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On the Pectic Substances of Mango Fruits

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ABSTRACT

Peels and fruit pulp of two Guinean mango varieties (Ceni and Springfield) were studied. The polyuronide content of the dried fruit material varied from 14·6 to 21·3% depending on the type of raw material (variety and part of the fruit) and methods of treatment prior to drying. By hydrochloric acid extraction at 85°C and pH = 1·5, the pectic substances were extracted most fully from the dried mango peels (Ceni, 24·5% and Springfield, 22·3%) and least fully from the fleshy part of ordinary mango (Ceni, 5·8%). The molecular mass of the pectins obtained ranged from 72 000 to 83 000 and the gel strength was between 162 and 232° according to Tarr-Baker.

The content of bound amino acids in the pectic preparations obtained was in the 1–7% range and did not depend on the degree of esterification of pectin.

The carbohydrate composition of the pectins obtained was estimated to be in the following ranges: galacturonic acid (40–70%); arabinose (2–4%); rhamnose (1–2%); xylose (1–7%); mannose (1–3%); galactose (14–22%) and glucose (8–22%).

INTRODUCTION

Pectin is obtained mainly from the waste materials of the production of apple, orange, grapefruit and lemon juices (Kertesz, 1951). Desaccharified sugar beet slices also find limited application as a raw material for the production of pectin (USSR) (Sosnovski, 1957). Considerable interest has also been shown in using shelled sunflower heads, first in the 1950s (Bulgaria, USSR, Canada, etc.) and later in the 1970s (USA, Canada and China) (Stoikoff, 1948; Shewfelt & Worthington, 1953;

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Sosnovski, 1957; Stoikoff & Kratchanov, 1966; Lin *et al.*, 1976) but without starting production of sunflower pectin on a regular basis (Lin *et al.*, 1976; Kratchanov & Bratanoff, 1982). The development of pectin production worldwide brought about the search for new sources of raw materials. Some authors report (Saed *et al.*, 1975; Beerh *et al.*, 1976; Srirangarajan & Shrikhande, 1976, 1977, 1979) that the fruit of the mango grown in Sudan and India could be used for the production of pectin based on their high pectin content (over 20% in the dried fruit raw material). The yield, degree of esterification and gel strength of the pectin obtained depend on the type of raw material used (variety, conditions of processing) and the extraction method. The comparative studies on the polyuronic acid content of various fruit raw materials done by Voragen *et al.* (1983) indicate that the fruit of mango and papaya have the relatively highest polyuronic acid contents, comparable to that of apples and citrus fruits. Mango is the major fruit raw material in the Republic of Guinea and the production of mango juice yields considerable amounts of fruit mass which still remain unutilized.

The present paper contains the first results from our research into opportunities for using the mango waste materials in the production of pectin.

MATERIALS AND METHODS

Raw material

The experiments were done using ordinary 'Ceni' mango and cultivated 'Springfield' mango both grown in Guinea, 1988 crop. The raw material was prepared for the experiments in the following way: the skins were peeled off and the stones were separated from the fruit flesh. The stones were not studied at all. The peels were divided into two. One lot was dried at 50°C and the other was twice treated with ethanol preheated to 70°C, pressed and dried at 50°C. The fruit flesh was twice processed with 96% ethanol preheated to 70°C, pressed and dried at 50°C.

Extraction of the pectic substances

20 g of dried raw material were mixed with 600 ml of diluted hydrochloric acid (pH = 1·5) preheated to 85°C. The mixture was mechanically stirred for 60 min, maintaining the temperature at 85°C. The acid extract was separated from the fruit mass by filtering and pressing through a

cloth and the pectin was coagulated with an equal volume of ethanol. The pectin coagulate was washed once with 70% hydrochloric ethanol then with 70% ethanol until the reaction was neutral and finally with 96% ethanol to speed up drying which was done at 50°C.

Fractional extraction

50 g of dried mango peels pretreated with ethanol were successively subjected to extraction under mechanical stirring with water, 0·5% ammonium oxalate and 0·5% hydrochloric acid in the following way:

(1) Three times with water at 85°C. First (for 30 min) with 1 litre, then twice (for 10 min each time) with 0·5 litre. The filtrates were collected and coagulated with an equal volume of ethanol containing 1% hydrochloric acid. The coagulate was further processed as described above.
(2) with 0·5% ammonium oxalate at 85°C. First (for 30 min) with 1 litre and then twice (for 10 min each time) with 0·5 litre. The filtrates were collected and coagulated with hydrochloric ethanol as indicated above.
(3) Extraction once (for 30 min) with 0·5% hydrochloric acid (0·5 litre). The filtrate was coagulated with an equal volume of ethanol. The coagulate was washed and dried as indicated above.

Analytical methods

The polyuronic acid content (PUAC) of the raw material was determined by the Gee *et al.* (1958) method. The analysis of the pectins was carried out titrimetrically after the neutralization method of Owens *et al.* (1952). The gel strength was determined by the Tarr-Baker method (Bender, 1949) and by the IFT-SAG method (IFT Committee, 1959). The molecular mass was determined by the viscosimetric method.

The amino acid composition was determined on Biotronic LC6001, manufactured in the FRG, after hydrolysing at 110°C the pectin sample with 5·7 N HCl for 24 h.

The pectin monosaccharide composition was determined using gas chromatography after enzyme hydrolysis of 1% water solutions of pectin (pH = 4·2; 50°C; for 96 h) with 5 mg of enzyme preparation with PGA 170 000 u/g. The hydrolysate was filtered and successively passed through cationite Wofatit KPS (H^+) and anionite Amberlite IRA 400 (CH_3COO^--form). The hydrolysate which passed through and the

washing waters were gathered and evaporated to dryness in vacuum. The monosaccharide content was determined on a Tracto vap 2470 T Carlo Erba gas chromatograph after silanization with hexamethylsilane in the presence of pyridine and trifluoroacetic acid.

RESULTS AND DISCUSSION

The chemical characteristics of the studied raw materials from ordinary and cultivated mango are given in Table 1. The results indicate that the treatment of the raw material with ethanol before drying led to increased polyuronic acid content and cellulose and to decreased ash content. It was to be expected because this sort of treatment takes out the alcohol-soluble components. The lower degree of esterification of the polyuronides of the non-alcohol treated raw material was probably due to the action of the pectinesterase (Ashraf Tahir & Malik, 1977) present in the raw material whose activity increased at the initial stage of drying because of the favourable moisture content and temperature. The pectolytic enzymes were deactivated in the samples treated with alcohol before drying. The difference in degree of esterification was more pronounced in the samples of cultivated mango, probably because of its higher pectinesterase activity. This problem requires special investigation.

Table 2 presents data on the pectin yield as a result of 60 min acid extraction at 85°C and pH = 1·5. It should first of all be noted that the pectin yield from the fruit flesh was rather low (5·8 and 9·3%) for their relatively high polyuronic acid content (over 16%). This indicates that the polyuronides of this part of the fruit are too strongly bonded with the remaining biopolymers in the fruit tissue to be taken out in a solution under the conditions of the 60 min acid extraction. Similar results were obtained from our studies on pectin extraction from the fruit flesh of oranges. The fruit peels are of greater interest from the point of view of a future pectin technology for they are prevalent in the waste from the production of mango juice. Pectin with quite a high yield (18–25%) and a good gel strength (over 200° after Tarr-Baker) was obtained from the mango peels under the usual extraction conditions for the pectin production. It is obvious that mango pectin resembles mostly apple pectin both in its chemical composition (polyuronic acid content and degree of esterification) and in its gel strength.

It can be seen that in our experiments the pectin yield reached 25% for a single extraction, while in other previous publications the mango pectin yield was reported to vary from 10 to 19% under the conditions

TABLE 1
Characteristics of Raw Materials

Sample No.	*Raw material*		*PUAC (%)*	*Degree of esterification (%)*	*Cellulose (%)*	*Ash (%)*	*Humidity (%)*
1	Ordinary mango Ceni	Dried peels, not treated with ethanol	18·4	82·1	8·8	4·0	6·7
2		Dried peels, treated with ethanol	21·3	83·0	14·2	3·0	7·1
3		Dried pulp, treated with ethanol	16·0	78·8	14·8	1·4	7·6
4	Cultivated mango Springfield	Dried peels, not treated with ethanol	14·6	78·6	9·9	2·8	7·9
5		Dried peels, treated with ethanol	17·7	84·0	13·5	1·9	9·8
6		Dried pulp, treated with ethanol	17·0	63·5	13·2	1·3	8·3

TABLE 2

Characteristics of Pectins Obtained from Mango through Acid Extraction (pH = 1·5; t = 85°C; hydromodule 1 : 30 and duration = 30 min)

Sample No.	*Raw material*		*Yield (%)*	*Degree of esterification (%)*	*PUAC (%)*	*Gel strength*		*Molecular mass*
						°TB	*SAG method*	
1	Ordinary mango Ceni	Dried peels, not treated with ethanol	17·0	75·3	66·8	232	174	—
2		Dried peels, treated with ethanol	24·5	76·2	61·2	223	165	77 000
3		Dried pulp, treated with ethanol	5·8	77·4	63·6	207	155	72 000
4	Cultivated mango Springfield	Dried peels, not treated with ethanol	20·2	75·4	42·0	223	162	—
5		Dried peels, treated with ethanol	22·3	77·9	52·1	213	160	83 000
6		Dried pulp treated with ethanol	9·3	62·3	60·1	162	125	—

of exhaustive extraction. This should be ascribed not only to the difference in variety but also to the difference in the experiment conditions — raw material pretreatment and extraction method.

The mango pectins isolated by us do not differ substantially in their degree of esterification from the pectins obtained by Beerh *et al.* (1976). Srirangarajan and Shrikhande (1976, 1977, 1979) obtained mango pectins with a considerably higher methoxyl content, while the degree of esterification calculated by us varied from 82 to 94·4%. Nevertheless, the overall conclusion is that pectic substances in the mango fruit (especially in the peels) are characterized by a relatively high degree of esterification, over 80%. The data in Table 2 also indicate that the yield of pectin increased after treating the raw material with ethanol. This conclusion was more clearly pronounced in the experiments with ordinary mango. The data about the gel strength are also of interest: the pectins obtained from ordinary mango have better gelling properties. It should also be noted that with the exception of the pectin from cultivated mango fruit flesh all other cases yield highly esterified pectin, 75–78%. The molecular mass varied from 72 000 to 83 000.

Table 3 contains data about the fractional composition of mango pectin through successive extraction with water, ammonium oxalate and diluted hydrochloric acid. The experiments were carried out using alcohol washed peels of ordinary mango. The data indicate that the water soluble fraction of the pectic substances prevails (over 70% of the total yield). It should also be noted that the total yield in the fractional extraction of pectin was slightly smaller than the one obtained from single acid extraction at pH = 1·5 (cf. Table 2, experiment 2). This fact could be explained by assuming that part of the pectic substances were degraded as the extraction time was increased (up to 3 h in the experiments in Table 3). The data about the gel strength come to support this assumption: the pectins obtained through fractional extraction have a 25–35% lower gel strength than the pectin obtained by single extraction

TABLE 3
Fractional Extraction of Pectin from Peels (Treated with Ethanol) of Ordinary Mango

Fraction (No.)	*Extracting agent*	*Yield (%)*	*Degree of esterification (%)*	*PUAC (%)*	*Gel strength*	
					°TB	*SAG method*
1	Water	15·3	86·9	73·8	177	135
2	0·5% ammonium oxalate	5·6	75·6	68·0	156	120
3	0·5% hydrochloric acid	0·3	—	—	—	—

at pH = 1·5 (Table 2). We assume that mango pectin is rather unstable when thermally treated in water solution for a long time, something which has been overlooked by Srirangarajan and Shrikhande (1977, 1979) who carried out the extraction at 95–100°C. Systematic research is obviously required in this direction as well, applying the methods for studying the degradation processes in pectin extraction from fruit offered by Pantchev *et al.* (1989).

There are occasional reports in the literature about the presence of bound proteins in pectins. Knee (1973) investigated the polysaccharides and glycoproteins of apple fruit cell walls and found amino acid content in some acid- and alkali-soluble polyuronides. The amount of amino acid component varied in a wide range (from 2 to 90%). This implies that pectic substances are likely to have covalent links with protein substances. Moisseeva *et al.* (1974) found the presence of an amino acid component in apple pectins. By paper chromatography, they determined the qualitative and quantitative amino acid composition of the investigated pectins. Some data on the amino acid composition of the apple fruit cell walls have also been reported by Neukom *et al.* (1980). Kratchanov and Popova (1990) found a considerable reduction (2–3 times) of the amino acid content of apple pectin by chromatographic treatment with hydrochloric acid ethanol. No mention is made of studies on pectins obtained from citrus fruit. Therefore, we studied the amino acid composition of several of the mango pectins obtained in the present research. For comparison we present in Table 4 data about apple pectin obtained by us under laboratory conditions. The data show that the pectins isolated from the fruit flesh have the highest amino acid content (5–7%). The pectin isolated from mango peels have a lower content of proteins and amino acids (1·1–4%). The general impression is that pectins from cultivated mango have a higher amino acid content. It should be noted that no correlation could be drawn between the degree of esterification of pectin and its amino acid content, therefore the ion interactions are not essential in this case for the binding of proteins and amino acids with the pectin. The data indicate that the different pectins do not differ substantially in their qualitative amino acid composition, even the samples were very different in their total amino acid content.

Finally, in Table 5 we present data on the carbohydrate composition of some of the mango pectic preparations obtained by us. It can be seen that the two pectins contain the same neutral monosaccharides. No differences were established in the qualitative composition and in comparison with the data of Voragen *et al.* (1983) about the carbohydrate composition of pectin from mango of unknown origin purchased in Vageningen, Holland. Substantial differences between the mango pectins

TABLE 4
Amino Acid Composition of Pectins from Mango

Indices	*Mango pectins, acid extraction of:*				*Mango pectin of ordinary mango, peels (water extraction)*	*Apple pectin (acid extraction)*
	Ordinary mango		*Cultivated mango*			
	Peels	*Fr. flesh (treated with ethanol)*	*Peels*	*Fr. flesh*		
1. Est. degree (%)	76·2	77·4	77·9	62·3	86·9	74·0
2. Total protein content (%)	3·3	5·6	1·1	7·4	4·7	1·1
3. Amino acid composition % of the total protein content						
Asp	10·4	9·8	10·7	10·0	10·8	12·0
Thr	5·3	4·8	5·1	5·5	4·4	5·5
Ser	5·7	5·5	5·9	5·8	6·1	5·8
Glu	13·6	13·9	13·1	14·5	14·7	14·8
Pro	5·1	4·4	5·2	4·5	4·3	—
Gly	5·1	4·7	5·4	4·6	5·8	5·1
Ala	6·0	5·9	5·8	3·6	5·9	5·4
Cys	—	—	—	—	—	—
Val	6·5	7·1	6·1	5·2	6·4	8·9
Met	1·6	1·5	1·8	3·4	1·4	—
Ile	5·8	6·3	5·6	5·0	5·6	3·7
Leu	9·4	10·9	9·8	10·8	9·6	6·9
Tyr	4·3	3·6	3·6	3·5	3·7	4·4
Phe	4·8	6·3	5·8	5·6	5·7	5·3
His	4·3	3·4	4·1	5·3	4·7	8·9
Lys	6·1	6·4	6·6	7·9	5·6	7·3
Arg	5·0	5·2	5·4	4·6	5·3	6·0

TABLE 5
Carbohydrate Composition of Pectins from Mango

Type of pectin	*D-Gal acid*	*Neutral sugars*					
		Ara	*Rha*	*Xyl*	*Man*	*Gal*	*Glu*
Ordinary mango (not treated peels) (w/w%)	65·8	4·1	1·6	1·4	3·3	14·0	7·6
Molar %, against D-Gal, acid	100·0	8·1	2·9	2·7	5·4	22·9	12·4
Cultivated mango (not treated peels) (w/w%)	42·0	1·9	1·5	7·0	1·6	22·1	21·9
Molar %, against D-Gal, acid	100·0	5·9	4·2	21·6	4·1	56·9	56·3

in our study were observed, however, in the quantitative ratio of monosaccharides. If we assume that neutral sugars are chemically (glycoside) bound with D-galacturonic acid, then it would be more interesting to discuss the molar ratio of neutral sugars against D-galacturonic acid. It follows from the data in Table 5 that with the exception of L-arabinose and D-mannose in all the remaining cases there is a considerable increase in the content of neutral sugars in the pectin from cultivated mango, most strongly expressed in D-glucose and slightly less so in D-xylose and D-galactose. The change with L-arabinose, D-mannose and L-rhamnose is negligible.

CONCLUSION

It has been established that the acid extraction of mango peels can give a high yield (over 20%) of highly esterified pectin with good gelling properties, similar to those of apple pectin. The polyuronic acid content of the different parts of the mango fruit ranges from 14 to 21%. The pectin yield depends on the type of raw material and methods of preliminary treatment. The yield of pectin from the fruit flesh is the lowest (6%) and that of the fruit peels the highest (25%), after pretreating the raw material with ethanol. It has been shown that the content of the water soluble pectin fraction is the highest.

The content of bound amino acids in the pectic preparations obtained has been determined. It ranges from 1 to 7% but the different pectins do not differ in their qualitative amino acid composition. Pectins isolated from the two varieties of mango do not differ substantially in their qualitative carbohydrate composition either: arabinose (2–4%), rhamnose (1–2%), xylose (1–7%), mannose (1–3%), galactose (14–22%) and glucose (8–22%). The polyuronic acid content ranges from 42 to 66%.

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