PECTIN SUBSTANCES OF ESSENTIAL-OIL CROPS

II. ISOLATION AND CHARACTERIZATION OF THE PECTIN OF *Rosa canina*

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Continuing a study of the pectins of essential-oil crops of the Crimea [1] in order to utilize wastes, in the present paper we give information on the pectin isolated from the petals of the rose *Rosa canina* L. (family Rosaceae). By heating the rose petals (variety Krasnaya Krymskaya) with benzene–ethanol (3:1) at 50-60°C for 5-6 h three times, followed by treatment with hot water, we eliminated lipids, pigments, and water-soluble polysaccharides. The pectins were extracted with mixture of 0.25% solutions of ammonium oxalate and oxalic acid at 60-70°C, followed by precipitation with ethanol. The precipitate was dialyzed against distilled water. The residue after dissolution in buffer solution was again precipitated with ethanol (the operation was repeated three times). The precipitate was subjected to freeze-drying. Yield 2-3%. The pectin isolated, with $[\alpha]_D^{20}$ + 219° (c 0.075; H_2O), consisted of a flocculant white or pink powder. It was readily soluble in water and practically insoluble in the majority of organic solvents. Elementary analysis (%), C, 32.51; H, 3.75; N, 1.97.

Its quantitative characteristics, obtained titrimetrically [2] were (%): free carboxy groups CF, 14.98; methoxylated carboxy groups CE, 6.83; degree of esterification, λ, 28.01; methoxy groups, CH_3O, 4.02.

The molecular weight was determined viscosimetrically [3], and was calculated from the equation $[\eta] = K \cdot M^{\alpha} = 1.1 \cdot 10^{-5} \cdot M_w^{1.22}$. The specific viscosities of the pectin for concentrations of 0.5, 0.25, 0.125, and 0.067% were, respectively, 4.80, 1.61, 0.55, and 0.15; M_w = 25,400 a.u. The calculated molecular weight [4] with a correction for the degree of polymerization was 27,290 a.u. (relative error 7.4%).

The IR spectrum (KBr tablets) had the following characteristic peaks (cm^{-1}): 3450 s, 2950 w, 1750 m, 1610 s, 1390 s, 1302 m, 1220 m, triplet at 1075-1040-990, 930 m, 860 w, 805 w, and 750 w (Fig. 1).

In the products of complete acid hydrolysis (2 N H_2SO_4, 100°C, 16-20 h) by paper chromatography in the butanol–benzene–pyridine–water (5:3:3:1) and butanol–pyridine–water (6:4:3) systems, we detected galacturonic acid, galactose, glucose, arabinose, xylose, and rhamnose. By ion-exchange chromatography [5] on a Technicon carbohydrate analyzer (DA-4-X anion-exchange resin, column 25 × 0.6 cm, eluent 0.5 N sodium borate buffer with pH 9.0, temperature 55°C, rate of gradient elution 90 ml/min) we obtained the following ratio of the carbohydrates (Fig. 2): rhamnose : mannose : arabinose : galactose : xylose : glucose 5.0 : 1.0 : 6.0 : 4.9 : 1.1 : 4.7. The areas of the peaks were calculated by the described-triangle method [6].

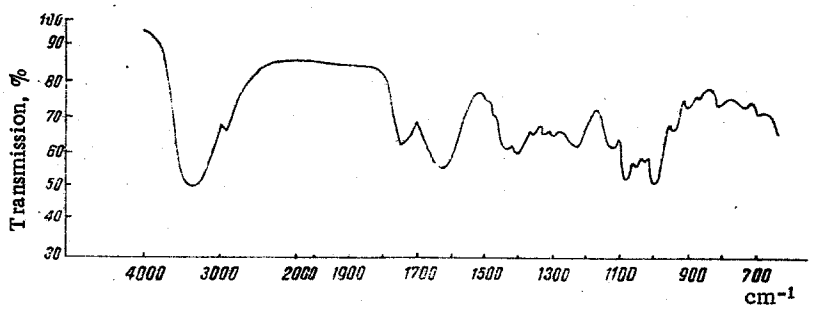

Fig. 1. IR spectrum of rose pectin.

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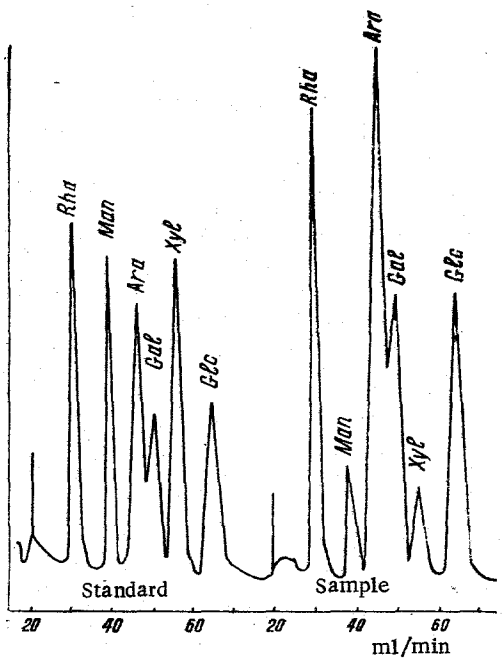

Fig. 2

Partial acid hydrolysis of the pectin (10% H_2SO_4, 95°C, 2 h) gave a hydrolyzate in which galacturonic acid, galactose, arabinose, and rhamnose together with traces of mannose and xylose were detected by paper chromatography.

The IR spectrum of the galacturonan obtained above had the following peaks (cm^{-1}): 3300 s, 2900 w, 1738 m, 1620 m, 1400 m, 1330 m, 1230 m, triplet at 1095-1040-1010, 942 m, 830 w, and 715 w.

Periodate oxidation of the pectin (0.4% solution of sodium periodate, 4°C, 12 days) followed by hydrolysis and analysis of the products by paper chromatography showed the presence of galacturonic acid, glucose, arabinose, and xylose. Periodate oxidation of the pectin followed by treatment of the reaction product with concentrated nitric acid led to the detection in the butanol—ethanol—pyridine—water (5:1:3:3) system with Bromocresol Purple as chromogenic agent of spots of formic, oxalic, and tartaric acids.

The formation of four-carbon fragments on exhaustive oxidation and the results of IR spectroscopy (triplet of a pyranose ring at 1075-1040-990 cm^{-1}) showed the presence of a 1,4-bond between the galacturonic acid and the monosaccharides.

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