POLYSACCHARIDES OF Ungernia.

XII. CARBOHYDRATE COMPONENTS OF Ungernia vvedenskyi

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We have previously studied the water-soluble polysaccharides (WSPs) of the bulbs of Ungernia vvedenskyi [1]. In the present paper we give the characteristics of the pectin substances (PSs) and hemicelluloses (HCs) of the bulbs and also of the WSPs of the leaves collected in the first ten days of July, 1982. The WSPs and PSs were obtained as described earlier [2]. Extraction of the residues of the raw material with 5% and 10% NaOH followed by neutralization, dialysis, and precipitation with ethanol gave the HCs. To determine their monosaccharide compositions, the polysaccharides were hydrolyzed (2 N H_2SO_4, 24 h, 100°C). The compositions of the hydrolysates were established with the aid of PC and GLC. The relative amounts of the sugars were determined from the areas of the peaks on GC chromatograms of the acetates of the corresponding aldonitriles.

The amounts of polysaccharides (in percentages of the air-dry raw material) and the ratios of the monosaccharides are given below:

Yield of polysaccharides (%) and ratio of the monosaccharides	Leaves			Bulbs	
	WSPs *(4,5)*	PSs *(13,0)*	HCs *(6,5)*	PSs (2,0)	HCs *(4,0)*
Rhamnose	5,0	6,0	14,3	1,4	—
Xylose	Tr.	2,3	52,0	Tr.	2,0
Arabinose	4,1	1,0	23,3	1,0	1,9
Mannose	1,0	Tr.	1,0	9,6	19,9
Glucose	4,1	Tr.	15,5	10,0	26,2
Galactose	4,8	3,2	7,8	4,3	—
Galacturonic acid	+	+	+	+	+

The PSs predominated in the leaves (13%); they consisted of a light brownish powder readily soluble in water $[\alpha]_D^{20}$ +140 (c 0.25: water) that were precipitated completely from aqueous solution by aluminum sulfate. The amount of uronic anhydride in the PSs of the leaves, determined by the decarboxylation method [3] was 52%. The IR spectrum of the pectin showed absorption bands at 3400, 1710, 1600, 1445, 1310, 1160, 1120, 1030, and 960 cm^{-1}.

Partial hydrolysis of the PSs (2 N H_2SO_4, 4 h, 100°C) yielded a polygalacturonide with $[\alpha]_D^{20}$ +240° (c 0.5; water). In a hydrolysate of the latter, only galacturonic acid was detected by PC. The PSs were decomposed under the action of pectinase, and galacturonic acid was found in the products of enzymatic hydrolysis. The enzymatic hydrolysis of the PSs of the Ungernia leaves and that of mangel-wurzel pectin, took place similarly, which shows the presence of an α-(1 → 4) bond between the galacturonic acid residues. The high values of the specific rotations of the PSs and of the polygalacturonide also show the α configuration of the glycosidic bonds.

The hemicelluloses of the leaves and the bulbs differed in composition. The HCs of the leaves contained mainly xylose and arabinose residues.

The hemicelluloses of the bulbs, in which mannose and glucose residues predominated, consisted of a mixture of different polysaccharides giving the starch reaction with iodine. For separation, the mixture was treated with water, giving a soluble fraction A, and the insoluble residue was treated with 2 N NaOH giving fraction B. The fractions were reprecipitated via the copper complexes. On neutralization with CH_3COOH, a polysaccharide deposited from fraction A in a hydrolysate of which only glucose was found. From fraction B a polysaccharide containing D-glucose and D-mannose in a ratio of 1:1.3 was isolated.

Thus, the carbohydrate complexes of U. vvedenskyi contains a water-soluble polysaccharide (a natively

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acetylated mannan), pectin substances, a glucan, a glucomannan, and starch. It follows from a comparison of the results obtained with those given in the literature [4, 5] that U. vvedenskyi differs with respect to its polysaccharide composition from other genera of the family Amaryllidaceae.

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POLYSACCHARIDES OF *Eremurus*. XVIII. A GLUCOMANNAN FROM THE TUBEROUS ROOTS OF *Eremurus tadshicorum*

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A preliminary investigation of the polysaccharides of Eremurus tadshicorum Vved. has been reported previously [1]. We now give information on the study of the structure of a glucomannan isolated from the water-soluble fraction of E. tadshicorum.

According to the results of gel filtration on Sephadex G-100, the polysaccharide was polydisperse. To obtain a homogeneous fraction of the polysaccharide, an aqueous solution (1%, 500 ml) was precipitated with various volumes of ethanol (0.5; 1; 1.5; 4). The yields of the fractions were (%): T_1, 1.7; T_2, 75.1; T_3, 9.8; T_4, 3.0.

For further chemical studies we took fractions T_2 and T_3, constituting the bulk of the water-soluble polysaccharide. In hydrolysates of T_2 and T_3 we detected glucose and mannose in ratios of 1:5 and 1:9.8 respectively. Fractions T_2 and T_3 proved to be homogeneous on gel filtration on Sephadex G-100; their molecular weights calculated on the basis of ultracentrifugation were 63,000 and 47,000, respectively and their specific rotations were $[\alpha]_D^{22}$ −33° (c 1.0; water) and $[\alpha]_D^{22}$ −35° (c 1.0; water), respectively. Their IR spectra (UR-20, tablets with KBr) contained absorption bands at 1730 and 1250 cm^{-1} (ester group).

To determine the types of bonds between the monosaccharides, the glucomannans (T_2 and T_3) were first acetylated and were then methylated by Haworth's [2] and Purdie's [3] methods, which gave permethylates of glucomannans with OCH_3 contents of 42.3% for T_2 and 41.54% for T_3. The permethylates of T_2 and T_3 were subjected to formolysis and hydrolysis. In the hydrolysates, by TLC [4] and GLC [5] in comparison with standard samples, 2,3,6-tri-O-methylmannose and 2,3,6-tri-O-methylglucose as the main products, and also a very small amount of 2,3,4,6-tetra-O-methylmannose, were identified in both cases, which indicates completeness of methylation and linear structures for T_2 and T_3. The hexose residues in the glucomannan molecules are linked by 1 → 4 bonds. There are mannose residues at their nonreducing ends.

To determine the configurations of the glycosidic bonds we used the method of oxidizing the acetylated polysaccharides with chromium trioxide [6]. When peracetates of the glucomannans T_2 and T_3 were oxidized with chromium trioxide, no mannose or glucose was detected in the oxidation products, which shows the presence of a β-glycosidic bond. This is in harmony with the values of the optical rotations of the polysaccharides.

The results of methylation were also confirmed by the results of ^{13}C NMR spectroscopy. To interpret the signals in the spectrum we used the results of the analysis of ^{13}C NMR spectra of other polysaccharides obtained previously [7]. The ^{13}C NMR chemical shifts (CSs) of the glucomannan T_2 are given below:

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