

Oxidative Stability of Cashew Oils from Raw and Roasted Nuts

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Abstract Cashew nut oils, extracted from raw and roasted whole cashew nuts, were examined for their fatty acid composition, color change and oxidative stability. Fatty acids were analyzed using gas chromatography, and a spectrophotometric method was used to determine the color changes of the resultant oils. Oxidative stability was determined under accelerated oxidation conditions by employing conjugated diene (CD) and thiobarbituric acid reactive substances (TBARS) assays. The contents of monounsaturated (MUFA), polyunsaturated (PUFA) and saturated (SAFA) fatty acids were 61, 17 and 21%, respectively. Oleic acid was the major MUFA whereas linoleic acid was the main PUFA present in cashew nut oils. Oxidative stability of the oil as determined by CD values after 72 h of storage under Schall oven condition at 60 °C was 1.08 and 0.65 for the raw and high temperature roasted cashew nut, respectively. The TBARS values, expressed as malondialdehyde equivalents decreased with increasing roasting temperature. Thus roasting of whole cashew nuts improved the oxidative stability of the resultant nut oils.

Keywords Color · GC · SAFA · MUFA · PUFA · CD · TBARS

Introduction

Tree nuts and their oils are known to contain bioactive and health promoting substances and as such have long been considered to serve as important components of the human diet. Epidemiological evidences indicate 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, particularly oleic acid, and phytosterols, among others [1]. Miraliakbari and Shahidi [2–4] have reported the compositional characteristics of nut oils and the antioxidant activity of their minor components.

Fats, oils, and lipid containing foods are oxidized at different rates which results in their sensory and nutritional deterioration. One of the most important parameters that influence lipid oxidation is the degree of unsaturation of fatty acids involved. The presence of natural compounds with different chemical structures that exhibit antioxidant activity may also affect the rate of oxidation [5–8]. Another lipid alteration is lipid hydrolysis, with consequent formation of free fatty acids (FFA), by chemical or enzymic action. This phenomenon is of particular interest in water containing lipid matrices, such as butter and virgin olive oil during olive processing. Although the original causes and the consequences of oxidative and hydrolytic degradation processes are quite different, they seem to interact with one another and reduce the shelf life of edible oils.

Oxidative stability is an important parameter for the quality assessment of fats and oils. Autoxidation is affected by atmospheric oxygen and the oxidation process proceeds via free radical reactions involving unsaturated fatty acids [9]. The primary products formed are hydroperoxides, which subsequently break down in a series of complex reactions, to yield secondary products including alcohols

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and carbonyl compounds. These can be oxidized further to carboxylic acids [9].

Tree nut oils are primarily composed of triacylglycerols. They also contain diacylglycerols, monoacylglycerols, free fatty acids, and other minor components, including natural antioxidants and fat soluble vitamins. 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, such as linoleic acid, and small amounts of saturated lipids [10].

During the roasting process, a pleasant aroma and taste is developed that is transferred to the oil upon extraction. The conventional method for the preparation of condiment oils, such as sesame and red pepper oils, involves cleaning, roasting and pressing but not refining [11]. The roasting process is the key step for making condiment oil, since the color, flavor, composition, and quality of oils are influenced by the process. Some studies have shown that the chemical composition of oil is independent of the roasting temperature used for its preparation [11–14]. However, there are no published reports on lipid class compositions of roasted cashew nut oils, and their oxidative stabilities. Therefore, this study was conducted to investigate the changes in color, fatty acid composition and oxidative stability of the oil extracted from whole cashew nuts roasted at two different temperatures.

Materials and Methods

Materials

Raw shelled cashews with testa was obtained from Green Field Bio Plantation (Pvt.) Ltd., Colombo, Sri Lanka. Fatty acid standards, anhydrous sodium sulfate, 2,2,4-trimethylpentane, 1, 1, 3, 3-tetramethoxypropane, and 2-thiobarbituric acid (2-TBA) were purchased from Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada). Hexane, chloroform, methanol, sulfuric acid, and 1-butanol were purchased from Fisher Scientific Ltd (Ottawa, ON, Canada).

Sample Preparation

Roasting was carried out using two different processing temperatures. For low temperature (LT) processing, raw whole cashew nuts were roasted in a forced convection hot-air oven at 70 °C for 6 h. In this, cashew kernels weighing approximately 100 g were spread in a single layer on a stainless steel wire mesh tray placed in the center of the oven during hot-air roasting. After roasting, the hot cashew kernels were cooled in a desiccator at room temperature, and then kept in sealed plastic bags at 4 °C, until further

analysis. Under industrial cashew processing operations, both small and large scale cashew producers use these conditions to obtain good quality products [15]. For high temperature (HT) processing, raw whole cashew nuts were roasted in a forced air convection oven at 130 °C for 33 min. This temperature and time combination was the optimum roasting conditions for cashew kernels based on hedonic sensory evaluations according to Wanlapa and Jindal [16]. Raw whole cashew nuts were used as the control to compare the effect of the two different roasting conditions employed.

Raw and roasted whole cashew nuts, were ground separately using a coffee bean grinder (Model CBG5 series, Black & Decker, Canada Inc. Brockville, ON, Canada) to obtain a fine powder which passed through mesh 16 (sieve opening 1 mm, Tyler test sieve, Mentor, OH). Each sample was then defatted by blending with hexane (1:5, w/v, 5 min, 3×) in a Waring blender (Model 33BL73, Waring Products Division Dynamics Co. of America, New Hartford, CT) at ambient temperature (20 °C). The resulting oil in hexane mixture was filtered through a Whatman No. 4 filter paper using a Buchner funnel. The residue was re-extracted twice with the same solvent for oil recovery and the filtrates from the three extractions were combined, and solvent evaporated in vacuo (Rotavapor model 461, Buchi, Flawil, Switzerland) at 40 °C to reduce the volume. The hexane-oil mixture so obtained was then passed through anhydrous sodium sulfate placed over a filter paper in a funnel, followed by evaporation of the remaining solvent in vacuo at 40 °C. The resulting oil was weighed and transferred into glass bottles, capped with nitrogen, and stored at –80 °C until used for further analysis.

Determination of Color Development

The color of raw, low temperature (LT) and high temperature (HT) treated whole cashew nut oil was determined. As an index of color development, the absorbance at 420 nm of 5% (w/v) solutions of oils in chloroform as recommended by Yoshida et al. [17] was measured spectrophotometrically.

Fatty Acid Composition Analysis

Fatty acid methyl esters (FAME) were prepared from each oil sample and analyzed using gas chromatography (GC) as described by Wang and Shahidi [18]. In brief, the FAMES were prepared using methanol and 6% sulfuric acid according to the official AOCS [19] method. Methyl esters of FA were extracted with hexane and 1 µL aliquot of the extracts was autoinjected for GC analysis (HP-5890, series II, Agilent Technologies Canada Inc., Mississauga, ON, Canada). The gas chromatograph was equipped with a

flame ionization detector (FID). The column used was a Supelcowax-10 fused-silica capillary column (30 m × 0.25 mm diameter, 0.25 μm film thickness; Supelco Canada Ltd., Oakville, ON, Canada). The carrier gas was helium, and the total gas flow rate was 20 mL/min. Identification and quantification was carried out using known standards (Sigma-Aldrich Canada Ltd., Oakville, ON, Canada).

Determination of Oxidative Stability

The oxidative stability of cashew nut oils was studied under accelerated Schall oven conditions. Two grams of cashew nut oil samples were accurately weighed into 10-mL clear glass sample vials and loosely capped before being placed in a forced air oven (Thelco, Model 2, Precision Scientific Co., Chicago, IL) in the dark and heated to 60 °C. For each sample, six vials were loaded into the oven, and samples were removed after 0, 6, 12, 24, 36, 48, and 72 h and then stored at −80 °C until used for determination of conjugated dienes (CD), and thiobarbituric acid reactive substances (TBARS). All determinations were carried out in triplicate.

Determination of Conjugated Diene Content

The CD contents were determined according to the method explained by Wang and Shahidi [18]. In brief, A specified amount of oil (0.02–0.03 g) was weighed into a 25-mL volumetric flask, and made up to the mark with 2,2,4-trimethylpentane. The solution was thoroughly mixed before reading its absorbance at 234 nm (Model HP 8452A diode array spectrophotometer, Agilent Technologies, Palo Alto, CA). Pure 2,2,4-trimethylpentane was used as a reference. CD values were calculated using the following equation: $CD = \text{Absorbance of solution at 234 nm} / C \cdot l$ where C = concentration of oil in g per 100 mL, l = length of the cuvette in cm (IUPAC, 1987).

Analysis of Thiobarbituric Acid Reactive Substances

Thiobarbituric acid reactive substances (TBARS) values were determined according to the official AOCS [19] method. The oil (50–100 mg) was weighed into a 25-mL volumetric flask and made up to volume with 1-butanol. Aliquot (5 mL) of this solution was transferred into a screw capped test tube to which freshly prepared 5 mL of 2-TBA reagent (500 mg 2-TBA in 250 mL 1-butanol) was added. Contents were thoroughly mixed and heated in a thermostated water bath at 95 °C. After 2 h the samples were removed from the water bath and cooled in an ice bath. The absorbance was then read at 532 nm. A standard curve was prepared using 1,1,3,3-tetramethoxypropane as the

malondialdehyde (MDA) precursor and the results were expressed as mmol MDA equivalents/g oil.

Statistical Analysis

Results were expressed as means ± standard deviations (SD) of at least three independent experiments. Differences were estimated by the analysis of variance (ANOVA) followed by Tukey's "honest significant difference" test. Differences were considered significant at $p \leq 0.05$. All statistical analyses were performed using the free statistical software SPSS 13.0 version (SPSS Inc., Chicago, IL).

Results and Discussion

Oil Yield

The oil yield of cashew nuts roasted under different conditions ranged from 41.30 ± 0.40 to $42.58 \pm 0.38\%$ (Fig. 1). The roasted cashew nut yielded a significantly ($p < 0.05$) higher percentage of oil than that of raw cashew nut. This was probably due to a certain amount of protein denaturation which could improve oil extractability of cashew nuts [20]. Furthermore, the temperatures employed in this study may cause high damage to the cell membranes leading to the high extractability of oil [21, 22]. The oil yields obtained in this study are in the range of those reported by others for cashew nuts ($40.4 \pm 2.0\%$) on a weight basis [23, 24].

Color Development of Cashew Nut Oil

Figure 2 presents the absorbance values of cashew oils from raw and roasted nuts as indices for color development

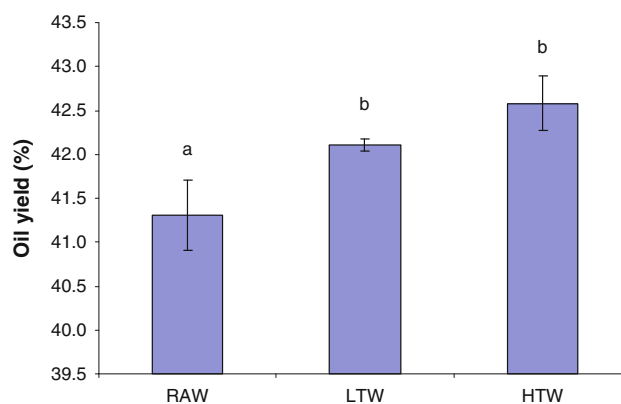


Fig. 1 Yield of cashew oil at different roasting conditions. Data are expressed as means ± SD ($n = 3$). Means ± SD followed by the same letter, on bars are not significantly different ($p > 0.05$). RAWO raw whole cashew nut oil, LTWO low temperature roasted whole cashew nut oil, HTWO high temperature roasted whole cashew nut oil

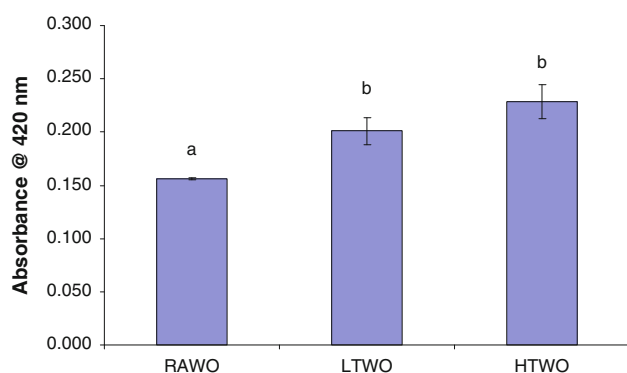


Fig. 2 Color development (absorbance at 420 nm) of cashew nut oil under different roasting conditions. Data are expressed as means \pm SD ($n = 3$). Means \pm SD followed by the same letter, on bars are not significantly different ($p > 0.05$). RAWO raw whole cashew nut oil, LTWO low temperature roasted whole cashew nut oil, HTWO high temperature roasted whole cashew nut oil

in the products. The absorbance of cashew nut oil at 420 nm increased significantly ($p < 0.05$) upon roasting and the color of oils changed gradually from light yellow to deep brown. The absorbance values ranged from 0.1563 ± 0.001 to 0.2282 ± 0.015 . The results of this study showed that the color formation in the oil was influenced by the roasting temperature employed. The Maillard reaction products (MRP) are formed in thermally processed foods due to non-enzymatic reactions between reducing sugars and free amino acids [25]. The increase in color of oils with increasing roasting temperature appears to be due to the formation of MRPs at elevated roasting temperatures. Thus, the present results lend support to earlier findings, which indicated an increase in the color of oils with increasing roasting temperature of rice germ and sesame seed oils [11, 13, 26].

Fatty Acid Composition

The fatty acid composition of an oil can be used as an indicator of its stability, physical properties, and nutritional value. Fatty acid profiles of the raw and roasted cashew nut oils determined by GC are presented in Table 1. The major monounsaturated fatty acid (MUFA) present in cashew nuts was oleic acid (C18:1n-9), which was present at 60.57–61.33. Meanwhile, linoleic acid (C18:2n-6) was the most abundant polyunsaturated fatty acid (PUFA) present at 16.79–17.03 % with a lesser amount of α -linolenic acid (C18:3n-3). The primary saturated fatty acids (SFA) identified in cashew nuts were palmitic acid (C16:0) and stearic acid (C18:0) present at 10.21–10.31% and 9.57–10.14%, respectively. In accordance with the present study, Venkatachalam and Sathe [27] reported oleic, linolenic, palmitic, and stearic acid contents of raw cashew oil at 61.15, 16.88, 10.70, and 9.33%, respectively. In addition, Ryan

Table 1 Fatty acid composition of cashew nut oil extracted under different roasting conditions

Fatty acid, %	RAWO	LTWO	HTWO
16:0	10.31 \pm 0.05 ^a	10.21 \pm 0.00 ^a	10.28 \pm 0.00 ^a
16:1n-9	0.34 \pm 0.01 ^a	0.34 \pm 0.00 ^a	0.33 \pm 0.00 ^a
16:3n-4	0.06 \pm 0.01 ^a	0.03 \pm 0.00 ^a	0.11 \pm 0.00 ^b
17:0	0.13 \pm 0.00 ^a	0.12 \pm 0.00 ^a	0.14 \pm 0.00 ^a
18:0	9.83 \pm 0.06 ^a	9.57 \pm 0.05 ^a	10.14 \pm 0.01 ^a
18:1n-9	60.57 \pm 0.11 ^a	61.33 \pm 0.04 ^a	60.68 \pm 0.00 ^a
18:2n-6	17.03 \pm 0.11 ^a	16.79 \pm 0.07 ^a	16.79 \pm 0.00 ^a
18:3n-3	0.21 \pm 0.01 ^a	0.22 \pm 0.00 ^a	0.19 \pm 0.00 ^a
20:0	0.74 \pm 0.01 ^a	0.67 \pm 0.01 ^a	0.64 \pm 0.01 ^{ab}
21:1n-9	0.19 \pm 0.01 ^a	0.19 \pm 0.01 ^a	0.17 \pm 0.00 ^a
22:0	0.14 \pm 0.00 ^a	0.12 \pm 0.01 ^a	0.11 \pm 0.01 ^{ab}
24:0	0.11 \pm 0.01 ^a	0.09 \pm 0.01 ^a	0.09 \pm 0.00 ^a

Data are expressed as means \pm SD ($n = 3$). Means \pm SD followed by the same letters, on raw are not significantly different ($p > 0.05$)

RAWO raw whole cashew nut oil, LTWO low temperature roasted whole cashew nut oil, HTWO high temperature roasted whole cashew nut oil

et al. [23] and Toschi et al. [28] also reported similar values for the above mentioned fatty acids found in raw cashew nut oils.

In general, the ratio of total SFA to MUFA to PUFA of cashew nut oils was 1.2:3.6:1.0. This ratio remained unchanged for oils extracted from raw, LT, and HT treated whole cashew nuts, suggesting that roasting had little or no effect on the fatty acid profile of the oils tested. Several authors have reported that FA compositions of rice germ, sesame seed and safflower seed oils prepared under different roasting temperatures and time combinations remained unchanged [11, 13, 21, 26]. This is perhaps due to the relatively stable and less unsaturated type of fatty acids presents in the cashew nut oil.

Oxidative Stability of Cashew Nut Oils

The oxidative stability of cashew nut oils were tested by determining their contents of CD and TBARS. The results obtained clearly demonstrated greater oxidative stability of cashew nut oils prepared under accelerated oxidation conditions with increased roasting temperature. Table 2 shows the changes in the contents of CD and TBARS (mmol MDA equivalents/g of oil) in cashew nut oils during storage at 60 °C. Generally, the CD values of oils extracted from roasted cashew nuts were significantly ($p < 0.05$) lower than that extracted from raw cashew nut, thus suggesting the better oxidative stability of the oil from roasted nuts.

CD show the degree of formation of primary products of lipid oxidation due to a shift in double bond positions upon oxidation of methylene interrupted lipid dienes or polyenes

Table 2 Oxidative stability of cashew nut oil extracted under different roasting conditions

Storage time (h)	CD values			TBARS (mmol MAD eq/g of oil)		
	RAWO	LTWO	HTWO	RAWO	LTWO	HTWO
0	0.91 ± 0.00 ^a	0.90 ± 0.10 ^a	0.81 ± 0.01 ^a	0.10 ± 0.08 ^a	0.12 ± 0.01 ^a	0.02 ± 0.06 ^a
6	0.93 ± 0.01 ^a	0.90 ± 0.05 ^a	0.57 ± 0.13 ^b	0.21 ± 0.01 ^a	0.21 ± 0.01 ^a	0.17 ± 0.02 ^b
12	1.23 ± 0.08 ^a	0.99 ± 0.00 ^b	0.83 ± 0.04 ^b	0.30 ± 0.01 ^a	0.24 ± 0.04 ^a	0.18 ± 0.06 ^b
24	1.14 ± 0.23 ^a	0.84 ± 0.02 ^a	0.68 ± 0.17 ^b	0.25 ± 0.01 ^a	0.23 ± 0.04 ^a	0.09 ± 0.06 ^b
36	1.31 ± 0.19 ^a	0.83 ± 0.10 ^b	0.72 ± 0.03 ^b	0.17 ± 0.03 ^a	0.13 ± 0.04 ^a	0.08 ± 0.04 ^b
48	1.34 ± 0.51 ^a	0.89 ± 0.08 ^a	0.69 ± 0.08 ^b	0.15 ± 0.04 ^a	0.12 ± 0.01 ^a	0.11 ± 0.01 ^a
72	1.37 ± 0.29 ^a	0.74 ± 0.12 ^b	0.66 ± 0.02 ^b	0.11 ± 0.01 ^a	0.12 ± 0.01 ^a	0.11 ± 0.01 ^a

Data are expressed as means ± SD ($n = 3$). Means ± SD followed by the same letters, on raw are not significantly different ($p > 0.05$)

RAWO raw whole cashew nut oil, LTWO low temperature roasted whole cashew nut oil, HTWO high temperature roasted whole cashew nut oil, CD conjugated diene, TBARS thiobarbituric acid reactive substances, MAD eq malondialdehyde equivalents

[29]. CD contents of cashew nut oils increased gradually as the storage time increased. Oxidative stability of cashew nut oils, based on changes of CD contents, followed the same order as those evaluated by the TBARS method in this study. Therefore, the oils from cashew nut roasted at high temperatures had a significantly ($p < 0.05$) higher oxidative stability than oil from raw cashew nuts or those roasted at a low temperature. These results are in agreement with those previously reported for sesame oils that indicated a better oxidative stability for sesame oil from seeds subjected to a higher roasting temperature [30]. Lee et al. [21] also reported that oxidative stability of safflower oil prepared from seeds roasted at different temperatures (140–180 °C) was increased with increasing roasting temperature.

TBARS values provide a measure of the secondary oxidation products in the oil. The TBARS values, expressed as mmol MDA equivalents per g, of oil extracted from raw or roasted cashew nuts increased slowly during the storage period for all samples. Moreover, TBARS values of oils (Table 2) from raw, LT, and HT treated cashew nut oil were 0.105 ± 0.02 , 0.120 ± 0.01 , and 0.113 ± 0.01 mmol MDA equivalents per g of oil, respectively, for oil samples after 72 h of storage under Schall oven conditions at 60 °C. These results are in agreement of with those of Abou-Gharbia et al. [31] who studied the effect of processing on oxidative stability of sesame oil extracted from intact and dehulled seeds.

The better oxidative stability of cashew oil prepared from nuts roasted at high temperature was possibly due to the formation of Maillard browning reaction products during the roasting process which are known to positively influence products' shelf life [32].

Conclusions

Cashew nut oil extracted from raw and roasted whole cashew nuts were examined for their fatty acid

composition, color change and oxidative stability. In general fatty acid composition remained unchanged for cashew nut oils extracted from raw as well as roasted whole nuts. Oleic acid was the major fatty acid followed by linoleic, palmitic, and stearic acids in all oil samples tested. Oxidative stability, as determined by the contents of CD and TBARS, increased with increasing roasting temperature. The color of oil extracted from roasted whole cashew nuts exhibited a higher absorbance value compared to that from raw whole cashew nut, possibly due to the formation of MRP which are known to render antioxidant effects. Thus, roasting of whole cashew nuts improved the oxidative stability of their extracted oils. Further studies are warranted to shed light on the chemical identity of the active components in cashew nut oil samples and to evaluate their contribution to the stability of the oils extracted from roasted whole cashew nuts.

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