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Preparation of Acetonides from Soybean Oil, Methyl Soyate, and Fatty Esters

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Ⓢ *Supporting Information*

ABSTRACT: This paper describes the preparation of a new type of branched vegetable oil and its methyl ester that involves the formation of acetonides. A facile and environmentally friendly synthesis has been found to produce acetonides that entails the use of ferric chloride as a catalyst and is conducted at room temperature. The products have been fully characterized with the help of model compounds, including elemental analysis, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), and gas chromatography−mass spectrometry (GC−MS).

KEYWORDS: Epoxidized soybean oil, acetonide, acetone, branched oleochemical, ferric chloride

■ INTRODUCTION

In addition to being important agricultural and food items, vegetable oils are also renewable raw material for the development of novel substances.[1−4] It is known that the introduction of branches into the alkyl chains is highly desirable, and many approaches have been reported to produce branching.[5−11] Thus, in lubricants the presence of branching can produce improved low-temperature characteristics, higher hydrolytic stability, and lower viscosity index.[3] For methyl soyate, partial freezing in cold climates is considered an obstacle to its continued development and commercialization.[5,7]

In our laboratories, we have been exploring environmentally friendly and energy-conserving reactions involving triglyceride oils.[12−15] It has been reported in the literature that an epoxide and a ketone will react in the presence of an inorganic acid to form a cyclic ketal.[16] Doll and Erhan[17] reported the reaction of epoxidized methyl oleate (EMO) and 2-pentanone using inorganic acids. They found high conversions with phosphoric acid (100% yield) and sulfuric acid (69% yield) but less encouraging results for tosic acid (4% yield) and copper sulfate (0% yield). They carried out this reaction at 50−70 °C. Probably because of the acid present, some byproducts and degradation products were found in gas chromatography (GC) analysis.

Whereas methyl oleate may be interesting, we are more interested in soybean oil and methyl soyate, making branched products out of them and providing full analytical characterization. We are also interested in producing an alternative reaction pathway that is energy-conserving and environmentally friendly. Two things we want to avoid are the use of inorganic acids and high temperature. A different reaction pathway toward cyclic ketal formation, using $FeCl_3$ as the catalyst, was reported by Saha et al.[18] We have used this catalyst and found it to be suitable for the conversion of soybean oil to cyclic ketal at room temperature.

As a result, an energy-conserving but still effective reaction has been observed. Furthermore, $FeCl_3$ can be recycled, thereby minimizing the disposal of potential waste chemicals. An advantage of epoxidized soybean oil (ESBO) is that it is commercially available, with an annual production of about 40 000 tons/year.[19]

For the cyclic ketal reaction, we have chosen acetone as the reactant because of its low cost and general availability. The resulting acetonide can be readily hydrolyzed to give the diol;[20] the diol can be regenerated to acetonide via $FeCl_3$.[21] Thus, the acetonide branching is reversible. Furthermore, acetone is relatively safe and can be removed with less environmental hazard. As far as we know, this is the first report of the synthesis of soybean oil acetonide and methyl soyate acetonide in the literature.

■ MATERIALS AND METHODS

Materials. Methyl oleate (Sigma-Aldrich, St. Louis, MO, Tech 70%; Nucheck Prep, Elysian, MN, >99%), hydrogen peroxide (Sigma-Aldrich, St. Louis, MO, ACS reagent, 30% solution), formic acid (Sigma-Aldrich, 96%, ACS reagent), hexanes (Sigma-Aldrich, St. Louis, MO, >95%, HPLC grade), NaCl (Fisher, Fairlawn, NJ, ACS reagent), $NaHCO_3$ (Fisher, Fairlawn, NJ, ACS reagent), acetone, and ferric chloride were all used as received.

EMO (methyl 9,10-epoxy stearate) and epoxidized methyl linoleate (EMLO) have been prepared in our laboratory as described elsewhere[11,22,23] to make a variety of different oleochemicals. The same epoxidation reaction can be used for soybean oil and methyl soyate. For expediency, we acquired ESBO (4.2 oxirane moieties per triglyceride) and epoxidized methyl soyate (5.6% oxirane content) from Arkema, Philadelphia, PA, and used them as received.
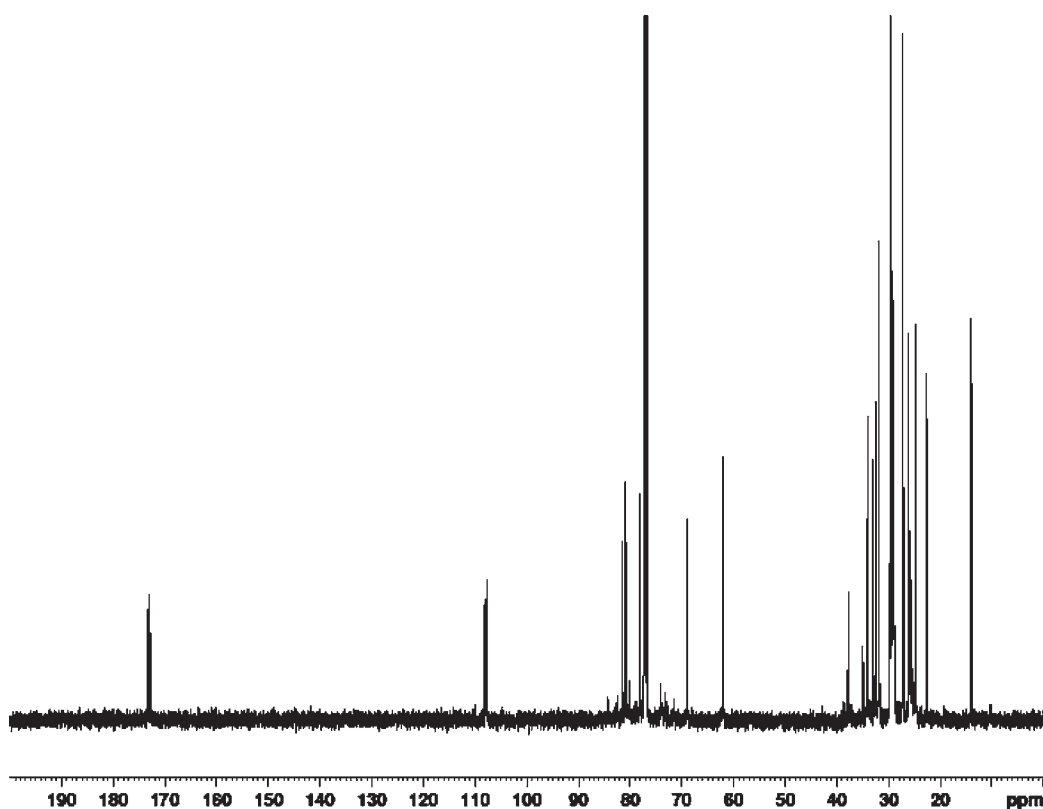
**Figure 1.** ^{13}C NMR spectrum (in $CDCl_3$) of acetonides from ESBO.

Reaction of Epoxy Ring with Acetone. The procedure entailed mixing together epoxidized fatty acid esters/soybean oil with acetone in the presence of ferric chloride for 24 h at room temperature. In the procedure, 3 g of ESBO and 20 mL of acetone were placed in a 50 mL round-bottom flask. Ferric chloride, 10−45 mg, was added to the reaction mixture, which was stirred for 24 h at room temperature. Acetone was evaporated in a rotary evaporator. To the remaining portion, 40 mL of ethyl acetate was added and the mixture was transferred to a 100 mL separatory funnel. Ferric chloride was removed by washing it with ethylenediaminetetraacetic acid (EDTA) solution. An equivalent amount of EDTA was used. Finally, the ethyl acetate layer was washed with water and brine, dried with sodium sulfate, filtered, and filtrate-evaporated to give the acetonide. The yield was 3.52 g, corresponding to 92% of the maximum theoretical yield of acetonide. Similar reactions were performed using EMO, EMLO, and epoxidized methyl soyate to give corresponding acetonides.

Characterization. Nuclear magnetic resonance (NMR) was performed on a Bruker (Boston, MA) Avance 500 NMR spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C. Bruker Icon NMR software was used on a HP ×1100 Pentium 4 workstation. Peaks were referenced to tetramethylsilane (TMS) at 0.00 ppm. Calculation of ^{13}C NMR chemical shifts was performed with ACD/Laboratories 6.00 ACD/CNMR predictor software, running on a Gateway Pentium 4 CPU with a 2.53 GHz processor.

Fourier transform infrared (FTIR) spectra of the starting material and products were recorded on a Thermonicolet (Madison, WI) Nexus 470 FTIR instrument with a Smart ARK accessory containing a diamond crystal. Data were collected and processed on a Dell 2.46 GHz computer, equipped with Windows 2000, Optiplex GX260 Pentium 4, and Omnic 6.2 software.

GC−mass spectrometry (MS) was performed on an Agilent (Santa Clara, CA) 5-7890A gas chromatograph equipped with a 7683B series injector and a 5975C mass detector. The instrument programs and data

Scheme 1. Reaction of EMO with Acetone, with ^{13}C NMR Assignments Shown for the Acetonide Ring Carbons
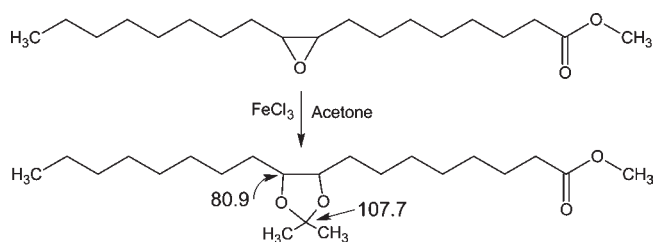
acquisition were handled by a Windows-XP-equipped HP-Compaq DC7700 computer with a 3.39 GHz Pentium D processor using Agilent MSD Enhanced Chemstation, version E01.00.237. The GC column was Supelco SPB-35 (30 m × 320 μm). A helium flow rate of ∼0.3 mL min^{-1},[10] an injection volume of 0.1 μL, and a 50:1 split ratio were used. The temperatures were as follows: inlet, 220 °C; detector, 220 °C; auxiliary transfer line, 250 °C; and mass selective detector (MSD), 150 °C. The initial temperature of 150 °C was held for 2 min and then ramped to 280 °C at 15 °C min^{-1}, where it was held for 20 min. The detector was run in the electron impact (EI) mode and set to scan for m/z ratios from 50 to 500 Da.

Elemental analysis was carried out with a Leco CHN-2000 analyzer. Each sample was run in triplicate, and the average values were taken.

■ RESULTS AND DISCUSSION

The reaction of ESBO with acetone in the presence of ferric chloride readily yielded a reaction product. The product, however, gave a number of different peaks in the ^{13}C NMR spectrum (Figure 1). To elucidate the chemical structure of this product and
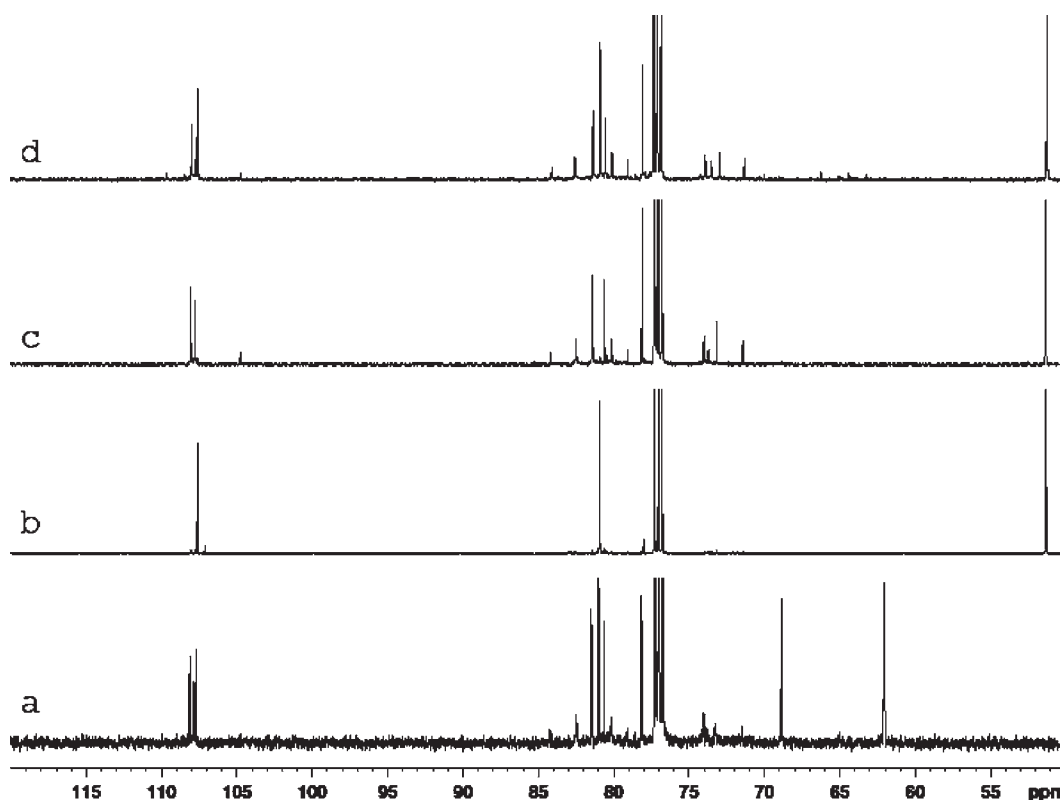
Figure 2. ^{13}C NMR expanded spectra (in CDCl$_3$) of acetonides from (a) ESBO, (b) EMO, (c) EMLO, and (d) epoxidized methyl soyate.

to understand the reaction better, we used model compounds and carried out the reactions on EMO and EMLO.

Methyl Oleate Acetonide. The reaction scheme for methyl oleate acetonide is shown in Scheme 1. The reaction is carried out by mixing the EMO with acetone and ferric chloride. No solvent is added, except for the unreacted acetone. The ferric chloride serves as a Lewis acid catalyst. It is not consumed and can be readily recovered after the reaction and reused.

The reaction appears facile with epoxy methyl oleate. The presence of even 0.58% ferric chloride (by weight relative to methyl oleate) catalyzes the reaction and reacts out 100% epoxide in 24 h at room temperature. Elemental analysis for the methyl oleate acetonide gave 70.79% C, 11.63% H, and 0.20% N. The calculated values are 71.31% C, 11.42% H, and 0% N, in good agreement with expected values.

The ^{13}C NMR spectrum of the reaction product indicates a rather clean reaction. Only the 50−120 ppm region is shown in Figure 2b. The peaks at 107.7 and 80.9 ppm correspond to the quaternary carbon and the two methines on the acetonide, respectively (the peak at 80.7 ppm is actually split into two closely spaced peaks because the two methines on the acetonide are slightly non-equivalent). The methoxy peak for the ester appears at 51.2 ppm. The peaks at ca. 129 ppm (not shown) are the residual double bond from oleate, which is not epoxidized.

The infrared (IR) spectrum of the reaction product is also consistent with the structure. Figure 3a shows the IR spectra of the starting epoxy methyl oleate, and Figure 3b shows the methyl oleate acetonide. In comparison to epoxy methyl oleate, the acetonide has an additional doublet at 1370 cm^{-1} for gem-dimethyl[24] and peaks at 1200, 1100, 1080, and 1060 cm^{-1} for the ketal.[25] The GC−MS analysis shows one main GC peak, with the following significant m/z peaks beyond 150 Da in the mass

spectrum: 356, 263, 279, 213, and 170. Two peaks are diagnostic: 356 for $[M-CH_3]^+$ and 213 for the fragmentation product $[C_8H_{17}-C_5H_8O_2]^+$ (1,2-decanediol acetonide).

Methyl Linoleate Acetonide. This acetonide can be similarly made with EMLO. The reaction scheme is shown in Scheme 2. At 0.77% ferric chloride (by weight relative to methyl linoleate), all of the epoxide has reacted in 24 h at room temperature. Elemental analysis gave 66.46% C, 10.40% H, and 0.06% N. The calculated values were 67.84% C, 10.47% H, and 0% N, in good agreement with expected values.

The ^{13}C NMR spectrum is more complex than that of methyl oleate acetonide (Figure 2c). Two peaks are found at 108.1 and 107.8 ppm, corresponding to racemic (*trans*) and meso (*cis*) isomers, respectively. The epoxide peaks at 53−58 ppm have disappeared, as expected. At the 70−85 ppm region, the four main peaks can be assigned to the meso (*cis*) and racemic (*trans*) isomers of the diacetonide. With the use of ^{13}C chemical-shift rules and in analogy to other polymer structures,[26,27] we can assign 77.2 and 80.6 ppm to the meso (*cis*) isomer and 78.1 and 81.4 ppm to the racemic (*trans*) isomer. The racemic isomer is found to be slightly more preponderant (~56:44 racemic/meso) (the peaks at 81.4 and 77.2 ppm are actually split into closely spaced doublets at the magnetic field strength used because those two methines at the acetonides are slightly non-equivalent). It may be noted that there are also several smaller peaks in this region that are not yet positively identified.

The IR spectrum (Figure 3c) of the reaction product is similar to that of methyl oleate acetonide, thereby confirming the presence of acetonide functionality (viz., peaks at 1370, 1200, 1100, 1080, and 1060 cm^{-1}). The GC−MS analysis shows two main GC peaks (area ratio of ~64:36), with the same mass spectra. By analogy to NMR data, the larger peak is assigned to the racemic isomer and the smaller peak is assigned to the meso
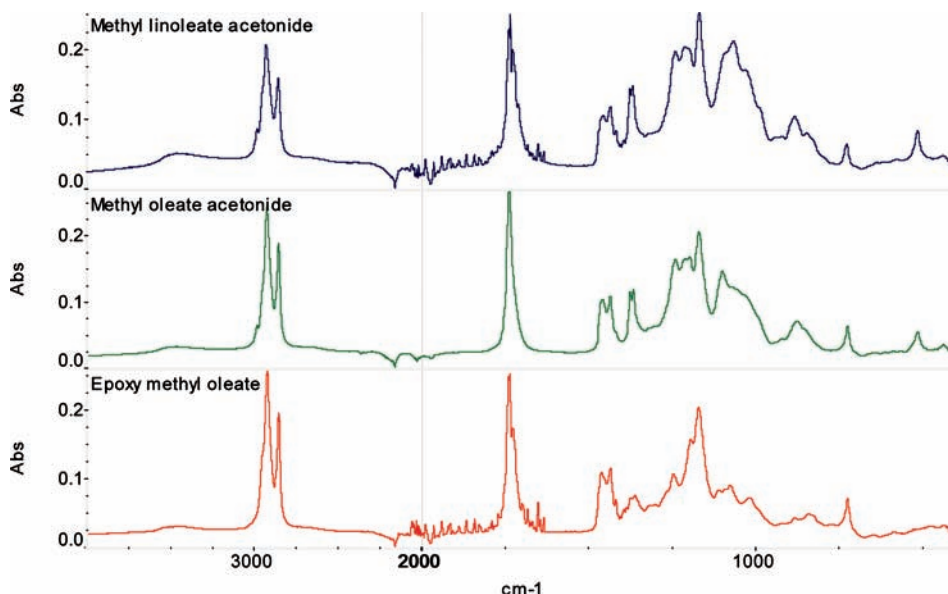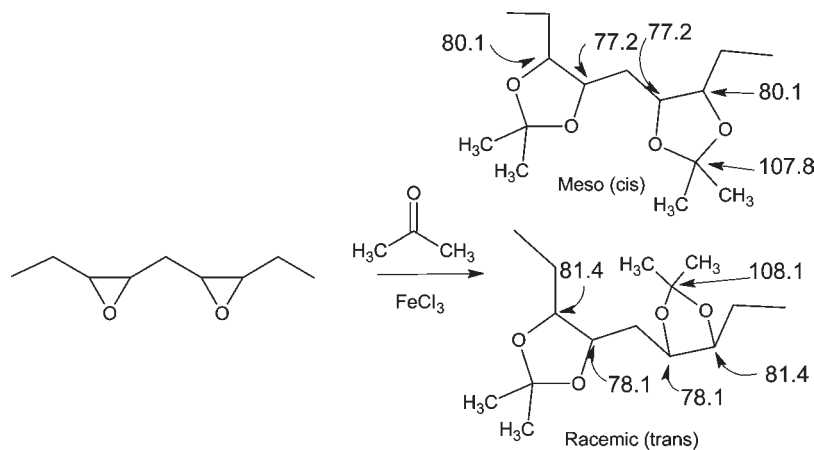
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Figure 3. FTIR spectra of (a) epoxy methyl oleate, (b) methyl oleate acetonide, and (c) methyl linoleate acetonide.

Scheme 2. Reaction of EMLO with Acetone, with ^{13}C NMR Assignments Shown for the Acetonide Ring Carbons

isomer. The following are the significant m/z peaks beyond 150 Da in the mass spectra: 427, 309, 277, 241, 193, and 171. Two peaks are diagnostic: 427 for $[M-CH_3]^+$ and 171 for the fragmentation product $[C_5H_{11}-C_5H_8O_2]^+$ (1,2-heptanediol acetonide).

Soybean Oil Acetonides. We now return to the ^{13}C NMR spectrum of soybean oil acetonides (Figure 2a). A comparison of Figure 2a with the spectra of methyl oleate acetonide and methyl linoleate acetonide (spectra b and c of Figure 2) indicates that the peaks in the soybean oil acetonide spectrum are the composite of the peaks in the spectra of methyl oleate acetonide and methyl linoleate acetonide. Thus, the peak for oleate acetonide is at 81 ppm, and the peaks for linoleate diacetonide are at 77.2 and 80.6 ppm (meso isomer) and 78.1 and 81.4 ppm (racemic isomer). Note that the peaks at 62 and 69 ppm in Figure 2a are due to the glyceride.

For the acetone–ESBO reaction, we have carried out a study with different dosages of ferric chloride (Table 1). The loss of epoxide has been monitored by ^{1}H NMR. From the results

Table 1. Dependence of the ESBO Reaction on the FeCl$_3$ Level, Obtained at Room Temperature for 24 h

weight of ESBO (g)	weight of FeCl$_3$ (mg)	volume of acetone (mL)	FeCl$_3$/ESBO (wt %)	loss of epoxide (%)
3	10	20	0.33	0
3	15	20	0.50	50
3	30	20	1.00	100
3	45	20	1.5	100

shown in Table 1, it is clear that 1.0% ferric chloride is needed to achieve 100% reaction of epoxide in the case of ESBO.

Methyl Soyate Acetonides. We also carried out the same acetonide reaction with epoxidized methyl soyate. The reaction proceeded in a similar fashion. The ^{13}C NMR spectrum of the reaction product (Figure 2d) is almost the same as that of soybean oil acetonide (Figure 2a), except for the absence of the glyceride peaks at 62 and 69 ppm. Thus, the spectrum consists of reaction products of

both oleate acetonide (81 ppm) and linoleate diacetonide (meso at 77.2 and 80.6 ppm and racemic at 78.1 and 81.4 ppm).

From the above results, it appears that the reaction described herein can readily form acetonides out of soybean oil, methyl soyate, methyl linoleate, and methyl oleate. There are many advantages of this reaction. First, the acetonide reaction produces a branched fatty acid moiety, which can provide improved properties for methyl soyate and soybean oil. Second, we use ferric chloride (a Lewis acid), and it is less likely to cause hydrolysis of the ester or glyceride. We also use room temperature for the reaction, resulting in less energy usage. Finally, acetone is cheap and has a good environmental profile.

■ ASSOCIATED CONTENT

⑤ Supporting Information. Gas chromatogram of the reaction product between EMO and acetone (Figure S-1), mass spectrum of reaction product between EMO and acetone (Figure S-2), gas chromatogram of the reaction product between EMLO and acetone (Figure S-3), mass spectrum of reaction product between EMLO and acetone (Figures S-4 and S-5), and ^{13}C NMR spectra (in CDCl$_3$) of 76−83 ppm region of acetonides (Figure S-6). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DISCLOSURE

■ ACKNOWLEDGMENT

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