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Extraction and determination of physico-chemical characteristics of Pili nut oil

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Abstract

Canarium ovatum oil Engl. (pili nut oil) was extracted by using cold press method and then the physico-chemical properties of the oil samples, roasted pili nut oil (RPNO) and unroasted pili nut oil (UPNO) such as iodine value (IV), peroxide value (PV), acid value (% FFA), solid fat content (SFC), fatty acid composition and triacylglycerol (TAG) composition were determined. The percentage of oil yield and iodine value for RPNO and UPNO were showed no significant different, wheareas there were significantly different for the peroxide value and percentage of free fatty acid. The solid fat content for RPNO and UPNO were similar to the palm olein oil and both completely melt at 25°C. Both samples, RPNO and UPNO were contained 50.70% and 52.59% of oleic acid and were found not contain the trisaturated TAGs.

Introduction

According to Coronel (1996), Agricultural research has traditionally focused on staple crops that produce the majority of the food supply while relatively little attention has been given to minor (or underutilized or neglected) crops. The limited information available on many important and frequently basic aspects of neglected and underutilized crops hinders their development and their sustainable conservation. In Malaysia, the Department of Agriculture Sabah has planted pili for research purposes.

The kernel or known as the pili nut is the most important part of the pili fruit. Pili nut can be eaten raw, roasted or coated with sugar. The oil extracted from pili nut has a light yellowish colour, mainly the glycerides of oleic (44.4% to 59.6%) and palmitic acids (32.6 to 38.2%) and is suitable for culinary purposes (Janick and Paull, 2008). According to Arribas (1994), the pili kernel is about 70% oil and it resembles olive oil which is has possibility to replace the imported olive oil for sardine manufacture, salad dressing and other food preparations. The quality of pili nut oil is also said to be comparable to that of olive oil due to its high content of monounsaturated fatty acid which is oleic acid (Haard, 1985). More information on pili nut oil and its properties is needed to promote the utilization and development of this new oil. Therefore, the research was focused on determination of physicochemical properties of roasted pili nut oil (RPNO) and unrosted pili nut oil (UPNO) extracted by using mechanical press machine (cold press method).

Materials and Methods

Materials

Roasted and unroasted pili nuts were supplied by Department of Agriculture Sabah (DoA), Kota Kinabalu, Sabah.

Method of extraction

Roasted pili nut oil (RPNO) and unroasted pili nut oil (UPNO) were extracted by using mechanical press machine (cold press method) and the percentage of oil yield were determined. Both samples were stored in sealed glass bottle at -20°C until analyzed.

Iodine value (IV)

Iodine value was determined according to PORIM test methods p3.2 (1995). Sample was weighed accurately to the nearest 0.0001g in the glass weighing scoop or vial. The weight of the sample to be used varies according to its expected iodine value. About 0.5 g of pili nut oil was weighed and put into a 500 ml flask. 20 ml cyclohexane was added to dissolve the fat. Warm the flask slightly to

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facilitate dissolution of the fat if necessary. 25 ml of the Wijs solution was added, stopper was inserted, shake gently and the bottle was placed in the dark for 1 hour. After standing, 20 ml of the potassium iodide solution and 100 ml of water was added. Titrate with the sodium thiosulphate solution until the yellow colour due to iodine had almost disappeared. 1 to 2 ml of starch indicator solution was added and titration was continued until the blue colour just disappears after very vigorous shaking. Three determinations on the same test sample was carried out. A blank test was carried out simultaneously under the same conditions. Expression of results:

$$\text{Iodine value} = \frac{12.69N\ (\ V2 - V1)}{W}$$

Where: N is the exact normality of the sodium thiosulphate solution used; V2 is the volume in millilitres, of the sodium thiosulphate solution used for the blank test; V1 is the volume in millilitres, of the sodium thiosulphate solution used for the determination; W is the weigh, in grams, of the test portion.

Peroxide value (PV)

Peroxide value was determined according to PORIM test methods p2.3 (1995). 5.00 ± 0.05 g of the pili nut oil was weighed into the 250 ml flask. 30 ml of the acetic-chloroform solution was added. The flask was swirled until the sample was dissolved in the solution. 0.5 ml of saturated potassium iodide was added with a graduated pipette. The solution was swirled for 1 minute and then 30 ml of distilled water was added. For freshly produced oils, a few drops of starch solution were added. Titrate with 0.01N sodium thiosulphate solution, adding it gradually and with constant and vigorous shaking. The titration was continued, the flask was vigorously shaking near the end-point to liberate all the iodine from the chloroform layers. The sodium thiosulphate solution was added drop wise until the blue colour just disappears. A blank test was carried out in parallel with the determination. The blank titration must not exceed 0.1 ml of the 0.01 N sodium thiosulphate solution. The peroxide value, expressed in miliequivalents of active oxygen per kilogram of sample is:

$$\frac{(Vs - Vb)N \times 1000}{W}$$

Where: Vs is the volume in milliliters, of the sodium thiosulphate solution of normality N, used for the determination; Vb is the volume , in milliliters of the sodium thiosulphate solution used for the blank test; W is the weight, in grams, of the test portion; N is the normality of the sodium thiosulphate solution.

Acid value (% FFA)

Acid value was determined according to PORIM test methods no. p2.5 (1995). 0.5 g of pili nut oil was weighed into an Erlemeyer flask. 50 ml isopropanol was added in a flask and bring the solution to the boil over a hot plate. 0.5 ml of phenolphthalein was added and neutralized by dropwise addition of 0.1 N potassium hydroxide till a faint, but permanent pink colour was obtained. Expression of result: FFA % as oleic acid:

$$\frac{28.2 \times N \times V}{W}$$

Where: N = normality of NaOH solution; V = volume of NaOH solution used in ml; W = weigh of sample.

Solid fat content (SFC)

The percentage of solid fat content was determined based on MPOB test method (2005), (nonstabilized serial procedure) by using Bruker Minispec pulsed Nuclear Magnetic Resonance (pNMR) Analyzer Model No. 120 (Rheinstetten, Germany). The samples inside the pNMR tube were melted at 70°C for 30 min in an oven before analysis. The predetermined temperatures used for measurement were 0, 5, 10, 15, 20, 25, 30, 35 and 37.5°C.

Fatty acid composition

The fatty acid composition was determined according to MPOB test method (2005).

Triacylglycerol (TAG) composition

The TAG composition was determined according to MPOB test method (2005).

Statistic

Data obtained were tested for significance using ANOVA and Duncan Multiple Range Test at $p < 0.05$ using SAS version 9.2. Experiment was performed in triplicate and the result were expressed as mean ± standard deviation.

Results and Discussion

Table 1 shows the percentage of oil yield, iodine value, peroxide value and percentage of free fatty acid of roasted pili nut oil (RPNO) and unroasted pili nut oil (UPNO). Both samples, RPNO and UNPO were

Table 1. Chemical properties of roasted pili nut oil (RPNO) and unroasted pili nut oil (UPNO)

Sample	Chemical properties			
	Oil yield (%) /dry wt basis	Iodine value	Peroxide value (meq per kg of oil)	Acid value (% FFA as oleic acid)
RPNO	65.69 ± 6.15 [a]	32.44 ± 0.73 [a]	7.70 ± 0.02 [a]	1.27 ± 0.31 [a]
UPNO	64.13 ± 3.56 [a]	31.54 ± 1.31 [a]	1.98 ± 0.02 [b]	0.53 ± 0.03 [b]

[ab] Means with the same letter are not significantly different.

Table 2. Fatty acid composition of roasted pili nut oil (RPNO) and unroasted pili nut oil (UPNO)

Samples	Fatty Acid Composition (%)					
	Oleic (C18:1)	Palmitic (C16:0)	Stearic (C18:0)	Linoleic (C18:2)	Linolenic (C18:3)	Palmitoleic (C16:1)
RPNO	50.7	28.19	9.34	10.61	0.73	0.43
UPNO	52.59	28.73	9.91	7.79	0.62	0.37
[a]Almond	58-81	6-9	0-1	12-32	-	-
[a]Cashew	57-65	9-14	6-12	16-19	-	-
[b]Peanut oil	41.5	11.4	4.0	34.9	0.2	0.1
[c]Olive oil	78.4	11.3	2.6	5.7	0.5	0.8
[d]Cocoa butter	35.2	25.2	35.5	3.2	0.2	-

[a] Ucciani, 1995.
[b] Taira, 1985; Hammond *et al*., 1997.
[c] Muhamed *et al*., 2002.
[d] Pease, 1985.

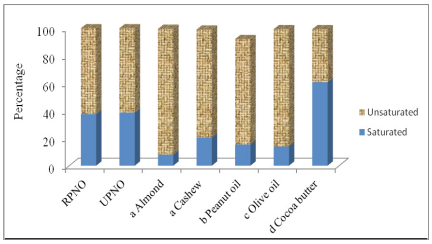

Figure 1. Saturated and unsaturated fat of roasted pili nut oil (RPNO) and unroasted pili nut oil (UPNO)

[a] Ucciani E., 1995.
[b] Taira, H., 1985; Hammond, E.G. *et al*., 1997.
[c] Muhamed A.I. *et al*., 2002.
[d] Pease, J.J., 1985.

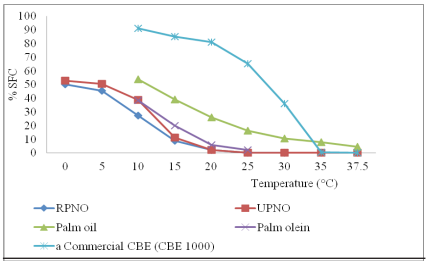

Figure 2. Solid fat content of roasted pili nut oil (RPNO) and unroasted pili nut oil (UPNO)

[a] Wong Soon, 2002

extracted by using cold press method and there was no significant different on the percentage of oil yield and iodine value. PV measures the degree of oxidation which is related to the shelf life of an oil before the oil goes rancid (oxidative rancidity). Temperature, light, moisture and exposure to oxygen have been found to be the main contributing factors to oxidation (Jan *et al.*, 1988; Mate *et al.*, 1996; Koyuncu and Askin, 1999; Stark *et al*., 2000). Furthermore, according to Gertz *et al.* (2000), the oxidation is also influenced by antioxidants and the fatty acid composition of the oils. According to Naz *et al.* (2005), autoxidation occurs via self-propagating free radical mechanism. Since direct reaction of unsaturated fatty acids with O_2 is thermodynamically difficult, production of first few radicals necessary to start propagation (initiation) must occur by some catalytic means. It has been proposed that the initiation step may take place by decomposition of preformed hydroperoxides due to heat or exposure to light or by mechanisms where singlet O_2 is the active species involved. Upon formation of sufficient free radicals the chain reaction is propagated by the abstraction of hydrogen atoms adjacent to double bonds of fatty acids, followed by O_2 attack at these locations and resulting in the production of peroxy radicals. The PV and the percentage of free fatty acid for both sample showed a significantly different. The PV of RPNO and UPNO were 7.70 and 1.98, whereas the value of % FFA were 1.27% and 0.53%. The peroxide value and the percentage of free fatty acid of RPNO was higher than UPNO might be because of the roasting temperature that being exposed to the nuts. However, oxidative rancidity or autoxidation cannot be stopped by lowering the temperature of storage since it is a chemical reaction with low activation energy (Naz *et al*., 2005). Furthermore, oxidative rancidity is caused by the oxidation of the double bonds of the fatty acids and it is in agreement with the result in Table 2 and Figure 1.

According to Table 2 and Figure 1, the saturated and unsaturated fat in RPNO were 37.53% and 62.47% whereas in UPNO, the content of saturated and unsaturated fat were 38.64% and 61.37%. The unsaturated fatty acid in RPNO was found quite higher than UPNO and this result was compatible with the result of peroxide value and percentage of free fatty acid. Furthermore, according to Haard (1985), this fatty acid profile is comparable with that of olive oil which is about 85% unsaturated. Both samples, RPNO and UPNO were contain low saturated fat and high of unsaturated fatty acid (Table 2 and Figure 1). These fatty acids may also reduce total and low-density lipoprotein (LDL) cholesterol and decreasing the risk of cardiovascular disease (Lopez-Huertas, 2010). Both samples, RPNO and UPNO contain high percentage of oleic acid and also contain polyunsaturated fatty acid. According to the WHO (2003), the most effective replacement for saturated fatty acids in terms of coronary heart disease (CHD) outcome are polyunsaturated fatty acids (PUFA) and oleic acid. Furthermore, isocaloric replacement of about 5% of energy from saturated fatty acids by oleic acid (or PUFA) has been estimated to reduce coronary heart disease risk by 20 - 40% mainly via LDL – cholesterol reduction (Kris-Etherton, 1999). It is clear that pili nut oil is in the family of the high-priced monounsaturated oils. Based on table 2, the main composition of fatty acid in RPNO were

Table 3. Triacylglycerol (TAG) composition of roasted pili nut oil (RPNO) and unroasted pili nut oil (UPNO)

TAG (%)	Samples					
	RPNO	UPNO	Almond seed oil [a]	Olive oil [b]	Palm oil [c]	Cocoa butter [d]
OLL	0.4	0.1	10	1.1	0.5	-
PLL	1.1	0.3	3	0.7	2.5	
OLO	2.4	1.1	15	-	1.7	0.8
PLO	6.3	3.7	-	-	9.9	1.7
PLP	2.8	1.9	-	-	9.5	0.5
OOO	8.2	7.7	21	44	4.3	2.2
POO	54.3	61.1	3	23.3	22.8	2.3
POP	13	12.5	-	-	29	14.8
SOO	4.9	4.9	-	5	2.5	2.9
POS	6.1	6.2	-	-	5.1	36.8
SOS	0.4	0.5	-	-		25.3

[a] Holčapek *et al*., 2003.
b Boskou, 1996.
c Tan *et al.*, 1997.
d Soekopitojo *et al*., 2009.

50.70% oleic acid (C18:1), 28.19% palmitic acid (C16:0), 9.34% stearic acid (C18:0) and 10.61% linoleic acid (C18:2). Meanwhile, in UPNO, there were 52.59% oleic acid (C18:1), 28.73% palmitic acid (C16:0), 9.91% stearic acid (C18:0) and 7.79% linoleic acid (C18:2). Generally, from the result, both samples, RPNO and UPNO contain high percentage of monounsaturated fatty acid (MUFA) and low percentage of polyunsaturated fatty acid (PUFA) and this result is in agreement with the finding of Eritsland, (2000) where, oxidative stress is considered an important mechanism in the pathogenesis of inflammation, cancer and atherosclerosis. Free radicals preferentially target PUFAs because of their multiple double bonds. In contrast, MUFAs are less prone to peroxidation because they contain only one double bond, and it is hypothesized that pili nut oil would lead to less oxidative stress. According to Augusto *et al.* (2012), the solid fat content (SFC) is an important physical property of lipids, which express the solid fraction amount at each temperature. Percentage of solid fat content not greater than 32% at 10°C is essential for good spread ability at refrigeration temperature. Based on Figure 2, unroasted pili nut oil (UPNO) was harder than roasted pili nut oil (RPNO) at refrigerator temperature and at 10°C, the percentage of solid fat content of RPNO and UPNO at 10°C were 27.45% and 38.68%. This result is in agreement with the fatty acid composition in both samples, where RPNO contain quite higher of unsaturated fatty acid compared to UPNO. SFC at 20°C - 22°C determines the stability and resistance of fats to oil exudation at room temperature. A SFC value of more than 10% is needed in order to avoid oil exudation (oiling off) (Noor Lida and Ali, 1998). Both samples had SFC less than 10% at 20°C - 22°C. It means that unroasted and roasted pili nut oil exhibit oil exudation. Both samples, after extraction, were in a liquid form at room temperature, thus, the SFC curve for both samples, RPNO and UPNO were similar with of palm olein and according to Figure 1, both samples were completely melt at temperature of 25°C. Based on Table 3, the main TAG components in RPNO were 54.3% of 1-palmitoyl-2-oleyl-3-oleyl-sn-glycerol (POO), 13% of 1,3-dipalmitoyl-2-oleoyl-glycerol (POP), 8.2% of Triolein (OOO) and 6.1% of 1-palmitoyl-2-oleyl-3-stearoyl glycerol (POS) whereas in UPNO there were about 61.1% of 1-palmitoyl-2-oleyl-3-oleyl-sn-glycerol (POO), 12.5% of 1,3-dipalmitoyl-2-oleoyl-glycerol (POP), 7.7% of Triolein (OOO) and 6.2% of 1-palmitoyl-2-oleyl-3-stearoyl glycerol (POS) respectively. From the result, the highest composition of TAG in both samples was1-palmitoyl-2-oleyl-3-oleyl-sn-glycerol (POO). According to Pham and Kwon (1992) and Bhati (1987), this TAG result and information should be useful because fatty acid positions could be highly important aspect of the biosynthetic process and in the tailoring process.

Conclusion

Roasted and unroasted pili nut oil extracted by using mechanical press machine (cold press method) showed there were no significant different on the percentage of oil yield and iodine value but there were significantly different for the peroxide value and percentage of free fatty acid. Both samples were completely melt at 25°C, contained high percentage of oleic acid and were found not contain the trisaturated TAGs.

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