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EXTRACTION AND CHARACTERIZATION OF OIL FROM AFRICAN STAR APPLE (CHRYSOPHYLLUM ALBIDUM) SEEDS FOR UTILIZATION IN THE LEATHER INDUSTRY

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ABSTRACT

The leather industries in Nigeria depend largely on imported fatliquors at exorbitant rates and that has affected the leather value chain, to avert this, there is the need to look into our indigenous plants to make this product available. In this light African star apple (Chrysophyllum Albidum) seed was considered for its affordability and availability. The seed was collected and some physico-chemical parameters analysed and presented as follows: Moisture content (18.3%); Saponification value (222.05mgKOH/g); Acid value (3.8mgKOH/g); Free Fatty Acid value (2.54mgKOH/g); Peroxide value (5.5mgKOH/g); Specific gravity (0.90g/cm^3); Refractive index (1.3573); Ester value (218.25); Iodine value (28mg/100g of sample); Percentage yield of oil (13%).Some heavy metals of interest such as: Iron, lead and nickel were analysed to ascertain their concentrations in the sample using Atomic Absorption Spectrophotometer (AAS). Functional groups present were analysed using Fourier Transform Infrared Spectroscopy (FTIR) as follows: -OH; Alkyl group –C-H; -CHO from aldehyde and amide –N-H, alkanes –C=C stretch. Furthermore GC-MS was employed to validate the degree of saturation and unsaturation of fatty acids and alcohols. The GC-MS key results include: Palmitic acid (21.22%), stearic acid (8.08%),tridecanoic (9.94%),tridecenal (2.25%),docosanoic (0.92%); oleic (12%), linoleic (11.91%) and fatty alcohol (palmitoleic 40.40%). Palmitic and stearic acid play important role in the production of fatliquor though surface active agents are needed to lower its viscosity.ChrysophyllumAlbidum can be used in combination with groundnut or castor seed oils because of its low yield (13%) for fatliquor production in the leather industry.

Keywords*: Chrysophyllum Albidum, oil, Characterization, utilization, fatliquor.*

Introduction

African Star apple (*chrysophyllum albidum*) is an indigenous tropical fruit, edible fruit which is classified as a plant and belong to the family Sapotaceae and it is distributed throughout the southern part of Nigerian (Oboh *et al., 2009*).In the southwestern Nigeria, the fruit is called "*Agbalumo*" and popularly referred to as "*Udara*" in southeastern Nigeria. This fruit is distributed in the low land rain forest zone and mostly found in the villages. The fruits generally are not only consumed fresh but also used to produce jam jellies, syrup and several types of soft drinks. It is also used for medical purpose due to properties of stalk and fruit (Isalam, 2002). The fruit pulp is rich in vitamin C, iron and an excellent source of raw material for industries, Tannins, flavonoids, trepenoids, proteins, carbohydrates and resins are the phytochemicals that led to the isolation of eleagnine, tetrahydro-2-methyiharinan and skatole (Ehiagbonare *et al*., 2008). Elagnine was found to be the main compound responsible for its antimicrobial activity. *Chrysophyllum albidum* may not cause any adverse effect on the biochemical and hematological indices of toxicity (Vursavas *et al*., 2005). The oil extracted from this plant is intended for use as lubricant in the leather industry.Leather is one of the oldest man-made materials and as such has been made from natural materials with sustainable processes for thousands of years. But industrialisation also changed the manufacturing of leather. Although still starting from a natural raw material, modern processes of leather making often involve a significant consumption of energy and non-renewable resources. Fat-liquors are often based on natural materials or chemically modified natural materials to a significant extent. Most often, these materials are formulated together with other components of petrochemical origin. The methods for chemical modification include: oxidation/sulfitation, sulfatation, sulfonation, sulfochlorination, sulfoxidation, esterification, saponification, and alkoxylation (Leonardus et al., 2012). The choice of fat-liquors used in a wet end recipe has a great influence on the haptic properties of the final leather article – such as softness, touch, fullness, grain tightness - but also on its technical performance. Fat-liquors can have a significant impact on the light fastness and especially the heat-fastness of the article, and are often the decisive factor for the fogging behaviour. Chemically, fish oils, animal oils and vegetable oils are all triglycerides. The differences arise from the composition of fatty acids within the triglyceride. This has a major influence on the fastness properties of the oils. Ageing, which can be recognised by discolouration and the development of unpleasant odour, occurs mainly because of the so-called autoxidation process (Leonardus et al., 2012). This is a radical chain reaction which takes place at CH_2 groups of the fatty acid chain. Due to radical stabilisation this reaction is facilitated by double bonds adjacent to the

attacked CH_2 group, and for this reason unsaturated fatty acids are more prone to autoxidation than saturated ones. The reaction happens most easily if two double bonds are adjacent to the same CH_2 group, as found in fatty acids such as linoleic and eicosapentaenoic acid. On the other hand, a higher amount of unsaturated fatty acids in the triglyceride when used in a fat-liquor formulation tends to provide better softness in application. A simple method to determine the degree of unsaturation is the iodine value, and this is often used to characterise natural oils (Leonardus et al., 2012). The plant and other features are presented pictorially in Figure 1.0 (Plate 1.1 – 1.4).

Plate 1.1: The Plant of *chrsoyphyllum albidium.*

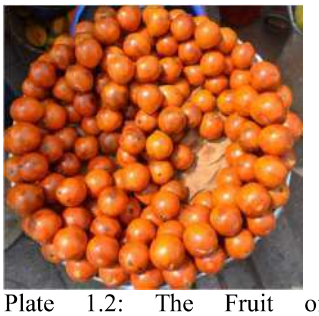


Plate 1.2: The Fruit of *chrysophyllum abidium*

Plate 1.3: Seeds of *Chrsoyphyllum albidium*

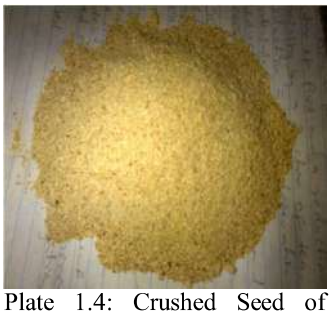


Plate 1.4: Crushed Seed of *chrsoyphyllum albidium*

Figure 1.0: Representation of chrsoyphyllum albidium

Methodology

Collection of Sample: The Fresh fruits of African star apple seed were purchased from local market at Samaru-Zaria, Kaduna State, Nigeria. The African star apple seed under-went various processing units prior to extraction.

Moisture Content (%): Five grams of the sample was weighed in duplicate into the porcelain dish for drying. The samples were dried at a temperature of 100^{o}C for 6hours. The samples were re-weighed at every 2-hours interval until constant weights were obtained. The losses in weight were reported as moisture content loss. The dried samples were cooled in a desiccator to prevent moisture uptake (Dauda, 2014; SLC 2/3a OMCA, 1996).

Solvent Extraction of African Star Apple Seed Oil: A volume of 300ml of n-hexane was transferred into a round bottom flask and 30g of the sample was placed in the thimble for extraction. The Soxhlet was heated at 65°C-75°C respectively. When the solvent was boiling, the vapour rise through the vertical tube into the condenser at the top. The liquid condensate dripped into the filter paper thimble in the centre, which contains the solid sample. The extract seeps through the pores of the thimble and fills the siphon tube, where it flows back into the round bottom flask. This was allowed to continue for 30 minutes. It was then removed from the tube, dried on the water bath, cooled in the desiccators and weighed again to determine the amount of oil extracted according to SLC – 4 (IUP 4- OMCA,1996).

Saponification value: Two grams of *chrysophyllium albidum* oil was weighed into a round-bottom flask, 25cm^3 of 0.5 M ethanolic potassium hydroxide was added followed by two dispersion beads and the mixture was boiled for 30 minutes in reflux condenser. The mixture was removed from the heat source and 1cm^3 of phenolphthalein was added. The mixture was then titrated with 0.5 M hydrochloric acid until a pink colour persisting for more than 15 seconds was observed. Blank titrations excluding the oil were performed (Emmanuel et al., 2014; SLC ¼ OMCA, 1996).

Acid value: For this determination, 12.5cm^3 of both ethyl ether and absolute alcohol were measured into a conical flask and 5 g of *chrysophyllium albidum* oil was added. The mixture was shaken and 0.5cm^3 of phenolphthalein was added and agitated vigorously. The mixture was then titrated with 0.1 M potassium

hydroxide until a pink colour that persisted for 15 s was observed (Emmanuel et al., 2014; SLO 1/5 OMCA, 1996).

Peroxide value: Two gram of *chrysophyllium albidum* oil sample was weighed into 500cm^3 conical flask, 10cm^3 of chloroform was added to dissolve the sample quickly by stirring, then 15cm^3 of acetic acid was added and 1ml of freshly prepared saturated potassium iodide solution was added. The flask was then closed immediately, stirred for 1minute and kept for exactly 5minutes away from light at room temperature. 75cm^3 of water was added to the flask and then shaken vigorously. Few drops of starch solution were added as indicator. The liberated iodine was titrated against 0.01N sodium thiosulphate solution. The same procedure was carried out for the blank omitting test sample (Emmanuel et al., 2014).

Specific gravity: A pycnometer of 25cm^{3}was cleaned and dried, filled with water and weighed at room temperature (27°C). The pycnometer was emptied, dried, cooled and weighed again on an electronic balance. The apparatus was filled with *chrysophyllium albidum* oil and weighed (Emmanuel et al., 2014).

Ester value: One gram of *chrysophyllium albidum* oil was weighed into a 200cm^3 flask and 5cm^3 of ethanol (95%) added. To the mixture was added 5 drops of phenolphthalein indicator, and titrated with 0.1 M ethanolic potassium hydroxide until the colour turned pink. Twenty centilitres of 0.5 M potassium hydroxide was added along with 2 glass beads. A reflux condenser was turned on and the content was boiled for one hour. The mixture was removed from the heat source and 25cm^3 of distilled water was added along with 0.2cm^3 of phenolphthalein. The mixture was titrated to neutrality with 0.5 M hydrochloric acid (Emmanuel et al., 2014).

Iodine Value: One gram of *chrysophyllium albidum* oil sample was weighed into conical flask. 10cm^3 of chloroform and 12.5cm^3 of Dam's reagent was added to the flask. Stopper was then inserted and the content of the flask vigorously swirled. The flask was then placed in the dark for 1hr 30minutes. At the end of the time, 10cm^3 of potassium iodide solution and 75cm^3 of water were added. The content of each flask was titrated with 0.1mol/L sodium thiosulphate solution until the yellow colour due to the iodine almost disappeared. Few drops of starch were then added and titration continued until the blue colour disappeared after vigorous shaking. The same procedure was used for the blank (Emmanuel et al., 2014; SLO 1/6 OMCA, 1996).

Digestion: Quantitatively, 2g of crushed *chrysophyllium albidum* sample was transferred into a beaker and digested with 10cm^3 hydrofluoric acid and 1.0cm^3 aqua regia, which is hydrochloric acid and nitric acid (3:1) in a Kjeldah flask. Thereafter, 5.0cm^3 perchloric acid was added and again heated to dryness for 3 hours, and then cooled. Distilled water of 50cm^3 was added and heated for 15 minutes, allowed to cooled, filtered and made up to 100 cm^3.The filtrate was taken for the determination of heavy metal such as are Iron, Lead and Nickel using Atomic Absorption Spectroscopy (Deepali and Gangwar, 2010).

Fourier Transform Infrared Spectrophotometer and Gas chromatography-Mass spectroscopy Analysis of *chrysophyllium albidum* seed oil

The seed oil was extracted by Soxhlet extraction method and was carried out using n-hexane as the extracting solvent. 30 g of the pulverized seed were extracted in 300cm^3 of the solvent, the extraction continued until enough oil were extracted for the analysis, using FT-IR-8400 Soil coated with KBr, and GC-MS-QP2010 Plus Shimadzu, Japan. The following parameters were observed for GC-MS: column oven temperature (80°C), injection temperature and mode (250°C and split), flow control mode (linear velocity), pressure (108.0 kPa), column flow (1.58 ml/minute), linear velocity (46.3 cm/second) ion source temperature (230°C), interface temperature (250°C), solvent cut time (2.50 minute), detector gain mode (relative), detector gain (0.00kV), threshold (1000) and n-hexane as the methylating solvent (Emmanuel et al., 2014).

Results and Discussion

Table 1.0 present results from physico-chemical analysis of chrysophyllum albidum, crushed sample for moisture content and other parameters as presented.

Table 1.0:Physicochemical characteristic of African star apple seed oil

S/No	Parameter	Units	Values
1	Moisture content	%	18.3
2	Saponification value	(mgKOH/g)	222.05
3	Acid value	(mgKOH/g) oil	3.8
4	Free fatty acid value	(mgKOH/g oil)	2.54
5	Peroxide value	(mg/kg oil)	5.5
6	iodine value	(mg/100g oil)	28
7	Specific gravity	(g/cm^3)	0.90
8	Refractive index at 28^{0}C		1.357
9	Precentage yeild of oil	%	13
10	Viscosity at 28^{o}C		12.20
11	Ester value		218.25

The moisture contentof the Chrysophyllum albidium seed oil was analysed to be 18.3%, this result shows that the seed is not good for storage due to it's high moisture content which may lead to decay or degredation of vital components of the seed intended for oil.The saponification value of Chrysophyllum albidium seed oil of 222.05mgKOH/g agrees with that reported by Musa et al., (2015), (228.4 mg KOH/g), but higher than that reported by Adebayo et al., (2012). (177.30mgKOH/g). The higher the saponification value of oil, the higher the lauric acid content of that oil. The lauric acid content and the saponification value of oil serve as important parameters in determining the suitability of oil. Acid value can be used to check the level of oxidative deterioration of oil by enzymatic or chemical oxidation. It is a measure of the degree of unsaturation of oil and corresponds to the amount of potassium hydroxide required to neutralize free fatty acids. The lower the acid value of oil, the fewer free fatty acids it contains which makes it less exposed to rancidity. The acid values obtained for the oils in this study was (3.8mgKOH/g) this was higher than the result

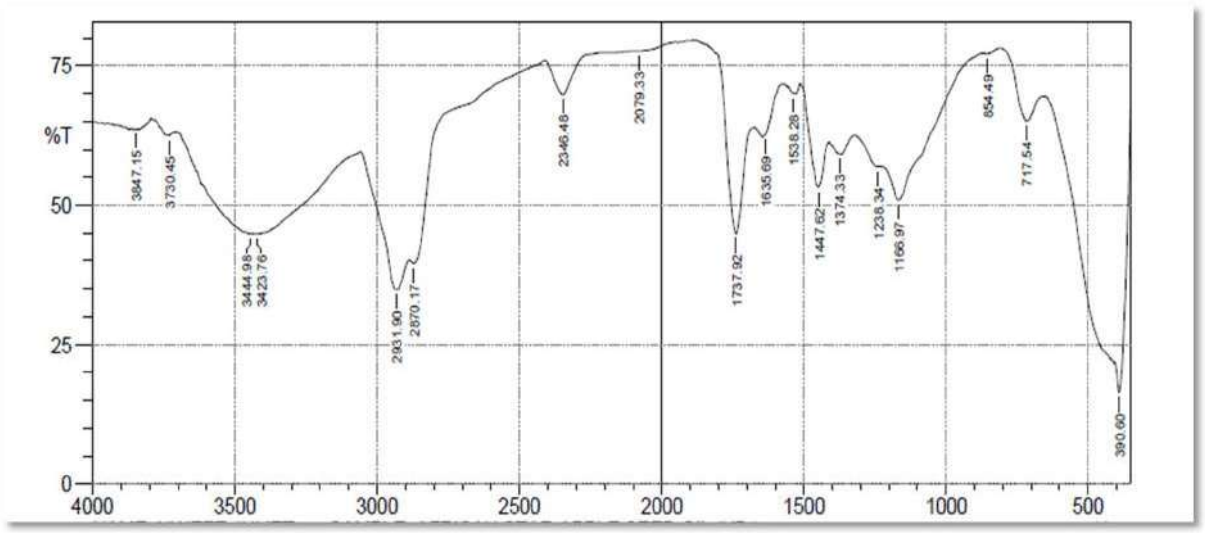
reported by Musa et al., (2015), (2.52mgKOH/g) but lower when compared to Adebayo et al., (2012), (5.20mgKOH/g). The peroxide value obtained for Chrysophyllum albidium seed oil in this study was (5.5meq/kg) permitted maximum peroxide level of not more than 10 M equivalent of peroxide oxygen/Kg of the oils is allowed for consumption this result was higher than the ones reported by Musa et al., (2015), (1.45meq/kg) and Adebayo et al., (2012), (1.65meq/kg). Peroxide value indicates the deterioration level of oils. Oils with higher peroxide values are more unsaturated than those with lower peroxide values which leads to peroxidation during storage. Highly unsaturated oils are known to absorb more oxygen and develop higher peroxide values, and oils with higher peroxide values are prone to rancidity. Iodine value is the measure of degree of unsaturation of oil it also determines the stability of oils to oxidation, and allows the overall unsaturation of the fat to be determined qualitatively. The lodine value of (28.7 mgI_2/g) for this study was below 100 usuallyclassified as non drying oil. These classes of oil are usually suitable for production of soap and lubricating oil(Adebayo *etal*., 2012) the higher the lodine value the higher the unsaturated bond. Specific gravity is a physical properties of the seed oil. The specific gravity of C. albdium seed oil (0.90g/cm^3) compared with that of the studies for guna seed with value 0.987g/cm^{3}reported by Lew Kowitseh (1909). This shows that the oil is less dense than the water. Refractive index measures the purity of the oil,the index value of 1.357 shows that the oil was of low purity than the value reported by ASTM values that ranges from 1.476-1.479 (ASTM, D960-52, 1952)

Table 2.0: Heavy Metal Concentration in *chrsoyphyullm albidium*.

Metal	concentration (ppm)
Lead (Pb)	0.0334
Iron(Fe)	0.2102
Nickel (Ni)	0.0286

Table 2.0, shows some heavy metals concentration (ppm) of the raw oil as follows: lead (Pb),iron (Fe),and nickle (Ni) with concentrations of 0.0334, 0.2102, 0.0286, respectively. These indicate that metals found in the african star apple seed oil are mild, when compared with its nutritional value,heavy metals may be toxic or poisonous even at low concentration, they cannot be degraded or destroyed, but some of them like iron are essential for maintaining the human body metabolism (Ogbe *etal*., 2011).

In Table 3.0, the result from FT-IR shows that, African star apple seed oil contained –OH group, –C=O from aldehyde group,Amide –N-H and AIkyl –C – H, Alkanes –C=C stretch. Hydrocarbon molecule can also contain functional group these are groups that contain atleast one atom which is neither carbon or hydrogen,these functional group can affect the chemical behavior, the chemical properties of organic compound depends on their functional groups.



Wavenumber (cm-1)

Figure 2.0: FT-IR Results for African star apple seed oil

Table 3.0: Analysis of (FTIR) Result for African star apple seed oil

S/No	Frequency, (cm$^{-1)}$	Functional group
1	34449.8	-OH group
2	2870.17	Alkyl group –C-H
3	1737.92	From Aldehyde group –CHO
4	1635.69	Amide group –N-H stretch
5	2079.33	Alkanes group C=C stretch

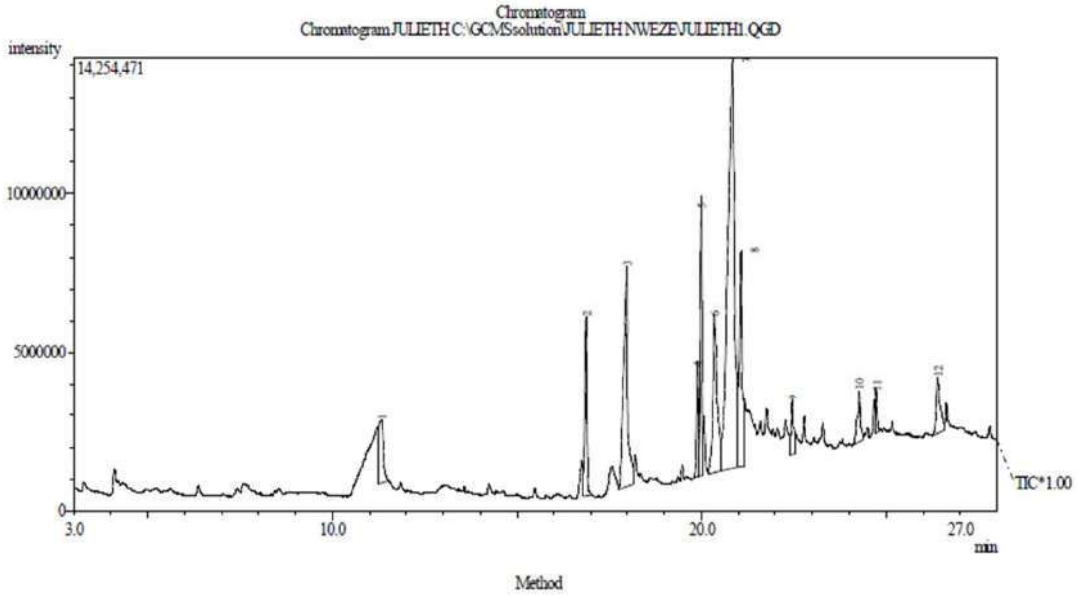


Figure 3.0: GC-MS of African star apple seed oil

Table 4.0:Results for *chrysophyllum albidium* using GC-MS

S/No	FATTY ACIDS AND ALCOHOL	% Area	MOLECULAR FORMULAR
1	1,3-propanediol	4.20	$C_3H_8O_2$
2	Palmitic acids	21.22	$C_{17}H_{34}O_2$
3	Stearic acids	8.67	$C_{18}H_{36}O_2$
4	Oleic acids	12	$C_{19}H_{36}O_2$
5	Linoleic acids	11.91	$C_{19}H_{34}O_2$
6	Tridecanoic	9.94	$C_{13}H_{26}O_2$
7	Tetradecenal	2.25	$C_{14}H_{26}O_4$
8	Docosanoic	0.93	$C_{22}H_{44}O_2$
9	Palmitoleic	40.40	$C_{16}H_{30}O_2$

Table 4.0, shows the results from Gas Chromatography Mass Spectroscopy (GC-MS) analysis. As an analytical technique, GC-MS was used to determined fatty acids present in african star apple seed oil which shows the saturated and unsaturated fatty acids present in the oil,saturated fatty acids found were:palmitic 21.22%,stearic 8.08%, tridecanoic 9.94%, tridecenal 2.25%,docosanoic 0.93%,while the unsaturated fatty acids are: oleic 12%, linoleic 11.91% and (fatty alcohol) palmitoleic 40.40%, were present in the oil. Saturated fatty acids play roles in the fat-liqour by causing the fatty spue on the leather surface due to it's high melting tempearture, which can be eliminated by the addition of surface active agent, this is a substance used to lower the surface tension of medium in which it is dissolved, the interfacial tension with other phase, and is positively adsorbed at the liquid-vapour interface and other interfaces (Vihampa, 2010).

Conclusion

African Star Apple *(Chrysophyllum albidum)* obtained from Samaru market were analysed. The following chemical properties were determined: Moisture content, saponification value, acid value, peroxide value, iodine value, specific gravity, refractive index and percentage yield of the oil using n-hexane as the solvent. The oil showed good prospects in relation to some of its physico-chemical parameters analysed. The heavy metals analysed were within the permissible range and may not cause danger when used as a lubricating agent in the leather industry as fat-liquor. Fourier Transform Infrared Spectrophotometer was employed to ascertain the functional groups present (FTIR-8400S, SHIMADZU) and Gas Chromatography- Mass Spectroscopy (GC-MS-QP2010 PLUS SHIMADZU, JAPAN) was used to determined fatty acids present in african star apple seed oil which shows the saturated and unsaturated fatty acids. The yeild of the oil was poor (13%) but can be used in combination with castor seed or groundnut oils in the production of fatliquor.

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