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Research into Changes of Pectic Substances in Apricots and Peaches Processed by Osmotic Dehydration*

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SUMMARY

The influence of osmotic dehydration on the degradation of pectic substances of apricots ('San Castrese' variety) and clingstone peaches ('Carson' variety) during processing and storage in flexible pouches was studied. The three pectin fractions, water soluble (WS), oxalate soluble (OS) and residual pectin (protopectin) (RP), were determined in fresh fruits, after blanching, after osmotic dehydration and on packed fruits after 2, 4 and 6 months storage. The anhydrogalacturonic acid content of the three fractions was determined quantitatively by using ion-exchange high-performance liquid chromatography while the methanol was determined by gas chromatography. Textural changes were followed by compression and using penetration tests performed with an Instron and overall preference was determined organoleptically. The analysis of the pectic compositions of the two types of fruits confirmed the role of the protopectin in preserving the fruits' firmness during processing. The differences of composition, highlighted by the distribution of differently soluble fractions of total pectin in the two species of fruits, was sufficiently large to account for the different response to the osmotic dehydration process and storage. The RP fraction of the two fruits and the respective textural and organoleptic values showed a

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good correlation. The 'protopectin/soluble pectin' ratio, introduced here, may prove valuable as an index of the suitability of the fruits for osmotic dehydration. Further investigations of the generality of this correlation for different species of fruits would be a desirable development from this present research.

INTRODUCTION

The osmotic dehydration of fruits has received increasing attention in recent years as a gentle, energy efficient dehydration treatment to produce shelf-stable fruits. A commercial process consisting of osmotic dehydration of fruit pieces followed by packaging and mild heat treatment was recently proposed (Maltini & Torreggiani, 1981; Maltini *et al.*, 1983).

This process, which is still at the experimental stage, presents some problems which arise because of the differing responses of different fruit species. Apricots, in particular, are liable to lose their firmness, yielding poor quality products, while peaches remain firm, and the quality is unaffected.

The different behaviour of the two fruits could be attributed to differences in their pectin substances. This is emphasized in various research reports on the correlation between textural characteristics and both qualitative and quantitative measures of pectin composition of the fruit during ripening (Pressey *et al.*, 1971; Shewfelt & Smit, 1972; Buescher & Furmansky, 1978), storage (Ben-Arie & Lavee, 1971; Bartley & Knee, 1982), processing (Kanujoso & Luh, 1967; Gierschner, 1981; Navarro *et al.*, 1982) and including quick-freezing (Polesello & Maltini, 1970; Polesello & Crivelli, 1971). The crucial role of protopectin is also well recognized (Doesburg, 1965; Souty & Perret, 1970; Souty & Jacquemin, 1976). However, the softening effect of processing on certain cultivars of apricots is so great that this fruit presents great difficulty both in canning (Souty *et al.*, 1981*a*), and in quick-freezing (Nicotra *et al.*, 1971; Crivelli *et al.*, 1972).

We have carried out this research investigation into the behaviour of one cultivar of apricots and one of clingstone peaches during an osmotic dehydration process, and during storage, with the aim of evaluating how changes in the pectin fraction relate to the loss in firmness during processing.

METHODS AND MATERIAL

Fruits and osmotic process

The following fruits were used: apricots ('San Castrese' variety) and industrial clingstone peaches ('Carson' variety), harvested when commercially mature. The inedible parts of the fruits were removed before osmotic treatment. Apricots were stoned and cut into halves; peaches were lye-peeled (dipped into 7% NaOH at 80°C for 40 s), stoned and cut into ~2 cm thick slices. The fruits were then water-blanched. Apricots were blanched at 75°C for 1 min 30 s and peaches at 95°C for 15 s. Such blanching conditions did not inactivate the endogenous enzymes, except on the surface; unfortunately higher temperatures would affect the 'fresh' taste of the fruit and would cause the hydrolysis of the protopectin (Souty & Jacquemin, 1976). The fruits were then dehydrated using a 70° Brix sucrose syrup with 1% of ascorbic acid added as an antioxidant. The dehydration was carried out at an ambient temperature of ~25°C, for 6 h for apricots and 4 h for peaches, reaching dry matter values of ~20–25%.

After the osmotic concentration fruits were drained, vacuum packed in plastic pouches (250 g, Doypack-Grace Italiana, Passirana di Rho, Milan, Italy), pasteurized (75°C for 30 min) and stored at an ambient temperature of ~25°C. In these conditions the products are microbiologically stable (Leistner *et al.*, 1977; Maltini & Torreggiani, 1981; Maltini *et al.*, 1983).

Analytical methods

The investigations were conducted on fresh fruits, after blanching, osmosis and storage for 2, 4 and 6 months. Each sample consisted of the contents of three bags. Samples were analysed for alcohol insoluble solids (AIS), for total pectic substances, for water-soluble (WS) and oxalate-soluble (OS) pectins and for insoluble residual pectin (RP) considered to be protopectin, but also for firmness and for organoleptic characteristics.

Extraction of AIS

A sample (500 g) was processed by a Ultraturrax homogenizer with 2 litres of 96% boiling ethanol. The mixture was allowed to stand for at

least 2 h and filtered through a G3 sintered funnel. The precipitate was washed successively with 96% ethanol, then acetone until it became colourless, and finally was dried, weighed and ground to a fine powder. The yields are expressed as g for 100 g of sample (Barbier & Thibault, 1982).

Fractionation of pectin substances

The analysis of the AIS for pectin was performed according to the procedure described by Barbier & Thibault (1982) modified as illustrated in Fig. 1.

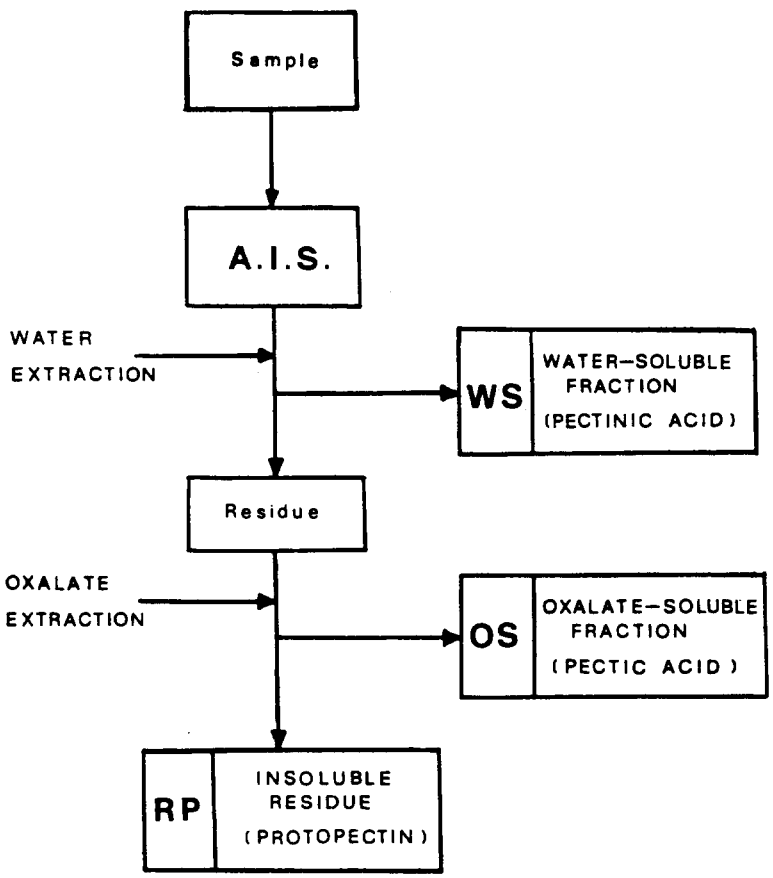

Fig. 1. Flow diagram of the fractional extraction of pectic substances.

Water-soluble pectin (WS). A sample (500 mg) of the AIS was dispersed at room temperature by magnetic stirring in 50 ml of H_2O for 60 min. The slurry was filtered. The extraction was repeated and the filtrates (WS) were collected and concentrated in a rotary evaporator at a temperature below 40°C to a final volume of 50 ml.

Oxalate-soluble pectin (OS). Thirty millilitres of 0·005 M Na oxalate at pH 5·6 was added to the residue at room temperature, the slurry was stirred for 60 min and filtered. The extraction was repeated, the filtrates (OS) were collected and concentrated as for the above pectin (WS) to a final volume of 25 ml.

Residual-pectin (RP). The residue was finally suspended in H_2O to give a final volume of 100 ml.

Determination of pectin substances

This was effected by the determination of galacturonic acid and methanol in the fractions WS, OS, RP.

The methanol was quantified using the procedure of Forni *et al.* (1984); de-esterification of the pectin was performed by alkaline hydrolysis of fractions and the methanol released was determined by gas chromatography (Porapak-Q column, FID dectector, printer–plotter data processor). In another aliquot of the same solution (WS or OS or RP), the galacturonic acid was determined using a procedure modified from that of Forni *et al.* (1981) and Giangiacomo *et al.* (1982) based on the depolymerization of pectic substances by enzyme Rohament-P, kindly donated by SCIB, Brescia, Italy. The galacturonic acid released was measured by HPLC (Jasco Trirotar II HPLC system with a Shodex SE11 RI detector and a Shimadzu CR1B printer–plotter data processor) on a Partisil SAX (25 cm × 4·5 mm i.d.) column, eluting with an aqueous 0·002 M K_2HPO_4 solution buffered at pH 7·47 (Long, 1968) at a flow rate of 1·2 ml min^{-1}.

After the determination of the galacturonic and methoxyl contents in the fractions WS, OS and RP, the amount of pectin was calculated using

$$((A-B)\times 176)+(B\times 190)=\%\text{ pectin}$$

where A=% of equivalents of free and esterified carboxyl groups = % galacturonic acid/176 and B=% of equivalents of esterified carboxyl groups = % methoxyl/31.

The pectin was then expressed as a percentage of dry weight of fruit or % AIS (Tables 1 and 2).

Firmness evaluation

Prior to recovery of the AIS, the firmness of the fruits was measured with an Instron Universal Testing Machine (model 1140) using two different methods.

Compression test (for apricots). The samples were compressed by a 4 cm diameter flat plunger; the plunger was stopped after depressing the surface of the fruits by 3 mm. The maximum compression force (kg) was determined at a crosshead speed of 10 cm min^{-1}. The figures in Table 3 represent the average of 30 determinations.

Penetration test (for peaches). The maximum force was recorded when a 5 mm diameter plunger penetrated 15 mm into a prism of peach flesh (height 15 mm), cut from the middle of each sample. Again, the figures in Table 3 represent the average of 30 determinations, obtained with a crosshead speed of 20 cm min^{-1}.

Sensory evaluation

Sensory evaluations were carried out through a preference test (Larmond, 1977) using a nine-point hedonic scale ranging from 1 (dislike extremely) to 9 (like extremely) and taking into account appear-

TABLE 1
Fresh Fruits Composition

Fruits	*% on dry weight*		*% on AIS*				
	AIS	*Total pectin*	*Total pectin*	*WS*[a]	*OS*[b]	*RP*[c]	*RP/(WS+OS)*[d]
Apricots	14·78	2·46	16·65	6·30	1·15	9·2	1·25
Peaches	11·90	2·63	22·10	3·78	0·41	17·90	4·26

[a] WS = water-soluble pectin.
[b] OS = oxalate-soluble pectin.
[c] RP = residual pectin (protopectin).
[d] RP/(WS + OS) = residual pectin/soluble pectin: 'protopectin index'.

TABLE 2
AIS and Pectin Content of Fruits After Blanching, Osmosis and During Storage

Fruits	*Stage of process*	*Storage period (months)*	*% on dry weight*					
			AIS	*Total pectin*	*WS*[a]	*OS*[b]	*RP*[c]	*RP/(WS+OS)*
Apricots	Blanching	0	16·09	2·58	1·02	0·16	1·40	1·18
	Osmosis	0	10·55	1·52	0·67	0·07	0·78	1·05
		2	9·80	1·43	0·83	0·08	0·52	0·57
		4	9·98	1·34	0·76	0·12	0·46	0·52
Peaches	Blanching	0	12·77	2·84	0·52	0·07	2·26	3·80
	Osmosis	0	10·61	2·40	0·43	0·07	1·90	3·80
		2	10·50	1·87	0·59	0·08	1·21	1·80
		4	11·63	2·15	0·55	0·08	1·52	2·41
		6	10·63	1·63	0·33	0·10	1·19	2·76

[a] WS = water-soluble pectin.
[b] OS = oxalate-soluble pectin.
[c] RP = residual pectin (protopectin).

TABLE 3
Fruits' Firmness of Apricots (Compression Test) and Peaches (Penetration Test)

Fruits	*Stage of process*	*Storage period (months)*	*Textural firmness (kg)*
Apricots	Blanching	0	11·49
	Osmosis	0	3·12
		2	1·79
		4	2·01
		6	1·67
Peaches	Blanching	0	1·48
	Osmosis	0	1·11
		2	1·00
		4	1·13
		6	1·07

ance, flavour and texture. The panel was composed of 10 judges and each test was repeated twice. Analysis of variance and Duncan's multiple range test were used to determine statistically significant differences ($P \leqslant 0{\cdot}05$).

RESULTS

Raw fruits

Table 1 shows that the two fruits analysed had comparable amounts of pectic substances expressed as % dry weight. The apricots contained more AIS though less total pectin than peaches, probably due to the presence of other polysaccharides which did not significantly affect the firmness of the fruits. Furthermore, the AIS of the apricots was lower in residual pectin RP (protopectin), so that the index RP/(WS + OS) was only about one-third that of the peaches (Table 1).

Since the protopectin content of fruit has been reported to be very closely associated with tissue firmness (Souty & Jacquemin, 1976), the value obtained from apricots and peaches could predict their behaviour on osmotic processing.

Fruits after blanching

The effect of blanching (Table 2) was the same for both fruits; very little increase was recorded in the levels of AIS and pectic substances.

Fruits after osmosis

Exchange between the soluble substances of the fruits and those in the osmotic syrup occurs during the process. An increase of sugars, expressed as % fresh weight, of 3.7% for the apricots 'San Castrese' and 1.8% for the peaches 'Carson', was reported by Giangiacomo *et al.* (1985). The change in the pectic substances during the process was different for the two fruits (Table 4). For apricots there was a decrease in the amounts of the AIS and the total pectic substances, and particularly the residual protopectin (RP). The changes were smaller for the peaches. The index RP/(WS + OS) was reduced by 16% for the apricots and 10% for the peaches (Table 2). The apricot tissue seems

TABLE 4
Balance of Pectic Components and AIS During the Osmosis[a]

Fruits	*ΔP (%)*				
	AIS	*Total pectin*	*WS*	*OS*	*RP*
Apricot	−6·9	−9·6	+5·6	+3·4	−17·0
Peaches	+0·2	+0·2	−4·0	+3·8	−0·6

[a]The data reported are calculated with the formula:

$$\Delta P(\%) = \left(\frac{(P_f\, C_f) - (P_i\, C_i)}{(P_i\, C_i)} \right) \times 100$$

where P_f = fruit's weight after the osmosis, P_i = fruit's weight before the osmosis, C_f = % of the component after the osmosis and C_i = % of the component before the osmosis.

TABLE 5
Sensory Evaluations

Fruits	*Stage of process*	*Storage period (months)*	*Appearance*	*Flavour*	*Texture*
Apricots	Blanching	0	7·15[a]	7·50[a]	7·00[a]
	Osmosis	0	6·17[a]	4·50[a]	4·33[b]
		2	5·00[b]	3·42[b]	4·33[b]
		4	3·33[c]	3·17[b]	3·08[b]
Peaches	Blanching	0	8·02	7·15	7·00
	Osmosis	0	7·00	6·83	6·58
		2	7·13	6·50	6·42
		4	7·00	6·79	6·92
		6	6·67	6·21	7·08

[a, b, c]Mean values within a column not followed by the same letter are significantly different ($P \leq 0{\cdot}05$).

to be less permeable to the osmotic effect of the sugar syrup than the peach tissue.

These variations were consistent with the organoleptic data (Table 5) and the Instron results (Table 3). After osmosis apricots were significantly less firm whereas the peaches showed little difference.

Fruits during storage

During the first 2 months of storage the solubility of the pectic substances underwent further changes, probably reaching an equilibrium state among the different forms of pectins after this time. The residual pectin (RP) both of apricots and peaches suffered a similar loss (33% and 36%, respectively, when expressed as a percentage of RP at time 0) while soluble pectins increased (23% in apricots and 37% in peaches for WS and 14% in both fruits for OS). RP/(WS + OS) ratios decreased to 0·57 in apricots and to 1·8 in peaches after 2 months storage. During this period some pectins were probably depolymerized to alcohol-soluble oligomers, which were not estimated as AIS, as the total pectin in the two fruits was lowered.

After 4 months of storage, there were no significant changes except for peaches, where a 20% increase in residual pectin was found, corresponding to an increase in the firmness (Table 3).

When storage is further extended, the behaviour of the products diverged. The apricots softened to the point where they became unacceptable and hence were discarded. In contrast the peaches preserved an acceptable firmness for 6 months, although both AIS and total pectin content fell. However, while WS pectin dropped to about 40%, the residual pectin RP was reduced by 20% resulting in an increase in the RP/(WS + OS) ratio. In this species the RP content was sufficient to sustain the firmness of the product as confirmed by the organoleptic and textural measurements (Tables 3 and 5).

DISCUSSION AND CONCLUSIONS

The analysis of pectic composition of the two types of fruits confirmed the role of the protopectin in preserving firmness during processing. The differences displayed by the apricots in comparison with the clingstone peaches overall lay rather more in the composition of their pectic substances than in their total pectin content.

The differences in composition exhibited after calculating the percentage soluble fractions in the total pectin of the two fruits (Fig. 2) suggested that these components might be responsible for the different behaviour of the fruits on osmotic dehydration and storage.

Apricots had initially a content of less than 60% of protopectin (RP) and about 35% of water soluble pectin (WS) of total pectins, in

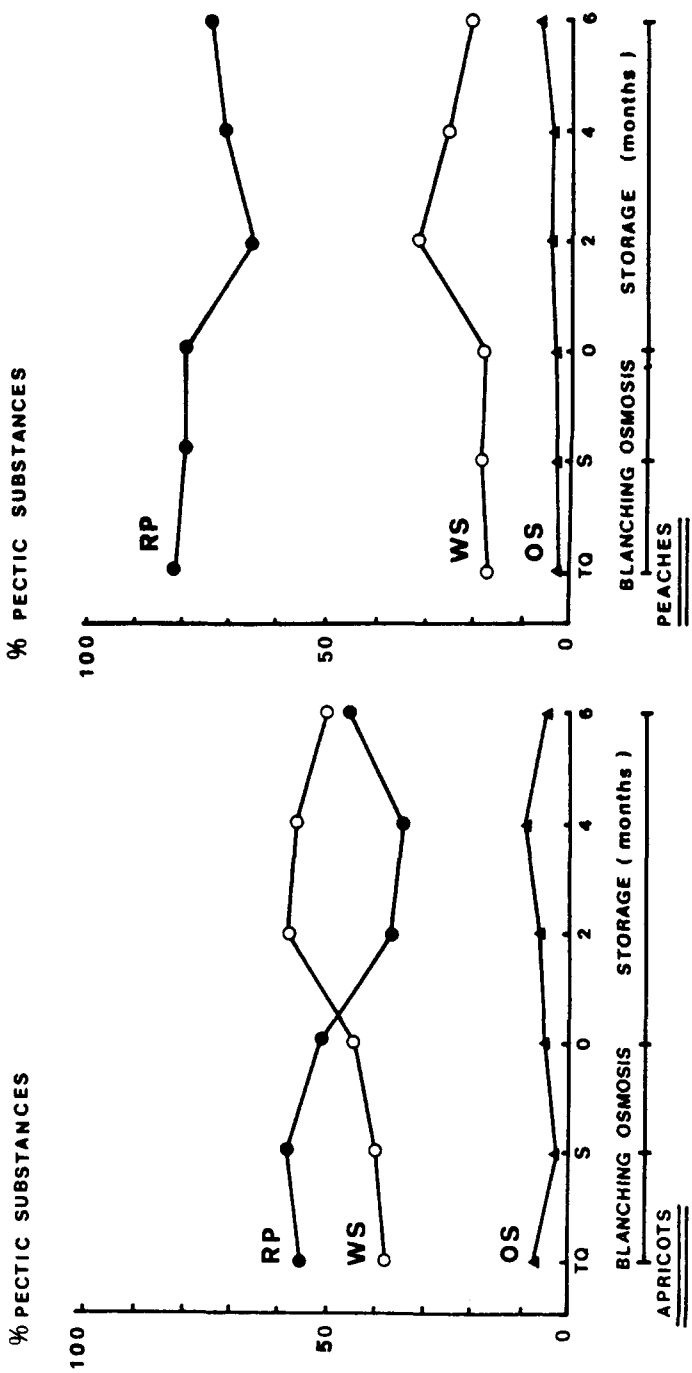

Fig. 2. Distribution of pectic substances in the fraction: WS, OS and RP. TQ = raw fruits and S = blanched fruits.

agreement with the figures quoted by Souty *et al.* (1981*b*). After 2 months of storage, the WS fraction was the major component (60%), while the RP fraction fell to 35%. The consequential loss of firmness was enough to make them unacceptable. The first 2 months of storage seem to be the most critical period for the osmotically dehydrated fruits.

In contrast, the initial total pectin of clingstone peaches was composed of 80% of the RP fraction and about 20% of the WS fraction; the OS fraction was negligible (Fig. 2). This composition did not change greatly during the process. The changes in the distribution of the pectin fractions observed during the storage did not appear large enough to greatly affect the firmness of the product.

It is evident when we compare the RP fraction of the two fruits with their respective textured and organoleptic values (each one normalized in respect of the blanched product (Fig. 3)) that the pectic constituents exert a definite effect on textural stability. Apricots yielded an organoleptically unacceptable product, owing to the very high loss in protopectin during the process. On the contrary, for the clingstone peaches, the organoleptic quality was not influenced by the low loss of protopectin, although a certain softening was detected from the Instron values.

Clearly the technological virtue of this work is that it suggests on the basis of these two species that the processor may determine which species and varieties of fruit are suitable candidates for the osmotic dehydration process. The exact nature of the biochemical mechanisms whereby these changes in pectin structures and pectin degradations are initiated and effected is still obscure and awaiting further investigation.

From the reported data, it appears that when the protopectin is present as 80% of the total pectin content corresponding to a RP/(WS + OS) > 4 (as was the case for clingstone peaches 'Carson') good quality should be assured for the product. On the contrary, when protopectin is present at only 60% of total pectin (RP/(WS + OS) < 2) (as in the case of the apricots 'San Castrese'), the fruits would not be suitable for the process.

The protopectin/soluble pectin ratio (Table 1) might therefore be taken as an index of suitability of the fruits for osmotic processing and possibly for other processes too. Such a ratio could be used to screen

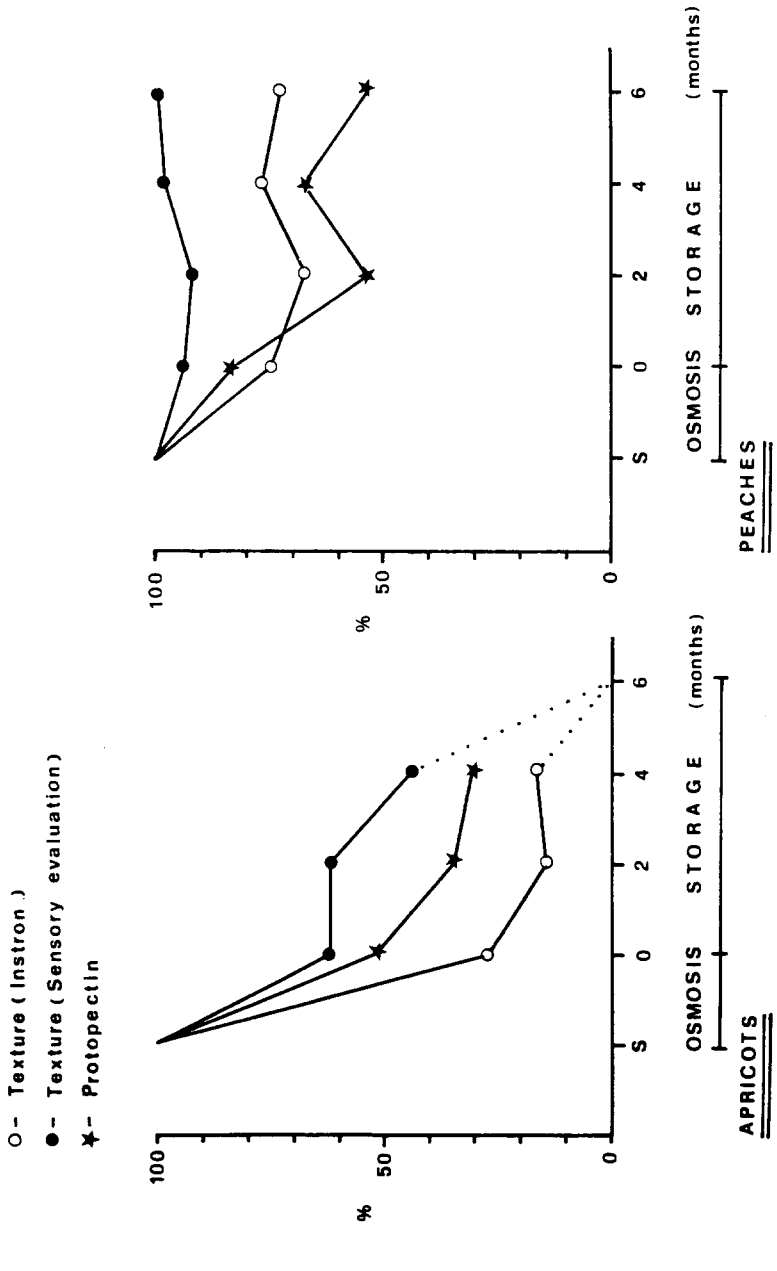

Fig. 3. Comparison of texture measurements (Instron and sensory evaluation) and protopectin content (all values are referred to S). S = blanched fruits and O = osmotically processed fruits.

the cultivars of apricots, selecting those with values > 4 and thereby improving the processing and storage properties of the products.

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