BRIEF COMMUNICATIONS

CARBOHYDRATES OF *Allium*.

VI. STACHYOSE FROM THE SEEDS OF *A. suvorovii*

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Continuing an investigation of the carbohydrates of plants of the family Alliaceae, we have studied the carbohydrate composition of *Allium suvorovii* Rgl. The dry comminuted material after inactivation of the enzymes with 96% ethanol was subjected to extracted with 80% ethanol. After purification of the filtrate with type OU-B carbon and evaporation, a dry ethanol-soluble residue of mono- and oligosaccharides was obtained (12%). Then the successive extraction of the water-soluble polysaccharides (1.5%), of the pectin substances (2.5%) [1], and of hemicelluloses A (3.6%) and B (1.2%) was performed [2].

By paper chromatography (PC, FN-7, 24 h; water-saturated phenol; ethanolic solution of urea, condition 1), three spots were detected in the ethanol-soluble fraction with chromatographic mobilities in relation to fructose of 1.0, 0.69, and 0.3.

The first two spots were identified as fructose and glucose and the third sugar had an R_f value lower than that of raffinose.

The third, unidentified, sugar was separated from the mixture of fructose and glucose by preparative gel chromatography on a column of Sephadex G-15 (60 × 3 cm). Its molecular weight, as determined on a column of Sephadex G-75 (65 × 0.8 cm), was 650, i.e., it was a tetrasaccharide. On complete acid hydrolysis of the tetrasaccharide (0.5 N H_2SO_4, 4 h), by PC (FN-17, 24 h, butanol—pyridine—water (6:4:3); aniline phthalate – condition 2), galactose (more intense spot), glucose and fructose were detected, which corresponds to the composition of stachyose. Its melting point was 99-100°C, which corresponds to the melting point of stachyose hydrate, $[\alpha]_D^{22}$ +139.6° (H_2O); according to the literature, for stachyose hydrate: $[\alpha]_D^{20}$ +139.2° [3].

Acetylation with acetic anhydride in pyrydine gave a peracetate of the tetrasaccharide which consisted of a white powder readily soluble in chloroform and ethanol. The specific rotation of the tetrasaccharide peracetate was $[\alpha]_D^{22}$ +119.3° (c 4; ethanol, and according to the literature for stachyose peracetate $[\alpha]_D^{20}$ +120° (c 3.8; ethanol) [4]; consequently, the tetrasaccharide was actually stachyose.

Glucose and fructose (main spot) were detected in a hydrolysate of the water-soluble polysaccharides by PC (condition 1) which means that they were a combination of glucofructans.

The pectin isolated was a cream-colored powder readily soluble in water with $[\alpha]_D^{22}$ +147° (c 0.25; water). Its galacturonic anhydride content determined by a standard method [5] was 31%, and its OCH_3 content 3.2%.

By paper chromatography (condition 2) in a hydrolysate (2 N H_2SO_4, 100°C, 48 h) of the pectin substances arabinose glucose, and galacturonic acid were detected, and in hydrolysates of hemicelluloses A and B were found galactose, glucose, and arabinose.

Thus, the carbohydrate composition of the seeds of *Allium suvorovii* Rgl. has been characterized. A tetrasaccharide – stachyose – has been isolated from the ethanol—soluble fraction and has been characterized. This is the first time that stachyose has been isolated from this plant.

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POLYSACCHARIDES OF *Eremurus*.

XX. FRUCTOOLIGOSACCHARIDES FROM *E. lactiflorus*

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Glucofructans have been isolated previously from the tuberous roots of *Eremurus lactiflorus*. According to PC (water-saturated phenol system; revealing agent and alcoholic solution of urea), the total glucofructans formed a mixture of fructooligosaccharides consisting of residues of fructose (main spot) and glucose.

In order to isolate a homogeneous oligosaccharide, the combined material (1.2 g) was separated by gel chromatography on a column of Sephadex G-15 (1.3 × 60 cm). The oligosaccharides were eluted with water, the fractions being monitored by the phenol–sulfuric acid method. The eluates corresponding to the peaks of the individual oligosaccharides were combined and evaporated and the residues were treated with acetone. This gave white pulverulent sugars. Nonreducing penta- and hexaoligosaccharides were isolated (yields 22.4% and 15.6%, respectively), which, according to PC, were individual substances. The ratio of fructose to glucose according to ^{13}C NMR spectroscopy was 5:1 for the hexaoligosaccharide and 4:1 for the pentaoligosaccharide.

Their IR spectra had bands at 940, 880, and 820 cm^{-1}. The PC and GLC analyses of a hydrolysate of the products of Smith degradation showed the presence of glycerol. The oligosaccharides were methylated, by Hakomori's method. After formolysis and hydrolysis of permethylates of the oligosaccharide, the following sugar derivatives were identified by comparison with markers by TLC on Silufol (methyl ether–1% ammonia (30:4) system) and by GLC [1]: 3,4,6-tri-O-Me-D-fructose, 1,3,4,6-tetra-O-Me-D-fructose, and 2,3,4,6-tetra-O-Me-D-glucose.

The results of periodate oxidation and methylation indicated the presence of a 2 → 1 bond between the monosaccharide residues.

The ^{13}C NMR spectroscopy of the oligosaccharides (using a Bruker WR-60 instrument, for the substances in D_2O at 50°C with methanol as internal standard at 50.15 ppm relative to tetramethylsilane) likewise showed the presence of 2 → 1 bonds. The glucose was present at the nonreducing ends of the oligosaccharides and was attached to C-2 of a fructose residue as was shown by the peak of the chemical shift of the C-1 atom of α-D-Glc_p (93.1 ppm).

This is the first time that these oligosaccharides have been isolated from plants of the genus *Eremurus*.

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