academicJournals

Vol. 10(23), pp. 649-654, 15 December, 2015
DOI: 10.5897/SRE2015.6216
Article Number: 5E4FA5C56694
ISSN 1992-2248

http://www.academicjournals.org/SRE

Scientific Research and Essays

Full Length Research Paper

Synthesis and characterization of copper metal soaps from *Thevetia peruviana* and *Hura crepitans* seed oils

Joseph Bodunde Owolabi[1]*, Kazeem Adelani Alabi[2] and Labunmi Lajide[1]

[1]Department of Chemistry, Federal University of Technology, P. M. B. 74. Akure, Ondo State, Nigeria.
[2]Department of Chemical Sciences, Fountain University. P. M. B. 4491, Osogbo, Osun State, Nigeria.

Received 25 March, 2015; Accepted 30 October, 2015

***Thevetia peruviana* (TP) and *Hura crepitans* (HC) seed oils with 73 and 65% unsaturation, respectively as analyzed by gas chromatography-flame ionization detector (GC-FID) chromatogram were used for the synthesis of copper metal salt. The sodium carboxylate (soluble soap) prepared from the oils by saponifying with sodium hydroxide were reacted with solution of copper salt to produce the metal soaps. The yield was encouraging ranging from 60 to 65%. The progress of the reaction was monitored and confirmed using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR). The difference in absorption frequencies of the FTIR spectra of the oils and their corresponding soaps indicates their production. Confirming it further, the appearance of the characteristic peaks of ^{1}H NMR and ^{13}C NMR of the metallic soaps affirm the synthesis of these compounds. The seeds are thus good sources of raw materials (oleochemicals) for the production of valuable industrial and domestic products.**

Key words: *Thevetia peruviana*, *Hura crepitans,* metal soaps, industrial, sodium hydroxide, synthesis.

INTRODUCTION

The replacement of petrochemicals by oleochemical feedstocks in many industrial and domestic applications has resulted in an increase in demand for bio-based products and as such recognizing and increasing the benefits of using renewable materials. Seeds are important sources of nutritional oils, and they also have industrial and pharmaceutical importance (Oderinde et al., 2009). Current emphasis on sustainable development has made it imperative to search for industrial raw materials from renewable sources. Seed oils are at the centre of this search as many useful products and industrial materials have been produced from them. One of such materials is metal carboxylates otherwise called metal soaps. Metallic soaps have been described as alkaline-earth or heavy metal long-chain carboxylates (Barth, 1982), which are insoluble in water, but soluble in non-aqueous solvents. The soaps of the heavy metals have important applications. Soaps of barium, cadmium, lead, zinc and calcium have found practical application as thermal stabilizers for poly (vinyl chloride) (Owen and

*Corresponding author. E-mail: qasimade@gmail.com.

Msayib, 1989; Bacalogulu and Fisch, 1994). Calcium and magnesium soaps are used as corrosion inhibitors in non-polar media. Lead, manganese, cobalt and zinc soaps are used in paints to accelerate drying while copper soaps are well known for their fungicidal properties (Salager, 2002). Therefore, the present work has added to the available fungitoxic chemicals beforehand and consequently, they can find uses in agrochemical industries and could also serve as precursors for urea or thiourea complexes formation. Silver carboxylates are used as the source of silver in thermographic and photothermographic materials (Binnemans et al., 2004). Some found have been used in greases, cosmetics and textiles (Egbuchunam et al., 2005). The studies on the nature of these soaps are of great importance for their use in industries and for explaining their characteristics under different conditions. The physicochemical properties of different metallic soaps have been investigated by several researchers. Upadhyaya and Sharma (1997) studied thermal, infrared, and x-ray diffraction analysis of manganese and zinc soaps. A number of seed oils have been characterized but the vast majority have not been explored for the preparation of metal carboxylates despite being the most abundant source of carboxylic fatty acids. The seed oils used are also among those that have not been explored for the synthesis of fatty acid carboxylate. Many of the reports on the characterization and properties of metal soaps have been carried out on soaps prepared using pure fatty acids with little attention on the use of triglycerides, inspite of their abundance and low cost, as starting materials for the preparation of metal soaps (Egbuchunam et al., 2007). Therefore, since there are no published evidences according to our literature search showing that *Thevetia peruviana* and *Hura crepitans* have been utilized for the production of copper metallic soap, it was considered necessary to make use of these abundantly available plant seed oils for the production of the metallic soaps and their productions were monitored and confirmed using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectrometers.

MATERIALS AND METHODS

T. peruviana seeds were collected from various locations at high school area in Akure, Ondo State in September, 2012. The good quality seeds were hand-picked to separate them from bad ones. *H. crepitans* seeds were obtained from a tree in front of School of Agriculture and Agricultural Technology, Federal University of Technology, Akure, Ondo State in October, 2012. They were sundried, ground into powder and preserved in a air tight container for further processing. Copper chloride ($CuCl_2.7H_2O$), ethanol and sodium hydroxide used were purchased from Merck, Darmstadt, Germany.

Chemical analysis of *T. peruviana* and *H. crepitans* oil

Powered *T. peruviana* and *H. crepitans* seeds (50 g each) were placed in a stoppered container with 1 L n-hexane and allowed to stand at room temperature for a period of 24 h with frequent agitation. The mixture was strained, the damp solid material pressed, and returned into the container. The process was repeated for 7 days to ensure complete extraction. The oil was concentrated by simple distillation which gave 62 and 54% yield for TP and HC oils, respectively. The extracted oil was analyzed for its iodine, saponification, and acid values using the methods described by the Association of Official Analytical Chemists (AOAC, 1994).

Fatty acid composition of the oils

Fatty acid methyl esters of the oils were prepared by saponification. 50 mg of the fat contents was mixed for 5 min at 95°C with 3.4 ml of the 0.5 M KOH in dry methanol. The mixture was neutralized by using 0.7 M HCl. 3 ml of the 14% BF_3 in methanol was added. The mixture was heated for 5 min at 90°C to achieve complete methylation process. The fatty acid methyl esters were thrice extracted from the mixture with redistilled n-hexane. The content was concentrated to 1 ml for gas chromatography analysis, 1 µl of this was injected into the injection port of GC which was oven programmed with Model HP 6890 powered with HP Chemstation Rev. A 09.01 [1206] software equipped with flame ionization detector and a capillary column HP INNOWax (30 m × 0.25 mm × 0.25 µm) to obtain individual peaks of fatty acid methyl esters. The inlet and detector temperatures were set at 250 and 320°C, respectively. Nitrogen gas was used and the split ratio was 20:1 with hydrogen pressure at 22 psi. The fatty acid methyl esters peaks were identified by retention times in comparison with calibration curve of the standards analyzed under the same conditions.

Preparation of the metallic soaps

Copper chloride salt solution (O.5 M of $CuCl_2.7H_2O$) was prepared and kept in an amber bottle. 10 cm^3 of 0.5 M HCl was added to 20 cm^3 of 10% soluble soap solution prepared above and titrated against the copper chloride salt solution with continuous stirring until complete precipitation was observed. The mixture was then filtered. The residue (Carboxylate) was washed with warm water, air-dried followed by cleaning with petroleum ether and re-crystallized in benzene. The percentage yield was calculated by dividing the actual value (gram of the product produced after drying) with the theoretical value obtained from the equation of the reaction.

Spectroscopic analysis

Fourier transform infrared (FTIR)

The FTIR spectra of *T. peruviana* and *H. crepitans* acids and corresponding copper soaps were obtained with a Perkin-Elmer grating spectrophotometer at a resolution of 4 cm^{-1} between wave numbers 4000 and 400 cm^{-1}, using potassium bromide disc method.

NMR spectroscopy

^1H NMR and ^{13}C NMR spectra of these samples were obtained with Agilent-NMR-vnmrs 400 with pulse sequence: proton (s2pul), temperature 26.0°C/299.1°K, relaxation delay 1.000 s, pulse 45.0 degrees, aqueous time 2.556 s, and width 6410.3 Hz spectrometer using deuterated chloroform ($CDCl_3$) as the solvent.

Table 1. Fatty acid composition of *Thevetia peruviana*.

S/N	Retention time (mm)	Names	Shorthands	Relative percentage
1	13.887	Myristic acid	C14:0	0.18
2	15.317	Palmitic acid	C16:0	19.10
3	16.305	Palmitoleic acid	C16:1	0.01
4	18.055	Stearic acid	C18:0	7.31
5	18.934	Oleic acid	C18:1	53.40
6	19.520	Linoleic acid	C18:2	19.03
7	20.721	Linolenic acid	C18:3	0.25
8	21.821	Arachidic acid	C20:0	0.11
9	22.689	Arachidonic acid	C20:1	0.40
10	23.835	Behemic acid	C22:0	0.06
11	25.003	Erucic acid	C22:1	0.10

Table 2. Fatty acid composition of *Hura crepitans*.

S/N	Retention time (mm)	Names	Shorthands	Relative percentage
1	14.440	Myristic acid	C14:0	0.18
2	16.044	Palmitic acid	C16:0	21.67
3	16.677	Palmitoleic acid	C16:1	0.57
4	17.369	Margaric acid	C17:0	0.31
5	18.060	Stearic acid	C18:0	9.66
6	18.941	Oleic acid	C18:1	26.91
7	19.526	Linoleic acid	C18:2	36.61
8	20.658	Linolenic acid	C18:3	0.75
9	21.911	Arachidic acid	C20:0	2.48
10	23.972	Behemic acid	C22:0	0.31
11	25.623	Lignoceric acid	C24:0	0.49

RESULTS AND DISCUSSION

Percentage fatty acids compositions

Table 1 presents the fatty acids constituents of *T. peruviana* oil. The saponifiable matter of the oil contains different fatty acids. Oleic acid had the highest percentage (53.40%) followed by palmitic acid (19.10%) and linoleic acid (19.03%). Moderate amount of stearic acid (7.3%) was found. Myristic, palmitoleic, linolenic, arachidic, arachidonic, behenic, and erucic acids were found in very low quantity; 0.2, 0.01, 0.3, 0.1, 0.4, 0.1, and 0.1%, respectively. The results shown in Table 1 for the fatty acid composition of TP are in full agreement with those reported by Olupona and Atteh (2008).

Table 2 represents the fatty acids constituents of *H. crepitans* oil. The saponifiable matter of this oil also contains different fatty acids. Linoleic acid had the highest percentage (36.6%) followed by oleic acid (26.9%), and palmitic acid (21.7%). Moderate amount of stearic acid (9.7%) was found. Arachidic acid was found in low quantity (2.5%). Myristic, palmitoleic, margaric, linolenic, behenic, and lignoceric acid were found in very low quantity; 0.2, 0.6, 0.3, 0.8, 0.3, and 0.5%, respectively (Tables 3 and 4).

As no modifications occur on the alkyl chain of triglyceride during soap preparation, the metal soaps spectra still show absorption bands which are characteristics of the oils. CH_2 antisymmetric and symmetric stretching vibrations occur with varying intensities in the region 2926 to 2927 cm^{-1} for *T. peruviana* and *H. crepitans* oils, respectively and between 2857 and 2922, 2857 and 2925 cm^{-1} for the metal soaps, respectively. Typical antisymmetric stretching vibration for carboxylate occurs between 1589 and 1611 cm^{-1} (Olujinmi et al., 2011).

The difference in absorption frequencies of carbonyl group of fatty acid and its corresponding metal soap also confirms the formation of soaps. 1714 and 1721 cm^{-1} for *T. peruviana* fatty acid and *T. peruviana* soap and 1708 and 1710 cm^{-1} for *H. crepitans* fatty acid and *H. crepitans* soap respectively. The carbonyl group either shift or disappear in the spectra of its complexes accompanied by the appearance of two bands in the 1569 to 1631 cm^{-1}

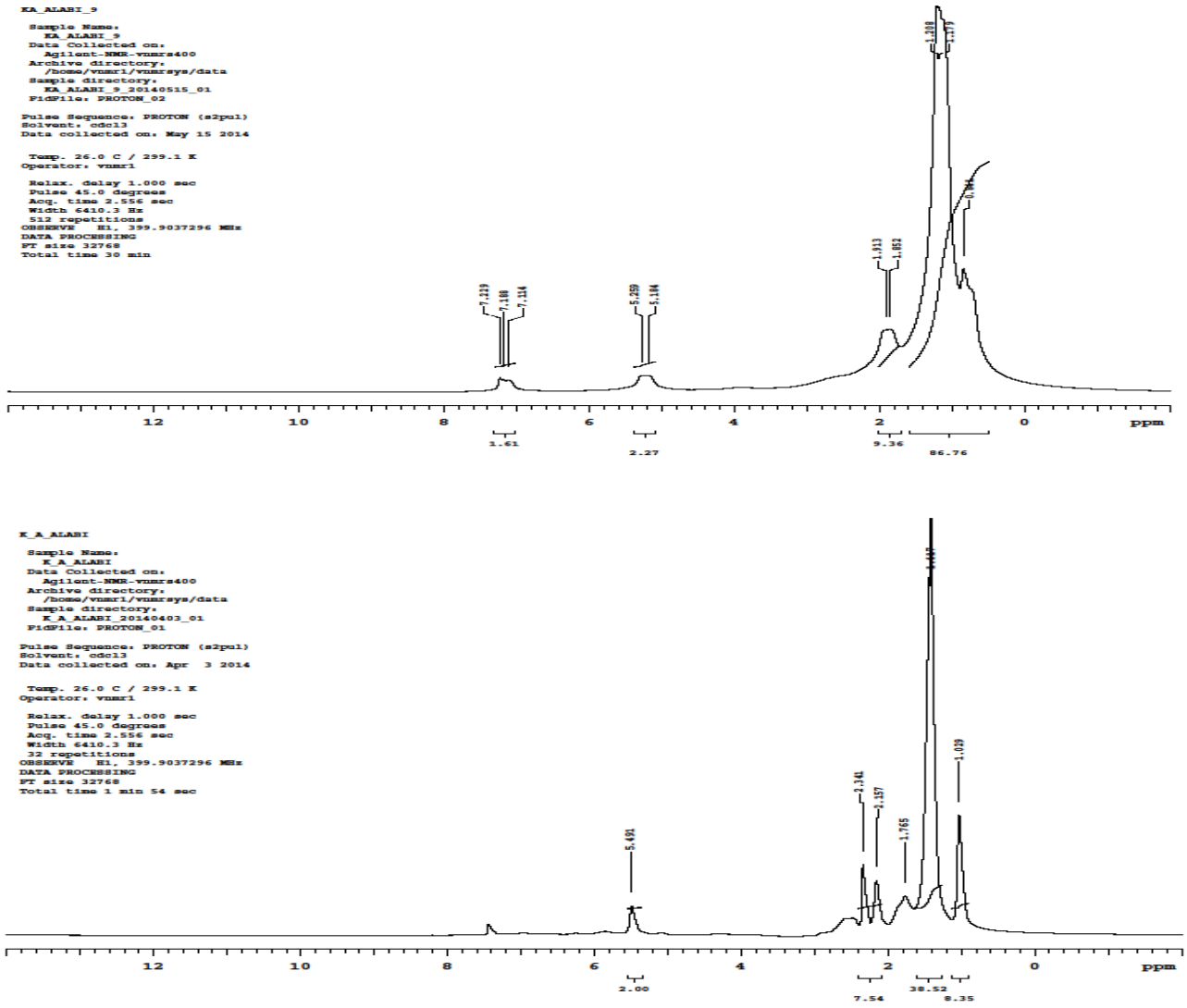

Figure 1. ^{1}H NMR spectra of *Thevetia Peruvian*a and *Hura crepitans* soaps.

range due to υ_{as} (COO^{-}) and one in the 1350 to 1413 cm^{-1} range assigned to υ_{s} (COO^{-}). Accordingly, the antisymmetric and symmetric stretching vibration modes υ_{as} (COO^{-}) and υ_{s} (COO^{-}) of the COO^{-} group should help in elucidating the structure of our complexes (Mesubi, 1982).

The absorption in the vicinity of 717 to 722 cm^{-1} in the spectra of these soaps are associated with the rocking vibration of a chain of successive methylene groups – (CH_2) and are sensitive to the crystallization of soap (Anushri et al., 2012).

The ^{1}H NMR spectra of the soaps (*T. peruviana* and *H. crepitans*) are shown in Figure 1. The peaks at around 0.841 and 1.029, 1.208 and 1.417, 1.852 and 1.768, and 1.913 and 2.157 ppm were attributable to the terminal methyl protons, protons of the repeating methylene units, and protons of the methylene group *β* and *α* to the carbonyl group, respectively (Gunstone, 2008; Tariq et al., 2011). The signal at 2.341 ppm in *H. crepitans* was assigned to allylic methylene protons while the peaks at 5.259 and 5.491 ppm were considered to be from the olefinic protons, confirming the presence of unsaturation in the soaps as indicated by the FTIR and gas chromatography-flame ionization detector (GC-FID) results.

Figure 2 presents the ^{13}C NMR of these products. The signals between 14.021 ppm and 31.844 ppm for *T. peruviana* and between 14.173 and 34.560 ppm for *H. crepitans* represent the repeating methylene groups, while the signals at 76.942 and 77.170 ppm are characteristic absorption regions for C-O group. The signals at 129.924 and 130.075 ppm, respectively indicate the presence of double bonds (C=C) as evident in their fatty acid profile (Tables 3 and 4) and the earlier

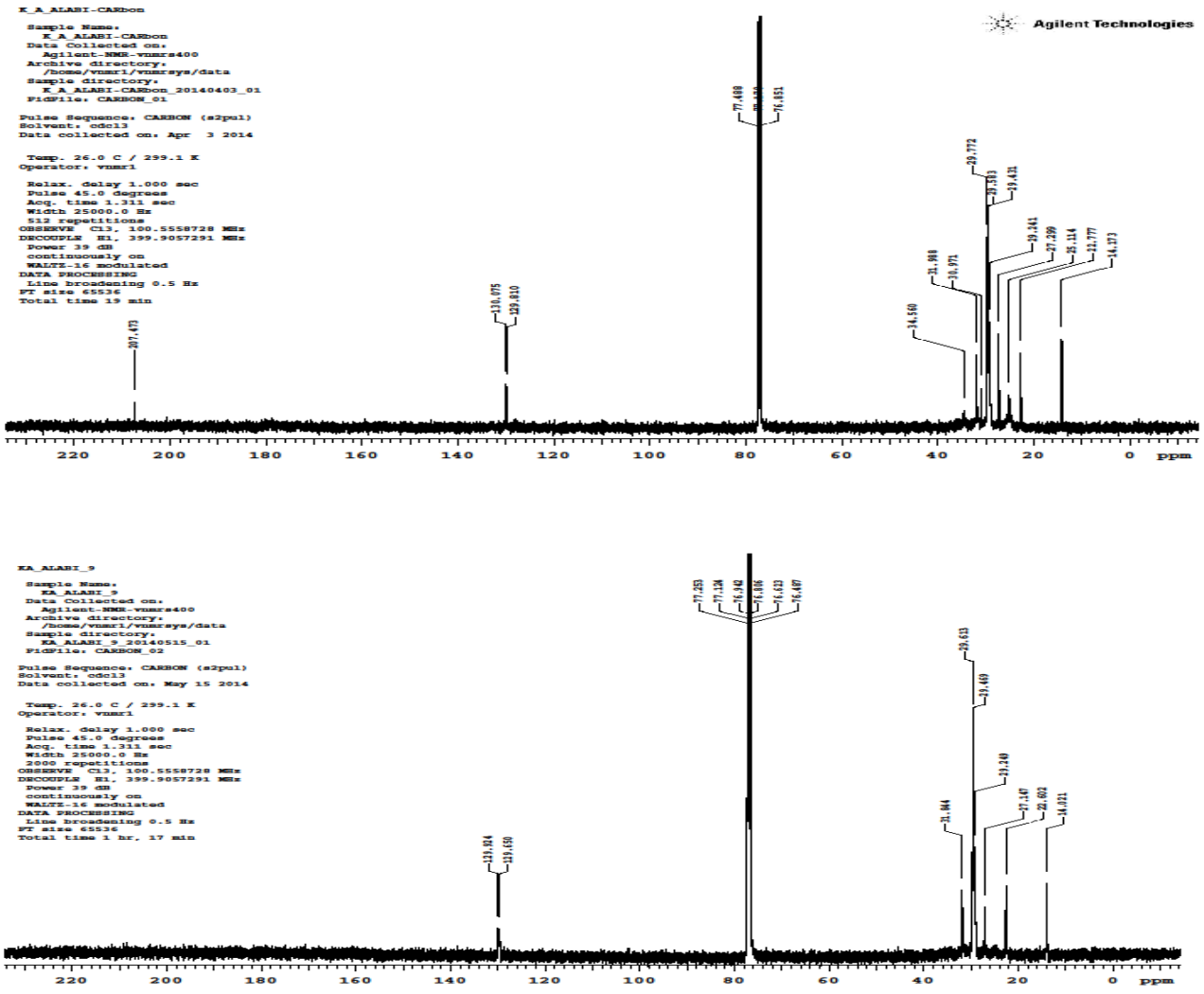

Figure 2. ^{13}CNMR spectra of *Thevetia Peruvian*a and *Hura crepitans* soaps.

Table 3. Percentage saturation and unsaturation.

Sample	Saturation	Unsaturation	Remarks
T. peruviana oil	26.76	73.19	Both are good raw materials for various industrial uses such as polymer because of high percentage of unsaturation.
H. crepitans oil	35.1	64.84	

^{1}H NMR spectra; the most prominent fraction was Oleic (C18:1) and the absorption at 207.473 ppm by the *H. crepitans* soap represents the carbonyl carbon, but was not significant in that of *T. peruviana* soap which could have been more deshielded down the field, thus the machine could not record it.

Conclusions

In this study, the oils were extracted, purified and used directly because the physico chemical parameters were earlier reported by Olupona and Atteh (2008) and Okolie et al. (2012). The copper soaps were actually synthesized from sodium soap with the percentage yield ranging from 60 to 65%. The progress of the synthesis was monitored using both FTIR and nuclear magnetic resonance.

Conflict of Interests

The authors have not declared any conflicts of interest.

Table 4. Frequencies (cm^{-1}) of absorption maxima with their assignments, of *T. peruviana* and *H. crepitans* acids and soaps.

S/N	Assignment	*T. peruviana* acid	*H. crepitans* acid	*T. peruviana* soap	*H. crepitans* soap
1	CH_2, C-H asymmetric stretch	2926vs	2927vs	2922vs	2925vs
2	CH_2, C-H symmetric stretch	-	-	2857s	2857s
3	C=O stretch	1714vs	1708vs	1721s	1710s
4	COO^- asymmetric stretch	-	-	1589vs	1611s
5	COO^- symmetric stretch	-	-	1428ms	1426s
6	C-O stretch + O-H in plane deform	1453ms	1455ms	-	-
7	Progressive bands (CH_2, twist and wag)	1276w	1284w	1313w, 1179w	1239w
8	CH_3 rocking	1036vw	-	1105w	-
9	OH out of plane deform	931w	-	-	968w
10	CH_2 rocking	721w	-	722w	717w

vs: Very strong; ms: medium; s: strong; w: weak; m: medium; vw: very weak.

REFERENCES

Anushri G, Upadhyaya SK, Kamal K (2012). Infrared absorption spectra, x-rays diffraction studies and thermal behavior of cerium and thorium laurate. Int. J. Theor. Appl. Sci. 4(1):1-5.

AOAC, Official Methods of Analysis (1994). Association of Official Analytical Chemist, Arlington, Va, USA, 14th edition, Vol. 67.

Bacalogulu R, Fisch M (1994). Degradation and stabilization of poly (vinyl chloride) II. Kinetics of the thermal degradation of poly (vinyl chloride). Graw-Hill Encyclopedia of Science and Technology. McGraw-Hill Inc. USA. Polym. Degrad. Stab. 45:488.

Barth TFW (1982). Soaps In: McGraw-Hill Encyclopedia of Science and Technology. McGraw-Hill Inc. USA, P 488.

Binnemans K, Van Deun R, Thijs RB, Vanwelkenhuysen I, Geuens I (2004). Structure and mesomorphism of silver alkanoates. Chem. Mater. 16:2021-2027.

Egbuchunam TO, Balkose D, Okieimen FE (2007). Structure and thermal behaviour of polyvalent metal soaps of rubber seed oil. J. Chem. Soc. Niger. 32(2):107-116.

Egbuchunam TO, Okieimen FE, Aigbodion AI (2005). Studies in the thermal stability of metal soaps of parkia seed oil. Chem. Tech. J. 1:18-23.

Gunstone FD (2008). Oils and Fats in the Food Industry. Food Industry Briefing, Blackwell Publishing Company, London, UK.

Mesubi MA (1982). An infrared study of zinc, cadmium, and lead salts of some fatty acids. J. Mol. Struc. 81:1-2, 61-67.

Oderinde RA, Ajayi IA, Adewuyi A (2009). Characterisation of seed and seed oil of *Hura crepitans* and kinetics of degradation of the oil during heating. EJEAFChe pp. 201-208.

Okolie PN, Uaboi-Egbenni PO, Ajekwene AE (2012). Extraction and Quality Evaluation of Sandbox Tree Seed (*Hura crepitan*) Oil. World J. Agric. Sci. 8(4):359-365.

Olujinmi MF, Ighodalo CE, Catherine OE (2011). Relative thermal stability of metal soaps of *Ximenia americana* and *Balanites aegyptiaca* seed oils. Sci. Res. Essays 6(9):1922-1927.

Olupona J, Atteh J (2008). Physico-chemical characteristics and fatty acid composition of oil from *Thevetia peruviana* seed, 8th *European Poultry Conference.*

Owen ED, Msayib KJ (1989). Catalyzed degradation of poly(vinyl chloride). III. Zinc (II) chloride catalysis. J. Polym. Sci. 27:399-408.

Salager J (2002). Surfactants: Types and uses. FIRP.

Tariq M, Ali S, Ahmad F (2011). Identification, FTIR, NMR (^1H and ^{13}C) and GC/MS studies of fatty acid methyl esters in biodiesel from rocket seed oil. Fuel Process. Technol. 92(3):336-334.

Upadhyaya SK, Sharma PS (1997). Thermal, infrared and x-ray diffraction studies on manganese and zinc soaps. Asian J. Chem. 9:388.