



Selected Under-exploited Plant Oils in Nigeria: A Correlative Study of their Properties

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Abstract

This study examined the physicochemical properties of seven under-exploited plant oils in Nigeria, namely; *Hevea brasiliensis* seed oil (HBSO), *Prunus dulcis* seed oil (PDSO), *Azizia africana* aril cap oil (AAACO), *Jatropha curcas* seed oil (JCSO), *Sesamum indicum* seed oil (SISO), *Canarium schweinfurthii* seed oil (CSSO) and *Hura crepitans* seed oil (HCSO). Characteristics such as colour, percentage yield, specific gravity, freezing/melting point, acid value, free fatty acid, iodine value, and saponification value were investigated. The results showed that they have different colours and are liquid at room temperature. The percentage yield of the extracted oils varied from 34 to 55.39%. The specific gravities which were observed to agree with what is obtainable in most vegetable oils were in the range of 0.91 in PDSO to 0.948 in CSSO. The freezing/melting points show that CSSO (8.89 °C), AAACO (6.39 °C) and JCSO (3.18 °C) have greater amounts of saturated fatty acids than SISO (-6.21 °C), HCSO (-15.34 °C) and HBSO /PDSO (-18 °C). The acid values and free fatty acids of the oils were in the range of 2.13–17.49 mg KOH/g and 1.07–9.648%, respectively. The iodine values of HBSO, PDSO, JCSO, and SISO (104–128.9 mg iodine/100 g) and AAACO and CSSO (68–77 mg iodine/100 g) placed them in the semi-drying and non-drying class, respectively. Their saponification values (137.2 to 210 mg KOH/g oil) suggest their possible applications in the soap industry. The results generally present a deductive justification for the usage of the studied plant seed oils for some industrial and other applications.

Keywords: Plant seed oils, physicochemical properties, potential applications

Introduction

The potentials of some plant seeds in Nigeria have not been thoroughly investigated and as such, under-utilized over time. Significant effort is, therefore, required to develop the industrial potentials of undervalued agricultural plant seeds in the country. For economic viability, the oil and meal from plant seeds should also be utilized (Ajayi et al. 2006, Kamel and Kakuda 1992). To ensure the complete utilization of the

seeds and meals of these types of plant materials, more studies should be carried out to investigate their possible applications. The meals of these seeds containing plant materials can be transformed into nutrients for either feed or food, or into manure, hence serving as an essential additions to industrial products or food sources (Fernandes et al. 2017, Kamel and Kakuda 1992). Edible or non-edible oils can be extracted from the seeds of these fruit plants (Maliki et al.

2020a, Maliki et al. 2020b, Nkwor et al. 2020). These oils are used for nutritional purposes or as raw materials for the production of drying oils, soaps and detergents, lubricants, surface coatings, fatliquoring of leather in tanneries, pharmaceuticals, cosmetic and emulsifiers.

More attention is usually given to the edible oil containing seeds as opposed to the non-edible ones, without realizing that some non-edible oils in some seeds possess invaluable industrial applications that can make them more economically valuable than their edible counterparts. Currently, the need to preserve resources allocated for the importation of oils for indigenous utilizations and industrial applications proffers reinvigorated incentives in the quest for innovative sources to complement the conventional ones (Akubugwo and Ugbogu 2007). More attention has hence been directed to under-utilized local plant seeds for viable advancement and utilization.

There are several under-exploited plant oil seeds in Nigeria. These include *Hevea brasiliensis* (Willd.) Muell.-Arg. (HBSO), *Prunus dulcis* Mill. seed oil (PDSO), *Azelia africana* Sm. ex Pers aril cap oil (AAACO), *Jatropha curcas* L. seed oil (JCSO), *Sesamum indicum* L. seed oil (SISO), *Canarium schweinfurthii* Engl. seed oil (CSSO) and *Hura crepitans* L. seed oil (HCSO). The rubber tree (*Hevea brasiliensis*) is from the South American tropical tree of the spurge family (Euphorbiaceae). An almond (family Rosaceae) is comprised of two varieties, viz, *Prunus amara* (bitter almond), and *Prunus dulcis* (sweet almond). Studies have shown that almond seeds contain about 50% oil which can chiefly be extracted from sweet almonds (Fernandes et al. 2017). The almond seed oil has several characteristics including immunity-boosting, anti-hepatotoxicity and anti-inflammatory effects (Kodad and Socias 2008). It can also be used to decrease irritable bowel syndrome symptoms, the incidence of colon cancer and so on (Ahmad 2010). *Azelia africana* is a

deciduous plant extensively scattered in several countries of Africa (Nkwor and Ukoha 2020). It belongs to the family Fabaceae, sub-family Caesalpiniaceae and can customarily be located in dry and humid forests (Ozgunay et al. 2007). In Nigeria, its seeds are often used as soup thickeners. The aril cap, though discarded and without any commercial value, can be used in the extraction of oil (Nkwor and Ukoha 2020). *Jatropha curcas* is cultivated majorly in the recovery of wastelands and as a hedge around fields and gardens. *Sesamum indicum* has been grown from pre-historic times and its seed oil used as cooking oil in many continental and intercontinental dishes. *Canarium schweinfurthii*, also known as black date, is an exotic tree that is abundantly available in Sub-Sahara Africa (Kuate 2017, Nkwor et al. 2019b). In Nigeria, the oil-rich kernel seed is consumed cooked and sometimes made into a vegetable butter. The oils can be utilized as good substitutes for conventional vegetable oil (Kuate 2017). *Hura crepitans* is an evergreen perennial tropical plant belonging to the family Euphorbiaceae (Otabor et al. 2019). Its trees are generally used to give shade in front of parks, public buildings, and residential areas in Africa. The seeds contain a surprisingly high percentage of non-edible oil (Nkwor et al. 2019a). Among the studied vegetable oils, *Jatropha curcas*, *Hura crepitans* and *Hevea brasiliensis* are non-edible due to the presence of antinutrients in them. *Jatropha curcas* has been reported to have toxins such as curcin and phorbol-esters (Goel et al. 2007). The oil from *Hura crepitans* can be used as a purgative even in small amounts (Abdulkadir et al. 2013). *Hevea brasiliensis* contains cyanogenic glucoside that yields poisonous prussic acid (HCN). Previous studies have reported its applications in the production of fatliquor (Nkwor and Ukoha 2020), alkyd resin (Otabor et al. 2019), grease (Awoyale et al. 2011), biofuels (Shambhu et al. 2013), metal soaps (Umoren et al. 2013), etc.

The potentials of the above-mentioned plant seeds are not fully utilized both commercially and domestically, in Nigeria. This research therefore, was carried out to investigate their further potentials as viable sources of oil for possible industrial and other applications.

Materials and Methods

The rubber (*Hevea brasiliensis*) seeds were obtained from the Rubber Research Institute of Nigeria, Benin City, Nigeria. Almond seeds were collected from the University of Benin City, Edo State. *Afzelia africana* aril caps, *Jatropha curcas* seeds, and *Sesamum indicum* seeds were harvested from a local farm at Ikwo, *Hura crepitans* seeds were obtained from its shade plants at Fatilami park, Abakaliki, while *Canarium schweinfurthii* seeds were harvested from Onueke town both in Ebonyi State. All the collected seeds were matured, ripe and collected in air-tight containers. Apart from *Canarium schweinfurthii* and *Afzelia africana* aril cap, all the collected seeds were sun dried. Samples of the seeds were authenticated at the Herbarium Unit of the Department of Biological Sciences, Ahmadu Bello University, Zaria, Nigeria, Department of Research Operations, Rubber Research Institute of Nigeria, Benin City, Nigeria. Analytical grade phenolphthalein, sulphuric acid, sodium hydroxide, sodium chloride (brine), potassium hydroxide, hydrochloric acid, Wijs solution, carbon tetrachloride, ethanol, diethyl ether, thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), *n*-hexane and distilled water were used in this study.

Sample preparation and oil extraction

The seeds were dried, and deshelled. The aril caps were removed from the seeds. These samples were sundried to decrease the moisture content before crushing. The vegetable oils were extracted using *n*-hexane as a solvent with the aid of the Soxhlet-apparatus.

Characterization of the oil samples

Standard procedures for physicochemical properties determination were used to characterize the extracted oil samples. The characterized parameters included acid value, saponification value, iodine value, specific gravity, free fatty acid and colour (physical observation). The freezing/melting points of the oils were examined employing a differential scanning calorimeter (DSC 2 Star System (Mettler Toledo)).

Determination of free fatty acid

The free fatty acid (FFA) values of the oil samples were evaluated as follows: 0.002 kg of oil sample was transferred into a volumetric flask containing 50 ml of 95% ethanol/diethyl ether, 1/1, v/v mixture with continuous stirring. Two drops of phenolphthalein indicator were added to the oil/solvent mixture. The mixture was then titrated with potassium hydroxide solution until the colour turned to pink (British Standard Institution 1976, Otabor et al. 2019). The acid value (AV) was calculated by the formula depicted in Equation 1.

$$AV = \frac{56.1 \times N \times V}{M} \quad \text{Eq. 1}$$

Where: V = the number of mL of KOH solution used;

N = the normality of KOH solution;

M = the mass in g of the sample.

Measurement of saponification value

Saponification value was measured as previously described (Mutar and Hassan 2017). A mixture of 25 mL of 1.0 M alcoholic KOH and 0.002 kg of the oil sample contained in a 100 mL volumetric flask was allowed to react for 45 minutes through a condenser joined to the flask to complete the saponification reaction. Cooling of the flask and the condenser were adequately carried out but not to the point of the development of gel. Thereafter, the condenser was elevated to add 1 mL of phenolphthalein into the mixture. Titration with 0.5 N hydrochloric acid (HCl) was

carried out on the solution until the pink colour faded away. A blank measurement was concurrently estimated with the sample. The formula in Equation 2 was employed in the determination of the saponification value.

$$\text{Saponification value} = \frac{56.1 \times N \times (V_2 - V_1)}{W}$$

Eq. 2

Where: W = weight of the sample (g);
V1 = volume of hydrochloric acid that was utilized during the test (mL);
V2 = volume of the hydrochloric acid employed in the blank (mL);
N = normality of the hydrochloric acid used.

Determination of iodine value

Iodine value was determined as previously described (Isaac and Nsi 2013). In a conventional ascertainment, 25 mL of Wijs solution was transferred into a volumetric flask containing a mixture of carbon tetrachloride (15 mL) and oil sample (1 g) using a pipette with constant stirring. The mixture was made to stand in the dark for 30 minutes at room temperature. This was accompanied by the addition of distilled water (150 mL) and 10% potassium iodide (KI) solution (20 mL) to the mixture. The titration of the mixture with 0.1 N thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) solution was consequently carried out till the yellow colour almost disappeared. The starch indicator solution (1.5 mL) was added and the titration was continued until the blue colour faded. The measurement of the blank was carried out simultaneously. Estimation of the iodine value was carried out utilizing Equation 3.

$$\text{Iodine value} = \frac{12.69 \times N \times (V_2 - V_1)}{W}$$
 Eq. 3

Where: W = weight of the sample (g);
V1 = volume of hydrochloric acid that was employed during the test (mL);
V2 = volume of the hydrochloric acid used during the blank preparation (mL);
N = normality of the hydrochloric acid used.

Determination of acid value

The acid values of the samples were determined as detailed by a previous procedure (Hulsbosch et al. 2018). The sample (2 g) was measured into a 100 mL beaker; 5 mL ethanol was added and heated on a water bath to dissolve. The solution was titrated against 0.1 M NaOH using 3-4 drops phenolphthalein as the indicator and shaken constantly until a pink colour persisted. The acid value is a conventional expression of the percentage of free fatty acid (Eq. 4).

$$AV = \frac{A \times M \times 40}{W}$$
 Eq. 4

Where: M = the concentration of NaOH;
A = mL of 0.1M NaOH used;
W = weight in grams of the sample;
AV = Acid value.

Determination of specific gravity

The specific gravities of the oil samples were determined using the standard procedure of American Oil Chemistry Society (Cunniff et al. 1997). A washed dried 25 mL wide mouth pycnometer was weighed (W0). It was then filled with the sample and reweighed again (W1). The sample was replaced with water and weighed to give W2. The specific gravity of the sample was calculated using the following formula:

$$SG = \frac{W_1 - W_0}{W_2 - W_0}$$
 Eq. 5

Where;
SG = Specific gravity;
W1-W0 = Mass of substance;
W2-W0 = Mass of an equal volume of water.

Results and Discussions

The physicochemical properties of the investigated plant oils are presented in Table 1.

A visual examination of the extracted oils revealed brown, dark yellow, dark orange, golden yellow, golden yellow, dark green and golden yellow colourations for HBSO, PDSO, AAACO, JCSO, SISO, CSSO, and HCSO, respectively. These colours are consistent with the observations of previous

studies (Akminul Islam et al. 2013, Fernandes et al. 2017, Nkwor et al. 2019a, Nkwor et al. 2019b, Nkwor and Ukoha 2020, Otabor et al. 2019, Wei et al. 2016). The

PDSO, JCSO, SISO and HCSO all displayed a yellow colour. However, the yellowish colour displayed by the PDSO was observed to be slightly darker.

Table 1: Physiochemical properties of the oils extracted plant oils

Properties	HBSO	PDSO	AAACO	JCSO	SISO	CSSO	HCSO
Colour	brown	dark yellow	dark orange	golden yellow	golden yellow	dark green	golden yellow
Percentage yield (%)	34	54.41	55.39	49.21	54.7	51.32	52.76
Specific gravity (g/cm ³) (at 20 °C)	0.92	0.91	0.941	0.903	0.923	0.948	0.920
Freezing/melting point (°C)	-18	-18	6.39	3.18	-6.21	8.89	-15.34
Acid value (mg KOH/g)	17.49	2.48	12.99	7.54	2.13	11.36	6.17
Free fatty acid (% as oleic acid)	9.648	4.63	6.50	3.77	1.07	5.68	3.09
Iodine value (g iodine/100 g)	128.9	115.78	77	104	107	68	117
Saponification value (mg KOH/g)	137.20	189.85	185	205	192	198	210

Hevea brasiliensis seed oil = HBSO, *Prunus dulcis* seed oil = PDSO, *Azizelia africana* aril cap oil = AAACO, *Jatropha curcas* seed oil = JCSO, *Sesamum indicum* (Sesame) seed oil = SISO, *Canarium schweinfurthii* seed oil = CSSO, and *Hura crepitans* L. seed oil = HCSO

The percentage yields of the oils extracted from the various seed types varied from one seed type to the other as they gave percentage yields ranging from 34.0 to 55.39%. Rubber seed oil recorded the least yield (34%) when compared to the other studied oils. This, however, is lower than the yield of 44% obtained by Oyekunle and Omode (2008). According to the percentage yield classification, all the studied seeds can be categorized as high oil yielding seeds. Therefore, the oil yields obtained from *H. brasiliensis*, *P. dulcis*, *A. africana*, *J. curcas*, *S. indicum*, *C. schweinfurthii* and *H. crepitans* are deemed economical for industrial production of plant seed oils. The obtained yields are very commendable since the yields obtained in all the studied oils gave

percentages that were higher than the reported reasonable yield range of 26 to 42% established by Kyari (2008) for *Butyrospermum parkii*, *Lophira lanceolata*, *Sterculia setegera*, *Detarium microcarpum*, *Blighia sapida* and *Schorocarya birrea*. The oil yields of 9.71–48% reported by a previous study from some plant seeds such as palm kernel seeds, groundnut seed and pumpkin seeds were lower than most of the oil yields extracted from the seeds used in this study (Eze 2012). An important parameter that usually affects the yield of oil is the mode of extraction. It has been reported that the most reliable and feasible method for the extraction of oil from a large number of seeds is through the use of a hydraulic press (Singh and Saroj 2009).

The specific gravity, which is the weight of an oil sample relative to that of an equal volume of water, was observed to be in the range of 0.91 in PDSO–0.948 in CSSO. These specific gravity values are in agreement with what is obtainable in most vegetable oils (Onyeike and Acheru 2002). These values were lower than that of water. They correspond to the typical values observed for common seed oils. As such, they can be easily applied as water evaporation retardants particularly in dry areas where severe water deficiency is a serious problem (Oyekunle et al. 2007). Because seed oils are predisposed to more accelerated biodegradation than fossil fuels, there is no fear of any possible long-term environmental pollution. Notwithstanding, the water for which the oils may serve as retardants should not be consumed as peroxidation of the oils may confer off-odour due to the rancidity of the oils in the water with time. The short-term usage of this application includes conserving water for watering seedlings and molding blocks (Oyekunle et al. 2007).

Oxidative deterioration of oils can be stimulated by their free fatty acid contents via chemical oxidation and/or enzymatic and other physical factors like heat and light to form off-flavour component (Ajayi 2010). The acid value and free fatty acid of the oils extracted from the seeds of *H. crepitans* (6.17 mg KOH/g, 3.09% as oleic acid) and *S. indicum* (2.13 mg KOH/g, 1.07% as oleic acid) are low. These low values are indicative of the fact that they apparently could be preserved for a lengthy period without deterioration through oxidative rancidity. Previous studies have shown that for an oil to be considered for cooking, the free fatty acid content of the oils should not exceed the limits of 0.0–3.0% (Ajayi 2010, Onyeike and Acheru 2002). According to the aforementioned free fatty acid limits for cooking, the increasing order of free fatty acid values of the studied edible oils depicted in Table 1, which also corresponds to their possible usage as cooking oils is in this order:

SISO < PDSO < CSSO < AAACO. This, therefore, means that the lower the free fatty acid content of oil, the better its use as cooking oil. However, HCSO, HBSO, and JCSO cannot be used for cooking as a result of the toxins in them.

The measure of the level of unsaturation of the fatty acids in the oils is achievable through the determination of the iodine value (IV) and could be used to quantify the number of double bonds present in the oil which reveals the susceptibility of oil to oxidation. The iodine values ranged from 68 (g iodine/100 g) in CSSO to 128.9 g iodine/100 g in HBSO. The high iodine value recorded by HBSO is an indication that it has the highest percentage of unsaturated fatty acids in comparison to all the other studied oils. Conversely, CSSO had the smallest percentage of unsaturated fatty acids as recorded by its iodine value which is the least among the seven extracted oils. The iodine values indicate that apart from the AAACO and CSSO, the studied oils generally have high degrees of unsaturation. It has been reported that the double bonds in oils with high iodine values are prone to modification for industrial applications due to the reactivity of their bonds (Pathak et al. 2014). Chemical modification of vegetable oils introduces certain functionalities or chemical entities into the oil structure, thereby improving the reactivity and imparting desirable physical and chemical characteristics in them (Okieimen et al. 2005). Such modifications on the double bond include epoxidation (Okieimen et al. 2005, Lee and Song 2019), sulphonation (Nkwor and Ukoha 2020), hydroxylation (Okieimen et al. 2005), and chlorination (Jia et al. 2015)..

Drying, semi-drying, and non-drying oils are usually established based on the grams of iodine needed to saturate the double bonds of 100 g of oil (iodine value). The different classifications of oil based on their drying properties using iodine values reported by several studies have been seen to vary over

the years by different authors. For example, a study reported the following: semi-drying oils, iodine value 125–140 g iodine/100 g; drying oils, iodine value >140 g iodine/100 g; non-drying oils, iodine value < 125 g iodine/100 g (Rheineck and Austin 1968). Such established ranges of values for drying categories of oil differ slightly from recent reports. Thus, more recently, studies have reported the following: when the iodine value of oil is less than 100, it is classified as non-drying oil (Ogundiran and Ojo 2012, Singh et al. 2018). Iodine values ranging from 100 to 130 g iodine/100 g can be classified as semi-drying oils (Ogundiran and Ojo 2012); Oils that have iodine values ranging from 130 to 190 g iodine/100 g can be considered drying oils (Chia-Wei et al. 2019, Karak 2012, Singh et al. 2018). The classification reported by Ibeto et al. (2012) and Singh et al. (2018) are slightly different as they classified the iodine value of semi-drying oil and non-drying oils in the range of 110–140 g I₂/100 g and <110 g I₂/100 g, respectively. According to the established drying categories of oil, HBSO, PDSO, JCSO and SISO can be classified as semi-drying oils because their iodine values fall within the 100–140 g iodine/100 g range for semi-drying oil. However, these semi-drying oils can be made to dry into a solid film when they are treated with heat. They can be used as raw materials for binders such as epoxy esters, alkyd resins, and uralkyds. Since the AAACO and CSSO fall in the range of iodine value less than 100 (g I₂/100 g sample), they can, therefore, be classified as non-drying oils. They can be utilized as excellent hydraulic brake fluids and lubricants, skin care merchandises and sporting gear or to condition flexible materials such as leather boots (Eze 2012). Several medicinal applications of non-drying and semi-drying oils such as PDSO, SISO, CSSO and JCSO have been reported (Abdelgadir and Van Staden 2013, Ahmad 2010, Anilakumar et al. 2010, Kuete et al. 2015).

The saponification value is the amount of alkali needed to turn a fat or oil into soap. The determined values of all the extracted oils ranged from 137.20 to 210 mg KOH/g. Some of the observed values are somewhat greater than those detailed in the literature for plant seed oils (Anang et al. 2019, Milovanović and Pićurić-Jovanović 2005, Otabor et al. 2019, Zahir et al. 2017), but lower than those for coconut oil and several other oils (Atasie and Akinhanmi 2009, Ghani et al. 2018, Kamel et al. 1985). However, the saponification values of all the studied oils are in line with the accepted range of values that can be utilized in the production of soap and shampoos (Atasie and Akinhanmi 2009, Ghani et al. 2018). Because it has been established that oil with a higher value of saponification will produce a better soap with more improved properties than soap prepared from oil with lower saponification values, it means, therefore, that the suitability of the studied oils usage in soap production is in the order: HCSO > JCSO > CSSO > SISO > PDSO > AAACO > HBSO. The saponification value is also an indicator of the average molar mass of the fatty acid present in the oil. The saponification value has a direct relationship with the molar mass of the fatty acid content of the oil (Ajani et al. 2019). Apart from the HBSO which recorded a saponification value of 137.2 mg KOH/g, all the other oils showed a narrow range of 185–210 mg KOH/g, which in turn signified a relatively close range of molecular weights for all the extracted oils. The freezing/melting points of the extracted oils were observed to be in this order: CSSO (8.89 °C) > AAACO (6.39 °C) > JCSO (3.18 °C) > SISO (–6.21 °C) > HCSO (–15.34 °C) > HBSO / PDSO (–18 °C).

The observed freezing/melting points show that CSSO, AAACO, and JCSO have greater amounts of saturated fatty acids but lower proportions of unsaturated fatty acids than those of HBSO, SISO, HCSO and PDSO, as freezing/melting points have been shown to decrease with increment in the

levels of unsaturation (Saadi et al. 2011). The low freezing/melting points of the non-toxic oils may be applied in the production of easy-to-digest/soft margarine and oil creams, while the other non-toxic oils with higher freezing/melting points would be invaluable in the production of confections. It was reported that the freezing/melting point is among the key factors that should be considered when measuring the lubricating power of fats and oils (Devi and Khatkar 2016). For instance, low freezing/melting point non-toxic oils can be used to produce cookies with a higher spread as compared to cookies made with the other non-toxic oils with a higher freezing/melting point (Devi and Khatkar 2016). The suitability of the studied non-toxic oils for deep frying can also be examined from their freezing/melting points as it has been established by a previous study that oils with higher freezing/melting points are more suitable for deep frying than oils with lower freezing/melting point (Emmanuel and Peter 2018). This study shows that CSSO and AAACO have better deep-frying properties than SISO and PDSO.

Conclusion

This study has shown that the seven studied plants are excellent sources of raw oils. From their colours, acid values, free fatty acid contents, iodine values and saponification values studies, most of the oils, if refined, could be useful in emulsifier formulation, deep-frying, baking ventures and as part of pastry/bakery ingredients. The additional physicochemical characteristics of the oils as unveiled by this research show their ability to be utilized as lubricants, as raw materials for the production of detergents, lather shaving creams and fatliquor. The results generally present a deductive justification for the usage of the studied plant seed oils for industrial products and other possible applications.

Conflicts of interest/Competing interests

The authors declare no conflict of interest.

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