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Turkish Tombul Hazelnut (*Corylus avellana* L.). 2. Lipid Characteristics and Oxidative Stability

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The quality of crude hazelnut oil extracted from Tombul (Round) hazelnut, grown in the Giresun province of Turkey, was determined by measuring lipid classes, fatty acids, and fat soluble bioactives (tocopherols and phytosterols). Oxygen uptake, peroxide value, thiobarbituric acid reactive substances, and α-tocopherol levels of stripped and crude hazelnut oils in bulk and oil-in-water (o/w) emulsion systems were also evaluated as indices of lipid oxidation over a 21 day storage period at 60 °C in the dark. The total lipid content of Tombul hazelnut was 61.2%, of which 98.8% were nonpolar and 1.2% polar constituents. Triacylglycerols were the major nonpolar lipid class and contributed nearly 100% to the total amount. Phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol were the most abundant polar lipids, respectively. Sixteen fatty acids were identified, among which oleic acid contributed 82.7% to the total, followed by linoleic, palmitic, and stearic acids. Unsaturated fatty acids accounted for 92.2% of the total fatty acids present. Among oil soluble bioactives, α-tocopherol (38.2 mg/100 g) and β-sitosterol (105.5 mg/100 g) were predominant in hazelnut oil and comprised 88 and 93% of the total tocopherols and phytosterols present, respectively. The results also showed that both stripped and crude hazelnut oils were more stable in terms of lipid oxidation in the bulk oil as compared to those in an o/w emulsion.

KEYWORDS: Tombul hazelnut; hazelnut oil; lipid classes; fatty acids; tocopherols; phytosterols; oxidative stability; bulk systems; emulsions

INTRODUCTION

Turkey is the main hazelnut producer in the world (approximately 650 000 MT in 2001, unshelled basis), contributing approximately 70% of the total global production, followed by Italy (about 130 000 MT/year), the U.S. (about 45 000 MT/year), and Spain (about 25 000 MT/year). Turkey's total export revenue from hazelnut and hazelnut products is approximately 1 billion U.S. dollars annually (*1*).

Hazelnut oil is becoming increasingly popular in the Black Sea region and most parts of Turkey. Annual production of hazelnut oil in Turkey has increased considerably in recent years, from 5165 MT/year in 1990 to 33 471 MT/year in 2001 (*1*). More than two-thirds of the families in the Giresun province of Turkey consume hazelnut oil for cooking, deep frying, and salad dressing instead of other vegetable oils. It is, therefore, of great interest to assess the quality of hazelnut oil extracted from the Tombul hazelnut.

Among nut species, hazelnut plays a major role in human nutrition and health, because of its special fatty acid composition, which includes oleic and linoleic acids as well as the presence of tocopherols and sterols. Hazelnut provides an excellent source of energy due to its high oil content of approximately 60% (*2*). Several research groups have reported the benefits of inclusion of nuts in the human diet (*3*−*7*). These effects could be related to the fatty acid profile of hazelnut oil, which is rich in MUFA and PUFA (*8*−*10*). Studies have shown that diets low in saturated fat and high in MUFA are effective in controlling blood lipid levels, a likely consequence of which may be rendering beneficial effects on the risk of CHD (*11*−

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13). In addition, diets rich in MUFA (high in hazelnut oil) exert positive effects in the reduction of blood pressure, reduction of mean total CHOL, decrease of LDL CHOL, increase of HDL CHOL, and decrease of blood TAG in humans (*7*, *14*−*16*).

Tocopherols are particularly important in hazelnut oil because they have a nutritional function for humans as vitamin E and display antioxidant activities in vivo and in vitro; α-tocopherol has the highest vitamin E activity (*17*). In addition, tocopherols, in association with polyphenols and other substances, contribute to the stabilization of hazelnut oil and their quantity may reflect the oxidative state of the oil. There is also growing research interest in the role of these compounds beyond their antioxidative function. Although the mechanism of their action is not yet clearly understood, there is strong evidence that tocopherols play an important role in the prevention of some chronic diseases such as heart disease and certain types of cancers (*18*).

Recently, the health aspects of β-sitosterol, which is found in high amounts in hazelnut oil (*19*), in the reduction of CHOL levels and the prevention of many diseases and various types of cancer (colon, prostate, and breast) have been reported. This includes inhibition of tumor growth and stimulation of apoptosis (*19*−*24*).

Evaluation of oxidative stability of bulk oil vs o/w emulsions has shown that differences observed depend on the nature of minor components in the systems involved. However, interpretation of the results has not always been straightforward. Such inconsistent results may originate from changes in oxidation conditions and application of analytical methods that measure different endpoints of lipid oxidation (*25*). Oxidative stability of fats and oils depends on their environment, and there are differences in their rate of oxidation in the bulk vs o/w emulsions (*25*−*28*). Lipid oxidation negatively affects the flavor, odor, color, and nutritional value of foods during storage, and this may also limit the utilization of hazelnut oil in processed and fortified foods as well as nutritional supplements. It is, therefore, important to evaluate the oxidative stability of hazelnut oil as affected by processing and storage conditions.

The objectives of this research were to investigate lipid class, fatty acid, tocopherol, and sterol compositions of crude hazelnut oil extracted from Turkish Tombul hazelnut and to assess oxidative stability of both stripped and crude hazelnut oils in bulk and o/w emulsion systems. The health aspects of these components, where possible, are also discussed.

MATERIALS AND METHODS

Samples. The sun-dried (commercial way of drying) premium class natural Tombul (Round) hazelnut variety (*Corylus avellana* L.) was procured from the Giresun province of Turkey at the beginning of the harvest season (August 2001) and kept unshelled in a dark room at 5 °C until analyses were carried out (all analyses were completed within 3 months). The hazelnuts were shelled before analysis. All chemicals were obtained from Sigma-Aldrich-Fluka Company Ltd. (Dorset, U.K.), unless otherwise specified. NBD-labeled PC was obtained from Avanti Polor Lipids, Inc. (Alabaster, AL). The oil used for different analyses was extracted from the Tombul hazelnut.

Total Fat Content. The total fat content was determined in accordance with the official method (Soxhlet method, 920.39C) of the Association of Official Analytical Chemists (*29*).

Analysis of Fatty Acids. FAMEs were prepared from hazelnut oil and determined by GC according to the method described by Slover and Lanza (*30*) with minor modifications. FAMEs were prepared using boron trifluoride in methanol (20% of BF_3 in methanol) and extracted with *n*-hexane and then analyzed by GC. For this purpose, samples (1 μL) were injected into a Supelcowax 10 column (60 m × 0.25 mm i.d., 0.25 μm film thickness; Supelco, Bellefonte, PA) coated with poly(ethylene glycol). The column was connected to a Hewlett-Packard 5890 Series II (Little Falls, Wilmington, DE) gas chromatograph equipped with a FID. The oven temperature was programmed as follows: 180 °C for 2 min, raised to 200 °C at 2 °C/min, held at 200 °C for a further 10 min, and then raised to 215 °C at 2 °C/min and kept there for 10 min. The injector and detector temperatures were 200 and 250 °C, respectively. Helium was used as the carrier gas at a flow rate of 1.5 mL/min. FAME identification was based on retention times compared with those of standard FAMEs.

Analysis of Lipid Classes. Identification and quantification of major lipid classes were carried out by Iatroscan TLC−FID.

(i) Instrumentation. The crude lipids were chromatographed on silica gel-coated Chromarods S III and then analyzed on an Iatroscan MK-5 (Iatroscan Laboratories Inc.,Tokyo, Japan) analyzer equipped with a FID connected to a computer loaded with TSCAN software (Scientific Products and Equipment, Concord, ON) for data handling. A hydrogen flow rate of 160 mL/min and an air flow rate of 2000 mL/min were used in operating the FID. The scanning speed of the rods was 30 s/rod.

(ii) Preparation of Chromarods. The Chromarods were soaked in concentrated nitric acid overnight, followed by thorough washing with distilled water and acetone. The Chromarods were then impregnated by dipping in a 3% (w/v) boric acid solution for 5 min in order to improve separation. Finally, the cleaned Chromarods were scanned twice to burn any remaining impurities.

(iii) Standards and Calibration. A stock solution of each of the nonpolar lipids, namely, FFA (oleic acid), CE, CHOL, MAG (monoolein), DAG (diolein), and TAG (triolein), and the polar lipids, namely, PC, PE, PI, PS, LPC, LPE, CL, and SM, was prepared by dissolving them in chloroform/methanol (2:1, v/v) and storing them at −20 °C. A range of dilutions of the stock solution from 0.1 to 10 mg/mL was prepared for use as working standards. Each compound was developed individually and run on the Iatroscan FID to determine its purity and R_f value. For each compound, the peak area was plotted against a series of known sample concentrations to obtain the calibration curve.

(*iv*) *Iatroscan TLC−FID Analysis of Lipids.* The total lipid extract was dissolved in chloroform/methanol (2:1, v/v) in order to obtain a concentration of 1 mg lipid per mL. A 1 mL aliquot of sample was spotted on silica gel-coated Chromarods S III and conditioned in a humidity chamber containing saturated $CaCl_2$ for 20 min. The Chromarods were then developed in two solvent systems. First, hexane/diethyl ether/glacial acetic acid (80:20:2, v/v/v) was used as the solvent system for nonpolar lipids (*31*). Following their development, the Chromarods were dried at 110 °C for 3 min and scanned completely to reveal nonpolar lipids. For polar lipids, the Chromarods were first developed in the same solvent system as used for nonpolar lipids and then dried at 110 °C for 3 min to remove solvents. This was scanned partially to a point just beyond the MAG peak to burn the nonpolar lipids. These partially scanned Chromarods were developed in a second solvent system of ethyl acetate/propan-2-ol/chloroform/methanol/0.25% aqueous KCl (25:25:25:10:9, v/v/v/v/v) for the separation of polar lipid classes (*31*). After they developed, the Chromarods were dried at 110 °C for 3 min and scanned completely to reveal polar lipids. The identity of each peak was determined by comparison with a chromatogram of standards acquired concurrently with the samples. The percentages of individual lipid classes (by weight) were determined using the standard curves procured for each authentic standard.

Analysis of Tocol Isomers. Tocol isomers were analyzed according to the HPLC method of Katsanidis and Addis (*32*) with a slight modification. A 2 g sample of grated hazelnut was homogenized (PowerGen 700, Fisher Scientific, Pittsburgh, PA) for 30 s with 8 mL of absolute methanol inside a 100 mL plastic tube. Subsequently, 10 mL of HPLC grade water was added and the mixture was homogenized again for 15 s. After that, 8 mL of hexane was added and the mixture was rehomogenized for another 15 s. Finally, the plastic tube was capped and centrifuged (Damon/IEC Division, Needham Heights, MA) at 629*g* for 10 min at 4 °C. After 10 min, the upper layer (hexane) was collected carefully into an airtight amber bottle (10 mL capacity) for HPLC analysis. Vials were flushed with nitrogen and stored at 2 °C prior to the HPLC analysis because tocol isomers are very sensitive to air and heat.

The collected hexane layer was filtered through a GELMAN Acrodisc LC13 PVDV 0.45 μm pore size syringe filter (PALL Life

Sciences, Ann Arbor, MI) and injected (20 μL) into a Zorbax Silica column (220 mm × 4 mm i.d.; Rockland Technologies, Chadds Ford, PA). The unit consisted of a Varian 9050 UV detector, Varian 9010 solvent delivery system, and Varian Star 5.3 software (Varian Chromatography Systems, Walnut Greek, CA). The mobile phase (filtered through a 0.45 μm Millipore filter and degassed prior to use) was 1% 2-propanol in hexane at a flow rate of 1.3 mL/min. The UV detector was set at 295 nm. Pure standards of tocol isomers were used for identification and quantification in hazelnut oils according to the calibration curves so constructed. Tocol levels in hazelnut oils were calculated using the percentage of oil content measured in Tombul hazelnut (61.2%).

Analysis of Phytosterols. (*i*) *Saponification.* Phytosterols were determined by GC according to the method described by Slover et al. (*33*). Approximately 100 mg of oil was placed in a screw-capped glass tube and 1 mL of IS containing ~40 mg of 5α-cholestane was added. The solvent was removed with a stream of nitrogen while tubes were heated to 40−45 °C in a water bath. The removal of all traces of solvent, particularly chloroform, was essential to avoid degradation of unsaponifiables, especially sterols. After the solvent was removed, the tubes were removed from the heat and 8 mL of 3% ethanolic solution of pyrogallol was added while keeping the tubes under nitrogen for an additional 2 min without interrupting the nitrogen flow. Saturated aqueous KOH (0.5 mL) was added, and the tubes were quickly sealed with Teflon-lined screw caps. The samples were vigorously mixed using a Vortex for ~5 s and then heated for 8 min in a water bath at 80 °C. The tubes were shaken vigorously three times during that period. After 8 min, the tubes were removed from the water bath and cooled under cold tap water for 15 s.

(*ii*) *Extraction of Unsaponifiables.* Cyclohexane (20 mL) was added to the saponified sample, followed by 12 mL of distilled water. The tubes were recapped, shaken vigorously for exactly 2 min, and then centrifuged at 1200*g* for 5 min. The clear upper layer of cyclohexane was transferred to another glass test tube, and the extraction process was carried out three times. The pooled cyclohexane layer was evaporated to dryness using nitrogen.

(*iii*) *Derivatization.* Pure dry pyridine (50 μL) and 50 μL of BSTFA containing 1% TMCS were added to the extracted unsaponifiables, and the tubes 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 reaction mixture in pyridine was injected directly into the GC column.

(*iv*) *GC.* For this purpose, a fused-silica capillary column SAC-5 (30 m × 0.25 mm i.d., 0.25 μm film thickness; Supelco) was used. The column was connected to a Hewlett-Packard 5890 Series II (Little Falls) gas chromatograph equipped with a FID, an automatic liquid sampler (HP 7673), and a glass splitter system. The GC oven temperature was set at 240 °C isothermal. The injector and detector temperatures were 270 and 300 °C, respectively. Helium was used as the carrier gas at an inlet pressure of 11 psi, and the split ratio was 1:40. The sterols were identified by comparing the relative retention times of 5α-cholestane with those of corresponding standards.

Oxidative Stability of Hazelnut in Oil Systems. *(i) Stripping of Oil.* Crude hazelnut oil was stripped by column chromatography (72 cm length × 6 cm i.d.) on silica gel 60 (spherical, 40−50 μm, Kanto Chemical Co. Inc., Tokyo, Japan) to remove polar compounds and natural tocopherols. For this purpose, a 35 g portion of the oil was charged on the column and eluted with *n*-hexane, followed by 7% (v/v) diethyl ether in *n*-hexane.

(*ii*) *Preparations of o/w Emulsion.* A 50 mL portion of the o/w emulsion containing 15 g of stripped hazelnut oil and 1.5 g of Tween-20 in 0.05 M phosphate buffer (pH 7.0) was prepared as a control sample by using an Ultrasonic Disruptor UD-200 (Tomy Tech USA, Inc., Fremont, CA) for 6 min at 20 °C.

(*iii*) *Oxidation of Stripped Hazelnut Oil.* For determination of PV and TBARS, a 25 mL portion of each test emulsion was placed in an Erlenmeyer flask. The flask was kept in an oven set at 60 °C in the dark. For determination of O_2 uptake, a 10 mL portion of the emulsion was taken in a glass vial (60 mL) and subsequently sealed tightly with an aluminum cap with PTFE silicone liner (20 mm, Supelco). The oils were stored at 60 °C in the dark while being shaken gently.

Table 1. Lipid Classes of Oil Extracted from Tombul Hazelnut[a]

nonpolar lipids (98.8%)		polar lipids (1.2%)	
TAG	~100%	PC	56.4 ± 3.4%
		PE	30.8 ± 4.6%
		PI	11.7 ± 1.8%

[a] Data are expressed as mean ± SD ($n = 3$).

(*iv*) *Oxidation of Crude Hazelnut Oil.* A parallel study (at a different time) was carried out to evaluate the oxidative stability of crude hazelnut oil in bulk and o/w emulsion systems. Similar o/w emulsion preparations and oxidation conditions to those explained above were employed. Determination of PV and O_2 uptake was carried out throughout the 21 day storage period, whereas TBARS and α-tocopherol were determined only on day 1 and day 21.

(*v*) *Analysis of PV.* The formation of peroxides was measured by determining PV by employing a slightly modified version of the procedure reported by Ohshima et al. (*34*, *35*) using a flow injection system with a DPPP (Dojindo Co., Kumamoto, Japan) postcolumn fluorescence detection. Briefly, a mixture of 1-butanol:methanol (2:1, v/v) was used as the mobile phase at a flow rate of 0.5 mL/min. The DPPP solution (5 mg of DPPP and 100 mg of BHT in a 200 mL 1-butanol:methanol (2:1, v/v) mixture) was pumped into a stainless steel reaction coil (40 mm × 0.25 mm i.d.) at a flow rate of 0.3 mL/min. The peroxides in the sample reacted with DPPP to form DPPP oxide in the coil and were subsequently detected with a fluorescence HPLC monitor RF535 (Shimadzu, Kyoto, Japan) at an Em wavelength of 380 nm and an Ex wavelength of 535 nm. NBD-labeled PC was used as an IS and detected at Em 534 nm and Ex 460 nm using a Shimadzu spectrofluorometric detector RF 10AxL, which was set in the flow line behind the first fluorescent detector. A calibration curve was constructed as follows: cumene hydroperoxide (Aldrich Chemical Co. Inc., Milwaukee, WI) was mixed with NBD-labeled PC as an IS in methanol. The peak area ratios of cumene hydroperoxides vs the IS were plotted against the mole ratio of the compounds to obtain a calibration curve. PV was expressed as meq of hydroperoxide/kg of hazelnut oil.

(*vi*) *Analysis of TBARS.* The TBARS value was determined according to the official method (Cd19-90) of the American Oil Chemist's Society (*36*). Results were expressed as mg of malonaldehyde equivalents/kg of hazelnut oil.

(*vii*) *Analysis of O_2 Uptake.* The O_2 uptake was measured according to the GC method of Ohshima et al. (*37*). A 0.1 mL portion of the headspace gas from the vial was withdrawn using a gastight microsyringe (24 G needle) and then injected into a glass column (1.7 m length × 2.5 mm i.d.) packed with molecular sieve 5A (80−100 mesh, Nihon Chromato Co. Ltd., Tokyo, Japan). The column was connected to a Shimadzu gas chromatograph GC3BT equipped with a TCD. Helium was used as a carrier gas at an inlet pressure of 1.2 kg/cm^2. O_2 uptake was expressed as mL of O_2 uptake/g of hazelnut oil.

(*viii*) *Analysis of α-Tocopherol.* α-Tocopherol was determined according to the HPLC procedure of the official method (Ce8-89) of the American Oil Chemist's Society (*36*).

Statistical Analysis. Data were analyzed by SAS software (*38*). The mean and SD were determined, and the differences between treatments were tested by ANOVA. The level of significance was $p < 0.05$. All determinations were performed in triplicate, unless otherwise specified.

RESULTS AND DISCUSSION

Lipid Classes. The total lipid content of Tombul hazelnut was 61.2 ± 1.0%. The lipid extract from hazelnut was composed of nonpolar (98.8%) and polar (1.2%) components. The main nonpolar lipid class, as identified by Iatroscan TLC−FID, in hazelnut oil was TAG, which contributed nearly 100% to the total (**Table 1**). TAGs are the major storage reserve in hazelnut (*19*). However, traces of DAGs, FFAs, and sterols were also present. The polar lipids were comprised of three lipid classes, namely, PC, PE, and PI, which contributed 56.4, 30.8, and

Table 2. Fatty Acids Composition of Oil Extracted from Tombul Hazelnut[a]

fatty acids	(%)
14:0	0.03 ± 0.00
15:0	0.02 ± 0.00
16:0	4.85 ± 0.02
16:1	0.16 ± 0.00
17:0	0.04 ± 0.00
17:1	0.07 ± 0.00
18:0	2.73 ± 0.00
18:1ω9	82.72 ± 0.04
18:2ω6	8.89 ± 0.01
18:3ω3	0.10 ± 0.00
20:0	0.14 ± 0.00
20:1ω9	0.16 ± 0.00
22:0	0.03 ± 0.00
22:1ω9	0.03 ± 0.01
24:0	0.01 ± 0.00
24:1ω9	0.02 ± 0.00
∑ SFA	7.85
∑ MUFA	83.16
∑ PUFA	8.99
(∑ MUFA + ∑ PUFA)/(∑ SFA)	11.74

[a] Data are expressed as mean ± SD ($n = 3$); ∑, total.

11.7% to the total polar lipids, respectively. Parcerisa et al. (*9*) reported that TAGs were the major nonpolar lipid class (98.4%) while MGDG, PI, and PC were the main polar lipid classes of hazelnut oil. MGDG was most predominant in the polar lipid fraction. Parcerisa et al. (*39*) further analyzed nonpolar and polar lipid components of hazelnut oil during fruit development and showed that TAG was the main nonpolar and PC, PE, and PI were the most abundant polar lipid classes. In addition, traces of phosphatidic acid were present. Thus, results obtained in the present study lend further support to the previously published data.

Fatty Acids. The fatty acid composition of Tombul hazelnut oil is shown in **Table 2**. Sixteen fatty acids were identified among which oleic acid (18:1ω9) contributed 82.72% to the total, followed by linoleic acid (18:2ω6) at 8.89%, palmitic acid (16:0) at 4.85%, and stearic acid (18:0) at 2.73%. The remaining fatty acids contributed only 0.8% to the total fatty acids present. Parcerisa et al. (*9*) reported that oleic acid was dominant in the nonpolar lipid class (TAG), whereas linoleic, palmitic, and stearic acids were most predominant in the polar lipid class in hazelnut oil.

It has been reported that the ratio of oleic acid to linoleic acid varies among varieties of hazelnuts and that the concentrations of the two were inversely related (*2*, *19*, *40*). The present results are comparable to those reported in the literature (*2*, *8*, *10*, *19*, *41*−*43*). However, it should be noted that the variety, geographical origin, growing practices, use of fertilizer, harvesting time, season, climate, latitude, and storage conditions (light, temperature, and humidity) influence hazelnut fatty acid composition, both between and within varieties (*2*, *8*, *10*, *19*, *39*, *44*).

The total SFA made up a small proportion (<8.0%) of the fatty acids of hazelnut oil, whereas total MUFA was the highest (>83%). Unsaturated fatty acids (MUFA + PUFA) accounted for 92.2% of the total fatty acids present. Beneficial effects of high levels of MUFA (mainly oleic acid) in hazelnut oil for the human diet have been reported (*7*, *9*, *14*−*16*). As compared to other nuts and vegetable oils, hazelnut oil has been reported to contain the highest proportion of oleic acid (*42*, *45*).

It has been reported that the total SFA ranged from 13.7 to 24.4% for Italian, Tunisian, and Greek olive oils (*46*, *47*). These values are significantly higher than the 7.85% observed in the hazelnut oil in this study (**Table 2**). Therefore, hazelnut oil, in terms of its high proportion of unsaturated fatty acids, is much more desirable.

On the other hand, unsaturated fatty acids are susceptible to autoxidation (*2*, *8*). The rates of oxidation of fatty acids are approximately 1:10:100:200 for stearic (18:0), oleic (18:1ω9), linoleic (18:2ω6), and linolenic (18:3ω3) acids, respectively (*48*). Therefore, varieties with a lower level of linoleic acid and a higher level of oleic acid at the same level of stearic acid are more stable to oxidative changes. Pershern et al. (*49*) used the ratio of unsaturated to SFA to predict the shelf life of hazelnuts oils; the lower the ratio was, the longer was the shelf life. This ratio was 11.74 for Tombul hazelnut oil (**Table 2**), which is higher than values reported for other Turkish varieties of hazelnut oil (*43*).

Table 3. Tocopherol and Phytosterol Compositions of Oil Extracted from Tombul Hazelnut[a]

tocopherols	mg/100 g oil	phytosterols	mg/100 g oil
α-tocopherol	38.23 ± 0.83	campesterol	7.15 ± 0.38
β-tocopherol	1.15 ± 0.03	stigmasterol	0.89 ± 0.10
γ-tocopherol	3.89 ± 0.29	β-sitosterol	105.48 ± 8.37
δ-tocopherol	0.18 ± 0.03		
total	43.45 ± 1.17	total	113.52 ± 8.78

[a] Data are expressed as mean ± SD ($n = 3$).

Tocopherols. The content of tocopherols in freshly extracted oil of Tombul hazelnut is shown in **Table 3**. Among the tocopherols identified, α-tocopherol was most abundant accounting for 88% of the total (38.23 mg/100 g), followed by γ-tocopherol (3.89 mg/100 g), β-tocopherol (1.15 mg/100 g), and a small amount of δ-tocopherol (0.18 mg/100 g).

Savage et al. (*19*) compared the tocopherol content of oils extracted from six different commercial hazelnut cultivars (Whiteheart, Barcelona, Butler, Ennis, Tonda di Giffoni, and Campanica) grown in New Zealand. They also reported that α-tocopherol was the major tocopherol present with concentrations ranging from 19.9 to 40.9 mg/100 g, followed by γ-tocopherol (from 1.9 to 14.9 mg/100 g), β-tocopherol (from 0.6 to 1.7 mg/100 g), and δ-tocopherol (from 0.1 to 0.7 mg/100 g) in the oils. In addition, Ebrahem et al. (*42*) compared the tocopherol content of 17 varieties of hazelnut oil. Their results also showed that α-tocopherol was the predominant tocopherol in all hazelnut varieties, being highest in Tombul (43.4 mg/100 g oil) and lowest in Ennis (30.2 mg/100 g oil). Although β-tocopherol and δ-tocopherol were found in small amounts, no δ-tocopherol was detected in their study. Varietal differences in tocopherol content of hazelnut cultivars have been reported in both studies. Geographical origin, climate, harvesting year, storage conditions, culture conditions, and the composition of soil might also affect the tocopherol composition of hazelnut oils.

Hazelnut oil has been reported to contain the highest α-tocopherol level among nut oils, and only sunflower oil contained a higher content of α-tocopherol than that of hazelnut oil (*42*, *50*, *51*). Depending on varieties, hazelnut oil contained 2−3 times more α-tocopherol than extra virgin olive oil (*50*, *52*).

Phytosterols. The most common phytosterols, namely, β-sitosterol, campesterol, and stigmasterol, were found in Tombul hazelnut oil (**Table 3**). Among them, β-sitosterol comprised 93% of the total (105.48 mg/100 g), followed by campesterol (7.15 mg/100 g) and a minor amount of stigmasterol (0.89 mg/100 g). No CHOL was present.

Phytosterol contents found in this study were slightly lower than those reported in the oils extracted from six different commercial hazelnut cultivars grown in New Zealand (*19*). Also, small amounts of CHOL, Δ5-avenasterol, Δ7-avenasterol, and Δ7-stigmasterol were reported (*19*). This could be due to either varietal, geographical location, harvesting period, or environmental conditions (*53*). Significant differences in individual and total phytosterol content in hazelnut oils among different cultivars have been reported (*19, 43*).

β-Sitosterol content of olive oil was 102 mg/100 g (*45*), which is slightly lower than that of hazelnut oil (105.48 mg/100 g). β-Sitosterol has been reported to be the main sterol in olive oil (75−90% of the total sterol) (*47, 54, 55*).

There is an increasing interest in commercial sources of phytosterols to be used as "nutraceuticals" for addition to margarines and spreads as it appears that they can inhibit the uptake of CHOL from the diet. Phytosterols have been known to reduce the level of serum total and LDL CHOL by lowering their intestinal absorption. Numerous well-designed studies have documented the beneficial role of phytosterols on serum CHOL (*24, 56−61*). The consumption of margarine containing 10% phytosterols resulted in a 13% reduction in total and LDL CHOL in normal and mildly hypercholesterolemic patients (*57*). In addition, recent reports claim that phytosterols have beneficial effects in the treatment of benign prostatic hyperplasia, rheumatoid arthritis, allergies, and stress-related illnesses and may inhibit the development of colon cancer (*62*).

High plasma CHOL levels are a known risk factor for the development of CHD (*24*). Studies have suggested that lowering plasma CHOL levels may reduce the incidence of a first heart attack, overall death from heart disease, and the need for heart surgery. Phytosterols have received FDA clearance as GRAS substances. In the U.S., foods containing plant sterol esters can carry health claims (*63*). Hence, the consumption of foods such as hazelnut oil, which contain phytosterols, provides potential health benefits.

Oxidative Stability of Hazelnut in Oil Systems. To evaluate the oxidative stability of both stripped and crude hazelnut oils in bulk and o/w emulsion systems, the levels of O_2 uptake, PV, TBARS, and α-tocopherol were determined as indices of lipid oxidation. **Figure 1A**,**B** shows the changes in O_2 uptake of stripped and crude hazelnut oils in bulk and o/w emulsion systems, respectively. The amount of O_2 absorbed in the bulk of stripped hazelnut oil showed a steady increase during 21 days of storage; however, a much higher rate of O_2 consumption ($p < 0.01$) was observed after 4 days in the o/w emulsion as compared to that of the bulk oil system (**Figure 1A**). For crude hazelnut oil, the amount of O_2 absorbed in both oil systems increased linearly and in a similar fashion, but the level of O_2 consumption in o/w emulsion was again higher than that of the bulk oil (**Figure 1B**). The O_2 consumption rate behaved differently in both bulk and o/w emulsion systems. The tocopherols in crude hazelnut oil act as natural antioxidants and slow the rate of O_2 consumption. In addition, crude hazelnut oil contains minor components other than tocopherols. For example, FFAs promote oxidation, but phospholipids, especially PE, inhibit oxidation in a synergistic manner with α-tocopherol. Therefore, better stability of crude hazelnut oil as compared to its stripped counterpart would be due to the combined effect of antioxidative and prooxidative compounds present in the oil.

The changes of PV for both stripped and crude hazelnut oils in bulk and o/w emulsion systems are illustrated in **Figure 2A**,**B**, respectively. In the bulk system of stripped hazelnut oil, PV remained almost unchanged at a very low level (<3.38 meq/kg oil) over 21 days (**Figure 2A**), whereas the peroxides accumulated in the o/w emulsion to a high level after 12 days of storage. With respect to crude hazelnut oil (**Figure 2B**), PV in the o/w emulsion reached a plateau after 17 days and then decreased throughout the rest of the storage period, whereas PV in the bulk oil system showed a gradual increase. Different patterns of oxidation were observed in both stripped and crude hazelnut oils. The bulk stripped hazelnut oil had a much lower PV than that of the crude oil over the entire storage period. The removal of initial hydroperoxides and their secondary products as well as photosensitizing pigments, such as chlorophylls, if present in the oil may slow down the oxidation of stripped oil.

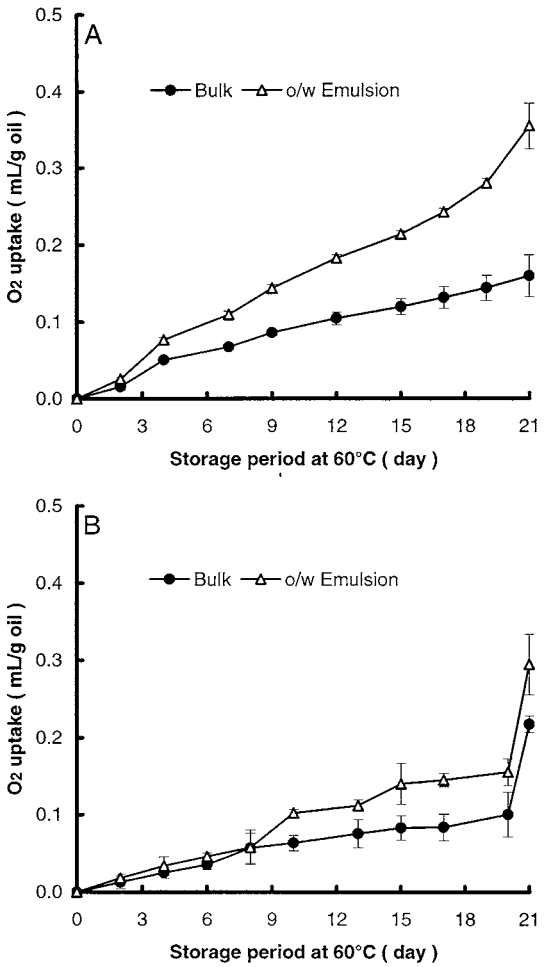

Figure 1. Changes in O_2 uptake levels of stripped (**A**) and crude (**B**) hazelnut oils in bulk and in o/w emulsion. Error bars show the variations of five determinations in terms of SD.

Changes in TBARS values of stripped hazelnut oil in both bulk and o/w emulsion systems are illustrated in **Figure 3A**. The initial levels of TBARS in both bulk and o/w emulsion systems were 0.002 and 0.21 mg/kg oil, respectively. The level in the bulk oil system showed a slight increase up to day 12 (0.025 mg/kg oil) and then decreased to 0.004 mg/kg oil until day 21. In contrast, the level of TBARS in the o/w emulsion system showed a fluctuating trend with higher levels. TBARS reached a plateau (0.51 mg/kg oil) after 19 days and then decreased to 0.23 mg/kg oil on day 21. For crude hazelnut oil, the initial concentrations of TBARS were very low (<0.005 mg/kg oil) in both bulk and o/w emulsion systems. Meanwhile, the level of TBARS in the o/w emulsion on day 21 was about seven times higher than that in the bulk oil system (**Figure 3B**). The much higher level of TBARS in crude hazelnut oil as

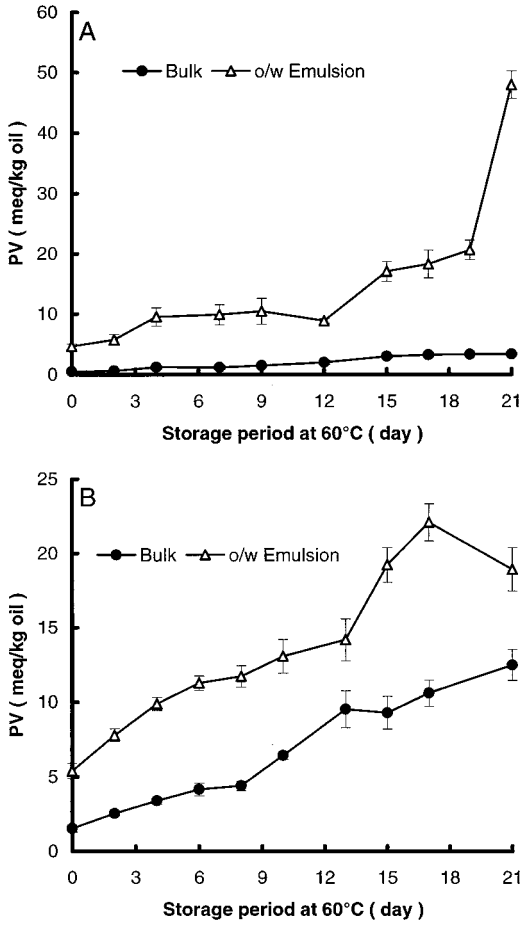

Figure 2. Changes in PV levels of stripped (**A**) and crude (**B**) hazelnut oils in bulk and in o/w emulsion. Error bars show the variations of five determinations in terms of SD.

compared to stripped hazelnut oil could again be due to the stripping process in which the initial oxidation products and possibly the photosensitizing chlorophylls in the stripped oil were almost completely removed.

Results illustrated in **Figures 1**−**3** demonstrate that stripped and crude hazelnut oils in both bulk and o/w emulsion systems behaved differently with respect to their oxidative stability. During a 21 day storage period, the o/w emulsion of both hazelnut oils was quite unstable as compared to the corresponding bulk oil systems. A similar oxidation pattern was observed for sunflower oil (*64*), algae and fish oils (*25*), and stripped and nonstripped borage and evening primrose oils (*27*). The large difference in oxidation behavior of hazelnut oil in bulk and o/w emulsion systems may be due to a number of factors that accelerate oxidation in the o/w emulsion. Previous studies have shown that the type of emulsifier and concentration in fish oil-based structured lipid emulsions affected their oxidation rates (*65*). A higher emulsifier concentration in mayonnaise gave lower PVs (*66*). It has been documented that the presence of metals such as iron can lead to deterioration of lipids in o/w emulsion systems (*25*, *67*, *68*). To optimize the stability of hazelnut oil in the o/w emulsion, a better understanding of the role of its constituents is required. Different concentrations and types of emulsifier as well as characteristics of the buffer used as a continuous phase need to be investigated. Moreover, the influence of the physical state and size of the droplets, the molecular structures of lipids and antioxidant components, the pH, and the effects of various food ingredients still need to be elucidated.

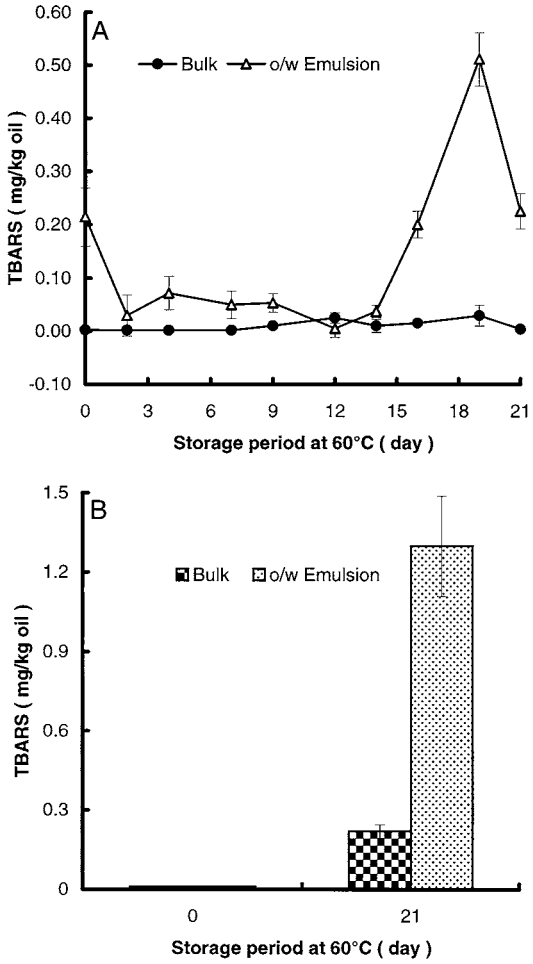

Figure 3. Changes in TBARS values of stripped (**A**) and crude (**B**) hazelnut oils in bulk and in o/w emulsion. Error bars show the variations of five determinations in terms of SD.

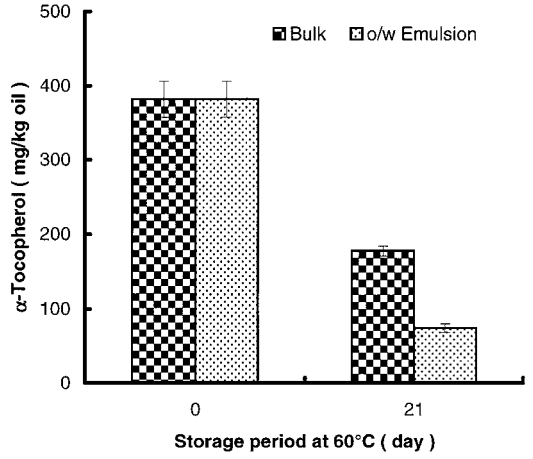

Figure 4. Changes in α-tocopherol contents of crude hazelnut oil in bulk and in o/w emulsion before and 21 days after oxidations. Error bars show the variations of five determinations in terms of SD.

Another important aspect in the stability of hazelnut oil is the role of natural antioxidants in both systems. Tocopherols are the most important antioxidants present in vegetable oil-derived foods. No detectable amount of α-tocopherol was found in stripped hazelnut oil. **Figure 4** shows the changes in α-tocopherol of crude hazelnut oil in both systems. The results showed that α-tocopherol in the bulk oil was more stable than that of the o/w emulsion. The level of α-tocopherol was reduced

(54% in bulk and 81% in the o/w emulsion) upon storage for 21 days. The higher loss of α-tocopherol in the o/w emulsion system appears to correspond to the higher rate of oxidation, which negatively affects the stability of products.

Ohshima et al. (*37*) observed a synergistic effect between the amount of α-tocopherol and the variation of phospholipids in fish lipids by using O_2 uptake, PV, and TBARS as oxidation indices. α-Tocopherol may act as an antioxidant or prooxidant, depending on the test system, the concentration, and the method used to follow oxidation (*69*). Huang et al. (*70*) found that the antioxidant activity increased as the concentration and oxidation time in both bulk and o/w emulsion systems increased. The results presented above suggest that the role of α-tocopherol in bulk and o/w emulsions still requires further clarification. Therefore, experiments on the effect of concentration of α-tocopherol and storage time as well as the effects of others natural compounds present in hazelnut oil, such as ascorbic acid and its antioxidant effects in the systems, need to be investigated.

CONCLUSIONS

TAGs were the dominant lipid class in Tombul hazelnut oil and contributed nearly 100% to the total nonpolar lipids. The proportion of different polar lipid components was according to the trend PC > PE > PI. The fatty acid profile of the hazelnut oil was dominated by oleic acid, which contributed 82.7% to the total, followed by linoleic, palmitic, and stearic acids. Unsaturated fatty acids accounted for 92.2% of the total fatty acids present. Four tocopherols and three phytosterols were positively identified, among which α-tocopherol and β-sitosterol predominated, respectively. These results suggest that hazelnut oil serves as a good source of natural antioxidants and bioactives, thus reflecting its nutraceutical potential in different food and specialty applications. In addition, hazelnut oil, a rich source of MUFA (mainly oleic acid), may be considered as a supplement for daily diet plannings in order to reduce the risk of CHD by lowering total, LDL, VLDL, and TAG levels and increasing HDL CHOL levels (*16*). The results clearly showed that both stripped and crude hazelnut oils were more stable in terms of lipid oxidation in the bulk oil system as compared to that of the o/w emulsion. Differences in the oxidative stability of hazelnut oils in bulk and o/w emulsion systems may be affected by many factors including the size of emulsion droplets, the emulsifier, the presence of metals such as iron in aqueous solution, the pH, and the emulsification method.

ABBREVIATIONS USED

ANOVA, analysis of variance; BHT, butylated hydroxytoluene; BSTFA, bis(trimethylsilyl)trifloroacetamide; CE, cholesterol ester; CHD, coronary heart disease; CHOL, cholesterol; CL, cardiolipin; DAG, diacylglycerol; DPPP, diphenyl-1-pyrenylphosphine; Em, emission; Ex, excitation; FAME, fatty acid methyl esters; FDA, Food and Drug Administration; FFA, free fatty acid; FID, flame ionization detector; GC, gas chromatography; GRAS, generally recognized as safe; HDL, high-density lipoprotein; HPLC, high-performance liquid chromatography; IS, internal standard; LDL, low-density lipoprotein; LPC, lysophosphatidylcholine; LPE, lysophosphatidylethanolamine; MAG, monoacylglycerol; meq, milliequivalents; MGDG, monogalactosyldiacylglycerol; MUFA, monounsaturated fatty acids; MT, metric tons; NBD, 12-{7-nitro-2-1,3-benzoxadiazole-4-yl}amino[dodecanoyl]; o/w, oil-in-water; O_2, oxygen; PC, phosphatidylcholine; PE, phosphatidylethanolamine; PI, phosphatidylinositol; PS, phosphatidylserine; PUFA, polyunsaturated fatty acids; PV, peroxide value; SAS, statistical analytical systems; SD, standard deviation; SFA, saturated fatty acids; SM, sphingomyelin; TAG, triacylglycerol; TBARS, thiobarbituric acid reactive substances; TCD, thermal conductivity detector; TLC−FID, thin-layer chromatography−flame ionization detector; TMCS, trimethylchlorosilane; UV, ultraviolet; VLDL, very low-density lipoprotein.

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