JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Synthesis, Characterization, and Evaluation of 10-Undecenoic Acid-Based Epithio Derivatives as Multifunctional Additives

Gorla Geethanjali, Korlipara V. Padmaja, Arukali Sammaiah, and Rachapudi B. N. Prasad*

Centre for Lipid Research, CSIR—Indian Institute of Chemical Technology, Hyderabad 500 007, Andhra Pradesh, India

ABSTRACT: Novel epithio compounds from alkyl epoxy undecanoates (*n*-alkyl, C_1, C_4, and C_6; isoalkyl, C_3, C_4, and C_8) were synthesized using an ammonium thiocyanate in ionic liquid 1-methylimidazolium tetrafluoroborate/H_2O (2:1) solvent system in 85−90% yields by gas chromatographic (GC) analysis. The synthesized products were characterized by ^1H and ^{13}C nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy (FTIR), gas chromatography, and GC mass spectral (GC-MS) analyses and evaluated for their antioxidant, extreme pressure (EP), and antiwear (AW) properties in three different base oils, namely, epoxy jatropha fatty acid *n*-butyl esters (EJB), di-2-ethylhexyl sebacate (DOS), and mineral oil (S-105). Among the synthesized products, *n*-butyl epithio undecanoate exhibited superior antioxidant property (229.2 °C) compared to butylated hydroxytoluene (BHT, 193.8 °C) in base oil DOS and comparable performance in EJB and S-105 base oils. All of the epithio derivatives exhibited significantly enhanced weld point for the base oils EJB and DOS at 2 wt % level and displayed moderate enhancement in S-105 base oil. Methyl epithio undecanoate at 0.6% concentration exhibited considerable improvement in the wear scar of DOS base oil. The synthesized epithio derivatives have potential as multifunctional additives in lubricant formulations.

KEYWORDS: *10-undecenoic acid, epithio derivatives, ionic liquid, extreme pressure additive, antiwear, antioxidant, biolubricant, synthetic ester, mineral oil*

INTRODUCTION

The increasing use of non-petroleum lubricant base stocks will require new environmentally friendly and multifunctional lubricant additives. Currently, the majority of lubricant additives are petroleum based, providing an opportunity for a biobased lubricant additive that is eco-friendly, cost-effective, and of superior quality with compatibility for biolubricants.[1] Using renewable raw material oils and fats of vegetable and animal origin offers new synthesis for the chemical industry.[2] The structural modification of long-chain fatty acid derivatives such as addition reactions to double bonds or epoxy groups gives compounds containing either sulfur, phosphorus, or halogen, or a combination of these elements. These compounds may exhibit good antiwear (AW) or extreme pressure (EP) lubricating characteristics and, in some cases, function in both capacities.[3−7] Organic sulfur compounds have been widely used in lubricating compositions for their EP as well as AW properties.[8] Sulfur compounds can also be used as antioxidants, and some of them are considered natural antioxidants in lubricating oils.[9−11] Many attempts were made by various workers on sulfurization of vegetable oils to find replacement for sulfurized sperm whale oil, a biobased antiwear and EP additive. These attempts were not successful as the sulfurization of vegetable oils resulted in high viscous resinous products that displayed a tendency to corrode copper, excessive foaming, thickening during gear box tests, and exhibit low thermal stability. These products were mostly insoluble in base oils and required the addition of nonwax fatty acid methyl esters to improve their solubility.[12,13]

Epithio compounds are very effective lubricant additives, in particular EP/AW and antioxidant additives, and are superior to other sulfur products.[14] The synthesis of C_{18} fatty acids containing a thiophene nucleus has been reported.[15,16] Three-membered heterocyclic fatty acids containing an S atom were used as intermediates leading to the preparation of thionitrile derivatives.[17] Kuranova et al. have prepared trisubstituted five-membered sulfur heterocycles by reacting methyl 9,10:12,13-diepithiostearate with HBr or Cl_3CCOOH.[18] Preparation of a number of epithio C_{18} fatty esters from methyl oleate, linoleate, ricinoleate, and derivatives of ricinoleate is reported.[16] Epoxy fatty esters on treatment with dimethylthioformamide and trifluoroacetic acid in dichloromethane were converted to their corresponding 2,3-epithio fatty esters. $2,2^1$-Epoxy fatty esters were transformed to $2,2^1$-epithio fatty esters by similar reaction and were characterized by ^1H and ^{13}C NMR spectroscopy. Methodologies reported for the synthesis of episulfides involve the use of catalysts and reagents, namely, dichlorodisulfides, iodothiocyanate, sulfuryl lithium, dimethylthioformamide, thiourea, potassium thiocyanate, and ammonium thiocyanate, using ruthenium catalyst[19] and other methods that are either corrosive or expensive. Furthermore, the reported methods suffer from disadvantages such as moderate yields, elevated temperatures, and requirement of stoichiometric amounts of catalyst. Furthermore, in view of developing new ecofriendly biolubricant multifunctional additives, we report the synthesis and characterization of novel epithio derivatives of 10-undecenoic acid, a commercially available derivative of castor oil, followed by their evaluation for their antioxidant, antiwear, and extreme pressure properties in three types of base fluids.

Received: July 14, 2014
Revised: October 31, 2014
Accepted: November 4, 2014

■ MATERIALS AND METHODS

Materials. 10-Undecenoic acid was obtained from Jayant Oil Mills (Mumbai, India). Methanol, propan-2-ol, butan-1-ol, 2-methylpropan-1-ol, hexan-1-ol, 2-ethylhexan-1-ol, hexane, and ethyl acetate were procured from Qualigens Fine Chemicals (Mumbai, India). Dichloromethane, *m*-chloroperbenzoic acid (m-CPBA), aniline, butylated hydroxytoluene (BHT), paraffin oil, ammonium thiocyanate, 1-methylimidazole, and HBf4 were purchased from Sigma-Aldrich (St. Louis, MO, USA). Hydrogen peroxide (30% aqueous solution), xylene, and *p*-toluenesulfonic acid (p-TSA) were purchased from M/s sd fine-chem Ltd., Mumbai, India. Formic acid solution (85%) and sulfuric acid (AR grade) were purchased from M/s Rankhem, New Delhi, India. Sebacic acid was procured from Sisco Research Laboratories (Mumbai, India). Jatropha oil was obtained from a local company. LZ 1359 and tricresyl phosphate (TCP) was used as control in antiwear and extreme pressure analyses, respectively. All of the chemicals were of analytical reagent grade and used as received.

Methods. The analytical determinations of the sebacic acid and jatropha oil derivatives were accomplished according to the official methods of the American Oil Chemists' Society (AOCS) as follows: acid value (AOCS Cd 63), iodine value (IV, AOCS Da 15-48), and oxirane value (OO, AOCS Cd 9-57). The base oil lubricant properties such as density, viscosity, and viscosity index were evaluated per methods described previously.[20] ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AR X 400 spectrometer (400 MHz) and a Varian spectrometer at 75 MHz, respectively, and TMS was used as an internal standard. IR spectra were recorded in chloroform on a PerkinElmer Fourier transform (model Spectrum BX; Shelton, CT, USA) FT-IR spectrometer neat as thin film. The spectrum was recorded in absorbance mode.

A gas chromatograph Agilent 6890N series was employed to analyze the fatty acid composition using an HP-1 column (30 m × 0.25 mm × 0.5 μm). The flame ionization detector and injector were at 300 °C. The oven temperature was programmed at 150 °C for 2 min and then increased to 300 °C at 10 °C/min. The carrier gas used was nitrogen at a flow rate of 1.5 mL/min. The GC-MS analysis was carried out using an Agilent 6890 gas chromatograph connected to an Agilent 5973 mass spectrophotometer at 70 eV (m/z 50−600; source at 230 °C and quadruple at 150 °C) in the EI mode using an HP-1 MS capillary column (30 m × 0.25 mm × 0.5 μm). The oven temperature was programmed at 150 °C for 2 min, 10 °C/min to 300 °C, and 20 min at 300 °C. The carrier gas used was helium at a flow rate of 1.0 mL/min.

The antioxidant activity of the synthesized epithio derivatives in three base oils was evaluated using a differential scanning calorimeter (DSC Q 2000, TA Instruments) under oxygen atmosphere. The oxidative onset temperature (OOT) was measured for base oils with and without added additives in dynamic mode. The temperature programming was set at 25−300 °C, ramped at 10 °C/min, and purified oxygen was passed through the sample enclosure at 50 mL/min. The oxidative onset temperature was determined from the start of the exothermic reaction peak in the DSC thermogram.

The load-carrying capacity and antiwear properties of synthesized additives were investigated using a Stanhope SETA four-ball tester. All of the wear tests were conducted at a rotating speed of 1200 rpm under a load of 40 kg, with a duration of 60 min. An optical microscope was used to determine the wear scar diameters (WSD) of the three lower balls with an accuracy of ±0.01 mm, and these diameters were averaged and cited as the WSD reported in this paper. The extreme pressure tests were run at 1475 rpm, ambient temperature at variable load, and test duration for 1 min or until the balls welded, whichever occurred first. The extreme pressure properties of three base oils with and without added additive at different concentrations were evaluated as weld point loads and are reproducible to within one loading increment (±10 kg for 10 kg loading increments).

The surface analysis of wear scar developed on the steel balls during the antiwear analysis was studied using a Hitachi S-3000N scanning electron microscope (SEM) with energy/wavelength dispersion, at a voltage of 20 kV.

Synthesis of Di-2-ethylhexyl Sebacate. Sebacic acid (200 g, 0.99 mol), 2-ethylhexanol (465 mL, 2.97 mol), *p*-toluenesulfonic acid (2 g, 1 wt % of KFA), and xylene, 100 mL, were taken in a four-necked round-bottom flask and stirred at 130−140 °C for a period of 8 h. The reaction was monitored by TLC. The crude product was distilled at 180 °C temperature and 5 mmHg to remove excess alcohol and xylene. The distilled product was extracted with hexane and washed with water until it was acid free, passed through Na_2SO_4, concentrated, and dried under vacuum. The product was further purified using basic alumina column chromatography by elution with hexane to obtain di-2-ethylhexyl sebacate with an acid value of <0.1. The yield of the product was found to be 95%. The structure of the product was characterized by FT-IR, EI-MS, and ^{1}H NMR spectral studies.

Synthesis of Epoxy Jatropha Fatty Acid *n*-Butyl Esters (EJB). *n*-Butyl esters of jatropha fatty acids[21] (125 g, 0.385 mol), formic acid (26.6 g, 0.577 mol), and sulfuric acid (1.7 mL, 2 wt % of HCOOH and hydrogen peroxide) were taken in a three-necked round-bottom flask equipped with an overhead stirrer. A 30% aqueous hydrogen peroxide solution (117.9 mL, 1.155 mol) was added slowly to the contents under strong mechanical stirring at 15−20 °C over a duration of 1 h. After addition, the temperature was raised to 55−60 °C for 5 h. The product was extracted with ethyl acetate and washed with water until it was acid free, then passed through anhydrous sodium sulfate, and dried under reduced pressure to yield the product with oxirane oxygen content of 4.4%. The yield of the epoxy jatropha fatty acid *n*-butyl esters was found to be 95%. The structure of the product was characterized by FT-IR and ^{1}H NMR spectral studies.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85−0.95 (t, $-CH_2{-}C\underline{H}_3$), 1.2−1.4 (m, $-C\underline{H}_2{-}CH_3$), 1.4−1.5 (m, $C\underline{H}_2{-}CHOCH-$), 1.6−1.7 (m, $C\underline{H}_2{-}CH_2{-}CO-$), 2.8−3.1 (m, $-C\underline{H}OC\underline{H}-$), 2.3 (t, $-CH_2{-}C{=}O$), 4.05 (t, $-C\underline{H}_2{-}O{-}C{=}O$); IR (neat, cm^{-1}) 2927 (C−H), 1740 (C=O), 826 (epoxy ring), 1172 (C−C (=O)−O).

Preparation of Ionic Liquid [HMIM]BF_4. 1-Methylimidazole (6 g, 0.0738 mol) was taken into a three-necked round-bottom flask. The temperature of the medium was sustained at 0 °C, and 48% tetrafluoroboric acid (9.54 mL, 0.0738 mol) was added slowly to it for 40 min, and then the reaction was further continued at room temperature for 2 h. After completion of the reaction, the contents were kept under high vacuum to remove moisture at 80−90 °C. The product was subjected to ethyl acetate washings to remove excess imidazole followed by drying under reduced pressure to obtain a light yellow viscous liquid.

Synthesis of Alkyl 10-Undecenoates (2a-f). 10-Undecenoic acid was esterified with different alcohols, namely, methanol, propan-2-ol, butan-1-ol, 2-methylpropan-1-ol, hexan-1-ol, and 2-ethylhexan-1-ol, in the presence of p-TSA (1 wt % of the acid) for a duration of 4−5 h to yield alkyl 10-undecenoates **2a**−**f**). The synthetic procedure is reported elsewhere.[22]

Synthesis of Alkyl 10-Epoxyundecanoates (3a−f). Alkyl 10-undecenoates were epoxidized using *m*-chloroperbenzoic acid to yield alkyl epoxy undecanoates. The synthetic procedure is reported elsewhere.[22]

Typical Procedure for the Preparation of Butyl 10-Epithioundecanoate (4a−f). *n*-Butyl 10-epoxyundecanoate (2 g, 0.0078 mol) and ammonium thiocyanate (0.594 g, 0.0078 mol) were taken into a round-bottom flask. Ionic liquid [HMIM]BF_4 (4 g) and water (2 g) in a 2:1 ratio were added to the contents, and the resultant reaction mixture was stirred at 60 °C for a period of 23 h. The progress of the reaction was monitored by TLC using hexane/ethyl acetate (90:10 v/v). After completion of the reaction, the crude product was extracted using ether, and the ethereal solution was washed with water and dried over sodium sulfate. The combined ether extracts were concentrated using a rotary evaporator. The structure of the product was established by GC-MS and GC (90%). The crude product was purified using silica gel column chromatography using hexane and ethyl acetate (80/20) to afford *n*-butyl 10-epithioundecanoate (1.44 g, 68% of isolated yield). The product was characterized by ^{1}H NMR, IR, GC, and GC-MS spectral data.

Methyl 10-Epithioundecanoate (ESUME, 4a): 1.29 g, 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS) 1.2−1.40 (m, 12 H, $-CH_2$), 1.4−1.65 (m, 2H, $C\underline{H}2{-}CH2{-}C{=}O$), 1.75−1.85 (m, 2H, $H_2\overbracket{CSC}H{-}CH_2$), 2.15−2.18 (d, 2H, $\underline{H}_2\overbracket{CSC}H$), 2.25−2.35 (t, 2H, $-CO{-}CH_2$), 2.48–2.52 (d, $\underline{H}_2\overline{CSC}\underline{H}$), 3.6–3.65 (t, 2H $-O-C\underline{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5–30.0 ($-CH_2-$), 25.8 ($-CH_2-CH-S-\underline{C}H_2$), 29.5 ($-CH_2-\underline{C}H-S-CH_2$), 34.0 ($-\underline{C}H_2-C{=}O$), 51.0 ($\underline{C}H_3-O-C{=}O$), 36.2 ($-\underline{C}H_2-CH-S-CH_2$), 174.5 ($-COO-$); IR (neat, cm^{-1}) 2929 ($-C-H$ stretching), 1736 ($-C{=}O$), 612 ($-C-S-$ stretching), 1042 ($-C-S-$ asymmetric stretching), 1172 ($C-C({=}O)-O$); EIMS *m*/*z* 230 [M]$^+$, 215, 173, 199.

2-Propyl 10-Epithioundecanoate (ESIPUES, 4b): 1.29 g; 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS) 1.20–1.36 (q, 6H, $-CH-(C\underline{H}_3)_2$), 1.42–1.66 (m, 14 H, $-C\underline{H}_2$), 1.75–1.85 (m, 2H, $H_2\overline{CSC}H-CH_2$), 2.15–2.18 (d, 2H, $\underline{H}_2\overline{CSC}H$), 2.2–2.3 (t, 2H, $-CO-C\underline{H}_2$), 2.48–2.52 (d, $\underline{H}_2\overline{CSC}\underline{H}$), 3.14–3.18 (d, 2H, $O-CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14 ($\underline{C}H_3-CH_2-$), 21.7 ($(\underline{C}H_3)_2-CH-$), 22.6–32.2 ($-CH_2-$), 34.3 ($-\underline{C}H_2-C{=}O$), 36.5 ($-\underline{C}H_2-CH-S-CH_2$), 30.5 ($-CH_2-\underline{C}H-S-CH_2$), 174.5 ($-COO-$); IR (neat, cm^{-1}) 2927 ($-C-H$ stretching), 1736 ($-C{=}O$), 612 ($-C-S-$ stretching), 1042 ($-C-S-$ asymmetric stretching), 1174 ($C-C({=}O)-O$); EIMS *m*/*z* 281 [M + Na]$^+$, 259, 199, 181.

2-Methyl-1-propyl 10-epithioundecanoate (ESC-4UES, 4c): 1.20 g; 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS) 0.86–0.95 (t, 3H, $-C\underline{H}_3$), 1.18–1.65 (m, 18 H, $-C\underline{H}_2$), 2.2–2.3 (t, 2H, $-CO-C\underline{H}_2$), 1.72–1.8 (m, 2H, $H_2\overline{CSC}H-CH_2$), 2.12–2.17 (d, 2H, $\underline{H}_2\overline{CSC}H$), 2.28–2.32 (t, 2H, $-CO-CH_2$), 2.42–2.48 (d, $U_2\overline{CSC}\underline{H}$), 3.85–3.95 (t, 2H $-O-C\underline{H}_2-(CH_2)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) 14 ($\underline{C}H_3-CH-$), 19 ($(\underline{C}H_3)_2-CH-$), 21.7 ($(\underline{C}H_3)_2-CH-$), 22.6–32.2 ($-CH_2-$), 34.5 ($-\underline{C}H_2-C{=}O$), 36.5 ($-\underline{C}H_2-CH-S-CH_2$), 30.5 ($-CH_2-\underline{C}H-S-CH_2$), 70.3 ($-\underline{C}H-O-C{=}O$), 173.5 ($-COO-$); IR (neat, cm^{-1}) 2929 ($-C-H$ stretching), 1736 ($-C{=}O$), 619 ($-C-S-$), 1042 ($-C-S-$ asymmetric stretching), 1163 ($C-C({=}O)-O$); EIMS *m*/*z* 295 [M + Na], 216, 199.

Butyl 10-Epithioundecanoate (ESnBU-UES, 4d): 1.44 g; 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS) 0.9–1.0 (d, 3H, $-CH_3$), 1.2–1.40 (m, 14 H, $-CH_2$), 1.4–1.45 (m, 2H, $C\underline{H}2-CH_2-C{=}O$), 1.75–1.85 (m, 2H, $H_2\overline{CSC}H-CH_2$), 2.1–2.15 (d, 2H, $\underline{H}_2\overline{CSC}H$), 2.2–2.3 (t, 2H, $-CO-CH_2$), 2.45–2.5 (d, $H_2\overline{CSC}\underline{H}$), 4.0–4.1 (t, 2H, $-O-C\underline{H}_2-(CH_2)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) 13.5 ($\underline{C}H_3-CH_2-$), 19.0 ($CH_3-\underline{C}H_2-$), 25.0–30.5 ($-CH_2-$), 34.2 ($-\underline{C}H_2-C{=}O$), 36.5 ($-\underline{C}H_2-CH-S-CH_2$), 31.0 ($-CH_2-\underline{C}H-S-CH_2$), 26.0 ($-CH_2-CH-S-\underline{C}H_2$), 64.1 ($-\underline{C}HO-C{=}O$), 173.8 ($-COO-$); IR (neat, cm^{-1}) 2929 ($-C-H$ stretching), 1736 ($-C{=}O$), 619 ($-C-S-$), 1163 ($-C-C({=}O)-O$); EIMS *m*/*z* 295 [M + Na], 216, 199.

Hexyl 10-Epithioundecanoate (ESnHE-UES, 4e): 1.37 g; 66.5%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS) 0.95–1.0 (d, 3H, $-CH_3$), 1.3–1.50 (m, 18 H, $-CH_2$), 1.45–1.5 (m, 2H, $C\underline{H}2-CH_2-C{=}O$), 1.8–1.85 (m, 2H, $H_2\overline{CSC}H-CH_2$), 2.1–2.15 (d, 2H, $\underline{H}_2\overline{CSC}H$), 2.25–2.3 (t, 2H, $-CO-CH_2$), 2.45–2.5 (d, $H_2\overline{CSC}\underline{H}$), 4.05–4.1(t, 2H, $-O-C\underline{H}_2-(CH_2)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 ($\underline{C}H_3-CH_2-$), 22.5 ($CH_3-C\underline{H_2}-$), 28.5–29.4 ($-CH_2-$), 25.5–26 ($-CH_2-CH-S-\underline{C}H_2$), 31.5 ($-CH_2-\underline{C}H-S-CH_2$), 34–34.2 ($-\underline{C}H_2-C{=}O$), 36.0 ($-\underline{C}H_2-CH-S-CH_2$), 64.5 ($-\underline{C}HO-C{=}O$), 174 ($-COO-$); IR (neat, cm^{-1}) 2929 ($-C-H$ stretching), 1738 ($-C{=}O$), 615 ($-C-S-$), 1163 ($-C-C({=}O)-O$); EIMS *m*/*z* 323 [M + Na]$^+$, 199.

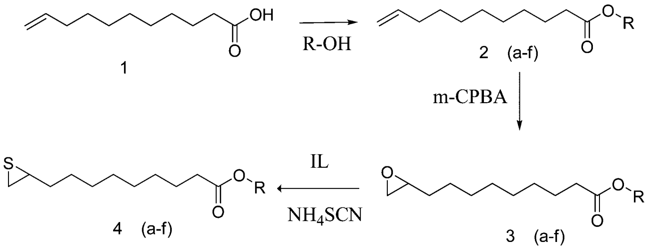
2-Ethylhexyl 10-epithioundecanoate (ES2ET-HE-UES, 4f): 1.3 g; 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS) 0.8–0.95 (t, 6H, $-(C\underline{H}_3)_2$), 1.20–1.50 (m, 21 H, $-C\underline{H}_2$), 1.75–1.85 (m, 2H, $H_2\overline{CSC}H-CH_2$), 2.12–2.17 (d, 2H, $\underline{H}_2\overline{CSC}H$), 2.25–2.35 (t, 2H, $-CO-C\underline{H}_2$), 2.48–2.52 (d, $H_2\overline{CSC}\underline{H}$), 3.95–4.0 (t, 2H $-O-C\underline{H}_2-(CH_2)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.8 ($\underline{C}H_3-CH_2-$), 14 ($\underline{C}H_3-CH_2-$), 22.1–32.4 ($-CH_2-$), 30.5 ($-CH_2-\underline{C}H-S-CH_2$), 36.5 ($-\underline{C}H_2-CH-S-CH_2$), 38.5 ($-CH_2-C{=}O$), 66.5 ($-\underline{C}HO-C{=}O$), 174 ($-COO-$); IR (neat, cm^{-1}) 2929 ($-C-H$ stretching), 1732 ($-C{=}O$), 619 ($-C-S-$), 1042 ($-C-S-$ asymmetric stretching), 1171 ($-C-C({=}O)-O$); EIMS *m*/*z* 351 [M + Na]$^+$, 199.

RESULTS AND DISCUSSION

In the present study epithio undecanoates were synthesized from epoxy undecanoates in a green reaction medium, ionic liquid. The use of ionic liquid for the synthesis of epithio compounds helps in carrying out the reaction under mild and neutral conditions to afford epithio undecanoates in high yields. The performance of the epithio derivative as multifunctional additives was evaluated in three base oils: epoxy jatropha *n*-butyl esters (EJB), di-2-ethylhexyl sebacate (DOS), and paraffin (S-105) base oil.

The epoxy undecanoates were used as starting material to synthesize epithio undecanoates using ammonium thiocyanate in stoichiometric ratio (Scheme 1). All of the reactions were completed within 20–24 h, affording high yields of alkyl 10-epithioundecanoates as revealed by GC analysis (85–96%). The products were purified using silica gel column chromatography using hexane and ethyl acetate (80:20) to afford pure alkyl 10-epithioundecanoates with an isolated yield of 60–68%. The FT-IR spectra of the epoxy undecanoate derivatives are characterized by a stretching vibration frequency at 835 cm^{-1}, which is attributable to the epoxy stretching vibration frequency and asymmetric ring deformation at 916 cm^{-1}. In contrast, the IR spectral feature observed in epithio derivatives is the disappearance of these peaks, indicating complete conversion of epoxy to epithio group in the synthesized products. Two new peaks appeared at 619 and 1011 cm^{-1}, which are attributable to the symmetric and asymmetric epithio ring deformation,[23−25] proving the successful conversion of epoxide to epithio group. The FT-IR spectra also exhibited the characteristic absorptions of aliphatic carbons around 2987 and 2865 cm^{-1} and an ester group ($-COO-$) around 1735 cm^{-1}.

Scheme 1. Synthesis of Epithio Undecanoates



R= a, $-CH_3$; b, $-CH-(CH_3)_2$; c, $-CH_2-CH-(CH_3)_2$; d, $-(CH_2)_3-CH_3$; e, $-(CH_2)_5-CH_3$; f, $-(CH_2)_5-CH-(CH_3)_2$.

In ^{1}H NMR spectra of alkyl 10-epithioundecanoates, signals at 2.2 and 2.5 ppm corresponding to methylene and methine protons, respectively, confirmed the epithio ring introduction into the molecule, respectively. In epithio undecanoate derivatives the disappearance of peaks at 2.8–2.9 ppm corresponding to $-CH-$ protons of the epoxy carbon confirmed the epithio ring formation. Both the infrared spectra and NMR spectra of these epithio derivatives indicated the absence of an epoxy group in the epithio derivatives. The GC-MS and GC chromatograms also indicated the absence of an epoxy group, indicating complete conversion into an epithio group. Signals in ^{13}C NMR at 31.0 and 26.0 ppm confirm the presence of an epithio ring in the synthesized products. The adjacent methylene group of the epithio system was shifted to 36.0 ppm due to a β effect from the sulfur atom, also confirming the product formation.

Performance Evaluation of the Epithio Derivatives as Antioxidants. The antioxidant activity of the synthesized epithio derivatives and commercial antioxidant BHT were evaluated using three base oils, EJB, DOS, and S-105. The oxidative onset temperature (OOT) of the pure base oils was found to be 164.4, 180.2, and 193.6 °C, respectively. The fatty acid composition of synthesized biolubricant base oil EJB revealed that almost all of the unsaturation converted to epoxy group as follows: C18:1 epoxy, 44.1%; C18:2 mono epoxy, 3%; and C18:2 di epoxy, 26%. The basic lubricant properties such as viscosity, viscosity index, and density exhibited by the three base oils are shown in Table 1. The additive percentage in base oils was optimized using base oil (DOS) spiked with additive butyl 10-epithioundecanoate (**4d**) ranging from 0.5 to 4% and their OOTs are 181.8, 188.1, 229.2, 230.5, and 232.5 °C, respectively. The maximum antioxidant activity was observed at 2 wt % concentration, and even though the additive dosage was increased to 3 and 4%, a negligible increase in antioxidant activity was observed. Hence, the antioxidant efficacies of synthesized epithio derivatives and commercial antioxidant, BHT, were evaluated at 2 wt % concentration in the base oils. All of the epithio undecanoates exhibited superior performance compared to BHT in DOS base oil, whereas **4d** exhibited comparable performance with BHT in EJB and S-105 base oils. The nature of the ester alkyl group of the epithio undecanoate derivatives displayed different antioxidant activities in the three base oils tested. Products prepared from short-chain alcohols (methyl and *n*-butyl) exhibited better performance, and as the chain length increased (2-ethylhexyl), the antioxidant activity decreased. There is a clear effect of the length of the alkyl chain of the ester moiety of epithio derivatives on antioxidant potency, resulting in products (**4a** and **4d**) with greater antioxidant ability to stabilize base oil than their corresponding epithio derivative, **4e**. Similar results have been published earlier for ether derivatives of hydroxytyrosol and amino alcohols,[21,25] and in which the shorter alkyl side chains improved the scavenger activity and the reducing ability of hydroxytyrosol, and the presence of longer linear chains (C_7-C_9) decreased such antioxidant effects.[26] A cutoff effect in the antioxidant efficacy in relation to the alkyl chain length was also reported by Sorensen et al. on alkyl ferulates. The most efficient alkyl ferulates were methyl and butyl ferulate, whereas octyl ferulate was pro-oxidative, and the pro-oxidative effect increased further with an increment in the alkyl chain length from C_8 to C_{12}. Further elongation of the alkyl chain length to C_{16} and C_{20} resulted in weak pro-oxidative effects to weak antioxidative effects.[27] This might be also due to readily available sites for oxidation, making them more sensitive to cleavage than shorter ester chain lengths.[28−31] The three epithio derivatives prepared with iso alkyl epoxy undecanoates exhibited less antioxidant activity compared to straight-chain epithio derivatives. This could be related to the steric effect of side chains present in the ester chain of isoalkyl epithio derivatives.

Table 1. Physicochemical Properties of Base Oils

property		EJB	DOS	S-105
density 15 °C (g/cm^3)		0.915	0.920	0.835
viscosity	40 °C, cSt	11.15	12.38	10.28
	100 °C, cSt	3.09	3.26	3.36
viscosity index		126	126	117

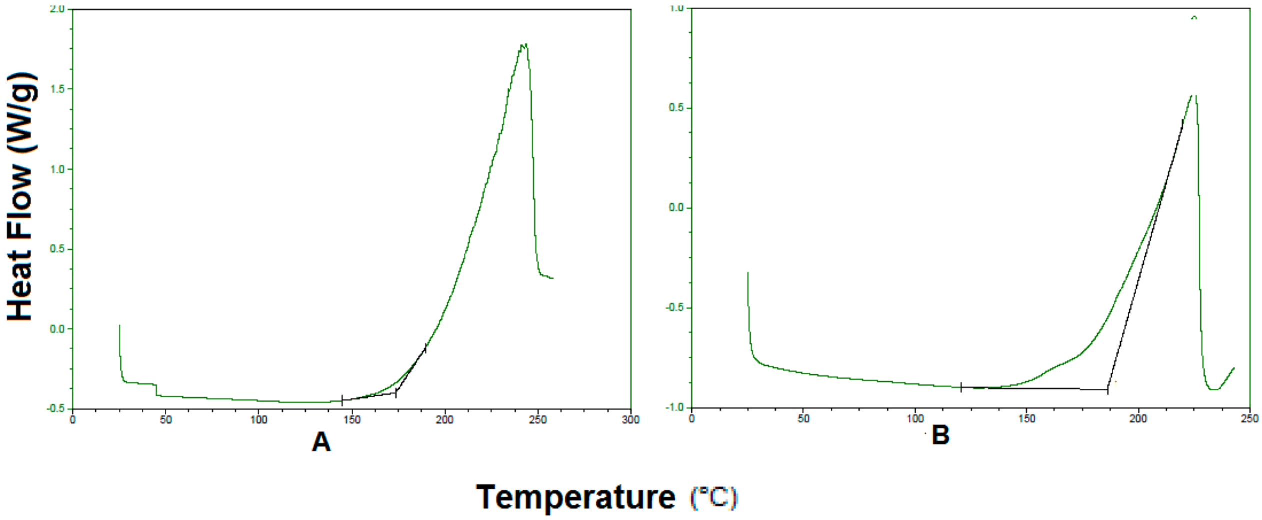
Epithio derivatives with methyl and butyl ester chain lengths exhibited comparable antioxidant activities in base oil EJB. The same trend was observed in DOS and S-105 base oils, and the results are summarized in Table 2. The optimum chain length C_4 exhibited superior OOT of 229 °C among the synthesized additives in DOS base oil. In the case of S-105 base oil, as the chain length increased from C_1 to C_4, an increase in activity, and on further increase in chain length (C_8), a decrease in activity were observed. Butyl 10-epithioundecanoate exhibited excellent antioxidant activity among all of the synthesized additives in the three base oils EJB, DOS, and S-105 with OOTs of 180.6, 229.2, and 242 °C, respectively, followed by **4a**. A typical dynamic DSC curve is given in Figure 1, showing the dynamic curve of a base oil without any additive and of a base oil with **4d** at 2 wt % concentration in EJB and S-105 base oil.

Table 2. Antioxidant Property of the Synthesized Additives (2 wt %) in Three Lubricant Base Stocks

	oxidative onset temperature (OOT) (°C)		
sample name[a]	EJB	DOS	S-105
no additive	164.4	180.2	193.6
ESUME	177.6	195.1	216.5
ESIPAUES	162.7	206.2	214.4
ESC-4UES	156.1	200.1	215.9
ESnBU-UES	180.6	229.2	242.0
ES-2ET-HE-UES	169.7	199.5	199.2
BHT	180.3	193.8	243.3

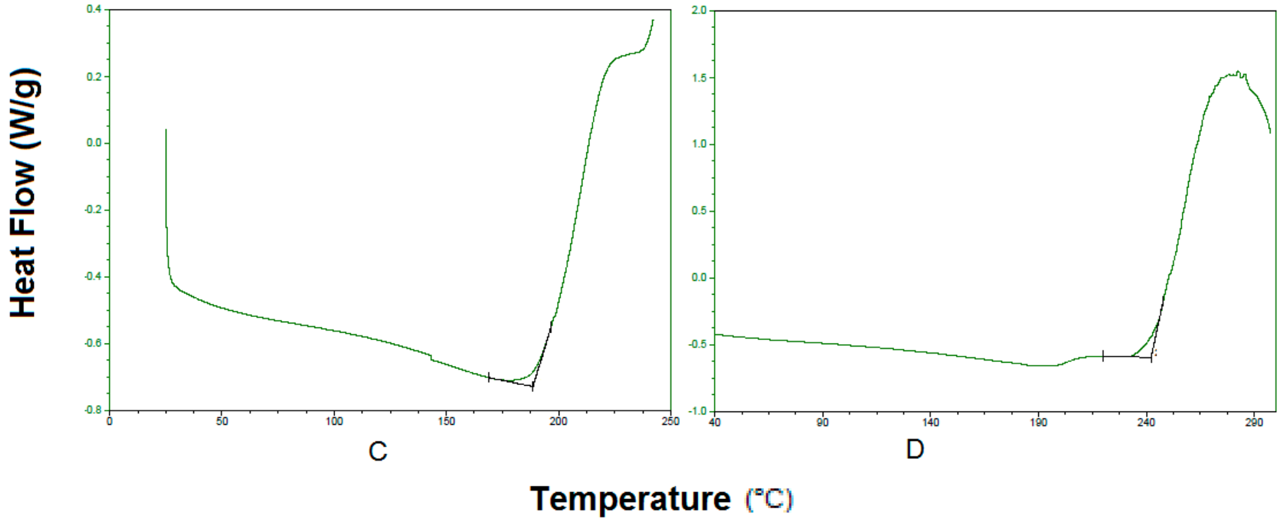
[a] ESUME, methyl 10-epithoundecanoate; ESIPAUES, 1-(2-propyl) 10-epithoundecanoate; ESC-4UES, 2-methyl-1-propyl 10-epithoundecanoate; ESnBU-UES, 1-butyl 10-epithoundecanoate; ES-2ET-HE-UES, 2-ethylhexyl 10-epithoundecanoate; BHT, butylated hydroxytoluene.

Performance Evaluation of the Synthesized Epithio Derivatives as Extreme Pressure Additives. The weld point (WP) in extreme pressure property can be defined as the load at which welding of the balls due to the friction between the stationary three balls and the rotating top ball is high enough to weld. The WP of a test sample can be evaluated within ±10 kg by increasing the smaller load close to the weld point. Higher WP indicates the better EP properties of the test sample. Compounds containing certain elements such as sulfur, phosphorus, and halogens are known to be capable of participating in tribochemical reactions with the friction surfaces and generating in situ tribofilms that reduce friction under extreme pressure conditions.[32] Therefore, the synthesized alkyl epithio undecanoates were evaluated for their EP activity using three base oils, EJB, DOS, and S-105, and the results were compared with those of commercial EP additive, TCP. In the absence of EP additives the three base oils displayed weld points of 160, 120, and 120 kg, respectively. The base oil doped with the additives was stirred under magnetic stirring for 30 min at 40 °C to attain the homogeneity of the sample. Butyl epithio undecanoate and base oil DOS were used for optimization of additive concentration. The improvement in weld point of the base oil was analyzed at different concentrations ranging from 0.5 to 4%, and their weld points were 130, 140, 170, 160, and 150 kg, respectively. From the results 2 wt % was the optimum concentration at which the maximum weld point was observed. Even though the concentration was increased further to 3 and 4%, a decrease in weld point was observed. The blending of EP additives with the base oils resulted in increased weld point of three base oils as shown in Table 3. As the chain length of the ester moiety of the episulfide undecanoate increased from C_1 to C_4, the weld point of the base oil EJB increased from 160 to 210 kg. Surprisingly, methyl and butyl ester chains of episulfide undecanoate exhibited similar weld points of 210 kg. In the case of the 2-ethyhexyl ester of episulfide undecanoate the decrease in weld load of 180 kg was observed. The same trend was observed in base oils DOS and



A: Base Oil- Epoxy Jatropha Fatty Acid n-Butyl Esters (EJB)

B: Base Oil+n-Butyl-Epithio-Undecanoate



C: Base Oil-Mineral Oil (S-105)

D: Base Oil+ n-Butyl-Epithio-Undecanoate

Figure 1. Nonisothermal DSC curves of base oil with and without antioxidant.

S-105. This shows a decrease in load-carrying capacity with increasing chain length of the alcohol moiety of the fatty acid ester of epithio derivatives. These results demonstrate the effects of molecular structure on lubricity property. This is in good agreement with the general observation that shorter chain lengths reduce molecular interactions and decrease the temperature stability of a protective lubricant film.[33] *n*-Butyl 10-epithioundecanoate exhibited comparable performance with commercial additive TCP in both base oils EJB and DOS and inferior performance in S-105. The synthesized additives exhibited better compatibility with biolubricant base oil (EJB) and synthetic ester (DOS) compared to mineral base oil (S-105), which indicates a better synergistic effect of the epithio derivatives with these two oils than with mineral oil. Similar enhancements of load-carrying capacity in biobased base stocks relative to mineral oil have been reported.[34] Results indicate that the prepared compounds exhibited improved EP activity, and they can be effectively used as EP additives for biobased lubricant basestocks.

Performance Evaluation of Epithio Derivatives as Antiwear Additives. The investigation of the antiwear ability of methyl and butyl epithio undecanoates was done by varying their concentration in base oil DOS. Figure 2 shows the variation of the WSD of the lower steel balls with different additive concentrations. It is observed from the figure that the addition of additives in base stock, even at small concentrations, can

Table 3. Effect of 2 wt % Concentration of the Extreme Pressure Additive on Three Base Oils

	weld load (kg)		
sample name	EJB	DOS	S-105
no additive	160	120	120
ESUME	210	170	160
ESIPAUES	180	140	130
ESC-4UES	180	140	130
ESnBU-UES	210	170	160
ESnHE-UES	170	130	120
ES-2ET-HE-UES	180	140	130
TCP	210	160	200

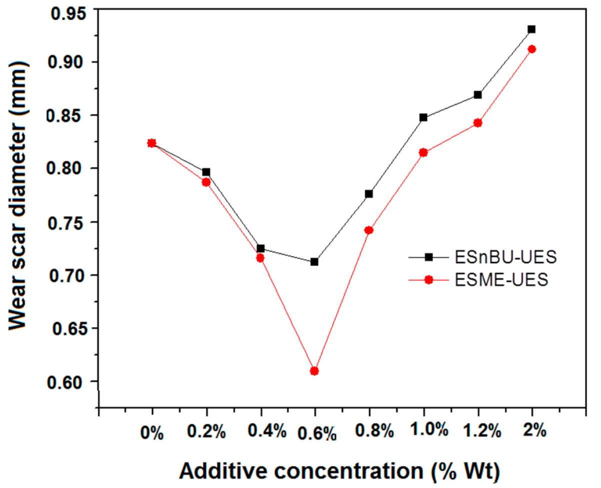


Figure 2. Wear scar diameter of the synthesized antiwear additive at different concentrations. ESnBU-UES, butyl epithio undecanoate; ESME-UES, methyl epithio undecanoate.

significantly reduce the WSD of the system. In particular, the introduction of 0.6 wt % methyl epithio undecanoate led to a decrease of the WSD by >26%. The addition of commercial antiwear additive LZ1359 also improved the AW property of the base fluid by 30%. The WSD decreased gradually with further increase of the additive concentration, implying that the AW property of the additive is dependent on its concentration in the base stock. When the additive concentration was below 0.6%, the WSD was smaller, indicating that additives demonstrated better AW property at a low concentration of 0.6%. This may be attributed to the formation of a more effective AW film by the additives through competing adsorption with base oil at a low concentration. The slight increase in the WSD with increasing additive concentration has also been reported in the literature.[35,36] This might be ascribed to corrosion of metal caused by the sulfur element present in the additives.

Worn Surface Analysis. Figure 3 shows the SEM images of the worn surface of steel balls lubricated with base oil DOS alone and with **4a** added oil at 0.6% concentration. The wear scar obtained from the test lubricated with base oil alone exhibited more scratches and deeper furrows compared with the scar produced with base oil with 0.6 wt % epithio derivative (**4a**). It can also be observed that the worn surface of steel balls lubricated by base oil with **4a** is shallower and smoother than that lubricated by base oil alone. This result further verifies that **4a** possesses good AW ability.

In conclusion, we have synthesized a series of novel epithio derivatives from 10-undecenoic acid. The addition of epithio derivatives as multifunctional additives to the base oils resulted in the enhancement of antioxidant, extreme pressure, and antiwear properties. Among the reported products, butyl 10-epithoundecanoate exhibited superior antioxidant and extreme pressure properties.

AUTHOR INFORMATION

Corresponding Author

*(R.B.N.P.) Phone: +91 040 27193370. Fax: +9140 27193370. E-mail: rbnprasad@iict.res.in.

Notes

The authors declare no competing financial interest.

REFERENCES

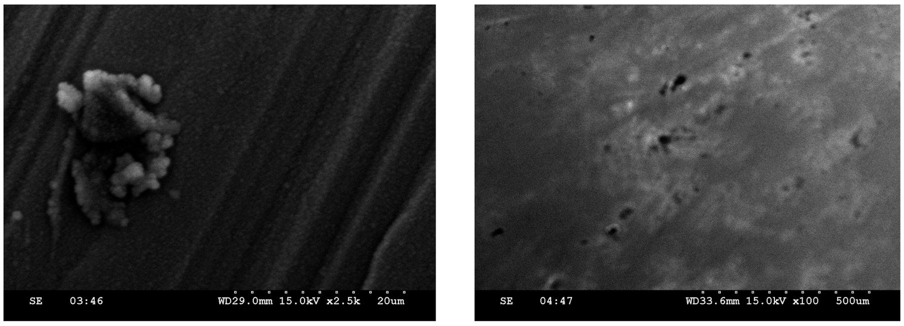
(1) Choi, U. S.; Ahn, B. G.; Kwon, O. K.; Chnat, Y. J. Tribological behavior of some antiwear additives in vegetable oils. *Tribol. Int.* **1997**, *37*, 677−683.

(2) Biermann, U.; Friedt, W.; Luhs, W.; Machmuller, G.; Metzger, J. O.; Klaas, M. R.; Schafer, H. J.; Schneider, M. P. New synthesis with oils and fats as renewable raw materials for the chemical industry. *Angew. Chem., Int. Ed.* **2000**, *39*, 2206−2224.

(3) Gunderson, R. J.; Hart, A. H. *Synthetic Lubricants*; Reinhold Publishing: New York, 1962; p 388.

(4) Mod, R. A.; Magne, F. C.; Sumrell, G.; Koos, R. E. Lubricants and lubricant additives: III. Performance characteristics of some thioacetate, phosphorodithioate, and hexachlorocyclopentadiene derivatives of stearic acid amides and esters. *J. Am. Oil Chem. Soc.* **1977**, *54*, 589−591.

(5) Magne, F. C.; Mod, R. R.; Sumrell, G.; Koos, R. E.; Parker, W. E. Lubricants and lubricant additives: II. Performance characteristics of some substituted fatty acid esters. *J. Am. Oil Chem. Soc.* **1975**, *52*, 494−497.



(a) 2-Ethylhexyl sebacate (Base oil)

(b) 0.6%ESUM+ base oil

Figure 3. SEM morphologies of worn surfaces of base oil (a) and additive-doped base oil (b).

(6) Mod, R. R.; Magne, F. C.; Sumrell, G.; Koos, R. E. Lubricants and lubricant additives: III. Performance characteristics of some thioacetate, phosphoro dithioate and hexachlorocyclopentadiene derivatives of stearic acid amides and esters. *J. Am. Oil Chem. Soc.* **1977**, 589−591.

(7) Chibber, V. K.; Chuadhary, R. B.; Tyagi, O. S.; Anand, O. N. Antiwear and antifriction characteristics of tribochemical films of alkyl octa-decenoates and their derivatives. *Lubri. Sci.* **2006**, *18*, 63−76.

(8) Forbes, E. S.; Reid, A. J. D. Liquid phase adsorption/reaction studies of organo-sulfur compounds and their load carrying mechanism. *ASLE Trans.* **1973**, *16*, 50−60.

(9) Allum, K. G.; Ford, J. F. The influence of chemical structure on the load-carrying properties of certain organo-sulphur compounds. *J. Inst. Petrol.* **1965**, *51*, 145−161.

(10) Davey, W.; Edwards, E. D. The extreme-pressure lubricating properties of some sulphides and disulphides, in mineral oil, as assessed by the four-ball machine. *Wear* **1958**, *1* (4), 291−304.

(11) Allum, K. G.; Forbes, E. S. The influence of chemical structure on antiwear properties of organic disulfides. *J. Inst. Petrol.* **1967**, *53*, 173−185.

(12) Wakim, J. M. Cosulfurized products of high iodine valve triglyceride and nonwax ester of monoethenoid fatty acid as lubricant additives. U.S. Patent 3,986,966, 1976.

(13) Sharma, B. K.; Adhvaryu, A.; Erhan, S. Z. Synthesis of hydroxy thio-ether derivatives of vegetable oil. *J. Agric. Food Chem.* **2006**, *54*, 9866−9872.

(14) Michaelis, P. Epithio compounds as additives for lubricants. U.S. Patent 4,217,233, 1980.

(15) Gunstone, F. D.; Hussain, M. G.; Smith, D. M. Fatty acids, part 42. The preparation and properties of methyl monomercapto stearates, some related thiols and some methyl epithiostearates. *Chem. Phys. Lipids* **1974**, *13*, 71−91.

(16) Marcel, S. F.; Lie Ken, Jie.; Zheng, Y. F. Synthesis and physical properties of some 2,3- and 2,2^1-epithio C_{18} fatty acid derivatives. *Chem. Phys. Lipids* **1988**, *49*, 167−178.

(17) Gupta, R.; Ahmad, S. M., Jr.; Ahmad, F.; Osmin, S. M. *Indian J. Chem. B* **1978**, *25*, 429−431.

(18) Kuranova, I. L.; Snetkova, E. V. *J. Org. Chem.* **1978**, *43*, 2923−2925.

(19) Iranpoor, N.; Kazemi, F. Stereospecific formation of *S*-styrene sulfide: efficient conversion of epoxides to thiiranes catalysed with Ru. *Tetrahedron* **1997**, *53*, 11377−11382.

(20) Geethanjali, G.; Sony, M. K.; Padmaja, K. V.; Karuna, M. S. L.; Prasad, R. B. N. Preparation and properties of lubricant base stocks from epoxidized karanja oil and its alkyl esters. *Ind. Eng. Chem. Res.* **2013**, *52*, 16598−16605.

(21) Sammaiah, A.; Padmaja, K. V.; Prasad, R. B. N. Synthesis and evaluation of novel acyl derivatives from jatropha oil as potential lubricant basestocks. *J. Agric. Food Chem.* **2014**, *62*, 4652−4660.

(22) Geethanjali, G.; Padmaja, K. V.; Sreedhar, B.; Prasad, R. B. N. Preparation of alkyl 11-anilino-10-hydroxy undecanoates and evaluation of their antioxidant activity. *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 740−746.

(23) Rao, C. N. R.; Raghavan, V. R.; Kasturi, T. R. Contribution to the infrared spectra of organosulphur compounds. *Can. J. Chem.* **1964**, *42*, 36−42.

(24) Derzhinskii, A. R.; Kalugin, V. E.; Prilezhaeva, E. N. Syntheis and reaction of 2,3-epoxy(epthio)propyl alkyl sulphides, sulfoxides and sulphones (translation). *Izv. Akad. Nauk SSSR* **1984**, *6*, 1392−1395.

(25) Bell, J. P.; Don, T.-M.; Voong, S.; Fernandez, A.; Ku, W. Synthesis and properties of epoxy-episulfide resins. *Angew. Makromol.* **1996**, *240*, 67−81.

(26) Pereira-Caro, G.; Madrona, A.; Bravo, L.; Espartero, J. L.; Alcudia, F.; Cert, A.; Mateos, R. Antioxidant activity evaluation of alkyl hydroxytyrosyl ethers, a new class of hydroxytyrosol derivatives. *Food Chem.* **2009**, *115* (1), 86−91.

(27) Sorensen, A. D. M.; Lyneborg, K. S.; Villeneuve, P.; Jacobsen, C. Alkyl chain length impacts the antioxidative effect of lipophilized ferulic acid in fish oil enriched milk. *J. Funct. Foods* **2014**, DOI: 10.1016/j.jff.2014.04.008.

(28) Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Ester hydroxyl derivatives of methyl oleate: Tribological, oxidation and low temperature properties. *Bioresour. Technol.* **2008**, *99*, 7333−7340.

(29) Sharma, B. K.; Adhvaryu, A.; Liu, Z.; Erhan, S. Z. Chemical modification of vegetable oils for lubricant applications. *J. Am. Oil Chem. Soc.* **2006**, *83*, 129−136.

(30) Tan, C. P.; Che Man, Y. B.; Selamat, J.; Yusof, M. S. A. Comparative studies of oxidative stability of edible oils by differential scanning calorimetry and oxidative stability index methods. *Food Chem.* **2002**, *76*, 385−389.

(31) Pardauil, J. J.; Souza, L. K.; Molfetta, F. A.; Zamian, J. R.; Rocha Filho, G. N.; da Costa, C. E. Determination of the oxidative stability by DSC of vegetable oils from the Amazonian area. *Bioresour. Technol.* **2011**, *102*, 5873−5877.

(32) Biresaw, G.; Laszio, J. A.; Evans, K. O.; Compton, D. L.; Bantchev, G. B. Synthesis and tribological investigation of lipoyl glycerides. *J. Agric. Food Chem.* **2014**, *62*, 2233−2243.

(33) Baek, S.Y.; Kim, Y.-W.; Chung, K.; Yoo, S.-H.; Kim, N. K.; Kim, Y.-J. Synthesis of succinic acid alkyl half-ester derivatives with improved lubricity characteristics. *Ind. Eng. Chem. Res.* **2012**, *51*, 3564−3568.

(34) Asadauskas, S. Z.; Biresaw, G.; McClure, T. G. Effects of chlorinated paraffin and ZDDP concentrations on boundary lubrication properties of mineral and soybean oils. *Tribol. Lett.* **2010**, *37* (2), 111−121.

(35) Zhou, M. L.; Li, F. F.; Zeng, X. J. Synthesis of two novel additives and study of their tribological properties in rapeseed oil. *China Petrol. Process. Petrochem. Technol.* **2007**, *3*, 29−33.

(36) Jianwei, Y.; Fenfang, L.; Yihui, H. Tribological performance of two potential environmentally friendly ash less vegetable oil additives. *China Petrol. Process. Petrochem. Technol.* **2010**, *12*, 43−48.