PECTIN SUBSTANCES OF THE STEMS AND FRUIT HUSKS OF Fagopyrum saggittatum

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The polysaccharides were extracted from the raw material with a 0.5% solution of ammonium oxalate. They were investigated by various methods: partial and complete acid hydrolysis, fractionation on a column of DEAE-cellulose, IR spectroscopy, enzymatic hydrolysis, etc. It was shown that the protopectin of the stems and fruit hulls of common buckwheat are similar to the pectin substances of other higher plants and are characterized by a low degree of esterification.

The present work is a continuation of investigations on the comparative characterization of the polysaccharides of the stems and fruit husks of Fagopyrum sagittatum Gilib. (common buckwheat) [1-3].

The polysaccharides extracted from the raw material with a 0.5% solution of ammonium oxalate were investigated. The fact that they belonged to the protopectins was shown by their fairly high content of polygalacturonic acid (63.0 for the stems and 56.3% for the buckwheat husks). In addition to acid components, neutral monoses were also present in the hydrolysates of the polysaccharides from the stems and buckwheat husks (% by weight): galactose – 6.0 and 13.7; arabinoses – 7.1 and 8.6; rhamnose – 5.6 and 2.0; xylose – 2.5 and 3.3; glucose – traces.

The amounts of functional groups in the protopectins of the stems and buckwheat fruit husks were, respectively, (% by weight): free COOH – 13.4 and 17.7; $COOCH_3$ – 2.7 and 6.5; $OCOCH_3$ – 0.2 and 0.1. The pectin substances of the buckwheat husks were distinguished by a higher degree of methoxylation. On the whole, both samples of protopectins were characterized by a low content of methoxy groups and can be assigned to the weakly esterified group. The degrees of polymerization of the polysaccharides of the stems and of the liquid husks were low, amounting to 72 and 63, respectively, $[\alpha]_D^{20}$ + 198° and + 169° (c 0.2; 0.1 N. NaOH). The IR spectra of the carbohydrates investigated were similar to those of the pectin substances of other plants [4].

The protopectins of the stems and buckwheat fruit husks were split by pectinase to the extent of 69.0 and 73.2%, respectively, the polysaccharide from the husks being hydrolyzed by the enzyme at a greater rate.

On fractionation on a column of DEAE-cellulose, both polysaccharides were separated into three fractions. An investigation of the monosaccharide compositions of the hydrolysates from the individual fractions of the buckwheat husk protopectin showed that they differed in their ratio of monoses (%):

Monosaccharide	Eluent		
	0.1 M NaH_2PO_4	0.5 M NaH_2PO_4	0.1 N NaOH
Galacturonic acid	52.8	56.7	61.2
Galactose	21.8	18.8	16.3
Arabinose	14.7	12.9	11.8
Xylose	6.3	5.6	3.5
Rhamnose	1.1	1.9	2.3
Glucose	0.4	–	–

The maximum amount of galacturonic acid was found in the fraction eluted by sodium hydroxide solution.

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On the partial hydrolytic degradation of the protopectins of the stems and buckwheat husks, polyuronides were obtained. The acid and enzymatic hydrolysis of these samples led to the formation of D-galacturonic acid alone. The polyuronides were split completely by pectinase, and their IR spectra contained absorption bands typical for galacturonans.

The high positive rotations of the galacturonans of the stems and buckwheat fruit husks, which amounted to $[\alpha]_D^{20}$ + 217° and + 219° (c 0.2; 0.1 N NaOH), respectively, in combination with the results given above, permit us to consider that the core of the pectin substances of the stems of the buckwheat husks is a chain of α-D-galacturonic acid residues in the pyranose form linked in the 1 → 4 manner. This is characteristic for the pectin substances of higher plants.

EXPERIMENTAL

Descending PC was performed in the following systems: 1) butan-1-ol—pyridine—water—benzene (5:3:1); and 2) butan-1-ol—acetic acid—water (4:1:5). The following reagents were used to reveal the spots: 1) acid aniline phthalate; and 2) an alkaline solution of silver nitrate.

The GLC of the samples was carried out on a Chrom-4 instrument with a flame-ionization detector using a 1.2-m steel column with the solid phase Chromaton N-AW-DMCS impregnated with 5% of XE-60 at an evaporator temperature of 220°C and a column temperature of 140-200°C, the carrier gas being helium at a rate of flow of 30 ml/min.

Isolation of the Protopectins. The raw material was ground and was treated successively with ether, 82% ethanol, and water. The protopectins were extracted with a 0.5% solution of ammonium oxalate at 90°C and were precipitated with ethanol. They were purified by three reprecipitations, and starch was eliminated by amylolysis [5] and mineral substances by dialysis.

Functional groups were determined by standard methods [6]. The amounts of free and methoxylated carboxy groups were determined spectrometrically and that of acid groups by steam distillation.

The degree of polymerization of the protopectins was established viscometrically [6].

The acid hydrolysis of the pectin substances was performed with 2 N sulfuric acid at 100°C for 14 h. The hydrolysate was neutralized with barium carbonate and was filtered, and the filtrate was studied by PC. Part of the hydrolysate in the form of the corresponding polyol acetates was investigated by GLC.

The enzymatic hydrolysis of the samples was performed with the pectinase from the culture fluid of Aspergillus awamori at 37°C. The depth of hydrolysis was monitored from the accumulation of reducing substances.

The pectin substances were fractionated on a column (3 × 40 cm) of DEAE-cellulose in the phosphate form. Stepwise elution was carried out with water, with 0.1, 0.3, and 0.5 M solutions of potassium dihydrogen phosphate, and a 0.1 N solution of sodium hydroxide. The emergence of the fractions was monitored with the anthrone reagent. The pectin substances of the stems and buckthorn fruit husks were eluted with 0.1 and 0.5 M solutions of potassium dihydrogen phosphate and 0.1 N sodium hydroxide. The fractions were dialyzed and precipitated with ethanol. The fractions of the protopectin of the buckwheat husks were subjected to acid hydrolysis and the products were chromatographed.

CONCLUSION

The protopectins of buckwheat stems and fruit husks are similar to the pectin substances of other higher plants and are characterized by a low degree of esterification.

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LIPIDS OF THE FRUIT OF Diospyros kaki

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The composition and amounts of the various groups of liposoluble compounds in the rind and flesh of persimmon fruit of the varieties Hachiya and Hyakume have been established by a combination of chromatographic and chemical methods. The identity of the qualitative composition of the lipids of the flesh and rind of the fruit and quantitative differences in the amounts of individual groups have been found. A total of 24 groups of compounds were identified, the main ones of which were monogalactosyldiglycerides, carotenoids, diacylglycerols, ceramide oligosides, digalactosyldiglycerides, phosphatidylglycerols; phosphatidylcholines, and free and glycosylated sterols. In the fatty acid composition of the lipids unsaturated fatty acids – linolenic, oleic, linoleic, and palmitoleic – predominated (> 70%).

Lipids, which are present in fruit in comparatively low concentrations, largely determine the organoleptic properties and food value of the products and their stability on storage, and also the conditions of technological treatment [1]. In connection with the development of new ways of preserving products based on persimmon fruit possessing high dietetic and medicinal properties [2], we have investigated the lipid spectrum of fresh green fruit of Diospyros kaki L. of the widely grown varieties Hachiya (I), and Hyakume (II), gathered in November, 1985, on the plantations of the training farm of the Azerbaidzhan Agricultural Institute (Kirovobad).

The lipids were isolated from homogenates of the component elements of the fruit (rind, flesh) by a modified Bligh–Dyer method [3]. The purified (washing with 0.5% $CaCl_2$ solution) lipid extracts were separated successively by column and thin-layer chromatography. The preliminary identification of the groups of lipids was carried out by comparing the chromatographic mobilities of the samples under investigation and of markers, and also with the use of specific color reagents. The definitive identification of the chromatographically homogeneous groups of lipids was carried out on the basis of the results of a study of the compositions of the products of severe acid hydrolysis.

The amounts of the total lipids in the flesh of the persimmon fruit were 1195 and 1020 mg/kg, respectively, for varieties (I) and (II). The concentrations of the lipids in the rind were several times higher [4325 mg/kg for variety (I), and 7744 mg/kg for variety (II)]. On the whole, the amounts of lipids in the persimmon fruit were substantially higher than in apples, grapes, and citrus fruits [4].

The predominating groups of lipids in the persimmon are (Table 1) monogalactosyldiglycerols, carotenoids, diacylglycerols, ceramide oligosides, digalactosyldiglycerols, phosphatidylglycerols, phosphatylcholines, and free and glycosylated sterols.

The qualitative compositions of the lipids of the rind and flesh were identical, but the group distributions had certain differences. The largest fraction of the flesh lipids consisted of the neutral lipids (NLs), and of the rind it consisted of the glycolipids (GLs).

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