Microwave Roasting Effects on the Physico-chemical Composition and Oxidative Stability of Sunflower Seed Oil

Fozia Anjum[a], Farooq Anwar[a,*], Amer Jamil[a], and M. Iqbal[b]

Departments of [a]Chemistry and [b]Botany, University of Agriculture, Faisalabad-38040, Pakistan

ABSTRACT: The purpose of the present study was to explore the influences of microwave heating on the composition of sunflower seeds and to extend our knowledge concerning the changes in oxidative stability, distribution of FA, and contents of tocopherols of sunflower seed oil. Microwaved sunflower seeds (*Helianthus annuus* L.) of two varieties, KL-39 and FH-330, were extracted using *n*-hexane. Roasting decreased the oil content of the seeds significantly ($P < 0.05$). The oilseed residue analysis revealed no changes in the contents of fiber, ash, and protein that were attributable to the roasting. Analysis of the extracted oils demonstrated a significant increase in FFA, *p*-anisidine, saponification, conjugated diene, conjugated triene, density, and color values for roasting periods of 10 and 15 min. The iodine values of the oils were remarkably decreased. A significant ($P < 0.05$) decrease in the amounts of tocopherol constituents of the microwaved sunflower oils also was found. However, after 15 min of roasting, the amount of α-tocopherol homologs was still over 76 and 81% of the original levels for the KL-39 and FH-330 varieties, respectively. In the same time period, the level of δ-tocopherol fell to zero. Regarding the FA composition of the extracted oils, microwave heating increased oleic acid 16–42% and decreased linoleic acid 17–19%, but palmitic and stearic acid contents were not affected significantly ($P > 0.05$).

Paper no. J11258 in *JAOCS 83*, 777–784 (September 2006).

KEY WORDS: Chemical composition, fatty acid composition, microwave roasting, oxidative stability, sunflower oilseeds, tocopherol.

Roasting and expelling are key steps for making condiment oils because the color, flavor, composition, and quality of the oil all are influenced by processing conditions (1). Microwave ovens are present in the majority of homes and today more people use microwave ovens for cooking and reheating than ever before. Nowadays convenience foods that have been subjected to minimal processing are flooding the market (2,3).

The application of microwave oven heating to culinary techniques and food processing is a recent addition to traditional cooking techniques such as roasting, boiling, and frying. Food products designed for microwave heating are popular because of their quick preparation time and convenience. The heating of food in a microwave oven is caused by interaction of an electromagnetic field with the chemical constituents of food. These interactions instantaneously generate heat because of molecular friction and excitation (2–4) and suggest applications in cooking, baking, dehydrating, thawing, tempering, pasteurizing, and sterilizing.

Although there is sufficient information available on the consequences of microwave heating on the composition and nutritional quality of food, there has been speculation on the ease of free radical formation when fatty foods are exposed to microwave energy (5). The differential heating behavior of food components can result in severely uneven heating of certain foods rich in fats and proteins (6).

The effects of microwave heating on different animal and vegetable fats have been investigated (7) as have its influences on thermo-oxidative stability of common oils and fats in household use (1,8). Little has been published on the changes in composition and oxidative stability of the oils during microwave oven heating (9).

Changes in chemical composition and levels of minor constituents affect the functional and nutritional characteristics of oils (10). Some reports suggest that retention of nutrients such as vitamins in microwaved foods is improved when the roasting time is shortened. However, other studies indicate that nutrient retention during microwave processing is not much greater than that in conventional cooking (11).

The presence of tocopherol homologs (α-, β-, γ-, and δ-) in food provides some protection against oxidation. Their amount in vegetable oils is governed by the contents of unsaturated FA (12). Unsaturated oils contain up to 1 $g \cdot kg^{-1}$ or more of tocopherols, whereas more saturated oils contain almost none. The determination of tocopherol homologs in the oil of sunflower kernels is important owing to their antioxidative effects and their positive nutritional effects in human metabolism. Microwave heating has been shown to result in the thermal oxidation of tocopherol (10,13).

Sunflowers are an important economic crop worldwide. Sunflower seed oil is light in taste and appearance and supplies more vitamin E than any other vegetable oil. It is rich in polyunsaturates (linoleic acid) and monounsaturates (oleic acid) and low in saturates (14). Because of the high level of PUFA, though, sunflower oil is susceptible to oxidation during frying and roasting (2,4).

The purpose of present study was to explore the influences of microwave roasting on the composition of two different locally grown varieties of sunflower oilseeds and to extend our knowledge concerning the changes in oxidative stability and the distribution of FA and of tocopherols in sunflower oil extracted after different microwave roasting treatments.

*To whom correspondence should be addressed.
E-mail: fqanwar@yahoo.com

MATERIALS AND METHODS

Sunflower seeds. Seeds of two commercially available sunflower hybrid varieties (KL-39 and FH-330) were procured from Ayub Agriculture Research Institute (Faisalabad, Pakistan). Each seed typically weighed 120–200 mg. The seeds were stored in polyethylene bags until analysis. Duplicate samples of seeds were collected.

Reagents and standards. All chemicals (analytical and HPLC) used in this study were from either E. Merck (Darmstadt, Germany) or Sigma-Aldrich (Buchs, Switzerland) unless otherwise noted. Pure standards of tocopherols [DL-α-tocopherol, (+)-δ-tocopherol, and (+)-γ-tocopherol] and FAME were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO).

Microwave roasting of sunflower seeds. Sunflower seeds placed in Pyrex petri dishes (10.0 g in each petri dish) were roasted in a consumer-model microwave oven at a frequency of 2450 MHz (medium power setting, oven capable of generating 500 W) for 5, 10, and 15 min. After roasting, sunflower seeds were allowed to cool to ambient temperature and thoroughly mixed prior to crushing and oil extraction.

Moisture contents of samples exposed to microwave heating were expressed as apparent moisture, and this was calculated after each exposure time by dividing the weight of moisture loss by the weight of the sample before heating.

Oil extraction. After microwave roasting, thoroughly mixed seeds were crushed by using a consumer-model electric grinder. The crushed or flaked seeds were conditioned/heated (100°C) in an electric oven (VOC-300 SD; Eyela, Tokyo, Japan) for an hour. Then each batch (~75 g) of sunflower seeds was fed into a Soxhlet extractor fitted with a 500-mL round-bottomed flask and a condenser. The extraction was carried out on a water bath (75–80°C) for 8–9 h with 300 mL of *n*-hexane (b.p. 68°C). After extraction, the solvent was distilled off under vacuum in a rotary evaporator (Eyela Rotary Vacuum Evaporator N. N. Series equipped with an Aspirator and a Digital Water Bath SB-651; Rikakikai, Tokyo, Japan) at 45°C (15).

Analysis of oilseed residues. (i) Protein contents. Protein contents were determined according to the AOAC official method (16) using a micro-Kjeldhal apparatus. Each meal sample (2 g) was digested for about an hour with 2 g of digestion mixture (Cu, Fe, and K sulfates in the ratio of 9:1:90 by wt) and 10 mL of concentrated H_2SO_4. When digestion was completed, the solution became clear. The solution was then made up to 100.0 mL in a volumetric flask with distilled water.

For the nitrogen determination, 5 mL of 2% boric acid solution was first taken in a beaker with a few drops of methyl red as indicator. Then 10 mL of the digested mixture, 10 mL of 40% NaOH solution, and 10 mL of distilled water were transferred to the distillation chamber. Ammonia was liberated, and it combined with NaOH to form NH_4OH, which was then received into the boric acid solution to form ammonium borate (pink color to yellow). Distillate (ammonium borate) was then titrated with 0.1 N H_2SO_4. The volume of acid that had been added at the point when the color of the distillate changed from yellow to pink was recorded.

Protein was calculated according to the following formula: %protein = %N × 6.25.

(ii) Fiber contents. Fiber contents were determined according to the standard International Standard Organization (ISO) method (17). Two grams of finely ground defatted meal were weighed and then boiled with 250 mL of 0.1275 N H_2SO_4, followed by the separation and washing of insoluble residues. The residues were then boiled with 250 mL of 0.313 N NaOH followed by the separation, washing, and drying of residues. The dried residues were weighed and ashed in a muffle furnace (TMF-2100; Eyela) at 600°C, and the loss of mass was determined gravimetrically.

(iii) Ash contents. Ash contents were determined by the standard ISO method (18). Two grams of meal were carbonized by heating on a gas flame and then ashed in an electric muffle furnace at 600°C until a constant mass was achieved.

Analysis of extracted oil. (i) Physical and chemical parameters of oils. Determination of density, refractive index, FFA, PV, iodine value, saponification value, unsaponfiable matter, and *p*-anisidine value of the extracted oil was carried out according to the standard IUPAC methods (19). Color was determined by Lovibond tintometer (Tintometer Ltd., Salisbury, United Kingdom) using a 1-in. (2.5 cm) cell. Specific extinctions at 232 and 268 nm were determined using a Hitachi U-2001 spectrophotometer. Samples were diluted with iso-octane to bring the absorbance within limits (0.2–0.8), and (${}^{1\%}\varepsilon_{1cm(\lambda)}$) values were calculated following the method of IUPAC (19).

(ii) Tocopherol contents. Tocopherol analyses were performed by HPLC following the method of Lee *et al*. (20). A high-performance liquid chromatograph (Sykam GmbH, Kleinostheim, Germany) equipped with an S-1121 dual piston solvent delivery system and s-3210 UV/vis diode array detector was used. One gram of sunflower oil was accurately weighed and made up to volume with acetonitrile in a 10-mL volumetric flask wrapped in aluminum foil paper to inhibit photo-oxidation. A 20-μL sample of the mixture was injected into an analytical Hypersil (Thermo Electron GmbH, Karlsruhe, Germany) ODS reversed-phase (C18) column (250 × 4.6 mm; 4 μm particle size) fitted with a C18 guard column. The mobile phase consisted of a mixture of HPLC-grade methanol and acetonitrile (65:35, vol/vol). The chromatographic separation was performed by isocratic elution of the mobile phase at a flow rate of 1 mL·min^{-1} at 30°C. The detector was set at 292 nm. Tocopherols were identified by comparing the retention times of the unknowns with those of pure standards of α-, γ-, and δ-tocopherols and quantified on the basis of peak area percentage. The peak areas were recorded and calculated by a computer with SRI peak simple chromatography data acquisition and integration software (SRI Instrument, Torrance, CA)

(iii) Determination of FA composition. FAME were prepared by IUPAC standard method 2.301(18) and analyzed on a Shimadzu gas chromatograph model 17-A fitted with an SP-2330 (Supelco, Inc., Bellefonte, PA) methyl lignocerate-coated (film thickness 0.20 μm) polar capillary column (30 m × 0.32 mm) and an FID. Oxygen-free nitrogen gas at a flow rate of 5 mL/min was used as carrier gas. Other conditions were as follows: initial

oven temperature, 180°C; ramp rate, 5°C/min; final temperature, 220°C; injector temperature 200°C; detector temperature, 250°C. FAME were identified by comparing their relative and absolute retention times with those of authentic standards. Quantification was done by a Chromatography Station for Windows (CSW32) data-handling program (Data APEX Ltd., Prague, The Czech Republic). The FA composition was reported as a relative percentage of the total peak area. The internal standard was nonadecanoic acid.

Statistical analysis. Two samples of each variety of sunflower oilseeds (microwave-treated) were analyzed individually in triplicate, and the results were reported as mean ± SD. Statistical significance of the differences between mean values was assessed by two-way ANOVA (21).

RESULTS AND DISCUSSION

Proximate analysis. Results of the proximate analysis of the unroasted (control sample) and roasted sunflower seeds are shown in Table 1. The hexane-extracted oil contents of unroasted sunflower oilseeds of varieties KL-39 and FH-330 were 35.8 and 38.8%, respectively. In roasting seeds for 5, 10 and 15 min, the oil content of both varieties decreased significantly with time ($P < 0.05$).

The moisture contents of the unroasted sunflower oilseeds of variety KL-39 and FH-330 were 7.0 and 6.3%, respectively. Contents of protein, fiber, and ash were 24.94 and 21.00; 7.01 and 9.50; and 5.00 and 5.50%, respectively.

Roasting of the seeds did not affect the fiber, ash, and protein contents significantly ($P > 0.05$). The losses in the weight of seeds of KL-39 and FH-330 after roasting for 5, 10, and 15 min amounted to 3.2, 4.6, 6.8, and 2.4, 5.2, and 6.4%, respectively. The longer the roasting time, the greater was the loss in weight of the seeds. This trend agreed with the findings of Yoshida *et al.* (2,4), who reported the loss in weight of sunflower seeds. This loss in weight may reflect total volatile substances, but it was considered to be mostly due to the loss of moisture. In the present analysis, the loss in weight of sunflower oilseeds was found to be greater as compared with those reported by Yoshida *et al.* (2), which might be attributable to variations in the genetic makeup and the original moisture contents of the varieties of sunflower oil seeds investigated. Yoshida and Kojimoto (9) and Yoshida *et al.* (3,5) reported that after roasting for different times, changes in the weight of peanut and sesame seeds may be due to the presence of moisture and volatile components. In contrast to these, Yoshida *et al*. (12) reported no significant differences in the weight loss among different cultivars of soybeans at different roasting times. Oomah and Mazza (22) reported that microwave oven-drying could be used as a quick method for moisture determination in oilseeds such as canola, flax, and mustard. Statistical analysis showed no significant differences ($P < 0.05$) in the weight loss of sunflower seeds of both varieties at different roasting times.

Microwave roasting effects on physical and chemical properties of sunflower oil. Different physical and chemical parameters of the sunflower seed oils of varieties KL-39 and FH-330 before and after microwave roasting are compared in Table 2. The refractive indices (40°C) of the control oils (extracted from unroasted sunflower seeds) were 1.4610 and 1.4640, respectively. With increasing microwave roasting time (5–15 min), the refractive index of the oils decreased, which might be due to the decrease of M.W. or probably to polymerization of unsaturated FA in the oils. These changes are statistically significant ($P < 0.05$).

The density of the control oils was 0.880 and 0.855 $mg \cdot mL^{-1}$. Roasting increased the densities of the oils in a time-dependent manner. After 15 min of roasting, the densities were 5.11 and 7.13% above the original values. This increase in values may reflect the occurrence of polymerization, which makes the oil denser.

The color of the oil extracted from microwaved sunflower seeds changed from light yellow (5 min of roasting) to yellow (10 min of roasting) to brown (15 min of roasting). Thus, by increasing the roasting time, browning substances were developed. Browning substances are very polar due to active radicals. The longer the roasting time, the greater was the intensification of the color. The formation of browning substances in many thermally

TABLE 1
Proximate Analysis of Roasted/Unroasted Sunflower Oilseeds[a]

			Roasted		
Contents	Variety	Control	5 min	10 min	15 min
Dry weight (%)	KL-39	93.00 ± 1.30	89.80 ± 1.52	88.40 ± 1.36	86.20 ± 1.80
	FH-330	93.70 ± 1.75	91.30 ± 1.77	88.50 ± 1.45	87.30 ± 1.52
Oil contents (%)	KL-39	35.80 ± 0.85	30.25 ± 0.70	30.02 ± 1.01	28.72 ± 0.81
	FH-330	38.78 ± 0.78	38.58 ± 1.12	37.81 ± 1.17	36.56 ± 0.90
Protein contents (%)	KL-39	24.94 ± 0.84	24.94 ± 0.87	24.21 ± 0.45	24.25 ± 0.85
	FH-330	21.00 ± 0.90	20.69 ± 0.62	20.70 ± 0.63	20.59 ± 0.54
Fiber contents (%)	KL-39	7.01 ± 0.36	7.00 ± 0.38	6.79 ± 0.16	6.71 ± 0.19
	FH-330	9.50 ± 0.34	9.50 ± 0.38	9.41 ± 0.43	9.02 ± 0.29
Ash contents (%)	KL-39	5.00 ± 0.40	4.98 ± 0.29	4.90 ± 0.28	4.82 ± 0.22
	FH-330	5.50 ± 0.35	5.50 ± 0.26	5.48 ± 0.31	5.45 ± 0.40

[a]Values are presented as mean ± SD of duplicate samples analyzed individually in triplicate. The control is unroasted sunflower seed sample.

TABLE 2
Physical and Chemical Properties of Roasted/Unroasted Sunflower Seed Oils[a]

Contents	Variety	Control	Roasted		
			5 min	10 min	15 min
Color (red units)	KL-39	1.60 ± 0.12	2.70 ± 0.16	5.60 ± 0.12	6.80 ± 0.41
	FH-330	1.30 ± 0.05	2.00 ± 0.09	3.60 ± 0.15	4.00 ± 0.22
Color (yellow units)	KL-39	16.00 ± 1.13	27.04 ± 1.23	40.00 ± 1.19	50.44 ± 3.10
	FH-330	13.00 ± 1.14	19.64 ± 0.99	36.00 ± 1.40	40.44 ± 2.42
Refractive index (n_D 40°C)	KL-39	1.4610 ± 0.002	1.4610 ± 0.002	1.4570 ± 0.003	1.4550 ± 0.001
	FH-330	1.4640 ± 0.002	1.4630 ± 0.003	1.4600 ± 0.002	1.4590 ± 0.002
Density (24°C) ($mg◊mL^{-1}$)	KL-39	0.880 ± 0.001	0.880 ± 0.001	0.915 ± 0.001	0.925 ± 0.003
	FH-330	0.855 ± 0.002	0.910 ± 0.001	0.911 ± 0.001	0.916 ± 0.002
Iodine value (g of I/100 g of oil)	KL-39	138.04 ± 1.90	128.1 ± 1.60	124.4 ± 1.60	113.5 ± 1.80
	FH-330	140.00 ± 1.40	135.0 ± 1.00	123.5 ± 1.51	120.5 ± 1.45
Unsap matter (%)	KL-39	0.59 ± 0.04	0.59 ± 0.05	0.40 ± 0.02	0.40 ± 0.04
	FH-330	0.40 ± 0.02	0.38 ± 0.04	0.35 ± 0.01	0.30 ± 0.04
Saponification value (mg of KOH/g of oil)	KL-39	189.07 ± 2.35	189.33 ± 2.10	204.00 ± 3.50	233.00 ± 3.20
	FH-330	185.00 ± 3.12	190.02 ± 3.60	203.62 ± 4.35	238.13 ± 4.00
FFA (% as oleic acid)	KL-39	0.800 ± 0.02	0.850 ± 0.02	0.866 ± 0.01	0.945 ± 0.02
	FH-330	0.745 ± 0.02	0.933 ± 0.01	0.996 ± 0.02	1.070 ± 0.03

[a]Values are presented as mean ± SD of duplicate samples analyzed individually in triplicate. The control is oil extracted from unroasted sunflower oilseeds.

processed foods results from Maillard-type nonenzymatic reactions, caramelization, and phospholipid degradation and increases with increasing roasting time (1). Yen (23), Yoshida and Kojimoto (9), and Kim *et al.* (24) reported that an increase in roasting time and temperature of seeds such as rice germ and sesame seeds resulted in a significant increase in the color of oils. Megahed (25) reported that oil extracted from peanuts showed gradual darkening and higher Lovibond color indices with increasing heating time. Hafez *et al.* (26) demonstrated that TAG were slightly hydrolyzed by microwaves to produce FFA; and an increase in microwave roasting time was accompanied by an increase in the browning substances and phospholipids degradation, which may be attributed to the increase of polar lipids. Phospholipids were reported to cause browning of the oil during roasting (27). Therefore, an increase in browning substances may be attributable to the increase in contents of other lipids, such as glyceroglycolipids, in the oil. Hassanein *et al.* (28) reported that color intensity increases with the formation of browning substances, as a result of phospholipid degradation during microwave heating. Changes in red and yellow color with heating of the two varieties of sunflower oils were significantly ($P < 0.05$) different.

Saponification values of the control sunflower oil samples of varieties KL-39 and FH-330 were 189.0 and 185.0 $mg \cdot g^{-1}$, respectively. After 15 min of microwave roasting of sunflower seeds, the saponification values of the extracted oils were 23 and 28.72% greater than the original values, respectively. The longer the roasting time, the greater was the saponification value. Saponification value was significantly increased ($P < 0.05$) after 10 and 15 min of roasting in both varieties of sunflower oil.

The unsaponifiable matter (unsap) values of the control sunflower oil varieties KL-39 and FH-330 were 0.590 and 0.404%, respectively. The unsap values of the two hybrid varieties were significantly different ($P < 0.05$). As the roasting time increased, there was a significant decrease ($P < 0.05$) in the values of unsap. In contrast, the unsap of rice bran oil increased with increased roasting time (29).

The FFA values of the KL-39 and FH-330 control oils were 0.80 and 0.74%, respectively. As the seeds were roasted, the FFA contents increased significantly ($P < 0.05$), in agreement with the results of Yoshida *et al*. (6), who found that FFA in sunflower seed oil increased with increasing roasting time. The increase in FFA of the oil might be attributed to hydrolysis of TAG by microwaves to produce FFA and DAG, as reported for olive oil (30), peanuts and sesame seeds (4,5,10). Fukuda (31) reported that roasted sesame oil contained more FFA than other purified vegetable oils.

Iodine values of control oils of KL-39 and FH-330 were 138.0 and 140.0 g of I/100 g of oil, respectively. As roasting time increased, the iodine values of the extracted oils decreased. These decreases may be attributable to reductions in the number of unsaturation sites as a result of oxidation, polymerization, or breakage of the long-chain FA. However, Jung *et al*. (32) reported that the iodine values of red pepper seed oils did not change with roasting time. In sunflower seed and peanut oils, Yoshida *et al*. (2,33) found that roasting caused a significant decrease ($P < 0.05$) in molecular species containing more than four double bonds.

Iodine value is often used as a rough criterion of stability of oil during roasting, as the more unsaturated oils are unstable to thermal oxidation. More precise indication of stability is given by the amounts of PUFA present, e.g., linoleic and linoleinic acids, which have more than one double bond in the molecule. These oxidize more rapidly than oleic acid, which has one double bond. Thus for two oils with the same iodine value, the oil with the higher linoleic acid content will oxidize more rapidly than the oil with the higher oleic acid content. Changes with

TABLE 3
Effect of Roasting on Oxidative Stability of Sunflower Seed Oil

Contents	Variety	Control	Roasted		
			5 min	10 min	15 min
$\varepsilon_{1cm}^{1\%}$ (λ 232 nm)	KL-39	4.10 ± 0.33	6.47 ± 0.31	8.01 ± 0.59	9.46 ± 0.52
	FH-330	9.66 ± 0.43	11.53 ± 0.70	12.68 ± 0.65	17.04 ± 0.58
$\varepsilon_{1cm}^{1\%}$ (λ 270 nm)	KL-39	0.60 ± 0.05	0.61 ± 0.05	0.95 ± 0.09	1.06 ± 0.07
	FH-330	0.58 ± 0.05	0.77 ± 0.05	0.87 ± 0.09	0.99 ± 0.07
PV (mequiv/kg of oil)	KL-39	3.77 ± 0.12	4.01 ± 0.12	4.05 ± 0.26	6.93 ± 0.19
	FH-330	2.60 ± 0.12	4.01 ± 0.09	4.95 ± 0.16	5.65 ± 0.21
p-Anisidine value	KL-39	3.24 ± 0.19	2.29 ± 0.19	2.42 ± 0.21	3.48 ± 0.18
	FH-330	4.99 ± 0.25	1.40 ± 0.17	2.30 ± 0.11	2.50 ± 0.12

[a]Values are presented as mean ± SD of duplicate samples analyzed individually in triplicate. The control is oil extracted from unroasted sunflower oilseeds.

roasting time in iodine values of oils of both varieties of sunflower were significant ($P < 0.05$).

Effect of roasting on oxidative stability of sunflower oil. Different parameters studied for the oxidative stability of the oils extracted from control and roasted sunflower seeds of varieties KL-39 and FH-330 are shown in Table 3.

PV serves as an indicator of the extent of formation of primary oxidation products in oils whereas the *p*-anisidine value reflects the degree of secondary oxidation product formation (12) There were appreciable increases in PV and *p*-anisidine values at 10 min of roasting, and more pronounced differences ($P < 0.05$) were observed after 15 min of roasting. Yoshida *et al.* (5) reported a minor increase in PV and *p*-anisidine value in peanut seed oil after 30 min of roasting, and a gradual increase with longer roasting time in sesame seed oil (9,10). In general, PV do not represent the absolute state of oxidation of oil because hydroperoxides are unstable on heating. This results in rapid transformation to secondary products (34). However, the indicators for secondary oxidation products were very low during microwave heating. *p*-Anisidine values were the most sensitive of the parameters enumerated in Table 3 to changes in the chemical properties of purified fats heated in a microwave oven. Lee *et al*. (1) suggested that the greater the roasting time, the greater would be the increase in PV of the safflower oil. Microwave heating accelerates the formation of some undesirable and harmful compounds (e.g., oxidation products, pigments) during the roasting of peanuts. Thais *et al*. (35) and Vieira and Regitano (36) investigated the effects of microwave heating on the oxidative stability of refined canola, corn, and soybean oils by measuring absorptivity in the UV spectrum and by chemical analysis (PV and acid values). PV showed a significant difference ($P < 0.05$) in the initial stage of heating (0–6 min) for all oils. After this period PV could not be correlated with absorptivity at 232 nm owing to the instability of hydroperoxides at high temperatures.

The specific extinctions at 232 and 270 nm, which reflected the oxidative deterioration and purity of the oils (12), were 4.104 and 0.600, and 9.664 and 0.581 in the control oils of varieties KL-39 and FH-330, respectively. When the oilseeds were subjected to microwave roasting, the extracted oils showed a significant ($P < 0.05$) increase in the formation of conjugated dienes and trienes. Similar findings were reported by Megahed (25), but Yoshida *et al.* (33) showed that roasting caused a significant decrease ($P < 0.05$) in the amount of diene and triene species present in TAG. Vieira and Regitano-D'Arce (36) reported that oxidative stability of corn oil is dependent on the absorptivities at 232 and 270 nm, which increased during microwave exposure.

Tocopherol distribution. The effects of microwave roasting on tocopherol contents of the oils of the two varieties of sunflower seeds (varieties KL-39 and FH-330) are shown in Table 4. α-Tocopherol was the predominant component (958.86 and 887.10 $mg \cdot kg^{-1}$, respectively), γ-tocopherol was undetected in both varieties, and δ-tocopherol contents were 37.00 and 44.00 $mg \cdot kg^{-1}$, respectively. After 15 min of roasting, the level of α-tocopherols was reduced to 731.34 (24%) and 721.23 $mg \cdot kg^{-1}$ (19%) for KL-39 and FH-330, respectively. δ-Tocopherol was reduced to zero. Yoshida *et al.* (7) reported that α-tocopherol showed the highest rate of loss,

TABLE 4
Effect of Roasting on Tocopherol Components[a]

Contents	Variety	Control	Roasted		
			5 min	10 min	15 min
Tocopherol (α)	KL-39	958.86 ± 19.55	894.36 ± 12.79	838.26 ± 20.90	731.34 ± 15.52
	FH-330	887.10 ± 14.45	741.29 ± 20.85	739.12 ± 16.40	721.23 ± 18.98
Tocopherol (δ)	KL-39	37.00 ± 2.52	31.67 ± 1.31	11.00 ± 0.51	ND
	FH-330	44.25 ± 1.49	43.48 ± 2.60	01.60 ± 0.17	ND

[a]Values are presented as mean ± SD of duplicate samples analyzed individually in triplicate. ND = not detected. The control is oil extracted from unroasted sunflower oilseeds.

TABLE 5
Effect of Roasting on the FA Composition (%) of Sunflower Oils

Contents	Variety	Control	Roasted		
			5 min	10 min	15 min
Palmitic	KL-39	8.06 ± 0.23	8.07 ± 0.19	8.05 ± 0.30	8.08 ± 0.23
	FH-330	7.42 ± 0.14	8.00 ± 0.16	8.05 ± 0.21	7.42 ± 0.27
Stearic	KL-39	4.04 ± 0.32	4.00 ± 0.20	4.04 ± 0.15	4.05 ± 0.01
	FH-330	3.35 ± 0.18	3.38 ± 0.26	3.41 ± 0.10	3.40 ± 0.06
Oleic	KL-39	30.82 ± 0.45	36.15 ± 0.60	40.30 ± 0.42	43.79 ± 0.70
	FH-330	39.68 ± 0.68	39.36 ± 0.50	44.03 ± 0.40	45.97 ± 0.64
Linoleic	KL-39	53.93 ± 0.63	46.89 ± 0.89	39.01 ± 0.61	43.58 ± 0.55
	FH-330	49.53 ± 0.55	45.80 ± 0.35	43.82 ± 0.65	40.68 ± 0.72

[a]Values are presented as mean ± SD of duplicate samples analyzed individually in triplicate. The control is oil extracted from unroasted sunflower oilseeds.

followed by β-, γ-, and δ-tocopherol, during microwave heating. Our results were comparable with those of Yoshida *et al.* (6,10,37). Yoshida and Takagi (38) reported that >80% tocopherol of the original level in soaked soybean oils still remained after 20 min of microwave roasting. Barrera-Arellano *et al*. (39) found that α-tocopherol losses were very rapid and independent of the unsaturation of the TAG system under their conditions. α-Tocopherol degraded faster in less unsaturated lipids. Takagi *et al*. (11) reported that, with increasing roasting times, as much as 40% of the individual tocopherols present in the seed coat of the soybean was lost at 12 min of roasting. On the other hand, over 80% of the tocopherols were retained in the cotyledons and axis after 20 min of roasting.

The amount of tocopherols in animal fats exposed to microwave heating was significantly ($P < 0.05$) destroyed after 8 min of heating. The loss increased in the order δ- < β- < γ- < α-tocopherol (7). However, Lee *et al*. (1) reported that the contents of α-tocopherol in safflower oil gradually increased as roasting temperature increased up to 160°C but then decreased up to 180°C. According to Yen (23), the level of tocopherol in sesame oils prepared by electric oven heating increased with roasting temperature up to 200°C but decreased up to 260°C. Yoshida *et al*. (38) also reported that the tocopherol concentration gradually decreased at a similar rate in oils prepared from soybeans roasted in a microwave oven and that percentages of the losses increased significantly after 12 min of exposure time. Moreau *et al.* (40) showed that a significant amount of γ-tocopherol in corn hull was bound to proteins or linked to phosphates or phospholipids and that heat broke these bonds. Therefore, these results suggested that changes of tocopherol contents in the oils were dependent on roasting temperature and processing time.

FA composition. FA compositions of control and roasted sunflower seed oil are given in Table 5. The principal FA components of the control sunflower oil varieties KL-39 and FH-330 were palmitic (C16:0) stearic (C18:0), oleic (C18:1), and linoleic acid (C18:2) in concentrations of 8.06, 7.42; 4.04, 3.35; 30.82, 39.68; and 53.93, 49.53%, respectively. When both these varieties were roasted in a microwave oven for 5, 10, and 15 min, there was little change in the FA composition of the oils. Oleic and linoleic acids were more affected by microwave heating than palmitic and stearic acids. The longer the roasting time, the higher was the percentage of the oleic acid and lesser was that of linoleic acid. After 15 min of roasting, oleic acid was increased to a level of 43.79 and 45.97%, respectively, whereas linoleic acid contents were decreased to 43.58 and 40.68 % for KL-39 and FH-330 sunflower oils, respectively. The results of the FA analysis showed no formation of any *trans* FA during microwave roasting. Yoshida *et al*. (10,38) observed a decrease in the amount of PUFA in soybean oil. The composition was generally characterized by relatively higher percentages of saturated FA (palmitic or stearic acids) and relatively lower percentages of unsaturated FA such as oleic or linoleic acid. The trends became more pronounced with the progress of roasting. Yoshida *et al.* (5) reported a minor decrease in FA composition of the TAG fraction but a more pronounced decline in the phospholipids fraction after 12 min of roasting. Hassanein *et al.* (28) reported that heat treatment causes a worsening of the nutritional quality of the fatty fraction. As a consequence, the contents of unsaturated FA and PUFA decreased, with greater variations in the oils heated by microwave than by a conventional oven, while the saturated FA contents did not change substantially. Similarly Yoshida *et al*. (3) reported that with continuous roasting, small but significant differences were observed in the patterns of the FA composition. However in contrast to our results Yoshida *et al*. (4,6) reported no significant ($P > 0.05$) loss in the FA distribution within 12 min of roasting in sunflower seed oil. Yen (23), Yoshida and Kojimoto (9), and Kim *et al*. (24) found no differences in FA composition of rice germ and sesame seed oils prepared at different roasting temperatures and times. Yoshida and Kojimoto (9) reported that a significant ($P < 0.05$) difference occurred in FA composition of phospholipids of sesame oil after 12 min of microwave heating. The heat treatments also caused an increase in the *trans*-isomers of unsaturated FA. Tomioka and Morioka (41) reported that oxidative deterioration of FA in fish meat was significantly promoted by heating, and the effects of microwave heating were much larger than those of conventional heating. However, Ramezanzadeh *et al*. (42) reported that linoleic and linolenic acid contents of microwave-heated rice bran did not change significantly ($P < 0.05$) from those in raw rice bran. Echarte (43) reported that

microwave heating hardly modified the FA profiles of either chicken and beef patties.

REFERENCES

1. Lee, Y.C., I.H. Kim, J. Chang, Y.K. Rhee, H.I. Oh, and H.K. Park, Chemical Compositions and Oxidative Stability of Safflower Oil Prepared with Expeller from Safflower Seeds Roasted at Different Temperatures. *J. Food Sci. 69*:33–38 (2004).
2. Yoshida, H., Y. Hirakawa, and S. Abe, Influence of Microwave Roasting on Positional Distribution of Fatty Acids of Triacylglycerols and Phospholipids in Sunflower Seeds (*Helianthus annuus* L.), *Eur. J. Lipid Sci. Technol. 103*:201–207 (2002).
3. Yoshida, H., S. Abe, Y. Hirakawa, and S. Takagi, Roasting Effects on Fatty Acid Distributions of Triacylglycerols and Phospholipids in Sesame (*Sesamum indicum*) Seeds, *J. Sci. Food Agric. 81*:620–626 (2001).
4. Yoshida, H., Y. Hirakawa, and S. Abe, Roasting Influence on Molecular Species of Triacylglycerols in Sunflower Seeds (*Helianthus annuus* L.), *Food Res. Int. 34*:613–619 (2001).
5. Yoshida, H., Y. Hirakawa, Y. Tomiyama, and Y. Miz, Effect of Microwave Treatment on the Oxidative Stability of Peanut (*Arachis hypogeae*) Oils and the Molecular Species of Their Triacylglycerols, *Eur. J. Lipid Sci. Technol. 105*:351–358 (2003).
6. Yoshida, H., Y. Hirakawa, S. Abe, and Y. Mizushina, The Contents of Tocopherols and Oxidative Quality of Oils Prepared from Sunflower (*Helianthus annuus* L.) Seeds Roasted in a Microwave Oven, *Ibid. 104*:116–122 (2002).
7. Yoshida, H., I. Kondo, and G. Kojimoto, Effects of Microwave Energy on the Relative Stability of Vitamin E in Animal Fats, *J. Sci. Food Agric. 58*:531–534 (1992).
8. Albie, T., A. Lanzon, A. Guinda, M. Leon, and M. C. Perez-Camino, Microwave and Conventional Heating Effects on the Thermoxidative Degradation of Edible Fats, *J. Agric. Food Chem. 45*:3795–3798 (1997).
9. Yoshida, H., and G. Kojimoto, Microwave Heating Effects Composition and Oxidative Stability of Sesame (*Sesamum indicum*) Oil, *J. Food Sci. 58*:616–625 (1994).
10. Yoshida, H., J. Shigezaki, S. Takagi, and G. Kojimoto, Variations in the Composition of Various Acyl Lipids, Tocopherols and Lignans in Sesame Seed Oils Roasted in a Microwave Oven, *J. Sci. Food Agric. 68*:407–415 (1995).
11. Takagi, S., H. Lenaga, C. Tsuchiya, and H. Yoshida, Microwave Roasting Effects on the Composition of Tocopherols and Acyl Lipids Within Each Structural Part and Section of a Soybean, *Ibid. 79*:1155–1162 (1999).
12. Anwar, F., T. Anwar, and Z. Mehmood, Methodical Characterization of Rice Bran Oil from Pakistan, *Grasas Aceites 56*:126–127 (2005).
13. Yoshida, H., K. Matsuda, Y. Hirakawa, and Y. Mizushina, Roasting Effects on the Distribution of Tocopherols and Phospholipids Within Each Structural Part and Section of Soybeans, *J. Am. Oil Chem. Soc. 80*:665–674 (2003).
14. Shahbaz, A., and F. Hassain, Oil Yield and Fatty Acid Composition of Spring Sunflower, *Pak. J. Biol. Sci. 12*:2063–2064 (2000).
15. ISO (International Standard Organization), Oilseed Determination of Hexane Extract (or light petroleum ether extract) Called "Oil Contents," ISO, Geneva, Standard No. 659 (1979).
16. AOAC, *Official Methods of the Association of Official Analytical Chemists*, 14th edn., AOAC, Arlington, VA, 1984, Method 28.110.
17. ISO, Animal Feeding Stuff, Determination of Nitrogen and Calculation of Crude Protein Contents, ISO, Geneva, Standard No. 5983 (1981).
18. ISO, Oilseeds Residues, Determination of Total Ash, ISO, Geneva, Standard No. 749 (1977).
19. International Union of Pure and Applied Chemistry (IUPAC), *Standard Methods for the Analysis of Oils and Fats and Derivatives,* 7th revised and enlarged edn., edited by C. Paquot and A. Hautfenne, Blackwell Scientific, London 1987.
20. Lee, B.L., A.L. New, and C.N. Ong, Simultaneous Determination of Tocotrienols, Tocopherol, Retinol and Major Carotenoids in Human Plasma, *Clin. Chem. 49*:2056–2066 (2003).
21. Steel, R.G.D., and J.H. Torrie, *Principles and Procedures of Statistics,* 2nd edn., McGraw-Hill, Singapore, 1992.
22. Oomah, B.D., and G. Mazza, Microwave Oven Drying for Moisture Determination in Flax, Canola and Yellow Mustard Seeds, *Lebensm. Wiss. Technol. 25*:523–526 (1992).
23. Yen, G.C., Influence of Seed Roasting Process on the Changes in Composition and Quality of Sesame (*Sesamum indicum*) Oil, *J. Sci. Food Agric. 50*:563–570 (1990).
24. Kim, I.H., C.J. Kim, M.J. You, K.W. Lee, C.T. Kim, S.H. Chung, and B.S. Tae, Effect of Roasting Temperature and Time on the Chemical Composition of Rice Germ Oil, *J. Am. Oil Chem. Soc. 79*:413–418 (2002).
25. Megahad, M.G., Microwave Roasting of Peanuts: Effects on Oil Characteristics and Composition, *Nahrung 45*:255–257 (2001).
26. Hafez, Y.S., G. Singh, M.E. Mclellan and L. Montore-Lord, Effects of Microwave Heating on Nutritional Quality of Soybean, *Nutr. Rep. Int. 28*:413–421 (1983).
27. Husain, S.R., J. Tarao, and S. Matsushita, Effect of Browning Reaction Products of Phopholipids on Autoxidation of Methyl Linoleate, *J. Am. Oil Chem. Soc. 63*:1457–1460 (1986).
28. Hassanein, M.M., S.M. El-Shami, and M.H. Al-Mallah, Changes Occurring in Vegetable Oils Composition Due to Microwave Heating, *Grasas Aceites 54*:343–349 (2003).
29. Ko., S.-N., C.-J. Kim, C.-T. Kim, H. Kim, S.-H. Chung, S.-M. Lee, H.-H. Yoon, and I.-H. Kim, Changes of Vitamin E Content in Rice Bran with Different Heat Treatment, *Eur. J. Lipid Sci. Technol. 5*:225–228 (2003).
30. Cossignani, L., M.S. Simontti, A. Neri, and P. Damiani, Changes in Olive Oil Composition Due to Microwave Heating, *J. Am. Oil Chem. Soc. 75*:931–937 (1998).
31. Fukuda, Y., Food Chemical Studies on the Antioxidants in Sesame Seed, *Nippon Shokuhin Kogyo Gakkaishi* (*J. Jpn. Soc. Food Sci.) 37*:484–492 (1990).
32. Jung, M.Y., J.Y. Bock, S.O. Baik, J.H. Lee, and T.K. Lee, Effects of Roasting on Pyrazine Contents and Oxidative Stability of Red Pepper Seed Oil Prior to Its Extraction, *J. Agric. Food Chem. 47*:2203–2206 (1999).
33. Yoshida, H., S. Takagi, and Y. Hirakawa, Molecular Species of Triacylglycerols in the Seed Coats of Soybeans (*Glycine max* L.) Following Microwave Treatment, *J. Food Chem. 70:*63–69 (2000).
34. Gray, J.I., Measurement of Lipid Oxidation; A Review, *J. Am. Oil Chem. Soc. 55*:539–546 (1978).
35. Vieira, T.M.F.S., and M.A.B. Regitano D'Arce, Stability of Oils Heated by Microwave: UV Spectrophotometeric Evaluation, *Ciên. Tecnol. Aliment. 18*:433–437 (1998).
36. Vieira, T.M., and M.A.B. Regitano D'Arce, UV Spectrophotometric Evaluation of Corn Oil Oxidative Stability During Microwave Heating and Oven Test, *Nahrung 46*:279–282 (2002).
37. Yoshida, H., S. Takagi, and S. Mitsuhashi, Tocopherol Distribution and Oxidative Stability of Oils Prepared from the Hypocotyl of Soybeans Roasted in a Microwave Oven, *J. Am. Oil Chem. Soc. 76*:915–920 (1999).
38. Yoshida, H., and S. Takagi, Vitamin E and Oxidative Stability of Soybean Oil Prepared with Beans at Various Moisture Contents Roasted in a Microwave Oven, *J. Sci. Food Agric. 72*:111–119 (1996).

39. Barrera-Arellano, D., V. Ruiz-Mendez, J. Velasco, G. Marquez-Ruiz, and M.C. Dobarganes , Loss of Tocopherol and Formation of Degradation Compounds in Triacylglycerol Model Systems Heated at High Temperature, *J. Sci. Food Agric. 79*:1923–1928 (1999).
40. Moreau, R.A., K.B. Hicks, and M.J. Powell, Effects of Heat Pretreatment on the Yield and Composition of Oil Extracted from Corn Fiber, *J. Agric. Food Chem. 47*:2867–2871 (1999).
41. Tomioka, F., and M. Morioka, Oxidative Deterioration of Neutral Lipids and Phospholipids in Pacific Saury by Microwave Heating, *Nippon Kaseigaku Kaishi 43*: 1103– 1110 (1992).
42. Ramezanzadeh, F.M., R.M. Rao, W. Prinyawiwatkul, W.E. Marshall, and M. Windhauser, Effects of Microwave Heat, Packaging, and Storage Temperature on Fatty Acid and Proximate Compositions in Rice Bran, *Nahrung. 45*:129–132 (2001).
43. Echarte. M., D. Ansorena, and I. Astiasaran, Consequences of Microwave Heating and Frying on the Lipid Fraction of Chicken and Beef Patties, *J. Agric. Food Chem. 49*:5662–5667 (2001).

[Received October 11, 2005; accepted June 8, 2006]