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ORIGINAL PAPER

Chemical Characterization and Physical Properties of Solvents Derived from Epoxidized Methyl Soyate

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Abstract Reactions of epoxidized methyl soyate (EMS) with alcohols, carbon dioxide, and acetone yielded liquids with solvent properties that make them more suitable than methyl soyate for dissolving polar substances. The reactions of EMS in the presence of Amberlyst-15 with alcohols, including methanol, ethanol, *n*-butanol, and 2-methoxyethanol, produced a series of solvents containing ether (–OR) and alcohol (–OH) groups. Reactions of EMS with carbon dioxide and acetone gave products with carbonate and ketonide functional groups, respectively. The complex mixture of compounds present in the product, EMS(MeOH), resulting from the reaction of EMS with MeOH, was characterized by MS and NMR investigations. In addition to products resulting from MeOH addition across the epoxide ring, were major amounts of cyclic tetrahydrofuran derivatives that were derived from reactions of methyl linoleate (18:2) with MeOH. All of the solvents were characterized by high boiling points and low vapor pressures. Their viscosities were higher than that of methyl soyate. Especially notable were their very high Kauri-butanol values, which ranged from 280 to 852, all of which are much higher than that (57) of methyl soyate. Such high KB values indicate that these solvents have very favorable solubilizing properties, which is illustrated by the ability of EMS(MeOH) to readily dissolve both polar (e.g., MeOH) and non-polar (e.g., hexane) compounds.

Keywords Soybean oil · Methyl soyate · Epoxidized methyl soyate · Epoxidized soybean oil · Methyl linoleate · Solvents · Solubility · Amberlyst-15 · Kauri butanol · LC APCI

Abbreviations

ESO	Epoxidized soybean oil
EMS	Epoxidized methyl soyate
FAME	Fatty acid methyl ester(s)
*m*CPBA	*meta*-chloroperbenzoic acid
NMR	Nuclear magnetic resonance spectroscopy
LC–MS	Liquid chromatography-mass spectrometry
APCI	Atmospheric pressure chemical ionization
TBAB	Tetra(*n*-butyl)ammonium bromide
KB	Kauri-butanol
VOC	Volatile organic compound(s)
$Cr(acac)_3$	Chromium *tris*-acetylacetonate

Introduction

Although methyl soyate is used primarily as a biodiesel fuel [1, 2], it is also used as a solvent in a variety of applications such as parts cleaning, paint strippers, and removers/cleaners [3, 4]. Methyl soyate (MS) has a low vapor pressure (<0.1 mm Hg), a viscosity of 3.9–4.3 cSt, and a reported Kauri-butanol value of 58 [5, 6]. Its advantages over conventional solvents are biodegradability, low VOC, and low toxicity [5, 6]. However, one of its main disadvantages as a solvent is its very non-polar nature, which means that it is most useful for dissolving non-polar substances. A goal of the present project was to modify methyl soyate in ways that would render it as a suitable solvent for more polar substances. To this end, we sought to introduce oxygen-containing groups into the hydrocarbon chain of the unsaturated fatty acids in methyl soyate.

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Although there is some evidence that alcohols can be added directly across double bonds in the unsaturated fatty acids in methyl soyate [7], the conditions (concentrated sulfuric acid at elevated temperature) are harsh and impractical for commercial production. The direct addition of methanol across the double bonds of methyl linoleate (18:2) and methyl oleate (18:1) using BF_3·MeOH as the Lewis acid catalyst is also known [8], but a large excess of the costly and difficult-to-recover BF_3·MeOH reagent is required. In exploratory studies, we used a variety of acid catalysts (*p*-toluenesulfonic acid, iron(III) chloride, Nafion SAC-13, and Amberlyst-15) to catalyze the reaction of methyl soyate with methanol. However, only trace amounts of products resulting from the addition of methanol across the double bonds were detected.

We therefore activated the methyl soyate double bonds by converting them to their corresponding epoxides, which are known to react with alcohols to give products that contain alkoxy, and hydroxy groups [9, 10]. Our strategy was to convert methyl soyate (MS) to epoxidized methyl soyate (EMS), which would then be reacted with alcohols, CO_2, and acetone (Scheme 1). All of these types of reactions of EMS have been reported previously (see "Results and Discussion" section). Extensive ^{1}H and ^{31}P NMR, mass spectrometric, and chromatographic studies were used to establish the molecular species present in several of the solvents. The product resulting from the reaction of EMS with methanol, using epoxidized soybean oil as the starting material, was prepared on a relatively large scale (1.0 L). Physical properties (i.e., Kauri-butanol values, boiling points, melting points, solubilities of water in them, and viscosities) were determined for the products resulting from the reactions of EMS with alcohols, carbon dioxide, and acetone. Of particular relevance to the solvent properties of these liquids are their unusually high Kauri-butanol values, which range from 280 to 852, all of which are much higher than that of methyl soyate (57).

Experimental Section

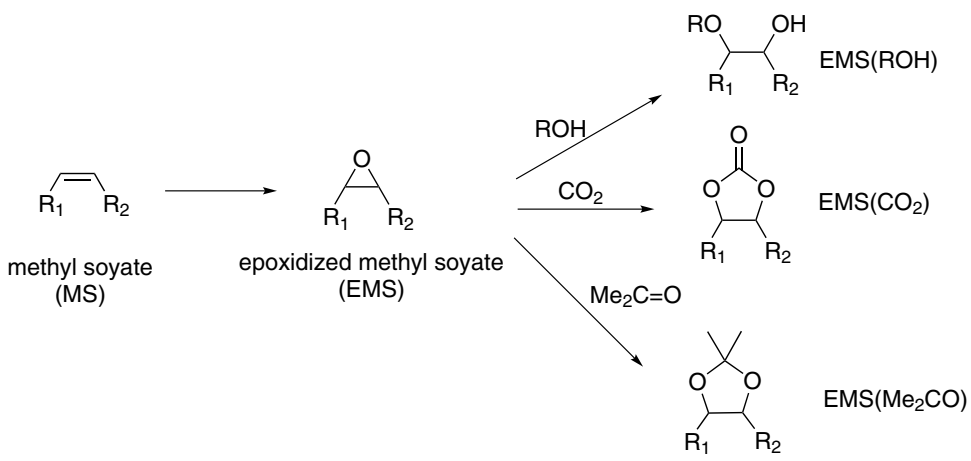
Materials

All starting materials were commercially available unless otherwise noted. Epoxidized soybean oil (ESO) was supplied by Arkema and ChemCeed. High-oleic soybean oil (HOSO) was supplied as Frymax by Stratas Foods LLC. Methyl oleate (18:1) (>70 %), Amberlyst-15 (hydrogen form, dry, 18–23 mesh, 4.7 equiv –SO_3H/kg), tetra(*n*-butyl)ammonium bromide, 2-methoxyethanol, phosphorus trichloride, pinacol, and triethylamine were purchased from Sigma-Aldrich. Amberlyst-15 was activated by heating in an oil bath at 100 °C for 24 h under vacuum (1 Torr) and stored under a nitrogen atmosphere prior to use. Methyl linoleate (18:2, >95 %) and methyl linolenate (18:3, >70 %) were purchased from TCI America. All reactions were conducted under a nitrogen atmosphere, except where indicated otherwise. The kinematic viscosities and Karl Fischer water contents of the solvents were determined by Galbraith Laboratories, Inc.

Kauri-butanol values were determined according to the ASTM D1133 standard using a standardized Kauri-butanol solution obtained from Lab Express International (Fairfield, NJ). The A and B values provided by the supplier were 104.8 and 38.2, respectively.

Liquid Chromatography–Mass Spectrometry (LC–APCI)

LC–MS experiments were performed on an Agilent QTOF 6540 accurate mass MSMS instrument with an atmospheric pressure chemical ionization (APCI) ion source. HPLC experiments employed a C18 reversed-phase column (1.8 μm particle size, 4.6 × 50 mm) and 1-μL injection. The solvent phase was 85 % MeOH/15 % H_2O at a flow rate of 0.8 mL/min.



Scheme 1 Preparation of solvents from methyl soyate

NMR Data Collection

^{1}H- and ^{13}C-NMR spectra of samples dissolved in $CDCl_3$ were obtained on Varian VXR-300 and -400 instruments. ^{31}P-NMR spectra were collected on a Bruker AVIII-600 instrument with a relaxation delay time of 3 s.

Epoxidation of Methyl Linoleate (18:2) to E18:2

Methyl linoleate (1.0 mL, 3.0 mmol) was dissolved in CH_2Cl_2 (10 mL) in a round-bottom flask at 0 °C. To this solution was added *m*CPBA (1.4 g, 6.4 mmol), and then the reaction mixture was stirred with a magnetic stir bar and allowed to gradually warm to room temperature. After 16 h, the solution was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$ solution. The organic phase was dried with $MgSO_4$ and concentrated in a rotary evaporator to afford crude E18:2. The product was purified by flash silica gel chromatography (4:1 hexanes/ethyl acetate as the solvent phase, column size 20 × 2.5 cm) to give E18:2 as a clear liquid (960 mg, 2.9 mmol, 97 % yield). The NMR spectrum of this compound matches that reported in the literature [11].

Epoxidation of Methyl Linolenate (18:3) to E18:3

The epoxidation of 18:3 was performed in the same manner as described for the epoxidation of 18:2, except that 3.1 equivalents of *m*CPBA per mol of 18:3 (1.0 mL, 3.1 mmol) were used. The reaction conditions and workup procedure were the same as for E18:2, including purification by flash silica gel chromatography (1.02 g, 3.0 mmol, 97 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 3H, CO_2CH_3), 3.21–3.03 (3H), 3.01–2.88 (3H), 2.29 (t, $J = 6$ Hz, 2H, CH_2CO_2), 1.82–1.70 (4H), 1.68–1.21 (14H), 1.06 (t, $J = 6$ Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 176.93, 57.20, 56.12, 54.49, 54.41, 54.29, 54.22, 51.68, 34.68, 29.51, 29.38, 29.23, 28.11, 27.99, 26.75, 26.66, 25.10, 21.37, 10.70; HRMS: (APCI) *m/z* calculated for $C_{19}H_{32}O_5$ 341.2323, found 341.2312 (MH^+).

Preparation of EMS from ESO, 10-mL Scale

In a procedure similar to that reported in reference [11], 10 mL of ESO was mixed with 50 mL of methanol in a round-bottom flask under a flowing nitrogen atmosphere. The reaction mixture was heated to 60 °C in order to dissolve the ESO. At this point, 0.10 g of solid NaOMe was added to the reaction mixture, which was allowed to react by heating at 60 °C and stirring with a magnetic stir bar for 1 h. The solution was then allowed to cool to room temperature, and the methanol was removed with a rotary evaporator. The glycerol by-product, containing dissolved NaOMe catalyst, was then removed from the desired product using a separatory funnel to afford EMS as a colorless, transparent liquid. ^{1}H-NMR analysis of the liquid showed that ESO was completely converted to EMS.

Preparation of EMS from ESO, 1.0-L Scale

A procedure similar to that used for the 10-mL scale procedure (above) was followed for the conversion of ESO to EMS on a 1.0-L scale. In a 5-L three-necked round-bottom flask equipped with two reflux condensers, 1.0 L of ESO was mixed with methanol (ca. 1 L) under a flowing nitrogen atmosphere. The reaction mixture was heated to 60 °C in order to dissolve the ESO. Solid NaOMe (10 g) was added to the reaction mixture, which was allowed to react while heating at 60 °C and stirring with a paddle stirrer for 1 h. The solution was then allowed to cool to room temperature, and the methanol was removed using a rotary evaporator. The glycerol by-product, containing dissolved NaOMe, was then removed from the desired product using a separatory funnel to afford EMS. Analysis by ^{1}H-NMR spectroscopy showed complete conversion of the ESO to EMS based on the absence of peaks for the glycerol protons.

Reactions of Epoxides with Alcohols: a Typical Procedure

The epoxide (E18:1, E18:2, E18:3, or EMS, ca. 1 mL) was dissolved in 50 mL of methanol in a round-bottom flask with a magnetic stirrer. To this was added 0.1 g of activated Amberlyst-15. The mixture was heated to 60 °C for 4 h with stirring under a nitrogen atmosphere, and then it was allowed to cool to room temperature after which the catalyst was separated by filtration. The methanol was then removed with a rotary evaporator followed by removal of a yellow coloration from the resulting product by dissolving it in an equal volume of hexanes followed by treatment with ca. 1 g of decolorizing carbon. The carbon was removed by filtration through a pad of Celite, and the hexanes were removed using a rotary evaporator. The resulting product was purified by flash silica-gel chromatography (4:1 hexanes/ethyl acetate) to give the product as a light yellow liquid. Characterizations of the products are discussed in the "Results and Discussion" section.

For larger scale conversions of EMS to EMS(MeOH), e.g., 1.0 L, a similar procedure was followed using equal volumes of EMS and MeOH with a paddle stirrer operating at a speed of 180–200 rpm. The EMS(MeOH) was characterized as discussed in the "Results and Discussion" section.

EMS(EtOH) was prepared using the same procedure as for the preparation of EMS(MeOH) using ethanol as the alcohol reactant. Excess ethanol was removed by rotary evaporation. The characterization of this product is discussed in the "Results and Discussion" section.

EMS($HOCH_2CH_2OCH_3$) was prepared in the same manner as EMS(MeOH) using 2-methoxyethanol as the

alcohol. The excess 2-methoxyethanol was removed via vacuum distillation (60 °C, 1 Torr).

Carboxylation of EMS

In a procedure similar to that reported in reference [12], EMS (100 mL) and TBAB (10 g) were combined in a 200 mL Parr bomb reactor. The vessel was sealed and charged with 150 psi of carbon dioxide. The reaction mixture was heated to 120 °C for 16 h with paddle stirring at 120 rpm. The reaction was then cooled to room temperature, and the reaction vessel was depressurized in a hood. The resulting mixture was then dissolved in diethyl ether (200 mL), and the organic solution was washed with water to remove the TBAB. The ether was removed by rotary evaporation to give EMS(CO_2) as an orange liquid, which was characterized as described in the "Results and Discussion" section.

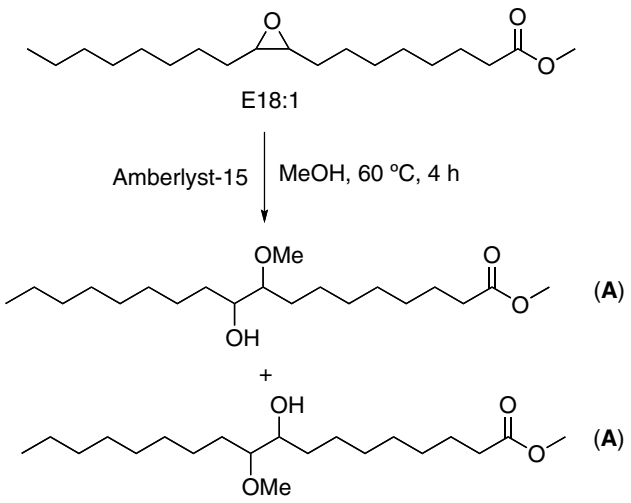
Preparation of EMS Acetonide, EMS(Me_2CO), from EMS

The acetonide EMS(Me_2CO) was prepared from EMS and acetone using a literature procedure [13]. The ^{1}H- and ^{13}C-NMR spectroscopic data for the product match those in the literature.

^{31}P-NMR Experiments on Products Derivatized with a Chlorophospholane

As described in the "Results and Discussion" section, the presence of –OH groups in products resulting from reactions of alcohols with the epoxides was detected and quantitated by ^{31}P-NMR spectroscopy after derivatizing them with the chlorophospholane reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane [14–16]. This reagent was prepared according to the following modified literature procedure [14]. In an oven-dried round-bottom flask, pinacol (2.7 g, 23 mmol) was dissolved in 10 mL of dry diethyl ether under a nitrogen atmosphere. To this solution was added phosphorus trichloride (2.0 mL, 23 mmol) and pyridine (3.7 mL, 46 mmol) at 0 °C. The mixture was stirred for 4 h, while allowing it to warm to room temperature. The ether solvent was removed with a rotary evaporator, and the chlorophospholane product was distilled under vacuum (100 °C, 1 Torr) to give the desired reagent. The compound was stored under nitrogen at 0 °C.

^{31}P-NMR experiments were performed on solutions prepared by dissolving the derivatized MS samples (typically ~0.05 mmol) in 1 mL of $CDCl_3$ in an NMR tube. To this was added a known amount (0.02–0.05 mmol) of phenol as an internal standard and excess amounts of both triethylamine (0.05 mL, 0.85 mmol) and the chlorophospholane (0.05 mL, 0.31 mmol). Finally, 1–2 mg of $Cr(acac)_3$ was added to the mixture as an NMR relaxation reagent. The mixture was shaken and allowed to stand at room temperature for 30 min before analysis by ^{31}P-NMR spectroscopy.



Scheme 2 Reaction of E18:1 with methanol

NMR and Mass Spectroscopic Data for the Compounds and Mixtures (Structures of Compounds are given in Schemes 2, 4, and 5)

Methyl 10-hydroxy-9-methoxyoctadecanoate (**A**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 3H, CO_2CH_3), 3.47 (m, 1H), 3.40 (s, 3H, OCH_3), 2.97 (m, 1H), 2.29 (t, $J = 7$ Hz, 2H, CH_2CO_2), 1.63–1.24 (26H), 0.85 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 174.50, 84.52, 84.48, 82.28, 72.83, 58.32, 56.13, 51.67, 34.31, 33.62, 32.11, 30.21, 30.12, 29.99, 29.76, 29.49, 29.41, 29.31, 25.98, 25.91, 25.14, 22.89, 14.33; HRMS: (APCI) *m/z* calculated for $C_{20}H_{40}O_4$ 345.2999, found 345.2993 (MH^+).

Methyl 8-[3-hydroxy-5-(1-methoxyhexyl)tetrahydrofuran-2-yl]octanoate (**B**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94–3.76 (2H), 3.46–3.35 (2H), 3.65 (s, 6H, CO_2CH_3), 3.32 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3), 2.41 (t, $J = 7$ Hz, 4H, CH_2CO_2), 2.14–2.05 (m, 1H), 1.91–1.84 (m, 1H), 1.69–1.29 (20H), 0.87 (t, $J = 6$ Hz, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 174.54, 170.05, 166.60, 83.04, 82.40, 82.40, 82.24, 81.35, 80.42, 80.31, 74.24, 74.07, 74.01, 57.23, 56.84, 56.12, 51.67, 34.31, 34.05, 33.72, 33.62, 33.47, 32.18, 32.12, 29.97, 29.75, 29.43, 29.39, 29.34, 29.28, 29.00, 28.89, 26.41, 26.23, 26.05, 25.79, 25.14, 22.87, 22.78, 14.24; HRMS: (APCI) *m/z* calculated for $C_{20}H_{38}O_5$ 359.2792, found 359.2787 (MH^+).

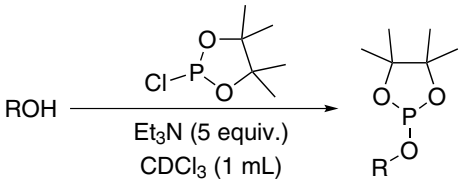
Methyl 10,12-dihydroxy-9,13-dimethoxyoctadecanoate (**C**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.02 (m, 1H), 3.86 (m, 1H), 3.76 (m, 1H), 3.64 (s, 3H, CO_2CH_3), 3.60 (m, 1H), 3.41 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 3.07 (br, 2H), 2.28 (t, $J = 6$ Hz, 2H, CH_2CO_2), 1.64–1.23 (20H) 0.85 (t, $J = 6$ Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 174.55, 84.49, 84.44, 74.04, 73.97, 58.29, 51.68, 38.86, 34.38, 32.29, 31.98, 29.82, 29.39, 29.36, 28.96, 26.35, 25.94, 25.13, 22.83, 14.26; HRMS: (APCI) *m/z* calculated for $C_{21}H_{42}O_6$ 391.3054, found 391.3049 (MH^+).

Methyl 9-hydroxy-9-(4-hydroxy-5-pentyltetrahydrofuran-2-yl)nonanoate (**D**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.22 (br, 1H), 4.10 (m, 1H), 3.94 (m, 1H), 3.73 (m, 1H), 3.64 (s, 3H, CO_2CH_3), 3.45 (br, 1H), 3.35 (m, 1H), 2.28 (m, 2H), 2.01 (m, 1H), 1.81 (m, 1H), 1.65-1.21 (20H), 0.86 (t, $J = 7$ Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 178.35, 178.34, 84.48, 80.44, 79.34, 74.23, 73.42, 71.65, 71.23, 51.70, 38.75, 38.06, 34.39, 34.27, 33.24, 32.25, 32.19, 32.09, 31.83, 31.72, 29.90, 29.70, 29.64, 29.43, 29.33, 29.26, 29.11, 28.90, 26.15, 25.57, 25.10, 24.86, 22.80, 14.26; HRMS: (APCI) *m/z* calculated for $C_{19}H_{36}O_5$ 345.2636, found 345.2632 (MH^+).

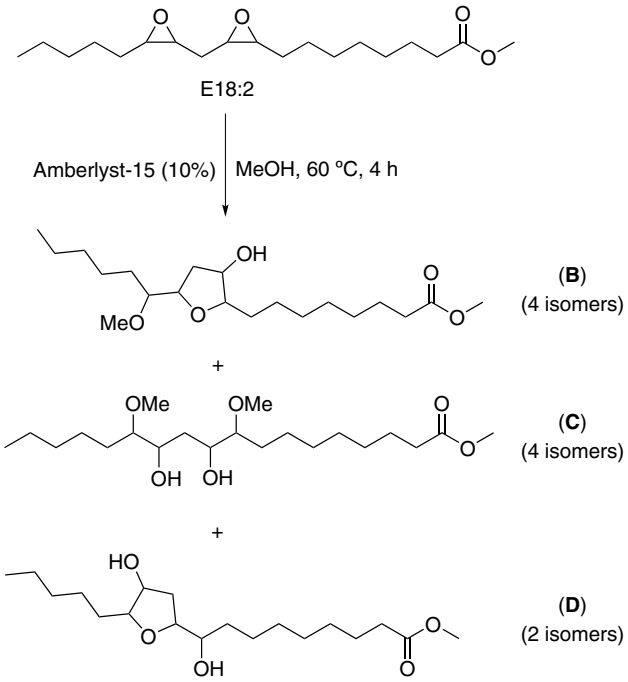
Methyl 10,12,15-trihydroxy-9,13,16-trimethoxyoctadecanoate (**E**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (2H), 3.66 (s, 3H, CO_2CH_3), 3.43 (s, 6H, OCH_3), 3.29 (s, 3H, OCH_3), 3.02 (2H), 2.45 (2H), 2.30 (t, $J = 6$ Hz, 2H, CH_2CO_2) 1.70–1.26 (16H), 0.89 (t, $J = 6$ Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 174.88, 81.33, 81.03, 80.99, 76.72, 75.01, 74.64, 57.25, 57.06, 56.14, 56.12, 51.68, 33.81, 32.15, 30.85, 30.28, 30.22, 29.45, 29.33, 27.42, 26.54, 26.25, 25.16, 22.80, 14.27; HRMS: (APCI) *m/z* calculated for $C_{22}H_{44}O_8$ 437.3109, found 437.3100 (MH^+).

Methyl 8-[3-hydroxy-5-(3-hydroxy-1,4-dimethoxyhexyl)tetrahydrofuran-2-yl]octanoate (**F**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.24 (m, 1H), 4.04 (m, 1H), 3.88 (m, 1H), 3.78 (m, 1H), 3.66 (s, 3H, CO_2CH_3), 3.43 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.29 (m, 1H), 2.43 (m, 1H), 2.30 (t, $J = 6$ Hz, 2H, CH_2CO_2), 1.86–1.16 (16H), 0.88 (t, $J = 6$ Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 172.97, 86.45, 81.03, 81.50, 74.11, 74.05, 71.78, 58.34, 57.01, 56.13, 52.62, 51.68, 34.55, 34.31, 32.57, 32.27, 30.60, 29.88, 29.74, 29.64, 29.41, 29.34, 29.29, 27.28, 26.99, 26.82, 26.49, 26.24, 25.91, 25.72, 25.28, 22.85, 14.28; HRMS: (APCI) *m/z* calculated for $C_{21}H_{40}O_7$ 405.2847, found 405.2844 (MH^+).

Methyl 8-[5-(1,3-dihydroxy-4-methoxyhexyl)-3-hydroxytetrahydrofuran-2-yl]octanoate (**G**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 3H, CO_2CH_3), 3.61 (2H) 3.32 (s, 3H, OCH_3), 3.28 (m, 1H), 3.14 (m, 1H), 3.05 (2H), 2.29 (t, $J = 6$ Hz, 2H, CH_2CO_2), 1.66–1.24 (16H), 0.92 (t, $J = 6$ Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 186.98, 87.10, 84.20, 83.11, 82.28, 51.68, 34.37, 34.29, 32.15, 31.75, 31.51, 30.38, 30.05, 30.01, 29.97, 29.42, 29.11, 26.44, 26.01, 25.14, 25.08, 24.86, 22.84, 14.81; HRMS: (APCI) *m/z* calculated for $C_{20}H_{38}O_7$ 391.2690, found 391.2670 (MH^+).



Scheme 3 Reaction of alcohols with chlorophospholane



Scheme 4 Reaction of E18:2 with methanol

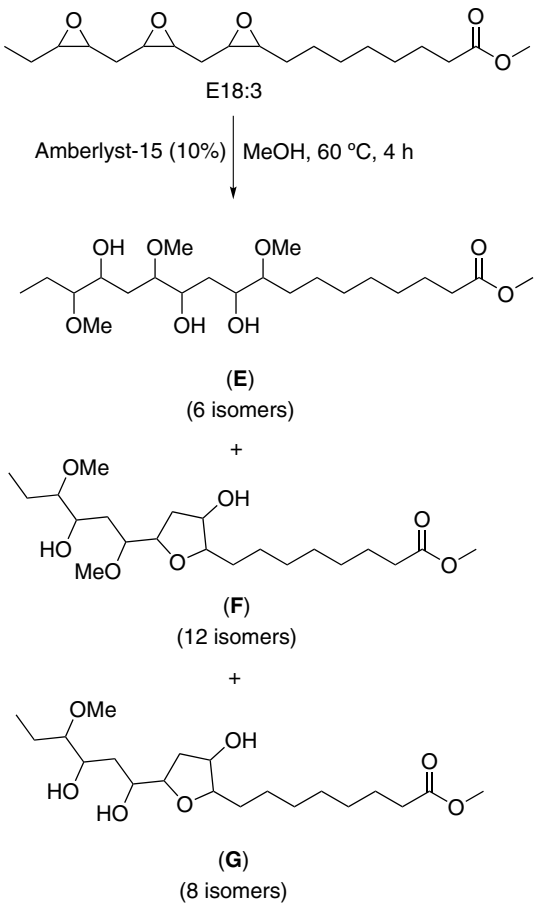
^{31}P-NMR Data for the Phospholane-Derivatized Products (Structures of Compounds are given in Schemes 2, 3, 4, and 5)

E18:1(MeOH) (**A**). ^{31}P NMR (600 MHz, $CDCl_3$): δ 146.88, 146.87.

E18:2(MeOH). ^{31}P NMR (600 MHz, $CDCl_3$): δ 148.47, 147.89, 147.75, 147.69, 147.60, 147.57, 147.54, 147.52, 147.48, 147.45, 147.38, 147.12, 147.09, 146.99, 146.94, 146.83, 146.81, 146.76.

Compound **B**. ^{31}P NMR (600 MHz, $CDCl_3$): δ 147.49, 147.45, 146.82, 146.75.

Compound **C**. ^{31}P NMR (600 MHz, $CDCl_3$): δ 147.81, 147.75, 147.67, 147.63, 147.51, 147.43, 146.90, 146.88.



Scheme 5 Reaction of E18:3 with methanol

Compound **D**. ^{31}P NMR (600 MHz, $CDCl_3$): δ 147.54, 147.49, 147.01, 146.95.

E18:3(MeOH). ^{31}P NMR (600 MHz, $CDCl_3$): δ 148.13, 148.08, 147.92, 147.90, 147.71, 147.69, 147.66, 147.61, 147.53, 147.47, 147.42, 147.40, 147.38, 147.35, 147.33, 147.31, 147.22, 147.18, 147.14, 147.10, 147.06, 147.04, 147.02, 146.99, 146.97, 146.94, 146.91, 146.86, 146.82, 146.77, 146.72, 146.68, 146.63, 146.59, 145.96, 145.91, 145.58, 145.48.

EMS(MeOH). ^{31}P NMR (600 MHz, $CDCl_3$): δ 148.47, 147.89, 147.75, 147.69, 147.60, 147.57, 147.54, 147.52, 147.48, 147.45, 147.38, 147.12, 147.09, 146.99, 146.94, 146.88, 146.87, 146.83, 146.81, 146.76.

Results and Discussion

Epoxidation of Methyl Soyate

Two common methods for the epoxidation of olefins employ either hydrogen peroxide and formic acid [17–20] or meta-chloroperbenzoic acid (*m*CPBA) [21]. The former achieves this transformation in lower yields (~90 vs 99 % for *m*CPBA), but the latter requires stoichiometric amounts of an expensive reagent and is therefore not economical on a large scale. Therefore, in small-scale reactions (i.e., 1.0 mL of alkene), the *m*CPBA method was preferred, while the hydrogen peroxide approach was used in scaled-up reactions.

A typical fatty acid composition of soybean oil is 51 % linoleate (18:2), 25 % oleate (18:1), 9 % linolenate (18:3), 12 % palmitate (16:0), and 3 % stearate (18:0). In the epoxidation of MS to EMS, the double bonds in 18:1, 18:2, and 18:3 are epoxidized while the saturated FAME (16:0 and 18:0) do not react. In order to analyze the composition of the EMS, it was useful to examine the products obtained from the epoxidation of the individual components of methyl soyate. Both E18:1 and E18:2, which had been previously reported [21], were prepared from 18:1 and 18:2 using *m*CPBA as the oxidant. Although not previously reported, we also prepared the tri-epoxide E18:3 using *m*CPBA.

Another method for the production of EMS involves the transesterification of epoxidized soybean oil (ESO) with methanol using sodium methoxide as the catalyst [11]. ESO was previously prepared by the complete epoxidation of soybean oil [22]; it is commercially available and is relatively inexpensive. The reaction of ESO with methanol in the presence of sodium methoxide gave EMS in quantitative yield. This was demonstrated by the disappearance of the triglyceride proton signals and the appearance of the methyl ester group in the ^{1}H-NMR spectrum of EMS. The NMR spectrum also showed that the epoxide group is stable under the transesterification conditions.

Reactions of Epoxides with Alcohols

Reaction of E18:1 with Methanol to Give E18:1(MeOH)

Using conditions similar to those reported previously [23, 24], we reacted E18:1 with methanol in the presence of Amberlyst-15 catalyst (which contains $-SO_3H$ Brønsted acid groups) to produce E18:1(MeOH). This reaction gives two regioisomers (**A**) depending on the mode of alcohol addition to the epoxide group (Scheme 2). Analysis of this regioisomeric mixture by LC-APCI showed two peaks in the chromatogram with 5.3 and 5.6 min retention times, and both displayed molecular ion peaks of 345 (MH^+) for **A**. Although the peaks are not completely separated, their integrations are in an approximately 1:1 ratio. In the ^{1}H-NMR spectrum of E18:1(MeOH), the ester methyl (3.65 ppm) and the ether methyl (3.40 ppm) signals integrate in a 1:1 ratio, which is consistent with the presence of equal numbers of ester and ether methyl groups, as is expected for the isomeric compounds with structures **A**.

An alternate method of characterizing these new compounds involves the use of a chlorophospholane reagent [14], which reacts with alcohol groups in organic compounds (Scheme 3). This method has been used for the detection and quantitation of phenolic groups in coal liquids [25, 26], as well as for the quantitation of mono- and diglycerides in olive oil [15, 16]. The ^{31}P-chemical shift is very sensitive to its chemical environment, which allows for the quantitation of –OH groups in molecules with very similar chemical environments as in the **A** isomers of E18:1. Treatment of E18:1(MeOH) with chlorophospholane and analysis by ^{31}P showed two peaks at 146.88 and 146.87 that integrate in a 1:1 ratio. This result is additional evidence that E18:1(MeOH) consists of the two **A** regioisomers proposed in Scheme 2.

High oleic soybean oil (HOSO) was transesterified by reaction with methanol in the presence of sodium methoxide catalyst to give HO18:1. Analysis of the ^{1}H-NMR spectrum [27, 28] of HO18:1 showed that it consisted primarily (86 %) of 18:1. After HO18:1 was epoxidized and then reacted with methanol, the product EHO18:1(MeOH) was isolated. Its ^{1}H, ^{13}C, and ^{31}P-NMR spectra were the same as those of E18:1(MeOH).

Reaction of E18:2 with Methanol to Give E18:2(MeOH)

The di-epoxide E18:2 reacts with methanol, under the same conditions as for the reaction of E18:1 (Scheme 2), to form a mixture of compounds we designate as E18:2(MeOH) (Scheme 4). To our knowledge, this reaction has not been reported in the literature. Analysis of the products by LC-APCI showed five distinct peaks in the LC chromatogram at 1.4, 1.7, 1.8, 2.2, and 2.5 min.

Flash silica-gel column chromatography of E18:2(MeOH) yielded fractions that contained pure **B**, **C**, and **D**. Integration of the methyl ester group in each fraction against a Ph_3CH standard yielded the molar percentage composition of each of these compounds in E18:2(MeOH) which is 53 % **B**, 26 % **C**, and 21 % **D**. The cyclic methanolysis product **B** is clearly the major product of the acid-catalyzed reaction of E18:2 with methanol.

The peak in the LC chromatogram at 1.7 min has a molecular ion peak ($MH^+ = 391$) that corresponds to the proposed structure of **C** in Scheme 4. This compound represents the product resulting from methanol addition to both of the epoxide rings to give a product containing two –OH and two –OMe groups. Depending on the site of attack of the alcohol on the epoxides, there are four possible regioisomers of this compound. An ^{1}H-NMR spectrum of pure compound **C** shows peaks for the ester methyl (3.64 ppm) and the ether methyl groups (3.40, 3.41 ppm) that integrate in a 1:2 ratio, which is consistent with two ether methyl groups for each ester methyl group in structure **C**.

The peaks at 2.2 and 2.5 min in the LC chromatogram both show MH^+ molecular ion peaks for compound **B** in Scheme 4. This product is presumably formed as a result of MeOH addition to one of the epoxides. The epoxide oxygen in the resulting intermediate then adds to a carbon of the second epoxide to give the cyclic 5-membered ether ring. Depending on the initial site of attack of the methanol on the E18:2 epoxides, the formation of four isomers of **B** is possible. (This mechanism is drawn in detail in the supporting information). Cyclic ethers of this type have been reported from the reaction of E18:2 with water under acidic conditions where the presence of the cyclic ether group in these products was indicated by LC–MS fragmentation analysis as well as by NOE NMR spectroscopy [29, 30]. The proposed structure **B** is based on the molecular ion fragment in the APCI spectrum, which gives the molecular formula corresponding to **B**. This structure is further corroborated by the ^{1}H-NMR spectrum which shows that the methyl ester (3.65 ppm) and methyl ether (3.32 and 3.28 ppm) groups integrate in a 1:1 ratio, showing that for each ester methyl there is one ether methyl group.

The peaks at 1.4 and 1.8 min both have molecular ion peaks ($MH^+ = 345$) in their mass spectra that correspond to the cyclic hydrolysis product **D** in Scheme 4. The two peaks indicate that this compound exists as two regioisomers, presumably differing by the initial site of water attack on the epoxide groups to form the dihydroxy tetrahydrofuran products **D**. The retention times of **D** in E18:2(MeOH) correspond exactly to the retention times of the pure **D** prepared from E18:2 according to Ref. [30]. The formation of hydrolysis compound **D** indicates that water is formed during the reaction of E18:2 with methanol in the presence of the acidic Amberlyst-15. The origin oand other alcohols) in the presence off this water is not obvious, but a possibility is that dehydration of methanol to give dimethyl ether and water occurs; such an Amberlyst-15-catalyzed dehydration of alcohols has been reported previously [31].

The ^{31}P-NMR spectrum of the product of the reaction of E18:2(MeOH) with the chlorophospholane derivatizing agent showed 16 distinct phosphorus signals in the 146–148 ppm region. A sample of pure compound **B** displayed four ^{31}P-NMR peaks, indicating the presence of 4 –OH groups, suggesting that this component is a mixture of 4 regioisomers, each of which has a single –OH group. Compound **C** features 8 peaks in its ^{31}P-NMR spectrum, indicating the presence of 8 hydroxy groups, which is consistent with its proposed structure. The four possible regioisomers of this structure would each possess two hydroxy groups. Finally, the phosphorylated product **D** exhibits four distinct ^{31}P-signals, which is consistent with the presence of two regioisomers, each of which possesses two different hydroxy groups. Thus, the sixteen ^{31}P-NMR peaks observed in the spectrum of E18:2(MeOH) is consistent

with the number of peaks expected for a mixture of **B**, **C**, and **D**.

Reaction of E18:3 with Methanol to Give E18:3(MeOH)

The tri-epoxide E18:3 was reacted with methanol in the presence of Amberlyst-15 under the same conditions as described above for E18:1 and E18:2. To the best of our knowledge, this reaction has not been reported previously. Analysis of the product by LC-APCI showed three distinct peaks with molecular ion formulas that correspond to compounds **E** ($MH^+ = 437$, 1.0 min), **F** ($MH^+ = 405$, 1.2 min), and **G** ($MH^+ = 391$, 0.9 min) (Scheme 5). The E18:3(MeOH) mixture was also separated by flash silica gel chromatography, and the amounts of compound in each fraction were quantified by integration of the ester methyl peaks in the ^{1}H-NMR spectra of the compounds. The composition was found to be 10 % **E**, 51 % **F**, and 39 % **G**. Thus, the major component in E18:3(MeOH) is the cyclic methanolysis compound **F**.

The molecular ion for compound **E** corresponds to the acyclic compound that results from MeOH addition to each of the three epoxides in E18:3. The ^{1}H-NMR spectrum yields an ester methyl/ether methyl integration ratio of 1:3, which is consistent with the proposed structure of **E**. The molecular ion peak suggests that compound **F** contains a cyclic tetrahydrofuran ether compound similar to that in **B.** Presumably this ring forms as the result of MeOH addition to one of the epoxides, followed by intramolecular cyclization with a second epoxide to give the cyclic ether. The third epoxide ring is simply opened upon reaction with methanol to give **F**. Integration of the ^{1}H-NMR spectrum of **F** yields a 1:2 ester methyl/ether methyl ratio, which is consistent with the proposed structure for **F**.

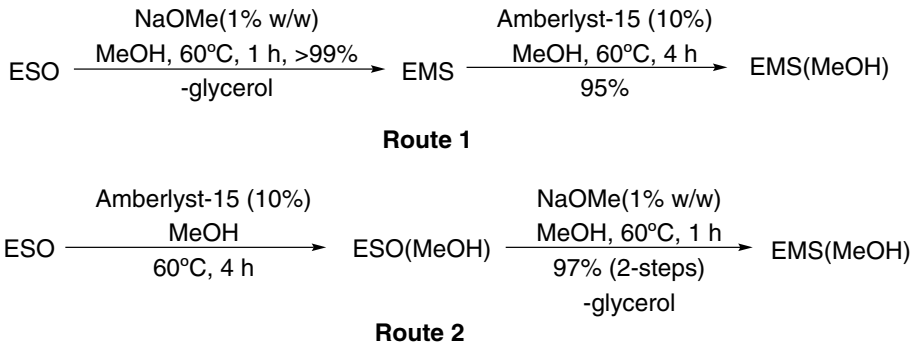
Compound **G** results from the addition of water to one epoxide followed by cyclization to give the cyclic ether group; reaction of the remaining epoxide with methanol gives the final product **G**. The ^{1}H-NMR spectrum of this compound provides an ester methyl/ether methyl integration of 1:1, which is consistent with the structure proposed for **G**.

The ^{31}P-NMR spectrum of the mixture resulting from the reaction of E18:3(MeOH) with the chlorophospholane reagent showed 38 peaks in the 145–148 ppm region. The large number of peaks may be attributed to the large number of alcohol-containing products, including regioisomers, in E18:3(MeOH). In addition, many of the peaks are poorly resolved, thus making it difficult to make assignments of the molecular species in E18:3(MeOH).

Reaction of EMS with Methanol

Considering the complex mixture of compounds in EMS, the product resulting from its reaction with methanol is expected to be even more complex. There are two potential methods of producing EMS(MeOH) using ESO as the starting material. The first involves the base-catalyzed transesterification of ESO to EMS, followed by an acid-catalyzed reaction of the epoxide groups in EMS with methanol to give EMS(MeOH) (Route 1 in Scheme 6). The second route involves the acid-catalyzed reaction of the epoxide groups in ESO with methanol to form ESO(MeOH) as an intermediate, which is then transesterified with methanol in a base-catalyzed reaction to give EMS(MeOH) (Route 2 in Scheme 6). The primary advantage of Route 2 is that it involves fewer mechanical steps. Route 1 requires removal of the methanol solvent by evaporation after the transesterification step in order to separate the glycerol side product and NaOMe catalyst; then methanol must be re-added to the EMS in the second step to give EMS(MeOH). Route 2, on the other hand, utilizes the same methanol solvent for both steps of the process, because the Amberlyst-15 catalyst can be removed simply by filtration. Then the NaOMe catalyst can be added to the reaction solution for the second step.

Both of the aforementioned routes to EMS(MeOH) were investigated. Route 1 yielded quantitative conversion of ESO to EMS in the first step, followed by a 95 % yield for the conversion of EMS to EMS(MeOH) in the second step. In contrast, the first step of Route 2 gave a gummy substance that coated the Amberlyst-15 catalyst during the reaction. This compound, which is presumed to be



Scheme 6 Routes for the conversion of ESO to EMS(MeOH)

Table 1 LC-APCI data for EMS(MeOH)

Fraction	Retention time (min)	MH^+	Formula	Percentage comp. (%)[a]	Proposed structure
1	0.900	391.2670	$C_{20}H_{38}O_7$	0.4	**G**
2	1.017	405.2844	$C_{21}H_{40}O_7$	0.1	**E**
3	1.167	437.3100	$C_{22}H_{44}O_8$	1.5	**F**
4	1.385	345.2632	$C_{19}H_{36}O_5$	8	**D**
5	1.663	391.3049	$C_{21}H_{42}O_6$	14	**C**
6	1.811	345.2633	$C_{19}H_{36}O_5$	10	**D**
7	2.187	359.2787	$C_{20}H_{38}O_5$	13	**B**
8	2.548	359.2785	$C_{20}H_{38}O_5$	22	**B**
9	5.317	345.2993	$C_{20}H_{40}O_4$	13	**A**
10	5.645	345.2993	$C_{20}H_{40}O_4$	19	**A**

Compound labels are indicated in bold

[a] Percentage compositions are based on ^{1}H-NMR integrations of ester methyl peaks in spectra of each of the fractions against a Ph_3CH standard

polymerized ESO, also reduced the activity of the catalyst. Moreover, recycling of the catalyst in Route 2 was not feasible, as the separation of the catalyst from the gummy polymer proved to be unsuccessful. This gummy material does not form when using Route 1. Therefore, although Route 2 involves fewer mechanical steps, Route 1 was more efficient and was used for the synthesis of EMS(MeOH) for all subsequent studies.

It should be noted that the reaction of ESO with MeOH (and other alcohols) in the presence of H_2SO_4 catalyst at 80–100 °C was previously reported [32]. Under these conditions, complete epoxide ring opening occurred but only partial transesterification. No tetrahydrofuran-type structures, such as **B** or **F**, were identified among the components of those products.

The product, EMS(MeOH), of the Route 1 reaction was analyzed by LC-APCI (Table 1). The retention times and molecular ions observed are identical to those obtained from products of the reactions of E18:1, E18:2, and E18:3 with methanol, discussed above. The EMS(MeOH) was separated into 10 fractions by flash chromatography on a silica column. The percentage molar compositions of the individual fractions are based on ^{1}H-NMR integrations of the ester methyl peaks relative to the Ph_3CH standard. The products, **E**, **F**, and **G,** derived from E18:3, make up only a small percentage (~2 %) of the functionalized products in EMS(MeOH) (Table 1). The E18:1(MeOH) compounds **A** make up 31 % of the mixture which is consistent with the fact that 18:1 makes up ~30 % of the unsaturated compounds in methyl soyate. The family of E18:2(MeOH) compounds, **B**, **C**, and **D**, derived from E18:2, make up the largest percentage (67 %) of the functionalized EMS(MeOH).

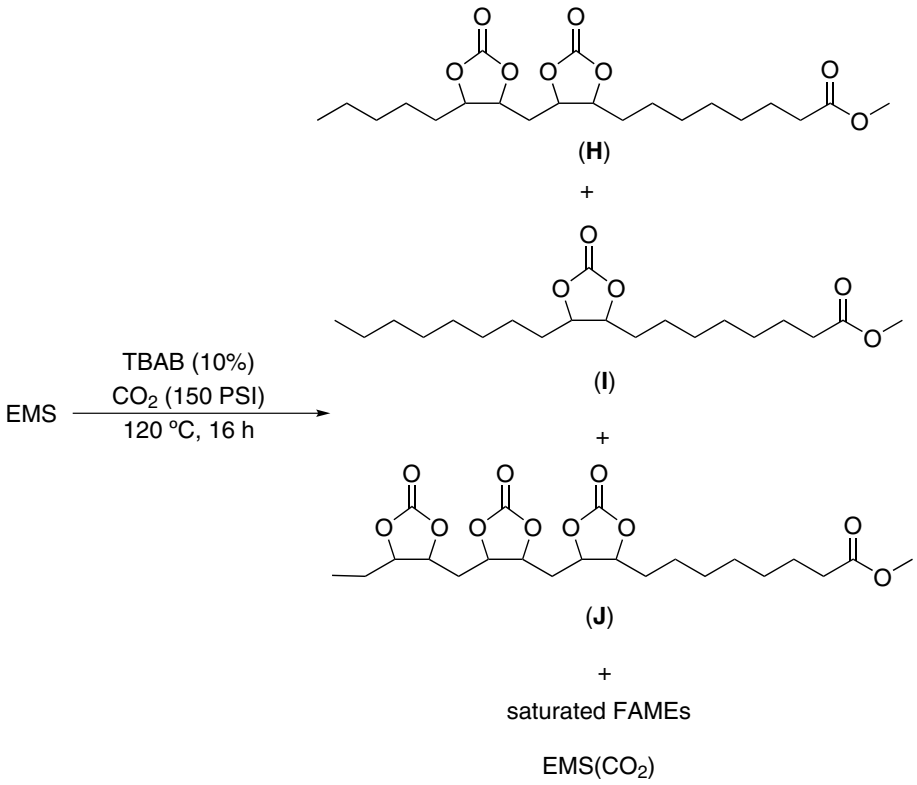
Ethanol, *n*-propanol, *n*-butanol, and 2-methoxyethanol were also reacted with EMS in the presence of Amberlyst-15 under conditions similar to those used with methanol to give other solvents EMS(ROH). More sterically hindered alcohols such as *iso*-propanol, *sec*-butanol, and *tert*-butanol gave low yields of the expected epoxide ring-opened products.

The ^{31}P-NMR spectrum of EMS(MeOH) functionalized with the chlorophospholane revealed peaks for the compounds present in both E18:1(MeOH) and E18:2(MeOH) with the same chemical shifts as those observed in the pure samples as discussed earlier. Integrations of these peaks showed that the E18:1(MeOH) and E18:2(MeOH) compounds are present in a 1:2.54 ratio. On the basis of the ^{31}P-NMR spectrum, 72 % of the alcohol (–OH) groups in EMS(MeOH) are derived from reactions of E18:2, while 28 % are derived from reactions of E18:1. Interestingly, no ^{31}P-NMR peaks for phosphorylated E18:3(MeOH) were detected in phosphorylated EMS(MeOH), which may be due to the relatively small amount of E18:3 in EMS(compared with E18:2 and E18:1) and to the large number of different alcoholic groups in E18:3(MeOH), as observed in ^{31}P-NMR spectra of phosphorylated products of E18:3(MeOH) (see above).

Reaction of EMS with Carbon Dioxide to Form EMS(CO_2)

Epoxidized methyl soyate (EMS) was previously reacted with carbon dioxide using tetra(*n*-butyl)ammonium bromide (TBAB) as the catalyst [12]. The product of this reaction was characterized by IR spectroscopy, which established the presence of carbonate groups. After we prepared EMS(CO_2) by this method, the resulting product was separated by flash silica gel chromatography to give pure fractions of compounds **H** and **I** (Scheme 7). These compounds were characterized by LC-APCI, which exhibited MH^+ ion peaks at 415 and 357, respectively. Analysis of the pure fractions by ^{1}H-NMR spectroscopy revealed that EMS(CO_2) contained 63 % **H** and 37 % **I**. None of compound **J** was found after column purification. The only product of the carboxylation of E18:2 is **H** and similarly, the only products of the reactions of E18:1 and E18:3 with CO_2 are **I** and **J**, respectively. None of the epoxide remains

Scheme 7 Carboxylation of EMS to EMS(CO_2)



after these reactions, as evidenced by the complete loss of epoxide peaks in the ^{1}H-NMR spectra.

Reaction of EMS with Acetone to Form EMS(Me_2CO)

The acetonide of EMS was prepared according to a literature procedure [13], which involves treatment of EMS in the presence of a Lewis acid ($FeCl_3$) using acetone as the solvent as well as reactant (Scheme 8). The product is a mixture of acetonides, **K**, **L**, and **M,** as evidenced by the presence of the MH^+ molecular ions in an LC-APCI analysis of the crude product EMS(Me_2CO). The previous literature report [13] characterized the product by its ^{13}C-NMR spectrum, which contained a peak at 107 ppm indicative of quaternary carbons; this peak was also observed in our studies.

Physical Properties of the Solvents

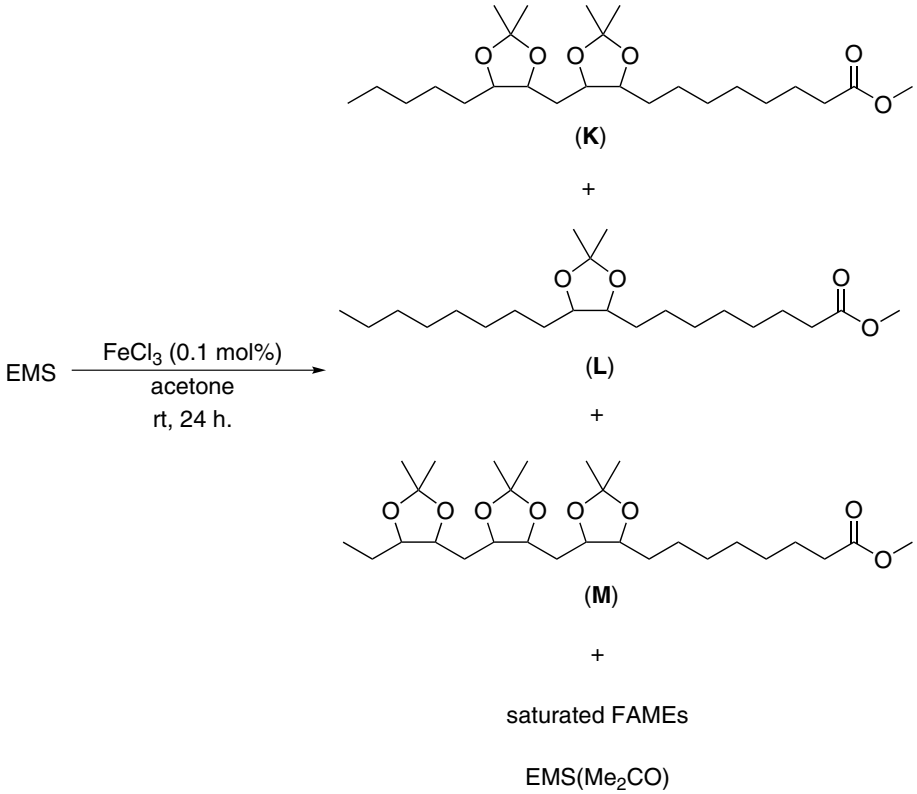
Kauri-Butanol (KB) Values

One of the standard methods of characterizing the solution properties of solvents is the determination of their Kauri-butanol values [33, 34]. This method involves the titration of a standard solution of Kauri gum in *n*-butanol with the solvent of interest until the solution reaches a cloud point. The amount of solvent titrant required is used to calculate the KB value. In general, a larger KB value indicates a more effective solvent. Recently, Knöthe and Steidley [33] reported a modified Kauri-butanol procedure that used only 5 g of Kauri-butanol solution instead of the 20 g used in the standard method [35]; they found the same KB values as those determined with 20 g. We have found that the amount of Kauri-butanol solution used for these titrations can be decreased further to 1.00 g while still giving the same or nearly the same KB values as those obtained with 5 and 20 g. For example, we obtained the same KB value (30) for hexanes using 1.00 or 5.00 g of Kauri-butanol solution. For *p*-xylene, the KB value on a 5.00 g scale was determined to be 97, while on a 1.00 g scale, it was 101. The use of 1.00 g of the Kauri-butanol solution required a modification of the KB Eq. 1. Here, *X* is the amount (1.00 g) of the KB solution used, C is the volume (mL) of

$$\mathrm{KB} = \left\{(65)[(20C/X) - B]/(A - B)\right\} + 40 \quad (1)$$

tested solvent required to reach the endpoint, A is the volume of toluene (mL) required to titrate 20 g of KB solution as provided by the KB solution supplier, and B is the volume (mL) of a toluene-heptane blend required to titrate 20 g of KB solution as provided by the KB solution supplier. For the particular KB solution that was used in our titrations, $A = 104.8$ and $B = 38.2$. Therefore, for our determinations that utilized 1.00 g of KB solution, the KB equation is shown below.

Scheme 8 Reaction of EMS with acetone to give EMS(Me_2CO)



$$KB = \left[(65)(20C-B)/(A-B)\right] + 40 \quad (2)$$

The KB values of the solvents prepared in the present study are shown in Table 2. It is clear that each of these solvents has a considerably higher KB value than that of methyl soyate (57, Table 2, Entry 1); note that our measured KB value is very similar to that (58) reported previously [5, 6], although a higher value of 82.7 has also been reported for methyl soyate [34]. Of the solvents prepared in the present investigation, the KB value is lowest for EMS(Me_2CO) (280, Entry 3). EMS(which possesses epoxide functional groups) has a KB value of 249 (Entry 2). By contrast, all of the prepared solvents reported herein have higher KB than those in Entries 1 and 2. It is interesting that the KB value (610) for EHO(MeOH), derived from high oleic soybean oil, is much higher than the KB value (369) for EMS(MeOH) derived from standard soybean oil. The major component in EHO(MeOH) has structure **A**, which is the product of the methanolysis of E18:1 (Scheme 2); this structure is presumably at least partially responsible for its higher KB value as compared with that of EMS(MeOH) in which the major structure is the cyclic tetrahydrofuran derivative **B** formed in the reaction of E18:2 with methanol (Scheme 4). It appears to be the combination of the polar groups and the hydrocarbon chain that gives these solvents such unprecedentedly high KB values.

Table 2 KB Values of prepared solvents using 1.00 g of Kauributanol solution

Entry	Solvent	Amt. solvent used (mL)	KB value
1	Methyl soyate	2.8	57
2	EMS	12.6	249
3	EMS(Me_2CO)	14.2	280
4	EMS(MeOH)	18.6	366
5	EMS(CO_2)	28.2	553
6	EHO(MeOH)	31.1	610
7	EMS($HOCH_2CH_2OCH_3$)	37.0	725
8	EMS(EtOH)	43.5	852

Melting Points and Initial Boiling Points

The procedure for determining the melting points reported in Table 3 involved first freezing the solvent (~10 mL) in a dry ice/acetone bath and allowing the solvent to slowly warm to room temperature, noting the temperature, MP(start), at which the solvent first began to show liquid and then the temperature, MP(end), at which the solid was completely melted. All the boiling points in Table 3 were performed at 1 Torr pressure because of their high boiling points at atmospheric pressure. The initial boiling points listed in Table 3 are temperatures of the solvents at which they first began to bubble.

Table 3 Physical properties of prepared solvents

Entry	Solvent	Initial BP (1 Torr) °C	MP (start) (°C)	MP (end) (°C)	Karl Fischer water sol. (%)	Viscosity at 25.0 °C (cSt)
1	Methyl soyate	51.5	−49.1	1.0	0.05 [36]	3.9–4.3 [3, 4, 37]
2	EMS(MeOH)	68.8	−33.0	6.5	0.539	69.67
3	EMS(EtOH)	72.8	−33.4	4.6	0.522	59.42
4	EMS($HOCH_2CH_2OCH_3$)	55.0	−39.0	2.2	0.487	38.69
5	EMS(CO_2)	53.1	−23.9	9.3	0.242	178.4

When compared to the melting point of methyl soyate, all of the prepared solvents have higher melting points. Likewise, they all have higher initial boiling points than methyl soyate. All of them would therefore have higher normal boiling points than methyl soyate, which has a normal boiling point of 216 °C [3, 4]. The vapor pressures of EMS(MeOH), EMS(EtOH), EMS($HOCH_2CH_2OCH_3$), and EMS(CO_2) were measured with a mercury manometer. In every case, the vapor pressure was very low (<1 mmHg at 19 °C).

Solubility of Water in the Solvents

Karl Fischer titration reveals that water is extremely insoluble in methyl soyate (0.05 % water) [36]. All of our solvents, however, dissolve more water than methyl soyate (Table 3) especially those derived from reactions of EMS with alcohols (ca. 0.5 %). The solvent without –OH groups, EMS(CO_2) has a lower water solubility of 0.24 %, presumably because of its reduced ability to participate in hydrogen-bonding.

A wide range of organic solvents are readily soluble in EMS(MeOH). These include methanol, ethanol, acetonitrile, diethyl ether, toluene, and hexane.

Viscosities of the Solvents

Kinematic viscosities of the solvents were also determined (Table 3). Methyl soyate is reported to have a viscosity of ~4 cSt [3, 4, 37], whereas our functionalized solvents possess viscosities ranging from 39 cSt for EMS($HOCH_2CH_2OCH_3$) to 178 cSt for EMS(CO_2), which are all much higher than that of methyl soyate. Presumably the added polar –OH and –OR groups are largely responsible for the high viscosities of the alcohol-derived solvents EMS(ROH), as has been reported [38, 39] for the methyl ester of ricinoleic acid, with a viscosity of 15.4 cSt at 40 °C. The unusually high viscosity of EMS(CO_2) is consistent with the previously-reported high viscosities of carbonated soybean and vernonia oils [40].

Summary and Conclusions

The goal of this project was to convert methyl soyate (biodiesel derived from soybean oil) into a solvent that possesses properties that would make it capable of dissolving a broad range of polar and non-polar substances. One measure of the solubilizing properties of a solvent is its Kauributanol value. All of the solvents described in this paper, EMS(MeOH), EMS(EtOH), EMS($HOCH_2CH_2OCH_3$), EMS(CO_2), and EMS(Me_2CO), have substantially higher KB values (280–852) than that (57) of methyl soyate (MS). Because of the low cost of MeOH and potential low cost of EMS(MeOH), we characterized EMS(MeOH) in the greatest detail and found that it consisted of molecular components that contained –OH and –OMe functional groups near the center of the C_{18} hydrocarbon chains. The major component (**B** in Scheme 4) also contained a cyclic tetrahydrofuran unit derived from methyl linoleate (18:2). It is presumably these polar groups that give EMS(MeOH) its high KB value (366). The higher concentration of **A** in EHO(MeOH), derived from high-oleic soybean oil, reasonably accounts for the even higher KB value (610) of this solvent.

The excellent solvent properties of EMS(MeOH) are also reflected in its ability to dissolve solvents ranging from hydrogen-bonding, polar solvents such as methanol to non-polar solvents such as hexane. The versatile solubilizing properties of EMS(MeOH) and our other solvents, together with their low volatilities (VOC), will hopefully make them useful in a variety of solvent and surfactant applications.

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