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PECTINS FROM THE PEEL OF *Citrus unshiu**

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The carbohydrate composition of tangarine peel is studied. Water-soluble carbohydrates, pectins, are isolated. Their physicochemical properties are determined. Regulation of the degree of esterification is examined.

Wastes from citrus juice production were examined as possible sources of pectins. The quantitative characteristics of pectins obtained from tangarine peel depend on the type and growing conditions. We studied the carbohydrate composition of peels from ripe and green tangarine (*Citrus unshiu*) grown in South Korea. Pectins in tangarine pulp and fruit as a whole have been studied [1, 2].

Air-dried material was ground and treated with 96° alcohol. Water-soluble carbohydrates were extracted (Table 1).

Table 1 shows that the extraction of mono- and polysaccharides is greatest at 50°C for 2 h (Expt. No. 8). Water-soluble polysaccharides were determined gravimetrically after precipitation by alcohol. Monosaccharides were isolated by preparative paper chromatography. Glucose, fructose, and saccharose were identified among the sugars.

The material remaining was successively hydrolyzed and extracted with acids to remove the pectins (PS). The yield of PS was directly dependent on the nature and concentration of extractant (Table 2).

Table 2 shows that PS are extracted in greatest yield by a mixture of HCl and H_3PO_4. The PS from tangarine peel pulp that are extracted from both sources are hygroscopic light-cream-colored powders. They give a negative reaction with iodine and are soluble in water. Their physicochemical properties are different (Table 3).

Peels of ripe fruit have a lower yield of PS, decreased viscosity of an aqueous solution, and lower MM and degree of esterification. However, the statistical exchange volume and ash content increase. IR spectra of the PS from ripe and green tangarine peel pulp exhibit absorption bands corresponding to stretching vibrations of carboxyl (near 1745 cm^{-1}) and ester carbonyls (at 1750 cm^{-1}). These are especially characteristic of all PS [3, 4]. Thus, the band at 1745 cm^{-1} in the spectrum of the demethoxylated pectin is much more intense than that in the spectrum of the starting pectin.

TABLE 1. Aqueous Extract of Tangarine Pulp

Expt. No.	Time, h	Temperature, °C	Source:extractant ratio	Quantity		
				dry substances, %	sugars, % of source mass	polysaccharides, %
1	1.0	20	1.10	2.1	11.9	0.5
2	1.0	30	1.10	2.6	12.1	0.53
3	1.0	40	1.10	3.0	14.3	0.76
4	1.0	50	1.10	3.25	15.3	1.11
5	2.0	20	1.10	3.0	12.3	1.3
6	2.0	30	1.10	3.1	13.8	2.1
7	2.0	40	1.10	3.25	15.1	2.7
8	2.0	50	1.10	3.5	15.3	3.3

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TABLE 2. Hydrolysis-extraction of Pectins from Tangarine Pulp

Expt. No.	Hydrolyzing agent	Conc. of hydrolyzing agent	Pulp:extractant ratio	Pectin yield, %	Content in source, %
		Peel of ripe fruit			
1	HCl	0.5	1:15	9.2	60.1
2		1.0	1:15	12.2	61.2
3		1.5	1:15	10.8	63.7
4	HNO_3	0.35	1:15	5.7	64.7
5		0.5	1:15	6.4	66.3
6	H_3PO_4	0.3	1:15	10.0	64.7
7		0.4	1:15	10.9	65.4
8		1.0	1:15	13.1	67.7
9	HCl + H_3PO_4	0.15+0.2	1:15	13.4	83.2
		Peel of green fruit			
10	HCl + H_3PO_4	0.15+0.2	1:15	16.0	88.2

TABLE 3. Physicochemical Properties of Pectins

Pectin	Rel. viscosity, [η], MPa	Mol. mass	Stat. exchange volume, mg-g/eq	Degree of esterif., λ, %	Free COOH groups, %	$COOCH_3$ groups, %	Ash, %
Peel of ripe fruit	3.6	52274	52.4	75.0	6.39	14.67	1.5
Peel of green fruit	4.78	64220	46.7	78.4	5.81	16.1	1.2

TABLE 4. Alkaline Saponification of Pectins

Expt. No.	Reagent	Reagent conc.	Time, min	Yield, %	λ, %	K_c	K_m	OAc groups, %
1	NH_4OH	0.5	60	89.1	75.4			
2	in 90° alcohol	1.0	60	83.2	74.0	5.4	14.53	0.87
3		1.5	60	75.4	70.0	2.43	4.78	0.8
4		2.0	60	78.0	66.0	6.9	12.8	
5	NaOH	0.5	60	77.9	68.0	6.7	14.93	0.34
6	in 90° alcohol	1.0	60	77.1	65.0	8.68	14.67	0.32
7		1.5	60	72.3	63.4			
8		2.0	60	68	59.0	9.2	13.1	0.2
9	NaOH	0.01	60	77	69.6	6.39	14.67	0.34
10	in water	0.15	60	75	65.5	7.2	13.68	0.29
11		0.2	60	72	60.1	8.9	12.78	0.25

Compared with the starting pectin, the demethoxylated one has a broad band with a maximum at 3460 cm^{-1} that is due to stretching vibrations of hydroxyl groups. Highly methoxylated pectins have vibrations in the range 2960-2940 cm^{-1}, which are characteristic of symmetric and asymmetric methoxyl vibrations. These vibrations are weaker in the demethoxylated pectin.

Bands in the range 1200-1000 cm^{-1} are assigned to C–C, C–O, and C–C–C stretching vibrations of pyranose rings. They are characteristic of highly methoxylated and demethoxylated pectins. The band at 890 cm^{-1} comes from the 1→4 bond and is characteristic of all pectins.

The degree of esterification of the pectin was regulated in various ways. From a processing point of view, the most

acceptable is treatment of the extract by alkaline solutions before concentration on ultrafiltration devices (Table 4). Table 4 shows that PS with various physicochemical properties can be obtained depending on the nature, reagent concentration, and solvent. This makes them useful in the food and medicine industries.

EXPERIMENTAL

IR spectra were recorded on a Perkin—Elmer IR Fourier spectrophotometer (2000 model, 100 scans, 4 cm^{-1} resolution).

The amounts of free and methoxylated groups were determined by titration [4]; OAc groups, by the literature method [5]. The molecular mass of the PS was found by viscosimetry [6].

Paper chromatography in descending mode used Filtrak FN-13 paper and butanol—pyridine—water (6:4:3).

Extraction of PS was effected on a boiling-water bath by various acids (HCl, HNO_3, H_3PO_4) for 60-20 min. The extracts were precipitated after filtration and concentration by alcohol in a 1:3 ratio. The precipitate was dried in a desiccator at 100±5°C.

PS in solution were precipitated after saponification by aqueous and alcoholic solutions of ammonia and alkali as described above.

REFERENCES

1. S. J. Moon, K. H. Sohn, and M. H. Lee, *Hanguk Sikp'um Kwahakhoe Chi*, **14**, 63 (1982).
2. H. Miura, S. Haginuma, and T. Mizuta, *Shokuryo Kenkyusho Kenkyu Hokoku*, **19**, 290 (1965).
3. M. P. Filippov, *Infrared Spectra of Pectins* [in Russian], Shtiintsa, Kishinev (1973), p. 78.
4. G. B. Buzina, O. F. Ivanova, and L. B. Sosnovskii, *Khlebopek. Konditer. Prom.*, No. 4, 35 (1965).
5. N. V. Shelukhina, R. Sh. Abaeva, and G. B. Aimukhamedova, *Pectin and Its Preparation Parameters* [in Russian], Ilim, Frunze (1987), p. 87.
6. S. L. Kovalenko and O. D. Kurilenko, *Izv. Vyssh. Uchebn. Zaved., Pishch. Tekhnol.*, 175 (1972).