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Fatty Acid, Triacylglycerol, Phytosterol, and Tocopherol Variations in Kernel Oil of Malatya Apricots from Turkey

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The fatty acid, sn-2 fatty acid, triacyglycerol (TAG), tocopherol, and phytosterol compositions of kernel oils obtained from nine apricot varieties grown in the Malatya region of Turkey were determined (P < 0.05). The names of the apricot varieties were Alyanak (ALY), Çataloğlu (CAT), Çöloğlu (COL), Hacıhaliloğlu (HAC), Hacıkız (HKI), Hasanbey (HSB), Kabaaşı (KAB), Soğancı (SOG), and Tokaloğlu (TOK). The total oil contents of apricot kernels ranged from 40.23 to 53.19%. Oleic acid contributed 70.83% to the total fatty acids, followed by linoleic (21.96%), palmitic (4.92%), and stearic (1.21%) acids. The sn-2 position is mainly occupied with oleic acid (63.54%), linoleic acid (35.0%), and palmitic acid (0.96%). Eight TAG species were identified: LLL, OLL, PLL, OOL + POL, OOO + POO, and SOO (where P, palmitoyl; S, stearoyl; O, oleoyl; and L, linoleoyl), among which mainly OOO + POO contributed to 48.64% of the total, followed by OOL + POL at 32.63% and OLL at 14.33%. Four tocopherol and six phytosterol isomers were identified and quantified; among these, y-tocopherol (475.11 mg/kg of oil) and β -sitosterol (273.67 mg/100 g of oil) were predominant. Principal component analysis (PCA) was applied to the data from lipid components of apricot kernel oil in order to explore the distribution of the apricot variety according to their kernel's lipid components. PCA separated some varieties including ALY, COL, KAB, CAT, SOG, and HSB in one group and varieties TOK, HAC, and HKI in another group based on their lipid components of apricot kernel oil. So, in the present study, PCA was found to be a powerful tool for classification of the samples.

KEYWORDS: Apricot kernel oil; fatty acid; *sn*-2 fatty acids; triacylglycerol; tocopherol; phytosterol; principal component analysis

INTRODUCTION

Turkey is the leading fresh apricot producer in the world. The Malatya region, of Eastern Turkey, is particularly important for apricot production and processing. According to the data from the Food and Agriculture Organization (FAO), the average annual production of fresh apricots was calculated as 450000 tons for the years 1998–2005 (1). Apricot kernels, which may be accepted as a byproduct, are consumed as appetizers or used as food additives after removing the stone parts. The proportion of the kernel in the fresh apricot is ca. 1.5% (2). So, the average production of apricot kernels for that time period is about 7000 tons per year. The oil content of apricot kernels ranges from 27.7 to 66.7%, with the average value of 47.2% (3). When these values are taken into account, it is possible to produce about

3500 tons of apricot kernel oil per year. Insufficient quantities of edible oil in the world have become a major economic and nutritional problem. The need for edible oil must be met by new resources or substitutes (3).

The physical and chemical properties of apricot kernel, including some lipid profiles, have been reviewed by Alpaslan and Hayta (4). It has been reported that apricot kernel oil contains unsaturated fatty acids which vary from 91.5 to 91.8%. The major fatty acids are oleic (58.3–73.4%) and linoleic (18.8–31.7%). It has also been reported that the apricot kernel oil contains neutral lipids (95.2–95.7%), glycolipids (1.3–1.8%), phospholipids (2%), and phytosterols consisting of 11.8 mg/ 100 g of campesterol, 9.8 mg/100 g of stigmasterol, and 177.0 mg/100 g of sitosterol (4).

Monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA), as well as minor lipid components such as tocopherols and phytosterols, play an important role in human nutrition and health. Diets rich in these compounds decrease blood pressure and total blood cholesterol levels in humans (5–7). Apricot

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Table 1. Total Oil Content^a (in Fresh Weight) and Fatty Acid Composition of Apricot Kernel Oils

								fatty acids (%)						
varieties	total oil content (%)	C16:0	C16:1	C17:0	C17:1	C18:0	C18:1 ω 9	C18:2\(\omega\)	C18:3 ω 3	C20:0	C20:1 ω 9	SSFA	∑MUFA	ΣPUFA
Alyanak Çataloğlu Çöloğlu Hacıhaliloğlu Hasanbey Kabaşı Soğancı Tokaloğlu	44.57 ± 0.12 c 47.07 ± 0.82 d 50.77 ± 0.82 e 53.19 ± 0.25 f 47.21 ± 0.09 d 40.23 ± 0.41 a 43.35 ± 1.08 bc 46.48 ± 1.89 d 42.86 ± 0.73 b 46.19 ± 4.02	4.50 ± 0.01 a 0 4.84 ± 0.01 b 0 4.84 ± 0.01 c 0 0 6 4.94 ± 0.00 c 0 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	(61 ± 0.00 bcd (55 ± 0.02 a (56 ± 0.02 d (58 ± 0.02 d (58 ± 0.03 e (50 ± 0.01 bc (62 ± 0.01 bc (62 ± 0.01 bc (62 ± 0.01 bc (63 ± 0.02 cd (63 ± 0.02 cd	0.04 ± 0.01 a 0.05 ± 0.00 a 0.05 ± 0.00 a 0.07 ± 0.02 a 0.05 ± 0.01 a 0.04 ± 0.00 a 0.05 ± 0.01 a 0.05 ± 0.01 a 0.05 ± 0.01 a 0.04 ± 0.00 a	0.12 ± 0.00 a 0.13 ± 0.01 ab 0.12 ± 0.00 a 0.14 ± 0.03 b 0.12 ± 0.00 a 0.12 ± 0.00 a 0.12 ± 0.00 a 0.13 ± 0.01 ab 0.12 ± 0.00 a	1.12 ± 0.01 b 1.23 ± 0.01 d 1.23 ± 0.02 d 1.37 ± 0.02 f 1.37 ± 0.01 b 1.11 ± 0.01 d 1.33 ± 0.01 d 1.33 ± 0.00 e 1.31 ± 0.01 d	71.00 ± 0.02 e 72.51 ± 0.02 h 70.72 ± 0.06 d 70.72 ± 0.06 d 67.01 ± 0.20 b 70.13 ± 0.02 c 66.53 ± 0.05 a 71.66 ± 0.03 f 75.83 ± 0.02 l	22.30 ± 0.01 f 20.41 ± 0.03 b 22.05 ± 0.03 e 24.41 ± 0.06 c 24.83 ± 0.22 h 22.93 ± 0.02 g 26.14 ± 0.03 d 27.17 ± 0.01 a 17.17 ± 0.01 a	0.11 ± 0.01 d 0.08 ± 0.00 c 0.07 ± 0.01 a 0.08 ± 0.00 ab 0.08 ± 0.01 bc 0.07 ± 0.00 ab 0.07 ± 0.01 abc 0.07 ± 0.01 abc 0.07 ± 0.01 abc 0.08 ± 0.00 ab	0.10 ± 0.00 b 0.10 ± 0.01 b 0.10 ± 0.01 b 0.10 ± 0.01 d 0.12 ± 0.01 c 0.09 ± 0.00 ab 0.10 ± 0.01 b 0.11 ± 0.01 c	0.10 ± 0.01 a 0.00 ± 0.01 a 0.09 ± 0.01 a 0.09 ± 0.01 a 0.09 ± 0.01 a 0.10 ± 0.01 a 0.11 ± 0.01 a 0.11 ± 0.01 a	5.77 ± 0.02 a 6.22 ± 0.00 c 6.32 ± 0.02 d 6.32 ± 0.02 d 7.13 ± 0.05 f 6.05 ± 0.01 b 6.39 ± 0.01 d 6.39 ± 0.01 d 6.39 ± 0.01 d 6.39 ± 0.01 d 6.39 ± 0.01 d 6.30 ± 0.01 d	71.83 ± 0.01 e 73.29 ± 0.02 h 71.58 ± 0.05 d 72.89 ± 0.05 g 67.96 ± 0.18 b 70.94 ± 0.03 c 67.41 ± 0.05 a 72.51 ± 0.03 f 76.69 ± 0.01 l	22.40 ± 0.01 f 20.49 ± 0.03 b 22.11 ± 0.02 e 22.11 ± 0.06 c 24.91 ± 0.06 c 24.91 ± 0.02 b 23.00 ± 0.03 d 26.21 ± 0.03 d 21.18 ± 0.03 d 17.31 ± 0.01 a

Each value is the mean \pm standard deviation of triplicate determinations. Means with different letters in the column for each apricot kernel oil are significantly different (P < 0.05)

kernel oil is an excellent source of MUFA, tocopherols, and phytosterols, and may prove to have beneficial effects.

Although the lipid characteristics of the apricot kernel oils from different regions of the world have been reported (8-12), there is little information available on the fatty acid, sn-2 fatty acid, triacylglycerol (TAG), tocopherol, and phytosterol compositions of apricot kernel oil extracted from the most cultivated apricot varieties in the Malatya region of Turkey. The present study therefore compares some important lipid compositions of apricot kernel oils, to establish, if any, the differences in the lipid compositions of the nine apricot kernel oil varieties.

MATERIALS AND METHODS

Samples. Apricot varieties (Alyanak, Çataloğlu, Çöloğlu, Hacıhaliloğlu, Hacıkız, Hasanbey, Kabaaşı, Soğancı, and Tokaloğlu) from the Malatya region were harvested at commercial maturity stage from the Malatya Fruit Research Institute between the first and third weeks of July 2005. A total of 100 apricot samples were collected from at least four different trees in each cultivar and pooled. The samples were transported in the boxes within 10 h. Stones from the apricot fruits were removed, and individual stones were hammered in order to obtain the kernel. The kernels were dried until about 3.5% moisture at open air conditions and were placed into polyethylene bags and stored at 4 °C until further analysis. All analyses were performed at least in duplicate.

Reagents and Standards. Tocopherol sets (each contains one 50 mg vial each of DL- α -tocopherol, D- β -tocopherol, D- γ -tocopherol, and D- δ -tocopherol, catalog no. 613424) were purchased from Calbiochem (La Jolla, CA). Tris(hydroxymethyl)aminomethane, thin layer chromatography (TLC) plates (silica gel 60 G), n-hexane, and 2-propanol were obtained from Merck (Darmstadt, Germany). Porcine pancreatic lipase (EC 3.1.1.3, type II, crude), 2',7'-dichlorofluorescein (for TLC, 90% purity), sodium cholate, sterol standards (campesterol, stigmasterol, β -sitosterol, dihydrocholesterol, 5α -cholestane), triolein, trilinolein, and tristearin were purchased from Sigma (St. Louis, MO). Triglyceride mix (tricaprin, tricaprylin, trilaurin, trimyristin, tripalmitin) and a fatty acid methyl ester (FAME) mixture (37 component FAME mix, 10 mg/ mL of the FAME reference standard mix in methylene chloride, catalog no. 47885-U) were purchased from Supelco (Bellefonte, PA). N-O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA, 98%) and chlorotrimethylsilane (TMCS, 98%) were obtained from Acros (Geel, Belgium). Pyrogallol (98%) was purchased from Fluka (Seelze, Germany). Pyridine was obtained from JT Baker (Griesheim, Germany). All other chemicals and reagents for the analysis were analytical or chromatographic grades.

Analytical Methods. *Total Oil Content (AOAC Official Method 920.39C) (13).* The kernels, from each variety, were separately ground in a mortar to pass 1-2 mm screens. The total oil contents of the samples (5 g) were determined in a Soxhlet apparatus using 200 mL of petroleum ether (boiling point range 40-60 °C) for a period of 8 h.

Ether extracts containing apricot kernel oil were subjected to vacuum evaporation at 40 °C using a rotary evaporator RE 100 (Bibby Sterilin Ltd., Staffordshire, U.K.) to remove ether. The total oil content was determined in triplicate by using three samples of each variety, and average values were reported. The residual solvent was removed under a stream of nitrogen, and the lipids were stored at -20 °C under nitrogen until further analysis.

Fatty Acid Analysis. Fatty acid methyl esters (FAMEs) were prepared using potassium hydroxide in dry methanol (2 N) and extracted with n-hexane as described in AOCS Official Method Ce 2-66 (14). One microliter of the FAMEs was analyzed with an HP 5890 series II gas chromatograph (GC) (Hewlett-Packard Company, Wilmington, DE) equipped with a flame ionization detector (FID) and an HP 7673A automatic injector (Agilent Technologies, Palo Alto, CA). A fused silica DB23 capillary column (60 m \times 0.25 mm i.d., 0.25 μ m film thickness; J&W Scientific, Folsom, CA) was used. The oven temperature was programmed as follows: 170 °C for 3 min, increased to 220 °C at 3 °C/min, and kept at 220 °C for 15 min. The injection and detector temperatures were 250 and 260 °C, respectively. The carrier gas was

Table 2. sn-2 Fatty Acid Compositions^a of Apricot Kernel Oils

	fatty acids (%)							
varieties	C16:0	C18:0	C18:1ω9	C18:2ω6				
Alyanak	$0.83 \pm 0.02\mathrm{c}$	$0.34 \pm 0.01 \mathrm{bc}$	61.65 ± 0.17 b	37.18 ± 0.16 e				
Çataloğlu	$0.84 \pm 0.06\mathrm{c}$	$0.43\pm0.05\mathrm{cde}$	$65.43 \pm 0.07 \mathrm{de}$	$33.30 \pm 0.18 \mathrm{c}$				
Çöloğlu	$1.31 \pm 0.03 \mathrm{e}$	$0.62\pm0.04\mathrm{f}$	$61.29 \pm 0.10 \mathrm{b}$	36.79 ± 0.16 e				
Hacıhaliloğlu	$1.08\pm0.04\mathrm{d}$	0.54 ± 0.10 ef	$66.41 \pm 0.07 \mathrm{e}$	$31.96 \pm 0.01 \mathrm{b}$				
Hacıkız	1.54 \pm 0.07 f	$0.77 \pm 0.06 \mathrm{g}$	$58.48 \pm 0.92 \mathrm{a}$	$39.21 \pm 1.05 \mathrm{f}$				
Hasanbey	$0.63 \pm 0.03\mathrm{b}$	$0.42\pm0.02\mathrm{cd}$	$63.86 \pm 0.38 \mathrm{c}$	$35.09 \pm 0.43 \mathrm{d}$				
Kabaaşı	$1.26 \pm 0.02 \mathrm{e}$	0.51 ± 0.01 de	58.64 ± 0.74 a	$39.59 \pm 0.74 \mathrm{f}$				
Soğancı	$0.52 \pm 0.02 \mathrm{a}$	$0.22 \pm 0.02 \mathrm{a}$	$64.91\pm0.10\mathrm{cd}$	34.35 ± 0.10 cd				
Tokaloğlu	$0.59\pm0.01\mathrm{ab}$	0.31 ± 0.00 ab	$71.17 \pm 0.86 \mathrm{f}$	$27.51 \pm 0.29 a$				
average	0.96 ± 0.36	0.46 ± 0.17	63.54 ± 4.04	35.00 ± 3.80				

^a Each value is the mean \pm standard deviation of duplicate determinations. Means with different letters in the column for each apricot kernel oil are significantly different (P < 0.05).

Table 3. Triacylglycerol Compositions^a of Apricot Kernel Oils

		$triacylglycerols^b$ (%)								
varieties	LLL	OLL	PLL	OOL + POL	000 + P00	S00				
Alyanak	2.74 ± 0.01 f	14.59 ± 0.25 d	$0.11 \pm 0.05 \mathrm{ab}$	$33.93 \pm 0.12\mathrm{f}$	47.15 ± 0.24 c	1.46 ± 0.07 a				
Çataloğlu	$2.52 \pm 0.00 \mathrm{d}$	$13.60 \pm 0.11 \mathrm{c}$	$0.11 \pm 0.01 \ ab$	$32.15 \pm 0.01 c$	$49.85 \pm 0.15 \mathrm{e}$	$1.78\pm0.02~\mathrm{cd}$				
Çöloğlu	$2.57 \pm 0.06 \mathrm{de}$	$15.01 \pm 0.04 \mathrm{e}$	$0.07 \pm 0.04 a$	$33.41 \pm 0.08 \mathrm{e}$	$47.26 \pm 0.02 \mathrm{c}$	1.68 ± 0.0 bc				
Hacıhaliloğlu	$2.38 \pm 0.01 \mathrm{c}$	$13.00 \pm 0.09 \mathrm{b}$	0.10 ± 0.05 ab	$31.59 \pm 0.16 \mathrm{b}$	$51.09 \pm 0.18 \mathrm{g}$	$1.82\pm0.06\mathrm{d}$				
Hacıkız	2.92 ± 0.06 g	$17.43 \pm 0.08 \mathrm{f}$	$0.14 \pm 0.00 \ ab$	$34.70 \pm 0.02 \mathrm{g}$	$43.19 \pm 0.08 \mathrm{b}$	$1.62 \pm 0.07 \mathrm{b}$				
Hasanbey	$2.65\pm0.02\mathrm{ef}$	$14.48 \pm 0.16 \mathrm{d}$	$0.10 \pm 0.06 ab$	$31.89 \pm 0.20 \mathrm{c}$	$49.23 \pm 0.25 \mathrm{d}$	$1.69\pm0.04~\mathrm{bc}$				
Kabaaşı	$3.49 \pm 0.09 \mathrm{h}$	$17.67 \pm 0.16 \mathrm{f}$	$0.17 \pm 0.02 \mathrm{b}$	34.91 ± 0.16 g	42.38 ± 0.36 a	$1.39 \pm 0.0 \mathrm{a}$				
Soğancı	$2.10 \pm 0.03 \mathrm{b}$	$13.00 \pm 0.16 \mathrm{b}$	$0.06 \pm 0.00 a$	$32.66 \pm 0.02 m d$	$50.42 \pm 0.21 \mathrm{f}$	$1.74 \pm 0.01 \ \mathrm{bcc}$				
Tokoloğlu	$1.91\pm0.02\mathrm{a}$	$10.19 \pm 0.06 a$	$0.08\pm0.03\mathrm{ab}$	$28.47 \pm 0.01 \text{ a}$	$57.23 \pm 0.13 \mathrm{h}$	$2.13\pm0.08~\textrm{e}$				
average	2.58 ± 0.46	14.33 ± 2.31	$\textbf{0.10} \pm \textbf{0.03}$	$\textbf{32.63} \pm \textbf{1.97}$	48.64 ± 4.44	$\textbf{1.70} \pm \textbf{0.21}$				

 $[^]a$ Each value is the mean \pm standard deviation of duplicate determinations. Means with different letters in the column for each apricot kernel oil are significantly different (P < 0.05). b Trilinoleoylglycerol (CLL), oleoyl-diinoleoylglycerol (OLL), palmitoyl-diinoleoylglycerol (PLL), dioleoyl-linoleoylglycerol (OOL), palmitoyl-dioleoylglycerol (POL), trioleylglycerol (OOO), palmitoyl-dioleoylglycerol (POO), stearoyl-dioleoylglycerol (SOO).

nitrogen, and the flow rate was 1 mL/min. The split ratio was 1/65. FAME identification was based on retention times as compared with those of the standard FAME mixture. Results were expressed as percentage of peak area without any corrections. Fatty acid analysis was performed in triplicate for single samples of each variety, and average values were reported.

sn-2 Fatty Acid Analysis (AOCS Official Method Ch 3-91) (14). This method entails several steps: selective hydrolysis of the 1,3-position of fatty acids in the apricot kernel oils with pancreatic lipase; separation of the obtained monoacylglycerols (MAG) by thin-layer chromatography, using silica gel 60 plates and a developing solvent mixture of hexane, diethyl ether, and formic acid in the proportions 70/30/1 (v/v/v); identification of the MAG band (R_f about 0.035) under UV light; and, finally, analysis of the MAGs by GC following conversion of the MAGs to methyl esters as described in the section Fatty Acid Analysis. Sn-2 fatty acid analysis was performed in duplicate for single samples of each variety, and average values were reported.

Triacylglycerols. Triacylglycerol compositions of apricot kernel oils were determined by reversed-phase high performance liquid chromatography (RP-HPLC) with slight modifications of AOCS Official Method Ce 5b-89 (14). Briefly, 0.1 g oil was dissolved in 2 mL of acetone and filtered through a 0.45 μm pore size syringe filter (Millipore, Bedford, MA). Twenty microliters of filtered oil was directly injected into the ThermoFinnigan HPLC system integrated with an autosampler including temperature control for the column (SpectraSystem AS3000), a degasser system (SpectraSystem SCM1000), and a quaternary gradient pump (SpectraSystem P4000) (ThermoFinnigan, San Jose, CA). Detection was performed with a SpectraSystem RI-150 refractive index detector (ThermoFinnigan, San Jose, CA). The chromatograms were processed using a software package for system control and data acquisition (ChromQuest 4.0). The chromatographic separation of the compounds was achieved with a Luna C18 column (250 mm × 4.6 mm; 5 μ m; Phenomenex, Torrance, CA) operated at 35 °C. An isocratic solvent system consisting of acetone-acetonitrile (60:40, v/v) was used at a flow rate of 1 mL/min. Peaks were identified by taking into account the relative retention times of triglyceride standards, and results were expressed as percentage of peak areas. Triacylglycerol determinations were performed in duplicate for single samples of each variety, and average values were reported.

Tocopherols. The tocopherol composition of oils was determined according to Karabulut et al. (15). Normal phase HPLC was used to analyze tocopherols using a ThermoFinnigan HPLC system as given above. The chromatographic separation was achieved with a Luna Silica column (250 mm \times 4.6 mm, 5 μ m; Phenomenex, Torrance, CA), and the column temperature was maintained at 30 °C. Separation of tocopherols was based on isocratic elution with *n*-hexane (99%) and isopropanol (1%) at 1 mL/min. The injection volume of the samples was 20 μ L. The eluate was monitored at 292 nm by using a SpectraSystem UV6000LP photodiode-array detector (ThermoFinnigan, San Jose, CA). The compounds were identified by comparing their retention times and UV spectra with authentic standards. Tocopherols were quantified based on peak areas compared with external standards. Tocopherol analysis was performed in triplicate for single samples of each variety, and average values were reported.

Phytosterols. Phytosterols were determined according to the method of Slover et al. (16) with some modifications. Approximately 0.5 g of oil was placed in a screw-capped glass bottle, and 1 mL of internal standard solution containing 0.50 mg of 5α -cholestane in hexane was added. The solvent was removed with a stream of nitrogen while bottles were heated to 40-45 °C in a water bath. After the solvent was removed, the residue was dissolved with 10 mL of pyrogallol–ethanol (3%, w/v). Then, 1 mL of saturated aqueous KOH was added. The bottles were shaken vigorously and mixed using a Vortex mixer and then placed into an 80 °C water bath for 20 min. The bottles were mixed four times during that period. After the heating period, the bottles were removed from the water bath and cooled using tap water. Hexane (20 mL) and distilled water (10 mL) were added to each sample bottle. The bottles were recapped, shaken vigorously for 2 min, and then centrifuged at 179g for 5 min. The clear upper layer of hexane was transferred to another bottle and evaporated to dryness at 40 °C under a gentle stream

Table 4. Tocopherol Contents^a of Apricot Kernel Oils

	tocopherol isomers (mg/kg of oil)								
varieties	α-tocopherol	eta-tocopherol	γ -tocopherol	δ -tocopherol	total				
Alyanak	18.18 ± 0.05 d	0.32 ± 0.08 a	563.40 ± 1.13 g	18.94 ± 0.15 f	600.85 ± 1.03 g				
Çataloğlu	$18.89 \pm 0.22 \mathrm{d}$	0.34 ± 0.04 a	$484.17 \pm 2.07 \mathrm{d}$	$12.83\pm0.41\mathrm{cd}$	$516.23 \pm 2.58 \mathrm{d}$				
Çöloğlu	$26.87 \pm 0.24 \mathrm{f}$	0.23 ± 0.04 a	$516.56 \pm 4.73 \mathrm{f}$	$12.32 \pm 0.29 \mathrm{bc}$	$555.99 \pm 5.15 \mathrm{f}$				
Hacıhaliloğlu	$16.43 \pm 0.07 \mathrm{b}$	$0.32 \pm 0.02 \mathrm{a}$	$438.44 \pm 1.10 \mathrm{b}$	$11.58 \pm 0.41 \mathrm{b}$	466.78 ± 1.27 b				
Hacıkız	$14.89 \pm 0.10 \mathrm{a}$	$0.64 \pm 0.27 \mathrm{b}$	$438.19 \pm 4.11 \mathrm{b}$	$15.24 \pm 0.81 \mathrm{e}$	468.97 ± 4.74 b				
Hasanbey	$15.53 \pm 0.20 \mathrm{a}$	$0.71 \pm 0.18 \mathrm{b}$	$514.06 \pm 4.42 \mathrm{f}$	$11.22 \pm 0.90 \mathrm{b}$	541.52 ± 5.36 e				
Kabaaşı	$26.52 \pm 1.27 \mathrm{f}$	$0.44 \pm 0.03 \mathrm{ab}$	502.23 ± 2.11 e	$13.80\pm1.28\mathrm{d}$	543.00 ± 3.84 e				
Soğancı	21.02 ± 0.23 e	$0.21 \pm 0.01 a$	$472.37 \pm 4.67 \mathrm{c}$	$8.56 \pm 0.31 \mathrm{a}$	502.16 ± 5.04 c				
Tokaloğlu	$17.30\pm0.57~\mathrm{c}$	$0.19\pm0.33a$	$346.53 \pm 8.38 a$	$9.30\pm0.17a$	373.31 ± 9.21 a				
average	19.51 ± 4.46	0.38 ± 0.19	475.11 ± 62.35	12.64 ± 3.14	507.64 ± 65.89				

^a Each value is the mean \pm standard deviation of triplicate determinations. Means with different letters in the column for each apricot kernel oil are significantly different (P < 0.05).

Table 5. Sterol Compositions^a of Apricot Kernel Oils

			S	terol isomers (mg/100	g of oil)		
varieties	campesterol	stigmasterol	β -sitosterol	$\Delta^{ extsf{5}} ext{-avenasterol}$	Δ^{5-24} -stigmastadienol	Δ^7 -stigmasterol	total
Alyanak	11.29 ± 0.22 b	$2.19 \pm 0.12 \mathrm{b}$	$294.22 \pm 3.86\mathrm{d}$	21.92 ± 1.18 a	1.80 ± 0.09 a	$3.16 \pm 0.72 \mathrm{b}$	$334.59 \pm 5.33 \mathrm{bc}$
Çataloğlu	$12.76\pm0.80~\text{cd}$	$1.39 \pm 0.43 \mathrm{a}$	$278.60 \pm 5.90 \mathrm{c}$	$38.32 \pm 0.51 \mathrm{c}$	$2.69 \pm 0.26 \mathrm{b}$	$2.26 \pm 0.12 a$	$337.91 \pm 7.79 \mathrm{bc}$
Çöloğlu	$11.62 \pm 1.22 \mathrm{bc}$	$1.38 \pm 0.22 a$	$264.93 \pm 6.10 \mathrm{b}$	$39.89 \pm 1.54 \mathrm{cd}$	$2.99\pm0.02\mathrm{bc}$	$4.68\pm0.06\mathrm{d}$	$325.49 \pm 9.16 \mathrm{b}$
Hacıhaliloğlu	15.50 \pm 0.28 f	$2.85 \pm 0.22 \mathrm{c}$	$280.30 \pm 0.92\mathrm{c}$	$41.22 \pm 2.08 \mathrm{d}$	$2.71 \pm 0.17 \mathrm{b}$	$3.27 \pm 0.41 \mathrm{b}$	$345.85 \pm 1.24 \mathrm{cd}$
Hacıkız	$14.24 \pm 0.51 \mathrm{e}$	1.98 ± 0.01 ab	$293.92 \pm 4.28 \mathrm{d}$	$56.83 \pm 1.16 \mathrm{f}$	$4.82\pm0.27~\mathrm{d}$	$4.30\pm0.05\mathrm{cd}$	$376.10 \pm 5.72 \mathrm{e}$
Hasanbey	$8.84 \pm 0.11 \ a$	$3.17 \pm 0.10 \mathrm{c}$	$264.06 \pm 0.84 \mathrm{b}$	$54.40 \pm 0.34 \mathrm{f}$	$3.01\pm0.12\mathrm{bc}$	$3.67\pm0.09\mathrm{bc}$	$337.16 \pm 0.48 \mathrm{bc}$
Kabaası	$11.44 \pm 0.06 \mathrm{b}$	$3.81\pm0.15\mathrm{d}$	$280.73 \pm 3.44 \mathrm{c}$	$49.99 \pm 1.72 \mathrm{e}$	$3.38 \pm 0.31 \ c$	$2.96 \pm 0.49 \mathrm{ab}$	$352.31 \pm 1.14 \mathrm{d}$
Soğancı	$11.17 \pm 0.10 \mathrm{b}$	1.47 ± 0.46 a	251.40 ± 2.83 a	$29.72 \pm 0.82 \mathrm{b}$	$2.64\pm0.09\mathrm{b}$	4.23 ± 0.10 cd	$300.63 \pm 3.09 \mathrm{a}$
Tokaloğlu	$\rm 12.89 \pm 0.07 \ d$	$1.70\pm0.04~\mathrm{ab}$	$254.84 \pm 2.19 a$	$31.95 \pm 0.14 \mathrm{b}$	$1.69 \pm 0.26 a$	$4.39\pm0.01~\text{cd}$	$307.46 \pm 2.08 a$
average	$\textbf{12.19} \pm \textbf{1.93}$	$\textbf{2.22} \pm \textbf{0.87}$	273.67 ± 15.7	40.47 ± 11.67	2.86 ± 0.92	$\textbf{3.66} \pm \textbf{0.80}$	335.07 ± 22.75

^a Each value is the mean \pm standard deviation of duplicate determinations. Means with different letters in the column for each apricot kernel oil are significantly different (P < 0.05).

of nitrogen. The phytosterols were analyzed with a GC instrument equipped with an FID detector and a fused silica capillary column ZB-5 $(30 \text{ m} \times 0.25 \text{ mm i.d.}, 0.25 \text{ mm film thickness}; Phenomenex, Torrance,$ CA) as the trimethylsilyl (TMS) ether derivatives. To prepare TMS ether derivatives of sterols, 100 μ L of a 1:1 (v/v) mixture of anhydrous pyridine and BSTFA containing 1% TMCS was added to the extracted unsaponifiables and the vials were securely capped with Teflon-lined caps and thoroughly mixed. The samples were held at room temperature for at least 15 min before GC analysis. The injection volume was 1 μ L, the split ratio was 1/10, and the carrier gas was nitrogen at 1.0 mL. The injector, column, and detector temperatures were 280, 260, and 290 °C, respectively. The total phytosterol content was determined considering all peaks of sterol eluted between campasterol and Δ^7 avenasterol. Identification was achieved by comparing the relative retention times from samples with those obtained with standards and olive oil. Peaks were quantified by 5α -cholestane as an internal standard. Δ^5 -Avenasterol, Δ^{5-24} -stigmasterol, and Δ^7 -avenasterol were tentatively identified by comparison with refs 17 and 18. β -Sitostanol and Δ^5 avenasterol eluted very closely, and therefore, they were quantified as Δ^5 -avenasterol. Phytosterol contents were determined in triplicate for single samples of each variety, and average values were reported.

Statistics. Several statistical methods were applied to data. First, the data were analyzed by analysis of variance (ANOVA) using SPSS version 9.0. (SPSS Inc., Chicago, IL). When significant (P < 0.05) differences were found among the kernel oils extracted from different apricot varieties, a Duncan multiple range test was used for comparisons.

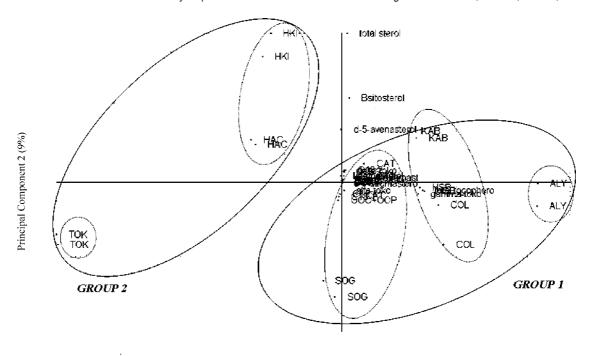
Principal component analysis (PCA) was performed using the varimax rotation between all variables of the samples on the ANOVA results in order to simplify the results obtained. The Varimax rotation method maximizes the sparseness of each of a group of modes by means of an orthogonal rotation. As a result of a Varimax rotation, a new set of modes is produced; each of these new modes will have a few components with large amplitude and many with small or nearly zero amplitude. The Varimax procedure is performed on the subspace of PCs necessary to reconstruct the data to the determined accuracy and not just those correlated to outcome.

The ANOVA was performed on the scores to determine the principal components (PCs) that gave significant differences (P < 0.05) between variables. PCA was carried out using The Unscrambler 9.6 version (CAMO, Software AS, Oslo, Norway). Hierarchical cluster analysis (HCA) was performed using Euclidean distance and average linkage without standardizing the variables. The HCA was performed using SPSS version 9.0.

RESULTS AND DISCUSSION

Total Oil Content and Fatty Acid Composition. The total oil content of kernels from different apricot varieties is presented in **Table 1**. The oil contents, which were found to be significantly different (P < 0.05), ranged from 40.23% (Hasanbey) to 53.19% (Hacıhaliloğlu) with an average value of 46.19%. Therefore, apricot kernel oils could be considered as a rich source in terms of oil content. The total oil contents found in the present study are, in general, comparable to those reported in the literature (4) and lower than those of sweet apricot kernel oils (12).

The fatty acid profiles of apricot kernel oils are shown in **Table 1**. Ten fatty acids were identified, among which oleic acid (18:1 ω 9) contributed 70.83% (average) to the total, followed by linoleic acid (18:2 ω 6) at 21.96%, palmitic acid (16:0) at 4.92%, and stearic acid (18:0) at 1.21%. Changes in the fatty acid composition of apricot kernel oils, except heptadecanoic acid (C17:0), were found to be significant (P < 0.05). Also, significant differences were found between the varieties for total saturated fatty acids (SFAs), total monounsaturated fatty acids (MUFAs), and total polyunsaturated fatty acids (PUFAs). The total SFAs made up small proportions (ranged from 5.77 to 7.13%) of the fatty acids in apricot kernel oils, whereas MUFAs were higher (ranged from 67.41 to 76.69%). The high percentage of linoleic acid in apricot kernel oils makes this oil of high



Principal Component 1 (89%)

Figure 1. Biplots of principal components 1 (89%) and 2 (9%) showing the sample scores and variable loadings from principal component analysis of the data from lipid components for kernel oils from apricot varieties. Apricot kernel oils were abbreviated as Alyanak (ALY), Çataloğlu (CAT), Çöloğlu (COL), Hacıhaliloğlu (HAC), Hacıkız (HKI), Hasanbey (HSB), Kabaaşı (KAB), Soğancı (SOG), and Tokaloğlu (TOK).

nutritional value, as linoleic acid is one of the three essential fatty acids. Average unsaturated fatty acids (MUFAs + PUFAs) accounted for 93.73% of the total fatty acids. The levels of palmitic and oleic acids presented in this study are, in general, comparable to those reported in the literature for different apricot kernel oils (4). On the other hand, higher values have been reported for linoleic acid, ranging from 26.0 to 31.7% (4). When compared to other nut and vegetable oils, including almond (60.93 g/100 g of lipid), cashew nut (61.15 g/100 g of lipid), macadamia nut (58.51 g/100 g of lipid), pecan (66.66 g/100 g of lipid), pistachio (50.29 g/100 g of lipid) (19), berry seed (ranges from 12.4 to 22.9 g/100 g of oil) (20), coconut (7%), palm (43%), rapeseed (54%), and soybean (25%) (21), apricot kernel oil contains the highest proportion of oleic acid. Hence, apricot kernel oils may be used for the production of salad or frying oils.

The fatty acid composition of apricot kernel oils is important from several perspectives, including nutritional quality (the MUFAs and PUFAs being considered more desirable than the SFAs) and possible health benefits offered by MUFAs and PUFAs. When MUFAs (most important: oleic acid) and ω -6 PUFAs (most important: linoleic acid) are supplied instead of SFAs in metabolic studies, they lower total and LDL cholesterol significantly (22, 23). The ability of some unsaturated vegetable oils to reduce the serum cholesterol level may focus attention on apricot kernel oil due to its higher unsaturated oil content.

sn-2 Fatty Acids. The compositions of the fatty acids in the sn-2 position of the apricot kernel oils are shown in Table 2. Changes in the fatty acids of apricot kernel oils in the sn-2 position were found to be significant (P < 0.05). The sn-2 position was mainly occupied with oleic acid (63.54%, ranged from 58.48% in Hacıkız to 71.17% in Tokaloğlu), linoleic acid (35.0%, ranged from 27.51% in Tokaloğlu to 39.59% in Kabaaşı), and palmitic acid (0.96%, ranged from 0.52% in Soğancı to 1.54% in Hacıkız). Similar positional distributions of fatty acids have been reported in peanut oil for oleic, linoleic, and palmitic acids in the ranges of 58, 39, and 1 (mol%),

respectively (24). The composition of the fatty acids in the *sn*-2 position reported in this study can also be considered as reference data for the apricot kernel oils; to the authors' knowledge, no data are available on these compounds.

Triacylglycerol Composition. The fatty acid composition can be used to evaluate the stability and nutritional quality of fats and oils; however, in order to appreciate their physical and functional properties, determination of the type and amounts of TAG species existing in the oil is also essential (25).

The TAG compositions in apricot kernel oils are summarized in **Table 3**. Changes in the TAG compositions of apricot kernel oils were found to be significant (P < 0.05). A complete separation of some TAG species was not achieved under our chromatographic conditions. Therefore, some of them were given together, as shown in Table 3. Eight TAG species were identified, among which mainly trioleoylglycerol + palmitoyldioleoylglycerol (OOO + POO) contributed at 48.64% (average) to the total, followed by dioleoyl-linoleoylglycerol + palmitoyloleoyl-linoleoylglycerol (OOL + POL) at 32.63% and oleoyldilinoleoylglycerol (OLL at 14.33%). When the amount of each fatty acid was considered, the proportion of OOO in the total of OOO + POO was quite a bit higher than that of POO. A similar approach could be used for OOL + POL. Apricot kernel oil from the Tokaloğlu variety contained the highest amount of the OOO + POO TAG species (57.23%), which includes OOO, the main TAG species in olive oil.

There is a small amount of SFAs (6.27%) in total (**Table 1**). So, tri- or disaturated TAG species were not detected. Apricot kernel oils contain higher amounts of di- and triunsaturated forms of TAG, containing mainly oleic acid. There are no published data for comparison of TAG species of the apricot kernel oil from different regions.

Tocopherol Contents. Tocopherols are natural antioxidant compounds which stabilize oils. The tocopherol contents of kernel oils obtained from different apricot varieties exhibited significant variations (P < 0.05) among the varieties, except for β -tocopherol, as indicated in **Table 4**. Four tocopherol

* * * * HIERARCHICAL CLUSTER ANALYSIS * * * *

Rescaled Distance Cluster Combine

Dendrogram using Average Linkage (Between Groups)

CASE 0 10 20 25 15 Label Num HSB 11 HSB 12 COL 5 Cluster 1 COL 6 KAB 13 KAB SOG 15 SOG 16 Cluster 2 CAT CAT 4 ALY 1 2 HAC 7 HAC 8 HKI 9 HKI 10

Figure 2. Hierarchical cluster analysis data from lipid components for kernel oils from apricot varieties. Apricot kernel oils were abbreviated as Alyanak (ALY), Çataloğlu (CAT), Çöloğlu (COL), Hacıhaliloğlu (HAC), Hacıkız (HKI), Hasanbey (HSB), Kabaaşı (KAB), Soğancı (SOG), and Tokaloğlu (TOK).

isomers were identified and quantified, among which γ -tocopherol was the most abundant, with an average concentration of 475.11 mg/kg of oil, contributing 93.6% to the total, followed by α -tocopherol (19.51 mg/kg of oil), δ -tocopherol (12.64 mg/ kg of oil), and a small amount of β -tocopherol (0.38 mg/kg of oil). These results are in good agreement with data previously reported on apricot kernel oils from Egypt (26). Based on a chromatogram available in the literature (27), apricot kernel oils contain α - and δ -tocotrienols in trace amounts. The peak areas of these tocotrienol isomers are smaller than that of β -tocopherol (which matches the average value of 0.4 mg/kg oil). The apricot kernel oil from the Alyanak variety, although low in α -tocopherol compared to the oils from Çöloğlu and Kabaaşı, showed the highest total tocopherols, followed by the oil from Çöloğlu. The oil from the Alyanak variety exhibited the highest concentration of γ -tocopherol (563.40 mg/kg of oil). The results obtained can be used to characterize these apricot kernel oils and facilitate their differentiation from the other oils.

TOK

17 18

Tocopherols are the best known and most widely used antioxidants. They can be classified as tocopherols and tocotrienols, and within each of these two classes, there are four isomers $(\alpha_{-}, \beta_{-}, \gamma_{-}, \text{ and } \delta_{-})$, making a total of eight tocopherol isomers (28, 29). The predominance of one or the other tocol depends on the oil origin. For example, α -tocopherol is the major tocopherol in olive oil (\sim 95%) (30) and sunflower oil $(\sim 94\%)$ (28), while γ -tocopherol is predominant in cactus pear pulp oil (\sim 80%) (30), in soybean oil (\sim 60%), in corn oil (\sim 57%), and in canola oil (\sim 66%) (28). In general, α - and γ -tocopherol comprise more than 60% of the total vitamin E content in a majority of vegetable oils, with some exceptions, such as in palm oil, which is characterized by a high amount of α -tocopherol (\sim 30%) and tocotrienols (\sim 60%) (32). Although it is generally accepted that α-tocopherol has a higher hydrogen donation ability than γ -tocopherol, the latter was often found to be a better antioxidant in some cases (33). When compared to many vegetable oil and nut oils, apricot kernel oils contain a considerable amount of total tocopherols, consisting mainly of γ -tocopherol. Consequently, apricot kernel oils, especially oil from the Alyanak variety, which has the highest amount of γ -tocopherol, can be used for edible purposes alone or mixed with the other vegetable oils to enhance their oxidative stability. However, further investigations are needed for determination of the oxidative stability of apricot kernel oils.

Phytosterol Composition. Table 5 shows the results obtained for the phytosterol compositions of the kernel oils from different varieties of apricot. Six phytosterol isomers were identified, among which β -sitosterol was by far the predominant one. It ranged from 251.40 mg/100 g of oil and to 294.22 mg/100 g of oil in the Soğancı and Alyanak varieties, respectively, with an average content of 273.67 mg/100 g of oil, contributing 81.6% to the total. The second and third phytosterols were always Δ^{3} avenasterol and campesterol with mean values of 40.47 and 12.19 mg/100 g of oil, respectively. All other phytosterol isomers, consisting of stigmasterol, Δ^{5-24} -stigmastadienol, and Δ' -stigmasterol, were present on average in amounts lower than 5 mg/100 g of oil. It was reported that Δ^{5} -avenasterol has an essential antipolymerization effect, which could protect oils from oxidation during prolonged heating at high temperatures (34). The sterol compositions of apricot kernel oils from different apricot varieties showed significant variations (P < 0.05) from one variety to another.

There are no literature data for comparison of the phytosterol compositions of apricot kernel oils from different regions. Meanwhile, compared to some edible oils, apricot kernel oil contained higher levels of total phytosterol, with the average value of 335.1 mg/100 g of oil compared to those of soybean (203–285 mg/100 g of oil), safflower (192 mg/100 g of oil), peanut (167 mg/100 g of oil), olive (68–261 mg/100 g of oil), cottonseed (292 mg/100 g of oil), coconut (70 mg/100 g of oil), palm (66 mg/100 g of oil), borage (226 mg/100 g of oil), sunflower (263 mg/100 g of oil) (35), and hazelnut (164.9 mg/100 g of oil) oils (36).

Phytosterols, primarily β -sitosterol, campesterol, and stigmasterol, are membrane constituents of plants that effectively reduce serum LDL cholesterol and atherosclerotic risk (37). Hence, the consumption of apricot kernel or its oils that contain phytosterols provides potential health benefits.

Existing differences between sterol compositions make them the most suitable for determining the botanical origin of oils and, hence, detecting adulteration among vegetable oils (38). In fact, rape seed oil contains a significant amount of brassicasterol (100-1100 mg/kg), while olive oil has a high level of β -sitosterol (683–2610 mg/kg) and Δ ⁵-avenasterol (34–266 mg/ kg). The amount of Δ^5 -avenasterol, stigmasterol, and its isomers (Table 5) may be used as a tool for adulteration of apricot kernel oil with other oils.

Principal Component Analysis (PCA). PCA was applied to those variables which presented significant (P < 0.05)differences among the samples to clarify separation of them and interpretation of the results. Significant differences among the samples on the first two principal components on the PCA were determined by ANOVA. The results of PCA indicated that the samples were distinguished according to the levels of their lipid components. A biplot of the sample scores and variable loadings for PC1 and PC2 is shown in Figure 1. PC1 and PC2 explained 89 and 9% of the variation between the lipid components of the samples. PCA of the results indicated that the samples were located in two main groups which include subgroups. HCA of the same results highlighted closely related clusters (Figure 2), which were indicated as ovals on the biblot.

The first group (cluster 1) clustered the samples Hasanbey (HSB), Çöloğlu (COL), and Kabaaşı (KAB), indicating the samples contained similar levels of some tocopherol components. The next group (cluster 2) consisted of Soganci (SOG) and Cataloğlu (CAT), and this indicates that these samples had similar fatty acid and TAG compositions. The last group (cluster 4) consisted of Hacıhaliloğlu (HAC) and Hacıkız (HKI), which were characterized as having a higher abundance of sterol contents. The samples Alyanak (ALY) (cluster 3) and Tokaloğlu (TOK) (cluster 5) were located as an individual group and separated from the other samples.

The samples can be classified into two big groups: (group 1) HSB, COL, KAB, SOG, CAT and ALY; (group 2) HAC, HKI, and TOK. The ALY sample contained significantly higher levels of β -sitosterol and γ -, δ -, and total tocopherol, and a higher percentage of OOL + POL, while these lipid components were scarcely present in the TOK sample. The samples including HAC, HKI, and KAB were described as having a higher abundance of β -sitosterol, Δ^5 -avenasterol, and total sterols than those other samples. According to multivariate statistical analysis, the apricot kernel oils in this study were characterized with some lipid components, i.e., TAG, tocopherol, and sterol contents. These techniques were an efficient approach to evaluate and interpret easily the data and gave useful information on the investigated lipid characteristics of apricot kernel oil.

In conclusion, apricot kernel oil could be utilized successfully as a source of edible oils. Apricot kernel oil is a rich source of MUFA and PUFA, including mainly oleic (about 70%) and linoleic acids, respectively, which have been associated with beneficial health effects, and compared to many oils, it has the advantage of presenting lower contents of SFAs. Hence, apricot kernel oil may be used for the production of salad or frying oils. Apricot kernel oil contains higher amounts of the di- and triunsaturated forms of TAG, containing mainly oleic acid. In addition, apricot kernel oil could be considered as a good source of bioactive compounds such as tocopherols and phytosterols, consisting mainly of the γ -isomer and β -sitosterol, respectively. PCA was successfully applied to data and gave useful information on the investigated lipid characteristics of apricot kernel oil. On the other hand, there are no reports available on the fatty acids located on the sn-2 position or on the TAG, tocopherol, and phytosterol contents of apricot kernel oils; hence, this study may be important in terms of the potential nutritional, functional, and economic utility of apricot kernel oils as a new source of oil. However, further in vivo and in vitro investigations are needed for determining health effects and the oxidative status of apricot kernel oils.

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