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Full Length Research Paper

Fatty acids, metal composition and physico-chemical parameters of Igbemo Ekiti rice bran oil

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Rice bran was digested for metal analysis while the oil extracted from the bran was analysed for metal and fatty acid profile. Using cold and hot extraction methods, the oil contains high levels of unsaturated fatty acid (oleic acid: 52.10 and 34.8%), (linoleic acid: 22.1 and 27.1%) for the cold and hot extractions, respectively. Major saturated fatty acids present include palmitic acid (16.2, 14.9%) and myristic acid (ND, 1.9). The metal composition of the crude rice bran appeared higher but not statistically significant at 95% confidence interval compared with that of the rice bran oil. Cu was 36 times > CODEX range of 0.1- 0.4 ppm in the oil and the concentration of Fe in the oil was 61.28 ppm. The peroxide value (31 meqO_2/kg) and the Iodine value (72 g I_2/ 100 g oil), were found while the saponification value (156 mgKOH/g) and the refractive index value (1.39) obtained for the rice bran oil are within the range reported for the oil in literature. The high unsaturated and essential fatty acids in the oil implies that it has potential for cooking and industrial use if refined to reduce the Fe and Cu overload, and could be an alternative to palm oil.

Key words: Rice bran, rice bran oil, fatty acids, heavy metals, physico-chemical parameters.

INTRODUCTION

Nigeria has over 150 million people (Ottong, 2013) and estimated to be 170,123,740 as at July 2012 (WFB, 2013), which are particularly used to palm oil, ground nut oil and soya beans oil as edible oil. With the growing population, there is need to look for alternative edible oil that will reduce problems such as atherosclerosis (also known as arteriosclerotic vascular disease or ASVD) caused by saturated fats. In identifying new source of edible oil, there is need to carry out the physicochemical parameters of the oil so as to determine its edibility in terms of metal composition, taste, colour and fatty acid composition.

One method used for discovering adulterations is determining the composition of fatty acids on the basis of chromatographic analysis of their methyl esters (Casas et al., 2009). The major components of lipids are fatty acids and their physical, chemical, and physiological properties depend largely on its fatty acid composition. The quality and freshness of vegetable oil is determine by the fatty acid constituents, this is because long chain organic acids are not very volatile compounds (Ken'ichi and Yumeto, 2010; Justyna and Waldemar, 2011).

Rice bran is the main source of rice oil. The majority of available bran continues to be used for animal feeds without the oil extracted. The food industry uses minor quantities of stabilized rice bran as a source of dietary fibre, protein, and desirable oil; however, less than ten percent of this valuable oil is used for edible oil production. The limitation to the edibility is as a result of the presence of lipase enzyme, after rice milling it acts as a catalyst, the triglyceride of oil is quickly hydrolyzed into glycerol and free fatty acids (Pourali et al., 2009).

More recent efforts have emphasized the nutritional benefits of rice bran oil with low free fatty acid content and are being extracted with hexane from extrusion stabilized bran. Non-stabilized bran, although having a high free fatty acid, can also be used for production of oil. With non-stabilized bran, the extraction is similar to that of stabilized fine powder (Barber and Benedito de Barber, 1980; Frank, 2005). The major fatty acids in the rice bran oil are palmitic and linoleic acids along with oleic acid, capable of treating cardiovascular disease (Cicero and

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Derosa, 2005; Frank, 2005). It is rich in vitamins and minerals, including vitamin E, thiamine, niacin, aluminium, calcium, chlorine, iron, magnesium, manganese, phosphorus, potassium, silicon, sodium, zinc and antioxidant (Hu et al., 1996; Xu et al., 2006; Pourali et al., 2009).

The determination of metals in vegetable oils and fats has been given a considerable attention by researchers in the past and in recent times because metal causes deleterious effects on the quality and stability of the oils and fats. Metals such as copper and iron have been known for oxidative activities in fats and oil at low concentration of 0.005 and 0.03 ppm, respectively (Farooq et al., 2004; Black, 1975; Marfec and Bulinski, 1997).

Several methods for this analysis, including atomic absorption spectrophotometry (AAS) have been published in the literature (Anzan and Gonzalez, 2000; Elson et al., 1981; Flider et al., 1981; Hammond et al., 1999; McGinley, 1991; Persmers et al., 1971; Sleeters, 1985). A number of physical and chemical parameters have been established for the purpose of assessment of quality and purity as well as for identification of oils. These constants include; saponification, acid, peroxide, Iodine and ester values as well as percentage unsaponifiable matter, melting/solidification temperature, refractive index, specific gravity, smoke point and total phenol.

Saponification value is the number of milligram of potassium hydroxide required to neutralize the fatty acids resulting from the complete hydrolysis of 1 g of the fat or oil sample. Since the potassium hydroxide neutralizes the free fatty acid present in the original oil as well as those obtained by the hydrolysis of the glycerides, saponification value measured the total acids. The acid value determined the amount of free fatty acids present in most oils while the Iodine value gives an indication of the proportion of unsaturated acids in the oil or fat, that is, it is a measure of the degree of unsaturation of the fatty acids in the oil or fat. The refractive index shows the physical attractiveness of pure oil. The index of each fat falls within a narrow range and can be used as characteristic of fat in checking purity or searching for components of a mixture (Olaniyi and Ogungbamila, 1991; Ramachandran, 2001; Akubugwo and Ugbogu, 2007).

Rice production and consumption is common in Asian countries and the production of rice bran oil commonly called healthy oil which is believed to reduce body cholesterol is often in use (Economic Research Services, USDA, 2004). In Africa countries including Nigeria, rice production is a common practise. Igbemo rice (brown rice) is grown and milled locally in the South western Nigeria. Nigerians prefer the local rice because of its agreeable taste and smell (Longtau, 2000). The rice bran is used by small scale industries for animal feeds. There is no available data or information on edible oil production from rice bran in this area, although, the area is well known for rice production in the South west Nigeria.

Thus, this study aimed at characterizing the fatty acid composition of the Igbemo rice bran oil and determining its metal composition and its physicochemical parameters, thus, verifies its suitability for consumption, and providing data base for further studies on its usefulness.

MATERIALS AND METHODS

The rice was harvested in middle of July 2011, soaked in water for about three days, then parboil until the paddy rice started splitting, drained, sun dried, and milled to separate the bran from the grains. The rice bran was obtained by milling rice grain with a local grinding machine, followed by sieving to separate grain from bran and the bran (not stabilized) was stored in a cool and dry place. Palm oil and soybean oil were obtained at the local market in Ile-Ife for comparison of the metal analysis of the oil.

Reagents and glassware

Sulphuric acid, nitric acid, carbon tetrachloride and hydrogen peroxide were analytical reagent grade from E. Merck. All glassware, were first washed with liquid soap, rinsed and soaked in a mixture of distilled water and 5% HNO_3 for 24 h to remove other impurities left, they were drained after washing. Multi elemental standard solutions were prepared using the dilution of certified standard solutions (1000 ppm, Fluka Kamica) of corresponding metal ions analysed.

Extraction of rice bran oil

The conventional techniques of extraction of rice bran oil were employed using soxhlet extraction (hot process) and solid-solvent extraction (cold process).

Cold method

Rice bran extract was prepared according to a method of Choi et al. (2007). 1.5 kg of dried rice bran was extracted thrice with 8, 5 and 5 L of 80% aqueous methanol at room temperature for 48 h and filtered through Whatman No. 2 filter paper and evaporated under vacuum using a rotary evaporator (Heidolph, Germany) to an oily semi-solid. The residual crude methanolic rice bran extract was weighed (65.4 g) corresponding to 4.36% yield.

Hot method

20 g of the powdered rice bran samples were packed into a thimble, and extracted thrice with 100 ml each n-hexane by reflux using soxhlet extractor for 18 h. The respective n-hexane extracts were then combined and concentrated to dryness under vacuum on the rotary evaporator (Heidolph model, Germany). The n-hexane brown oil extracts obtained were weighed and stored in the refrigerator until it is required for further analysis.

The solvent partitioning of crude rice bran extract was carried out with n-Hexane. The semi-solid crude rice bran extract was suspended in distilled water and separately partitioned with 700 ml n-Hexane three times. The combined organic layers of each n-Hexane fractions were concentrated in vacuo at 40°C to give (the n-Hexane fraction) which is a golden brown oil of about 45 ml.

Derivatization of the rice bran oil

15 mg of the oil sample was weighed into a test-tube and 2.0 ml 0.5 M KOH added. The solution was heated in a water bath maintained at about 85°C for 10 min. The resulting solution was then neutralized with 0.7 M HCl after which 3.0 mL of BF_3-CH_3OH solution was added. The resulting solution was heated further for about 10 min in water bath at 85°C and the methylated oil was then extracted with petroleum ether (40 to 60°C). The fatty acid methyl ester was separated by a Buck model 861°C gas chromatograph with RESTEK 100 M MXT-1 (100 m, 0.25 mm ID, 0.2 µm) columns (Ladoke Akintola University, Ogbomoso). Helium was the carrier gas at a flow rate of 65 Psi and a syringe injection). The temperature was programmed from 60 at 10°C min^{-1}, then 180°C at 4°C min^{-1} and finally 235°C. The total run time was 27.7 min. Detection was by flame ionization detector (FID) at 220°C. Identification and quantification of the methyl esters was made by comparison of retention times with standard fatty acid methyl esters.

Digestion of rice bran and rice bran oil for mineral analysis

The samples (Rice bran and rice bran oil) were digested separately for mineral analysis by the wet digestion method. 0.5 g of the sample was weighed and transferred into 75 mL micro digestion tubes. 4 ml concentrated H_2SO_4 and 2 ml H_2O_2 were added carefully. The tubes were heated in a block digester (preheated to 270°C) for 30 min at International Institute of Tropical Agriculture (IITA) Ibadan; they were then taken out and allowed to cool. Another portion (2 mL) of H_2O_2 was added and heated continuously until digestion is complete (appearance of clear solution indicated complete digestion). The mineral content was determined using a Buck Model 205 Atomic Absorption Spectrophotometer at the IITA, Ibadan after which the equipment had been calibrated using 100 mg/L of the standard solution of each element to be determined. The r^2 was found to be 0.99 and more for each element (Table 2), with a good calibration curve.

Saponification value (S. V.)

Oil sample (2.0 g) was accurately weighed into a conical flask and 25 ml of 0.5 N alcoholic KOH were added. A blank was also prepared by placing 25 ml of alcoholic KOH in a similar flask. Reflux condensers were fitted to both flasks and the contents were heated in a water bath for one hour, swirling the flask from time to time. The flasks were then allowed to cool a little and the condensers washed down with a little distilled water. The excess KOH was titrated with 0.46 M HCl acid using phenolphthalein indicator (AOAC method, 1990).

The saponification value was calculated using the following equation:

$$\text{S. V.} = \frac{(b - a) \times F \times 28.05}{\text{Weight of sample}}$$

Where b = titre value of blank (ml), a = titre value of sample (ml), F = factor of 0.46 M HCl = 1 (in this case) and 28.05 = mg of KOH equivalent to 1 ml of 0.46 M HCl.

Acid value (A. V.)

Ethanol was boiled on a water bath for a few minutes to remove dissolved gases, and neutralized by adding a few drops of phenolphthalein and about 10 ml 0.1M potassium hydroxide (KOH) until a pale pink colour was obtained. Oil sample (6.0 g) was weighed into a conical flask and 50 ml of hot previously neutralized alcohol was added. The mixture was later boiled on a water bath. The hot mixture was then titrated with 0.1N potassium hydroxide (KOH) solution until the pink colour (stable for few minutes) returned (AOAC method, 1990).

The acid value (A. V.) was calculated from the following expressions:

$$\text{A. V.} = \frac{\text{Titre value (ml)} \times N \times 56.1}{\text{Weight of sample}}$$

Where N = normality of KOH = 0.1M (in this case), 282 = molar mass of oleic acid and 56.1 = molar mass of KOH.

Iodine value (I. V.)

Oil sample (0.250 g) was weighed into a quick-fit conical flask and then dissolved with 10 mL $CHCl_3$ and 25 ml Hanus reagent. The flask and its content were placed in the dark for about 30 min with occasional shaking. 10 ml of 15% KI solution was later added with thorough shaking and the solution on the side of the flask and the stopper was washed down with 100 ml of distilled water. 25 ml of this solution was then titrated with standard 0.1N sodium thiosulphate solution, added gradually with constant shaking until the yellow solution turned almost colourless. Two drops of freshly prepared starch indicator was added and titration continued in drops until the blue black colour entirely disappeared. Blank determinations were conducted (AOAC method, 1990).
The Iodine value was calculated using:

$$\text{I. V.} = \frac{(B - S) \times N \times 126.9}{\text{Weight of sample (in g)}}$$

Where, B = Blank titre value (ml), S = Sample titre value (ml) and Normality of $Na_2S_2O_3$ = 0.1N.

Peroxide value (P. V.)

This was done by the AOAC method (1990). Oil sample (5.0 g) was accurately weighed into a conical flask, and dissolved in solvent mixture containing 12 ml chloroform and 18 ml glacial acetic acid. To the solution 0.5 ml of a saturated aqueous potassium iodide solution was added. The flask was stoppered and allowed to stand for 1 min. 30 ml of water was added and the solution was titrated with 0.1 M sodium thiosulphate solution until the yellow colour had almost gone. About 0.5 ml of starch solution was introduced and titration continued with the reagent added slowly until the blue black colour disappeared. During the titration, the flask was continuously and vigorously shaken to transfer the liberated Iodine from the chloroform layer to the aqueous layer. A blank titration was also performed, and the peroxide value was obtained from the formula (Olaniyi and Ogungbamila, 1991):

$$\text{P. V.} = \frac{F \times (A - B) \times 10}{\text{Weight of oil (in g)}}$$

Table 1. Fatty acid composition of the Cold and Hot extracts of the rice bran fixed oils.

Fatty acids carbon chain	Common name	Systematic name	Relative % abundance	
			Cold	Hot
C14:0	Myristic	Tetradecanoic	ND	1.9
C16:0	Palmitic	Hexadecanoic	16.2	14.9
C17:1	Margaric(daturic)	*cis*-9-heptadecenoic acid	ND	1.1
C18:0	Stearic	Octadecanoic	1.5	9.0
C18:1	Oleic	Cis-9-octadecanoic	52.1	34.8
C18:2	Linoleic	Cis,Cis-9,12-octadecadienoic	22.1	27.1
C18:3	α-Linoleic	Cis,Cis-9,12,15-octadecatrienoic	1.5	2.8
C20:3	Dihomo-γ-linolenic	8,11,14-eicosatrienoic	2.0	1.7
C20:4	Arachidonic	5,8,11,14- eicosatetraenoic	1.0	1.9
C21:0	Heneicosylic	Heneicosanoic	3.0	3.4
C24:1	Nervonic	Cis-15-tetracosenvic	0.8	1.6

ND- Not Detected.

Where F = Factor of 0.1N $Na_2S_2O_3$, A = Sample titre value and B = Blank titre value.

Refractive index (μ)

The refractive index of the rice bran oil at room temperature was determined using Carl Zeiss 110849, Made in West Germany. The oil drop was placed on the slide and directed towards a source of light. It was then observed through the lens after adjustment had been made to give a semi- circle on the glass prism in the refractometer. The reading was then taken.

Statistical analysis

Data were analysed using Statistical Package for the Social Sciences (SPSS, version 16.0, Inc., Chicago, USA). Statistically significant differences between groups were compared using analysis of independent t-test at probability level of 95%. The data were displayed as mean ± standard deviation.

RESULTS AND DISCUSSION

The fatty acid profile obtained for the rice bran oil extract using both the cold and the hot extraction methods are presented in Table 1. The oil is dominated by the high percentage of polyunsaturated fatty acids (PUFA) than its saturated counterparts. While the hot method gave more fatty acids profiles for the oil, the cold method seems to be more favourable since it gave relatively high percentage of the important unsaturated fatty acids (e.g. oleic acid (52.1% in cold extraction and 34.8% in hot extraction) and linoleic acid (22.1% in cold and 27.1% in hot extraction), respectively. Major saturated fatty acids present include palmitic acid (16.2, 14.9%) and myristic acid (ND, 1.9) for the cold and the hot extraction, respectively. This fatty acid profile of rice bran oil put the oil at an advantage over conventional vegetable oils (e.g. palm oil) that are characterised with high percentage of saturated fatty acids, and therefore can pose health risk such as atherosclerosis, a disease associated with heart attack. For example, the proportion of palmitic acid obtained for the oil in this study is much lower compared to 44.5% in palm oil (Martos et al., 2009).

In contrast, the higher percentage of oleic acid obtained in rice bran oil (52.1%) in this work is higher than 24.7, 7.4, 7.5, 22.9, 19.0 and 11.2% reported for palm oil, castor oil, coconut oil, cotton seed oil linseed and melon seed oils, respectively (Weast, 1972-1973). The oil also contain lower percentage of α-linoleic acid ($C_{18:3}$), γ-linolenic ($C_{20:3}$) and arachidonic acid ($C_{20:4}$). Oleic, Linoleic and linolenic acids are important essential fatty acids required for growth, physiological functions and body maintenance (FAO and WHO, 1993). The abundance of unsaturated fatty acids in the oil is desirable from nutritional and health points of view as unsaturated fatty acids consumption will not lead to heart related diseases. Also, aside the use of the oil as food in frying and baking, and since oils rich in unsaturated fatty acids have been reported to reduce the risk of heart diseases associated with cholesterol (Law, 2000), therefore the potential applications of the studied rice bran oil in industrial processes such as production of paints and emulsions, plastics, drying agents, lubricants and as additives in pharmaceuticals and drug productions because of its abundance of important and essential unsaturated fatty acids cannot be overemphasised.

The results of the calibration (Table 2) showed correlation coefficient (r^2) not less than 0.99 in agreement with (Miller and Miller, 2000) that a good calibration should not be less than 0.99 for a good working condition of equipment for analysis. The metal concentration of the rice bran is higher in value than that of rice bran oil (Table 3). This is because the oil was a component extracted from the bran. These metals were originally present in the

Table 2. Calibration curve for the metals.

Element	Calibration curve (r^2) value
Ca	0.99990
Mg	0.99990
K	0.99996
Na	0.99997
Zn	1.00000
Fe	0.99995
Cu	0.99999
Pb	0.99980
Cr	0.99995
Cd	1.00000
Ni	1.00000
B	0.99995
As	0.99995

Table 3. Comparison of the mineral composition of rice bran and crude rice bran oil.

Element	Rice bran	Rice bran oil
Ca (%)	2.26 ± 0.01	1.26 ± 0.01
Mg (%)	0.880± 0.065	0.467 ± 0.007
K (%)	0.23 ± 0.08	0.04 ± 0.04
Na (mg/kg)	36.131 ± 0.003	31.080 ± 0.001
Fe (mg/kg)	54.13 ± 0.00	61.28 ± 0.00
Zn (mg/kg)	28.35 1± 0.005	8.271± 0.003
Cu (mg/kg)	1.566 ± 0.003	0.724 ± 0.038
Mn (mg/kg)	71.12 ± 0.00	28.52 ± 0.00
Pb (mg/kg)	0.05± 0.01	0.01 ± 0.01
As (mg/kg)	0.01 ± 0.00	0.01 ± 0.05
Cr (mg/kg)	0.01 ± 0.00	0.01 ± 0.00
Se (mg/kg)	0.02 ± 0.00	0.01 ± 0.00
Cd (mg/kg)	0.01 ± 0.00	0.01 ± 0.00
Ni (mg/kg)	0.13 ± 0.00	0.10 ± 0.01
B (mg/kg)	2.18 ± 0.06	1.99 ± 0.00

rice bran while some amounts of it were extracted along with the crude rice oil during extraction processes. Concentration of Iron was particularly higher in the oil (61.28 mg/kg) than in the rice bran (54.13 mg/kg). This could be due to the presence of iron complexes or phosphatides that are readily easily extracted along with the oils during its extraction. But statistical analysis using t-test at 95% confidence level revealed that the t-calculated was 0.20 and the t-table is 2.14, meaning that there is no significant difference in the metal composition of the rice bran and the crude rice bran oil. The paired sample correlation was 0.86, supporting the above result, and also indicating that the data were in agreement and of the same source.

Retail soya oil and palm oil metal composition were compared with the crude rice bran oil and was found to be comparable (Table 4). The paired t-test carried out at probability of 0.05 depicted no significance difference in the mean metal composition of the edible palm oil and crude rice oil, t calculated was found to be 0.93 and t table 2.14, $t_{cal} < t_{tab}$. The paired correlation was 0.94. The same trend was observed in the evaluation of the t test of crude rice oil with retail soya oil $T_{cal} < t_{tab}$ with t cal = 0.38 and metal paired correlation of 0.94 showing no significant difference in the metal composition of the two oil.

However, the edibility of crude rice oil could not be ascertain without testing for other physicochemical parameters such as the peroxide value, Iodine value, saponification value, acid value and refractive index. The

Table 4. Mineral composition in rice bran oil and some selected edible oils.

Element	Palm oil	Soybean oil	Rice bran oil
Ca (%)	1.65 ± 0.01	1.12 ± 0.07	1.26 ± 0.01
Mg (%)	0.640 ± 0.016	0.451± 0.108	0.467 ± 0.007
K (%)	2.17 ± 0.05	1.95 ± 0.10	0.04 ± 0.04
Na (mg/kg)	8.668 ± 0.002	59.567 ± 0.002	31.080 ± 0.001
Fe (mg/kg)	73.23 ± 0.00	57.23 ± 0.00	61.28 ± 0.00
Zn (mg/kg)	11.928 ± 0.030	7.863± 0.090	8.271± 0.003
Cu (mg/kg)	0.931± 0.063	0.612 ± 0.014	0.724 ± 0.038
Mn (mg/kg)	33.72 ± 0.01	29.13 ± 0.00	28.52 ± 0.00
Pb (mg/kg)	0.01 ± 0.01	0.01 ± 0.00	0.01 ± 0.01
As (mg/kg)	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.05
Cr (mg/kg)	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
Se (mg/kg)	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
Cd (mg/kg)	0.00 ± 0.00	0.06 ± 0.00	0.01 ± 0.00
Ni (mg/kg)	0.12 ± 0.00	0.12 ± 0.00	0.10 ± 0.01
B (mg/kg)	3.18 ± 0.00	2.14 ± 0.00	1.99 ± 0.00

Table 5. Physicochemical parameter of Igbemo rice bran oil compared with literature value.

Physicochemical parameter	Crude rice bran	Refined rice bran	This study (Igbemo rice bran)
Refractive Index	1.46-1.47	1.46-1.47	1.39
Iodine value (gI_2/100g)	85-105	90-105	72
Saponification value (mgKOH/g)	175-195	180-195	156
Acid value (mgKOH/g)	80.0	0.5	28.0
Peroxide value ($meqO_2$/kg)	-	-	31

Source: Ramachandran (2001).

oil content of rice bran varies in each variety, and depends to an even greater extent on the processes and conditions obtained during rice milling. Rice bran has 15 to 25% of oil associated with it (Kusum et al., 2011). The percentage yield of oil in this study is 4.36%.

The peroxide value is used as an indicator of deterioration of oils. Fresh oils have peroxide values lower than 10 $meqO_2$/kg and before oil becomes rancid, its peroxide value must be between 20 and 40 $meqO_2$/kg (Akubugwo and Ugbogu, 2007). Peroxide formation is an indication that lipid oxidation is on-going, these compound react with low molecular weight metals to produce free radicals that are capable of further lipid oxidation (Kilic and Richards, 2003). The peroxide value of the crude rice bran oil was found to be 31 $meqO_2$/kg (Table 5) which was within the range of rancid oils (20 to 40 $meqO_2$/kg). This could be as a result of high concentration of Cu and Fe in the crude rice oil. Copper is the strongest pro-oxidant for oils, and for the best stability, the content of copper should be below 0.02 ppm (Farooq et al., 2004; Black, 1975; Marfec and Bulinski, 1997; Smouse, 1994). The concentration of Cu in this study is 36 times higher than what is expected in oil for best stability. High levels of Iron and Copper could be traced to the containers used in parboiling and the milling machines. According to the reports (Smouse, 1994), for the best stability of oils, the level of Iron should be below 0.1 ppm and 0.10 to 0.40 ppm was recommended for copper by Codex STAN 19 (Codex, 1981), this will enhance the stability and edibility of the oil and prolong the shelf life. The concentration of Fe in this study for crude rice oil was 61.28 ppm, and this value might explain the high peroxide value obtained for the oil probably due to oxidative process induced by the high iron content.

There could be other components present in the oil that could result in rancidity. The Iodine value for the rice bran oil in this study was found to be 72 g I_2/ 100 g oil and (Table 5) lower than 85 to 105 g I_2/ 100 g oil value for crude rice bran oil and 90 to 105 g I_2/ 100 g oil for refined rice bran oil reported by Ramachandran (2001). The progressive reduction in Iodine value usually could be attributed to lipid oxidation (Chan and Cotton, 1987). The higher the Iodine value, the higher the degree of unsaturation. When Iodine value is lower, it means that the double bond of the polyunsaturated fatty acid (PUFA)

Table 6. Standard conditions of Buck Model 205 atomic absorption spectrophotometer at the IITA, Ibadan.

Metal	Wavelength (Nm)	Slit	Detection limit (mg/L)	Linear range (mg/L)
As	193.7	0.7	0.25	25.0
B	249.7	0.7	-	450
Cd	228.9	0.7	0.01	2.00
Ca	422.7	0.7	0.05	5.00
Cr	357.9	0.7	0.04	5.00
Cu	324.8	0.7	0.005	5.00
Fe	248.3	0.2	0.05	5.00
Pb	279	0.7	0.08	20.00
Mg	285.2	0.7	0.005	1.50
Mn	279.5	0.7	0.03	2.50
Ni	233	0.2	0.05	4.00
K	766.5	0.7	0.01	3.00
Se	196.0	0.2	0.50	25.00
Na	589.0	0.2	0.005	2.00
Zn	213.9	0.7	0.005	2.50

of the oil had been attacked and oxidation of the oil had taken place. Thus, there is progressive reduction of the nutritional value of the oil. Oils rich in unsaturated fatty acids have been reported to reduce heart diseases associated with cholesterol (Law, 2000). In this case the Iodine value was 72 g I_2/ 100 g oil is suggestive of oil that have been oxidised since the rice bran was not stabilised before extraction and no preservative was added to the extracted oil. Although, Falade et al. (2008) explained that high Iodine values also have its own disadvantages; for instance, the oil will be more susceptible to oxidative deterioration thereby making them difficult to store.

Saponification value is used in checking adulteration. The saponification value was found to be 156 mgKOH/g which is less than 175 to 195 mgKOH/g reported by Ramachandran (2001) for crude rice bran oil. High saponification value of 156 mgKOH/g is indicative that the oil investigated in this work has potential for uses in the industries.

Acid values are used as an indicator for edibility or otherwise of oils and suitability for use in industries (Akubugwo and Ugbogu, 2007). Acid value for crude rice bran oil is about 80.0 and 0.5 mgKOH/g (Table 6) for refined rice bran oil (Ramachandran, 2001). The acid value for the rice bran oil was found to be 28.0 mgKOH/g which is within the range of values for crude rice bran oil and refined rice bran oil, this showed that the free fatty acid was high. Some enzymes that are present in the rice bran include α-amylase, β-amylase, ascorbic acid oxidase, catalase, cytochrome oxidase, lipase, lipoxygenase, peroxidase and many others. Particular attention should be given to lipase, lipoxygenase and peroxidase, because of their potential in reducing the quality and shelf life of rice bran. Lipase promotes the hydrolysis of the oil in the bran into glycerol and free fatty acids (FFA) thus making the rice bran oil to be unstable (Orthoefer, 1996, 2005; Pourali et al., 2009). It is well known that free fatty acids are more susceptible to lipid oxidation, leading to rancidity and production of off-odour compared to intact fatty acids in the triglycerides (FAO/WHO, 1993), thus stabilising the rice bran before extraction is needed because rice bran contains active enzymes (Barber and Benedito de Barber, 1980).

The refractive index of the rice bran oil was found to be 1.39. This value is very close to 1.46-1.47 reported by Ramachandran (2001) for crude rice bran oil. This indicates that the rice bran oil analyzed in this study is comparable in thickness to that reported by Ramachandran (2001) and most drying oils have refractive indices between 1.48 and 1.49 (Oluba et al., 2008).

There are a number of factors that influence the quality of rice bran oil. Immediate extraction and processing are considered as of prime importance, as delayed extraction can lead to problems, such as color changes and deterioration of organoleptic quality and flavours (Kusum et al., 2011).

Conclusions

Conclusively, the fatty acid profile of the crude rice bran showed that it is good for consumption if well refined because it contains high percentage of oleic and linoleic acids which could prevent heart related diseases, and therefore serve as an alternative to conventional oils such as palm oil in domestic shores. The rancid nature of the crude rice oil requires attention and stabilising the rice bran before storage for extraction will be necessary.

The crude rice bran oil in this study has the potential for both domestic and industrial uses base on some of its fatty acids profile and physico-chemical properties provided Copper and Iron overload are taken care of by thorough industrial processes.

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