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CARBOHYDRATES OF Peganum harmala

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The carbohydrate complex of the epigeal part of Peganum harmala L. includes mono- and oligosaccharides, water-soluble polysaccharides, hemicelluloses, and an acidic polysaccharide, similar to the pectin substances of higher plants. It is based on a fragment constructed of α-(1 → 4)-linked D-galacturonic acid residues in the pyranose form.

In the present paper we give the results of an investigation of the carbohydrates isolated from the epigeal part of Peganum harmala L. (harmel peganum) collected in the flowering phase in May, 1981 in Dzhizak province, UzSSR. The air-dry raw material was treated with 96% ethanol to eliminate low-molecular-weight compounds and pigment substances. The mono- and oligosaccharides were isolated by extraction with 80% ethanol, and they were found by PC to include galactose, glucose, fructose, and sucrose. From the residue of the raw material, the water-soluble polysaccharides [1], pectin substances [2], and hemicelluloses [3] were isolated successively.

The amounts of the polysaccharides and their monosaccharide compositions according to PC and GLC [3] are given below (% on the air-dry mass of the plant):

Type of polysaccharide	Yield	*Gal*	*Glc*	*Man*	*Xyl*	*Ara*	*Rib*	*Rha*
Water-soluble	3,8	6,5	1,5	1	Tr..	7,8	Tr.	2,8
Pectin substances	4,8	1,3	1,0	—	Tr..	4,2	Tr.	1,4
Hemicelluloses								
A-1	5,0	1	6,3	Tr.	3,4	1,6	Tr.	1,4
B-1	4,28	9,9	36,5	2,2	9,0	10,0	1	10,0
A-2	2,56	3,3	7,6	2	9	5,6	Tr.	1
B-2	2,18	6	17,2	6,9	5,6	2,4	1	1,2

The water-soluble polysaccharide consisted of a white powder not giving a blue coloration with iodine, i.e., it did not contain a glucan of the starch type. D-Galactose and L-arabinose predominated in its hydrolysate.

The pectin substances had the form of a flocculent white odorless mucilaginous powder soluble in water and practically insoluble in the majority of organic solvents, $[\alpha]_D^{20}$ +140, water, which contained about 1% of nitrogen. The titrimetric method [4] gave the following quantitative characteristics (%): free carboxy groups, K_c – 8.1; methoxylated carboxy groups, K_c – 7.2; degree of esterification – 47; methoxy groups – 5.2. In the

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products of complete acid hydrolysis, in addition to the monosaccharides mentioned above, we found a considerable amount of galacturonic acid, which was identified by PC and by electrophoresis with markers. Galacturonic acid was also found in the products of enzymatic hydrolysis with pectinase. Its high amount (>50%), the hydrolysis with pectinase, and also precipitation with Cetavlon and aluminum sulfate showed that the polysaccharide isolated belonged to the class of pectins. The IR spectrum contained characteristic absorption bands (780, 840, 1030-1080, 1250, 1340, 1380, 1445, 1650, 1750, 2260, 2940, 3200-3400 cm^{-1}) and was similar to the spectra of the pectins of higher plants [5].

The high positive specific rotation of the pectin, its hydrolysis by pectinase, and the presence in the IR spectrum of absorption bands at 780 and 840 cm^{-1} indicated that the basis of the pectin was a polymeric chain of 1 → 4-linked D-galacturonic acid residues.

Partial hydrolysis of the pectin yielded a galacturonide with $[\alpha]_D^{20}$ +250 (c 0.5; 0.1 N NaOH). The products of enzymatic hydrolysis and acid hydrolysis were found to contain mainly D-galacturonic acid with traces of D-glucose and L-arabinose.

Aqueous solutions of the pectin possessed a considerable viscosity. Below we give information on the dependence of the relative (η_{rel}), the specific (η_{sp}), and the reduced (η_{red}) viscosities on the concentration of the solutions:

Concentration of pectin, c, %	Time of outflow of the solution, t", sec	$\eta_{rel} = \frac{t''}{t'}$	$\eta_{sp} \frac{t''-t'}{t'}$	$\eta_{red} \frac{\eta_{sp}}{C}$
0,06	74	1,85	0,85	14,1
0,12	110	2,75	1,75	14,6
0,25	238	5,95	4,8	19,2
0,5	1192	29,8	28,8	57,0

They indicate a good gelling capacity of the pectin isolated.

The alkali-soluble polysaccharides (hemicelluloses) were present in considerably smaller amounts than the water-soluble polysaccharides and pectin substances. The fractions isolated with 5% and 10% solutions of NaOH differed little in their qualitative composition but were very different in their quantitative contents of the individual monosaccharides.

EXPERIMENTAL

The descending PC of the sugars was carried out in the butan-1-ol–pyridine–water (6:4:3) system on FN-11 paper (GDR). The polysaccharides were hydrolyzed with 2 N H_2SO_4 at 100°C for 10-48 h followed by neutralization with $BaCO_3$. Paper electrophoresis was performed on a horizontal instrument at 1000 V, 5 mA, in 1% CH_3COOH on FN-7 paper for 5 h. Monosaccharides were detected with aniline hydrogen phthalate in water-saturated butanol at 110°C. The conditions for performing GLC have been described previously [3]. The relative amounts of the sugars were determined from the areas of the peaks. IR spectra were taken on a UR-20 instrument (tablets with KBr). Viscosities were measured on an Ostwald viscometer having a capillary with a diameter of 0.73 mm, at 21°C. The time of outflow of the solvent, t' = 40 sec.

The isolation of the water-soluble polysaccharides and of the pectin substances was carried out as described previously [1, 2]. The hemicelluloses (HCs) were extracted with 5% aqueous NaOH solution, and the extract was neutralized with acetic acid. This yielded a precipitate (HC A-1). The filtrate was dialyzed and evaporated, and three volumes of ethanol were added, to give HC B-1. HC A-2 and HC B-2 were obtained similarly from a extract with 10% alkali. The amounts and monosaccharide compositions of the polysaccharides are given above.

Enzymatic Hydrolysis. A solution of 100 mg of the pectin in 10 ml of water was treated with 10 mg of pectinase (Fluka) diluted with hydrochloric acid, pH 4. The mixture was incubated at 37°C for 48 h and was then boiled for 5 min to stop enzymatic hydrolysis. The hydrolysis products were analyzed by the PC method. D-galacturonic acid was detected.

Isolation of the Galacturonan. The pectin (1 g) was treated with 2 N H_2SO_4 (1:30) at 100°C for 4 h. The precipitate of galacturonan was separated off and was washed with 1% H_2SO_4 solution, with 80% ethanol, with acetone, and with ether. Yield 0.41 g, $[\alpha]_D^{20}$ +250° (c 0.5; 0.1 and NaOH). Galacturonic acid was detected in the products of its complete acid hydrolysis by PC and electrophoresis.

SUMMARY

The carbohydrate complex of the epigeal part of Peganum harmala L. includes mono- and oligosaccharides, water-soluble polysaccharides, hemicelluloses, and an acidic polysaccharide similar to the pectin substances of higher plants. It is based on a fragment constructed of α-1 → 4-linked D-galacturonic acid residues in the pyranose form.

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NEUTRAL LIPIDS OF THE OIL OF TOMATO SEEDS

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The composition of the oil of tomato seeds with respect to the classes of lipids has been studied. The presence of less than 1% of oxidized triacylglycerides has been established. A stereospecific analysis of the main lipid component of the oil – triacylglycerols – has been performed. It has been shown that the first position is enriched with saturated fatty acids as compared with the third position, and the second position contains 95% of unsaturated fatty acid residues, as in the majority of plant triacylglycerols.

Every year in the USSR the gross tomato harvest amounts to more than 3.5 million tonnes [1], of which about 50% is processed in the preserving industry. When it is considered that their oil content is 25-30%, the seeds, which are obtained as a waste material (the proportion of seeds in tomatoes being 0.5-2.5%), are sufficient for the production of about 7 thousand tonnes of edible oil. Furthermore, this oil is recommended for use in the manufacture of cosmetic and pharmaceutical products and paints [2].

Information exists on the physicochemical properties, fatty-acid composition, and amount of unsaponifiables of the seed oil of tomatoes of various varieties, forms, and industrial samples. According to some figures, the seed oil contains oxidized lipids but their assignment to the classes of organic substances and the determination of the amounts of individual lipid components of the oil has not been carried out [2-7].

In order to evaluate tomato seed oil as a promising food product, we have studied it [3] in relation to the classes of lipids present in it. The oils were isolated from various of industrial waste seeds of the Tashkent preserving factory – samples I, II, and III. The oil from each of the samples was separated by column chromatography into a number of fractions by solvent systems 1-7. Complex fractions of the oil were additionally separated by comparative thin-layer chromatography in suitable solvent systems. The assignment of the chromatographically individual zones of the substances to various classes of lipids was made on the basis of a combination of the mobilities of the substances in a thin layer of silica gel in comparison with the mobility of model substances, of qualitative reactions, of spectral characteristics, and of the products of chemical reactions.

It was established that the lipids present in largest amount in these samples of oils belonged to the following classes:

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