EFFECT OF METHOD OF EXTRACTION ON THE QUALITY OF COCONUT OIL

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ABSTRACT

Coconut oils prepared by pressing copra (commercial coconut oil) and boiling water extracts of scraped coconut kernel (home-made coconut oil) were analyzed in order to study the effect of method of extraction on their quality. Acid value and peroxide value were 89% and 95% respectively higher in commercial coconut oil compared to home-made coconut oil indicating that commercial coconut oil is more prone to oxidation. Saponification value was 12 % higher in home-made coconut oil while there was no significant difference in the iodine value of the two types of coconut oils. Only minor differences in the fatty acid composition between commercial coconut oil and home-made coconut oil were observed. The total content of phenolic compounds in home-made coconut oil was 84 % higher than that in commercial coconut oil. These results indicate that quality of coconut oil is highly dependent on the method of extraction.

Keywords: Coconut oil, Extraction method, Phenolic compounds, Fatty acids

INTRODUCTION

Two methods of extraction, i.e., expression of copra and boiling of water extracts of scraped coconut kernel (coconut milk), are commonly used to produce coconut oil. Expression of copra is carried out in the large-scale production of coconut oil (commercial coconut oil) and boiling of coconut milk is limited to small-scale production of coconut oil (home-made coconut oil) for domestic purposes. It is traditionally known that home-made coconut oil exhibits better qualities compared to commercial coconut oil. For example, home-made coconut oil has a pleasant odor and a longer shelf-life while commercial coconut oil has a neutral odor with a shorter

shelf-life. It has been shown that peroxide formation is significantly slower in home-made coconut oil compared to commercial coconut oil (Seneviratne & Dissanayake 2003a).

Unrefined vegetable oils contain approximately 98-99 % of saponifiable compounds and approximately 1-2 % of nonsaponifiable compounds. Saponifiable compounds include triglycerides and free fatty acids. Nonsaponifiable fraction contains phenolic acids, flavonoids, hydrocarbons and numerous other organic compounds. Several parameters related to both saponifiable and nonsaponifiable fractions have to be considered for the evaluation of the quality of unrefined oils. Acid value (AV), peroxide value (PV), saponification value (SV) and iodine value (IV) are considered as parameters related to the saponifiable fraction and total phenol content is an important parameter related to the nonsaponifiable fraction of cooking oils. As quality parameters related to saponifiable fraction, AV and PV are useful to evaluate the oxidative stability while IV and SV are measures of the chemical nature of fatty acids.

Even though the nonsaponifiable fraction is a minor component in cooking oils, phenolic compounds present in the nonsaponifiable fraction exert several physiological effects on human nutrition and strongly influence the quality of oil. Phenolic compounds in virgin olive oil are responsible for several organoleptic characteristics (Gutiérrez *et al.*, 1989) and oxidative stability (Montedoro *et al.*, 1993). More over, phenolic compounds in olive oil display pharmacological properties (Maestro Durán *et al.*, 1994) and antioxidant properties (Baldioli *et al.*, 1996). Beneficial health effects arising from the antioxidant properties of the phenolic fraction of olive oil have been well documented (Visioli & Galli, 1998). There are several reports on the variation of phenol content of virgin olive oil with the variety, location and degree of ripeness of olive fruits (Montedoro & Garofolo, 1984; Esti *et al.*, 1998). However, there have been only very few reports on the effect of extraction method on the phenol content of olive oil (Nergiz & Ünal, 1991) and such reports for other vegetable oils are even meager.

The effect of phenol content and metal ion content on the oxidative stability of coconut oil has already been reported (Seneviratne & Dissanayake 2003a; Seneviratne & Dissanayake 2003b). In the present study, AV, PV, SV, IV and phenolic content of commercial coconut oil and home-made coconut oil were evaluated in order to determine the effect of method of extraction on the quality of coconut oil. Compositions of individual fatty acids of the two types of coconut oils were also determined.

MATERIALS AND METHODS

Sample collection

Nuts of the same maturity stage (12 - 14 months) of "Ordinary Tall" coconut cultivars were used to obtain coconut oil. Coconut milk was prepared by extracting scraped coconut kernel with water. Four oil samples were prepared by boiling coconut milk within 24 hours after the harvest. Coconuts from the same batch were used to prepare copra. Four copra samples were prepared by drying coconut kernels under the sunlight for three weeks. Coconut oil from these four copra samples was prepared by pressing copra in a small-scale expeller available in oil mills in Sri Lanka.

Reagents and standards

Gallic acid was purchased from Analytical Reagent, Mumbai, India. Sodium tungstate for the preparation of Folin-Denis reagent for phenol analysis was purchased from Tomas Baker, Mumbai, India. Standards for fatty acid methyl esters for gas liquid chromatographic (GLC) analysis were purchased from Fluka Chemicals, Switzerland.

Determination of quality parameters

AV, PV, SV and IV were determined by standard methods given in text books (Kirk & Sawyer, 1991). AV was determined by titrating a solution of coconut oil in a 1 : 1 mixture of ethanol and diethylether with a solution of standard KOH using phenolphthalein as the indicator. SV was determined by base hydrolysis of coconut oil with excess KOH and titrating unreacted KOH with a standard solution of HCl using phenolphthalein as the indicator. IV was determined by reacting coconut oil with a solution of ICl followed by an iodometric titration. PV was determined by thiocyanate assay method (Masuda *et al.*, 1966).

Determination of total phenolics

Folin-Denis reagent was prepared according to the procedure reported by Perry *et al.* (2001). 20.0 g of coconut oil was sonicated with 20 ml of ethanol : water (70 : 30) mixture for 2 hours. The mixture was centrifuged and 1.0 ml of the resultant clear solution was mixed with 1.0 ml of Folin – Denis reagent. After 3 minutes, 1.0 ml of 35% Na₂CO₃ solution was added and the mixture was diluted to 10.0 ml with distilled water. After 45 minutes, the mixture was centrifuged and absorbance was measured with respect to a blank with no added phenolic extract at 745 nm using a

UV-Visible Spectrophotometer (Model : Shimadzu UV – 160). This procedure was repeated 3 times for one 20.0 g portion of coconut oil. Phenolic compounds were not detected in coconut oil after the third extraction. The total phenol content was expressed as gallic acid equivalents.

Methylation of fatty acids

Methylation of fatty acids was carried out according to the procedure described by Fernandez *et al.* (2000) with some modifications. 0.10 g of the oil sample was placed in a leak-proof tube and 4 ml of a mixture of anhydrous methanol : toluene : Conc. H_2SO_4 (88 : 10 : 2 v/v) was added to the tube. The mixture was heated at 80 °C for 1 hour and cooled to room temperature. Fatty acid methyl esters (FAME) were extracted with *n*-hexane (1 ml x 4) and a saturated NaCl solution was added to clear the hexane layer. The extract was filtered through a column of anhydrous Na_2SO_4 and stored in an amber-colored vial until gas liquid chromatographic (GLC) analysis. The esterification process was monitored by thin layer chromatography (TLC) to make sure that the reaction is complete. For this purpose, TLC plates were developed with the solvent system, hexane : ethyl ether : formic acid (75 : 25 : 1 v/v). Spots were visualized by spraying 25 % H_2SO_4 reagent.

Fatty acid analysis by Gas Liquid Chromatography (GLC)

The hexane solution of FAME in a vial was concentrated to 1 ml by evaporating the solvent under a stream of N_2 . The concentrated extract was subjected to gas chromatography. A Thermo Finnigan Trace GC (K01332734500000, Strada Rivoltana-20090 Rodano (Milan)-Italy) equipped with a capillary column Rtx^R-WAX (Crossbond with PEG, 30 m x 0.32 mm i.d. 0.25 μm) and a flame ionization detector (FID) was used for this analysis. The injector and detector temperatures were set at 230 °C and 250 °C respectively. Helium gas was passed as carrier gas at a flow rate of 0.5 ml/min and analyses were performed on split mode (split ratio 100: 1). Column temperature was programmed at 130 °C (3 min), 130 °C to 210 °C at 45 °C/min and 210 °C (12 min). 0.4 μl of the sample was injected into the GLC system. Signals in the GLC chromatogram were identified by comparison of the retention times with the retention times of authentic fatty acid methyl ester standards. The quantities of fatty acids were obtained by integration of the peak areas in GLC chromatograms.

Statistical Analysis

Statistical analyses were performed using ANOVA followed by Tukey's pairwise comparison test and 2 sample t-test.

RESULTS AND DISCUSSION

Coconuts of same maturity from 'Ordinary Tall' coconut cultivars were used to minimize variations in the raw material. Free fatty acid content (AV) of coconut oil is given in the Table 1. AV of commercial coconut oil is 89% higher than that of home-made coconut oil and the PV of commercial coconut oil is 95 % higher than that of home-made coconut oil. It has been shown that free fatty acid content in coconut oil varies with the processing time and storage time of copra (Seneviratne *et al.*, 2002). The rancidity occurs as a result of the oxidation of free fatty acids in oils. Lower free fatty acid and peroxide contents in home-made coconut oil would be two important factors that contribute to its higher oxidative stability compared to that of commercial coconut oil.

Table 1: Quality parameters of home made (HO) and commercial (CO) coconut oils

Source	AV (mg of KOH/g)	SV (mg of OH/g)	IV (g of I ₂ /100 g)	PV (absorbance at 500 nm)	Total phenol content (mg/kg)
HO	0.40 ± 0.02 ^a	274 ± 2 ^a	6.6 ± 0.2 ^a	0.034 ± 0.002 ^a	506 ± 20 ^a
CO	3.5 ± 0.9 ^b	241 ± 3 ^b	6.2 ± 0.3 ^a	0.62 ± 0.04 ^b	72.1 ± 5.6 ^b

Each data point represents the mean of eight replicates ± S.E; Different superscript letters in the same column denote a significant difference (p<0.05).

Even though the fatty acid composition of coconut oil is reported in several articles, the source and the method of oil extraction in the reported compositions are not elaborated. In this study, the fatty acid composition of the home-made coconut oil and commercial coconut oil were analyzed by GLC and the relevant chromatograms are given in Figs 1 and 2 respectively. Fatty acid composition given

in Table 2 indicates that the values are within the same range of values reported by Kaunitz (1972).

Figure 1: GLC chromatogram of the fatty acid methyl esters of home-made coconut oil

Figure 2: GLC chromatogram of the fatty acid methyl esters of commercial coconut oil

Table 2: Fatty acid compositions of home-made (HO) and commercial (CO) coconut oils

Source	C 6:0	C 8:0	C 10:0	C 12:0	C 14:0	C 16:0	C 18:0	C 18:1	C 18:2
HO	0.63 ± 0.04	9.2 ± 0.1 ^a	6.5 ± 0.1	49.6 ± 0.2 ^a	19.2 ± 0.1	7.2 ± 0.1	2.4 ± 0.1	4.5 ± 0.1	1.1 ± 0.1
CO	0.53 ± 0.04	8.6 ± 0.1 ^b	6.4 ± 0.2	48.7 ± 0.2 ^b	18.9 ± 0.1	7.6 ± 0.2	2.4 ± 0.1	4.9 ± 0.2	1.3 ± 0.1

Each data point represents the mean of three replicates ± S.E; Different superscript letters in a same column denote a significant difference at 5 % level by one way ANOVA & Tukeys's pair wise comparison test.

SV of home-made coconut oil is 12 % higher than that of commercial coconut oil. Higher saponification value for a triglyceride indicates a higher medium chain fatty acid composition. However, the fatty acid composition, determined by GLC (Table 2) indicates that the medium chain fatty acid composition of home-made coconut oil is only 2 % higher than that of commercial coconut oil. There is no direct correlation between the SV and the percentage of medium chain fatty acids for a mixture of triglycerides. In addition, the SV for unrefined vegetable oils may also be affected by the compounds in the nonsaponifiable fraction. For example, compounds such as phenolic acids that can react with KOH may also contribute to the higher saponification value of home-made coconut oil.

There was no significant difference in the IV of the two types of coconut oils ($p > 0.05$) indicating that there is no difference in the degree of insaturation in the fatty acids present in home-made and commercial coconut oils.

The most striking difference between home-made coconut oil and commercial coconut oil is in the phenol content (Table 1). Total phenol content of home made coconut oil was 506 ± 20 mg while that of commercial coconut oil was 72 ± 6 mg as gallic acid/kg oil. Higher phenol contents for home-made coconut oil extracted from more mature coconut nuts have also been reported (Seneviratne & Dissanayake, 2003a) indicating that phenol content varies with the maturity of

coconut nuts. Total phenol content of home-made coconut oil is usually about 84 % higher than that of commercial coconut oil indicating that extraction methods have a remarkable impact on the total phenol content of coconut oil. Phenolic acids and flavonoids are polar compounds that are usually soluble in water and alcohols. Scraped coconut kernel is extracted with water to prepare coconut milk in home-made process of coconut oil extraction and most of the phenolic compounds dissolve in this water extract of coconut kernel. These phenolic compounds are slowly incorporated into coconut oil during boiling and evaporation of water in the home-made process.

It is a usual practice to consider triglyceride fraction and neglect the nonsaponifiable fraction of cooking oils in the assessment of health effects and nutritional properties. However, phenolic compounds such as phenolic acids and flavonoids present in plants are natural antioxidants that are responsible for several beneficial health effects. Recent findings demonstrate that phenolic compounds in food inhibit the oxidation of low-density lipoprotein (LDL), thus reducing the risk of coronary heart disease (CHD) (Visioli & Galli, 1998). Lower incidence of CHD in the Mediterranean area has been hypothesized to arise from the protective effect of phenolic compounds present in olive oil (Hertog *et al.*, 1995). There is an increasing number of data from epidemiological and controlled studies to correlate the intake of flavonoids and phenolic acids with the lower incidence of CHD (Hertog *et al.*, 1993; 1995). A direct relationship between the phenol content and the oxidative stability of virgin olive oil has been described (Nergiz & Ünal, 1991). The reported value of total phenol content for unrefined olive oil is ~800 mg/kg oil as gallic acid (Monti *et al.*, 2001). Total phenol content of home-made coconut oil is more than 60 % of this value and therefore the total phenol content of home-made coconut oil is comparable with that of unrefined olive oil. As such, it is reasonable to expect significant beneficial health effects from the phenolic compounds in coconut oil.

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REFERENCES

- Baldioli, M., M. Servili, G. Perretti & G.F. Montedoro 1996. Antioxidant activity of tocopherols and phenolic compounds of virgin olive oil. *Journal of the American Oil Chemists' Society* 73 (11): 1589-1593.

- Esti, M., L. Cinquanta & E. La Notte 1998. Phenolic compounds in different oil varieties. *Journal of Agricultural and Food Chemistry* 46: 32-35.
- Fernandez, M.V., F.E. Martinez & R. Garces 2000. Metabolism of triacylglycerol species during seed germination in fatty acid sunflower (*Helianthus annuus*) mutants. *Journal of Agricultural and Food Chemistry* 48: 770-774.
- Gutiérrez, F., M.A. Albi, R. Palma, J.L. Rios & J.M. Olías 1989. Bitter taste of virgin olive oil: correlation of sensory evaluation and instrumental HPLC analysis. *Journal of Food Science* 54: 68-70.
- Hertog, M.L.G., E.J.M. Feskens, M.B. Katan, & D. Kromhout 1993. Dietary antioxidant flavonoids and risk of coronary heart disease in the Zutphen Elderly Study. *Lancet* 342: 1007-1011.
- Hertog, M.G.L., D. Kromhout, C. Aravanis, H. Blackburn, R. Buzina, F. Fidanza, S. Giampaoli, B.S. Simic, H. Toshima, E.J.M. Feskens, P.C.H. Hollman & M.B. Katan 1995. Flavonoid intake and long-term risk of coronary heart disease and cancer in Seven Countries Study. *Archives of Internal Medicine* 155: 381-386.
- Kaunitz, H. (1972). Nutritional properties of coconut oil. *Ceylon Coconut Quarterly* 23: 85-91.
- Kirk, S.R. & R. Sawyer 1991. *Pearson's Composition and Analysis of Foods*, (9th Edition), Longman Scientific and Technical, Harlow, England.
- Maestro-Durán, R., Leòn R. Cabello & V. Ruiz Gutierrez 1994. Phenolic compounds from olive (*Olea europea*). *Grasas Aceites* 45: 265 – 269.
- Masuda, H., K. Yuasumoto & K. Iwami 1966. Antioxidative action of indole compounds during the auto oxidation of linoleic acid. *Eiyo to Shokuryo* 19: 210-214.
- Montedoro, G. F. & L. Garofolo 1984. The quantitative characteristics of virgin olive oils. The influence of variable such as variety, environment, preservation,

- extraction conditioning of the finished product. *Rivista Italiana Sostanze Grasse* 61: 157-168.
- Montedoro, G.F., M. Servili, M. Baldioli, R. Selvaggini, E. Miniati & A. Macchioni 1993. Simple and hydrolysable phenolic compounds in olive oil. 3. Spectroscopic characterization of the secoiridois derivatives. *Journal of Agricultural and Food Chemistry* 41: 2228-2234.
- Monti, S.M., A. Ritieni, R. Sacchi, K. Skog, E. Borgan & V. Fogliano 2001. Characterization of phenolic compounds in virgin olive oil and their effect on the formation of carcinogenic/mutagenic heterocyclic amines in a model system. *Journal of Agricultural and Food Chemistry* 49: 3969-3975.
- Nergiz, C. & K. Ünal 1991. Effect of method of extraction on the total polyphenol, 1,2- diphenol content and stability of virgin olive oil. *Journal of the Science of Food and Agriculture* 56: 79-84.
- Perry, N.B., E.J. Burgess & V.I. Glennie 2001. *Echinacea* Standardization: Analytical Methods for Phenolic Compounds and Typical Levels in Medicinal Species. *Journal of Agricultural and Food Chemistry* 49: 1702-1706.
- Seneviratne, K.N., K.D.L.S. Dharmaraja & D.M.S. Dissanayake 2002. Preliminary studies on the oxidation of coconut oil. *Proceedings of the Annual Research Symposium 2002, Faculty of Graduate Studies, University of Kelaniya*, (Abstract), p. 36.
- Seneviratne, K.N. & D.M.S. Dissanayake 2003a. The effect of phenols content on the oxidative stability of coconut oil. *Proceedings of the Proceedings of the Annual Research Symposium 2003, Faculty of Graduate Studies, University of Kelaniya*, (Abstract), p. 79.
- Seneviratne, K.N. & D.M.S. Dissanayake 2003b. Effect of metal ions on the oxidative stability of coconut oil. *Proceedings of the 59th Annual Session of Sri Lanka Association for the Advancement of Science*, (Abstract), p. 228.
- Visioli, F. & C. Galli 1998. Olive oil phenols and their potential effects on human health. *Journal of Agricultural and Food Chemistry* 46: 4292-4296.