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STRUCTURE OF THE XYLOGLUCAN OF THE LEAVES OF *Heracleum sosnowskyi*

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The results are given of investigations of the polysaccharide complex of the leaves of *Heracleum sosnowskyi*. The complex was isolated from the leaves by extraction with alkali.

We have previously studied the structure of the xylans and glucans of a number of fodder plants [1, 2]. The cell walls of developing plant tissues contain a xyloglucan [3]; this has been found in the midribs of tobacco leaves [3] and in seeds [4]. In view of the probability of the presence of this saccharide in the leaves of herbs, we have isolated it from the leaves of *Heracleum sosnowskyi* Manden. collected in the Main Botanical Garden of the Academy of Sciences of the Moldavian SSR in Kishinev in 1981.

The monomeric composition of the hemicelluloses (HMCs) isolated was represented by uronic acid, galactose, arabinose, and xylose in a percentage ratio of 14.5:7.3:30.9:12.8:35.5. The scheme of fractionation of the HMCs included the following steps: the production of a water-soluble fraction of the HMCs, the chromotography of this fraction on DEAE-cellulose to separate the acidic fragments from the neutral fragments, and then subfractionation on a cellulose column. As a result of the fractionation, a neutral xyloglucan was isolated. After

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its acid hydrolysis, galactose, glucose, arabinose, and xylose were found in the hydrolysate in a molar ratio of 4:60:7:42. The homogeneity of the polysaccharide was shown in parallel by gel chromatography on Sephadexes G-100 and G-200 and by electrophoresis.

The specific optical activity was $[\alpha]_D^{20}$ + 42°, which agrees with available information in the literature for xyloglucans from other sources.

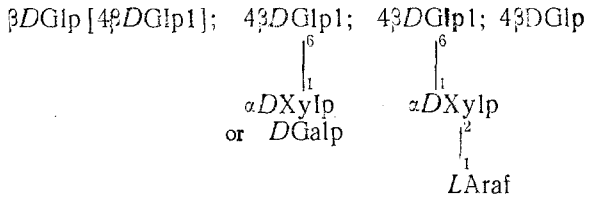
Under certain conditions, xyloglucans interact with an iodine reagent [5]. Analysis showed that the maximum absorption of the iodine complex of the xyloglucans of the leaves of *H. sosnowskyi* was at 630 nm. According to literature sources, the absorption bands of the complexes are located at 620-640 nm [5].

After the acetolysis of the polysaccharide and the appropriate working up of the reaction products [3], cellobiose was obtained, which confirms the presence of a cellulose-like core in the macromolecule of the polymer isolated.

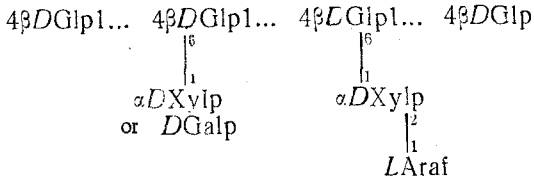
The structure of the xyloglucan was established by Hakomori methylation [6]. It was shown by paper chromatography (PC) and gas–liquid chromatography (GLC) that the methylated xyloglucan contained residues of 2,3,5-tri-O-methyl-L-arabinose, 2,3,4-tri-O-methyl-D-xylose, 3,4-di-O-methyl-D-xylose, 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,6-tri-O-methyl-D-glucose, 2,3-di-O-methyl-D-glucose, and 2,3,4,6-tetra-O-methyl-D-galactose in a molar ratio of 7:22:20:1:27:33:4.

The methylation results confirmed the presence in the xyloglucan of 1–4 bonds between glucopyranose residues. The polysaccharide is branched. The side chains are represented by xylopyranose, arabinofuranose, and galactopyranose residues.

As the results obtained showed, the following fragments are characteristic for the structure of the xyloglucan of the leaves of *H. sosnowskyi:*



The chain of the xyloglucan can be represented in the following way:



EXPERIMENTAL

Paper chromatography was carried out by using the following solvent systems: 1) butan-1-ol–pyridine–water (6:4:3); 2) pyridine–butan-1-ol–benzene–water (3:5:1:3); and 3) butan-1-ol–ethanol–water (5:1:4). The spots were revealed with aniline phthalate. GLC was performed on a Chrom-4 chromatograph with a FID using a 2000-mm column with helium as the carrier gas, the temperature of the evaporator being 220°C and that of the column 140-200°C.

The electrophoresis of the xyloglucan was carried out in borate buffer, pH 11.2, at a current strength of 15 mA and a voltage of 500 V for 6 h. Staining of the electrophoretogram gave a single spot at the position of deposition.

Gel chromatography was carried out on columns of Sephadexes G-100 and G-200. The xyloglucan was deposited on the column in the form of a 5% solution and it was eluted with 0.5% NaOH. In both cases, fractionation gave a single symmetrical peak. The yields of the fractions were monitored by the anthrone reaction.

The hemicelluloses were isolated from dried comminuted leaves of *H. sosnowskyi.* The raw material was defatted with diethyl ether and was treated repeatedly with water at 80°C, and the pectin substances were eliminated by heating the raw material with a 0.5% solution of ammonium oxalate. The residue was extracted with a 6% solution of KOH at 20°C in an atmosphere of nitrogen, the extract was acidified with acetic acid to pH 4, and the HMCs were precipitated with ethanol.

Fractionation. The HMCs were extracted with water at 100°C for 2 h and the insoluble part was removed by centrifugation. The water-soluble HMCs (0.4 g) were transferred to a column of DEAE-cellulose in the acetate form (2 × 100 cm) and were eluted stepwise with water, 5 M acetate buffer, acetate buffer with pH 6, and 0.1 and 0.5 N NaOH. The yields of the fractions were monitored by the anthrone method. The fraction eluted by water was precipitated with ethanol to give 25 mg of product. On acid hydrolysis, this yielded uronic acid, galactose, glucose, arabinose, and xylose in a percentage ratio of 13.6:15.3:12.8:18.5:40.8 and was not studied further. Analysis of an acid hydrolysate of the fraction eluted by 0.5 N NaOH showed the presence of galactose, glucose, arabinose, and xylose in a molar ratio of 4:60:7:42.

Kooiman's Iodine Reaction. An aqueous solution of iodine in 1% potassium iodide (0.5 ml) was added to an aqueous solution of the polysaccharide (1 ml) containing 0.05-0.3 mg of the xyloglucan. A coloration developed in the course of 60-90 min. The spectrum was recorded in the 500-700 nm region.

The acetolysis of the xyloglucan was carried out by the method of Eda and Kato [3]. A mixture of 2 ml of glacial acetic acid, 2 ml of acetic anhydride, and 0.2 ml of sulfuric acid was added at 0°C to 10 mg of the xyloglucan. The mixture was kept at 40°C for three days and then at room temperature for 2 days. The resulting solution was poured into ice water and the acetylation products were extracted with chloroform. The mixture of acetates was dissolved in dry methanol (2 ml) and deacetylated by the addition of a 1 M methanolic solution of sodium methanolate (2 ml). After deacetylation, cellobiose was detected by the PC method with solvent system 1.

The xyloglucan was methylated by Hakamori's method [6] in dimethyl sulfoxide with a solution of the methylsulfinyl carbamion and methyl iodide. The completeness of methylation was confirmed by thin-layer chromatography on Al_2O_3 plates and also by IR spectroscopy. The methylated products were subjected to formolysis with 90% formic acid at 100°C for 1 h, and then to hydrolysis with 0.25 M sulfuric acid at the same temperature for 14 h. The hydrolysate was investigated by PC and GLC.

CONCLUSION

The alkali-soluble hemicelluloses have been isolated from the leaves of *Heracleum sosnowskyi* Manden. The water-soluble fraction of the hemicelluloses has been characterized; it contains a xyloglucan which is a branched polymer. The main chain of the xyloglucan is constructed of β-glucosidic residues linked to one another by 1–4 bonds, and the side chains are represented by xylose, arabinose, and galactose residues.

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