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Gas Chromatographic Analysis of Sugars and Sugar-Alcohols in the Mesocarp, Endocarp, and Kernel of Almond Fruit

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Water-soluble carbohydrate composition of mesocarp (hulls), endocarp (shells), integument, and kernels of the almond was determined by GC on an SE-30 column under isothermal conditions. The Kovâts' retention indices of the Me_3Si derivatives of sugars and sugar–alcohols were determined. The oligosaccharide content (sucrose and raffinose), expressed in grams of sugar per 100 g of total sugars, increased from the outside to the inside of the fruit (i.e., hull to kernel), while reducing sugars and sorbitol decreased appreciably.

In previous papers (Saura-Calixto and Cañellas, 1982; Saura-Calixto et al., 1983), the chemical composition of mesocarp (hull), endocarp (shell), and kernel integument of almond fruits were reported. These papers embraced a study of the dietary fiber, mineral elements, and amino acid composition.

Sugar content of mediterranean almond kernels varies between 4 and 8% of dry matter with sucrose the principal constituent (Casares and López Herrera, 1952; Saura-Calixto et al., 1980; Vidal-Valverde et al., 1978; Zuercher and Hadorn, 1976). The previous few reports on carbohydrate composition of the subproducts (hulls, shells, and teguments) of almonds, which are finding increased uses in industry and animal nutrition, include the work of Sequeira and Leiw (1970) identifying fructose, glucose, sucrose, sorbitol, and inositol in hulls.

We now report on the sugar and sugar–alcohol composition of various parts of the almond fruit.

EXPERIMENTAL SECTION

Preparation of Samples for Analysis. Samples used corresponded to a mixture of the principal varieties of almonds cultivated on the island of Mallorca, Spain, commercially named "Mallorca Propietor". Different parts of the fruit were mechanically separated, homogenized, and ground to pass through a 0.5-mm sieve. Eighty percent aqueous ethanol at 50 °C was employed to extract sugars, and the solvent was removed by vacuum distillation on a rotavapor to yield dry residues. Kernel oil was previously extracted with ethyl ether by using a Soxhlet extractor.

The procedure of Sweeley et al. (1963) and conditions described by Laker (1980) were followed to prepare trimethylsilyl derivatives (Me_3Si derivatives). One milliliter of anhydrous pyridine, 0.6 mL of hexamethyldisilazane, and 0.4 mL of trimethylchlorosilane were added to dry samples containing 10–20 mg of carbohydrates and shaken occasionally. Derivatization occurs at room temperature with quantitative yields. Similar treatment was carried out with 10 mg of each standard and with different standard mixtures. Previously, standard sugars were equilibrated for 24 h in an aqueous solution, which was then evaporated to dryness at 40 °C under vacuum before trimethylsilylation (Sawardeker and Sloneker, 1965).

Derivatization reagents and sugar and sugar–alcohols standards were products used as reference substances for chromatography supplied by Carlo Erba and Merck.

Gas Chromatographic Analysis. Gas–liquid chromatography was carried out on a Model Sigma 3B Perkin-Elmer chromatograph equipped with a Sigma 10B station data integrator using a stainless steel column (3 m × 0.3 cm) packed with 3% SE-30 on Supelcoport 80/100. Assays were performed under isothermal conditions. The operating conditions for Me_3Si derivatives of samples

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Table I. Kováts Retention Indices (I) of Me_3Si Derivatives of Water-Soluble Sugars and Sugar–Alcohols on SE-30[a]

	monosaccharides (210 °C)		
ribose (α)	1669	gluclose (α)	1924
ribose (β)	1693	glucose (β)	2012
2-D-ribose (α)	1466	galactose (α)	1892
2-D-ribose (β)	1502	mannose (α)	1836
arabinose (α)	1633	galactose (β)	1939
xylose (α)	1729	mannose (β)	1945
lyxose (α)	1610	L-rhamnose (α)	1642
xylose (β)	1782	L-rhamnose (β)	1725
arabinose (β)	1663	sorbose (α)	1903
lyxose (β)	1668	sorbose (β)	1927
sorbital	1988	fructose (α)	1843
inositol	2139	fructose (β)	1859
mannitol	1979	mesoerythritol	1528 (at 170 °C)
	Disaccharides		
210 °C		230 °C	
sucrose	2709	sucrose	2728
lactose	2704	lactose	2719
cellobiose	2888	cellobiose	2890
trehalose	2797	trehalose	2823
maltose	2802	maltose	2812
		meliboise	2950
		lactulose	2715
	Trisaccharides (290 °C)		
raffinose	3545		

[a] Minor peaks (<1%) corresponding to galactose, arabinose, and xylose have not been considered.

and standards were as follows: flow of the carrier gas (nitrogen), 35 mL/min; column temperature, 170, 210, 230, and 290 °C; detector temperature (flame ionization), 300 °C; injector temperature, 300 °C; sample size, 0.3μL.

In order to determine Kováts' retention indices (I) of Me_3Si derivatives, several mixtures of n-alkanes (C_{10}–C_{24}) were injected under the same operating conditions. The gas holdup time (t_M) was calculated by the Peterson and Hirsch method (1959), and I values were statistically calculated by the computer method of Grobler and Bálisz (1974).

Identifications of carbohydrates were made by comparing the Kováts' indices of samples and standards. Quantitative analyses were performed by comparing the peak corrected areas. Several mixtures of standards with known composition were prepared to determine the response factor of Me_3Si derivatives for each sugar and sugar–alcohol at different temperatures. Response factors were used to correct peak areas, and quantitative analyses were made by the internal normalization method (Tranchant, 1972).

RESULTS AND DISCUSSION

Assays of gas chromatographic analysis of sugars are generally carried out under programmed temperature conditions, and the retention data are expressed as relative retention time to a reference standard (Laker, 1980; Churms, 1982).

However, it is well-known that the precision of Kováts' indices is greater than that of the other chromatographic values and the results obtained are more acceptable and uniform since the retention system permits use of results obtained in other laboratories (Budahegy et al., 1983). For this reason we have used Kováts' indices, which were determined under isothermal conditions, to obtain a greater accuracy. Assays between 170 and 210 °C are adequate for the separation of Me_3Si-monosaccharides and sugar–alcohols. Higher temperatures are neccessary to obtain adequate resolution of oligosaccharides, e.g., 230 °C for disaccharides and 290 °C for raffinose. Table I lists the I values of Me_3Si derivatives for the compounds used.

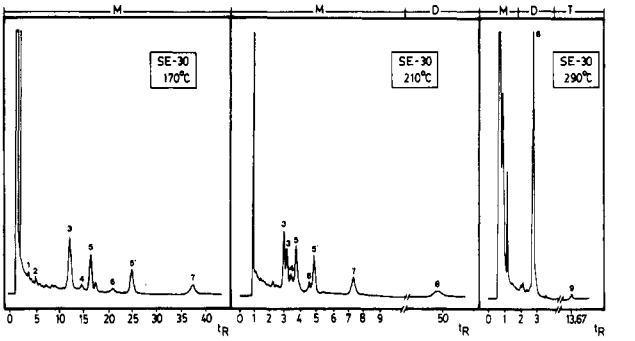

Figure 1. Chromatogram corresponding to the sugar composition of the kernel integument on SE-30 at different temperatures. Sugar: 1, arabinose; 2, xylose; 3, fructose; 4, galactose, doubtful assignment (?); 5 and 5', glucose; 6, sorbitol; 7, inositol; 8, sucrose; 9, raffinose (peak between 5 and 6, unknown).

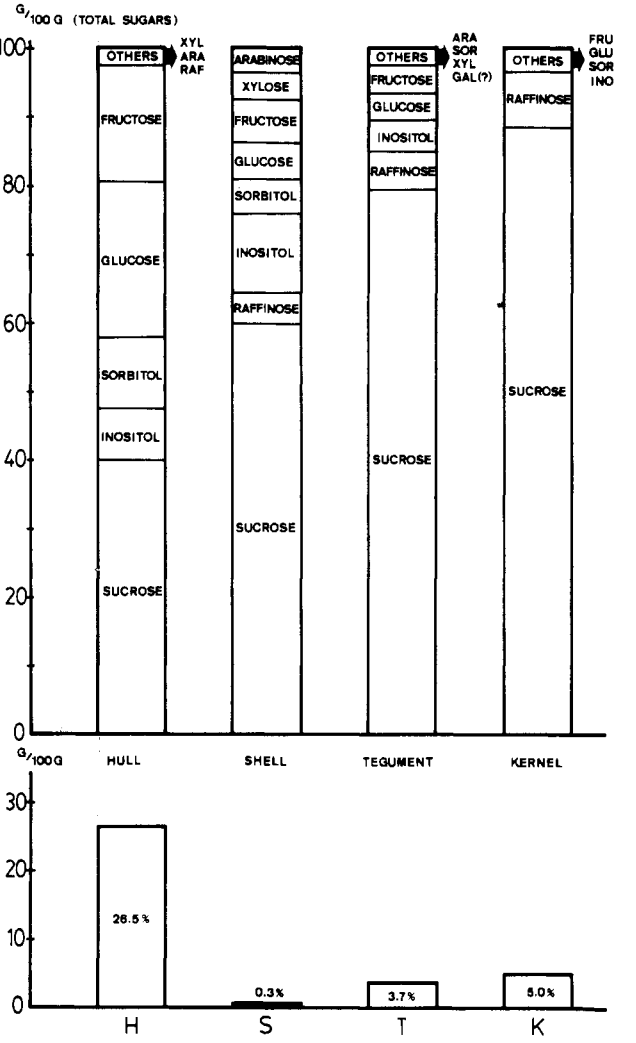

Figure 2. Scheme showing the quantitative composition of sugar fraction (H = hull; S = shell; T = tegument; K = kernel.).

A typical chromatogram, corresponding to the kernel integument, is shown in Figure 1. The composition of sugars and sugar–alcohols originating from the different parts of almond fruit are shown in Figure 2.

It can be observed that sucrose is the major component in all cases. Inositol, sorbitol, and reducing sugars, especially glucose and fructose, are present in significant amounts in hulls, shells, and integuments. In the kernel, however, only traces of these components are found, and these had not been previously detected by using thin-layer chromatography or colorimetric methods (Casares and

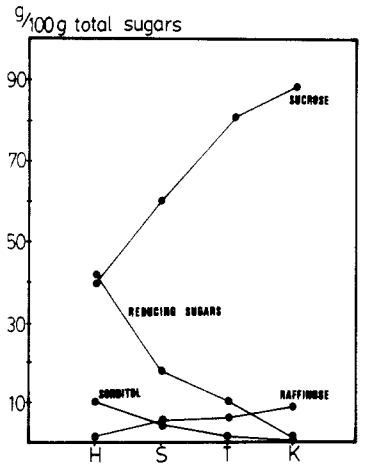

Figure 3. Variation of the principal sugar components in the different parts of the almond fruit.

López Herrera, 1952; Saura-Calixto et al., 1981).

A comparison of sugar composition, expressed in grams of sugar per 100 g of total sugars, in the different parts of almond fruit (Figure 3) shows an increase of oligosaccharides (raffinose and sucrose) from the outside to the inside of the fruit, i.e., from the hull to the kernel, while reducing sugars and sorbitol decrease appreciably.

Registry No. Sucrose, 57-50-1; raffinose, 512-69-6; sorbitol, 50-70-4.

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Free and Bound Terpene Compounds in Papaya (*Carica papaya*, L.) Fruit Pulp

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Papaya (*Carica papaya*, L.) fruit pulps were prepared by three different methods: (i) by adding sodium azide; (ii) by adding mercurous ion; (iii) without any enzyme inhibition during homogenization of ripe fruits. After solvent extraction of the pulps, containing added internal standard, quantitative capillary gas chromatography of the concentrated extracts showed that the concentrations of benzyl isothiocyanate, linalool, two isomer furanoid linalool oxides, and terpene hydrocarbons were much lower as a result of enzyme inhibition with Hg^{2+}. Consequently, linalool does not occur in free form in the ripe fruit but is formed by enzymic activity during fruit processing due to cell disruption. The identities of the volatiles were confirmed by capillary gas chromatography–mass spectrometry.

The aroma composition of papaya (*Carica papaya*, L.) fruit has been extensively investigated by different authors (Katague and Kirch, 1965; Flath and Forrey, 1977; MacLeod and Pieris, 1983; Idstein and Schreier, 1984), leading to the identification of major volatiles such as benzyl isothiocyanate, terpene hydrocarbons like (*E*)- and (*Z*)-ocimene, limonene, sabinene, and (*Z*)-neoalloocimene, and terpene alcohols like linalool, α-terpineol, nerol, and geraniol as well as the (*E*)- and (*Z*)-linalool oxides. In all these studies, fruit tissue homogenization was a part of the sample preparation sequence. In this paper, it will be demonstrated that some terpene compounds are formed during fruit pulp processing due to disruption of cell structure and do not occur in their free forms in the fruit.

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EXPERIMENTAL SECTION

Sample Preparation and Extraction. Three different methods of sample preparation were employed for pulp preparation from selected fresh papaya (*C. papaya*, L., var. Solo) fruits of the same fully ripened stage. After the fruit was peeled and the seeds were carefully removed, 1.5-kg portions of intact fruit tissue were added to each of the following: (i) 1.5 L of an 0.05 M aqueous NaN_3 solution containing 50 mL of 0.1 M phosphate buffer (pH 7.5); (ii) 1.5 L of an 0.1 M aqueous $HgCl_2$ solution; (iii) 1.5 L of distilled water. After homogenization, dilution (1:3 w/w) with distilled water, and addition of an internal standard (150 μg/kg 2-octanol), the diluted pulps were individually subjected to solvent extraction using a pentane–dichloromethane mixture (2:1) (Drawert and Rapp, 1968). Each extract was carefully concentrated by distillation (Vigreux

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