JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Oxidative Stability of Tree Nut Oils

HOMAN MIRALIAKBARI AND FEREIDOON SHAHIDI*

Department of Biochemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X9

The oxidative stability of selected tree nut oils was examined. The oils of almond, Brazil nut, hazelnut, pecan, pine nut, pistachio, and walnut were extracted using two solvent extraction systems, namely, hexane and chloroform/methanol. The chloroform/methanol system afforded a higher oil yield for each tree nut type examined (pine nut had the highest oil content, whereas almond had the lowest). The fatty acid compositions of tree nut oils were analyzed using gas chromatography, showing that oleic acid was the predominant fatty acid in all samples except pine nut and walnut oils, which contained high amounts of linoleic acid. The tocopherol compositions were analyzed using high-performance liquid chromatography, showing that α- and γ-tocopherols were the predominant tocopherol homologues present; however δ- and β-tocopherols were also detected in some samples. The oxidative stability of nonstripped and stripped tree nut oils was examined under two conditions, namely, accelerated autoxidation and photooxidation. Progression of oxidation was monitored using tests for conjugated dienes, peroxide value, *p*-anisidine value, and headspace volatiles. Primary products of oxidation persisted in the earlier stages of oxidation, whereas secondary oxidation product levels increased dramatically during the later stages of oxidation. Hexanal was the major headspace aldehyde formed in all oxidized samples except walnut oil, which contained primarily propanal. Results showed that chloroform/methanol-extracted oils were more stable than hexane-extracted oils in both the accelerated autoxidation and photooxidation studies. Oils of pecan and pistachio were the most stable, whereas oils of pine nut and walnut were the least stable.

KEYWORDS: Tree nut oils; antioxidants; conjugated dienes; peroxide value; *p*-anisidine value; headspace volatiles; oxidative stability

INTRODUCTION

Several tree nut varieties serve as valuable oil crops due to their high oil yield, unique flavors, and healthful lipid composition. Tree nut oils are primarily composed of triacylglycerols, but also contain diacylglycerols, monoacylglycerols, free fatty acids, and other minor components, including natural antioxidants and fat-soluble vitamins. Tree nuts in many cases provide rich sources of food lipids, up to 75%, on a weight basis, as such (*1*). Generally, tree nut oils are somewhat similar to peanut oil and are rich in monounsaturated fatty acids, predominantly oleic acid, but contain much lower amounts of polyunsaturated fatty acids, predominantly linoleic acid, and small amounts of saturated lipids (*1*). Only walnut oil contains α-linolenic acid to any appreciable extent. In many parts of the world, such as the Middle East and Asia, tree nuts are cultivated for use as oil crops and are important sources of energy and essential dietary nutrients as well as phytochemicals (*2*). Tree nut oils are also components of some skin moisturizers and cosmetic products (*3*).

Tree nuts and their oils are known to contain several bioactive and health-promoting substances. Tree nuts have long been considered to be an important component of the Mediterranean diet (*4*), and in July 2003 the U.S. Food and Drug Administration (FDA) allowed a qualified health claim stating that consumption of 1.5 oz (42 g) per day of most tree nuts may reduce the risk of heart disease. Epidemiological evidence indicates that the consumption of tree nuts may exert several cardioprotective effects, which are speculated to arise from their lipid component that includes unsaturated fatty acids, phytosterols, and tocols (*4*). Recent investigations have also shown that dietary consumption of tree nut oils may exert even more beneficial effects than consumption of whole tree nuts, possibly due to the replacement of dietary carbohydrates with unsaturated lipids and/or other components present in the oil extracts (*4*).

Oxygen-dependent deterioration of lipids or lipid oxidation has long been recognized as a major problem in the storage of fats and oils. Lipid oxidation imparts undesirable flavors and aromas, compromises the nutritional quality of fats and oils, and leads to the production of toxic compounds. In fats and oils, the lipids involved in the oxidation process contain unsaturated fatty acids such as oleic, linoleic, linolenic, and long-chain polyunsaturated fatty acids; however, other unsaturated lipids present in fats and oils such as cholesterol and other sterols do become oxidized during this process (*5*). The rate at which

* Corresponding author telephone (709) 737-8552; fax (709) 737-4000; e-mail fshahidi@mun.ca.

10.1021/jf8000982 CCC: $40.75
Published on Web 05/22/2008

Table 1. Recovery of Stripped Oils Using the Solvent Stripping Process from Hexane- and Chloroform/Methanol-Extracted Oils[a]

nut	oil yield (%)	
	hexane-extracted	chloroform/methanol extracted
almond	97.8 ± 0.1a	97.3 ± 0.1b
Brazil nut	96.0 ± 0.1d	95.2 ± 0.1f
hazelnut	96.9 ± 0.1c	96.1 ± 0.1d
pecan	96.2 ± 0.1d	95.5 ± 0.1e
pine nut	97.7 ± 0.1a	97.1 ± 0.1b
pistachio	96.7 ± 0.1c	96.2 ± 0.1d
walnut	96.6 ± 0.1c	96.2 ± 0.1d

[a] Values bearing different letters are significantly ($p \leq 0.05$) different for each type of solvent-extracted oil.

fatty acids are oxidized increases with the degree of unsaturation and decreases with the presence of lipid-soluble antioxidants. The oxidation of edible fats and oils can be controlled by application of antioxidants, using processing techniques that minimize loss of tocopherols and other natural antioxidants, inactivation of prooxidant metals and enzymes, exposure to oxygen, heat, and light, hydrogenation of polyunsaturated fatty acids, and the use of an inert gas or vacuum packaging to expel atmospheric oxygen before long-term storage.

Much of the existing literature attributes the beneficial health effects of tree nuts and tree nut oils to their high oleic acid content. We have previously reported the compositional characteristics of nut oils and the antioxidant activity of their minor components (*6, 7*). However, information regarding oxidative stabilities of nut oils as influenced by their minor components is lacking. Therefore, the objective of this study was to assess the oxidative stability of tree nut oils under accelerated autoxidation and photooxidation conditions. A further objective of this work was to compare the effects of two oil extraction solvents, namely, hexane and chloroform/methanol, on the previously stated components and variables.

MATERIALS AND METHODS

Materials. Commercially available shelled and unsalted almonds, Brazil nuts, hazelnuts (filberts), pecans, pine nuts, pistachios, and walnuts were purchased fresh from local markets in St. John's, NL, Canada, or acquired from the International Treenut Council (Reus, Spain) or its affiliates. Samples were stored at −20 °C until use. All chemicals were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada) or Fisher Scientific (Ottawa, ON, Canada), unless otherwise stated. All solvents were of ACS grade, or better, unless otherwise specified.

Fat Extraction. *Hexane Extraction.* Forty grams of each tree nut sample was first ground into a fine powder (300 μm) and combined with 400 mL of hexanes, followed by homogenization at 8000 rpm using a Polytron (Polytron model PT 3000, Kinematica, Littau, Switzerland) for 3 min. The resulting mixture was filtered through a Whatman no. 4 filter paper with suction using a Büchner funnel. The residue was re-extracted twice; the filtrates from the three extractions were combined, and a portion of the solvent was removed from the extract using a rotary evaporator (Rotavapor model 461, Büchi, Flawil, Switzerland) at 40 °C. The hexane−oil mixture was then passed through a layer of anhydrous sodium sulfate placed over a filter paper in a funnel, and the remaining solvent was removed using a rotary evaporator at 40 °C. The resulting oil was weighed and transferred into 10 mL sample vials, capped with nitrogen, and stored at −80 °C until use.

Chloroform/Methanol Extraction. This was carried out in a similar manner as described for hexane extraction, but using chloroform. The residue was re-extracted twice with 400 mL of 1:1 (v/v) chloroform/methanol. The resultant oil was then redissolved in chloroform and then processed and stored in the same manner as the hexane-extracted oil.

Lipid Analysis. *Fatty Acid Analysis.* Fatty acid methyl esters (FAMEs) were prepared for each oil sample and were analyzed using gas chromatography, as described elsewhere (*6–8*). The FAMEs were prepared using methanol and sulfuric acid. The fatty acid profile of the oils have previously been reported (*6*).

Tocopherol Composition. *Tocopherol Extraction.* The tocopherol compositions of tree nut oil samples were analyzed as previously described (*7, 9*), with minor modifications. Five hundred milligrams of oil was accurately weighed into 50 mL glass tubes, followed by the addition of 5 mL of KOH (60%, w/v), 5 mL of ethanol, and 10 mL of ethanolic pyrogallol (6%, w/v). The glass tubes were then sealed and subsequently heated at 70 °C for 6 h. The tubes were then cooled, and 5 mL of deionized water was added. The mixture was subsequently extracted with 15 mL of hexane/ethyl acetate (9:1, v/v) using a benchtop vortex (Fisher Scientific, Ottawa, ON, Canada) for 3 min. Next the hexane/ethyl acetate fraction was carefully transferred into a 50 mL round-bottom flask using a pipet. The extraction process was repeated three times. The pooled extracts were evaporated to dryness and redissolved in 0.5 mL of HPLC grade methanol and filtered through a 3 μm pore size syringe filter before HPLC analysis.

The linearity and reproducibility of the extraction process were confirmed for each tocopherol homologue by testing the recovery of pure tocopherols and tocopherol mixtures from stripped corn oil (Acros Organics, Geel, Belgium) with externally added tocopherols.

Tocopherol Analysis. The tocopherols in tree nut oil samples were analyzed using an Agilent model 1100 HPLC/UV-DAD/MS system (Agilent Technologies, Palo Alto, CA) as previously described (*10*), with minor modifications. Separation of tocopherol homologues was achieved using a Phenomenex fused silica analytical column (250 mm × 4.6 mm; Phenomenex, Torrance, CA) packed with 5 μm particles. Forty microliters of the tocopherol extract was loaded onto the column and then eluted isocratically using hexane/2-propanol (98:2, v/v) with a flow rate of 1 mL/min at ambient temperature. Tocopherol homologues were quantified using an ultraviolet diode array detector (UV-DAD) at a wavelength of 290 nm. Quantification of tocopherol homologues was achieved by comparison of each sample peak response to that of the corresponding authentic standard. To confirm the identity of each tocopherol peak, the HPLC/UV-DAD effluent was channeled into an Agilent 1100 APCI-MS operating in the negative mode. The MS conditions were as follows: auxiliary gas flow, 10 units; sheath gas pressure, 70 psig; capillary temperature, 150 °C; vaporizer temperature, 400 °C; corona current, 5 μA; scan time, 1 s; scan range, m/z 40−600. Analysis of chromatographic and spectral data was performed using Agilent Chemstation software.

Stripping of Tree Nut Oils. Minor components were removed from tree nut oils as previously described (*11, 12*), with minor modifications. Twenty grams of oil was combined with 200 mL of hexane in a lightly tarred 500 mL separatory funnel. To this was added 100 mL of methanol, and the separatory funnel was sealed and agitated for 5 min with periodic venting. The separatory funnel was then sealed with nitrogen and stored at 4 °C for 1 h. The methanol fraction was decanted into a 1 L round-bottom flask. After the methanol extraction process, the hexane fraction was washed once with cold (4 °C) deionized water, and then the hexane fraction was passed through sodium sulfate. Hexane was removed from the recovered solution using a rotary evaporator at 40 °C. The resulting stripped oil was weighed to assess oil recovery. The stripped oil was then transferred to 10 mL sample vials and stored under nitrogen at −80 °C until use.

Oxidative Stability of Tree Nut Oils. *Accelerated Oxidation Studies.* The oxidative stability of stripped and nonstripped tree nut oils was studied using two accelerated oxidation conditions, namely, accelerated autoxidation and accelerated photooxidation.

Accelerated Autoxidation Conditions. Six grams (±0.01 g) of stripped or nonstripped tree nut oil samples was accurately weighed into 10 mL clear glass sample vials and loosely capped before being placed in a forced-air oven (Precision Scientific Co., Chicago, IL) in the dark and heated to 60 °C. For each sample, six vials were loaded into the oven, and one was removed after 12 h and 1, 3, 6, 9, and 12 days and stored at −80 °C until used for testing. The experiment was done in triplicate (*13*).

Table 2. Tocopherol Content (Milligrams per Kilogram) and Compositions of Nonstripped and Stripped Tree Nut Oils[a,b]

compound	α-tocopherol	γ-tocopherol	δ-tocopherol	β-tocopherol	total
		Nonstripped Oils[c]			
A-H	231.2 ± 0.4f	12.6 ± 0.5n	nd	nd	243.8 ± 1.1h
A-CM	257.4 ± 0.9e	17.7 ± 0.3m	nd	10.9 ± 0.4c	286.0 ± 2.4g
BN-H	12.8 ± 0.5l	138.2 ± 1.1h	17.6 ± 0.6a	nd	168.6 ± 2.2j
BN-CM	14.4 ± 1.8l	168.2 ± 0.4g	18.9 ± 0.4a	nd	201.5 ± 2.5i
HN-H	365.0 ± 0.5b	96.8 ± 1.6j	nd	nd	461.8 ± 1.9c
HN-CM	372.4 ± 1.1a	136.4 ± 1.3i	nd	nd	508.8 ± 1.7a
P-H	13.7 ± 0.6l	440.2 ± 0.3b	nd	nd	453.9 ± 1.8g
P-CM	18.2 ± 0.7k	472.9 ± 1.2a	nd	nd	491.1 ± 1.6b
PN-H	114.6 ± 0.5h	229.5 ± 0.8f	23.2 ± 0.6a	31.8 ± 0.8a	399.1 ± 1.7h
PN-CM	166.3 ± 0.7g	247.4 ± 0.6e	21.7 ± 0.3a	22.6 ± 0.7b	458.0 ± 1.4c
PO-H	286.9 ± 1.0d	30.6 ± 0.7l	16.8 ± 0.3a	nd	334.3 ± 1.7f
PO-CM	327.8 ± 0.7c	47.8 ± 1.1k	22.1 ± 0.5a	nd	397.7 ± 1.7e
W-H	33.1 ± 0.8j	349.4 ± 1.3d	19.8 ± 0.5a	nd	402.3 ± 1.9e
W-CM	38.0 ± 0.4i	375.8 ± 1.2c	23.4 ± 0.4a	nd	437.2 ± 1.8d
		Stripped Oils			
A-H	68.4 ± 0.6f	4.8 ± 0.5n	nd	nd	73.2 ± 0.9i
A-CM	95.2 ± 0.8d	6.8 ± 0.2m	nd	nd	106.7 ± 1.0h
BN-H	5.1 ± 0.5j	50.8 ± 0.4i	5.9 ± 0.2b	nd	61.8 ± 0.9j
BN-CM	5.9 ± 0.5j	60.7 ± 0.7g	8.4 ± 0.2a	nd	75.0 ± 1.3i
HN-H	154.9 ± 0.6b	43.8 ± 0.4j	nd	nd	198.7 ± 0.8b
HN-CM	165.3 ± 0.7a	54.1 ± 0.9h	nd	nd	219.4 ± 1.3a
P-H	5.9 ± 0.4j	159.5 ± 0.8b	nd	nd	165.4 ± 1.2e
P-CM	6.9 ± 0.3j	162.3 ± 0.7a	nd	nd	169.2 ± 1.0d
PN-H	41.6 ± 0.5g	92.8 ± 0.4f	9.0 ± 0.4a	11.3 ± 0.3a	154.7 ± 1.1g
PN-CM	74.2 ± 0.4e	97.0 ± 0.7e	8.7 ± 0.4a	8.5 ± 0.2b	188.4 ± 0.9c
PO-H	94.9 ± 0.6d	13.7 ± 0.4l	7.2 ± 0.3a	nd	115.8 ± 1.0u
PO-CM	124.8 ± 0.7c	27.4 ± 0.4k	9.4 ± 0.3a	nd	161.6 ± 1.1f
W-H	15.3 ± 0.4i	130.2 ± 0.7d	8.7 ± 0.4a	nd	154.2 ± 1.3g
W-CM	17.3 ± 0.4h	142.4 ± 0.5c	10.3 ± 0.4a	nd	170.0 ± 1.0d

[a] Abbreviations used: A-H, almond oil, hexane extracted; A-CM, almond oil, chloroform/methanol extracted; BN-H, Brazil nut oil, hexane extracted; BN-CM, Brazil nut oil, chloroform/methanol extracted; HN-H, hazelnut oil, hexane extract; HN-CM, hazelnut oil, chloroform/methanol extracted; P-H, pecan oil, hexane extracted; P-CM, pecan oil, chloroform/methanol extracted; PN-H, pine nut oil, hexane extracted; PN-CM, pine nut oil, chloroform/methanol extracted; PO-H, pistachio oil, hexane extracted; PO-CM, pistachio oil, chloroform/methanol extracted; W-H, walnut oil, hexane extracted; W-CM, walnut oil, chloroform/methanol extracted; nd, not detected. [b] Values in the same column with different letters are significantly ($p \leq 0.05$) different. [c] Values for tocopherol contents of nonstripped oils are from ref *7* and have been given for comparative purposes.

Accelerated Photooxidation Conditions. Stripped or nonstripped tree nut oils (2.0 g ± 0.01 g) were accurately weighed into 4 mL clear glass sample vials and placed in stainless steel transmethylation blocks, such that light was able to come into contact with the oils from the top of the vials only. The transmethylation blocks containing samples were then placed in a mirrored box [70 cm (l) × 35 cm (w) × 25 cm (h)] equipped with two cool white fluorescent lights suspended 10 cm above the sample vials. The fluorescent radiation was at 2650 lx, and the temperature within the photooxidation chamber was maintained at 27 ± 1 °C. For each sample, six vials were loaded into the photooxidation chamber, and one was removed after 4, 8, 12, and 24 h and 2 and 3 days and then stored at −80 °C until tested. The experiment was done in triplicate (*11*).

Quality Indicator Tests. The quality indicator tests used to assess the oxidative deterioration of stripped and nonstripped tree nut oils were conjugated dienes, using the IUPAC method (*15*), and peroxide values, according to the AOCS method (*14*), and these were used for assessing primary oxidation products. The *p*-anisidine values [AOCS (*14*)] and static headspace chromatographic analysis of volatile aldehydes (*16*) were used for monitoring secondary oxidation products.

Static Headspace Gas Chromatographic Analysis. A Perkin-Elmer 8500 gas chromatograph equipped with an HS-6 headspace sampler (Perkin-Elmer Corp., Montreal, QC, Canada) was used for headspace analysis. Volatile aldehydes were separated using a Supelcowax-10 fused silica capillary column (30 m length, 0.32 mm i.d., 0.10 μm film thickness; Supelco, Oakville, ON, Canada). Ultrahigh-purity (UHP) helium was used at 1.19 bar (120.58 kPas) as the carrier gas and a split ratio of 7:1. The oven temperature was maintained at 40 °C for 5 min and then ramped to 200 °C at 20 °C/min and held there for 5 min. The injector and FID temperatures were set at 280 °C during the analysis. Volatile aldehydes were identified by comparison of their retention times with those of authentic standards.

Statistical Analysis. All experiments were performed in triplicate; mean values and standard deviations were calculated for each case. Analysis of variance (ANOVA) followed by Tukey's studentized range test was performed at the $p \leq 0.05$ level using Minitab statistical software version 14 (Minitab Inc., State College, PA) to evaluate the significance of differences among different mean values (*17*).

RESULTS AND DISCUSSION

Oil Yield, Chemical Characteristics, and Stripping of Tree Nut Oils. The oils used in this study were extracted from fresh raw tree nuts. Comparison of the oil extraction processes with hexane and chloroform/methanol showed that the latter solvent system afforded a higher oil yield for all tree nut varieties studied, whereas the hexane solvent system gave oil with higher clarity, implying that hexane extraction provides a more refined oil compared to the chloroform/methanol solvent system. The oil contents were highest for pine nut extracted with hexane (73.9%) or chloroform/methanol (75.4%), whereas almond had the lowest oil contents of 51.2% with hexane and 53.5% with chloroform/methanol. The oil contents for other hexane-extracted oils were as follows: Brazil nut, 67.4%; hazelnut, 60.4%; pecan, 71.5%; pistachio, 52.3%; and walnut, 70.6%. Corresponding values for chloroform/methanol extracted oils were 68.9, 61.9, 73.4, 54.1, and 72.5%, respectively, indicating that the latter solvent system was more effective in oil extraction, especially their minor components (*18*). The oil yields reported here are in good agreement with those in the literature (*1, 18*), listing values of 50.6% for almond, 66.4% for Brazil nut, 72.0%

Table 3. Formation of Conjugated Dienes in Tree Nut Oils during Autoxidation at 60 °C[a,b]

oil	storage period					
	0 days	1 day	3 days	6 days	9 days	12 days
almond oil						
hexane extracted	0.956d	1.095g	1.578g	1.969 °	4.796p	6.451j
chloroform/methanol extracted	1.744b	1.812e	2.096f	2.455n	4.863p	6.757j
stripped hexane extracted	2.636a	2.929c	3.519d	9.475e	15.289f	15.914c
stripped chloroform/methanol extracted	2.270b	2.492d	2.528f	8.832f	12.930i	15.331d
Brazil nut oil						
hexane extracted	1.768b	2.455d	3.049e	4.163l	7.741m	15.767d
chloroform/methanol extracted	0.692e	0.820h	2.060f	2.421n	2.899r	3.686l
stripped hexane extracted	1.301c	1.793e	2.131f	8.725f	14.783g	15.341e
stripped chloroform/methanol extracted	1.423c	1.965e	2.464f	7.593g	13.401h	14.430f
hazelnut oil						
hexane extracted	1.096d	1.858e	2.277f	4.789k	6.951n	7.199j
chloroform/methanol extracted	1.492c	2.422d	2.883e	4.491l	5.789 °	6.131k
stripped hexane extracted	1.704b	2.086e	2.339f	6.925i	11.859j	12.033g
stripped chloroform/methanol extracted	1.467c	2.241d	2.757e	6.374j	10.857l	11.092h
pecan oil						
hexane extracted	0.502e	0.547h	0.849i	1.305p	1.920t	2.821m
chloroform/methanol extracted	0.267f	0.287i	0.346j	0.394q	1.029v	1.245 °
stripped hexane extracted	0.945d	1.183g	1.429g	2.398n	5.829 °	6.719j
stripped chloroform/methanol extracted	0.897d	1.259g	1.709g	2.720m	5.791 °	6.036k
pine nut oil						
hexane extracted	1.216c	1.537f	2.953e	7.628g	19.865e	24.745b
chloroform/methanol extracted	1.067d	1.058g	1.623g	2.315n	5.829 °	7.920i
stripped hexane extracted	1.509c	2.322d	4.043c	17.962d	34.677b	0.493p
stripped chloroform/methanol extracted	1.524c	2.008e	3.099e	18.472c	37.351a	5.825k
pistachio oil						
hexane extracted	0.481e	0.473i	0.495j	1.292p	2.379s	3.898l
chloroform/methanol extracted	0.992d	1.002g	1.029h	1.237p	1.401u	1.689n
stripped hexane extracted	1.145c	1.185g	1.219h	1.934 °	4.635p	6.945j
stripped chloroform/methanol extracted	0.936d	1.047g	1.138h	1.789 °	4.253q	6.673j
walnut oil						
hexane extracted	0.554e	0.681h	4.161c	7.247h	13.153i	29.998a
chloroform/methanol extracted	0.535e	0.986g	1.593g	4.279l	11.494k	17.507c
stripped hexane extracted	0.684e	4.834a	13.623a	41.262a	27.953d	5.965k
stripped chloroform/methanol extracted	0.693e	4.291b	12.315b	39.742b	28.512c	7.452j

[a] Values in the same row bearing different letters are significantly ($p \leq 0.05$) different. [b] Standard deviations did not exceed 0.100 for any data point (data not shown).

for pecan, 68.4% for pine nut, 46.4% for pistachio, and 65.2% for walnut, all on a weight basis.

The oxidative status of the extracted oils showed that peroxide values for all oils were in the range of 0.015−0.058 mequiv of oxygen/kg of oil and their *p*-anisidine values varied between 0.120 and 0.821, all of which are well below the recommended values for oil acceptability (*19*). These findings show that the fat extraction processes employed here were gentle enough to preserve the oxidative integrity of the oils, as expected for fresh products.

A liquid−liquid phase partitioning system was used to strip minor components from tree nut oil samples (solvent stripping process). This method was chosen over solid phase stripping processes (*11*) because of the relative ease of the solvent stripping process and to reduce oxidative deterioration of the minor component extracts which were used in other studies. The recovery of stripped oil was between 95.2 and 97.8%, with hexane-extracted almond oil affording the highest stripped oil recovery and, as expected, chloroform/methanol-extracted Brazil nut oil affording the lowest stripped oil recovery (**Table 1**) because of higher content of minor, non-triacylglycerol, components when this solvent system was used. A similar solvent stripping process was employed by Khan and Shahidi (*11*) and Ramadan et al. (*12*) to extract antioxidative components from different oils and reporting 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity of the corresponding oil extracts. However, the nature of the active compounds involved was not investigated (*12*).

Fatty Acid Composition of Tree Nut Oils. The fatty acid compositions of tree nut oils used in this study were reported elsewhere (*6*). Oleic acid was the predominant fatty acid in all samples examined, except for pine nut oil and walnut oil, which contained predominantly linoleic acid (C18:2 n-6), but the latter also contained α-linolenic acid (C18:3 n-3). The extraction solvent did not significantly ($p > 0.05$) influence the fatty acid composition of the oils. Fatty acid compositions of the stripped tree nut oils were not significantly ($p > 0.05$) different from their parent oils, as reported elsewhere (*6*).

Tocopherol Contents and Compositions of Tree Nut Oils. Comparison of the hexane- and chloroform/methanol-extracted oils for total tocopherol contents showed that the latter system afforded oils with higher tocopherol contents, with differences reaching significance ($p \leq 0.05$) in all nut oil samples studied (**Table 2**), presumably because of their better solubility in this solvent system. Among nonstripped samples, hazelnut oil contained the highest tocopherol content (462−508 mg/kg of oil), followed by pecan oil (454−490 mg/kg) and then pine nut

Table 4. Increase in Peroxide Values (Milliequivalents of Oxygen per Kilogram of Oil) of Tree Nut Oils during Autoxidation at 60 °C[a,b]

oil	storage period				
	0 days	3 days	6 days	9 days	12 days
almond oil					
hexane extracted	0.040a	0.076g	0.102h	0.153i	0.335g
chloroform/methanol extracted	0.030b	0.044g	0.057i	0.107i	0.164h
stripped hexane extracted	0.023b	0.212e	0.285f	0.393g	0.531f
stripped chloroform/methanol extracted	0.015b	0.157f	0.246f	0.346g	0.458g
Brazil nut oil					
hexane extracted	0.047a	0.142f	0.233f	0.370g	0.661e
chloroform/methanol extracted	0.030b	0.061g	0.104h	0.140i	0.197h
stripped hexane extracted	0.015b	0.156f	0.554d	1.195d	1.992c
stripped chloroform/methanol extracted	0.023b	0.162f	0.446d	0.935e	1.415d
hazelnut oil					
hexane extracted	0.031b	0.079g	0.125g	0.200h	0.307g
chloroform/methanol extracted	0.059a	0.065g	0.094h	0.150i	0.200h
stripped hexane extracted	0.015b	0.280c	0.389e	0.458f	0.519f
stripped chloroform/methanol extracted	0.015b	0.252d	0.369e	0.437f	0.467g
pecan oil					
hexane extracted	0.030b	0.053g	0.085h	0.119i	0.158h
chloroform/methanol extracted	0.023b	0.026g	0.030j	0.036j	0.045i
stripped hexane extracted	0.023b	0.097g	0.149g	0.228h	0.346g
stripped chloroform/methanol extracted	0.015b	0.073g	0.131g	0.205h	0.309g
pine nut oil					
hexane extracted	0.030b	0.206e	0.466d	0.822e	1.317d
chloroform/methanol extracted	0.016b	0.081g	0.155g	0.228h	0.291g
stripped hexane extracted	0.023b	0.296c	0.859c	1.506c	2.305b
stripped chloroform/methanol extracted	0.015b	0.274c	0.827c	1.428c	2.259b
pistachio oil					
hexane extracted	0.023b	0.035g	0.065i	0.088i	0.116h
chloroform/methanol extracted	0.015b	0.021g	0.031j	0.036j	0.037i
stripped hexane extracted	0.015b	0.037g	0.098h	0.211h	0.438g
stripped chloroform/methanol extracted	0.015b	0.037g	0.097h	0.206h	0.428g
walnut oil					
hexane extracted	0.030b	0.839b	1.711b	1.921b	2.142c
chloroform/methanol extracted	0.015b	0.208e	0.238f	0.287h	0.334g
stripped hexane extracted	0.015b	1.109a	2.276a	3.656a	4.736a
stripped chloroform/methanol extracted	0.015b	1.065a	2.226a	3.585a	4.629a

[a] Values in the same row bearing different letters are significantly ($p \leq 0.05$) different. [b] Standard deviations did not exceed 0.050 for any data point (data not shown).

oil (399−458 mg/kg). Hexane-extracted Brazil nut oil contained the lowest amount of tocopherols (169 mg/kg of oil).

The solvent stripping process employed in this work was able to reduce the amount of total tocopherols in tree nut oils by 57−70%; however, no individual tocopherol homologue could be completely stripped from oil samples. α-Tocopherol and γ-tocopherol were present in all tree nut oils, with α-tocopherol predominating in almond, hazelnut, and pistachio, whereas γ-tocopherol predominated in pecan, pine nut, walnut, and Brazil nut oils. δ-Tocopherol was present in Brazil nut, pine nut, pistachio, and walnut oils (17−23 mg/kg of oil). β-Tocopherol was detected only in chloroform/methanol-extracted almond and pine nut oils in low amounts (<32 mg/kg of oil). α-Tocopherol was the predominant tocol in almond oil (390−439 mg/kg) and hazelnut oil (382−472 mg/kg); both are reported to contain smaller amounts of γ-tocopherol (12.5 and 61.2 mg/kg, respectively) (*1, 20*). The predominant tocopherol in pecan oil was γ-tocopherol (176 mg/kg), followed by α-tocopherol (10 mg/kg) and then δ- and β-tocopherols (6.2 mg/kg) (*1*). Pistachio oil has been reported to contain 270 mg/kg of tocopherols (primarily α-tocopherol) (*1*), whereas walnut oil was reported to contain 268−436 mg/kg of total tocopherols. The predominant tocol isomer in walnut oils was γ-tocopherol (>90%), followed by α-tocopherol (6%) and then β- and δ-tocopherols (*21*). The tocopherol compositions reported here are in agreement with those reported in the literature (*18*). Mention should also be made that γ-tocopherol is known to serve as a better in vitro antioxidant than α-tocopherol. The stability of the oils might then be affected by their tocopherol profiles.

Oxidative Stability of Tree Nut Oils under Accelerated Autoxidation Conditions. The oxidative stability of nonstripped and stripped tree nut oils was monitored using tests for conjugated dienes, peroxide value, *p*-anisidine value, and headspace analysis of volatiles. Results showed that chloroform/methanol-extracted oils were more resistant to oxidation than hexane-extracted oils. Minor component stripped oils were less stable than their nonstripped counterparts, which shows the importance of minor components in oils on their oxidative stability. The stripping process was effective for both chloroform/methanol-extracted and hexane-extracted oils, because both stripped oil types exhibited low oxidative stability. Among the oils studied, chloroform/methanol-extracted pecan oil showed the highest oxidative stability, with the lowest levels of both primary and secondary oxidation products after 12 days of accelerated oxidation. The relatively high stability of extracted pecan oil is likely due to its rich content of tocopherols and possibly phospholipids, and a low degree of unsaturation, as reflected in its low iodine value. The importance of minor

Table 5. *p*-Anisidine Values of Tree Nut Oils during Autoxidation at 60 °C[a,b]

oil	storage period				
	0 days	3 days	6 days	9 days	12 days
almond oil					
hexane extracted	0.120f	1.437h	2.335n	3.247s	3.923s
chloroform/methanol extracted	0.561b	1.095h	2.015n	2.464t	3.061t
stripped chloroform/methanol extracted	0.267d	4.839f	11.739e	19.743e	29.058c
stripped hexane extracted	0.465b	5.294e	11.201f	17.493g	24.389f
Brazil nut oil					
hexane extracted	0.189e	1.936h	3.853l	6.059p	8.576p
chloroform/methanol extracted	0.821a	1.272h	1.780n	2.392t	3.327t
stripped hexane extracted	0.264d	4.429g	9.221g	13.948h	19.746g
stripped chloroform/methanol extracted	0.371c	3.700g	7.139i	11.137j	16.048i
hazelnut oil					
hexane extracted	0.592b	2.138h	4.120l	6.023p	8.262p
chloroform/methanol extracted	0.288d	1.695h	3.274m	4.893r	6.555r
stripped hexane extracted	0.255d	3.943g	8.193h	12.294i	16.428i
stripped chloroform/methanol extracted	0.343c	3.492g	7.419i	11.489j	15.386j
pecan oil					
hexane extracted	0.433b	2.162h	4.006l	5.589q	7.172q
chloroform/methanol extracted	0.294d	0.702i	1.398 °	2.330t	3.243t
stripped hexane extracted	0.344c	2.583h	5.302l	8.153m	11.876m
stripped chloroform/methanol extracted	0.257	2.683h	5.732k	8.682l	12.686l
pine nut oil					
hexane extracted	0.267d	2.081h	4.359k	10.286k	17.567h
chloroform/methanol extracted	0.493b	2.105h	4.423k	8.473m	14.029k
stripped hexane extracted	0.281d	7.043c	14.382c	22.395c	29.711b
stripped chloroform/methanol extracted	0.552b	6.382d	13.492d	21.014d	28.549d
pistachio oil					
hexane extracted	0.545b	0.763i	1.017p	1.484u	1.910u
chloroform/methanol extracted	0.635b	0.691i	0.790q	1.285u	1.731u
stripped hexane extracted	0.518b	2.385h	5.092l	7.854n	10.473n
stripped chloroform/methanol extracted	0.493b	2.372h	4.727l	6.937 °	9.361 °
walnut oil					
hexane extracted	0.230d	4.202g	9.535g	18.826f	29.591b
chloroform/methanol extracted	0.462b	1.472	6.640j	13.782h	24.880e
stripped hexane extracted	0.193e	9.736a	20.472a	34.284a	52.562a
stripped chloroform/methanol extracted	0.237d	8.583b	18.936b	30.847b	48.836a

[a] Values in the same row bearing different letters are significantly ($p \leq 0.05$) different. [b] Standard deviations did not exceed 0.150 for any data point (data not shown).

components of chloroform/methanol-extracted pecan oil against lipid oxidation is apparent when its oxidative stability is compared to that of its hexane-extracted counterpart with lower amounts of minor components. However, hexane-extracted pecan oil did exhibit the highest oxidative stability among the hexane-extracted oils examined. This observation was also noted for other tree nut oils such as walnut oil and pine nut oil, which were least stable and most unsaturated. Chloroform/methanol-extracted pistachio oil also exhibited high oxidative stability, which was second only to chloroform/methanol-extracted pecan oil. Oils of almond and hazelnut exhibited intermediate stabilities. However, hexane-extracted Brazil nut oil exhibited a stability similar to that of stripped hexane- and chloroform/methanol-extracted Brazil nut oil, which implies that hexane did not effectively extract the antioxidative components from it.

Conjugated Dienes and Peroxide Values of Autoxidized Tree Nut Oils. Conjugated dienes and peroxides are both primary products of oxidation and persist during the early stages of lipid oxidation. Formation of conjugated dienes in tree nut oils during the 12 day oxidation test is summarized in **Table 3**. In all oils examined, chloroform/methanol-extracted oils and their stripped counterparts were more resistant to the formation of conjugated dienes than their corresponding nonstripped hexane-extracted oils. Among the samples examined, stripped hexane-extracted almond oil possessed the highest initial conjugated dienes value (2.6), followed by stripped chloroform/methanol-extracted almond oil (2.3). Hexane-extracted pistachio oil had the lowest initial conjugated dienes (0.5).

Stripped chloroform/methanol-extracted almond oil had lower conjugated diene levels than its stripped hexane-extracted counterpart after 12 days of storage under Schaal oven conditions (15.3 and 15.9, respectively). The chloroform/methanol extract of Brazil nut oil showed very low levels of conjugated dienes after 12 days (3.7), which is very interesting considering that this oil has a high degree of unsaturation compared to other oils examined and also because its hexane-extracted counterpart and stripped counterparts contained 4.5−5 times higher conjugated diene levels. Hexane- and chloroform/methanol-extracted hazelnut oils exhibited conjugated diene levels similar to those of almond oils after 12 days; however, stripped hazelnut oils possessed lower conjugated dienes than stripped almond oils, which is likely due to the fact that almond oils have higher amounts of unsaturated lipids than hazelnut oils (**Table 3**). This may imply that the antioxidative components in almond oil are more effective in reducing lipid oxidation than those present in hazelnut oil. Chloroform/methanol-extracted pecan oil possessed the lowest level of conjugated dienes among samples examined

Table 6. Headspace Aldehyde Compositions (Micrograms of Aldehyde per Gram of Oil) of Tree Nut Oils during Autoxidation at 60 °C[a]

oil	aldehyde	storage period day 3	day 6	day 9	day 12
almond oil					
hexane extracted	hexanal	4.1	16.0	32.6	56.0
	nonanal	0.0	2.1	7.4	17.0
chloroform/methanol extracted	hexanal	0.0	22.0	29.5	36.0
	nonanal	0.0	0.0	1.4	9.0
stripped hexane extracted	hexanal	21.1	60.4	85.4	122.3
	nonanal	2.5	6.7	11.4	16.6
stripped chloroform/methanol extracted	hexanal	25.7	64.4	92.7	134.4
	nonanal	0.0	3.5	8.4	14.2
Brazil nut oil					
hexane extracted	hexanal	7.6	31.7	49.6	81.7
	nonanal	0.0	0.0	0.0	13.2
chloroform/methanol extracted	hexanal	2.3	18.7	24.4	37.4
	nonanal	0.0	0.0	0.0	2.5
stripped hexane extracted	hexanal	31.5	79.4	109.7	150.4
	nonanal	2.7	21.4	28.4	42.4
stripped chloroform/methanol extracted	hexanal	28.5	73.6	100.5	123.9
	nonanal	3.4	14.5	26.4	34.7
hazelnut oil					
hexane extracted	hexanal	3.2	37.5	49.6	82.6
	nonanal	0.0	0.0	0.0	7.22
chloroform/methanol extracted	hexanal	8.1	28.4	42.5	66.1
	nonanal	0.0	0.0	0.0	2.14
stripped hexane extracted	hexanal	24.6	61.6	79.4	136.1
	nonanal	0.0	6.3	11.6	23.2
stripped chloroform/methanol extracted	hexanal	17.5	48.3	87.4	124.2
	nonanal	0.0	7.2	12.6	20.3
pecan oil					
hexane extracted	hexanal	1.7	13.8	19.5	27.8
	nonanal	0.0	0.0	0.0	2.5
chloroform/methanol extracted	hexanal	0.0	8.5	11.8	19.7
	nonanal	0.0	0.0	0.0	0.0
stripped hexane extracted	hexanal	20.5	57.6	86.7	120.5
	nonanal	0.0	4.8	8.7	12.4
stripped chloroform/methanol extracted	hexanal	14.6	57.6	72.8	116.5
	nonanal	0.0	4.8	8.4	15.3
pine nut oil					
hexane extracted	hexanal	2.5	64.7	126.7	166.3
	nonanal	0.0	19.6	28.4	48.5
chloroform/methanol extracted	hexanal	1.7	42.7	64.7	120.0
	nonanal	4.6	19.5	29.6	37.6
stripped hexane extracted	hexanal	42.7	138.7	216.8	302.1
	nonanal	5.1	18.6	26.8	37.8
stripped chloroform/methanol extracted	hexanal	48.3	127.9	201.3	286.5
	nonanal	3.7	17.5	23.5	34.4
pistachio oil					
hexane extracted	hexanal	3.5	18.5	31.3	43.5
	nonanal	0.0	1.7	5.6	13.3
chloroform/methanol extracted	hexanal	1.4	14.3	26.9	34.7
	nonanal	0.0	2.8	7.5	10.8
stripped hexane extracted	hexanal	14.7	41.4	63.5	94.6
	nonanal	0.0	3.7	5.8	12.5
stripped chloroform/methanol extracted	hexanal	10.4	39.6	52.7	92.4
	nonanal	0.0	2.3	5.1	9.3
walnut oil					
hexane extracted	propanal	43.8	69.5	118.6	188.3
	hexanal	31.6	49.4	78.4	72.7
	nonanal	9.5	19.8	31.8	43.2
chloroform/methanol extracted	propanal	21.6	58.3	84.8	137.5
	hexanal	5.9	20.6	34.6	53.2
	nonanal	2.1	12.3	21.5	29.4
stripped hexane extracted	propanal	43.8	118.6	163.6	262.4
	hexanal	31.6	78.4	116.7	167.3
	nonanal	9.5	31.8	53.7	82.6
stripped chloroform/methanol extracted	propanal	39.8	119.6	149.7	251.5
	hexanal	20.8	68.3	102.6	154.3
	nonanal	12.3	29.5	52.6	68.0

[a] Sample means were calculated from triplicate analyses; standard deviations were within the range of 0.1−9.0 μg/g, with higher mean values having larger standard deviations (data not shown).

Table 7. Formation of Conjugated Dienes in Tree Nut Oils during Photooxidation[a,b]

	sampling period 0 h	4 h	8 h	12 h	24 h	48 h	72 h
Nonstripped Oils							
A-H	0.956d	1.862i	2.683g	3.347p	8.153q	10.967n	14.257 °
A-BD	1.744b	4.950c	3.563f	4.174 °	8.267q	11.487m	14.933n
BN-H	1.768b	4.174d	5.183e	7.077m	13.160n	26.804e	34.845e
BN-BD	0.692e	1.394j	3.502f	4.116 °	4.928t	6.266r	8.146r
HN-H	1.096d	3.159f	3.871f	8.141k	11.817 °	12.238k	15.910l
HN-BD	1.492c	4.117d	4.901e	7.635l	9.841p	10.423 °	13.550p
P-H	0.502e	0.930k	1.443i	2.219r	3.264v	4.796s	6.234s
P-BD	0.267f	0.488l	0.588k	0.670s	1.749w	2.117u	2.751u
PN-H	1.216c	2.613h	5.020e	12.968g	33.771e	42.067b	54.686b
PN-BD	1.067d	1.799i	2.759g	3.936 °	9.909p	13.464i	17.503j
PO-H	0.481e	0.804k	0.842j	2.196r	4.044u	6.627q	8.615q
PO-BD	0.992d	1.303j	1.749h	2.103r	3.382v	3.971t	4.733t
W-H	0.554e	1.158j	7.074c	12.320h	22.360i	50.997a	66.296a
W-BD	0.535e	1.676i	2.708g	7.274m	19.540l	29.762c	38.690c
Stripped Oils							
A-H	2.636a	4.979c	5.982d	16.108e	25.991f	27.054d	35.170d
A-BD	2.270b	4.236d	4.298f	15.014f	21.981j	26.063f	33.882f
BN-H	1.301c	3.048g	3.623f	14.833f	25.131g	26.080f	33.904f
BN-BD	1.423c	3.341f	4.189f	12.908g	22.782h	24.531g	31.890g
HN-H	1.704b	3.546f	3.976f	11.773i	20.160k	20.456h	26.593h
HN-BD	1.467c	3.810e	4.687e	10.836j	18.457m	18.857i	24.514i
P-H	0.945d	2.011i	2.429g	4.077 °	9.909p	11.422m	14.849n
P-BD	0.897d	2.140i	2.905g	4.624n	9.845p	10.261 °	13.340p
PN-H	1.509c	3.947e	6.873c	30.535d	63.497a	0.838v	1.090u
PN-BD	1.524c	3.414f	5.268e	31.402c	58.951b	9.903p	12.873q
PO-H	1.145c	2.015i	2.072h	3.288p	7.880r	11.807l	15.348m
PO-BD	0.936d	1.780i	1.935h	2.948q	7.230s	11.344m	14.747n
W-H	0.684e	8.218a	23.159a	70.145a	48.520c	10.141 °	13.183p
W-BD	0.693e	7.295b	20.936b	67.561b	47.470d	12.668j	16.469k

[a] Abbreviations used: A-H, almond oil, hexane extracted; A-CM, almond oil, chloroform/methanol extracted; BN-H, Brazil nut oil, hexane extracted; BN-CM, Brazil nut oil, chloroform/methanol extracted; HN-H, hazelnut oil, hexane extract; HN-CM, hazelnut oil, chloroform/methanol extracted; P-H, pecan oil, hexane extracted; P-CM, pecan oil, chloroform/methanol extracted; PN-H, pine nut oil, hexane extracted; PN-CM, pine nut oil, chloroform/methanol extracted; PO-H, pistachio oil, hexane extracted; PO-CM, pistachio oil, chloroform/methanol extracted; W-H, walnut oil, hexane extracted; W-CM, walnut oil, chloroform/methanol extracted. [b] Values in the same column with different letters are significantly ($p \leq 0.05$) different. All samples were analyzed in triplicate. Standard deviations did not exceed 0.100 for any data point (data not shown).

after 12 days of oxidation (1.2), followed by chloroform/methanol-extracted pistachio oil (1.7). Among hexane-extracted oils, hexane-extracted pecan oil had the lowest conjugated dienes level after 12 days of storage under Schaal oven conditions (2.8), followed by hexane-extracted pistachio oil (3.9). Hexane-extracted walnut oil contained the highest level of conjugated dienes after the 12 days under accelerated oxidation conditions (30.0), followed by hexane-extracted pine nut oil (24.7); the chloroform/methanol-extracted counterparts of these oils were considerably more stable, with conjugated diene levels of 17.5 and 7.9, respectively, but were still highest among all non-stripped oils examined. The stripped oils of walnuts possessed the highest conjugated diene levels among all samples examined, followed by the stripped oils of pine nuts; this observation can easily be attributed to the high degree of unsaturation of these oils, in combination with their lack of antioxidative minor components.

The results of the peroxide value determined for tree nut oils subjected to accelerated oxidation are shown in **Table 4**. Examination of these results shows that the rate of formation of peroxides during autoxidation resembles the formation rate of conjugated dienes in oils examined, and the ranking order of oxidative stability, derived using maximum peroxide value

Table 8. Headspace Aldehyde Compositions (Micrograms of Aldehyde per Gram of Oil) of Tree Nut Oils during Photooxidation[a]

oil	aldehyde	storage period 12 h	24 h	48 h	72 h
almond oil					
hexane extracted	hexanal	3.0	15.9	26.9	37.4
	nonanal	0.0	1.5	4.8	11.4
chloroform/methanol extracted	hexanal	1.2	12.3	23.1	29.8
	nonanal	0.0	2.4	6.5	9.3
stripped hexane extracted	hexanal	12.6	35.6	54.6	81.4
	nonanal	0.0	3.2	5.0	10.8
stripped chloroform/methanol extracted	hexanal	8.9	34.1	45.3	79.5
	nonanal	0.0	2.0	4.4	8.0
Brazil nut oil					
hexane extracted	hexanal	6.5	27.3	42.7	70.3
	nonanal	0.0	0.0	0.0	11.4
chloroform/methanol extracted	hexanal	2.0	16.1	21.0	32.2
	nonanal	0.0	0.0	0.0	2.2
stripped hexane extracted	hexanal	27.1	68.3	94.3	129.3
	nonanal	2.3	18.4	24.4	36.5
stripped chloroform/methanol extracted	hexanal	24.5	63.3	86.4	106.6
	nonanal	2.9	12.5	22.7	29.8
hazelnut oil					
hexane extracted	hexanal	2.8	32.3	42.7	71.0
	nonanal	0.0	0.0	0.0	6.2
chloroform/methanol extracted	hexanal	7.0	24.4	36.6	56.8
	nonanal	0.0	0.0	0.0	1.8
stripped hexane extracted	hexanal	21.2	53.0	68.3	117.0
	nonanal	0.0	5.4	10.0	20.0
stripped chloroform/methanol extracted	hexanal	15.1	41.5	75.2	106.8
	nonanal	0.0	6.2	10.8	17.5
pecan oil					
hexane extracted	hexanal	1.5	11.9	16.8	23.9
	nonanal	0.0	0.0	0.0	2.2
chloroform/methanol extracted	hexanal	0.0	7.3	10.1	16.9
	nonanal	0.0	0.0	0.0	0.0
stripped hexane extracted	hexanal	17.6	49.5	74.6	103.6
	nonanal	0.0	4.1	7.5	10.7
stripped chloroform/methanol extracted	hexanal	12.6	49.5	62.6	100.2
	nonanal	0.0	4.1	7.2	13.2
pine nut oil					
hexane extracted	hexanal	2.2	55.6	109.0	143.0
	nonanal	0.0	16.9	24.4	41.7
chloroform/methanol extracted	hexanal	1.5	36.7	55.6	103.2
	nonanal	4.0	16.8	25.5	32.3
stripped hexane extracted	hexanal	36.7	119.3	186.4	259.8
	nonanal	4.4	16.0	23.0	32.5
stripped chloroform/methanol extracted	hexanal	41.5	110.0	173.1	246.4
	nonanal	3.2	15.1	20.2	29.6
pistachio oil					
hexane extracted	hexanal	3.0	15.9	26.9	37.4
	nonanal	0.0	1.5	4.8	11.4
chloroform/methanol extracted	hexanal	1.2	12.3	23.1	29.8
	nonanal	0.0	2.4	6.5	9.3
stripped hexane extracted	hexanal	12.6	35.6	54.6	81.4
	nonanal	0.0	3.2	5.0	10.8
stripped chloroform/methanol extracted	hexanal	8.9	34.1	45.3	79.5
	nonanal	0.0	2.0	4.4	8.0
walnut oil					
hexane extracted	propanal	37.7	59.8	102.0	161.9
	hexanal	27.2	42.5	67.4	62.5
	nonanal	8.2	17.0	27.3	37.2
chloroform/methanol extracted	propanal	18.6	50.1	72.9	118.3
	hexanal	5.1	17.7	29.8	45.8
	nonanal	1.8	10.6	18.5	25.3
stripped hexane extracted	propanal	37.7	102.0	140.7	225.7
	hexanal	27.2	67.4	100.4	143.9
	nonanal	8.2	27.3	46.2	71.0
stripped chloroform/methanol extracted	propanal	34.2	102.9	128.7	216.3
	hexanal	17.9	58.7	88.2	132.7
	nonanal	10.6	25.4	45.2	58.5

[a] Sample means were calculated from triplicate analyses; standard deviations were within the range of 0.1−9.0 μg/g, with higher mean values having larger standard deviations (data not shown).

levels, was identical to the order obtained using maximum conjugated diene values (pecan oil > pistachio oil > hazelnut oil ≥ almond oil > Brazil nut oil > pine nut oil > walnut oil; chloroform/methanol-extracted oils > hexane-extracted oils; nonstripped oils > stripped oils).

***p*-Anisidine Values and Headspace Volatile Compositions of Autoxidized Tree Nut Oils.** The *p*-anisidine value and headspace analysis are both tests for secondary products of lipid oxidation. The *p*-anisidine value is an empirical test, whereas headspace analysis can produce quantitative data on oil volatiles formed during lipid oxidation. *p*-Anisidine values of autoxidized tree nut oils are shown in **Table 5**. Results show that chloroform/methanol-extracted oils, presumably containing higher contents of minor components and a fewer initial oxidation products, were more resistant to the formation of *p*-anisidine reactive substances when compared to hexane-extracted oils. Also, nonstripped oils were more stable than stripped oils for all nut oil samples studied, again because of their higher content of antioxidative minor components. Among the samples studied, chloroform/methanol-extracted pistachio oil exhibited the lowest *p*-anisidine value after 12 days of storage under accelerated Schaal oven conditions, followed by hexane-extracted pistachio oil, chloroform/methanol-extracted pecan, almond, and Brazil nut oils, and chloroform/methanol-extracted hazelnut oil. Hexane-extracted walnut oil had the highest *p*-anisidine value among nonstripped oil samples examined after 12 days under accelerated oxidation conditions, presumably because of its high degree of unsaturation and lower content of minor components.

Hexanal and nonanal were the most widely detected headspace volatiles observed in tree nut oils subjected to accelerated oxidation; propanal was present only in walnut oil, which is the only nut oil containing α-linolenic acid (**Table 6**). Hexanal is an oxidation product of linoleic acid, an omega-6 fatty acid. Its presence in meat and other lipid sources containing linoleic acid has been reported in the literature (*16*). In addition, nonanal is an oxidation product of oleic acid, an omega-9 fatty acid (*22*). No headspace aldehydes were detected in oil samples before commencement of the stability studies. Chloroform/methanol-extracted oils contained lower amounts of headspace aldehydes compared to their hexane-extracted counterparts at each sampling point of the accelerated autoxidation studies. Stripped oils contained 2−4 times the amount of headspace aldehydes compared to their nonstripped counterparts. Among nonstripped samples, hexane-extracted walnut oil contained the highest amount of total aldehydes after 12 days of storage under accelerated oxidation under Schaal oven conditions, followed by chloroform/methanol-extracted walnut oil, hexane-extracted pine nut oil, and chloroform/methanol-extracted pine nut oil. Chloroform/methanol-extracted pecan oil contained the lowest amount of total aldehydes at each sampling point. Surprisingly, chloroform/methanol-extracted Brazil nut oil contained the third lowest level of headspace aldehydes on day 12, after chloroform/methanol-extracted pecan oil and hexane-extracted pecan oil, which was unexpected considering its high level of linoleic acid. Nonanal was detected in all samples on day 12 except chloroform/methanol-extracted pecan oil and was the least predominant aldehyde in all samples in which it was detected.

Photooxidative Stability of Tree Nut Oils. The photooxidative stability of stripped and nonstripped tree nut oils over 72 h was examined using a previously described protocol (*11*). Results of the photooxidation studies showed that chloroform/methanol-extracted oils were more resistant to conjugated diene formation than hexane-extracted oils. Stripped oils were less

resistant to conjugated diene formation than their nonstripped counterparts (**Table 7**). Among nonstripped samples, hexane-extracted walnut oil had the highest levels of conjugated dienes after 72 h, followed by hexane-extracted pine nut oil and then hexane-extracted Brazil nut oil. Chloroform/methanol-extracted pecan oil had the lowest levels of conjugated dienes after 72 h of photooxidation, followed by chloroform/methanol-extracted pistachio oil. Interestingly, chloroform/methanol-extracted Brazil nut oil was considerably more stable than its hexane-extracted counterpart; this trend was also observed for conjugated diene formation in Brazil nut oil during the autoxidation studies and may indicate the presence of antioxidants that render stabilities to the oil under both autoxidative and photooxidative conditions.

Results of headspace analyses of photooxidized tree nut oils are given in **Table 8**; hexanal and nonanal were the most prevalent aldehydes present, with propanal existing only in walnut oil. Chloroform/methanol-extracted pecan oil contained the lowest level of total headspace aldehydes among all samples after 72 h, followed by hexane-extracted pecan oil, chloroform/methanol-extracted Brazil nut oil, and then chloroform/methanol-extracted pistachio oil. Among nonstripped samples, hexane-extracted walnut oil contained the highest amount of total headspace aldehydes after 72 h of photooxidation, followed by chloroform/methanol-extracted walnut oil and then hexane-extracted pine nut oil. The headspace aldehyde compositions of photooxidized tree nut oils were similar to those observed for autoxidized oils, but higher amounts of total headspace aldehydes were detected during the accelerated oxidation under Schaal oven conditions; thus, the oils examined enjoyed a reasonable photooxidative stability under the conditions examined. However, the overall trends observed in the photooxidative stability studies were similar to those noted under Schaal oven condition oxidation; oils that exhibited high photooxidative stability also exhibited high autoxidative stability. This implies that the antioxidative minor components of oils such as chloroform/methanol-extracted pecan, pistachio, and Brazil nut oils impart both photooxidative and autoxidative stability to them. Further studies on minor component compositions of these and other tree nut oils are warranted.

LITERATURE CITED

(1) U.S. Department of Agriculture (USDA) Nutrient Database version 17; www.nal.usda.gov/foodcomp; accessed May 28, 2005.

(2) Bonvehi, J. S.; Coll, F. V.; Rius, I. A. Liquid chromatographic determination of tocopherols and tocotrienols in vegetable oils, formulated preparations, and biscuits. *J. AOAC Int.* **2000**, *83*, 627–634.

(3) Madhaven, N. Final report on the safety assessment of *Corylus avellana* (Hazel) seed oil, *Corylus americana* (Hazel) seed oil, *Corylus avellana* (Hazel) seed extract, *Corylus americana* (Hazel) seed extract, *Corylus avellana* (Hazel) leaf extract, *Corylus americana* (Hazel) leaf extract, and *Corylus rostrata* (Hazel) leaf extract. *Int. J. Toxicol.* **2001**, *20*, 15–20.

(4) Hu, F. B.; Stampfer, M. J. Nut consumption and risk of coronary heart disease: a review of epidemiologic evidence. *Curr. Atheroscler. Rep.* **1999**, *3*, 204–209.

(5) Lundberg, W. O. Autoxidation and antioxidants. In *Free Radicals in Biology*; Lundberg, W. O., Ed.; Wiley: New York, 1961.

(6) Miraliakbari, H.; Shahidi, F. Lipid class composition, tocopherols and sterols of tree nut oils extracted with different solvents. *J. Food Lipids* **2008**, *15*, 81–96.

(7) Miraliakbari, H.; Shahidi, F. Antioxidant activity of minor components of tree nut oils. *Food Chem.* **2008**, . in press.

(8) Alasalvar, C.; Shahidi, F.; Ohshima, T.; Wanasundara, U.; Yurttas, H. C.; Liyanapathirana, C. M.; Rodrigues, F. B. Turkish Tombul hazelnut (*Corylus avellana* L.). 2. Lipid characteristics and oxidative stability. *J. Agric. Food Chem.* **2003**, *51*, 3797–3805.

(9) Gomez-Coronado, D. J.; Barbas, C. Optimized and validated HPLC method for α- and γ-tocopherol measurement in *Laurus nobilis* leaves. New data on tocopherol content. *J. Agric. Food Chem.* **2003**, *51*, 5196–5201.

(10) Chatzimichalakis, P. F.; Samanidou, V. F.; Papadoyannis, I. N. Development of a validated liquid chromatography method for the simultaneous determination of eight fat-soluble vitamins in biological fluids after solid-phase extraction. *J. Chromatogr., B* **2004**, *15*, 289–296.

(11) Khan, M. A.; Shahidi, F. Photoxidative stability of stripped and non-stripped borage and evening primrose oils and their emulsions in water. *Food Chem.* **2002**, *79*, 47–53.

(12) Ramadan, M. F.; Kroh, L. W.; Morsel, J. T. Radical scavenging activity of black cumin (*Nigella sativa* L.), coriander (*Coriandrum sativum L.*), and niger (*Guizotia abyssinica* Cass.) crude seed oils and oil fractions. *J. Agric. Food Chem.* **2003**, *51*, 6961–6969.

(13) Khan, M. A.; Shahidi, F. Effects of natural and synthetic antioxidants of the oxidative stability of borage and evening primrose triacylglycerols. *Food Chem.* **2001**, *75*, 431–437.

(14) AOCS. *Official Methods and Recommended Practices of the American Oil Chemists'Society*4th ed.; AOCS Press: Champaign, IL, 1990.

(15) IUPAC. *Standard Methods for the Analysis of Oils and Fats and Derivatives*7th ed.; Blackwell Scientific Publishing: Oxford, U.K., 1987.

(16) Shahidi, F.; Pegg, R. B. Hexanal as an indicator of meat flavour deterioration. *J. Food Lipids* **1994**, *1*, 177–186.

(17) Snedecor, G. W.; Cochran, N. G. *Statistical Methods*, 7th ed.; Iowa University Press: Ames, IA, 1980.

(18) Shahidi, F.; Miraliakbari, H. Tree nut oils. In *Bailey's Industrial Oil and Fat Products*, 6th ed.; Shahidi, F., Ed.; Wiley-Interscience: Hoboken, NJ, 2005; pp 175−193.

(19) Dobarganes, M.; Ruiz, G. Regulation of used frying fats and validity of quick tests for discarding the fats. *Grasas Aceites* **1998**, *49*, 331–335.

(20) Maguire, L. S.; O'Sullivan, M.; Galvin, K.; O'Connor, T. P.; O'Brien, N. M. Fatty acid profile, tocopherol, squalene and phytosterol content of walnuts, peanuts, hazelnuts and the macadamia nut. *Int. J. Food Sci. Nutr.* **2004**, *55*, 171–178.

(21) Savage, G. P.; Dutta, P. C.; McNeil, D. L. Fatty acid and tocopherol contents and oxidative stability of walnut oils. *J. Am. Oil Chem. Soc.* **1999**, *76*, 1059–1065.

(22) Ramirez, M. R.; Estevez, M.; Morcuende, D.; Cava, R. Effect of the type of frying culinary fat on volatile compounds isolated in fried pork loin chops by using SPME-GC-MS. *J. Agric. Food Chem.* **2004**, *52*, 7673–7643.

Received for review January 11, 2008. Revised manuscript received March 7, 2008. Accepted March 12, 2008. We are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support in the form of a discovery grant to F.S.

JF8000982