PHYSICO-CHEMICAL AND GC-MS ANALYSIS OF SOME SELECTED PLANT SEED OILS; CASTOR, NEEM AND RUBBER SEED OILS

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Abstract: Oils were extracted from castor, neem and rubber seeds plants using Soxhlet apparatus and their physical and chemical (physico-chemical) properties were determined. The acid values were 12.69, 12.64 and 7.60 mg KOH/g for castor, neem and rubber seed oil, respectively. The iodine value of castor oil was 97.61 gI_2/100g while that of neem oil was 84.20 gI_2/100g and rubber seed oil has an iodine value of 136.21 gI_2/100g. However, after dehydration the iodine value of castor seed oil increased to 131.00 gI_2/100g which made the dehydrated castor seed oil a drying oil just as rubber seed oil. The free fatty acids in castor seed oil are palmitic acid (9.25%), ricinoleic acid (74.42%), linoleic acid (6.55%), stearic acid (7.60%) and oleic acid (2.18%). The neem seed oil GC-MS analysis revealed eight prominent free fatty acids which are myristic acid (0.92%), palmitic acid (27.81%), margaric acid (0.50%), linoleic acid (45.56%), stearic acid (19.69%), arachidic acid (3.83%), behenic acid (1.05%) and heptacosanoic acid (0.64%). Rubber seed oil free fatty acids include myristic acid (0.57%), palmitic acid (23.12%), linoleic acid (50.04%), stearic acid (20.32%), oleic acid (2.39%), arachidic acid (1.44%) and linolenic acid, omega- 3 fatty acid, an essential unsaturated fatty acid (2.12%). Other uses of the free fatty acids were also proffered besides their used for the preparation of alkyd resins.

Keywords: Transesterification, methylesters, free fatty acid, gas column mass spectroscopic (GC-MS)

Introduction

Fats and oils are generally known as lipids. Plant oils are known to be triglycerides of fatty acids. Vegetable oils are made of over 90% triglycerides which consist of three fatty acids attached to glyceryl group.

Despite the apparent popularity of petroleum products as raw materials in different areas of application, fats and oils are better used in surface coatings, soaps, cosmetics, pharmaceuticals, lubricants, surfactants and polymer processing. Their wide acceptance in these fields of applications is attributable to the fact that they are of renewable resources and possess other qualities such as sustainability, biodegradability and are environmental friendly. Environmental friendliness is becoming more significant consideration in recent times due to the pressing environmental challenges of climate change and global warming. This development has given rise to a number of investigations on the quality and applications of vast number of African seed oils. It has also triggered the demand for more oils needed to expand the present supplies in the oleo-chemical industry (Uzoh and Nwabanne, 2016).

The industrial value of any plant oil depends on its specified fatty acids and the ease with which it can be modified or combined with other chemicals (Ikwuagwu *et al*, 2000). It has also been reported that the most reactive sites in fatty acids are the carboxyl group and double bonds, methylenes adjacent to them are activated and thereby increasing their reactivity. Only rarely do saturated chains show reactivity. Carboxyl groups and unsaturated centres usually react independently, but when in close proximity, both may react through neighboring group participation. In enzymatic reactions, the reactivity of the carboxyl group can be influenced by the presence of a nearby double bonds (Scrimgeour, 2005).

The castor oil plant, *Ricinus communis,* is a flowering plant in the spurge family, Euphorbiaceae. It belong to the genus *Ricinus,* and subtribe, Riciniae. Castor bean (*Ricinus communis)* is an important drought-resistant shrub which is believed to be native of Ethiopian region of tropical Africa and has become naturalized in tropical and temperate regions throughout the world. Castor seed which is often refers to as castor bean (*Ricinus communis L.*) is the source of castor oil. The demand for Castor oil has grown in international market because of its over 700 applications which include medicines, cosmetics, production of biodiesel, plastic, lubricants and also its high oil content which varies between 35-52% depending on the variety of the seeds and the methods of extraction (Aldo *et al,* 2012). Due to these uses of castor seed oil, it becomes imperative for its detailed free fatty analysis to be carried out.

Fig. 1: Castor plant and its seeds

Neem seed oil is obtained from Neem plant (*Azadirachta indica*). The tree is a native of South East Asia and is a member of the Mahogany family *Meliaceae* (Okonkwo, 2004). Neem tree is popularly known in Nigeria as *Dongonyaro.* The neem tree is noted for its drought resistance. Normally, the plant thrives in an area with annual rainfall between 400-1,200 millimetres (16-47 in). It can also grow in regions with annual rainfall below 400 mm. Neem grows in different types of soil and can tolerate high to very high temperatures but cannot survive in temperature below 4^0C (39^0F). All parts of this tree are of different biological activity and the most economic part of neem tree is the oil obtained from the kernel of its seed (Noorul and Gayathri, 2016). Neem seed oil has been used in various parts of the globe for medicinal and agricultural purposes (Kumar *et al.*, 2010). This plant oil has been employed in the production of various items such as soap, commercial pesticides and cosmetics, lamp oil, candle production and lubricating oil (Peter, 2000). Neem seed oil has been found to be of great health use as it has an anti-germ property which it displayed from its insecticidal soap (Kovo, 2006). In spite of these numerous applications of neem seed oil, there are limited information on its free fatty acids compositions.

Fig. 2: Neem plant and its seeds

Fig. 3: Rubber plant and its seeds

The rubber plant which is widely used as a natural source of rubber have been reported to have oil rich seeds of about 40% depending on the location and country where it is grown. Rubber seed oil has been thought to have little economic importance except for the preparation of soap, alkyd resins, biodiesel and lubricating oil simply because little has been reported about its detailed free fatty compositions (Njoku *et al.*, 1996). In this research work, the free fatty acids, physical and chemical properties of castor, neem and rubber seeds oils were determined so as to enhance their industrial applications.

Experimental

Materials

All chemicals reagents used for this work were of analytical grade and were used without further purification except otherwise stated.

Extraction of castor, neem and rubber seed oils

The castor, neem and rubber seed oil were extracted using solvent extraction method using process optimization technique in which a mixture of n-hexane and ethanol was used for the solvent extraction as reported by Tunmise and Oladipupo (2012) at solvent composition of 80.77% n-hexane. The percentage of oil extracted was calculated from Equation 1

$$\text{Percentage oil extracted} = \frac{mass\ of\ extract}{mass\ of\ sample} x\,100 \text{……eqn 1}$$

Physico-chemical properties castor, neem and rubber seed oils

The physico-chemical properties which are the specific gravity, colour, acid value, saponification value and iodine value of the castor, neem and rubber seeds oils were determined according to ASTM standard methods (Nway and Mya, 2008; Ikhuoria *et al.*, 2007). For each of the oil, two samples were analyzed for each parameter and the mean values were recorded.

GC-MS analysis of castor, neem rubber seed oils

The GC-MS analyses of the oil were carried out as reported by Warra (2015) and Yusuf *et al.* (2015). This technique involved subjecting the oil to methylation process to increase the volatility of the oil for auto injection into the Mass Spectrophotometer (Marvin, 2008). This analysis of the fatty acids in the oil samples was carried out at National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria with Shimadzu QP2010 plus series gas chromatography coupled with Shimadzu QP2010 plus mass spectroscopy detector (GC-MS) system.

Fig. 4: Extracted and methylated castor seed oils

Preparation of dehydrated castor seed oil (DCO)

The extracted castor seed oil was dehydrated in a round bottom flask with 2% (wt%) of $NaHSO_4$ catalyst as reported by Nway and Mya in 2008. The system was heated to temperature of about 140^{0}C under vacuum and the dehydration time was 75 min. The physico-chemical properties especially the iodine value of the dehydrated castor oil was carried out using AOAC standard methods.

Results and Discussion

Physico-chemical properties of castor, neem and rubber seed oils

The physical and chemical (physico-chemical) properties of castor, Neem and Rubber seed oils are shown in Table 1. The colour of the crude castor oil was colourless, the neem was very light brown while that of the rubber seed was brown as revealed in Table 3.1. The colours of the oils were similar to other plant seed oils and Warra in 2015 has earlier reported castor seed oil to be colourless. The colourless nature of castor oil is an advantage over other seed oils because its end products will need little or no discolouration.

The specific gravity of the three plants oil are as shown in Table 1. The specific gravity crude castor oil was 0.960; the neem was 0.935 while that of the rubber seed oil was 0.922 signifying that they are all lighter than water. The specific gravity of castor seed oil was slightly different from that reported by Yusuf *et al.* (2015) which was 0.959 while the ASTM Standard for castor seed oil is 0.957-0.961.

The acid value of oil is defined as the number of milligrammes of KOH required to neutralize the free fatty acids in one gramme of the oil. From Table 1, the acid value of the castor oil was 12.69 mg KOH/g, the neem seed oil was 12.64 mg KOH/g while that of the rubber seed was 7.60 mg KOH/g. The high acid values for the three oils (with castor seed having the highest value) will negatively affect the efficiency of their transesterification which will result in low yield in biodiesel production during base-catalyzed transesterification process. However, appreciable yield can be obtained from the three plant oils (castor, neem and rubber seed oils) if acid-catalyzed transesterication is employed (Abbas, 2011). The acid values of the analyzed oils also indicated a considerable amount of free fatty acids which therefore made them suitable for the production of soap.

Saponification value (SV), which is related to the molecular weight of the oil sample is the number of milligramme of KOH required to saponify onegramme of the oil sample. The saponification values are 184.30, 192.35 and 190.93 mg KOH/g for castor, neem and rubber seed oil respectively. The high saponification values for the three oils indicate normal triglycerides and shows that the oils can be used for the production of cream, soap and shampoo.

The iodine value of an oil or fatty acid is the amount of halogen absorbed under specified conditions and is expressed as the number of grammes of iodine per 100 g of fatty acid or oil sample. It is a measure of the degree of unsaturation present in the oil sample and the kind of unsaturation. Table 1 also revealed that the iodine value of castor, neem and rubber seed oils are 97.61, 84 and 136.21 gI_2/100g, respectively. The result indicated that castor and neem seed oils are classified as non drying oil therefore cannot be used for the production of alkyd resins used in coating industry but can be used for the production of soap. However, rubber seed oil has its iodine value greater than 130 which shows that it is a drying oil and can therefore be used for the production of "alkyd" resins which can serve as a better substitute for linseed oil used in oil paint."Alkyd" resins are important class of resins used as binder in gloss or oil paints. The term alkyd is a modification of the original name "alcid", reflecting the fact that they are derived from alcohol and organic acids (Erhan, 2005). The average molecular weight of the oil is inversely related to the saponification values of the plant oils (Panda, 2010).

Profiles of free fatty acids in castor seeds oil

The free fatty acids profile of Castor seed oil is given in Table 2 and the GC-MS chromatograph of the oil is shown in Fig. 5. Obviously, other compounds were revealed in the GC-MS analysis of the castor seed oil but in the course of this work, attention is only given to the free fatty acids present in the oil sample because of their industrial applications and their role in the synthesis of alkyd resins. The same principle was also applied in the free fatty acids analysis of neem and rubber seed oils.

Table 1: Physico-chemical properties of castor, neem and rubber seed oils

S/N	Physico-Chemical Properties	Castor Seed Oil [Mean Value (X)]	Neem Seed Oil [Mean Value (X)]	Rubber seed Oil [Mean Value (X)]
1.	Colour	Colourless	Very light Brown	Light brown
2.	Specific gravity	0.960	0.935	0.922
3.	Acid value (mg KOH/g)	12.69	12.64	7.60
4.	Saponification value (mg KOH/g)	184.30	192.35	190.93
5.	Iodine value (gI_2/100g)	97.61	84.20	136.210
6.	Average Molecular Weight (Mw)	304.40	291.66	293.83

Table 2: Profiles of free fatty acids in castor seeds oil

S/N	Free fatty acids	Trivial names of free fatty acids	Retention Time (RT)	Molecular Formular	% Conc.
1.	Hexadecanoic Acid	Palmitic Acid	14.83	$C_{16}H_{32}O_2$	9.25
2.	12-Hydroxy,9-Octadecenoic Acid	Ricinoleic Acid	15.04	$C_{18}H_{33}O_3$	74.42
3.	9,12-Octadecadienoic Acid	Linoleic Acid	16.53	$C_{18}H_{31}O_2$	6.55
4.	Octadecanoic Acid	Stearic Acid	16.72	$C_{18}H_{34}O_2$	7.60
5.	9-Octadecenoic Acid	Oleic Acid	19.94	$C_{18}H_{32}O_2$	2.18

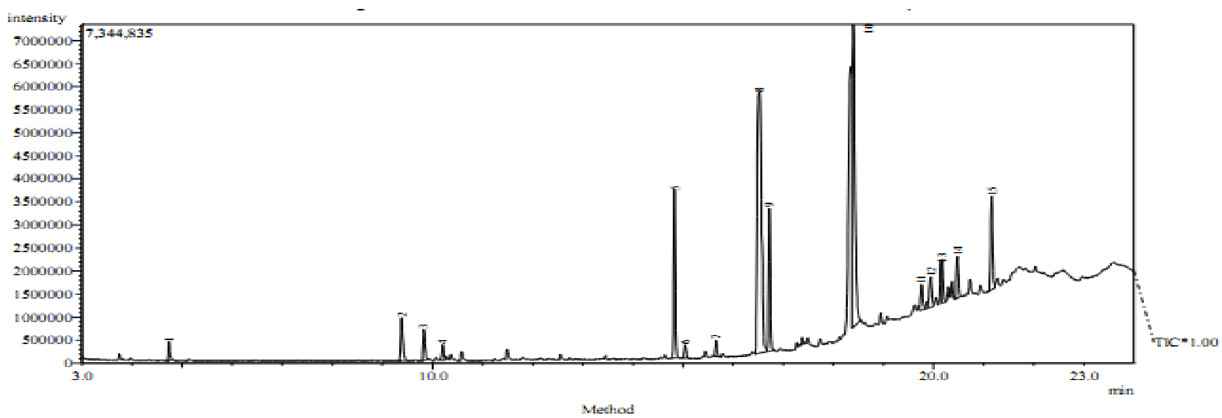


Fig. 5: GC-MS chromatograph of crude castor seed oil

Figure 5 showed the GC-MS Chromatograph of castor seed oil analyzed. The identified peaks in the GC-MS chromatograph; their mass spectra with their fragmentation pattern were compared with the spectra in the database of Mass spectra library of National Institute of Standards and Technology (NIST) 2012 for identification of the free fatty acids. The prominent free fatty acids in castor seed oil are shown in Table 2. The concentrations of the free fatty acids were also determined using the area of the identified GC peaks.

Hexadecanoic acid which is also known as Palmitic acid is one of the two prominent saturated fatty acidsidentified and it accounted for about 9.25% of the total fatty acids. Palmitic acid when extracted is of great economic value as Warra in 2015 reported that the sodium salt of Palmitic acid is used to produce soap, cosmetic and release agents.

12-Hydroxy,9-Octadecenoic acid (which is widely known as Ricinoleic acid) accounted for about 74.42% of the free fatty acids in the plant oil and this value falls within the range (70-90%) reported by Foglia *et al.* (2000) for castor oil samples in USA. The presence of Ricinoleic acid in castor oil makes it unique among vegetable oils as it remains the only commercial source of a hydroxylated fatty acid (Uzoh and Nwabanne, 2016). Simple modification of the this plant oil usually resulted in the removal of the hydroxyl group in the fatty acid chain of Ricinoleic acid thereby creating double bonds which ultimately transformed the oil from non drying to drying oil which is used for the production of alkyd resins used in surface coating. This additional double bonds created was revealed in increase in the iodine value after dehydrating the oil.

9,12-Octadecadienoic acid (also known as Linoleic acid) accounted for about 6.55% of the fatty acids in the oil. Linoleic acid has been reported to have anti–inflammatory and moisture retention effects and for these reason it is becoming more popular in beauty industry (Darmastadt *et al.*, 2002).

Octadecanoic acid (Stearic acid) which was about. 7.60% in occurrence in the castor oil, is the most common saturated fatty acid (Bockisch, 1998). Stearic acid is a saturated fatty acid with an 18-carbon chain and has the IUPAC name octadecanoic acid which has a chemical formula $C_{18}H_{34}O_2$. Stearic acid is mainly used in the production of detergents, soaps, and cosmetics such as shampoos and shaving cream products (Gunstone, 2004).

9-Octadecenoic acid (oleic acid) which was about 2.18% of the fatty acid in castor is used commercially in the preparation of oleates and lotions, and as a pharmaceutical solvent (PubChem, 2014). Oleic acid is used as moisturizer and a number of cosmetic companies add it to lotions and soaps in order to boost their ability to nourish the skin (Warra, 2015).

GC-MS spectra of the free fatty acid and methyl esters of free fatty acids in castor oil and their mass fragmentation patterns

The molecular mass and fragmentation patterns of the free fatty acids in castor seed oils are shown Figure 6-10. Virtually all the free fatty acids appeared in their methyl ester derivatives as a result of methylation of the oil prior to the analysis by the GC-MS equipment. Methylation increased the volatility of the oil in order to correspond to the Programme Temperature Volume (PTV) of the injector of the GC-MS machine. The methyl derivatives correspond to those of the parent substances except that the molecular ions are 14 mass higher but with the same fragmentation patterns (Jans-Joachim, 2009). Therefore, the methyl esters of the free fatty acids corresponds to the free fatty acids except that the molecular mass of the methyl esters are higher by 14 than their corresponding free fatty acids but have the same fragmentation patterns.

Fig. 6: Methyl ester of ricinoleic acid

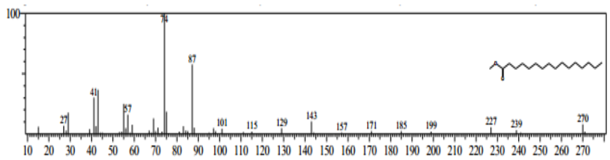


Fig. 7: Methyl ester of palmitic acid

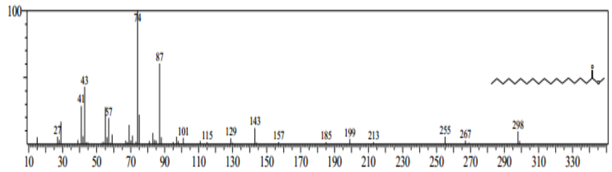


Fig. 8: Methyl ester of stearic acid

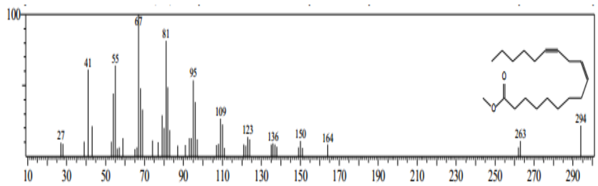


Fig. 9: Methyl ester of linoleic acid

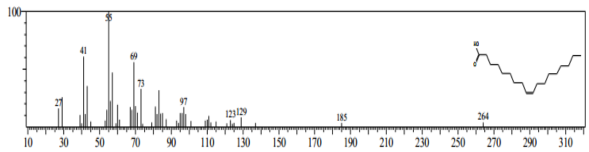
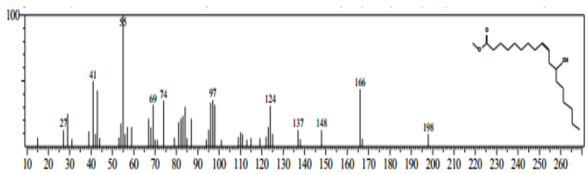


Fig. 10: Oleic acid



Physico-chemical properties of dehydrated castor seed oil (DCO)

The physico-chemical properties of the dehydrated castor seed oil is given in Table 3. The physical and chemical properties of the dehydrated castor were similar to the crude castor seed oil except for the acid value and iodine value. The result in Table 3 showed the acid value increased from 12.69 to 18.75 mg KOH/g signifying more free fatty acids in the medium. The iodine value of the crude castor seed oil also increased from 97.61 to 131.00 gI_2/100g after dehydrated. This means that during dehydration, abstraction of the hydroxyl groups in ricinoleic acid created double bonds which absorbed iodine molecules during iodine value test and this ultimately converted the oil to a drying oil. Being a drying oil, it can therefore be used for the preparation of "alkyd resins" used in gloss paint coatings.

Table 3: Physico-chemical properties of dehydrated castor seed oil (DCO)

S/N	Physico-chemical Properties	Castor Seed Oil [Mean Value (X)]	Dehydrated Castor Oil [Mean Value (X)]
1.	Colour	Colourless	Dark Brown
2.	Specific gravity	0.960	0.934
3.	Acid value (mg KOH/g)	12.69	18.75
4.	Saponification value (mg KOH/g)	184.30	189.40
5.	Iodine value (gI_2/100g)	97.61	131.00
6.	Average Molecular Weight (Mw)	304.89	296.20

Table 4: Profiles of the fatty acids in neem seed oil

S/N	Free fatty acids	Trivial names of free fatty acids	Retention Time (RT)	Molecular Formular	% conc.
1.	Tetradecanoic Acid	Myristic Acid	12.77	$C_{14}H_{28}O_2$	0.92
2.	Hexadecanoic Acid	Palmitic Acid	14.89	$C_{16}H_{32}O_2$	27.81
3.	Heptadecanoic Acid	Margaric Acid	15.83	$C_{17}H_{34}O_2$	0.50
4.	9,12-Octadecadienoic Acid	Linoleic Acid(Omega-6 Acid)	16.61	$C_{18}H_{31}O_2$	45.56
5.	Octadecanoic Acid	Stearic Acid	16.79	$C_{18}H_{34}O_2$	19.69
6.	Eicosanoic Acid	Arachidic Acid	18.80	$C_{20}H_{40}O_2$	3.83
7.	Docosanoic Acid	Behenic Acid	20.09	$C_{22}H_{44}O_2$	1.05
8.	Heptacosanoic Acid	–	21.61	$C_{27}H_{54}O_2$	0.64

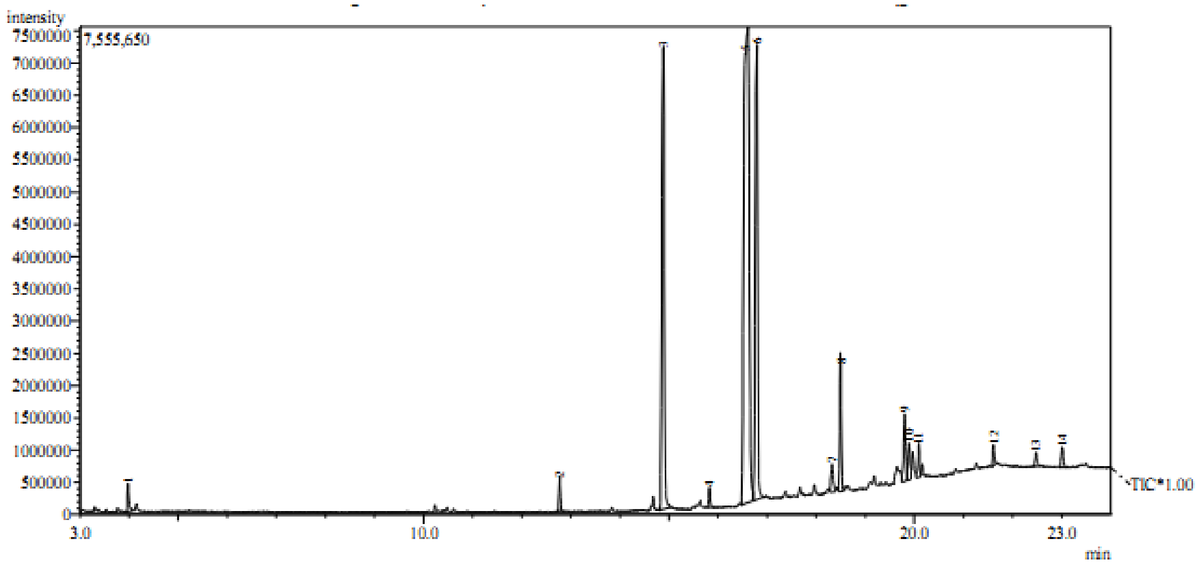


Fig. 11: GC-MS chromatograph of neem seed oil

Profiles of free fatty acids in neem seeds oil

The GC-MS chromatograph of neem seed oil and the free fatty acids with their percentage compositions are shown in Fig. 11 and Table 4, respectively. Some of the free fatty acids in castor seed oil discussed earlier are also present in neem seed oil although with vary percentage composition. Therefore, we shall discuss only free fatty acid not mentioned above but were found in neem seed oil. These are Tetradecanoic acid (Myristic acid), Heptadecanoic acid (Margaric acid), Eicosanoic acid (Arachidic acid), Docosanoic acid (Behenic acid) and Heptacosanoic acid.

Tetradecanoic acid (Myristic acid) is a common saturated fatty acid which with lauric acid have been reported as saturated fatty acids most strongly related to the average serum cholesterol concentrations in humans (German and Dillard, 2010). Heptadecanoic acid or Margaric acid is a saturated fatty acid that does not occur in high concentration in any animal fat or plant oil (Beare-Rogers *et al.*, 2001) and in neem seed oil, Heptadecanoic acid accounted for only 0.50% of the total fatty acids in the oil. Eicosanoic Acid (Arachidic acid) is also a saturated fatty acid with 20-carbon chain. Eicosanoic acid percentage concentration in neem seed oil is about 3.83% and when extracted can be used for the production of detergent, photographic materials, lubricants and because of its surfactant related properties it is also used cosmetics. Docosanoic acid which is also called Behenic acid ($C_{22}H_{44}O_2$) has 1.05% concentration in the plant oil. Behenic acid is often used to give hair conditioners and moisturizers their smoothing properties (Warra, 2015). Heptacosanoic acid also referred to as Heptacosylic acid or Carboceric acid is a 27-carbon chain saturated fatty acid with chemical formula $C_{27}H_{54}O_2$. Heptacosanoic acid has a percentage concentration of 0.64 in neem seed oil.

GC-MS spectra of the methyl esters of free fatty acids in neem seed oil and their mass fragmentation patterns

Figures 12 to 19 give the methyl esters of the free fatty acids present in neem seed oil. Earlier it has been said that the methyl derivatives correspond to those of the parent substances except that the molecular ions are 14 mass higher but with the same fragmentation patterns (Jans-Joachim, 2009). Therefore, the methyl esters of the free fatty acids corresponds to the free fatty acids except that the molecular mass of the methyl esters are higher by 14 than their corresponding free fatty acids but have the same fragmentation patterns.

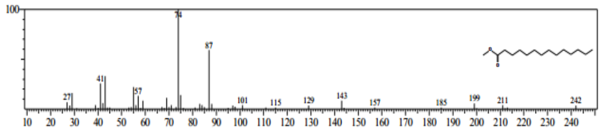


Fig. 12: Methyl ester of myristic acid

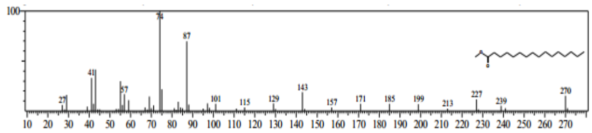


Fig. 13: Methyl ester of palmitic acid

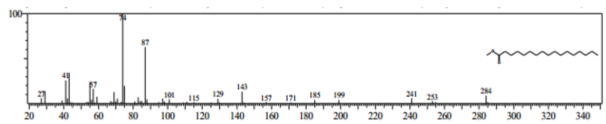


Fig. 14: Methyl ester of margaric acid

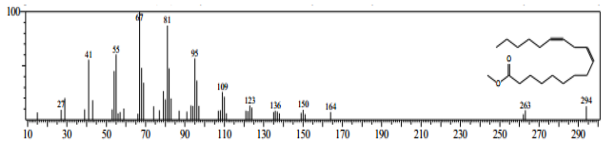


Fig. 15: Methyl ester of linoleic acid

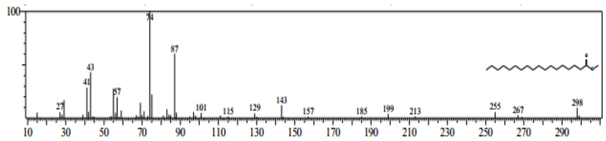


Fig. 16: Methyl ester of stearic acid

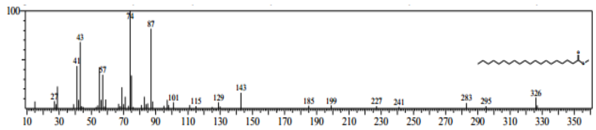


Fig. 17: Methyl ester of arachidic acid

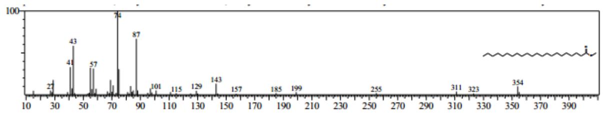


Fig. 18: Methyl ester of behenic acid

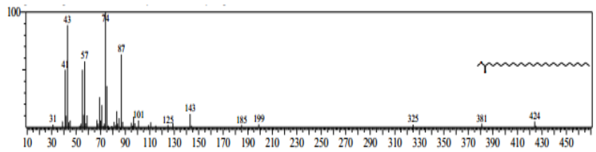


Fig. 19: Methyl ester of heptacosanoic acid

Profile of free fatty acids in rubber seeds oil

The fatty acids in rubber seed oil are given in Table 5 which Fig. 20 gave the GC-MS Micrograph of the rubber seed oil. 9,12-Octadecadienoic acid ($C_{18}H_{32}O_2$)which is known as Linoleic acid (an Omega-6 acid) has the highest percentage concentration which was 50.04%. This high level of unsaturated fatty acid must have undoubtedly responsible for the high iodine value of the oil which makes suitable for the production of alkyd resins used in gloss paint. Other fatty acids in the rubber seed oil has been discussed earlier under Castor and Neem seed oils with the exception of 9,12,15-Octadecatrienoic acid also known as Linolenic acid (an Omega-3 acid). 9,12,15-Octadecatrienoic acid or Linolenic acid is an indispensable dietary component in mammals.

Table 5: Profile of free fatty acids in rubber seeds oil

S/N	Free fatty acids	Trivial names of free fatty acids	Retention time (RT)	Molecular formular	% Conc.
1.	Tetradecanoic Acid	Myristic Acid	12.77	$C_{14}H_{28}O_2$	0.57
2.	Hexadecanoic Acid	Palmitic Acid	14.88	$C_{16}H_{32}O_2$	23.12
3.	9,12-Octadecadienoic Acid	Linoleic Acid (Omega-6 Acid)	16.60	$C_{18}H_{32}O_2$	50.04
4.	Octadecanoic Acid	Stearic Acid	16.78	$C_{18}H_{36}O_2$	20.32
5.	9-Octadecenoic Acid	Oleic Acid (Omega-9 Acid)	18.32	$C_{18}H_{32}O_2$	2.39
6.	Eicosanoic Acid	Arachidic Acid	18.49	$C_{20}H_{40}O_2$	1.44
7.	9,12,15-Octadecatrienoic Acid	Linolenic Acid (Omega-3 Acid)	19.88	$C_{22}H_{44}O_2$	2.12

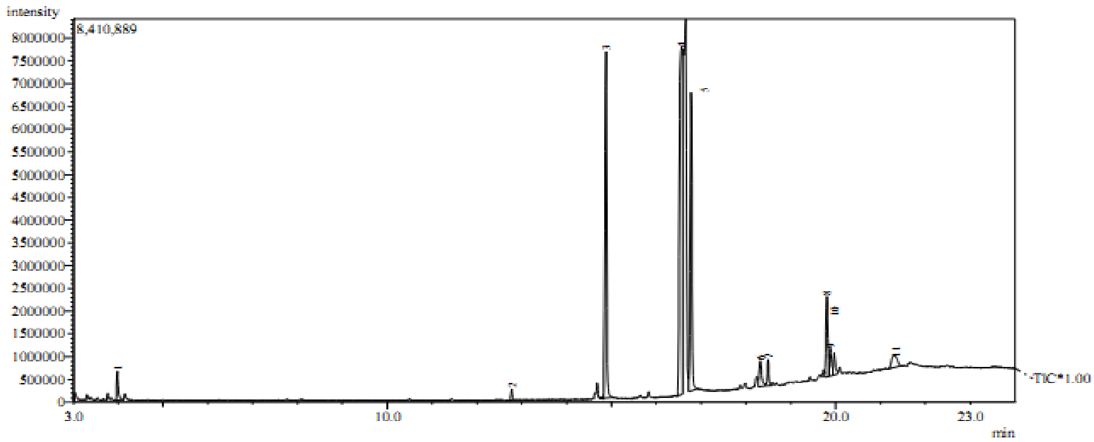


Fig. 20: GC-MS micrograph of rubber seed oil

Table 6: Summary of the free fatty acids in castor, neem and rubber seeds oils

S/N	Parameters (%)	Castor Seed Oil (CSO)	Neem Seed Oil (NSO)	Rubber Seed Oil (RSO)
1	Saturated Fatty Acid (SFA)	16.85	54.44	45.45
2	Mono Unsaturated Fatty Acids (MUFA)	76.60	-	2.39
3	Poly Unsaturated Fatty Acids (PUFA)	6.55	45.56	52.16

GC-MS spectra of the methyl esters of free fatty acids in rubber seed oil and their mass fragmentation patterns

The methyl esters of the free fatty acids in rubber seed oil are given in Fig. 21 to 27; these Figures give the free fatty acids and the fragmentation patterns of the fatty acid present in rubber seed oil.

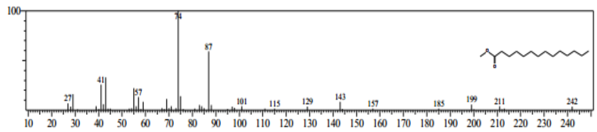


Fig. 21: Methyl ester of myristic acid

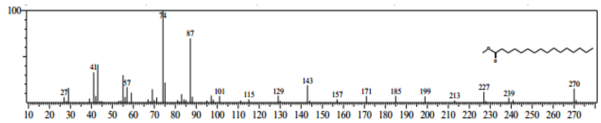


Fig. 22: Methyl ester of palmitic acid

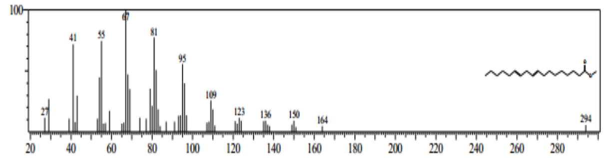


Fig. 23: Methyl ester of linoleic acid

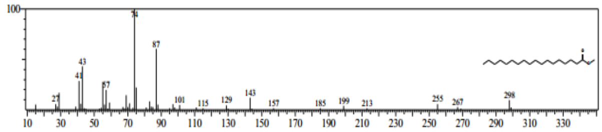


Fig. 24: Methyl ester of stearic acid

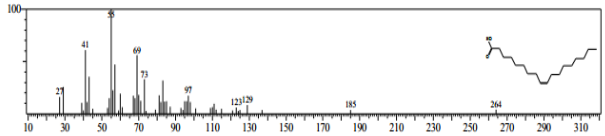


Fig. 25: Methyl ester of oleic acid

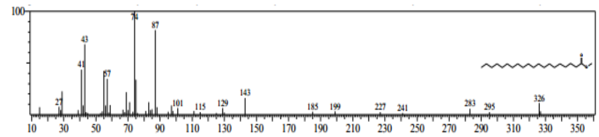


Fig. 26: Methyl ester of arachidic acid

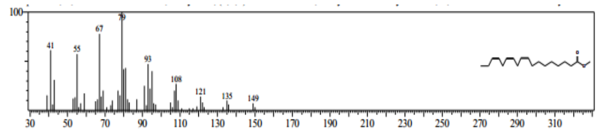


Fig. 27: Methyl ester of linolenic acid

Summary of the free fatty acids in castor, neem and rubber seeds oils

The summary of the free fatty acids present in the castor, neem and rubber seed oils analyzed were given in Table 6. Castor seed oil has Saturated fatty acid (SFA) of 16.85%, Mono unsaturated fatty acids (MUFA) of 76.60% and total Poly unsaturated fatty acids (PUFA) of 6.55%. Neem seed oil has no Mono unsaturated fatty acid. However, neem has saturated fatty acid which amount to a total of 54.44% and poly unsaturated fatty acid of 45.46%. the rubber seed oil has Saturated fatty acids of 45.45%, Mono unsaturated fatty acids of 2.39% and total Poly unsaturated fatty acids of 52.16%.

Conclusion

The free fatty acids in castor, neem and rubber seed oils have been identified and their percentage compositions in the various oils have also been given. The results showed that neem is a non-drying oil and can only be used to synthesize a non-oxidizing alkydand because it is not capable of coherent film formation by oxidation it is advised that such alkyd resin be reacted with otherpolymer types to produce cured films. On the other hand, dehydrated castor and rubber seed oils are drying oil which can be used to prepare an oxidizing alkyd resin which is able to form film by oxidation.

References

Abbas M 2011. Optimization of Biodiesel Production from *Jatropha* Seed Oil using Microbial Lipase-Catalyzed Transesterification Reactions. Department of Biochemistry, Ahmadu Bello University, Zaria, Nigeria, pp. 42-42.

Aldo O, Temu AK, Ogwok P & Ntalikwa JW 2012. Physico-Chemical properties of Biodiesel from Jatropha and Castor oils. M.Sc Thesis. Department of Chemical and Mining Engineering, University of Dar es Salaam-Tanzania, pp. 6-20.

ASTM D 1647-89, 1994. Resistance of dried film to vanishes, water and "alkalie". Annual book of American society for testing and material standards. *Philadelphia*, PA, 06: 268-9.

Beare-Rogers J, Dieffenbacher A & Holm JV 2001. Lexicon of lipid nutrition (IUPAC) *Technical Report. Pure and Appl. Chem.*, 73(4): 685-744.

Bockisch M 1998. Fats and Oils Handbook. AOCS Press, Champaign, Illinois, p. 58 Cayman Chemical Supplier 2014. Available at www.caymanchem.com.

Darmastadt GL, Mao-Qiang M, Chi E, Saha SK, Ziboh VA, Black RE, Santosham M & Elias PM 2002. Impact of tropical oils on the Skin barrier: Possible implications for neonatal health in developing countries. *Acta Paediatrica*, 91(5): 546-554.

Erhan Bat 2005. Synthesis and Characterization of Hyperbranched and Air Drying Fatty Acid Based Resins. M.Sc Thesis, Middle East Technical University, pp. 25-26.

Foglia TA, Jones KC & Sonnet PE 2000. Selectivity of lipases: Isolation of fatty acids from castor, coriander and *Meadowfoam* oils. *Eur. J. Lipid Sci. Techn.*, 102(10): 612-617.

German JB & Dillard CJ 2010. Saturated fats: A perspective from lactation and *Milkcomposition. Lipids*, 45(10): 915-923.

Gunstone FD 2004. The Chemistry of Oils and Fats Sources, Composition, Properties and Uses. Blackwell Publishing Ltd, UK, p. 54.

Ikhuoria EU, Maliki M & Okieimen FE 2007. Synthesis and characterization of chlorinated rubber seed oil alkyd resins. *Progress in Organic Coatings*, 59: 134–13.

Ikwuagwu OE, Ononogbu IC & Njoku OU 2000. Production of biodiesel using rubber

[*Hevea brasiliensis (*Kunth. Muell.)] seed oil. *Industrial Crops and Products*, 12: 57-62. www.elsevier.com/locate/indcrop

Jans-Joachim Hubschmann 2009. Handbook of GC/MS; Fundamental and Applications, 2nd Edition, WILEY-VCH, Verlag Gbmh, Weinheim.

Kovo AS 2006. Application of full 4^2 factorial design for the development and characterization of insecticidal soap from neem oil. *Leonardo Electronic J. Practices and Techn.*, 8: 29-40

Kumar PS, Ghosh DG & Pander CS 2010. Biological Action and Medicinal Properties of various Constituents of *Azadirachta indica* (*meliaceae* an overview). *Annals of Biological Research*, 1(3): 23-34.

Marvin CM 2008. GC/MS A practical Users Guide, 2nd Edition, John Wiley and Sons Inc., Hoboken, New Jersey, Canada, p. 36.

National Research Council (NRC) 1992. *Neem: A Tree for Solving Global Problems.* National Academy Press, Washington, DC

NIST 2012. National Institute of Standards and Technology. Standard Reference Data Programme, GC-MS NIST Library Information Manual. United States of America.

Njoku OU, Omonogbu CI & Owusu JY 1996. An investigation of oil of rubber (*Hevea bransiliensis*). *J. Rubber Resources Institute*, Sri Lanka, 78: 52- 59.

Noorul Aneesa and Gayathri 2016. Beneficial effects of neem oil-An update review. *J. Pharmac. Sci. and Res.*, 8(8): 756-758.

Nway NH & Mya MO 2008. Manufacture of alkyd resin from castor oil. *Proceedings of World Acad. Sci., Engr. and Techn.*, 36: 928-934.

Okonkwo EM 2004. Employment Creation and Opportunities in Manufacturing Sub-sectors: A case for neem tree in Nigeria. *Bullion, Publication of Central Bank of Nigeria*, 28(3): 30-35.

Panda H 2010. Alkyd Resins Technology Handbook, Asia Pacific Business Press Inc., p. 1.

Peter F 2000. *Global Neem Usage*. Deutsche Gesellschaft fdÜr Technische Zusanmmenarbeit (GTZ) GmbH Eschborn, Germany.

PubChem 2014. Elaidic acid. Accessed 12/12/2014 at pubchem.ncbi.nlm.nih.gov/compound/ Elaidic acid.

Scrimgeour Charlie 2005. Chemistry of Fatty Acids Scottish Crop Research Institute Dundee, Bailey's Industrial Oil and Fat Products, Sixth Edition, Six Volume Set. John Wiley & Sons, Inc, Scotland.

Tunmise LA & Oladipupo OO 2012. Optimization of neem seed oil extraction process using response surface methodology. *J. Natural Sci. Rese.*, 2(6): 66 – 76.

Uzoh CF & Nwanbanne J 2016. Investigating the effect of catalyst type and concentration on the functional group conversion in castor seed oil alkyd resin production. *Advances in Chem. Engr. and Sci.*, 6: 190-200.

Warra AA 2015. Physico-chemical and GC/MS analysis of wild castor (*Ricinus communis*

L.) seed oil. *Applied Science Reports*, 9(3): 123-128.

Yusuf AK, Mamza PAP, Ahmed AS & Agunwa U 2015. Extraction and characterization of castor seed oil from wild *Ricinus communis* Linn. *Int. J. Sci., Envt. and Techn.*, 4(5): 132 – 140.