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STRUCTURE AND PROPERTIES OF APPLE PECTIN

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Some molecular and structural features of apple pectins obtained by various methods have been revealed through an analysis of the results of physical and physicochemical investigations.

Pectin substances are promising plant polymers for both the food and the medicinal industries [1-5]. We have studied structural features of apple pectin (APC) obtained by alkaline, acid, and enzymatic methods [6-9].

Microscope investigations in transmitted and polarized light showed that apple pectin obtained by the enzymatic method (APC-A) was characterized by film-like particles of elongated shape, large but fairly inhomogeneous in dimensions (35-2000 μm), dissolving readily on treatment with water (Table 1, Fig. 1).

In the pectin obtained by the alkaline method (APC-B) we observed many small particles of rounded form, sometimes transparent, fairly homogeneous in dimensions (7-70 μm), insoluble in water. However, in water all the particles swelled and became transparent and more homogeneous.

In the pectin obtained by the acid method (APC-C) we observed particles inhomogeneous in dimensions (7-100 μm) and form, mainly rounded, frequently aggregated with one another, fairly large elongated formations sometimes being found. On treatment with water, the particles first swelled strongly, and then, in the course of a day, dissolved.

Regardless of the method of preparation, the particles did not shine in polarized light, which showed the amorphous nature of all three samples. This was confirmed by x-ray studies, which gave diffractograms with a very weak diffuse peak (almost straight lines with a slight hump). It was also shown by electron-microscope investigations. In the SEM photographs for all the APCs (Fig. 2) it was possible to see particles of rounded form and various dimensions with a smoothed structure and defects, the number of which was greater for a sample of APC-A.

Dispersed samples of APC (Fig. 3) showed the structureless mass that is characteristic for amorphous polymers. Furthermore, for a sample of APC-A a fiberlike mass was observed, and for APC-B condensed rounded particles, which is connected with their different capacities for interacting and being broken down in one and the same dispersion medium (ethanol).

Sorption studies (Table 2) showed that the samples of pectin possessed different sorption capacities according to the method of preparation.

Thus, while APC-A sorbed 3.9% at 65% relative humidity, APC-B absorbed 5.4%, and APC-C 7.46% at the same relative humidity. The specific surfaces calculated by the BET equation amounted to 151.05, 108.08, and 76.50 m^2/g, respectively, for samples of APC-A, -B, and -C, the lower values in the last two cases obviously being connected with the denser structure and higher molecular mass of the APC-A.

A more substantial difference between the samples was revealed at the molecular level in IR-spectroscopic investigations, particularly in the region of the stretching vibrations of OH and C−O groups and the deformation vibrations of OCH_3 groups.

Characteristic for the APC-A were fairly well-pronounced absorption bands in the 3600 and 3263 cm^{-1} regions, showing the presence, in considerable number, of free and bound OH groups, respectively. For the APC-C, in the region of the stretching vibrations of free C−OH groups we observed only a shoulder at 3500 cm^{-1} and a well-defined absorption band of bound OH groups (3311 cm^{-1}). For APC-B there was only a broad band in the 3400 cm^{-1} region showing the presence of OH groups bound by H-bonds of differing intensities.

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TABLE 1. Characteristics of Samples of Apple Pectin

Sample	Mol. mass, thousands	Content, %		Dimensions, μm			Behavior in water
		$-OCH_3$	-COOH	minimum	maximum	mean	
APC-A	90–100	90	9.8	35	2000	500	+++
APC-B	30–35	35	65	7	70	28	++
APC-C	60–65	65	34.9	7	97	29	+

*+++) dissolves completely; ++) swells; +) swells, dissolves in 24 h.

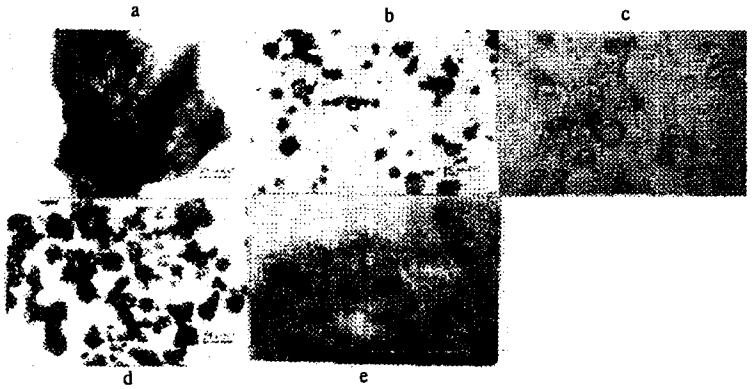

Fig. 1. Optical photographs of APC before and after swelling in water: *a*) APC-A; *b*) APC-B; *c*) APC-B in H_2O; *d*) APC-C in H_2O; *e*) APC-C in H_2O [sic].

For all the types of pectins we observed an absorption band in the region of 1749 cm^{-1}, characteristic for the stretching vibrations of C–O in carboxy groups. However, the intensity and sharpness of this band decreased in the following sequence: APC-A > APC-C > APC-B. In the last case, it was accompanied by the appearance of an absorption band in the 1620 cm^{-1} region due to the deformation vibrations of an intramolecular H-bond in a COOH group. The same can also be said for an absorption band due to deformation vibrations of OCH_3 groups, which was observed for APC-A and APC-C in the 1450 cm^{-1} region and was broadened and shifted to the 1420 cm^{-1} region for APC-B. These facts correlate with the results of determinations of the numbers of OCH_3 groups, which increased in the same sequence: APC-A > APC-C > APC-B. Together with the presence of H-bonds, this is responsible for the different capacities for dissolution of pectins obtained by different methods (see Table 1).

Thus, depending on the method of preparation, it is possible to obtain from a single source pectin substances with definite physicochemical properties for an intended use.

EXPERIMENTAL

Samples A, B, and C were obtained in accordance with [2, 4, and 7], respectively.

The microscope investigations in transmitted and polarized light were conducted on an MBI-6 optical microscope. The external appearance, shape, presence of anisotropy, and behavior of the samples during treatment with solvents were determined. The electron-microscope investigations of dispersed preparations [10] were conducted in a SEM-100 of the transmission type. The samples were dispersed in a Disk-2 vibromill. The dispersion in alcoholic solution, after deposition on a grid and drying, was shadowed with chromium in a VUP-4 vacuum apparatus. Electron-microscope investigations in the scanning regime were conducted with the aid of a REM-200, for which the samples were first coated with a layer of silver.

X-ray investigations were performed on a DRON-3M diffractometer with monochromatic CuK_α radiation at a voltage of 25 V and a current strength of 15 mA [11].

Sorption measurements [12] were conducted on a McBain vacuum balance with a quartz spiral in the interval of 0-100% relative humidity. By applying the BET equation to the results obtained, we calculated the specific surface (S_{sp}) and the volum (W_0) and mean effective radius of the capillaries (r_c).

TABLE 2. Sorption of Water Vapor by Samples of Apple Pectin

Relative humidity, %	Sorption, %		
	APC-A	APC-B	APC-C
10	8.7	1.15	2.30
30	1.90	2.90	4.80
50	3.00	4.35	6.30
65	3.90	5.40	7.40
80	5.30	7.05	9.50
90	7.00	9.50	12.10
100	15.30	16.30	26.60
	Sorption characteristics		
X, g/g	0.0218	0.0307	0.0429
S_{sp}, m^2/g	76.50	108.08	151.05
W_0, cm/g	0.153	0.163	0.266
r_c, Å	40.0	30.0	35.0

Fig. 2. SEM photographs of APC samples: *a*) APC-A; *b*) APC-C.

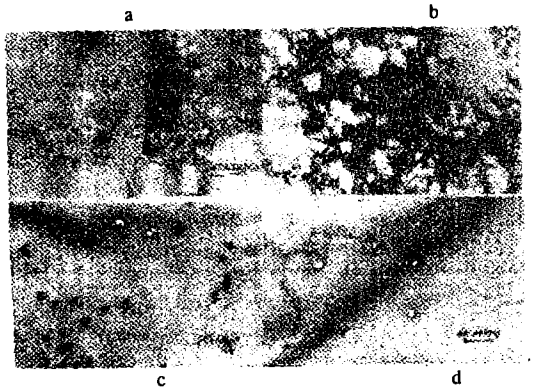

Fig. 3. Electron-microscope photographs of dispersed samples of APC: *a, b*) APC-A; *c*) APC-B; *d*) APC-C.

The numbers of free and methoxylated groups were determined by a titrimetric method [13].

The molecular masses of the pectin were found viscometrically [14].

IR spectra were obtained on a Perkin-Elmer single-beam IR Fourier spectrometer (model 2000, 100 scans, resolution 4 cm^{-1}) [15, 16].

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