BRIEF COMMUNICATIONS

CARBOHYDRATES OF ALLIUM.

V. GLUCOFRUCTANS OF *Allium cepa*

M. A. Khodzhaeva and E. S. Kondratenko*

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Continuing an investigation of the carbohydrates of plants of the family Alliaceae, we have studied the water-soluble polysaccharides (WSPSs) of the bulbs of *A. cepa* (garden onion).

After the elimination of ballast substances with chloroform and 96% ethanol, the comminuted material was subjected to extraction with 80% ethanol. Fructose, glucose, and sucrose were detected in the ethanol-soluble fraction (9.7% on the absolutely dry raw material) by paper chromatography [PC, system 1: butanol—pyridine—water (6:4:3)].

Subsequent extraction with water, elimination of protein by Sevag's method [1], and precipitation with acetone gave the WSPSs (12% on the absolutely dry raw material). They consisted of a white amorphous powder readily soluble in water at 30-40°C and similar to inulin. When chromatographed on Sephadex G-75 (61 × 1.8 cm), the initial WSPSs proved to be polydisperse. A homogeneous fraction was isolated by preparative gel chromatography on Sephadex G-50 (45 × 3.5 cm).

Six fractions (1-6) differing in their elution volumes and, consequently, in their molecular masses, were obtained:

	1	2	3	4	5	6
Elution volume, ml	135	166	198	267	340	470
Yield, %	20	2	1	35	20	11
Molecular mass	5000-6000	4000	—	2100	1000	320-700

Fraction 4 was homogeneous and had the highest yield on the initial WSPSs, which served as a reason for its more detailed study.

Fructose and glucose were found in an acid hydrolysate of this fraction with the aid of PC (system 1), and the amount of fructose, determined by Kolthoff's method [2] was 77%. Consequently, fraction 4 of the WSPSs was a glucofructan. Its IR spectrum contained absorption bands characteristic for glucofructans of the mixed type [3].

The ^{13}C NMR spectrum of the glucofructan showed chemical shifts of 105.0 ppm (C-2) and 76.5 ppm (C-4), which are characteristic for fructofuranose units within a chain linked by 2 → 1 and 2 → 6 β-glycosidic bonds. The ratio of the 2 → 1 and 2 → 6 bonds calculated from the intensities of the signals was 5.6:1.

The α-D-Glcp had characteristic chemical shifts of 93.5 and 93.7 ppm and was present at the "reducing" end of the glucofructan, attached to the C-2 atoms of the inulin units.

The chemical shift of 97.15 ppm also indicates the presence of β-D-Glcp attached to the sixth carbon atom of the inulin part of the molecule, and for a comparison of integral intensities it follows that 20% of the inulin units are substituted by β-D-Glcp.

The assignments of the signals of the other carbon atoms are given below† (solution in D_2O, 60°C, CH_3OH — internal standard — 50.15 ppm):

*Deceased.

†Interpreted in accordance with [4].

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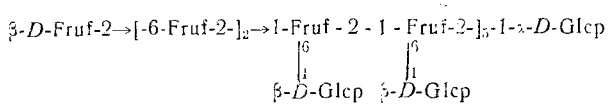
	C-1	C-2	C-3	C-4	C-5	C-6
Residues of 2 → 1-bound fructofuranose units	62.35	104.5	78.3	76.1	82.6	63.7
Residues of 2 → 6-bound fructofuranose units	61.0	105.0†	78.65	76.5 ‡	81.65	64.7
α-D-Glucopyranose residues	93.5	72.5	73.9	70.8	73.0	61.0
β-D-Glucopyranose residues	97.15	72.7	73.2	70.5	72.5	62.1

The methylation of the glucofructan by Hakomori's method gave a permethylate with $[\alpha]_D^{22}$ −33.3°, which was subjected to formolysis followed by hydrolysis. The product of the hydrolysis of the permethylate was subjected to thin-layer chromatography [TLC, system: benzene–acetone (2:1)] and 2,3,4,6-tetra-O-methyl-D-glucose, 1,3,4,6-tetra-O-methyl-D-fructose, 1,3,4-tri-O-methyl-D-fructose, 3,4,6-tri-O-methyl-D-fructose, and 3,4-di-O-methyl-D-fructose were identified by comparison with authentic samples.

The analysis of the products of the hydrolysis of the permethylate was confirmed by IR and ^{13}C NMR spectra. Summing all the conclusions, it is possible to put forward the following structure for the glucofructan from the bulbs of *A. cepa*:



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WATER-SOLUBLE POLYSACCHARIDES OF SOME REPRESENTATIVES OF THE FAMILY VACCINIACEAE

E. G. Martynov and E. A. Stroev

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We have investigated the ripe fruit of *Vaccinium vitis-idaea* L. (cowberry), *Vaccinium oxycoccus* L. (small cranberry), and *Vaccinium myrtillus* L. (myrtle whortleberry) collected, respectively, in the environs of the villages of Ushmar and Neshkino in the Klepikovskii region and the village of Murmino in the Ryazanskii region of Ryazan province. The chemical compositions of the fruits of these plants has been studied inadequately, which also applies to the water-soluble polysaccharides (WSPSs).

After preliminary purification [1], the air-dry raw material (moisture content 9.5-11.0%), from the 1980-1982 harvest was extracted with hot water at 90-95°C (1:20) for 1.5 h. The extract was filtered and evaporated, and the residue was treated with 96% ethanol (1.5 volumes). The precipitate of WSPSs was separated off, washed with ethanol and with acetone, and dried in vacuum over P_2O_5 for 12 h. The yield of polysaccharides (PSs) from the cowberries was 2.4%, from the myrtle whortleberries 2.5%, and from the small cranberries 2.6%. Their ash contents (6.4, 6.5, and 5.2%, respectively) were determined by igniting samples of the PSs in a muffle furnace at 600°C.

The WSPSs were determined by reprecipitating aqueous solutions with acidified ethanol, dialysis through a semipermeable membrane, and treatment with KU-2 cation-exchange resin

I. P. Pavlov Ryazan Medical Institute.

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