STRUCTURE OF THE GLUCOMANNAN OF Fraxinus excelsior

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The glucomannans of plant raw materials have been studied comparatively little [1-4]. They are present in small amounts in wood and are absent from many species of annual plants. We have isolated the glucomannan from the wood of Fraxinus excelsior (European ash).

As a quantitative chromatographic analysis of hydrolyzates of the initial and methylated polysaccharides showed, the glucomannan is constructed of residues of glucopyranose and mannopyranose in a ratio of 5 : 2, respectively. The presence of pyranose rings was confirmed by IR spectroscopy: absorption in the 700-900 cm^{-1} region is characteristic of them. The monosaccharide residues are connected by a β linkage, as is shown by absorption in the 890 cm^{-1} region and the negative value of the optical rotation of the methylated polysaccharide.

The results of the periodate oxidation of the glucomannan, of a study of the decomposition products of the reduced polyaldehyde, and of methylation show that the chain of the polymer is not branched. The consumption of periodate corresponded to one mole per mole of hexose residue. Among the hydrolysis products of the reduced polyaldehyde of the glucomannan were found erythritol and small amounts of glycerol, which are derived from the terminal residues of the chain of the macromolecule. Another proof of the linearity of the chain is the absence of a glycosylerythrol among the decomposition products. Consequently, the Smith degradation takes place in the following way:

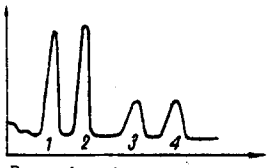
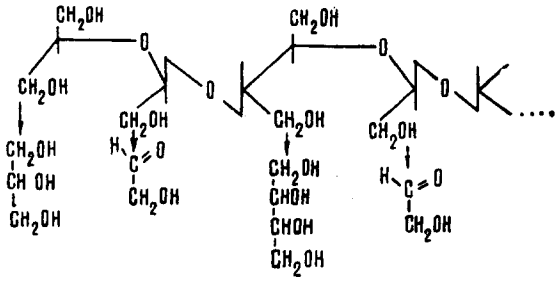


Fig. 1. Gas–liquid chromatography of a hydrolyzate of the methylated glucomannan of ash wood: 1 and 2) α and β isomers of 2,3,6-trimethylmannose; 3 and 4) α and β isomers of 2,3,6-trimethylglucose (stationary phase 15% of Apiezon L on Chromaton, t = 160°C).

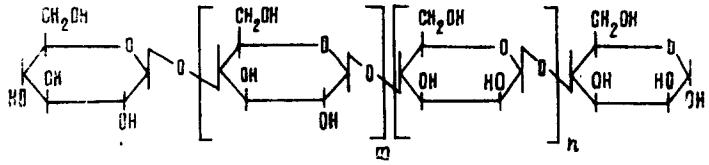


and the polysaccharide has a linear structure. The methylated monoses were separated by gas–liquid chromatography.

TABLE 1

Oxidation time, days	$NaIO_4$ consump.	HCOOH liberated
	moles per mole of hexose residue	
2	0,76	0,04
3	0,93	0,06
4	1,10	0,07
5	1,12	0,07

The molecular weight of the polymer is 6800 and the degree of polymerization 42. On the basis of the facts given above, the structure of the macromolecule of the glucomannan of European ash wood can be represented in the form



where m + n = 40.

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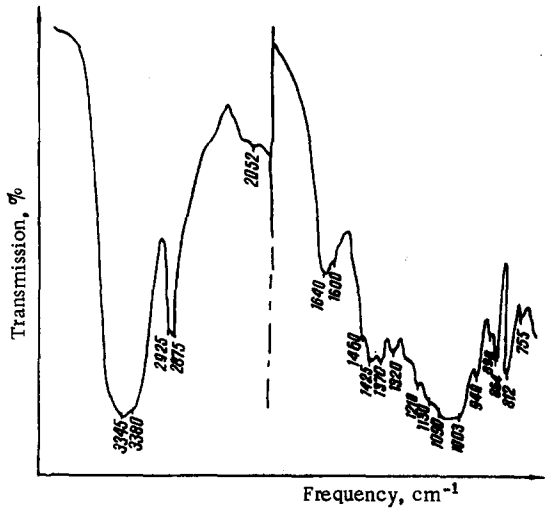
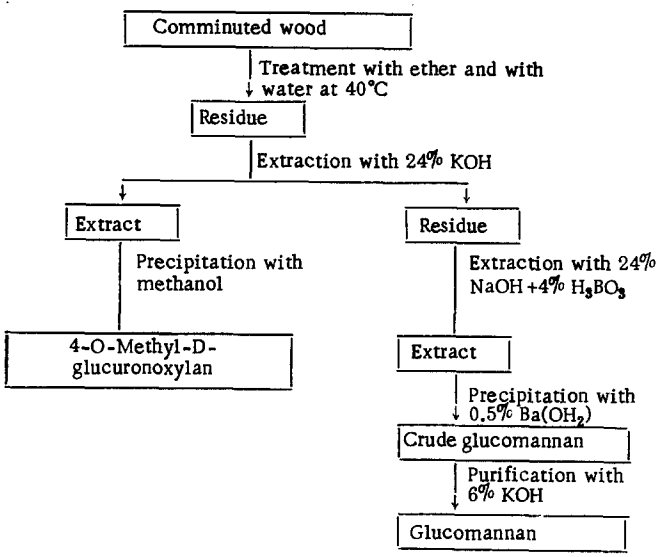


Fig. 2. IR spectrum of the glucomannan.

Scheme 1



EXPERIMENTAL

Isolation of the Glucomannan. Chips of the wood of Fraxinus excelsior were treated with ether. They were extracted with water at 40°C. After this, the glucomannan was obtained according to Scheme 1. The purity of the product isolated was checked chromatographically. The hydrolyzate contained only mannose and glucose in a ratio of 5 : 2.

Periodate Oxidation. The glucomannan was oxidized with 0.3 M sodium periodate in the dark at room temperature for various times (Table 1).

Thus, the oxidation of the glucomannan was complete in four days. The consumption of periodate amounted to 1 mole per mole of hexose residue, and the yield of formic acid was 0.07 mole.

Smith Degradation. The polyaldehyde obtained was reduced with sodium tetrahydroborate. The resulting polyol was hydrolyzed with 0.2 N HCl at room temperature for 6 h. The hydrolysis products were identified by paper chromatography using as solvent benzene–pyridine–butanol–water (1 : 3 : 5 : 3) and as the spraying agent a 0.1 M solution of sodium metaperiodate followed by a 1% solution of potassium permanganate.

Erythritol and traces of glycerol were found among the degradation products.

Methylation of the Glucomannan. The reaction was performed in tetrahydrofuran with solid caustic soda and dimethyl sulfate. The completeness of methylation was checked by thin-layer chromatography on plates of Al_2O_3 and also on an IR spectrograph from the constancy of the absorption bands in the 2910 cm^{-1} region; $[\alpha]_D^{20}$ −18° (c 1; chloroform).

In view of the close R_f values of the trimethyl derivatives of glucose and mannose, their separation by paper chromatography is impossible [5]. Consequently, we used gas–liquid chromatography. The ratio between the monomers was found from the intensities of the peaks (Fig. 1).

The calculation performed showed that the ratio between the trimethylmannose and the trimethylglucose was 5 : 2. This correlates well with the chromatographic analysis of the corresponding unmethylated monomers.

IR Spectra. These were taken on an IKS-14 double-beam spectrograph. The absorption bands in the 700–900 cm^{-1} region corresponded to the vibrations of pyranose rings. A β linkage is characterized by an absorption band in the 890 cm^{-1} region (Fig. 2).

Determination of the Molecular Weight. In view of the poor solubility of the glucomannan isolated, it was difficult to determine its molecular weight by the viscosimetric method. The molecular weight was calculated from the results of the periodate oxidation.

Because of the linearity of the polymer, 3 moles of formic acid should be obtained from the whole macromolecule, while the amount found was 0.07 mole per anhydroglucose unit, i.e., $0.07 \cdot DP = 3$, whence $DP = 3/0.07 = 42$, and the molecular weight is 6800.

SUMMARY

The glucomannan of the wood of Fraxinus excelsior has been isolated. It has been shown that it is a linear polymer consisting of mannopyranose and glucopyranose units connected by β linkages in a ratio of 5:2.

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