STRUCTURE OF THE XYLAN OF THE STEMS OF *Brassica napus*

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The results are given of an investigation of the polysaccharide complex of the stems of winter rape. The complex was isolated by the alkaline extraction of the stems and contained 79.80% of polysaccharide, 2.4% of ash substances, and 8.75% of "crude" protein. The carbohydrate fraction consisted of a glucuronoxylan. Under the conditions of gel filtration and electrophoresis the complex was not separated into carbohydrate and protein components. When the xylan was subjected to partial hydrolysis, a number of neutral and acidic oligomers were found. The characteristic of the neutral oligomers are given.

We have previously studied the structures of the xylans of the stems of a number of traditional fodder crops [1, 2] and have shown that the xylans of the stems of leguminous plants belong to the class of glucoronoxylans and those of cereals to the class of araboglucuronoxylans.

In the present paper we give the characteristics of the structure of the glucoronoxylan of the stems of *B. napus* L. *oleifera* (winter rape) — a promising fodder herb.

The comminuted stems were first treated with ether, water, and aqueous ammonium oxalate solution, after which the xylan was extracted with a 6% solution of potassium hydroxide in an atmosphere of nitrogen. The xylan obtained was purified by repeated dissolution in 6% potassium hydroxide, dialysis, and subsequent precipitation with ethanol. The purity of the product obtained was checked from the constancy of the ratio of the carbohydrate components in the hydrolysate after each reprecipitation.

The homogeneity of the xylan was shown by gel filtration on Sephadexes and by paper electrophoresis.

The polysaccharide contained (% on the absolutely dry substance): RSs 79.80; ash 2.4; and nitrogen 1.4, or 8.75 of "crude" protein. The molecular ratio of xylose and uronic acids was 10:1.

In the fractionation on Sephadexes, in addition to the polysaccharide component a protein was isolated, which indicates a possible interrelationship between them.

The specific rotation of the xylan was $[\alpha]_D^{20}$ −62°. This shows the existence of a β bond between the xylopyranose units, as was also confirmed by the results of IR spectroscopy.

A hydrolysate of the methylated xylan was found to contain 2-O-methyl-D-xylose, 3-O-methyl-D-xylose, 2,3-di-O-methyl-D-xylose, and 2,3,4-tri-O-methyl-D-xylose in a molar ratio of 1:4:33:1.2.

Thus, it can be stated that the polysaccharide chain of the xylan is constructed of β-D-xylopyranose residues linked through the 1 → 4 carbon atoms. The side chains contain uronic acid and xylose residues attached at the positions of carbon atoms 2 and 3 of the main chain.

The acidic and neutral oligosaccharides obtained by partial hydrolytic degradation were separated on a column of Amberlite IR-45 in the acetate form. The chromatogram showed the presence among the neutral components of xylose, xylobiose, xylotetraose, xylopentaose, and xyloheptaose, and among the acidic components β-D-glucuronic and 4-O-methyl-D-glucuronic acids and aldobiuronic acids containing D-glucuronic and 4-O-methyl-D-glucuronic acids and aldotriuronic and aldotetrauronic acids containing only D-glucuronic acid, together with a number of unidentified acidic compounds. The oligomers were isolated by paper chromatography. The individualities of the oligomers isolated were confirmed by rechromatography on paper.

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The degrees of polymerization of the oligomers investigated, determined from their reducing capacities in the hydrolysis process [3], were 2, 4, 5, and 7, which agrees with the R_f values of the corresponding fragments determined by calculation from the relation

$$R_m = \log\left(\frac{1}{R_f} - 1\right) [3],$$

where m is the number of units in the oligomer chain.

The structures of the oligomers were found by the Hakamori methylation method [4]. The molar ratios of the hydrolysis products of the methylated oligomers were as follows:

Oligomer	2-O-Me-D-Xylose	2,3-di-O-Me-D-Xylose	2,3,4-tri-O-Me-D-Xylose
Xyolotetraose	-	3	1
Xylopentaose	-	4	1
Xyloheptaose	1	4	2

The results of an investigation of the hydrolysates of the methylated neutral xylooligomers showed that the xylotetraose and xylopentaose consisted of fragments of linear sections of the xylan molecule, and the xyloheptaose was a branched fragment and had at the branching point xylose at the position of the carbon atom 2 of one of the xylopyranose residues forming the chain of this oligomer.

EXPERIMENTAL

Isolation and Purification of the Xylan. The xylan was isolated from the comminuted stems of winter rape. The raw material was defatted with ether and was then treated with water at 80°C until, according to the anthrone test, carbohydrates had been completely eliminated, and then with a 0.5% solution of ammonium oxalate to eliminate pectin substances. The residue was extracted with 6% KOH solution by a method described previously [1]. The polysaccharide was purified by three reprecipitations from the dialyzed extract. The purity of the product was determined by using paper chromatography as a control (from the constancy of the composition of the carbohydrate components in a hydrolysate).

Paper electrophoresis was carried out in borate buffer, pH 11.2 at a current strength of 15 mA and a voltage of 600 V for 6 h. After visualization of the phoretograms, a single spot close to the starting line was found.

Gel filtration was performed on columns containing Sephadexes G-75 and G-100. A 4% solution of the xylan was introduced into the column, and the eluent was 4% NaOH. The fractions were monitored by the anthrone method, (carbohydrates) and by Lowry's method (proteins). The fractions corresponding to a peak were combined, dialyzed, concentrated in vacuum, and hydrolyzed. The carbohydrate composition was characterized by the GLC method.

The partial hydrolysis of the xylan was carried out with 0.1% HCl in the water bath under reflux for 2 h. The filtrate was separated off and was neutralized with $BaCO_3$, and the neutralized solution of the mixture of acidic and neutral components was fractionated with the aid of Amberlite IR-45 in the acetate form using as eluents water and 25% CH_3COOH. The neutral and acidic components were investigated separately by chromatography. The neutral components were separated by rechromatography on paper in the following solvent systems: 1) pyridine—butan-1-ol—water—benzene (3:5:3:1), and 2) butan-1-ol—acetic acid—water (4:1:5).

The carbohydrate compositions of the oligomers were determined after hydrolysis with 1 N H_2SO_4 for 1 h by paper chromatography. The acidic oligomers were separated in the solvent ethyl acetate—acetic acid—formic acid—water (18:4:1:3).

SUMMARY

1. The stems of winter rape contain a glucuronoxylan the composition of which includes D-glucuronic and 4-O-methyl-D-glucuronic acids.

2. In the structure of its macromolecule, the rape xylan is similar to the gluconoxylan isolated previously from the stems of leguminous herbs and broad-leaved trees. It differs by the degree of branching of the chain and the ratio of monose residues in it.

3. For each branch in the polymer chain there are no less than 7 xylose residues, which indicates a block structure of the macromolecule.

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COMPOSITION OF THE COATS AND KERNELS OF THE SEEDS OF *Nepeta pannonica* AND *Lavandula vera*

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The lipid compositions of the coats and kernels of the seeds of *Nepeta pannonica* and *Lavandula vera* have been studied. It has been established that the lipids of the seed coats of the two species of plants differ substantially in their composition. The lipids of the kernels of *Nepeta* have been found to contain free fatty acids with chain lengths of from C_{20} to C_{35}. Ursolic acid and its acetate have been isolated from extracts of the seed coats of *Lavandula*, and dimethyladipic acid from the seed oil of this species.

Recently, a considerable number of publications devoted to the surface lipids of various plant organs, and, in particular, the stems and leaves, has appeared [1]. The surface lipids play an important role in the interaction of the plants with the environment, controlling their water balance and protecting them from pathogens. These lipids consist of a complex mixture the usual components of which are hydrocarbons, waxes, free fatty acids, high-molecular-weight alcohols, aldehydes, terpenes, and flavones.

The lipids of seed coats have been less studied. It has been reported [2] that the lipid layer of seed coats contains the above-mentioned classes of compounds and, in particular, hydrocarbons, waxes, and triterpenes, with more rarely, aldehydes and ketones. At the same time, some of the compounds mentioned have been detected in the lipids of the seed kernels of many plants [3]. Suprunov [4] states that in the seed of *Schizandra chinensis* (family Schizandraceae), the essential oil, waxes, and pigments are present exclusively in the solid coat, and the oil of the kernel consists of triacylglycerols together with sterols and tocopherols. A fatty oil without impurities can therefore be obtained from seeds that have been treated previously with ethanol or acetone.

The question of whether certain classes of lipids belong to the suface lipids or are characteristic of the kernel is of particular interest in those cases where new compounds unusual for neutral lipids have been detected [5].

In order to investigate differences in the lipid compositions of the coats and kernels of seeds, we have investigated the seeds of two species of the family *Labiatae* — *Nepeta pannonica* (Hungarian catmint) and *Lavandula vera* (*Lavandula officinalis*; true lavender). The latter species is cultivated for the production of its essential oil. There is information in the literature only on the composition of the fatty acids of the total lipids of *Nepeta pannonica* [6].

The seeds of *Nepeta pannonica* were collected in August, 1978, in the valley of the R. Chon-Kemin, Kirghiz SSSR, and those of *Lavandula vera* in July, 1977, in the "Dolina Roz" ["Valley of Roses"] collective farm in the Moldavian SSR. They were very small with a smooth surface in the case of the lavender and with a rough surface in the case of the catmint, and

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