simple synthetic routes to strained hydrocarbons that may be difficult to prepare by conventional methods.[55] As is illustrated by some of the examples outlined above though, very complex product mixtures can be obtained, particularly with bichromophoric systems. What is remarkable, however, is the high degree of regio- and stereospecificity associated with many of the photo-transformations.

In addition to the academic interest that these reactions provide, the advent of the excimer laser has introduced useful technological and medical applications[56] that involve interactions of far-UV photons with organic solids.[57] As a result, it can be expected that this field will develop rapidly in coming years.

We thank our co-workers, including T. Baum, J. A. Ors, and A. R. Rossi, whose ideas and experimental skill contributed a great deal toward the work described here.

Registry No. Cyclopropane, 75-19-4; allylcyclopropane, 4663-23-4; vinylcyclopropane, 693-86-7.

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Chemical Modification and Selective Fragmentation of Polysaccharides

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The fact that polysaccharides display an enormous variety of structures[1] may be obscured by the very abundance of starch and cellulose as chemically monotonous homopolysaccharides. In fact, the vast majority of polysaccharides are heteroglycans with two or more constituent sugars, frequently in several linkage types. The complete assignment of covalent structures still presents a major challenge to the organic chemist since it involves not only sequencing, as for proteins and nucleic acids, but also the determination of ring size, linkage type, and anomeric configuration for each of the monosaccharide units. Furthermore, repetitive features, which are always present, may be masked by departures from regularity. Some of these departures from strict regularity are of major importance since they provide the basis for the expression of desirable physical properties,[2] e.g., in gel formation, or give rise to the precise structural domains involved in specific biological activity.

Three broad classes of polysaccharides illustrate different balances between structural regularity and deviations from regularity. Many bacterial polysaccharides[3] (Figure 1, top), of the capsular type and in the *O*-antigenic regions of lipopolysaccharides, show a high degree of structural regularity resulting from the biosynthetic assembly on a lipid carrier of oligosaccharide repeating units of some 3–8 residues which are then polymerized. The presence of a regular repeating unit is a simplifying factor in structure determination. Consequently, with the use of two-dimensional NMR techniques and fast atom bombardment mass spectrometry, complete structures can be worked out with a minimum of chemical degradations.[4,5] Where degradations are required, specific bacteriophage enzymes are especially useful since they yield a single oligosaccharide closely related to the natural repeating unit.[6]

In contrast to most polysaccharides from bacteria, many of those from mammalian and plant sources show departures from simple regularity of structure. The mammalian glycosaminoglycans[7] (Figure 1, middle) are synthesized initially with rather simple repeating disaccharide structures of the AB type but then undergo postpolymerization changes in which each type of unit may be modified. The blood anticoagulant heparin provides an excellent example of one such polysaccharide in which very precise alterations to certain sequences of sugar residues produce the specific pentasaccharide region which binds to antithrombin III.[7]

Plant polysaccharides,[8] in addition to being essentially passive structural components of cell walls, may also be the source of biologically active fragments which are liberated by the action of specific enzymes.[9]

At first sight many plant glycans appear to be of a simple type in possessing repetitive interior chains, which form the basis for their structural classification

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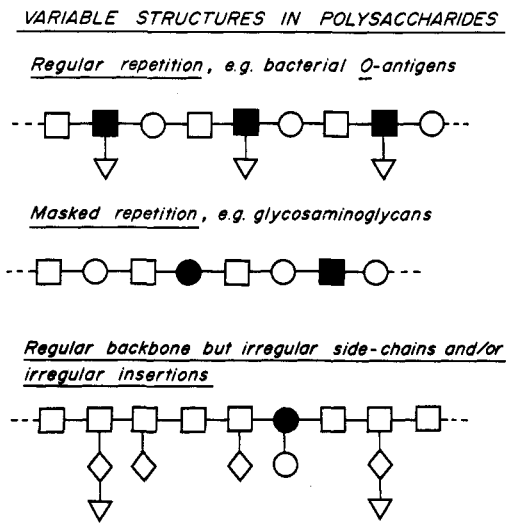

Figure 1. Diagrammatic representation of structurally repetitive polysaccharide sequences and departures from regularity.

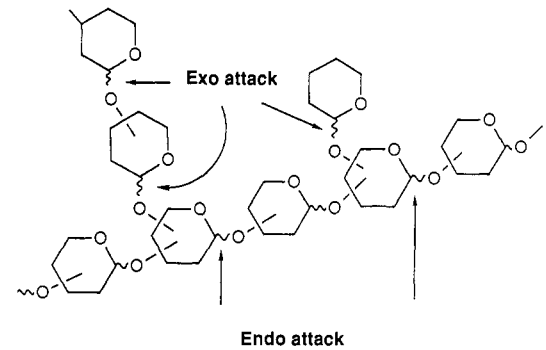

Figure 2. Degradations of polysaccharides by exo and endo attack. Typical examples of exo attack are hydrolysis with exo enzymes, partial acid hydrolysis of acid-sensitive terminal glycosidic linkages, and Smith degradation involving the removal of periodate-vulnerable outer chain residues. Examples of endo attack are hydrolysis with endo enzymes, base-catalyzed β-elimination of 4-O-substituted hexuronates, and specific structural modifications of internal chain residues leading to the formation of linkages susceptible to selective cleavage.

into families, such as the xylan, arabinogalactan, glucuronomannan, and pectin-related galacturonan and rhamnogalacturonan groups.[8,10] Departures from simple regularity may be through the attachment of side chains of different types or degrees of extension or, less frequently, the insertion of different units in the main chain (Figure 1, bottom). For departures from regularity to be included, repeating units, if present, as in the highly branched plant arabinogalactans,[8] must be larger than those in bacterial and mammalian polysaccharides.

Progress in establishing detailed structures has been slow for plant polysaccharides which contain high proportions of uronic acids in the interior chains. In the absence of satisfactory methods for internal chain cleavage with retention of outer chain units, only limited evidence for regularity of backbone structure has been available and even less on detailed sequences of residues in side chains. To provide some answers to these problems, we have explored new types of selective fragmentation initiated after structural modification of polysaccharides.

Approaches to Chemical Selectivity in Partial Fragmentation

Among classical methods of polysaccharide structure determination,[11] partial hydrolysis and related acid-catalyzed depolymerizations have been widely used. Although wasteful of material, these procedures have been turned to advantage where there are large differences in rates of glycoside hydrolysis, as in the selective cleavage of furanosidic linkages, or where the resistance to hydrolysis of glycosiduronic acids permits the ready formation of acidic oligosaccharides. However, structure determination by partial fragmentation remains incomplete unless overlapping sequences of sugar residues can be generated by other types of reactions. The polysaccharides to be considered here contain outer sugar residues whose glycosidic linkages are relatively vulnerable to acid hydrolysis. Stepwise degradations by acid, or enzymic attack by glycosidase or exoglycanase action[12] with loss of outer residues (Figure 2), may generate simpler degraded polysaccharides but with loss of information on points of attachment of the cleaved units. Endoglycanases are rarely available with the desired specificity and with the ability to approach densely branched interior chains and thus liberate segments with outer chains still attached. Accordingly, our attention has turned to chemical means of achieving "endo" attack, taking advantage of functional groups already present or introduced through specific structural modifications.

Ideally a selective fragmentation procedure for polysaccharides would be analogous to the cyanogen bromide degradation of protein.[13] Such a degradation for a polysaccharide should proceed with a chemical selectivity different from and complementary to that observed in partial acid hydrolysis and related reactions and desirably give rise to a modified sugar residue which clearly originates from the site of cleavage, but with retention of other glycosyl residues in unaltered form. A close analogy to the cyanogen bromide degradation of proteins is the nitrous acid deamination of the equatorially oriented 2-amino-2-deoxy-D-glucopyranosides and -D-galactopyranosides with 2,5-anhydrohexose formation accompanied by glycoside cleavage.[11] This reaction has been extensively used in polysaccharide studies,[14-16] but it is not suitable for extension to methylated derivatives.[17]

Where degradations can be performed on methylated polysaccharides there are the following advantages: (1) solubility in organic solvents, (2) suitability for linkage analysis (the stock-in-trade of the polysaccharide chemist), and (3) the generation, in selective fragmentations, of hydroxyl groups only at sites of cleavage in glycosyl (after reduction) and aglycon residues. The one major limitation of the use of methylated glycans, apart from the loss of base-labile ester substituents, is that

(10) These families may include a range of species from the structurally simpler but less readily isolated cell wall polysaccharides to the more complex but easily obtainable exudate gum components.

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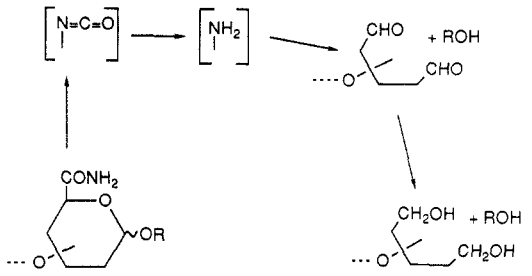

Figure 3. Hofmann–Weermann degradation of glycosiduronamides: NaClO, pH 12.5; CH_3CO_2H, pH 5; $NaBH_4$.

for uronic acid containing polysaccharides (glycuronans) methylation, necessarily carried out under basic conditions, may be accompanied by some base-catalyzed β-elimination from hexuronate esters. The methylated glycuronan may therefore not be entirely representative of the parent polysaccharide. Limited depolymerization need not be a serious complication provided that (i) sufficiently long repeating sequences remain and (ii) the origins of modified residues at the inadvertently formed chain termini are recognized. A more serious situation could arise if high proportions of certain units in side chains are lost in the methylation process. In such instances these losses must be balanced against the advantages that accrue from the use of methylated derivatives.

An alternative approach to acid-catalyzed fragmentation involves base-catalyzed degradation initiated at esterified uronic acid residues[18–20] or at carbonyl groups[21] formed by oxidation of specific hydroxyl groups in otherwise methylated glycans. Hydroxyl groups are protected and the advantages of working with methylated derivatives are realized, but the sugar residues at which degradation is initiated are destroyed. Additional structural information may be lost if further degradation takes place from exposed reducing sugar residues.

We have now developed procedures for the controlled depolymerization of glycuronans with retention of recognizable fragments from uronic acid residues. Structural modifications are required for the introduction of functional groups at which fragmentation is sought. Our main objective has been to reverse the cleavage preference, wherein glycosiduronic acid linkages are the most resistant to acid hydrolysis, and to achieve instead selective fragmentation at these linkages. The first reaction to be explored in our laboratory was the Hofmann–Weermann hypochlorite degradation which had been first applied to nonreducing terminal glycosiduronamides by Kochetkov and his collaborators[22] (Figure 3). The reaction was extended to the cleavage of nonterminal linkages in methylated polysaccharides.[23] Formation of a pentodialdose without other chain scission through hydrolysis of the intermediate 5-aminopentopyranoside, followed by reduction with sodium borohydride, furnished base-stable pen-

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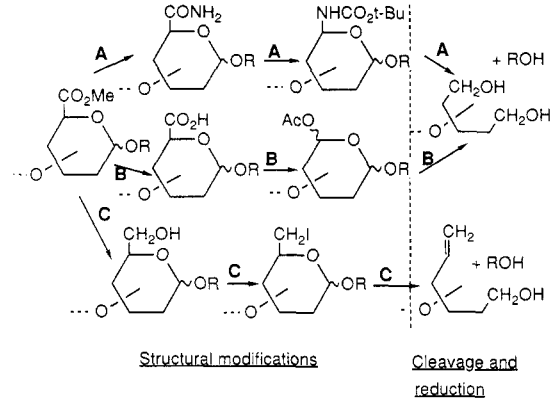

Figure 4. Selective fragmentations of methylated glycuronans with net cleavage of glycosiduronic acid linkages and exposure of hydroxyl groups in pentitol, 1,2-dideoxyhexenitol, and aglycon residues for further substitution (acetylation or trideuteriomethylation): (A) NH_3; $Pb(OAc)_4$, *t*-BuOH; HCO_2H; $NaBH_4$. (B) NaOH; $Pb(OAc)_4$, benzene; $NaBH_4$. (C) $LiAlH_4$; NIS, PPh_3; Zn dust, EtOH–H_2O, $NaBH_4$.

titols and pentitol-terminated oligosaccharides.

Although the reaction sequence proved to be satisfactory in principle, the extent of reaction was variable, and completeness of reaction could not be ascertained until the products of depolymerization and subsequent derivatization had been separated and characterized. To overcome these deficiencies, an alternative procedure and two other reaction sequences which employed a common strategy were developed (Figure 4). The common strategy involves (i) a series of structural modifications of uronic acid residues to furnish, without depolymerization, a latent site for fragmentation, followed by (ii) deliberate chain scission to yield characteristic derivatives which clearly originate from those uronic acids and carry attached glycosyl substituents. For potential reaction sequences suitably substituted di- or trisaccharides may be used as model compounds to establish the feasibility of high preparative yields being obtained at each stage, but this is no guarantee that reactions at the polymer level will proceed at similar rates or to an equivalent extent. All structural modification and cleavage steps should be monitored spectroscopically and/or chemically to ensure as complete reaction as possible since transformed and untransformed units in the same chain cannot be separated. Shortfalls in any of the structural modification steps leading to the introduction of a required functional group or in its selective cleavage will result in incomplete depolymerization. For transformations where only one type of structural unit is affected spectroscopic analysis, if adequately sensitive, may be sufficient. However, where the units undergoing change are in two or more structural environments, methylated sugar analysis is desirable to ensure that each type of unit is duly modified.

Cleavage of β-D-Glucopyranosiduronic Acid Linkages

The first two procedures (Figure 4, A and B) for the selective cleavage of modified glycosiduronic acid linkages involve a net oxidative decarboxylation with formation of masked pentodialdose derivatives. The overall objective of the Hofmann–Weermann hypochlorite degradation, but with an accompanying check on the completeness of modification, was achieved by

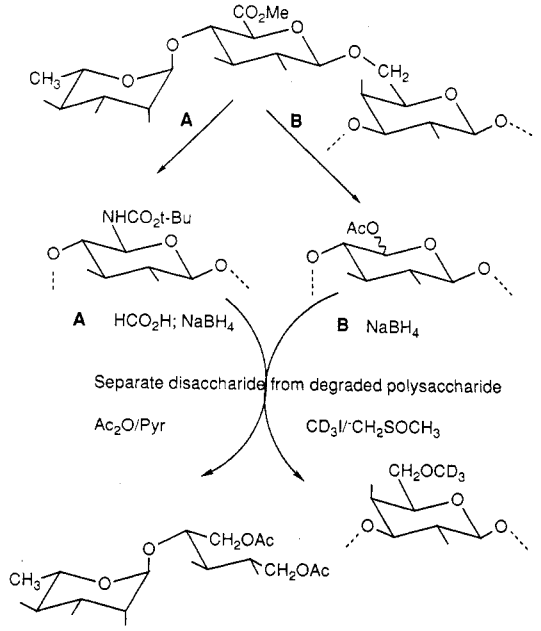

Figure 5. Cleavage of glucosiduronic acid linkages in outer trisaccharide segments of methylated gum arabic by routes A and B (as in Figure 4) with isolation of derivatives of 4-*O*-α-L-rhamnopyranosyl-D-xylitol and attenuated outer chains in otherwise unaltered methylated polysaccharide. (In this and other figures undesignated substituents — are OCH_3 and ⌐ are CH_2OCH_3.)

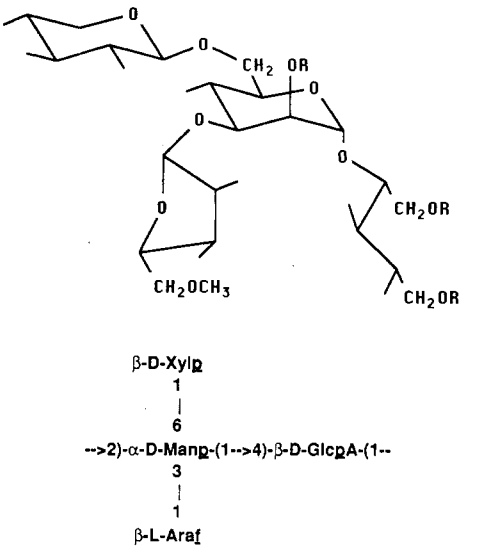

Figure 6. Peralkylated tetrasaccharide alditol (R = CD_3) formed from the segment of leiocarpan A shown in shorthand form. The methylated polysaccharide was degraded by both routes A and B (Figure 4), followed by trideuteriomethylation.

Hofmann–Curtius type rearrangements. Intermediate isocyanates were intercepted by reaction with *tert*-butyl alcohol to give isolable *tert*-butyl carbamates[24] (Figure 4, A), which were hydrolyzed with formic acid at room temperature with minimum cleavage of other glycosidic linkages in methylated glycans. Comparable selectivity in carbamate hydrolysis of acetylated glycans was not observed.[25]

A reaction sequence which is more direct in both the structural modification and selective cleavage steps is based on the decarboxylation–acetoxylation reaction developed by Kitagawa and his collaborators.[26] Methylated glucosiduronic acids are treated with lead tetraacetate in boiling benzene, and completeness of reaction may be checked by the disappearance of ionizable carboxyl groups and by chemical analysis for the absence of uronic acid components in the modified polysaccharide (Figure 4, B). The formation of epimeric pairs of 5-acetoxypentopyranosides is not a matter of consequence since reductive cleavage with sodium borohydride[27] occurs cleanly with formation of the same pentitols and pentitol-terminated oligosaccharides.

Both degradative procedures were effective in achieving a high degree of selective cleavage of D-glucosiduronic acid linkages in the outer chains of methylated gum arabic (Figure 5).[24,27] In a much more stringent test depolymerization between alternate sugar residues in the inner chains of the methylated derivative of leiocarpan A, an exudate gum glucuronomannan, furnished two oligosaccharides carrying intact side chains attached to segments derived from the fragmented main chain.[28] Figure 6 shows the structure of the peralkylated tetrasaccharide alditol derived from the designated segment of leiocarpan A. Exposed hydroxyl groups in the liberated oligosaccharides were identified by trideuteriomethylation, and the complete structures of the oligosaccharide derivatives were established by ^1H NMR and ^{13}C NMR spectroscopy, mass spectrometry of the oligosaccharide derivatives, and methylated sugar analysis by conversion into partially methylated alditol acetates (for GLC–MS) on hydrolysis, reduction, and acetylation.[28]

The decarboxylation–acetoxylation sequence (Figure 4, B) has been used to obtain new structural information on other polysaccharides of the glucuronomannan family.[8,29–31] Degradation of the methylated polysaccharides led to the isolation of partially methylated oligosaccharide alditols, each of which contained a 4-*O*-α-D-mannopyranosyl-D-xylitol unit with an exposed hydroxyl group at C-2 of the mannose residue. Figure 7 shows the variety of single unit side chains attached to both types of main-chain residues in polysaccharides of this family. The isolation of these compounds confirms the presence in each polysaccharide main chain of alternating 2-linked α-D-mannopyranose and 4-linked D-glucuronic acid residues. More importantly, the characterization of these oligosaccharides provides the first direct evidence for the sites of attachments and anomeric configurations of sugar residues in attendant side chains.

The Hex-5-enose Degradation

Pectins and structurally related exudate gums present similar problems to those of the glucuronomannans in that they also possess glycuronan interior chains. There are even further variations in the detailed arrangements of sugar residues in that (i) the backbone chains range from 4-linked α-D-galacturonans to rhamnogalact-

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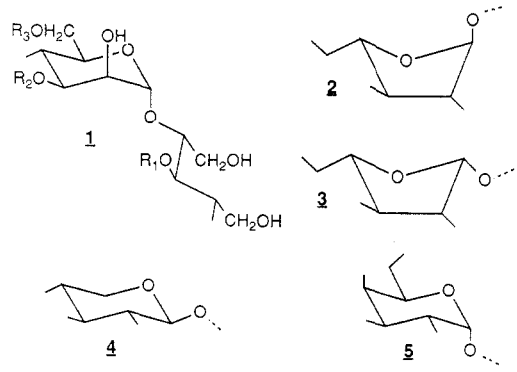

Polysaccharide source	OR_1	OR_2	OR_3
Leiocarpan A			4
Leiocarpan A		3	4
Drosera mucins[29]		5	
Drosera mucins	2		
Tobacco arabinoglucuronomannan[30]	2		
Drosera binata mucin	2	5	
Tobacco arabinoglucuronomannan		2	

Figure 7. Methylated oligosaccharide alditols formed from methylated glucuronomannans by the decarboxylation–acetoxylation route (Figure 4, B) contains a common 4-*O*-α-D-mannopyranosyl-D-xylitol unit (**1**) to which may be attached glycosyl substituents (**2**–**5**) [**2** = α-L-arabinofuranosyl, **3** = β-L-arabinofuranosyl, **4** = β-D-xylopyranosyl, and **5** = α-D-galactopyranosyl].

uronans with alternate 4-linked α-D-galacturonic acid and 2-linked α-L-rhamnopyranose residues and (ii) the side chains which may be attached to one or another backbone residue may include short stubs of one to three residues or polysaccharide subunits with multiple residues of D-galactose and/or L-arabinose,[8] and sometimes as in rhamnogalacturonan II with unusual sugars not encountered elsewhere in plant glycans.[32] The two degradative sequences which were quite effective for the cleavage of β-D-glucosiduronic acid linkages were, for reasons which are yet unexplained, rather ineffective for those of α-D-galactosiduronic acid. A different approach was therefore taken to the fragmentation of these polysaccharides.

The degradative sequence (Figure 4, C) involves the generation of primary hydroxyl groups, e.g., by reduction of uronic acid residues, conversion to 6-deoxy-6-iodohexopyranosides, reductive cleavage with zinc dust (cf. ref 33), and treatment of the liberated 5,6-dideoxyhex-5-enoses to give the corresponding 1,2-dideoxyhex-1-enitols. Studies on model oligosaccharides showed that otherwise methylated 6-deoxy-6-iodo-α-D-galactopyranosides with glycosyl substituents at various positions are smoothly degraded and that the derived hexenitol-terminated oligosaccharides are readily characterized by acetylation or further alkylation as for the corresponding saturated alditol derivatives.[34] Primary hydroxyl groups in oligosaccharide derivatives were conveniently iodinated by triflation followed by

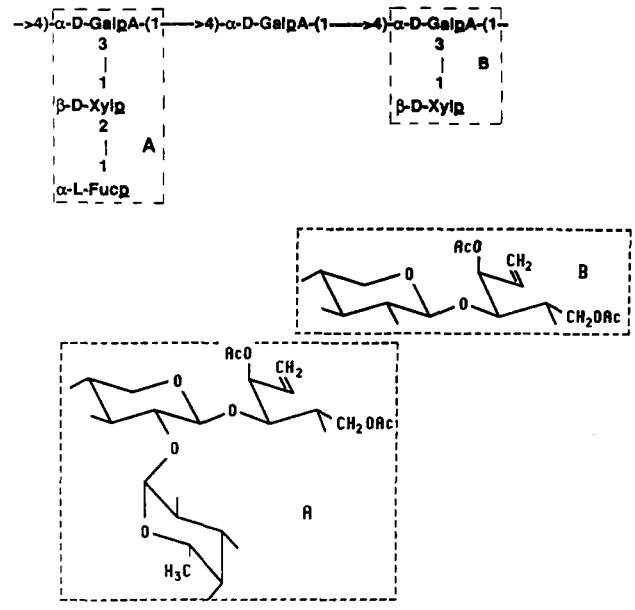

Figure 8. Hex-5-enose degradation of carboxyl-reduced methylated tragacanthic acid with reactions shown in Figure 4 (C) and leading, after acetylation, to hexenitol-terminated oligosaccharides which bear the side chains attached to the original galacturonan chain (as designated in shorthand form).

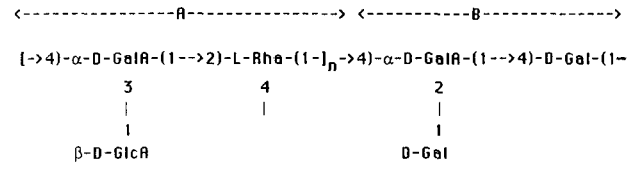

Figure 9. Structural regions proposed for *Sterculia* gums in earlier studies.[40] (All residues in Figures 9 and 11 are pyranoid.)

iodide displacement.[35] For polysaccharides, iodination of primary hydroxyl groups proceeds more reliably by reaction with *N*-iodosuccinimide (NIS) and triphenylphosphine.[36] The overall conversion into 6-deoxy-6-iodoglycosides is conveniently assessed by reaction with tributylstannane[37] to give residues of the corresponding 6-deoxyhexoses, which are characterized by standard methylated sugar analyses.

The hex-5-enose degradation has been applied to two exudate gums whose backbone structures are at opposite ends of the galacturonan–rhamnogalacturonan spectrum. Tragacanthic acid has an α-D-galacturonan backbone to which are attached incompletely defined short side chains.[38] Iodination of the carboxyl-reduced methylated glycan was achieved by the Binkley procedure,[35] and treatment with zinc dust, followed by reduction and acetylation, gave two hexenitol-terminated oligosaccharides (Figure 8), thus providing unambiguous evidence for the nature and mode of attachment of side chains.[39]

Exudate gums of the *Sterculia* family[8] contain rhamnogalacturonan chains with repeating disaccharide units in which each type of sugar residue may be in-

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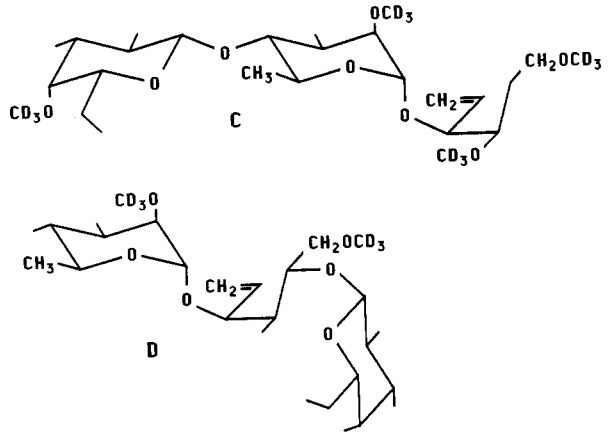

Figure 10. Two peralkylated hexenitol-terminated trisaccharides (C and D) from the hex-5-enose degradation of carboxyl-reduced methylated *Sterculia* gums.

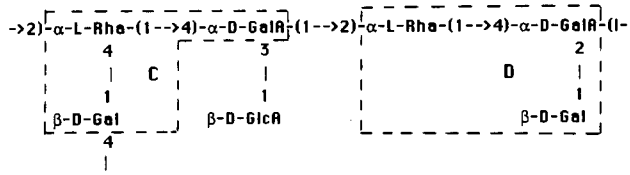

Figure 11. Revised partial structure (shorthand array) for *Sterculia* gums with rhamnogalacturonan backbone and attached side chains indicating regions C and D from which the hexenitol-terminated trisaccharides (Figure 10) are derived.

volved in branching (Figure 9, region A). In addition, units of another disaccharide with an attached side chain (Figure 9, region B) were postulated as segments which interrupted at intervals and were continuous with the rhamnogalacturonan regions.[40] Other neutral sugar residues, present mainly as end groups, were not placed with certainty. Carboxyl-reduced methylated *S. urens* and *S. caudata* gums have been subjected to the hex-5-enose degradation, as for the corresponding derivative of tragacanthic acid, to give, in each case, a series of peralkylated oligosaccharides. The characterization of the two major trisaccharide components[41] (Figure 10) has necessitated revision of the earlier partial structures and points to the presence of uninterrupted rhamnogalacturonan chains bearing a variety of side chains (Figure 11). The β-D-galactopyranose residues in the gums are present only in side chains but are of two different types. A disaccharide methyl glycoside, necessarily arising from the "reducing" terminus of the methylated glycans, was formed in sufficient quantity to suggest that depolymerization involving base-catalyzed β-elimination had taken place during alkylation (cf. ref 42). Such a reaction could account for the observation that galacturonic acid residues linked to galactose in the previously postulated region B (Figure 9) were not detected as constituents of the methylated gums and have yet to be accounted for in the revised structure.

In principle, the hex-5-enose degradation is not restricted to carboxyl-reduced glycuronans since reaction could be initiated wherever selective iodination of primary hydroxyl groups can be achieved. Experiments to date have drawn attention to two quite different

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(42) McNeil, M.; Darvill, A. G.; Albersheim, P. *Plant Physiol.* **1982**, *70*, 1586.

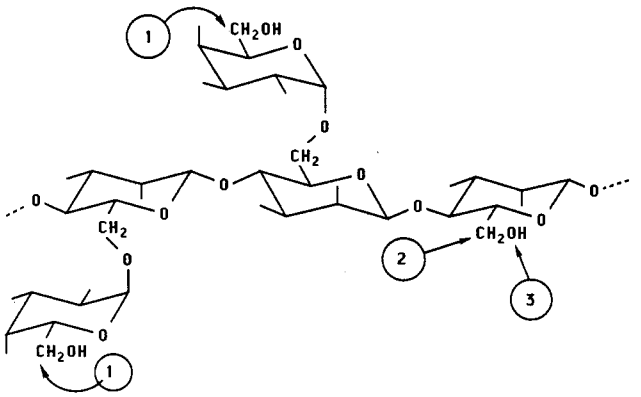

Figure 12. Selective iodination of primary hydroxyl groups in otherwise methylated galactomannans: (1) C-6 of α-D-galactopyranose residues is available for displacement if protected against intramolecular displacement by substitution of O-3; (2) C-6 of unbranched β-D-mannopyranose residues is relatively unreactive, although (3) alkylation at O-6 occurs without difficulty.

problems. In common with other investigators[43] we have confirmed[44] that selective iodination at primary hydroxyl groups, which proceeds satisfactorily for unprotected D-glucopyranosides and D-mannopyranosides, cannot be achieved for D-galactopyranosides without 3,6-anhydro derivative formation unless secondary hydroxyl groups are blocked. In addition, lack of reactivity of supposedly accessible primary hydroxyl groups may be due to chain conformational restrictions. An attempt was made to effect iodination at C-6 of D-galactopyranose end groups and unbranched D-mannopyranose residues in otherwise methylated derivatives of galactomannans (Figure 12), such as guaran. The protected D-galactopyranose residues, which often undergo nucleophilic displacements at C-6 sluggishly,[45] reacted completely. However, iodination at C-6 unbranched D-mannopyranose residues was largely unsuccessful, even though alkylation at O-6 (methylation or even tritylation) occurred without difficulty.

Conclusions

The search for specific fragmentations of polysaccharides by chemical rather than enzymic procedures involves an appreciation of the multifaceted requirements for selectivity in the reactions of carbohydrate polymers. Practical considerations include trivial but very real solubility problems and the fact that surface reactions, which proceed smoothly for compounds of low molecular weight, may simply not take place at reasonable rates with polysaccharide substrates, e.g. anodic oxidation as an alternative to decarboxylation–acetoxylation with lead tetraacetate.[24]

The methods which we have developed were generated in response to particular structural problems and have yet to be proved general, but they have enabled us to probe previously inaccessible regions of a number of polysaccharide structures. The overall strategy adopted in seeking to introduce sites for fragmentation, and in monitoring the steps involved and in the subsequent cleavage, may prove to be more generally useful than the tactics employed in particular circumstances.

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The fragmentation procedures were designed primarily to generate oligosaccharides from regions of structure where regularity is absent or has yet to be demonstrated. Most of the structurally informative molecules characterized so far have been in the tri- and tetrasaccharide range. Since fast atom bombardment mass spectrometry already provides the means for the determination of molecular weights and sequential aspects of structure for carbohydrate polymers of up to ~30 residues, future progress will be critically dependent on advances in techniques for chromatographic separations of oligosaccharides of increasing size as individual species.

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Probing Intermolecular Interactions with Picosecond Photon Echo Experiments

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I. Introduction

Because a tremendous amount of chemistry occurs in condensed phases, a detailed understanding of intermolecular interactions and dynamics on a microscopic level is very important. A molecule in a medium, whether it is a liquid, a glass, a membrane, or a crystal, feels a constantly changing array of intermolecular interactions. Heat is molecular motions: changing molecular positions and orientations. Since intermolecular interactions are distance- and angle-dependent, any condensed-phase system confronts us with a complex, time-dependent problem. Application of picosecond nonlinear spectroscopic experiments to condensed-phase systems is providing detailed new probes of fundamental condensed matter phenomena.

In this paper we will briefly discuss two problems: the nature of the electronic states of interacting solute molecules and the coupling of electronic states of a solute molecule to the mechanical degrees of freedom of the medium. These examples will illustrate the unique nature of the information that can be obtained from fast nonlinear experiments. In the picosecond photon echo experiments presented below, the samples are mixed molecular crystals or organic molecules in organic glasses. Molecular crystals have a long history as prototype molecular systems. Problems of electronic and vibronic spectroscopy, spin–orbit coupling, and intersystem crossing, to name a few, have received detailed study in molecular crystal systems. A mixed crystal contains guest molecules (solute) in a host crystal. The mixed crystal is a solid solution in which the guest molecules are randomly distributed spatially, but unlike a liquid solution, there is orientational order.

In contrast to a crystal, organic molecules in an organic glass do not experience environments which have orientational order. Molecules in a glass, as in liquid solution, have a wide distribution of environments which are associated with the structures of the solvent shells around each molecule. Unlike a crystal, the glass environments are not fixed, even at very low temperature (1.5 K).[1] In organic glasses, a particular local mechanical configuration is separated from other configurations by small potential barriers. Tunneling and thermal activation result in constantly changing environments around a solute molecule. This is somewhat akin to a liquid solution, except the time scale on which the environments change is orders of magnitude faster in a liquid.

In a crystal, heat manifests itself as vibrations of the lattice, i.e., acoustic and optical phonons.[2] Acoustic phonons derive from molecular translations in the gas phase, whereas optical phonons derive from molecular rotations. The restoring forces present in the densely packed crystal couple the motions of the individual molecules. This coupling transforms the gas-phase translations and rotations into collective vibrational motions of the solid, the phonons. Thermal population of many different phonon modes produces an environment about a solute molecule which is constantly and rapidly fluctuating about some equilibrium lattice configuration. In a glass, similar fluctuations occur, but in addition, the local configuration can actually change.

If a sample is optically excited at the S_0 to S_1 transition frequency of a dilute solute (no solute–solute interactions) at very low temperature (phonon-induced fluctuations and configuration changes frozen out), then the only dynamics will be relaxation of the molecular

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