BRIEF COMMUNICATIONS

POLYSACCHARIDES OF THE WASTES FROM *Punica granatum*

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We have studied the amounts of carbohydrate components in the wastes of the pomegranate *Punica granatum* L. (*Punicaceae*) (crushed residue with peel) from the Samarkand preserving combine "Serp i Molot."

The dry comminuted raw material was freed with chloroform from colored ballast substances (0.94% of the weight of the dry raw material) and was extracted with 96% and 80% ethanols. The 96% ethanol extracted from the raw material 28% of tanning substances with a quality index of 64% and free sugars — fructose and glucose (PC; butanol—pyridine—water (6:4:3); aniline hydrogen phthalate; system 1) amounting to 4.4% of the air-dry raw material.

In the ethanol-soluble fraction (80% ethanol, 23% on the air-dry raw material), fructose, glucose, and traces of raffinose were also detected.

Water extracted the water-soluble polysaccharides (1.5%), a mixture of 0.5% solutions of oxalic acid and ammonium oxalate at 70°C extracted pectin substances (2.8%), and a 10% solution of caustic soda extracted hemicelluloses A (0.6%) and B (1.6%).

Approximately the same amounts of carbohydrate components have been described in the peel of the pomegranate [1].

Our aim was a further study of the composition and properties of the carbohydrate components of interest.

The water-soluble polysaccharides consisted of a cream-colored powder insoluble in organic solvents and not colored by a 0.5 N solution of iodine. In the product of its complete acid hydrolysis (2 N H_2SO_4, 8 h) we detected by PC arabinose, xylose, galactose, rhamnose, and galacturonic acid (system 1).

The monosaccharide composition of the pectin substances was determined after acid hydrolysis (2 N H_2SO_4, 48 h, 100°C) with the aid of PC (system 1) and of the GLC of the corresponding aldononitriles on a Tsvet-101 instrument with a flame-ionization detector, a steel column (200 × 0.3 cm) filled with 5% of silicone XE-60 on Chromaton NAW (0.200-0.250 mesh), carrier gas helium (60 ml/min), 210°C (conditions 1). The ratio of glucose, galactose, xylose, rhamnose, arabinose, mannose, and pectin substances found was (in moles) 1:1.25:8:5.25:20:4.2. PC (system 1) also revealed the presence of galacturonic acid. As we see, the monosaccharide composition of the pectin substances was identical with the composition of the water-soluble polysaccharide.

On analyzing the initial pectin we found (%): free carboxy groups, K_f, 1.35; methoxylated carboxy groups, K_e, 2.48; degree of esterification λ, 64; methoxy groups, CH_3O, 3.55.

The amount of uronic anhydride in the pectin substances was 46.6%, determined by a standard method [2].

After the precipitation of the pectin substances by methanol and evaporation of the mother solution a dry residue was obtained (6.6% of the air-dry raw material). In the products of its acid hydrolysis (0.5 N H_2SO_4, 100°C, 6 h), PC (water-saturated phenol, with a 5% ethanolic solution of urea as the revealing agent) showed strong spots of glucose and fructose, i.e., this product was a glucofructan.

The IR spectrum of the glucofructan had absorption bands characteristic for polysaccharides of the inulin type [3].

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The molecular weight of the glucofructan determined on a column of Sephadex G-100 was 31,000.

The monosaccharide compositions (2 N H_2SO_4, 100°C, 48 h) of the hemicelluloses A and B were represented by the sugars rhamnose, xylose, arabinose, mannose, glucose, and galactose (51.1:3:1:traces:2.4:3.4 and 6.5:1:1.2:1.43:1.8:1.26, respectively, in moles).

Thus, the carbohydrate composition of pomegranate residues has been characterized. The quantitative and qualitative compositions of the polysaccharides isolated have been determined. The pectin substances isolated are distinguished by a high degree of methoxylation.

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COUMARINS OF SPECIES OF THE GENUS *Campanula*

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As reported previously [1], fraxetol 7-O-D-glucopyranoside (isofraxoside) has been isolated from the epigeal parts of *Campanula alliariifolia* and *C. letschchumensis* collected in the flowering stage.

Continuing a study of the coumarin compositions of bellflowers of the section *Cordifolia* (Fom.) Fed. [2], from the leaves and flowers of *C. alliariifolia* and *C. ochroleuca* Kem.-Nath (KBASSR [Karabdino-Balkar Autonomous Soviet Socialist Republic], gorge of R. Cherek-Balkarskii) we have obtained an aqueous-ethanolic extract which, after concentration, was treated successively with petroleum ether, chloroform, and ethyl acetate. The chloroform fraction was evaporated, and the resin was deposited on a column of Al_2O_3 (Brockman activity grade III) and was eluted with chloroform–methanol (4:1 by volume). The total material obtained was separated on a column of silica gel (type KSK) by repeated fractionation with chloroform–methanol in various proportions [3].

Another two crystalline substances (I and II) belonging to the hydroxycoumarin group were isolated [6].

Substance (I), $C_{16}H_{18}O_{10}$, light yellow acicular crystals with mp 204°C, $[\alpha]_D^{20}$ 86.6°. The UV region of the spectrum of the substance showed one fairly strong maximum at $\lambda_{max}^{CH_3OH}$ 350 nm. The IR spectrum contained bands characteristic of the coumarin nucleus [4]. On the basis of its hydrolysis products and physicochemical properties, the substance was identified as fraxoside (8-β-D-glucosyloxy-7-hydroxy-6-methoxycoumarin) [5], isolated previously from *Fraxinus potamophila* Herd. [3].

Substance (II), $C_{10}H_8O_5$, formed yellow plates with mp 228-234°C (from aqueous ethanol (1:1)). According to the results of alkaline degradation, UV and IR spectroscopy, and a mixed melting point, and also those of a chromatographic comparison with an authentic sample, the substance was characterized as 7,8-dihydroxy-6-methoxycoumarin (fraxetol) [1, 6] or fraxetin [5].

Fraxoside and isofraxoside have been detected chromatographically in the species *C. alliariifolia* Willd., *C. leskovii* Fed., *C. letschchumensis* Kem-Nath., and *C. makashvilli* E. Busch. out of the many populations growing in the Western Caucasus, while fraxitol and fraxoside were present only in the species *C. ochroleuca* Kem.-Nath., *C. dolomitica* E. Busch.,

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