

RANCIDITY OF WALNUTS AND ALMONDS AFFECTED BY SHORT TIME HEAT TREATMENTS FOR INSECT CONTROL

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ABSTRACT

Short time heat treatments effectively control insect contamination of nuts containing substantial quantities of polyunsaturated fatty acids susceptible to oxidative rancidity. Walnut kernels contain greater concentrations of polyunsaturated fatty acids than almond kernels. The objectives of this research were to investigate the lipid stability of shelled walnuts and almonds as affected by short time heat treatments and accelerated storage temperatures. Heating treatments were at 55C for 2 min, 55C for 10 min, 60C for 2 min or 60C for 10 min to simulate predetermined deinfestation treatments. Untreated control and heat treated shelled walnut and almond kernels were stored at 25C for 5, 15, 30 and 60 days or 35C for 2, 5, 10 and 20 days to simulate the shelf lives of walnut and almond kernels at 4C for 2 years. Oils extracted from untreated and short time heat treated walnut kernels exhibited higher peroxide values than oils extracted from untreated and short time heat treated almond kernels under equivalent conditions. Oils extracted from untreated walnut kernels exhibited significantly ($P \leq 0.05$) higher peroxide values than oils extracted from short time heat treated walnut kernels after 5, 15, 30, and 60 days of storage at 25C, or after 2, 5, 10, or 20 days of storage at 35C. Oils extracted from untreated almond kernels exhibited higher peroxide values than oils extracted from short time heat treated almond kernels after 5, 15, 30, or 60 days of storage at 25C, or after 2, 5, 10 or 20 days of storage at 35C. Oils extracted from untreated walnut kernels and oils extracted from short time heat treated walnut kernels exhibited higher peroxide values than oils extracted from almond kernels after storage at 25C or 35C. Short time heat treatment does not enhance development of rancidity during accelerated storage of walnut or almond kernels.

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INTRODUCTION

Short time heat treatments based on radio frequency energy can be used to control insect pests of concern in international trade of tree nuts (Tang *et al.* 2000). Walnuts and almonds are often fumigated or heated to remove contaminating insects. Walnuts and almonds contain high concentrations of polyunsaturated fatty acids susceptible to oxidative and hydrolytic rancidity. Walnut kernels contain 62% total lipids, 18% carbohydrate, 14% protein, 6% minerals, and 3.7% moisture. Fatty acids in walnut kernels include approximately 32% linoleic acid and 7% linolenic acid (USDA 1984). Almond kernels contain 52% total lipids, 20% carbohydrate, 20% protein, 5% minerals, and 4.4% moisture. Fatty acids in almond kernels include approximately 11% linoleic acid and 0.4% linolenic acid (USDA 1984). The unsaturated fatty acids in walnuts and almonds are susceptible to oxidative rancidity, which produces undesirable volatile compounds and off-flavors. Light, trace minerals, antioxidants, elevated temperatures, and the presence of unsaturated fatty acids enhance the oxidation of walnuts and almonds. Macrae *et al.* (1993), and Young and Cunningham (1991) stated that almonds and almond products have a longer shelf-life compared to other nuts because they contain smaller concentrations of polyunsaturated fatty acids and larger concentrations of tocopherol antioxidants. Almond kernels contain higher concentrations of alpha-tocopherol (~24 mg per 100 g) than walnut kernels (~2.62 mg per 100 g) (USDA 1984).

Young and Cunningham (1991) reported that almonds, macadamia nuts, and pistachios are acceptable after 6 to 9 months storage at 38C, while cashews, hazelnuts, peanuts, pecans, and walnuts are acceptable after only 2 to 5 months storage at 38C without becoming rancid as judged by sensory panels. Fourie and Basson (1989) stated that few flavor differences in almonds could be detected after 12 months of storage at room temperature. Macadamia nuts tend to develop oxidative rancidity rapidly during storage at room temperature, but can be stored at 2C for up to a year without becoming rancid. Macadamia nuts are acceptable after 3 months storage at room temperature and after 18 months storage at -18C. The oxidative stability of nut kernels decreases with an increase in storage temperature.

Chemical analyses for assessing oxidative rancidity include peroxide value (PV) reported as milliequivalents of peroxide per kilogram of oils. Peroxide values of walnut kernel oils less than 3.0 meq/kg indicate acceptable quality walnuts (Quality Nut Co., Empire, CA). Peroxide values of almond kernel oils less than 2.0 meq/kg indicate acceptable quality almonds (Paramount Farms, Bakersfield, CA). The primary oxidation of kernel oils produces peroxides and hydroperoxides. Autoxidation of unsaturated fatty acids is a continuous process leading to secondary oxidation products such as aldehydes, ketones, alcohols, and aliphatic hydrocarbons (Gutteridge 1986; Allen and Hamilton 1999).

Chemical analyses for assessing secondary oxidation products include thiobarbituric acid (TBA) and *para*-anisidine values. TBA value is expressed by converting absorbance readings to milligrams of malonaldehyde per kilogram of oils. *Para*-anisidine value is defined as 100 times the absorbance of a solution containing 1 g of oil in 100 mL of isooctane and *para*-anisidine solvent in a 1 cm cuvette observed at 350 nm. *Para*-anisidine value determines the concentration of aldehydes in oils, principally 2-alkenals, and 2,4-alkadienals produced during oxidation.

Hydrolytic rancidity results from hydrolysis of triacylglycerols in the presence of lipases and moisture. The analysis used to assess hydrolytic rancidity is fatty acid value. Fatty acid value is the determination of fatty acids in oils by titration against a standardized alkali solution. The nut industry provides standards for fatty acid values of kernel oils that define acceptable quality. Fatty acid values less than 1.5%, calculated as oleic acid, indicate acceptable quality walnuts (Quality Nut Co., Empire, CA). Fatty acid value less than 1.0%, calculated as oleic acid, indicate acceptable quality almonds (Paramount Farms, Bakersfield, CA).

The objective of this research was to investigate the lipid stability of shelled walnut and almond kernels as affected by: (1) predetermined disinfestation of walnut and almond kernels heat treatment at 55C or 60C for 2 or 10 min; and (2) accelerated storage temperatures to simulate the shelf-life of walnut and almond kernels at 4C for 2 years, as calculated from Q_{10} .

MATERIALS AND METHODS

Seeds of Walnuts and Almonds

Shelled walnuts, *Juglans regia* (cv. Chandler), were harvested in September, 1998 and obtained from Quality Nut Co. (Empire, CA). Shelled almonds, *Prunus dulcis* (cv. Nonpareil), were harvested in August, 1998 and obtained from Paramount Farms (Bakersfield, CA). Shelled walnuts and almonds were stored for ~ 3 months at recommended optimum storage conditions of 2 to 4C and 65 to 70% relative humidity in polyethylene bags before conducting short time heat treatments.

Heat and Storage Treatments

The experiment was divided into four heating treatments and two storage temperatures. Heating treatments selected were 55C for 2 min, 55C for 10 min, 60C for 2 min, or 60C for 10 min (Fig. 1 to 4) as predetermined by Wang *et al.* (2002a, b) to deinfest unshelled walnuts and almonds (Fig. 5). Temperatures were measured by using thermocouples.

Untreated control and heat treated shelled walnut and almond kernels were stored at 25C for 5, 15, 30, and 60 days or at 35C for 2, 5, 10, and 20 days to simulate the shelf-life of walnut and almond kernels at 4C for 2 years as

calculated from Q_{10} based on \log_{10} . $Q_{10} = \frac{E_A}{R} * \frac{4.34}{T(T+10)}$

where: E_A = activation energy (KJ/mol);
 R = Universal gas constant (0.0038314 KJ/K * mol); and
 T = Temperature (K).

Q_{10} of 3.41 at 35C was based on E_A of 100 kJ/mol (Taeukis *et al.* 1992).

Moisture Content

The moisture content of walnut and almond kernels was determined by official method 934.06 and recommended practices of the American Oil Chemists Society (AOCS 1995). Walnut or almond kernels were blended in a coffee bean grinder (Braun, Woburn, MA) for 1 min. Five grams of the blended walnut or almond kernels were weighed into tared disposable aluminum weighing dishes. Walnut and almond kernels were dried for 6 h in a vacuum oven at 70 ± 1 C under pressure ≤ 100 mm Hg (13.3 kPa) with air flow (ca two bubbles/s). Blended walnut and almond kernels were cooled in a desiccator before being weighed. Moisture content was calculated on a wet basis:

$$MC_{wb} = \frac{\text{wt of nuts before drying} - \text{wt of nuts after drying}}{\text{wt of nuts before drying}} * 100$$

Oil Extraction

Approximately 150 g of untreated control or heat treated shelled walnut kernels or 250 g of untreated control or heat treated shelled almond kernels were weighed to obtain approximately 40 g of kernel oil. Shelled walnut and almond kernels were pressed with a Carver Laboratory Press (Fred S. Carver Inc., Summit, NJ) to obtain walnut and almond oils. The pressed oils were stored in amber glass containers (100 mL) at room temperature (21C). Chemical analyses were initiated within 3 h after pressing. Chemical analyses for assessing oxidative rancidity were peroxide values, thiobarbituric acid (TBA), and *para*-anisidine values (AOCS 1997). Hydrolytic rancidity was determined by titrating fatty acid values (AOCS 1989). Table 1 presents standard peroxide and fatty acid values recognized as indices of acceptable quality for shelled walnut or almond kernels.

TABLE 1.
RECOGNIZED STANDARDS OF ACCEPTABLE QUALITY SHELLED WALNUT
AND ALMOND KERNELS

Types	Peroxide value* (meq/kg of oil)	Fatty acid value* (% Oleic)	Ref
Walnuts	< 1.0	< 2.0	1
	< 3.0	< 1.5	2
Almonds	< 2.0	< 1.0	3

*Standard values followed by nut industry.

Ref: ¹Diamond of California (Stockton, CA)

²Quality Nut Co. (Empire, CA)

³Paramount Farms (Bakersfield, CA)

Chemical Analyses for Oxidative Rancidity

Chemical analyses for assessing oxidative rancidity were peroxide values, thiobarbituric acid (TBA), and *para*-anisidine values. Positive calculated values of peroxide values indicate the formation of peroxides and hydroperoxides in shelled walnut and almond kernels. Negative calculated values of TBA and *para*-anisidine values indicate undetectable concentrations of aldehydes in shelled walnut and almond kernels.

The primary oxidation of nut kernels produces peroxides and hydroperoxides. The secondary oxidation of nut kernels produces oxidation products such as aldehydes. Therefore, large values indicate that the rate of oxidative rancidity can be attributed to poor lipid stability in walnut and almond kernel oils.

Peroxide Value (PV)

Peroxide value analysis was done by official method Cd 8-53 and recommended practices of the American Oil Chemists Society (AOCS 1997). This method determines iodine liberated from potassium iodide by the peroxides present in the oil.

$$\text{Peroxide value (milliequivalents peroxide/kg of oil)} = \frac{(S-B) \times N \times 1000}{m}$$

where: B = volume of sodium thiosulfate solution (mL) after titration against the mixture of acetic acid-chloroform solution, and saturated KI solution. The blank titration must not exceed 0.1 mL of the 0.1 N sodium thiosulfate.

S = volume of sodium thiosulfate solution (mL) after titration against the oil solution.

N = normality of sodium thiosulfate solution (0.1 N).

m = weight of the extracted oil, g.

2-Thiobarbituric Acid (TBA)

Thiobarbituric acid (TBA) analysis was done by official method Cd 19-90 and recommended practices of the American Oil Chemists Society (AOCS 1997). TBA value is defined as the increase of absorbance at 530 nm due to the reaction of 2-thiobarbituric acid with malonaldehyde or other aldehydes. Secondary oxidation products such as 2-alkenals and 2,4-alkadienals react with 2-thiobarbituric acid forming condensation products and produce red chromogen that absorbs at 530 nm, while other aldehydes produce a yellow chromogen that absorbs at 450 nm. TBA value is expressed by converting absorbance readings to milligrams of malonaldehyde per kilogram of oil.

$$TBA \text{ value} = \frac{50 \times (A - B)}{m}$$

where: A = absorbance of the extracted oil after reaction with 1-butanol and the TBA reagent.

B = absorbance of the mixture of 1-butanol and the TBA reagent; designated as a blank.

m = weight of the extracted oil, mg.

Para-anisidine value (p-AV)

Para-anisidine value analysis was done by official method Cd 18-90 and recommended practices of the American Oil Chemists (AOCS 1997). The *para*-anisidine value is defined as 100 times the absorbance of a solution containing 1 g of oil in 100 mL of isooctane and *para*-anisidine solvent in a 1 cm cuvette observed at 350 nm. The *para*-anisidine value determines the concentration of aldehydes, principally 2-alkenals, and 2,4-alkadienals produced during oxidation.

$$para\text{-anisidine value (p-AV)} = \frac{25 \times (1.2A_s - Ab)}{m}$$

where: A_s = absorbance of the extracted oil after reaction with *para*-anisidine reagent.

- Ab = absorbance of the extracted oil.
m = weight of the extracted oil, g.

Chemical Analyses for Hydrolytic Rancidity

Fatty Acid Values. Fatty acid value analysis was done by official method Ab 5-49 and recommended practices of the American Oil Chemists Society (AOCS 1989). Fatty acid value is the quantitative determination of fatty acids in oil by titration against a standardized alkali solution (NaOH).

$$\text{Fatty acids, calculated as oleic acid, \%} = \frac{V \times N \times 28.2}{m} \times 100\% \text{ oleic aci}$$

where: V = volume of standardized NaOH solution after titration against the mixture of extracted oils and isopropyl alcohol, mL.

N = normality of NaOH solution used, 0.25 N.

m = weight of the extracted oil, g.

STATISTICAL ANALYSIS

The experiments were conducted in duplicate on two replications of each heating treatment and each pressed oil from walnut and almond kernels. The general linear model procedure (SAS 1989) was used to determine significant differences ($P \leq 0.05$) among peroxide values, thiobarbituric acid (TBA), *para*-anisidine, and fatty acid values of untreated, heat treated, and stored walnut and almond kernels.

RESULTS AND DISCUSSION

Moisture Content of Walnut Kernels

The initial moisture content of untreated walnut kernels was 4.36%. The moisture content of walnut kernels after heat treatment 55C for 2 min or 10 min, or 60C for 2 min or 10 min were 3.27, 3.21, 3.27 and 3.04%, respectively. Untreated walnut kernels exhibited higher moisture content than short time heat treated (STHT) walnut kernels. Walnut kernels after heat treatment at 60C for 10 min exhibited the lowest moisture content compared to walnuts heated at 55C or 60C for 2 min, or 55C for 10 min. High temperatures and long heating times generally reduce moisture content more than low temperatures and short heating times. Heat treatments may inactivate enzymes such as lipoxygenase or lipase, enzymes that catalyze oxidative and hydrolytic rancidity.

Moisture Content of Almond Kernels

The initial moisture content of untreated almond kernels was 5.70%. The moisture content of almond kernels after heat treatment at 55C for 2 min or 10 min or 60C for 2 min or 10 min were 5.39, 5.21, 5.26 and 5.04%, respectively. Untreated almond kernels exhibited higher moisture content than SHT almond kernels. Almond kernels after heat treatment at 60C for 10 min exhibited the lowest moisture content compared to almonds heated at 55C or 60C for 2 min, or 55C for 10 min.

Wahab *et al.* (1984) reported that reduction in fruit moisture content as well as minimizing the enzymatic activity could be attributed to prestorage heating. McGlamery and Hood (1951) reported that inhibition of enzymatic and retardation of rancidity occurred when unshelled pecans were subjected to 80C for 15 min. Loss of moisture and inactivation of enzymes such as lipase and esterase during heat treatment may inhibit the onset of hydrolytic rancidity (Allen and Hamilton 1999).

Chemical Analyses for Oxidative and Hydrolytic Rancidity of Walnut Kernel Oils

Peroxide Values. The initial mean peroxide values of oils extracted from untreated walnut kernels was 0.39 meq/kg of oil. The initial mean peroxide values of oils extracted from SHT walnut kernels heated at 55C for 2 min or 10 min, or at 60C for 2 min or 10 min were 0.27, 0.30, 0.32, or 0.35 meq/kg of oil, respectively. However, no significant differences ($P > 0.05$) were observed between oils extracted from untreated control walnut kernels and oils extracted from SHT control walnut kernels (Fig. 1).

Walnut Kernels Stored at 25C. Oils extracted from untreated walnut kernels exhibited significantly higher ($P \leq 0.05$) peroxide values than oils extracted from SHT walnut kernels after 5, 15, 30, and 60 days of storage at 25C (Fig. 1). The peroxide values of oils extracted from untreated walnut kernels and oils extracted from SHT walnut kernels increased sharply after 30 days of storage at 25C (Fig. 1). An increase in peroxide value indicates hydroperoxides formed and the onset of oxidative rancidity (Hui 1992).

Quality Nut Co. (Empire, CA) recognizes a standard for acceptable walnuts that contain 3.0 meq of peroxides in a kilogram of walnut kernel oil. Oils extracted from SHT walnut kernels exhibited peroxide values within the limits for acceptable quality even after 60 days of accelerated storage at 25C.

Wahab *et al.* (1984) reported that pecan kernels stored at room temperature exhibited higher peroxide values than pecan kernels heated at 160C for 5 min or 10 min, or at 180C for 5 min or 10 min stored at room temperature.

Peroxide values of oils extracted from the heated pecan kernels tended to decrease as the time and temperature of storage increased (Wahab *et al.* 1984).

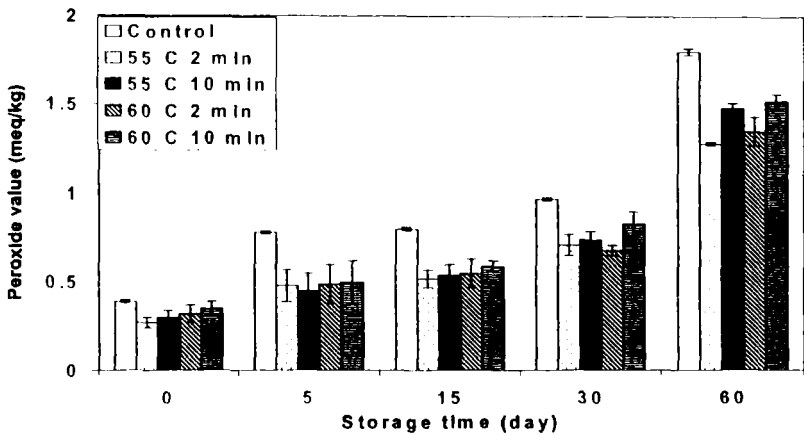


FIG. 1. PEROXIDE VALUES OF OILS EXTRACTED FROM WALNUT KERNELS HEATED AT 55°C OR 60°C FOR 2 OR 10 MIN AND STORED AT 25°C

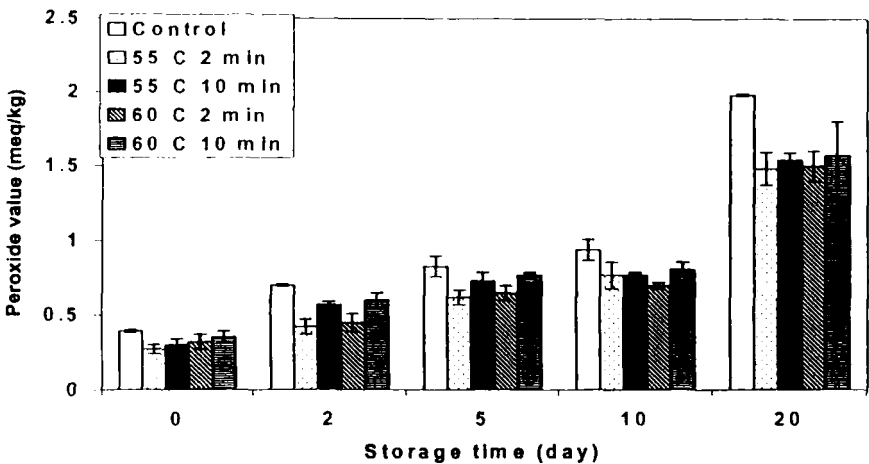


FIG. 2. PEROXIDE VALUES OF OILS EXTRACTED FROM WALNUT KERNELS HEATED AT 55°C OR 60°C FOR 2 OR 10 MIN AND STORED AT 35°C

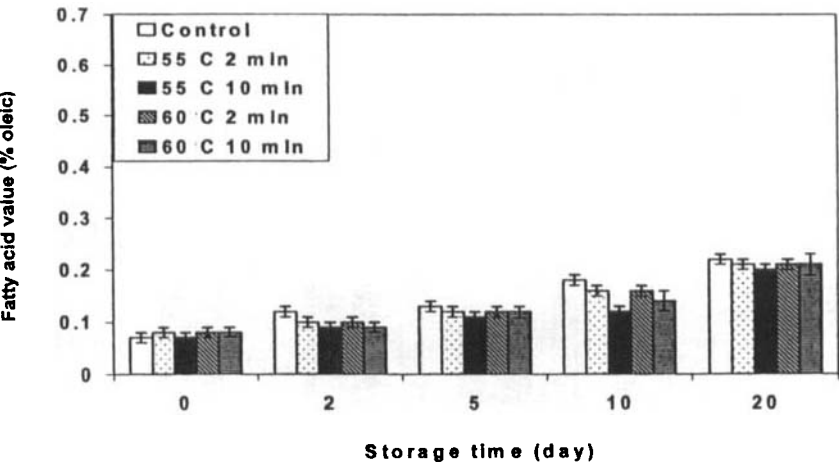


FIG. 3. FATTY ACID VALUES OF OILS EXTRACTED FROM WALNUT KERNELS HEATED AT 55C OR 60C FOR 2 OR 10 MIN AND STORED AT 25C

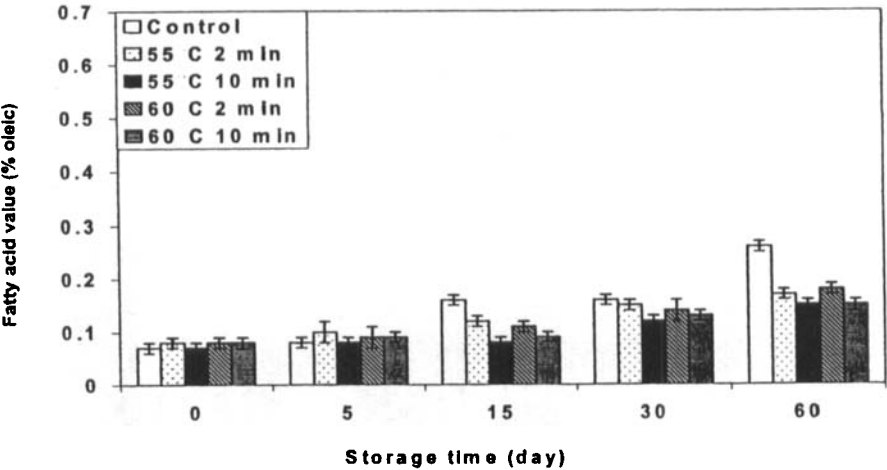


FIG. 4. FATTY ACID VALUES OF OILS EXTRACTED FROM WALNUT KERNELS HEATED AT 55C OR 60C FOR 2 OR 10 MIN AND STORED AT 35C

Walnut Kernels Stored at 35C. Oils extracted from untreated walnut kernels exhibited higher peroxide values than oils extracted from STHT walnut kernels after 2, 5, 10, and 20 days of storage at 35C (Fig. 2). The peroxide values of oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels increased slightly after 10 days of storage at 35C (Fig. 2). No significant differences in peroxide values ($P > 0.05$) were observed between oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels after 2, 5, and 10 days of storage at 35C.

The peroxide values of oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels increased sharply after 20 days of storage at 35C (Fig. 2). The mean peroxide value of oils extracted from untreated walnut kernels after 20 days of storage was 1.98 meq/kg of oil. The peroxide values of oils extracted from the four short time heat treatments of walnut kernels after 20 days of storage at 35C were 1.48, 1.54, 1.50, and 1.57 meq/kg of oil, respectively (Fig. 2). Oils extracted from untreated walnut kernels exhibited significantly ($P \leq 0.05$) higher peroxide values than oils extracted from STHT walnut kernels after 20 days of storage at 35C (Fig. 2). Peroxide values of walnut kernel oils less than 3.0 meq/kg indicate acceptable quality walnuts (Quality Nut Co., Empire, CA). Both untreated and STHT walnut kernels exhibited peroxide values within the limit of acceptable quality shelled walnut kernels.

Walnut kernels are more susceptible to oxidative rancidity than almond kernels because walnut kernels contain greater concentrations of unsaturated fatty acids such as oleic, linoleic, and linolenic acids. The relative ratio of oxidation for oleic, linoleic, and linolenic acids is 1:10:20.

Thiobarbituric Acid Values (TBA)

The initial mean TBA value of oils extracted from untreated walnut kernels was 0.09. The initial mean of TBA values of oils extracted from STHT walnut kernels heated at 55C for 2 min or 10 min, or 60C for 2 min or 10 min were 0.12, 0.09, 0.10, and 0.09, respectively. TBA values of oils extracted from STHT walnut kernels after storage at 25C or 35C exhibited inconsistent TBA values. Zacheo *et al.* (2000) reported that the TBA assay is often criticized for its lack of specificity and accuracy. However, there are additional limitations on the use of TBA. Dugan (1955) reported that sucrose and some compounds in wood smoke interfere with TBA, reacting with the TBA reagent to give a red color. Fennema (1996) reported that TBA is widely used in determining lipid oxidation; however, malonaldehyde is not always present in oxidized products. Fennema (1996) reported that malonaldehyde could react with proteins in oxidized products and result in false negative and inaccurate the TBA values.

Other aldehydes can also react with TBA reagent to give red chromogen, and other compounds such as nonextractable lipid, urea, sugar, oxidized protein, or other oxidized products present in foods can react with TBA reagent. Nevertheless, TBA is an attractive assay because it can be carried out on whole foods, and may detect oxidative damage to materials other than the extractable triacylglycerols. The TBA assay is said to be of little value with frying oils but useful in measuring early stages of rancidity in vegetable oils, lard, cooking oils and fresh foods. Akoh and Min (1998) reported that the exact reaction mechanism of oxidized products and TBA reagent is not well understood. Therefore, other analyses such as *para*-anisidine values were conducted to assess the concentration of aldehydes, principally 2-alkenal and 2,4-alkadienals.

TBA value is expressed by converting absorbance readings to milligrams of malonaldehyde per kilogram of oil. Mean TBA values of oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels contained concentrations of malonaldehyde less than 0.1 mg/mL (100 mg/kg).

Oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels contained very small concentrations of aldehydes. These imply that there is little development of oxidative rancidity in oils extracted from untreated and STHT walnut kernels. In addition, STHT may inactivate lipoxygenase enzymes and lower moisture content which can retard the development of oxidative and hydrolytic rancidity.

***Para*-anisidine Values**

The initial mean of *para*-anisidine values of oils extracted from untreated walnut kernels and oils extracted from heated walnut kernels as assayed by *para*-anisidine analysis were undetectable.

The *para*-anisidine analysis determines the quantity of aldehydes, principally 2-alkenal and 2,4-alkadienals in oils under acidic conditions (Akoh and Min 1998). Oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels contain concentrations of aldehydes less than 1 mg/mL (1000 mg/kg of oil). Oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels did not produce large concentrations of aldehydes, principally 2-alkenal and 2,4-alkadienals, which are common secondary oxidation products produced during oxidation.

Fatty Acid Values

The initial mean fatty acid value of oils extracted from untreated walnut kernels was 0.07%, calculated as oleic acid. The initial mean fatty acid values of oils extracted from walnut kernels heated at 55C for 2 min or 10 min, or 60C for 2 min or 10 min were 0.08, 0.07, 0.08, and 0.08%, respectively.

Walnut Kernels Stored at 25C. No significant differences in fatty acid values ($P > 0.05$) were observed between oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels after 5 days of storage at 25C (Fig. 3).

The fatty acid values of oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels increased after 5, 15, 30, and 60 days of storage at 25C (Fig. 3). The fatty acid values of oils extracted from untreated walnut kernels after 60 days of storage was 0.26%. The fatty acid values of oils extracted from STHT walnut kernels after 60 days of storage were at 0.17, 0.15, 0.18, and 0.15%. Oils extracted from untreated walnut kernels exhibited significantly ($P \leq 0.05$) higher fatty acid values than oils extracted from STHT walnut kernels after 60 days of storage at 25C (Fig. 3).

Fatty acid values less than 1.5% calculated as oleic acid indicate acceptable quality walnuts (Quality Nut Co., Empire, CA). Oils extracted from STHT walnut kernels exhibited fatty acid values within the limits for acceptable quality even after 60 days of accelerated storage at 25C.

Walnut Kernels Stored at 35C. The fatty acid values of oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels increased after 2, 5, 10, and 20 days of storage at 35C (Fig. 4). The fatty acid values of oils extracted from untreated walnut kernels after 20 days of storage was 0.22%. The fatty acid values of oils extracted from STHT walnut kernels after 20 days of storage were at 0.21, 0.20, 0.21, and 0.21%. No significant differences ($P > 0.05$) were observed between oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels after 20 days of storage at 35C (Fig. 4).

Fatty acid values less than 1.5% calculated as oleic acid indicate acceptable quality walnuts (Quality Nut Co., Empire, CA). Oils extracted from STHT walnut kernels exhibited fatty acid values within the limits for acceptable quality even after 20 days of accelerated storage at 35C.

Hydrolytic rancidity is caused by hydrolysis of triacylglycerols in the presence of enzymes such as lipase or esterase (Allen and Hamilton 1999). Ekstrand *et al.* (1993) reported an increase in fatty acid values in stored pecans, but a less pronounced increase in heated pecans.

Chemical Analyses for Oxidative and Hydrolytic Rancidity of Almond Kernel Oils

Peroxide Values. The initial mean peroxide value of oils extracted from untreated almond kernels was 0.35 meq/kg of oil. The initial mean peroxide values of oils extracted from short time heat treated almond kernels heated at

55C for 2 min or 10 min, or at 60C for 2 min or 10 min were 0.25, 0.31, 0.24, and 0.28 meq/kg of oil, respectively.

Almond Kernels Stored at 25C. Oils extracted from untreated almond kernels exhibited higher peroxide values than oils extracted from STHT almond kernels after 5, 15, 30, and 60 days of storage at 25C (Fig. 5). No significant differences ($P > 0.05$) were observed between oils extracted from untreated almond kernels and oils extracted from STHT almond kernels after 5, 15, and 30 days of storage at 25C. However, oils extracted from untreated almond kernels exhibited significantly ($P \leq 0.05$) higher peroxide values than oils extracted from STHT almond kernels after 60 days of storage at 25C (Fig. 5). The mean peroxide value of oils extracted from untreated almond kernels after 60 days of storage at 25C was 0.59 meq/kg of oil. The mean peroxide value of oils extracted from walnut kernels heated at 55C for 2 min or 10 min, or 60C for 2 min or 10 min after 60 days of storage at 25C were 0.48, 0.54, 0.49, 0.55 meq/kg of oil, respectively (Fig. 5).

Peroxide values of almond kernel oils less than 2.0 meq/kg of oil indicate acceptable quality almonds (Paramount Farms, Bakersfield, CA). Oils extracted from both untreated and STHT almond kernels exhibited peroxide values within the limits for acceptable quality even after 60 days of accelerated storage at 25C.

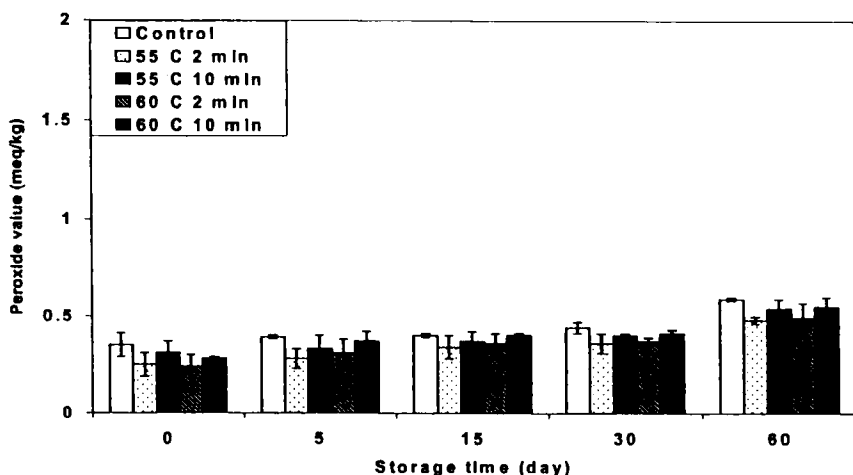


FIG. 5. PEROXIDE VALUES OF OILS EXTRACTED FROM ALMOND KERNELS HEATED AT 55C OR 60C FOR 2 OR 10 MIN AND STORED AT 25C

Almond Kernels Stored at 35C. Oils extracted from untreated almond kernels exhibited higher peroxide values than oils extracted from STHT almond kernels after 2, 5, 10, and 20 days of storage at 35C (Fig. 6). No significant differences ($P \geq 0.05$) were observed between oils extracted from untreated almond kernels and oils extracted from STHT almond kernels after 20 days of storage at 35C (Fig. 6).

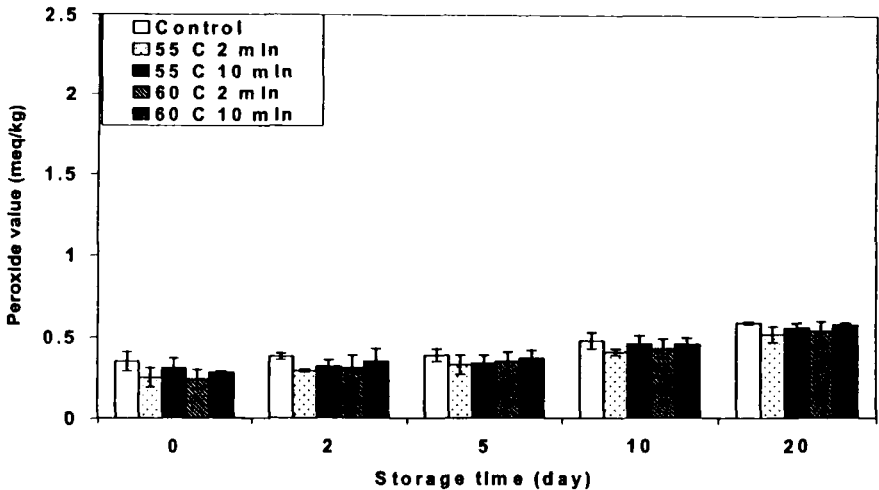


FIG. 6. PEROXIDE VALUES OF OILS EXTRACTED FROM ALMOND KERNELS HEATED AT 55C OR 60C FOR 2 OR 10 MIN AND STORED AT 35C

The major fatty acids in almond kernels are unsaturated fatty acids (Zacheo *et al.* 2000). Almond kernels contain approximately 33% oleic acid, 11% linoleic acid and 0.4% linolenic acids (USDA 1984). Zacheo *et al.* (2000) reported that shelled almonds did not exhibit significant changes in peroxide values after 2 years of storage at room temperature. Fourie and Basson (1989) reported that peroxide values in almonds change little during storage after 16 months of storage at room temperature and no flavor differences in almonds could be detected after 12 months of storage at room temperature. Mehran and Filsoof (1974) did not detect significant changes in peroxide values after 12 months storage of almonds at room temperature. Storage of almonds at low temperatures in low oxygen atmosphere resulted in less off flavor development. Nut quality is usually determined by detection of off flavors, and the most common loss in quality of nuts is observed as oxidative rancidity (Fourie and Basson 1989; Zacheo *et al.* 2000).

Thiobarbituric Acid Values (TBA). TBA analysis of oils extracted from untreated almond kernels was undetectable. The initial mean TBA values of oils extracted from SHTT almond kernels heated at 55C or 60C were 0.01 or less. No significant differences ($P > 0.05$) were observed between oils extracted from untreated almond kernels and oils extracted from SHTT almond kernels at 25C or 35C of storage.

Mean TBA values of oils extracted from untreated almond kernels and oils extracted from SHTT almond kernels contained concentrations of malonaldehyde less than 0.01 mg/mL. Oils extracted from untreated almond kernels and oils extracted from SHTT almond kernels contain very small concentrations of aldehydes. Zacheo *et al.* (2000) reported an increase in malonaldehyde content in almonds after 2 years of storage at room temperature. Hydroperoxides and malonaldehyde concentrations were detected 2 years after harvesting of almonds and storage at room temperature (Zacheo *et al.* 2000).

Para-anisidine Values. Para-anisidine analysis of oils extracted from untreated almond kernels and oils extracted from SHTT almond kernels were undetectable. Para-anisidine determines the quantity of aldehydes, principally 2-alkenal and 2,4-alkadienals in oils under acidic conditions (Akoh and Min 1998). Oils extracted from untreated almond kernels and oils extracted from SHTT almond kernels contain concentrations of aldehyde less than 1 mg/mL (1000 mg/kg of oil).

Fatty Acid Values. The initial mean fatty acid value of oils extracted from untreated almond kernels was 0.12%, calculated as oleic acid. The initial mean fatty acid values of oils extracted from SHTT almond kernels heated at 55C for 2 min or 10 min, or 60C for 2 min or were 0.12, 0.11, 0.12, and 0.13%, respectively. No significant differences ($P > 0.05$) were observed between oils extracted from untreated control almond kernels and oils extracted from SHTT control almond kernels (Fig. 7).

Almond Kernels Stored at 25C. The fatty acid values of oils extracted from untreated almond kernels and oils extracted from SHTT almond kernels increased after 5, 15, 30, and 60 days of storage at 25C (Fig. 7).

Almond Kernels Stored at 35C. The fatty acid values of oils extracted from untreated almond kernels and oils extracted from SHTT almond kernels increased after 2, 5, 10, and 20 days of storage at 35C (Fig. 8). No significant differences ($P > 0.05$) were observed between oils extracted from untreated almond kernels and oils extracted from SHTT almond kernels after 2, 5, 10 days of storage at 35C (Fig. 8). However, oils extracted from untreated almond kernels exhibited significantly ($P \leq 0.05$) higher fatty acid values than oils extracted from SHTT almond kernels heated at 55C for 2 min, or 60C for 2 min

after 20 days of storage at 35C. No significant differences ($P > 0.05$) were observed between oils extracted from untreated almond kernels and oils extracted from STHT almond kernels heated at 55C for 10 min, or 60C for 10 min after 20 days of storage at 35C (Fig. 8).

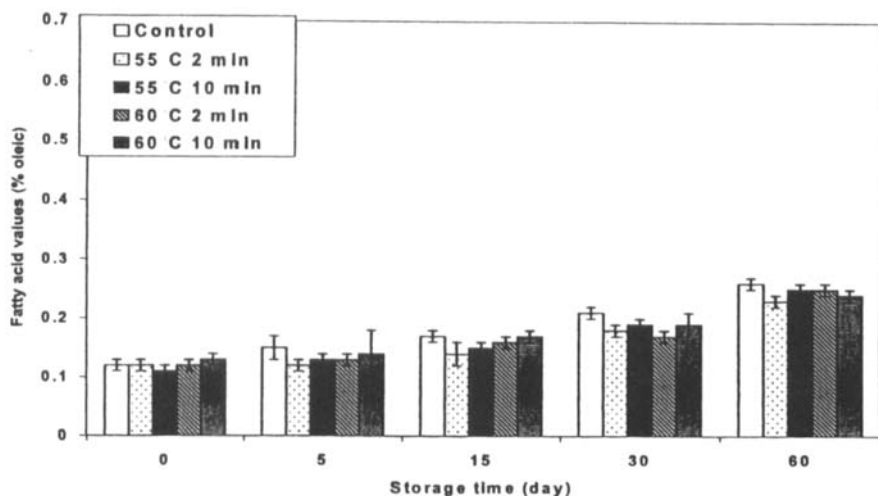


FIG. 7. FATTY ACID VALUES OF OILS EXTRACTED FROM ALMOND KERNELS HEATED AT 55C OR 60C FOR 2 OR 10 MIN AND STORED AT 25C

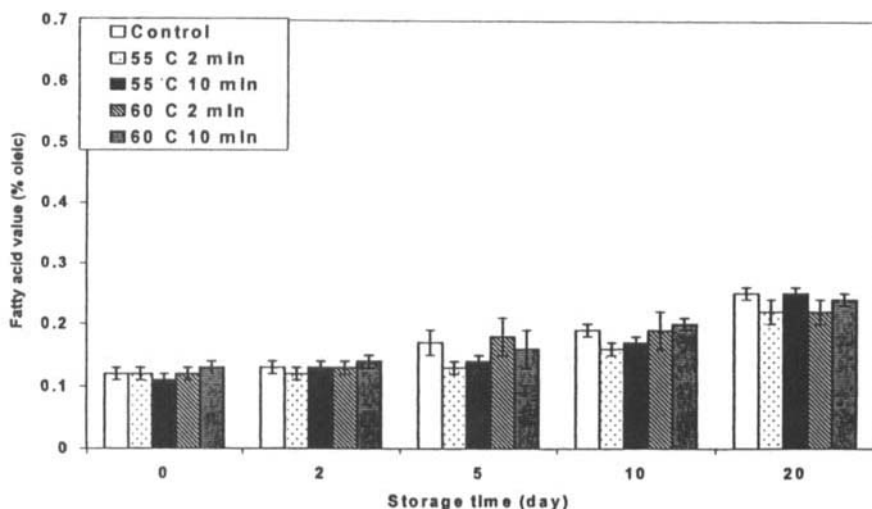


FIG. 8. FATTY ACID VALUES OF OILS EXTRACTED FROM ALMOND KERNELS HEATED AT 55C OR 60C FOR 2 OR 10 MIN AND STORED AT 35C

Comparison Between Walnut and Almond Kernel Oils

Peroxide Values. Oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels exhibited higher peroxide values than oils extracted from almond kernels after 25C or 35C of storage.

Quality Nut Co. (Empire, CA) recognizes a standard for acceptable quality walnuts of less than 3.0 meq of peroxides in a kilogram of walnut kernel oil (Table 1). Walnut kernels heat treated at 55C for 2 min or 10 min, or at 60C for 2 min or 10 min exhibited peroxide values within the limits for acceptable quality even after accelerated storage conditions of 60 days of storage at 25C, or 20 days of storage at 35C.

Paramount Farms (Bakersfield, CA) recognizes a standard for acceptable quality almonds of less than 2.0 meq of peroxides in a kilogram of almond kernel oil (Table 1). Almond kernels heat treated at 55C for 2 min or 10 min, or at 60C for 2 min or 10 min exhibited peroxide values within the limits for acceptable quality even after accelerated storage conditions of 60 days of storage at 25C, or 20 days of storage at 35C.

Almond kernels contain greater concentrations of *alpha*-tocopherol (~ 24.01 mg per 100 g) than walnut kernels (~ 2.62 mg per 100 g) (USDA 1984). Zacheo *et al.* (2000) reported that tocopherols in almond kernels are an important compound protecting almonds against lipid oxidation, which leads to prolonged storage life. *Alpha*-tocopherol is a natural antioxidant acting as a free radical scavenger by inactivating or scavenging free radicals, thus inhibiting initiation and propagation reactions which results in the retardation of oxidative rancidity. Zacheo *et al.* (2000) reported that lipoxygenase activity of almond kernels increased with aging time. However, lipoxygenase activity was lost after heating almond kernels at 80C for 10 min. Zacheo *et al.* (2000) recommended further investigation to assess the association of lipoxygenase activity, antioxidant concentration, and lipid oxidation of almonds.

Thiobarbituric Acid Values (TBA). Oils extracted from untreated walnut kernels and oils extracted from STHT walnut kernels exhibited higher TBA values than oils extracted from almond kernels. Neither walnut nor almond kernels contained large concentrations of malonaldehydes.

***Para*-anisidine values.** *Para*-anisidine analysis of oils extracted from walnut and almond kernels were undetectable.

Fatty Acid Values. Oils extracted from walnut and almond kernels exhibited similar fatty acid values in both untreated and STHT walnut and almond kernels.

Quality Nut Co. (Empire, CA) recognizes a standard for acceptable walnuts containing less than 1.5% titratable fatty acids calculated as oleic acid (Table 1). Walnut kernels heat treated at 55C or 60C exhibited fatty acid value within the limits for acceptable quality even after accelerated storage at 60 days of storage at 25C, or 20 days of storage at 35C.

Paramount Farms (Bakersfield, CA) recognizes a standard for acceptable quality almonds containing less than 1.0% titratable fatty acids calculated as oleic acid (Table 1). Almond kernels heat treated at 55C or 60C exhibited fatty acid values within the limits for acceptable quality even after accelerated storage conditions: 60 days of storage at 25C, or 20 days of storage at 35C to simulate the shelf-life of almond kernels at 4C for 2 years.

CONCLUSIONS

Peroxide values and fatty acid values indicate the development of oxidative and hydrolytic rancidity, respectively. Rancidity in walnut and almond kernels tends to be oxidative rancidity rather than hydrolytic rancidity. Oils extracted from walnut kernels oxidized faster than oils extracted from almond kernels as indicated by peroxide values.

Short time heat treatment of walnuts and almonds did not promote rancidity. Untreated control and heat treated shelled walnut and almond kernels were acceptable after 60 days of storage 25C or after 20 days of storage at 35C which is equivalent to storing walnut and almond kernels at 4C for 2 years. Short time heat treatments of 55C for 2 min or greater retard the development of oxidative rancidity in shelled walnuts and almonds during distribution and storage.

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