PERIODATE OXIDATION OF XYLANS OF VARIOUS STRUCTURES

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UDC 549.917 + 639.64

The results of a study of the mechanism of periodate oxidation have been given in a number of papers [1]. The synthesis of polyaldehyde derivatives of starch [2] and of cellulose [3] has been described. The oxidation of xylans has been performed, in the main, with the aim of characterizing their structures [4]. The nature of the selective oxidizability of the residues of various monosaccharides forming the links of the xylan macromolecule has been little studied [5, 6], and the structure of the polyaldehydes from these compounds is not clear.

We have subjected to oxidation with sodium periodate xylans having different structures: the araboglucuronoxylan of wheat straw of variety OD-16 and the 4-O-methylglucuronoxylan of the wood of Platanus orientalis.

The xylans were isolated from the initial raw material by alkaline extraction. They were purified by three reprecipitations via the copper complex. The characteristics of the plane-tree and straw xylans were as follows: molecular weights 30,000 and 16,000, respectively, DP 220 and 120, $[\alpha]_D^{20}$ −64 and −58°. According to chromatography the quantitative composition of a hydrolyzate of the straw xylan was 85% of D-xylose, 7% of L-arabinose, and 8% of D-glucuronic acid, and that of the plane xylan was 90% of D-xylose and 10% of 4-O-methyl-D-glucuronic acid.

When the xylans were treated with sodium periodate, the polysaccharides gradually dissolved. To obtain the oxidized xylans, we used freezing out, dialysis, and passage through ion-exchange resins. The dialysis method proved to be the most suitable in relation to the yield and purity of the product. As the analysis of the wash-waters after dialysis showed, degradation of the polysaccharide takes place during oxidation: the dialyzate contained xylose and oligosaccharides.

The consumption of $NaIO_4$ was determined in each individual case (iodometrically). The polyaldehyde isolated was characterized by its yield, by the proportion of carbonyl groups in it (by the hydroxylamine method), and by the number of unoxidized monose residues (hydrolysis and chromatography).

The results of the experiments are given in Tables 1 and 2.

The maximum oxidation of plane-tree xylan under our experimental conditions was achieved after 96 h, amounting to 83% of theoretical. The consumption of periodate remained constant for 96 and 120 h, and after the action of $NaIO_4$ for 120 h a process of overoxidation took place vigorously, as was shown by an increase in the consumption of periodate and a decrease in the amount of aldehyde groups. The uronic acid residues present at branchings were oxidized first; the rate of their degradation was fairly high, since after oxidation for only 5 hours only traces of them remained, and then they disappeared completely. The amount of xylose, which decreased sharply at the beginning of the oxidation, remained constant after 48 h. A hydrolysis of the polyaldehyde took place in parallel. With an increase in the time of oxidation, the number of glycosidic bonds decreased through ring opening and resistance to hydrolysis decreased, the glycosidic bonds adjacent to carboxyl groups being hydrolyzed first [1].

The increased rate of oxidation of the uronic acid residues and the "overoxidation" are apparently due not only to the cleavage of the C_2-C_3 bonds with the formation of a derivative of the monoaldehyde of meth-

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TABLE 1. Characteristics of the Polyaldehydes of Plane-Tree Xylan

Time of oxidation, h	Consump. of $NaIO_4$/mole of pentose resid.	Amt. of aldehyde groups, %	Yield of polyaldehyde, %	Monosaccharide composition, %
5	0,69	5,30	9	Uronic acid, traces of xylose 64
24	0,72	7,80	12	Not det.
48	0,76	17,30	32	Xylose 12
96	0,84	31,90	60	Xylose 10
120	0,84	30,00	58	Xylose 11
144	1,00	28,00	45	Xylose 10
168	1,20	24,30	36	Xylose 11

TABLE 2. Characteristics of the Polyaldehydes of Wheat-Straw Xylan

Time, h	Consump. of $NaIO_4$/mole of pentose resid.	Amt. of aldehyde groups, %	Yield of polyaldehyde, %	Content of unoxidized monose resid., %
Polyaldehyde A				
5	0,77	17,5	60	Uronic acid, traces of arabinose 2.7; xylose 47.0
24	1,10	24,2	15	Arabinose 2.0; xylose 14.0
Polyaldehyde B				
5	0,77	1,0	3,0	Uronic acid, traces of arabinose 3.10; xylose 30.0
24	1,10	5,5	5,0	-
48	1,20	7,0	12,0	Arabinose 2.2; xylose 4.6
96	1,20	28,0	12,0	Arabinose 2.3; xylose 5.0
144	1,30	12,0	12,0	Arabinose 3.1; xylose 11.5
168	1,40	9,0	12,0	Not det.

oxytartaric acid, but also to hydrolysis of the polyaldehyde. During the oxidation, an ever-increasing number of pyranose rings open. The aldehydes form, and then the carboxy groups in the α positions to the semiacetal bond reduce its stability. The bond mentioned hydrolyzes first [1]. This explains the sharp decrease (from 60 to 30%) in the yield of polyaldehyde after dialysis.

The oxidation of the araboglucuronoxylan takes place in a somewhat different manner. While on oxidation the plane-tree xylan passes into solution completely after only 5 h, the same process takes place gradually for straw xylan and is complete only after oxidation for 24 h. Consequently, we investigated two fractions of the xylan: a partially oxidized but not yet dissolved polyaldehyde A and a dissolved polyaldehyde B, which was isolated from the solution by dialysis (Table 2).

The yield of polyaldehyde A fell from 90% after oxidation for 1 h to 15% after 24 h. The amount of carbonyl groups rose to 28%. No glucuronic acid was present after oxidation for 5 h. The arabofuranose residues are more resistant to oxidation, some of them remaining unoxidized for 168 h. This resistance is probably due to the presence of a furanose ring and to the conformational structure of the arabinose. The lower rate of oxidation of the arabinose residues in comparison with the uronic acids is due to the influence of the trans-α-diol groupings in the molecules and to the fact that they are present in the furanose form.

The incomplete oxidation of the xylose residues depends on the presence of side branches formed through a bond with one of the α-glycol hydroxyls. Polyaldehyde B, in contrast to the amorphous polyaldehyde A, has the external form of a crystalline substance. Its yield is low and remains constant after oxidation for 24 h. The maximum amount of aldehyde groups is 28%, and then it decreases with an increase in the consumption of periodate, which is characteristic for the process of overoxidation [7, 8]. This fact is confirmed by the increase in the number of carboxyl groups in polyaldehyde B from 4.3% after oxidation for 96 h to 5.3% at 144 h, with a simultaneous decrease in the amount of aldehyde groups. In this case, no appreciable destruction of the polyaldehyde takes place, since its yield remains constant.

EXPERIMENTAL

The isolation and purification of the 4-O-methylglucuronoxylan of the plane and of the araboglucuronoxylan of wheat straw were performed by a previously described method [9].

The periodate oxidation of the xylan was performed with a 0.3 M aqueous solution of $NaIO_4$ at room temperature in the dark with periodic shaking for various times – from 5 to 144 h. In each case, ethylene glycol was added to the solution obtained and it was dialyzed against running water for several days until the reaction for iodine was negative (Beilstein test). The dialyzate was evaporated to a pasty state and was dried in vacuum. The polyaldehyde A was separated from the solution of the oxidant by filtration.

Determination of the Monosaccharide Compositions of the Polyaldehydes. The polyaldehydes were hydrolyzed with 2% HCl for 4 h in the boiling-water bath under reflux. The carbohydrate composition of the hydrolyzate was determined by paper chromatography in the benzene–butan-1-ol–pyridine–water (1 : 5 : 3 : 3) system with aniline phthalate as the chromogenic agent.

SUMMARY

1. The rate of oxidation of xylan with sodium periodate depends on the amount of oxidizable monosaccharide residues forming its links and on their quantitative ratio.

2. The rate of oxidation of monosaccharide residues of the structural links of the xylans is determined by their structure.

3. The highest rate of oxidation is characteristic for D-glucuronic acid residues and the lowest for L-arabofuranose residues.

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