IJST EXPLORE International Journal of Science and Technology
CENTRE OF PROFESSIONAL RESEARCH PUBLICATIONS
ISSN 2049-7318

International Journal of Science and Technology Volume 4 No. 5, May, 2015

Physicochemical and Fatty Acid Composition of Crude and Refined Oils of African Canarium

Ayoade, G.W, Amoo I.A and V.O.E. Akpambang
Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria

ABSTRACT

The physicochemical properties and fatty acid composition of crude and refined oil of *Canarium* seed were investigated using standard methods. Physicochemical properties of crude and refined oils were colour (dark green and greenish yellow), specific gravity (0.9516 and 0.8621), refractive index (1.4012 and1.3034), acid value (1.14 and 0.64) mgKOH/g, free fatty acid (0.96 and 0.34), peroxide value (1.08 and 0.71) meq/kg, iodine value (96.51 and 117.29), saponification value (148.3 and 126.8) mgKOH/kg, unsaponifiable matter (1.73 and 1.21) %, freezing point (-7.5 and 13.0) ^oC, melting point (43.0 and 39.0) ^oC, smoke point (187 and 203) ^oC, flash point (283 and 317) ^oC and fire point (345 and 358) ^oC respectively. The fatty acid composition of crude and refined oils respectively are; stearic (10.765 and 11.481) %, myristic (2.612 and 2.963) %, palmitic (0.358 and 0.574) %, capric (0.013 and 0.024) % and total saturated (15.042 and 13.748) %. The unsaturated are; oleic (31.621 and 35.386) %, palmitoleic (0.053 and 0.142) %, erudic (1.017 and 1.084) %, linoleic (23.724 and 28.612) % and linolenic (0.638 and 0.086) %, total unsaturated (57.053 and 66.370) %. The total fatty acid determined in crude and refined oils are (72.095 and 80.118) % and total undetected was 27.905 and 19.882 % respectively. The study concluded that the seed pulp of canarium is a good source of fat. The extracted oil of canarium seed is better consumed in refined form for its better physicochemical properties and unsaturated fatty acid composition.

Key words: *Canarium Seed, Physicochemical, Fatty Acid, Crude Oil, Refined Oil*

1. INTRODUCTION

Seeds have nutritive and calorific values which make them relevant in diets. They are also good sources of edible oils and fats (Odoemelan, 2005). Seeds are good sources of oil needed for cooking, cake meal, margarine and as valuable protein supplement for all farm animals. Seeds are also of value in the production of confectionaries such as cheese, sweets, crisps, sandwiches, cookies and for flavouring foods. They can be roasted, fried or boiled and eaten as snacks. Seed flours are incorporated into infant foods such as root and tuber based diets, which are low in protein in order to increase their protein content and improve flavor. Oil obtained from these plant seeds are essential in meeting global nutritional demands and are utilized for many food and other industrial purposes (Idouraine et al, 1996). Apart from their food and biochemical utilization, fats and oils are raw materials for the food, coating, paint, pharmaceutical, soap and detergent and cosmetic industries. Recently, the production of biofuel from fats and oils has been advocated. Factors or analytical parameters such as saponification value, iodine value, peroxide value, ester value and acid value have been found to be significant in assessing the various uses in which a given fat or oil can be effective. In Nigeria, the major sources of edible oils are peanut (*Arachis hypoea*) and oil palm (*Eloesis guineesis*). These oils are mainly used as cooking oils, for the production of soap, margarine and cosmetics (Ong et al, 1995). The importance of lipids in human diet cannot be over emphasized. In normal diet, about 20-25% of the caloric intakes consist of fats and oils. These substances are the most concentrated form of energy in human diet, when metabolized, fats produce about 9.5 kcal/g (Okaka *et al*., 2002). In view of the economic situation in the country and high level of oil consumption among the populace, it is essential to source for inexpensive and good quality seeds like *canarium* and other oil bearing wild plant seeds Ayoade, 2015. *Canerium* seed contained natural flavours, high fat content, pigments, moisture, nutritionally valuable minerals, (Ayoade, 2015) vitamins and naturally occurring antioxidants Ayoade, *et al* (2015), the oil also contain dirt's and unwanted impurities and compounds not suitable for consumption (Kordylas, 1991). This research is therefore aimed at purification of canarium oil through refining processes to enhance its chemical composition.

2. MATERIALS AND METHODS

2.1 Sample and sample preparation

The matured African canarium (*Canarium schweinfurthii)* seeds were purchased directly from a farmer in Pankshin Local Government in Jos, Plateau State, Nigeria. The seeds were brought to Akure authentication was done at the Department of Crop and Pest Management of The Federal University of Technology, Akure Ondo State, Nigeria. The seeds were screened in the Laboratory by hand-picking to remove the bad ones and soaked in warm water at 65^oC for about 20 minutes to soften the seed coat for easy removal. Seed flesh was then removed and ground using Marlex Excella mixer / grinding machine. The ground sample was extracted using soxhlet apparatus and n-hexane as solvent to obtain oil (crude) which was later refined and subsequently analyzed.

2.2 Refining process: The degumming, neutralization, washing, bleaching and deodorization methods described by

Ihekoronye and Ngoddy (1985) were adopted in refining the crude oil.

2.3 Physicochemical analysis

Physical properties: Colour of the oils was examined using Lovinbond tinctometer. Refractive index was measured using Abbe refractometer as described by Kirk and Sawyer (1991). Specific gravity of the oils were measured using specific gravity bottle, other properties such as melting, freezing, flash, smoke and fire points were determined using (ASTM, 1984; Morris, 1999).

Chemical properties: Saponification value, iodine value, soap content, acid value, free fatty acid and peroxide value was determined using Pearson (1991) method.

2.4 Fatty acid analysis

The oil from samples was converted to fatty acid methyl esters (FAME) through transmethylation using sodium hydroxide and methanol and analysed using method described by Akintayo, *et al* (2004).

2.5 Statistical analysis

The results of physicochemical properties of the oils were expressed as mean ± Standard Deviation (SD) of three replicates. Data obtained were statistically analysed using one way Analysis of Variance (ANOVA), a tool in Statistical Packages for Social Sciences (SPSS 14.0). The level of significance was set at $P < 0.05$. Means were separated with Duncan Multiple Range Test (DMRT).

3. RESULTS AND DISCUSSION

Table 1: Physicochemical properties of crude and refined oils of Canerium fruit

Physicochemical	Crude oil	Refined oil
Colour (Lovibond unit)	11.2 units (Dark green)	4.3 units (Greenish yellow)
Specific gravity @ 25ºC	0.9516 ± 0.13^a	0.8621 ± 0.07^b
Refractive index @ 35ºC	1.4012 ± 0.02^a	1.3034 ± 0.01^b
Viscosity (pal/.s) @ 25ºC	68.04 ± 1.01^a	56.28 ± 0.03^b
Moisture / volatile matter %	ND	ND
Acid value (mgKOH/g)	1.14 ± 0.03^a	0.64 ± 0.01^b
Free fatty acid (as oleic acid)	0.57 ± 0.01^a	0.32 ± 0.00^b
Peroxide value (meq/kg)	1.08 ± 0.01^a	0.71 ± 0.01^b
Iodine value (mg iodine/g)	96.51 ± 1.02^b	117.29 ± 0.84^a
Saponification value (mg/kg)	148.3 ± 1.13^a	126.8 ± 1.05^b
Unsaponifiable matter (%)	1.73 ± 0.01^a	1.21 ± 0.01^b
Soap content (ppm)	212.5 ± 2.01^b	128.63 ± 1.01^a
Freezing point ºC	-7.5 ± 0.15^a	-13.0 ± 0.11^b
Melting point ºC	43 ± 0.10^a	39 ± 0.05^b
Smoke point ºC	187 ± 2.17^b	203 ± 2.03^a
Flash point ºC	283 ± 3.14^b	317 ± 2.08^a
Fire point ºC	345 ± 3.01^b	358 ± 4.12^a

Mean ± standard deviation of triplicate determinations
Mean values followed by the same superscript within the rows are not significantly different at $p<0.05$

Physicochemical properties of crude and refined oils

The results of physicochemical properties of crude and refined *canerium* seed oils are presented in table 1. There was significant difference ($p<0.05$) in all the parameters analysed except volatile matter that was not detected. The colour of the oil samples improved from crude (dark green) to (greenish yellow). The improvement in colour from dark green to greenish yellow could be as a result of phosphoric acid, caustic soda and bleaching earth used for degumming, neutralisation and bleaching of the oil which might have removed the red pigment and some other impurities during the processing (Gibb *et al*, 2004). The colour of crude and refined oil samples were lower than values reported for crude and bleached sunflower oil by Oshodi and Abitogun (2010). The specific gravity (25ºC) of crude oil sample was higher than values reported for crude adenopus benth seed oil by Akintayo and Bayer (2002), and cashew nut oil by Amoo, (2005). The refractive index of crude oil was higher than that of refined oil, the value obtained for crude oil in this study was lower than values reported for crude adenopus benth seed oil by Akintayo and Bayer (2002), groundnut oil by Atasie, *et al*, (2009) and cashew nut oil by Amoo, (2005). The viscosity of crude oil was higher than that of refined oil, while moisture content was not detected in both crude and refined. These indicate that the oils are liquid at room temperature and may have good shelf life. The amount of acid value (mgKOH/g) and free fatty acid obtained in this study for crude and refined oil samples are lower than 1.7 and 0.96 reported by Amoo, (2005) for cashew nut oil, 5.99 and 3.01 reported for groundnut by Atasie, *et al*, (2009) 3.51% reported for crude fluted pumpkin by Christian (2006) and 2.85 % reported by Dawodu (2009). This indicates that refine process has significantly ($p<0.05$) reduced the acid value and free fatty acid contents of refined oil. Acid value of the oil suitable for edible purposes should not exceed 4 mg KOH/g (Pearson 1991), likewise the presence of excess free fatty acid and other fatty materials in oil bring about the offensive odour and taste in the oil on long storage Kirk and Sawyer (1991). Peroxide value is frequently used to measure the progress of oxidation in oil. Nielsen (2002) described the peroxide value as a measure of degree of lipid oxidation in fats and oils but not their stability. Therefore high peroxide value is an indication of high oxidative rancidity. The peroxide values obtained for canerium seed oil reduced from 1.08 of crude to 0.71meq/kg for refined oil sample which indicates that refining process has significantly ($p<0.05$) reduced the peroxide value. However, the peroxide values of both oil samples were below the maximum acceptable limit of 10meq peroxide/kg set by the Codex Alimentarius Commission for edible oils (CODEX, 2005; Abayeh *et al*, 1998). Low peroxide value of the oil samples indicates its high resistance to peroxidation and low rate of spoilage (Nielsen, 2002). Iodine value is a measure of the extent of unsaturation of fatty acid present in fat and oil Nielsen (2002). The higher the iodine value of particular oil, the higher the degree of unsaturation of the oil. The iodine value (mg iodine/g) obtained for canerium seed oil has significantly increased from crude to refined (96.51 and 117.29), this was an indication that the degree of unsaturation increases progressively as a result of refining which reduced the level of impurities in crude oil thereby increased its iodine value. Saponification value of crude and refined oil samples showed that there was significant difference ($p<0.05$) in degree of saponification from crude to refined oil. This decrease generally could be due to the neutralization of fatty acids which may have resulted from hydrolysis of the oil sample. According to Kirk and Sawyer (1991), the number of milligrams of potassium hydroxide (KOH) used to neutralize the fatty acids determine the degree of hydrolysis of the oil sample. The saponification values obtained for both oil are very low compared to groundnut oil (188-196 mgKOH/kg), corn oil (187-196 mgKOH/kg), palm oil (196-205 mgKOH/kg) (Cocks and Van Rede, 1966), cashew oil (243.2 mg/KOH/kg) (Amoo, 2005). The unsaponifiable matter of the crude canarium seed oil was 1.73% and that of refined oil has reduced to 1.21%. This value is low especially in the refined oil, which indicates that the oil samples are pure because most fats and oils of normal purity contain less than 2% of unsaponifiable matter (Pearson 1991). The soap content for both crude and refined oil shows a significant decrease in values as 212.50ppm for crude and 128.63ppm after refining. This decrease could be due to removal of fatty materials containing traces of soap in the refining process and could also be due to action of sulphuric acid contained during refining. The results of freezing and melting point of the oil samples indicates that the crude oil freeze at -7.5ºC and melt at 43.0ºC while the refined oil freeze at -13.0ºC and melt at 39.0ºC. There was significant ($p<0.05$) decreased in the values from crude to refined oil which could be as a result of removal of impurities. The values of smoke points, flash points and fire points increased significantly from crude to refined oil samples. The progressive increase in the values of smoke, flash and fire points of the oil samples from crude to refined indicates that the volatile organic material in the oil and the residual extraction solvents had been removed to infinitesimal level during the refining process (Nielson 2002).

Also, the high smoke, flash and fire points of the oil samples in conjunction with their low free fatty acid values make the oil to be suitable for stir-fry cooking (Samah, 2001), and is an indication of good combustion characteristics, therefore could be used as fuel or biofuel (bio diesel) production.

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Table 2: Fatty Acid Composition (%) of Crude and Refined Canerium Seed Oils

Fatty Methyl ester	Fatty acids (Saturated)	Carbon number	Crude oil (%)	Refined oil (%)
Methyl myristate	Myristic	14:0	2.963	2.612
Methyl stearate	Stearic	18:0	11.481	10.765
Methyl palmitate	Palmitic	16:0	0.574	0.358
Methyl caproate	Capric	10:0	0.024	0.013
	Total		**15.042**	**13.748**
	Mono unsaturated			
Methyl oleate	Oleic	18:1	31.621	35.386
Methyl palmitoleate	Palmitoleic	16:1	0.053	0.142
Methyl erucenoate	Erucic	22:1	1.017	1.084
	Total		**32.691**	**36.612**
	Poly unsaturated			
Methyl linoleate	Linoleic	18:2	23.724	28.672
Methyl linolenate	Linolenic	18:3	0.638	1.086
	Total		**24.362**	**29.758**
Total fatty acids detected			72.095	80.118
Total saturated fatty acids			15.042	13.748
Total unsaturated fatty acids			57.053	66.370
Total undetected fatty acids			27.905	19.882

Fatty acid Composition

Table 2 present the result of fatty acid composition of crude and refined canerium seed oils. The table showed that the saturated fatty acids detected in both oil were myristic, stearic, palmitic and capric acids. The stearic had the highest values among the saturated group for both crude and refined oils. The value of myristic acid obtained for crude and refined oil were significant compared with the values of palmitic and capric acid content that were found in traces level. There was progressive increase in all fatty acids detected from crude to refined oil which could be as a result of impurities present in crude oil sample. However, as the oil was being processed, it becomes more purified and this invariably increased the level of fatty acid content of the oil. The monounsaturated fatty acids detected were oleic, palmitoleic and erudic acids. Oleic acid has the highest percentage value among monounsaturated for both crude and refined oil. The values of oleic acid obtained for both oil are higher than 23.87% reported for crude oil of *Hura crepitans* by (Abdulkadir *et al*, 2013), 30.7% reported for *Anarcadium occidentale* by Aremu *et al*, (2007) and 11.7% reported by Akintayo and Bayer (2002), also higher than most legume seed oils reported by Adeyeye *et al*, (1999), Oshodi *et al*, (1993), Paul and Southgate (1985) and Ihekoronye and Ngoddy (1985), but lower than 41.11% reported for ground nut by Atasie, *et al*, (2009). The polyunsaturated fatty acids detected in both crude and refined oils of canarium fruit are linoleic and linolenic acids. The linoleic value for both crude and refined oils in this study are lower than 58.77% reported for crude adenopus benth seed oil by Oshodi (1996), 61.3% reported by Akintayo and Bayer (2002) for the same sample, and 59.18% reported for processed sunflower oil by Abitogun and Oshodi (2010). The high content of linoleic acid in both oils is an indication that the oil is of high nutritional value for linoleic acid being an essential acid with cholesterol-lowering activity (Messink and Katan, 1992; Akintayo and Bayer, 2002). However, the percentage of linolenic acid was detected in trace level with significant increased from crude to refined oil. The sum of saturated fatty acids in crude oil was higher than that of refined oil monounsaturated and polyunsaturated fatty acid levels were higher in refined oil than the crude oil. The total sum of fatty acids detected in crude oil is lower than that of refined oil, while total undetected fatty acid is higher in crude oil than refined one. It was generally observed that the percentage of both saturated and unsaturated fatty acids in refined oil was far higher than that of crude oil. This reveals that canerium seed oil is more of liquid (oil) than solid (fat) at ordinary temperature, hence it cannot easily congeal and this also confirms its edibility. Moreover, linoleic acid as reported by Gunstone and Norris (1983) usually cures Essential Fatty Acid (EFA) deficiency as it can be neutralized to the required C_{20} and C_{22} polyene acids. Essential Fatty Acid deficiency in human results in abnormal skin conditions such as scaliness and dermatitis, increased water loss, reduced regeneration of tissue and increase susceptibility to infection (Gunstone and Norris, 1983). Therefore, with high percentage of linoleic acid in canerium oil, it could be employed to cure essential fatty acid deficiency. Keys *et al*, (1979) and Garrow *et al*, (2004) reported that plasma cholesterol was raised by saturated fatty acids (SFA) and lowered by polyunsaturated fatty acids (PUFA). Therefore, as the processing improved the quality of oils especially with increase in unsaturated fatty acids, it is clear that the cholesterol of processed oil could be very low and this will make it very useful for foods preparation to reduce the incidence of heart attack (arteroscleroses) cause by high intake of cholesterol.

4. CONCLUSION

The results of physicochemical properties of crude and refined oils revealed that there was significant improvement in colour, specific gravity, refractive index and viscosity of the refined oil than that of crude which could be as result of removal of impurity by refining process. There was reduction in acid value, free fatty acid, peroxide value, saponification value, unsaponifiable matter and soap content of the refined oil, whereas the iodine value, melting, smoke, flash and fire points were significantly increased in refined oil compared to the crude oil thereby making the oil consumable in refined form. Fatty acid composition of the crude and refined oil showed the presence of saturated fatty acid at low concentration and high amount of unsaturated fatty acid especially in refined oil sample was established which makes it very useful for foods preparation to reduce the incidence of heart attack (arteroscleroses) cause by high intake of cholesterol.

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