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HEMICELLULOSES IN HARDWOODS GROWING ON SOUTHERN PINE SITES

J. K. N. Jones[1]
Chown Research Professor, Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

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ABSTRACT

Aspects of the chemistry of the two more common hemicelluloses found in hardwoods growing on southern pine sites are outlined. The 4-*O*-methylglucuronoxylans have been investigated chemically by several groups of workers and have been shown to consist of an essentially linear backbone of 1,4-β-linked D-xylopyranose residues. To this backbone are attached in a random fashion, α-linked 4-*O*-methyl-D-glucuronopyranosyl residues through position 2 of about one in ten of the D-xylopyranosyl groups. *O*-Acetyl residues may also be present. The glucomannans have received less attention. They consist of essentially linear polymers formed of 1,4-β-linked-D-glucopyranose and 1,4-β-linked-D-mannopyranose residues joined in random sequence and may also contain *O*-acetyl residues. The ratio of the sugars varies between 1:2 and 1:1.

Keywords: Southern hardwoods, hemicelluloses, chemical analysis, carbohydrates, pentoses, hexoses, xylans, glucomannans.

INTRODUCTION

The hemicelluloses of only three of the twenty-two major species of hardwoods (Angiospermae) growing on southern pine sites have received detailed investigation. Some 90 percent of these hardwoods, i.e. the six predominant species and thirteen other species, have received only superficial chemical examination (Table 1), and their polysaccharides have not been investigated using modern techniques. Because so little is known about these species, much research is needed so that the opportunity for their chemical utilization may be made possible. For this reason this article concentrates on the chemistry of the hemicelluloses of white oak (*Quercus alba*, L.), red maple (*Acer rubrum*, L.), and American elm (*Ulmus americana*, L.) (Timell 1964, 1965), describing techniques for determining the chemical structure of the xylans and glucomannans.

A hemicellulose may be defined roughly as a polysaccharide, of low molecular weight relative to that of cellulose, which is normally found in plant tissues. It is associated with cellulose and lignin and can be isolated from the original wood or from delignified material either by extraction with water or, more usually, by extraction with aqueous alkali. Most of the hemicelluloses isolated from land plants are essentially linear in structure. The major groups of polysaccharides investigated so far have been the *O*-acetyl-4-*O*-methylglucuronoxylans, the glucomannans, tensionwood galactans and polysaccharides extractable from wood with hot water (starch, pectin, etc.). Since the last two groups are of minor importance to the wood chemist, their chemistry will not be discussed here. The isolation and chemical investigation of the *O*-acetyl-4-*O*-methylglucuronoxylans, the dominating hemicellulose in hardwoods, have attracted, by far, the most investigators.

It is very difficult to determine (±1%), the absolute composition of a hemicellulose and to identify all the sugars in the polymer. First there is the problem of isolating a hemicellulose free from other polysaccharides and from such impurities as ash and water. Unlike proteins, polysaccharides are composed of a spectrum of molecular weights and are usually built up in a random fashion so they may vary in the com-

[1] Prof. Jones died in Kingston, Canada 13 April 1977.

TABLE 1. *Pentosan content of some hardwoods growing on southern pine sites*

Species	Wood volume[a] *million cu ft*	Proportion of pine site hardwood volume *percent*	Pentosan content (from *furfural*) *percent*
Sweetgum (*Liquidambar styraciflua* L.)	6,508	13.2	18.3–20.7
Oak, white (*Quercus alba* L.)	6,058	12.3	21.7–23.3
Hickory, spp. (*Carya* spp.)	4,173	8.5	16.2–18.7
Oak, southern red (*Q. falcata* Michx.)	3,994	8.1	21.5
Oak, post (*Q. stellata* Wangenh.)	3,444	7.0	17.8
Yellow-poplar (*Liriodendron tulipifera* L.)	3,421	7.0	18.4–19.1
Tupelo, black (*Nyssa sylvatica* Marsh.)	2,710	5.5	14.5–17.1
Oak, water (*Q. nigra* L.)	2,332	4.7	—
Oak, black (*Q. velutina* Lam.)	1,949	4.0	—
Oak, scarlet (*Q. coccinea* Muench.)	1,779	3.6	—
Maple, red (*Acer rubrum* L.)	1,751	3.6	17.1–18.3
Oak, chestnut (*Q. prinus* L.)	1,452	2.9	—
Oak, northern red (*Q. rubra* L.)	1,169	2.4	—
Oak, laurel (*Q. laurifolia* Michx.)	683	1.4	—
Elm, spp. (*Ulmus* spp.)	668	1.4	—
American elm (*U. americana* L.)	—	—	16.2–18.1
Oak, cherrybark (*Q. falcata* var. *pagodaefolia* Ell.)	579	1.2	—
Ash, spp. (*Fraxinus* spp.)	441	0.9	—
American ash (*F. americana* L.)	—	—	14.5–20.2
Sweetbay (*Magnolia virginiana* L.)	300	0.6	—
Oak, shumard (*Q. shumardii* Buckl.)	120	0.2	—
Hackberry, spp. (*Celtis* spp.)	57	0.1	—
Blackjack oak (*Q. marilandica* Muench.)	—	<1.0	20.1
Other hardwoods	5,628	11.4	—
Total	49,236	100.0	

[a] Christopher et al. (1976).

position of their endgroups. Because of the variability in the composition of the hemicelluloses, their acidic hydrolysis, which is usually a heterogeneous reacton, leads to problems. The furanosides are hydrolyzed more easily than the pyranosides, which in turn are more easily hydrolyzed than are the uronosides. In the hydrolysis of a complex hemicellulose, the furanosidic sugars (e.g., L-arabinose), which are more easily hydrolyzed, are more rapidly destroyed by hot acid when they are in the reducing form than are the nonreducing pyranosidic sugars. Similarly, complete hydrolysis of uronosides results in a substantial degradative loss of all sugars. It is therefore advisable to carry out an analysis in three steps; first using dilute (0.1N) acid to hydrolyze furanosides, second to follow the hydrolysis using stronger (2N) acid and thus to determine the pyranosides, and finally a prolonged hydrolysis to determine the uronosides. In all cases an internal standard (mannitol or erythritol), unaffected by the conditions of hydrolysis, should be added. This procedure will give the optimum yields of sugars (and in some cases indicate their transformation into isomers) and may lead to the detection of traces of some sugars (such as *O*-methylated sugars). The enzymic degradation of hemicelluloses may also lead to difficulties because of the formation of sugar artefacts (e.g. unsaturated sugars).

The quantitative (ca. 95%) isolation of pure hardwood xylans is difficult and has

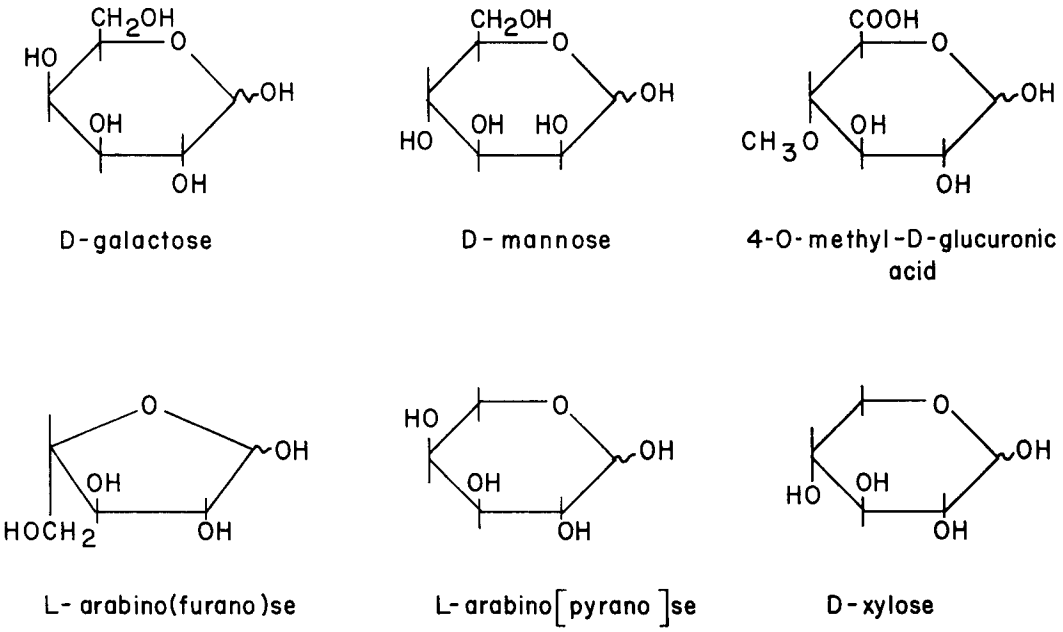


FIG. 1. Sugars present in hardwood hemicelluloses.

been achieved in a few cases only. Consequently the approximate amounts of these polysaccharides are better assessed by chemical analysis of the wood despite the difficulty in obtaining complete hydrolysis of the polymers without some destruction of the sugars. Nowadays because of improvements in technique, such as the use of specific sugar oxidases and the use of thin layer chromatography, paper chromatography, gas-liquid chromatography, and high pressure liquid chromatography, it is a comparatively simple matter to determine, quickly and accurately, the ratios of sugars produced on hydrolysis of the woods (however, see above precautions on hydrolysis technique). The major sugars determined quantitatively are D-galactose, D-glucose (mainly from cellulose), D-mannose, L-arabinose and D-xylose (Fig. 1, Table 2). Other sugars such as L-fucose, L-rhamnose, D-galacturonic acid, 4-*O*-methyl-D-glucuronic acid, and D-glucuronic acid may also be detected, usually in relatively small amounts. The methyl pentoses and D-galacturonic acid probably arise from pectic materials.

Direct extraction of hardwood sawdust

TABLE 2. *Chemical analysis of carbohydrates from some American woods*

Species	Percentage of extractive-free oven-dry wood						
	Acetyl	Uronic anhydride	Glucan	Mannan	Xylan	Galactan	Arabinan
Beach	3.9	4.8	47.5	2.1	17.5	1.2	0.5
Maple, red	3.8	3.5	46.6	3.5	17.3	0.6	0.5
Oak, southern red	3.3	4.5	40.6	2.0	19.2	1.2	0.4
Sweetgum	—	—	39.4	3.1	17.5	0.8	0.3
Elm, white	3.9	3.6	53.2	2.4	11.5	0.9	0.6

The author thanks the Forest Products Laboratory, USDA Forest Service, for permission to publish Table 2.

TABLE 3. *General characteristics of some 4-O-methylglucuronoxylans*

Species	Yield, in % of wood	Xylose ratio per acid residue	$[\alpha]_D$ degrees (in NaOH)	Pn
Quercus alba Oak, white	10	—	–75	—
Quercus robur Oak, English	7–12	11–12	–62 to –85 –85	—
Ulmus americana Elm, American	5–6	7	–70	185

Pn = Number-average degree of polymerization (number of xylose residues in the xylan backbone).

(extractive-free) with aqueous alkali makes it possible in many cases to isolate a de-*O*-acetylated xylan in yields of up to 95% (Table 3). Thus it is feasible to check the D-xylose content found by chemical analysis against the yield of xylan determined by direct alkaline extraction of the wood. However, the direct extraction of hemicelluloses from American elm sawdust does not give good yields of product. The yields of hemicelluloses depend upon the type of alkali used. Experience has shown that aqueous potassium hydroxide is more effective than aqueous sodium hydroxide in extracting 4-*O*-methylglucuronoxylans and it is more specific in that very little glucomannan is extracted at the same time. The sawdust is usually extracted in an atmosphere of nitrogen at or below room temperature if de-*O*-acetylated xylans of minimum degradation are required.

This procedure minimizes the alkaline degradation of polysaccharides but does not prevent the so-called "peeling off" reaction which results from degradation of the molecule from the reducing end (by β-elimination) (Fig. 2). To prevent this "peeling off" reaction, the polysaccharide molecules may be treated with sodium borohydride to convert their reducing ends to derivatives of xylitol. If sodium borotritiide (NaB^3H_4) is used, then the reducing ends of the molecules are labelled with tritium and may be identified later, thus giving the average molecular size of the molecules (Fig. 3). The 4-*O*-methyl-D-glucuronic acid portion of a 4-*O*-methyl-D-glucoronoxylan may itself be vulnerable to alkaline degradation under certain circumstances, again by β-elimination resulting first in demethylation and then in loss of uronic acid residues.

In some cases the yield of hemicelluloses from direct alkali extraction of wood is low. To improve the yield, the lignin should first be removed leaving a holocellulose. There are several procedures described in the literature that involve the use of chlorine, chlorine derivatives, or peracids. These reagents convert the lignin, oxidatively, to derivatives that can then be extracted under mild conditions with organic solvents or acids. Unfortunately, these procedures usually lead to loss of polysaccharides and may result in modification of the isolated polysaccharides. For example, the reducing endgroup of the polysaccharides may be converted to an aldonic acid derivative, a primary alcohol may be oxidized to a carboxylic acid or a secondary alcohol to a ketone. This last reaction is of considerable significance since it may make the polymers base-labile as shown in Fig. 2 ("peeling off" reaction). To overcome this possibility the delignified material may be treated with sodium borohydride before extracting the holocellulose with potassium hydroxide solution. This treatment converts ketones to secondary alcohols that are unaffected by the base. If a polysaccharide still containing its original *O*-acetyl groups is required, a holocellulose, obtained by chlorite treatment of the original wood (e.g. silver birch), may be extracted with methyl sulfoxide to yield a xylan containing a relatively high proportion of *O*-acetyl and uronic acid residues. However, it is impracticable to ex-

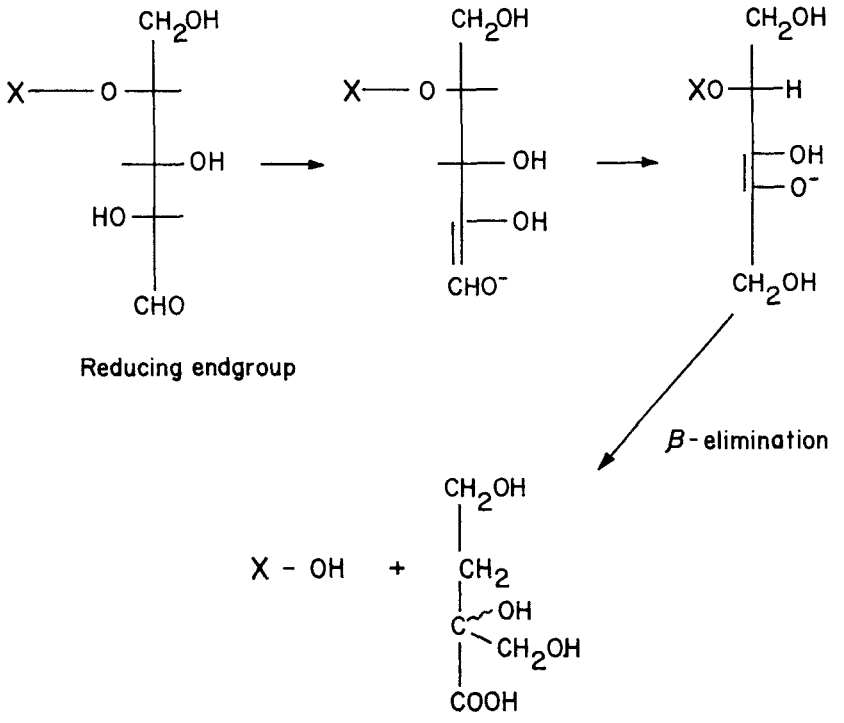


FIG. 2. Degradation of xylan by alkali.

tract all the hemicelluloses from a wood by any of these procedures. There usually remains a portion that appears to be bound to the lignin or to the cellulose fraction of the wood.

STRUCTURE OF THE 4-O-METHYL-D-GLUCURONOPYRANOSYLXYLANS

The original classical work begun in 1923 (O'Dwyer 1940) on the structure of the hemicelluloses of white oak was made difficult because little was known at that time of the chemistry of xylose and of uronic acids. Microchemical techniques were not available and the separation and identification of the sugars, involving the preparation of their complex hydrazones, were very complicated and inexact procedures. Nevertheless it was possible to isolate a hemicellulose that gave xylose and a uronic acid deriva-

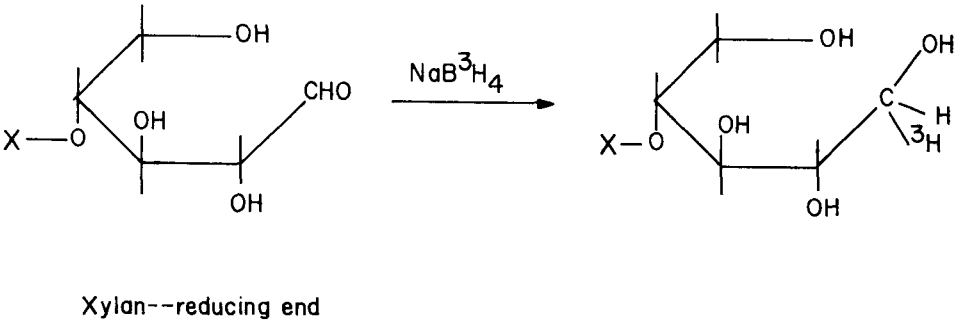


FIG. 3. Reduction of xylan with sodium borotritiide (NaB^3H_4).

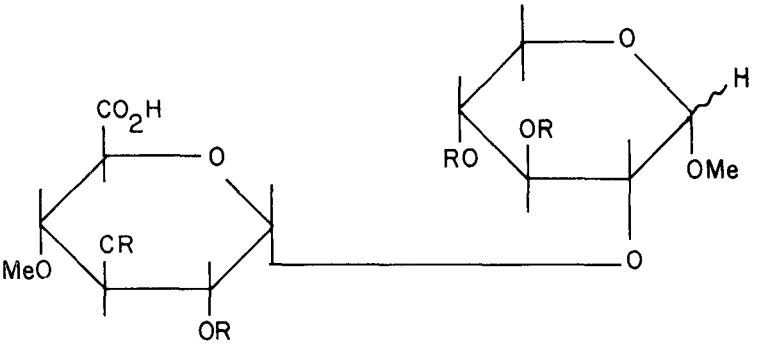
TABLE 4. *Xylan from various species of hardwood (extractive-free)*

Species	Percentage of extractive-free xylan				
	Pentosan	Xylose residues	(4-*O*-Methyl-glucurono)-xylan	*O*-Acetyl-(4-*O*-methyl-glucurono)-xylan	Experimental yield (direct extraction)
Acer rubrum					
Maple, red	20.2	18.6	21.3	25.1	—
Acer saccharum					
Maple, sugar	18.5	15.9	18.2	21.1	14.6 12.4
Ulmus americana					
Elm, American	15.3	12.3	14.9	18.8	5.3

tive in a ratio of 6:1. This hemicellulose contained methoxyl residues. On partial hydrolysis of the hemicellulose, the barium salt of an *O*-methylglycuronosylxylose was obtained. The present author examined a specimen of this salt in 1947, but even then insufficient background knowledge was available to determine its complete structure using the techniques available.

Partial hydrolysis by acids or enzymes is a major procedure now used to determine the sequence of sugars in hemicelluloses. This is possible because there are now so many analytical techniques that may be used to separate di-, tri-, tetra-, etc. oligosaccharides from one another. When aspen sawdust was hydrolyzed by acid and the components separated into neutral and acidic fractions, at least four materials were identified. These were: D-xylose, xylobiose, xylotriose and an aldobiouronic acid identified as 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose. The isolation of these components using a column of charcoal (Whistler and BeMiller 1962) gives some idea of the structure of the original hemicellulose.

A more powerful tool for the determina-



Methyl O-[methyl (2,3-di-O-acetyl-4-O-methyl-α-D-glucopyranosyl)-uronate]-(1→2)-3,4-di-O-acetyl-α-D-xylopyranoside

R = CO·CH3

FIG. 4. Methyl *O*-[methyl(2,3-di-*O*-methyl-α-D-glucopyranosyl)uronate]-(1→2)-3,4-di-*O*-acetyl-α-D-xylopyranoside IV, R=H characterized as R = CO · CH_3.

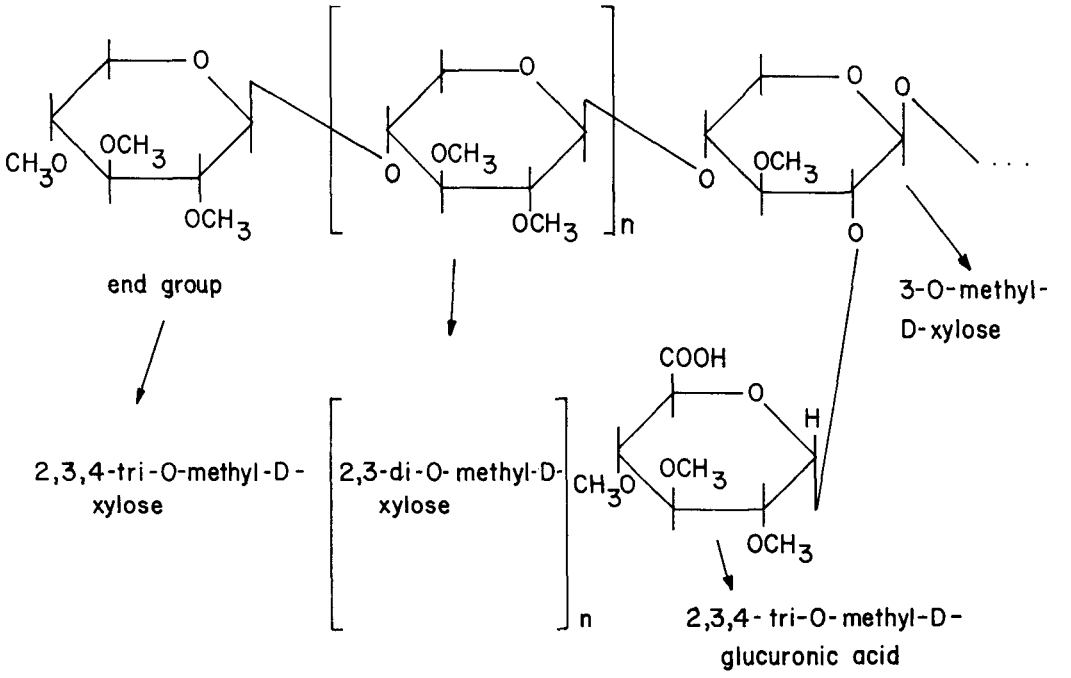


FIG. 5. Hydrolysis of methylated xylan.

tion of polysaccharide structure is the methylation procedure. In this technique free hydroxyl groups present in a hemicellulose molecule are converted to the corresponding methyl ethers using methyl sulfate and alkali, thus labelling them (Haworth 1915). The methylated derivative is then hydrolyzed, and the different components so produced are separated and identified. When 4-*O*-methyl-D-glucuronoxylan from red maple was put through this procedure, a fully methylated derivative was obtained that was soluble in organic solvents. After hydrolysis, four components could be detected chromatographically. These were separated and identified (Fig. 5) as 2,3,4-tri-O-methyl-D-xylose (endgroup), 2,3-di-*O*-methyl-D-xylose (the major component), 3-*O*-methyl-D-xylose and 2,3,4-tri-*O*-methyl-D-glucuronic acid (Aspinall et al. 1954). The last component resulted from the methylation of the side chains of 4-*O*-methyl-D-glucuronic acid which were attached to the 3-*O*-methyl-D-xylose residues. The linkage between the 2,3,4-tri-*O*-methyl-D-glucuronic acid and 3-*O*-methyl-D-xylose is relatively stable to acid. Consequently, a disaccharide composed of these two units is frequently encountered when methylated *O*-glucuronosylxylans are hydrolyzed by acids. This information, together with the knowledge that xylobiose, xylotriose and an aldobiouronic acid (Fig. 4) are produced on acidic hydrolysis of xylan, is unfortunately, not sufficient to permit an unambiguous structure to be allocated to this polysaccharide.

The newer methods of methylation (Sandford and Conrad 1966) using the methyl sulfoxide anion ($CH_3SOCH_2^-Na^+$) permit the complete and rapid methylation of a very small amount of material (ca. 20 mg). The gas-liquid chromatographic (g.l.c.) machine coupled to a mass spectrometer and computer now allow one to separate, identify, and determine quantitatively the components produced on hydrolysis of a minute amount of methylated hemicellulose. This procedure has been used in the case of some polysaccharides but

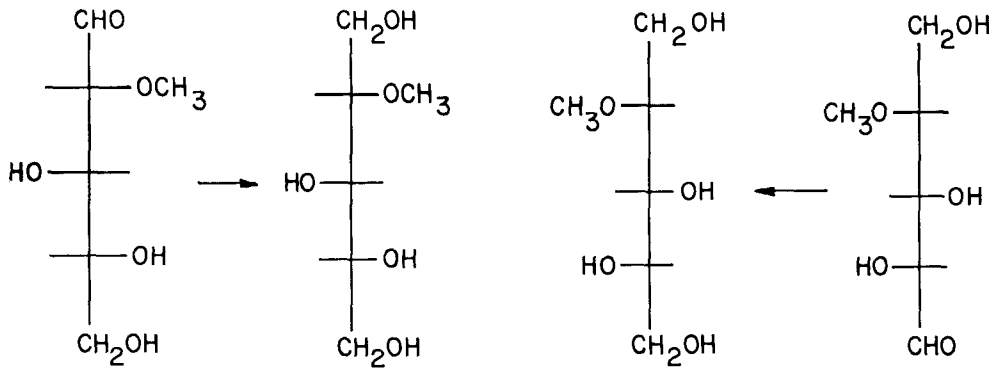


FIG. 6. Reduction of 2- and of 4-*O*-methylxylose.

has not yet, as far as the author is aware, been employed in the examination of a methylated hemicellulose. In some cases the *O*-methyl ether derivatives of the sugars may not be sufficiently volatile for analysis on the g.l.c. machine. Several procedures can be used to overcome this problem, but often at least two methods must be used to solve it. For example, the *O*-methyl ether may be acetylated or trimethylsilylated or it may be reduced and then acetylated or trimethylsilylated. In the first procedure a complicated mixture may be produced because of the possibility of formation of several glycosides. In the second case a much simpler pattern will be formed, but there may be ambiguities because of the stereochemistry of the sugars. For example 2-*O*-methylxylose on reduction yields 2-*O*-methylxylitol but 4-*O*-methylxylose yields a xylitol which is indistinguishable by the g.l.c. procedure (Fig. 6). Use of gas chromatography to separate trimethylsilylated derivatives of the polysaccharides found in most prepared foods has been described by Larson and Egberg (1977), using different columns for mono- and disaccharides and for tri- and tetrasaccharides. A recent publication has described the preparation of the oximes of the sugars that on acetylation yield the acetylated acyclic nitriles; the formation of isomers due to ring structure is thus avoided (Lance and Jones 1967).

The hardwood xylans consist, in the main, of a linear backbone of 1,4-linked β-D-xylopyranosyl residues to which are attached, by α-linkages, 4-*O*-methyl-D-glucuronopyranosyl units at irregular intervals (Timell 1961a). These xylans are physically and perhaps chemically heterogeneous and are composed, on the average, of about 190 sugar residues. Some of them are in part *O*-acetylated. An idea of the positions of the *O*-acetyl residues may be determined by periodate oxidation. This reagent oxidizes compounds that contain hydroxyl groups on each of two or more contiguous carbon atoms. If a hydroxyl group, whether on C-2 or C-3 of the xylose residue in a xylan molecule, is substituted by an *O*-acetyl residue that molecule will not be oxidized by periodate. Thus, if the number of *O*-acetyl residues corresponds to the number of unoxidized D-xylopyranosyl residues, then there will be approximately one *O*-acetyl residue for each unoxidized sugar. Allowance is made for the presence of unoxidized residues resulting from substitution at C-2 by uronic acid groups. A better method (see Fig. 7) (Bouveng 1961) is to treat the *O*-acetylxylan with phenyl isocyanate to prepare the fully substituted phenylcarbamate ester. The more stable phenylcarbamate ester is unaffected by mild acid hydrolysis, but the *O*-acetyl groups are removed. Methylation of the de-*O*-acetylated product with silver oxide and methyl iodide followed by treatment with lithium aluminum hydride to remove the *O*-phenylcarbamoyl groups gave a partially

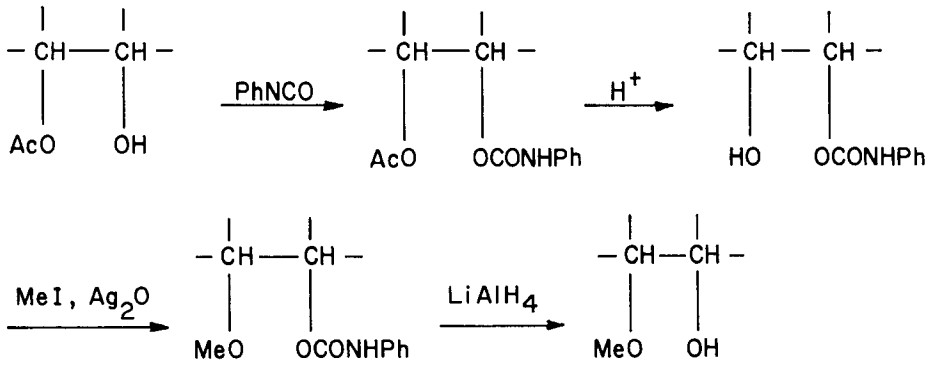


FIG. 7. Determination of the position of an *O*-acetyl residue in xylan.

methylated xylan. The position of the methoxyl groups and hence of the *O*-acetyls in the xylose residue was determined by conventional methods. Thus it was shown that *O*-acetyls exist as esters of hydroxyl groups on C-2 or C-3, and also on C-2 and C-3 of sugar residues in some cases (in a ratio of ca. 2:4:1 in the case of a xylan from white birch). Surprisingly some of these *O*-acetyl residues survive during the acid sulfite pulping process.

The periodate method of oxidation (Smith and Montgomery 1959) has been used to show that the xylan (from yellow birch) does not contain *O*-acetylated 4-*O*-methyl-D-glucuronic acid residues. When the 4-*O*-methyl-D-glucuronosylxylan is oxidized with periodate and the product is reduced by sodium borohydride, the resulting polyalcohol on hydrolysis, by dilute acid, does not yield any 4-*O*-methyl-D-glucuronic acid. This proves that each uronic acid molecule

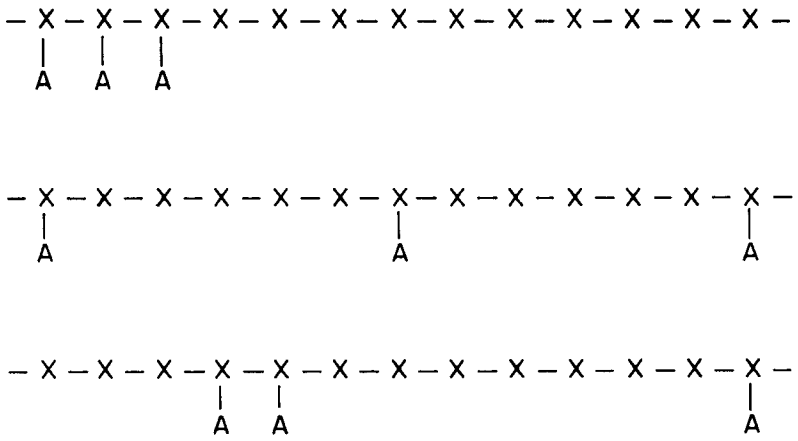


FIG. 8. Possible structures of hardwood xylan.

TABLE 5. *General characteristics of glucomannans from some hardwoods*

Species	Yield, in % of wood	Man/G	$[\alpha]_D$ degrees (in NaOH)	Pn	Nature of chain
Acer rubrum					
Maple, red	3.3	1.9	–31	70	linear
Acer saccharum					
Maple, sugar	1.1	2.3	–24	26	linear
Fagus grandifolia					
Beech, American	1.7(3.0[a])	1.7	–28	—	—

[a] Crude product, containing 13–14% of xylose residues.

has two adjacent hydroxyl groups (at C-2 and C-3) and therefore cannot have possessed any *O*-acetyl residues. Each grouping is therefore also an endgroup. In practically all xylans from hardwoods so far investigated, it has been shown that the uronic acid residues are α-linked to D-xylopyranose residues through C-2 of the pentose. Many structures are possible for the 4-*O*-methyl-D-glucuronosylxylan, some of which are shown in Fig. 8.

GLUCOMANNANS FROM HARDWOODS

Angiosperms contain little glucomannan (ca. 4%) relative to xylan (20–30%) and for this reason have been but little investigated. In a general method of isolation developed by Hamilton and Quimby (1957) and Timell (1961b), the wood is first delignified by chlorite and subsequently extracted with aqueous potassium hydroxide, which removes practically all the 4-*O*-methylglucuronoxylan. The residual wood is then extracted with sodium hydroxide containing borate which complexes with, and removes most of the glucomannan (Jones et al. 1956; Hamilton and Quimby 1957), leaving crude α-cellulose. The glucomannan can be purified either as a complex with barium hydroxide or as a copper complex that results when Fehling's solution is added to an alkaline solution of the glucomannan. Electrophoresis experiments indicate that these polysaccharides are essentially homogeneous. Physical methods of analysis (osmometry, etc.) indicate that they are composed, in the main, of about 100 sugar residues linked together in a linear fashion. The ratio of glucose to mannose in glucomannan is ca. 1:2 except in the genus *Betula* where it is ca. 1:1 (Timell 1961b).

Methylation studies (Mian and Timell 1960) on the glucomannan from red maple

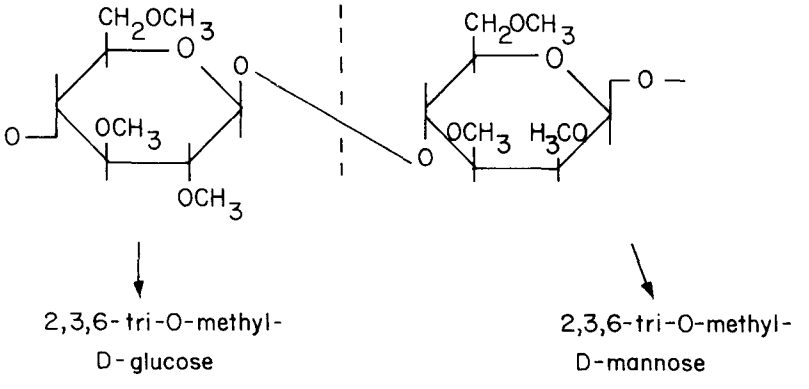


FIG. 9. Hydrolysis of methylated glucomannan.

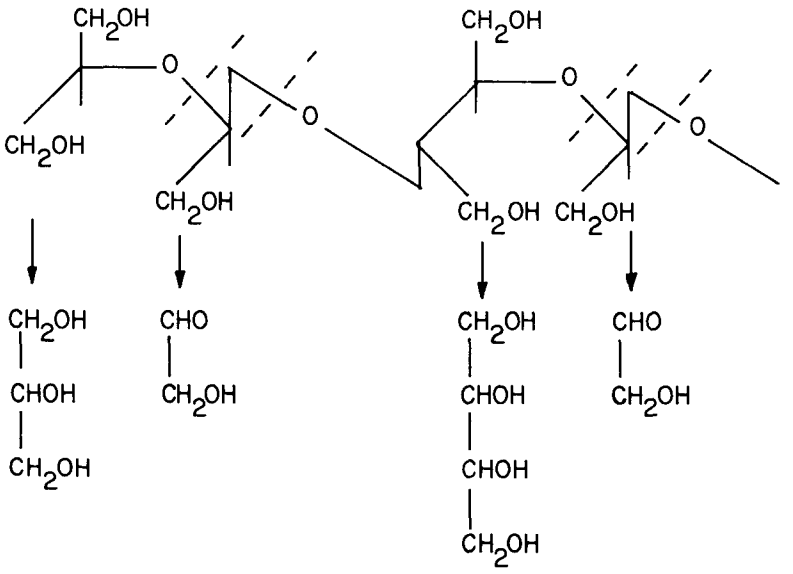


FIG. 10. Degradation of glucomannan using the procedure of F. Smith.

have shown that the sugars are 1→4 linked since after methylation and hydrolysis both 2,3,6-tri-*O*-methyl-D-glucose and 2,3,6-tri-*O*-methyl-D-mannose were produced together with small amounts of 2,3,4,6-tetra-*O*-methyl-D-glucose, which results from the nonreducing end of the polysaccharide (Fig. 9). The negative rotation (ca. –30°) of the polymer indicated that the sugars were linked by β-glycosidic linkages. Further evidence on this point resulted when the glucomannan from red maple was subjected to graded hydrolysis by dilute formic acid (Mian and Timell 1960). From the hydrolysis mixture the following sugars were isolated and identified: D-glucose (G), D-mannose (M), 4-*O*-(β-D-mannopyranosyl)-D-mannose (M-M), 4-*O*-β-(D-mannopyranosyl)-D-glucose (M-G), 4-*O*-(β-D-glucopyranosyl)-D-mannose (G-M), 4-*O*-(β-D-glucopyranosyl)-D-glucose (G-G) and *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-D-mannose (M-M-M). These results indicate that the sugars are probably randomly joined to one another in the linear polysaccharide chain. This suggestion was supported when maplewood glucomannan was degraded by the Smith and Montgomery (1959) procedure: i.e., (1) oxidation of the polymer by periodate (2) reduction of the product with sodium borohydride followed by (3) controlled hydrolysis with cold dilute acid (cf. Kooiman and Adams 1961). There resulted glycolaldehyde, erythritol, and traces of glycerol produced from the nonreducing end of the polysaccharide (Fig. 10). Thus glucomannan resembles a low molecular weight cellulose fraction in which two out of three D-glucose residues have been replaced in a random fashion by D-mannose residues (Fig. 11).

CONCLUSION

This brief account of the chemistry of the hemicelluloses from hardwoods includes very little information on the major hardwood species found on southern pine sites in Louisiana. It is evident that much further research is required if the chemistry of these trees is to be clarified. Modern techniques in carbohydrate chemistry should very much simplify and expedite this work.

Although elucidation of all details of southern hardwood hemicellulose chemistry has not been obtained, much background

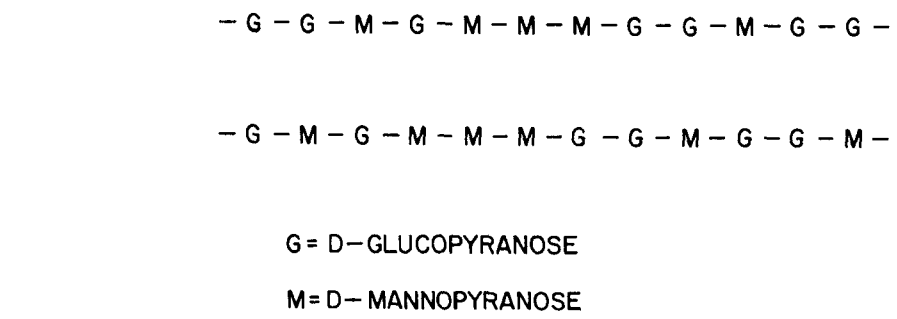


FIG. 11. Possible partial structures of glucomannan from red maple.

research on methods to extract hemicelluloses with a minimum of aromatic contaminants has been done. For example, Casebier et al. (1973a, b) have outlined the conditions to remove hemicelluloses from black gum (*Nyssa biflora*) using water prehydrolysis. Of course such methods of obtaining hemicelluloses result in mixtures of oligosaccharides, sugars, acids, etc. These heterogeneous mixtures will require separation before they are suitable for many subsequent chemical processes that often cannot tolerate mixtures.

Industrial use of hemicelluloses is possible, depending on the ultimate economics of any such venture after the problems of separating the sugar mixtures have been solved. As an example, while methods for production of furfural are available, production of furfural in conjunction with prehydrolysis kraft pulping of hardwoods at any given kraft mill will depend on size and location of the furfural marketplace, freight costs, cost of adding the furfural production capability to the pulp mill, and additional expenses directly incurred in furfural production.

REFERENCES

ASPINALL, G. O., E. L. HIRST, AND R. S. MAHOMED. 1954. Hemicellulose A of beechwood (*Fagus sylvatica*). J. Chem. Soc. 1954(2):1734–1738.

BOUVENG, H. O. 1961. Phenyl isocyanate derivatives of carbohydrates, I and II. Acta Chem. Scand. 15:87–95, 96–100.

CASEBIER, R. L., J. K. HAMILTON, AND H. L. HERGERT. 1973a. The chemistry and mechanism of water prehydrolysis on black gumwood: Effect of temperature at constant time. Tappi 56(3):135–139.

———, ———, AND ———. 1973b. The chemistry and mechanism of water prehydrolysis on black gumwood: Effect of time at constant temperature. Tappi 56(11):150.

CHRISTOPHER, J. F., H. S. STERNITZKE, R. C. BELTZ, J. M. EARLES, AND M. S. HEDLUND. 1976. Hardwood distribution on pine sites in the south. USDA For. Serv. Resour. Bull. SO-59. 27 pp. South. For. Exp. Sta., New Orleans, LA.

HAMILTON, J. K., AND G. R. QUIMBY. 1957. The extractive power of lithium, sodium and potassium hydroxide solutions for the hemicelluloses associated with wood cellulose and holocellulose from western hemlock. Tappi 40(9):781–786.

HAWORTH, W. N. 1915. A new method of preparing alkylated sugars. J. Chem. Soc. 107: 8–16.

JONES, J. K. N., L. E. WISE, AND J. JAPPE. 1956. The action of alkali containing metaborates on wood cellulose. Tappi 39:139–141.

KOOIMAN, P., AND G. A. ADAMS. 1961. Constitution of a glucomannan from tamarack (*Larix laricina*). Can. J. Chem. 39:889–896.

LANCE, D. G., AND J. K. N. JONES. 1967. Gas chromatography of derivatives of methyl ethers of D-xylose. Can. J. Chem. 45:1995–1998.

LARSON, PAUL A., AND DAVID C. EGBERG. 1977. Gas chromatographic analysis of sugars in food. Abstr. Papers Am. Chem. Soc. Meeting 173:AGFD 90.

MIAN, A. JABBER, AND T. E. TIMELL. 1960. Isolation and properties of a glucomannan from the wood of red maple (*Acer rubrum* L.). Can. J. Chem. 38:1511–1517.

O'DWYER, M. H. 1940. The hemicelluloses of the wood of English oak. V. The structure of hemicellulose B. Biochem. J. 34:149–152.

SANDFORD, P. A., AND H. E. CONRAD. 1966. The structure of *Aerobacter aerogenes* (S1) polysaccharide. I. A reexamination using im-

proved procedures for methylation analysis. Biochem. 5:1508–1517.

SMITH, F., AND R. MONTGOMERY. 1959. The chemistry of the plant gums and mucilages. Reinhold Publishing Corporation, New York, N.Y. Pp. 195–222.

TIMELL, T. E. 1961a. Isolation and properties of an *O*-acetyl-4-*O*-methyl-D-glucurono-D-xyloglycan from the wood of white birch (*Betula papyrifira*). J. Am. Chem. Soc. 82:5211–5215.

———. 1961b. Isolation and properties of a glucomannan from the wood of white birch (*Betula papyrifera*). Tappi 44: 844–848.

———. 1964. Wood hemicelluloses. Part I. Advances in Carb. Chem. 19:247–302.

———. 1965. Wood hemicelluloses. Part II. Advances in Carb. Chem. 20:409–483.

WHISTLER, R. L., AND J. N. BEMILLER. 1962. Carbon column chromatography. Academic Press, New York, N.Y. Pp. 42–44.