

A novel class of bio-lubricants are synthesized by epoxidation of 10-undecylenic acid-based esters

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SUMMARY: Mineral-based lubricants are being supplanted by bio-based lubricants because of environmental concerns and the depletion of fossil resources. The derivatives of edible and non-edible oils are considered potential alternatives to existing natural mineral oil base stocks in certain lubricant applications, where immediate interaction with the environment is predicted. A new class of epoxides were synthesized from the undecylenic esters of 2-ethyl hexanol, neopentyl glycol (NPG), and trimethylolpropane (TMP). These unsaturated esters were epoxidized by using meta chloro perbenzoic acid. The synthesized epoxides were characterized by spectral studies (¹HNMR, ¹³CNMR, IR) physio-chemical (density, specific gravity) and lubricant properties (kinematic viscosity, viscosity index, flash point, fire point, cloud point, pour point, copper strip corrosion). TMP epoxide has a high viscosity index, high flash point, and low pour point compared to 2-ethyl hexyl epoxide and NPG epoxide.

KEYWORDS: 2-ethyl hexyl epoxide; Biolubricants; Epoxidation; Esterification; NPG epoxide; TMP epoxide.

RESUMEN: Nueva clase de biolubricantes sintetizados mediante epoxidación de ésteres de ácido 10-undecilénico. Los lubricantes de base biológica están reemplazando a los lubricantes de base mineral debido a preocupaciones ambientales y al agotamiento de los recursos fósiles. Los derivados de aceite comestible y no comestible se consideran alternativas potenciales a las existencias base de aceite mineral natural existentes en ciertas aplicaciones de lubricantes, donde se predice una interacción inmediata con el medio ambiente. Se preparó una nueva clase de epóxidos a partir de ésteres a base de ácido undecilénico de 2-etilhexanol, neopentilglicol (NPG) y trimetilolpropano (TMP) mediante epoxidación con ácido metacloroperbenzoico como catalizador. Los epóxidos sintetizados se caracterizaron mediante estudios espectrales (¹HNMR, ¹³CNMR, IR) las propiedades fisicoquímicas (densidad, densidad específica) y lubricantes (viscosidad cinemática, índice de viscosidad, punto de inflamación, punto de combustión, punto de enturbiamiento, punto de fluidez, tira de cobre, corrosión). El epóxido a base de éster de TMP tiene un índice de viscosidad alto, un punto de inflamación alto y un punto de fluidez bajo en comparación con el epóxido a base de éster 2-etilhexílico y el epóxido a base de éster NPG.

PALABRAS CLAVE: Biolubricantes; Epoxidación, Epóxido; Epóxido a base de éster TMP; Éster de NPG; Propiedades fisicoquímicas.

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1. INTRODUCTION

Lubricants have a tremendous application in day-to-day life, machine-driven and automobile industries. Most of the existing lubricant oils are non-degradable, causing a tremendous effect on the environment. There has been considerable interest in biodegradable lubricants from renewable resources as substitutes for conventional non-renewable mineral-based lubricants. Environmental concerns and the decrease of fossil fuel reserves have triggered great interest in developing bio-based lubricants from renewable resources.

The performance of an engine can be improved by using various edible and non-edible oil-based lubricants. Vegetable oils are renewable resources and are eco-friendly. Synthesized or modified vegetable oil lubricants have been proven to possess excellent lubricant properties for various applications (Anjana and Preeti, 2013). Polyol esters from palm and palm kernel oils have excellent oxidative stability (Yunus *et al.*, 2004). Fatty esters from rubber seed oil and thumba seed oil synthesized from 2-ethyl hexanol, neopentylglycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) are good bio-lubricant base-stocks (Kamalakar *et al.*, 2013; Kamalakar *et al.*, 2015). High-performance polyol ester lubricants were synthesized from 10-Undecenoic acid (Padmaja *et al.*, 2012). The novel class of eco-friendly lubricants was synthesized from undecylenic acid (Cavalcante *et al.*, 2019). The polyol esters of Calophyllum inophyllum oils showed good tribological properties. (Srinivas *et al.*, 2020). Trimethylol triesters from waste cooking oils showed good lubrication properties (Lakkoju and Vemulapalli, 2020). Polyol ester-based bio-lubricants and their blends showed tribological properties (Kotturu *et al.*, 2020).

The double bonds present in synthesized esters undergo auto-oxidation which is susceptible to degradation on prolonged use, thus decreasing the lubricant efficiency. To improve the lubricant efficiency, double bonds present in esters can be modified chemically by epoxidation reaction.

Oils with unsaturated fatty acids were epoxidized using different catalysts. H_2SO_4 was an effective catalyst for forming an oxirane ring in the presence of H_2O_2 across the double bonds in vegetable oils (Abdullah and Salimon, 2010). Cottonseed oil was epoxidized using sulphuric acid (Dinda *et al.*, 2008), peracetic acid (Sinadinović-Fišer

et al., 2012), and soybean fatty methyl esters by performic acid (Campanella *et al.*, 2008), jatropha and castor oils by performic acid and peroxyacetic acid in acid ion exchange resin (Goud *et al.*, 2007). The epoxidation reaction of mahua oil with hydrogen peroxide (H_2O_2) and glacial acetic acid in the presence of an acidic medium was reported (Goud *et al.*, 2006a). Okieimen reported the epoxidation of rubber seed oil using peroxyacetic acid (Okieimen *et al.*, 2002). Vegetable oils such as oil from the Karanja seed (Goud *et al.*, 2006b), soybean oil (Petrovic *et al.*, 2002; Geethanjali *et al.*, 2013), canola oil, canola oil derivatives (Omonov *et al.*, 2016), jatropha seed oil (Goud *et al.*, 2007) and Parkia biglobosa seed methyl esters (Ikhuoria *et al.*, 2007) were also converted to respective epoxidized oils. Epoxidized vegetable oils have various applications as valuable intermediate or end products due to their biodegradability and non-toxicity (Armylisas *et al.*, 2017).

Epoxidized soybean oil exhibited improved low-temperature stability, thermo-oxidative stability friction and wear properties compared to existing lubricants (Erhan *et al.*, 2008, Adhvaryu *et al.*, 2005). Epoxidized jatropha oil showed better antioxidant properties than butylated hydroxyl toluene and zinc dimethyl dithiocarbamate (Sammaiah *et al.*, 2014). Epoxidised Rapeseed oil had superior oxidative stability, better friction reduction and high-pressure abilities (Wu *et al.*, 2000). Epoxidized fatty methyl esters from castor oil have more thermo-oxidative stability than their esters (Venubabu and Goud, 2014). The present study focused on synthesizing a novel class of epoxides from undecylenic esters of 2-ethyl hexanol, NPG and TMP. The synthesized products were assessed for lubricant properties and correlated with their corresponding esters.

2. MATERIALS AND METHODS

2.1. Materials

2-Ethylhexanol, 2,2-Dimethylpropane-1, 3-diol (NPG) and 2-ethyl2-(hydroxyl methyl)-1, and 3-propanediol (TMP) were supplied by ACRO Organics, India. Basic aluminum oxide, dichloromethane (DCM), ethyl acetate, hexane and toluene were supplied by Finar, India. mCPBA (m-chloro per benzoic acid) was supplied by LOBA Chemie, India. Undecylenic acid (UDA) was supplied by SDFCL, Mumbai, In-

dia. Silica gel (60-120 mesh) was supplied by Fisher Scientifics, Ahmadabad, India. Sodium thiosulphate (Hypo) and anhydrous sodium sulphate were supplied by Fisher Scientifics, Mumbai, India. Sodium bicarbonate (NaHCO_3) was supplied by Merck Specialties Pvt. Ltd., Mumbai, India. p-toluene sulphonic acid (pTSA) was supplied by AVRA labs, Hyderabad, India. All the above chemicals, required for synthesis, were used directly and without further purification.

2.2. Methods

2.2.1. Spectral analysis

A 1600 FT-IR Perkin-Elmer spectrometer (Norwalk, CT) was used for recording Infrared (IR) spectra with a liquid film between the NaCl cells. The stretching frequencies of the IR spectra were measured in cm^{-1} . A Bruker AVANCE 400 MHz spectrometer was used to record proton and Carbon - 13 Nuclear Magnetic Resonance Spectra (^1H and ^{13}C NMR) with respect to tetra methyl silane (TMS) an internal standard. The CDCl_3 was used as solvent in ^1H , ^{13}C NMR. The δ values were recorded in parts per million (ppm).

2.2.2. Characterization properties

Physico-chemical, and lubricant properties of synthesized esters and epoxy compounds were determined by standard ASTM (American standard testing method) methods. The density and specific gravity were tested by pycnometer at room temperature. The Kinematic viscosity at various temperatures (40 °C, 100 °C) was tested in a Kinematic viscosity bath. Flash point, and fire point were tested in a Cleveland flash and fire point apparatus. Cloud, and pour point were tested in the automatic cloud and pour point apparatus. Copper strip corrosion was tested in the Copper strip corrosion bath. All the above apparatus were procured from culture instruments India LLP, Bengaluru, India.

2.2.3. Determination of lubricant properties

Kinematic viscosity and viscosity index. The kinematic viscosity was measured at two different temperatures of 40 and 100 °C using an Ostwald direct flow type viscometer tube (type-C, D, E tubes, having definite constant values) in a 'CI' kinematic viscosity bath Digital and calculated according to

the ASTM D 445 method. The viscosity index was calculated according to the ASTM D 2270 method. Measurements were done thrice and average values were taken.

$$\text{Kinematic viscosity} = \frac{\text{constant value of viscometer}}{\times \text{time in seconds}}$$

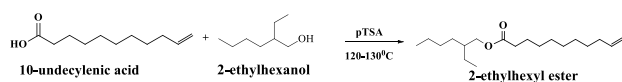
Cloud and pour point. The cloud and pour points were determined according to standard ASTM D 2500, ASTM D 97 methods using a 'CI' ultra crystal cloud and pour point apparatus. The cloud point of the samples was detected automatically in a cloud and pour point apparatus. The pour point of the samples was checked manually for every 1 °C decrease in temperature. Cloud and pour point determinations were made thrice and the average was reported.

Flash and fire points. The flash and fire points were determined according to ASTM D 92 method using a 'CI' Cleveland flash and fire point apparatus. The open-cup method for the detection of flash point was used by means of a vessel, which is exposed to the outside air. The sample was placed in the vessel and the temperature was raised gradually until it flashed and ignited at a certain point. After obtaining the flash point, the sample was heated until the fire came. The flash and fire points of all samples were determined thrice and the average was reported.

Copper strip corrosion. The copper strip corrosion of the samples was determined by using a 'CI' copper strip corrosion test apparatus as per the ASTM 130 method. A polished copper strip was immersed in the sample solution and heated at 100 °C for 3 h. After that, the tarnished copper strip was removed and assessed against an ASTM standard.

Synthesis of 2-ethylhexyl undec-10-enoate (2-ethyl hexyl ester) (a). 0.3839 moles of 2-ethyl hexanol (50 g), 0.5759 moles of UDA (106 g), 1% pTSA (total weight of 2-ethyl hexanol and UDA, 1.56 g) and toluene (100 mL) in an RB flask were refluxed at 120-130 °C. The reaction proceeded at 120-130 °C until 7 mL of water were collected in the dean-stark apparatus. The reaction progress was checked by observing thin layer chromatography (TLC) with 9:1 v/v hexane and ethyl acetate as eluent at regular intervals. After reaching the required product temperature of the reaction mixture, it was decreased to 23-25 °C. The toluene present in the reaction mixture was removed by a vacuum. The

excess or unreacted acid in the reaction mixture was neutralised using a saturated NaHCO_3 solution, and ethyl acetate was added to the aqueous solution. The organic (ethyl acetate) layer, which contained crude 2-ethyl hexyl ester, was separated using a separating funnel and thoroughly washed with water twice. Anhydrous sodium sulphate was used to remove moisture from the crude (2-ethyl hexyl ester) present in the organic layer. The crude 2-ethyl hexyl ester was purified by using the column chromatography technique. Basic aluminum oxide was used as a stationary phase, 10% ethyl acetate in hexane was used as a mobile phase in column chromatography. 96.8 g of pure 2-ethyl hexyl ester were obtained. The 2-ethyl hexyl ester was assessed by ^1H NMR, ^{13}C NMR and IR spectral studies.



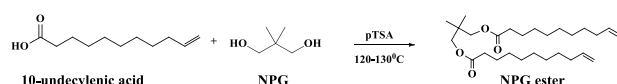
^1H NMR spectra: 0.8-9.0 (t, 6H, $-\text{CH}_3$), 1.2-1.6 (m, 18H, $-\text{CH}_2-$), 2.0-2.1 (m, 3H, $\text{C}=\text{C}-\text{CH}_2$) and $-\text{CH}(\text{CH}_2)_3$, 2.3-2.4 (t, 2H, $-\text{CO}-\text{CH}_2-$), 3.9-4.0 (m, 2H, $-\text{O}-\text{CH}_2-$), 4.9-5.0 (m, 2H, $\text{CH}=\text{CH}_2$), 5.7-5.8 (m, 1H, $-\text{CH}=\text{CH}_2$).

^{13}C NMR spectra: 66.5 ($\text{O}-\text{CH}_2$), 115.10 ($\text{CH}=\text{CH}_2$), 139.27 ($\text{CH}=\text{CH}_2$), 173.44 ($\text{C}=\text{O}$).

IR spectra: 3020 (str, $\text{C}=\text{C}-\text{H}$), 2929-2857 (str, $-\text{C}-\text{H}$), 1727 (str, $\text{C}=\text{O}$), 1217 (str, $\text{C}-\text{O}-\text{C}$), 771 ($\text{C}-\text{C}$).

Synthesis of 2,2-dimethylpropane-1,3-diyl diundec-10-enoate (NPG ester)(b). 0.678 moles of NPG (70.6 g), 1.356 moles of UDA (250 g), 1% pTSA (total weight of NPG and UDA, 3.2 g) and toluene (100 mL) were refluxed in a RB flask at 120-130 °C. The reaction took place at 120-130 °C until 24 mL of water were collected in the dean-stark apparatus. The reaction progress was monitored by observing TLC with 9:1 v/v hexane and ethyl acetate as eluent at regular intervals. After the formation of ester, the temperature of the reaction mixture was decreased to 23-25 °C. The toluene present in the reaction mixture was removed by vacuum. Ethyl acetate was added to the neutralized excess or unreacted acid present in the reaction mixture with a saturated NaHCO_3 solution in the aqueous solution. The organic (ethyl acetate) layer, which contains crude NPG ester, was separated

using a separating funnel and thoroughly washed with water twice. Anhydrous sodium sulphate was used to remove moisture from the crude (NPG ester) present in the organic layer. The crude NPG ester was purified using the column chromatography technique. Basic aluminum oxide was used as stationary phase, 10% ethyl acetate in hexane was used as a mobile phase in column chromatography. 245 g pure NPG ester were obtained. The NPG ester was assessed by ^1H NMR, ^{13}C NMR and IR spectral studies.



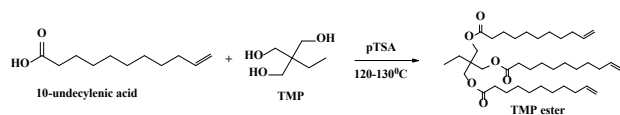
^1H NMR spectra: 0.9 (s, 6H, $-\text{CH}_3$), 1.2-1.4(m, 20H, $-\text{CH}_2-$), 1.5-1.6(m, 4H, $-\text{CO}-\text{CH}_2-\text{CH}_2-$), 2.0-2.1(q, 4H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 2.3-2.4(t, 4H, $-\text{CO}-\text{CH}_2-$), 3.9(s, 4H, $-\text{O}-\text{CH}_2-$), 4.9-5.0(m, 4H, $-\text{CH}=\text{CH}_2$), 5.7-5.9 (m, 2H, $-\text{CH}=\text{CH}_2$).

^{13}C NMR spectra: 68.76 ($\text{O}-\text{CH}_2$), 114.78 ($\text{CH}=\text{CH}_2$), 139.09 ($\text{CH}=\text{CH}_2$), 172.76 ($\text{C}=\text{O}$).

IR spectra: 3021(str, $\text{C}=\text{CH}$), 2927 (str, $\text{C}-\text{H}$), 1736 (str, $\text{C}=\text{O}$), 1214(str, COC), 755 ($\text{C}-\text{C}$).

Synthesis of 2-ethyl-2-((undec-10-enoyloxy)methyl)propane-1,3-diyl diundec-10-enolate (TMP ester) (c). 0.378 moles of TMP (52 g), 1.356 moles of UDA (250 g), 1% pTSA (total weight of NPG and UDA, 3.02 g) and toluene (100 mL) in a RB flask were refluxed at 120-130 °C. The reaction proceeded at 120-130 °C until 21 mL of water were collected in the dean-stark apparatus. The reaction progress was monitored by observing TLC with 9:1 v/v hexane and ethyl acetate as eluent at regular intervals. The temperature of the reaction mixture decreased to 23-25 °C. The toluene present in the reaction mixture was removed by vacuum. Ethyl acetate was added to the neutralized excess or unreacted acid in the reaction mixture using a saturated NaHCO_3 solution, in the aqueous solution. The organic (ethyl acetate) layer, which contains crude TMP ester, was separated using a separating funnel and thoroughly washed with water twice. Anhydrous sodium sulphate was used to remove moisture from the crude (TMP ester) present in the organic layer. The crude TMP ester was purified by using the column chromatography technique. Basic aluminum oxide was used as a sta-

tionary phase, 10% ethyl acetate in hexane was used as a mobile phase in column chromatography. 208 g of pure TMP ester were obtained. The TMP ester was assessed by ^1H NMR, ^{13}C NMR and IR spectral studies.

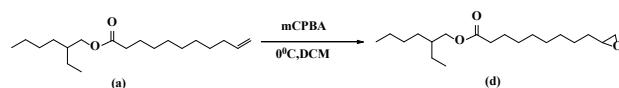


^1H NMR spectra: 0.8-1.0 (t, 3H, $-\text{CH}_3$), 1.2-1.3 (m, 30H, $-\text{CH}_2-$), 1.3-1.4 (m, 2H, CH_3-CH_2-), 1.5-1.7 (m, 6H, $-\text{CO}-\text{CH}_2-\text{CH}_2-$), 2.0-2.1 (q, 6H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 2.3-2.4 (t, 6H, $-\text{CO}-\text{CH}_2-$), 3.9 (s, 6H, $-\text{O}-\text{CH}_2-$), 4.9-5.0 (m, 6H, $-\text{CH}=\text{CH}_2$), 5.7-5.8 (m, 3H, $-\text{CH}=\text{CH}_2$).

^{13}C NMR spectra: 63.32 (O- CH_2), 114.20 (CH= CH_2), 138.69 ($\text{CH}=\text{CH}_2$), 171.97 ($\text{C}=\text{O}$).

IR spectra: 3021 (str, C=CH), 2927 (str, C-H), 1741 (str, C=O), 1162 (str, COC), 758 (C-C).

Synthesis of 2-ethylhexyl 9-(oxiran-2-yl) nonanoate (2-ethyl hexyl epoxide)(d). 2-ethyl hexyl ester (a) (35 g, 0.1146 moles) 175 mL of DCM (10 vol with respect to ester) were taken in a 1L RB flask and cooled to 0 °C. mCPBA (65% purity, 49 g, 0.1720 moles) was added to the reaction mixture at regular intervals for 3 h to maintain the temperature at 0 °C. The reaction was kept at ambient temperature and stirred overnight. The reaction progress was monitored by observing TLC. The reaction mixture was cooled to 0 °C. After completion of the reaction, the precipitated m-chloro benzoic acid was filtered. Ethyl acetate was added to the filtrate with 10% sodium thiosulphate solution, and then stirred thoroughly. The organic (ethyl acetate) layer was separated and washed twice with distilled water. The organic layer was dried over anhydrous sodium sulphate to remove moisture and concentrated under reduced vacuum to obtain crude 2-ethyl hexyl epoxide. Silica gel column chromatography was used to purify crude 2-ethyl hexyl epoxide with 1:1 ethyl acetate and hexane as an eluent to obtain 26 g of pure 2-ethyl hexyl epoxide. The pure 2-ethyl hexyl epoxide was assessed by ^1H NMR, ^{13}C NMR, IR spectral studies, and analyzed for physicochemical and basic lubricant properties.

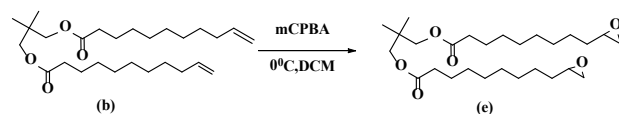


^1H NMR spectra: 0.9 -1.0 (t, 6H, $-\text{CH}_3$), 1.2-1.4 (m, 19H, $-\text{CH}_2-$ and $-\text{CH}(\text{CH}_2)_3$), 1.5-1.7 (m, 2H, $\text{H}_C-\text{HC}(\text{OCH}_2)$), 2.0-2.1 (t, 2H, $-\text{CH}_2\text{C}=\text{O}$), 2.3-2.5 (m, 2H, H_C-OCH_2), 2.7 (d, 1H, H_C-OCH_2), 4.0-4.15 (m, 2H, $-\text{CH}-\text{O}-\text{C}=\text{O}$).

^{13}C NMR spectra: 68.17 (O- CH_2), 46.43 (CHOCH_2), 51.85 (CHOCH_2), 173.20 ($\text{C}=\text{O}$).

IR spectra: 1724 (str, C=O), 1216 (str, $\text{C}-\text{O}-\text{C}$), 757 (C-C).

Synthesis of 2,2-dimethyl propane-1,3-diyl bis (9-(oxiran-2-yl) nonanoate (NPG epoxide) (e). NPG ester (b) (50 g, 0.1146 moles) 250 mL DCM (10 vol with respect to ester) were taken in a 1L RB flask and cooled to 0 °C. mCPBA (65% purity, 130 g, 0.4535 moles) was added to the reaction mixture at regular intervals for 3 h to maintain the temperature at 0 °C. It was allowed to cool to ambient temperature and stirred overnight. The reaction progress was monitored by observing TLC. The reaction mixture was cooled to 0 °C. After completion of the reaction, the precipitated m-chloro benzoic acid was filtered. A 10% sodium thiosulphate solution was added to the filtrate, along with ethyl acetate and stirred thoroughly. The organic (ethyl acetate) layer was separated and washed twice with distilled water. The organic layer was dried over anhydrous sodium sulphate to remove moisture and concentrated under reduced vacuum to obtain crude NPG epoxide. Silica gel column chromatography was used to purify crude NPG epoxide with 1:1 ethyl acetate and hexane as an eluent to obtain 36 g of pure NPG epoxide. The pure NPG epoxide was assessed by ^1H NMR, ^{13}C NMR, IR spectral studies, analyzed for physicochemical and basic lubricant properties.

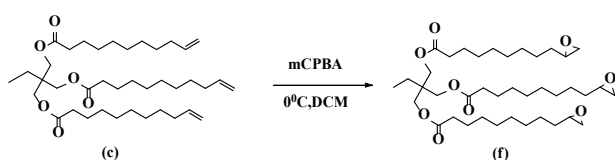


¹HNMR spectra: 0.98 (s, 6H, -CH₃), 1.3-1.4 (m, 24H, -CH₂-), 1.4-1.5 (m, 4H, H₃C—HC₂CH₂), 1.6-1.7 (m, 4H, -CH₂-CH₂C=O), 2.3-2.4 (4H, t, -CH₂C=O), 2.7-2.8 (m, 2H, HC₂CH₂), 2.9-3.0 (t, 4H, HC₂CH₂), 3.9 (s, 4H, -CH₂-O-C=O).

¹³C NMR spectra: 68.56 (O-CH₂), 46.44 (CHOCH₂), 51.86 (CHOCH₂), 172.94 (C=O).

IR spectra: 1727 (str, C=O), 1258 (str, C₂O), 755 (C-C).

Synthesis of 2-ethyl-2-((9-(oxiran-2-yl) nonanoxy) methyl) propane-1, 3-diyl (9-(oxiran-2-yl) nonanoate) (TMP epoxide)(f). TMP ester (c) (50 g, 0.0738 moles) 250 mL DCM (10 vol with respect to ester) were taken in a 1L RB flask and cooled to 0 °C. mCPBA (65% purity, 135 g, 0.4737 moles) was added to the reaction mixture at regular intervals for 3 h to maintain the temperature at 0 °C. The reaction was allowed to cool to ambient temperature and stirred overnight. The reaction progress was monitored by observing TLC. The reaction mixture was cooled to 0°C after completion of the reaction, and the precipitated m-chloro benzoic acid was filtered. A 10% sodium thiosulphate solution and ethyl acetate were added to the filtrate and stirred thoroughly. The organic (ethyl acetate) layer was separated and was washed twice with distilled water. The organic layer was dried over anhydrous sodium sulphate to remove moisture and concentrated under reduced vacuum to obtain crude TMP epoxide. Silica gel column chromatography was used to purify the crude TMP epoxide with 1:1 ethyl acetate and hexane as an eluent to obtain 35 g of pure TMP epoxide. The pure TMP epoxide was assessed by ¹HNMR, ¹³C NMR, IR spectral studies, and then analyzed for physicochemical and basic lubricant properties.



¹HNMR spectra: 0.9 (t, 3H, -CH₃), 1.3-1.4 (m, 32H, -CH₂-), 1.4-1.5 (m, 6H, H₃C—HC₂CH₂), 1.6-1.7 (m, 6H, -CH₂-CH₂C=O), 2.3-2.4 (t, 6H, -CH₂C=O), 2.7-2.8 (m, 3H, HC₂CH₂), 2.9-3.0 (t, 6H, HC₂CH₂), 4.0 (s, 3H, -CH-O-C=O).

¹³C NMR spectra: 68.19 (O-CH₂), 46.49 (CHOCH₂), 51.92 (CHOCH₂), 172.89 (C=O).

IR spectra: 1738 (str, C=O), 1256 (str, C₂O), 751 (C-C).

3. RESULTS AND DISCUSSION

Vegetable oils and synthesized polyol esters possess good lubricity, high viscosity index, and flash point along with lower volatility. In vegetable oils, the presence of a high degree of unsaturation lowers thermal and oxidative stability, which can be improved by the chemical modification of unsaturation such as epoxidation. Epoxidized castor oil possesses enhanced lubricity properties such as high density, viscosity and low pour point (Venubabu and Goud, 2014). Keeping this in mind, undecylenic acid-based epoxides of 2-ethyl hexanol, NPG and TMP based esters were developed. Undecylenic acid, a second-generation product of castor oil, was a suitable feedstock to prepare many novel products for various applications. Upon pyrolysis, castor oil gives undecylenic acid. Various esters are prepared from undecylenic acid using different alcohols such as 2-ethyl hexanol, NPG and TMP in the presence of pTSA. The yields of synthesized esters were in the range of 75-80%. A peak corresponding to ester O-CH₂ protons in ¹HNMR was observed at 3.9-4.0 ppm in 2-ethyl hexyl ester, 3.9 ppm in NPG ester, and 3.9 ppm in TMP ester. Multiple peaks corresponding to unsaturation were observed at 4.9-5.0 ppm, 5.7-5.8 ppm in 2-ethyl hexyl ester and TMP ester, 4.9-5.0 ppm and 5.7-5.9 ppm in NPG ester was observed (Figure 1). In the ¹³C NMR spectrum (Figure 2), the carbon signal for unsaturation was observed at the 115.10 ppm CH₂ peak, 139.27 ppm CH peak in 2-ethyl hexyl ester, 114.78 ppm CH₂ peak and 139.09 ppm for the CH peak in the NPG ester, 114.20 ppm CH₂ peak and 139.69 ppm or CH peak for TMP ester. A peak was observed at 173.44 ppm for 2-ethyl hexyl ester, 172.76 ppm for NPG ester, 171.97 ppm for NPG ester-assisted r C=O indicated ester linkage. C=O stretching

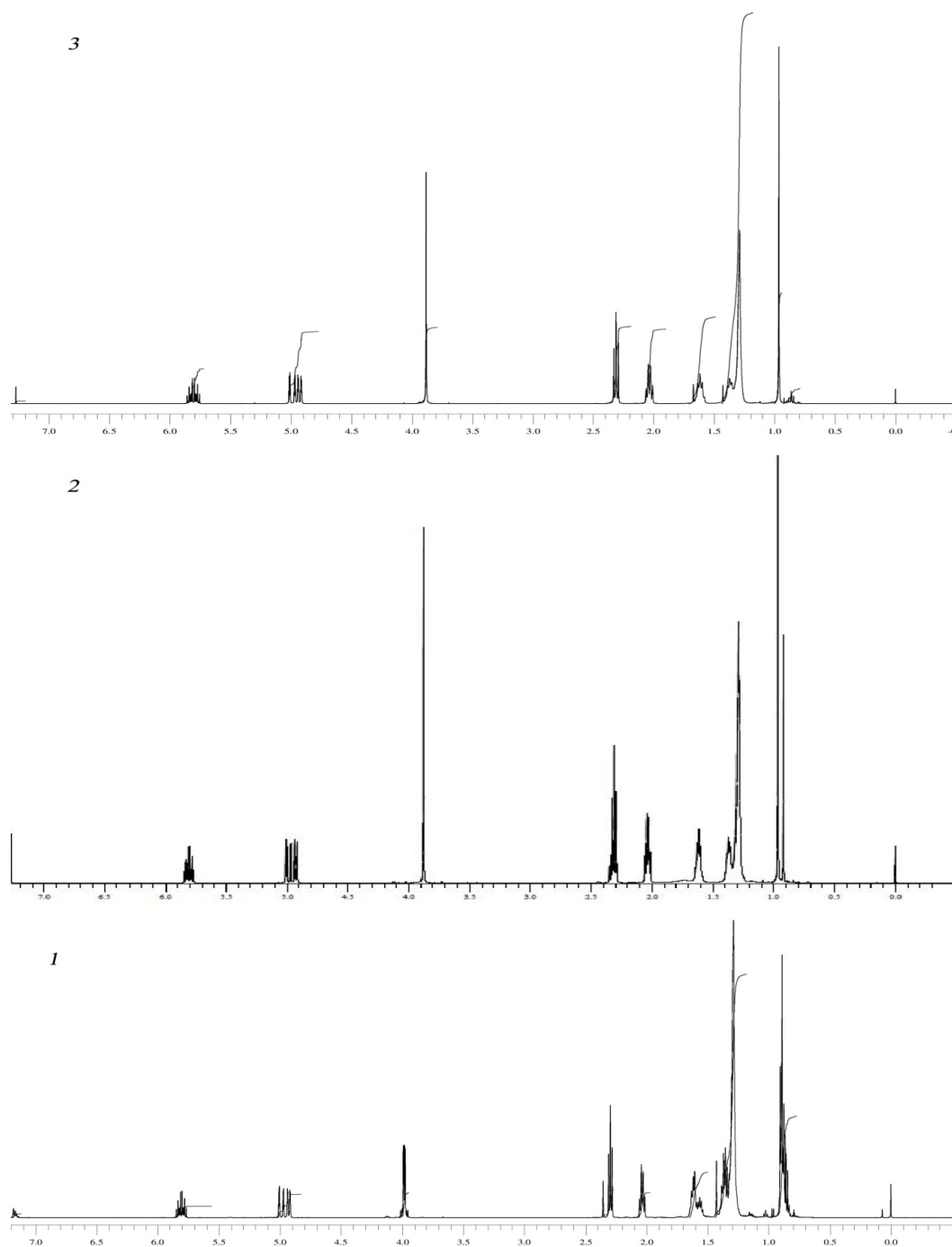


FIGURE 1. ¹H NMR spectra of various esters. 1) 2-ethyl hexyl ester, 2) NPG ester and 3) TMP ester

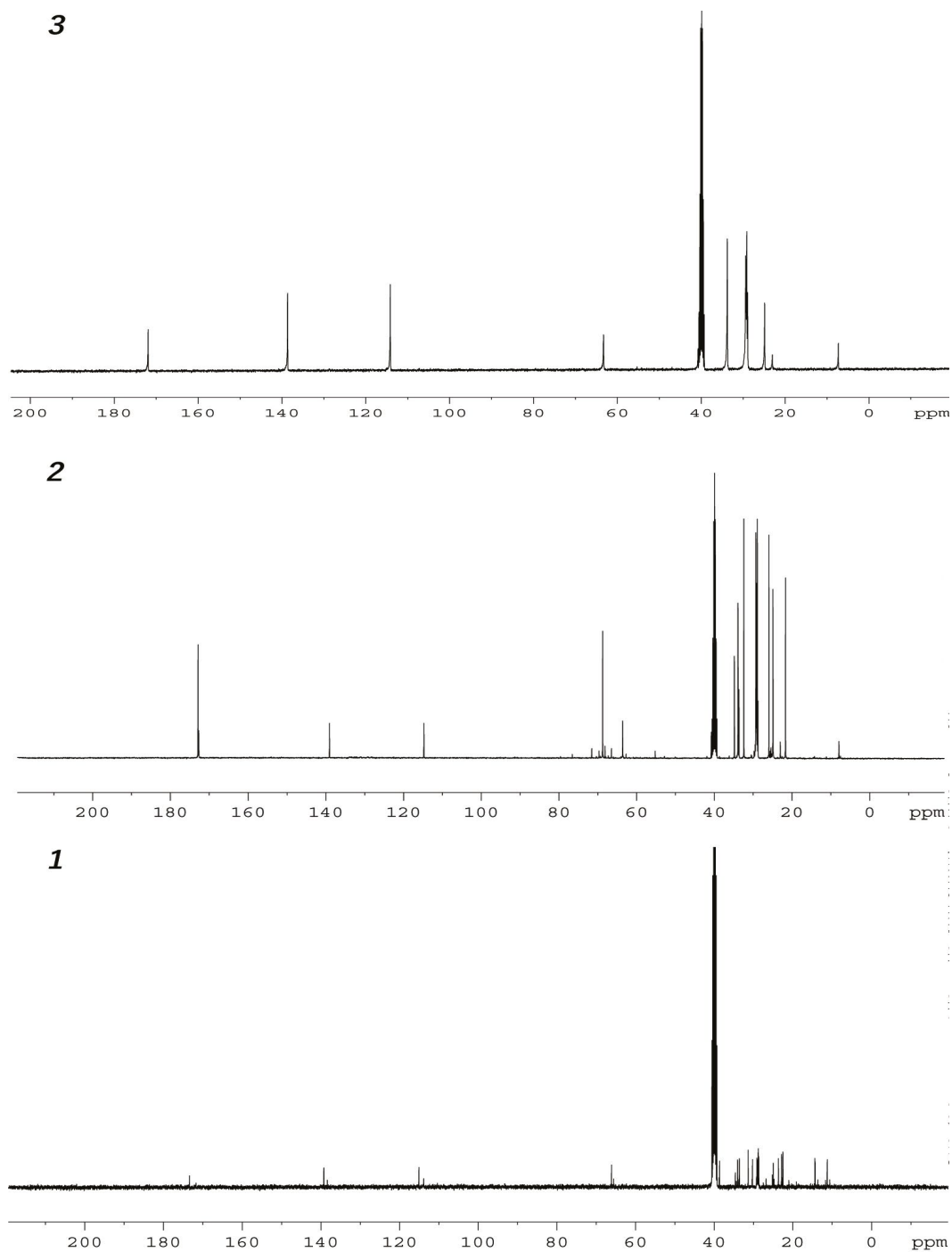


FIGURE 2. ¹³C NMR spectra of various esters. 1) 2-ethyl hexyl ester, 2) NPG ester and 3) TMP ester

was observed in the IR spectrum at 1727 cm^{-1} for 2-ethyl hexyl ester, 1736 cm^{-1} for NPG ester and 1741 cm^{-1} for TMP ester. C=C-H stretching at 3020 cm^{-1} for 2-ethyl hexyl ester, 3021 cm^{-1} for NPG ester and 3021 cm^{-1} for TMP ester were observed in the IR spectra, which confirmed the unsaturation group (Figure 3).

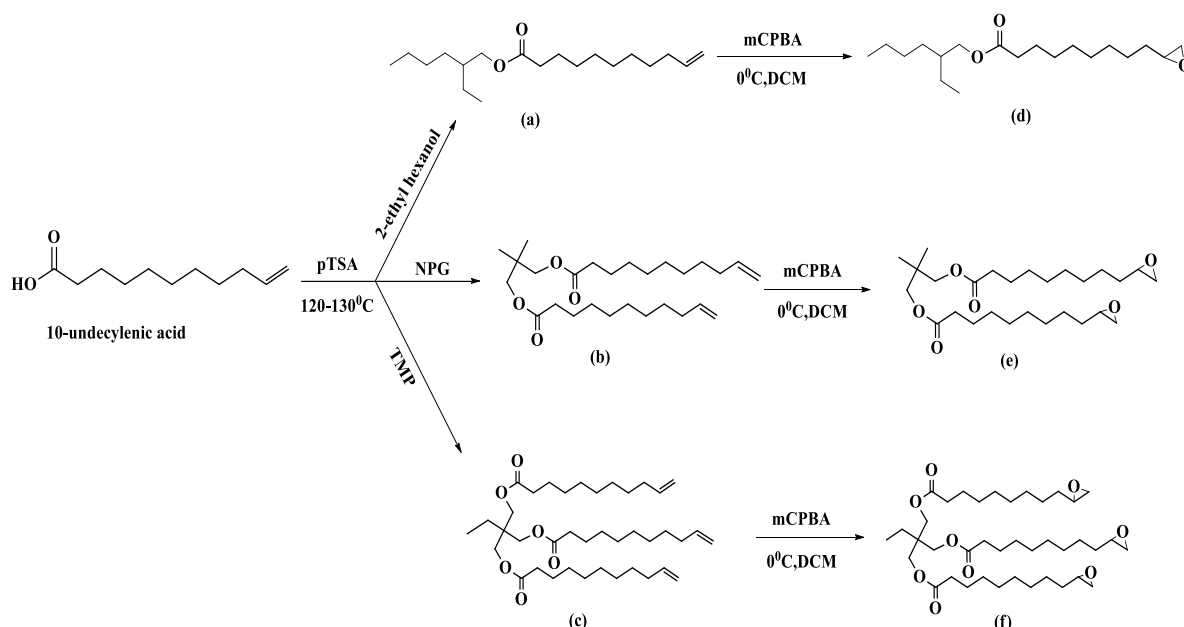
These esters were epoxidized using mCPBA in the presence of DCM. TLC is used to monitor the progress of the reaction. After completion, the reaction mixture was quenched with hypo and extracted with ethyl acetate. The organic layer (Ethyl acetate) was concentrated using a high vacuum to afford crude epoxide, and was purified by column chromatography.

The yields of synthesized epoxides were in the range of 70-75%. The epoxidized 2-ethyl hexanol, NPG and TMP based esters (Scheme-1) were characterized using $^1\text{H NMR}$ (Figure 4) $^{13}\text{C NMR}$ (Figure 5) and IR (Figure 6) spectral studies. The presence of epoxide ring protons in $^1\text{H NMR}$ was observed at 2.3-2.4 ppm as multiplet, 2.7-2.8 ppm doublet in 2-ethyl hexyl epoxide, 2.7-2.8 ppm as multiplet, 2.9-3.0 ppm as triplet in NPG epoxide, 2.7-2.8 ppm as multiplet, 2.9-3.0 ppm as triplet in

TMP epoxide. The multiplet at 5.0-5.5 ppm due to alkene proton in esters (a-c) disappeared in all epoxides, indicating the conversion of the alkene group to oxirane ring (d-f). In the $^{13}\text{C NMR}$ spectrum, two new peaks were observed at 46.43 ppm, 51.85 ppm in 2-ethyl hexyl epoxide, 46.44 ppm, 51.86 ppm in NPG epoxide, 46.46 ppm, 51.92 ppm in TMP epoxide, indicating carbon atoms for oxirane. The carbon signals at 114 ppm and 139 ppm for unsaturation in esters was absent, indicating the conversion of a double bond to oxirane.

The existence of $\text{C}-\text{O}-\text{C}$ stretching at 1216 cm^{-1} in the 2-ethyl hexyl epoxide, 1258 cm^{-1} in the NPG epoxide, and 1256 cm^{-1} in TMP epoxide observed in the IR spectra confirm the presence of the epoxide group. All synthesized epoxides were analyzed for physicochemical and lubricant properties. All properties were triplicated and data correspond to the mean of three determinations plus or minus standard deviation (Table 1).

Density. Density is a crucial property for all lubricant oils. Density was determined by means of a pycnometer at room temperature. The densities of 2-ethyl hexyl, NPG and TMP ester-based epoxides were 1.0351 ± 0.0004 , 1.0446 ± 0.0006 and 1.1606



Scheme-1: Preparation of various epoxides from 10-undecylenic acid

(a) 2-Ethylhexyl undec-10-enoate, (b) 2,2-Dimethyl propane-1,3-diyl diundec-10-enoate, (c) 2-Ethyl-2-((undec-10-enoyloxy)methyl)propane-1,3-diyl diundec-10-enoate, (d) 2-ethylhexyl 9-(oxiran-2-yl)nonanoate, (e) 2,2-dimethylpropane-1,3-diylbis(9-(oxiran-2-yl)nonanoate), and (f) 2-ethyl-2-((9-(oxiran-2-yl)nonanoxyl)methyl)propane-1,3-diyl(9-(oxiran-2-yl)nonanoate)

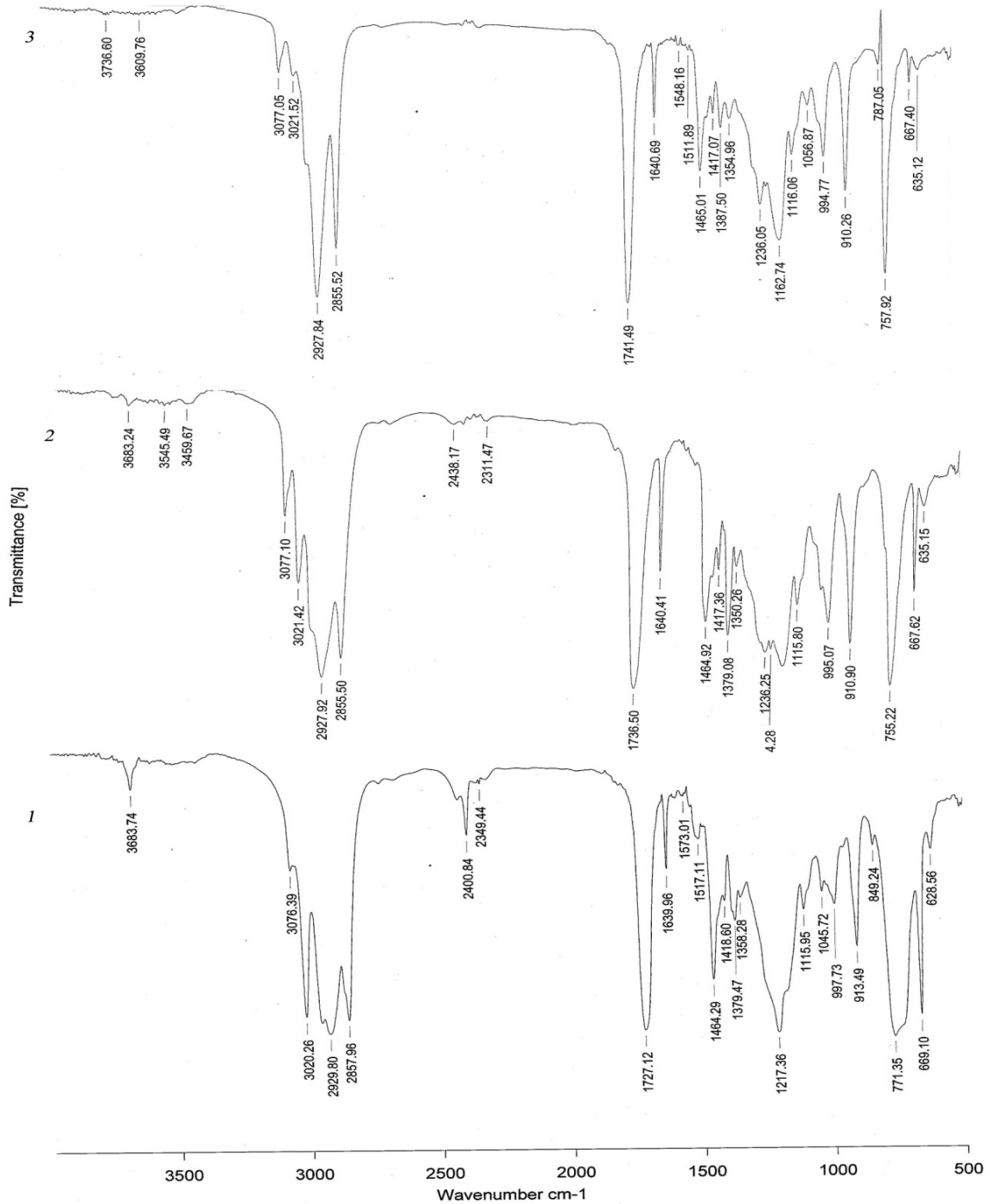


FIGURE 3. IR spectra of various esters. 1) 2-ethyl hexyl ester, 2) NPG ester and 3) TMP este

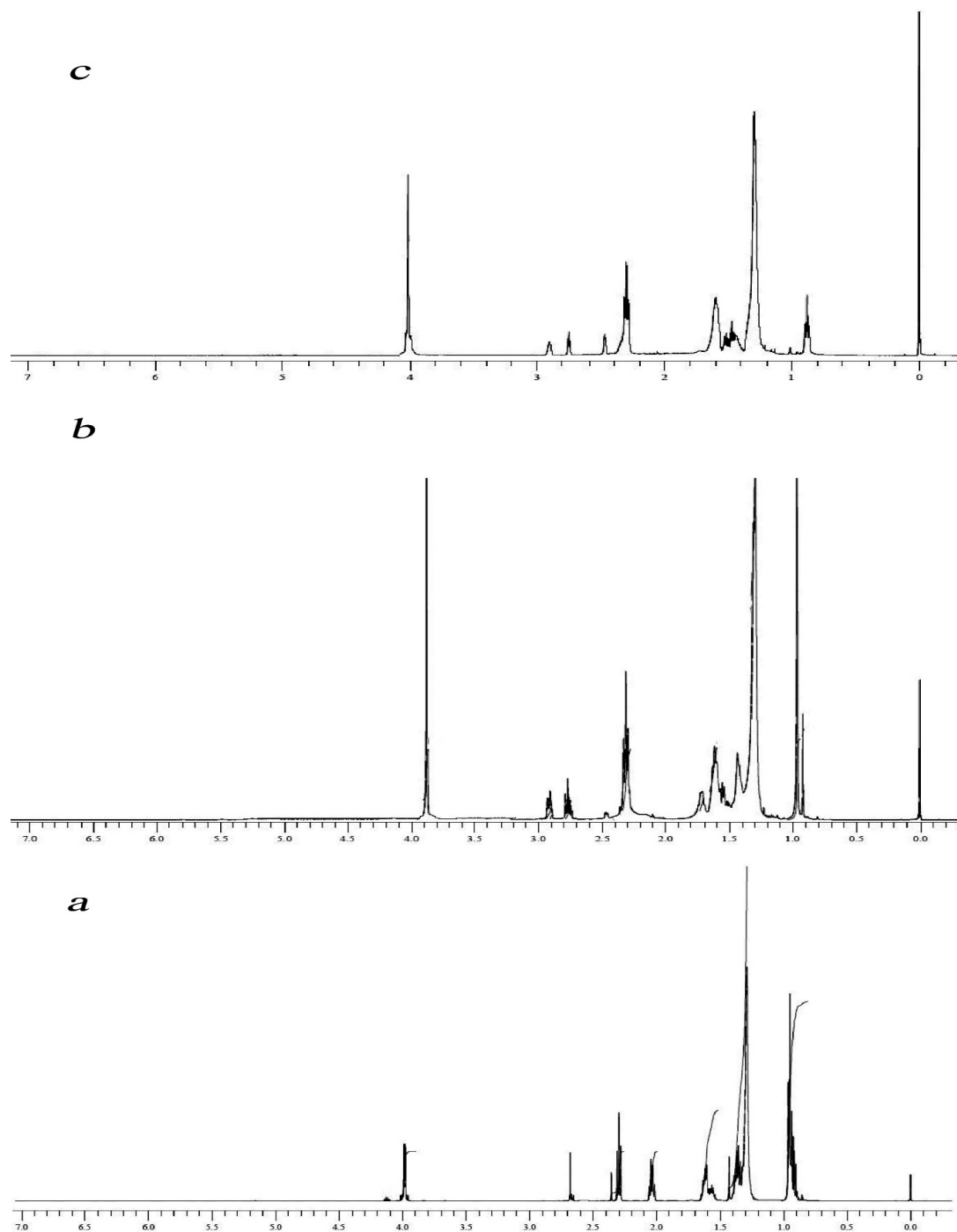


FIGURE 4. ¹H NMR spectra of various epoxides. a) 2-ethyl hexyl epoxide, b) NPG epoxide and c) TMP epoxide

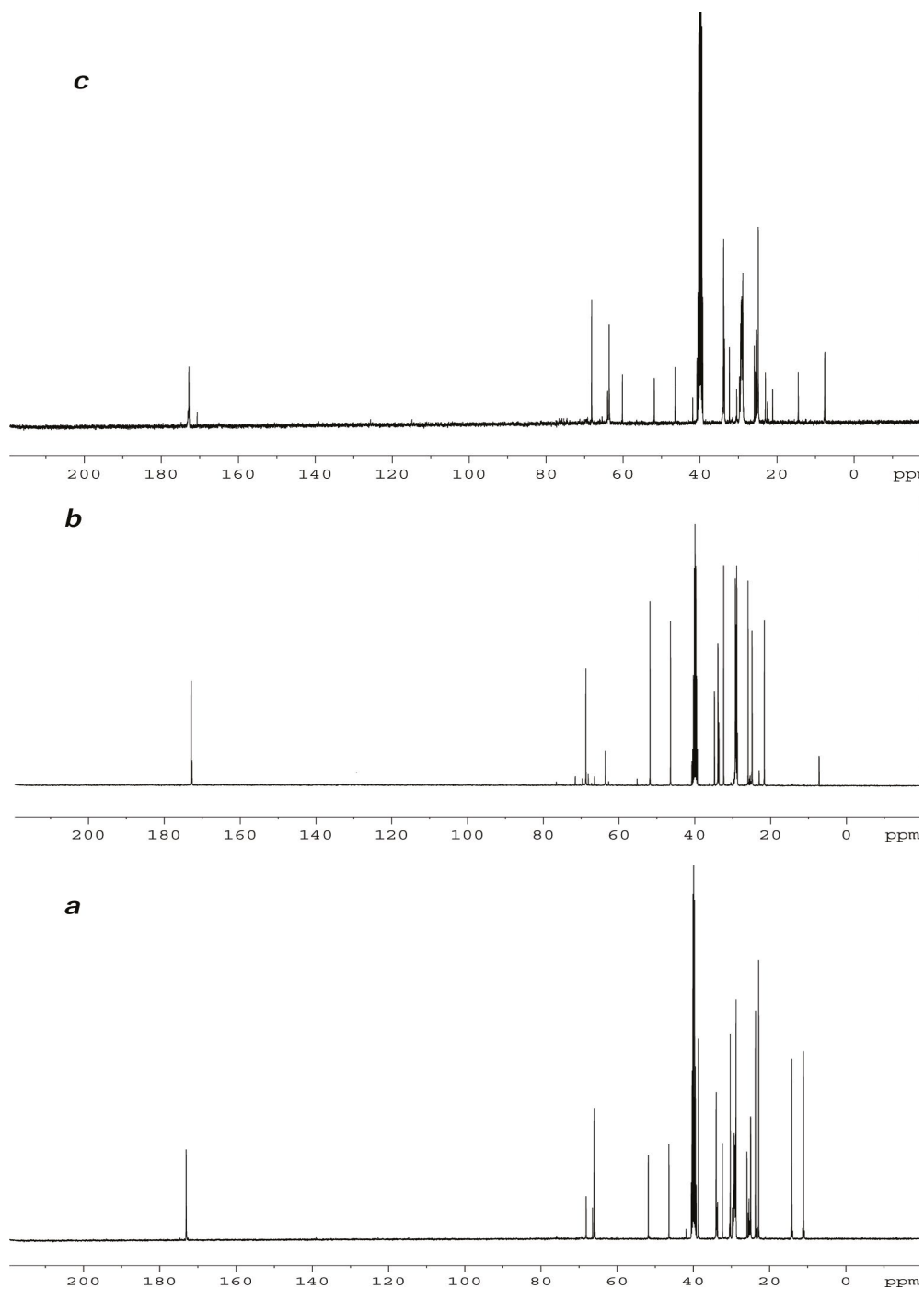


FIGURE 5. ¹³CNMR spectra of various epoxides. a) 2-ethyl hexyl epoxide, b) NPG epoxide and c) TMP epoxide

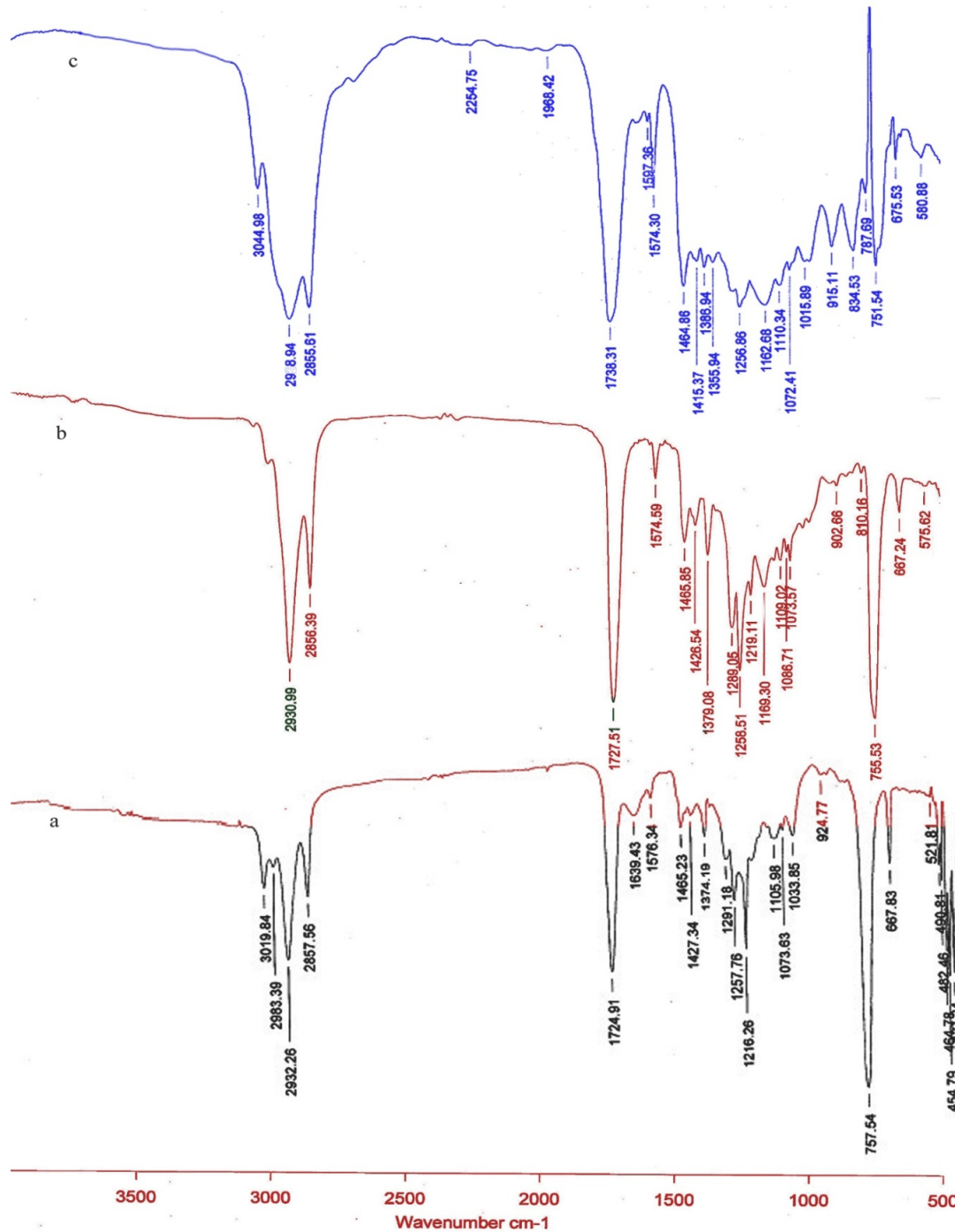


FIGURE 6. IR spectra of various epoxides. a) 2-ethyl hexyl epoxide, b) NPG epoxide and c) TMP epoxide

TABLE I. Physico-chemical properties of various epoxides of undecylenic esters

Properties	Methods	2-ethyl hexyl epoxide*	NPG epoxide*	TMP epoxide*
Density (g/cc)	-	1.0351 ± 0.0004	1.0446 ± 0.0006	1.1606 ± 0.0006
Specific gravity	-	1.0351 ± 0.0004	1.0446 ± 0.0006	1.1606 ± 0.0006
Moisture	-	0.0025	0.0021	0.002
Viscosity (40°C) cSt	ASTM D445	10.08 ± 0.025	37.34 ± 0.32	260 ± 0.325
Viscosity (100°C) cSt	ASTM D445	2.98 ± 0.269	7.6 ± 0.16	39.3 ± 0.485
Viscosity index (VI)	ASTM D2270	169	177	204
Flash point (°C)	ASTM D92	164 ± 2	270 ± 6	308 ± 2.1
Fire point (°C)	ASTM D92	173 ± 2.2	285 ± 0.066	314 ± 0.0723
Cloud point (°C)	ASTM D2500	-3.9 ± 0.1	-1.8 ± 0.2	3 ± 0.152
Pour point (°C)	ASTM D97	-35 ± 4	-25 ± 1.96	-12.5 ± 1.75
Copper strip Corrosion	ASTM-D-130	1a	1a	1a

*Data correspond to the mean of three determinations plus or minus standard deviation. The values are expressed as mean ± standard deviation (n=3)

± 0.0006 g/cc, respectively. These synthesized lubricants were referred to as high-density lubricant oils because of their higher density compared to water. So water floats on those lubricants. High-density lubricants are better to control contamination, because of aiding in the suspension, transport and particulate contamination removal. These contamination partials are held in suspension longer to be removed by filtration (Fitch, 1992).

Kinematic viscosity. The kinematic viscosity of 2-ethylhexyl, NPG and TMP-based esters ranges

from 1.89 ± 0.01 to 17.52 ± 0.02 cSt at 40 °C, which corresponds to low viscosity grade lubricants, which are useful for industrial applications. 2-ethyl hexanol epoxide, NPG epoxide and TMP epoxide viscosities range from 10 ± 0.025 to 260 ± 0.325 cSt at 40 °C. The viscosities increased with increasing molecular weight, acyl and epoxy groups. The kinematic viscosity at 100 °C of 2-ethyl hexanol, NPG and TMP ester-based epoxides ranges from 2.98 ± 0.269 to 39.3 ± 0.485 cSt (Figure 7). Among all epoxides, the TMP epoxide shows better viscosity, which is suitable for

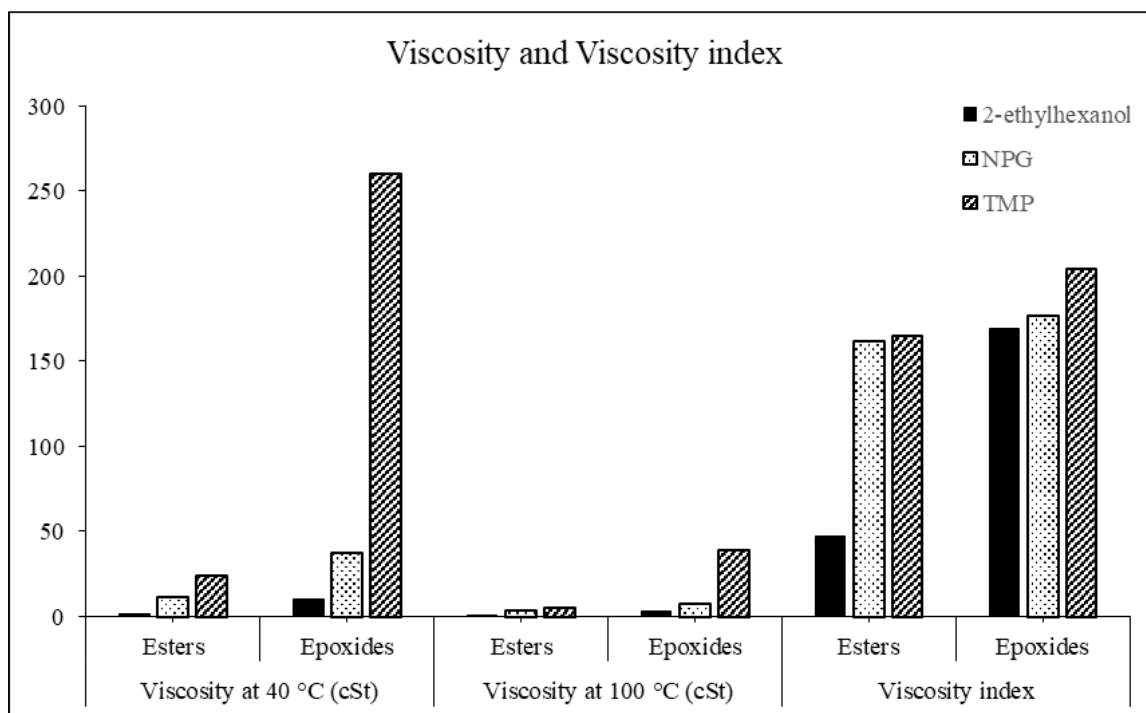


FIGURE 7. Viscosities of various esters and their epoxides.

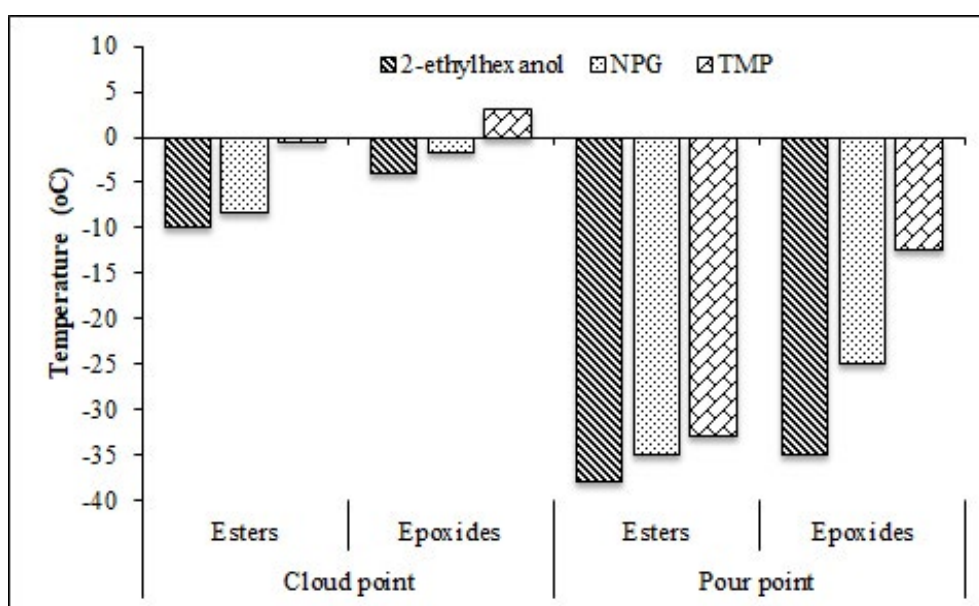


FIGURE 8. Cloud and pour points of various esters and epoxides.

various industrial applications such as an ISO VG 220 gear oil, metal working fluids and high-temperature applications.

Viscosity index. The viscosity indexes of 2-ethyl hexanol ester, NPG ester and TMP ester range from 47-210, indicating that they are suitable for multi-range applications. 2-ethyl hexanol epoxide, NPG epoxide and TMP epoxide exhibit a viscosity index in the range of 126-204. However, all synthesized ester-based epoxides show viscosity indexes of more than 126, which is a better viscosity index than mineral-based oil.

Flash and fire point. The flash and fire points of lubricants are usually known for higher temperature properties, and are used to determine the volatility and fire-resistance required during storage and transportation. The flash points of 2-ethyl hexanol ester, NPG ester and TMP ester were 138 ± 0.82 , 254 ± 0.82 , 286 ± 0.82 °C. The fire points were 147 ± 0.96 , 263 ± 0.96 and 294 ± 0.82 °C. The flashpoints of 2-ethyl hexanol ester-based epoxide, NPG ester-based epoxide and TMP ester-based epoxide were in the range of 164 ± 2 to 308 ± 2.1 °C. Fire points were 173 ± 2.2 to 314 ± 0.072 °C. All synthesized epoxides showed ≥ 164 °C flash and fire points, which indicates that they are within the range of standard lubricants. The flash and fire points were increased with increasing molecular weight, carbon chain length and acyl and epoxy groups. So, the synthesized epoxides were stable even at high temperatures and depicted a low tendency to evaporate (Figure 8).

Cloud and pour points. The cloud and pour point are imperative temperature properties at low temperatures for all lubricants. The cloud points of 2-ethyl hexanol ester, NPG ester and TMP ester were -10 ± 0.19 , -8.3 ± 0.10 and -0.6 ± 0.13 °C. The pour points were -38 ± 0.29 , -35 ± 0.38 , -33 ± 0.28 °C, respectively. The mono-branched alkyl ester exhibited a much lower pour point, which is suitable for many industrial applications. 2-ethyl hexanol epoxide, NPG epoxide and TMP epoxide showed cloud points ranging from -3.9 ± 0.1 to 3.0 ± 0.152 °C and pour points of -35 ± 4 to -12.5 ± 1.75 °C. 2-ethyl hexyl ester-epoxide exhibited a lower pour point, due to its low molecular weight and to being less branched. On the other hand, pour points were increased with increasing molecular weights in NPG and TMP ester-based epoxides. The data reveal that all epoxides showed low pour points, suggesting acceptable lubricants (Figure 9).

Copper strip corrosion. Corrosiveness of 2-ethyl hexanol ester, NPG ester and TMP ester and corresponding epoxides were found to be **1a** and are less corrosive, indicating that esters and their epoxides are resistant to moisture, as these esters and epoxides were prepared from UDA, a derivative of castor oil, which has less moisture content and absence of non-toxic chemicals like sulfur.

Microbial activity. The microbial activity was tested by the agar well diffusion technique accord-

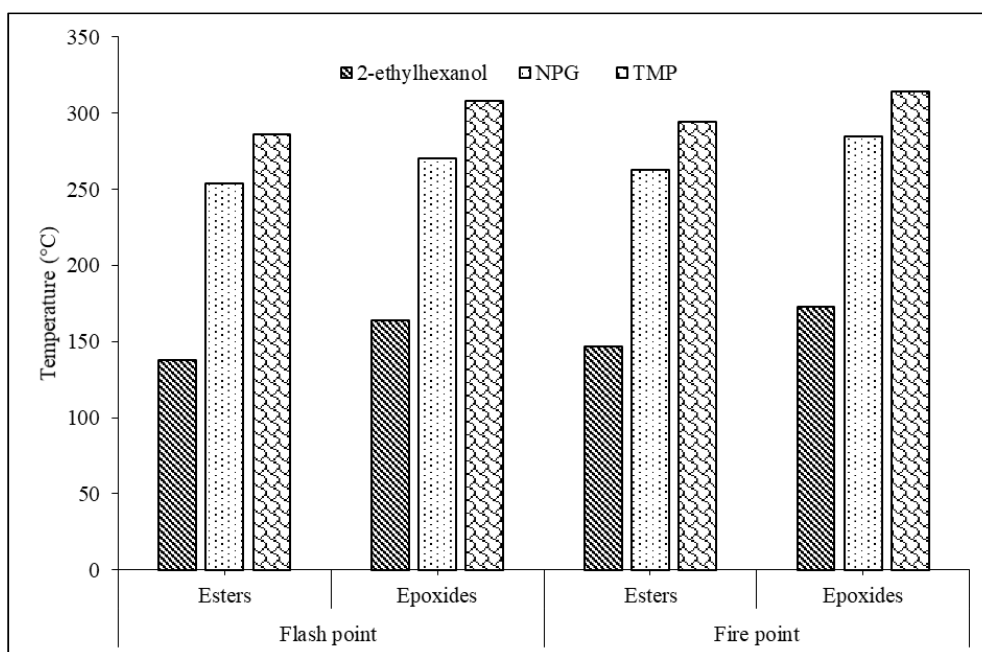


FIGURE 9. Flash and Fire points of various esters and epoxides. The values are expressed as mean \pm standard deviation ($n=3$).

ing to the standard procedure. The 2-ethyl hexanol ester, NPG ester and TMP ester and corresponding epoxides were treated against two gram-positive bacterial strains: *bacillus subtilis*, *staphylococcus aureus* and two-gram negative bacterial stains: *pseudomonas aeruginosa*, *klebsiella pneumoniae*. In this method, agar plates were inoculated with different strains of bacteria under restraining conditions and borewells (6 mm diameter) and filled with 150 $\mu\text{g}/\text{mL}$ of 2-ethyl hexanol ester, NPG ester and TMP ester and corresponding epoxides in a dimethyl sulphoxide (DMSO) solution and incubated at 37 $^{\circ}\text{C}$ for 24 h. After the incubation period, the diameter of the growth inhibition zones was measured. The inhibition zones were reported in millimeters (mm). Vegetable oil was used as standard. All tests were performed in triplicate.

The results of inhibition zone values for 2-ethyl hexanol ester, NPG ester and TMP ester and corresponding epoxides against bacterial strains such as *bacillus subtilis*, *staphylococcus aureus*, *pseudomonas aeruginosa*, *Klebsiella pneumoniae* are shown in Figure 10. According to Figure 10, all 2-ethyl hexanol ester, NPG ester and TMP ester and their corresponding epoxides did not show a zone of inhibition in gram-positive and gram-negative bacterial strains. This strongly suggests that the synthesized 2-ethyl hexanol ester, NPG ester and TMP es-

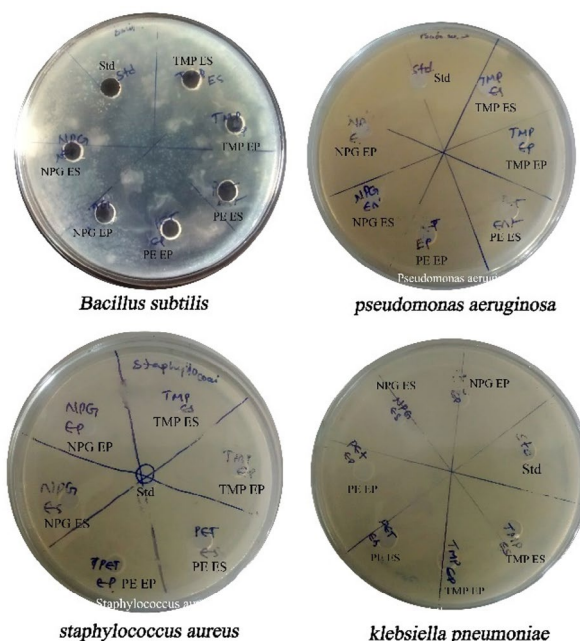


FIGURE 10. Zone of inhibition of synthesized esters and their epoxides against bacterial strains such as *staphylococcus aureus*, *bacillus subtilis*, *Klebsiella pneumoniae*, *pseudomonas aeruginosa*.

ter and their corresponding epoxides are non-toxic.

The synthesized epoxides showed an excessive viscosity index, flash point and lower volatility than the respective esters (Table 2). Among all the three synthesized epoxides, TMP epoxide showed

TABLE 2. Physico-chemical properties of various UDA-based esters

Properties	2-ethyl hexyl ester*	NPG Esters*	TMP ester*
Density (g/cc)	0.9051 ± 0.0002	0.9283 ± 0.0001	1.0046 ± 0.0001
Viscosity (40°C) cSt	1.89 ± 0.01	10.51 ± 0.02	17.52 ± 0.02
Viscosity (100°C) cSt	0.89 ± 0.01	3.31 ± 0.02	4.71 ± 0.02
Viscosity index	47.08	212.89	207.619
Flash point (°C)	138 ± 0.82	254 ± 0.82	286 ± 0.82
Fire point (°C)	147.75 ± 0.96	263.75 ± 0.96	294 ± 0.82
Cloud point (°C)	-10.78 ± 0.19	-8.43 ± 0.10	-0.65 ± 0.13
Pour point (°C)	-38.50 ± 0.29	-35.53 ± 0.38	-33.48 ± 0.28
Copper strip Corrosion	1a	1a	1a

*Data correspond to the mean of three determinations plus or minus standard deviation. The values are expressed as mean ± standard deviation (n=3)

a higher viscosity index, flash point, and lower pour point compared to 2-ethyl hexyl and NPG epoxides. TMP ester-based epoxide has a higher VI compared to various epoxidized vegetable oils such as castor methyl ester (Venubabu and Goud, 2014), rapeseed oil (Wu *et al.*, 2000), Karanja oil (Geethanjali *et al.*, 2013) and HP Lube parthan SL220 (Table 3). Epoxides, thus synthesized, can be a potential base-stock for lubricants. The standard lubricants widely used in the market for machinery are various ISO VG grades. The 2-ethyl hexanol epoxide, NPG epoxide and synthesized TMP epoxide are comparable to standard ISO VG grades.

Kinematic viscosity at 40 °C for NPG epoxide is 37.34 cSt. It is in the range of ISO VG 32 and 46 grades. Standard ISO VG 32 and 46 grades are widely used machinery lubricating oil and turbine oil. Kinematic viscosity at 40 °C for TMP epoxide is 260 cSt, which is in the range of standard ISO VG 220 and 320 grades. The Standard ISO VG 220 and 320 grades are widely used in machinery lubricating oil, bearing oils for steel plants and industri-

al gear oils.

The synthesized 2-ethyl hexanol epoxide, NPG epoxide and TMP epoxide can replace the existing mineral-based lubricating oils of ISO VG 32-46, ISO VG 220-320 grades in the market for machinery, turbine and industrial gear oil applications. The synthesized 2-ethyl hexanol epoxide, NPG epoxide and TMP epoxide is from a renewable source and is biodegradable without polluting the environment. These are recommended for all industrial machinery and other machine parts lubricated by a thin film of oil for anti-friction bearings, plain bearings, drive gears and the pinions of steel mills, where operating conditions are moderate.

4. CONCLUSIONS

The study involved a new class of epoxides synthesized from undecylenic esters as a bio lubricant base-stock. Undecylenic esters of 2-ethyl hexanol, NPG and TMP were epoxidized using mCPBA. The yields of 2-ethyl hexanol epoxide, NPG epoxide and TMP epoxide were in the range of 70-75%.

TABLE 3. Physico-chemical properties of various vegetable epoxides and HP Lube parthan SL220

Properties	Castor methyl ester ^a	Rapeseed oil ^b	Karanja oil ^c	HP Lube parthan SL220 [@]
Viscosity at 40°C (cSt)	35.81	86.74	256	241.9
Viscosity at 100°C (cSt)	-	12.72	28	31.34
Viscosity index	-	145	-	173
Pour point(°C)	8	-12	3	-45
Flash point(°C)	138	239	-	250
Copper strip Corrosion	1 ^a	1a	1a	1a

^aVenu babu *et al.*, 2014, ^bWu *et al.*, 2000, ^cGeethanjali *et al.*, 2013, [@]ISO Grade 220.

TMP epoxide showed higher viscosity, higher viscosity indices, higher cloud point, lower pour point, higher flash point, and higher fire point than 2-ethyl hexyl and NPG epoxide. 2-ethyl hexanol epoxide, NPG epoxide and TMP epoxide have superior lubricant properties compared to their corresponding esters.

2-ethyl hexanol epoxide, NPG epoxide and TMP epoxide with high viscosity indices, higher flash point, and lower pour points can be exploited for automotive and hydraulic fluid formulations. Undecylenic esters and their epoxides can be used for numerous applications due to their non-toxicity and biodegradability.

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