Synthesis of Estolide Esters from *cis*-9-Octadecenoic Acid Estolides

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ABSTRACT: Oleic acid (*cis*-9-octadecenoic acid) was converted in excellent yield to the estolide, which was then esterified with 2,2-dimethypropan-1-ol (neopentyl alcohol), *cis*-9-octadecen-1-ol (oleyl alcohol), and 2-propanol to generate the corresponding estolide esters. Higher-formula mass estolide esters were synthesized by reaction of the parent estolide with 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, and 1,5-pentanediol to give the corresponding diesters of oleic estolide, thus doubling the molecular size of the parent estolide. Pour points and viscosities were determined in order to evaluate these products for possible industrial application.

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KEY WORDS: 2,2-Dimethyl-1,3-propanediol, 2,2-dimethylpropan-1-ol, 2,2-dimethyl-1,3-propyl diester, esterification, neopentyl ester, *cis*-9-octadecenioc acid (oleic acid), *cis*-9-octadecen-1-ol, oleic estolide, oleyl ester, 1,5-pentanediol, 1,5-pentyl diester, perchloric acid, phosphoric acid, 1,3-propanediol, 2-propanol, 1,3-propyl diester, 2-propyl ester, sulfuric acid.

The nonfood industrial uses of vegetable oils have been restricted in many cases as a result of the limited functionality of the structure of the most common triglycerides beyond the olefinic and ester moieties. To broaden the industrial application of these seed oils the introduction of heteroatoms, branching, or saturation of double bonds is required. Saturation is essential to improve the oxidative stability of the oil, in addition to adding new functional characteristics. Functionalization of vegetable oils that leads to a robust demand is particularly important for new crops, as reasonable economic incentives are required for farmers to invest in an alternative crop. One approach to realizing the above goal for seed oils is *via* development of estolides. An estolide is the oxidative product of an acid-catalyzed intermolecular reaction between an olefinic double bond of an unsaturated fatty acid as acceptor and the oxygen of the hydroxyl moiety of a free carboxylic acid function as donor (1).

Estolides have been successfully produced from vegetable seed oils using a variety of catalysts. Use of industrial clays as catalysts resulted in low and impractical yields of estolides (2–4). Mineral acid catalysis, on the other hand, gave good to excellent estolide yields (1,5–6) and formed the basis of this process. Development of the process using oleic acid is of interest because this acid is a major component of many seed oils, including the new crops and high-oleic soybean. For new crop oils the estolides and their derivatives provide new and unique value-added components that increase the profitability of many new crops. For example, the fatty acids derived from the oil of meadowfoam (*Limnanthes alba*), a new crop, have given rise to a variety of new potential industrial products, which include environmentally benign lubricants (7). In this paper we report the synthesis of oleic estolides from oleic acid and modification of the estolide to the estolide esters using mono- and dihydroxyl alcohols with the objective of evaluating the physical properties of the new products in order to identify potential industrial applications.

EXPERIMENTAL PROCEDURES

Materials. Orthophosphoric acid, anhydrous sodium sulfate, toluene, sodium chloride, hexanes [high-performance liquid chromatography (HPLC) grade], ethyl acetate, acetone, and disodium hydrogen phosphate were obtained from Fisher Scientific (Chicago, IL), whereas oleic acid (90%), perchloric acid (70%), isopropyl alcohol (reagent grade), 1,3-propanediol (98%), oleyl alcohol (85%), neopentyl glycol (99%), 1,5-pentanediol (96%), and anhydrous zinc chloride were obtained from Aldrich Chemical Company (Milwaukee, WI).

Instrumentation. HPLC analysis on the reaction mixtures was carried out on a Thermo Separations (Fremont, CA) Spectra system SP8780XR autosampler/injector with an SP8800 ternary gradient pump coupled to a Varex ELSD II evaporative light-scattering detector operated at 46.5°C (Alltech Associates, Deerfield, IL). A Dynamax silica (25 cm × 4.6 mm, 60Å, 8 µm) column from Rainin Instruments Co. (Woburn, MA) was used, employing hexanes/acetone (80:20) as the eluting solvent in the isocratic mode. Final products were distilled from a UIC Inc. (Joliet, IL), high vacuum (2–4 × 10^{-3} Torr), short path, wipe-film KDL-1 laboratory unit. Pour points were determined in a pour point instrument built in-house, while viscosities were measured using a Temp-Trol Viscosity Bath (Precision Scientific, Chicago, IL). Fourier transform infrared (FTIR) spectra of products were run as smears on KBr discs using a Bomem MB-Series (Bomem Inc., Québec, Canada) spectrometer and using Grams 32 software (Galactic Industries Inc., Salem, NH). ^{1}H (400 MHz) and ^{13}C (100.62 MHz) nuclear magnetic resonance (NMR)

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spectra of products were obtained on a Bruker ARX-400 (Bruker Spectrospin, Billerica, MA) with a 5-mm dual proton/carbon probe.

Methods. (i) Oleic estolide. A 90%, *cis*-9-octadecenoic acid (3,550.0 g, 12.57 mol) was placed in a three-necked, 12-L jacketed reaction kettle equipped with a mechanical stirrer. The system was maintained at 45°C and purged with N_2. To the vigorously stirred oleic acid was added 70% perchloric acid (274 mL, 3.14 mol, 0.25 mol equivalent). Stirring continued for 24 h while reaction progress was monitored by HPLC until 83% conversion to the estolide was indicated; the reaction was then quenched with saturated Na_2HPO_4 to pH 5.5. The aqueous layer was removed, and the light yellow organic phase was washed with saturated NaCl followed by deionized water. The estolide was separated from the lactone by-product by a short path, wipe-film, high vacuum distillation at 160°C, 2×10^{-3} Torr to yield 2,718 g (85.1%). Infrared (IR) (smear on KBr disc) cm^{-1}: 3540–2500 w, 2925 vs, 2855 s, 1733 s, 1711 sh, 1462, 1377, 1246, 1176, 1112, 967, 721, and 663. ^{1}H NMR ($CDCl_3$) ppm: 5.4 (*m*, 1H), 4.8 (*m*, 1H), 2.3 (*t, J* = 7.5 Hz, 2H), 2.2 (*t, J* = 7.5 Hz, 2H), 1.9 (*m*, 2H), 1.6 (*bs*, 4H), 1.5 (*d, J* = 5.2 Hz, 5H), 1.2 (*m*, 45H), and 0.85 (*t, J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$) ppm: 180.0, 173.6, 130.30, 130.17, 73.93, 34.57, 34.01, 32.48, 31.79, 29.52, 29.49, 29.32, 29.27, 29.23, 29.19, 29.12, 29.06, 29.01, 25.18, 25.04, 22.56, and 13.98.

(ii) 2,2-Dimethyl-1-propyl ester. Neopentyl alcohol (99%, 10.8 g, 122 mmol) was placed in oleic estolide (60.8 g, 107.62 mmol) in a dry 500-mL round-bottomed flask. Toluene (100 mL) and orthophosphoric acid (1.0 mL, 14.7 mmol) were added, and the reaction mixture was refluxed to remove water with a Dean Stark setup. The reaction progress was monitored by HPLC until 90.7% conversion was attained; then the product mixture was cooled, diluted with hexanes, washed, dried (Na_2SO_4), and concentrated under reduced pressure to give 67.2 g of crude product. The latter was redistilled at 160°C to give 64.5 g (94%) of the neopentyl ester. IR cm^{-1}: 2954, 2927, 2855, 1738, 1465, 1377 d, 1246, 1173, 1008, 967, and 722. ^{1}H NMR ($CDCl_3$) ppm: 5.33 (*m*, 1H), 4.82 (*m*, 1H), 3.72 (*s*, 2H), 2.25 (*m*, 4H), 1.92 (*m*, 2H), 1.58 (*m*, 4H), 1.46 (*m*, 5H), 1.21 (*bs*, 38H), 0.89 (*s*, 6H), and 0.83 (*t, J* = 7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$) ppm: 173.43, 132.0, 130.17, 73.8, 73.37, 34.53, 34.02, 32.47, 31.77, 29.56, 29.51, 29.47, 29.39, 29.31, 29.21, 29.18, 29.10, 29.04, 26.29, 25.18, 25.02, 22.54, and 13.97.

Oleyl ester. Oleic estolide (94.5 g, 167.27 mmol) and toluene (120 mL) were placed in a 500-mL, three-necked, round-bottomed flask equipped with a Dean Stark apparatus. To this mixture technical grade (85%) oleyl alcohol (46.39 g, 172.8 mmol) and orthophosphoric acid (2.5 mL, 3.0%) were added, and the reaction mixture was refluxed for 165 min until HPLC indicated 92.9% conversion. The product mixture was cooled, diluted with hexanes, and washed with deionized water to pH 6. The organic phase was dried (Na_2SO_4), concentrated under reduced pressure, and distilled at 160°C (4×10^{-3} Torr) to give 116.9 g (97.7%) yield of oleyl ester. IR cm^{-1}: 3004, 2925, 2854, 1735, 1464, 1378, 1247, 1175, 967, 722, and 665. ^{1}H NMR ($CDCl_3$) ppm: 5.34 (*m*, 3H), 4.83 (*m*,1H), 4.02 (*t, J* = 6.7 Hz, 1H), 3.6 (*t, J* = 6.7 Hz, 1H), 2.23 (*m*, 4H), 1.95 (*m*, 5H), 1.56 (*m*, 8H), 1.47 (*bd, J* = 5.2 Hz, 4H), 1.24 (*m*, 63H), and 0.85 (*t, J* = 6.8 Hz, 9H). ^{13}C NMR ($CDCl_3$) ppm: 173.51, 130.2, 129.80, 129.64, 129.61, 73.87, 64.23, 62.81, 34.02, 31.78, 29.64, 29.59, 29.53, 29.49, 29.41, 29.29, 29.20, 29.11, 29.07, 28.51, 27.07, 27.04, 25.79, 25.19, 22.56, and 13.98.

2-Propyl ester. Oleic estolide (109.6 g, 0.194 mol) was added to dry 2-propanol (12.62 g, 18 mL, 0.21 mol) in a dry 500-mL three-necked, round-bottomed flask. The mixture was stirred with a magnetic stirrer, and orthophosphoric acid, 4.0 mL (6.2% by wt), and toluene (200 mL) were added. The stirred reaction flask was fitted with a Dean Stark arrangement for reflux, and the top of the condenser was protected from water vapor with a $CaCl_2$ tube. The reaction was then heated to *ca*. 85°C for 3 h until HPLC showed 94% conversion to the desired ester. The reaction mixture was cooled, diluted with hexanes, washed sequentially with saturated NaCl (2 × 100 mL) and water (3 × 150 mL) to pH 6. The organic layer was dried over Na_2SO_4, concentrated at 45°C under reduced pressure, and distilled at 160°C, 2×10^{-3} Torr to give 116.0 g (98.5%) of the 2-propyl ester of oleic estolide. IR cm^{-1}: 2927, 2854, 1734, 1467, 1375, 1248, 1178, 1111, 966.0, and 723.0. ^{1}H NMR ($CDCl_3$) ppm: 5.32 (*m*, 1H), 4.95 (*m*, 1H), 4.82 (*m*, 1H), 2.2 (*m*, 4H), 1.91 (*m*, 2H), 1.56 (*bs*, 4H), 1.45 (*d, J* = 5.1 Hz, 5H), 1.25 (*bs*, 32H), 1.18 (*dd, J* = 3.4, 3.4, 5.4 Hz, 6H), and 0.83 (*t, J* = 7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$) ppm: 173.45, 130.30, 130.10, 73.81, 73.74, 67.10, 34.52, 34.01, 32.46, 31.77, 29.55, 29.50, 29.47, 29.38, 29.30, 29.21, 29.17, 29.09, 29.03, 25.17, 25.01, 22.54, 21.67, and 13.95.

1,3-Propyl diester. Oleic estolide (500 g, 0.885 mol) was added to toluene (300 mL) in a dry flask equipped for reflux with a Dean Stark apparatus. Anhydrous $ZnSO_4$ (18.0 g), 1,3-propanediol (98%, 98.0 g, 1.28 mol), and orthophosphoric acid (4.0 mL) were added and the reaction was heated to gentle reflux to azeotrope off the condensation by-product, water. The reaction progress was followed by HPLC until 98% conversion was attained (27 h); then the reaction was cooled and diluted with hexanes, washed with saturated NaCl solution and water, and dried over Na_2SO_4. It was concentrated to 564.0 g of a viscous crude product that was then distilled at 160°C at 2×10^{-3} Torr to yield 468.9 g (90.5%) of 1,3-propyl diester of oleic estolide. IR cm^{-1}: 2925, 2857, 1735, 1464, 1377, 1174, 967, and 722. ^{1}H NMR ($CDCl_3$) ppm: 5.3 (*m*, 2H), 4.8 (*m*, 1H), 4.1 (*m*, 2H), 3.44 (*m*, 3H), 2.25 (4H), 1.9 (*m*, 6H), 1.57 (*bs*, 4H), 1.46 (*bd, J* = 5.0 Hz, 4H), 1.23 (*bs*, 43H), and 0.84 (*t, J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) ppm: 173.42, 130.22, 130.09, 128.84, 128.04, 73.80, 73.84, 67.29, 60.72, 34.53, 34.03, 32.47, 31.78, 31.74, 29.57, 29.52, 29.48, 29.40, 29.22, 29.19, 29.11, 29.05, 28.93, 25.19, 25.02, 22.55, and 13.97.

2,2-Dimethyl-1,3-propyl diester. Oleic estolide (200.0 g, 354 mmol) and 2,2-dimethyl- 1,3-propanediol (18.62 g, 178.8 mmol) were placed in a 1-L, three-necked flask equipped with a magnetic stirrer and a Dean Stark arrangement for reflux. Toluene (150 mL) and H_2SO_4 (2.0 mL, 1.68% of substrates) were then introduced into the mixture. Stirring started and the reaction mixture was heated to gentle reflux. Progress of the esterification was followed by HPLC. After 2.5 h, 95% conversion was obtained, the reaction vessel was cooled, and the mixture was diluted with hexanes and neutralized with Na_2HPO_4. The neutralized reaction mixture was then washed with brine and water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give 207 g of crude product. The crude product was distilled at 160°C (4×10^{-3} Torr) to yield 185.0 g (87%) of the desired product. IR (smear on KBr disc) cm^{-1}: 2928, 2854, 1735, 1465, 1378, 1248, 1173, 967, and 723. ^{1}H NMR ($CDCl_3$) ppm: 5.35 (*m*, 1H), 4.82 (*m*, 1H), 3.85 (*s*, 2H), 2.26 (*m*, 4H), 1.94 (*m*, 3H), 1.58 (*bs*, 4H), 1.47 (*m*, 4H), 1.25 (*bs*, 38H), 0.93 (*s*, 3H), and 0.85 (*t*, 14 Hz, 6H). ^{13}C NMR ($CDCl_3$) ppm: 173.5, 130.37, 130.33, 130.20, 130.14, 73.87, 68.87, 68.85, 34.57, 34.02, 32.48, 31.78, 29.57, 29.52, 29.48, 29.41, 29.27, 29.23, 29.19, 29.11, 29.05, 29.01, 25.19, 22.55, 21.62, and 13.99.

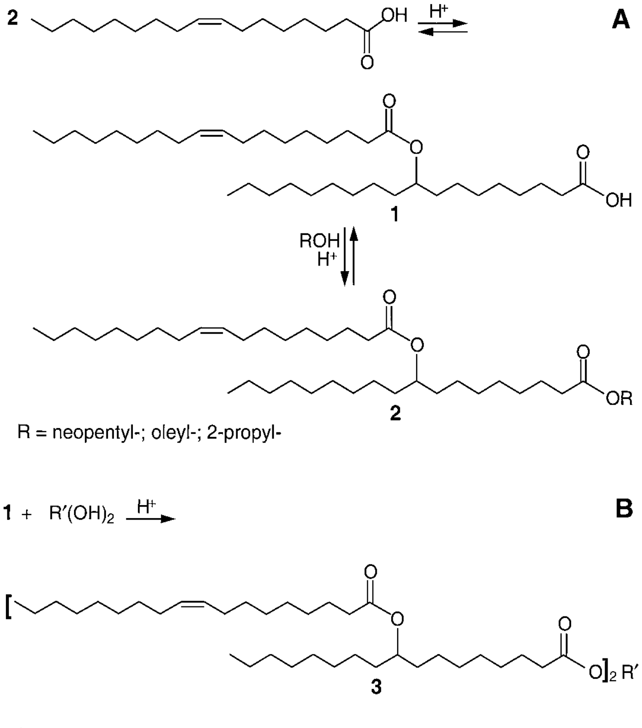
1,5-Pentyl diester. Oleic estolide (500.0 g, 885.1 mmol) was placed in a dry 2-L three-necked flask equipped for reflux and water removal. Pentanediol (96%, 47 g, 0.5 mol equivalent), orthophosphoric acid (3.0 mL, 44 mmol), and toluene (200 mL) were added. The reaction was heated to gentle reflux until quantitative conversion to the diester was achieved (30 h). The crude product was extracted and distilled at 160°C, 2×10^{-3} Torr to yield 509 g (96.0%) of 1,5-pentyl diester of oleic estolide. IR (smear on KBr disc) cm^{-1}: 2929, 2860, 1735, 1461, 1377, 1248, 1174, 1111, 966, and 724. ^{1}H NMR ($CDCl_3$) ppm: 5.33 (*m*, 1H), 4.8 (*m*, 1H), 4.0 (*m*, 2H), 3.6 (*t*, J = 6.5 Hz, 1H), 2.23 (*m*, 4H), 1.92 (*m*, 3H), 1.55 (*m*, 7H), 1.44 (*m*, 7H), 1.22 (*bs*, 42H), and 0.83 (*t*, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$) ppm: 173.53 (*d*), 130.27, 130.04, 73.87, 63.84, 62.37, 37.36, 34.55, 34.00, 32.46, 32.12, 31.77, 29.55, 29.50, 29.46, 29.39, 29.20, 29.17, 29.09, 29.03, 28.98, 28.32, 25.17, 22.54, and 13.97.

RESULTS AND DISCUSSION

Oleic estolide was synthesized in excellent yield, 85%, from 4 L of 90% neat oleic acid using 0.25 mole equivalent of 70% perchloric acid relative to starting carboxylic acid. The product obtained was a light, golden yellow oil. Its IR spectrum showed a weak broad characteristic band for carboxylic acids (3500–2500 cm^{-1}), very strong (2927–2850 cm^{-1}) alkyl absorptions, and a strong (1735 cm^{-1}) band of the secondary ester with a 1711 cm^{-1} shoulder for the C=O of the free carboxyl group. The ^{13}C NMR of this compound showed a 73.93 ppm resonance for the only tertiary carbon present. This compound was in marked contrast to the dark brown or black material obtained from sulfuric acid catalysis of the same reaction under analogous conditions. An additional advantage of perchloric acid catalysis in this reaction is that the perchlorate conjugate base does not readily form complexes (8). The impact of this behavior is the isolation of clean, pH stable (*ca.* 5), uncomplexed, mainly monomeric estolides at 45°C and 24 h reaction time. The level of oligomerization can, however, be raised by increasing the reaction temperature at the same perchloric acid loading. In contrast, sulfuric acid catalysis tends to result in higher oligomers at 55°C and 24 h (4), but the product seems to be complexed to the hydrogen sulfate ion, which causes a lowering of the pH of the estolide over time (Isbell, T.A., unpublished data).

Estolide esters. Esters of estolides in large batch preparations can be prepared in a one-pot reaction setup by graduating the order of the addition of reagents. For example, the appropriate alcohol can be added to the estolide reaction mixture at the point after maximal conversion of the enoic acid to the estolide has been reached, thus extending utilization of the catalyst and simplifying the workup of the reaction (Isbell, T.A., unpublished data). For smaller quantity requirements, however, the esters were made from two reactions. First, the estolide was made and isolated, followed by a subsequent esterification with the desired alcohol. In this manner, the following estolide esters were synthesized as shown in Schemes 1A and 1B.

Reaction of the monohydroxyl alcohols (neopentyl, oleyl, and 2-propyl) to the corresponding esters (Scheme 1A) was catalyzed by orthophosphoric acid in a system arranged for azeotropic removal of water from the reaction mixture while progress of the final ester formation was monitored by HPLC in hexanes/acetone (80:20) as solvent. Figures 1A and 1B show the conversion rates for neopentyl and oleyl ester formation, respectively. The reaction rates were observed to decrease in the following order: oleyl > neopentyl ≫ 2-propyl



SCHEME 1

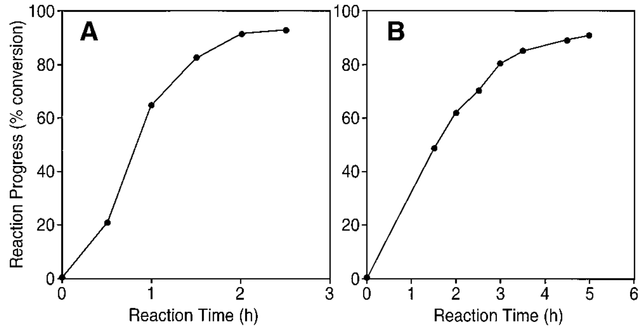


FIG. 1. (A) Esterification of oleic estolide with oleyl alcohol and (B) formation of neopentyl monoester of oleic estolide.

TABLE 1
Physical Properties of Esters of Oleic Estolide

Compound	HPLC[a] retention time (min)	Viscosity (cp) 40°C	Pour point (°C)
Oleic estolide	3.47	381.0	−21.0
Neopentyl ester	2.98	119.2	−32.8
Oleyl ester	2.74	104.8	−12.8
2-Propyl ester	3.0 (2.997)	89.2	−21.1
1,3-Propyl diester	2.79	251.8	−19.2
2,2-Dimethyl-1,3-propyl diester	2.75	119.2	−21.1
1,5-Pentyl diester	2.79	331.0	−12.8

[a] HPLC, high-performance liquid chromatography.

alcohol. The reaction conditions for 2-propanol were slightly complicated by the tendency of the secondary alcohol to dehydrate at the vigorous reflux needed for removal of condensed water in the course of the reaction. This reaction did go smoothly, however, when heated to about the boiling point of the alcohol in the presence of a desiccant such as anhydrous $ZnCl_2$ or $ZnSO_4$. The isolated yield of each ester was >90%. One notable spectral feature of the IR absorption of these estolide esters was the prominence of the band at 1734 cm^{-1} and the complete transparency of the 3500 to 3200 cm^{-1} region of the spectrum indicating the absence of any O–H stretch; the 1711 cm^{-1} band of the free carboxylic acid of the parent estolide also disappeared. The ^1H spectrum for the 2-propyl ester showed a heptet for the (HCO) at 4.95 ppm while the ^{13}C gave two resonances—73.81 and 73.74 ppm—for the two tertiary carbons of both the substituent and the substituted estolide. Table 1 shows the chromatographic retention times and flow characteristics for all the esters synthesized. The monoesters have very low color, with a range of pour points and viscosity values likely to be suitable for several applications.

The second set of estolide esters were derived from the parent estolide by esterification with 1,3-propanediol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), and 1,5-pentanediol (Scheme 1B) and were also isolated in good to excellent yields. These diesters effectively doubled the molecular mass of the parent estolide. The consequence of increased size in a polymer is usually changes in the flow characteristics such as viscosity and pour point of the resulting material. Because chain length and branching are important factors that affect rheological behavior of materials, we were curious as to how a combination of both branching and chain lengthening would manifest in the diesters of the estolide. The last three entries in Table 1 show mixed results. The 1,5-pentyldiester with the longest chain length exhibits the highest observed viscosity relative to the other diesters and also has an elevated pour point temperature. In the 1,3-propyl diesters, the unbranched propyl substituent appears to augment the viscosity, at the same time causing a slight increase in pour point temperature. The 2,2-dimethyl-1,3-propyldiester, on the other hand, shows a rather sizable attenuation in viscosity relative to its neighbors and fosters a much lower pour point. These data in the main are in accord with the expectation that materials with longer linear chain lengths generally exhibit higher viscosities because of their extended sweep in the medium. Branching in the chain tends to introduce sphericity in the molecule, a factor that attenuates the viscosity and enhances lower pour point temperatures. So, even with this small sample of molecules, we observe a compromise resulting from an interplay of the two opposing factors on each molecule.

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