POLYSACCHARIDES OF *Berberis vulgaris*

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European barberry contains a number of biologically active substances [1-3, 5] that are widely used in medical practice [1-4] and also in nutrition [5]. There is no information on the water-soluble polysaccharides (WSPSs) of European barberry in the literature.

We have studied the accumulation of the WSPSs in the inflorescences, fruit, and leaves of *Berberis vulgaris* L. (European barberry) and their monosaccharide composition.

The inflorescence were collected in the period of mass flowering (May 31), and fruit and leaves in the phase of technical ripening of the fruit (September 28) in the environs of Ryazan' in 1981. The polysaccharides (PSs) from the air-dry raw material (moisture content of the flowers and leaves 9.2-10.2%, and of the fruit 10.1-11.0%) that had been twice extracted with ethanol (1:10) for 2 h were extracted with hot water (90-95°C, 1:20) for 1.5 h. The aqueous extract was filtered and evaporated, and the residue was treated with 96% ethanol (1.5 volumes). The precipitate of the WSPSs was separated off, washed with ethanol and acetone, and dried in vacuum over P_2O_5 for 12 h. The yield of PSs from the inflorescences was 4.4%, from the fruit 2.5%, and from the leaves 7.0%. The ash contents of analytical samples of the WSPSs of the fruit (5.87%), the flowers (10.29%), and the leaves (11.05%) were determined by their combustion in a muffle furnace at 600°C, and their uronic anhydride content (82.3-85.1%) by complexometric titration [6].

The WSPSs were demineralized by the successive passage of their 1% aqueous solutions through a column of KU-2 (H^+) cation-exchange resin and AV-17 (OH^-) anion-exchange resin. The ash content of the demineralized WSPSs was 0.5-0.6%. All the WSPSs were distinguished by a high content of uronic anhydride, the amount of which in the samples of leaves was 84.3% and in the fruit and flowers 86.8%.

The demineralized PSs were hydrolyzed with 1 N H_2SO_4 (9 h). The hydrolysis products, after neutralization with $BaCO_3$, were investigated by descending paper chromatography in the 1-butanol—pyridine—water (6:4:3) system. The monosaccharides were revealed by treatment with aniline phthalate in a thermostat at 105-110°C for 10 min. All the samples of WSPSs consisted of seven monosaccharide components: D-galacturonic acid, D-galactose, D-glucose, L-arabinose, D-xylose, and L-rhamnose and one unidentified monosaccharide present in traces, chromatographically more mobile than L-rhamnose.

The quantitative ratios of galactose, fucose, arabinose, xylose, and rhamnose in the WSPSs were determined by direct densitometry of the chromatograms on a Joyce-Loebl automatic integrating microdensitometer of type III CS and proved to be: for the flowers (4:1:5.2:1.6:2.6), for the fruit (4:1:5.6:1.7:1.9), and for the leaves (4.3:1:6:1.5:2.1). The predominating components in the PSs of the inflorescences, the fruit, and the leaves were arabinose and galactose. The amount of glucose that accumulated in the WSPSs was less than that of the other sugars. No statistically significant differences [7] were found in the amounts of the monosaccharides mentioned or in the amounts of xylose and rhamnose, with the exception of the PSs of the inflorescences in which there was more rhamnose than xylose ($P < 0.05$). The results of the investigations permit the WSPSs of European barberry to be assigned to the class of pectin substances.

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POLYSACCHARIDES OF *Crataegus*.

II. POLYSACCHARIDES OF THE FRUIT OF *Crataegus meyeri*

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Continuing an investigation of the carbohydrates of plants of the genus *Crataegus* [1], we have studied the dynamics of the accumulation and the monosaccharide compositions of the water-soluble polysaccharides (WSPSs) and pectin substances (PcSs) of the fruit of *Crataegus meyeri* (Meyer's hawthorn).

The polysaccharides (PSs) from the air-dry raw material of the 1981-1982 crop collected in the Shakhbuz region of the Nakhichevan ASSR were isolated by a published method [3] and were purified by reprecipitation with acidified ethanol, dialysis through a semipermeable membrane, and treatment with KU-2 cation-exchange resin (H^+ form).

Samples of the PSs were hydrolyzed with 2 N H_2SO_4 at 100°C for 8 h. The resulting hydrolysates were neutralized with $BaCO_3$, filtered, passed through a column of KU-2 cation-exchange resin (H^+ form), concentrated, and studied by descending paper chromatography in the n-butanol—pyridine—water (6:4:3) and ethyl acetate—acetic acid—water (3:1:3) systems. The monosaccharides were revealed by treatment with aniline phthalate at 105°C for 10 min. The neutral monosaccharides in the individual samples and the amounts of galacturonic acid were determined quantitatively by literature methods [4 and 5, respectively].

Depending on the stage of ripeness of the fruit, the WSPSs and the PcSs in them accumulated differently (% on the air-dry weight):

Color of the fruit	Yield of PSs	Amount of galacturonic acid	Quantitative ratios of the sugar residues			
			arabinose	galactose	rhamnose	xylose
Water-soluble polysaccharides						
Green	11.6	39.8	43.0	1.0	—	—
Orange	12.2	42.4	4.2	2.1	Tr.	Tr.
Red	12.5	43.7	5.2	2.2	1.0	Tr.
Pectin substances						
Green	14.3	40.1	17.0	1.0	Tr.	—
Orange	10.4	48.5	8.4	1.4	Tr.	—
Red	8.7	52.8	2.0	1.7	1.0	—

The amount of WSPSs changed only slightly as the fruit ripened. However, the maximum amount of PcSs was found in the green fruit, and at the moment of complete ripeness of the fruit it had fallen by almost one half.

The quantitative monosaccharide composition of the PSs and also their quantitative ratios changed according to the state of ripeness of the fruit. The quantitative and qualitative characteristics of the PcSs from the ripe fruit were determined by the titrimetric method [6] (%): free carboxy groups, K_f — 3.50; methoxylated carboxy groups, K_e — 4.69; degree of esterification, λ — 57; content of methoxy groups, CH_3O — 3.12. Amount of galacturonic acid — 52.8%.

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