

Synthesis of Carbonated Fatty Methyl Esters Using Supercritical Carbon Dioxide

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The two-step syntheses of the cyclic carbonates carbonated methyl oleate (CMO) and carbonated methyl linoleate (CML) are reported. First, synthesis of epoxides through well-precedented chemical reactions of unsaturated fatty methyl esters with hydrogen peroxide and formic acid was accomplished. Next, a carbonation reaction with a simple tetrabutylammonium bromide catalyst was performed, allowing the direct incorporation of carbon dioxide into the oleochemical. These syntheses avoid the use of the environmentally unfriendly phosgene. The carbonated products are characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy and studied by thermogravimetric analysis (TGA). Also reported is the synthesis of a similar cyclic carbonate from the commercially available 2-ethylhexyl epoxy soyate. These carbonates show properties that may make them useful as petrochemical replacements or as biobased industrial product precursors.

KEYWORDS: Supercritical carbon dioxide; cyclic carbonate; methyl 8-(2-oxo-5-octyl-1,3-dioxolan-4-yl)-octanoate; carbonated methyl oleate; carbonated methyl linoleate

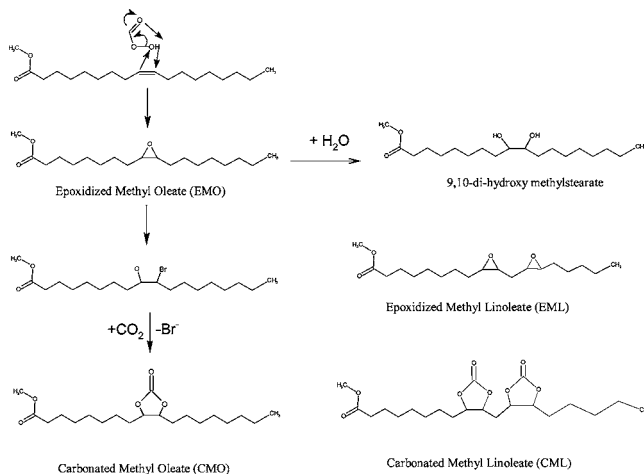
INTRODUCTION

With the price of crude oil near \sim \\$70/barrel, the need to use biobased resources is of high priority (1, 2). A recent area of interest has been in the synthesis of carbonates from agriculturally derived oleochemicals (3, 4). These carbonates have been used as emollients (3), fuel additives (5, 6), polymer precursors (7, 8), lubricants, or chemical solvents (3, 4). One particular area of interest has been in the synthesis of the cyclic carbonates of fatty esters, which have shown possible use as plasticizers (9, 10) or in biomedical applications (11). Both of these older synthetic methods required the use of phosgene, as well as organic solvents. Recently, Kenar and Tevis reported a novel synthesis of the cyclic carbonate methyl 8-(2-oxo-5-octyl-1,3-dioxolan-4-yl)octanoate (12) (carbonated methyl oleate, CMO) as well as the 2-ethylhexyl derivative from the corresponding chlorohydroxy materials. Using these syntheses, they were able to avoid the use of phosgene and build the cyclic system using ammonium hydrogen carbonate.

However, we decided to explore an alternative route (Scheme 1) to the synthesis of CMO through a well-precedented epoxide route. Using this route, we used supercritical carbon dioxide directly with a catalytic amount of tetrabutylammonium bromide. A similar reaction has been used for the carbonation of soybean oil under both atmospheric (7, 8) and supercritical carbon dioxide conditions.

Supercritical CO_2 has been used for over 20 years in the extraction of oils from agricultural products (13–15). Reactions

Scheme 1. Epoxidation of Methyl Oleate Using Performic Acid Followed by the Carbonation Using Tetrabutylammonium Bromide Catalyst^a



^a If the epoxidation reaction is not monitored directly, a dihydroxy stearate impurity may be produced. Epoxidized methyl linoleate (EML) and carbonated methyl linoleate (CML) are also shown.

of fatty materials have been preformed in supercritical CO_2 including polymerizations (16, 17), hydrogenations (18, 19), and esterifications (20, 21). In some of these systems, the supercritical CO_2 system has a higher reaction rate. For example, a transesterification of myristic acid shows 37% conversion in CO_2 versus only 4% in the corresponding acetonitrile system (21) at similar reaction times. The solubility parameters of fatty

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materials in supercritical CO₂ have been well studied (20). Esters are somewhat soluble in supercritical CO₂, with the trend of increased solubility with increasing fatty chain length (22). The solubility of hydrocarbons (23–25) and fatty esters (26) has also been shown to increase at higher reaction temperatures and pressures.

Our reaction is also environmentally advantageous because our system uses CO₂ directly. The carbonation reaction is completely atom efficient, following the second principle of green chemistry (27, 28). Without the use of the supercritical system, it may not be possible to get a satisfactory reaction rate. The supercritical CO₂ system employed herein is quite simple, requiring only a high-pressure reactor and a fairly inexpensive syringe pump.

We used the previously reported synthesis of epoxidized methyl oleate (EMO) (29) as a starting point to the synthesis of our desired product, carbonated methyl oleate (CMO). Additionally, we also report the synthesis of carbonated methyl linoleate (CML) and the carbonation of a commercially available epoxidized ester material using similar procedures.

MATERIALS AND METHODS

Materials. Methyl oleate (Sigma-Aldrich, St. Louis, MO), Tech 70% (Nu Check Prep, Elsyan, MN, >99%), methyl linoleate (Nu Check Prep, >99%), 2-ethylhexyl epoxy soyate (Arkema, Philadelphia, PA; VikoFlex 4050, 5.6% oxirane content), hydrogen peroxide (Sigma-Aldrich, ACS Reagent, 30% solution); formic acid (Sigma-Aldrich, 96%, ACS Reagent), hexanes (Sigma-Aldrich, >95%, HPLC grade), NaCl (Fisher, Fair Lawn, NJ, ACS Reagent), NaHCO₃ (Fisher, ACS Reagent), NaSO₄ (Sigma-Aldrich 99+, ACS Reagent), tetrabutylammonium bromide (Sigma-Aldrich 99%), and carbon dioxide (AirGas, Wilmington, DE; 50 lb siphon type high-pressure cylinder, UN1013) were used as received.

Instrumentation and Equipment. The reactor employed was a Parr (Moline, IL) 4560 mini benchtop unit equipped with a Parr 4843 controller and thermocouple. For the reported experiments, a 300 mL reactor body equipped with quartz viewing windows was used.

FTIR spectra of the starting material and products were recorded on a Thermo Nicolet (Madison, WI) Nexus 470 FTIR with a Smart ARK accessory containing a 45° ZeSe trough. Data were collected and processed on a Windows 2000 equipped Dell Optiplex GX260 Pentium 4, 2.46 GHz computer running Omnic 6.2 software.

Gas chromatography was performed on a Hewlett-Packard (Loveland, CO) 6890 GC system equipped with a 6890 series injector and an FID detector. A Supelco SPB 30 (30 m × 320 μm) was used with a helium flow rate of 1.2 mL min⁻¹. The temperature ramp used started at 180 °C and increased to 250 °C at 5 °C min⁻¹ and then to 290 °C at 15 °C min⁻¹.

NMR was performed on a Bruker (Boston, MA) Avance 500 NMR operating at 500 MHz for ¹H and at 125 MHz for ¹³C. Bruker Icon NMR software was used running on an HP X1100 Pentium 4 workstation. Peaks were referenced to sodium 3-trimethylsilylpropionate-2,2,3,3-*d*₄ (TSP) at 0.0000 ppm. Simulations of ¹³C NMR spectra were performed by ACD/Labs 6.00 ACD/CNMR predictor software, running on a Gateway Pentium 4 CPU with a 2.53 GHz processor.

Freeze-drying was performed with a Labconco (Kansas City, MO) Freezone 1. Samples were prefrozen in a dry ice/ethanol bath according to standard laboratory procedures.

Thermogravimetric analysis (TGA) was performed on a TA (La Canada, CA) TGA Q500. Data were collected and processed on a Windows 2000 × 86 Family 6 model 8 IBM computer with Advantage for Q series version 1.5.0.208 Thermal Advantage release 3.2.0 software. Samples were heated under nitrogen using a heating ramp of 2.0 °C min⁻¹ from 25 to 350 °C.

Epoxidations. The reaction was carried out using a slightly modified synthesis of Bunker and Wool (29). This synthesis was originally used by Swern (30, 31) and has been refined and studied over the years (32–34). First, 200.0 g (0.67 mol) of methyl oleate is placed in a 500

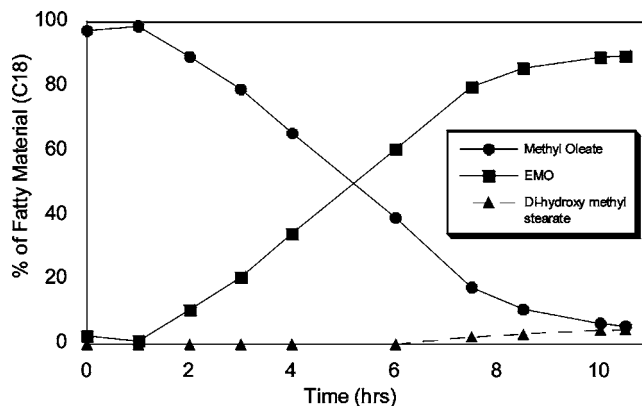


Figure 1. Reaction progress of the epoxidation reaction of methyl oleate (●) to epoxidized methyl oleate (EMO, ■). At longer reaction times, some dihydroxy stearate (▲) can be detected.

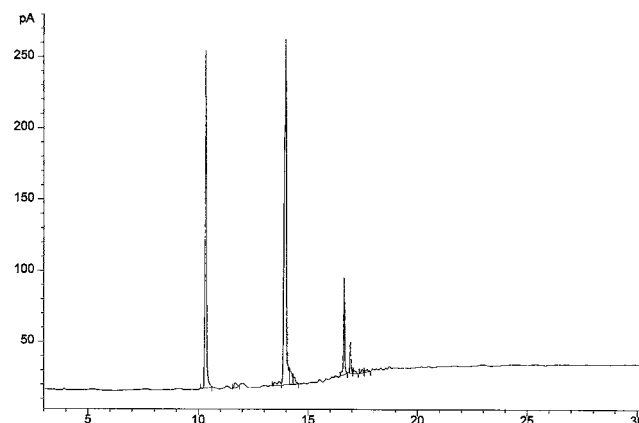


Figure 2. GC-FID trace of the epoxidation reaction of methyl linoleate at 3 h. In this trace it is possible to observe starting material (~10.3 min), singly epoxidized material (~14.0 min), and fully epoxidized methyl linoleate (EML; ~16.6 min).

mL round-bottom flask equipped with an overhead stirrer. Next, 102 g (2.2 mol) of formic acid was slowly added, forming a layered mixture. The reaction flask is cooled in an ice bath, and 163 g of 30% hydrogen peroxide (1.44 mol) is added over ~5 min while the temperature of the solution is monitored. The peroxide is added slowly enough such that the temperature of the solution does not exceed 18.4 °C, but rapidly enough to keep the reaction solution from solidifying. Gas bubbles are evident as the hydrogen peroxide is added. The reaction is allowed to proceed at room temperature, and aliquots are taken and analyzed by GC (Figure 3). The product is purified using a separatory funnel by dissolving the material in ~200 mL of hexanes and then discarding the aqueous/formic acid layer. Then, ~200 mL of saturated sodium bicarbonate solution is shaken with the hexane layer and removed. This is repeated until the pH of the solution is >7 (three times). Next, ~400 mL of saturated sodium chloride solution is added to the hexane layer, shaken, and removed with a separatory funnel three times. The hexane layer is dried over ~28 g of anhydrous sodium sulfate and filtered through a fritted funnel, and the hexane is removed with rotary evaporation (~60 °C; overnight). The product is a very slightly colored viscous liquid that slowly became cloudy when cooled below room temperature. The isolated yield was 221.1 g (97%). The product was stored over molecular sieves. Product purification has also been performed using Et₂O instead of hexanes, but solvent removal is more difficult.

The epoxidation of methyl linoleate was performed in an analogous manner using 200 g of starting material and yielding 221.7 g (95%) of epoxidized material. The final product is similar in appearance to the EMO, but tended to become cloudy more rapidly even at room temperature.

EMO: ¹H NMR (500 MHz, CDCl₃) δ 3.61 (s, 3, methoxy protons), 2.85 (t, 2, epoxide ring protons), 2.26 (t, 2, protons on carbon α to

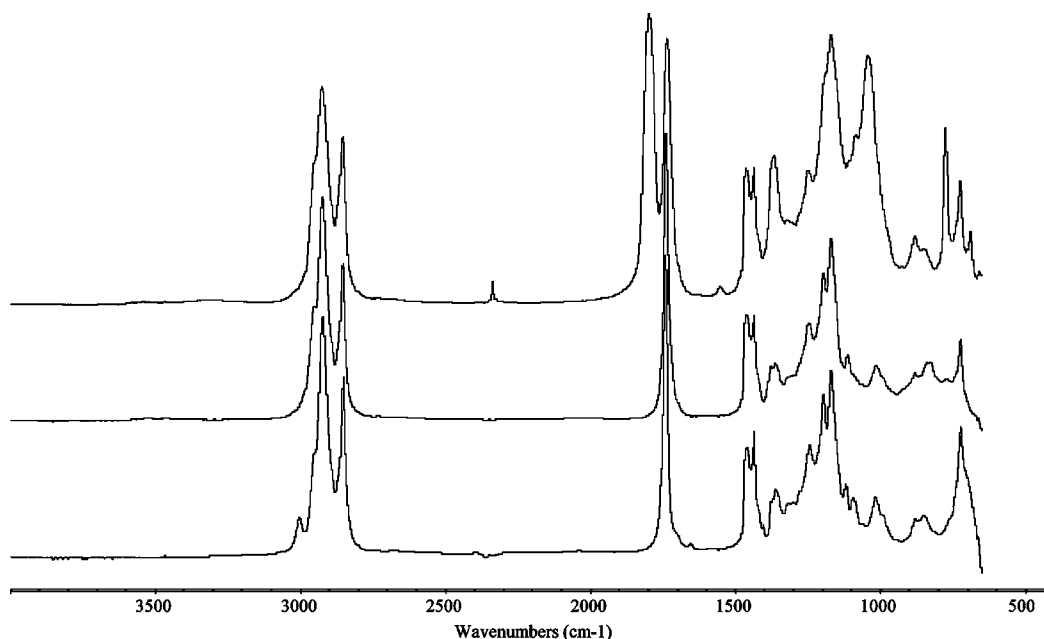


Figure 3. FT-IR spectra of methyl oleate (bottom), epoxidized methyl oleate (EMO; middle), and carbonated methyl oleate (CMO; top). The appearance of the bands at 827 and 840 cm^{-1} in the EMO spectrum confirm epoxidation. They are not present in the CMO spectrum, but a new carbonyl band at 1797 cm^{-1} is observed.

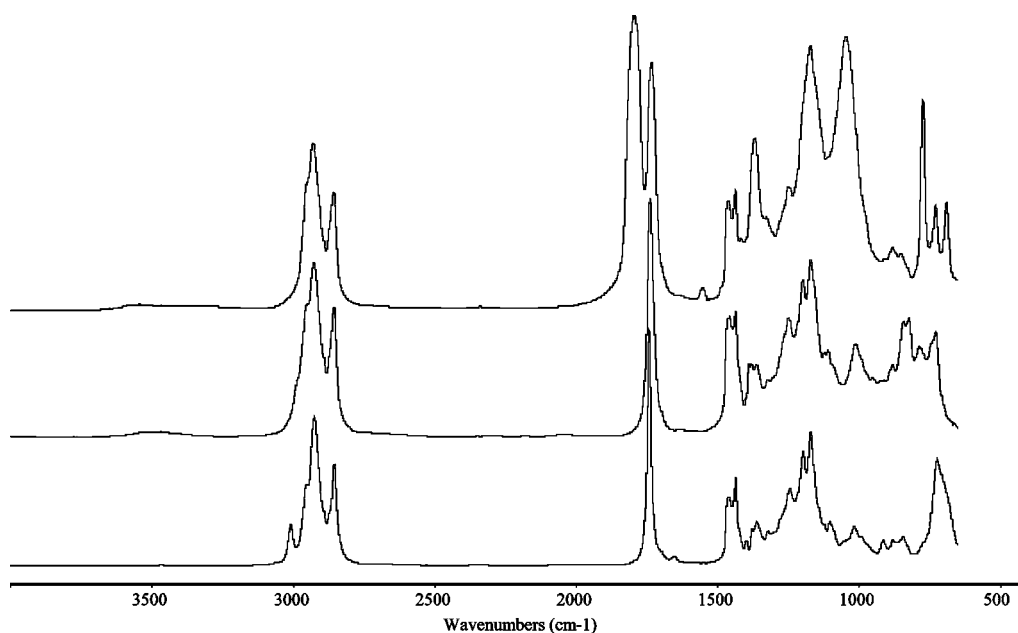


Figure 4. FT-IR spectra of methyl linoleate (bottom), epoxidized methyl linoleate (EML; middle), and carbonated methyl linoleate (CML; top). The appearance of the bands at 823 and 840 cm^{-1} in the EML spectrum, as well as the loss of the resolvable peak at 3009 cm^{-1} , confirms epoxidation and loss of unsaturated C–H signals. The epoxide peaks are not present in the CML spectrum, but a new carbonyl band at 1793 cm^{-1} is observed.

carboxy), 0.85 (t, 3, end of fatty chain), unresolvable signals from δ 1.3–1.6; ^{13}C NMR (125 MHz, CDCl_3) δ 174 (carbonyl carbon), 57, (epoxide carbons), 51 (methoxy carbon signals), 14, (end carbon of fatty chain), 20–35 (multiple signals). The spectral peaks and assignments are close to computed chemical shift and in order.

EML: ^1H NMR (500 MHz, CDCl_3) δ 3.66 (s, 3, methoxy protons), 3.12, 3.08, 2.98 (m, 4, epoxide ring protons), 2.30 (t, 2, protons on carbon α to carboxy), 0.91 (t, 3, end of fatty chain), unresolvable signals from δ 1.3–1.8; ^{13}C NMR (125 MHz, CDCl_3) δ 174 (carbonyl carbon) 54–57, (epoxide carbons), 51 (methoxy carbon signals), 14 (end carbon of fatty chain), 20–35 (multiple signals). The spectral peaks and assignments are close to computed chemical shift and in order.

Synthesis of Carbonated Fatty Esters. The EMO was heated in a warm water bath until fluid, and 29.5 g (0.096 mol) was poured into a 300 mL high-pressure reactor vessel. Next, \sim 1.59 g (0.0049 mol,

5.0 mol %, 5.0 wt %) tetrabutylammonium bromide (TBA^+Br^-) was dissolved into the oil with stirring. The reactor was closed and pressurized with CO_2 to \sim 500 psi. The reactor was then heated to 100 $^\circ\text{C}$, causing the pressure to rise. Once the reaction temperature was reached, the CO_2 pressure was further increased to 1500 psi and maintained there throughout the reaction with the necessary addition of CO_2 by the pressure-controlling pump. The reaction was run overnight (\sim 15 h). After the reaction was complete, the reactor was depressurized slowly to allow dissolved CO_2 to leave the carbonated product. The carbonated product is light brown and slightly more viscous than the epoxy material. Isolated yield was 33.03 g (93% yield of crude product). The product was characterized by ^1H NMR and IR spectroscopy. Carbonated methyl linoleate and carbonated vegetable oil esters (2-ethylhexyl soyate; VikoFlex 4050) were synthesized in an analogous manner always using 5 mol % of the TBA^+Br^- catalyst.

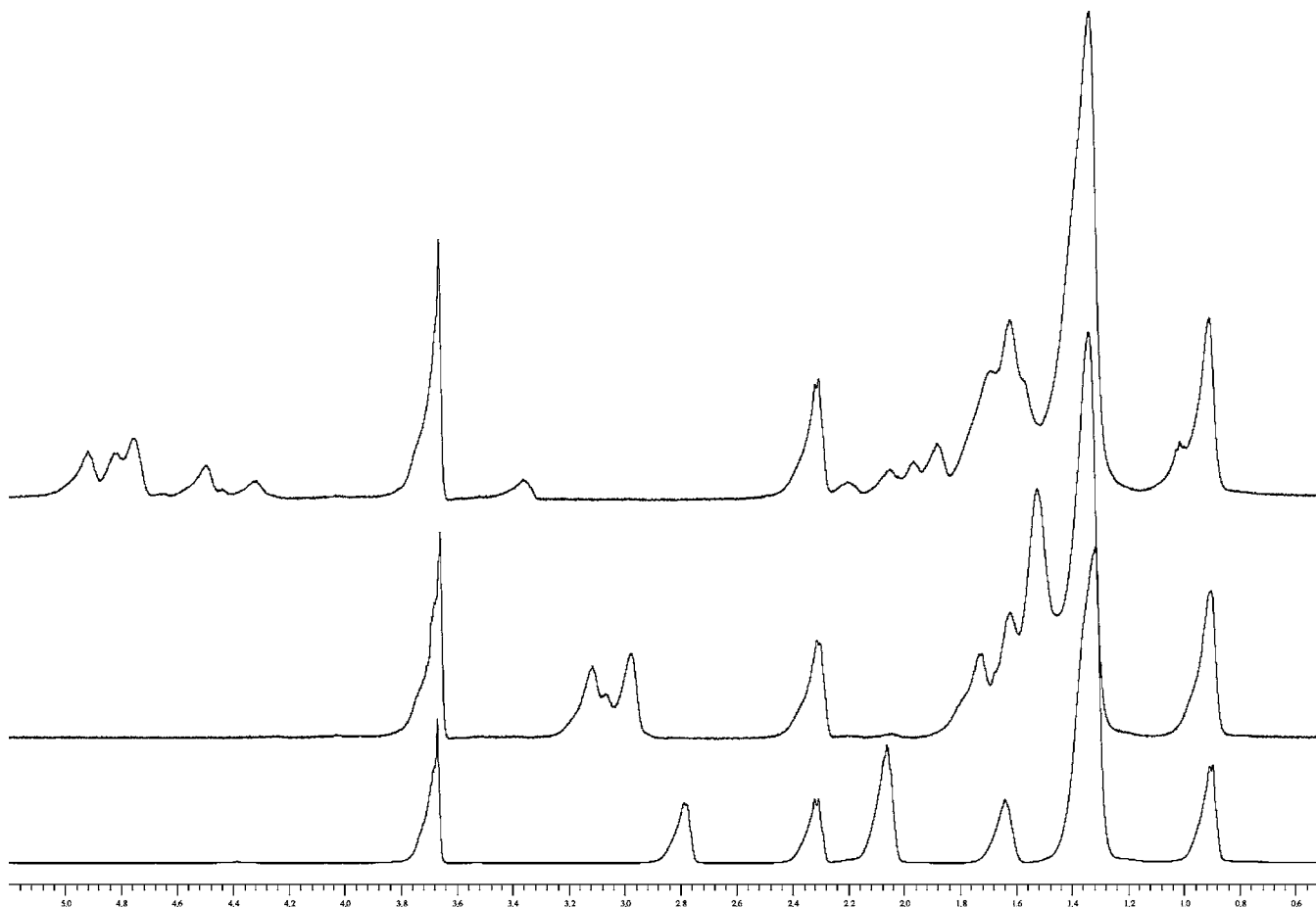


Figure 5. ^1H NMR spectra of methyl linoleate (bottom), epoxidized methyl linoleate (EML; middle), and carbonated methyl linoleate (CML; top). The appearance of the peaks 3–3.1 in the EML spectrum confirms epoxidation. The epoxide peaks are not present in the CML spectrum, but new peaks at 4.5–4.9 are indicative of the presence of the cyclic carbonate.

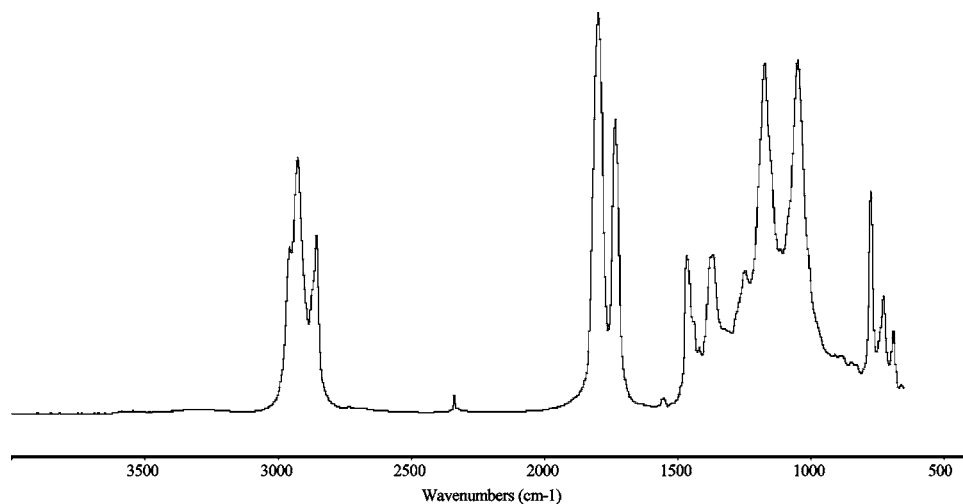


Figure 6. FT-IR spectra of carbonated 2-ethylhexyl epoxy soyate. The spectrum is similar to that of other carbonated methyl esters including the large carbonyl band at 1797 cm^{-1} .

The catalyst was removed from the products by a washing and sonication process. First, 25.79 g of CMO was suspended in 20 mL of H_2O and sonicated at $25\text{ }^\circ\text{C}$ for 3 h. This was repeated three times. The water and product layers were separated in a separatory funnel, and the product was dried on a rotary evaporator overnight at $40\text{ }^\circ\text{C}$. The water layer was freeze-dried, yielding 0.351 g of white TBA^+Br^- catalyst, which was confirmed to be intact by ^1H NMR spectroscopy. Product losses during the purification process were minimal, at $<3\%$, giving an overall experimental yield of 90%. The carbonated methyl linoleate and carbonated VikoFlex 4050 were purified in a similar manner and in similar yield. We have recently reported a method to

remove TBA^+Br^- catalyst by heating the sample to $190\text{ }^\circ\text{C}$ and taking advantage of a Hofmann reaction, which decomposes the catalyst to volatile product. However, TGA of the carbonated oleates shows some decomposition or volatilization at $\sim 190\text{ }^\circ\text{C}$, demonstrating that heat purification of these carbonates is not feasible.

CMO: ^1H NMR (500 MHz, CDCl_3) δ 4.63–4.22 (s, 2, cyclic carbonate ring protons), 3.65 (s, 3, methoxy protons), 2.29 (t, 2, protons on carbon α to carboxy), 0.87 (t, 3, end of fatty chain), unresolvable signals from δ 1.2–2.2; ^{13}C NMR (125 MHz, CDCl_3) δ 174 (methoxy carbonyl carbon), 154 and 154 (cyclic carbonate carbons), 79–82 (cyclic ring carbons), 51 (methoxy carbon signals), 14 (end carbon of

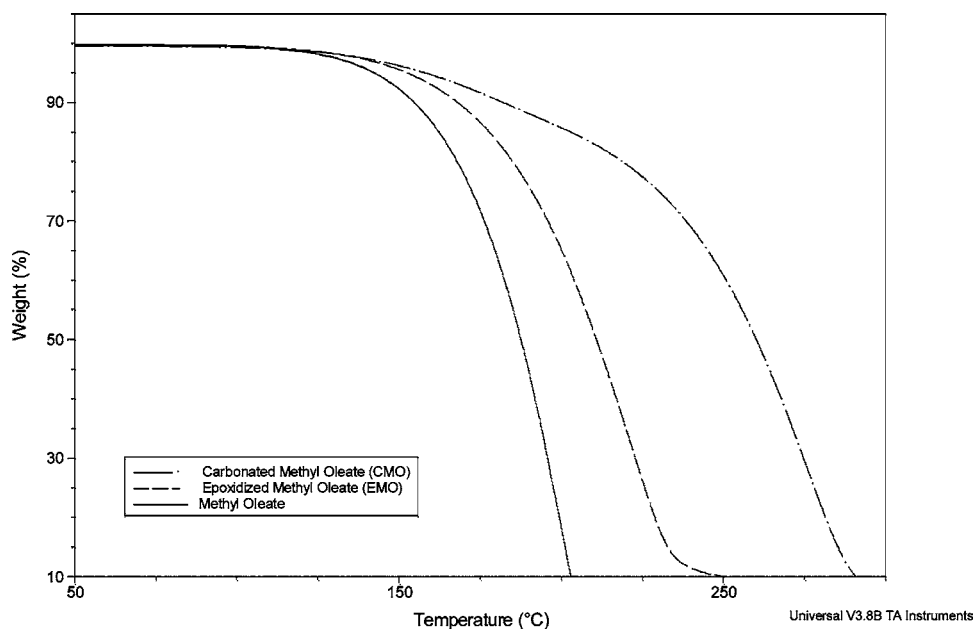


Figure 7. TGA of methyl oleate (solid line), epoxidized methyl oleate (EMO, dashed line), and carbonated methyl oleate (CMO, dot–dash line). The samples show 50% weight loss at 187, 211, and 260 °C, respectively.

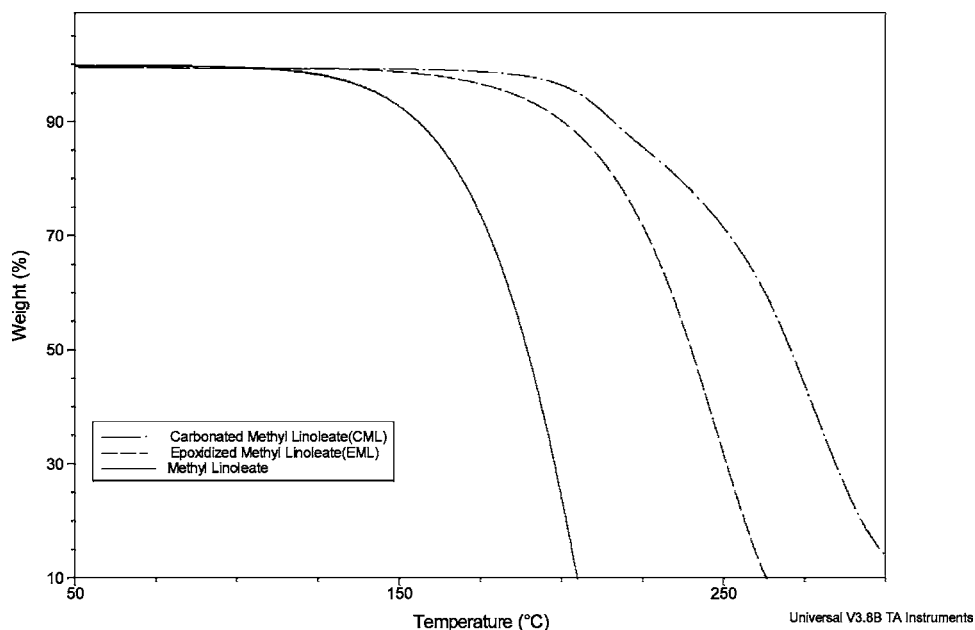


Figure 8. TGA of methyl linoleate (solid line), epoxidized methyl oleate (EML, dashed line), and carbonated methyl linoleate (CML, dot–dash line). The samples show 50% weight loss at 189, 231, and 271 °C, respectively.

fatty chain), 20–35 (multiple signals). These spectral peaks agree with the reported NMR for this compound (12), and the peaks and assignments are close to computed chemical shift and in order.

CML: ^1H NMR (500 MHz, CDCl_3) δ 4.93–4.49 (m, 4, cyclic carbonate ring protons), 3.67 (s, 3, methoxy protons), 2.32 (t, 2, protons on carbon α to carboxy), 0.90 (t, 3, end of fatty chain), unresolvable signals from δ 1.3–2.2; ^{13}C NMR (125 MHz, CDCl_3) δ 174 (carbonyl carbon), 154 (cyclic carbonate carbonyl carbon), 79–82 (cyclic ring carbons), 51 (methoxy carbon signals), 14 (end carbon of fatty chain), 20–35 (multiple signals). The spectral peaks and assignments are close to computed chemical shift and in order.

Carbonated 2-ethylhexyl methyl soyate: ^1H NMR (500 MHz, CDCl_3) δ 4.95–4.52 (2H-signal, cyclic carbonate ring protons), 3.68 and 3.68 (alkoxy protons), 2.91 (small residual epoxide signal <10% compared to δ 2.32), 2.32 (2-H triplet, protons on carbon α to carboxy), 0.91 (6.5-H unresolved multiplet, end of fatty chain and end of alkoxy chain), unresolvable signals from δ 1.2–2.2; ^{13}C NMR (125 MHz, CDCl_3) δ 174 (alkoxy carbonyl carbon), 154 (cyclic carbonate carbon), 75–79

(cyclic ring carbons), 66 (alkoxy carbon signals), 57 (small residual epoxide carbons), 14 (end carbon of fatty chain), 11 (end of alkoxy chain), 20–35 (multiple signals). The spectral peaks and assignments are close to computed chemical shift and in order.

RESULTS AND DISCUSSION

The syntheses of EMO and EML were performed using the well-precedented formic acid and hydrogen peroxide method. Vigorous stirring with an overhead stirrer was required to keep the layered system well mixed. The reactions were monitored by sampling aliquots of the oil layer and analyzing them by GC-FID. An initial amount of methyl palmitate in the starting material was used as an internal standard. The reaction was >90% complete in 10 h, when the reaction was stopped (Figure 1). In the GC chromatograms of the final data points, a small amount of 9,10-dihydroxy methyl stearate could be detected,

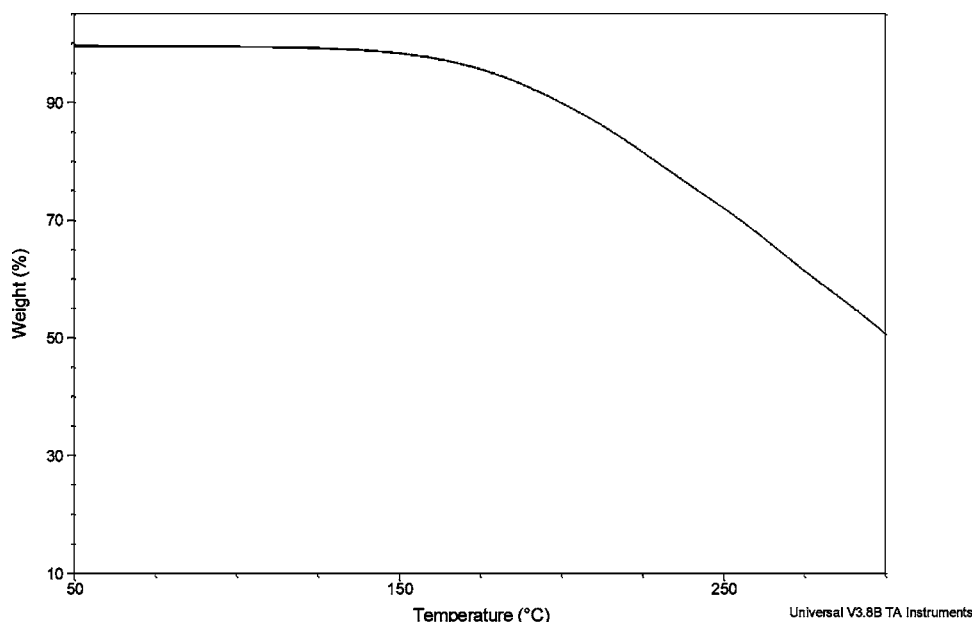


Figure 9. TGA of carbonated 2-ethylhexyl soyate. The sample shows 50% weight loss at 301 °C.

demonstrating the importance in following the reaction directly and stopping it at the appropriate time. A kinetic plot of $\ln([\text{methyl oleate}]_{\text{initial}}/[\text{methyl oleate}])$ versus time gives a pseudo-first-order rate constant of 0.005 min^{-1} , slower than that observed in a kinetic study of a similar reaction (34) that was stirred at 1150 rpm. This indicates that the epoxidation reaction exhibits mass transfer rate limitations under our conditions.

The epoxidation of the linoleic acid also went as expected and was slightly faster in the oleate case, as was observed by Wool et al. (34). At 3 h of reaction time, it is possible to detect the intermediate product with one epoxy group (Figure 2) as well as the final product; however, it was not isolated.

The carbonation reaction (Scheme 1) proceeded as expected. This reaction was considerably faster than the corresponding reaction observed for epoxidized soybean oil. Overnight reactions showed complete reaction by IR, ^1H NMR, and ^{13}C NMR spectroscopic methods. The IR spectra of the products (Figures 3 and 4) were very similar to that of carbonated soybean oil. As the methyl oleate (Figure 3) is changed from the unsaturated ester to the epoxide to the carbonate, corresponding spectral changes can be observed. Bands at ~ 823 and 847 cm^{-1} appear in the epoxide product and then disappear as the material forms the carbonate. More obvious is the appearance of the second carbonyl band (C=O stretch) at $\sim 1790 \text{ cm}^{-1}$. Similar changes in the spectra of the linoleate system (Figure 4) were observable as well as the disappearance of a more noticeable band at 3009 cm^{-1} , corresponding to the higher quantity of unsaturated cis-configured double bonds in the methyl linoleate starting material (35). The ^1H NMR spectra (Figure 5) of the products show reaction progress. Peaks corresponding to the protons on the epoxy carbons of EML can be seen at δ 2.98, 3.12, and 3.08. They disappear upon carbonation and are replaced by new signals at δ 4.49–4.93. A similar occurrence in the ^{13}C NMR spectra shows the change of the epoxy carbons as δ 54–57 being replaced by the cyclic carbonate ring carbons at δ 79–82. The new cyclic carbonyl carbon at δ 154 is also easily observed. The NMR spectra in the oleate system show similar results. Our reaction methodology also works on the commercially available 2-ethylhexyl epoxy soyate (VikoFlex 4050; Arkema), which has $>5.2\%$ oxirane content. This epoxide was carbonated in the same manner as EMO and EML and also gave a characteristic IR spectrum (Figure 6). It is also of note

that we performed the epoxidation and carbonation reactions with the highly expensive $>99\%$ pure methyl oleate as well as the inexpensive technical grade methyl oleate of $\sim 70\%$ purity, with equal effectiveness.

A study of the thermal stability of the carbonates was also warranted, especially for potential application as fuel or lubricant additives. We performed a TGA, under nitrogen, on a sample of each of the carbonates, and a comparative experiment was performed for each epoxide. The TGA (Figures 8, and 9) of the samples shows that CMO and CML show 50% weight loss at 251 and 271 °C, respectively. This is an improvement in high-temperature stability compared to ordinary methyl oleate and methyl linoleate, which show 50% weight loss at 187 and 189 °C under identical conditions. The epoxides show behavior intermediate between the carbonate and the olefinic material. This improved stability may allow the carbonates, and possibly the epoxides, to be used as lubricant additives (36). All of the carbonates are light brown materials and do not show the large increase in viscosity that has been observed in the carbonation of soybean oil.

We have performed the synthesis and characterization of cyclic carbonates from commercially readily available oleochemical products using a simple two-step reaction. Our synthesis uses environmentally friendly supercritical CO_2 as a reactant and avoids the use of phosgene. Continuous flow of this type of reaction has been shown to be feasible (37) and may be necessary for commercialization. The synthesized carbonates show higher temperature stability compared to the corresponding methyl esters or epoxidized methyl esters. They have potential uses as industrial lubricants or fuel additives, and they may prove to be effective starting materials in the development of non-isocyanate polyurethanes, polyesters, or polycarbonate materials, derived from natural sources. Other possibilities include use in the surfactant, personal care, and biomedical industries.

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