hydroxyethyl starch molecules of lower and higher molecular weight were no longer present after circulation. Smaller molecules could be filtered off at the glomerulus, whereas larger molecules could be removed either by cells of the reticuloendothelial system or by digestion with amylase.[1207] It was reported that high molecular weight (hydroxyethyl)starch was toxic to rabbits.[1208,1209] Irikura and coworkers,[1210] proposed the use of (hydroxyethyl)starch of DS 0.47–0.62 as a blood substitute, and compositions of (hydroxyethyl)starch with hemoglobin were also proposed.[906,1211] In humans, hydroxyethyl starch exhibited a low degree of antigenicity.[1212,1213] Immunogenicity was not observed in rabbits and guinea pigs.[1214] Studies *in vitro*[1207–1217] showed that hydroxyethyl starch is an extracellular cryophylactic agent for erythrocytes, and it was also useful in treating endotoxin shock.[1218] There was no anaphylactic reaction to (hydroxyethyl)starch, although another report indicated that rapid infusion evokes such a reaction.[1219] It supported rapid growth of two hematopoietic cell lines derived from patients with solid tumors. It was not metabolized by the cells. In the presence of (hydroxyethyl)starch, the rates of utilization of glucose and production of lactic acid were lower. The uptake of glucose by cells decreased upon increasing the concentration of (hydroxyethyl)starch.[1220]

A method for separating granulocytes from normal human blood using (hydroxyethyl)starch has been published.[1221] (Hydroxyethyl)starch appears to be

a superior anticoagulant which maximizes the granulocyte harvest.[1222] When reprecipitated from solutions of (hydroxyethyl)starch, γ-globulins of blood had better intravenous compatibility.[1223] (Hydroxyethyl)starch was also used for cryopreservation of mammalian cells.[1224–1228] After freezing blood solutions to −196 °C, the average erythrocyte recovery was 97.4% and the average saline stability was 83.4%.[1229] Blood that had been preserved by this method did not cause increased bleeding in monkeys.[1230] (Hydroxyethyl)starch was also used for cryoprotection of bone marrow.[1231] (Hydroxypropyl)starch undergoes fermentation by amyloglucosidase[1064] and other amylolytic enzymes.[922] It was reported that pancreatin digests (hydroxypropyl)starch, but the digestibility decreases exponentially with increasing DS.[1232–1234] Further studies on mice, rabbits, and dogs[1235,1236] indicated that certain doses produced serious and irreversible liver damage. Three-month tests in rabbits showed damaging effects to renal tubular epithelium, swelling of reticular cells of lymph nodes, and other symptoms.[1237] In pregnant mice, teratogenic effects to embryos and offsprings were not observed.[1238] Studies on rats with an orally administered ^{14}C labeled derivative showed that, after 96 h, 60% of the dose was excreted in feces, 20% was detected in expired carbon dioxide, and 15% was observed in the urine.[1239] The urine metabolites were 3-*O*-(2-hydroxyethyl)glucose and oligomers from the hydrolytic scission of the polysaccharide,[1239–1241] but in other studies[1242] oligosaccharides or maltose were not detected among metabolites. These findings varied for different test animals.[1243] (Hydroxyethyl)- as well as (hydroxypropyl)-starches have been shown to be useful in anerobic preservation of whole blood tissues containing living mammalian cells.[1244] It was also reported that (hydroxyethyl)starch and defroxamine, this is, *N*′-[5-[[4-[[5-(acetylhydroxylamino)pentyl]amino]-1,4-dioxobutyl]hydroxylamino]pentyl]-*N*-(5-aminopentyl)-*N*-hydroxybutanediamine, enhanced the recovery of regional wall motion in stunned myocardium.[1245]

(Hydroxypropyl)starch of DS 0.017–0.035 forms a blue complex with iodine, which was suggested for use to add color to swimming pools.[1246] An interesting method of synthesizing (hydroxypropyl)Sephadex was reported,[1247] and it was used in chromatographic separation of lipid and cholesterol materials. First, either maltodextrin or starch was hydroxypropylated under alkaline conditions, followed by a Lewis acid-catalyzed reaction of the product with alkene oxides bearing C-15–C-18 side-chains in 1,2-dichloroethane. A purification method of crude (hydroxypropyl)starch was published.[1248] (Hydroxypropyl)starch was also designed as a component of washing powders.[1249] (Hydroxypropyl)starch has been crosslinked with epichlorohydrin and covalently bonded to various dyes, for instance disodium 8-amino-5-[3-(sulfoethyl)sulfonyl]-anilino]-6-anthraquinonesulfonate[1250]

and Procion Yellow HE-3G.[1251] Such chromogenous starches are useful in the detection of enzymes.

A quantitative method of ether determination is based on hydrolysis of starch ether with hydrochloric acid to glucose.[1252] Hydroxyethyl groups can be determined using either pyrolysis gas-chromatography,[1253] gas-chromatographic analysis of reaction products with hydroiodic acid,[1254] HPLC,[1255] or nuclear magnetic resonance.[1256,1257] Standardized methods have also been reported for the determination of hydroxyalkyl groups.[1258,1259] HPLC can be used to analyze the distribution of hydroxyethyl groups in starch.[1260] High-performance exclusion chromatography is useful to determine the molecular weight of (hydroxyethyl)starch.[1261] Techniques involving FTIR[1262] and UV-visible[1263] are used to identify and quantify hydroxypropylation of starch.

Additional information on starch ethers has been reported by Pringsheim,[1264] Hjermstad[1265] as well as Banks and coworkers,[1266] and Mishler[1267] [only (hydroxyethyl)starch], Omae and coworkers[1268] [only (hydroxypropyl)starch adhesives], Hjermstad,[1269] Mehltretter,[1270] Moser[1271] [(hydroxyethyl)starch], Tuschhoff[1272] [(hydroxypropyl)starch], and Wurzburg[1273] (crosslinked starches).

X. Acetalation

1. Acetalation of Starch

Aldehydes readily react with alcohols into hemiacetals and acetals. The first reaction involves simple addition, whereas water is liberated in the second reaction. The reactions are acid-catalyzed and reversible. Acid catalysis is, however, not a necessary condition for the reaction to proceed. Frequently, particularly in the case of aliphatic aldehydes, the reaction proceeds without a catalyst. If both alcohol and aldehyde are bifunctional reagents, it is possible that cyclic structures may form or that polymerization may occur. Whether or not one or the other of these reactions occur depends on the energy factors, steric accessibility of the reaction sites, and finally, as in all reversible reactions, on the position of the equilibrium according to the concentration of reagents and products in the solution. Starch, being a polyalcohol, also reacts with aldehydes. This subject was formerly reviewed by Roberts.[1274]

Since aldehydes behave as bifunctional reagents, crosslinking of starch occurs. For example, Syniewski[1275] reported the reaction of starch with formaldehyde.

There are also patents for solid, water-insoluble products resulting from such a reaction.[1276,1277] In addition there are reports of the strengthening of artificial silk, starches, and cellulose after contact with formaldehyde.[1278] On the other hand model studies carried out by Tomasik and Schilling[1279] on the reaction of maltodextrins with formaldehyde and pyruvaldehyde suggested that neither of these, in contrast to glyoxal and glutaraldehyde, acted as crosslinker.

Prior to 1920, there was a strong controversy in the literature about the action of formaldehyde on starch. Formaldehyde was initially considered to be a starch hydrolyzing reagent. This observation was based mainly on the empirical effects of temperature, time, and formaldehyde concentration on starch gelatinization. For example, with 38% aqueous formaldehyde at 15–16 °C, it was reported that gelatinization was complete two days after blending the reagents.[1280–1285] The lack of blue color upon the reaction of iodine with formaldehyde-treated starch suggested starch decomposition. This lack of color was, in fact, evidence of structural changes in the starch as a result of a chemical reaction.[1286–1288] The varying degree of starch hydrolysis also confused researchers. This controversy ceased after Samec and Meyer[1289] documented the reaction of starch with formaldehyde and showed that both amylose and amylopectin reacted indiscriminately. It was also shown[1290] that a starch–formaldehyde acetal was formed reversibly and that transacetalation occurred upon the contact of the starch acetal with alcohols. Added electrolytes decompose the acetal, providing a quantitative procedure for starch recovery. Protective colloids revealed the opposite trend. Starch formed acetals also upon reaction with methyl vinyl ethers.[1291,1292]

A wide variety of reaction conditions have been proposed for the reaction of starch with aldehydes. Early studies entailed use of alkaline solutions, perhaps in order to gelatinize starch.[1276] Because of the known behavior of aldehydes in alkaline media (Cannizzaro disproportionation and aldol condensations of aldehydes with active active α-methylene groups), this reaction has no simple outcome. However, a process of acetalation in alkaline solutions was subsequently patented.[1293] An exothermic reaction was observed within 3–4 min using an excess of formaldehyde. It was also reported that α,β-unsaturated aldehydes reacted readily in slightly basic media.[1294]

Early patents reported formation of acetals with formaldehyde at pH < 2.[1295,1296] Interestingly, even when starch was pretreated with alkali,[1295] the reaction is complete within 3–28 h at pH 1.6–2.5 and at a temperature below gelation. The concentration of either formaldehyde or acetaldehyde was 0.075–0.5 wt.% of starch in suspension. It was reported that this reaction carried out in acidic media could be shortened to 1 h and that the viscosity of the final product depended on the

reaction time.[1297,1298] Unreacted aldehyde was removed by addition of sulfite after adjusting the pH to 6.3–7.0.[1299] Either hydrogensulfite or hydrosulfite could be used to remove the excess of aldehyde.[1300] Another method for removal of formaldehyde entailed use of ammonium hydroxide.[1301] Alternatively, hexamethylenetetramine (urotropine) could be used in a starch slurry, with heating.[1302]

The reaction in water at pH 7 required either 24 h at room temperature or 12 h at the boiling point.[1290] These observations were later confirmed by reaction of aliphatic aldehydes with starch over the temperature interval from room temperature to below the gelatinization temperature.[1303] The properties of the products obtained under identical reaction conditions were dependent on the starch variety. Aromatic aldehydes reacted with difficulty under these conditions, as the reactions lasted up to one week at 37 °C.[1303] The reaction may be performed without any catalyst, however, it required heating in a sealed tube at 160 °C for 3 h.[1304] At lower temperatures, an extended heating time was required and the proportions of water, formaldehyde and starch also affected the outcome of this reaction. As expected for this reversible reaction, an increase in water content shifted the reaction in favor of the reactants. An excess of formaldehyde stopped the reaction at the stage of hemiacetal formation.

Acetalation at pH close to 7, followed by heating to 120 °C, provided a cold-swelling product.[1305] It was also reported[1306] that starch reacted with glyoxal in acidic or neutral solutions at 50–75 °C to give a water-insoluble product, which was subsequently transformed into a water-soluble gel upon heating to 95–100 °C. The reaction of starch with paraformaldehyde was conducted in a closed vessel at 70–90 °C required 15–20 min to proceed without addition of any catalyst and solvent. Acetalation of starch with paraformaldehyde required heating at 200 °C for 3–4 h.[1307] Maintaining of strictly anhydrous conditions was suggested.[1308] But it was later shown that this reaction could be performed in an open vessel at 50–55 °C in a starch slurry.[1298,1309] Crosslinking of starch with polyacrolein has also been described.[1310] According to more recent information, starch and even mono- and di-saccharides can be effectively crosslinked with aldehydes and dialdehydes by stirring the components in aqueous solutions at room temperature for 4 h.[1311] Rapid acetalation of starch with formaldehyde was achieved by heating neutral starch slurry with the formaldehyde in a microwave oven, a reaction that required between 5 and 15 min.[94] The reaction of trichloroacetaldehyde (chloral) hydrate with starch (5:8 wt.%) was patented as a crosslinking process requiring neither catalyst nor heating.[1312] The reaction of alkyl propiolates with starch at a pH between 8.5 and 12.0 produced starch [2-(alkoxycarbonyl)ethylidene] acetals which readily decomposed in acidic media.[1313] It was reported that alkoxide–starch derivatives

could also be crosslinked with formaldehyde.[1314] In that study, the authors' goal was to decrease the aqueous solubility of the products by crosslinking. It was also reported that hydrophobicity of the acetal could be enhanced either by the addition of various inorganic salts or by crosslinking with amine-, amide-, and phenol-aldehyde resins.[1315]

2. Starch Acetalation with Aldehyde–Amine, Aldehyde–Amide, and Aldehyde–Phenol Resins

A cationic starch can be prepared by blending a condensate of formaldehyde plus an inorganic ammonium salt with starch and heating at 80 °C for up to 1 h.[1316] A great interest was developed with urea–formaldehyde resins that were made to react with such polyalcohols as starch.[1317–1319] It was reported that the reaction of starch with urea–formaldehyde resin required an acidic catalyst[592,1320–1325] and the use of such dispersants as polyphosphates.[1326] Ammonium metaphosphate catalyzed the reaction without the addition of any other acid catalyst.[1327] A product that formed a paste was produced by controlling the proportion of starch to aldehyde (either up to 20% of formaldehyde or up to 30% of acetaldehyde) and urea (up to 15%) at pH 2–4.[1328]

Carbon-13 cross-polarization-magic-angle spinning (^{3}CP/MAS) NMR spectroscopic studies[1329] showed that the most favorable starch-to-urea ratio in the formaldehyde resin was 6.0. Higher amounts of dimethylurea resulted in self-condensation of the latter. Condensations with ureidopyrimidones were also patented.[1330] The latter compound was formed *in situ* from urea and acrolein in acidic medium. Reactions with starch were also performed in a neutral medium.[1330] A specific approach was demonstrated by Kou Xiechun and coworkers.[1331] who first treated starch with urea and then copolymerized the resulting product with urea–formaldehyde prepolymer. The first step required pH ∼8 and the second step pH 5.5–6. A pH close to 7 was used when phenol was used instead of urea or when both urea and phenol were reacted with formaldehyde.[1332,1333] The combined use of urea–formaldehyde and phenol–formaldehyde resins was also reported[1334] as a method to improve adhesiveness of the product. Condensation of melamine–formaldehyde resins with starch could be carried out during molding and without the use of any catalyst.[1335] However, acids accelerated the reaction.[1336,1337] Magnesium chloride also catalyzed this reaction.[1338] Further studies revealed that such reactions proceed readily in alkaline solutions,[1339] in line with former

observations that alkaline media promote the reaction of starch with urea– and phenol–formaldehyde resins.[1340–1343]

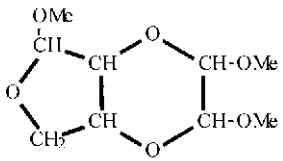
The sequence of reactions could be reversed, that is, starch could be treated first with either amines or amides followed by the addition of formaldehyde. The reaction of starch with amines or amides could be performed in such nonaqueous solvents such as toluene.[1344] A method of crosslinking starch with gelatin using formaldehyde was used to produce homeostatic sponges.[1345] Crosslinking of starch in blend with casein using formaldehyde was also reported. Reaction proceeded in an acidic aqueous solution.[1346] Crosslinking starch with formaldehyde in the presence of potassium cyanamide gave a water-insoluble product.[1347]

3. Acetalation of Starch Derivatives

Starch derivatives, such as oxidized and chlorinated starches, can be acetalated as already described for the reaction with glyoxal.[573] It is possible to acetalate (hydroxyethyl)starch instead.[1348] Viscous, water-soluble products resulted from the reaction of (carboxymethyl)starch with either formaldehyde or acetaldehyde in methanol in the presence of alkali,[1349] and this product could be obtained in granular form.[1340] Similarly, crosslinking by formaldehyde of a graft copolymer of starch and acrylamide under basic conditions was reported.[1351–1356] Crosslinking of (hydroxyethyl)amylose with1,5-pentanedial (glutaraldehyde) leads to a soluble product which was subsequently solubilized by treatment with ammonium hydroxide.[1357] A material of high mechanical strength was produced by crosslinking starch xanthate[1358] and starch xanthide[1359] with formaldehyde and polyphenols, followed by blending with added synthetic rubber. Starch carbamates, esters, and ethers were acetalated with formaldehyde in a process that was used to produce fire-resistant boards.[1360] It was reported that thixotropic starch could be produced by reacting of $POCl_3$-crosslinked starch with unsaturated aliphatic aldehydes.[1361] Acetalation of benzyl starch with formaldehyde, glyoxal, acrolein, crotonaldehyde, and polymers thereof has been patented.[1362]

Specific acetalation can be performed on starch dialdehyde. Unlike starch, acetalated by aldehydes, the aldehydo groups on starch dialdehyde lead to the formation of acetals with alcohols. Acetals are formed randomly along the macrochain, moreover, 1,4-dioxane rings (**25** and **26**) also formed as a result of new, hemiacetal bonds.[425,426] In such a manner, an allylated derivative was prepared with the use

of allyl alcohol.[587] It was reported that starch dialdehyde forms acetals with the hydroxyl groups of ethylene–vinyl alcohol copolymers.[603] Polyalcohols may also be involved in the acetalation of starch dialdehyde. Thus, starch dialdehyde could be polymerized with poly(vinyl alcohol)[564] and pullulan.[1363,1364]



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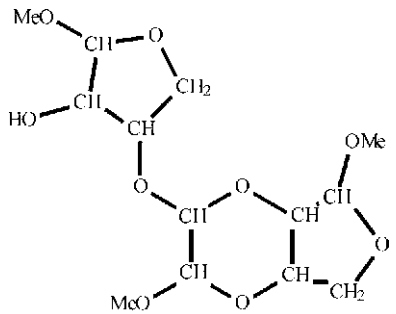

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It was also reported that crosslinking with urea or melamine proceeded in neutral[1365] or alkaline media.[1366]

Preparation of an acetal from 3,4-dihydro-2*H*-pyran and starch has been described.[1367] Water was not formed in this reaction, nor did crosslinking occur. Tetrahydropyran-2-yl derivatives of starch were also prepared when samples gelatinized in dimethyl sulfoxide were treated with 4-toluenesulfonic acid followed by 3,4-dihydro-2*H*-pyran. When the reaction mixtures were then transferred into ethanol, materials with a low degree-of-substitution were achieved. However, when the reaction mixture was poured into water, materials with an intermediate and high degrees-of-substitution were produced.[1291] This reaction proceeded with preference for the C-6 position of the glucose units.[1368]

4. Reactions of Starch Acetals

Reduction of acetals with $NaBH_4$ was reported,[1369] but no applications of the products were given. Crosslinking of starch acetals with epichlorohydrin and similar compounds was also described.[1370] A urea–formaldehyde–starch copolymer reacted with hydrogen peroxide and Cu(II) catalysts, thereby producing a starch solution with improved stability of viscosity.[1371]

5. Applications of Aldehyde-Crosslinked Starches

The chemical and physical stability of formaldehyde-crosslinked starch made these materials one of the first plastics that were made of starch.[1276,1277] Such products were fairly stable and responded favorably to heat and pressure.[1372] As a result, they were soon applied as paper coatings.[1320,1373] Starch acetals were also used as thickeners for paper coatings and for textile printing with dyes.[1374] Examples in the paper industry include the development of hydrophobic, cold-swelling,[1295,1303,1327] and water-soluble,[1293] materials. The product of crosslinking of starch with paraformaldehyde in the presence of hydrochloric acid had the same application,[1375] and the use of tannin as a phenol component was also reported.[1376] In addition, compounds produced by co-crosslinking with ketones were patented as adhesives for corrugated paper board[1377,1378] and also as water-stable sizing materials.[1337,1366] It was reported that adhesiveness could be improved by reacting starch with formaldehyde and ammonia[1379] or ammonium salts.[1380] Starch acetals were also used as plastics to impregnate fibrous substances,[1373] as a coating for heat-resistant fibers,[1309] as artificial lumber when mixed with sawdust,[1296] and as molding-compound binders, surfactants, and further crosslinking agents.[1310] Starch–formaldehyde acetal was also used as a cotton fabric size to improve the whiteness of household cloth after washing.[1381] Pastes made of starch and chloral hydrate had strong adhesive and antiseptic properties.[1312] Such material was evaluated as a critical factor regulating energy uptake by sheep[1382] and beef cattle[1383] that were fed with this product. It inhibited methanogenesis in the rumen.[1384] Aqueous solubility could also be controlled when the hydrophilicity of starch was enhanced by introducing carboxymethyl groups prior to crosslinking with aldehydes. Such products had increased viscosity[1349] and could be obtained in a granular form for cation-exchanger applications.[1350] Starch crosslinked with such unsaturated aldehydes as acrolein has a wide range of applications for binding of nonwoven textile fibers and filter elements, and thickeners/extenders for laminating fabrics.[1294] Ethandial (glyoxal) and starch after heating under reflux followed by crosslinking to produce a water-soluble material for liquid glues.[1270]

Chlorinated and/or oxidized starches crosslinked with glyoxal were used to produce a high-strength size for paper.[573] Coating adhesives were also prepared by crosslinking glycidyl esters.[1385] In addition, esters of starch with inorganic acids (such as starch phosphates) were crosslinked with various aliphatic and aromatic aldehydes in the presence of urea, melamine and similar compounds.[1322]

Several paper-coating applications involving starch crosslinked with urea–formaldehyde were also reported.[1320,1321,1324,1326,1339,1386,1387] Starch crosslinked with urea–formaldehyde was also proposed for the manufacturing of opacifying pigments (air-containing microcapsules) for paper.[1388] Starch crosslinked with urea–formaldehyde resins was proposed as a matrix for encapsulation of solid agrochemicals.[1389,1390] Encapsulation performance was improved when urea–formaldehyde resin was crosslinked to hydrophobic starch derivatives, for instance, benzylated starch.[1391] Resin consisting of urea–formaldehyde-crosslinked starch was proposed as a binder for nonwoven textiles.[1323] After blending with a silicone emulsion, this copolymer was proposed as workable duroplast composition.[1392] Products made from crosslinking starch with urea–formaldehyde resins[1317] and phenol–formaldehyde resins include binders of molding sands.[1332] Crosslinking was carried out with aldehyde and a aldehyde carbamate (3:1 ratio and above) to form a product of reduced swelling.[1393] When a melamine–formamide–starch polycondensate was additionally reacted with citric acid a cation-exchange material was obtained.[1394] Starch crosslinked first with either calcium or diammonium phosphate and then reacted with dicyanamide–aldehyde resin was patented as a fire-resistant material.[1395]

Materials from starch crosslinked with melamine–formaldehyde, methylated melamine–formaldehyde, and other amine–aldehyde resins were patented as binders for filter paper,[1336] milk filter sheet materials,[1338] and aqueous paper-coating compositions containing clay, titanium(IV) oxide, butadiene–styrene latex, and calcium octadecanoate.[1396,1397] Foams for filters were developed.[1398] A heat-setting adhesive was one of the first applications reported for starch crosslinked by urea–formaldehyde and phenol–formaldehyde resins.[1331,1340–1342,1347,1372,1399]

Molding powders have been prepared by crosslinking starch with melamine–formaldehyde resins. Poulverel[1333] described the combination of glycerol, gelatinized starch, urea, and phenol condensed in an acidic medium to afford water-insoluble plastics for paint binders, lubricants, molded articles, and varnish. Protein–acetal compounds that were prepared with gelatin formed sponges, which could be used instead of gauze and adhesive bandages.[1345] Acetals blended with casein were also used as food dyes.[1346] Polycondensates of aldehydes with amides of unsaturated carboxylic acids after reaction with starch produced agents for impregnating textiles, leather, wood, and paper.[1400]

Formaldehyde-crosslinked (hydroxyethyl)starch blended with borax was used to produce an adhesive,[1401] and with silver(I) halides to produce photochemical stencils.[1402] The use of 1,5-pentandial instead of formaldehyde has been used to produce a so-called “antifogging” composition for optical applications.[1357] Reinforced

rubbers were produced by crosslinking starch xanthate and blending the resulting product with styrene–butadiene–rubber latex.[1358,1359,1403,1404] Starch xanthide was also used for this purpose.[1405] Aldehyde crosslinking of various starch blends with synthetic macromolecules has also attracted attention. For example, formaldehyde crosslinking of a starch blend with poly(vinyl alcohol) produced a material that was resistant to boiling water and also capable of dye impregnation.[576] There are several reports of the crosslinking of starch and its carboxymethyl derivatives and various acrylates to produce absorbents for water.[1355,1356,1406,1407] Strengthening agents for paper were also prepared by grafting oxidized starch with acrylamides and converting them into amines followed by crosslinking with formaldehyde.[1408,1409] Wet-strength additives for paper sizing were developed[1410] by grafting unsaturated acetals onto starch and subsequently converting these acetal groups into aldehydes.

Starch dialdehyde acetalated with pullulan was applied as a cathode-mix binder in dry-cell batteries[1363] and in contact lenses.[1364] It was also reported that starch dialdehyde, after amination with ethylenediamine and crosslinking with 1,5-pentandial, immobilized trypsin.[1411] This preparation was proposed as a component of wound dressing.

XI. Esterification

1. Introduction

Starch, as a polyalcohol, readily forms esters with organic and inorganic reagents. Either one, two, or all three hydroxyl groups of the starch glucose units may be involved in esterification. The generally low selectivity of these groups in esterification is affected by the reagent, reaction conditions and the degree of chain branching in the amylopectin component. The reactions usually proceed in suspension. With granular starch, such reactions take place first of all on the granule surface. However, if the reagents penetrate the granules, reactions will involve both the amorphous and crystalline regions of the granule interiors. Esterification in biosynthetic processes for instance, sulfation, is usually regiospecific. For example, potato starch, which is naturally phosphorylated, bears this ester moiety exclusively in the 6-position of the glucose units and only of amylopectin.

Esters are capable of further modifications either in the acyl moiety or by involvement of remaining free hydroxyl groups. Crosslinking of these products is one of such chemical modifications.[1360]

2. Nitration (Starch Nitrates and Nitrites)

The great success of cellulose nitrates ("nitrocelluloses"), being esters of cellulose with nitric acid, had major impact on parallel studies on the nitration of starch. Celluloid and cellophane as cellulose products of low esterification, and highly esterified cellulose—nitrocellulose—were in common use as construction materials, wrapping foils, and explosives even after World War II. The chemical similarity of cellulose and starch motivated chemists towards studies of starch esterified with nitric acid.

Early work focused on the preparation of esters of the highest possible degree of esterification. Although one patent[1412] claimed a product with nitrogen content of 16.38%, a lower nitrogen level of 14.14% should most probably be taken as the highest credible figure, as it corresponds to a trinitrate.[1413] Although the properties of the ester were claimed to depend on the starch variety, these results were invalidated by Hackel and Urbanski.[1414] Significant differences were reported[1413] in the viscosities of solutions of esterified cellulose and starch having the same degree of nitration.

Despite several side reactions, including the formation of sulfuric esters, oxidation, hydrolysis, and carbonization (esterification has been carried out even in oleum), increasing the concentration of nitric acid was the crucial factor to achieve a high degree of esterification and a high overall yield. Maintaining a low reaction temperature was also beneficial.[1414–1420] Proteins and lipids should be removed prior to nitration, to avoid contamination by their nitration. This can be achieved by preliminary treatment of starch with a solution of 1.5–2% aqueous sodium hydroxide.[1421,1422] The remaining impurities cancan be removed by oxidation. Cereals can be nitrated in a similar process.[1423] Other processes have been reported, including simultaneous starch swelling and nitration,[1424] nitration after starch gelatinization during extrusion,[1425] and the use of porous starch flakes.[1426] Such modes of starch pretreatment allowed nitration to be conducted with more diluted nitration mixtures, for instance, 25 parts of nitric acid, 65 parts of sulfuric acid, and 10 parts of water.[1426] Nitration also occurred with a mixture of nitric and phosphoric acid to produce a material having 13.0% nitrogen content, and thus an almost completely trinitrated starch, for which 14.14% of nitrogen is calculated.[1427] This method of nitration inhibits acid-hydrolytic degradation of the starch structure.[1428] Materials of lesser stability result from nitration with nitric acid in acetic anhydride.[1429] Differences observed in susceptibility to nitration were paralleled by transformation from a crystalline to amorphous structure.[1430] These changes were reversible to a certain extent, as the crystalline

character could be recovered after nitrated starch was hydrolyzed back to soluble starch.[1427]

Urbanski and Hackel[1431] reported that the choice of reaction conditions was an important factor for the physical properties (for instance, viscosity) of the final product. It was shown[1432] that nitration with nitric acid alone gave a methanol-soluble product, "nitroamylose." Nitration with mixtures of nitric and sulfuric acids gave products partially soluble in methanol. The insoluble part consisted of amylopectin nitrates. Perhaps the highest degree of esterification occurs when either gaseous or liquid nitric anhydride (N_2O_5) was used,[1433–1435] and also in the presence of sodium fluoride in chloroform, which allows the reaction to proceed at temperatures close to ambient.[1436] Nevertheless, nitration with conventional nitration mixtures remained as an important process used in industry.[1437]

Amylopectin nitrate is more viscous than amylose nitrate.[1438] Solid esters are pure white, soluble in concentrated sulfuric acid, and also more hygroscopic than esterified cellulose. Their stability was high, their density exceeded that of the cellulose esters, and these materials also could not be exploded without the use of a detonator.[1439,1440] Amylose nitrate is more stable than amylopectin nitrate, and the latter was more stable than starch nitrate.[1441] There were differences between nitrocellulose and "nitrostarch" with respect to the sensitivity of their explosiveness to the composition of the atmosphere. The explosion temperature of nitrocellulose was independent of the atmosphere composition, whereas "nitrostarch" exploded at lower temperatures when the oxygen content in the atmosphere increased.[1442] Stabilization of "nitrostarch" was possible by either treating it with a boiling solution of cyanamide,[1443,1444] an acidic solution of sodium thiosulfate,[1445] by the formation of channel-inclusion complexes with organic compounds,[1446] or by suspending it in polyacrylamide slurries. The latter method was recommended as a safe way of transporting starch nitrate.[1447] Isolated starch nitrate could also be protected from hydrolysis by washing the crude isolated product with a solution of 50–90% ethanol[1448,1449] or by washing reacting acids out with a stream of water.[1450–1452] Isolated starch nitrate could also be protected by boiling crude starch nitrate in water under pressure,[1453] and eventually by the addition of sodium carbonate,[1441,1454] or by boiling in ethanol.[1455] Nevertheless, the extent of acid hydrolysis upon nitration is significant. Starch nitrate is actually an ester of an oligosaccharide of 6–7 glucose units[1456] and even maltose octanitrate.[1457] The isolation of "diamylose hexanitrate," "triamylose hexanitrate," and "amylose nonanitrate" was described.[1458]

Nitrated starches having a nitrogen content below 9% are not classified as explosives, although species of higher nitrogen content have explosive properties similar

to those of trotyl and picric acid.[1459] Amylose nitrate is even more explosive than amylopectin nitrate.[1460] The explosive power of starch nitrate could be increased by blending it with sucrose nitrate.[1461] The addition of small amounts of starch nitrate significantly increased the explosiveness of ammonium nitrate.[1462] Ammonium salts that were added to starch nitrate increased its explosiveness.[1463,1464] For higher degrees of explosiveness, starch was nitrated jointly with various additives, for instance, pentaerythritol, mannitol, D-glucitol, and other polyalcohols and polyhydroxy esters.[1465,1466] They could be used as the oxidizer salt phase with a carbonaceous fuel phase.[1467]

Other earlier applications of nitrated starch included propellants,[1468] nitrogen fertilizers used together with ammonium salts,[1469] a component of ignition preparations,[1470] and a lacquer component.[1471–1473] It has been used as a lacquer component because of its resinous properties, its ability to combine physically with synthetic resins,[1474] and also because of its solubility in alcohols and aromatic hydrocarbons.

The treatment of starch with dinitrogen tetraoxide or nitrosyl chloride gives a corresponding triester, starch trinitrite, which could be isolated at low temperatures in the form of a wet fibrous material that is immediately decomposed in protic solvents under acid catalysis, regenerating starch and nitrous acid.[1475]

Heats of formation of starch nitrate of the same degree of esterification were lower when the reaction was carried out solely with nitric acid instead of a nitrating mixture. These differences were interpreted as resulting from the formation of nitrosylsulfuric acid.[1476] Later investigations[1477] suggested that this effect might be due to different rates of hydrolysis and differences in the penetration of these nitrating agents into starch granules.

Alkaline hydrolysis of starch nitrate produced ammonia, cyanides, nitrites, and nitrates.[1478] Starch nitrate could be denitrated by use of diluted solutions of ammonium sulfite followed by the addition of hydrogen peroxide to remove colloidal sulfur.[1448] The strong nitrate band absorption in the infrared between 730 and 960 cm^{-1} complicates the identification of polysaccharides. The region suitable for identification of starch nitrates is between 900 and 1350 cm^{-1}.[1479] Nitration of "glyceryl starch" into a trinitrate was also reported.[1480] Starch nitrates readily react with an *N,N*-dimethylformamide–SO_3 complex to give trisulfates.[1481]

Additional studies on starch nitrates have been reported by Oelker,[1468] Kesseler and Roehm,[1482] Matla,[1483] Dejarme,[1484] Brissaud and Ronssin,[1485] Graefe,[1486] and Ceasar.[1487]

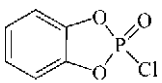
3. Phosphation and Other Reactions Leading to Phosphorus-Containing Starches

a. Introduction.—Almost all known varieties of native starch contain phosphorus. However, only potato starch contains chemically bound phosphorus, the so-called organic phosphorus. In potato starch, phosphoric acid esterifies a glucose unit of amylopectin at a frequency of once every 30–200 glucose units. The phosphoric acid moiety also makes potato starch a natural anionic biopolymer. In native potato starch, the phosphoric acid moiety contains mono- and di-valent cations. Their distribution in starch (only in the amylopectin portion) depends on the soil composition in which the plant grows. Usually these ions include potassium, sodium, calcium, and magnesium. These ions can be readily removed to give the free acid,[76,142] or they can be substituted by other metal ions.[639,1488] This is a common method of insolubilizing starch phosphates in water.[1489] Potato starch exhibits gelatinization behavior that is quite distinct from other starches, because of the phosphoric acid moiety and the cations that neutralize this moiety.[1490,1491] For example, starch phosphate is hydrolyzed in acidic media with difficulty, but it is more readily split by "diastase."[1492] Even so, the digestibility of synthetic starch monophosphate is less than that of unmodified potato starch.[1493] Such starch phosphates retain their buffering properties, and ammonium, sodium, and potassium salts of starch phosphates are used as metal corrosion inhibitors.[1494,1495]

Phosphoric acid moieties can be introduced chemically into starch by several methods, which are described next.

b. Phosphorus Oxychloride.—Early methods of synthesis involved treatment of starch with phosphorus oxychloride and calcium carbonate in chloroform.[1492] Calcium oxide and hydroxide can be used, as well as other chlorinated solvents, to produce calcium starch phosphates.[1496] The use of phosphorus oxychloride usually causes crosslinking. Crosslinked starch is more reactive than gelatinized starch.[1497] This reaction proceeds more readily when the starch is pre-treated by drying under a variety of conditions, including atmospheric drying in an oven, azeotropic drying with benzene, or by refluxing in pyridine.[1498] Phosphorylation in supercritical CO_2 has been described.[478] Another approach involves the swelling of starch granules in dilute aqueous sodium hydroxide.[1499–1501] In this case, the composition of the reaction medium appears to be critical for controlling the properties of the product. For example, oven-dried and benzene-dried starch reacted with phosphorus oxychloride to produce water-soluble products, whereas pyridine-pretreated starch gave water insoluble phosphates. The difference is probably attributable to simple

phosphorylation and crosslinking with either two or three linkages to the phosphorus atom. The reaction with phosphorus oxychloride also proceeded in pyridine, and amylose undergoes phosphorylation to a degree of substitution of 0.33, that is, each glucose carries one phosphoric acid moiety.[1502] A starch triphosphate has also been made, and two alternative structures were proposed: either O-6 carries the dibasic phosphoric acid residue, and O-2 and O-3 are crosslinked with another phosphate moiety, or the crosslinking involves O-6 and O-2, and O-3 carries the dibasic phosphato group.[1503] In the reaction of phosphorus oxychloride with starch in an aqueous solution at pH 11 with a neutral metal salt (for instance, sodium chloride) added,[1504,1505] the salt concentration controlled the degree of modification.[1506] It was also shown that the use of trisodium phosphate together with phosphorus oxychloride improved the thickening properties of the crosslinked product.[1507] Specific phosphorus oxychlorides and amides (**27**–**29**) provided a degree of substitution as high as 0.7–1.75 without significant starch degradation.[1508,1509] Starch crosslinked with phosphorus oxychloride still undergoes the blue reaction with iodine, but more slowly than that with unprocessed starch.[1510]



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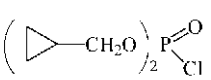

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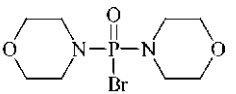

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c. Metaphosphates.—The most convenient method of phosphorylation entails use of inorganic phosphates in an aqueous solution at pH 7.[1511–1513] However, this method results in a product of lower DS. Using sodium metaphosphate ($NaPO_3$), a DS of 0.03 was produced in the form of mono- and di-starch phosphates.[1514] Granular, distarch phosphate can be produced by performing the reaction at a temperature below that necessary for starch gelatinization and at a pH of at least 9.[1515–1521]

d. Orthophosphates.—Reactions leading to orthophosphates were studied thoroughly by Suzuki and coworkers,[1522] who reported some critical relationships between reaction parameters and product properties. Changes in the pH and the amount of trisodium phosphate used had little effect on the viscosity of corn starch mixtures.[1523] The maximum concentration of phosphorus was incorporated within 3.5 h, beyond which time the viscosity of the product did not increase.[1524] It was also reported that an increase in the phosphate concentration from 1 to 20 g per

100 g of starch accelerated esterification by 14.6 times. The resulting esters had higher viscosities, whereas the gel stability and the gelatinization temperature were only slightly changed.[1525] Starch monophosphates with a DS ranging from 0.02 to 0.05 were prepared and their properties thoroughly studied.[1526] Upon an increase in the degree of substitution, their pasting temperature decreased slightly and the viscosity maximum increased slightly. In another approach, moist starch was blended with phosphates and fluidized in a stream of hot gas,[1527,1528] followed by roasting with 3.5% sodium tripolyphosphate at 130–150 °C for 5 h.[1529]

The role of size in the potato starch granule has also been studied.[1530] Dibasic phosphate groups are located at C-6 and C-2. Separate studies were carried out on sorghum,[1531] cassava,[1532] rice,[1533] sweet potato,[1534] wheat and corn,[1535] and rye and triticale[1491] starch. The following conditions for a wet process have been reported:[1536] the water-to-starch ratio should be maintained at 200:190, the sodium dihydrogenphosphate-to-disodium hydrogenphosphate ratio should be 4:10, conditioning should be performed at 45 °C for 40 min, predrying should occur at 40 °C until the water content is reduced to 8%, and esterification should be carried out for 4 h at 150 °C. A modification of this process was also patented.[1537] In another study, the reaction was carried out with phosphoric acid in ammonium hydroxide, which produced ammonium starch phosphate.[1538] The advantage of using this salt over sodium starch phosphates is that it produces thicker pastes in cold water. Phosphorylation with disodium hydrogenphosphate in diluted sulfuric acid[1539,1540] and phosphoric acid[1541–1543] was also demonstrated. As compared to similar mixtures prepared in alkaline and neutral solutions, these products had a higher range of gelatinization temperatures, increased swelling and aqueous solubility, decreased viscosity, and no setback.

Adjusting the pH might reduce the time necessary to prepare starch phosphate with a maximal phosphorus content.[1544] For example, at pH 9.68, 130.6 °C, and 14% sodium tripolyphosphate, the yield of phosphorylation product was maximum within 46 min. It was also reported that tripolyphosphate in an aqueous medium did not attack the granular structure of starch, even at pH 11.[1545] The use of $Na_5P_3O_{10}$ for the manufacture of starch monophosphates and $Na_3P_3O_9$ or starch diphosphates was proposed.[1546] In both cases the reaction blend was maintained for several hours prior to roasting. An aqueous suspension was subsequently prepared and was thermally modified on a drying roller. Other authors have discussed the role of preconditioning the reaction mixture in order to promote penetration of the reagent into the granule interior.[1536] Crosslinking of arrowroot and cassava starch with $Na_3P_3O_9$ was reported at a temperature of 45 °C and pH 10.5.[1547] A reaction period of one hour provided the highest paste viscosity.

Comparative studies of the effectiveness of various phosphorylating agents were performed on sweet potato starch.[1548] Sodium dihydrogenphosphate, disodium hydrogenphosphate, sodium metaphosphate, sodium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate, sodium trimetaphosphate, and phosphorus oxychloride were utilized in this study. It was reported that the gelatinization temperature increased, and the rate of swelling was decreased, when the pH exceeded 10. Sodium dihydrogen- and disodium hydrogen-phosphates provided the highest viscosity and gelatinization temperature. Sodium trimetaphosphate as well as phosphorus oxychloride, gave products having a high gelatinization temperature without any decreases in viscosity upon stirring at 95 °C for 1 h. Phosphorylation to produce a diester, which started in an alkaline solution at 60 °C followed by 8 h at pH 6.5.[1549] The addition of alkaline earth salts inhibited the coloration of starch phosphates upon heating.[1550] In the case of phosphorylation with sodium trimetaphosphate, the swelling power of the product reached 310 g of water per gram of modified starch.[1551]

It was reported that phosphorylation during extrusion required less reagents than by the use of classical phosphorylation. The response of various starch varieties to extrusion parameters was similar.[1552]

e. Phosphorus Pentaoxide and Phosphorus Pentasulfide.—Methods of crosslinking starch phosphates with phosphorus pentaoxide in aqueous alkaline solutions have been reported.[1553–1556] The phosphorylating agent is in fact a mixture of tetrametaphosphoric and tetrapolyphosphoric acid. Sodium hexametaphosphate and sodium tripolyphosphate did not perform as well as phosphorus pentaoxide. The use of the latter, either in benzene or pyridine, produced starch phosphate having a degree of substitution as high as 0.8. Perfect solubility in water suggested that there was no crosslinking and also that the acid groups resided as dibasic substituents.[1557,1558] The solid-phase phosphorylation of starch is possible.[1559] Starch was first activated on heating with sodium carbonate for 2 h at 80 °C before adding phosphorus pentaoxide. Phosphorylation took place at the 2-positions within the glucose units. The use of phosphorus pentasulfide (P_4S_{10}), either with or without DMF, gave the corresponding starch thiophosphate esters. Reactions without *N,N*-dimethylformamide were more successful for incorporating larger amounts of phosphorus and sulfur.[1560]

f. Phosphamides and Alkyl and Aryl Phosphates.—Tetrapolyphosphoric acid tributylammonium salt reacted with starch acetate to produce starch phosphate.[1561] A continuous process was patented.[1562] It was also found[1563] that the addition of

urea accelerated esterification when sodium di- and disodium mono-phosphates were allowed to react with starch at room temperature and pH 6.2 followed by heating the dried paste to 160 °C for 30 min. A similar idea was patented[1564] with use of sodium trimetaphosphate. Hexamethylenephosphoric triamide reacted with starch in an organic solvent yielding a product containing up to 0.7% P.[1565] The reaction product is capable of swelling in cold water, and the viscosities are nearly independent of temperature. The same authors explored further reactions of these products with epichlorohydrin.[1566] Depending on the reaction conditions, the products exhibited either anionic or cationic character. Cationic products were insoluble in water and organic solvents, and they could also be used as ion exchangers. Anionic products were capable of swelling in cold water and produced viscous solutions. Sodium *N*-phosphoryl-*N*′-methylimidazolium chloride,[1567,1568] *N*-benzoylphosphoramidic acid,[1569] as well as 2-carboxyarylphosphates (for instance salicyl phosphate and its 5-substituted derivatives, and also 2-carboxy-1-naphthyl phosphate) phosphorylated starch at temperatures between 15 and 54 °C over a wide range of pH. It was also reported that the addition of sodium sulfate increased the reaction yield.[1569] A wide variety of starches modified with trialkyl orthophosphates were patented.[1570] These processes were run on dry starch, but starch could also be slurried with dialkylpyrophosphates in water, followed by heating to 130–160 °C. Increasing the pH promoted formation of a more viscous product.[1571]

g. Hypophosphorus Acid.—When hypophosphorus acid, $H_2P(O)OH$, reacts with alcohols, ROH, it can be esterified into monoesters, $RHP(O)OH$. Such esters can further react with either epichlorohydrin or propylene oxide to produce diesters, $RHP(O)OR'$, where $R' = CH_2CH_2Cl$ and $CH_2CH(OH)Me$, respectively. Starch was one of the alcohols tested in this reaction.[1572]

h. Tetrapolyphosphoric Acid.—In a 3:1 mixture with trialkylamines, tetrapolyphosphoric acid phosphorylates starch into a monoester with a degree of substitution of up to 1.75. Esters were found stable to hydrolysis in alkaline media and less stable under acidic conditions.[1509]

i. Role of the Starch Variety.—The variety of starch used controls the effects of a given type of phosphorylation.[1573] Millet grain starch reacted with a mixture of sodium dihydrogen and disodium hydrogen phosphates, and the reaction was complete within 1 h upon heating to 170 °C.[1574,1575] This reaction was also complete within 2 h upon heating to 160 °C. Similar conditions were observed for potato starch.[1576]

Phosphorylation in corn starch was found to proceed mainly on the granule surface, however, the decreased iodine uptake suggested that the granule interiors (especially amylose) were attacked.[1577] Primary phosphate groups reside on the granule surface, whereas secondary phosphate groups are located in the granule interior.[1578] Comparative rheological, microscopic, and calorimetric studies were performed on starch phosphates, acetates, and hydroxypropyl starch, and the results indicated that all chemical modifications had a similar effect on the starch granule structure.[1579] The phosphate groups in starch phosphate with a DS of 0.016 occupied the C-2, C-3, and C-6 positions at concentrations of 28, 9, and 63%, respectively.[1580,1581] These groups exist in the dibasic form. Partial hydrolysis of starch accompanied phosphorylation, even when sodium hydrogenphosphate was the reagent.[1582] Further studies with ascending paper chromatography confirmed this assumption.[1583] This would explain the observation that starch phosphates and "amylophosphoric acid" of a comparable DS were dissimilar in terms of their physicochemical properties.[1584] Starch monophosphate always had a lower viscosity, a greater degree of water solubility, and a better paste transparency, than synthetic amylophosphoric acid.

Phosphates are also known that have the phosphoric acid moiety in a side chain bound to glucose units. Such compounds have been prepared from diethyl 2-chloro-1-hydroxyethyl phosphonate [$ClCH_2CH(OH)PO(OEt)_2$].[1585] The starch phosphonate ethers had a DS of 0.0138. In addition, 2-methyl-3-phosphono-2-oxazolinium chloride sodium salt was reacted with starch to produce stable, aqueous dispersions.[1586]

j. Reactions of Phosphated Starches.—Distarch phosphates can be modified by means of reacting them with epichlorohydrin, propylene oxide, or acetic anhydride. It was reported that starch granules remained intact, even after such modifications.[1587,1588] It was suggested that acetylation occurs in certain parts of starch granules and that hydroxypropylation was uniform throughout starch granules.[1589]

A thixotropic starch was produced in reactions of $POCl_3$-crosslinked starch with unsaturated aliphatic aldehydes.[1361] Starch phosphates have been crosslinked by various aliphatic and aromatic aldehydes in the presence of urea, melamine, and similar compounds. Among several aldehydes tested[formaldehyde, propanal (propionaldehyde), glyoxal, glutaraldehyde, 2-hydroxyadipaldehyde (2-hydroxy-1,6-hexanedial), and some aromatic aldehydes], only those products that had reacted with glyoxal were insoluble in water.[1322] Significant increases in viscosity occurred after starch phosphates having a low DS were treated with urea.[1590]

Products of low viscosity were obtained when urea was used together with phosphoric acid.[1591,1592]

Phosphation can occur simultaneously with acylation. Such reaction of starch in a mixture of 87% phosphoric acid and acetic acid with acyl anhydrides produced a gummy substance, which transformed into an amorphous solid upon purification.[1593]

Phosphoric acid could be used together with urea and sodium or potassium dihydrogen phosphate, and a 10% aqueous solution of the resulting product had a viscosity of 1500 MPa s at pH 7.8.[1594,1595] The viscosity of the product can be readily controlled by adjusting component proportions and other reaction parameters. Significant increases in viscosity are possible when the procedure is supplemented by the addition of urea, or urea mixed with sodium hydrogenphosphates. Amidated and phosphated products have been reported using such reactions.[1596] Other amides,[1597] amines, and ammonium salts[1598] can be used instead. The use of urea together with orthophosphoric acid and sodium pyrophosphate provided some control of the acidity of the reaction mixture.[1599] Acidity and nitrogen content of the product increased with reaction time and temperature, confirming that urea is chemically incorporated into the product. The application of metaphosphoric acid instead of orthophosphoric acid gave less-viscous products.[1600] Another set of preparations entails use of both phosphoric acids and urea.[1601] The reaction of starch with alkali metal phosphates and urea was analyzed,[1602] and optimal parameters were shown to depend on the starch variety. The addition of urea inhibited coloration and agglomeration of starch granules.[1603–1605]

Treating starch phosphates with chlorine in methanol increased their viscosity.[1606,1607] A viscous, semitransparent paste was obtained using corn starch for simultaneous esterification of phosphoric acid and succinic acid in the presence of urea.[1608] Polyphosphoric acid was also used, together with calcium carbonate and hydroxide as well as borax.[1609]

k. Phosphation of Starch Derivatives.—Starch derivatives have also been phosphorylated. For example, starch polyethers prepared from starch and alkylene oxides were phosphorylated with 100% phosphoric acid.[1610] A polyurethane foam was produced after further treatment with polyalkylene polyphenyl isocyanate. The phosphorylation of oxidized, quaternized and hydrolyzed starches by means of of sodium tripolyphosphate in an alkaline slurry has been patented.[1611] (Diethylamino)ethyl starch was phosphorylated to give the corresponding triphosphate sodium salt,[1612,1613] and the resulting product significantly improved pigment retention in pulp. Phosphonomethylaminoethyl analogs of such starch were prepared

by reaction of starch with *N*-(2-haloethyl)iminobis(methylenediphosphonic) acid or *N*-alkyl-*N*-(2-haloethyl)aminoethylphosphonic acid in alkaline media.[1614–1616] They served for the same purpose as diethylaminoethyl starch. *O*-Hydroxypropylated starch has been crosslinked by sodium trimetaphosphate.[1617] *O*-(Hydroxypropyl)starch has frequently been phosphorylated, for instance, it has been crosslinked by use of phosphorus oxychloride.[1618–1620] The addition of trisodium phosphate as a buffer was shown to increase its resistance to degradation.[1621]

Starch phosphates have been oxidized to carboxylic derivatives.[1622] Starches oxidized by NaOCl could be phosphorylated with $POCl_3$,[1623] causing crosslinking. The reaction of starch phosphate with glycidyltrimethylammonium chloride gave the corresponding phosphobetaine compound, starch poly[3-(*N*,*N*,*N*-trimethylammonio)-2-hydroxypropyl phosphate].[1624]

l. Phosphonium Cationic Starches.—Chloromethylphosphonic dichloride in pyridine caused crosslining of starch, and products were obtained, having a DS from 0.0013 to 0.75,[1625] that were water-insoluble and nonflammable.

Non-gelatinizing phosphonium starch ethers were obtained by treating starch with 2-chloroethyltributylphosphonium chloride.[1626] Allyltriphenylphosphonium bromide has been used to produce phosphonium cationic starches.[1627]

m. Applications of Phosphated Starches.—The main applications of phosphated starches are perhaps as food modifiers. Such modified starches act as encapsulators for food flavors and aromas, and include starch phosphates, acetylated distarch phosphates, and phosphorylated hydroxypropyl starch.[1628] Starch phosphates exhibit high viscosity and low peptization temperatures.[1629] Monostarch phosphate is reported to be suitable for food application because of its appearance, hygroscopicity, solution transparency, swelling, emulgation, retrogradation, separability from water during freezing, saccharification with “diastase,” and viscosity. Refrigeration of starch phosphates enhanced their transparency, but they are unstable at elevated temperatures in acidic media. Among several starch phosphates, those made of tapioca starch were most stable.[1630] Among starch acetates, (hydroxypropyl)starch, (carboxymethyl)starch, and sodium starch phosphate, pastes and films of the last had superior stability.[1631] A thickener for acid fruit juices and dairy products was produced on reaction of starch polyether with phosphorus oxychloride.[1632] The thickening and viscous properties of mono- and di-starch phosphates can be modified by interactions with lipids, which develop considerable stability on aging and also produce very stiff gels.[1633] The effects

of sucrose addition differ with the DS of the phosphate monoester.[1634] Esters having a DS as low as 0.055 exhibited decreased viscosity as the concentration of sucrose increased up to 55%. However, esters with a DS of 0.113 and 0.147 produced the opposite effect. Pretreatment of starch with enzymes and reaction of sodium hydrogenphosphate in acetic acid afforded a product designed as pudding starch.[1635]

Starch phosphates have been proposed for a variety of applications, including food thickeners and gelifying agents,[1636,1637] emulsion stabilizers,[1638,1639] and additives, that retain freshness in bread.[1640] The use of distarch phosphate is not recommended for the latter purpose.[1641] Starch phosphate enhances the taste of fish pastes.[1642,1643] Conditions for the preparation of phosphated maize amylopectin were optimized.[1644] Starch phosphate was patented as a poultry and ruminant fodder.[1645] Distarch phosphate was also acetylated and used as fruit pie filling because of its gelling properties and freeze–thaw resistance.[1646] Starch phosphate was also maleinated and sulfonated.[1647] A food thickener was produced by hydroxypropylation of starch crosslinked with sodium trimetaphosphate.[1618] Crosslinking with phosphorus oxychloride resulted in a food thickener that was resistant to freeze–thaw cycles.[1618–1680] Digestible food thickners are also produced using phosphorylated starch in the presence of urea.[1648] Barley starch phosphorylated with phosphorus oxychloride was hydroxypropylated and exhibited superior freeze–thaw stability over tapioca starch.[1649] Comparative studies on (hydroxypropyl)starch phosphate and unmodified tapioca starch revealed that the modified starch was more susceptible to digestion by pancreatic amylase than by fungal amylase, whereas plain tapioca starch was more readily digested by fungal rather than pancreatic amylase.[1650] Rats that were fed with tapioca starch exhibited depressed ^{59}Fe retention as compared to rats that were fed with (hydroxypropyl)distarch phosphate.[1651] These differences are undoubtedly attributable to structural changes of the modified starch matrix.[1652] It was reported that both tapioca and (hydroxypropyl)distarch phosphate bound similar amounts of calcium.[1653] Starch derivatives having a higher DS levels were reported to form renal lesions in hamsters.[1654]

Multigeneration studies on rats fed with phosphorylated starch showed no significant toxicological effects.[1655] Phosphorylated starch was patented as a component of pharmaceutical coatings[1656] and as a carrier of phosphorus radionuclides in metabolic studies.[1657]

Other applications include sizing agents, adhesives, and water-loss inhibitors.[1644,1658–1661] A granular distarch phosphate was reported as a paper adhesive[1515,1517–1521] and also as a sand binder for foundry molds.[1662] The

use of starch phosphates as a cotton fiber finish was also patented.[1663] Further applications of starch phosphates include use as a binder for reconstituted tobacco sheets,[1664] an adhesive for cigarette filters,[1665] for textile sizing,[1666,1667] as an additive to improve pulp filtration, as a paper coating and paper adhesive,[1668–1670] as an adhesive for corrugated board,[1671] as flocculants for coal wash tailings,[1672,1673] and as a sizing for glass fiber sheet.[1674] A coating of starch phosphate prevented scale deposition on reactor walls during polymerization of vinyl chloride.[1675] When added to toothpaste, starch monophosphates allowed a reduced level of concentration of polishing components and also prevented fluoride loss during storage.[1676]

Starch phosphate was combined with rosin and alum to increase the dry strength and ink retention characteristics of paper.[1677] Starch phosphates have also been used as soil conditioners to increase water retention.[1678] Starch phosphates improved the dispersion and dye reception of synthetic fibers,[1667] and are used to stabilize water,[1543] finger paints,[1679] and white coating colors.[1680] Phosphonoamidated starches are useful in paper sizing.[1681] Biodegradable films were produced by combining starch phosphate with poly(vinyl alcohol).[1682] Phosphonoacetyl starch added to polyacrylonitrile improved it affinity for dyes.[1683]

The reaction of starch phosphate with such proteins as soybean protein and casein was used to produce protective colloids for insolubilization of pigments in coatings and paper.[1684] The complexation of starch phosphate with protein insolubilizes the latter, particularly when starch phosphate is in the form of an ammonium salt.[1685]

Anionic–cationic starches have been used to produce water-insoluble films, thixotropic gels, and additives to improve the retention of titanium hydroxide in cellulose pulp.[1613] They are available as cationic starches to which a variety of anionic groups are introduced, including carboxylic, sulfate, sulfonic, and phosphate groups.[1686,1687] Starch phosphate and ketene dimer produced emulsions having a good burst factor, tensile strength, porosity, and ink reception.[1688] Starch phosphate sulfosuccinate was used to improve retention of titanium oxide in cellulose pulp.[1647] Phosphorylated amino and ammonio starches were produced as a skin-moisturizing additive to cosmetics.[1624] Phosphonium cationic starches were patented as sizes for glass fibers.[1689] Phosphobetaines, having the structure, starch-$OP(O)(O^-)OCH_2CH(OH)CH_2N^+R_3$, were patented as detergents and components of skin cleansers.[1690]

Starch phosphates have been also proposed as additives for oil-well drilling muds.[1636,1637] Starch phosphonate ethers were also suggested as fillers, binders, flocculants and sizes.[1585]

n. Miscellanous.—A refractometric method to determine the solubility of starch phosphate has been reported.[1691] Additional information on phosphorus containing starches can be found in several references.[1473,1507,1692–1695]

4. Sulfation, Sulfates, Sulfites, Thiosulfates and Sulfonates

a. Sulfates.—Starch sulfates have been known since 1843 when Blondeau[1696] and de Corolles[1697] described the esterification of starch with concentrated sulfuric acid. This process was not effective, however, because the starch was degraded. Esterification with diluted sulfuric acid was also not effective,[1698–1701] but milder sulfating agents gave better results, as with fuming sulfuric acid and sulfur trioxide in CS_2,[1702,1703] although these reagents were also too vigorous. The use of sulfur trioxide coordinated to such tertiary amines as trimethylamine,[1704–1707] triethylamine,[1704,1708–1712] benzyldimethylamine,[1704] and pyridine[535,1713–1715] was effective, but these amines have unpleasant odors, and therefore, other coordinating agents and solvents for sulfur trioxide were examined. These included *N,N*-dimethylaniline, 1,4-dioxane, bis[(dichloroethyl) ether],[1715] formamide,[1716] *N,N*-dimethylformamide,[1481,1717,1718] poly(2-vinylpyridine),[1719,1720] and dimethyl sulfoxide.[1721,1722] Among them, complexes with trimethylamine appeared to be the least effective, but their performance could be significantly improved when sulfation was carried out in either methanol or, preferably, in *N,N*-dimethylformamide.[1723,1707] Several reports are available on the use of chlorosulfonic acid and its sodium salt. Its reactivity is lowered by such solvents as pyridine[1724–1733] or formamide.[532,619,1716,1733–1738] Starch was also sulfated with thionyl chloride in chloroform at 5–7 °C for 6–12 h.[1739] Other sulfating agents reported for starch include alkali fluorosulfates,[1740] sulfamic acid in aqueous urea,[1741–1743] amidotrisulfonic acid sodium salt,[1744] and alkali *N*-alkylimidazole-*N*-sulfonates.[1745,1746] Similar sulfating agents were used for sulfation of such starch derivatives as (carboxy)starch and its esters[532,535,536,619,1734,1735] and (carboxymethyl)starch.[1747] Sulfation of esters in a solution of formic acid is effective.[536] (Hydroxyalkyl)starches have been sulfated with sulfuric, pyrosulfuric, or chlorosulfonic acids.[1748,1749] Sulfation occurs on the side-chain hydroxyl group. The use of bis(2-hydroxyethyl)sulfone with a blend of starch and cellulose caused crosslinking of starch with cellulose.[1750] Sulfation of a trimethylsilyl ether of starch in *N,N*-dimethylformamide causes cleavage of the trimethylsilyl groups.[1751]

The origin of the starch has no effect on the results of sulfation. Apart from the sulfating agent used, the reaction temperature is the most crucial parameter. Using SO_3–amine complexes, the degree of substitution increased from 0.2 to 2.0 as the temperature was raised from 55 to 90 °C[1723] and the reaction was in 80% complete within the first hour. Esterification involves all three 2-, 3- and 6-OH groups, but in reaction carried out in *N,N*-dimethylformamide preference for sulfation at O-6 was observed.[1707] Starch sulfates hydrolyze under acidic as well as alkaline conditions.[1707,1752] In alkaline media, the reaction rate does not follow simple kinetics. As the reaction progresses, its rate decreases regardless of the nature of the reaction medium.

Sulfate esters are more stable to enzymatic degradation than the original starch.[1753] The sulfated products are stabilized by transforming them into salts. Calcium, lead(IV), magnesium, and copper(II) salts did not precipitate from solution,[1724] although the barium salt does precipitate, providing the basis of a useful, gravimetric method for the determination of starch sulfates.[1754] Conversion of these salts into the hydrogensulfates can be effected by acidification with hydrogen chloride in 2-propanol solution containing small amounts of water.[1755] Products stable towards hydrolysis can be obtained by reacting starch with vinylalkylsulfones and vinylarylsulfones, respectively, with a basic catalyst.[1756,1757] Some biologically active sulfonamides, such as salicylazosulfapyridine, can be bound to (carboxymethyl)starch, either by crosslinking with epichlorohydrin in concentrated aqueous NaOH[1758] or by condensation of sulfonamides with oxidized starch with the involvement of their amino groups.[1759]

The literature describes starch derivatives containing a sulfonic group in ether-linked side-chains. Thus, a series of substituted phthalic anhydrides with, among others, sulfonic groups reacted with starch to give 2-carboxysulfophenyl starch derivatives.[1760] Starch derivatives having side-chain sulfonic groups also result from the reaction of starch with alkylsultones in alkali, as with propyl-,[1761–1765] butyl-,[1766] and tosyl-sultones.[1761,1766,1767] Shorter alkyl chains were introduced by reacting starch with sodium sulfoalkyl chlorides[NaO_3S-$(CH_2)_n$-Cl][1768,1769] or by reacting corresponding diazoalkyl compounds.[1770] Such products form acidic, transparent solutions and the salts have ben suggested as ion exchangers,[1748,1771] components of drilling muds,[1772] sizes and adhesives,[1764] and thickeners for water-color paints.[1773] Related compounds were resistant to mildew.[1770] Chlorosulfoalkylcarboxylates, on reaction with starch, introduce additional functional groups into starch.[1771] These starch derivatives have ampholytic properties and have been patented as biodegradable detergent builders,[1774] as components of gelatin–silver iodobromide phothographic emulsions,[1775–1777] and papers.[1778,1779]

Another group of compounds containing the sulfonic group consist of starches sulfated following esterification with such cyclic anhydrides as maleic and succinic anhydrides. Thus, esterification of phosphorylated and aminated starch with succinic anhydride, followed by sulfation with $Na_2S_2O_5$, produced a corresponding sulfosuccinate, which was used to improve the retention of TiO_2 in cellulose pulp.[1647,1780] Similar products were also prepared from dioctylmaleylated starch.[1781] Acylation was also carried out with sulfoanhydrides, for instance, sulfomaleic and sulfosuccinic anhydrides.[1782,1783]

A qualitative reaction for starch sulfates involves use of Toluidine Blue, which develops a blue color with starch and a violet color with starch sulfate.[1725,1784] These esters can also be identified by IR absorption spectroscopy.[1785,1786]

The functional properties of starch sulfates depend on the degree of polymerization and the method used for sulfation.[1787] Starch sulfates are readily water-soluble, and they typically form solutions having viscosities higher than those of soluble starch solutions of the same concentrations. In contrast to soluble starch, starch sulfates do not revert to solid gels.[1743] Quick-setting pastes of high thickness and good adhesiveness are available in this manner.[1705,1717,1719,1720] These properties cease, however, when the solutions are neutral or made alkaline.[1722] Starch sulfates have been used as protective colloids,[1702,1703] adhesives, thermosetting, edible glues,[1717,1728,1788,1789] thickeners for drilling muds,[1705,1790,1791] and water-color paints,[1792] additives to hydraulic binders,[1738,1793] components of electrostatic papers,[1794] additives for clay-ceramic masses,[1791] and components of water-insoluble coatings for paper, cardboard, wood, glass, and textiles.[1795,1796] Starch sulfate was mixed with gelatin to form a wall material for microcapsules produced by coacervation.[1797] Microcapsules are also produced by combining sodium starch acetate sulfate with gum arabic, polyacrylamide, and other compounds.[1798] Because of its polarity, starch sulfate interacts with proteins. Spun-protein fibers containing starch sulfate exhibited increased thermostability.[1799] Poly(acrylonitrile) was modified with starch sulfate in order to produce a material less susceptible to static electrification.[1800]

The structure and some biological properties of sulfated starch and, separately, amylose resemble those of heparin, the well-known blood anticoagulant.[1801] Several references describe the antipeptic activity of starch sulfates and their activation of the bradykinin-forming system.[99,1725,1726,1737,1754,1802–1808] The biological activity of starch sulfates increases with their degree of polymerization.[1804] Products of lower molecular weight are weaker anticoagulants, but they also cause less gastrointestinal hemorrage.[1731,1787] Amylopectin sulfate was also used as a potent inhibitor of pepsin.[1706] Sulfates of branched polysaccharides did not accelerate

coagulation[1803] and did not exhibit antilipemic activity.[1809] Sulfated and oxidized starches exhibited lower levels of such activity.[533,621,1799,1810–1813] The use of sulfated starch as blood anticoagulant has certain advantages over heparin. For example, it is less sensitive to large amounts of thrombokinase,[1802] and is also less toxic than sulfated cellulose, although it is less active than the latter.[1725–1727] Sulfated starch was proposed for treatment of hyperlipidemia. It decreased the cholesterol count and inhibited artherosclerosis.[532,535,1799] It was reported that 0.7–2 mg/kg was the lethal, intravenous dose of starch sulfate in mice.[1736] Rabbits fed with 30–40 mg/kg doses of starch sulfate developed increased lymphocyte counts after seven days.[1735] Sulfated (hydroxyalkyl)starches were proposed as biodegradable surfactants.[1814]

b. Sulfites.—Apart from direct synthesis of starch sulfites by use of involvement of SO_2,[1815] related products were also obtained by acetalation of starch with formaldehyde followed by reaction with sodium sulfite to give water-insoluble products containing 0.20% S.[1816]

c. Sulfonates.—Sulfonyl chlorides react with starch in aqueous sodium hydroxide[1815,1817] or pyridine[1818,1819] to give sulfonic esters. The action of 4-toluenesulfonic acid on starch in pyridine (the latter swells granular starch) at room temperature results in trisubstitution to give tritosylstarch. The reactivity of tosyloxy groups resembles that of halogen atoms. Replacement of these atoms and tosyloxy groups by nucleophilic substitution is commonly utilized. Thus, -*O*-(tritosyl)starch reacts with NaI in acetone to give monoiododitosyl esters containing iodine at only the primary position of the glucose units of starch.[1818,1820] The primary tosyloxy group can also be replaced by other halogen atoms,[1821] and the azide group, reduction of which with $LiAlH_4$ results in the formation of 6-amino-6-deoxystarch.[1822] Amines[1817] can also replace the primary tosyloxy group. In 2(3),6-di-*O*-(tosyl)amylose both tosyloxy groups could be replaced by hydrazine,[1823] on the other hand, tosylated and methanesulfonylated derivatives of 3,6-anhydroamylose were resistant to amination by hydrazine.[1824] In this manner, also starch xanthate[1825] and thiocyanatostarch[1826] have been prepared. 4-Aminobenzenesulfonyl fluoride was allowed to react with starch and a product having a DS of 0.12 was reported.[1827] Under vigorous conditions the tosyl group reacts with all 2-, 3-, and 6-OH groups to form -*O*-(tritosyl)starch, but the 6-position is the most reactive at lower levels of reaction. The chemical reactivity of tosyloxy groups also offers the possibility for elimination reactions. When the configuration of a tosyloxy group and the vicinal hydrogen atom allow β-elimination, an

unsaturated, deoxy starch can be prepared. 2,3-Unsaturated starch was prepared in this manner.[1828]

Alkylsulfonyl starches are obtainable with alkylsulfonyl chlorides in either alkaline solutions[1775] or pyridine.[1829] Long-chain alkyl groups (C_8, C_{10}, C_{18}) produce effective surfactants, even at low DS levels (0.023–0.099). Some of these inhibited the growth of *Escherichia coli*, *Bacillus subtillis*, and *Aspergillus niger*. Long-chain and aromatic-ring sulfones are available by reacting starch with sultones.[1761] Sulfoethylaminated starches have also been described.[1830]

2-(Acrylamido)-2-methylpropanesulfonic acid is a useful reagent for the preparation of such compounds.[1831] Side-chain substituted sulfones were prepared by reacting starch with corresponding vinyl sulfones. A basic catalyst is needed to perform these reactions in various solvents (such as diethyl ether, chloroform, benzene, and water).[1757]

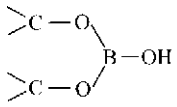
d. Thiosulfates.—Thiosulfates of starch reported in the literature include benzoylthiosulfate and benzoyloxythiosulfate,[1832,1833] produced by treating starch with the corresponding thiosulfates in an aqueous suspension at room temperature. They were designed as coating and sizing materials for the paper industry. The thiosulfate group can also be localized in ether-bound side-chains. Urea sulfamated starch was blended with 3-trimethylammonium-2-hydroxypropylated starch and used in construction boards in order to provide strong, interlayer bonding.[1834]

Additional information on the sulfation of starch has been reported by Whistler,[1835] Graefe,[1486] and by Tomasik and coworkers.[1836]

5. Boration and Silylation

a. Boron-Containing Starches.—Boron compounds, particularly boric acid, borax, and polyborates, have been added to various starch compositions as antimolding agents and/or for cosmetic use. These compounds cause thickening of starch paste,[1837–1848] indicative of either complex formation[1849] or crosslinking through formation od starch borate. Starch boric ester is described[1850] as crosslinking starch by the involvement of pairs of *cis*-hydroxyl groups of two glucose units, at positions 2 and 3. Three of these groups form intra-/inter-molecular ester bonds, whereas the fourth forms a donor–acceptor bond *via* its lone electron pair on the oxygen atom and the empty orbital of the boron atom. (**30** and **31**) Such compounds can be prepared by extrusion.[1851,1852] Starch acetate was extruded

with alkali metal borates having the general structure of $X_2B_4O_7$, X_3BO_3, XBO_2, XBO_3, X_2HBO_3, and XH_2BO_3, where X = Li, Na, K, to give materials usually designed for making corrugated board and binders.



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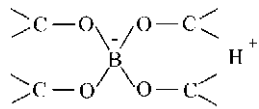

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Borax has frequently been used in conjunction with such reagents as (3-chloro-2-hydroxypropyl)trimethylammonium salts,[1853] epichlorohydrin or formaldehyde,[1401,1853,1854,1855] melamine–formaldehyde resins,[1856] (carboxymethyl) starch, oxidized (carboxymethyl)starch, (carboxymethyl)starch–acrylamide copolymer,[1857] and oxidized starch.[1858] Boric acid was also used jointly with formaldehyde,[1859] and starch dialdehyde has been crosslinked with boric acid.[526]

b. Silyl Starch Derivatives.—Silylation with chlorotrimethylsilane involves all three hydroxyl groups of the D-glucose residues of amylose. Reaction of tri-*O*-(trimethylsilyl)amylose with acetic anhydride occurs solely on the 6-*O*-silylated group. Desilylation of the remaining 2- and 3-silyloxy groups can be achieved by treating the compound with acetic acid.[1860]

Silylated starch derivatives have generally been prepared from starch and silanes containing either one or two reactive groups. In the first case, thermoplastics were formed that are soluble in hydrocarbons, chloroform, and diethyl ether, whereas, in the second case, thermosetting, insoluble polymers are produced. The reactive groups of silanes include chloro, amino, lower primary alkoxyl, lower secondary alkoxyl, and lower tertiary alkoxyl groups. Their reactivity decreases in that order.[1861] An *O*-trimethylsilylstarch having a degree of substitution of 2.2 was produced by using hexamethyldisalazane in formamide.[1862,1863] Trimethoxypropylsilane reacts in aqueous starch suspensions in the presence of either sodium aluminate,[1864] butyl titanate[1865] or during extrusion, without any catalyst.[1866] The reaction of starch in aqueous suspensions with dimethylsiloxane containing 2 mole% of $H_2N(CH_2)_2NH(CH_2)_3$ groups required approximately 10 min to proceed at 90 °C. The reaction products were designed as glues, binders, coatings, water-repellent sizes,[1867] and glass-fiber sizes.[1868] Polysiloxanes react with starch in the presence of either alkali aluminate, alkali hydroxide[1869] or urea, and also with thiourea.[1870] Several modifications of silylated starches were achieved by the use of silanes having the general structure $R(CH_2)_n\ Si(Me)_m(OR^1)_{3-m}$ where $R = NH_2$,

H, Me, Cl, $CH=CH_2$, SH, O, glycidoxy, $CH_2=CHMeCOO$, $R^1=C_1-C_6$ alkyl, $n=10$–20 and $m=0$–2.[1868,1871,1872] Such derivatives are biodegradable.

Silylated starch derivatives were tested with limited success as flocculants in the production of beet sugar.[1873]

6. Acylation

a. Anhydrides.—Because of the polyol character of starch, it originally seemed obvious that acylation of starch with carboxylic acid anhydrides would be the most convenient method of preparation. However, early attempts revealed that neither starch nor cellulose could be readily acetylated with acetic anhydride,[1874] because these polysaccharides are insoluble in acetic anhydride. Heating starch in acetic anhydride to 70 °C led to some depolymerization and the production of acetylated oligosaccharides.[1875] The addition of mineral acids solved this problem. Sulfuric and perchloric acids are the most effective catalysts, and the activity of hydrohalic acids, weaker catalysts, decreases in the order HI > HBr > HCl.[1876,1877] Magnesium perchlorate was reported to exhibit good catalytic properties.[1878] Acetylation in the presence of MgO or $Mg(OH)_2$, which control the acidity of the reaction mixture, has been recommended.[1879] The diffusion rate of catalyst and acylating agent into the granule interior is the rate-limiting step. Acetylation of starch in phosphoric acid was also patented.[1880] The results of acylation are influenced by hydrolysis of the esters in the acidic reaction medium.[1881] Other suggested catalysts, such as pyridine, zinc and aluminium chlorides, and sodium acetate, were not effective. Although direct acetylation with Ac_2O produced triesters, without activation, the reaction yield was not higher than 2%.[1882] The yield can be improved by "activation" of the starch, as by swelling of the starch granules.[1883] In this manner, starch pastes were produced in approximately 33 wt% aqueous solution, with subsequent precipitation by ethanol. The precipitate was suspended in glacial acetic acid through which a stream of chlorine was passed, and acylation was then effected by use of acetic anhydride with sulfur dioxide, (presumably via an acyl sulfite). The yield of starch triacetate reached 96.5%.[1884] Other catalysts used included zinc chloride,[1885] thionyl chloride, or magnesium perchlorate.[1886,1887] Sulfonyl chlorides could also be used without causing incorporation of sulfur and chlorine.[1888] Several pretreatment techniques was checked.[1889] Acetylation with acetic anhydride–pyridine gave good results,[1890,1891] and it was reported to be more efficient than reaction in anhydrous ammonia.[1892]

Diesters were formed when acetylation was conducted in the presence of formamide and potassium acetate under conditions inhibiting starch gelatinization.[1893] The use of *N,N*-dimethylformamide at pH 3.8,[1894] and acetylation in the presence of potassium acetate and quaternary tetralkylammonium salts[1895] were proposed. After swelling of starch with formic acid, subsequent acetylation with acetic anhydride at 95 °C was complete within 1 h.[1896] Starch may be esterified by means of acetic anhydride saturated with dry ammonia in the presence of sodium acetate,[1897,1898] and ammonium acetate and acetamide can also be used. The reaction at 140 °C was complete within 1 h, introducing 2.5–2.75 acetyl groups. This idea was extended to the use of fatty acid ammonium salts in a process where blends were vacuum-heated at 100 °C.[1899] Acetylation of starch with acetic anhydride in alkaline media is reported to be convenient,[1900–1903] and a Romanian patent[1904] described acetylation of starch under basic conditions with 2-propanol added. Acylation of starch during extrusion with anhydrides in the presence of sodium carbonate has been demonstrated.[1905] Esters were formed without depolymerization by the continous addition of acetic anhydride at pH 9–10 to a 1:1.5 starch–water suspension at 20 °C.[1906] Primary hydroxyl groups react first, and when the degree of acetylation reached 0.024, secondary hydroxyl groups begin to react. However, when tri-*O*-(trimethylsilyl)starch was acetylated, only the 6-$OSiMe_3$ group was substituted by the acetyl group. Removal of two remaining protecting groups provided 6-*O*-acetylstarch of high degree of substitution.[1860]

Acylation with methoxalic anhydride (the anhydride of the monmethyl ester of oxalic acid) in pyridine produced starch monomethoxalate.[1907]

Anhydrides of unsaturated acids could react in pyridine, as shown in the preparation of methacrylic esters.[1908,1909] As with acetic anhydride, higher aliphatic acyl anhydrides produced triesters,[1910] but benzoic anhydride produced only a diester. Subsequent acylation with benzoic and acetic anhydrides provided a mixed acetyldibenzoyl starch.[1911]

The use of cyclic anhydrides of dicarboxylic acids gave monoesters of the dicarboxylic acids.[1912–1915] Maleic anhydride reacted with slurried starch within 30 min at 45 °C at pH 7.5–8.5.[1916] Another procedure involved the blending of an acetone suspension of starch with maleic anhydride, followed by evaporation of the acetone, the addition of sodium hydroxide powder, and heating the blend at 120 °C for 7 h.[1917]

Various anhydrides show significant differences in reactivity. For instance, acetic anhydride reacted with starch in the presence of formamide, whereas phthalic anhydride required pyridine to react. This property was utilized in preparation of starch esters carrying two different acyl groups simultaneously.[1918,1919] Mixed starch esters may also be prepared by using a mixture of various anhydrides in

the presence of pyridine or *N,N*-dimethylformamide,[1920] as well as alkali.[1921–1923] The use of dianhydrides, for instance those available from the reaction of acids with acyl chlorides, led to the production of crosslinked starches that had reduced swelling after cooking. The products can be used as food thickeners.[1921,1923]

b. Acyl Chlorides.—The reaction of acyl chlorides with starch has been used to produce starch esters, particularly when esters of higher fatty acids are desired. Degradation of the starch resulted upon fast reaction with lower acyl halides.[1924,1925] On the other hand, starch retains its granular structure after reaction with phosgene.[1926] A reagent composed of acetyl bromide and hydrogen bromide in acetic acid was proposed for detecting non-(1→4)-glucopyranoside linkages, that is, the branching points of amylopectin.[1927] Higher acyl chlorides caused acylation upon heating; pyridine and quinoline were recommended as the catalysts, used either as the reaction medium[1928] or added as catalysts in toluene,[1929] benzene, and halogenated hydrocarbons,[1930–1932] Generating a moist mixture containing sufficient amounts of solvent and catalyst.[1933] Solubilization of starch prior to reaction affected the course of esterification. Diesters were formed when the starch was insoluble,[1934] otherwise, triacylated starch resulted. The preparation of starch benzoate using benzoyl chloride in propanol–aqueous sodium hydroxide added produced esters having a degree of substitution between 0.15 and 0.30.[1935] Acylation with acyl chlorides involving phase-transfer catalysis has been demonstrated;[1936] the starch ester was isolated from the toluene layer. The time of reaction was a critical parameter in the cinnamyolation of starch.[1937] Control of the reaction time allowed the production of desired levels of diacylated product. Starch, amylose, and amylopectin were all esterified in the same manner[1938] and the starch variety seemed to have no particular effect on the result of esterification. However, studies on acetylation of starch with acetic anhydride revealed that tapioca, wheat, rice, potato, and sweet-potato starch reacted at the same rate, while maize (corn) starch reacted more rapidly. On the other hand, the viscosity of all esters but that of potato starch was lower than that of maize starch.[1876] Several, less-common starch varieties were acetylated, and some differences in the degree of substitution between them were demonstrated.[1939] These differences might be related to the size of the starch granules.[1940] Optimal conditions for acetylation of tapioca starch involved 3–5 h of reaction at 30 °C and pH 7–9.[1941] An alternative method involving use of sulfuric acid as the catalyst was suggested.[1942] A temperature of 25 °C and a pH of 9–10 were proposed as optimal parameters for acetylation of sweet-potato starch.[1943] The properties of this starch derivative were studied in detail.[1944] Diacyl dichlorides and cyanuric chloride can be used to crosslink starch.[1945]

The reactivity of acyl chlorides determines the selectivity of the reaction.[1938] Benzoyl chloride provided disubstituted products rather than triesters,[1946–1948] but maltodextrins formed triesters. However, by adjusting the reaction conditions, mono- and di-esters of fatty acids could also be prepared.[1949] On the other hand, acetylation usually led to the triacetate.[1438] Chlorides of unsaturated acids, when treated with pregelatinized starch, did not require any solvent other than water. In this case, dissolved alkali played the role of catalyst. Mixed esters were also formed when mixtures of acyl chlorides[1950–1953] or acyl anhydrides were used.[1954,1955]

c. Carboxylic Acids.—Direct reaction of starch with carboxylic acids also produces starch esters. Additional information on this topic can be found in Section IV. Heating a starch blend with acetic acid to 80 °C was sufficient to produce starch acetate,[1956] but reaction at the boiling point could also be used.[1957] The degree of substitution could be controlled by regulating the volume of water withdrawn from the boiling reaction mixture.[1958] Starch and acids, when heated in the dry state[1959] react slowly to give the monoester during several days at room temperature, as shown with formic acid.[188] Esterification is catalyzed by sulfuric and phosphoric acids, but Cl_2O_5 or Cl_2O_7, being volatile, appear to be superior.[1960] A comparative study on the esterification of starch with propanoic acid and its anhydride showed that at 156 °C the acid esterified starch 8.7 times as fast as the anhydride[1961] and the degree of substitution was between 0.93 and 1.0. In the case of an acetic acid–acetic anhydride mixture, the reaction was fast until the degree of esterification reached 36%, beyond which the reaction rate decreased.[1962] When this reaction is catalyzed by sulfuric acid, the degree of substitution is higher,[1963] and the degradation of the polysaccharide is lower.[1964] Among aliphatic carboxylic acids, formic acid reacted most readily. When 90% formic acid was used, the degree of formylation reached >0.14 after 2 h at room temperature and increased up to 0.18 after 48 h at the same temperature, however, the use of anhydrous formic acid gave DS values of 0.2 and 0.24, at 2 and 48 h, respectively.[1965] Formyl groups reside mainly at C-6.[1966] Chloroacetic acid reacts with starch to form the corresponding ester, and the chlorine atom does not react.[1967,1968] Acylation of starch with a fatty acid as high as octadecanoic gave a degree of esterification of 0.7[1969,1970] when was carried out in xylene in the presence of sulfuric acid. Unsaturated acids also esterified starch, with retention of their double bonds.[1971,1972] A process of esterifying starch with gluconic acid was described.[1973] Transesterication of starch formate with other aliphatic acids in the presence of sulfuric acid is possible.[1974] Various other esters may be conveniently prepared by using a mixture of a desired acid plus trifluoroacetic acid.[1975] Dicarboxylic esters form half esters.[1976] In this

manner esters of citric and itaconic acids were also prepared,[1902,1977–1981] and the products exhibited good freeze–thaw stability. A benzenetetracarboxylic acid[1982] and butanetetracarboxylic acid[1983] strongly crosslinked starch.

d. Esters.—Vinyl[1984–1988] and allyl[1989] esters of carboxylic acids acylated starch at pH values ranging from 7.5 to 12.5 and the degree of substitution reached almost 0.1. These acylating agents were applied for acylation of cyanoalkylated starch[1990] and epichlorohydrin-crosslinked starch.[1991] There was a report that methyl esters of higher fatty acids, octanoate, dodecanoate, and hexadecanoate transesterified starch on heating in dimethyl sulfone.[1992] Esters of unsaturated acids reacted similarly.[1993] Esterification of starch with lactones is also a transesterification process, as in starch esterification by D-glucono-1,5-lactone.[1973] Carboxylic acid esters cause transesterification upon heating with starch in a microwave oven.[1994]

1,3-Lactones of saturated aliphatic acids also act as acylating agents when applied in alkaline conditions, whereas they formed ethers in neutral and acidic media.[1995] A wide range of starch esters could be prepared from starch and dialkyl, alkylaryl, and diarylchloroformates or chlorothioformates in aqueous solutions of sodium carbonate at 90 °C.[1996] Carbohydrate *trans*-carbonates esterify starch, leading to copolymers.[1997] Transesterification of esters of aliphatic acids and aliphatic alcohols by starch was patented[1998] in a process involving agitation of starch with ethyl esters in chloroform or other chlorinated alkanes. Triesters were formed with a degree of acylation greater than 2.4. The reaction yield was much lower when conducted in an aqueous slurry at pH 6.5. This procedure was described for producing diesters of dioic acids and esters of arylcarboxylic acids.[1999,2000] Acyl monophosphates have also been used for formation of starch esters. At 40 °C and pH 6.0, starch succinate containing 1.14% succinyl groups was formed within 90 min.[2001]

Starch carbonate diesters were formed by reaction of starch with alkylene carbonates under diminished pressure at 100–140 °C.[2002] The products were proposed as surgical dusting powders. Another method involved dimethyl sulfoxide as the reaction medium, triethylamine as the catalyst, and *trans*-carbonates of glycosides as the acylating agents. Thionocarbonates were used similarly. The degree of substitution was 0.4.[2003] Another method involves 1-acyl 1,1′-carbodiimidazole or dicarboxylic acid imidazolides at pH 8.0.[2004]

e. Carboxyamides.—Carboxyamides act as acylating agents when starch is heated in a carboxyamide solvent, as formamide[2005,2006] and acetamide.[2006] *N*-Acylimidazoles are good acylating agents.[2007]

f. Ketene, Diketene, and Acyl Peroxides.—Acetylation with ketene gave results comparable to acetylation with acetic anhydride in sulfuric acid; the product contained ~43% of acetyl groups.[2008] Acylation with diketene has been patented;[2009–2011] the reaction required an alkaline solution and produced starch acetoacetate. The acylation of starch and maltodextrins by means of acyl peroxides was also patented.[2012]

g. Physical and Chemical Properties of Acylated Starch.—A comparison of the thermal stability of amylose esters provided the following order of esters: amylose hexadecanoate > amylose acetate > amylose propanoate > amylose phenylacetate > amylose benzoate > amylose succinate > amylose phthalate. The overall activation energy decreased as the length of the acyl chain increases, and decomposition of these esters obeyed first-order kinetics.[2013,2014] Hexene, hexanone, methyl acetate, and allyl crotonate were identified as decomposition products of starch acetate.[2015] More-subtle temperature effects on acylated starch could be evaluated rheologically,[2016] The degree of substitution of starch acetates can be determined by enzymatic degradation, IR spectroscopy, and viscosimetry.[2017] Several hours of heating of starch acetate with CaO at 250–300 °C produced calcium acetate and acetone.[2018]

In other reactions of starch esters, for example, 2,3-di-*O*-acetylamylose reacted with *N*-iodosuccinimide in the presence of triphenylphosphine to give 2,3-di-*O*-acetyl-6-deoxy-6-iodoamylose.[2019] The ester bonds are fairly stable to acid-catalyzed hydrolysis. Starch esterified with acetylsalicylic acid administered to dogs did not increase the acetylsalicylic acid level to any significant extent in the animal's blood serum.[2020] The slow release of herbicides from their esters with starch was analyzed.[2021,2022] Alkaline hydrolysis of starch esters is easier than acid hydrolysis.[2023] The enthalpy of starch acetate formation was 143.5 kJ/mole, and acetylation decreased the susceptibility of the starch backbone to enzymatic hydrolysis and iodine uptake.[2024] The hydrolysis of starch and starch acetate in alkaline solutions obeys second-order kinetics.[1988]

h. Applications.—Acylation of starch improves several of its functional properties, particularly with respect to food cooking applications. Starch acylation is used to modify setback viscosity, gelatinization time, stability at low pH, freeze–thaw stability, storage characteristics, and other characteristics.[2025]

The acetate of potato amylose is more flexible than cellulose acetate, but the persistent length of the latter is significantly higher.[2026] Starch triacetate, amylose triacetate, and amylopectin triacetate are reported to be suitable for

gel-chromatographic packings,[2027] as well as film-[2028,2029] and fiber-forming[2030] material. Acylated cereals have been used to produce biodegradable plastics.[2031] Starch maleate and other monoesters of dibasic carboxylic acids have been proposed as resin adhesives.[2032,2033] Starch acetate could partly replace caseinate in cheese,[2034] and also replace sodium alginate in the printing of reactive dyes on textiles.[2035] Starch acetate can also be used as a surface treatment for paper.[2036] Starch esterified with octadecylsuccinic anhydride formed gels that were reversible upon changing the temperature and pH.[2037] The same material was used as a component of a binder for tapes[2038] and as an emulsifier.[2039] Polymeric microspheres can be produced by esterification of starch with acrylic acid.[2040] For the same application, starch was crosslinked by 1,1′-carbonyldiimidazole, phosgene, or ethyl chloroformate.[2041] Esters of cinnamic acids were useful as photosensitive resins, absorbents, liquid crystals, carriers for enzymes, chromatographic packings, and as reagents for optical applications.[2042] Starch acetoacetate was reported as a water-resistant adhesive.[2043]

Starch esters are used as emulsifying agents, thickeners and sizes,[1913,2044] binders for coal briquettes,[2045] additives for hydraulic binders,[1738] paper coatings,[2046] and adhesives.[2047] Starch acetates having a degree of substitution of 0.21–0.50 were prepared by a method retaining the granular structure, and the products were soluble in hot water. Films cast from such hot-water solutions are rigid and impermeable to oxygen. It was reported that jet cooking of such esters improved their aqueous solubility and the quality of the films produced.[2048,2049] Selective and nonselective neutral membranes from starch triacetate can be made.[2050] Starch acetate having a degree of esterification above 0.03 was blended with diluted alkali and urea to produce an adhesive.[2051] Starch acetate has been used in waste water treatment, especially in applications involving food processing. For example, proteins in sludge were taken to their isoelectric point and then sorbed onto starch acetate.[2052] In another application, processing of so-called parting paper for laminates by the use of an 8:3:12 blend of starch acetate, zirconium octadecanoate and silica or alginate was reported.[2053] Starch propanoate at concentrations of 0.5–5.0% was reported to stabilize water–oil emulsions and was, therefore, proposed as a component of salad dressings, flavoring oils, and cosmetics, and for encapsulation of lipids.[2054] A paint additive and a coating for glass fiber used starch benzoate stabilized by stirring at 100–250 °C under pressure.[2055,2056] This ester was blended with wheat flour to produce a glue.[2057] Esters of starch with branched alkanoic acids, after a similar process of stabilization, have also been proposed for use as glues. [2058–2060] Starch dodecanoate having a degree of substitution above 2 was patented as a base for chewing gum,[2061] and starch hexadecanoate was reported as a component of shampoos.[2062]

Esters of higher fatty acids were used to produce special optical effects in photographic films.[1969,1970]

The acylation of hydrolyzed starch with acid anhydrides in pyridine[2063–2065] gave products of interest for medical and cosmetic use, as well as applications similar to those of acylated starches.[2066]

Esters from unsaturated fatty acid chlorides are usually viscous or limpid oils soluble in hydrocarbons and turpentine, and whose primary applications are as varnishes, films, artificial threads, aqueous emulsions, and rubber-like plastics.[2067,2068] Heating them in an inert gas produced insoluble products formed by polymerization involving double bonds in the acyl moieites.[2069] As mentioned in the section on nitrates, acetates of amylose are less compact than amylopectin acetate.[1468] Esters of unsaturated acids have also been proposed as re-moistenable adhesives.[1971,1972]

Mixed esters were proposed for use as petrochemical dispersants[2070] and cardboard adhesives.[2071] They were also compounded with starch and borax for use in processing corrugated board.[2072]

The products of acylation of starch with maleic anhydride were proposed as cation exchangers,[2073] and also to encapsulate volatile flavoring oils and perfumes.[2074,2075] Starch maleate was proposed as a photographic hardener.[2076] The reaction of starch with maleic anhydride–styrene copolymer provided a biodegradable material.[2077] Starch succinate was also proposed as a dispersant for coatings, sizes, and adhesives.[2078] Esters of succinic acid derivatives carrying long-chain alkyl substitutents, for instance, octenyl groups, were proposed for making yarn,[2079] protecting coatings for photographs,[2080] and in combination with gelatin for the encapsulation of pharmaceuticals.[2081] A lipophilic starch 3-carboxy(octenyl)propanoate was obtained after treatment with alpha amylase, and was found useful as an encapsulating agent[2082] and as a paper size.[2083] Starch octenylsuccinate and tertadecenylsuccinate were components of sizing for glass fibers,[2084] and they were also reported to improve the quality of bread crumbs.[2085] Starch maleate, succinate, and starch terephthalate, all in form of sodium salts, were proposed as detergent builders,[2086] adhesives, and thickeners.[2087] Modification of foodstuffs was accomplished after modifying starch by the use of 4% succinic anhydride and 3% 1-octenylsuccinic anhydride.[2088] Starch octenylsuccinate was also proposed as a partial replacement of calcium caseinate in imitation cheese products[2089] and additives to meat pastes.[2090]

i. Acylation of Starch Derivatives.—Esterification occurs more readily with starch derivatives containing side-chain hydroxyl groups and also with starches that are partially depolymerized. Thus, (hydroxypropyl)starch can be esterified with carboxylic acids in liquid sulfur dioxide[2091] or simply by heating to 55 °C

with acetic anhydride for 2 h,[2092] or with other acid anhydrides.[2093] Tridecyl vinyl ether–maleic anhydride was used to produce rosin sizes.[2094] Esterification by styrene–maleic anhydride copolymer gave coating compositions[2095] and, esterification by ethylene–acrylate–maleic anhydride copolymer gave materials for films.[2096] Such an ester prepared at high pressure was proposed as a chewing gum base.[2097] Starch derivatives having hydroxyl groups in a side-chain, for instance 2,3-(dihydroxypropyl)starch, react readily with acetic anhydride in pyridine, and both of the side-chain hydroxyl groups are acetylated, as well as the remaining hydroxyl groups of the starch glucose units.[1480] The choice of the acylation method is not always arbitrary. In the case of allyl starch, acylation with acid anhydrides in pyridine is an effective method.[2098] Acylated oxidized starch[2099,2100] has been used as an adhesive for tape. Acetylation of starch phosphate did not replace the phosphate moiety.[2101,2102] Tapioca starch crosslinked first with phosphorus oxychloride followed by acetylation with acetic anhydride retained the phosphate groups and also exhibited reduced odor.[2103] Starch derivatives bearing side-chain ester groups were prepared by etherification of starch with esters of aliphatic 2-chlorocarboxylic acids.[2104] The sodium salt of 2-chlorocarboxylic acids could be used instead, and the products then required esterification.[2105,2106] Starch grafted with alkyl acrylates was acylated by means of acetic anhydride, either in pyridine or in sulfuric acid. Since grafting occurred principally at the 2-OH groups of the glucose residues, the 3- and 6-OH groups were acetylated.[2010] In unsubstituted glucose residues, the reactivity of the individual hydroxyl groups decreased in the order 6-OH>2-OH> 3-OH, as shown by analysis of the acetyl group distribution in acetylated starch, using ^{1}H and ^{13}C NMR.[2107] Starch has been acylated by a styrene–maleic anhydride copolymer, which was first hydrolyzed in ammonium hydroxide to give a product that is simultaneously an amide and ammonium carboxylate. Heating for 15 min at 90–95 °C produced a material proposed for paper sizing.[2108,2109] Hydroxyethylation of esterified starch, followed by further esterification of the product with octadecanoic acid has been described.[2110]

Acylated starch can be copolymerized to yield materials for films, lacquers, and fibers.[2111] Starch acetate copolymerized with epichlorohydrin was extruded to give cold-water swelling products with a high degree of friability.[2112] Epichlorohydrin-crosslinked starch has been acylated with 2,3-di-*O*-benzoyl-L-threaric anhydride.[2113] The reaction proceeded either in *N,N*-dimethylformamide or in toluene, and the non-crosslinked product has also been reported.[2114]

Acetylated adipate- and glycerol-crosslinked starch, administered at 62% in a cooked diet, was safe to experimental rats.[2115] Such esters, as well as acetylated starch phosphates, influenced mineral metabolism to a certain extent in rats, but

the effect was less significant that that of lactose.[2116] Up to 30 day tests with rats fed with starch octenylsuccinate showed that, although the growth of the rats and their hematological characteristics remained unaffected, their kidney and cecal weight increased.[2117] Female rats had higher concentrations of urinary magnesium and calcium than males. This correlated with the level of mineralization of the cortico-medullary junction.

Esterification of starch with some biologically active acids provided controlled-release herbicides, as demonstrated with starch and (cyanoethyl)starch esterfied with (2,4-dichlorophenoxy)acetyl chloride[2118] and with metronidazole (2-methyl-5-nitroimidazole-1-ethanol) hemiester.[2119] Esterification of (hydroxyethyl)starch with phthalic anhydride provided a coating material for tablets,[2120] and acetylation of (hydroxypropyl)starch provided a base for chewing gum.[2121] It was reported that esterification of (hydroxypropyl)starch with isophthalic acid–1,2-propanediol–trimellitic anhydride copolymer was used to produce paper size.[2122] Starch esterified with octanoic or oleic acid served as a gelatinizing agent for liquid oils and fats[2123] and cosmetic gels.[2124]

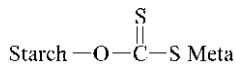
j. Miscellaneous.—A rapid and accurate method of the determination of acetyl groups in starch acetates involves transesterification with sodium methoxide in anhydrous methanol to give methyl acetate, determined by titration after saponification in an excess of alkali.[2125]

Additional information on starch acylation has been reported in several sources.[1886,1962,2068,2126–2133]

7. Xanthation

Artificial silk (viscose rayon) is spun from a viscous medium that is produced by reacting cellulose with carbon disulfide in alkali. The unusual success of this reaction prompted scientists to analyze similar reactions with starch, and indeed, starch viscose can be obtained.[2134,2135] The properties of xanthates (**32**), mainly the degree of substitution, depend on such reaction conditions as the proportions and concentrations of reagents, and the duration and temperature of the process. Xanthation of starch using 2–3 moles of sodium hydroxide in 5–20% aqueous solutions per mole of starch and 20–25 mL of carbon disulfide per 10 g of starch is complete within 24 h of shaking at room temperature. Further studies suggested a 3-molar NaOH solution as the most suitable.[2136] The temperature is a critical parameter and

should not exceed 49 °C in order to prevent formation of the trithiocarbonate.[2137] Within one hour there was 93% conversion of CS_2 into xanthates having a DS of up to 0.29.[2138–2142] The degree of substitution also depends on the particular metal hydroxide and its concentration. For example, 17.8% NaOH provided a DS of 0.4, whereas the same concentration of KOH produced a DS of 1.3.[45] It was reported that LiOH and NaOH exhibited similar results and that RbOH and CsOH, behaved similarly to KOH.



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Cereals, wheat bran, wheat gluten, maltodextrin, and dextran can also be xanthated,[2143,2144] and continous processes have been described.[2139,2145] The distribution of the xanthation sites between primary and secondary groups appears initially to be random, however, there is a preference for the primary hydroxyl groups when the reaction time is prolonged.[2141,2146,2147] Sodium amylopectin xanthate had a polydisperse random coil configuration in an aqueous solution of 1 M NaOH.[2148]

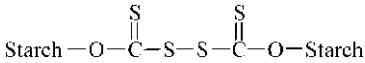
The kinetics of starch xanthation follows Eq. (*4*):

$$-\left(\frac{dv}{dt}\right) = kv^{n+1} \qquad (4)$$

where v is the concentration, t is the time, k is the rate constant, and n depends on the DS. When v is 0–25, 25–75, and 75–100 xanthate groups per 100 glucose residues, n is equal to 0, 1, and 2, respectively. The activation energy is 7.54×10^{-2} and 7.12×10^{-2} kJ/mole, at 25–40 and 40–50 °C, respectively.[2149] The reaction rate decreases with increasing concentration of alkali. Acidimetric determination of the xanthate groups can be performed by using sulfuric acid and then a sodium hydroxide solution.[2150]

Xanthates readily hydrolyze in acidic media, regenerating starch and CS_2.[2149] They also decompose during storage, especially products of low DS. Air oxidation transforms xanthates into xanthides (**33**). Some of the xanthate groups migrate, and monothiocarbonates are formed.[2151] Xanthides are also produced by oxidizing starch xanthate with sodium hypochlorite.[2152] Stabilization can be achieved by increasing the concentration of NaOH in solution, this is, by suppressing dissociation of the xanthate and its conversion into salts.[504] In the latter case, only water-insoluble salts are fully stable. Rapid drying of xanthate solutions is also

useful for this purpose.[2153] Reaction with 2-chloro-*N,N*-diethylacetamide also stabilizes xanthates.[2139] Stable products are also produced by esterification with other agents, for example, alkylglycidyl ethers[2154,2155] and alkyl diepoxides.[2156]



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Starch xanthate can be methylated as well as acetylated.[45] The first reaction is base-catalyzed and the second acid-catalyzed. Neither procedure decreases the DS of the modified xanthate. Cationization of starch xanthate occurs on reaction with the water-soluble poly(vinylbenzyltrimethylammonium) chloride.[2157] Xanthates have been cyanoethylated to produce rubber mixes.[2158,2159] Sulfonated products were made by reaction with sultones.[2160]

Xanthates undergo convertion into water-insoluble xanthides after prolonged exposure to air and/or contact with such oxidants as hydrogen peroxide, chlorine in alkali, or sodium nitrite.[503,2159,2161,2162] The xanthates can be recovered by cleaving the xanthide −C(S)−S−S−C(S)− bond by various reagents.[2163]

The viscosity of starch xanthate decreases rapidly with time, exactly the opposite of the behavior with cellulose xanthate.[2135] Nevertheless, starch xanthate has been used in 80:20 (w/w) blends with cellulose viscose.[2164–2168]

Attempts have been made to utilize starch xanthates for froth flotation of oxidized iron ores[2169,2170] and flocculation of coal powder suspensions.[2171,2172] Xanthate salts and xanthate esters have been used for soil conditioning. For example, corn germination and seedling growth were improved after such treatment.[2173] Similar materials were also proposed as a repellent.[2160] Xanthates have been used as collectors of heavy metal ions, and in combination with cationic polymers to form polyelectrolyte complexes.[2174–2178] Metal xanthates, particulary alkali metal xanthates, are used in paper products.[2137,2143,2144,2179,2180] Xanthates precipitate as insoluble xanthides during pulp processing, particularly when such oxidizing agents as chlorine, iodine, and nitrogen oxides, are present.[2181] For example, zinc xanthate was produced by this method and used used in latex compounding.[2182] Titanium xanthate was claimed to collect up to 78% uranium from sea water.[2183] Solutions of starch xanthates were also proposed as solvents for sulfide dyes.[2184,2185]

Ion exchangers have been produced from crosslinked xanthates, applied as either their sodium or magnesium salts.[2176,2186–2193] Crosslinked xanthates are also used to make molded articles and films.[2155] Reported crosslinkers include aldehydes, urea, isocyanantes, acids, acyl halides, alkyl and aryl halides, organosilyl halides,[2194]

diglycidyl esters,[2155] polyacrolein hydrogensulfite adduct,[2195] vinyl monomers with hydrogen peroxide,[2196] and epichlorohydrin.[2197] Crosslinked xanthates have been used in treatment of waste water to decrease the concentrations of selenium,[2198] zinc,[2199,2200] cadmium,[2200] nickel,[2201] antimony,[2202] mercury(II),[2200,2203] and other metal ions.[2204] A variety of elastomers, resins, rubbers and latexes were prepared by polymerization and copolymerization with starch xanthates, xanthides, and various related polymers and copolymers.[2182,2190,2205–2216] Epoxidized and crosslinked xanthates were proposed as thickeners.[2217]

Xanthates were also used for microencapsulation of pesticides; the pesticide and a soluble xanthate were blended in aqueous solution followed by acidification and the addition of a coupling agent to form a matrix.[2218–2227] Particles of nitrile–butadiene rubber (NBR) and styrene–butadiene rubber (SBR) were also encapsulated by starch xanthates.[2228]

Xanthides are used as internal adhesives for paper. The major application of xanthides is as an additive providing a high level of wet and dry strength to paper. In practice, xanthides are prepared from xanthates *in situ*.[2229,2230] It was reported that alum helps to retain xanthides in pulp.[2231] Xanthates having glycidyl groups are also used as papermaking additives that increase strength and fold endurance.[2154–2156] Polyampholytes for paper, using such esters as diethylaminoethyl and 2-hydroxy-3-(trimethylammonio)propyl xanthates were produced,[2232,2233] Xanthates and polyamide–polyamine–epichlorohydrin resins were also used to improve the wet-end strength of paper.[2205,2234–2237] As a component of styrene–butadiene rubber (SBR) and nitrile–butadiene rubber (NBR), the xanthide is used to avoid vulcanization with elemental sulfur.[2215,2231,2238,2239] In this application, the effectiveness is decreased by water or moisture[1404,2240–2242] but can be improved by the addition of diisocyanate,[2241] resorcinol, paraformaldehyde, and 3-aminopropyltriethoxysilane.[2242]

Xanthides are also used for trapping heavy-metal ions[2178,2226] for encapsulating pesticides, herbicides,[2243–2246]and nematocides,[2247] and producing nitrile–butadiene and styrene–butadiene rubbers, and other elastomer particles.[2228,2231,2248]

Cereal xanthates have been incorporated into greaseproof paper products.[2161] The strength of certain rubbers could be increased by coprecipitation of latex with xanthate.[2206,2249,2250]

A method for analyzing the starch component of starch xanthide involves destruction of the xanthide group in alkali, followed by treatment of a neutralized sample with alphaamylase and a determination of recovered D-glucose.[2251]

Additional information on xanthates can be found in several references.[1486,1836,2164–2168,2252]

XII. Halogenation

Halogenated starch may incorporate halogen atoms bound either covalently ionically, or by other interactions, such as van der Waals and dispersion forces. Bonding of the latter type is responsible for the formation of various starch–halogen and halogenated compound–starch complexes. Since they were recently reviewed[4] such compounds are omitted from this section.

Contact of polysaccharides with halogens may produce sorption complexes. The action of chlorine on cereals has been used to improve baking properties,[2253] but the observed effect could be due to the oxidative effect of chlorine on flour polysaccharides (consult Section VII) and other reactions of nonsaccharide flour components. Chlorination of flours increases their viscosity[2254,2255] and hydrophobicity.[2256] Chlorinated flours have also been reported as adhesives[2257] and as oil collectors.[2258,2259] Their stability can be increased by neutralization with ammonia.[2260]

Halogenation of starch via direct action of halogen is probably not possible unless liquid chlorine is used, with heating under pressure. Otherwise, starch merely undergoes some random glycosidic bond-cleavage, accompanied by oxidative degradation and very random chlorination.[2261] Cleavage of the glycosidic bond probably proceeds ionically as nucleophilic attack on the OH groups. Chlorine is more effective in this respect than bromine.[2262–2264] Bromine, in aqueous solution, oxidizes starch and the rate increases with increasing pH.[2265] In liquid chlorine, various compounds were formed, including mono- up to hexa-chloroketones, α-chloroaldehydes, chlorohydrins, and hypochlorites.[2266] The rate of reaction clearly depends on the degree of chlorine penetration into granules. Aged and pregelatinized starches reacts more readily. The reaction is catalyzed by hydrogen chloride and water, which promotes bond cleavage.[2267] The reaction might also proceed in a free-radical manner, because experiments with starch and anhydrous hydrogen chloride revealed formation of free radicals.[2268] In liquid chlorine, esters[2269] and ethers[2270] could also be chlorinated. Esters react more slowly. Chlorinated esters and ethers were proposed as intermediates in manufacturing resins, plastics, and constituents of coatings and sizes.

Among the known halogenating reagents that usually transform alcohols into haloalkanes, phosphorus pentachloride was reported to be superior.[2271] Such a reaction resulted in a "pentachlorostarch." Three chlorine atoms were those that replaced three hydroxyl groups in the D-glucose residues, and the two others replaced carbonyl groups resulting from the opening of the pyranose ring. Reflux of pentachlorostarch with sodium iodide in acetone removed two chlorine atoms and gave

a "trichlorostarch." These remaining chlorine atoms could readily be substituted by NaS^- and SH^- nucleophiles, leading to thio and disulfide starches.[2272]

Selective C-6 monohalogenation of starch, with high (up to 97%) yield can be achieved with triphenylphosphine and tetrahalocarbons.[2273]

Reaction of amylose with methanesulfonyl chloride in *N,N*-dimethylformamide at 60 °C for 0.5 h effected selective 6-mesylation.[486] Iodine atoms can be introduced, starting from tri-*O*-tosylstarch on reaction with sodium iodine, giving di-*O*-tosyl-6-iodostarch.[1818] 6-*O*-Tosylstarch reacts with anhydrous potassium fluoride in ethylene glycol, or with anhydrous hydrogen fluoride in dimethyl sulfoxide, to give 6-deoxy-6-fluorostarch[485,486] Halogen atoms (Cl, Br, I) at C-6 are readily replaced by the azido group. The treatment of starch with chloromethylo-*N,N*-dimethyliminium chloride also gives a chlorodeoxystarch.[1821]

Halogen molecules can be added to double bonds in starch derivatives, as demonstrated[487] by the addition of bromine to the 2,3-double bond of 2,3-dideoxy-2,3-didehydro-6-*O*-trityl-starch. The reaction proceeded in methanol in the presence of silver acetate.[487]

Another group of halogenated starches contains halogen atoms in substituents used to modify starch, as in starch esters containing halogen in the ester groups introduced into starch by reactions with halo acid chlorides or anhydrides,[2274] or by reaction with epichlorohydrin.[2275] 6-Iodoethylated starch was said to result from the reaction of (hydroxypropyl)starch with *N*-iodosuccinimide in the presence of triphenylphosphine.[2276] Such a starch derivative was cited as a potential contrast material for medical imaging by computerized tomography.[2277]

Preparation of a chlorostarch for improved pigment retention in paper has been reported.[2278] Acetalation of chlorinated starches was described[573] as a procedure for producing a high-strength paper size.

Additional information on halogenated starches has been reported by Whistler.[2279,2280]

XIII. Amination, Amino and Ammonio (Cationic) Starches

1. Introduction

Although aldehydes and their hemiacetals and acetals react reversibly with ammonia to form aldehyde ammonias, the direct amination of starch is not possible. Aqueous ammonia slowly degrades starch[17] as does liquid ammonia.[21]

In addition, gaseous ammonia at elevated temperatures inhibited the dextrinization of starch possibly because of the oxygen-free heating conditions. Pyrodextrins, which nevertheless did form, were free of nitrogen. Ammonia reacts with small amounts of the products of more-extensive starch and dextrin decomposition, producing an aroma resembling that of roasted peanuts.[25,2281] Drastic heating conditions were required (6 h of heating at 220 °C) to produce dextrins having small amounts (0.48%) of residual nitrogen.[25,2281] Cereal flours heated in gaseous ammonia lose their baking properties and develop a similar aroma.[2282] Amino acids roasted with starch gave anionic dextrins[2283] and also developed various secondary food aromas.[2284] More nitrogen (1.25%) was retained in dextrins that have been prepared by heating starch with either aniline or 2-aminobenzoic acid, with aniline at temperatures approaching its boiling point.[2285] Starch has frequently been treated with ammonia to loosen the compact structure of the granules and increase their reactivity. Pyridine has also been used for this purpose.[2286]

Starch can be aminated when either reductive aminolysis is employed,[2287] or by substitution of tosyloxy groups in tosylated starches. In the first case, heating starch in liquid ammonia or an amine in a stream of hydrogen in the presence of Raney nickel in a pressure vessel leads to amino starches. In the latter case, a 6-tosyl group introduced into amylose can be replaced by the azido group which is then reduced by $LiAlH_4$ to give 6-amino-6-deoxyamylose.[2288] 2,6-Di-*O*-tosylamylose can be converted by anhydrous hydrazine into hydrazine derivatives, which on reduction with Raney nickel give aminated starches.[1823]

In an approach to heparin analogs from starch and amylose a synthesis of 2-amino derivatives of these polysaccharides was developed.[2289] The 6-hydroxyl groups in the D-glucose residues were first protected by tritylation followed concurrent by protection of the 3-hydroxyl groups and oxidation at C-2 in reaction with dimethyl sulfoxide in acetic anhydride. The 2-keto groups then reacted with hydroxylamine in pyridine to give the corresponding oximes. The 2-aminopolysaccharides were obtained by reduction of the oxime with $LiAlH_4$. Deprotection, oxidation (O_2, Pt) at C-6, and *N*-sulfation led to potential heparin analogs.[1801,2289] *O*-(Tosyl)starch reacted also with sodium azide followed by acetylation and reduction with lithium aluminium hydride. In this manner, 6-amino-6-deoxystarch and 2(3),6-diamino-2(3),6-dideoxystarch were prepared.[1822] In another approach, oxystarch was reacted with either ammonia[2290] or dimethylamine[2291] under hydrogen with a Cu-Ni-Cr catalyst.

Starch reacts with proteins. In his early papers, Samec[2292] assumed that simple blending of potato starch with a protein resulted in the binding of basic groups of

the protein to acidic phosphoric acid groups of amylopectin. This hypothesis was later proven.[2293,2294] At elevated temperatures, Maillard-type reactions take place, which are responsible for the development of secondary food aromas. Covalent bonding of a protein with starch can be achieved by crosslinking both components with formaldehyde.[2295]

Several publications describe reactions of starch with reagents containing amino groups. The amino reagents used in such reactions are listed in Table II. Either starch amino esters or starch amino ethers result, depending on the reagent used.

2. Amino Esters

Most of the amino starches described in the literature contain amino groups in the side chains. They can be introduced either directly or indirectly. The latter case is illustrated by the reaction of starch with 4-nitrobenzoyl chloride, followed by reduction of the 4-nitrobenzoylated starch with aqueous sodium hydrogensulfite[2417] or thiourea dioxide[2418] to give (4-aminobenzoyl)starch.[2417]

The formation of a trinicotinate was reported.[2409] The best method of preparing this starch derivative involved reacting nicotinoyl chloride hydrochloride and starch in boiling pyridine.[2410] Starch isonicotinates and 4-(sulfinylamino)benzoates were subsequently prepared. Starch isonicotinate was further cationized by treating it in nitromethane solution with methyl 2-(chloroacetyl)lactate or benzoylhydrazide *N*-chloroacetate and 1-[2-(chloroacetoxy)propanoyl]-3-methylpyrazole.[2411]

3. Amino Ethers

Various aminoalkyl and alkylaminoalkyl halides react with starch in alkaline media and are readily available by the reaction of epichlorohydrin with primary, secondary, and tertiary amines and even aqueous ammonia. Prior to the reaction with starch, the quaternary ammonium compounds were either decomposed to free amines, or they reacted as amminium compounds to give cationic aminium starches. Cationic starches were produced by the reaction of starch with arylalkylaminoalkyl epoxides. In the presence of formaldehyde, inorganic ammonium salts provided the source of amino groups.[1316]

Products free of unreacted epihalohydrin were provided by glycidyltrialkylammonium acetates.[2390] Starch underwent crosslinking by epichlorohydrin

TABLE II
Amino Reactants with Starch

Group Introduced	Reagent	Reference
$C(NH_3^+)=NH$	Cyanamide	2296–2301
$C(NHCOC_{18}H_{35})=NH$	Acylguanidine	2302
$[C=NH(NHCOC_6H_4ONH)=NHC]$	Diacyldiguanidine	2302
$C([N(CH_2CH=CH_2)_2]=NH$	Diallylcyanamide	2303
CH_2NEt_2	Chloride	2304
$CH_2CH_2NH(CH_2CH_2NH)_nCH_2CH_2$	Dichloride	2305
$CH_2CH_2NMe_2$	Chloride	2306,2307
	Epoxide	2308,2309
$CH_2CH_2NEt_2$	Chloride	1689,2307,2310–2333
	Aziridine	2334,2335
$CH(CH_2N^+HEt_2Cl^-)_2$	Chloride	2336
CH_2CH_2-N-morpholyl	Chloride	2324,2337
$CH_2CH(NEt_2)_2$	Chloride	2338
$CH_2CH_2CH_2NMe_2$	Chloride	2307
$CH_2CH_2CH_2N^+Me_3Cl^-$	Chloride	2339–2341
$CH_2\ CH_2CH_2CH_2CH_2N^+Et_3Cl^-$	Chloride	2339,2342
$CH_2CH_2CH_2CH_2N^+Me_3Br^-$	Bromide	2339
$CH_2CH_2CH_2CH_2CH_2N^+Me_3Br^-$	Bromide	2339
$CH_2CH=CHCH_2N^+Me_3Cl^-$	Chloride	2339,2343–2346
CH_2CH_2NHCO-1-aziridine	Chloride	2347
$CH(Me)CH_2NMe_2$	Chloride	2306
$CH(Me)CH_2CH_2CH_2NEt_2$	Bromide	2306
$CH_2CH(OH)CH_2NH_2$	Chloride	2348
$CH_2CH(OH)CH_2NMe_2$	Epoxide	2307,2311
$CH_2CH(OH)CH_2NBu_2$	Epoxide	2318
$[CH_2CH(OH)CH_2]_2CHNHPh$	Diepoxide	2318
$CH_2CH(OH)CH_2$-N-pyrrolidyl	Epoxide	2307
$CH_2CH(OH)CH_2N^+Me_3Cl^-$	Chloride, bromide,	2340,2345,2349
	and epoxide	2350–2376
$CH_2CH(OH)CH_2N^+Me_3HSO_4^-$	Epoxide	2377
$CH_2CH(OH)CH_2N^+Me_3MeCOO^-$	Epoxide	2348
$CH_2CH(OH)CH_2N^+Et_3Cl^-$	Chloride	2378
	Epoxide	2378
$CH_2CH(OH)CH_2N^+Et_2(CH_2OH)Cl^-$	Chloride	2379
$CH_2CH(OH)CH_2N(CH_2CH_2OH)_2$	Epoxide	2380
$CH(CH_2OH)CH_2N^+Me_3Cl^-$	Chloride, bromide	2349,2381–2383
$CH_2CH(OH)CH_2N(Ph)Et$	Chloride	2324
$CHCH(OH)CH_2N(i\text{-}Pr)_2$	Chloride	2324
$CH_2CH(OH)CH_2N(CH_2Ph)_2$	Chloride	2384
$CH(CH_2OH)(CH_2)_{12}NMe_2$	Chloride	2349
$CH(Me)CH_2N^+Me_3Br^-$	Chloride, bromide	2349
$CH(Me)(CH_2)_4N^+Me_3Br^-$	Chloride	2349
$CH(CH_2OH)CH_2N(CH_2Ph)Me_2$	Chloride	2349
$CH(CH_2OH)CH_2N)Me_2$	Chloride	2349

TABLE II
(*Continued*)

Group Introduced	Reagent	Reference
$CH_2CH(OH)CH_2NMe_2$	Epoxide	2385
$CH_2CH_2(OH)CH_2N^+Me_3Cl^-$	Epoxide	2385–2387
$[CH_2CH(OH)CH_2]_3N$	Trichloride	2348
$CH_2CH(COOEt)NEt_2$	Bromide	2388
$CH_2CH(CONH_2)NEt_2$	Bromide	2389
$CH_2CH(OH)CH_2^+NMe_3$ AcO^-	Epoxide	2390
$CH_2CH(OH)CH_2NBu_2$	Epoxide	2306,2342
$CH_2CH(OH)CH_2NEt_2$	Epoxide	2391,2392
$CH_2CH(OH)CH_2N^+Et_3Cl^-$	Epoxide	2325,2393–2397
$CH_2CH(OH)CH_2CH_2N^+Me_3Cl^-$	Epoxide	2398–2400
$CH_2CH(OH)CH_2CH_2N^+Et_3Cl^-$	Epoxide	2398,2399,2401
$CH_2CH(OH)N(Me)CH_2Ph$	Epoxide	2398
$CH_2CH(OH)N^+(C_{12}H_{25})Me_2Cl^-$	Epoxide	2398
$CH_2CH(OH)N^+(Ph)Me_2Cl^-$	Epoxide	2398
$CH_2CH(OH)$N-piperidyl	Epoxide	2398
$CH_2CH(OH)N^+$-Et-piperidyl Cl^-	Epoxide	2398
$CH_2CH(OH)N^+$-Et-morpholyl Cl^-	Epoxide	597,2398
$CH_2CH(OH)N^+(CH_2CH{=}CH_2)_2Me$ Cl^-	Epoxide	2398
$CH_2CH(OH)N^+(C_{18}H_{36})Me_2Cl^-$	Epoxide	2398
$CH_2(Me)CH_2NMe_2$	Chloride	2311
$CH_2CH(OH)CH_2NBu_2$	Epoxide	2311
$CH_2CH(OH)CH_2$-1-pyridinium$^+Cl^-$	Chloride	2402
$CH_2CH(OH)CH_2$-1-(2-Me-pyridinium)$^+Cl^-$	Chloride	2402
$CH_2CH(OH)CH_2$-1-(2,6-di-Me-pyridinium)$^+Cl^-$	Chloride	2402
$CH_2CH(OH)CH_2$-1-(2,4,6-tri-Me-pyridinium$^+Cl^-$	Chloride	2402
CH(Me)CH(OH)N(Me)Ph	Epoxide	2311
CH(Me)CH(OH)-N-piperydyl	Epoxide	2306,2313
$(CH_2)_{18}N^+Me_3Cl^-$	Chloride	2403
CH(Me)CH(OH)N(Me)CH(OH)CHMe	Diepoxide	2404
$[CH(Me)CH(OH)]_2N(CH_2)_3N(C_{18}H_{35})CHCH(OH)Me$	Triepoxide	2405
$CH_2CH_2CONH_2$	Acrylamide	2406
CH_2CH_2-N-succinyl	*N*-vinylsuccinimide	2407
CH_2CH_2-N-pyrrolidonyl	*N*-vinylpyrrolidone	2407
CH_2CH_2-N-phthalyl	*N*-vinylphthalimide	2407
CH_2CH_2-N-oxazolidonyl	*N*-vinyloxazolidone	2407
CF_2CH_2-1-pyridinium$^+Cl^-$	Fluoride	2408
CO-3-pyridyl	Chloride	2409–2411
CO-4-pyridyl	Chloride	2411
CO-4-pyridinium$^+$ salts		2411
CO-C_6H_4-$NHSO_2H$-4	Chloride	2411
$CONHC_6H_4OEt$-4	Starch chloroformate	2412
$COCH_2$-1-pyridinium$^+Cl^-$	Chloride	2413
$COCH_2CH_2$-1-pyridinium$^+Cl^-$	Amide	2408

TABLE II
(*Continued*)

Group Introduced	Reagent	Reference
$CON(CH_2OH)CH_2N(alkyl)CH_2NH_2$	Triazone	2414
$COC_6H_4NH_2$-2	Isatoic anhydride	1921,2415
$OCH_2CH_2CONH_2$	Ether	2408
1,3,5-tris[$CH_2CH(O)CH_2$]	Hexahydro-*s*-triazine ether	2408
$SO_2C_6H_4NH_2$-2	Fluoride	2416
$SO_2C_6H_4NH_2$-3	Fluoride	1827,2416
$SO_2C_6H_4NH_2$-4	Fluoride	1827,2416
$SO_2C_6H_3Cl$-3-NH_2-4	Fluoride	1827,2416
$SO_2C_6H_3$ Me-3-NH_2-4	Fluoride	1827,2416

with simultaneous amination in the presence of perchloric acid. The 3-chloro-2-hydroxypropyl derivative initially formed was substituted by amines in the 3 position of the side chain. 2,2-Iminobis(ethanol) was also used.[2380] The same idea was utilized in the reaction of starch with propylene oxide and 2-aminoethanol.[2419] Several other amines have been used.[2420,2421] These materials were used to trap heavy-metal components of complex anions, for instance, $Cr_2O_7^{2-}$, $HgCl_4^{2-}$,$[Fe(CN)_6]^{4-}$ and others. Starch treated with epihalohydrins and diethylene triamine has also been used as a paper coating having good ink receptivity.[2422] Starch containing diethanolamine, ethylenediamine, and tetraethylenepentamine ligands effectively trapped heavy metal cations.[2423] For this purpose, starch was modified to contain either amino- or imino-hydroxamate substituents ($-CH_2NHCH_2CH_2CONHOH$ and $=NCH_2CH_2$ CONHOH, respectively).[2424]

Derivatives of methyl and ethyl secondary and tertiary amines have been frequently studied, but there are also several examples of starch derivatives containing other amines.[2384,2425] Chloride and bromide have been most frequently the anions of the quaternary moiety, but sometimes other quaternary salts have been prepared, for instance, acetate[2341,2390] and sulfate.[2377] In the latter case the chloride anion was exchanged by sulfate by using the corresponding anion exchanger. The sulfamate ($H_2NSO_3^-$) anion has also been introduced.[2426,2427] Such derivatives served as retention and dewatering aids and improved the strength and uniformity of paper. The exchange of anionic halides of cationic starches by phosphate anions can be achieved with countercurrent streams of cationic starch and disodium hydrogenphosphate.[2428]

Studies performed on the etherification of potato amylose and amylopectin with (diethylamino)ethyl chloride showed that amylose in the starch granule was more reactive than amylopectin.[2429] However, the relative reactivity of both starch components could be changed by physical pretreatment of the granules, for instance, by milling, heat–moisture treatment, freeze–thawing, and chemisorption. The physicochemical properties of amino starches depend on the starch variety reacted.[2430] Among potato, sweet potato, rice, wheat, and tapioca starch studied, the last reacted most readily.

The use of aminoalkyl epoxides prepared from amines and epichlorohydrins is convenient, but impurities present in the epichlorohydrin also caused crosslinking of starch. To eliminate this crosslinking, the use of allyl halides was proposed at the starting point. Allyl chloride was treated with amines and the product oxidized by hypochlorite to give the epoxide.[2393,2394] Allyltrialkylammonium compounds were treated with either chlorine or bromine in aqueous solution, and the resulting halohydrins were subsequently allowed to react with starch.[2349] Contact with either hydrochloric acid or enzymes decreased the molecular weight of cationic starches and improved their aqueous solubility.[2431] It was reported that one of the two bromine atoms in the ethyl ester of 2,3-dibromopropanoic acid reacts with starch. Diethylamine and the second bromine atom reacted with starch giving 2-[(ethoxycarbonyl)diethylammonio]ethyl starch.[2388]

Based on experiments with 2-(diethylamino)ethyl chloride, it could be observed that etherification of the glucose units occured preferably at the 2- and 3-hydroxyl groups, although the 6-hydroxyl groups were also involved to a certain extent.[2432] As etherification at the 2-position increased, substitution at 6-OH decreased, whereas substitution at 3-OH also substantially increased. The effects of reaction time, temperature, and the reagent ratio on the reaction of 3-chloro-2-hydroxypropylamines and glycidyltrimethylammonium salts with starch have been studied in more detail.[2348]

Side chains containing amino groups could also be introduced by treating starch either with aziridine,[2433] its sulfur dioxide complex,[2334] its derivatives, for instance, 2-chloroethyl-(1-carbonylamino)aziridine,[2347] or with ethers having a general structure ROCHR′CHR″X activated by a strong electron-withdrawing group X, such as NO_2, $CONH_2$, CHO, COMe, or a quaternized pyridine ring. Under some conditions, the activating groups could also enter the reaction and, as a consequence, crosslinking occurred. Reactions were catalyzed by alkali.[2408] N^1-Alkyl-N^3-methylhydroxy-N^5-H-triazin-4-ones reacted with starch (probably in the amido moiety of these compounds).[2414] Isatoic anhydride and its 5-chloro- and 5-nitro derivatives were also patented for the same use.[1921,2415] Starch

anthranilates fluoresce upon exposure to UV light.[2434] Following diazotization, the diazonium salts crosslinked. The transformation of (diethylamino)starch into an aldehyde by its reaction with 5-(hydroxymethyl)furan-2-aldehyde dimethyl acetal was proposed.[2434]

Aminoarenesulfonyl fluorides readily react with starch.[1827,2416] The structure of the starch aminating reagent has not been always fully recognized. For instance, amination of starch with the reaction product of 1-(2-hydroxyethyl)-2-*N*-heptadecenyl-2-imidazoline with either 1,4-dichloro-2-butene, epichlorohydrin, *n*-octyl chlorothioformate, divinyl sulfone, ethylene oxide, or acrylonitrile was reported.[2435] Such products exhibited good pasting characteristics, absorption of dyes, and optical clarity upon aging of the pastes.

Complexes of quaternary trialkylammonim halides with amylose and amylopectin were formed, which immediately precipitated from solution.[2436,2437] Ion-exchange resins were obtained by reacting dialkylaminoalkyl chlorides with starch crosslinked with glycerol 1,3-dichlorohydrin prior to formation of the amino ether.[2438] Strong crosslinking, necessary for ion-exchangers, was also achieved by the use of diepoxides.[2404] The introduction of alkylamino groups into starch, (hydroxypropyl)starch, and dialdehyde-crosslinked starch acetals was also patented as a method of preparing paper sizes[597,2316,2328] and textile finishes.[2439] The hydroxypropyl moiety could also be introduced to starch in a single substituent together with a cationic ammonio group, for instance, with (2-chloro-3-hydroxypropyl)trimethylammonium chloride[2440] and (3-chloro-2-hydroxypropyl)trimethylammonium chloride.[2387] Such cationized starch was then additionally phosphorylated with sodium hydrogenphosphate to form cationic and, simultaneously, anionic starch.[2441]

Aminated starches have been further converted. For example, dimethylaminoethyl starch could be converted into glycosides by alcoholysis,[2442] phosphorylated with sodium dihydrogenphosphate, and oxidized with hydrogen peroxide to carboxyl derivatives.[520] Additional information on this subject can be found in Section VII. 2-Hydroxypropyltrimethylammonium chloride starch has been crosslinked with epichlorohydrin.[2443] In contrast to amination, which requires basic solutions, phosphorylation occurs at pH 6.[2444]

Another approach to the synthesis of amino starches having amino groups in the side chains involves reactions of starch with nitrogen-functionalized vinyl monomers containing either amino groups (for instance, acrylamide) on moieties that can be transformed into amino groups (for instance, acrylonitrile, which can be reduced to the propylamino group after reaction with starch).[2445] Crosslinking by reacting starch with hexahydro-1,3,5-triacyloyl-*sym*-triazines is

also possible.[2446] Cyanoethyl starch reacted with ethylenediamine in the presence of sulfur or sulfur compounds to produce useful coagulants for paper sizes.[2447] Reactions of hypochlorite-oxidized starch with vinyl monomers has also been described.[2448] An interesting method for synthesis of cationized starch is the reaction of quaternized pyridine with starch monochloroacetate.[2449] A unique aspect of this synthesis, in contrast to other methods in which the starch reagent behaves as a nucleophile, is that the starch derivative acted as an electrophile with respect to the amino reagent. Other examples of such a reversed approach to the reactivity of the starch reagent include the reaction of *N*-chlorocarbamoylethyl starch with amines,[2450] *N*-chloroacetyl derivatives of amines with starch,[2451] starch with *N*-2-chloroethyl-4-(3-chloropropyl)pipieridine hydrochloride,[2452] and the reaction of starch chloroformate with phenethylamines. When 2-diethylamino-4,6-dichloro-*sym*-triazine was reacted with starch, only one chlorine atom of the reagent was involved, and crosslinking did not occur.[2453]

Several attempts have been made to bind dyes to starch, amylose, and amylopectin.[2307,2454,2455] Other starch-based dyes were prepared from starch and corresponding trichloropyrimidine or chlorotriazine derivatives. It was reported that these base-catalyzed reactions proceeded at room temperature within one day.[2456]

4. Amination of Starch Derivatives and Cereals

Cereal flours can also be cationized. For example, kneading machines have been used in which flour blends were processed with ethylenimine. Cationic efficiences were between 83 and 99%, and such functional properties as burst retention and tensile strength increased with increases in the ethylenimine concentration up to the level of 3 wt.%.[2457,2458] Such reactions were also carried out in a two-step process. First, starch was treated either with ethylene oxide or propylene oxide, followed by reaction with ethyleneimine.[2459] Aminoethylation of cereals[2459] and starch[2460] with aminoalkyl chlorides was carried out followed by epoxyethylation or epoxypropylation. In the reaction with starch, propane sultone was also used as a co-reagent.[2461–2464] Cationization of starch blends with millet corn and maltodextrin[2465] as well as degraded starches[2466] has been described.

Starch dialdehyde is also reported as a convenient precursors for cationization. Its reaction with betaine hydrazide hydrochloride gave the corresponding bis(dimethylmethanaminiummethylhydrazone) hydrochloride.[2467] Bromine-

oxidized starch was coupled with 1-aminodecane by reductive amination.[2468] Soon afterward, experiments were published on the reaction of amino polymers with starch and its derivatives, for instance, starch oxidized by sodium hypochlorite.[2469] Starch was also allowed to reacted with ammonia–epichlorohydrin–dimethylamine copolymer in the presence of hydrogen peroxide.[2470] Starch could be oxidized prior to this reaction.[588] Japanese patents claimed the reaction of starch with dimethylamine–formaldehyde–phenol–epichlorohydrin,[2471] with acrylic acid–sodium acrylate–*N,N′*-methylenebisacrylamide[2472] and with polyethylene glycol nonylphenyl ether–poly(vinyl alcohol)–epichlorohydrin–trimethylamine.[2473] The reaction of starch with poly(1-acryloyl-4,4-dimethylpiperazinium) methyl sulfate was also described for pulp krafting.[2474] Starch dialdehyde reacts with polyethyleneimine[2475] and with quaternary ammonium salts.[2476] Amino starches from the condensation of starch dialdehyde with *p*-phenylenediamine were reported to sorb mercury.[2477] Nitroalkanes condensed with starch dialdehyde and the products reduced with ammoniacal iron(II) hydroxide also produced aminopolysaccharides[539] (additional information on this subject can be found in Section VI).

The treatment of (cyanoethyl)starch with hydroxylamine[2478] and its salts gave a cationic amidoxime which was used as a paper strengthener,[2479] and it was also useful in the removal of heavy metal cations from wine.[2480] An amidoxime was also prepared from epichlorohydrin-crosslinked (cyanoethyl)starch.[2481] There are reports on cationic graft polymers, and these are detailed separately in Section XVI, together with other graft polymers.

The majority of published procedures for starch cationization involve processing of reagent and catalyst slurries. A continuous manufacturing process has been described.[2482,2483] Several dry-heating processes involve a tertiary amine, epichlorohydrin, and unswollen starch, reacting without catalyst at 80–135 °C,[2484] upon base catalysis,[2485] upon storing blended reagents,[2486,2487] and later by extrusion cooking.[2488–2490]

Cationic starches, for instance 2-hydroxy-3-trimethylammoniopropyl starch chloride, can be combined with anionic fluorescent whitening agents, such as diaminostilbenedisulfonate, in order to produce fluorescent starch.[2491] Unfortunately, despite their low cost and easy application, cationic starches have little prospect for use as soil stabilizers because of their low activity, which is independent of the metal ions present in the soil.[2492]

Several attempts have been made to prepare cationic ammonium starches with better performance and lower costs in a variety of industrial applications. Examples include starches blended with clay.[2493–2510]

5. Applications

Amino ethers (either free, or preferably cationized) have a broad range of current and potential applications in paper manufacturing as coatings and sizes that improve paper strength, retention of pigments and dyes, the production of conductive coatings, textile finishes, and other uses.[597,1689,2311,2316,2317,2320,2328,2332,2333,2336,2338,2385,2408,2422,2427,2439,2448,2477,2511–2527] The production of antihalation layers by suspending MnO_2 in cationic starches has been described.[2318] There is also a patent for improving the rheological properties of a clay ceramic mass by the addition of cationic starch.[2528] In the textile industry, cationic starches have been used as fiber sizes.[2313,2322] Use of cationic starches in the processing of poly(vinyl alcohol) was also reported.[2529] Cationic starches have also been used as starching agents in laundering.[2368]

Starch-based quaternary ammonium and aminium sizes exhibit effects that are strongly dependent on both the pH[2530] and temperature.[2531,2532] Cationic starches were also reported as components of various latexes,[2314] as additives that decrease fluid loss (filtration rate) during aqueous drilling of soils,[2533] and also as coatings for glass fibers.[2305] Some starch aminoalkyl esters and ethers were also reported as animal food supplements.[2534] Non-cationized aminostarches, such as diethylamino starch, 3-(*N*-phenylethylamino)-2-(hydroxypropyl)starch, 3-(diisopropylamino)-2-(hydroxypropyl)starch, and 2-(morpholinethyl)starch, were shown to improve the biodegradability of polyesters in soil.[2324,2397]

Starch anthranilates were proposed as optical brighteners. They improve the retention of inorganic fillers and fiber fines in paper processing.[2535,2536]

Biologically active phenethylamines can be bound to starch, providing stable and prolonged levels of a selected drug in an organism as a result of slow hydrolysis.[2412] Cationized starch can be obtained by crosslinking it with iminodiacetic acid.[2537] This product has been used to remove cadmium and copper from electroplating baths. The trisodium salt of 6-[2-sulfo-4-(4-amino-3-sulfo-1-anthraquinonamino)]anilino-4-[x-sulfoanilino]-1,3,5-triazine-2-yl-(hydroxyethyl) starch was prepared as a stationary phase for affinity chromatography of enzymes and enzyme-inhibitor applications.[2538]

Several applications of starches containing triazine groups were reported. Those containing alkyltriazinone groups were proposed as additives for waste flocculation.[2414] Use of ion-exchange resins for fractionating polysaccharides and other biopolymers was proposed.[2539] The disodium salt of (2-[8-hydroxy-3,6-bis(sulfo-1-naphthylamino)]-4,6-dichloro-*sym*-triazino) starch is useful in isoenzyme analysis.[2540]

(Diethylamino)ethyl starch hydrochloride has also been used to dewater starch slurries.[2541] The 2,4-bis(hydroxymethylamino)-*sym*-triazine-6-yl ether of starch phosphate was designed as antistatic additive for synthetic fibers.[2542] Amylopectin having Remazol Brilliant Blue R, Cibachron Blue, Procion Yellow, or Procion Brilliant Red bound to starch is useful in amylase determinations.[2306,2454,2455] The efficiency of a cationic starch in bleached pulp can be determined spectrophotometrically by using the Halopont Blue RNM pigment dispersed by an anionic agent.[2458]

Additional information on cationic starches can be found in several other publications.[1695,2543–2545]

XIV. Carbamoylation

1. Syntheses with Isocyanates

Starch reacts with isocyanates to produce carbamates (urethanes), which are esters of carbamic acid. Several reactions of starch with phenyl-, various aryl-, 1-naphthyl-isocyanates or 1,6-hexamethylene- and 2,4-tolyl-diisocyanates were conducted either in pyridine or morpholine below the boiling point of these solvents.[2546–2548] In each case all three hydroxyl groups of the glucose units reacted to give tricarbanilates, provided a sufficient amount of the isocyanate reagent was used.

Differences in the penetrating ability of the solvents might account for variations in behavior, however, dextrans, in which the penetration is perhaps of little importance, gave an insoluble carbanilate when the reaction was carried out in pyridine, whereas they give a soluble chiral product, when the reaction is performed in morphline. Starch carbanilates could be separated into amylose and amylopectin carbanilates upon stirring in ethyl acetate.[2548] Tricarbanilates of starch and modified starch have been used for molecular-weight characterization of starch and its modifications; the products were transformed into tricarbanilates, which were separated by high-performance gel-permeation chromatography.[2549] The use of toluene-2,4-diisocyanate caused crosslinking of starch, with one crosslink on average introduced for every 14th glucose unit, whereas hexamethylenediisocyante introduced one crosslink every 500 glucose unit.

The carbamates have hydrophobic surfaces and are resistant to swelling not only in water, but also in the presence of such strongly swelling reagents as 4 M aqueous

calcium chloride. The substituent effect in the aryl moiety of the carbamates was evaluated using measurements of specific rotation, melting points, solution viscosity, and solubility.[2550] The reaction is also feasible in aqueous solutions, but is hindered in toluene, triethylamine, and benzyldimethylamine. Further studies revealed that the reaction could be conducted in nonpolar solvents (for instance, benzene), provided a catalytic amount of pyridine was added. For reagents having two diisocyanate groups, either one group could react, or both could be consumed in different reactions.[2551] In this manner, water-soluble carbamates could be obtained. Starch polyurethanes can be produced in a twin-screw extruder.[2552] Ultraviolet crosslinking could be initiated when starch esters and/or ethers contained unsaturated (C=C) bonds.

Phenyl- and other aryl-carbamates of starch appeared to be nontoxic to *Aspergillus oryzae, Aspergillus niger, and Penicillium expansum*.[2550] 2-(Hydroxypropyl)starch carbamate was also tested without any particular success in enzyme-immobilizaton studies.[2553] Improvements in the weight gain of ruminants upon feeding with fodder supplemented with carbamates was reported.[2554]

Dialkylcarbamates were produced by the reaction of starch with dialkylacarbamoyl chlorides in aqueous suspensions, with reaction yields as high as 83%.[2555] These reactions are localized at the surface of starch granule.[2556]

Polyurethanes were subsequently prepared from hydroxyalkyl ethers of starch. Here, the reacting hydroxy groups of polysaccharide are mainly those in the side-chains. Polyurethanes were obtained in the form of rigid foams, which did not turn yellow during 5 months of aging.[2557,2558] By changing the ratio of starch-(or its polyhydroxyalkylene ether)-to-diisocyanate, flexible materials could be produced.[2559] The stability of the foams could be improved by the addition of such sulfur compounds as didodecanoyl thiodipropanoate and thiodiethylene bis(3,5-di-*tert*-butyl-4-hydroxy)hydrocinnamate as antioxidants.[2560] The use of swollen starch improved the elastic modulus of foams.[2561]

Modifications of polyether polyols are the subject of many patents. In several patented applications, either starch, high-amylose varieties, yellow dextrins[2562] or hydrolyzates from dextrins through to monosaccharides could be combined with various alkylene ethers or polyalcohols and were treated with propylene oxide. Such polyether polyols also controlled the foam rigidity. Polyurethane precursors of lower viscosity were claimed using 2-methoxyethanol,[2563] and ethylene oxide,[2564] and other alkylene oxides[2565] were proposed in place of propylene oxide to form polyether polyols. The use of partly esterified starches also brought good results. Esters of higher fatty acids, such as octanoic, dodecanoic, hexadecanoic, octadecanoic, and also aromatic acids including benzoic acid could

be crosslinked in nonpolar solvents. Increases in the degree of esterification improved the mechanical properties of starch-based polyurethanes.[2566] These results depended on the content of starch derivative content in the polyurethane. The highest reactivity was observed with esters having a degree of esterification as high as ~0.2.

2. Reactions with Acrylamides

Carbamoylethyl starch, a propanoamide starch ether, results upon by alkaline hydrolysis of the reaction product of acrylamide with starch.[2385,2406,2567] This reaction has been thoroughly studied.[2566,2568] Attempts to perform Hofmann rearrangement of the carbamoylethyl group by means of NaOCl gave the chloroamide. The reaction, having activation energy of 61.5 kJ/mole, obeyed second-order rate kinetics.[2569] The activation energies for starch oxidation by NaOCl and decarbamoylation were 71.1 and 87.9 kJ/mole, respectively.[2570] Thick pastes were obtained by reacting *N,N′*-methylenebisacrylamide at pH 5–6 and at temperatures between 27 and 55 °C.[2571] A reaction with *N*-hydroxymethylacrylamide required the use of an alkaline solution.[2572] The reaction could be carried out simultaneously with the involvement of formaldehyde.[2573] Either starch was first reacted with acrylamide and then crosslinked with *N,N′*-methylenebisacrylamide,[2574] or starch reacted first with *N,N′*-methylenebisacrylamide followed by polymerization with dimethylaminoethyl methacrylate.[2575] The product was designed as an anion exchanger. (Isobutoxymethyl)acrylamide gave a corresponding substituted carbamoyl starch.[2576] *N*-Hydroxymethylacrylamide reacted with starch with the elimination of water, and in this manner, the C=C double bond was retained.[2577] Other *N*-vinyl compounds have also been used, including *N*-vinylpyrrolidone, *N*-vinylsuccinamide, *N*-vinylphthalimide, and *N*-vinyloxazolidone.[2407,2578] Production of a so called "durable-press finish" for cotton by the addition of zinc nitrate was reported.[2579] Condensation of starch with polyacrylamide in the weight ratio of 1:4 was also patented.[2580] Quaternization of carbamoylalkylstarch is beneficial for paper sizing applications.[2581] Crosslinking of an acrylic acid–*N,N′*methylenediacrylamide–sodium acrylate–starch graft copolymer was reported to produce polyurethane foams having water sorbing characteristics.[2582,2583] Bis(acrylamide)acetic acid acted as a crosslinking agent, giving a superabsorbing product with a water holding capacity of 30–60%.[2584] In the reaction of starch with acrylamide 2-[(dimethylamino)methylcarbamoyl]ethyl starch ether was

produced.[2585] Crosslinking of a starch–acrylamide–*N,N′*-methylenediacrylamide graft copolymer was reported to produce hydrophilic polyurethane.[2586] Crosslinking copolymers of 80% starch dialdehyde copolymerized with isobutylene–maleic anhydride copolymer gave a waterproof polyurethane.[2587] Esters of starch with dicarboxylic acids could also be used instead.[2588] A process of co-crosslinking with cellulose nitrate was patented.[2589]

A convenient route to the production of starch carbamates was presented[2386,2590–2593] in which starch reacted with acrylonitrile and, subsequently, partly hydrolyzed into carbamates.

3. Reactions with Ureas

An alternative route to starch carbamates involves the reaction of starch with urea.[2594–2598] The reaction requires an elevated temperature.[2599] There are reports that reactions of starch with urea could be carried out simply by heating the reagents in a solid blend to 165 °C,[2600] 130 °C,[2601] and even at 110 °C,[2602] but there is also the report[2594] that evidently, heating to120 °C was insufficient because 70% of the nitrogen remained in the reaction mixture and only 14% of urea nitrogen was bound to starch. A group of Chinese workers applied high temperature and pressure in the presence of strong mineral acids.[2603,2604] This reaction was also performed in a microwave oven during 10–15 min and without any catalyst.[1994,2283] Later studies showed increased yields and range of carbamation by increasing the urea concentration as well as the reaction time and temperature.[2598] Formation of a triamidostarch having adhesive properties by the simple process of boiling urea and starch in an aqueous solution was reported.[2605] The reaction was much later extended to the use of urea in combination with hexamethylenetetramine (urotropine)[2606] and many other carboxyamides, which were heated with granular starch to 130–140 °C with or without the addition of phosphates.[2607,2608] A reaction carried out in boiling toluene gave a product containing 6.75% of nitrogen.[2098,2609,2610] A later patent claimed that lower temperatures were sufficient to perform the reaction.[2610–2612] The component ratio of 1:2 containing 10–15% moisture at 150 °C for 3 h seemed to be optimal reaction parameters.[2695] The reaction usually required an acid catalyst. Use of elevated pressure was reported, with the slurry being pressed through a nozzle. The solubility of polyurethanes depends on the same factors, and, additionally on the starch variety. The use of pregelatinized starch was beneficial for solubility of the final product. A starch-to-urea ratio of 3:1 in order to obtain a hot-melt adhesive was patented.[2601]

Urea derivatives were also used, for instance, *N*,*N*′-di(hydroxymethyl)-*N*,*N*′-ethyleneurea.[2613] It was reported that the use of bis(hydroxymethyl)urea required pH 4.1 at the initial stage of blending with corn starch. The reaction was made alkaline to litmus and heated for 2 h at around 80 °C.[2614] Similar reaction conditions were required for the reaction with bis(hydroxymethyl)ethyleneurea.[2615] Later, starch was condensed with cationic poly(urea amides) and cationic polyamides.[2616] Starch "anilides" were also prepared.[2617] The carbamoyl moiety can also be introduced into starch by reacting carboxyamides with active halogen atoms in the acyl groups. Thus 2,3-dibromopropanamide gave 2-carbamoyl-3-(diethylamino)ethyl starch.[2389]

Cationization of carbamates is possible by reacting starch with amides in the presence of mineral or carboxylic acids[2618] or by utilizing the Mannich reaction.[2619]

Water-soluble resins for textile sizing were obtained when starch was heated to 80–180 °C with either cyanamide or guanidine.[2620,2621] The products were stabilized by adjusting the pH to 11–11.5, or alternatively by adding $MgCl_2$, NaH_2PO_4, or $Al_2(SO_4)_3$.[2622] Formazans can also be included in this group of compounds. They are available from starch dialdehyde phenylhydrazones and benzenediazonium salts.[330]

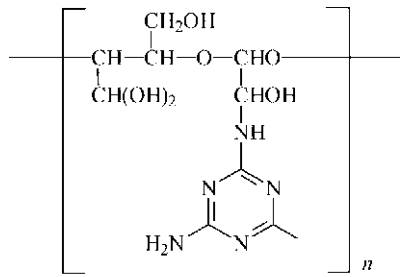
4. Reactions of Starch Polyurethanes

Modification of carbamoylated and carbaminated starches by oxidation and crosslinking with formaldehyde was reported.[2623] Crosslinking was used to produce fire-resistant construction boards.[1360] A size for cellulose fabrics was produced by crosslinking poly(carbamoylethyl)ethers of starch with formaldehyde.[1351]

5. Reactions of Starch Dialdehyde and Other Starch Derivatives

Starch dialdehyde condenses readily with amino amides[2624] and diamines,[2625] and forms oximes with hydroxylamine.[2626] The reaction of starch dialdehyde with isoniazid, 4′-formacetanilide thiosemicarbazone, 4′-aminobenzaldehyde thiosemicarbazone or thiosemicarbazone, produced the corresponding condensation products.[613–615,617,2627–2629] Hydrazones were readily formed when hydrazine and its derivatives were blended with starch dialdehyde and acidified with acetic acid[2543,2630] or simply on heating the reaction mixture.[2631] Condensation of starch

dialdehyde with melamine and its derivatives gave corresponding compounds of the general structure (**34**).[564,585,2632]



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Reaction of starch dialdehyde with urea gave a condensation product.[442,2633] Carboxyamides,[2624] including acrylamide,[524,585] were also allowed to react with starch dialdehyde. Condensation can occur between starch dialdehyde and macromolecules containing amido groups, for instance, epichlorohydrin-crosslinked polyamide resin,[598] ammonia–diethylamine–epichlorohydrin copolymer,[588] dicyanamide–formaldehyde resins,[565,566] quaternary alkylammonium compounds,[596,610,611] amino acids,[2634,2635] protein,[626,2636–2639] and aminoalkylated starch.[2515] The reactions are favored by low pH. The guanidino moieties of proteins entered the condensation the most readily.

Amidooximation of cyanoethylated starch is relevant here. The reaction of (cyanoethyl)starch with hydroxylamine at pH 7.1 and a temperature of 90 °C for 90 min produced a material used to chelate Fe(III) and Al cations.[2640] By reacting starch dialdehyde with acrylonitrile and hydrazine in alkaline solution, followed by adjusting the pH to 5–6 a glue was prepared.[2641]

6. Applications

Soluble carbamates have been considered for applications that include adhesives, pigmented coatings, paper coatings, and surfactants.[2551,2555] Starch carbamates having double bonds in the side chains are UV-curable and have been reported as coatings.[2642]

Starch carbamate block copolymers are biodegradable.[2643] During production, the reaction mixture can be supplemented with vegetable derivatives, molasses,

polysaccharide agricultural waste, and vegetable oil fractions. Biodegradability of such materials reaches 6.7% during 12 weeks of exposure to soil.[2644] In the late 1950's, starch was used as filler for polyurethane polymers in order to reduce the cost of the final products. Polyesters that were modified by reacting with diisocyanates were also molded with starch. Starch carbamate was also used for blending aminoplast or phenolic resins in order to produce wood adhesives.[2645] A synthetic leather was prepared from *p,p*'-diphenylmethane diisocyanate, polyester, and rice starch in the weight ratio of 4:1:2.5.[2646] Polyhydroxyalkyl ethers were also made by reacting starch with glycols or glycerol catalyzed by the boron trifluoride–diethyl ether complex.[2647] Alkylene oxides were also involved in the second, acid-catalyzed step of such reactions.[2648] The density of such a product was 0.034 g/mL. Starch was crosslinked with polymethylene polyphenyl isocyanates,[2648,2649] and the fire-extinguishing properties of such polyurethane were improved relative to that based on 2,4-tolylisocyanate. Fluorocarbons were also added as fire-retardants. The addition of aluminum hydroxide to improve the fire-resistance of foams was also reported.[2650] The addition of 1–2% of dipotassium 2−sulfooctadecanoate was reported to produce an open-cell polyurethane foam having over 90% open cells.[2651] Further improvements included crosslinking of polyols mixed with castor oil and the products from alcoholysis of the latter with glycol glycosides, using polymeric diisocyanates. The mixture of all components was pressure-molded at 140 °C and the properties of the products could be controlled by varying the ratio of the NCO to OH groups.[2652] In further modifications, starch was first hydrolyzed with polyphosphoric acid and then the hydrolyzate was processed with propylene oxide, and foam-stabilizing additives were introduced into the mixture, followed by reaction with polyphenylene polyethylene polyisocyanate. 1,1,3,3-Tetramethoxypropane was proposed as the stabilizer.[2653] Polyurethanes from flours have been utilized as adhesives for wood lamination.[2654]

Starch polyurethane foams could be converted into sorbents for water when starch–acrylonitrile or starch–methacrylonitrile graft copolymers were crosslinked with diisocyanates.[2655,2656] Such polyurethanes have been proposed as occlusive wound dressings,[2657] as well as sizes for cotton yarns.[2658] Starch polyurethanes for reinforced paper were produced in reaction of *N*-chlorocarbamoylethyl starch with cresol or thiolignin.[2659] The addition of mineral salts to polyurethanes prepared from starch and urea improved their performance as adhesives.[570]

Starch and urea were combined under pressure in order to produce an adhesive for corrugated paperboard[2616] and a thickener for frozen food.[2660] Carbamoylated starch could also be further reacted with formaldehyde and amines[2661] or with

acrylamide with accompanying dimethylaminomethylation,[2582] giving flocculants for sewage disposal applications.

The reaction of starch with bis(hydroxymethyl)ethyleneurea condensed with cationic poly(urea amides) and cationic polyamides was used to produce paper sizes, adhesives, and textile-finishing agents.[2616] Cationic starch that has been prepared from starch and cyanamide was patented for sizing wood and for synthetic wool fibers and fabrics.[2296,2298,2662] Reaction of starch urethanes with alkylene oxides and aldehydes was reported for use as hardenable compounds in waterproof films, coatings, and adhesives.[2663]

Thiosemicarbazones of starch dialdehyde and thiosemicarbazones and condensation products of starch dialdehyde with isoniazid were evaluated for their antituberculostatic activity, and showed positive effects with mice that were intravenously infected with *Mycobacterium tuberculosis*.[613,614,617,2627–2629] These results were contradicted by other authors[615,616] who showed acceleration of *M. tuberculosis* growth *in vitro* in contact with starch dialdehyde thiosemicarbazone. A potential application of this compound was suggested in tuberculosis taxonomy.

Starch dialdehyde crosslinked with diamines was also evaluated as a trap for Cr(III) and Cr(VI) ions.[2664]

7. Miscellaneous

The determination of the carbamoyl group in starch carbamates is based on cleavage of the carboxyamido group from the carbamate in alkaline hydrolysis. For this determination, the ammonia liberated is steam-distilled into boric acid followed by titration with 0.05 M aqueous sulfuric acid.[2665] Additional information on starch carbamates can be found in the article by Roberts.[2666]

XV. Other Sulfur-Containing Starches

Heating starch with sulfur and alkali for 12 h resulted in a product described as thiostarch, but its structure remains unknown.[2667] The structure is probably a starch complex of low molecular weight, for example, a thiaheterocyclic compound, as suggested by the other authors[2668,2669] who observed formation of these compounds

after heating starch in an atmosphere of hydrogen sulfide. Pyrolysis of starch with sulfur is a convenient method of generating hydrogen sulfide.[2670]

1. Thiocyanates

Thiocyanates acting as sulfur nucleophile, readily replace active halogen atoms in starch acylated with 2-chloroacyl anhydrides,[2671] as well as tosyloxy groups in *O*-tosyl starch.[1826,2672] Reduction of 6-deoxy-6-thiocyanatoamylose with $LiAlH_4$ gives 6-deoxy-6-mercaptoamylose.[2672] Biodegradable starch foams can be prepared from starch and poly(isocyanates) in an acid-catalyzed process.[2673]

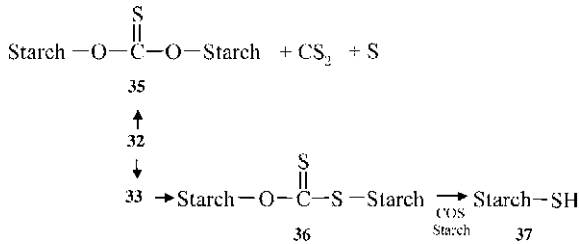
2. Thiocarbonates and Related Compounds

Thiocarbonates of the general structure, St–OC(O)SR, where St represents starch, result from the reaction of starch and chlorothioformates.[1996] Oxidation of these thiocarbonates with ClO_2, NaOCl, and $NaClO_2$ produced the monothiocarbonate disulfide[St–OC(O)SSC(O)O–St].[2674] Thionocarbonates and disulfides from them are useful as strengthening agents in paper manufacturing.[2674] Pyrolytic conversion of xanthates proceeds via intermediary dithiocarbonates[St–OC(S)S–St], which decompose further to thiolated starches.[2675] Thionocarbonates[St–OC(S)O–St] are the side products of this decomposition. It was reported that polysaccharide formazans produced thionic acid phenylhydrazides after reacting with H_2S at room temperature for 24 h.[2676]

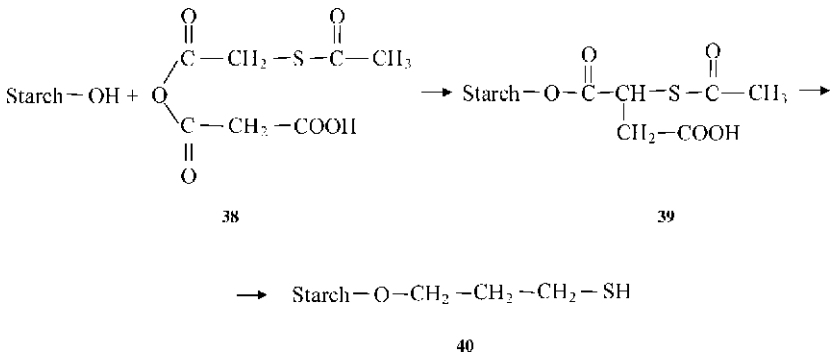
3. Thiols, Sulfides, and Sulfonium Salts

Starch thiols can have the SH group directly on the pyranose ring or in a side chain. There are several methods of synthesizing starch thiols of the first type. One of them is based on the pyrolysis of starch xanthates (**32**), but the reaction proceeds in two parallel routes: one producing thionates (**35**) and the other producing thiols (**37**).[2675,2677] Reduction of starch xanthates with $NaBH_4$ in alkali is another approach to thiols. Thiols prepared in this manner were subjected to graft polymerization with vinyl polymers. Nucleophilic substitution of the chlorine

atoms in "chlorostarch" with sodium hydrogensulfide gave thiols which are readily oxidized to disulfides. In this manner, unreacted hydrogen sulfide became trapped in a matrix of crosslinked starch.[2272]



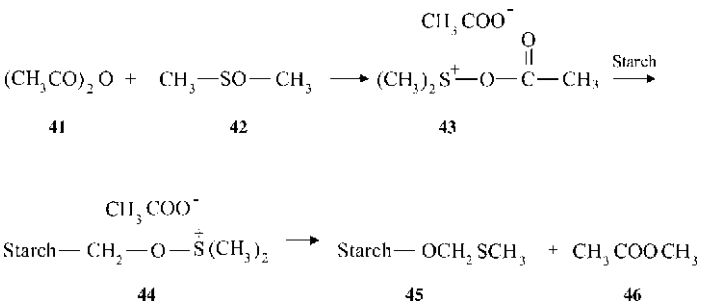
Thiols having the SH groups in side chains are available by various methods, as by reaction of starch with *N*-acylhomocysteine thiolactone.[2678] When starch reacts with epichlorohydrin, the chlorine atom in the resulting 2-hydroxy-3-chloropropyl ether can be substituted by the thiosulfato group, and the latter reduced with $NaBH_4$ to the thiol group.[2679] Thiols (**40**) were produced by reacting starch with either thiodiglycolic acid[2680] or acetylthiosuccinic anhydride (**38**).[2681]



(2-Hydroxy-3-chloropropyl)starch reacted with thioglycolic acid in tetrahydrofurane in the presence of sulfuric acid to give sulfur-crosslinked starch, which was water soluble and used for removing heavy metal ions from wastewater.[2682] Some thiols have been tested for their effectiveness in mobilizing methylmercury chloride during excretion from various organs of the human body. A significant decrease was shown in the concentration of methylmercury in the kidney, liver, and the blood of experimental animals.[2683]

Starch dialdehyde reacts with thiols to form dithioacetals.[525] Thiol groups in thiol acids undergo oxidation in air into disulfides.[2681]

The reaction of thiols with alkyl halides produces sulfides, which are converted into sulfonium halides in the presence of excess alkyl halides.[2680] Dimethyl sulfoxide (**42**) and acetic anhydride (**41**) react with starch[365] to cause oxidation at the C-3 and C-6 positions, and methylthiomethyl ethers are formed at O-6, according to the following reaction (**43**–**46**):



On the other hand, it has been demonstrated that amylose having the 6-OH group protected by the trityl group reacts with dimethyl sulfoxide in the presence of acetic anhydride to effect oxidation at C-2 and conversion of the 3-hydroxyl group into the methylthiosomethyl ether.[2289]

Dispersions of starch in dimethyl sulfoxide become stiff within 20 min when brought into contact with water.[2684] Sulfonium salts can be produced by the reaction of reagents already bearing the sulfonium moiety, as when starch is treated with 2-chloroethylmethylethyl sulfonium iodide in the presence of calcium hydroxide.[2685] The resulting formulations can be applied as paper coatings, paper adhesives, sizes, and thickeners.[2685,2686]

4. Thiourethanes

Thiourethanes reported in the literature[2142,2687–2689] are produced by treating starch xanthates with polyamines, hydrazine, diamines, or related compounds. An alternative route entails reaction of starch with thiourea at temperatures of approximately 100 °C.[2611] Viscous gels are produced whose rigidity depends on the molecular weight of the amine and the degree of substitution by xanthate. Thiourethanes were proposed as wet-end additives for paper manufacturing.[2611]

5. Thiosemicarbazones and Other Condensation Products with Starch Dialdehyde

Starch dialdehyde reacts in a manner typical for aldehydes, this is, it reacts with NH_2-X compounds, among them thiosemicarbazide and its derivatives.[615,2649] Thiosemicarbazones were prepared from starch dialdehyde and unsubstituted thiosemicarbazide in 2% aqueous butanol, and characterized as dithiosemicarbazone hydrates, possibly containing unreacted thiosemicarbazide, and monothiosemicarbazone hydrates. It was reported that the dithiosemicarbazones affected the growth of some bacteria and certain fungi,[615] promoting the growth of *Mycobacterium tuberculosis* (see Section XIV). Starch dialdehyde was used to carry other biologically active moieties condensed to its carbonyl groups. In this manner, 4,4'-diaminodiphenyl sulfone and sulfadimethoxine[4-amino-*N*-(2,6-dimethoxy-4-pyrimidinyl)benzenesulfonamide] were condensed with starch dialdehyde and the product used to treat mice infecteed with *Plasmodium bershei*.[2690]

XVI. Graft Polymers

1. Introduction

Reaction conditions necessary to carry out the modifications described earlier in this section usually result in some decomposition of amylose and amylopectin, even when simple substitution, addition, or crosslinking are involved. As a rule, graft copolymerization produces derivatives of significantly increased molecular weight. Starch grafting usually entails etherification, acetalation, or esterification of starch with vinyl monomers to introduce a reaction site for the further formation of a copolymeric chain. Such a chain would typically consist of either identical or different vinyl monomers (block polymers), or it may be grafted onto another polymer altogether.

Grafting of allyl starch[2691] and allyl glycidyl starch[2692] are examples of grafting onto to a starch side-chain reaction site. Such reactions are conveniently performed by means of interface catalysis.[2693,2694] Another example is starch maleate half-ester, which provides a double bond anchor for further grafting.[2695,2696] Grafting can also be achieved by abstraction of a labile atom, usually a hydrogen radical, from glucose units of starch by a developing polymer radical. This is equivalent to the transfer of the free-radical site and initiation of polymerization of the monomer

as a chain reaction. Attempts to avoid accompanying formation of a homopolymer are always challenging in the grafting of starch. Homopolymers can complex with starch.[2697] The anchoring of reactive sites on starch does not necessarily need to be a free-radical process, but copolymerization and grafting frequently follow a free-radical mechanism.

Depending on the grafting mode, the reaction may be considered either as graft coupling or graft polymerization. Graft coupling means that the water-soluble polymer binds to the granule surface by a covalent bond, and then the side chain expands through polymer–polymer coupling. Graft polymerization starts by fixation of the vinyl monomer on such a surface site of the granule, after which the side chain expands. Grafting was previously performed in suspension but also more refined techniques are reported. They are, for example, polymerization in isolated gel droplets,[2698] and in emulsions.[2699]

Swelling and disruption of starch granules are crucial factors that control grafting.[2700] Shorter and more frequent grafts were produced in unswollen material. Starch swollen at 85 °C gave grafts of extremely high molecular weight, whereas disrupted granules gave a more soluble product. Mechanochemical modification of starch into so-called α-starch was also beneficial to grafting.[2701]

2. Free-Radical Grafting

Free-radical generation (initiation), one of the most essential elements of grafting, can be grouped into physical and chemical methods. Among physical methods, freezing and thawing of starch solutions[2702] was reported to produce block polymers of starch with vinyl monomers, however, the grafting efficiency was rather low. More-effective methods include ball milling,[2703] mastication, and the application of a heavy shear stress,[2704,2705] extrusion,[2706,2707] microwave irradiation,[2708] convection dry heating in the range of 115–230 °C,[2709,2710] and ionizing radiation, which can be applied before or after blending starch with vinyl monomer. The last minimizes homopolymerization, although some depolymerization of starch occurs.[2711] Some metal salts also act as initiators.

a. Ionizing radiation.—Ionizing radiation was used to initiate diffusion of either acrylamide or vinyl acetate into the starch granule. Thus the pregelatinization of starch, its azeotropic drying, or other methods of starch pretreatment, could be enhanced by radiation. When starch was preirradiated and subsequently grafted

with acrylic acid, the rate of grafting decreased as the grafting efficiency approached a maximum. At a given radiation dose, the grafting rate was proportional to the first power of the concentration of preirradiated starch and to the 1.5 power of the initial concentration of acrylic acid.[2712] γ-Radiation was used to initiate starch graft co- and ter-polymerization with acrylamide-2-hydroxy-3-(methacryloyloxy)propyltrimethylammonium chloride[2713] and other quaternary ammonium salts.[2714,2715] The result of grafting depends, to a certain extent, on the method applied. For example, β-irradiation resulted in a higher degree of grafting than γ-irradiation, even if β-irradiation was used at lower doses.[2716] It was reported that the dose of γ-rays should not exceed 5.0 Mrad in order to avoid depolymerization of starch, and consequent decreases of the intrinsic viscosities of copolymer solutions.[2717–2719] It was also reported that γ-irradiation in the presence of a ceric(IV) initiator provided similar grafting efficiency, that is, between 33 and 31%.[2720] Again, the ceric(IV) initiator produced polymers of higher molecular weight than did hydrogen peroxide with ferrous salt. Mastication in aqueous suspensions merely produced homopolymers.[2721,2722] Catalysts used include polyamines, ammonia, aldehydes, monosaccharides, ascorbic acid, or tocopherol.[2723]

In another study, ethyl methacrylate was grafted onto electron-beam preirradiated starch, and an increased grafting ratio occurred as a result of graft copolymerization of individual starch granules.[2724,2725] This reaction was carried out in aqueous methanol. Grafting was accelerated by using such additives as glycerol, ethylene glycol, and cyclohexanol. This result is possibly attributable to changes in the overall viscosity of the medium, which inhibits decay of radicals propagated by methyl methacrylate.[2726,2727] On the other hand, it has been shown[2728] that water is a superior solvent, that methanol is nearly as good a solvent as water, and that ethanol is less effective for polymerization. The process is independent of the granule size[2729] and, generally, the source of starch.[2730] Small differences in the yield and add-on of granular graft polymers, which could be attributed to different starch origins, ceased after pregelatinization.[2731] However, the morphology of acrylonitrile-grafted starch granules depends on the starch variety.[2732] In particular, tuber starches were grafted inside granules, whereas legume starches grafted on the granule surfaces.

The mode of terminating graft polymerization onto preirradiated starch significantly affects the molecular-weight distribution of grafted poly(methyl methacrylate) chains.[2733] Peroxide or hydroperoxide radicals were formed by γ-radiation of starch.[2734] This procedure involved exposure to oxygen immediately after irradiation, followed by blending with either acrylic acid or acrylamide in an aqueous emulsion containing Fe(II), Ti(III), or Hg(I) salts as the initiators. In another study, scanning electron microscopy revealed that the polymer distribution

in grafted starch granules in ^{60}Co-initiated graft polymers depended on the type of vinyl monomer used.[2735] In the case of acrylamide–*N,N,N*-trimethylaminoethyl methacrylate sulfate, polymerization occurred throughout the entire granule interior when there was 16% add-on grafting. In contrast, polymerization occurred near the granule surface when 31% add-on polymer was used. Surface grafting was preponderated with the use of styrene. The granule size played only a minor role. Extrusion cooking of styrene–starch and methylacrylate-grafted starch copolymers resulted in deformed particles of polymer-grafted starch suspended in a homopolymer melt.[2736]

b. Ultraviolet Light.—Free radicals have also been generated by ultraviolet light (photolysis).[2737–2739] Visible light promoted grafting when a potassium pervanadate sensitizer was present.[2740] Ozone initiates grafting by developing peroxide functionalities on the starch backbone. Peroxides resulting from the reaction with ozone have been grafted with styrene,[2741,2742] methyl methacrylate,[2743] acrylonitrile and vinyl chloride,[2744] It was also reported that oxidation may be assisted by ferrous ions,[2745,2746] starch dialdehyde, the starch–KI_5 complex, or maltose.[2744] Grafting proceeded in an aqueous solution. Graft copolymers retained several properties of synthetic homopolymers, and solubility was the property most significantly altered as a result of crosslinking.[2747] Grafting of acrylamide on starch using the CS_2–ferrous ammonium sulfate–$K_2S_2O_8$ redox system was reported.[2748] In this case, starch reacts as a thiocarbonate. The reaction yield was maximized by using an acidic medium and that CCl_4 was the best reaction medium.

c. Peroxides.—Oxidation of starch by hydrogen peroxide (the activator) and Fenton reagent (the initiator) involves oxygen radicals. The starch radicals preferentially abstract hydrogen rather than cause growth of the polymer chain. It was reported that the oxidation of amino groups containing vinyl monomers (for instance, 2-dimethylaminoethyl methacrylate) was inhibited by transformation into their salts with nitric acid. Furthermore, this inhibition increased the molecular weight of the grafted branches, and simultaneously increased the amount of homopolymer.[2749,2750] The gelation of starch prior to grafting significantly decreased the grafting efficiency.[2751] An interface catalysis reaction was also utilized involving a two-phase, water–petroleum mixture containing a lyophilic nonionic surfactant.[2752] Benzoyl peroxide,[2753,2754] *tert*-butylperoxypivalate[2755] can be used as initiators. or *N,N*-azodiisobutyronitrile,[2756–2759] but the last produces more homopolymer. In the grafting of granular corn starch with methyl methacrylate, side chains resulting at a frequency of one glucose unit per 230–300 glucose

units were observed.[2760] Other initiating systems entailed the use of hydrogen peroxide with thiourea[2761] and thiourea dioxide together with hydrogen peroxide and $FeSO_4$.[2762] The latter system was used for graft copolymerization of glycidyl methacrylate with starch. The preparation of a series of anion-exchange graft copolymers from poly(glycidylmethacrylates) modified with various amines grafted on starch has been reported.[2763]

d. Peroxysulfates.—Peroxysulfates also initiate grafting.[2764–2769] Some degree of oxidation accompanies this type of grafting.[2770] It was suggested[2771] that the grafting initiator is the sulfate radical, which is transformed into the peroxysulfate radical. Such a radical can be generated by manganic(III) sulfate in sulfuric acid.[2772] Carrying out this reaction under nitrogen is advisable, although further experience showed that grafting may occur in an aqueous suspension at pH 7.[2773] Critical to this reaction are two factors: the time at which the peroxysulfate reagent is added and the subsequent time of its action. During grafting of acrylamide on starch, in the absence of monomer, oxidation resulted in the formation of more carboxylic groups during saponification as compared with products oxidized with monomer present.[2761] It was reported that the peroxysulfate initiator is suitable for grafting acrylic acid[2774] and *N,N′*-methylenebis(acrylamide) to give a good absorbent material.[2775] Fine, porous particles of high water-absorbance by inverse-phase suspension polymerization of starch with acrylic acid initiated by peroxysulfate.[2776] The addition of a small amount of cellulose increased the rates of monomer conversion and grafting.[2777] Another modification for grafting acrylic acid to starch involves use of alcohols (this is, from propanol to nonanol) as the solvent, and $K_2S_2O_8$–H_2O_2 as an initiator.[2778] Also, the activity of the $K_2S_2O_8$–thiosulfate combination was tested in graft copolymerization of butyl acrylate onto corn starch.[2779]

e. Azo Compounds.—Azo compounds were also tested as initiators. Preparing the starch complex with an azo compound prior to thermal decomposition was recommended.[2780] A much lower grafting efficiency (below 50%) was observed for vinyl acetate on granular corn starch, as opposed to grafting with methyl methacrylate and acrylonitrile.[2781] It is possible that this may be attributed to differences in the penetrating ability of particular vinyl polymers into the interior of the starch granule.[2758,2782] On the other hand, styrene grafted very effectively onto starch.[2783] Indeed, the results of grafting vinyl monomers on granular and gelatinized starch are different.[2784] This suggested grafting simultaneously with gelatinization during heating.[2785] *N,N*-Azodiisobutyronitrile[2756–2760] produces more homopolymer. In

the grafting of granular corn starch with methyl methacrylate, side chains resulting at a frequency of one glucose unit per 230–300 glucose units were observed.[2760]

f. Manganese Compounds.—Extensive studies were performed on graft copolymerization of methyl methacrylate, acrylonitrile, acrylamide, and acrylic acid onto starch[2786,2787] These studies involved testing the acetylacetonates of Mn(III), Co(III), Cr(III), and V(IV) as the initiators. Among them, Mn(III) appeared to be superior in all cases, and V(IV) was the least effective. An activation energy of 59.2 kJ/mole was reported for the graft copolymerization of methyl methacrylate initiated with Mn(III) acetylacetonate.

Manganese(III) ions initiate grafting acrylonitrile to potato starch.[2788–2790] It was reported that the Mn(III) initiator formed either from acidic $MnSO_4$ and either $KMnO_4$ or $Na_2P_4O_7$, potassium trioxalatomanganate in the dark or freshly prepared manganese(III) pyrophosphate.[2791] When the concentration of Mn(III) increased to within the range of $0.15–3 \times 10^{-3}$ M, the percentage of add-on increased, however, the graft frequency and the molecular weight of the graft polymer decreased. During initiation with manganese(III) pyrophosphate, the activation energy of grafting was 25.90 kJ/mole, and the rate constant was 3.37×10^2.[2792] The addition of sulfuric acid (10^{-2} M) promoted grafting.[2793] Use of gelled starch also promotes a high frequency of grafting and an increased molecular weight of the graft polymer. It was reported that raising the initiator concentration increased the frequency of add-on of grafts, however, the molecular weight of the product and the frequency of grafts decreased. These findings were observed both for the grafting of starch with acrylonitrile[2794] and methyl methacrylate.[2795] The grafting rate was independent of the polysaccharide conformation.[2796] The activation energy for graft polymerization of methyl methacrylate onto canna starch was 31.15 kJ/mole.[2797]

Methyl methacrylate has been grafted onto starch by the use of Mn(VII) ion initiator made from $KMnO_4$ in the presence of nitric acid.[2798] The reaction proceeded in aqueous methanol and increased with the amount of methanol in the solvent. After activation, $KMnO_4$ had to be removed, and higher concentrations of methanol in the reaction medium were used to deactivate residual Mn(IV) ions. The Mn(VII) ion-initiated acrylamide graft copolymerization when $KMnO_4$ was used either in sulfuric acid or organic carboxylic acids.[2799] The progress of the reaction could be controlled by the deposition of MnO_2. Such cations as Fe(III), Cu(II), or Li were beneficial to the reaction.[2800] Potassium permanganate cannot initiate homopolymerization of acrylamide above pH 4, but grafting to starch occurs even at pH 6.6.[2801] Mn(VII) ions in the presence of carboxylic acids can also initiate grafting of acrylic acid.[2802] There was no change in the first rate

constant for grafting acrylamide on starch when when comparing three initiators, namely $K_2S_2O_8$, benzoyl peroxide, and $KMnO_4$. However, the second rate constant decreased in the order just given. Another difference between these three initiators concerns the product viscosity, which was lower in two first cases and higher in the latter as compared to a solution of unprocessed starch.[2803]

g. Cupric Compounds.—The use of copper ammonium hydroxide to promote graft polymerization upon heating has been patented.[2804] Ziegler–Natta homogenous catalysts also effect graft copolymerization.[2805]

Aluminoxanes suppressed side reactions involving hydrogen transfer. They also formed cyclic structures with starch, giving copolymers that were coated with crystalline polyethylene. A catalyst composed of dicyclopentadienylzirconium dichloride and trimethylaluminium permitted polymerization of ethylene on starch in a toluene suspension at 60 °C for 2 h.[2806] Graft copolymerization of methyl methacrylate onto starch was also performed with an acetylacetone–copper(II) complex in trichloroacetic acid.[2807] The grafting yield and efficiency were proportional to the initiator concentration up to 7.0×10^{-3} mole/L.

Grafting of methyl methacrylate on starch occurs in an aqueous, saturated starch solution at 85 °C in the presence of carbon tetrachloride or copper(II) ions,[2808,2809] and the grafting efficiency could be as high as 72%. At a low concentrations of the vinyl compound, the reaction rate was proportional to its concentration. The reaction rate became independent of concentration at higher concentrations of the vinyl monomer. Grafting in the presence of 0.1 M nitric acid and ammonium selenate was also reported.[2810]

h. Ceric Compounds.—The ceric(IV) ion (from ceric ammonium nitrate) is a superior graft initiator as compared to iron and manganese, which act selectively.[2811] Batch and extrusion grafting processes have been described.[2812,2813] Comparative studies[2814] on the effectiveness of various catalysts in grafting cationic acrylamide to starch revealed that the reaction yield decreased according to the following order of catalysts used: Ce(IV) > Mn(VII) > H_2O_2–Fe(II). Another set of comparative studies on three initiators, H_2O_2–Fe(II), $K_2S_2O_8$, and $KMnO_4$ indicated the last as the one providing maximum grafting efficiency.[2815] The Ce(IV)–Mn(VII) system was effective in graft copolymerization of acrylamide onto starch.[2816] With Ce(IV), there is no crosslinking in the synthetic copolymer,[2817] although according to later studies[2818] there is crosslinking similar to that initiated by irradiation. Such an initiator, sometimes used together with either iron(II) ammonium sulfate or nitric acid, modifies starch into a form that is slightly dispersible in dimethyl sulfoxide

and even more dispersible in water.[2819,2820] The grafting efficiency increased with initiator concentration. Such a response to an increased concentration of initiator is opposite to that discussed earlier regarding the increased concentration of hydrogen peroxide initiator.[2821,2822] The most favorable proportion of reagents capable of producing the highest percentage of polyacrylamide grafting to starch was given as follows: 0.05 M cerium ammonium nitrate, 0.3 M HNO_3, and 1.0 M acrylamide at 50 °C.[2823] This reaction was further reexamined[2824] and some selectivity in that process was reported.[2825] The most favorable reagent ratio for grafting acrylonitrile to starch is 1:1–2 starch-to-nitrile for a 1 h reaction at 20–25 °C.[2826] At higher temperatures, between 65 and 95 °C, the initiator concentration should be between 2.0 and 8.0 mmole/L.[2827] Manipulation of the catalyst concentration allowed achievement of regularities in the structure of grafted material.[2828] The optimum conditions for grafting acrylic acid onto potato starch are 0.769 mole/L of acrylic acid and 2.632 mmole/L of the ceric catalyst, the starch was pretreated at 85 °C and then grafted at 40 °C for 2 h.[2829]

Graft copolymerization of methyl acrylate onto starch was confirmed to have free-radical character,[2825] and optimum concentrations of methyl acrylate, ceric initiator, and HNO_3 should be 1.08×10^{-3}, 5.0×10^{-3}, and 0.081 mole/L, respectively at 50 °C for 2 h (see also newer reports).[2830] Yield of grafting reached 95%. The reaction time and reagent concentration were confirmed crucial factors for grafting methyl methacrylate to starch.[2831] The optimum reaction parameters to maximize the graft percentage are: 4 h at 30–40 °C with Ce(IV) and methyl methacrylate concentrations are 4.5×10^{-3} and 4.0×10^{-1} mol/L, respectively.[2832] The stirring speed had no effect on the result of grafting.[2833] Several authors reported further modifications to the procedure.[2834–2836] Similar results were obtained for ethylacrylate grafting.[2837,2838] The reaction followed conventional kinetics of free-radical polymerization.[2839] For graft polymerization of vinyl acetate, the following concentrations of vinyl monomer and catalyst were given: 1.35 and 7.50 mmole/L, respectively, at 50 °C for 90–120 min.[2840]

The reactivity of vinyl monomers decreases according to the following order: acrylonitrile > ethyl acrylate > ethyl methacrylate.[2841] The rate of reaction of acrylonitrile was higher than that of acrylamide.[2842] Further studies[2843,2844] revealed that, although *N,N*-dimethylformamide permits facile removal of the homopolymer, the graft copolymer contained a few long chains. Water is a better reaction medium, because the overall yield was higher and more branches are formed.[2843–2846] Varying the concentration of aqueous methanol was used to control the properties of a graft copolymer.[2847,2848] Depleting the initiator upon grafting extended grafting in comparison to the common method of continous initiation, and the efficiency reached

a value as high as 90%. A maximum extent of grafting was attained at 10 mmole of Ce(IV) per gram of starch.[2849,2850] In the grafting of acrylamide, a water-soluble copolymer was obtained with no more than 3 grafts per starch molecule if the concentrations of acrylamide and ceric initiator are properly adjusted.[2851]

An interesting method of graft polymerization in a gas-phase suspension has also been described.[2698,2852] In this process, corn starch, monomers (acrylamide, acrylic acid, and their derivatives), initiators, molecular regulators, and crosslinking agents were dispersed in gas, which was used to help remove water and unreacted monomers. Graft copolymerization proceeded in isolated gel droplets. In contrast to the majority of graft polymerizations using cerium(IV) ammonium nitrate as initiator, this process involved the use of cerium(IV) sulfate. Comparative studies[2853] reveal the importance of the formation of the starch–vinyl monomer–ceric salt complex. The grafting frequency and the molecular weight of grafted acrylonitrile on gelatinized wheat starch is possible by the use of so-called chain modifiers.[2854] Several potential modifiers were tested, including ethanethiol, butanone, chloroform, ethanol, and 1-dodecanethiol. The last modifier promoted grafting, wheras ethanol caused chain shortening. It was also reported that copper(II) nitrate promoted grafting, and was a better modifier than copper(II) acetate. The amount of amylose in acrylonitrile grafted starch is proportional to the concentration of amylose in the grafted reaction mixture.[2855]

A continous process was developed having the following characteristics: when the acrylonitrile-to-starch ratio changed from 2:1 to 1:1 to 1:2, conversion varied from 87.3 to 77 to 97.7%, and the concentration of grafted acrylonitrile varied from 29.0 to 14.9 to 9.3%.[2856] Kinetic studies of graft copolymerization of acrylonitrile with gelatinized and granular starch in water with the ceric(IV) initiator revealed that the reaction rate is directly proportional to square root of the initiator concentration and to the 1.3 power of the acrylonitrile concentration.[2857] Values of the molar size dispersity were higher for the copolymer made from granular starch than from gelatinized starch.

i. Silver Compounds.—Silver(I) can also catalyze grafting.[2858] The rate of acrylonitrile grafting on starch was proportional to the square root of concentration of Ag(I) and starch. It is likely that Ag(II) ions are involved. Grafting of acrylonitrile and acrylamide on granular wheat starch in *N,N*-dimethylformamide was reported.[2712] Acrylonitrile grafting depends primarily upon the concentrations of both monomer and silver catalyst, whereas grafting of acrylamide is less sensitive to these factors. Higher concentrations of vinyl monomer promoted homopolymerization, which could be suppressed by a higher concentration of

catalyst. Under the most favorable reaction conditions, the grafting effciencies for acrylonitrile and acrylamide were 87 and 43%, respectively.

3. Vinyl Monomers and Other Reagents in Free-Radical Grafting

Several vinyl monomers, for instance, allyl alcohol, acrylamide, acrylonitrile, acrylic acid, and styrene, have been reported for grafting onto starch. Long-chain alkyl acrylates have also been used[2859–2863] as well as more complicated vinyl monomers, namely 2-hydroxyethylacrylate,[2864] 1-acrylamido-1-deoxy-D-glucitol,[2865] *N*-(acryloyloxyethyl)-*N,N,N*-trimethylammonium chloride together with hydroxypropyl methacrylate both grafted to trimethylaminoethyl chloride starch ether,[2866] *N*-methacryloyloxyethyl-*N,N,N*-trimethylammonium chloride, mono(2-methacryloyloxyethyl)acid phosphate in the presence of 2-hydroxyethylmethacrylate,[2867,2868] methoxyhexapropylene glycol methacrylate,[2869] mono(2-hydroxyethylmethacrylate) acid phosphate, acrylic acid–mono(2-hydroxyethyl acrylate)acid phosphate,[2870] isatoate acrylate,[2871] and phthalic anhydride.[2872] In addition, many other complex unsaturated compounds have been used, for instance, sodium 2,2-dimethyl-4-oxo-3-azahex-5-ene-1-sulfonate,[2873] 1-(2-methylprop-2-*N*-yl-1-sulfonate)amidoethylene,[2874] *N*-acryloyl-*N*′-cyanoacetohydrazide,[2875] and 2-acrylamido-2-methylpropanesulfonic acid.[2876] These compounds are usually grafted jointly with other vinyl monomers.

4. Ionic Grafting

There are also several examples of ionic graft copolymerization, for example, starch copolymerized with acrylonitrile, methacrylonitrile, acrylic and methacrylic esters, and several other vinyl monomers.[2877] Metal starch alkoxides served as anionic catalysts for polymerization of vinyl monomers. Suitable solvents included liquid ammonia, tetrahydrofuran, *N,N*-dimethylformamide, dimethyl sufoxide, or light petroleum fractions. The yield of graft copolymer usually increases with increase in alkoxide concentration, as shown, for instance, in the case of dedecanyl methacrylate.[2878] Low-molecular-weight polyisobutylene was also grafted on potato starch in a sequence of reactions. Thus, the terminal polyisobutylene double bond was oxidized with chromium(VI) oxide to the corresponding methyl ketone

derivative. It was oxidized with sodium hypobromite to the carboxylic acid, and then converted into the acid chloride by the action of thionyl chloride. The product reacted with starch in a Schotten–Baumann, anion-catalyzed reaction.[2879]

Anionic graft copolymerization was also applied to formaldehyde on starch[1314] and 4-vinylpyridine on starch.[2880] An alternative route to a starch–poly(ethylene oxide) graft copolymer was reported that simulates the free-radical process mentioned previously. Thus, starch alkoxide solution in dimethyl sulfoxide reacts with alkylene oxides. The polymerization efficiency was practically independent of the alkoxide concentration, however, it depended on the monomer concentration.[2881,2882] In another study, the reaction of dimethyl sulfoxide with potassium naphthalene (forming the dimsyl anion) was reported to be effective.[2883] Similarly, methacrylonitrile,[2884] methyl methacrylate,[2885] and acrylonitrile[2886] were grafted onto starch. In the case of methacrylonitrile, there was a certain limit to the concentration of monomer above which homopolymer was formed at a considerable rate. It was also reported that the yield of copolymerization product with methyl methacrylate increased with the alkoxide concentration, but again, higher concentrations of the monomer produced more homopolymer. Similar observations were made in the case of acrylonitrile. In this case, a high conversion of monomer took place even at low concentrations of alkoxide. Such an oxidant as sodium hypochlorite in alkali also initiated grafting of acrylamide on starch.[2887] Polyacrylamide was absent, this is, homopolymerization did not take place.

Graft copolymers were also produced by bubbling alkylene oxides through starch solutions in dimethyl sulfoxide in the presence of potassium naphthenate.[2888,2889] Another approach involved grafting poly(ethylene oxide) to starch. Poly(ethylene oxide) was converted into a chloroformate derivative and subjected to a reaction with starch alkoxide.[2890] Poly(alkylene glycol) could be grafted onto starch by means of cyclic aliphatic acid anhydride in the presence of 4-toluenesulfonic acid.[2891] The products were water soluble.

Poly(amino acids)[2892] and polypeptides[2893] can also be grafted onto starch. Starch was first alkylated in the presence of lithium naphthalene, and then the alkoxy derivatives were reacted with *N*-carboxy anhydrides. Poly(amide amines) were produced by reacting amines with dioic acids on starch and then crosslinking with epichlorohydrin or 1,2-dichloroethane.[2894] Grafting of starch with a synthetic polymer chain, for instance, polystyryl carboxylate anions prepared by an anionic polymerization, can be carried out on a blend of starch and cellulose functionalized by sulfonation, mesylation, or tosylation. In this manner, cellulose–starch graft copolymers were prepared.[2895]

Although it was originally suggested[2896,2897] that amylopectin is more sensitive to grafting than amylose, it was shown, in the grafting of methyl methacrylate, that amylopectin, due to its structure, favors homopolymerization of the vinyl monomer and does not readily copolymerize. The average molecular weight of grafted amylopectin was 475,000 and that of grafted amylose was 403,000. The number of grafted chains ranged from 2.4 to 4.6 $\times$ 10^{-3} and from 2.9 to 6.8 $\times$ 10^{-3} for amylopectin and amylose, respectively.[2898]

Predominant sites for initiating graft copolymerization are localized at C-1–C-2 end groups, and C-3–C-4 diol groups. The involvement of the 6-OH group is negligible.[2899] Infrared reflectance spectroscopy has been used in in structural studies of starch graft polymers,[2900] and routine IR spectroscopy can be used to analyze highly grafted polymers, in which bands characteristic of a substituent of the starting vinyl monomer can be distinguished.[2901,2902] Several of the aforementioned effects of reaction conditions upon the grafting of acrylonitrile to starch have been reexamined.[2903]

Studies[2784] on competitive graft copolymerization of acrylamide and 2-dimethylaminoethyl methacrylate nitrate led to the conclusion that the concentration of the methacrylate-originating moiety in the final graft copolymer was higher when the starch was swollen. Formation of grafted and ungrafted alternating copolymers by redox-initiated copolymerization of styrene and acrylonitrile in the presence of starch has been demonstrated.[2904] The formation of alternating copolymers was attributed to the formation of co-monomer complexes with starch. Starch was grafted starch with a blend of methyl methacrylate and styrene, and the grafted product contained more methacrylate units than the homopolymer that was formed simultaneously.[2905]

The grafting of methacrylonitrile together with C_1–C_6-alkyl methacrylates was reported as beneficial for increasing the molecular weight of the product.[2906,2907] As shown by ^{13}C NMR spectroscopy, at low conversion, a random statistical distribution of co-monomeric sequences was obtained, whereas high conversion was achieved by the formation of long sequences originating from alkyl methacrylate.[2908] Such studies were then extended to blends of methyl acrylate with vinyl acetate.[2909,2910] A 98.5% degree of grafting and a 90.3% grafting efficiency were achieved with concentrations of Ce(IV) ion and styrene of 7–7.5 mmole/L and 2–3 mole/L, respectively at 45 °C.[2911] The reaction was promoted by the addition of less than 5% acrylonitrile. An interesting study of the copolymerization of styrene and acrylonitrile on starch were reported.[2912] Under reaction conditions in which styrene did not graft to starch, the presence of acrylonitrile resulted in the formation of an acrylonitrile–starch–styrene graft polymer. Starch–acrylonitrile radicals were

originally formed which then accepted styrene. As with the copolymerization of a blend of acrylonitrile with ethyl acrylate to starch, acrylonitrile promoted incorporation of ethyl acrylate.[2913]

Generally, all graft polymers lacking polar groups are water-insoluble.[2914] However, a water-soluble graft polymer was produced by grafting acrylamide onto soluble starch.[2915] The swelling ability of starch was perhaps responsible for this result, although the penetrating ability of the vinyl monomer is also a factor.[2916] Methacrylamide is readily grafted onto starch, with yields close to quantitative.[2917] Once isolated from the reaction mixture, the products are water-insoluble. Gelatinization of starch prior to grafting was disadvantageous.[2918] The temperature and the sequence of admixing monomer and catalyst were crucial parameters.[2919,2920]

Aqueous dispersions of hydrolyzed copolymers at pH 7–8.5 were viscous, and the viscosity correlated with the amount of acrylonitrile added. The progress of grafting can also be monitored viscosimetrically.[2921] In contrast to hydrolyzed copolymers from granular starch, those produced from gelatinized starch behaved as polyelectrolytes.[2922] They consisted of swollen, deformable, closely packed gel particles.[2923] They could also be tailored to form products of a desired swelling ratio by controlling the solution viscosity[2934] as well as by coupling of suitable vinyl monomers.[2925] Free carboxylic groups in such copolymers (as well as in copolymers from starch and acrylic acid) interact via hydrogen bonds with the hydroxyl groups of starch glucose units, thereby influencing the chain conformation and enhancing in the crystalline character of the copolymers.[2926] Agglomeration and drying of such polymers does not decrease their absorptivity.[2927] Gels collapse in aqueous alcohols.[2928] Acid-catalyzed hydrolysis afforded a polyacrylonitrile derivative having oligosaccharide end groups.[2929]

A low degree of grafting decreases the thermal stability of the reaction product relative to that of starch alone. However, a high degree of grafting can improve thermal stability over that of starch alone, as shown by examples of starches grafted with acrylamide,[2930] acrylonitrile,[2901,2931] and alkylene methacrylates.[2882] A high level of grafting of methyl acrylate onto starch decreased the ultimate tensile strength of the graft polymer.[2932] Grafting disrupted the granular structure of starch and produced a compact structure more resistant to degradation by alpha amylase.[2933] An ethyl acrylate–starch graft polymer lost 20% of its weight within 27 days,[2836] and a methyl methacrylate–starch graft polymer lost approximately 32% of its weight after 40 days.[2934] Generally, the viscosity of starch solutions decreases on grafting because of an increase in the coil density of the macromolecule. In this case, the polymer becomes less flexible, and becomes more compact. In turn, this decreases the shear dependence on viscosity.[2935] In applications where low-viscosity

polymers are needed (for instance, in papermaking), the viscosity of the graft polymer can be decreased by the co-grafting of cinnamyl and maleyl moieties.[2936]

The vast majority of grafting studies have been performed with vinyl monomers. Other types of starch graft copolymers have been prepared from starch and lactones or lactides.[2937,2938] Such copolymers could be prepared using reagents in *N,N*-dimethylacetamide in the presence of lithium chloride and triethylamine.

5. Grafting Onto Modified Starches

It is possible that the grafting yield might be increased, and simultaneously, the amount of homopolymer formed decreased, in grafting on derivatized starch (this is, oxidized starch, starch dialdehyde, and so on).[2774,2939–2942] In the case of starch dialdehyde, acetal linkages were formed. Various starch derivatives have been used for grafting with vinyl monomers. Among them, starch xanthate was employed with hydrogen peroxide as the initiator. For example, it was reported that the reaction proceeded either under slightly acidic conditions[2210] or without acid addition.[2943] A foamed product resulted when the reaction was performed in a latex emulsion.[2944] (Carboxymethyl)starch was graft-copolymerized with acrylonitrile on initiation with the Ce(IV)–amine system,[2946] acrylamide,[501] and acrylic acid.[2947] (Cyanoethyl)amylopectin was grafted by ethylacrylate.[2948] Amylose triacetate was also copolymerized with styrene using a ceric(IV) initiator.[2942] Cationic starches were grafted with chloroprene,[2949] acrylonitrile,[2950–2952] acrylamide,[2953] methyl methacrylate,[2954] and isoprene,[2955] in all cases using ceric(IV) initiation. In the first case, latex was formed, and sonication at 20 kHz produced flexible films. In the latter case, a dispersion was produced consisting of spherical particles of 0.05–0.15 μm. Sonication at 20 kHz did not destroy these particles, but the viscosity was reduced by approximately two orders of magnitude.[2951]

In another study, starch anthranilate, resulting from esterification of starch with isatoic anhydride, was then diazotized, followed by grafting by acrylic acid in the presence of CuCl.[2956] Also, enzymatically hydrolyzed starch was subjected to graft copolymerization with acrylamide.[2957] In contrast, crosslinked starch was also grafted with acrylonitrile, followed by saponification.[2958,2959] Acrylonitrile-grafted starch, after hydrolysis, subsequently reacts with glycerol diglycidyl ether[2960] and other, more complex diglycidyl compounds, for example, diglycidyl methylphosphonate, nonaethylene glycol diglycidyl ether, and glycidyloxypropyltrimethoxysilane.[2961] Grafting of (hydroxypropyl)starch with

acrylonitrile followed by alkaline hydrolysis converts the cyano group into the carboxylic group.[2962] Crosslinked starch–acrylonitrile graft copolymers were prepared by crosslinking with epichlorohydrin or formaldehyde.[2963] In addition, thiolated starches of DS 0.005–0.162 were grafted with such vinyl monomers as acrylamide, acrylonitrile, acrylic acid, dimethylaminoethyl methacrylate, and styrene in the presence of hydrogen peroxide as an initiator.[1825] This initiator promoted grafting as well as coupling of thiol groups into disulfides, a reaction readily reversed by reduction with $NaBH_4$. Various modified starches can be used for grafting; starch modified by reaction with hypochlorite offers the most opportunities for creating products having widely diffrerent properties.[2964] Grafting and crosslinking in a single, batch processes were performed wherein acrylamide was grafted to starch using the Ce(IV) initiator and simulatenosuly, *N,N*-methylenebisacrylamide was used as crosslinker[2965] (after saponification, the product absorbed 5085 g water per gram of dry copolymer within 24 h at room temperature) and acrylic acid salts were after grafring were crosslinked with epichlorohydrin using ammonium peroxydisulfate as initiator.[2966] The method of isolating the polymer strongly affects its water-absorbing ability. In order to promote water absorption, it was suggested that gel-blocking and the addition of octadecanoic acid are to be avoided.[2967]

6. Isolation of Polymers

The most common method of isolating graft polymers is based on their selective solubility in certain organic solvents, which in turn allow separation of the graft polymer from the homopolymer.[2968] Solutions of graft polymers in organic solvents might be suitable for making thin films, fibers, and so on.[2969] The water content may be critical for the effectiveness of extraction. For example, the methylmethacrylate homopolymer is best extracted from its graft copolymer with starch when 25% moisture is present in the mixture.[2970] In the same study, various solvents exhibited the following order of extraction effectiveness: $CHCl_3 = CH_2CH_2Cl_2 > PhH > MeCOEt = Me_2CO = PhMe$. A specific isolation method was presented,[2971,2972] in which depolymerization of starch in the graft copolymer was achieved by oxidizing it with periodate and then the product was treated with methanolic alkali. A rapid method of analyzing starch graft copolymers entails swelling the grafted side chains in acetic acid followed by oxidation with perchloric acid and precipitation of the polymer side chain.[2973]

7. Modifications of Graft Polymers to Improve Their Functionality

Graft copolymers serve a variety of practical purposes, either in the as-prepared condition or in mixtures with other components. One example involves use of quaternary ammonium compounds derived from hydrogenated tallow[2974] to furnish water-dispersible products. In other studies, polyethylene and/or its graft polymers were filled with $CaCO_3$.[2975] Such polymers were also subjected to various reactions. For example, graft copolymers with methylmethacrylate react with hydrazine. It was reported that the resulting hydrazide was useful in trapping Ag(I) ions from electroplating wastewater.[2976] Reaction with hydroxylamine produced another good trap for heavy metals.[2977] Aminomethylation and hydroxymethylation of starch–acrylamide graft copolymers were also described,[2978] as well as grafting hydroxyalkyl acrylates and methacrylates.[2979] Such vinyl monomers were also grafted onto oxidized starch.[2980] Starch–acrylic ester graft-copolymers can be acylated more readily than untreated starch.[2981]

Polyacrylate-grafted starches were saponified in 10% KOH at 80 °C for 2 h[2982,2983] or under similar conditions.[2984–2987] The procedure decreases the viscosity, but this decrease after hydrolysis can be prevented by addition of various salts to the hydrolyzed reaction mixture, a result that was attributed to the counterion effect. The significance of this effect increases with the cation valency.[2988] The viscoelastic properties of these fluids depend on the history of the sample.[2989–2991] Hoffman degradation of acrylamide–starch graft copolymer[2992] gives an amino copolymer that can be subsequently cationized. The vinyl monomer used for grafting on starch also contributes to the polymer viscosity.[2993] In this study, styrene graft polymers usually had low viscosities. Starch–polyacrylamide graft polymers can be sulfomethylated by treatment with paraformaldehyde and sodium sulfite.[2994] Water-dispersible latexes can be formed by the use of various, starch-grafted copolymers that were crosslinked with glyoxal.[2995]

Carboxylates, resulting from saponification, are isolable in the form of alkali metal salts.[2996,2997] These carboxylates have a high liquid absorption capacity that is pH dependent. An acrylonitrile–starch grafted polymer absorbed 1000–2000 g of water per gram of polymer prior to its saponification.[2998] Similarly, acrylonitrile grafted onto corn-starch copolymer had superabsorbing properties, even when the grafting was initiated by ionizing radiation.[2999] The saponification of polyacrylonitrile branches tripled the water absorptivity relative to the original absorptivity prior to saponification.[3000] The amount of retained water also increased linearly with add-on. When grafting was initiated by ionizing radiation, controlled modification of liquid retention of the graft polymer produced was possible by adjusting the irradiation

time and the dose rate.[3001] The properties of water absorbed in the saponified product were studied by differential scanning calorimetry, which enabled a distinction to be made between two types of water, described as bound uncrystallizable water and free crystallizable water.[3002] The dynamic response to hydration in a superabsorbing polymer was studied by ^{13}C/crossed polarization, magic angle spinning (CPMAS)/NMR, and a correlation was found between the hydration time and induced polymer motions.[3003] On studies of the water sorption by acrylic acid–starch graft copolymers, high water-absorption was found to include random crosslinking and higher ionic concentrations.[3004] When the superabsorbent was anionic in character, it was shown that a saline solution decreased swelling, but multivalent ions evoked the opposite effect. Cationic superabsorbents were sensitive to the ionic strength of solutions, but they were insensitive to the type of multivalent cations used.[3005] Highly absorbing starches are available from starch reacting with such nonionic acrylic monomers as acrylamide and ionic sulfonic acid-substituted acrylic monomers,for instance, 2-acrylamido-2-methylpropanesulfonic acid,[3006–3009] acrylonitrile, and sodium allylsulfonate.[3010] The quality of such absorbents can be improved by bleaching with hydrosulfite, a process that is usually performed before saponification of amides, nitriles, and esters.[3011] Graft copolymers of sulfonated saponified acrylonitrile grafted ontotarch exhibit superior water absorption.[3012]

Choice of the method of separating such superabsorbents is critical for control of their storage stability. Separation is usually achieved by precipitation with a solvent. For example, it was reported that ethanol was superior in this respect, having the additional benefit of increasing the water absorbance of the precipitate.[3013] Ethanol, acetone, and 2-propanol did not perform as well as methanol. It was also reported that the precipitate should be neutralized before precipitation and should be dried under conditions preventing moisture loss.[3013] The superabsorbency could be increased by the use of crosslinked acrylic acid for grafting to starch.[3014] Random, intermolecular hydrogen-bonds were responsible for this effect.

Ion-exhange properties should also be mentioned. Saponification products usually exhibited fair water solubility.[3015] In order to decrease solubility, vinyl monomers were grafted onto crosslinked starch. Insoluble saponification products were reported to be good collectors of heavy metal ions.[3016] Improved collectors of heavy metal ions were prepared by saponification of acrylonitrile–epichlorohydrin–starch graft copolymers,[3017] and also by the use of vinyl monomers having sulfonic groups.[3018] It was reported that such compounds, not necessarily resulting from crosslinked starch, could also absorb brine, urine and feedlot waste, deodorants, enzymes, and soil conditioners, and they could also be used as hydroponic media.[3019] The metal-ion sorption (Q) of graft copolymers

containing the carboxylic group is time (t) dependent following the equation $Q = at/(1 + at)$.[3020] Hydrolysis only to the carboxyamide stage is also possible.

Hydrolysis of starch graft polymers formed with vinyl acetate was reported to produce poly(vinyl alcohol)-grafted starches using oxidized starches.[3021–3027] Hydrolysis of graft copolymer with 72% aqueous sulfuric acid and determination of glucose in the hydrolyzate by the Fehling reagent can be used.[3028]

Additional information on starch graft polymers can be found in reports by Watanabe and Nakano,[2701] Fanta,[3029] Lindsay,[3030] (this reference concerned only starch–acrylonitrile graft polymers), Stannett *et al.*,[3031] Tokuda,[3032] Ransby and Persson,[3033] Yoon Kee Jong,[3034] Chinnaswamy and Hanna,[3035] Zhang Yousong and Li Guangfeng,[3036] Doane,[3037] and Buchholz.[3038]

8. Applications of Graft Polymers

After more than a decade of intensive studies on graft copolymerization of vinyl monomers onto starch, the first applications for these materials appeared. A broad range of applications includes coatings,[3039] reinforcing materials for tires, rubber, and plastics,[2210] anticorrosion additives for water,[3040] flocculants (particularly graft copolymers having long chain trialkylammonium salts),[2777,3041] and retention aids for pigments and sizing agents for paper and textiles,[3042–3048] water dispersed latexes,[2951] components of electrostatographic toners,[3049] gas-chromatographic supports,[3050] components of deodorants,[3051] and various biodegradable materials.[3044,3052]

Ethylene, propylene, and other alkenes were grafted onto starch together with one of the following acrylamides: methacrylamide, acrylonitrile, acrylic acid, methacrylic acid and their alkali salts, 3-methacrylamidopropyltrimethylamine, 2-acrylamido-2-methylpropanesulfonic acid or its alkali salts, 2-methacryloylethanesulfonic acid and its alkali salts, styrene sulfonate, vinyl sulfonate, 2-methacryloyloxyethane.[3018] The copolymers exhibited a high degree of uptake of salts from aqueous electrolyte solutions. The products were also used as biodegradable materials.[3053] The product resulting from grafting 4-vinylpyridine onto starch, subsequently quaternized with ethyl bromide, was proposed as a bactericide of $LD_{50} > 3$ g/kg as elucidated in tests on rats.[3054,3055]

Saponified polyacrylate-grafted starches have been designed as drilling-mud additives, hydraulic fluids, and flocculants,[2982,3056] PVC gaskets,[3057] and components of biodegradable plastics.[3058–3060] Such copolymers, either free or as

their alkali metal salts, showed a high capacity for liquid absorption and only weak susceptibility to hydrolytic enzymes. For this reason they were added to paper in order to improve its absorption characteristics.[2996] Such materials can be incorporated into disposable diapers, surgical pads, gelatinous bandages, and paper towels for the absorbtion of urine, brine, and feedlot waste with simultaneous deodoration, soil conditiong (to increase its water absorbance), and other applications requiring water sorbency.[2751,2919,2986,2997,3005,3011,3044,3056,3090,3061–3077] Pressure-sensitive adhesives and tapes could also be made of such materials.[3078] Such graft copolymers can dehydrate gasoline[3079] and serve to dry coal powder.[3080] Enzymes can be immobilized by such copolymers.[3081–3089] The potassium salts, after hydration, produced gel sheets having good ion-exchange characteristics.[3015] Sodium salts were proposed as pharmaceutical adjuvants[3084] and encapsulants.[3085] Absorptivity of such copolymers can be increased by crosslinkling upon vacuum heating or by γ-radiation.[3086] Such co-polymers were used to trap radioactive waste.[3087] Other approaches for producing good collectors of metal ions involved grafting of acrylonitrile onto starch crosslinked by epichlorohydrin followed by saponification,[2959] and saponification of acrylonitrile copolymer followed by crosslinking with glycerol diglycidyl ether.[2960] Significant increases in water absorbtivity result upon grafting acrylonitrile to (sulfopropyl)starch or (carboxymethyl)starch, followed by saponification.[2984] A process involving modification of such polymers with fumed silica or alumina was developed[3088] to improve the rate of absorption of physiological fluids. Because of their swelling and non-Newtonian behavior, such products were also designed as thickeners[2924] and laminates for nonwoven fabrics.[3089] Copolymers of starch with hydrolyzed acrylonitrile and methylenebis(acrylamide) also served the same purpose.[3090,3091]

Graft copolymers of starch with acrylonitrile and 2-acrylamido-2-methylpropanesulfonic acid, after saponification, were claimed to be good sorbents.[3092] A composite of saponified acrylonitrile–starch–copolymer with vinyl formal polymers showed very good salt-rejection characteristics and served as membranes.[3093] The same material prepared with poly(vinyl chloride) has been used in gaskets for concrete pipes.[3057] Saponified acrylonitrile–starch graft copolymers blended with C_{12}–C_{16} alcohols provided excellent water-retention characteristics.[3094]

Acrylic acid or methacrylic acid–starch graft copolymers were proposed as flocculants for bauxites,[2714,3095] agents for sizing cotton,[3096–3098] tanning materials,[3099] paper additives,[3100] and also for sanitary napkins, diapers, tampons, and sick-bed sheets.[3101–3104] Particular attention was devoted to the use of vinyl monomer grafted onto crosslinked starch.[3105] Other applications include antiflammatory

and analgesic surgical dressings,[3106] re-moistenable adhesives (crotonic acid was also suitable for this purpose),[3107] additives for emulsions of lubricating oil used in metalworking,[3108] a thickener,[3109] hygroscopic container liners,[3110] and other moisture controlling systems,[3111,3112] for instance, concrete,[3113] cosmetic packs,[3114–3116] components of water-absorbent laminated printing sheets,[3117] an ink absorber for ink-jet printers,[3118] a component of automobile brake fluids,[3119] pharmaceutical tablet adjuvants,[3120] enzyme and drug encapsulating materials,[3121–3127] a water leaking inhibitor,[3128,3129] an oxygen sensor in sealed plastic bags containing food,[3130] paste-type electrodes in lead–acid batteries,[3102,3131–3135] components of cellular plastic moldings,[3136] and additives for removing metal ions and suspensions from liquid waste.[3137,3138] It was reported that such graft copolymers could also stabilize soil and other particles in water.[3139,3140] Such copolymers can hold pigments and, therefore, be used as components of water-based inks[3141] and pastes for textile printing applications.[3142–3144] A deodorant was prepared by blending this material with metallophthalocyanine.[3145] A moisture-permeable wallpaper was also patented.[3146] Acrylic acid grafting onto epichlorohydrin-crosslinked starch also gave a superabsorbent.[2967] Acrylic acid–acrylamide–starch graft copolymer, involving crosslinked starch for grafting, was proposed for a variety of applications including a cold-insulation material for food storage,[3147] a water sorbent for oil tanks,[3148] and dispersions of powdered coal in fuel oil.[3149]

Graft copolymerization of starch with acrylic acid and methylenebis(acrylamide) was used for applications that include cation-exchange resins,[3150] a water absorbent,[3151] and also for the encapsulation of agrochemicals, fertilizers, perfumes, and deodorants from which guest molecules could be slowly released.[3152,3153] A water absorbent was produced by grafting acrylic acid and 3-chloro-2-hydroxypropylacrylate onto starch.[3154] Acrylic acid–acrylamide–dimethylaminopropylacrylamide–starch copolymer was also designed for increasing the strength of paper.[3095,3155] Microcapsules were prepared from mixtures of acrylic acid–starch graft copolymer and siloxane[3156] as well as other additives.[2776,3157] Acrylate–acrylamide–starch copolymers were reported as dew-resistant paints.[3158] Superabsorbents were produced by acrylic acid–starch copolymers[2752] and crosslinked acrylic acid–starch graft copolymers.[3014,3159] Graft coplymerization of acrylic acid together with acrylic esters produced a high degree of water absorptivity.[3160] These materials were also proposed as cosmetic packs.[3116] Acrylic acid grafted onto (carboxymethyl)starch was also used to produce thickeners and flocculants.[2868] Acrylic acid–vinyl alcohol–starch graft copolymer has been used to dry coal powder[3080] and to coat paper.[3161] A composite of polyacrylate–starch graft copolymer with sodium sulfate decahydrate,

being hygroscopic, prevents solidification of dust and/or sand to which it was admixed.[3162] Methacrylic acid and ethylene dimethacrylate grafted onto starch gave a good adsorbent.[2985] A dust supressant was produced by combining acrylic acid–starch graft copolymer with surfactants.[3163] Improved freshness of fruits and vegetables was reported upon developing a layer of poly(vinyl chloride)–maleic acid copolymer on their surface.[3164]

Starch–acrylic acid–ethylene blended with urea and polyols formed films designed for biodegradable agricultural mulch.[3165] Starch–acrylic acid–vinyl acetate–acrylamide–*N,N*-methylenebisacrylamide pentapolymer formed a sizing material for yarns.[3166] Cationic starch grafted with acrylic acid and acrylamide gave a novel paper strengthening agent.[3167,3168] It was reported that acrylic acid grafted onto non-oxidized[3160,3169,3170] and oxidized starch[3171] gave a superabsorbent product for use with diapers, sanitary napkins, latex foam, and so on.[3172] Acrylic acid grafted together with acrylamide onto oxidized starch was used to produce a thickener.[3173] Acrylic acid grafted onto oxidized starch or (hydroxyethyl)starch produced a paper coating adhesive[3174] suitable for aluminium foils.[3175] Acrylic acid was grafted onto oxidized starch together with *N,N′*-methylenebisacrylamide, producing a superabsorbent material capable of absorbing 1248% water and 873% of saline.[3176] Oxidized starch grafted with acrylic acid and styrene with butadiene and sodium dodecylsulfate added was used to produce barrier coatings and sizes for paper.[3177,3178] Acrylic acid–starch–tetrakis(allyloxy)ethane graft polymer was reported to be a hydrophilic hydrogel with a high swelling capacity for usef in sanitary articles.[3179] A similar copolymer prepared with maleic anhydride was used in the same application.[3180] Cation-exchange composites were also prepared from starch, acrylic acid, and glycidylmethacrylate.[3181]

Starch–polyacrylonitrile graft copolymers exhibit high water absorbance[2987,3182] and since they resist high concentrations of salt, they have been used in secondary marine oil-recovery operations.[2983] In addition, they have been used to treat coal-water slurries,[3183] as a flocculant,[3184] as a paste for printing textiles,[3185,3186] as an anodic material in alkaline batteries,[3187,3188] and as an adhesive for surgical use[3189] including ostomy adhesives[3190] and waterproof sheets.[3191] They may also serve as construction materials for filters capable of detecting phase separation.[3192] Solutions useful as adhesives and coatings were obtained after solubilization in polar solvents, preferably nitroalkanes. These materials can be extruded into fibrils.[2969,3193] Starch–polyacrylonitrile graft copolymers also reduced the water content of emulsions, suspensions, and dispersions[3194,3195] and can be used as odor-absorbing materials.[3098,3191] Because of its powerful swelling capability, such a graft copolymer was patented as a building demolition agent, where

it is introduced into holes drilled in the construction materials and then, after contacting with water, it expands to an extent that cracks the construction.[3196] The addition of this material to poly(vinyl chloride) conferred biodegradability.[2942] Starch–polyacrylonitrile graft copolymers were also reported for use in production of water-permeable, waterproof fabrics.[3197]

Starch graft copolymers, either with acrylonitrile or methacrylonitrile, were used to stabilize soil containing up to 40% water.[3198] When mixed with quaternary ammonium compounds, they disperse rapidly in water.[2974] Grafting acrylonitrile together with isoprene onto [2-hydroxy-3-(tetramethylammonio)propyl]starch sulfate gave soapless latexes.[2955] A molten mixture of acrylonitrile–methyl methacrylate copolymer and graft acrylonitrile–starch copolymer formed so-called, self-crimping fiber.[3199] The same material was used to form water-absorbing molding compositions for toys.[3200] In combination with tragacanth, gum arabic and alginates it was used as a gel for treating skin and hair.[3201] Starch–acrylonitrile–styrene graft copolymers are also useful as thickeners.[3202] Starch–acrylonitrile–2–acrylamido–2–methylpropanesulfonic acid terpolymer showed a high degree of absorbency after saponification.[2876] Grafting of acrylamide onto either oxidized or (hydroxyethyl)starch produced a paper-coating adhesive.[3174] Saponified acrylonitrile–starch copolymer was an effective trap for copper(II) and cadmium ions at pH 7.[3203]

Acrylamide graft copolymer was proposed as a binder in paper coatings,[2785,3056] a flocculant,[3183,3204–3208] and also for use in enhanced oil-recovery applications.[3208–3211] It was also used as a thickener, particularly after its hydrolysis,[3212] for textile printing applications,[3213] and as collector of metal ions and suspensions from liquid waste.[3137] It was used to form readily removable dressings for wound secretions[3214] and also as a swelling polymer hydrogel for retaining soil humidity.[3215] Its use as a carrier of lysosome-encapsulated drugs was proposed.[3216] When hydrolyzed, it could be used as an extractant for protein.[3217] It could also be hydrolyzed with alpha amylase prior to its use as an additive to paper. A paste adhesive for tape was improved by blending it with metal ions.[2957] Grafting of acrylamide to poly(ethylene oxide)-crosslinked starch gave a resin for water absorption and retention.[3218] When applied jointly with dimethylaminoethylmethacrylate nitrate, it promoted flocculation of diatomaceous silica.[2784] Other patents report the use of acrylamide–acrylic acid–starch graft copolymer for flocculation of bauxite ore suspensions.[2714] Starch–acrylamide–allyl sulfonate graft copolymerization produced a flocculant for kaolin.[3219] Starch–acrylamide–*N,N′*methylenebis(acrylamide) graft polymer was reported as useful in diapers.[3220] 2-[(Methacryloxy)ethyl]tetramethylammonium

sulfate–starch–acrylamide as a cationic graft polymer was proposed for papermaking,[3221] and the use of a terpolymer with methacrylic acid instead of acrylic acid was also patented for the same application.[3222] Acrylamide–acrylic acid–amylopectin–dimethyldiallylammonium chloride graft copolymer was reported to provide good retention of pigments.[2693] A good absorbent was also produced by grafting acrylamide together with 2-acrylamido-2-methylpropanesulfonic acid on pregelatinized starch.[3006,3007,3223] Strengthening agents for paper include methacrylamide–starch graft copolymer,[3224] cationic starch grafted with acrylamide and acrylic acid,[3167] and grafting of *N*-acylvinylamides onto starch.[3225] Grafting of acrylamide onto oxidized starch as well as onto (hydroxyethyl)starch was reported to produce an adhesive coating for paper.[3174,3222] Ion-exchangers were produced from hydroxymethylated poly(acrylamide)–starch graft copolymer treated with various amines or ammonia.[3226]

Alkyl methacrylate–and alkyl acrylate–starch graft copolymers dissolved in polar solvents were designed as adhesives and coatings.[2969,3227] They could prevent soil erosion.[3228,3229] They were also proposed as stabilizers for aqueous dispersions[3230] and protective colloids.[3231] Methyl methacrylate grafted onto starch has uses as emulsifiers, adhesives, molding resins, and fibers.[3232] Being susceptible to attack by microorganisms, this copolymer confers biodegradability on blends of poly(vinyl chloride)[2942] and other materials.[2934,2997,3233–3236] They also perform well in filled plastics[3237] as strengthening agents for paper[3238,3239] and for nonwoven fabrics.[3240] Such graft copolymers were designed for encapsulating pesticides, fertilizers,[3241] drugs,[3242] and other bioactive materials.[3243] Methyl methacrylate–starch graft copolymer formed water-shrinking films useful as shrink-wrapping materials.[3244] Amylolytic *Arthrobacter* species readily adhered to such films.[3245] Acrylate–starch graft copolymers are used as a component of wallpaper to provide porosity.[3146] An adhesive was also produced by the use of hydroxyethylacrylate–starch graft copolymer after alkaline saponification and neutralizing with benzoic acid.[2864] Methoxyhexapropylene glycol methacrylate grafted onto starch produced films of good transparency and bending strength.[2869] Protective colloids were also formed by the same material.[3232] Graft copolymers of starch with methyl acrylate and *N,N,N*-tetramethylaminoethyl methacrylate sulfate were used as a latex material for stabilizing soil to water erosion.[3246] Hydroxyethylmethacrylate–mono(2-methacryloyloxyethyl)acid phosphate grafted onto starch phosphate was used to produce thickeners and flocculants[2868] as well as film-forming materials and adhesives.[3247] Composites of hydroxyethyl acrylate–starch graft polymers with poly(vinyl alcohol) were reported to produce films of very high tensile strength.[2979] Starch graft copolymers with glycidyl methacrylate were also reported to

immobilize peroxidase and glucose oxidase, cellulase, alpha amylase, and α-chymotrypsin enzymes.[3248] Industrial adhesives were produced by[(dimethylamino)ethyl]starch grafted with ethyl methacrylate.[3249] Alkyl acrylates grafted onto starch to which of glyoxal was added gave self-crosslinking latexes that were applied as a porous, polyester material.[2995] Acrylic acid–1,6-hexanediyl diacrylate–starch copolymer was patented as a component of gel lotions.[3250]

Starch–styrene graft copolymers were proposed as filled plastics[3251] and biodegradable materials.[2911] The addition of glycerol to an extrudate of this material to give a translucent, glossy, nonswelling ribbon. Starch–styrene–maleate copolymers served as dew-inhibiting paints.[3060,3252] Starch dialdehyde–styrene–acrylic acid terpolymer was reported as a sizing agent for paper.[3253]

Special graft copolymers were prepared from 4-vinylpyridine and starch. Such copolymers were then quaternized with alkyl halides to give bactericidal agents.[3053,3056]

Saponified vinyl acetate–starch graft copolymers were reported as sizes for yarns,[3026] air cleaners for dust removal,[3254] and as components of thermal recording materials.[3255] They were made from non-saponified vinyl acetate–starch graft copolymers.[3256] Graft copolymerization of starch with vinyl acetate also produced adhesives and thickeners[3025] as well as biodegradable plastics.[3257,3258] Isatoate acrylate grafted starch was reported as a laundry starch.[2871] Graft copolymerization of (2-hydroxypropyl-3-trimethylammonio)starch with monoethyl maleate and vinyl acetate was used as a sizing material for yarns.[3259]

Low-viscosity solutions resulted after vinyl alcohol–starch graft copolymers were digested with enzymes.[3027]

Starch grafted with allyl alcohol was used as a film-forming product and adhesive.[2861,3260] Starch allyl glycidyl ether grafted with acrylamide and acrylic acid was produced as a thickener;[3261] similarly starch allyl glycidyl ether grafted with 1-vinyl-3-(3-sulfopropyl)imidazolium hydroxide inner salt was designed as a thickener and stabilizer for aqueous media.[3262] Other derivatives involving grafting with allyl glycidyl ether and acrylamide were reported as paper strengthening agents.[2692] Derivatization of starch allyl glycidyl ether with diallylaminoethyl chloride and acrylamide was used to produce a water resistant, alkaline adhesive for corrugated paperboard.[3263]

Maleic acid–starch graft copolymers were used to precipitate waste suspensions and collect metal ions.[3137] The same material was also proposed as a re-moistenable adhesive,[3108] a swellable material,[2768] and a and encapsulant of some enzymes.[3264]

Graft co- and ter-polymers of starch with acrylamide and 2-hydroxy-3-methacryloyloxypropyl-tetramethylammonium chloride or 2-hydroxy-3-

methacryloyloxypropyl-tetramethylammonium sulfate were reported as selective depressants for silica in flotation of pebble phosphate ores and other ores,[2713] biodegradable drainage aids, and papermaking fillers.[3265,3266] Chlorides of the same copolymers were also patented as thickeners and flocculants.[2497]

When chloroprene was grafted onto cationic aminated starch, a latex was obtained that imparted wet strength to paper and also served as a pressureless adhesive for wood.[2951] Starch dialdehyde when grafted with acrylonitrile, methyl methacrylate, or both, produced a biodegradable filler for poly(vinyl chloride) plastics.[2942] Starch xanthates grafted with vinyl monomers were also used to produce additives for reinforced foamed rubber.[2944,2945]

Starch has been grafted with such silyl compounds such as 4-aminopropyltriethoxysilane to give a reinforced polymer that was subsequently reacted with maleic anhydride in the presence of benzoyl peroxide.[3267]

Biodegradable plastics were also obtained by grafting succinic acid monochloride on epichlorohydrin-crosslinked starch,[3268] and by grafting lactones and lactides onto starch.[2937]

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