THE STRUCTURE OF THE WATER-SOLUBLE ARABINOXYLAN OF WHEAT ENDOSPERM

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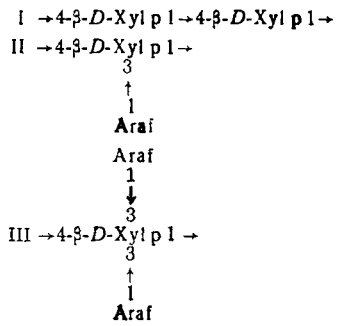
In contrast to other types of plant raw materials [1], the endosperm of wheat grain contains water-soluble xylans consisting of xylose and arabinose residues the structure of which has been studied little [2, 3] although their link with other components of the grain [4] and their influence on the quality of the flour obtained from it [5] are not a matter of doubt.

The present paper gives the results of an investigation of a water-soluble arabinoxylan isolated from the grain of a new variety of high-yielding wheat, Odesskaya-51 [6].

According to the results of electrophoresis and gel filtration, the xylan, purified by reprecipitation with ammonium sulfate and by enzymatic hydrolysis with a complex of the amylolytic enzymes of saliva [10], is homogeneous. On the basis of the results of hydrolysis and quantitative chromatographic analysis, we have found that this polysaccharide is constructed solely of D-xylose and L-arabinose in a ratio of 2 : 1. A similar ratio of these monosaccharides was found previously for American and Canadian varieties of wheat by Perlin [2] and by Montgomery and Smith [7]. Consequently, an arabinoxylan containing a considerable amount of arabinose residues is characteristic for wheat grain. The negative value of the specific rotation shows a predominant number of β-linkages between the monosaccharide units in the polymer.

Chromatographic analysis of a hydrolyzate of the methylated xylan gave a ratio between D-xylose, 2-O-methyl-D-xylose, 2,3-di-O-methyl-D-xylose, 2,3,4-tri-O-methyl-D-xylose, and 2,3,4-tri-O-methyl-L-arabinose of 1 : 6 : 10 : 0.1 : 8. This shows the presence in the structure of the xylan of sections of macromolecule of the types



For every fragment of type III the polymer chain contained six of type II and four of type I. Thus, the D-xylose residues in the chain are bound by β-(1 → 4) bonds, and the L-arabinose forms single-unit side chains attached to the xylose units at the position of the second carbon atom and, in a number of cases, at the second and third atoms by 1 → 2 and 1 → 3 bonds.

After the periodate oxidation of the xylan, the reduction of the resulting polyaldehyde to a polyol, the hydrolysis of the latter, and the identification of the hydrolysis products, xylose, glycerol, xylopyranosylglycerol, xylobiosylglycerol, and xylotriosylglycerol were found, which shows the irregular arrangement of the arabinose branching along the chain, in which individual blocks may exist together with a chaotic distribution. Aspinall et. al. [8] came to similar conclusions in a study of the arabinoxylan of rye flour.

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EXPERIMENTAL

Initial Raw Material. The experiments were performed with 70%-extraction flour obtained by grinding in a laboratory mill Odesskaya-51 wheat grains of the 1973 harvest grown in the All-Union Institute of Breeding and Genetics. Its composition (%) was: ash 0.50, protein 13.95, soluble mono- and oligosaccharides 1.26, pentosans 2.78, starch 78, cellulose 0.45, and fats 1.19.

Isolation of the Xylan. The gluten was washed out of 500 g of flour with water. The wash-waters, together with the suspension of starch, were centrifuged, and the centrifugate was boiled to coagulate the proteins and inactivate the enzymes. The proteins were precipitated by the successive addition of solutions of $CuSO_4$ and NaOH [9]. The solution was saturated with ammonium sulfate (70 g to 100 ml) and vigorously stirred. The xylan that precipitated was dialyzed, reprecipitated with $(NH_4)_2SO_4$, and subjected to the action of the amylolytic enzymes of saliva [10]. The purity of the polysaccharide isolated was judged from the constancy of the monosaccharide composition of a hydrolyzate after hydrolysis with 2% HCl.

Characteristics of the Xylan. The homogeneity of the polysaccharide was shown by paper electrophoresis in borate buffer and by gel filtration on Sephadex G-150. According to the results of chromatographic analysis, the hydrolyzate contained only xylose and arabinose (67.7 : 32.2%). The molecular weight determined by the viscosimetric method was 52,700, DP 400, $[\alpha]_D^{20}$ −96° in 2% NaOH.

Periodate Oxidation and Smith Degradation. The arabinoxylan was oxidized to with a 0.2 M solution of sodium periodate at room temperature. The number of moles of $NaIO_4$ per mole of pentose residue consumed after 24 h was 0.46, after 48 h 0.58, after 72 h 0.71, after 96 h 0.76, and after 120 h 0.76.

The oxidized and dialyzed xylan (0.5 g) was reduced with sodium tetrahydroborate (0.17 g). The polyol obtained was hydrolyzed with 0.2 N HCl at 20°C for 6 h. By paper chromatography [solvent: butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3)] the hydrolyzate was found to contain D-xylose, ethylene glycol, glycerol, and a product unidentified in the usual systems with a small R_f value.

To characterize the latter substance, the corresponding spot on the chromatogram was cut out and eluted with hot water, and the solution was concentrated in vacuum and rechromatographed in the butan-1-ol–acetic acid–water (4 : 1 : 5) system. Three components were detected – xylosylglycerol, xylobiosylglycerol, and xylotriosylglycerol.

Methylation was performed by Hakomori's method in dimethyl sulfoxide with a solution of the methylsulfinyl carbanion and methyl iodide. Complete methylation was achieved after four treatments. It was checked by thin-layer chromatography on a plate coated with Al_2O_3. The methylated product was subjected to formolysis with 90% HCOOH at 100°C for 1 h, and then to hydrolysis with 0.25 M H_2SO_4 at the same temperature.

The hydrolyzate was neutralized with barium carbonate, centrifuged, and evaporated to small volume in vacuum. The products of the methylated arabinoxylan were analyzed by paper chromatography: They contained D-xylose, a monomethyl-D-xylose, 2,3-di-O-methyl-D-xylose, 2,3,4-tri-O-methyl-D-xylose, and 2,3,4-tri-O-methyl-L-arabinose.

The position of the methyl group of the monomethyl xylose (C_2 or C_3) was determined by chromatography on paper impregnated with a solution of borax upon which monomethylxyloses have different mobilities. No 3-O-methylxylose was found. Consequently, branching takes place at C_3.

SUMMARY

The endosperm of Odesskaya-51 wheat contains a water-soluble arabinoxylan. Its main chain is constructed of β-D-xylopyranose units linked by β-(1→4) bonds. The side chains contain L-arabinofuranose residues attached to the main D-xylose chain at the second and third carbon atoms of the xylose units. The ratio of xylose to arabinose is 2 : 1.

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AN INVESTIGATION AND IDENTIFICATION OF POLYSACCHARIDES ISOLATED FROM ARCHEOLOGICAL SPECIMENS

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Carbohydrates may be preserved undisturbed for millions and thousands of millions of years in sedimentary rocks and fossilized plant and animal residues [1-5]. Of the polysaccharides in such specimens it is usually possible to determine cellulose, chitin, and starch [1-4], but it is not known how long the polysaccharides of other groups, especially gums, remain undisturbed. Plant gums were widely used in antiquity for preparing pigments [6], and therefore the investigation of an extremely unusual material – polysacchardies isolated from fragments of paintings – will enable us to determine whether gums remain unchanged for long periods. In the isolated experiments performed up to the present time, it has not been possible to identify the polysaccharides found in ancient paintings [7, 8].

Figure 1 shows the IR absorption spectra of compounds isolated from specimens of wall paintings of the following Central Asian buildings: a) Karatepe, second-fourth centuries; b) Pendzhikent, seventh-eighth centuries, c) Adzhinatepa, seventh century; d) Toprakkal, third-fourth centuries; e) Khiva, 19th century. A comparison of the spectra has shown that they are all very similar and consist of typical polysaccharide spectra. Thus, in the 3400-cm^{-1} region there is a broad and strong band of the stretching vibrations of bound OH groups, and at 2800-3000 cm^{-1} the band of the stretching vibrations of CH groups. Two bands are observed in the 1740 and 1620-1640 cm^{-1} regions in all the spectra. The first includes a band due to the stretching vibrations of C=O groups of unionized acids (some authors assign them to hydrate water [8]) and in the second there is the stretching vibration of the carbonyls of ionized acids forming complexes with inorganic ions [9, 10]. In the 1400-1450 cm^{-1} region there is the band of the planar deformation vibrations of CH groups, but bands corresponding to the vibrations of a carboxylate ion may also present here [10]. The stretching vibrations of the skeleton of the molecule are observed in the 1000-1100 cm^{-1} region. The difference of the spectra in this region is probably due to inorganic impurities and, in particular, to the presence of some traces of gypsum (particularly the absorption at $\sim$ 1000, 1120, and 1140 cm^{-1}) [11].

The characteristic nature of the features of the spectra for polysaccharides [7, 8, 10] emphasizes their distinct similarity to the IR spectrum of the gum of the apricot Armeniaca vulgaris (the gum was collected in the town of Tashkent) which is also given in Fig. 1f. The spectra of the gums of the sour cherry Prunus cerasus, of the mazzard cherry (Prunus avium), and of the apricot proved to be completely identical, and therefore it is impossible to distinguish the gums solely on the basis of a comparison of IR spectra.

The similarity of compounds *a* and b was also confirmed by a study of their composition by paper and thin-layer chromatography (Table 1). The same main components – xylose, mannose, and glucose – were detected in the two polysaccharides. In gas–liquid chromatography (GLC) of derivatives of a hydrolyzate of compound b it was found that it included, in addition to the monosaccharides already mentioned, considerable amounts of galactose and glucuronic acid. Consequently, in the cases described the gums of similar, but not identical, plants were apparently used. Since the spectra of the saccharides mentioned resemble the spectra of the gums of fruit trees (f) and are given in the literature [7], hydrolyzates of sour cherry and apricot gums were also analyzed by the GLC method. The compositions of these gums proved to be very similar (see Table 1), but the

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