RECENT ADVANCES IN CELLULOSE AND STARCH CHEMISTRY

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INTRODUCTION

Because of the intensive work being done on cellulose at the present time, the multiplicity of new facts and theories which are being adduced, renders comprehensive treatises on the chemistry of this carbohydrate obsolescent, almost as soon as the mechanics of assembly and publication are possible.

CELLULOSE STRUCTURE, HISTORICAL SUMMARY

For the benefit of those whose main interest has been in branches of Organic Chemistry other than that of cellulose, a brief account of the salient facts in connection with the study of the structure of this substance may be of interest before presenting the latest developments. So much has been published that in a review of this type only what appear, in the opinions of the authors, as the most fundamental work may be recounted and indulgence is asked if important researches seem to have been omitted.

As long ago as 1883 Flechsig (1) claimed that cellulose could be entirely converted into glucose. Ost and Wilkening (2) hydrolyzed cotton with sulfuric acid and obtained an almost theoretical yield of glucose, as estimated polarimetrically and by means of Fehling solution. Subsequently Willstätter and Zechmeister (3) showed that cellulose was soluble in 41 per cent hydrochloric acid and that such a solution upon standing resulted in the hydrolysis of cellulose to glucose. The polarimeter and Fehling solution both indicated a 95 per cent yield of glucose.

Since glucose was not quantitatively isolated, the proof that cellulose could be quantitatively hydrolyzed to glucose was open to criticism.

Cunningham (4) found that two such widely different types as cotton and esparto cellulose, the latter known to contain xylan, gave approximately the same optical rotation in solutions prepared according to the method of Willstätter and Zechmeister.

It was later found by E. C. Sherrard and A. W. Froehlke (5) that cotton cellulose, white spruce, Douglas Fir and yellow birch when dissolved in 40 per cent hydrochloric acid gave practically identical yields of glucose as estimated by means of optical rotation.

That cellulose is capable of hydrolysis quantitatively to glucose was firmly established through the work of Monier-Williams (6) who hydrolyzed cellulose with sulfuric acid and actually isolated pure crystalline glucose to the extent of 91 per cent, and the work of Irvine and Soutar (7) done at approximately the same time. The latter workers subjected cellulose to acetolysis with sulfuric acid in the presence of acetic anhydride and acetic acid and hydrolyzed the resulting glucose acetate with a methyl alcohol solution of hydrochloric acid, thereby obtaining α-methyl glucoside. This was, of course, readily converted to glucose. The yield obtained in this way was 85 per cent. Subsequently in 1922, Irvine and Hirst (8) through modification of the acetolysis method and the use of slightly stronger alcoholic HCl, brought the yield of glucose to 95.1 per cent of that demanded by the expression $(C_6H_{10}O_5)_x \rightarrow C_6H_{12}O_6$.

The methylation of cellulose also contributed to the cellulose $\rightarrow$ glucose question. Through the use of this reaction, Denham (9) introduced 25 per cent of methoxyl into cellulose. The product so obtained, when dissolved in 41 per cent hydrochloric acid and hydrolyzed, gave a crystalline sugar which was identified as 2,3,6 trimethyl glucose. And in 1923 Irvine and Hirst (10) demonstrated that 2,3,6 trimethyl glucose was the only sugar formed when cellulose is hydrolyzed to glucose.

The hydrolysis of cellulose quantitatively to glucose and the proof that 2,3,6 trimethyl glucose is the only glucose derivative

obtained by hydrolysis went far to clear the atmosphere in regard to cellulose structure and rid the subsequent speculations of many ambiguities which had existed prior to that time.   It enabled the casting out of much theoretical discussion which had previously appeared, such as the formula for cellulose presented by Cross and Bevan (11) about 1900 in which appeared four free hydroxyl groups.   The results of esterification studies had for a long time militated against such a view but the evidence presented in summary above made such a formula quite untenable.
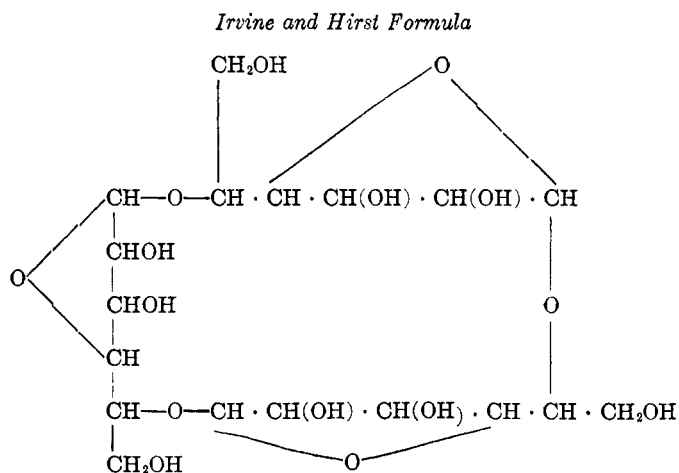
The present views of the structure of cellulose, as held by many workers, regard cellulose as represented by the formulation $[(C_6H_{10}O_5)_x]_y$, in which x equals the number of $C_6H_{10}O_5$ groups in the fundamental molecule and y equals the number of $(C_6H_{10}O_5)_x$ groups joined together by association, polymerization or other forces to produce the colloidal particle or micelle.   A notable exception is found in Kurt Hess and his co-workers (12) who maintain that the fundamental cellulose molecule is $(C_6H_{10}O_5)_1$. Their contention is based upon polarimetric data from the behaviour of cellulose in cuprammonium solution, and upon cryoscopic studies of the molecular weight of various derivatives. Recent publications by Pringsheim (13) appear to indicate that he is also of this belief.

On the other hand the isolation of a disaccharide from cellulose, namely cellobiose, leads many to the view that the linkage existing in cellobiose is present in cellulose.   Cellobiose is obtained by acetolysis of cellulose, with acetic anhydride, acetic acid and sulfuric acid, with subsequent hydrolysis of the cellobiose octa-acetate obtained.

Cellobiose octa-acetate was first isolated in the acetolysis of cellulose by Franchimont (14).   It was later studied by Maquenne and Goodwin (15) and other workers.   It appears to be one of the degradation products of cellulose.   The method of formation lends credence to the likelihood that it is a part of the cellulose molecule.   The maximum yield of cellobiose octa-acetate thus far obtained is 35 to 40 per cent.   This was accomplished by Haworth and Hirst (16).   The yield of cellobiose acetate from the acetolysis of cellulose triacetate and from cellulose appears

to be of the same order of magnitude (17). The Kurt Hess school, however, claim that in the acetolysis of cellulose the carbohydrate is first hydrolyzed to glucose and that cellobiose octa-acetate results from the recombination of two glucose molecules followed by acetylation of the resultant disaccharide.

Work by Irvine and Hirst (18) on the methylation of cellulose and subsequent hydrolysis of the ether thus produced led them to announce a formula for cellulose in which the x in the fundamental molecule was given as 3. The cellulose molecule is represented as an anhydro-trisaccharide as given below.

Irvine and Hirst Formula

$$CH_2OH \qquad\qquad O$$

$$CH—O—CH \cdot CH \cdot CH(OH) \cdot CH(OH) \cdot CH$$

$$CHOH$$

$$O$$

$$CHOH$$

$$O$$

$$CH$$

$$CH—O—CH \cdot CH(OH) \cdot CH(OH) \cdot CH \cdot CH \cdot CH_2OH$$

$$CH_2OH \qquad\qquad O$$

These authors have recently published the results of further work in support of this formula as given in a later paragraph.

Another tool which has proved of value in studying the structure of cellulose has been the use of x-rays. Cellulose and its derivatives yield x-ray spectrograms. Debye and Scherer (19) first recorded the observation that cellulose gave interferences with x-rays very similar to those of crystals, but apparently did not theorize upon their observation. The pioneer work in this field has been done by R. O. Herzog and H. Jancke, who published in 1920 (20) a paper dealing with the constitution of cellulose in which it was stated that $(C_6H_{10}O_5)_2$ represented the fundamental molecule of cellulose. In 1921 Herzog (21) modified

his views and stated that the cellulose unit contained 4 anhydro-glucose units and in 1925 (22) he suggested that the fundamental cellulose molecule might contain 1, 2, or 4 $C_6H_{10}O_5$ groups, but that in contra-distinction to Irvine (18) the value three was excluded by calculations from x-ray data.

With this rather meagre outline, in which an attempt has been made to recount the outstanding features of the work on the structure of cellulose, we pass to the more recent advances in this field, as well as that of the reactions of cellulose and its colloidal nature and behaviour as given in the succeeding paragraphs.

CELLULOSE STRUCTURE, PHYSICO-CHEMICAL RESEARCH

A very important contribution on the structure of cellulose as indicated by x-ray spectra is given in a paper by O. L. Sponsler and W. H. Dore (23). The authors studied the Röntgen diagram of fibers of Ramie and proposed a structure which appears to be consistent with the physical properties and chemical reactions of fibrous cellulose. They consider this substance to be made up of glucose units in the form of amylene oxide rings apparently united by primary valences in chains of indefinite length. These chains are parallel to the longitudinal axis of the fiber and are spaced rectangularly 6.10 x 5.40 Å.u. The ramie fiber is a hollow cylinder in which the crystal units are so placed that one of the diagonals of the 6.10 x 5.40 spacing always occupies a tangential position. The linkage of the chains is alternately from the 1 to 1 and the 4 to 4 carbon atoms of the glucose units. This precludes the presence of the cellobiose linkage in cellulose. They state that a group of eight glucose units is the simplest unit that can represent the structure of cellulose. This corresponds to the crystallographic unit with axes 10.80 x 12.20 x 10.25 Å.u.

The authors consider that the continuous primary valences account for the tensile strength of the fibers in a longitudinal direction while they are stabilized laterally by the secondary valences between the oxygen atoms of adjacent chains. Ester formation is shown to be possible. This may decrease the secondary valence force with a consequent separation of the longitudi-

nal chains and a resultant weakening of the fibrous structure. Sponsler and Dore (23) report a fair agreement with the data obtained by R. O. Herzog (24) but differ in their interpretation. This author (25) while admitting the possibility of the glucose units being glucosidically attached, considers it more likely that a number of $C_6H_{10}O_5$ groups are linked together according to Werner's theory of secondary valences.

E. Ott (26) in discussing the structure of the polysaccharides reports x-ray diagrams in support of the view that the crystallite of cellulose consists of three $C_6H_{10}O_5$ groups and that of lichenin seven. In another paper he (27) declares that cellulose hydrate, oxycellulose and hydrocellulose give diagrams identical with that of lichenin and believes that the crystallite constituents are the same, cellulose being a modification of lichenin. Herzog (28) finds lichenin yields a diagram similar to that of hydrated cellulose, but not identical with it.

Both cellulose nitrate and acetate when produced without destruction of the fibrous form show a crystalline structure according to Herzog (29) and to Ott (30).

Herzog (31) has observed differences in the Röntgen diagram of natural and mercerized fibers and finds that the same differences exist between cotton which has been esterified and deesterified without losing its fibrous form and that which has been in solution. From these data, since it is difficult to conceive that solution would cause a chemical alteration, he considers that mercerization produces a purely physical change. On the other hand, J. R. Katz (32) in a continuation of his previous work (33) adduces further data in support of his contention of the presence of an "alkali cellulose compound." In this instance he worked with alkali dissolved in dilute alcohol. By so doing the level portion of the Vieweg swelling curve disappears, but the same x-ray spectrographic change occurs as is observed in aqueous solutions of approximately the same concentration. When the cotton is washed with dilute alcohol, treated with an acetic acid solution to remove the last traces of sodium and dried, the spectrum of mercerized cellulose is obtained. This view is strengthened by the statement in another paper by Katz (34) that ramie

swollen by zinc chloride or calcium thiocyanate gives an unchanged spectrogram. That cellulose after swelling with HNO_3 and washing shows a Röntgen spectrum characteristic of mercerized cellulose has been shown by J. R. Katz and K. Hess (35). The concentration limits producing this effect are specific gravities 1.38 to 1.42. The so-called Knecht compound, $C_6H_{10}O_5 \cdot HNO_3$ is shown to have a constant composition and an x-ray diagram which differs from that of cellulose.

Work has been done by Herzog and Laski (36) on the absorption spectra of thin films of cellulose and nitrocellulose in the infra red as a possible clue to the structure of these compounds.

Alb. Frey (37) determined the refractive indices of various kinds of cellulose fibers and from the data obtained concluded that cotton cellulose and other types of fibrous cellulose are identical.

CELLULOSE STRUCTURE, CHEMICAL RESEARCH

Hess (12) in continuance of his work in support of the contention that $(C_6H_{10}O_5)$ is the molecular unit of cellulose has recalculated (38) the data given by Herzog (29) and found the number of $C_6H_{10}O_5$ groups per crystal unit to be 1.62 and 3.21 instead of 15.9 and 32.1 as originally recorded by Herzog. From this Hess concludes that the number 4 has nothing to do with the cellulose molecule. Herzog (39) admits the calculation error, but still maintains 2 or 4 $C_6H_{10}O_5$ mols per unit in the cellulose derivatives.

Hess (40) found from freezing point determinations in absence of air that di- and triacetyl cellulose dissolve in glacial acetic acid in concentrations of 0.05 to 0.6 per cent in monomolecular form corresponding to $C_6H_{10}O_5$. He favors the Naegeli micellar hypothesis and considers that glacial acetic acid is able to disperse the molecular building stones of the micelles. The above author (41) gives a review of his results obtained on the study of cellulose.

H. Pringsheim (13) heated cellulose triacetate in naphthalene and in tetrahydronaphthalene at 235°C. for two hours and observed that it is broken down without loss of material and without splitting off acetyl giving glucose anhydride triacetate. Saponi-

fication of this gives a substance which he calls cellosan, acetolysis of which yields cellobiose octa-acetate.   Hess (42) in a repetition of this work, finds that acetyl is split off during the heating.

The same author (43) observed in the methylation of glucoses a shifting of the oxygen bridge under certain conditions.   In another paper (44) the preparation of crystalline trimethyl cellulose is described.   From cryoscopic work in vacuo he found properties similar to those of cellulose acetate under the same conditions.   He concludes that methylation is the direct introduc-
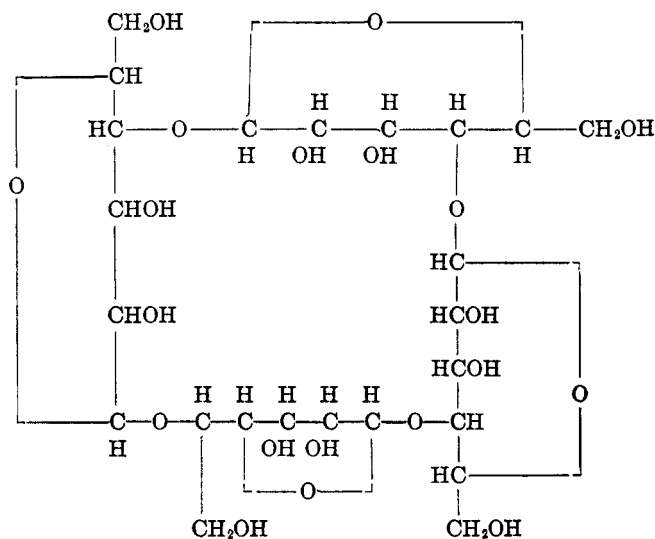

FIG. 1

tion of the methyl group except the possible wandering of the oxygen bridge.

Cellulose degraded by acetolysis and then deacetylated was shown by J. C. Irvine and G. J. Robertson (45) upon methylation and analysis of the products so obtained, to give 35 per cent anhydro-triglucose.   They believe that the triglucose unit must be at least one-third of the cellulose aggregate.

A constitutional formula for cellulose has been published by H. LeB. Gray (46), involving four $C_6H_{10}O_5$ groups or a multiple thereof as indicated in the structure given in figure 1.   This

structure is based on the spectrographic data and the chemical evidence that one hydroxyl per C_{24} unit possesses properties differing from the other eleven hydroxyls present. A hypothetical breakdown of such a molecule makes possible the existence of a disaccharide not known at the time of publication as well as cellobiose, celloisobiose and glucose. Upon methylation and hydrolysis it would yield 2,3,6 trimethyl glucose in accordance with Irvine (18).

By the acetolysis of cellulose, Hess and Hermann Friese (47) using the method of Ost with the sulfuric acid decreased to one-tenth, obtained a new derivative which they have determined to be a hexa acetyl biosan. Upon saponification an anhydro disaccharide is produced. Further degradation yields cellobiose and isocellobiose.

Fritz Micheel and Watroslow Reich (48) claim to have isolated from cellulose, by acetylation, deacetylation of the product obtained and reacetylation in pyridine, a new body which they believe may be related to the "Kittsubstanz" proposed by Herzog (49).

DISPERSOIDOLOGY OF CELLULOSE

During the past year the dispersoidology of cellulose and its derivatives has been the subject of many investigations. According to Herzog (50) electrolyte free polysaccharides do not swell in water. He considers that when swelling does take place the crystals break apart and the "Kittsubstanz" is partially destroyed. There are, in his opinion (51), two types of swelling agents; the first includes sodium hydroxide, cuprammonium and nitric acid; the second, salts and their water of crystallization. Under tension with the first type, the oblong crystallites imbedded in the "Kittsubstanz" become liquid. Release of the tension does not induce crystallization but results in coagulation.

W. Gordon (52) assumes the cotton fiber to have the properties of liquid crystals distributed in an amorphous cementing substance.

From the studies of solutions of cellulose in Schweitzer's reagent, Herzog and Krüger (53) concluded that the original

cellulose crystals whose size depended on the nature and previous history of the cellulose material, always dispersed into primary particles of the same size.

This appears to be contradicted by M. Numa (54) who claims that the color intensity of cuprammonium solutions of cellulose is directly related to the degree of dispersity.

Because of controversy concerning previous papers about the ripening of viscose, Herzog (55) published an account of the work which led to his papers on the viscose ripening process. The methods used for determining particle size are given. He states, in one of his papers (56) that the ripening of viscose is a coagulation phenomenon in which secondary particles consisting of series of rod shaped micelles are formed.

An investigation of the viscosity of viscose solutions led E. Berl and A. Lange (57) to conclude that ripening of viscose is not a polymerization effect of the cellulose xanthate molecule but that the cellulose formed by the splitting off of xanthic acid coagulates.

W. Von Neuenstein (58) states that cellulose nitrate and cellulose acetate solutions which have become thin on standing increase in viscosity when stirred. This effect is probably due, in his opinion, to the breaking up of secondary micelles.

Many data concerning cellulose nitrate solutions have been published by J. W. McBain, C. E. Harvey and L. E. Smith (59). They consider the solution of cellulose nitrate to be a direct combination between the solvent and suitable complementary chemical groups in the solute. Loose ramifying aggregates of colloidal particles held by local and specific bonds of residual affinity are believed to account almost entirely for the apparent viscosity of such solutions.

A study of the jellies formed by cellulose triacetate with benzyl alcohol and water has been made by H. J. Poole (60).

P. Karrer (61) observed the rate of zymolysis of cellulose by snail cellulase. He concuded the resistance to zymolysis is decreased by processes which cause a loosening of the micellar structure.

ALKALI CELLULOSE

Work on the action of alkali hydroxides on cellulose has brought forth numerous papers during the past year. The conclusions, in the main, represent those previously arrived at, with slight discrepancies.

Herzog (50) considers that the mass of water imbibed cannot be related to the heat of mercerization. However, Katz (62) believes that the taking up and liberation of water in the treatment of cellulose with alkali of different strengths plays an important part.

Making certain assumptions, W. Gordon (52) has derived a formula from which contraction on mercerization can be calculated.

Liquid ammonia at $-33°$ to $-35°$ according to G. Bernard (63) causes swelling of cotton fiber nearly equal to that produced by NaOH. The action of 22 per cent ammonium hydroxide on raw and wax free cellulose is similar to that of sodium hydroxide, but not as intensive. The products of the action of 22 per cent ammonium hydroxide still show intact external structure of cellulose and show no change in furfural, copper number, swelling power and fat content. If cellulose is treated with 22 per cent ammonia at $200°$ for forty-eight hours, a brown powder is obtained containing 20 per cent of nitrogen.

In the preparation of viscose E. Heuser and Schuster (64) found that lithium, potassium, sodium and rubidium hydroxides form true viscoses. With the first three the ratio of alkali to cellulose is one alkali hydroxide molecule per $(C_6H_{10}O_5)_2$. In the case of rubidium three $C_6H_{10}O_5$ groups are required per molecule of $Rb(OH)$.

Emil Heuser (65) discusses the relationship between degree of swelling of cellulose fibers and concentrations and electro conductivity of aqueous and alcoholic alkaline hydroxide solutions at the point of quantitative formation of alkali cellulose as determined by means of x-ray.

Further work has been done on solutions of cellulose in sulfuric and hydrochloric acids by K. Atsuki and F. Minaki (66) (67). In each case two points of inflection in the rotation-time curves were observed. The viscosity decreases rapidly until the first point of inflection is reached after which it remains nearly constant as the cellulose changes from colloid to crystalloid products.

According to Lieser (68) HCl supersaturated at zero degrees converts cellulose quantitatively into alkali soluble cellulose. Schwalbe's copper number shows no apparent increase in the reducing power of the product. The cellulose degradation cannot be explained, but the author considers that it is not a case of hydrolysis.

VISCOSE

Several interesting papers concerning viscose have appeared. Among these the following may be mentioned.

E. Berl and Johann Bitter (69) by the conversion of cellulose which had been alkylated, so as to contain one to two and one-half alkyl groups per C_6 unit, into viscose, arrive at the conclusion that there must be two free hydroxyl groups in the cellulose molecule for complete xanthation.

A paper by Heuser and Schuster (70) states that $(C_6H_{10}O_5)_2$ is the lowest xanthate formed. This breaks down to give a compound corresponding to $(C_6H_{10}O_5)_3$ and then to one of $(C_6H_{10}O_5)_4$. After this the breakdown is indefinite.

In a series of articles J. d'Ans and A. Jager (71) discuss the ripening of viscose. Experimental work shows that the decrease in the number of xanthate groups is regular and that the rate of separation of xanthate groups increases with rising temperature. The properties of the viscose solution and the number of xanthate groups have a clear relationship.

R. Bernhardt (72) suggests that acetic acid may be used for following the course of ripening of viscose.

CELLULOSE ESTERS

The literature of the cellulose derivatives has been increased by the publication of many papers. A few of the more important contributions are given.

A study of the nitration of various celluloses was made by M. G. Morin (73) in which he makes various suggestions for the use of new materials in the production of cellulose nitrate.

F. Blechta (74) confirms the fact that the instability of gun cotton is due primarily to the presence of sulfuric acid esters of cellulose. By a new method of stabilization with concentrated nitric acid he has shown that nitro hydrocellulose and nitro oxycellulose are not in themselves unstable. The prejudicial effect on the stability of crude nitrocellulose of N_2O_3 in the nitric acid has been confirmed. A short boiling with dilute caustic soda solution renders the nitrous acid esters harmless.

A description of the methods of analysis of cellulose nitrate is given by R. Gabillion (75) (76).

The hydrogen ion method for the determination of the stability of nitro-cellulose as proposed by N. L. Hansen is discussed by L. Metz (77).

From the experiments on the esterification of alkali cellulose with acid chlorides G. Kita et al. (78) arrive at the conclusion that only the chemically combined alkali takes part in the esterification. The same authors (79) treated dried cotton paper with stearyl or palmityl chloride in pyridine for eighteen hours, under reflux and obtained products the analysis of which indicated the formation of tri-esters.

H. Gault and P. Ehrmann (80) by the action of the chlorides of lauric, palmitic and stearic acids on hydrocellulose "Girard" prepared the mono- di- and tri-esters of the respective acids. Esters of fatty acids of cellulose containing more than five carbon atoms are described in a series of papers by the same authors (81).

The naphthenic acid esters of cellulose have been prepared by G. Kita and coworkers (82) (83). A description of the compounds is given.

Hydrophilic cotton, "Girard" hydrocellulose, cellulose from

cuprammonium, from viscose and alkali cellulose were used. An improvement was made by using $SOCl_2$ instead of the usual PCl_5 or PCl_3 in the preparation of the acid chlorides used.

The viscosity of cuprammonium solutions of cotton cellulose has been investigated by F. C. Hahn and H. Bradshaw (84) who find that higher viscosities are obtained with linters than with long fibered cotton.

O. Faust (85) has found that artificial silk fibers or films of all types when stretched show double refraction, and lose the property again when released.

ANALYTICAL

A. Kiesel and N. Semigasnovski (86) have published a method for determination of cellulose in plant material, by first hydrolyzing with dilute HCl to remove easily hydrolyzable material and then hydrolyzing the cellulose with sulfuric acid and determining the glucose obtained.

A discussion of the determination of alpha cellulose is given by P. Waentig (87) in which he mentions several unsatisfactory aspects of the procedure and offers recommendations for remedying them.

BIOCHEMICAL

In the investigation of pine wood, J. Marcusson (88) observed during rotting the cellulose is converted to oxidized cellulose and pectins.

S. Winogradski (89) has described the isolation in pure culture of a cellulose digesting vibrio. The gelatinous substance obtained is thought to be a colloidal form of oxycellulose.

A very sensitive method for detecting differences between the various types and varieties of cellulose, through hydrolysis with snail cellulase is described by P. Karrer (61). He has also shown that in the hydrolysis of cellulose by this enzyme the further addition of the same does not carry the action beyond that obtained by the original present. It is the opinion of the author that cellulose consists of two constituents which differ in their behaviour toward enzymes.

In another paper P. Karrer and P. Schubert (90) communicate the results of their study of the rate of enzyme action of snail cellulase on cellulose and viscose filaments. They conclude that the seration of the surface, the character of the surface membrane and possible salt occlusion are important contributory factors in this reaction.

J. A. Viljoen, E. B. Fred, and W. H. Peterson (91) reported the isolation in pure culture of a thermophilic organism which destroys cellulose at 65°. After growth on cellulose free media it is unable to ferment cellulose.

<div align="center">MISCELLANEOUS</div>

That the age of the fiber, whether living or dead, is neglected, though chemical and colloid changes may take place, is noted by C. G. Schwalbe (92). He mentions that standard cellulose should be used in all investigations and refers to the work of the American Chemical Society's Committee.

P. Ehrmann (93) gives a review of the chemistry of cellulose and its derivatives with 123 references.

A review of the structure of the cotton fiber by A. J. Turner (94) has been published with a bibliography of sixty-five references.

<div align="center">STARCH</div>

C. L. Alsberg, E. P. Griffing, and J. Field (95) describe a method of preparing a starch solution, by first grinding in a ball mill followed by sifting 2 per cent of the ground material into distilled water, and stirring for approximately one hour. The liquid is centrifuged at 2000 r.p.m. for one-half to one hour. The supernatant liquid is stored in a bottle, the surface being covered with toluene. Clear solutions are obtained in this manner, which will keep for many months and are considered superior for use as an indicator to Lintner's soluble starch or starch paste.

In a series of communications Kikuo Nagai (96) reported the results of ultra-microscopic studies on the fermentative processes of starch and on the starch-iodine reaction. Also starch digestion with pancreatin.

A study of the acid hydrolysis of starch by D. R. Nanji and R. G. L. Beazeley (97) led to the conclusion that the gelatinization of ordinary starch is due to the calcium salt of the amylophosphoric ester rather than to the ester itself. It was found that soluble starch was able to take up calcium from water when the amount present was as low as 1 part of calcium per 100,000 parts of water.

A triacetyl amylose was obtained by Max Bergmann and Ewald Knehe (98) by the acetylation of amylose in pyridine. Saponified with alcoholic potassium, amylose is regenerated which shows all of the properties of the original material, and when reacetylated in the same manner gives the same triacetate. From this the authors conclude that amylose is a strongly aggregated glucose anhydride and not a polysaccharide.

R. Kuhn and W. Ziese (99) found that upon the degradation of monomethyltrihexosan a 6-methyl-glucose is obtained. The results definitely exclude Pringsheim's (100) formulas for the hexosan. The authors conclude that the view generally held that oxygen bridges occur in starch through the C-6 position must be abandoned.

J. C. Irvine and J. MacDonald (101) found that the exhaustive methylation of starch yielded three products of constant composition and properties; (1) dimethyl starch with 32 per cent methoxyl, (2) methylated starch containing 36.3 per cent methoxyl, and (3) trimethyl starch, 43.7 per cent methoxyl. The last two yielded 2,3,6 trimethyl methyl glucoside, when hydrolyzed with methyl alcohol and hydrochloric acid. The 2,3,4 product which is derived from maltose could not be found.

In a paper on the constitution of starch, A. Pictet (102) shows that a linear relationship exists between the molecular optical rotatory power of degradation products of starch and their coefficients of polymerization. He considers that a condensation of three molecules of hexahexosan, $(C_6H_{10}O_5)_6$, is the simplest molecule of soluble starch. In these molecules, $(C_6H_{10}O_5)_{18}$, all of the atoms are held by their ordinary valences. In starch these molecules are probably associated.

In a continuation of his work on the chemistry of starch, H.

Pringsheim and J. Leibowitz (103) discuss the molecular magnitude and association of polyamyloses. The same author (104) gives a summary of his views on the constitution of cellulose and starch.

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