XYLAN FROM THE GLUMES OF COTTON BOLLS

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Xylan from cotton bolls has mol. wt. 15,600, degree of polymerization 118, $[\alpha]_D$ +68°. Complete acid hydrolysis of the xylan forms xylose, arabinose, glucose, galactose, and a uronic acid in molar ratios of 94:8:12:5:7.

The mild acid hydrolysis of the substance split off 14 moles of xylose, 8 moles of arabinose, 5 moles of galactose, and an aldobiuronic acid. The latter was isolated in the form of the barium salt, and the neutral sugars were separated on a column of cellulose. This gave D-xylose with mp 144-146°C, $[\alpha]_D$ +92° (c 0.5; water); phenylosazone with mp 163-165°C, $[\alpha]_D$ −22° (c 0.2; methanol); and D-galactose with mp 167-168°C, $[\alpha]_D$ +150° (water).

Since under these conditions the bonds of the main chain are not affected, the monoses split off are apparently present in side chains.

The residue of the xylan after mild alkaline hydrolysis was hydrolyzed completely with sulfuric acid. The hydrolyzate yielded 71 moles of xylose and 12 moles of glucose (calculated on the initial xylan). After the fermentation of the glucose with yeast of the "Leningrad" race, L-xylose was isolated with mp 140-141°C, $[\alpha]_D$ −31.9° (water).

The fact that glucose is split off only as the result of severe hydrolysis shows similar strengths of the bonds between the xylose and glucose units in the polysaccharide molecule. These sugars (L-xylose and D-glucose) most probably form the main chain of the xylan.

The facts given show that the xylan from cotton boll glumes differs considerably from the xylan from the stems of the cotton plant both in the composition of the main chain and in the diversity of the side chains. The xylan from the stems of the cotton plant contains both optical isomers of xylose.

The hydrolysis of the completely methylated xylan formed the products shown in Table 1.

The formation of 98 moles of 2,3-di-O-methylxylose shows that the main chain of the xylan molecule consists of 1→4-linked anhydroxyloses. The glucose present in the main chain is also linked with

TABLE 1. Products of the Hydrolysis of the Methylated Xylan

Methylated sugars	R_g* in systems		No. of moles per mole of xylan
	1	2	
2,3,4-Tri-O-methylxylose	0,93	0,97	7
2,3,4,6-Tetra-O-methylgalactose	0,86	0,88	5
2,3-Di-O-methylxylose	0,76	0,81	98
2,4-Di-O-methylxylose	0,66	0,68	8
2,3-Di-O-methylarabinose	0,63		6
3,6-Di-O-methylglucose	0,51	0,54	14
O-Methylglucuronic acid (I)	0,18	0,32	3
O-Methylglucuronic acid (II)	0,13	0.20	4

* R_g determined in relation to 2,3,4,6-tetra-O-methylglucose.

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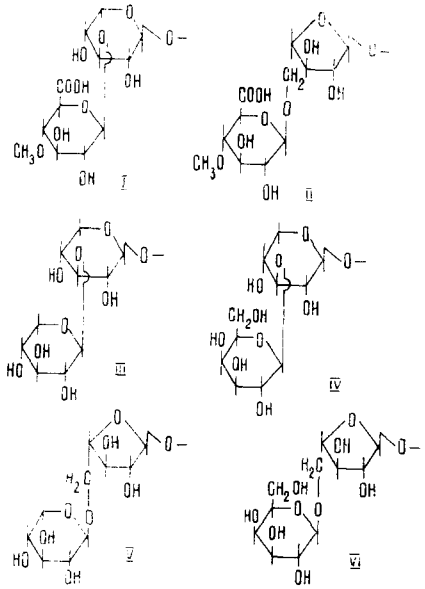
the xylose residues by 1→4 bonds, which is confirmed by the formation of 3,6-di-O-methylglucose on methylation. The positive rotation of the polysaccharide constructed mainly of L-xylose is due to the β configuration of the glycosidic bonds. Since among the products of hydrolysis of the methylated xylan there was no monomethylxylose, the side chains can be attached only at the C_2 position of the glucose units.

The terminal links of the xylan molecule are D-xylose, D-galactose, and glucuronic acid, as was shown by the isolation of 2,3,4-tri-O-methylxylose and 2,3,4,6-tetra-O-methylgalactose, and also of two methylated uronic acids. The formation of 2,4-di-O-methylxylose and 2,3-di-O-methylarabinose is apparently due to the fact that both these sugars are present in the side chains and are attached by 1→3 and 1→5 bonds, respectively.

On the basis of these facts it is possible to put forward the following structures (I, II, III, IV, V, and VI) for the side chains of the xylan from cotton bolls:

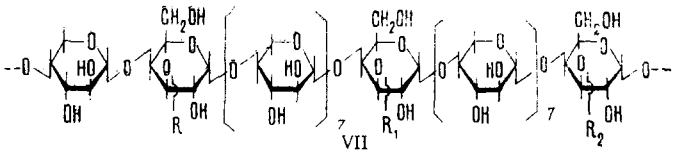


Since the methylated aldobiuronic acid isolated from the hydrolyzates of the cotton boll xylan has the same chromatographic mobility as the acid obtained from the xylan of the stems of the cotton plant [2], the side chain in which they are present has structure (I).

Additional experimental work is necessary to confirm the structures of these side chains.

The results of a study of the products of the hydrolysis of the initial and the methylated xylan permit the conclusion that the main repeating link in it consists of seven β-1→4-L-anhydroxylopyranose units and one β-1→4-D-anhydroglucopyranose unit to which a side chain formed of the fragments (I, III, IV, V, and VI) is attached at the C_2 position.

According to the yield of 3,6-di-O-methylglucose, the xylan molecule contains 14 branching points. Consequently, the most probable structure of the xylan from cotton boll glumes is (VII).



VII

R = I; R_1 = V or VI; R_2 = III or IV

The results of the investigation performed have shown that in the cotton plant, as in other plants, the xylans isolated from different organs have different structures. As a rule, the xylans from the stems of a plant have a simpler structure. This is apparently connected with their physiological function.

The xylan from the stems of the cotton plant contains β-1→4 bonds [2] and belongs to the polysaccharides of type A, its molecule consisting of a rigid ribbon-like chain [3]. Consequently, it is a structural polysaccharide.

The xylan from the boll glumes also belongs to the polysaccharides of type A. However, the presence of glucose residues in the main chain and of arabinose and glucuronic acid in the side chains makes its molecule looser and more accessible to the action of enzymes [4]. For such a xylan, in addition to its function as a skeletal substance, a function as a reserve material is also possible.

EXPERIMENTAL

Paper chromatography was performed on Whatman No. 1 paper with the following solvent systems: 1) butan-1-ol–ethanol–water–0.1% ammonia (40 : 10 : 49 : 1), 2) ethyl acetate–pyridine–water (5 : 1 : 5), and 3) ethyl acetate–acetic acid–formic acid–water (18 : 9 : 4 : 1).

The quantitative determination of the sugars and their methylated derivatives was performed by paper chromatography with the use of a type DFÉ-10 densitometer.

The complete hydrolysis of the xylan was performed as described previously [2]. The barium salt of an aldobiuronic acid, and xylose, arabinose, glucose, and galactose were identified by paper chromatography.

The mild hydrolysis of the xylan was performed similarly to the process described previously [2]. The sugars obtained after inversion were separated on a column of cellulose. The column was eluted with system 3, 5-ml fractions being collected. The monosaccharide composition of the fractions was checked by paper chromatography in system 3. This led to the isolation of D-xylose with mp 144-146°C (from ethanol), $[\alpha]_D$ +92° (c 0.5; water), phenylosazone with mp 163-165°C (ethanol–water), $[\alpha]_D$ −22° (c 0.2; methanol), and D-galactose with mp 167-168°C (from water), $[\alpha]_D$ +150° (water). Arabinose was eluted in admixture with xylose and was identified by comparison with an authentic sample by paper chromatography in systems 1, 2, and 3.

The degraded xylan was hydrolyzed completely [2]. Xylose and glucose were found chromatographically in the hydrolyzate. After the fermentation of the glucose with baker's yeast of the "Leningrad" race, L-xylose was isolated with mp 140-141°C (from ethanol), $[\alpha]_D$ −31.9° (in water), phenylosazone with mp 158-159°C, $[\alpha]_D$ +20° (methanol). The L-xylose gave no depression of the melting point in admixture with the L-xylose isolated from the stems of the cotton plant [2]. Literature figures for synthetic L-xylose: mp 144°C, $[\alpha]_D$ −18.6° (water) [5].

Methylation of the Xylan. Sodium hydride (0.26 g) was rapidly added to 5 ml of absolutely dry dimethyl sulfoxide. The mixture was stirred at 50°C for 80 min to form a greenish solution of the dimethylsulfinyl anion. Then a solution of 0.2 g of the xylan in 12 ml of absolutely dry dimethyl sulfoxide was added to the solution of dimethylsulfinyl anion. The mixture was cooled to 20°C and was kept at room temperature for 10 h. Then 10 ml of dry methyl iodide was added to the mixture with ice-water cooling. The solution was left at room temperature for 3 hours. Then it was poured into 200 ml of water and extracted with chloroform. The chloroform extract was washed twice with water. The chloroform was distilled off to dryness, toluene was added to the residue, and it was again distilled to dryness. A viscous yellowish syrup was obtained. Yield 0.148 g. The IR spectrum of this substance contained no bands characteristic for hydroxy groups.

The hydrolysis of the methylated xylan was performed in the same way as previously. The results of a chromatographic investigation of the hydrolyzates of the methylated xylan are given in Table 1. The methylated sugars were identified with comparison with authentic samples and by comparison of the R_g values that we obtained with those given in the literature.

SUMMARY

1. The structure of the xylan from cotton boll glumes has been studied. The results of the analysis of the products of the hydrolysis of the initial and the methylated xylan have shown that its main chain consists of β-1→4-L-xylopyranose and β-1→4-D-glucopyranose units. There are 14 branching points. The terminal residues of the xylan molecule are D-xylose, D-galactose, and 4-O-methylglucuronic acid. The side chains are attached to the main chain at the C_2 positions of the glucose units, and they contain, in addition to the terminal monosaccharides, D-xylose and L-arabinose attached to the main chain by 1→3 and 1→5 bonds, respectively.

2. It has been established that the main repeating unit of the molecules of the xylan from the boll glumes consists of seven or eight β-1→4-L-xylopyranose and one β-1→4-D-glucopyranose units, a side chain being attached to the latter in the C_2 position.

3. The most probable structure of the molecule of the xylan from the boll glumes has been proposed.

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