

POLYDISPERSITY OF PECTINS AND SOME PHYSICO-CHEMICAL PROPERTIES OF THEIR SOLUTIONS

K. T. Norkulova

UDC 664.692

Pectin solutions obtained in the presence of HNO₃, HCl, H₂SO₄, and H₃PO₄ have been studied by viscometry, turbidity spectra, and ultracentrifugation. Cotton pectin extracts with phosphoric acid proved to be the most unstable. The molecular masses of pectins obtained from various materials (apple, lemon, and grape press residues, beet pulp, and cotton boll valves) ranged between 14,000 and 37,000. The polydispersity of the pectins isolated was studied.

A necessary condition for the extraction of pectin substances is a predominance of the intermolecular cleavage of the protopectin over intramolecular cleavage, with the object of retaining the pectin nature of the material to the maximum degree. The nature of the pectin depends mainly on the type and concentration of the acids used (hydrochloric, nitric, sulfuric, phosphoric, oxalic, etc.) and also on the action of heat [1-3]. It is possible to obtain products with different degrees of polydispersity, which is reflected in their properties and determines features of their practical use. The investigation of the main indices of extracts of pectins obtained under various conditions is important both for technical operations and for improving the quality of the final product.

The supermolecular structures of the pectin solutions were investigated on the basis of their turbidity spectra, which give an idea of the structures of the biopolymers, the nature of their solubilities, and the presence of gel fractions. The turbidity spectra were recorded in the wavelength interval of 400-630 nm and graphs were plotted of the dependence of the tangent of the angle of slope α in a double-logarithmic scale of λ versus D (where λ is the wavelength, and D the optical density). The values of $\tan \alpha$ from the corresponding nomograms with allowance for the refractive indices of the polymer and the solvent were recalculated to r_w — the weighted mean radius of the polymer particles in solution. The graphical dependences of $\log \lambda$ on $\log D$ for pectin solutions obtained in the presence of various acids are shown in Fig. 1. This relationship has a linear nature, and for cotton pectin, irrespective of the nature of the acid, all four lines are parallel to one another, with the same angle of inclination to the axis of abscissas. In the case of citric and malic pectins, a linear relationship was also retained but the angle of inclination was somewhat different, which apparently witnesses a different conformational state of the polymer macromolecules in the solutions studied. Similar results were obtained for other known pectins that have been studied — for example, beet pectin [4].

It has been established that cotton pectin extracts obtained in the presence of phosphoric acid tend to undergo structuration with time:

τ , h	24	48	72	96	120	144
Kinematic viscosity, η , mm ² /sec	4.03	3.64	3.80	3.43	3.42	3.43

Immediately after the isolation of the pectin extract, the viscosity of the solution was at a maximum, and it then fell but stabilized after 96 h.

A study of the viscosity and the turbidity spectra of pectin extracts obtained in the presence of nitric, hydrochloric, and sulfuric acids showed their stability. The indices of cotton pectin extracts in 0.5% phosphoric acid confirmed their variability on storage.

Tashkent State Technical University, fax (3712) 29 48 36. Translated from *Khimiya Prirodnikh Soedinenii*, No. 3, pp. 349-353, May-June, 1998. Original article submitted February 23, 1998.

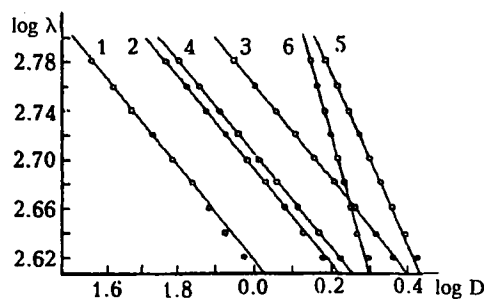


Fig. 1. Graph of the relation $\log \lambda = f(\log D)$ for the turbidity spectra of cotton pectin extracts obtained in the presence of phosphoric (1), nitric (2), hydrochloric (3), and sulfuric (4) acids and of malic (5) and citric (6) extracts obtained in the presence of hydrochloric acid.

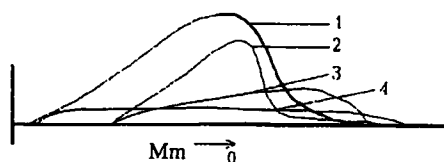


Fig. 2. Molecular-mass distributions of samples of pectins from: 1) cotton boll valves (lab. sample); 2) apple press residues (Bendery); 3) beet pulp (Krasnodar); 4) apple press residues (lab. sample).

τ , h	0	21	48	88	192
λ , nm	110	150	825	825	350
Number of particles in 1 cm ³ , $N \cdot 10^{10}$	10	0.01	0.007	0.007	0.16

Immediately after the isolation of the pectin extract, its particles had the smallest dimensions (110 nm). In storage they underwent aggregation, with an increase in size, but after 192 h they began to break down, which is possibly explained by a disaggregation of the gel fraction. The table gives physicochemical indices of pectin solutions obtained from various plant raw materials. As can be seen from it, all the pectin extracts contained a gel fraction, and this was particularly considerable in cotton pectin obtained in the presence of sulfuric and phosphoric acids. After its elimination from all the pectin extracts (with the exception of the apple and lemon extracts) the supermolecular particles disappeared, but the density rose somewhat and the ash content of the pectin extracts fell. The characteristic viscosities $[\eta]$ of cotton, beet, apple, and lemon pectins were determined by the viscometric method, and these proved to be between 0.6 and 1.29. The molecular masses of the pectins were: beet — 14,000; cotton — 15,500; grape — 21,000; lemon — 25,800; and apple — 37,000.

In order to determine the molecular uniformity and the degrees of polydispersity of these pectins, they were subjected to ultracentrifugation. Figure 2 shows curves of the molecular-mass distribution of samples of pectin from various plant sources. The curves have been transferred from a photoplate with a magnification of 20 times.

Curves of samples of pectin obtained from cotton boll valves (laboratory specimen) and apple press residues (industrial sample, Bendery) had a well-defined monodispersity: i.e., with a single maximum (Fig. 2, curves 1 and 2) and no low-molecular-mass tail or a fraction separate from the main fraction.

The results of the ultracentrifugation of beet pectin (industrial sample, Krasnodar) and apple pectin obtained under laboratory conditions from apple press residues differed from the curves considered above by shallowness, dispersity, and the absence of a well-defined peak (Fig. 2, curves 3 and 4). Here, again, there were no separate fractions in the low-molecular-mass region.

Thus, the results of a study by viscometry and turbidity spectra of the properties of pectin extracts obtained in the presence of various acids have revealed an interesting fact: solutions obtained in the presence of HNO_3 , HCl , and H_2SO_4 are

TABLE 1. Physicochemical Indices of Pectin Solutions*

Pectin extract	Hydrolyzing agent	Pectin content, %	d , g/cm ³	η , mm ² /sec	r_w	$N \cdot 10^{10}$	Ash content, %	Gel fraction, %
Apple	HCl	0.735(0.720)	1.0143(1.0171)	11.60(12.10)	750(200)	0.010(1.200)	0.06(0.06)	0.002(0.001)
Grape	"	0.285(0.303)	1.1802(1.1901)	3.17(3.35)	-(-)	-(-)	0.03(0.21)	0.020(-)
Lemon	"	0.480(0.510)	1.0107(1.0110)	9.15(9.00)	1000(710)	0.001(0.006)	0.06(0.06)	0.030(0.010)
Cotton	"	0.300(0.270)	1.0040(1.0061)	1.70(1.65)	330(-)	0.220(-)	0.06(0.05)	0.014(-)
"	HNO ₃	0.340(0.320)	1.0000(1.0000)	2.00(2.00)	110(-)	10.5(-)	0.08(0.08)	0.026(-)
"	H ₂ SO ₄	0.540(0.500)	1.0095(1.0050)	3.75(3.65)	140(-)	4.8(-)	0.14(0.14)	0.110(-)
"	H ₃ PO ₄	0.450(0.410)	1.0093(1.0084)	3.17(3.30)	110(-)	10.0(-)	0.78(0.71)	0.180(-)

*The figures in parentheses are results for centrifuged samples.

stable, while those obtained with H_3PO_4 are unstable. The kinematic viscosity of solutions, initially 4.03, fell to 3.43 mm²/sec and then remained constant. The small supermolecular particles (110 nm) observed immediately after the isolation of a cotton pectin extract then aggregated to a size of 825 nm, and after the lapse of a considerable time of storage (192 h) they broke down. Cotton pectin and apple pectin (industrial sample, Bendery) have a well-defined monodispersity, while beet pectin has a curve with a single maximum but the curve is disperse and shallow and the peak is ill-defined.

EXPERIMENTAL

Pectin extracts were obtained from apple, grape, and lemon press residues, and cotton boll valves by hydrolysis with various acids in the water bath at 85°C. The liquor ratio for the apple press residues was 1:15; grape – 1:6; lemon – 1:35; cotton – 1:10; extraction time 150 min. The extracts obtained were centrifuged on a T-23 laboratory centrifuge at $C = 5000$ m/sec for 30 min. The turbidity spectra of the pectin extracts were taken on a Spekol-II spectrophotometer with a cell having $l = 1$ cm. For ultracentrifugation we used a MOM-3180 ultracentrifuge with Philpot-Svensson optics, speed of rotation 60,000 rpm, at 20°C. The determinations were conducted under identical conditions: time of centrifugation – 120 min, pectin concentration of the solutions – 0.5%. Solutions of the pectins in 1% aqueous NaCl were investigated. Molecular masses were calculated by the Kuhn–Mark equation $[\eta] = K_m M^\alpha$ [5], where $K_m = 1.1 \cdot 10^{-4}$, $\alpha = 1.22$.

REFERENCES

1. N. S. Karpovich, L. V. Donchenko, and V. V. Nelina, Pectin. Production and Use [in Russian], Urozhai, Kiev (1989), p. 12.
2. N. P. Shelukhina, R. Sh. Abaeva, and G. B. Aimukhamedova, Pectin and the Parameters of Its Production [in Russian], Ilim, Frunze (1987), p. 42.
3. U. Irnazarova, Kh. A. Arifkhodzhaev, and Kh. T. Salomov, Pishch. Prom-st', No. 2, 55 (1991).
4. N. P. Shelukhina, Z. R. Nogoibaeva, and G. B. Aimukhamedova, An Investigation of the Fractional Composition of Sugar Beet Pectins [in Russian], Ilim, Frunze (1980), p. 14.
5. S. A. Glikman and S. Sh. Orlov, Dokl. Akad. Nauk, No. 3, 89 (1990).