

A STUDY OF THE PECTINS OF WILD APPLES

M. Kh. Malikova, D. A. Rakhimov, É. L. Kristallovich,
N. D. Abdullaev, and I. U. Mukumov

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Pectins have been isolated from five species of wild apples and have been characterized. They contain galacturonic acid, galactose, glucose, and arabinose residues. The titrimetric indices of the substances isolated have been determined. It has been shown by IR spectroscopy the pectins isolated are extracted partially in the form of pectic acids.

The genus *Malus* (apple), family Rosaceae is represented on Uzbekistan territory by ten species [1]. The properties of the fruit of many species of wild apple are not inferior to those of the fruit of the cultivated varieties. Since traditional sources of pectins are citrus and apples, we have studied the pectins of wild apples as a matter of topical interest [2-4]. The pectin substances (PSs) isolated were amorphous cream-colored powders readily soluble in water with the formation of viscous solutions. Their molecular masses determined viscosimetrically [5] ranged from 61,000 to 64,000 c.u. The main functional groups of the PSs were determined by the titrimetric method [6] (Table 1).

The isolated PSs were characterized by the presence of free carboxy groups and a high degree of esterification. The qualitative monosaccharide composition of the PSs consisted of galacturonic acid, galactose, glucose, arabinose, and rhamnose (Table 2). The PSs included starch, as was shown by a positive reaction with iodine, and, according to GLC, a considerable amount of glucose. Characteristic for the PSs was a high positive specific rotation, which we also observed for the wild apples (see Table 1).

The pectins of the plants contained in their main chains acid salts of polygalacturonic acids with different degrees of methylation. Some of the hydroxy groups of the PSs could be acetylated. Thanks to this diverse nature of the groupings, the IR spectrum of the PSs were fairly complex [7]. In addition, the pectins could be present in various modified forms: H—PA (pectic acid); CH₃—PA (methylated pectic acid); and Na—PA (sodium pectate). In view of this, it was of interest to study the PCs of different varieties of apples by IR spectroscopy. For this purpose we used the PSs of the wild apples (PSs I-V), the PS of a dry concentrate (PS—DC), the PS of a purified dried concentrate (PS—PDC), and apple PS from the FRG. The SP—DC and PS—PDC were used to obtain fruit-paste candy in an experimental technological laboratory.

A comparison of the IR spectra showed their great similarity, with some differences. In the IR spectra of the PS—FRG, PS—I, and PS—III a fairly intense maximum was observed at 1650 cm⁻¹, indicating a fairly high content of water of crystallization. In the other PS samples the intensity of the absorption band corresponding to the presence of water of crystallization, as in the standard PS—FRG, was very low. In the IR spectra of the pectins isolated and of the standard, no absorption bands were observed at 1223 and 1270 cm⁻¹ corresponding to ν_{C-O} of esters, nor were absorption bands at 1600 (ν_{ASCOO^-}) and 1400 cm⁻¹ (ν_{SCOO^-}). This fact confirmed the absence of acetate groups and of ionized carboxy groups (Table 3).

A broad eminence in the 2400-2600 cm⁻¹ region relating to hydrogen bonds in a carboxyl—carboxyl dimeric grouping confirmed the assignment of the absorption band at 1750 cm⁻¹ to the stretching vibrations of the carbonyls of carboxy groups.

Thus, the frequencies in the IR spectra show that the pectins under investigation were isolated partially in the form of pectic acids.

TABLE 1. Physicochemical Characteristics of the Wild Apple Pectins

Malus species	Yield, %	η_{red} (c 0.25; water)	$[\alpha]_D^{20}$ (c 0.125; water)	Mol. mass. c.u.	Amount of GalUA, %	Quantitative characteristics*				
						K _f	K _e	K _r	λ	OCH ₃
V. M. persicifolia	5.0	14.8	+125	61000	52.8	1.35	7.2	8.55	84.2	5.84
H. M. sieversii	4.8	12.0	+150	62000	53.6	1	6.12	7.12	86	5.31
III. M. Kudrjashevii	5.0	16.0	+125	63000	54	1	7.74	8.74	88.5	4.71
IV. M. anisophylla	4.6	18.8	+142	63000	54.4	1.44	10.35	11.8	87.7	8.13
V. M. transchianica	4.8	12.0	+133	64000	51.2	1.26	8.1	9.36	86.5	7.9

*K_f) Free carboxy groups; K_e) methoxylated carboxy groups; K_o) sum of K_f and K_e;
 λ) degree of methoxylation.

TABLE 2. Qualitative and Quantitative Monosaccharide Compositions of the Wild-Apple PSs

Pectin	Ratio of neutral monosaccharides				
	Gal	Glc	Ara	Rha	GalUA
I	+	23,4	1,5	1	+
II	+	13	7,14	1	+
III	+	3,4	1	0,3	+
IV	+	2,88	5,39	1	+
V	+	4,16	3	1	+

TABLE 3. Absorption of the Absorption Band Maxima in the IR Spectra of Pectins

Frequency, ν , cm ⁻¹	Presumed types of vibrations
3460	ν (OH) _C , ν (H ₂ O)
2400—2600	ν OH _A
1750	ν (C=O) A
1650	δ (H ₂ O)
1600 ν_{AS} (COO ⁻)	
1400 ν_S (COO)	ν (C—C), ν (C—O) ⁻ of pyranose rings
1000—1200	C—O—C of ether bridges
1223, 1273 ν (C—O) of an ester group	

ν) Stretching; δ) deformation vibrations; A) stretching vibrations of carboxyls; C) stretching vibrations of alcohol groups.

EXPERIMENTAL

Paper chromatography was conducted on Filtrak-FN 11.7 paper in the butan-1-ol—pyridine—water (6:4:3) system. Acid aniline phthalate was used to reveal the spots. The GLC of the samples was conducted on a Chrom-5 instrument under the following conditions: steel column (0.3 × 200 cm), 5% of Silicone XE-60 on Chromaton (0.200-0.250 mm), 210°C, carrier gas helium, 60 ml/min. Aldonitrile acetates were obtained by the method of [8]. IR spectra were taken on a UR-20 instrument (KBr tablets).

To determine molecular masses we used an Ostwald viscometer with a diameter of 0.73 mm. The main functional groups were determined by a known procedure [6].

Isolation of the Pectin Substances. The dry comminuted raw material (50 g) was first extracted with water (1:20) with constant stirring at room temperature for 2 h and was filtered off, and the residue of the dry material was extracted with a mixture of 0.5% solutions oxalic acid and ammonium oxalate (1:1) in a ratio of 1:20 at 80-85°C for 2-2.5 h. The extracts were concentrated in a rotary evaporator, dialyzed, centrifuged, and precipitated with alcohol (1:5).

Monosaccharide Composition. A 100-mg sample of a PS was hydrolyzed with 2 N H₂SO₄ in a sealed tube at 100°C for 20-24 h. The hydrolysate was neutralized with barium carbonate, deionized with KU-2 cation-exchange resin (H⁺), evaporated, and chromatographed on paper.

The quantitative determination of galacturonic acid was carried out by the colorimetric carbazole method [9].

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