πSynthesis and Evaluation of a Series of α-Hydroxy Ethers Derived from Isopropyl Oleate

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ABSTRACT: Several fatty derivatives with bulky moieties were prepared by treatment of epoxidized isopropyl oleate with a number of alcohols in the presence of sulfuric acid catalyst to provide a series of α-hydroxy ethers in good yield. The materials were analyzed for cold flow performance through cloud point and pour point determinations. The most promising α-hydroxy ether produced in this study, with respect to both low temperature behavior and economic criteria, was isopropyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate, which has a cloud point of –23°C and pour point of –24°C.

Paper no. J11424 in *JAOCS 83*, 959–963 (November 2006).

KEY WORDS: Biodiesel, cloud point, α-hydroxy ethers, isopropyl esters, pour point.

Biodiesel, defined as the monoalkyl esters of FA derived from vegetable oil or animal fat, is an attractive alternative to conventional diesel fuel (CDF) for combustion in diesel engines. Biodiesel (BD) has a number of fuel properties that are comparable with No. 2 diesel fuel (D2), including viscosity, gross heat of combustion, and cetane number (1–4). Blends of BD with ultra low-sulfur D2 (ULSD2) show improved lubricity characteristics over that of unblended ULSD2 (5) and reduced exhaust emissions, which include particulate matter, hydrocarbons, sulfur dioxide, carbon monoxide, and smoke (1,4,6–11). However, in most cases the use of BD results in an increase in NO_x emissions over that of CDF (7,8,12,13). Furthermore, another challenge facing BD in North America is the issue of relatively poor low-temperature performance, which may limit its use during winter months (14). For example, methyl soyate (MS: BD derived from transesterification of soybean oil) has a cloud point (CP) of approximately –2°C compared with –16°C for D2 (15). Several approaches for improving the low-temperature behavior of BD are under development, such as blending with CDF, transesterification with long- or branched-chain alcohols, crystallization fractionation, treatment with already commercialized cold-flow improver (CFI) additives developed for CDF, and the use of synthetic CFI additives novel to BD fuel (16).

Crystallization of any substance requires the arrangement of molecules in an orderly pattern. Introduction of branching into a linear, long-chain ester generally disrupts intermolecular associations at low temperatures, which may reduce the crystallization onset (T_{CO}) temperature (17). Recent work demonstrated that isopropyl soyate (IPS) has similar emissions behavior to MS, superior low-temperature performance, and slightly increased viscosity (18). Earlier work (19) showed the CP of IPS to be –9°C (vs. about –2°C for MS) and T_{CO} to be more than 11°C lower than for MS (Table 1). With these studies in mind, we set out to produce an isopropyl fatty ester that contains a branching moiety along the alkyl backbone as a potential CFI additive for BD fuel.

Nucleophilic addition to an oxirane moiety to provide a wide range of products is a well-established process and will not be reviewed here; however, the interested reader is directed elsewhere (20). Careful selection of the appropriate reagents will introduce branching into the oxirane system. Such an approach was undertaken in this study (Fig. 1) in which a variety of alcohols in the presence of sulfuric acid catalyst was added to an oxirane moiety to afford a series of α-hydroxy ethers (21,22). The introduction of branching to the fatty epoxide may impart lower CP and PP by affecting macrocrystalline formation at low temperatures. Applied to FA esters, such materials could prove useful as biodegradable CFI additives for BD fuel and potentially as lubricants in diverse applications such as hydraulic fluids, metalworking fluids, crankcase oils, drilling fluids, two-cycle engine oils, wear-resistant fluids, and greases (23).

MATERIALS AND METHODS

Materials. Formic acid (88%) was obtained from Fisher Scientific (Pittsburgh, PA) and used without further purification. All other chemicals and reagents were obtained from Aldrich Chemical (Milwaukee, WI) and used without further purification. Technical-grade oleic acid was found to contain, by GC–MS analysis, ~10% linoleic acid and a trace amount (<1%) of other fatty materials, such as stearic acid.

TABLE 1
Crystallization Onset Temperature (T_{CO}, °C), CP (°C), PP (°C), and Kinematic Viscosity (υ; mm²/s @ 40°C) of Methyl and Isopropyl Esters of Soybean Oil Compared with No. 2 Diesel Fuel[a]

Material	T_{CO}[b]	CP[b]	PP[b]	υ[c]
MS	5.2	–2	–3	4.5926
IPS	–6.0	–9	–12	5.2649
D2	–11.9	–17	–24	2.8911

[a]CP, cloud point; PP, pour point; D2, no. 2 diesel fuel; MS, methyl soyate; IPS, isopropyl soyate.
[b]From Reference 19.
[c]From Reference 18.

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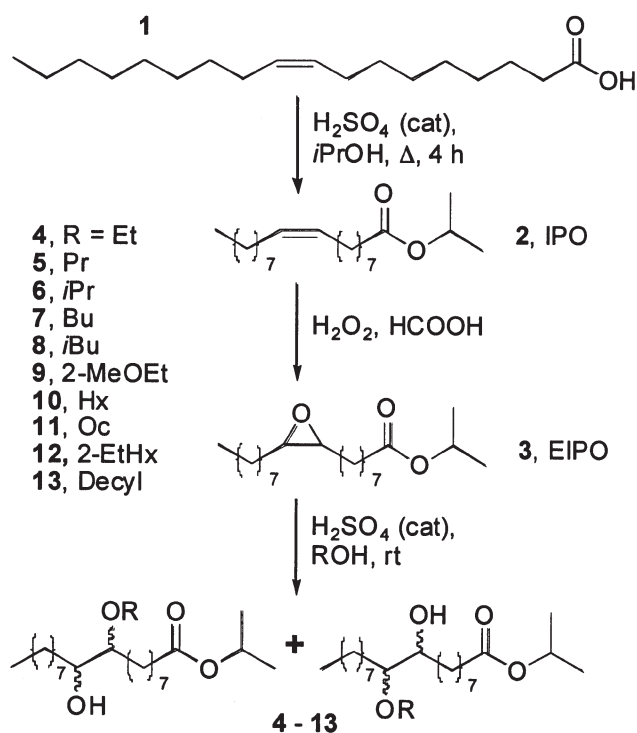
FIG. 1. Synthesis of α-hydroxy ethers from oleic acid.

Esterification of oleic acid. To a solution of oleic acid (**1**, 100.0 g, 319 mmol) in 2-propanol (150.0 mL) in a single-neck round-bottomed flask equipped with a magnetic stir bar was added at room temperature (rt) H_2SO_4 (conc., 0.90 mL, 5.2 mol%), which was heated at reflux with stirring for 4 h. After cooling to rt, the solvent was removed *in vacuo* using a rotary evaporator and the resultant oil dissolved in hexanes (100 mL). After washing with $NaHCO_3$ (sat. aq., 2×10 mL) and brine (2 $\times 10$ mL), the organic phase was dried ($MgSO_4$), filtered, concentrated *in vacuo*, and placed under vacuum for 6 h to afford isopropyl oleate (IPO, **2**) as a clear oil (101.3 g, 98% overall yield). GC–MS analysis indicated the product contained ~5%

isopropyl linoleate. No further purification was performed. ^{1}H NMR: δ 5.36 (2H, vinyl), 5.02 (COOC**H**(CH_3)_2), 2.27 (2H, α to ester), 2.02 (4H, α to vinyl), 1.62 (2H, β to ester), ~1.3 (20H, fatty backbone), 1.25 and 1.23 (6H, methyl protons of head group), 0.89 (3H, protons on terminal carbon); ^{13}C NMR: δ 173.43 (carbonyl C of ester), 129.97 and 129.74 (vinyl), 67.30 (COO**C**H(CH_3)_2), 34.71 (α to carbonyl), 33.86 and 32.26 (α to vinyl group), 14.11 (terminal C). FTIR: 2923 and 2853 cm^{-1} (sharp CH_2 str), 1733 (sharp carbonyl str), 1667 (olefin str), 1466 (CH_2 bend vib), 1374 (CH_3 sym bend vib), 1249, 1179, and 1108 (ester C–O str), 965 (vinyl C–H out-of-plane bend), 723 (CH_2 rocking vib). MS (EI): *m/z* 324 (M$^+$), 281 (M – *i*Pr-H).

Epoxidation of IPO. To a stirred solution of IPO (**2**, 10.0 g, 27.7 mmol) and formic acid (88%, 5.0 mL, 117 mmol) cooled in an ice bath (4°C) was added slowly H_2O_2 (30% in H_2O, 8.0 mL, 78 mmol). The reaction was then allowed to proceed at rt with vigorous stirring (800+ rpm) until GC–MS analysis indicated that **2** had been consumed (14–16 h). After the reaction was transferred to a separatory funnel, the lower aqueous phase was removed, and hexanes (20 mL) was added to the upper oily phase. The organic phase was then washed with $NaHCO_3$ (sat. aq., 2×5 mL) and brine (2×5 mL), dried ($MgSO_4$), filtered, concentrated *in vacuo*, and placed for 6 h under vacuum to provide epoxidized isopropyl oleate (EIPO, **3**) as a clear oil (9.36 g, 99% overall yield). GC–MS analysis indicated the presence of ~5% isopropyl 9,10-dihydroxystearate in the sample as well. No further purification was performed. ^{1}H NMR: δ 4.99 (COOC**H**(CH_3)_2), 2.87 (2H, epoxy), 2.24 (2H, α to ester), 1.60 (2H, β to ester), 1.48 (4H, α to epoxide), ~1.3 (20H, fatty backbone), 1.22 and 1.20 (6H, methyl protons of head group), 0.85 (3H, protons on terminal C); ^{13}C NMR: δ 173.32 (carbonyl C of ester), 67.29 (COO**C**H(CH_3)_2), 57.21 and 57.17 (epoxide), 34.64 (α to ester head group), 31.83 and 31.04 (α to epoxide), 14.07 (terminal C). FTIR: 2923 and 2853 cm^{-1} (sharp CH_2 str), 1733 (sharp carbonyl str), 1466 (CH_2 bend vib), 1374 (CH_3 sym bend vib), 1249, 1179, and 1108 (ester C–O str), 723 (CH_2 rocking vib), 1145 (ether C–O–C sym str), 896 (C–C asym ring str), 824 ("12 micron band;" Ref. 24) and a small peak at 3500

TABLE 2
Reaction Time (h), Yield (%), CP (°C), and PP (°C) of α-Hydroxy Ethers Derived from Epoxidized Isopropyl Oleate

R Ether	Reaction time[a]	% Yield	CP[b]	PP[b]
Ethyl, **4**	24	84	−2	−8
Propyl, **5**	72	81	−5	−11
Isopropyl, **6**	3, Δ	82	−5	−12
Butyl, **7**	72	84	−21	−22
Isobutyl, **8**	144	84	−21	−23
2-Methoxyethyl, **9**	96	85	−11	−14
Hexyl, **10**	168	82	−23	−23
Octyl, **11**	216	84	−23	−23
2-Ethylhexyl, **12**	240	85	−23	−24
Decyl, **13**	240	84	−23	−24

[a]Reactions are performed at room temperature unless otherwise noted; Δ denotes reflux.
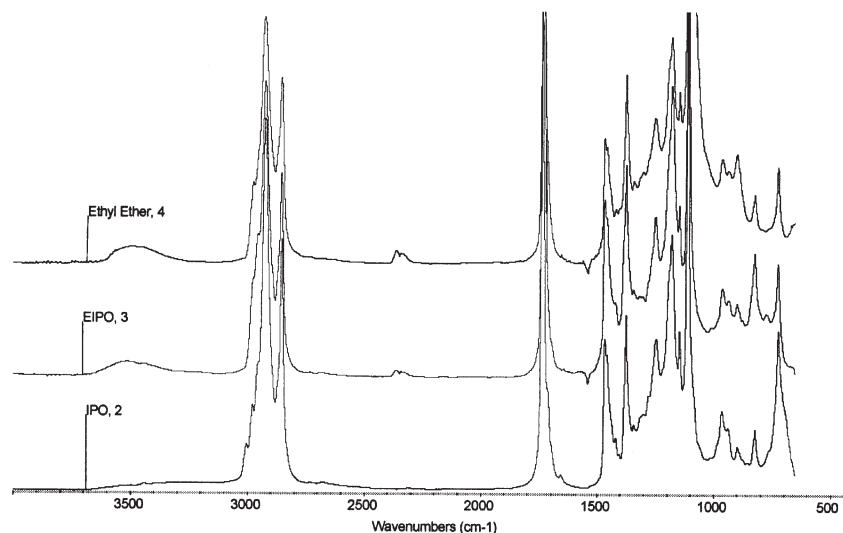[b]Means ($n = 3$), SD ±2°C.

FIG. 2. FT-IR spectra of isopropyl oleate (IPO) (**2**), epoxidized IPO (EIPO) (**3**), and isopropyl 9(10)-ethoxy-10(9)-hydroxystearate (**4**). Note: absorbance at about 2400 cm^{-1} on **3** and **4** is due to CO_2.

(OH stretch) indicative 9,10-dihydroxy by-product in small (~5%) quantity. MS (EI): m/z 340 (M$^+$), 323 (M – 16 – H), 264 (M – iPr – 16 – H).

Ring-opening of epoxide. To a stirred solution of 1.0 M EIPO (**3**, 1.0 g, 2.79 mmol) in an alcohol (2.8 mL) was added H_2SO_4 (conc., 10.0 mol%) and stirring continued at rt until GC–MS analysis indicated that **3** was consumed (24 to 240 h). Hexanes (5 mL) was then added, and the solution was washed with NaHCO$_3$ (sat. aq., 1 × 0.5 mL) and brine (2 × 1 mL), dried (MgSO$_4$), filtered, concentrated *in vacuo*, and placed for 6 h under vacuum to yield α-hydroxy ethers **4–13**. See Table 2 for reaction time and percent yield information for **4–13**. See Figures 2 and 3 for FTIR and ^{1}H NMR data of ethyl ether **4**. All other ethers (**5–13**) are similar to **4**.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV-500 spectrometer (Rheinstetten, Germany) 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) as solvent. FTIR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) with a Smart ARK accessory containing a 45 ZeSe trough in a scanning range of
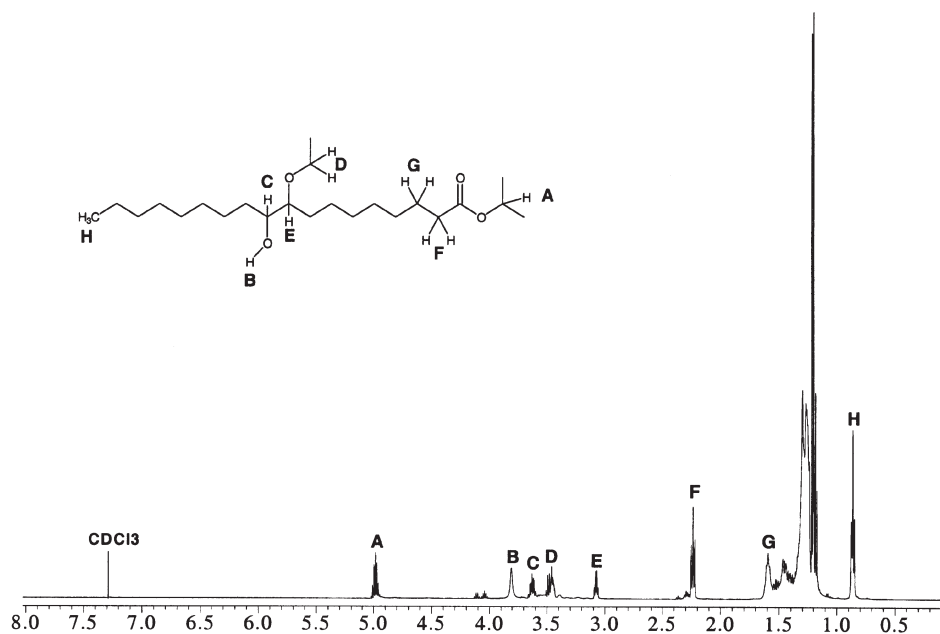

FIG. 3. ^{1}H NMR Spectrum of isopropyl 9-ethoxy-10-hydroxystearate in CDCl$_3$.

650–4000 cm^{-1} for 32 scans at a spectral resolution of 4 cm^{-1}.

Reactions were monitored by GC–MS every 8 or 24 h using a Hewlett-Packard (Loveland, CO) 5870 series II GC system equipped with a 6890 series injector and a 5970 Series MSD in EI mode. A Supelco SPB-35 (30 m × 320 mm) column was used with a helium flow rate of 0.9 mL/min. The temperature program started at 150°C and increased to 290°C at 10°C/min, which was followed by a hold time of 10 min. The inlet and detector temperatures were set to 250 and 280°C, respectively. The injection volume was 1 mL with a split ratio of 70:1.

Low-temperature performance. CP and PP determinations were made in agreement with ASTM D 5773 (25) and ASTM D 5949 (26) using a Phase Technology Analyzer Model PSA-70S (Phase Technology, Richmond, British Columbia, Canada). Each sample was run in triplicate, and an average value is reported. CP and PP data are rounded to the nearest whole degree.

RESULTS AND DISCUSSION

Synthesis. An earlier synthesis of α-hydroxy ethers (22) describes treatment of epoxidized oleic acid with an alcohol and acid catalyst to yield products analogous to **4**–**13**. However, in the earlier study the ether moiety (R′, see Fig. 1) and the ester head group (R) are identical (R = R′ = Me, Et, Pr), which is unavoidable with the synthetic scheme employed by Gast and colleagues (22). The current work describes the synthesis of a series of novel α-hydroxy ethers where R R′, thereby imparting much greater synthetic flexibility for the production of a large number of ether derivatives with the same head group. Unfortunately, no mention of the low-temperature performance (CP or PP) of the α-hydroxy ethers produced in the earlier study is made. Such an analysis would have made for an interesting comparison with the compounds produced in this study.

After the straightforward Fischer esterification (27) of oleic acid (**1**) to IPO (**2**), a modified epoxidation protocol (28) originally developed by Swern (29) was used to provide EIPO (**3**). The reaction was monitored by GC–MS analysis and terminated when >95% of **2** was consumed (14–15 h). Further analysis by GC–MS of the final product indicated the presence of a small amount (~5%) of isopropyl 9,10-dihydroxystearate, demonstrating the importance of monitoring the reaction closely to avoid unwanted over-reaction.

Following a protocol set forth by Aggarwal *et al.* (21) and Gast *et al.* (22), ring opening of the oxirane moiety to afford a series of α-hydroxy ethers (Fig. 1) was accomplished by treatment of a 1.0 M solution of **3** with a number of alcohols in the presence of acid catalyst (H$_2$SO$_4$). The series of reactions was monitored by GC–MS until **3** was consumed to afford α-hydroxy ethers **4**–**13** (Table 2) in moderate yield (81–85%).

A number of observations were made regarding the reactivity of alcohols with **3**. For instance, the use of methanol as reagent resulted in transesterification to provide methyl 9(10)-methoxy-10(9)-hydroxystearate at rt (already reported in Ref. 22) and none of the desired isopropyl ester. Conversely, secondary alcohols (2-propanol and 2-butanol) were unreactive at

rt. At elevated temperatures (40°C to reflux temperature of alcohol), ring opening with secondary alcohols would proceed quickly (3–4 h), but unwanted transesterification would again occur. Of course, in the case of 2-propanol, transesterification is irrelevant because **3** is already an isopropyl ester. Furthermore, branched primary alcohols (such as isobutanol and 2-ethylhexanol) react more slowly than their linear counterparts (1-butanol and 1-octanol, respectively). For instance, reaction of 1-butanol with **3** to provide **7** (Table 2) was complete in 72 h; however, isobutanol afforded **8** in a comparatively sluggish 144 h. Additionally, as the chain length of the alcohol reagent was increased, a corresponding decrease in reactivity (increase in reaction time) was observed. For example, **10** was formed from 1-hexanol in 168 h, which is of course significantly slower than the aforementioned butyl ether (**7**) produced from 1-butanol (72 h). Lastly, no effort was made to distinguish the regiochemistry (9-alkoxy-10-hydroxystearate vs. the equally likely 10-alkoxy-9-hydroxystearate regioisomer) of the α-hydroxy ethers formed (**4**–**13**), nor their stereochemistry (*R* or *S* at carbons 9 and 10), which is chiefly due to both the chromatographic means required for such an analysis and more importantly, the economics involved at potentially larger scales. If such adducts are to be eventually used as commercial CFI additives for BD fuel, then production costs relating to synthetic complexity and purification requirements are of paramount importance. Therefore, the α-hydroxy ethers prepared in this study (**4**–**13**) were tested without further purification.

Low-temperature behavior. The α-hydroxy ethers (**4**–**13**) described above were screened for low-temperature behavior through determination of both CP and PP. EIPO (**3**), the precursor for the synthesis of **4**–**13**, was found to have a CP of –6°C and PP of –7°C, which is an improvement over MS but not as good as IPS (Table 1). Among the ethers, ethyl ether **4** was the only derivative discovered to be less resistant to low temperatures than **3** (Table 2). The three-carbon ethers, propyl (**5**) and isopropyl (**6**), were comparable to **3** whereas the remaining ethers of longer chain length (**7**–**13**) were found to be far superior to **3**. For instance, decyl ether **13** has a CP of –23°C and a PP of –24°C. Not surprisingly, as the chain length of the alcohol increases, a corresponding improvement in low-temperature behavior is observed. This is due to the greater ability of the longer-chain ethers to disrupt macrocrystalline formation more effectively at reduced temperatures. Another observation of note is the positive effect of branching within the alcohol reagent on the low-temperature performance of the resultant α-hydroxy ether. For instance, butyl ether **7** has CP and PP values of –21 and –22°C, respectively, whereas isobutyl ether **8** has slightly improved values of –21 and —23°C, respectively. A similar trend was also observed for both the C$_3$ (**5** and **6**) and C$_8$ ethers [octyl (**11**) and 2-ethylhexyl (**12**)]. Furthermore, a dramatic improvement in the cold flow properties of α-hydroxy ethers is observed when the ether group contains 4 or more carbons (**7,8,10–13**) vs. ethers with 3 or fewer carbons (**4–6,9**). In conclusion, from both a cold flow performance and economic standpoint, 2-ethylhexyl ether **12** is the most desirable derivative because 2-ethylhexanol is the cheapest of the

C_4 and above alcohols used in this study. Thus, future work will entail evaluating **12** and other promising α-hydroxy ethers at additive levels in MS. Lastly, additional physical property examination (such as thermal and oxidative stability, viscosity, lubricity, surfactant behavior, etc.) may provide interesting insight into the utility of these derivatives.

ACKNOWLEDGMENTS

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