PROCEEDINGS OF THE

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INTRODUCTION

Chemistry is concerned with the composition of things and how these compositions come about. Our modern knowledge of the composition of living matter rests heavily upon the pioneering work of Emil Fischer and his school on the nature of the sugars and the amino acids. The present symposium is concerned with modern carbohydrate chemistry in its impact on biology, a broad topic necessarily embracing material of both plant and animal origin. The contributors have been selected from those laboratories making significant contributions to the area and with a view toward international representation, the selection has been necessarily limited.

The reagent phenylhydrazine served Emil Fischer as an entry into the maze of sugar chemistry but the exact structures of its reaction products with the sugars have only been solved in the last few years by Mester, a now transplanted member of the Zemplén school in Budapest, who utilized the formazan reaction, established many years ago by von Pechmann. Heidelberger, of Rutgers, elaborated the topic that all polysaccharides are immunologically specific and are therefore useful in the elucidation of the structure of the innumerable polysaccharides found in nature. Hestrin, of Israel, directed attention to the enzymic trans-D-fructosylation reactions of a bacterial levansucrase system and the avalanche-like process of polyrepetitive transfer by which the giant molecules of levan are produced. Blix, of Uppsala, traced the history of the sialic acids from their crystallization in his laboratory in 1936 to the final elucidation, in 1958, of their unique nine-carbon-atom structures. Studies in their biological action appear promising, especially in relation to virus action. Kuhn, of Heidelberg, summarized the subject of natural products containing amino sugars, to which field he has made significant contributions. He pointed out that the capacity for synthesizing these substances is not well developed in the newborn and, after later attaining its maximum, again decreases with age. Stacey, of Birmingham, reviewed the present status and biological significance, especially in relation to heredity and the cancer problem, of the nucleic acids of plants and animals and emphasized the difficult nature of the carbohydrate chemistry involved. Jones, of Canada, summarized the biosynthesis and natural occurrence of monosaccharides, a topic in which he has long held an active interest. Reichstein, of Basel, reported on the exhaustive investigations of his laboratory on the nature of the many unusual sugars occurring in the cardiac aglycons. Courtois, of Paris, told of the numerous oligosaccharides occurring in some

plants that contain sucrose in combination with one or more moles of D-galactose. Araki, of Japan, reported the remarkable work which has largely elucidated the unusual nature of the seaweed polysaccharides agar and carrageenan in which 3,6-anhydro-L(and D-)-galactose is a component. Hirst, of Edinburgh, outlined the present status of the chemical nature of the plant gums which rank amongst the most complicated of those known to chemists while Whistler, of Purdue, did the same for the somewhat related field of the plant "hemicelluloses".

Acknowledgment is herein made to the assistance of Dr. F. Shafizadeh in the many details concerned with arrangements for this Symposium and to Dr. Walter von Bebenburg and Mr. Alan Chaney for valued assistance in the final editing.

M. L. WOLFROM

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HEMICELLULOSES

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Mr. Chairman, Members of the Symposium. It is a pleasure for me to talk with you about an area of polysaccharide chemistry that not only offers such abundant problems in fundamental carbohydrate chemistry, but that also is growing rapidly and is so important to industrialists. I am especially pleased to talk here on this subject because I know how much members of this group have contributed, not only to hemicellulose chemistry, but to carbohydrate chemistry as a whole.

In recent years hemicelluloses have been reviewed periodically. I reviewed the "Advances in Hemicellulose Chemistry" before the International Congress of Pure and Applied Chemistry at Stockholm in 1953. Professor E. L. Hirst gave a very clear and complete account of the progress made before 1955 in his Pedler Lecture[1] and now here again we will try to summarize certain recent developments, points of special interest and possible lines of future work.

Hemicelluloses assume particular significance because of their extensive occurrence as cell wall components in all higher land plants (*Spermatophyta*). They constitute about 25–35% of woods and about 25–40% of agricultural crop residues, such as wheat straw, corn stalks and cobs and soybean hulls. The chemical and physical nature of these various polysaccharides is important, therefore, not only because of interest in their fundamental chemistry, but because they are in such great abundance that in the future they will become of industrial use, perhaps the bases of new industries.

NOMENCLATURE

At this early point one should say a word about the nomenclature used in connection with this group. The greatest nomenclature problem here might be the name hemicellulose itself. It is so poorly defined that the American Polysaccharide Nomenclature Sub-committee of the American Carbohydrate Nomenclature Committee could come to no uniform agreement on its meaning and made no recommendation concerning it. Perhaps, as believed by many, the term hemicellulose should be dropped. The group of polysaccharides which it represents could be designated

simply as non-cellulosic cell-wall polysaccharides. This would include pectin, which might not be objectionable since pectin is already included among the hemicelluloses as they are defined by some workers. If no one knows how to define hemicelluloses, let us, for the sake of this review, say that they are the non-cellulosic-non-pectin polysaccharides in the cell walls of higher plants.

Natural Cross-bonds and Odd Linkages

Much discussion still exists on whether hemicelluloses occur in the free state in plant cell walls or are covalently linked, in part, with cellulose and lignin. The origin of the problem is the need to explain the difference in solubility of some cell-wall polymers before and after isolation. Low solubility of the polymers while in the cell wall is ascribed by many workers to covalent bonds. There is today fairly good evidence for a chemical combination between lignin and hemicellulose.[2] On the other hand, another large group of investigators believe the low solubility of certain cell-wall polysaccharides results from the numerous secondary forces which hold them to other cell-wall components and also from their intimate association with other types of molecules with which they are entangled and overlaid. Evidence which suggests entangling includes the observation[3] that as the cell wall is ground, the finer particle sizes yield proportionally more extractable hemicellulose. Furthermore, extractability of hemicelluloses decreases under conditions which swell cellulose. Proof of the occurrence or non-occurrence of covalent cross-links between cell-wall polysaccharides or polysaccharides and lignin may not be obtained for some time because of the great difficulty in proper characterization of a polymer, both before and after its removal from its natural matrix, and because of the difficulty in clearly distinguishing whether covalent bonds are broken under extractive conditions. While the preponderance of evidence seems to indicate that most cell-wall polysaccharides are in physical admixture only, some covalent cross-bonding must surely exist. If not formed enzymatically during the development of the cell wall, the energetics resulting from hydrogen ion concentration and concentration of reactants in cell formation are such that some few purely chemical reactions could occur. Limited chemical synthesis of linkages seems entirely reasonable.

This purely chemical formation of bonds also seems to be one reasonable explanation for the unusual glycosidic bonds found in many polysaccharides. During the past few years much has been heard of the so-called "anomalous" linkage found in such otherwise uniformly linked polysaccharides as cellulose, xylan and starch amylose. The occurrence of an odd or unusual glycosidic bond among hundreds of uniform linkages seems to me to be fully expected and reasonable. It might arise from a

momentary aberration in the catalytic activity of the normal synthesizing enzyme, which is caused by a variation in solution kinetics or concentrations in the plant cell; or it might arise from the intrusive action of another enzyme. If, however, enzymes are above reproach there is the entirely reasonable possibility of linkage formation by a purely chemical reaction.

Purification

A major problem prevalent in examinations of hemicelluloses is the difficulty inherent in obtaining a pure polysaccharide that may be subjected to an unequivocal structural investigation. Separation of hemicelluloses from plant material and from each other is tedious and requires the exercise of utmost judgment and technical ability if pure polysaccharides are to be obtained in a natural and undegraded condition.

So far, alkaline extraction of holocellulose has proved useful as a means for the isolation of a group of polymers which can later be separated. The oxidative action of chlorite is minimal and this reagent has been widely used to delignify plant material. Alkaline extraction of the holocellulose can, however, bring about many changes in the polysaccharides. The destruction occurring in the presence of oxygen is well known. But even under oxygen-free conditions alkaline degradation might result. The degradation of polysaccharides in alkalis has been investigated extensively by the research group at the British Rayon Research Association and Dr. J. N. BeMiller and myself have written a review[4] on alkaline degradation of polysaccharides. Fortunately, perhaps, when chlorite is used to produce holocellulose a rather specific oxidation transforms the reducing end of the polysaccharide chain to glyconic acid residues. This change stabilizes some molecules to purely alkaline degradation which must begin at a reducing end group.[5] Alkaline degradation still occurs in those hemicellulose molecules which may contain carbonyl or carboxyl groups on non-terminal sugar units.

Possibly one of the great disadvantages in alkaline extraction of hemicelluloses is that any naturally occurring ester groups are saponified. Acetyl groups appear to be present in wood hemicelluloses and there is evidence that they are linked to D-xylose units.[6] Analysis indicates that woods with small hemicellulose contents have small acetyl contents. It would be interesting to prove whether natural hemicelluloses are acetylated or formylated and if derived to show the location of the ester linkage. An extractant which appears promising for the removal of hemicellulose fractions with the original acyl groups still present is dimethyl sulfoxide.[7]

Solutions of potassium hydroxide have been extensively used to extract hemicelluloses from various pulps including holocellulose. One of its

advantages is that on neutralization of the extract with acetic acid the potassium acetate formed has good solubility in ethanol and may be removed thereby. Schoettler[8] has found potassium hydroxide solutions better extractants for aspenwood xylan than are sodium hydroxide solutions. However, sodium and lithium hydroxide solutions are more effective than potassium hydroxide solution for dissolving glucomannans from Western Hemlock holocellulose.[9]

Still the most difficult problem in hemicellulose chemistry is that of the effective separation of a chemically homogeneous polysaccharide. All known methods of polymer separation have been applied to the hemicelluloses but without general success. Electrophoresis[10-14] is one way of testing chemical homogeneity of polysaccharide materials, but it is not applicable to macroseparations.

Most attempts to fractionate hemicelluloses make use of precipitation. Numerous investigators have complexed polysaccharides with copper salts. Fehling's solution[15-19] is often used, while solutions of cupriethylenediamine,[20] cupric chloride,[21] cupric sulfate[22] and cupric acetate,[23,24] have also been employed. In most instances the copper complex which precipitates is removed by filtration or centrifugation and decomposed by an ethanolic solution of acid or chelating agent; the polysaccharide is then washed free of inorganic ions.

An interesting precipitant for polysaccharides which has been investigated at Birmingham is cetyltrimethylammonium bromide.[25-28] When added to a neutral mixture of acidic and neutral polysaccharides it will precipitate the acidic ones as insoluble quaternary ammonium salts. Neutral polysaccharides which have been complexed with borate will precipitate in the same manner.[29]

A purification procedure found satisfactory in many applications is the fractional precipitation of dilute polysaccharide solutions by the gradual addition of ethanol. There are many examples of this fractionation method and so, perhaps, I may be permitted to illustrate with the technique used at Purdue. A mixture of acidic hemicelluloses from corn cob at 2% concentration and at pH 2 was separated into numerous fractions by repeated additions of ethanol to succeeding points of incipient turbidity, and individual fractions removed by centrifugation. In this way the fractionation curve shown in Fig. 1 was obtained. While pH 2 is recommended for analytical observation, it is obviously too acidic for preparative separations[30] where a neutral pH should be used to prevent hydrolysis (Fig. 1).

Molecular Structures

Structural information on the different polysaccharides constituting the hemicellulose group has been obtained using the various classical methods

so well known among polysaccharide chemists. In addition, the now well-accepted method of fragmentation analysis has greatly increased the worker's ability to make structural proposals. Although the β-D-(1→4) glycosidic linkage between D-xylopyranose units is established as common in hemicelluloses, it may be well to review the occurrence of certain

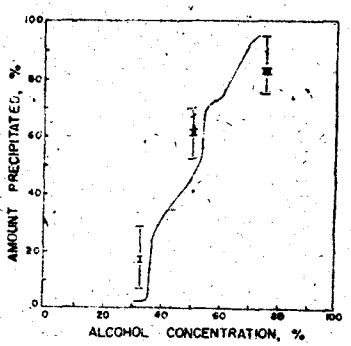

Fig. 1. Fractional precipitation curve for the B group polysaccharides of corn cob at 2% concentration and pH 2.

molecular fragments that establish other linkage types. Usually, fragments are obtained by graded acid hydrolysis, but sometimes they are acquired through enzymatic hydrolysis.

Bishop and Whitaker, at Ottawa, isolated an enzyme from *Myrothecium verrucaria* which hydrolyzed linear chains of β-(1→4)-linked D-xylose units.[31] Application of the enzyme to wheat straw hemicellulose[32] yielded, among other products, L-arabinofuranosyl-(1→3)-β-D-xylopyranosyl-(1→4)-D-xylose.[33]

Sørensen, in Denmark, working with enzymes from *Choetomium globosum*, *Streptomyces* and *Micromonospora* found that two enzymes are active in the hydrolysis of xylan, an exoenzyme which is able to act on xylosidic chains with three or more D-xylose units and an endoenzyme which is able to split xylobiose.[34]

At Purdue, an enzyme extract from the culture medium of *Aspergillus foetidus* hydrolyzed corn cob xylan primarily to xylobiose with no production of D-xylose.[35] An extract of the mold mycelium was separated on a cation-exchange resin into two fractions, one of which hydrolyzed xylan and xylooligosaccharides to D-xylose without producing significant amounts of transient oligosaccharides and another which hydrolyzed xylan to a mixture of D-xylose and xylooligosaccharides. Fractionation of the mycelium extract on either Celite or carboxymethylcellulose produced a fraction which did not hydrolyze xylan but did hydrolyze hemicellulose B.

As information on hemicelluloses accumulates, it is apparent that the

major portion of non-cellulose polysaccharides present in the cell walls of higher plants consist of derived xylans. From some viewpoints this group of polysaccharides is surprisingly uniform. In only a few instances has a naturally occurring pure xylan been encountered. Almost always the xylan contains other glycosidically bound sugar units. Most common groups are L-arabinofuranosyl and 4-*O*-methyl-α-D-glucopyranosyluronic acid. The former occur most frequently as single unit side chains joined to D-xylose units at position C2 and, less often, at C3. The uronic acid units are sometimes unmethylated, but in either case they are most frequently bound to position C2 of D-xylose units. These uronic acids are always end units or single unit side chains. Sometimes the substituted xylan is linear, but frequently it is branched at least once. Much less abundant but none the less widespread in nature are substituted xylans which contain still other types of sugar units, such as D-galactose and, infrequently, L-galactose and L-rhamnose.

Important structural tissue usually contains a greater proportion of linear or nearly linear polysaccharides than does tissue which is less important structurally.

Corn cobs contain a large proportion of branched polysaccharides, but seed hulls or seed coats contain a larger proportion of very highly branched polysaccharides.

This discussion will pertain to those cell-wall polysaccharides which have been the subject of work since 1955 and, hence, we will not describe certain structures elucidated earlier which include such well formulated polysaccharides as the hemicellulose of esparto grass.

Ever since the historical work of O'Dwyer it has been customary to extract plant material with alkaline solutions and separate the eluted polysaccharides into at least two portions by neutralization of the extract. Polysaccharides which precipitate at this point are called hemicellulose A and are principally linear molecules with few uronic acid groups. Polysaccharides which remain in solution are sometimes termed hemicellulose B and are mainly branched chain molecules.

The earliest fragments isolated, and those most easily obtained from hemicelluloses are the aldobiouronic acids which are found among the hydrolysis products of practically all hemicelluloses. It is well known that the glycoside bonds in these modified disaccharides are resistant to acid hydrolysis and hence are present after other glycosidic bonds have hydrolyzed. The common uronic acid component is 4-*O*-methyl-D-glucuronic acid which has been isolated from some 30 different hemicelluloses of annual plants and trees. Underived D-glucuronic acid apparently does not occur abundantly and, so far, has been observed in hemicelluloses from annual plants more often than in hemicelluloses from wood.

The aldobiouronic acid 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose has been obtained from American beechwood,[18] aspen wood,[36] black spruce,[37] corn cob,[38] Eucalyptus regnans,[39] European beechwood,[40] Finnish birch,[41] flax straw,[42] kapok,[43] loblolly pine,[44] maritime pine,[45] milkweed floss,[43] Monterey pine,[46] Norway spruce,[47] oat hulls,[48] Scots pine,[37] wheat bran,[49] western hemlock,[50] white elm,[51] white birch[43] and yellow birch.[43]

While the linkage of D-glucuronic acid and 4-*O*-methyl-D-glucuronic acid is most often to position C2 of D-xylose, linkage to position C3 has been observed. Thus, hemicellulose of sunflower heads yields 3-*O*-(α-D-glucopyranosyluronic acid)-D-xylose,[52] and the hemicellulose of Monterey pine[46] and possibly that of maritime pine[53] and wheat straw[54] yield 3-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose. Jute[55] has been reported to yield a similar aldobiouronic acid, except that the methyl group is at position C3. A hemicellulose from plum leaf has given on hydrolysis 2-*O*-methyl-D-xylose[56] which is the first recognition of a methylated aldopentose in nature.

A hemicellulose from oat straw isolated by Aspinall at Edinburgh had a D.P. of 40–45 and consisted of a linear chain of (1→4)-linked β-D-xylopyranose units with one 4-*O*-methyl-D-glucopyranosyluronic acid unit connected to position 2 of a D-xylose unit on each chain, and one L-arabinofuranosyl unit attached to the chain for approximately each 32 D-xylose units[57] (Fig. 2).

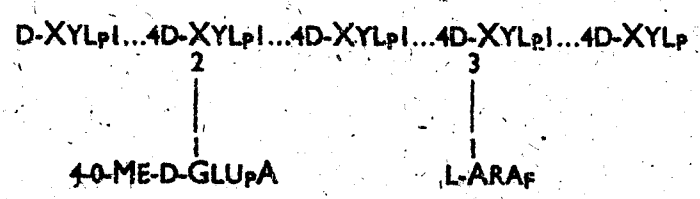

Fig. 2. Section of oat straw hemicellulose.

By alkali extraction, delignified flax straw has yielded a polymer of D.P. of about 135 that appears to be a xylan chain to which is attached some fifteen 4-*O*-methyl-D-glucopyranosyluronic acid units. However, the molecule is somewhat unusual in that it possesses two L-rhamnose units, perhaps one of which is a terminal reducing unit.[43,58]

A hemicellulose extracted with alkali from defatted barley husk has been investigated by Aspinall.[59] Methylation procedures suggest that the polysaccharide is composed of a slightly branched xylan skeletal structure to which is attached at least three types of side chains: D-glucopyranosyluronic acid units directly linked to D-xylose units at position C2, side chains terminated by L-arabinofuranose units linked to D-xylose units at position C3, and side chains terminated by D-xylopyranose units linked

to the backbone chain at position C3 of D-xylose units. Further evidence for the last-mentioned side chain was the isolation of the disaccharide 2-*O*-D-xylopyranosyl-L-arabinose from the products of mild acid hydrolysis of the polymer.

A homogeneous polysaccharide has been extracted by lime water from the seed coat of corn kernels.[60] The central xylan chain is highly branched as shown by structural examination of the polysaccharide remaining after most or all of the sugar units which were attached by furanose linkages have been removed by hydrolysis in dilute acid. Examination of the hydrolyzate[61] showed, in addition to L-arabinose, the presence of 3-*O*-α-D-xylopyranosyl-L-arabinose and *O*-L-galactopyranosyl-(1→4)-*O*-D-xylopyranosyl-(1→2)-L-arabinose.[62] Thus these two oligosaccharides constituted side chains on the branched xylan nucleus and were probably joined to the nucleus by furanosyl linkages. Both D- and L-galactose are to be found; each present only as non-reducing chain end units. At least some of the D-galactose is attached directly to the xylan nucleus as shown by the isolation after partial hydrolysis of 4-*O*-β-D-galactopyranosyl-D-xylose.[63] Also attached directly to the xylan nucleus at C2 positions are D-glucopyranosyluronic acid groups, which were identified as the aldobiouronic acid.[64,65]

Corn cobs contain several polysaccharides which can be extracted from their holocellulose by alkaline solution. Acid neutralization precipitates about three-fourths of the material as a linear xylan with perhaps one D-glucopyranosyluronic acid unit per molecule. It is from this xylan that we were originally able to isolate the polymer homologous series of oligosaccharides extending from xylobiose to xyloheptaose.[66,68] The remaining one-fourth of the hemicellulose which is soluble in the neutralized extract is a mixture of three or more polysaccharides as indicated by fractional precipitation data (Fig. 1). Recently, two of these have been separated in pure form and have been characterized.[69,70]

One of these polysaccharides is an arabinoxylan (Fig. 3) with a molecular weight of 13,700, containing 10.6% L-arabinose and 89.4% D-xylose. It

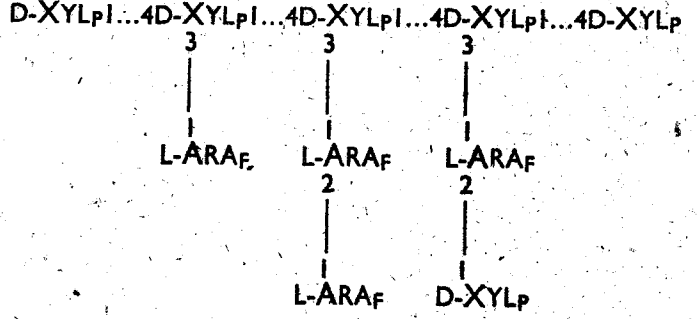

Fig. 3. Section of corn cob hemicellulose B.

seems to be a linear xylan chain with 4 side chains totalling 7 L-arabinofuranose units for each 30 units of the D-xylose chain. Some of the L-arabinose side chains may be terminated with D-xylose units since on partial hydrolysis 2-*O*-α-D-xylopyranosyl-L-arabinose is isolated. None of the side chains bears more than a single branch.[71] The second pure polysaccharide is a highly branched tetraheteroglycan (D.P. 150) containing 59.1% of D-xylose, 21.9% of L-arabinose, 11.3% of mono-*O*-methyl-D-glucuronic acid and 7.6% of D-galactose. All of the latter two units occur as non-reducing end units. There seem to be 10 side chains for every 44 sugar units and one mono-*O*-methyl-D-glucuronic acid unit for each 9–11 sugar units.

The constitution of a hemicellulose isolated from wheat bran has been investigated by Adams and Bishop at Ottawa.[49,72,73] It contained L-arabinose, D-xylose and uronic acid in about a 5:4:1 ratio. Slow hydrolytic removal of approximately 35% of the L-arabinose suggested that it was part of a chain, an indication which was borne out by methylation work. Most of the L-arabinose is probably in chains consisting only of L-arabinofuranose units joined to a linear xylan nucleus. The D-glucopyranosyluronic acid is connected to D-xylose units at position C2 as a single unit side chain. An enzyme from *Myrothecium verrucaria*, which hydrolyzes xylan, did not attack this polysaccharide except after most of the L-arabinose units were removed by extensive hydrolysis.

An acidic hemicellulose from wheat leaf chlorite holocellulose has been extracted by Adams[74] and has been purified through the copper complex. In addition to uronic acid, the polysaccharide contained D-xylose and L-arabinose in the ratio of 13:1. Since almost all of the L-arabinose could be removed by mild hydrolysis without loss of D-xylose, furanose units were probably attached individually to the xylan nucleus. This was also shown by methylation work. Evidence was obtained to suggest that an L-arabinose unit constitutes the reducing end of the chain. The xylan nucleus contains approximately 30 units and is branched with one D-glucopyranosyluronic acid unit attached to position C2. Three L-arabinofuranose units are attached individually at position C3 of the D-xylose units (Fig. 4).

Wheat straw hemicelluloses contain a number of closely related polysaccharides. To the backbones of the molecules are, of course, attached

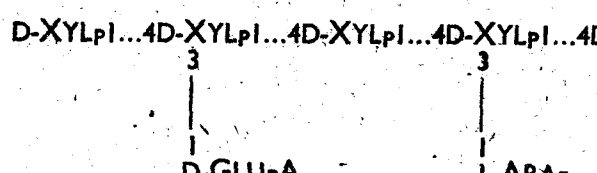

Fig. 4. Section of wheat-leaf hemicellulose.

L-arabinofuranose and D-glucopyranosyluronic acid units.[76-79] L-Arabinose units are all single unit side chains linked to the backbone chain through position C3 of D-xylose. Direct evidence of this is Bishop's isolation of the trisaccharide *O*-L-arabinofuranosyl-(1→3)-*O*-β-D-xylopyranosyl-(1→4)-D-xylose.[38] D-Glucuronic acid units are linked to the main chain through position C2 of D-xylose, as are the 4-*O*-methyl derivatives. The xylan chain of one hemicellulose appears to be branched, perhaps by a (1→3) linkage. It differs from another wheat-straw hemicellulose which is free of L-arabinose and is unbranched.[80] A hemicellulose isolated at Edinburgh by direct extraction from wheat straw has a D.P. of 71–76[79] (Fig. 5).

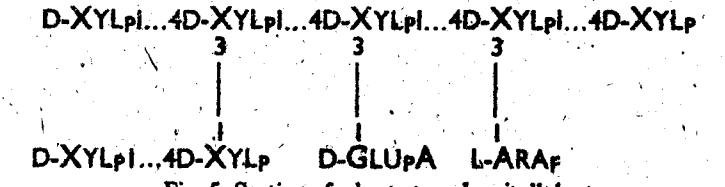

Fig. 5. Section of wheat-straw hemicellulose.

Beechwood hemicellulose A has a high content of uronic acid.[40] A polysaccharide from European beechwood contains 9.5% of 4-*O*-methyl-D-glucuronic acid. It consists of a linear chain of about 70 β-D-xylopyranose units linked (1→4) with about every tenth unit bearing a 4-*O*-methyl-D-glucuronopyranosyluronic acid unit attached to position 2 (Fig. 6).

Fig. 6. Section of European beechwood hemicellulose A.

A water-soluble hemicellulose extracted from American beechwood chlorite holocellulose[18] has been found by Adams at Ottawa to contain about 45 D-xylopyranose units in a Y-shaped arrangement with the branch at position 2 of a D-xylopyranose unit and with 5 single unit side chains of 4-*O*-methyl-α-D-glucopyranosyluronic acid units joined by (1→2) bonds (Fig. 7).

A hemicellulose has been extracted by alkali from chlorite holocellulose

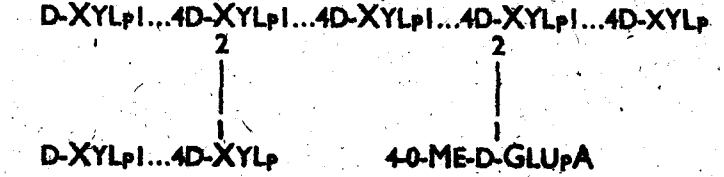

Fig. 7. Section of American beechwood hemicellulose.

of the softwood, Norway spruce.[47] It consists of an 80–85 unit xylan chain with every fifth unit carrying a single 4-*O*-methyl-D-glucuronic acid residue linked through to position 2. This xylan resembles the xylan of beechwood, differing slightly in chain length and in the proportion of 4-*O*-methyl-D-glucuronic acid residues linked as side chains.

From white birch holocellulose, Timell[48,81] at McGill obtained a hemicellulose consisting of an unbranched xylan chain of about 110–190 units with every tenth or eleventh D-xylopyranose unit carrying a single 4-*O*-methyl-D-glucopyranosyluronic acid unit attached to position 2. This general structure is thus similar to the substituted xylan from European beech.[40]

Western hemlock as investigated at Minnesota yields a hemicellulose[50,82] of unestablished size which appears to consist of a linear xylan substituted with three 4-*O*-methyl-D-glucopyranosyluronic acid groups and one L-arabinofuranosyl group for every twelve D-xylopyranose units.

Polysaccharides containing D-mannose units are often difficult to remove from wood, and at one time, they were thought to be mannans covalently linked to cellulose. However, it has become obvious that the D-mannose in coniferous woods and pulp is present as a component of glucomannans. By partial depolymerization of slash pine *alpha* cellulose, Leech[83], isolated 4-*O*-β-D-glucopyranosyl-D-mannose (also obtained from loblolly pine by Jones[84]). The parent glucomannan has been isolated from western hemlock,[85] white spruce[16] and Norway spruce.[86,87] D-Glucose to D-mannose ratios vary from 1 : 3 to 1 : 4. Glucomannans appear to be linear polymers with β-D-(1→4) linkages, and Lindberg finds the polymers from Norway spruce range in D.P. from 70 to 140. Glucomannans can be isolated in the crude form by hot water extraction of spruce holocellulose[7] which is swollen in dimethyl sulfoxide, and they can be purified by precipitation as the copper complex.[88] Jones[89] shows that they may be extracted directly in rather concentrated form by alkaline borate solutions

Biosynthesis and Physiological Rôle

Although cellulose is regarded as a structural polysaccharide with no food-reserve function, there is less agreement concerning the function of the hemicelluloses.

Investigations on the rôle of hemicelluloses in plants have been sporadic. The first results of work with woody plants were interpreted as evidence that the hemicelluloses were reserve polysaccharides. In fact, one finds the term "reserve cellulose" applied to them in early books on plant physiology.

The work of Murneek[90] was based on percent compositions. Investigations with grape stems by Winkler and Williams[91] failed to show any