THE CHEMICAL STRUCTURE OF THE HEMICELLULOSES

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The cellulose fibrils in the walls of plant cells which have undergone lignification are embedded in an amorphous mass of material consisting mainly of a mixture of lignin and various polymeric carbohydrates. For want of a better name it is at present convenient to refer to these polysaccharides as hemicelluloses, but when detailed knowledge of their chemical structures becomes available it will be practicable to refer to them by more appropriate chemical names. To some extent that possibility has now been reached and, as the result of intensive investigations carried out in many laboratories over the past few years, it has become clear that the greater portion of the hemicellulose group of substances consists of materials belonging to a small number of distinct and clearly recognizable families of polysacccharides. These include the large and very varied families of the xylans, the glucomannans and the arabogalactans, with the possibility that other family groups such as the β-glucans of barley and oats, some mannans and some galactomannans may also be regarded as hemicelluloses. In some instances, the distinctions between hemicelluloses on the one hand and plant gums and mucilages on the other have become vague and indefinite and it will be necessary to restrict the present discussion mainly to the typical hemicelluloses of wood. Considerable progress has been made in the determination of the main structural features of these materials, most of which appear to be present in the cell wall as mixtures of polysaccharides, the individual molecules of which have a similar general structure but differ amongst themselves in their degree of polymerization and in a wide variety of minor features, such as the nature, number and position of the side chains attached to the main chain of the molecular structure. This recognition of the occurrence of many plant polysaccharides as families of closely related substances, rather than as a collection of exactly identical molecules, has had an important bearing on the development of ideas in polysaccharide chemistry, and in many ways, therefore, the present time is appropriate for a review of structure in the hemicellulose group. The present account must, however, be restricted to general conclusions and to indications of gaps in our knowledge. Fuller accounts of the experimental evidence with detailed references are already available in recently published articles[1].

Interest in these materials is of long standing. Xylan or Wood Gum was described by Thomsen and by Wheeler and Tollens and used as a source of the xylose which it yielded on hydrolysis[2]. A similar material can be obtained from esparto grass and, in view of the convenience of this source,

much of the early work centred on the xylan obtained from esparto by alkaline extraction. Application of the methylation method revealed that the main structural feature is a chain of (1——→4)-linked β-D-xylopyranose units[3] (*Figure 1*), a conclusion which was substantiated later by the isolation of a series of oligosaccharides consisting of 1——→4-linked xylose residues[4].

In subsequent investigations, attempts were made to determine the chain-length by the end-group procedure, but difficulties were at once encountered in that two kinds of non-reducing terminal groups were found to be present, namely D-xylopyranose and L-arabofuranose. The amount of the L-arabofuranose end group varied from fraction to fraction as the crude xylan was purified and fractionated by use of its copper complex.

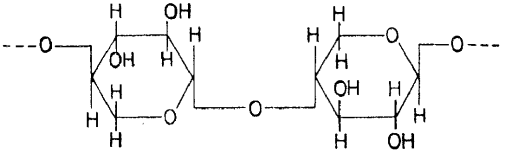

Figure 1. Main chain in xylan

One of the main points at issue at this stage was the question whether there were present two distinct polysaccharides—a true xylan in admixture with a true araban—or a single polysaccharide in which both xylose and arabinose residues were united in one molecular structure. That true xylans did exist was proved by examination of arabinose-free material obtained by exhaustive fractionation of the xylan from esparto. The main structural features of this are indicated in *Figure 2* which depicts a main chain of (1——→4)-linked β-D-xylopyranose units, probably with one branch chain of similarly combined xylose residues, the molecular size being of the order of 80–100 xylose residues.

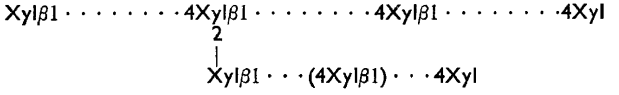

Figure 2

On the other hand, fractions containing arabinose were readily obtainable from esparto and from other sources, and Perlin[5] isolated from wheat flour a xylan fraction which contained almost as much arabinose as xylose. A study of this by the methylation procedure and by other methods clearly showed that single L-arabofuranose residues were attached to a main chain of xylose residues, in many instances substituting the hydroxyls at both C–2 and C–3 of the same xylose residue. These arabofuranose residues were readily removed by gentle hydrolysis with acid, leaving a xylan similar to the arabinose-free material from esparto mentioned above. The general molecular structure of wheat flour xylan is, therefore, the one shown in *Figure 3* and, by analogy, the arabinose-containing fractions from esparto may be expected to have a generally similar structure but with a smaller proportion of arabinose residues.

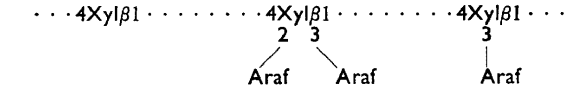

Figure 3

Direct proof of the attachment of L-arabofuranose residues to a xylose unit in the main chain has been obtained in two different ways. In one instance, a wheat straw xylan was subjected to partial hydrolysis by means of a cellulolytic enzyme present in the mould *Myrothecium verrucaria*[6]. This gave rise to a series of oligosaccharides containing both xylose and arabinose residues, one of these being the trisaccharide *O*-L-α-arabofuranosyl-(1⟶3)-*O*-β-D-xylopyranoysl-(1⟶4)-D-xylopyranose (see *Figure 4*). The mode of action of the enzyme on the original xylan is indicated in the same figure.

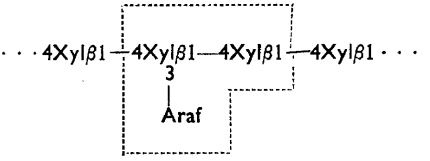

Figure 4

Another method, developed by Aspinall[7] and used in the course of work on rye-flour xylan, is to oxidize selectively by a catalytic procedure the primary alcoholic groups of the terminal L-arabinose residues to carboxylic acid groups. The arabofuranosyl linkage then becomes comparatively resistant to hydrolysis and, after partial hydrolysis of the oxidized polysaccharide, an aldobiouronic acid (L-arabofuranosyl uronic acid)-(1⟶3)-D-xylose was obtained (*Figure 5*) and proof was thereby provided of the mode of attachment of the arabinose residue to the xylan chain.

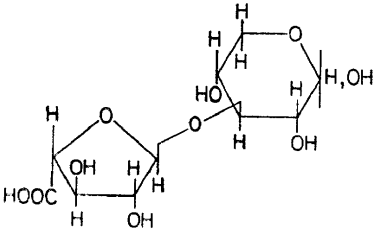

Figure 5

The arabinose residues in xylans are usually terminal units attached glycosidically to C–3 of a xylose residue. Frequently, however, non-terminal L-arabofuranose residues are encountered, as in the xylan of barley husks and in the complex group of hemicelluloses present in corn (maize) cobs, maize fibre and maize hulls. The xylan from barley husks may be taken as an example[8]. The structural evidence here clearly points to the presence of side chains containing a β-xylopyranose unit linked to C–2

of an L-arabofuranose residue (D-Xylβp1-L-Araf1 . . .) probably attached to the main chain as indicated in *Figure 6.*

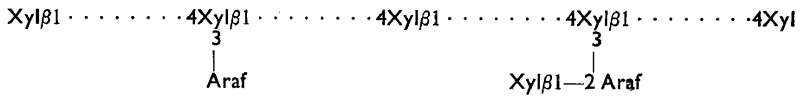

Figure 6. General features of structure of barley husk xylan

Other widely distributed units which are found to be attached directly to the main chain, usually but not invariably, *via* the C–2 of a xylose residue are D-glucuronic acid and its 4-*O*-methyl derivative (see *Figure 7*). These acidic residues were first recognized in a xylan from the pear (fruit). They occur in some wheat straw xylan fractions (where both 1–3 and 1–2 branch point linkages have been reported), although with wheat straw as also with wheat flour, barley flour, rye flour and esparto, fractions can be obtained which are devoid of acidic residues. In most of these instances it seems likely that both D-glucuronic acid and its 4-*O*-methyl ether are present in the xylan, whereas residues of 4-*O*-methyl D-glucuronic acid are typical of the xylans present in both soft and hard woods, where the uronic acid contents may be as high as 20 per cent and 15 per cent respectively. Normally, these residues are linked top osition 2 of a xylose residue in the interior of the main chain, but occasionally, as for example in the xylan from oak heart-wood, it is likely that a uronic acid residue of this type is present as the terminal unit of the chain.

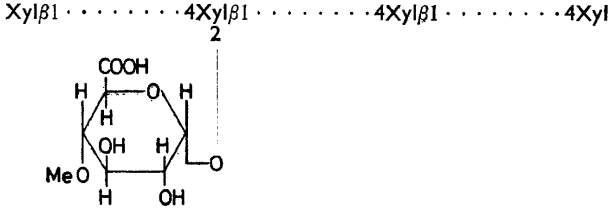

Figure 7

The question of the possible occurrence of branching in the main chain of xylose residues is still undecided in most instances, largely owing to difficulties in the accurate determination of molecular weights in the region (D.P. *ca* 50–150) in which most of the xylans occur. There is some evidence of a single branch point (see *Figure 2*) in the molecular structure of the arabinose-free esparto xylan mentioned previously. Furthermore, the xylan from Loblolly pine must contain a branched structure since there are three xylose end groups per molecule. Similar branched structures may occur in the xylans from North American beechwood, jute, milkweed floss and kapok[1].

It is evident from this summary that xylans from a wide variety of sources conform to the same general structural pattern characterized by a main chain, which may be branched, of β-1,4-linked xylopyranose residues, with side chains of L-arabofuranose, D-glucuronic acid (or its 4-*O*-methyl

derivative) and of L-arabofuranose carrying a xylopyranose residue attached at the C–2 position. From one xylan to another, frequently even in different fractions of a xylan from one plant source, the proportions in which these side chains are present may vary widely—an observation of special interest in connection with the mechanism of biogenesis of the xylans. In general, however, all these materials can be regarded as coming within one family group of polysaccharides, the main structural feature of which is the backbone of 1,4-linked xylose residues. This structural unit is a characteristic feature of the hemicelluloses of woody substances from both monocotyledonous and dicotyledonous plants, but it is clear that this mode of occurrence of xylose is by no means universal in the plant world. Xylans are prominent amongst the polysaccharide components of many algae and, in at least two cases which have been examined in some detail, β-xylopyranose residues linked through positions 1 and 3 play an important part in the structure. In the xylan from the red seaweed *Rhodymenia palmata*, both 1,3-and 1,4- links are present in the proportions of approximately 25 per cent and 75 per cent respectively (*Figure 8*)[9].

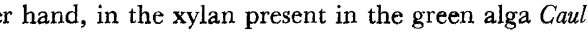

Figure 8. Xylan of *Rhodymenia palmata*

On the other hand, in the xylan present in the green alga *Caulerpa filiformis* the main chain is undoubtedly composed entirely of 1,3-linked β-xylose residues[10]. The principal structural features of this xylan, which may possess a branched xylose backbone, are indicated in *Figure 9*.

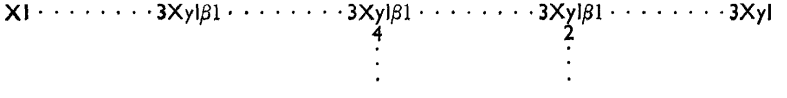

Figure 9. Xylan of *Caulerpa filiformis*

The question may be raised as to whether these algal xylans are to be regarded as hemicelluloses in the sense in which the word is usually employed, and structural comparisons may, therefore, be inappropriate. Nevertheless, they may well be constituents of the cell wall of the plants concerned and may be more nearly related to the hemicelluloses of the land plants than to the plant mucilages and wound gums which frequently contain xylose residues as components of extremely complex molecular structures. These, however, are outside the scope of the present discussion. It is probable also that the xylans which are found in the so-called "gum fractions" of the flour and grain of cereals have a biological function different from that of the wood hemicelluloses, although they show marked resemblances in their structural features, namely a backbone of β-1,4-linked xylose residues with side chains of arabofuranose units. Some of these may be highly complex polysaccharides resembling the true gums, with other sugar residues present also, *e.g.* galactose and mannose[11].

Many points of detail in the chemistry of the hemicelluloses still remain obscure. Reference has already been made to the need for more information concerning the molecular weight distribution of the various members

of the group, which appear to be, in general, both polymolecular and polydisperse despite their comparatively small D.P. values. This problem, at one time an extremely difficult one, would appear to be capable of resolution by the techniques now available. There are, however, many other still more formidable problems, one or two of which may be mentioned at this stage.

It will be evident from the descriptions and the formulae given above that no detailed information is available concerning the positions along the chain of the xylose residues which carry the side chains. The relative proportions in which these substituents are present can be determined, but, except in one or two special cases, *e.g.* Perlin's wheat flour arabinoxylan[12], neither the order in which they occur, nor their placing along the main chain has been ascertained. One of the difficulties here stems from the extreme lability of the furanoside linkage which joins the arabinose residues to the main chain. The usefulness of the method of linkage analysis by partial hydrolysis of the polysaccharide is thereby much restricted. Attempts to overcome this are now being made by taking advantage of the fact that the glycosidic link in uronic acids is much stronger than that of the corresponding sugar. If, therefore, the arabinose residues can be oxidized at C–5 giving a —COOH group in place of the original —CH_2OH group (*Figure 5*), the rate of removal of the arabinose residue is greatly diminished and it may be feasible to make use of the method of partial hydrolysis to gain knowledge of the distribution of side chains in the molecule (see above). At present it is not known whether the side chains (Aral—, GpAl—, 4Me-GpAl—, Xyll—→2Aral) are attached randomwise to the main chains or are present in ordered sequences.

Another problem is raised by the apparent stability of xylans to alkali. Many of them, indeed, are isolated by extraction with alkali under far from mild conditions. There is some evidence from molecular weight measurements that, in some cases, xylans which have been extracted without use of alkali undergo slow degradation when treated with aqueous alkali. The breakdown is of the type which would be expected if the first residue in the chain possessed a free reducing group (*Figure 10*).

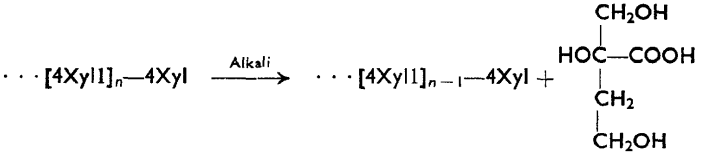

Figure 10

By contrast, xylans which have been acted upon by sodium borohydride to eliminate any free reducing group are stable to alkali. It seems likely that the peeling off reaction would be stopped by the presence of a 2-substituted xylose residue close to the end of the chain. On the other hand, when the main chain carries a substituent at C–3, the ready elimination of the side chain is not necessarily followed by rearrangement of the xylose residue to an alkali-stable saccharinic acid unit (*Figure 11*), but a second

elimination may occur, thus allowing the peeling reaction to continue as indicated in *Figure 10* [13].

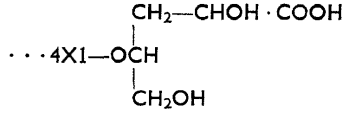

Figure 11

Another possible reason for the comparatively small reducing power of xylans as they are usually encountered may be that the chlorite treatment, often used for delignification during the preparation of the holocellulose, results in oxidation of the first residue to xylonic acid.

Mention of holocellulose raises yet another unsolved problem in hemicellulose chemistry, namely the mode of occurrence of the xylans in the cell wall itself. The marked difficulty with which many of these materials are separated from the other constituents has prompted suggestions, for which there is some supporting evidence, that in the cell wall the xylans are chemically combined in much larger macromolecular structures, perhaps as esters of their glucuronic acid residues with other carbohydrates and perhaps also through ether links to lignin. An indication of the complexity of the problem is revealed in Timell's work on the effect of the normal delignification procedures in reducing the molecular size of the xylan components of the cell wall[13a].

The vigorous methods used in the past for the isolation of hemicelluloses would inevitably result in the hydrolysis of ester groups attached to the polysaccharides. That such groups, particularly *O*-acetyl, may be present has been revealed by the use of mild reagents such as dimethyl sulphoxide for the extraction of glucuronoxylans from holocellulose preparations[14]. In this way, xylan fractions containing up to 17 per cent of acetyl groups have been isolated. It has been reported that some glucomannans from coniferous woods also contain acetyl groups and the question arises as to whether the presence of acetyl groups in natural xylans is general. Attempts have been made to determine the location of these acetyl groups by the methylation procedure using methyl iodide and silver oxide in dimethyl formamide. Difficulties are encountered owing to de-acetylation during the reaction and to the possibility of migration of the acetyl groups in the presence of silver oxide. In more recent studies[15], the free hydroxyl groups were protected by formation of the phenylcarbamoyl derivative (use of phenyl isocyanate), the acetyl groups removed and the product methylated. Control experiments indicated that, under the conditions employed, migration of phenylcarbamoyl groups did not occur, and the protecting group could be removed readily by reductive fission. Some idea of the distribution of the acetyl groups in a birch wood xylan is given by the following figures. The xylan contained some 13 per cent of acetyl apportioned in such a way that 58 per cent of the xylose residues were free from acetyl groups, 24 per cent were acetylated at C–3, 12 per cent at C–2, whilst 6 per cent had acetyl groups on both C–2 and C–3. The uronic acid residues were apparently not acetylated.

The materials considered up to this point have all been xylans in respect of their main structure. Xylose residues occur also in the much more complicated polysaccharides present in corn cobs, maize fibre, maize hulls, and in other cereal brans. Amongst these, a wide variety of sugar residues is encountered, these being present in all probability in a complex mixture of individual polysaccharides, some of which closely resemble the plant gums and mucilages in their properties. There are indeed indications that polysaccharides of these types are widely distributed in nature, and their inclusion in the hemicellulose fraction may be due in part at least to the difficulty of separating cell wall materials from those present in the cell sap.

As an example, brief reference may be made to the hemicellulose of maize fibre[16]. This does contain material similar in its main structure to the glucurono-xylans mentioned above, but whether the remaining residues are present exclusively as side chains, or partly in this way and partly as independent polysaccharides, is not known with certainty. This material is unusual amongst land plants in containing residues of both L- and D-galactose which are here present solely as end groups. Application of the methods of methylation and linkage analysis has revealed the presence of the following residues as component parts of larger molecules. The products containing reducing arabinose residues probably arose by fission of furanosyl linkages between the side chain and a xylan backbone. D-Gall-; L-Gall-; α-D-GpA-(1–2)-D-Xylp1-; α-D-GpA-(1–4)-D-Xylp1-; α-D-GpA-(1–4)-β-D-Xylp-(1–4)-D-Xylp1-; α-D-Xylp-(1–3)-L-Ara1-; L-Galp-(1–4)-D-Xylp-(1–2)-L-Ara1-; β-D-Galp-(1–4)-D-Xylp1-; and β-D-Galp-(1–5)-L-Araf1-.

The presence of galactose and arabinose in maize fibre hemicellulose indicates a resemblance between this material and the plant mucilages. A still closer relationship is evident in materials found in many conifers in association with polysaccharides of the xylan type. In illustration of this reference may be made to recent work on the hemicelluloses of *Pinus pinaster*[17] and to the group of galactoarabans typified by the ϵ-galactan of the European larch[18]. From *Pinus pinaster* on partial hydrolysis followed by examination of the aldobiouronic acids so liberated, *O*-(α-D-glucosyluronic acid)-(1–2)-D-xylose and *O*-(4-*O*-methyl-α-D-glucosyluronic acid)-(1–2)-D-xylose were obtained, characteristic of the glucuronoxylans of woody materials, but, in addition, several other acidic fragments were also isolated. These included the aldobiouronic acid *O*-(α-D-galactosyluronic acid)-(1–4)-D-xylose, which appears to be present in many woods, both of angiosperms and gymnosperms, but is absent from cereal straws and from chlorite holocelluloses prepared from wood. It was accompanied by *O*-(β-D-glucosyl-uronic acid)-(1–6)-D-galactose, a trisaccharide containing the residue β-D-GpA-(1–6)-D-Galp1 . . ., and the aldobiouronic acid *O*-(α-D-galactosyluronic acid)-2-L-rhamnose. All of these are characteristic of gums and mucilages rather than of cell wall materials and may not arise from the hemicellulosic portion of the wood. In this connection it may be noted that maple sap[19], as distinct from maple wood, has been found to contain polysaccharides composed of residues of galactose, arabinose and rhamnose (see below), whilst the combination of galactose, galacturonic acid and rhamnose occurs in some pectic materials[20] and also in various mucilages (linseed, *Ulmus fulva*, *Plantago ovata*, Cholla gum, Okra mucilage *etc.*).

As indicated above, angiosperm wood xylans contain only small proportions, if any, of arabinose residues. The situation is different however with the gymnosperms. In the xylan of the European larch, for example, arabinose residues are definitely present, and this may be true also of the Norway Spruce[21]. The mode of attachment of the arabinose units to C–3 of the xylose residues is normal, but in the case of the larch xylan it is not yet certain whether these arabinose units are directly linked to the main chain or whether to side chains of 1,4-linked xylose residues. Larch wood differs again from the hard woods in its composition in that it contains considerable proportions of an arabinogalactan or perhaps a mixture of such polysaccharides. Early work showed that fractionation of the crude ϵ-galactan from European larch could be effected and more recent work has definitely revealed the heterogeneity of some arabino galactans from larch. On the other hand, some samples of ϵ-galactan fail to reveal evidence of heterogeneity when examined in the ultracentrifuge. Structural examination of this apparently homogeneous material revealed in the first place that, on mild hydrolysis, the disaccharide 3-*O*-β-L-arabinopyranosyl-L-arabinose could be isolated. This disaccharide residue (L-Arapβ1-3-Aral . . .) occurs also in gum arabic and in other plant gums. Further examination by the methylation procedure showed that the arabinose residues in the polysaccharide could be accounted for almost completely as disaccharide units, which are linked as such to a main structure consisting of D-galactose residues. The results of linkage analysis and methylation experiments show that this galactose framework is highly branched and consists of D-galactose residues linked together by 1,3- and 1,6-linkages. Further experiments, including the application of F. Smith's reductive procedure to periodate oxidized ϵ-galactan, and linkage analysis investigations following catalytic oxidation of unsubstituted —CH_2OH groups in the galactan. The sum total of the evidence so obtained favours a structure for ϵ-galactan depicted in *Figure 12* in which the side chains R^1 and R^2 are L-Arapl-3L-Araf1 and D-Galpl-6D-Galpl- respectively, in proportions such that 1 in 12 of the D-galactose residues of the ϵ-galactan carried an arabinose side chain. This structure consists of a main chain containing 1,3-linked galactose residues with branches of 1,6-linked D-galactose residues united to the main chain at C–6 positions, and it now appears that at any rate the majority of the arabinose side chains are attached directly to the main chain and not to the side chains of galactose residues[22].

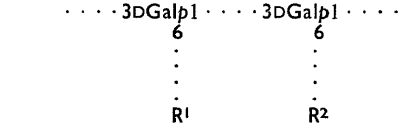

Figure 12

Studies on other arabinogalactans carried out in Canada[23] and in Sweden[24] reveal structural features similar to but not identical with those indicated for larch ϵ-galactan. There is strong reason, therefore, for the view that the arabinogalactans form a family of closely related polysaccharides possessing a highly branched structure of D-galactose residues joined by 1,3- and

1,6-linkages, to which are attached, in varying proportions, residues of L-arabopyranose and L-arabofuranose, some of the arabinose units being in the form -3L-Araf1-3L-Araf1- and some in the disaccharide unit previously mentioned. In Western larch arabinogalactan—and possibly in others—it is probable that some of the galactose residues are linked through the 1,4- positions in addition to 1,3- and 1,6-linkages[23] and it is clear that much further work will be required before unique molecular structures can be assigned. There is an obvious analogy with the structure of the main chain in gums of the Acacia type (chains of 1,3-linked galactose residues with branches of galactose side chains linked through the 1,6-positions). A backbone of 1,3-linked D-galactose residues with side chains of L-arabofuranose and L-rhamnopyranose units occurs also in the arabinogalactan present in maple sap[19]. It is of interest that up to the present no indication has been obtained of the presence in hemicellulose fractions of separate arabans of the kind often found in pectic materials. It must be remembered, however, that difficulties of separating the mixed polysaccharides are great and that it may well be the case that some of the materials studied come from the cell sap as well as from the cell wall. The complexity of the situation may be further illustrated by reference to a galactan present in large amounts in spruce compression wood, which shows a high degree of lignification. Although full details of structure are not yet available it is already known that part of the galactan consists of a chain of β-1,4-linked D-galactose residues, and is similar in structure to the galactan which is normally present in pectic materials (*Figure 13*)[26].

Galβ1 · · · · 4Galβ1 · · · · 4Gal

Figure 13. Galactan in spruce compression wood

The similarity extends even further in that D-galacturonic acid residues are present, probably in the form of a polygalacturonic acid of the pectic acid type. It is possible, therefore, that on occasions pectic materials may constitute a considerable proportion of the carbohydrate materials in a wood cell wall.

It is clear that wood hemicelluloses, particularly those from soft woods, contain a large variety of polysaccharides but, in view of their importance, reference must be made to yet another group, namely the glucomannans, or galactoglucomannans, which are present in considerable amounts in coniferous woods, to a lesser extent in some hard woods, and are found also in the seeds of many land plants. True mannans are also known, for example, the mannans present in ivory nuts, the molecular structure of which contains chains of (1–4)-linked β-D-mannopyranose residues[27]. A true mannan of similar structure is present in the marine alga *Porphyra umbilicalis*[28], but claims that mannans containing no other type of sugar residue can be isolated from spruce sulphite pulp and spruce holocellulose require confirmation. On the other hand, there is no doubt that the glucomannans which comprise up to half the hemicellulose content of some coniferous woods contain units of both mannose and glucose in their molecular structure[29,30] and this is true also of the Iles mannan of some species of *Amorphophallus*[29], and of the glucomannans from lily bulbs and iris seeds[30].

Separation of the glucomannan portion of wood hemicellulose from other components is by no means easy. The glucomannans are on the whole less readily extracted than the xylans, and in isolating them advantage may be taken of this fact and of their ready precipitation by barium hydroxide[31]. Purification may also be effected by precipitation of their copper complexes and fractionation of their acetates. Glucomannans from coniferous woods give, on hydrolysis, D-glucose and D-mannose in proportions ranging between 1:3 and 1:4, and some samples give rise also to small amounts of D-galactose. The galactopyranose residues are present as terminal units and it is not yet possible to say whether the galactose is part of a glucomannan polysaccharide or whether it occurs in a separate galactomannan of the type already known in guaran[32], which consists of chains of 1,4-linked β-mannose residues with galactose side chains consisting of single galactose residues linked to C–6 positions of the mannose chain (*Figure 14*).

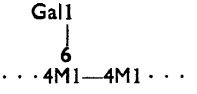

Figure 14. Guaran

Considerable attention has been given recently to structural investigations in the glucomannan of woody materials. Materials studied include polysaccharides from Loblolly pine[33], Western red cedar[34], Norwegian spruce[35], Sitka spruce[36], European larch[37], Red maple[38], Western Hemlock[39], Scots pine[40], Jack pine[41], White birch[42], Eastern white pine[43], and Aspen[44].

In some instances, materials free from galactose have been isolated and examined[45], whilst in others both galactose-containing and galactose-free fractions have been obtained from the same holocellulose. The glucomannans so far examined have revealed a striking similarity in molecular structure in that they consist essentially of linear molecules composed of residues of D-glucose and D-mannose linked through their 1,4-positions. On linkage analysis they give rise to the disaccharides 4-*O*-β-D-mannopyranosyl-D-mannose (Mβ1–4M), 4-*O*-β-D-glucopyranosyl-D-mannose (Glucβ1–4M), cellobiose (Glucβ1–4Glu) and 4-*O*-β-D-mannopyranosyl-D-glucose (Mβ1–4Glu). It is clear, therefore, that the molecular structure involves both glucose and mannose residues and there can be no question of a mixture of a mannan and a glucan. Oligosaccharides have also been identified after partial hydrolysis. These include several trisaccharides *e.g.* the substances Mβ1–4Mβ1–4M and Glucβ1–4Glucβ1–4M. From Norwegian Spruce no less than five of the eight theoretically possible trisaccharides containing mannose and glucose were isolated. Some caution in interpretation of the nature of the glycosidic links is necessary in view of the remarkable anomerization which mannosyl linkages can undergo in the presence of acids. The evidence as it stands, based partly on linkage analysis, partly on methylation and partly on periodate oxidation followed by degradation of the oxidized polysaccharide by F. Smith's method (borohydride reduction followed by hydrolysis), is in favour of the general structure for these glucomannans shown in *Figure 15*. In this structure

there is a random arrangement of the mannose and glucose residues, which may occur either as single units or as blocks of two, three or more of the same

$$\cdots\cdot 4\text{Glu}\beta 1\cdot\cdot\cdot\cdot 4\text{M}\beta 1\cdot\cdot\cdot\cdot$$

Figure 15. General features of molecular structure of glucomannans

kind in succession. It is just possible that the glucomannan of Loblolly pine may be an exception in that the glucose residues may be present as single units. The glucomannan from *Amorphophallus sp.* (*Iles mannan*) has the same general structure and, although smaller proportions of mannose-containing polysaccharides occur in the hard woods, the available evidence indicates that in these also (*e.g.* red maple[38], aspen[44], white birch[42]) the same type of structure is present. Ferns also appear to contain glucomannans (or galactoglucomannans) of the same general type in their hemicellulose fractions[46]. The question of branching in the main chain of some of these polysaccharides is still under investigation and further information is needed concerning the part played by the galactose residues when they are present. The latter give tetramethyl-D-galactopyranose after methylation of the polysaccharide and hydrolysis and must, therefore, occur as end groups. In the case of Norwegian Spruce hemicellulose, partial hydrolysis of the galactoglucomannan gives rise to the disaccharide Galα1–6M and the trisaccharide Galα1–6Mβ1–4M, indicating a mode of linkage which is found in guaran, but the evidence at present available does not permit any decision to be made as to whether or not polysaccharides of the guaran type are present in these hemicelluloses in admixture with glucomannans or galactoglucomannans. There is, however, evidence obtained during a study of the enzymic hydrolysis of a Jack Pine glucomannan that xylose residues present in side chains are constituent parts of the molecule. In the general patterns of their structures there would seem to be a close similarity between the xylan family and the glucomannan family. Like other polysaccharides of the hemicellulose group the glucomannans have comparatively small molecular weights (D.P. in the region of 100 in those cases where measurements have been made).

The greater part of cell wall materials in wood, other than cellulose itself, are included in the family groups which have been referred to above, namely the xylans (including arabinoxylans and glucuronoxylans), the galactoarabans and the glucomannans. It is evident that other polysaccharides also are present in many woods to a greater or lesser extent, and with improved methods of extraction and fractionation it should soon be possible to characterize these and determine the general features of their structures. Even so, however, only a beginning will have been made in the chemical study of the hemicelluloses and it will still be necessary to deal with the detailed structure of these polysaccharides and the way in which variations in structural detail occur within the family groups of molecules present in a single cell wall. Knowledge of the organization of the hemicelluloses within the cell wall and of the nature of their association with the cellulose and lignin components is at present scanty in the extreme and enquiry is needed into the possibility that certain members of the hemicellulose group may occur both in the cell wall and in the cell sap. There

remains, therefore, despite the rapid progress made during the past few years, a long programme of work awaiting both chemists and biochemists before our knowledge of the structure, function and biosynthesis of the hemicelluloses could be regarded as adequate.

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