Synthesis and characterization of poly(hydroxylalkanethiol-ether) derivatives of *Plukenetia conophora* oil

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Abstract

Biobased additives for metal working or industrial oils are desirable due to their eco-friendly nature. In this work, 1-butanethiol, 1-decanethiol and I-octadecanethiol were employed to synthesize three useful poly(hydroxyalkanethio-ether) derivatives of *Plukenetia conophora* oil. The optimum experimental conditions of solvent, catalysts, time and temperature were investigated. The reactions were monitored and products confirmed by FTIR and NMR spectroscopy. The physico-chemical properties, polymer molecular weight and oxidative stability of the products were carried out to determine their end-use applications. Using perchloric acid as catalyst and a temperature of 50^0C, the reactions proceeded smoothly to the desired products after 3, 3.5 and 5hr for butylthio-ether, decylthio-ether and octadecylthio-ether derivatives of Plukenetia conophora oil respectively, while retaining the triglyceride structure of the oil. The resulting derivatives of Plukenetia conophora oil possess potentials for application in formulation of lubricants and industrial fluids.

Keywords:Plukenetia conophora oil, polyhydroxylalkanethiol-ether, epoxy ring opening.

1. Introduction

The rising cost of petroleum and increased demand coupled with environmental concerns has always created a renewed interest in utilization of vegetable oil as bio based lubricants. Vegetable oil-based products have several advantages over petroleum based products because they are from renewable sources, non toxic, biodegradable and relatively inexpensive (Salunkhe et al., 1992, Bockish, 1981). Vegetable oils have proved to be excellent lubricants and functional fluids (Zahour and Normany, 1988, Willing, 2001) due to their low volatility, high molecular weight of the triacylglycerol molecule, narrow range of viscosity change with temperature, good lubrication characteristics which may be attributed to the polar ester group and high solubilising power for polar contaminants and additive molecules (Sharma et al., 2006). The double bond sites in the triacyglycerol structure of vegetable oils also offer sites for additional functionalization for further improving their technical properties (Sharma et al., 2009).

In spite of the above enumerated advantages of vegetable based oil lubricants, the high degree of unsaturated fatty acid in the composition of many vegetable oils however causes them to have low thermal and oxidative stability (Akintayo, 2007). High thermal and oxidative stability is required during various tribological processes when the oil structure has to withstand extreme temperature variations, and maintain excellent boundary lubricating properties through strong physical and chemical adsorption with the metal (Sharma et al., 2009).

Organic sulphur compounds have been widely used in improving the thermal and oxidative stabilities of lubricants. Wakim (1976) demonstrated that direct sulfurization of triglycerides gave resinous products mostly insoluble in base oils. Sharma et al., (Sharma et al., 2006) had reported a novel synthetic approach for introducing sulphur containing compound at the double bond sites of the triglycerides of soyabean oil while retaining the triglycerides structure and its associated benefits. This paper reports the synthesis of thioether hydroxyl derivative of *Plukenetia conophora* oil (PKCO) using the method described by Sharma et al., (2006). PKCO has been reported to consist of 70.1% linolenic, 11.7% oleic, 0.6% stearic and 0.8% palmitic acids (Akintayo and Bayer, 2002). It is therefore a very high unsaturation level oil and in particular high content of linolenic acid compared to soyabean oil which has been popularly studied for lubricant applications. Lubricants derived from PKCO are expected to present interesting properties for useful applications in the industry. The experimental conditions for the synthesis involving different thiols, solvent, catalyst amount, time and temperature were also intended to be optimised for laboratory scale up. Further studies are ongoing to determine the tribological properties of these products in order to determine their usefulness as antifriction and antiwear chemicals for automotive and other industrial applications.

2. Experimental

Materials

Plukenetia conophora seeds were purchased from Erekesan market in Ado-Ekiti, Ekiti State Nigeria. The good seeds were washed with water and air dried and later milled using Christy mill. Oven dried samples (103^0C) were extracted by soxhlet method using n- hexane. The crude oil was refined by agitating with 18M NaOH (1:30g/g of alkali: powder) for 15min. The resultant mixture was heated to 75-80^0C to break the soap stock and the neutral oil separated by centrifugation.

Perchloric acid (ACS reagent, 90% w/w), methylene chloride, sodium carbonate anhydrous magnesium sulphate, glacial acetic acid (100%), AR grade hydrogen peroxide (30wt%), Amberlite IR-I20H ion exchange resion, 62 % HBr in acetic acid (Merck, Darmstadt, Germany) and 1-butanethiol, 1-decanethiol, 1-octadecanethiol and deuteriated chloroform(99.8%), Sigma-Aldrich Chemie GmbH (Taufikirchen, Germany) were used as received.

2.1 Preparation of Epoxidised *Plukenetia conophora* oil (EPKCO).

PKCO (415g, 300mM C=C) was placed in a three neck round bottom flask and glacial acetic acid (90g, 0.05mols of acid; 1mol C = C) was added while stirring thoroughly at room temperature. The catalyst, 62.25g Amberlite IR-120H ion exchange resin (15% based on weight of oil) was now added and temperature increased to 55°C while stirring for 30min. Then 510g H_2O_2 (1.5moles H_2O_2: 1C = C) was added drop wisely to the reaction mixture over 1 hr. After complete addition of H_2O_2, temperature was increased to 65^0C and reaction allowed to continue for 12hr. The rapid stirring was maintained throughout the experiments so that fine dispersion of oil was achieved. After the experiment, the product mixture was poured into ice water and extracted with diethyl either. The ether layer was washed with dilute sodium bicarbonate followed by distilled water until neutral to pH. The organic layer was then dried over $MgSO_4$, filtered under vacuum and solvent removed over rotary evaporator. The isolated yield of the colourless oil was 442g (95.5 wt % theoretical yield). Oxirane number: 7.2.

HNMR (400 MHz, $CDCl_3$): ∂_H (ppm) = 0.85(t, 3H) terminal methyl; 0.97(t, 3H) terminal methyl homoallylic in linolenic fatty acid; 4.2-4.4(d,2H) glycerol methylenes; 5.2-5.3(m,IH) glycerol methine; 2.9-3.3 (m, IH) epoxy protons; 1.5(m, 2H) -$C\underline{H}_2$-epoxy; 1.7(dd,2H) epoxy-$C\underline{H}_2$-epoxy; 1.0-1.1 (t, 3H) terminal methyl of triepoxystearate.

2.2 Synthesis of poly (hydroxyl alkanethio-ether) derivatives of PKCO form EPKCO

25g (25.4mM) of EPKCO and 19.6ml (183 mM) of 1- butanethiol were dissolved in 400ml of methylene chloride in a three necked 1000ml round bottom flask under dry nitrogen atmosphere. Perchloric acid (2.54g dissolved in 20ml CH_2Cl_2) was used as catalyst and added dropwisely to the reaction mixture while stirring. After the catalyst addition, temperature was raised to 50^0C and reaction was allowed to continue for 3hr when FTIR analysis of aliquot of mixture indicated completion of reaction. The reaction was then cooled to room temperature and the organic phase washed with 200ml of aqueous 5% sodium bicarbonate solution and deionized water until no trace of acid catalyst remained in the system. The organic phase was dried with anhydrous magnesium sulphate overnight and filtered and solvent removed over rotavapour at 80^0C to yield the poly(hydroxybutanethiol-ether) derivative (BThPKCO) of *Plukenetia conophora* oil. The above procedure was repeated using 38ml of decanethiol, 61.8ml of octadecanethiol to yield the poly(hydroxydecanethiol-ether) (DThPKCO) and poly(hydroxy octadecanethiol-ether) (ODThPKCO) derivatives respectively. Reaction times for the other derivatives were 3.5 and 5hr respectively.

2.3 Physicochemical Characterisation

2.3.1 Cloud and Pour points: Pour point procedures followed ASTM D 97.

The automated low temperature immersion bath (Model FT902, Julabo, Labotechnic GmBH, Seelbach, Germany), capable of maintaining temperatures down to - 90^0C ± 0.1^0C and cooling rate of -3^0C/min in isopropyl alcohol was employed. Test jars, thermometers, corks and rubber rings fully met D97 specifications. In the study all the runs were carried out at least in duplicate. The D97 test call for determining pour point at segments of 3^0C and in this study no attempt was made to differentiate them into smaller segments. All samples were stored of 50^0C for at least 1hr prior to test to minimize possible effect of thermal history.

2.3.2 Total Acid No: The total acid number (TAN) refers to the potassium hydroxide weight (expressed in milligrams) required to neutralize the acid functions present in 1g of sample. The sample (0.2g) was dissolved in 5ml of ethanol. The solution was then titrated by a solution of potassium hydroxide (0.1M KOH). Phenolphthalein was used as the indicator. Each sample was titrated three times, and the TAN was calculated according to equation 1;

$$TAN = \frac{V \times N \times 56.1}{W}$$

where W = weight of sample in grams, V = volume in ml of KOH solution used for the titration, N = molar concentration of KOH used.

2.3.3 Oxirane Value: Oxirane oxygen content of the samples was determined using the titrimetric method with hydrobromic acid solution in acetic acid (Paquot, 1979). From the oxirane content, the percentage relative conversion to oxirane was determined using the following formula; Relative conversion to oxirane = $(Oo_{ex}/Oo_{th}) \times 100$ where Oo_{ex} is the experimentally determined content of oxirane oxygen, and Oo_{th} is the theoretical maximum oxirane oxygen content in 100g of oil determined using the expression;

$Oo_{th} = \{(IV_0/2A_i)/100 + (IV_0/2A_i)\ A_0\} x\ A_0 \times 100$

Where A_i =126.9 and A_0 (16.0) are the atomic weights of iodine and oxygen respectively and IV_0 is the initial iodine value of the oil sample (Mungro et al., 2008).

2.3.4 NMR Analysis

All the ^{1}HNMR spectra were recorded quantitatively using Bruker Avance – 400 (Brucker instruments, Inc Karlsruhe, Germany) Fourier transform spectrometer operating of 400.6 mHz, using a 5mm dual probe. Sample solutions were prepared in $CDCl_3$, 15% v/v concentration. Proton NMR spectra were obtained from 16 co-added FIDs. The gated decoupling pulse sequence was used with the following parameters: number of scans, 512; acquisition time, 1.3665; pulse width, 10.3Ns; free induction decay was transformed and zero filled to 300k to give digital resolution of 2Hz / point.

2.3.5 FTIR Analysis

FTIR spectra of the starting material, reaction aliquots, and final products were recorded on a Fourier transform infrared spectrometer, Tensor 27FT/IR – H1026302 (Bruker OPTKS, GmbH, Germany)). Test samples were pressed between two KBr disks (25mm x 5mm) to give transparent oil films for analysis by FTIR. A regular scanning range of 600-4000cm^{-1} was used for 16 repeated scans of a spectral resolution of 4cm^{-1}. The frequency and intensity of each band was obtained automatically by using the find peak command of the instrument OPUS software.

2.3.6 Pressure Differential Scanning Calorimetric Analysis

Oxidative stability experiments were carried out using pressurized differential scanning calorimetry (PDSC), DSC 2910 thermal analyzer from TA instrument (Newcastle, DE). A 1.5-2.0mg sample that resulted in a film thickness of less than 1mm was placed in an aluminum pan hermetically sealed with a pinhole lid. This was oxidized in the presence of dry air 1,378.95 kPa (200psi) in the static mode. Each experiment utilized a 10^{0}C per minute heating rate from 50^{0}C to 350^{0}C. The oxidation onset (OT^{0}C) and signal maximum temperature (SMT^{0}C) of oxidation were extrapolated from the exotherms in each case. Each sample was run in triplicate and average values rounded to the nearest whole degree are reported.

2.3.7 Gel Permeation Chromatographic Analysis

Polyester molecular weight was determined using SEC system LC-20A from Shimadzu equipped with an SIL-20A autosampler, PL gel 5µm MIXED-D Column (Polymer laboratories, 300mm x 7.5mm, 100, 500, 103 and 104A^0) and an RID-10A refractive index detector in THF(flow rate 1ml/min) at 50^{0}C. All determinations of molecular mass were performed relative to linear poly (methyl methacrylate) standards (Polymer Standard Service, MP102-981.000Da).

3. Results and Discussion

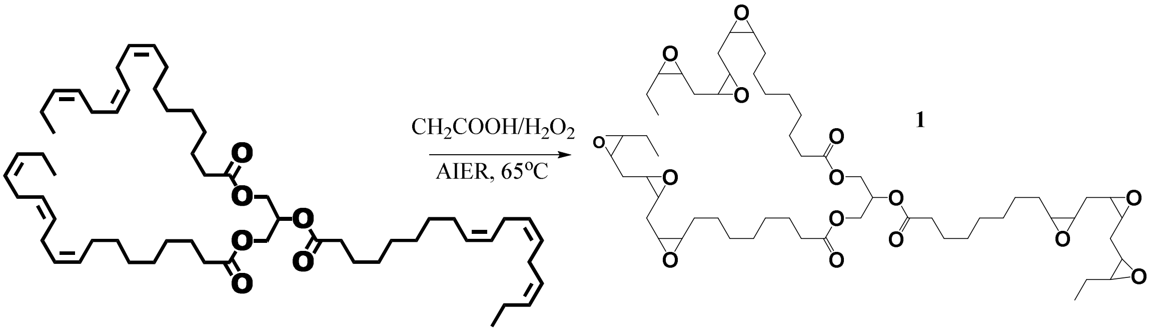
The fatty acid composition of the Plukenetia conophora oil employed in this work has been reported earlier (Akintayo and Bayer, 2002)) as 70.1% linolenic, 17.05% linoleic, 11.7% oleic, 0.6% stearic and 0.8% palmitic acid. With this data available, relevant data like number of moles of carbon-carbon double bonds per mole of triacylglycerol and the average molecule weight of the triglycerides were calculated (Table 1). The information was used to determine catalyst and reagents intakes for the subsequent catalytic modification reactions.

Table 1: Basic data calculated for *Plukenetia conophora* oil based on its fatty acid Composition

Parameter	Value
Average number of moles of double bonds per mole of Triacylglycerol of PKCO	6.3
Average molar mass of fatty acid of PKCO (g)	278.4
Molecular weight of PKCO (g)	873
Number of moles of double bond per 100g PKCO	0.723

The epoxidised PKCO, (Scheme 1) was obtained as a colorless liquid in quantitative yield (95.5 wt%).

Scheme 1: Epoxidation of *Plukenetia conophora* oil using acidic ion exchange resin



Epoxidation experiments were initially carried out with two different carboxylic acids (formic acid and acetic acid) in presence of Amberlite IR-120H, an acidic ion exchange resin (AIER) as catalyst to find out the best carboxylic acid. Other parameters optimized were temperature, acid to ethylenic unsaturation molar ratio, hydrogen peroxide to ethylenic unsaturation molar ratio and the AIER loading. Epoxidation of PKCO was carried out most effectively and with minimum oxirane average using acetic acid - acidic ion exchange resin combination at a temperature of 65^0C, an acetic acid to ethylenic unsaturation molar ratio of 0.5:1, a hydrogen peroxide to ethylenic unsaturation molar ratio of 1.5:1, and a catalyst (AIER) loading of 15wt% of total PKCO used. Under these conditions, ^{1}HNMR showed complete conversion of the carbon-carbon double bonds by the absence of the characteristic peaks of olefinic and allylic hydrogens at ∂_H (ppm) 5.3-5.4 and 2.6-2.8 respectively as shown in Figures 1 and 2.

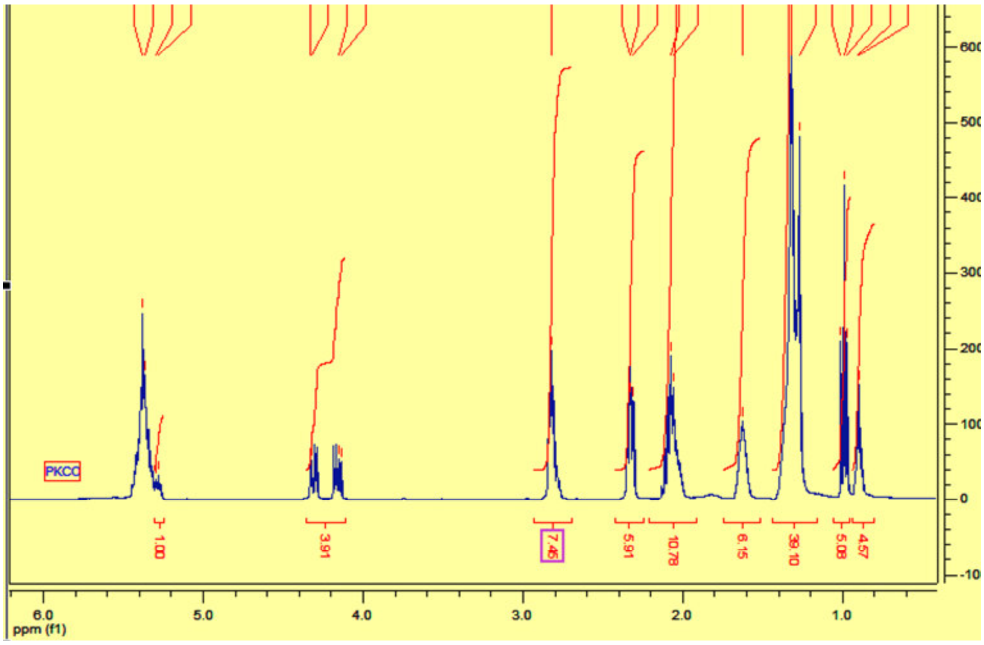


Figure 1: Proton NMR of *Plukenetia conophora* Oil

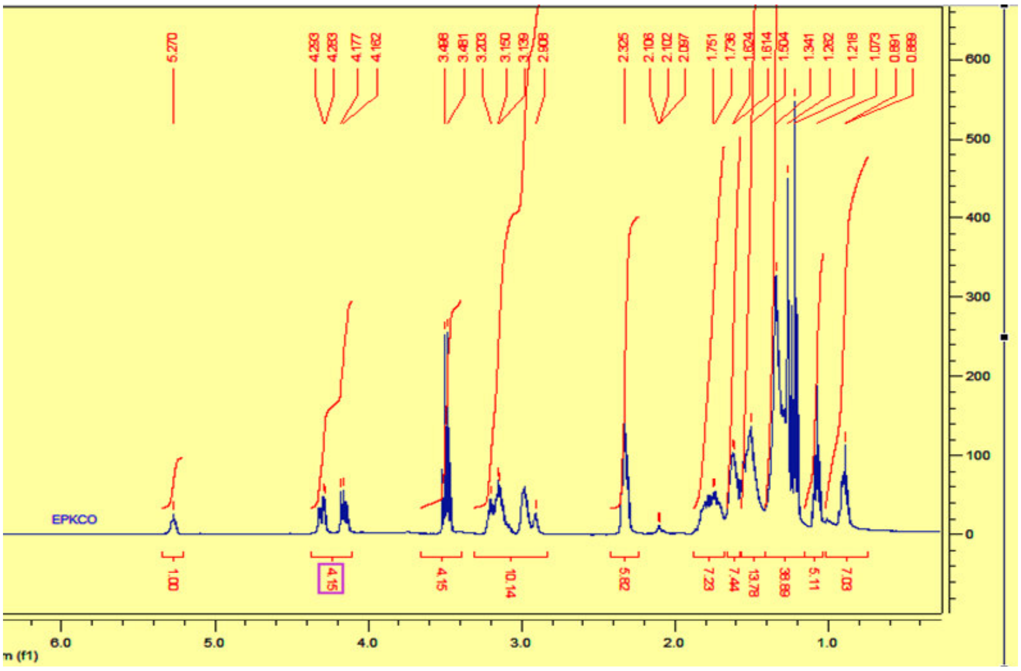


Figure 2: Proton NMR of Epoxidised *Plukenetia Conophora* Oil

New peaks from the hydrogen atoms on the epoxide unit are present in the region 2.8-3.1ppm (fig 2). Figure 2 also shows peaks at 3.4-3.6 due to formation of some diols of indicating opening of some of the epoxy groups. This attack of the oxirane ring by acetic acid in acid catalysed process has generally been observed and reported though the AIER is also known to cause less oxirane ring opening compared to mineral acids (Campamela and Baltanas, 2004). Percentage epoxy in the final product as indicated by figure 2 is 10.14/14.29 =71% and the percentage diol is 29%. These results were corroborated by titrimetric determination of the oxirane oxygen which indicated approximately 71% epoxy oxygen remaining in the final product compared to the thematically predicted oxirane oxygen (Table 2).

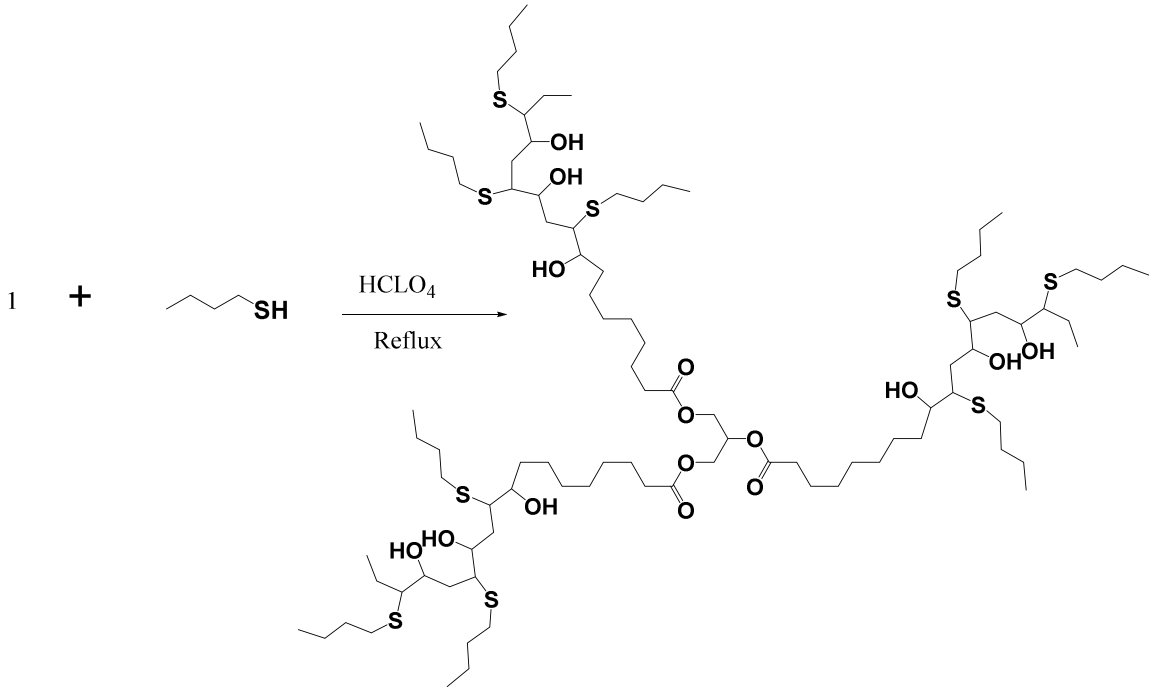
Table 2: Total acid value (TAV) and Oxirane Oxygen (Oox) in *Plukenetia conophora* Oil and some modified products.

	TAV (mgKOH/g)	Oxirane oxygen
PKCO	3.20	-
EPKCO	1.40	7.16, 10.1[b]
BTh PKCO	1.25	0
DTh PKCO	0.50	0
ODTh PKCO	0.45	0

a- experimentally determined oxirane value
b- theotical oxirane value.

Sulfur groups are effective friction and wear reducers and incorporation of sulfur in the triacylglycerol of PKCO is expected to improve the oil friction and wear properties (Savin et al., 1997). The acid catalysed ring opening of the EPKO by a thiol to form the hydroxyl thio-ether derivative is presented in scheme 2.

Scheme 2: Reaction of epoxidised Plukenetia conophora oil with 1-Butanethiol



In the synthesis of the different hydroxyl thio-ether derivatives of PKCO, it is important that the triacylglycerol backbone is retained in order to maintain excellent biodegradable character of the product. Acids generally have the tendency to hydroxyl the ester group; thereby destroying the triacylglycerol (Sharma et al., 2006). But when epoxy group(s) is present on the triacylglycerol chain as we have in epoxidised oils, they are more susceptible to ring opening by the acid catalyst than the hydrolysis of the ester of the triacylyglycerol. Sharma et al. (2006) had also reported that the reaction of the thiol group with the epoxy is more facile as compared with water or alcohol because the nucleophillicity of sulfur is higher than oxygen.

The challenge in this work is therefore to carefully optimize reaction conditions such as catalyst, catalyst amount, reaction temperature, solvent, retention time in a way that leads to the different alkanethiols reacting with the EPKCO to produce the hydroxyl thio-ether derivatives of PKCO without hydrolysis of the ester groups of the EPKCO.

Preliminary experiments to react different alkanethiols with EPCKO in presence of different Lewis acids (BF_3, $AlCl_3$, PCl_5) at both low and elevated temperatures resulted in no change in epoxy peaks in the FTIR which indicated that there was no epoxy ring opening implying that the catalysts did not initiate the thiol reaction with epoxy groups.

As reported by Sharma et al. (Sharma et al., 2006) we also found an oxy acid, $HClO_4$ suitable for the desired reaction, but only at mild reaction temperature 50^0C. Reaction of EPCKO with the different alkanethiols at 50^0C in methylene chloride went to completion at different reaction times, 3, 3.5 and 5hr for butanethiol, decanethiol and octadecanethiol respectively. Titrimetric determination of the oxirane oxygen had indicated that the EPKCO has approximately 7.2 moles of epoxy groups. Hence the maximum amount of thiol that was added in the reactions was 7.2 times per mole of EPKCO. In all cases, excess alkanethiol was removed by successive washings of the sample with methanol, followed by vacuum evaporation of the residual material at 90^0C for 3hr to yield a crude hydroxyl thio-ether product. The reaction progress was monitored by FTIR. The crude hydroxyl thio-ether product was further purified by flash chromatography to yield the purified hydroxy thio-ether product which was then analysed by ^{1}H NMR, FTIR and GPC.

Figure 3 shows the proton NMR spectra of DThPKCO with peak area integration.

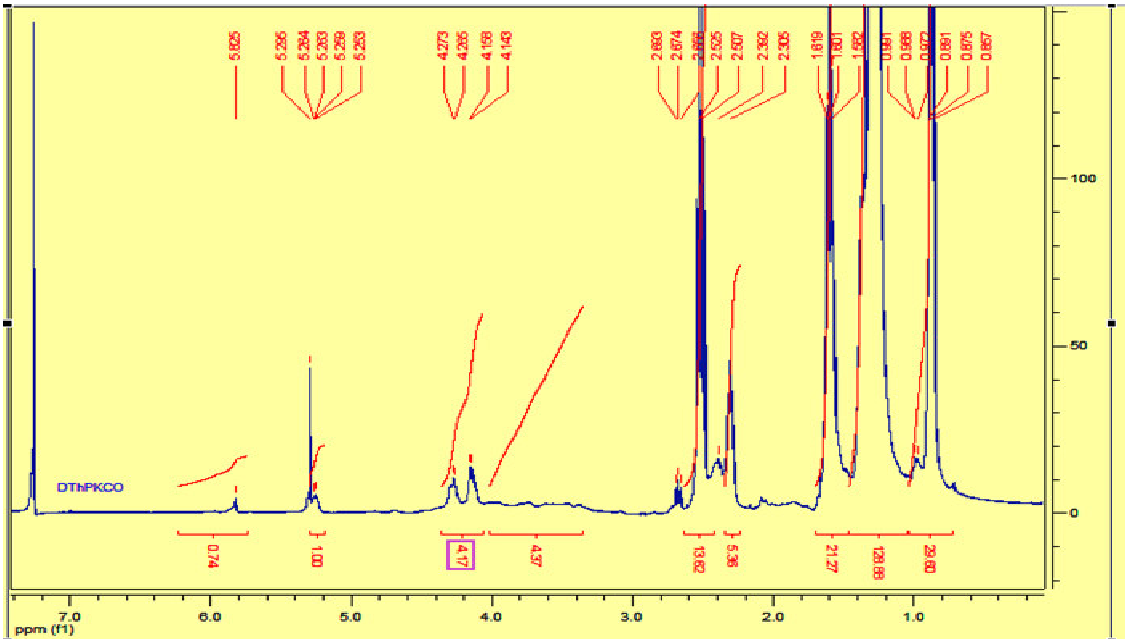


Figure 3: Proton NMR of polyhydroxydecanethiol-ether of *Plukenetia conophora* Oil

DThPKCO retains most of the characteristic peaks of EPKCO except the ones at ∂_H 2.9-3.2 ppm for protons attached to epoxy group, ∂H 1.4-1.5ppm for protons of methylene groups adjacent epoxy group and ∂_H 1.73-1.75ppm for CH_2 protons adjacent to two epoxy groups. Some additional peaks at ∂_H 5.8-5.9ppn corresponding to –OH and broad peaks in the range ∂_H 3.4 – 3.8 ppm from –C$\underline{H}$(OH) were identified. Figure 3 also shows new peaks at ∂_H 2.4-2.6ppm for –CH_2 adjacent to carbons linked to the thio-ether group and ∂_H 2.65-2.70ppm for CH-S-C$\underline{H}_2$ in the product.

By comparing, the proton counts (by integration) of the methylene peak at ∂_H 2.4 – 2.6 ppm for the α –CH_2 to the carbon linked to the thio-ether group and the methyl peak at ∂_H 0.85-0.95 ppm for C$\underline{H}_3$ of the thio-ether branch, it was possible to determine the extent of epoxy ring opening. We reference the integral values to 1.00 for one methine proton of –CH_2 – C$\underline{H}$ - CH_2 backbone at ∂_H 5.1 – 5.3 ppm and obtained an approximate value of 4.0 for the four – CH_2 protons of the backbone at ∂_H 4.1 – 4.3ppm and value of 6.0 for the six protons of α –CH_2 to >C =O at ∂_H 2.2 – 2.4ppm. These values confirmed that the triacylglycerol backbone structure of the vegetable oil was intact. The absence of -C$\underline{H}$ protons of the epoxy ring at ∂_H 2.9-3.2 ppm and an integral value of approximately 14 for α –CH_2 protons to carbon linked to the thio-ether group at ∂_H 2.4-2.6ppm suggested addition of approximately seven molecules of thiol per triacylqlycerol molecule. This was further confirmed by an integral value of approximately 30 for – CH_3 – protons of the thio-ether branch (approximately 21 protons) and fatty acid chains of triacylglycerol (9 protons).

These spectral analyses confirmed that we achieved the controlled ring opening of EPKCO to the desired product of DThPKCO. Similar proton NMR spectra were obtained for the BThPKCO and ODThPKO as presented in Figure 4.

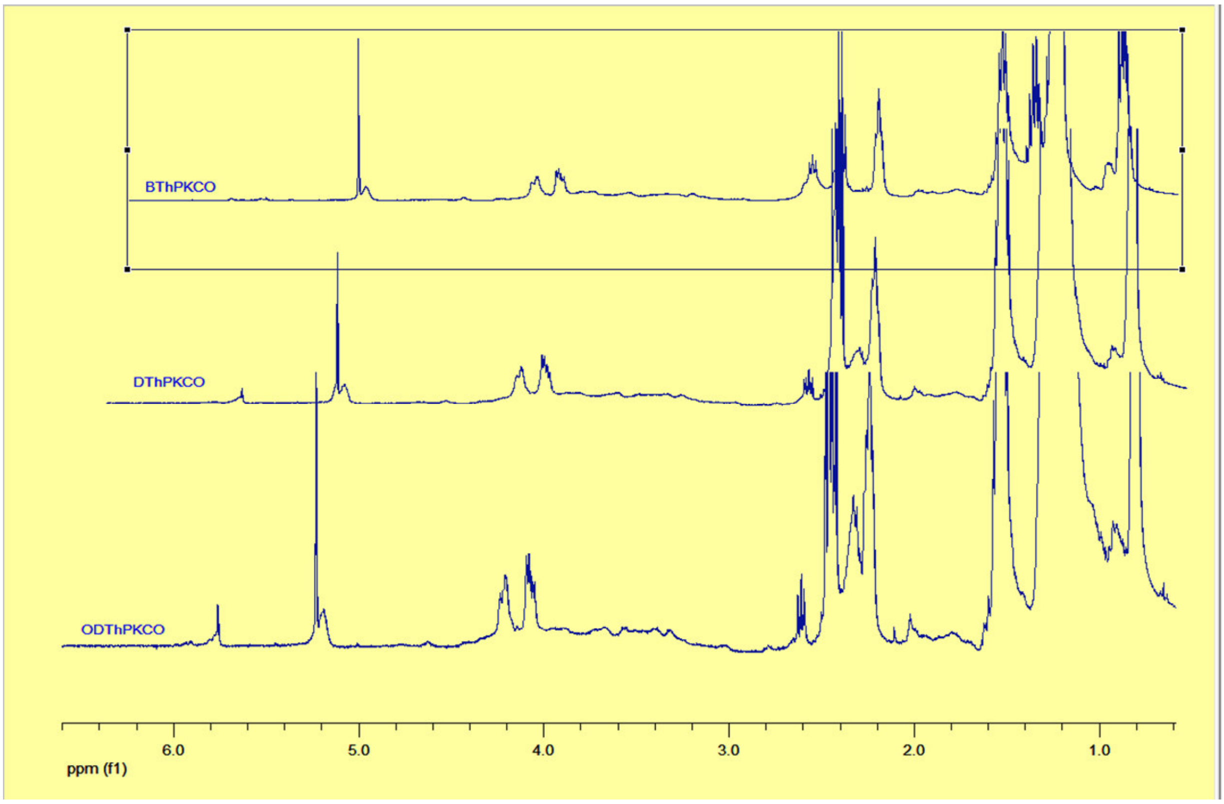


Figure 4: Proton NMR of BThPKCO, DThPKCO and ODThPKCO

FTIR spectra of PKCO, EPKCO and the polyhydroxylalkane thiol ethers are presented in Figure 5.

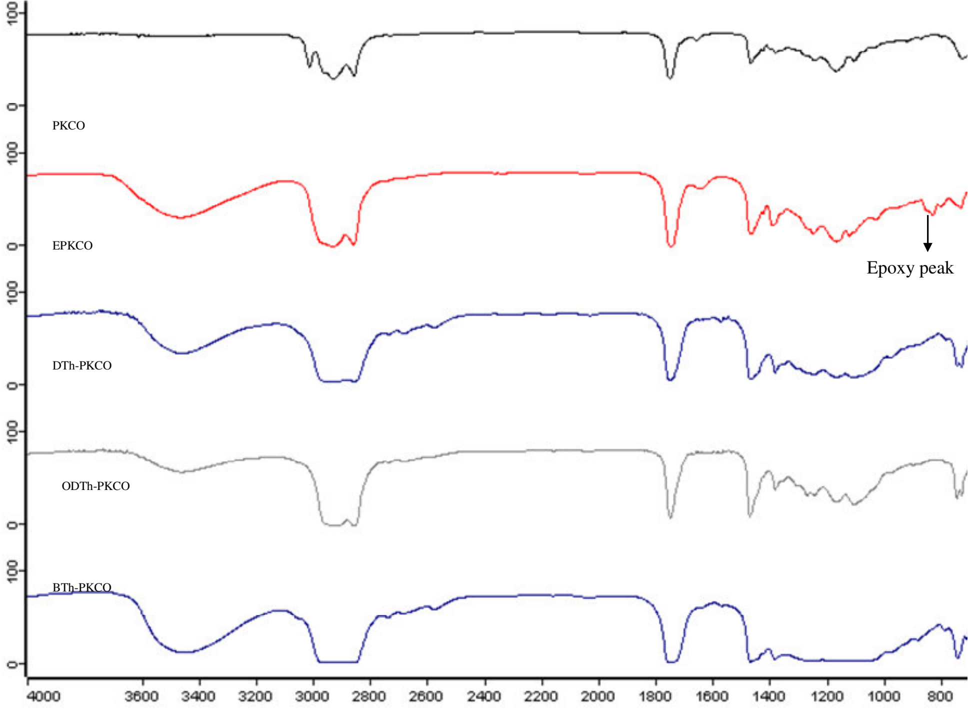
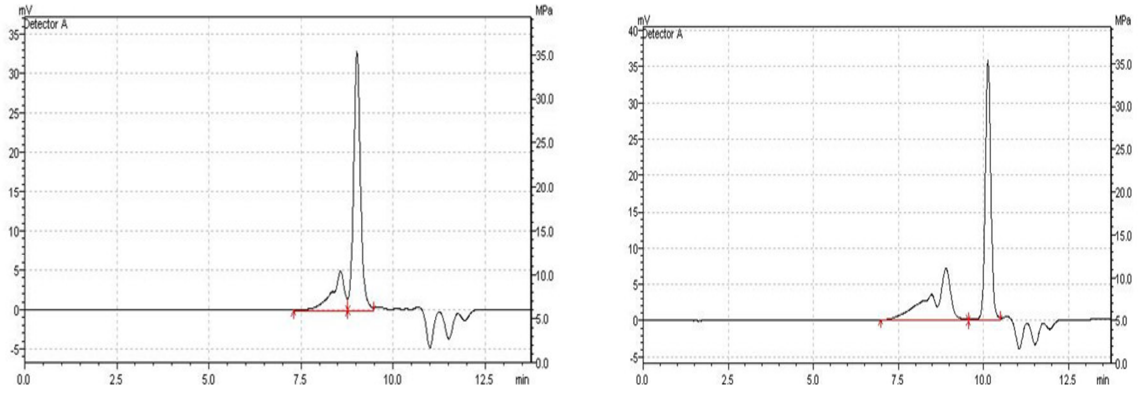


Fig 5: FTIR Spectra of PKCO, EPKCO, BThPKCO, DThPKCO and ODThPKCO

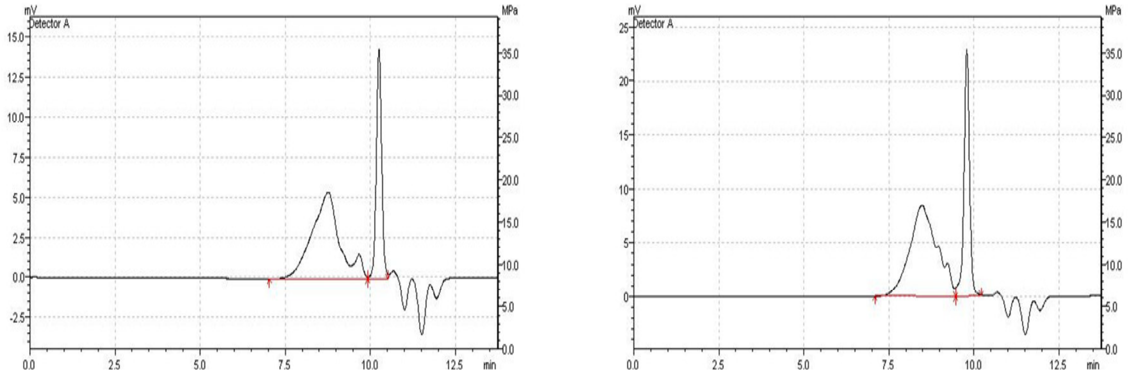
The EPKCO showed the epoxy absorption band at 821cm^{-1}. This peak was however absent in BThPKCO, DThPKCO and ODThPKCO suggesting that the EPKCO underwent a complete epoxy ring opening under the reaction conditions to form the polyhydroxythio ether products. According to scheme 2, the epoxy ring opening would generate hydroxyl groups and this was confirmed by the presence of broad peaks at 3200-3500 cm^{-1}(attributed to hydrogen bonded OH groups) in the FT-IR spectra of BThPKCO, DThPKCO and ODThPKCO. The complete epoxy ring opening was also confirmed results of titrimetric determination of oxirane oxygen. Table 2 shows that while the EPKCO had oxirane oxygen of 7.16, the derivatives all had oxirane oxygen of zero. The total acid value (TAV) of PKCO, EPKCO and the derived products were also determined to confirm if there was formation of free fatty acids during the reaction which would suggest the breakdown of the triacylglycerol backbone. While the PKCO had a TAV of 3.20mgKOH/g, the EPKCO, BThPKCO, DThPKCO and ODThPKCO had TAV of 1.40, 1.25, 0.5 and 0.45mgKOH/g respectively. This further confirms that there was no hydrolysis of the ester linkages and that the triglyceride structure was retained in all the products.

GPC analysis gives information about the formation or otherwise of higher or lower molecular weight products beside the desired product i.e. the epoxide ring opening reactions. The result of the GPC measurements of the EPKCO, BThPKCO, DTHPKCO and ODThPKCO is presented in Figure 5. EPKCO presents a small percentage of higher molecular weight products, likely formed by cross-linking reactions or self polymerization renting of the epoxide groups. The BThPKCO, DThPKCO and ODThPKCO however presented some lower molecular weight products likely resulting from slight decomposition of the oil molecule during the reaction. The percentages of these unwanted products are however small and it is believed that they could be eliminated by more careful control of the reaction conditions.



EPKCO

BThPKCO



DThPKCO

ODThPKCO

Figure 6: GPC traces of EPKCO, BThPKCO, DThPKCO and ODThPKCO

The cold flow properties of the modified PKCO product were determined using cloud and pour point analyses. The results of the measurement are presented in table 3.0. Pour point value for PKCO and EPKCO are -18^{0}C and 6^{0}C respectively. The resulting polyhydroxy alkanethiol derivatives are however characterized by lower pour point. The pour point decreased with increasing chain length of ester until DThPKCO. This may be explained to be due to the increasing steric hindrance thereby preventing crystallization and resulting in lower pour point. The ODThPKCO however led to an unusual increase in pour point having a value of +25^{0}C as compared to the DThPKCO with pour point of -33^{0}C.. The cloud point of PKCO is -12^{0}C. Modification of the oil either by epoxidation or by alkane thiols led to an increase in the value of cloud point. There was however no difference in the cloud point of the modified products.

The Pressure Differential Scanning Calorimetry (PSDC) is widely used in the lubricant industry for measuring oxidative stability (Erhan et al., 2008). The onset temperature of oxidation (OT) is the temperature when a rapid increase in the rate of oxidation is observed in the system while the signal maximum temperature of oxidation (SM) is the temperature at which maximum heat is evolved during the oxidative degradation of the sample (Erhan et al., 2008). The PSDC result of PKCO and the derived products is presented in table 3.0. The epoxidised PKCO and the polyhydroxy alkanethiols derivatives had improved oxidative stability as measured by the OT and SMT values. The increase in oxidation stability may be attributed to the removal of double bond present in the native oil in these samples. However, there was no significant change in the oxidative stability of the products with increase in the chain length of the branching groups.

Table 3.0: Oxidative Stability and Cold flow properties of PKCO and derived products.

Sample	Cloud Point (^0C)	Pour Point (^0C)	Onset Temperature (OT) (^0C)	Signal Maximum Temperature (SM) (^0C)
PKCO	-12	-18	126	145
EPKCO	-3	-16	185	196
BThPKCO	-3	-21	183	190
DThPKCO	-3	-33	180	190
ODThPKCO	ND	+25	181	191

5. Conclusion

Some vegetable oil based derivatives with potentials for useful application have been synthesized by selective reaction between the epoxy group of epoxidised *Plukenetia conophora* oil and some alkanethiols. The reactions were catalysed by $HClO_4$ at 50^0C and optimum time for conversion without crosslinking were 3, 3.5 and 5hr for the butylthio-ether, decylthio-ether and octadecylthio-ether derivatives of *Plukenetia conophora* respectively. The products demonstrated some interesting oxidative stability and cold flow properties that reveal their potential applications as lubricants and industrial oils

References

Akintayo E.T and Bayer E. (2002). Characterisation and some possible uses of Plukenetia conophora and Adenopus breviflorus benth seed oils. Biores. Tech. 85, 95.

Akintayo E.T. (2007). Ethylmethydioxirane epoxidation of Plukenetia conophora oil. Bull Chem. Soc. Ethiop. 21(1), 95-102

Bockish, M., Ed. Fats and Oils handbook, (1998) AOCs Press: Champoin, IL, p 838

Campamela A and Baltanas M.A. (2004). Degradation of the oxirane ring of epoxidised vegetable oils with solvated acetic acid using cation-exchange resin. Eur. J. Lipid Sci. Technol. 106, 524-530

Erhan S.Z., Sharma B.K., Liu Z. Advaryu A. (2008). Lubruicant base stock potential of chemically modified vegetable oils. J. Agric Food Chem., 56, 8919-8925.

Mungro R., Pradham N.C., Goud V.V., Dalai A.K. (2008). Epoxidation of canola oil with hydrogen peroxide catalysed by acidic ion exchange resin. J. Am. Oil Chem. Soc. 85: 887- 896

Paquot C. (1979). Standard methods for the analysis of oils, fats and derivatives part I. 6th edition. Pergamon. Oxford. Pp. 66-70

Salunkhe, D.K., Charon, J.K., Adsule, R.N., Kadam, S.S. (1992). World Oil Seed Chemistry, Technology and Utilization; Van Nastrand Reinhold: New York, Pp 1-8

Savin R., Tuli, D.K., Martin V., Rai M.M., bhatnagar A.K (1997). Development of N, P and S containing multifunctional additivesd for lubricants. Lubr. Eng. 53, 21-26.

Sharma B.K. Adhvaryu A., and Erhan S.Z. (2009). Friction and wear behavior of thioether hydroxy vegetable oil. Tribology International 42, 253-358

Sharma B.K., Adhvaryu A., and Erhan S.Z. (2006) Synthesis of hydroxyl thio-ether derivative of vegetable oil. J. Agric Food Chem.. 54, 9866-9872.

Wakim, J.M. U.S. Pat 3, 986, 966 (Oct 10, 1976).

Willing, A. (2001) Lubricants based on renewable resources – an environmentally compatible alternative to mineral oil products. Chemosphere, 43, 89-98

Zahour, F.A., Normany, H.M. (1988). Vegetable oils and lubricants Grasas Aceites (Senilla) 39, 235 – 238