

trations of neochlorogenic acid, procyanidin B3, and catechin were observed in most cultivars while the caffeic acid content was relatively small. Since the contribution of chlorogenic acids to the enzymatic browning reaction was less significant than that of other phenolic compounds (Lee and Jaworski, 1988), attention should be given to catechin and procyanidin B3.

PPO activity in peaches also varied greatly among different cultivars (Table I). Eden showed the highest PPO activity (4505 units/g) among 15 cultivars, followed by Triogem and Velvet, which exceeded 3000 units/g. Veecling had the lowest in PPO activity (1449 units/g), which was less than one-third that of Eden. It was observed that the degree of actual browning of individual peach cultivars was correlated to its PPO activity: peach cultivars having higher PPO activity showed a higher rate of browning (e.g., Eden). Conversely, peaches low in PPO activity, such as Harmony, showed a lower rate of browning. When degree of browning was plotted against total phenolics (Figure 4), they showed a relatively close correlation ( $r = 0.67$ ). A similar relationship was observed between degree of browning and the PPO activity ( $r = 0.65$ ).

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**Registry No.** PPO, 9002-10-2; catechin, 120-80-9; procyanidin B3, 23567-23-9; chlorogenic acid, 327-97-9; neochlorogenic acid, 906-33-2; caffeic acid, 331-39-5.

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## Sugar Content of Almond, Pecan, and Macadamia Nuts

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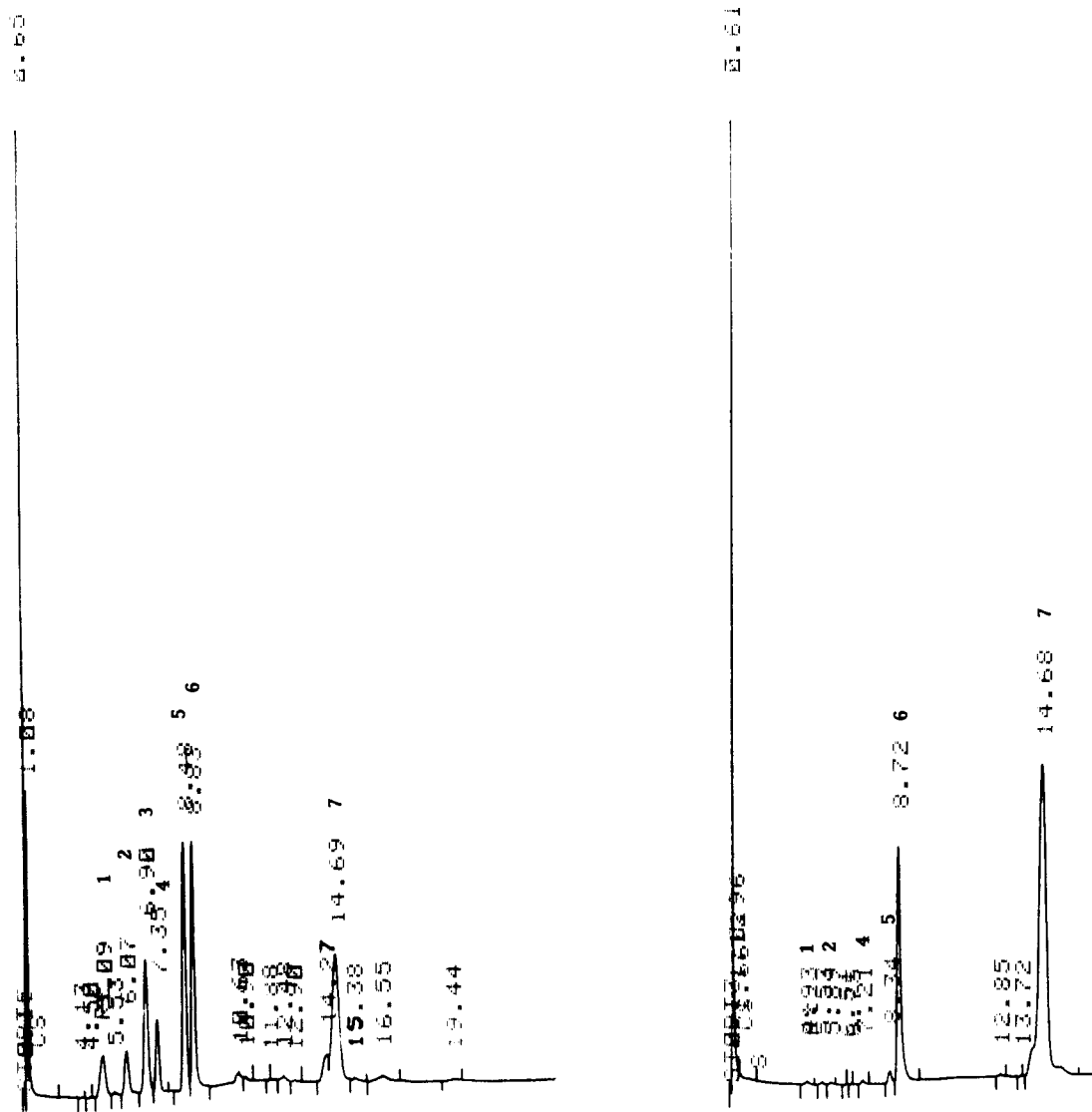
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The individual sugar contents of five almond cultivars, pecan, and macadamia nuts were determined by a gas chromatographic method. Good separations of carbohydrates were obtained within a short time with use of a combination of OV-1 and OV-225 as stationary phase. Sucrose was identified as the main constituent in almond, pecan, and macadamia nuts. Small quantities of other sugars and sugar alcohols were detected.

Saura-Calixto et al. (1981) quoted reports from literature on determinations of sucrose in almond milk by means of paper chromatography; glucose and fructose in almonds; and fructose, glucose, sucrose, sorbitol, and inositol in almond shells by gas chromatography. Sucrose was

reported to be the main constituent of carbohydrates in almonds. They confirmed these reports by determining total sugars by means of paper chromatographic, colorimetric, volumetric, and gravimetric methods and reported a mean value of 5.52 g of sucrose/100 g of almonds. They confirmed that sucrose was the main carbohydrate constituent. Saura-Calixto et al. (1984) again confirmed the presence of sucrose in almonds but also found traces of fructose, glucose, sorbitol, and inositol.

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**Figure 1.** Chromatograms of sugar standards (left) and the typical sugar content of almonds (right). Sugars: 1, fructose; 2,  $\alpha$ -glucose; 3, sorbitol; 4,  $\beta$ -glucose; 5, inositol; 6, internal standard; 7, sucrose.

Sorbitol and inositol are included in the sugar determinations although they are not sugars. They are alditols, carbohydrate derivatives with a close resemblance to sugars, also known as sugar alcohols (Koeppen, 1974). They were specifically included in the determination because researchers like Saura-Calixto et al. (1984) and Wood and McMeans (1982) detected them during kernel development of almonds and pecan nuts.

The total sugar content of Mediterranean almond kernels fluctuates between 4 and 8% (dry mass), with sucrose as the main constituent. Oligosaccharide concentrations (raffinose and sucrose) in almond increase from the outside to the inside, thus from the shell to the kernel. Reducing sugars and sorbitol decrease in the same direction (Saura-Calixto et al., 1984).

American-grown pecan kernels contain mainly fructose, glucose, sucrose, and inositol during the developing stage, but the concentrations decrease as the kernels mature (Wood and McMeans, 1982). The total sugar content of pecan cultivars grown in Egypt is approximately 3% (El-Hamady et al., 1984).

Cavaletto et al. (1966) determined total and reducing sugars by a colometric method on vacuum-dried, fat-free macadamia kernels. Values for total sugars (5.56%) and reducing sugars (0.04%), expressed as a percentage of dry weight, were reported. Prichavudhi and Yamamoto

(1965) determined total sugars (4.57%) and reducing sugars (0.06%) by the same methods as the previous authors.

Many other values for total sugar content of different nuts are stated in literature. Almonds contain approximately 4.3% (Rosengarten, 1984), macadamia nuts 8.2% (Jamieson, 1943), and pecan nuts approximately 3.2% (Wood and McMeans, 1982).

The objectives of this study were to quantify the individual sugars present in almonds, pecan, and macadamia nuts by a gas chromatographic method and to determine whether the sugar composition differs among these nuts.

#### EXPERIMENTAL SECTION

**Materials.** Shelled pecan (Moore), macadamia (Nelmar), and five almond cultivars (Burbank, Peerless, Ne Plus Ultra, Ai, Davey) were used.

**Methods.** Prior to being dried and defatted, kernels were ground to fine particles in a Waring Blender at low speed to minimize temperature increases. Nine replications of duplicate suspensions of vacuum oven dried (70 °C), defatted (Soxhlet) samples (ca. 2 g,  $\pm 1$  mg) were made in distilled water (20 mL), heated to boiling point, cooled to room temperature, quantitatively diluted to 100 mL with ethanol, and filtered. Gas-liquid chromatography was performed with a Hewlett-Packard 5831 A gas chromatograph equipped with a flame ionization detector and an electronic integrator. The first 1.2 m of a glass col-

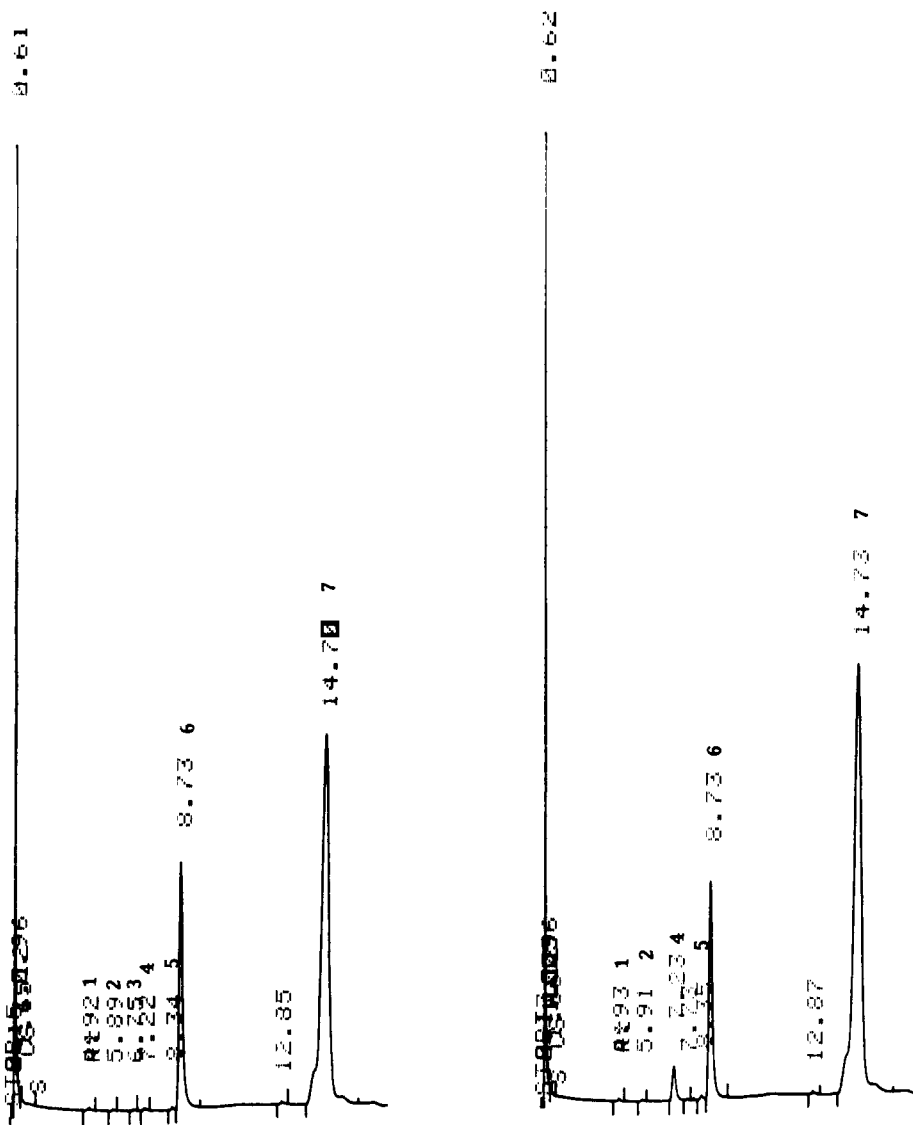


Figure 2. Chromatograms of the typical sugar content of pecan (left) and macadamia (right) nuts. Sugars: 1, fructose; 2,  $\alpha$ -glucose; 3, sorbitol; 4,  $\beta$ -glucose; 5, inositol; 6, internal standard; 7, sucrose.

Table I. Individual Sugar Content of Almonds, Pecan, and Macadamia Nuts

nut	cultivar	sugar content, <sup>a,b</sup> g/100 g			
		inositol	glucose	fructose	sucrose
pecan	Moore	0.01 (0.00)	0.01 (0.01)	0.02 (0.01)	2.02 (0.25)
macadamia	Nelmar	0.02 (0.01)	0.08 (0.01)	0.03 (0.03)	4.09 (0.57)
almond	Burbank	0.11 (0.02)	0.07 (0.03)	0.08 (0.04)	3.37 (0.30)
	Peerless	0.06 (0.02)	0.02 (0.01)	0.06 (0.03)	3.10 (0.35)
	Ne Plus Ultra	0.04 (0.02)	0.02 (0.01)	0.05 (0.04)	3.28 (0.26)
	Ai	0.08 (0.02)	0.03 (0.02)	0.08 (0.06)	4.11 (0.44)
	Davey	0.12 (0.02)	0.04 (0.01)	0.13 (0.04)	4.68 (0.85)

<sup>a</sup> Standard deviation in parentheses. <sup>b</sup> Trace amounts of sorbitol found in pecan (Moore) and almond (Burbank).

umn (3 m  $\times$  2 mm (i.d.)) was packed with 1.5% OV-1 and the last 1.8 m with 2% OV-225 (Koeppen, 1976). Chromosorb W (60–80 mesh) was used as carrier material. Nitrogen was used as carrier gas at 15 mL/min. The supply of hydrogen and air to the detector was set at 42.5 and 255 mL/min, respectively. The initial oven temperature was 155 °C. After 1.5 min it was elevated by 5 °C/min for 5 min, after which the oven temperature was elevated by 10 °C/min until 225 °C was reached. Detector temperature was 300 °C, and the temperature of the injection block was 250 °C. An equilibrium time of 2 min at the initial temperature was allowed for equilibrium before injection of each sample. The total determination took 25 min.

**Preparation of Standards.** All standards were monohydrate sugars stored in a desiccator over calcium chloride. A standard solution was prepared by dissolving D-glucose (180 mg,

$\pm 0.01$  mg), D-fructose (180 mg,  $\pm 0.01$  mg), sucrose (342 mg,  $\pm 0.01$  mg), sorbitol (182 mg,  $\pm 0.01$  mg), and inositol (180 mg,  $\pm 0.01$  mg) in distilled water (20 mL). It was then quantitatively diluted with ethanol to 100 mL (Koeppen, 1980).

**Silylation Procedure.** Aliquots (200  $\mu$ L) of the standard sugar solution and sample extract were evaporated to dryness over calcium chloride under reduced pressure at room temperature in septum-sealed vials. The internal standard solution (220  $\mu$ L/256.00 mg of triphenylethylene/100 mL of pyridine) was added to dissolve the dried material by agitating it in an ultrasonic bath for ca. 15 min. After agitation, hexamethyldisilazane (200  $\mu$ L), followed by trifluoroacetic acid (25  $\mu$ L), was added. Vials were capped and ultrasonically treated to obtain a homogeneous, clear solution (Koeppen, 1980). Samples were injected with an automatic injection system (ca. 1.5  $\mu$ L). The

syringe was washed with hexane between injections. Quantification was done with an electronic integrator relative to the area of the internal standard. Results were converted to the original nut kernel basis.

## RESULTS AND DISCUSSION

The sugar determination method of Koeppen (1980) was used with a combination of OV-1 and OV-225 columns (Koeppen, 1976). OV-1 has frequently been used for sugar analyses because of its great thermal stability, and OV-225 is recommended for the rapid separation of sucrose, lactose, and maltose (Koeppen, 1976). Koeppen (1976) also used a combination of OV-1 and OV-225 for analyses previously performed on OV-1 alone.

This combination column was used in preliminary tests on the different nuts to identify the individual sugars present. No traces of maltose could be detected in the nuts, but the column produced good, reproducible separations of mono- and disaccharides as well as sugar alcohols. The column was therefore used for the quantitative determinations of the individual sugars, but maltose was excluded in this study.

Analytical conditions were adapted to obtain reproducible separations in the shortest possible analysis time. Koeppen (1976) reported satisfactory separations for mono- and disaccharides with OV-1 in a total analysis time of 23 min and with OV-225 in 15 min (Koeppen, 1980). In the present study, the adapted analytical program used with the combination of OV-1 and OV-225 as stationary phase also made it possible to obtain good separations of mono- and disaccharides in 15 min. Allowing for cooling and equilibration at the initial temperature, subsequent samples could be injected at 25-min intervals with the automatic sampler. Typical chromatograms are illustrated in Figures 1 and 2.

With this method, Koeppen (1976) reported individual values for each sugar that did not vary by more than  $\pm 0.05\%$  from the average of three replications. In the present study the averages represent 18 values. Sucrose was identified as the main constituent in almonds, pecan, and macadamia nuts (Table I). However, in pecan nuts the sucrose content was lower than in the other nuts. The differences in sucrose content among the five almond cultivars possibly occurred because the determinations were not done on kernels of the same maturity, due to differences in date of harvest and variations in moisture content. Traces of glucose and fructose were also identified in all the nuts. The total reducing sugar content

(glucose and fructose) of pecan nuts was lower than in the other nuts. The results for macadamia nuts did not differ much from the values stated in the literature. Traces of sorbitol were only detected in pecan nuts and one of the individual almond cultivars (Burbank). Although inositol also occurred in trace amounts, it was more prominent in the almond cultivars than in pecan and macadamia nuts.

**Registry No.** Inositol, 87-89-8; glucose, 50-99-7; fructose, 57-48-7; sucrose, 57-50-1; sorbitol, 50-70-4.

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