

## Synthesis of Hydroxy Thio-ether Derivatives of Vegetable Oil

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Bio-based additives are desirable commodities due to their eco-friendly nature. These additives can demonstrate physical and chemical properties comparable to those of conventional mineral oil-based products. Sulfur incorporated triacylglycerol can function as an antiwear/antifricition additive for lubricants. The synthesis of four useful hydroxy thio-ether derivatives of vegetable oils, from commercially available epoxidized soybean oil and common organic thiols, is reported in this paper. The common thiols used herein were 1-butanethiol, 1-decanethiol, 1-octadecanethiol, and cyclohexyl mercaptan. Currently, there is no reported literature describing the synthesis of hydroxy thio-ether derivatives of vegetable oil. The reaction was monitored, and products were confirmed by NMR and FTIR spectroscopies. Experimental conditions involving various thiols, solvent, catalyst amount, time, and temperature were optimized for research quantity and laboratory scale-up. The synthetic process retains the vegetable oil structure, eliminates polyunsaturation in the molecule, and adds polar functional groups on triacylglycerol. These products can be used as agriculturally-based antiwear additives for lubricant applications.

**KEYWORDS:** Epoxidized soybean oil; thiols; thio-ether derivative; vegetable oil; epoxy ring opening

### INTRODUCTION

Vegetable oil-based products have advantages over petroleum-based products because they are from renewable resources, environmentally friendly, nontoxic, biodegradable, and relatively inexpensive (1, 2). The need to utilize bio-based resources is especially important considering the high cost of petroleum (3, 4). Vegetable oils are an excellent candidate for use as lubricants and functional fluids (5, 6) because they have very low volatility due to the high molecular weight of the triacylglycerol molecule, narrow range of viscosity change with temperature, good boundary lubrication characteristics due to the polar ester group, and high solubilizing power for polar contaminants and additive molecules. They are very attractive for industrial applications that have the potential for environmental contact through accidental leakage, dripping, or generating large quantities of after-use waste materials requiring costly disposal (7, 8). In addition, the vegetable oil structure offers sites for additional functionalization, allowing for the improvement of existing technical properties such as thermo-oxidative stability, low-temperature properties, and lubricity.

Vegetable oil in its natural form has poor thermo-oxidative stability (9–12) due to the presence of bisallylic protons. They are highly susceptible to radical attack and undergo oxidative degradation to form polar oxy compounds leading to an increase in oil soluble deposits, oxygenates, acids, and oil viscosity.

Vegetable oils also show poor corrosion protection (13). The ester functionality present in the triacylglycerol structure renders these oils susceptible to hydrolytic breakdown (14). Therefore, contamination with water in the form of emulsions must be prevented at every stage. Because of the presence of saturated fatty acids, they have poor low-temperature behavior (15, 16), as most vegetable oils undergo cloudiness, precipitation, poor flow, and solidification at  $-10\text{ }^{\circ}\text{C}$  upon long exposure to cold, in sharp contrast to mineral oil-based lubricants. Tribochemical degrading processes (17, 18) also occur in vegetable oils under severe conditions of temperature, pressure, shear stress, metal surface, and environment. To meet the stability requirement during various tribochemical processes, the oil structure has to maintain excellent boundary lubricating properties through strong physical and chemical adsorption with the metal. Incorporation of sulfur in the oil structure may improve adsorption properties (12, 17).

The double bonds present in vegetable oils offer an opportunity to chemically modify its structure to improve some of these properties. One useful reaction for the modification of vegetable oils has been epoxidation. The epoxidation method of oleochemicals has been known for many years (19, 20), and the process has been studied for vegetable oils also (21). Epoxidized soybean oil (ESBO) is commercially available and is widely used as a plasticizer. ESBO have been used to synthesize polymer composites (22–24). ESBO have also been used as a starting material for preparing chemically modified vegetable oils that are being studied in the lubricant (25–27),

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and limited studies on the conversion to lubricant additives has also been performed (28, 29).

In an effort to find replacements for sulfurized sperm whale oil, early attempts to sulfurize vegetable oils resulted in products that displayed a high level of intermolecular cross-linking and were thus characterized by unacceptable high viscosities. Miwa et al. (30) reports the reaction of jojoba oil with elemental sulfur, but the products from unrefined jojoba oil thickened badly during gear lubricant tests. Similarly, Princen and Rothfus (31) found that sulfurization of the unaltered meadowfoam oil triglyceride oil yielded a factice that was unacceptable as a lubricant additive. Various attempts to sulfurize wax esters of meadowfoam oil yielded products that had good lubrication properties but were characterized by one or more deficiencies, such as excessive foaming, unacceptable thermal stability, and thickening during gear box tests. Also, Kammann and Phillips (32) found that sulfurized vegetable triglyceride oils resulted in rubbery products, in some cases even at 12% sulfur content. Likewise, Wakim (33) reported that the sulfurization of triglycerides yield resinous products mostly insoluble in base oils and require the addition of nonwax fatty acid methyl esters to improve their solubility.

In this paper, a novel synthetic approach for the synthesis of hydroxy thio-ether derivatives of vegetable oils is reported. The synthesis is carried out by epoxy ring opening of the epoxidized soybean oil by organic thiols. They are the butyl thio-ether of hydroxy vegetable oil (BTHV), the decyl thio-ether of hydroxy vegetable oil (DTHV), the cyclohexyl thio-ether of hydroxy vegetable oil (CTHV), and the octadecyl thio-ether of hydroxy vegetable oil (OTHV). The thiols have been selected to give a variety of different materials that will allow us to study the effect of branch size and functionality on their performance properties. The current process retains the vegetable oil structure and its associated benefits (high flash point, viscosity index, lubricity, and eco-friendliness), while it allows for the removal of polyunsaturation in the fatty acid chain with the addition of polar functional groups that may increase surface adsorption on metal. Separate studies are in progress to determine the physical and performance properties of these products. These thio-ether derivatives will serve the function as antifriction and antiwear specialty chemicals in automotive and industrial applications.

## MATERIALS AND METHODS

**Materials.** Epoxidized soybean oil (Vikoflex 7170) from Arkema Inc. (Philadelphia, PA, 100% epoxidized, 7% (w/w) epoxy oxygen or 4.2 epoxy groups per triacylglycerol molecule), perchloric acid (ACS Reagent, 70% w/w), methylene chloride, sodium bicarbonate, and anhydrous magnesium sulfate from Fisher Scientific (Fairlawn, NJ) and 1-butanethiol, 1-decanethiol, cyclohexyl mercaptan, 1-octadecanethiol, and deuterated chloroform (99.8% D) from Sigma-Aldrich Chemicals (St. Louis, MO) were used as received.

**Syntheses of Poly(hydroxythio-ether) Derivative of Vegetable Oil from Epoxidized Soybean Oil.** The reaction was carried out with a mixture of 25 g (26 mmol) of ESBO and 9.86 g (109.4 mmol) of 1-butanethiol dissolved in 400 mL of methylene chloride, in a three-necked round-bottomed flask (1000 mL), under a dry nitrogen gas atmosphere. Perchloric acid (2.612 g) was used as the catalyst and added dropwise to the reaction mixture that was constantly agitated by a magnetic stirrer. After the addition was complete, the temperature was raised to 45 °C for refluxing. The reaction was allowed to proceed at 45 °C, and aliquots were taken and analyzed by FTIR. The reaction was judged to be complete after 4 h. After the reaction was complete, the mixture was cooled to room temperature, and the organic phase was washed with 200 mL of aqueous 5% sodium bicarbonate solution and deionized water (each 2 times) to remove any trace of acid catalyst remaining in the system. The organic phase was dried with anhydrous

magnesium sulfate for 12 h and filtered. The solvent was removed under reduced pressure at 80 °C, and the final product (BTHV) was stored under a dry vacuum overnight. The product obtained in 90–95% yield had a yellowish–brown color with garlic-like smell. The previous procedure was repeated using 109.4 mmol of 1-decanethiol (19 g), cyclohexyl mercaptan (12.7 g), and 1-octadecanethiol (31.3 g) for the preparation of DTHV (75% yield), CTHV (62% yield), and OTHV (71% yield) hydroxy thio-ether derivatives, respectively. The reaction times for complete reactions were 4.5 h (DTHV), 3 h (CTHV), and 5.5 h (OTHV).

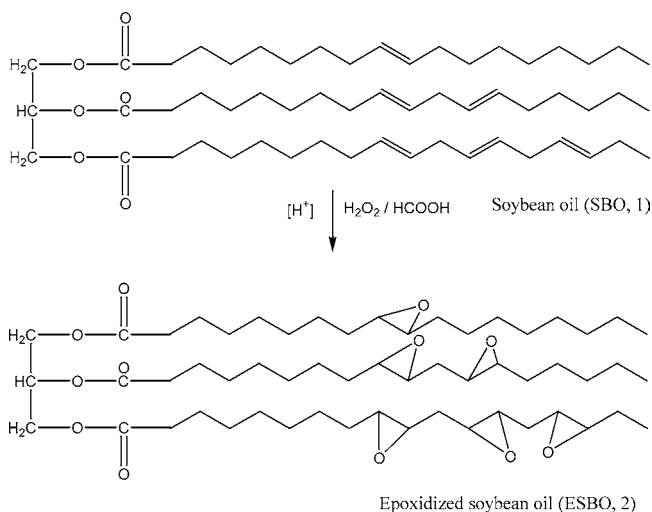
**NMR Analysis.** All the  $^1\text{H}$  NMR spectra were recorded quantitatively using a Bruker (Boston, MA) Avance 500 NMR spectrometer operating at 500 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$ , using a 5 mm dual probe. Bruker Icon NMR software was used running on an HP x1100 Pentium 4 workstation. For the  $^1\text{H}$  experiment, sample solutions were prepared in deuterated chloroform in 15% v/v concentrations. Proton NMR spectra were obtained from 16 co-added FIDs with a delay time of 1 s. Peaks were referenced to sodium 3-trimethylsilylpropionate-2,2,3,3- $d_4$  (TSP) at 0.0000 ppm. The peaks were identified by performing simulations of  $^1\text{H}$  NMR spectra using ACD/Labs 6.00 ACD/CNMR predictor software, running on a Gateway Pentium 4 CPU with a 2.53 GHz processor.

**FTIR Analysis.** FTIR spectra of the starting material, reaction aliquots, and products were recorded on a Thermo Nicolet (Madison, WI) Nexus 470 FTIR. Test samples of the reaction aliquots and products were pressed between two KBr disks (25 mm  $\times$  5 mm) to give transparent oil films for analysis by FTIR. A regular scanning range of 600–4000  $\text{cm}^{-1}$  was used for 32 repeated scans at a spectral resolution of 4  $\text{cm}^{-1}$ . Data were collected and processed on a Windows 2000 equipped Dell Optiplex GX260 Pentium 4, 2.46 GHz computer running Omnic 6.2 software. All spectra were baseline corrected and normalized to the average of the methylene peaks at 2927 and 2855  $\text{cm}^{-1}$ . Peak integration was performed with a routine provided in Omnic software. The area of the epoxy absorbance band, which existed in the epoxidized soybean oil as two overlapping peaks centered at 846 and 824  $\text{cm}^{-1}$ , was measured above a drawn baseline connecting the two minimums between 880 and 790  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

Vegetable oil consists of triacylglycerol molecules where the fatty acids are derived mainly from oleic (C18:1, one unsaturation in the fatty acid chain), linoleic (C18:2), and linolenic (C18:3) acids attached to a glycerol backbone. The relative distribution of fatty acids (FAs) in the molecule is largely based on the seed type and its genetic makeup. Regular soybean oil fatty acid distribution typically consists of  $\text{C}_{16} = 11\%$ ,  $\text{C}_{18} = 5\%$ ,  $\text{C}_{18:1} = 24\%$ ,  $\text{C}_{18:2} = 54\%$ , and  $\text{C}_{18:3} = 6\%$ . It has been established that presence of multiple double bonds in the vegetable oil triacylglycerol structure accelerates oxidative degradation (34). High polyunsaturation in the molecule would also result in low thermal and oxidative stability, while a higher degree of saturation would make the oil solid at room temperature. The removal of unsaturation in the soybean oil (SBO, **1**) by converting it to epoxy groups in epoxidized soybean oil (ESBO, **2**), shown in **Scheme 1**, significantly improves the thermal and oxidative stability of the oil (35).

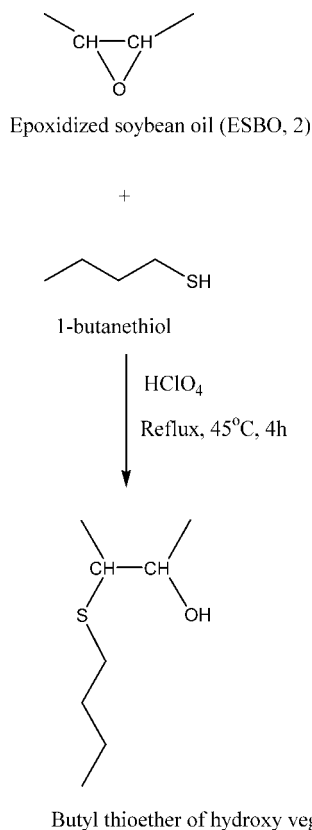
Our goal in this study is to open the epoxy ring of ESBO using various thiols. As sulfur groups are effective friction and wear reducers, sulfur incorporation in the triacylglycerol structure may enhance the friction and wear properties of soybean oil (36). The acid-catalyzed ring opening to form the hydroxy thio-ether derivatives was a simple straightforward reaction as well (**Scheme 2**). This synthesis is also an effective way of introducing branching at unsaturated sites as well as sulfur incorporation using a one-step intramolecular mechanism. In all of the reaction cases, we monitored the reaction progress closely by taking aliquots of the reaction solution and analyzing them by FTIR.

**Scheme 1.** Epoxidation of Soybean Oil (SBO) Using Performic Acid To Give Epoxidized Soybean Oil (ESBO)<sup>a</sup>

<sup>a</sup> The average triacylglycerol structures of SBO and ESBO have 4.2 double bonds and epoxy rings, respectively.

The retention of the triacylglycerol backbone is very important to maintain excellent biodegradable character of vegetable oils. Unfortunately, the acid has a tendency to hydrolyze the ester group and thereby destroy the triacylglycerol structure. However, the presence of one or two epoxy groups per fatty acid chain in the soybean oil (depending on the oleic and linoleic content) makes it highly susceptible to acid-catalyzed ring opening in a suitable protic medium. Moreover, the reaction of the thiol group with the epoxy group is more facile as compared with water or alcohol because the nucleophilicity of sulfur is higher than oxygen. The reaction of elemental sulfur with triacylglycerol molecules may result in sulfurized vegetable oils with unacceptably high viscosities due to a high level of intermolecular cross-linking (30–33). However, for our purpose, cross-linking is undesirable and will make the product useless as a lubricant or additive. This can be prevented by careful epoxy ring opening of epoxidized soybean oil using thiols to obtain the polyhydroxy thio-ether derivative of SBO, **3** (BTHV), as shown in **Scheme 2**. On visual inspection, the viscosity of **3** is substantially increased due to hydrogen bonding through the —OH pair, as compared to **2**, but is much lower than the viscosities of cross-linked sulfurized vegetable oils.

The reaction parameters such as catalysts, catalyst amount, reaction temperature, solvent, reaction time, and thiols were optimized for research quantity and laboratory scale-up. Initial attempts to use Lewis acid catalysts such as  $\text{BF}_3$ , with thiols at elevated temperatures, resulted in no change in epoxy peaks in FTIR, which means that there is no epoxy ring opening. These catalysts did not initiate the thiol reaction with epoxy groups. It was found that perchloric acid was the right type of catalyst to carry out the desired reaction as shown in **Scheme 2**. Other catalysts may also be used, provided that they are capable of simultaneously opening the oxirane ring and promoting the addition of the thiol residue without hydrolyzing the ester group and thereby cleaving the fatty acid chains from the glycerol backbone. We varied the catalyst amount from 2.6 to 3.5 g of perchloric acid and found that even with a lower amount, the reaction completed rapidly. We also used a reaction temperature of 90 °C for 1-butanethiol/ESBO in hexane initially. However, those conditions were proved to be too severe and thus hydrolyzed the ester group of the triacylglycerol structure. We turned our attention to a more mild reaction temperature of 45

**Scheme 2.** Reaction of Epoxidized Soybean Oil (ESBO) with 1-Butanethiol that Produces a Butyl Thio-ether of Hydroxy Vegetable Oil (BTHV)

°C in methylene chloride, which prevented the hydrolysis of the triacylglycerol structure. Initially, ESBO was reacted with 1-butanethiol/perchloric acid in refluxing methylene chloride for 5 h at 45 °C. We found that the reaction went to completion in 3.5 h. Thus, ESBO, 1-butanethiol, and perchloric acid were reacted at 45 °C. Each average molecule of ESBO has approximately 4.2 mol of epoxy groups. Thus, the maximum amount of thiol that should be used is 4.2 times per mol of ESBO. We varied the thiol amount from 4.2 to 8.4 mol for each mole of ESBO. Thus, 4.2 mol of 1-butanethiol and 1 mol of perchloric acid for each mole of ESBO was optimum. Other thiols such as 1-decanethiol, cyclohexyl mercaptan, and 1-octadecanethiol were used for opening the epoxy ring of ESBO. All other reaction conditions were the same except for the reaction time, which was 4.5 h for product DTHV, 3 h for CTHV, and 5.5 h for OTHV. These reaction times were optimized by monitoring reaction aliquots using FTIR.

Figure 1 shows the proton NMR spectra of epoxidized soybean oil, **2**, with peak area integration. <sup>1</sup>H NMR studies on **2** indicate that one methine proton of the —CH<sub>2</sub>—CH—CH<sub>2</sub>— backbone was observed at  $\delta$  5.1–5.3 ppm, four methylene protons of the —CH<sub>2</sub>—CH—CH<sub>2</sub>— backbone at  $\delta$  4.1–4.4 ppm, four CH<sub>2</sub> protons adjacent to two epoxy group at  $\delta$  1.65–1.85 ppm, —CH— protons (approximately nine protons) of the epoxy ring at  $\delta$  2.8–3.2 ppm, six protons of  $\alpha$ -CH<sub>2</sub> to >C=O at  $\delta$  2.2–2.4 ppm, six protons of  $\beta$ -CH<sub>2</sub> to >C=O at  $\delta$  1.55–1.7 ppm, protons of  $\alpha$ -CH<sub>2</sub> to epoxy group at  $\delta$  1.4–1.55 ppm, protons of saturated methylene groups  $\delta$  1.1–1.4 ppm, and terminal —CH<sub>3</sub> group protons at  $\delta$  0.8–1.0 ppm region. **Figure 2** shows the proton NMR spectra of the decyl thio-ether of hydroxy vegetable oil with peak area integration. DTHV retains most of the characteristic peaks of ESBO, **2**, except the ones at

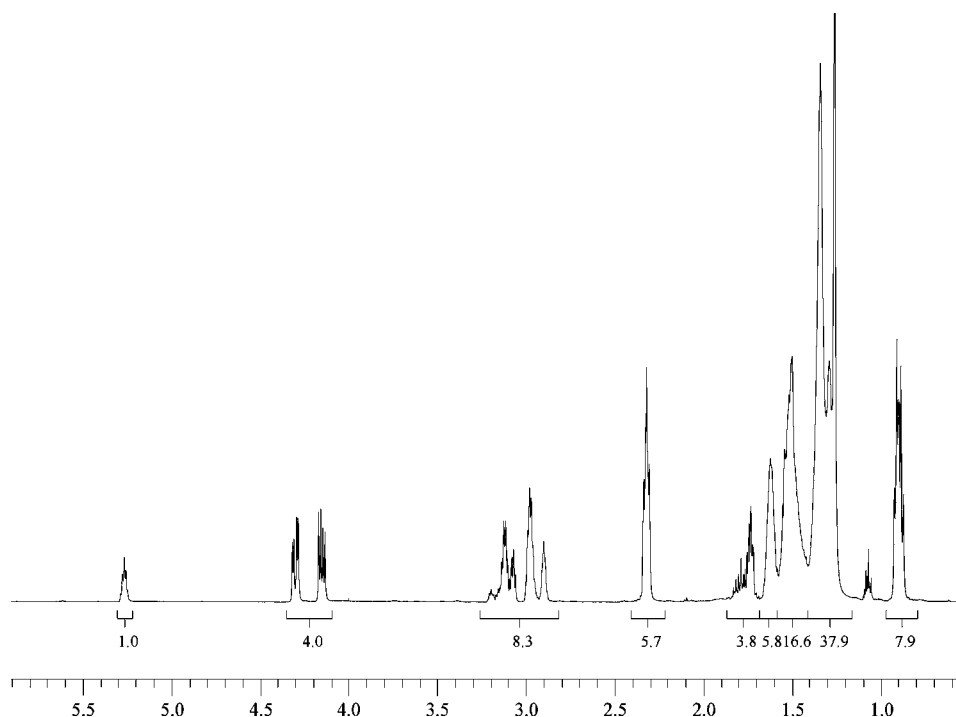


Figure 1. Proton NMR spectra of epoxidized soybean oil with peak area integration.

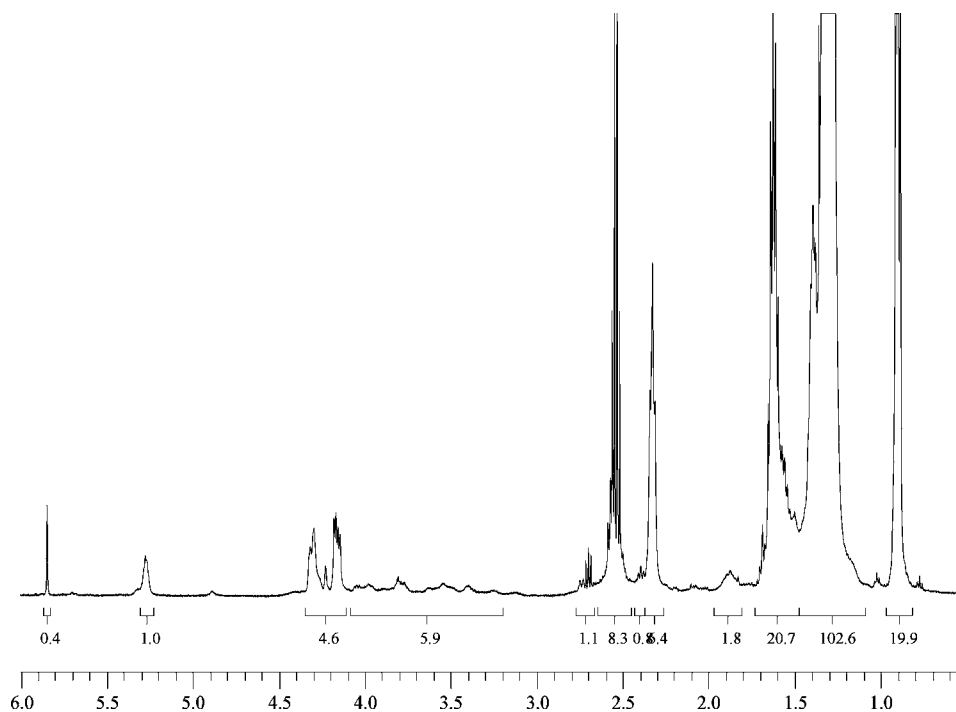
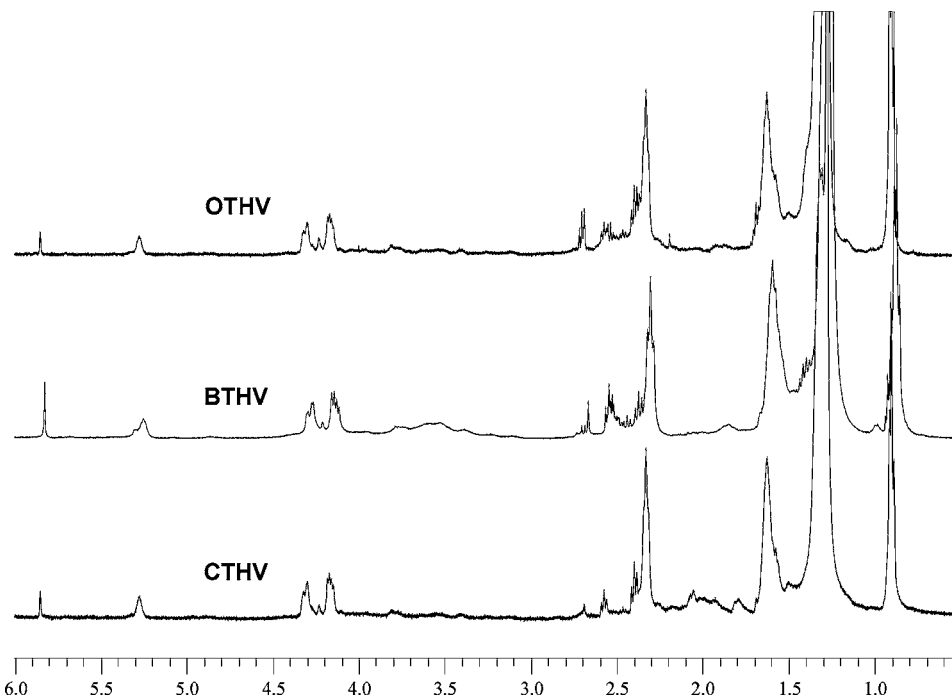


Figure 2. Proton NMR spectra of decyl thio-ether of hydroxy vegetable oil with peak area integration.

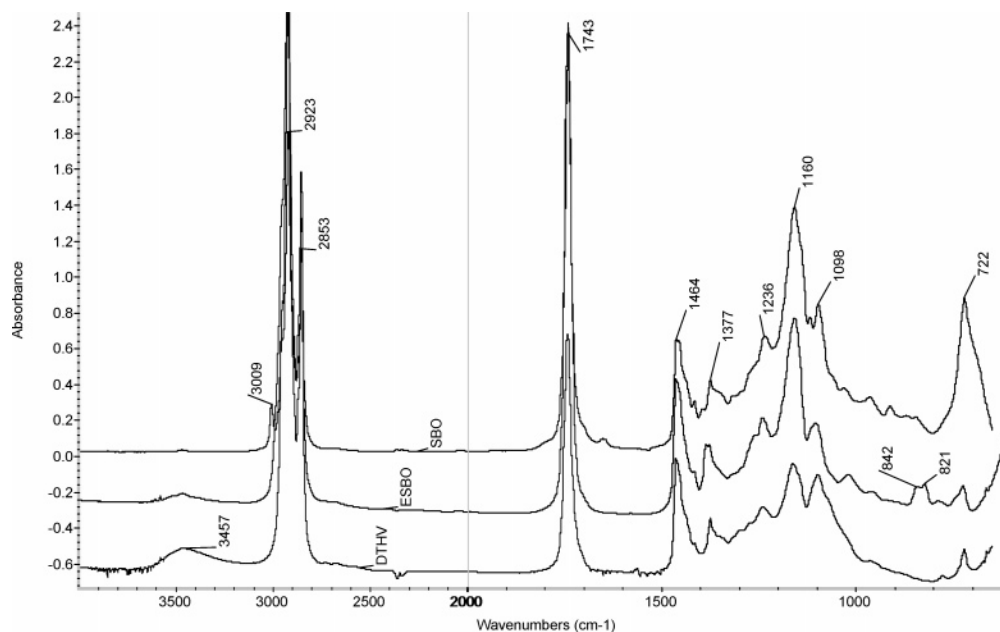
$\delta$  2.8–3.2 ppm for protons attached to epoxy groups,  $\delta$  1.4–1.55 ppm region for protons of methylene groups adjacent to the epoxy group, and  $\delta$  1.65–1.85 ppm for  $\text{CH}_2$  protons adjacent to two epoxy groups. Some additional peaks at  $\delta$  5.8–5.9 ppm corresponding to  $-\text{OH}$  and several broad overlapping peaks in the range  $\delta$  3.2–3.8 ppm from  $-\text{CH}$  (OH) were identified. The relative position of the hydroxyl peak (singlet, 5.8–5.9 ppm) varied from  $\delta$  4.8–6.0 ppm with respect to their abundance and position in the fatty acid chain of product **3** (Scheme 2). This in addition to peaks at  $\delta$  2.4–2.6 ppm from  $-\text{CH}_2$  adjacent to carbons linked to the thio-ether group and at  $\delta$  2.65–2.75

ppm from  $-\text{CH}-\text{S}-\text{CH}_2-$  was also identified in derivative **3**. Relative intensity and chemical shift of individual peaks from protons at substituted carbon sites in **3** varied slightly with the amount and position of epoxy rings in **2**.

By comparing the proton counts (by integration) of the methylene peak at  $\delta$  2.4–2.6 ppm for  $\alpha\text{-CH}_2$  to the carbon linked to the thio-ether group and the methyl peak at  $\delta$  0.8–0.95 ppm for  $\text{CH}_3$  of the thio-ether branch, we determined the extent of epoxy ring opening. The integral values can be referenced to 1.00 for one methine proton of the  $-\text{CH}_2-\text{CH}-\text{CH}_2-$  backbone at  $\delta$  5.1–5.3 ppm or to 4.00 for four methylene



**Figure 3.** Proton NMR spectra of octadecyl (OTHV, top), butyl (BTHV, middle), and cyclohexyl (CTHV, bottom) thio-ether of hydroxy vegetable oil.



**Figure 4.** FTIR spectra of soybean oil (SBO, top), epoxidized soybean oil (ESBO, middle), and decyl thio-ether of hydroxy vegetable oil (DTHV, bottom). The reaction progress can be judged by the loss of the ESBO epoxide band at 842 and 821  $\text{cm}^{-1}$  and the appearance of a broad OH band at  $\sim 3457 \text{ cm}^{-1}$ .

protons of the  $-\text{CH}_2-\text{CH}-\text{CH}_2-$  backbone at  $\delta$  4.1–4.4 ppm. We referenced all the integrals with respect to 1.00 for one  $-\text{CH}$  proton of backbone at  $\delta$  5.1–5.3 ppm and obtained an approximate value of 4.00 for four  $-\text{CH}_2$  protons of the backbone at  $\delta$  4.1–4.4 ppm and 6.00 for six protons of  $\alpha\text{-CH}_2$  to  $>\text{C}=\text{O}$  at  $\delta$  2.2–2.4 ppm. These values confirmed that the triacylglycerol backbone structure of vegetable oil is intact. The absence of  $-\text{CH}-$  protons of the epoxy ring at  $\delta$  2.8–3.2 ppm and an integral value of approximately 8.00 for  $\alpha\text{-CH}_2$  protons to carbon linked to the thio-ether group at  $\delta$  2.4–2.6 ppm suggested addition of approximately four molecules of thiol per triacylglycerol molecule. This has been further confirmed by an integral value of approximately 20.0 for  $-\text{CH}_3-$  protons of

the thio-ether branch (approximately 12 protons) and fatty acid chains of triacylglycerol (nine protons). Several broad overlapping peaks in the range  $\delta$  3.2–3.8 ppm for  $-\text{CH}$  (OH) have an integral value of approximately 6.0. Considering four protons assigned to epoxy ring opened product, there are two extra unidentified protons. The previous spectral data suggest that controlled ring opening of **2** was followed by a simultaneous formation of hydroxyl group and a thio-ether chain at the epoxy carbon sites in product **3**. Similar proton NMR spectra were obtained for the octadecyl (OTHV), butyl (BTHV), and cyclohexyl (CTHV) thio-ether of hydroxy vegetable oils as shown in **Figure 3**.

The FTIR spectra of soybean oil, epoxidized soybean oil,

and decyl thio-ether of hydroxy vegetable oil show well-resolved peaks at 722, 1098, 1160, 1236, 1377, 1464, 1743, 2853, 2923, and 3431  $\text{cm}^{-1}$  (Figure 4). The absorption due to the epoxy group at 821 and 842  $\text{cm}^{-1}$  in ESBO is not observed in DTHV. This fact suggests that ESBO undergoes complete ring opening under the reaction condition to form thio-ether derivatives of hydroxy vegetable oils. The consequent generation of free hydroxyl groups resulted in broad peak (3550–3200  $\text{cm}^{-1}$ ) for hydrogen-bonded -OH groups, and these are readily broken on dilution. The presence of these intermolecular hydrogen bonds also causes an increase in viscosity of the reaction product 3.

FTIR analysis of reaction aliquots was used to measure the reaction efficiency by estimating the fraction of an unreacted epoxy group remaining in the product oil. From spectral peak integration of the epoxy peak in the spectrum of the reaction product, it was observed that the area of the epoxy peak decreased with time. The epoxy peak was completely absent in the reaction product at the end of the reaction time, indicating that the epoxy ring opening reaction was 100% complete. As discussed in the NMR section, there was an addition of approximately four molecules of thiol per triacylglycerol molecule. So, if we consider 4.2 epoxy rings in average triacylglycerol molecule, the NMR data indicate that 95% of the epoxy groups was converted to thio-ether hydroxy derivatives, while the remaining epoxy rings were opened through competing hydrolysis. The total acid number (TAN) of the starting material SBO, ESBO, and reaction product were determined to check if there was any formation of free fatty acids during the reaction. The TAN values were an average of three experiments with standard deviations of <0.08. Soybean oil has a TAN value of 1.12 mg of KOH/g, ESBO has 0.12 mg of KOH/g, and all four reaction products have less than 0.5 mg of KOH/g. This further confirms that there is no hydrolysis of a triacylglycerol backbone to form free fatty acids in these reaction conditions.

The oxidation stability of these reaction products was measured using pressurized differential scanning calorimetry (PDSC). This oxidation stability test is widely used in the lubricant industry and is considered reliable for base oils as well as finished lubricants (37). The sample is heated in a hermetically sealed aluminum pinhole pan at 10  $^{\circ}\text{C}/\text{min}$ , under 200 psi (1379 kPa) of dry air. The onset temperature (OT) is the temperature at which a rapid increase in the rate of oxidation is observed and obtained by extrapolating the tangent drawn on the steepest slope of reaction exotherm to the baseline. A high OT would suggest a high oxidation stability of the oil (10, 12, 37). The onset temperatures determined for the starting material and reaction products are an average of three independent experiments with standard deviations of <1.0. The onset temperature for SBO was 134  $^{\circ}\text{C}$ , while for ESBO and reaction product BTHV, the OT was 195 and 181  $^{\circ}\text{C}$ , respectively. Both the ESBO and the thio-ether hydroxy derivative showed a higher oxidation stability than SBO as a result of the removal of polyunsaturation from the triacylglycerol structure of soybean oil. However, at higher temperatures (>250  $^{\circ}\text{C}$ ), rapid degradation of the epoxidized SBO occurs when the oxirane rings open under an oxidizing environment to give polymeric oxidation products through a radical pathway (35).

In conclusion, we have demonstrated the synthesis of potentially useful vegetable oil-based nontoxic additive compounds. The epoxy groups of the epoxidized soybean oil were reacted selectively with various thiols to give thio-ether hydroxy derivatives of soybean oil using a simple catalyst, reaction temperature, and time for maximum conversion, without cross-

linking and with no disruption of the ester linkages of the triacylglycerol structure of vegetable oil. Preliminary research on these compounds has shown interesting oxidation and lubricity properties. Furthermore, a greater affinity of sulfur (present in thio-ether hydroxy derivatives of vegetable oil) for metal surfaces will improve the friction and wear behavior, otherwise unattainable with SBO and ESBO. Further work on detailed tribochemical evaluation of these compounds is in progress. The thio-ether hydroxy derivatives of vegetable oil may find use as antiwear additives in bio-based industrial lubricants.

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