One-Pot Synthesis of Chemically Modified Vegetable Oils

BRAJENDRA K. SHARMA,[†,‡] ZENGSHE LIU,[†] ATANU ADHVARYU,[†,‡] AND
SEVIM Z. ERHAN*,[†]

*Food and Industrial Oil Research Unit, USDA/NCAUR/ARS, 1815 N. University Street,
Peoria, Illinois 61604, and Department of Chemical Engineering, Pennsylvania State University,
University Park, Pennsylvania 16802*

Vegetable oils are promising candidates as substitutes for petroleum base oils in lubricant applications, such as total loss lubrication, military applications, and outdoor activities. Although vegetable oils have some advantages, they also have poor oxidation and low temperature stability. One of the ways to address these issues is chemical modification of fatty acid chain of triglyceride. We report a one-pot synthesis of a novel class of chemically modified vegetable oils from epoxidized triacylglycerols and various anhydrides. In an anhydrous solvent, boron trifluoride etherate is used as catalyst to simultaneously open the oxirane ring and activate the anhydride. The reaction was monitored and products confirmed by NMR, FTIR, GPC, and TGA analysis. Experimental conditions were optimized for research quantity and laboratory scale-up (up to 4 lbs). The resultant acyl derivatives of vegetable oil, having diester substitution at the sites of unsaturation, have potential in formulation of industrial fluids such as hydraulic fluids, lubricants, and metal working fluids.

INTRODUCTION

Most lubricants currently originate from petroleum base stocks that are toxic to the environment, making it increasingly difficult for safe and easy disposal. The demand for "green" lubricants (*1*) is increasing due to concerns about the loss of petroleum lubricants to the environment (*2*), the high cost of petroleum (*3, 4*), and increasingly strict government regulations controlling their use.

Vegetable oils are nontoxic, renewable resources and lower cost alternatives to synthetic fluids (*5, 6*). They have low volatility, excellent lubricity, favorable viscosity temperature characteristics, and higher solubilizing capacity for contaminants and additives than mineral base oils. The most serious disadvantage of vegetable oils is their poor oxidative stability (*7, 8*), primarily due to the presence of bis allylic protons. These protons are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxy compounds, which ultimately results in insoluble deposit formation and an increase in oil acidity and viscosity. Studies have also shown that most vegetable oils undergo cloudiness, precipitation, poor fluid flow, and solidification at low temperatures. Genetic modification and use of additives can overcome these shortcomings to some extent. Another way to improve these properties of vegetable oils is chemical modification of fatty acid chains

of triglycerides at sites of unsaturation. It has been shown that changing the structure of the fatty acid chain has a large effect on the physical properties (*9*) of the triglycerides. These changes can significantly increase the performance of a lubricant material (*10–14*). The improvement of lubricity properties of triglycerides upon the introduction of branching has also been demonstrated (*10*).

One useful reaction for the modification of vegetable oils has been epoxidation of double bonds with hydrogen peroxide, either in acetic acid or formic acid (*15–17*). Epoxidized soybean oil (ESBO) is commercially available at a reasonable cost and is a promising intermediate for chemical modification because of reactive epoxy groups. These vegetable oil epoxides have also been used to synthesize polymer composites (*18–22*), hydrogels (*23*), and oleochemical carbonates (*24, 25*), and limited studies on the conversion of terminal epoxides to surfactants have also been performed (*26, 27*). The diester derivatives of triglycerides prepared using a two-step reaction (*10, 28*) were reported to have good oxidative stability and low temperature performance properties and utility in formulation of hydraulic fluids, metal working fluids, and other industrial fluids.

In this study, we report the synthesis of acyl derivatives of vegetable oils utilizing various acid anhydrides. Various anhydrides have been selected to give a variety of different products that will allow us to study the effect of branch size. We also report the process optimization and large-scale synthesis of an acyl derivative of vegetable oil using ESBO and hexanoic anhydride. Reactions were monitored using FTIR, and unreacted anhydride was determined using thermogravimetric analyzer

* Corresponding author. Tel.: 1-309-681-6532. Fax: 1-309-681-6340.
E-mail: Sevim.Erhan@ars.usda.gov.
[†] USDA/NCAUR/ARS.
[‡] Pennsylvania State University.

(TGA). Acyl derivatives of soybean oil were characterized using FTIR, gel permeation chromatography (GPC), and ^{1}H and ^{13}C NMR. These studies may help in the effort to find alternatives to petroleum-based products.

EXPERIMENTAL PROCEDURES

Materials. The ESBO (100% epoxidized, ∼4.2 epoxy groups per triacylglycerol molecule) was obtained from Elf Atochem Inc. (Philadelphia, PA) and used without any further purification. Boron trifluoride diethyl etherate (purified, redistilled), acetic anhydride (99.5%), propionic anhydrides (97%), butyric anhydride (≥97.5%), isobutyric anhydride (97%), valeric anhydride (97%), hexanoic anhydride (97%), hexanes, acetone, methyl oleate, methyl linoleate, monoolein, diolein, and triolein were obtained from Sigma-Aldrich (St. Louis, MO), while heptanoic anhydride (99%), sodium chloride, and sodium bicarbonate were obtained from Fisher Scientific (Fairlawn, NJ) and used as received. Polystyrene standards with molecular weights of 1700, 2450, 5050, 7000, 9200, and 10 665, were obtained from Polymer Laboratories Ltd. (Amherst, MA).

Analysis. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker (Boston, MA) Avance 500 NMR operating at a frequency of 500.13 and 125.77 MHz, respectively, using a 5 mm broadband inverse Z-gradient probe in CDCl$_3$ (Cambridge Isotope Laboratories, Andover, MA), and Bruker Icon NMR software was used. Peaks were referenced to sodium 3-trimethylsilylpropionate-2,2,3,3-d_4 (TSP) at 0.0000 ppm. Each spectrum was Fourier transformed, phase corrected, and integrated using ACD spectrum manager. The integration values in ^{1}H spectra were referenced to 4.00 between the range of 4.1 and 4.4 ppm. Simulations of ^{13}C NMR spectra were performed by ACD/Laboratories 6.00 ACD/CNMR predictor software.

FTIR spectra were recorded on a Thermo Nicolet (Madison, WI) Nexus 470 FT-IR system in a scanning range of 650–4000 cm^{-1} for 32 scans at a spectral resolution of 4 cm^{-1} with a pair of KBr crystals in thin film. Data were collected and processed using Omnic 6.2 software.

GPC profiles were obtained on a PL-GPC 120 high-temperature chromatograph (Polymer Laboratories, Amherst, MA) equipped with a column, autosampler, and built-in differential refractive index detector. The starting material and products were dissolved in THF. THF was used as the eluent with flow rate of 1.00 mL/min at 40 °C. The injection volume was 100 μL. Two PL gel 3 μm mixed E columns (300 mm × 7.5 mm) were used in series. The GPC was calibrated using a mixture of polystyrene (MW 1700, 2450, 5050, 7000, 9200, and 10 665), methyl oleate (296.48), methyl linoleate (294.48), monoolein (353), diolein (619.2), and triolein (885.4) in THF at 40 °C.

Product purity was obtained by determining unreacted anhydrides in the final products using TGA (model Q 500, TA Instruments, New Castle, DE), while heating the sample (3 μL) in platinum pans at 20 °C/min to 500 °C with high-resolution sensitivity 1.00 and resolution 3.00 in the presence of nitrogen. Hexanoic anhydride (HA) is a high-boiling sample and was found to evaporate before 200 °C. No evaporation loss below 200 °C was detected in ESBO. On using a solution of 20% HA in ESBO, at 200 °C, ∼20% weight loss was detected, which can be assigned to anhydride present in that mixture. On this basis, weight loss at 200 °C was assigned as unreacted anhydride content in the sample.

Oxirane titrations were performed on starting material and various diester products as per AOCS method Cd 9-57 to determine oxirane oxygen.

Total acid number (TAN) for the chemically modified samples was determined as per AOCS method Cd 3d-63. The TAN values of the staring material and the product mixture indicate the presence of free fatty acids and carboxylic acids generated during the reaction.
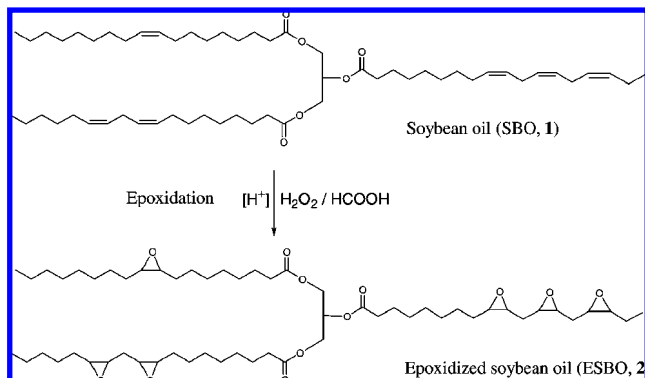
Synthesis of Acyl Derivatives of Vegetable Oils. The acylation reaction reported here is based on facile diacylation of glycidyl tosylate reported by Ali and Bittman (*29*), which has been modified for oleochemical use by our laboratory in the past (*10*). In a dry three-neck 500 mL round-bottom flask fitted with a condenser were placed 50 g of ESBO (52.6 mmol) and 47.28 g of hexanoic anhydride (220.9 mmol, 1:4.2 mol equiv) in 400 mL of methylene chloride. Boron trifluoride etherate (0.52 g, 3.7 mmol) was added and the mixture was

stirred and refluxed for 3 h under dry nitrogen atmosphere. After the reaction mixture cooled to room temperature, the product was purified by washing three times each with 100 mL of 5% NaHCO$_3$ solution followed by 100 mL of brine solution. The methylene chloride layer was dried over anhydrous magnesium sulfate (overnight) and filtered through a fritted funnel. The solvent was removed with rotary evaporation (∼60 °C; overnight) under reduced pressure, and residual anhydride was removed by Kugelrohr evaporation under reduced pressure (0.2 torr vacuum) at 70 °C to recover the diester derivative of SBO triacylglycerol. The product (HxSO1) was then stored under vacuum. The above procedure was repeated using acetic, propionic, butyric, isobutyric, valeric, and heptanoic anhydride for preparation of diester derivatives ASO1, PSO1, BSO1, iBSO1, VSO1, and HpSO1, respectively. The products were characterized by FTIR, GPC, and ^{1}H and ^{13}C NMR. Residual anhydrides in products were determined using TGA, while unreacted oxiranes and total acid numbers were determined using the aforementioned AOCS methods.

Larger-Scale Syntheses. Large-scale synthesis of HxSO1 was carried out in 20 L cylinderical reaction vessel. First, 8 L of ethyl acetate was used as solvent. The hexanoic anhydride (1419 g, 6.63 mol) was then placed in a 20 L reaction flask equipped with an overhead stirrer and, for temperature control, a heating mantle. The temperature was then raised to 35 °C and stirred to ensure thorough mixing. The catalyst boron trifluoride diethyl etherate (15.6 g, 0.11 mol) was then added to the anhydride solution in the reaction flask, and the temperature of the flask was raised to 55 °C. In a separate beaker, 1500 g (1.58 mol) of ESBO was dissolved in 2 L of ethyl acetate. This ESBO solution was then added slowly to the reaction flask. Once the addition was complete, the temperature of the reaction mixture was raised to 70 °C, when it started refluxing. The reaction mixture was stirred at a speed of 200 rpm. Heating and stirring continued at this temperature for another 5.5 h. The reaction was periodically monitored by taking aliquots and analyzing by FTIR for disappearance of the epoxy peak. In this reactor, and under these conditions, the reaction was judged to provide maximum conversion after 5.5 h. The reaction mixture was then cooled to room temperature, and the product was purified by washing three times each with 3 L of 5% NaHCO$_3$ solution followed by 3 L of brine solution. The ethyl acetate layer was dried over anhydrous magnesium sulfate (overnight) and filtered through a fritted funnel. The solvent was removed with rotary evaporation (∼60 °C; overnight) under reduced pressure. The residual anhydride was removed by vacuum distillation at 90 °C followed by Kugelrohr evaporation under reduced pressure (0.2 Torr vacuum) at 70 °C to recover the diester derivative of SBO triacylglycerol. The product (HxSO1) was then stored under vacuum. The isolated yield was 1590 g (1.17 mol, 74% yield). Similarly three more large-scale batches (one 500 g, two 700 g of ESBO) of HxSO1 were prepared in a 12 L round-bottom reaction flask equipped with an overhead stirrer. The reaction time for maximum conversion was ∼3.5 h in these three cases. The isolated yield for these three combined batches was 1949 g (1.44 mol, 72% yield).

ASO1 ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 5.26 (t, 1, CH proton of –CH$_2$**CH**CH$_2$– glycerol backbone), 5.4–4.6 (m, 2.4, CH protons, at the point of substitution CHO-acyl, in fatty acid chain), 4.32–4.08 (m, 4, CH$_2$ proton of –**CH$_2$**CH**CH$_2$**– glycerol backbone), 3.2–2.8 (m, 6.1, CH protons of the epoxy ring), 2.5–2.23 (t, 6, CH$_2$ protons α to fatty chain carboxy group), 2.2–1.83 (s, 7.3, CH$_3$ protons on the end of the acyl side chain), 1.8–1.2 (m, 70, unresolvable signals from CH$_2$ protons of fatty acid chain), 0.95–0.72 (t, 9, CH$_3$ protons on the end of the fatty chain). ^{13}C NMR: (125 MHz, CDCl$_3$) δ 173.1 (carbonyl carbon of the fatty chain), 172.7 (carbonyl carbon of the acyl side chain), 75–74 (fatty acid carbon of the branching site **C**HO-acyl), 68.9 (glycerol CH carbon), 62.1 (glycerol CH$_2$ carbon), 54.1–57.2 (epoxy carbons), 34.0–22.6 (multiple signals from the fatty carbon chain), 21.2 (CH$_3$ end carbon of the acyl side chain), 14.0 (CH$_3$ end carbon of the fatty chain). The spectral peaks and assignments are close to the computed chemical shift and in the correct order.

The ^{1}H and ^{13}C NMR data of diester derivatives PSO1, BSO1, iBSO1, VSO1, HxSO1, and HpSO1 are given in Supporting Information.

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Scheme 1. Epoxidation of Triacylglycerol of Soybean Oil (SBO) Resulting in Epoxidized Soybean Oil (ESBO)

Scheme 2. Ring-Opening Reaction of the Oxirane Ring of Epoxidized Soybean Oil (ESBO) Using Acid Anhydrides Resulting in Acyl Derivatives of Soybean Oil (SBO)


RESULTS AND DISCUSSION

The removal of unsaturation in the soybean oil by converting it to epoxy groups (**Scheme 1**) significantly improves the thermal and oxidative stability of the oil (*30*). It has already been established that the presence of multiple double bonds in the vegetable oil fatty acid chains accelerates oxidative degradation (*31*). The epoxidation of soybean oil, **1**, is a straightforward reaction (**Scheme 1**) and is done on industrial scale. The soybean oil is first either partially or completely epoxidized. The resultant oxirane rings are then available for reaction with anhydride. Epoxidation may be carried out as described by Bunker and Wool (*22*) and Doll and Erhan (*32*). The degree of epoxidation should be such that there is at least one and preferably two oxirane rings per triglyceride molecule. Typically, the epoxidation is carried to completion. Epoxidized soybean oil, **2**, for example, would have three to seven oxirane rings per molecule. The epoxidized soybean oil used here was obtained in high purity with oxirane oxygen content of 7% (w/w) or 4.2 epoxy groups per triacylglycerol molecule. In this study, we performed the straightforward ring opening of the oxirane ring of ESBO, **2**, using a nucleophilic reagents, resulting in formation of diesters at double bond sites (9,10; 12,13; 15,16) of fatty acid chains of triacylglycerol (**Scheme 2**). The conversion of **2** to **4** is postulated to proceed via initial attack of the anhydride carboxylic oxygen on one of the carbons of the epoxy ring affording intermediate **3**, which undergoes acyl migration to give acyl derivative of SBO, **4**. This kind of ring-opening reaction was performed previously in our laboratory with other nucleophilic reagents like water (*31*), thiol (*33*), and amine (*34*). The nucleophilic attack by acetic anhydride on the oxirane ring of ESBO in the presence of BF$_3$−ether catalyst resulted in ring-opened product ASO1, as shown in **Scheme 2**.

In all of the reaction cases, we monitored the reaction progress closely by taking aliquots of the reaction solution at 4 h intervals and analyzing them by FTIR for the disappearance of the epoxy absorption band (823 and 842 cm^{-1}) and change in relative intensities of 1465 and 1377 cm^{-1} bands in the fingerprint region (**Figure 1**). The ring opening of epoxy ring has also been confirmed by their respective ^{1}H NMR spectra (**Figure 2**). The intensity of peaks in the region 3.2–2.83 ppm (CH protons in the epoxy ring) decreased and new peaks at 4.8–5.4 ppm (protons at the point of substitution −CHOCOR in the fatty acid chain) appeared in all diester products. With these reaction conditions and catalyst, the ring opening is predominantly the major reaction with minimal ester hydrolysis. This is observed from the retention of NMR peaks of backbone glycerol structure in ring-opened derivatives. These are the NMR peaks at 5.2–5.3 and 4.1–4.4 ppm for CH and CH$_2$ proton of −CH$_2$CHCH$_2$−
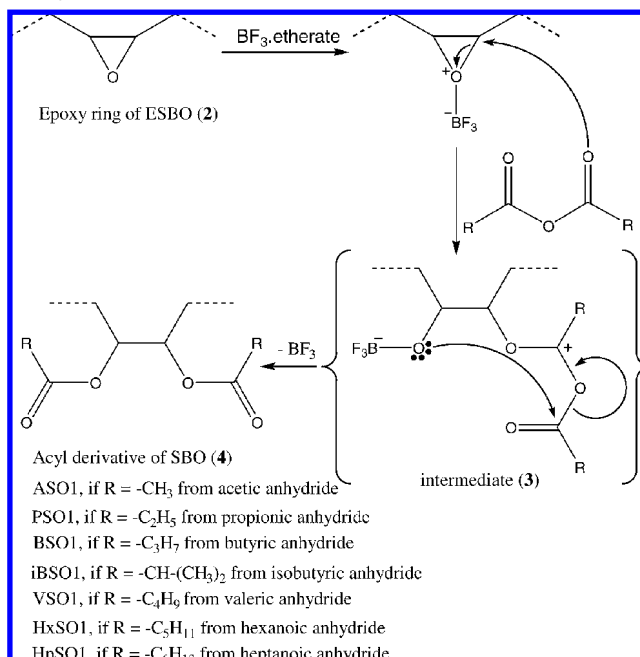
glycerol backbone, respectively. Further, the presence of ^{13}C NMR peaks at 173.2 ppm due to carbonyl carbon of triacylglycerol, 68.9 and 62.1 ppm, respectively, for CH and CH$_2$ carbons of −CH$_2$CHCH$_2$− glycerol backbone in all diester products confirms that the glycerol−fatty acid linkage is intact. The retention of the triacylglycerol backbone is important for maintaining the high biodegradability of the product.

To optimize the reaction conditions, five reaction parameters were varied. The parameters were catalysts, anhydrides, molar ratio of anhydrides to ESBO, reaction time, and reaction temperature. We found that boron trifluoride etherate in an anhydrous solvent was the most effective catalyst to simultaneously open the oxirane ring of ESBO and activate the anhydride, compared to other catalysts (perchloric acid, sulfuric acid, hydrochloric acid) tested. We used various anhydrides (acetic, propionic, butyric, isobutyric, valeric, hexanoic, and heptanoic anhydride), and hexanoic anhydride provided the best result in terms of epoxy ring opening. We determined the reaction time by running the reaction for up to 48 h and found no change in percent conversion after 3 h. Initially, we tried a solventless method and ESBO was reacted with acetic anhydride/BF$_3$. However, without solvent, conditions proved to be too aggressive for ESBO self-polymerization and the ESBO did not react with anhydride. We turned our attention to a more practical solvent method to carry out the reaction, with methylene chloride or ethyl acetate as solvent. Thus, ESBO, hexanoic anhydride, and boron trifluoride etherate as the catalyst in methylene chloride were reacted, and the optimal conditions were 50 °C for 3 h. We found that a similar reaction can be conducted in ethyl acetate solvent also, and the temperature in that case was 70 °C. On average, each mole of ESBO has 4.2 mol of epoxy groups. Thus, in principle, the maximum theoretical amount of anhydride that should be used is 4.2 mol per mole of EBSO. We varied the anhydride amount from 2.1 to 8.4 mol for each mole of ESBO. Thus, 4.2 mol of anhydride and 0.07 mol of boron trifluoride diethyl etherate for each mole of ESBO were optimal and opened about 1.25–2 epoxy groups depending on anhydrides. However, residual epoxy group remained in the
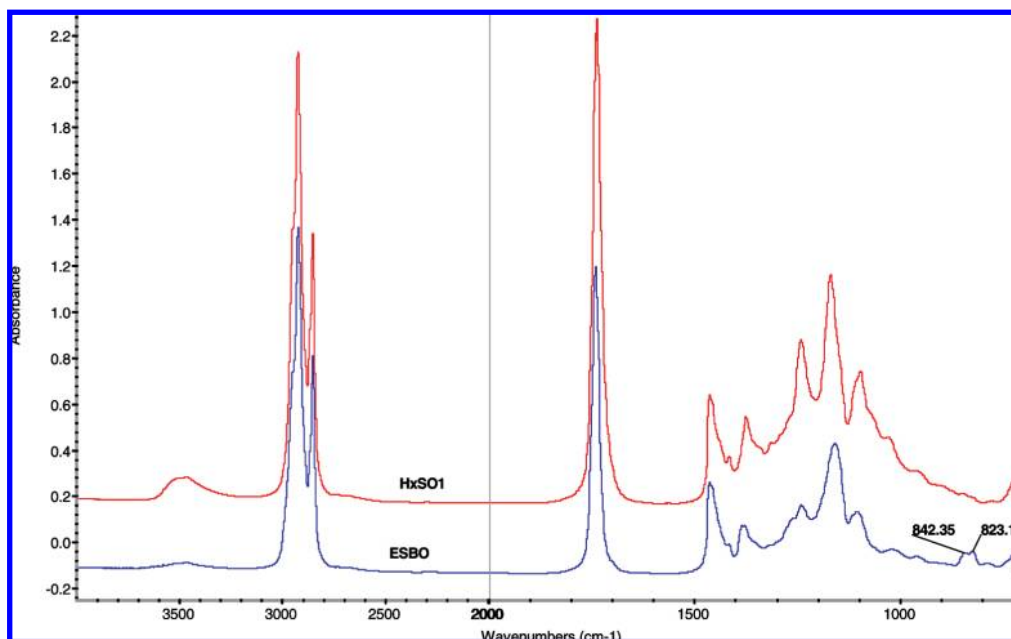
Figure 1. FTIR spectra of ESBO (bottom) and HxSO1 (top). The reaction progress can be judged by the loss of the ESBO epoxide peaks at 823 and 842 cm^{-1} and the relative growth of the carbonyl ester band at ~1743 cm^{-1}.
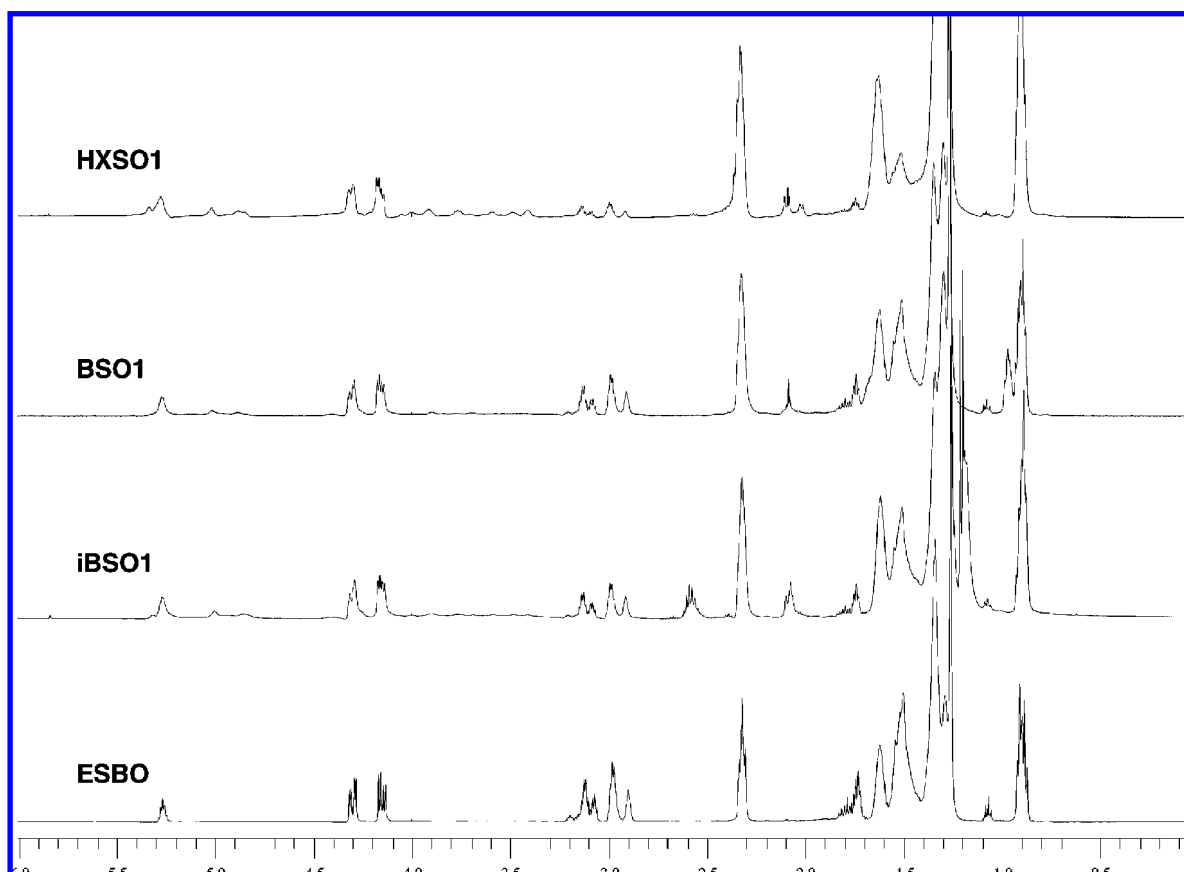
Figure 2. ^{1}H NMR spectra of ESBO, iBSO1, BSO1, and HxSO1. The reaction progress can be judged by the decrease in intensity of epoxide CH peaks in the region 3.2–2.83 ppm and the appearance of new peaks at 4.8–5.4 ppm.

product. This modification led to a decrease in the viscosity of acyl derivatives compared to ESBO, due to loss of epoxy structures, but the viscosity is higher than that of SBO.

The final products were identified and the structure was confirmed by FTIR and NMR analysis. The extent of ring opening was also calculated by performing oxirane titrations

on final products, while unreacted anhydride was determined using TGA. GPC was used to check the extent of polymerization in these reaction conditions.

FTIR Characterization of Diester Products. The presence of functional groups was monitored using FTIR analysis. The FTIR spectra of the starting material and product in the HxSO1
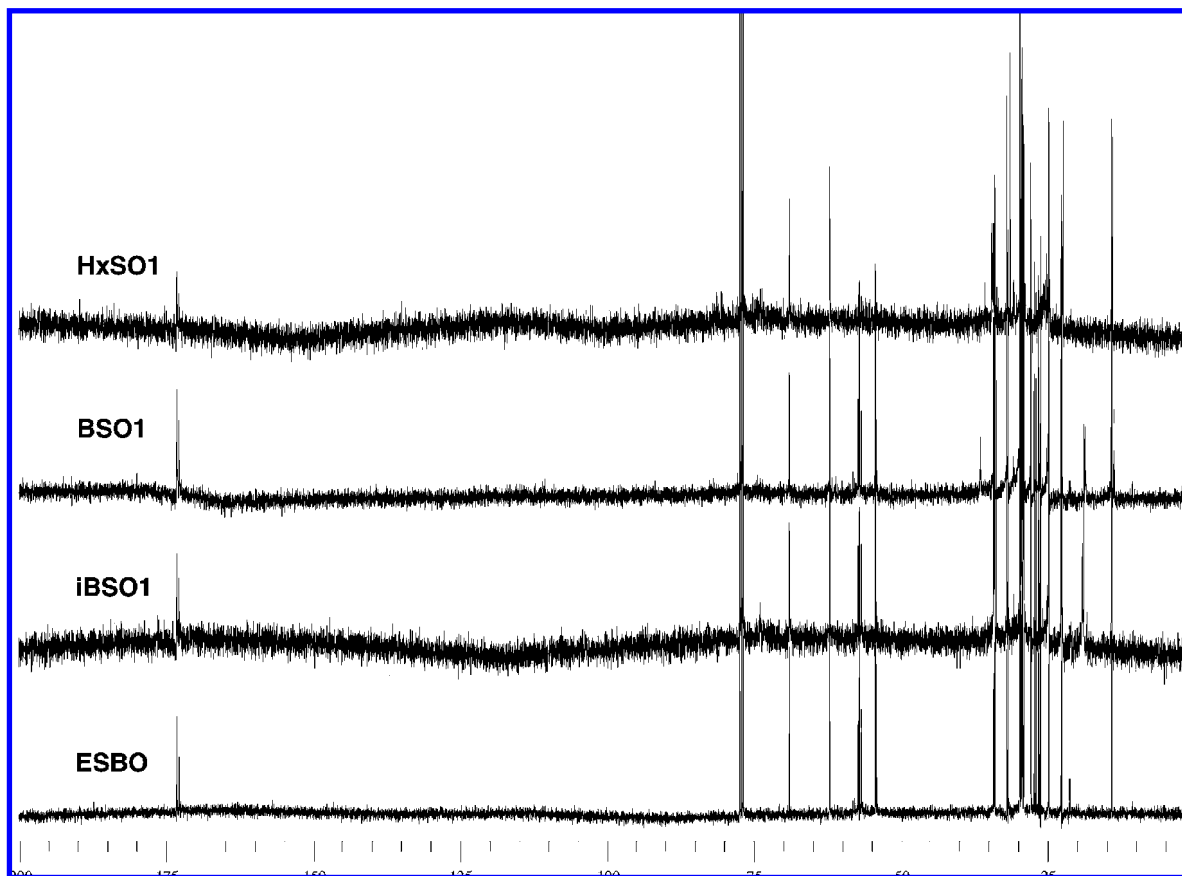
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Figure 3. ^{13}C NMR spectra of ESBO and acyl derivatives of soybean oil iBSO1, BSO1, and HxSO1.

reaction (**Figure 1**) show loss of epoxide bands from ∼823 to 842 cm^{-1} and a corresponding increase in the ester carbonyl at ∼1743 cm^{-1}, confirming more ester structures in the product.

The FTIR spectra (**Figure 1**) of all these products have some common peaks at 2926 and 2855 cm^{-1} (methylene asymmetric stretching), 1743 cm^{-1} (triglycerides carbonyl stretching), 1465 cm^{-1} (CH$_2$ bending vibration), 1377 cm^{-1} (CH$_3$ symmetrical bending vibration), 724 cm^{-1} (CH$_2$ rocking vibrations), and additional peaks at 1242, 1160, and 1104 cm^{-1} due to stretching vibrations of C−O group in esters (*35*). Formation of the ASO1 products was also confirmed by the increase in peak intensity ratio 1465:1377 cm^{-1}. In ESBO, the intensity of the 1377 cm^{-1} peak is almost half-that of the 1465 cm^{-1} peak, while in ASO1, due to addition of methyls (COCH$_3$) in the structure, the peak at 1377 cm^{-1} (CH$_3$ bending vibrations) almost doubled compared to that at 1465 cm^{-1} (CH$_2$ bending vibration). Also the intensities of peaks such as 1743 (ester carbonyl) and 1160 cm^{-1} (C−O stretching of esters) relative to that of the 2926 cm^{-1} peak has increased in HxSO1 compared to ESBO (**Figure 1**). This is due to the increase in ester functionalities in the structure. A similar trend was observed in spectra of ASO1, PSO1, BSO1, iBSO1 and HpSO1, confirming the formation of the final diester products.

NMR Characterization of Diester Products. Figure 2 shows the ^1H NMR spectra of ESBO, iBSO1, BSO1, and HxSO1 in CDCl$_3$. The quantitative ^1H NMR spectral data of ASO1 are given in the experimental section, while for others it is provided in Supporting Information. **Figure 3** shows the ^{13}C NMR spectra of ESBO, iBSO1, BSO1, and HxSO1 in CDCl$_3$. The proton NMR peaks that are common in ESBO and products are 2.25–2.5 ppm for CH$_2$ protons α to >C=O, 1.68–1.85 ppm for CH$_2$ protons in between two epoxides, 1.58–1.68 ppm for CH$_2$ protons β to >C=O, 1.15–1.58 ppm for all other CH$_2$

protons, and 0.8–1.0 ppm for terminal CH$_3$ protons. The number of protons shown for each product in the experimental section and Supporting Information is computed using a reference value of four protons for peaks at 4.1–4.4 ppm corresponding to four CH$_2$ protons of –CH$_2$CHCH$_2$– in the glycerol backbone of triacylglycerol structure. It can be seen that intensity of peaks at 3.2–2.83 ppm due to the epoxy group decreased in all the products. All the diester products have new peaks at 4.8–5.4 ppm in their ^1H NMR spectra due to CH protons at the branching site (−CHOCOR) on fatty acid chain, while the corresponding carbon peak appears at 74–76 ppm in their ^{13}C NMR spectra.

The presence of additional peaks at 1.83–2.2 ppm due to methyl protons of the –COCH$_3$ group in ^1H NMR and corresponding methyl carbons at 21.2 ppm and carbonyl carbons at 172.7 ppm in ^{13}C NMR confirms the formation of ASO1 product. The formation of PSO1 product is confirmed by an increase in the area of the peak at 2.5–2.23 ppm due to CH$_2$ protons α to carboxy group of acyl side chain, the appearance of a new peak at 1.15 ppm due to methyl protons on the end of the acyl side chain, and the corresponding methyl carbon peak at 10.8 ppm in the ^{13}C NMR spectrum. The product BSO1 is confirmed by an increase in area of the peak at 2.5–2.23 ppm due to CH$_2$ protons α to the carboxy group of the acyl side chain, the appearance of a new peak at 1.06–0.95 ppm due to CH$_3$ protons of the acyl side chain, and a new peak at 18.4 ppm in the ^{13}C NMR spectrum due to the CH$_2$ carbon α to the end carbon of the acyl side chain. Apart from other peaks, the product iBSO1 has the following identifiable peaks: 2.55 ppm due to CH protons α to the carboxy group of the acyl side chain, 1.2–1.0 ppm due to CH$_3$ protons on the end of the acyl side chain in the ^1H NMR spectrum, 19.4 ppm due to CH$_3$ end carbons of the acyl side chain in the ^{13}C NMR spectrum. The

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Table 1. Total Acid Number, Percent Unreacted Anhydride Content, Percent Conversion Based on Oxirane Titrations, and ^{1}H NMR Data of Various Acyl Derivatives of SBO

		% conversion			
	NMR-number of epoxy carbons used in reaction	based on NMR epoxy rings used	based on oxirane titrations	% anhydride using TGA	total acid number
SBO				0	0.10
ESBO	0	0	0	0	0.23
ASO1	2.5	29.1	32.9	0.2	0.73
PSO1	2.9	33.7	34.5	0.2	0.70
BSO1	3.4	39.0	41.3	0.4	0.79
iBSO1	3.0	34.4	36.8	0.7	0.55
VSO1	3.2	37.2	39.5	0.9	1.57
HxSO1	3.9	45.3	47.9	0.7	2.54
HpSO1	3.2	37.2	41.5	0.3	3.83

formation of product VSO1, HxSO1, and HpSO1 is confirmed by an increase in the area of peaks at 2.5–2.23 ppm due to CH_2 protons α to carboxy group of acyl side chain and 0.95–0.72 ppm due to CH_3 protons of acyl side chain in their ^{1}H NMR spectra. In the ^{13}C NMR spectra, the appearance of a new peak at 22.0 ppm in VSO1 due to the CH_2 carbon α to the end carbon of the acyl side chain and a new peak at 34.4 ppm in HxSO1 and HpSO1 due to the CH_2 carbon α to the carboxy group of the acyl side chain confirms their formation. These observations confirm the formation of diester products through one-step reaction of ESBO and various anhydrides.
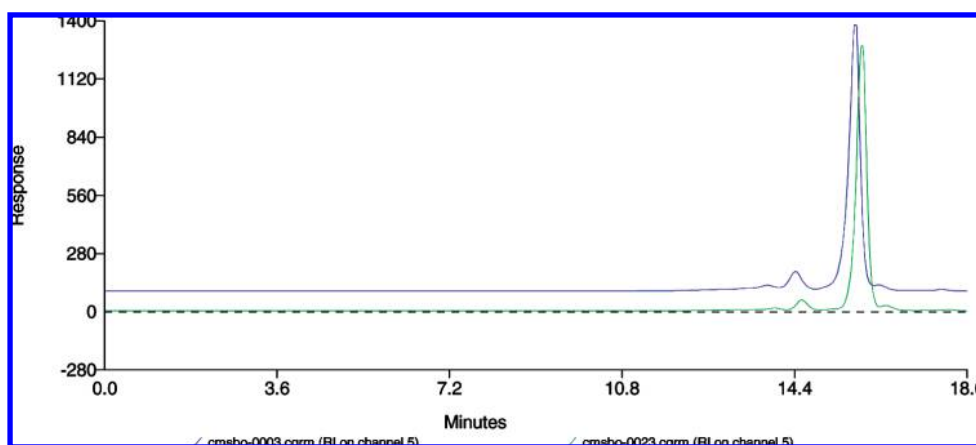
The percentage conversion calculated from ^{1}H NMR data for signals in the range 3.2–2.8 ppm (CH protons of epoxy ring) yield values in the range of 29–45%, as shown in **Table 1**. Similar results were obtained from oxirane titrations shown in **Table 1**. The oxirane titrations were performed to measure unreacted epoxy rings present in the products. A good correlation (regression constant 0.95) was found between oxirane oxygen determined using oxirane titrations and CH protons of the epoxy ring. For some of the products, such as ASO1, PSO1, and iBSO1, the number of acyl groups attached on the fatty acid chain were calculated using specific ^{1}H NMR peaks arising from branching groups and were found to be similar to the reacted oxirane carbons. Out of 8.6 carbon sites available for substitution in an average triacylglycerol molecule, about 2.5−4 sites were substituted by these acyl branching groups, while others remain as unopened epoxy rings. Proton NMR spectra and oxirane titrations illustrated the fact that unreacted epoxy groups are retained in the product mixture. Due to the steric geometry of the ESBO

molecule, complete conversion to diester products could not be achieved and allows only one substituent per fatty chain on an average. This explanation seems valid, as the conversion decreased when ESBO was reacted with isobutyric anhydride (bulky group) compared to butyric anhydride.

GPC Analysis. GPC was performed on ESBO and diester products to check the extent of internal polymerization. The GPC chromatograms of all of the samples showed similar trends. It was found that the polymerization under these reaction conditions was minimal, and only some degree of oligomerization (∼6%) occurred at some stage of the reaction (**Figure 4**). Apart from the main peak of expected products, there were 4–5% dimers and 1–1.5% trimers in the final diester products. As expected, the retention time of the product peak on the GPC chromatogram decreased with increasing molecular weight of the products. The GPC molecular weight (M_w) of main product peaks for starting and final products are ESBO, 845; ASO1, 883; PSO1, 887; iBSO1, 884; BSO1, 890; and HxSO1, 905, as estimated by using a calibration mixture of polystyrene, fatty acid methyl ester, and mono-, di-, and triolein. Because of such a small change in the molecular weights of starting material ESO and final products, no separate peaks for products were observed.

Anhydride Determination. The amount of unreacted anhydride was quantified using the TGA method discussed in the experimental section. It was found that in reactions with high-boiling anhydrides such as butyric, valeric, hexanoic, and heptanoic anhydride, a considerable amount of unreacted anhydride remained in the product even after vacuum distillation. Using TGA, the unreacted anhydride in the crude BSO1 obtained after vacuum distillation was found to be 24%. Kugelrohr distillation was then used at 70 °C under 0.2 Torr vacuum to remove the unreacted anhydride from all the products, which brought down the unreacted anhydride in the final products to less than 1%. **Table 1** shows the amount of unreacted anyhydride left in the final products. The anhydride content for large-scale synthesis of HxSO1 was also less than 1%.

FTIR was also used to monitor the removal of unreacted anhydride during vacuum and Kugelrohr distillation in the final diester products. The anhydride carbonyl peak appears at 1818 cm^{-1} and is easily distinguishable from the ester carbonyl peak at 1743 cm^{-1}. Complete removal of unreacted anhydrides using Kugelrohr distillation in final diester products (as shown in FTIR spectrum of HxSO1 in **Figure 1**) was confirmed by the absence of the 1818 cm^{-1} peak in their spectra.

Figure 4. GPC chromatogram of ESBO (bottom) and ASO1 (top).

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The total acid number (TAN) indicates the presence of free fatty acids and carboxylic acids generated during the reaction. The TAN values of the staring material ESBO and the final products were determined using an AOCS official method and are shown in **Table 1**. Soybean oil has a TAN value of 0.1 mg of KOH/g, whereas ESBO showed a TAN value of 0.23 mg of KOH/g. The diester reaction products showed TAN values in the range of 0.55–3.83 mg of KOH/g. In general, the TAN value of diester product increased with increasing the chain length of acid anhydrides. During the anhydride removal process through vacuum and Kugelrohr distillation, some of the high-boiling unreacted anhydride may have decomposed into acids instead of being removed. This leads to higher acid numbers for products prepared using high-boiling anhydride such as valeric, hexanoic, and heptanoic anhydride.

In conclusion, we have demonstrated a simple one-step synthesis of potentially useful acyl derivatives of soybean oil. The epoxy groups of the ESBO were selectively reacted with anhydrides of different chain length using a simple nucleophilic ring-opening reaction to give acyl derivatives of soybean oil using catalyst and solvent for minimum polymerization and with little disruption of the ester linkage. Hexanoic anhydride and boron trifluoride etherate catalyst were found to be the best for maximum epoxy ring opening. It is easy to envision that chemical modification of vegetable oils could lead to a number of applications. Preliminary research on these compounds has shown interesting oxidation stability, lubricity, and pour-point properties. These branched soybean oils may find use in some lubricant end-use applications as such or when formulated with other functional components, such as extreme-pressure additives, antiwear additives, pour point depressants, other base stocks, diluents, and the like. Therefore, as an extension of this work, we are currently investigating lubricant properties of the branched soybean oils presented here.

Supporting Information Available: The ^{1}H and ^{13}C NMR data of diester derivatives PSO1, BSO1, iBSO1, VSO1, HxSO1, and HpSO1. This material is available free of charge via the Internet at http://pubs.acs.org.

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