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Controlling Viscosity in Methyl Oleate Derivatives Through Functional Group Design

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Fatty acid methyl ester (FAME) derivatives have received considerable attention as potential biofuel additives and as sustainable lubricants. One common strategy for the modification of FAMEs, such as methyl oleate, involves epoxidation of the C9–C10 alkene followed by oxirane ring-opening to introduce branches into the FAME backbone. This strategy has been shown to improve cold-flow properties and oxidative stability relative to the parent oleates, and some derivatives have shown promise as lubricants. However, the effect of this strategy on viscosity has not been well established, if at all. Here we present the viscosity properties of methyl oleate derivatives as controlled by rational functional group manipulation with important implications for the preparation of bio-derived lubricants, where viscosity properties must be tightly controlled. The effect of selected derivatives as cold-flow additives in biodiesel is also reported.

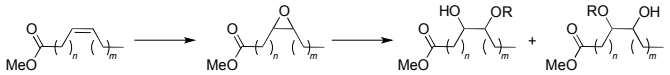
Introduction

The development of renewable sources of energy and materials is essential due to the impact of CO_2 emissions on the global climate and the finite nature of fossil fuel reserves. Biomass is an important, renewable source for organic chemicals, and lipid feedstocks are an attractive chemical platform due to their wide availability and relative chemical purity.[1] Accordingly, vegetable oil derivatives are being investigated for applications including building blocks for "oleochemical polyols" and "natural oil polyols";[2, 3] hydraulic fluids;[4] surfactants[5, 6] and adhesives.[7] Modified fatty-acid methyl esters (FAMEs), derived from unsaturated vegetable oils, have received particular attention in regards to their potential as biodiesel cold-flow additives[8-11] and as lubricants base stocks or additives.[12, 13] Vegetable oils have inherently low volatility, high viscosity indices and good lubricity, as well as good compatibility with mineral oils and additives and are readily biodegradable.[14] Their poor low-temperature fluidity and oxidative stability, however, prevents their use in most industrial applications.[13]

Recently Phung *et al*. employed a whole oil modification strategy to improve the cold-flow properties of biodiesel.[15] They combined the use of cobalt-mediated oxidation of triacylglycerides in acetic acid, at 150 °C, followed by esterification of the resulting mono- and di-carboxylate fragments with methanol to afford C7–C14 FAME and α□ω-di-ester mixtures. This work was for the express purpose of preparing biodiesel-like materials with improved cold flow properties compared with the original triacylglyceride mixtures. Particular success was reported with low-grade tallow. The process lowered the cloud-point from 14 °C to 1 °C, making the product mixture much more suitable for blending with conventional FAME biodiesel or petrodiesel feeds.

In contrast to that approach, the work reported here is aimed at the functionalisation of just the oleate fraction of vegetable oil through the use of specific chemical modifications. The resulting modified oils are investigated primarily for lubrication properties.

Direct chemical modification of FAMEs is a straightforward strategy for improving both cold-flow properties and oxidative stability. One common method of derivatisation involves epoxidation and oxirane ring-opening of an unsaturated FAME such as methyl oleate (Scheme 1).[9, 16, 17] Ring-opening reactions with both carboxylic acid[18-20] and alcohol[9, 10] nucleophiles have been investigated, generating α-hydroxy esters and ethers respectively. This approach introduces side-chains or branches to the FAME backbone. These branches are thought to inhibit crystal packing, thereby improving low temperature fluidity.[8] Concurrent removal of the sites of unsaturation improves oxidative stability.[17, 20]



Scheme 1. General strategy for addition of functionality to a double-bond in FAME, *via* ring opening of the epoxide with a carboxylic acid or alcohol nucleophile, leading to 2 regioisomers.

Numerous studies have shown that the introduction of side-chains consistently improves the cold flow properties of vegetable oil derivatives as measured by pour point, crystallisation onset temperature or cold filter plugging point (CFPP).[18, 20, 21] These properties have been shown to improve with both the number and size of the branches. Further reduction in pour point is generally seen where the side-chains themselves contain branching.[17, 21, 22]

Although removal of back-bone unsaturation through the addition of side-chains improves the oxidative stability of these materials relative to that of the parent unsaturated FAME up to a point, significant increases in molecular weight due to large or multiply branched side-chains eventually lead to a decrease in oxidative stability: suggesting that there are limitations to this approach.[23, 24]

Several FAME derivatives prepared through functionalization of an epoxide "handle" have shown promise as potential lubricants.[13, 20, 25] Erhan and co-workers used alcohol and anhydride nucleophiles to open the oxirane ring, followed by capping of the free hydroxyl group as an ester to generate a number of soybean oil derivatives with good lubricating properties.[26, 27] More recent studies showed that capping was not required for good cold-flow properties (measured by cloud-point) or oxidative stability (pressurised DSC), and that these α-hydroxy esters were effective at reducing the coefficient of friction and wear scars when used as an additive in hexadecane.[18]

The effect of the oxirane ring opening strategy on viscosity, another key parameter for lubricants, has not been systematically studied. However, in those cases where viscosity measurements are reported, the branched derivatives tend to have higher viscosity than the parent FAMEs,[21, 28] and increasing branch chain length results in an increase in viscosity, as does the use of branches bearing polar functional groups.[29, 30] Where reported, the viscosity index, a measure of the temperature stability of the viscosity, also tends to increase with the length of branches.[31, 32] However, the effect of polar functional groups on this parameter is not clear.

Due to the improved cold-flow properties of pure branched FAME derivatives as compared to the parent FAME from which they are synthesised, these compounds have also been investigated as potential additives to improve the low temperature performance of biofuels. The effects observed in these studies have at most resulted in a −2 °C improvement in pour point when short chain α-hydroxy ethers were used at up to 5 %w/w additive loading in biodiesel.[8, 21] Despite these modest gains, research in this area remains active.

An advantage of the epoxidation/oxirane ring opening strategy is the ease with which functional groups with differing properties can be introduced onto the FAME backbone, along with the desired level of branching. Esters, ethers and free hydroxyl groups were employed in the present study to systematically control viscosity properties in FAME derivatives, allowing the positive lubricating properties of this class of bioderived materials to be exploited through judicious manipulation of viscosity.

Methyl oleate was selected as a model FAME due to its abundance in typical feedstocks.[33] Based on previous studies,[21, 22] side-chains bearing cyclic R-groups were chosen to investigate whether the expected improvement in cold-flow properties (with only a minimum increase in molecular weight) is systematically correlated to any changes in viscosity behaviour.

To this end, 13 methyl oleate derivatives were prepared with hydroxy- or methoxy- substituents *alpha*- to the side-chain, or with no *alpha*-substitution (Figure 1). Cyclic branches were attached to the oleate backbone through ether or ester linkages. A further three derivatives with transesterified head-groups were prepared for comparison, giving a total of 16 compounds for viscosity testing. All compounds were isolated and analysed as a mixture of regioisomers at the C9/C10 positions of the parent FAME.

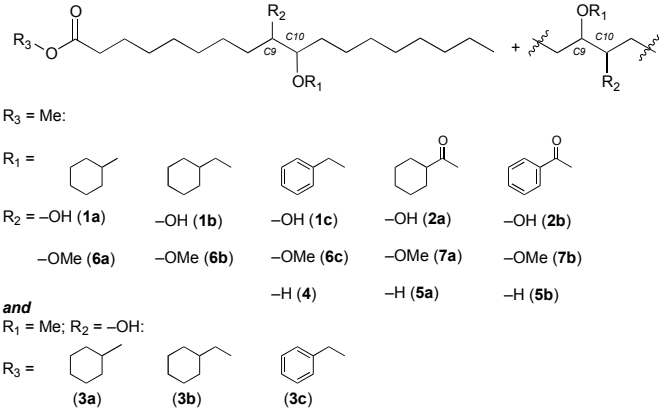


Figure 1. Overview of the substitution patterns for the compounds prepared and tested in this study.

Results and Discussion

Background

Vegetable oils have significant potential as feedstocks for bio-derived lubricants and biodiesel additives. They already possess many properties favorable for these applications. However, the poor cold-flow properties and low oxidation stability of vegetable oils and derivatised FAMES remains a significant hurdle to overcome. Although modification of the double bond is a successful strategy for improving oxidative stability[17, 20] and the introduction of branches through epoxidation and subsequent ring opening has been found to improve cold-flow, this tends to be at the expense of viscosity.[18] Hence, to systematically explore the effect of common modification strategies on viscosity, 16 methyl oleate derivatives were synthesised and their viscosity tested.

Synthesis of α-hydroxy derivatives

A series of methyl oleate derivatives with cyclic branches and a variety of different substituents in the α-position relative to the cyclic branch was prepared. Epoxidation of methyl oleate followed by acid-catalysed oxirane opening was used to

synthesise α-hydroxy ethers (**1a**–**c**) and esters (**2a**–**b**). Epoxidation was readily achieved in high yield (95%) using formic acid and peroxide according to the method of Erhan and co-workers.[34] Subsequent ring opening gave moderate yields of the desired substrates (33–65%). The reaction proceeds most efficiently using carboxylic acid nucleophiles, and the primary alcohols gave better yields than cyclohexanol, as would be expected based on steric considerations. A high yield was readily attained using methanol as the nucleophile (91%, see next section), further suggesting that steric hindrance was a major obstacle to high conversion in these reactions. All products were purified by column chromatography and fully characterised prior to further testing. Apart from steric hindrance, unwanted transesterification was also observed in some cases, accounting for the moderate yields of desired products. An example is shown in Figure 2, where the methyl ester head-group of **1c** was replaced by a benzyl group derived from the alcohol used to open the epoxide ring.

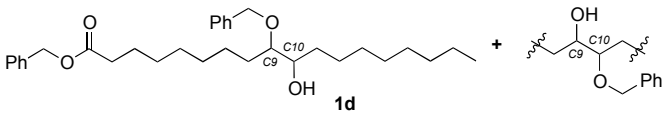


Figure 2. Structure of dibenzyl-substituted byproduct (**1d**) and its regioisomer isolated from the preparation of **1c**, accounting for reduced yield.

Synthesis of alkyl 9(10)-methoxy-10(9)-hydroxystearates

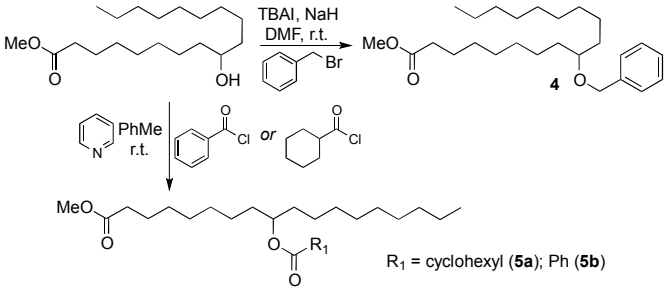
Ring opening of methyl 9,10-epoxystearate with methanol was used to obtain methyl 9(10)-methoxy-10(9)-hydroxystearate in good yield (91%). Transesterification using conventional sulfuric acid catalysis (10 wt%) and an excess of alcohol gave alkyl 9(10)-methoxy-10(9)-hydroxystearates (**3a**–**c**) in moderate yield (38–74%) with the poorest yield observed again for the relatively hindered cyclohexanol nucleophile. In all cases, the alcohol was required to be in excess in order to favour the formation of the desired transester products.

Synthesis of des-hydroxy derivatives

Des-hydroxy ethers and esters were of primary interest, as these analogues lack the free hydroxyl group arising from the traditional oxirane ring opening. This hydroxyl group is expected to be a major contributor to viscosity, due to its hydrogen-bonding capability. Des-hydroxy ether **4** was synthesised by a Williamson ether synthesis from benzyl bromide using sodium hydride as the base. Only a very low yield of desired product was obtained (10%), likely due to steric hindrance of the fatty-acid nucleophile. The des-hydroxy esters (**5a**–**b**) were readily synthesised in moderate to good yield (69–83%) from the appropriate acid chlorides in the presence of pyridine base (Scheme 2).

Synthesis of α-methoxy derivatives

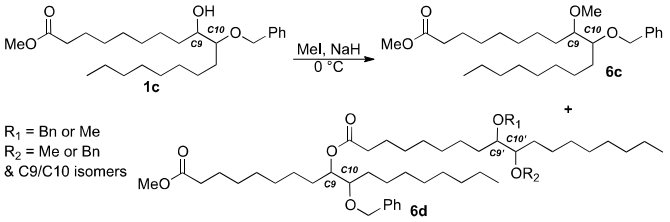
An alternative strategy for reducing viscosity was to cap the free hydroxyl with a methyl group. Accordingly methyl oleate derivatives (**1a**–**c** and **2a**–**b**) were treated with methyl iodide in dimethylformamide using sodium hydride as the base to give α-methoxy compounds (**6a**–**c** & **7a**–**b)** in moderate yields (36–59%).



Scheme 2. Synthetic route for des-hydroxy compounds from methyl monohydroxystearate. Only the C9-isomer is shown for clarity.

During these reactions some of the starting material was consumed through the formation of estolide byproducts, as shown in Scheme 3. Despite these side-reactions, the α-methoxy subset of products was considerably more accessible synthetically than the des-hydroxy ether **4**.

Using these methodologies, 16 derivatives were prepared with varying functionality at the C9/10 positions and with a range of ester head groups. The effect of these modifications on viscosity was then investigated. The range of substrates prepared allowed for three key comparisons to be made: ether branches *vs.* ester branches, internal substitution *vs*. head-group transesterification, and a methyl-capping strategy as compared with complete removal of the hydroxyl group in the des-hydroxy derivatives.



Scheme 3. Formation of estolide byproduct **6d** during methyl capping of α-hydroxy compound **1c**.

Viscosity of fatty-acid derivatives

Viscosity, a measure of the internal friction within a liquid, is the main parameter that determines how the liquid flows. For lubricants, viscosity determines the thickness of the lubricating film formed, and control over this property is necessary for the manufacture of lubricants appropriate for different applications. Despite the wide range of different fatty-acid derivatives that have been prepared and reported for consideration as lubricants in general, strategies for achieving control over the viscosity of these compounds have not been investigated systematically.

As oxygen containing functional groups are known to impact viscosity,[35] manipulation of these groups by design is a promising strategy for fine tuning of viscosity. The current compound set was tested using glass capillary viscometry at both 40 °C and 100 °C and from these data, an activation energy of viscous flow was calculated,[36] correcting for the

expected density change based on biodiesel data[37] (see SI for details of calculations).

Branched α-hydroxy ethers **1a–c** displayed viscosities of around 30–40 cSt at 40 °C and those of α-hydroxy esters were substantially higher at around 80–110 cSt (Table 1). Accordingly, the α-hydroxy-ethers require less energy to flow than do their ester analogues.

Table 1. Viscosity data for α-hydroxy compounds (R_3 = Me).

R_1O– substituent	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	E_A (kJmol^{-1})
cyclohexyloxy **1a**	36.8 ±0.1	5.23 ±0.02	32.4 ±0.2
cyclohexanemethoxy **1b**	39.0 ±0.2	5.46 ±0.02	32.6 ±0.2
benzyloxy **1c**	30.8 ±0.1	4.89 ±0.02	30.6 ±0.2
cyclohexanecarboxy **2a**	80.4 ±0.3	8.08 ±0.03	38.0 ±0.2
benzoyloxy **2b**	109.4 ±0.4	8.65 ±0.06	41.8 ±0.2

The rationale behind introducing mid-chain branches in the previous studies has been to disrupt crystal packing and thereby improve cold-flow properties.[8] It is not unreasonable to expect for such a strategy to have a similar effect on viscosity. In support of this hypothesis, the transesterified products **3a–c** had uniformly higher viscosities, at 40 °C, than their structural isomers (**1a–c**), in which the analogous ester motif is attached as the chain head-group rather than at a mid-chain branch point (*cf.* Table 1, entries 1–3 with Table 2). The corresponding activation energies, however, are comparable between the two subsets of compounds, indicating that transesterification of the methyl ester head group to these larger substituents has a minimal effect on the actual energy required for these molecules to slip past one another when an α-hydroxy-group is present on the main chain.

Table 2. Viscosity data for transesterified methoxy/hydroxy compounds. (R_1 = OMe)

R_3O– substituent	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	E_A (kJmol^{-1})
cyclohexyl ester **3a**	47.5 ±0.2	6.13 ±0.03	33.9 ±0.2
cyclohexanemethyl ester **3b**	47.5 ±0.2	6.31 ±0.02	33.4 ±0.2
benzyl ester **3c**	32.3 ±0.2	5.18 ±0.03	30.4 ±0.2

Des-hydroxy compounds **4** and **5a–b** displayed the lowest viscosity relative to the analogous methoxy- and hydroxy-derivatives (Table 3, entries 1–3). The fact that this subset of compounds has consistently low activation energies supports the hypothesis that hydrogen bonding in these relatively non-polar materials contributes significantly to their overall viscosity. The low yielding synthetic route for these compounds however, particularly the benzyloxy derivative, makes this modification strategy harder to implement on a large scale. As a consequence, methyl capping of the free hydroxyl group in compounds **1a–c** & **2a–b** to give α-methoxy compounds **6a–c** and **7a–b**, respectively, was explored as a facile approach for the reduction of viscosity properties (Table 3 entries 4–8). All α-methoxy compounds have lower viscosities and activation energies than their α-hydroxy analogues (*cf.* Table 3, **6a–c** & **7a–b** with Table 1), in spite of their slightly higher molecular weights. The lower viscosities can be attributed to the lower polarity of the methoxy-group relative to the hydroxyl-group and resultant loss of hydrogen bond donating ability. It is also noteworthy that the same mid-chain ether/ester influence on viscosity, previously seen with compounds **1a–c** & **2a–b** (Table 1), is present in this subset, with **7a** and **7b**, having higher activation energies than the ethers **6a–c**.

Table 3. Viscosity data for des-hydroxy and α-methoxy compounds (R_3 = Me).

R_1O– substituent	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	E_A (kJmol^{-1})
Des hydroxy-compounds:			
benzyloxy **4**	14.3 ±0.1	3.49 ±0.02	23.6 ±0.2
cyclohexanecarboxy **5a**	20.4 ±0.1	4.24 ±0.02	26.2 ±0.2
benzoyloxy **5b**	24.4 ±0.1	4.46 ±0.02	28.3 ±0.2
α-methoxy compounds:			
cyclohexyloxy **6a**	24.2 ±0.1	4.39 ±0.02	28.4 ±0.2
cyclohexanemethoxy **6b**	23.8 ±0.1	4.43 ±0.05	28.0 ±0.2
benzyloxy **6c**	16.3 ±0.2	3.76 ±0.01	24.5 ±0.2
cyclohexanecarboxy **7a**	29.1 ±0.1	5.02 ±0.01	29.2 ±0.2
benzoyloxy **7b**	44.9 ±0.3	6.10 ±0.02	33.1 ±0.2

The viscosity data at 40 °C and 100 °C was also used to calculate the viscosity indices (VI's) of all 16 compounds according to ASTM standard D2270-04[†] (Table 4). A high viscosity index indicates thermal stability of viscosity properties, which is particularly important for lubricant applications that involve machine parts, subject to heat sources other than friction.

Table 4. Calculated Visocosity Indices (VI's) based on the measured viscometry data.

Compound	Viscosity Index	Compound	Viscosity Index
α-hydroxy-		*α-methoxy-*	
cyclohexyloxy **1a**	55 ± 4	cyclohexyloxy **6a**	82 ± 4
cyclohexanemethoxy **1b**	61 ± 2	cyclohexanemethoxy **6b**	93 ± 5
benzyloxy **1c**	69 ± 3	benzyloxy **6c**	106 ± 3
cyclohexanecarboxy **2a**	52 ± 2	cyclohexanecarboxy **7a**	97 ± 2
benzoyloxy **2b**	12 ± 4	benzoyloxy **7b**	72 ± 3
Transesterified		*deshydroxy-*	
cyclohexyl ester **3a**	61 ± 3	benzyloxy **4**	130 ± 3
cyclohexanemethyl ester **3b**	72 ± 3	Cyclohexanecarboxy **5a**	116 ± 3
benzyl ester **3c**	84 ± 3	benzoyloxy **5b**	88 ± 3

The α-hydroxy-ethers **1a–c** have higher viscosity indices than the esters **2a–b** and overall, the less viscous the compound the higher its VI (and thus the higher its stability at elevated temperatures). Despite being a favourable attribute for a potential lubricant, none of these VI's are sufficient for the compounds to be considered commercially, at least on their own. These results are consistent with those previously published for modified FAMEs.[18, 22, 28]

In contrast, the transesterified products **3a–c** have higher measured viscosities and VI's than do their methyl ester isomers **1a–c**. Hence, head-group transesterification appears to be a method for fine-tuning viscosity *without deleteriously affecting the viscosity index of a FAME derivative.*

The des-hydroxy compounds **4** and **5a–b** had the highest VIs of the 16 compounds synthesised in this study. These three show the most promise for lubrication applications due to this high VI. Nevertheless, the α-methoxy subset (**6a–c** & **7a–b**) display

higher VI's than do their α-hydroxy analogues, with all but the benzoyloxy derivative **3e** having VI's above 80: the typical lower limit for commercial lubricants. Of particular note are the cyclohexanemethoxy ether **6b** and its ester analogue **7a**. In this case, the expected viscosity increase moving from an ether to an ester linkage is observed, but without the usual concomitant decrease in the VI. Methylation of the free hydroxyl group has, thus, proved to be an effective strategy for both reducing the viscosity and improving the viscosity index.

The above results provide two key strategies for controlling viscosity properties in FAME derivatives. Firstly, the VI can be uniformly improved by capping the secondary alcohol generated from the oxirane ring opening as the corresponding methyl ether. Secondly, viscosity may be tailored without adversely affecting the VI through head group ester modification and, in some cases, through the judicious choice of ester and either linkages.

Cold-Flow Properties of fatty-acid derivatives.

Low temperature behaviour of the derivatives was measured by differential scanning calorimetry (DSC) and is provided in the Supplementary Information. This technique is well established as a measure of cold-flow properties for a range of fatty-acid based molecules, including derivatives of methyl oleate. Crystallisation onset temperatures measured by DSC correspond well (within ± 5 °C) with cloud-point, as determined by ASTM standards.[38]

The des-hydroxy derivatives (**4** & **5a**–**b**) showed crystallisation onset temperatures between −70 and −80 °C. This represents a significant improvement in cold-flow properties compared to the parent methyl oleate (cloud-point −19 °C). Whereas the des-hydroxy derivatives showed freezing events as a clear exothermic peak, corresponding to a crystallization event, most of the remaining compounds show only a change in slope at very low temperatures: interpreted as a glass transition (T_G) rather than a liquid to solid phase change.

There is no reported relationship between the observed glass transitions and cold-flow for branched fatty-acid alkyl ester derivatives. Glass transitions generally arise from supercooling of a viscous liquid such that nucleation does not take place, resulting in an amorphous, solid**-**like state. Hence, if any crystalline state does exist for a given compound, the nucleation temperature is expected to be above the observed glass transition. It is therefore not clear for the compounds shown in Figure 1, whether there was a freezing point at higher temperature than the observed glass transitions, and whether it was bypassed due to the speed of the initial cooling protocol. To probe the thermal properties of these compounds further, a 2 °C min^{-1} cooling rate was tested for selected compounds, however, no additional crystallization peaks were observed. Based on cloud-point data for structurally similar compounds reported in the literature, it is likely that these compounds will possess cold-flow properties consistent with their use as lubricants.[3] Previously published studies of related compounds also suggest that the derivatives described here will have improved oxidative stability compared to the parent oleate ester, and will display lubricity properties within a suitable range for biolubricant applications.[9, 18, 20]

Fatty Acid Derivatives as Biodiesel Cold-Flow Improvers

There has been considerable interest in the use of branched FAME derivatives as cold-flow improvers for biodiesel. Results reported thus far have been mixed, ranging from no effect to a 2 °C reduction of pour point at 5 %w/w additive loading for some α-hydroxy ethers of isopropyl stearate.[8, 9]

The compounds reported here were tested as cold-flow improvers in biodiesel at 15 %w/w additive loading using DSC (see Supplementary Information). Reductions in crystallisation onset temperatures of 2 °C were observed at this loading for all compounds tested and are hence consistent with the available literature. The implication from the above results is that whilst the oxirane ring-opening strategy may be an effective method of whole-oil modification, the resulting compounds do not compete with traditional cold-flow improvers at concentrations that are commercially feasible.

Conclusions

A suite of 16 compounds derived from methyl oleate, a renewable chemical feedstock, was designed rationally, synthesized and their viscosity properties systematically studied to assess each compound's suitability for lubricant applications. Introduction of cyclic branches into methyl oleate derivatives resulted in compounds whose activation energies for viscous flow ranged from 22.8–41.0 $kJmol^{-1}$.

Two clear structural trends were observed: Ethers were preferable to esters as side chains; removal or capping of the hydroxyl group, from ring opening of the intermediate epoxide, resulted in the most suitable candidates for renewable bio-based lubricants, clearly reaching commercially relevant performance parameters.

Furthermore, transesterification was shown to be a simple method to uncouple the viscosity from the VI in a subset of analogues and, hence, there is the potential for further improvement of both of these parameters by combining back-bone hydroxyl-group removal and replacement of the terminal methyl ester group with an alternative substituent such as a benzyl ester.

Given their uniformly poor performance as cold-flow improvers for biodiesel, even at high loading, it is concluded that similar, simple double-bond functionalised oleate derivatives are unlikely to be practical for this purpose.

Experimental

Materials

The following reagents were used as received: methyl oleate, formic acid (98% purity), benzoic acid, cyclohexanecarbonyl chloride, cyclohexanecarboxylic acid, cyclohexanemethanol, benzyl bromide (all Aldrich), hydrogen peroxide (30 %w/v aq.), sulfuric acid (98%), cyclohexanol, benzyl alcohol, petroleum benzine 40–50 °C (light petroleum), hexane, ethyl

acetate, methanol, sodium hydride (60 % w/w dispersion in mineral oil), benzoyl chloride, tetrabutylammonium iodide (all Merck), sodium bicarbonate, sodium sulfate, perchloric acid, pyridine, (all Ajax), methyl iodide (APS). Deionised water, generated using a Milli-Q (Millipore) Ultrapure Water System, was used unless otherwise stated. All column chromatography was performed using chromatographic Silica Media LC60A 40–63 μm (Grace). Toluene and dimethylformamide (both Ajax) were dried over microwave activated 4 Å molecular sieves (Aldrich).

Chromatographic analysis

Reactions were monitored by thin layer chromatography (TLC) or by gas chromatography-mass spectrometry using a GCMS-QP2010 Gas chromatograph mass spectrometer (EI) with an Rtx-5MS column (30 m × 0.25 mm × 0.25 μm).

Viscosity measurements

Measurements of kinematic viscosity were performed using Cannon-Manning Semi-Micro calibrated glass capillary viscometers in a controlled temperature bath (see Supplementary Information for further details). Errors were calculated as two standard errors of the mean of a minimum of five replicates plus the standard error of the viscometer.

Differential Scanning Calorimetry

DSC was performed on a Mettler Toledo DSC823e. Samples (10.0 mg) were weighed into an aluminium pan and the container hermetically sealed. Each sample was measured for two cycles of heating to 80 °C and cooling to −100 °C at 5 °C min−1, with the sample held isothermally for 10 minutes in between heating and cooling runs and purge gas set at 40 mL min−1 nitrogen. Data were collected and analysed using Mettler Toledo STARe Software version 9.30.

Synthesis

METHYL 9,10-EPOXYSTEARATE

Cold 30 %w/v hydrogen peroxide aqueous solution (1.6 mL, 16 mmol) was added dropwise to a mixture of methyl oleate (2.0 g, 6.7 mmol) and 99% formic acid (1.0 mL, 23 mmol) on ice. The mixture was stirred vigorously at room temperature to form an emulsion (14 h) then diluted with hexanes (6 mL) and washed with saturated sodium bicarbonate solution (3 × 1 mL) and brine (2 × 1.5 mL), dried over sodium sulfate and concentrated under reduced pressure to give methyl 9,10-epoxystearate.

OXIRANE OPENING WITH ALCOHOLS AND ACIDS

Method A (alcohols): Cyclohexanol, cyclohexanemethanol or benzyl alcohol (128 mmol, 10 eq) was combined with 98 %w/v sulfuric acid (126 mg, 1.28 mmol) and methyl 9,10-epoxystearate was added (4.00 g, 12.8 mmol). The mixture was stirred at 30 °C and monitored (TLC) until the epoxide was consumed (3–40 h). The oil phase was then diluted with light petroleum (50 mL) and washed with saturated, aqueous sodium bicarbonate solution (2 × 10 mL) and brine (3 × 10 mL) then dried over sodium sulfate and the solvent evaporated under reduced pressure. The excess alcohol was then removed using a Kugelrohr apparatus (100–120 °C, 30–60 min) and the products **1a**–**c** were purified by column chromatography (4–5 %v/v ethyl acetate/light petroleum).

Method B (acids): A solution of cyclohexanecarboxylic acid or benzoic acid (98.3 mmol) in toluene (40 mL) was treated with methyl 9,10-epoxyoleate (3.10 g, 9.92 mmol) and heated at 100 ˚C (93–112 h) until the epoxide was consumed (TLC). The mixture was diluted with light petroleum (50 mL) and washed with saturated, aqueous sodium bicarbonate solution (4 × 20 mL) and brine (2 × 10 mL), dried over sodium sulfate and the solvent evaporated under reduced pressure. The products **2a**–**b** were then purified by column chromatography (4.5–6 %v/v ethyl acetate/light petroleum).

TRANSESTERIFICATION REACTIONS

Methyl 9(10)-methoxy-10(9)-hydroxystearate (1.50 g, 4.35 mmol) was combined with either cyclohexanol, benzyl alcohol or cyclohexanemethanol (48 mmol) and concentrated sulfuric acid added (70 mg, 0.71 mmol). The mixture was heated to 80 °C for 4 h then diluted with light petroleum (20 mL) and washed with saturated, aqueous sodium bicarbonate solution (2 × 1 mL), water (3 x 5 mL) and brine (3 × 5 mL) then dried over sodium sulfate and the solvent evaporated under reduced pressure. Excess alcohol was recovered using a Kugelrohr apparatus (100 °C, 30 min, 1.5 mbar) and the products **3a**–**c** purified by column chromatography (5–9 %v/v ethyl acetate/hexane).

DES-HYDROXY ETHER AND ESTER SYNTHESIS

Methyl 9(10)-monohydroxystearate[39] (1.0 g, 3.2 mmol) was treated with tetrabutylammonium iodide (117 mg, 0.32 mmol) in dimethyformamide (10 mL) and benzyl bromide added (2.3 mL, 19 mmol). Sodium hydride was added to the stirred solution in two batches (60 %w/w dispersion in mineral oil, 2 × 80 mg) 24 h apart and the reaction stirred for a further 6 h. Light petroleum (10 mL) was added and the mixture was acidified with cold 1 M hydrochloric acid, then extracted with light petroleum (3 × 15 mL). The organic extracts were washed with water (2 × 10 mL) and brine (3 × 10 mL) and dried over sodium sulfate and the solvent evaporated under reduced pressure. The oil was then combined with methanol (2.5 mL) and sulfuric acid (98%, 25 μL) and refluxed for 1.5 h. Water (2 mL) and light petroleum (5 mL) were added and the organic phase was separated. The aqueous phase was further extracted with light petroleum (3 × 10 mL) and the combined organic extracts were washed with water (2 × 2 mL) and brine (2 × 5 mL), dried over sodium sulfate and the solvent evaporated under reduced pressure. The product (**4**) was purified by column chromatography (2 %v/v ethyl acetate/light petroleum).

Methyl 9(10)-monohydroxystearate[39] (1.50 g, 4.8 mmol) was combined with pyridine (477 μL, 5.9 mmol) in toluene (2.25 mL) and cyclohexanecarbonyl chloride or benzoyl chloride (≈700 μL, 5.2 mmol) in toluene (1.5 mL) was added dropwise. The mixture was stirred at room temperature for 2 h until almost complete (TLC), then diluted in light petroleum (50 mL) and washed with water (2 × 10 mL), 1 M hydrochloric acid (3 × 10 mL), followed by 10 %w/v sodium carbonate (3 × 10 mL),

water (2 × 10 mL) and brine (3 × 10 mL) then dried over sodium sulfate and the solvent evaporated under reduced pressure. The products **5a**–**b** were purified by column chromatography (3–4 %v/v ethyl acetate/light petroleum).

METHYL CAPPING REACTIONS

A stirred solution of hydroxy compounds **1a**–**c** or **2a**–**b** (~1.25 g, 2.88 mmol) in DMF (15 mL) was treated with sodium hydride (60 %w/w dispersion in mineral oil, 0.13 g, 3.2 mmol). Methyl iodide (1.1 mL, 17 mmol) was then added and the reaction stirred at room temperature (1–3 h). Light petroleum was added (20 mL) and the mixture cooled on ice and acidified with hydrochloric acid (5 mL) then extracted with light petroleum (3 × 20 mL). The combined organic extracts were then washed with water (3 × 10 mL) and brine (2 × 10 mL), dried over sodium sulfate and the solvent evaporated under reduced pressure to give a crude oil, which was purified by column chromatography (2–4 %v/v ethyl acetate/hexane) to afford the products **6a**–**c** & **7a**–**b**.

Product Characterisation

IR spectra were recorded using a Bruker Tensor27 FT-IR spectrometer from 4000–600 cm^{-1} (NaCl, thin film). ^1H (300.13 MHz) and $^{13}C\{^1H\}$ (75.48 MHz) NMR spectra were recorded on a Bruker Avance DPX300 spectrometer at 300 K and referenced internally to residual solvent signals at 7.26 and 77.16 ppm, respectively, for $CDCl_3$. High resolution mass spectra (HRMS) were obtained using a Bruker 7T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer in positive ion ESI mode.

METHYL 9(10)-CYCLOHEXYLOXY-10(9)-HYDROXYSTEARATE 1A

HRMS ESI+ (*m/z*) 435.34448 calculated for $C_{25}H_{48}O_4Na^+$, found 435.34443. ^1H NMR (300 MHz, $CDCl_3$) δ 3.66 (s, 3H, CO_2CH_3), 3.48–3.38 (m, 1H, C**H**OH), 3.35–3.24 (m, 1H, OC**H**$(CH_2)_2$), 3.19 (q, *J* = 5.2 Hz, 1H, C**H**OCH$(CH_2)_2$), 2.38–2.23 (m, 3H, CHO**H**, CH_2CO_2), 1.97–1.08 (m, 36H), 0.88 (t, *J* = 6.4, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 174.4 (**C**O_2), 80.0(1) (CH), 79.9(5) (CH), 77.1 (CH), 72.6 (CH), 51.5 (CO_2CH_3), 34.2–22.8 (19 CH_2), 14.2 (CH_2CH_3). IR ν(cm^{-1}): 3468 (O–H), 2930 (C–H), 2856 (C–H), 1743 (C=O), 1453 (C–H).

METHYL 9(10)-CYCLOHEXANEMETHOXY-10(9)-HYDROXY-STEARATE 1B

HRMS ESI+ (*m/z*) 449.36013 calculated for $C_{26}H_{50}O_4Na^+$, found 449.35990. ^1H NMR (300 MHz, $CDCl_3$) δ 3.61 (s, 3H, CO_2CH_3), 3.48–3.38 (m, 1H, C**H**OH), 3.36–3.29 (m, 1H, OC**H**H′Ar), 3.19–3.11 (m, 1H, OCH**H′**Ar), 2.99 (app. q, *J* = 5.4 Hz, 1H, C**H**OCH_2Ar), 2.38 (t, *J* = 4.9 Hz, 1H, O**H**), 2.25 (t, *J* = 7.5 Hz, 2H, CO_2CH_2), 1.76–0.86 (m, 37H), 0.83 (t, *J* = 6.3 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 174.2 (**C**O_2), 82.7 (CH), 82.6 (CH), 76.4(3) (O**C**H_2), 76.4(0) (O**C**H_2), 72.7 (CH), 51.4 (CO_2CH_3), 38.6 (CH), 34.1–22.7 (19 CH_2), 14.1 (CH_2CH_3). IR ν(cm^{-1}): 3468 (O–H), 2925 (C–H), 2854 (C–H), 1743 (C=O), 1450 (C–H).

METHYL 9(10)-BENZYLOXY-10(9)-HYDROXYSTEARATE 1C

HRMS ESI+ (*m/z*) 443.31318 calculated for $C_{26}H_{44}O_4Na^+$, found 443.31305. ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.22 (m, 5H, Ar–**H**), 4.65 (d, *J* = 11.4 Hz, 1H, C**H**H′Ph). 4.50 (d, *J* = 11.4 Hz, 1H, CH**H′**Ph), 3.66 (s, 3H, CO_2CH_3), 3.58–3.48 (m, 1H, C**H**OH), 3.26 (app. q, *J* = 5.5 Hz, 1H, C**H**OBn), 2.64–2.36 (m, 1H, O**H**), 2.30 (t, *J* = 7.5 Hz, 2H, CO_2CH_2), 1.71–1.16 (m, 26H), 0.89 (t, *J* = 6.2 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 174.2 (**C**O_2), 138.6 (CH_2**C**$(CH)_2$), 128.4 (CH), 127.9 (CH), 127.7 (CH), 82.4 (CH), 82.4 (CH), 72.7 (CH), 72.4 (CH_2), 51.4 (CO_2CH_3), 34.1–22.7 (14 CH_2), 14.1 (CH_2CH_3). IR ν(cm^{-1}): 3467 (O–H), 3064 (C–H aromatic), 3030, 2927 (C–H), 2855 (C–H), 1741 (C=O), 1456 (C–H).

METHYL 9(10)-CYCLOHEXANECARBOXY-10(9)-HYDROXY-STEARATE 2A

HRMS ESI+ (m/z) 463.33940 calculated for $C_{26}H_{48}O_5Na^+$, found 463.33937. ^1H NMR (300 MHz, $CDCl_3$) δ 4.81 (td, *J* = 6.6, 3.8 Hz, 1H, CO_2CH), 3.66 (s, 3H, CO_2CH_3), 3.61–3.50 (m, 1H, C**H**OH), 2.40–2.24 (m, 3H, C**H**CO_2, CH_2CO_2), 1.98–1.85 (m, 2H), 1.81–1.13 (m, 35H), 0.87 (t, *J* = 6.6 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 175.9 (CH**C**O_2), 174.2 (**C**O_2CH_3), 76.0 (CH), 75.9 (CH), 72.6 (CH), 51.4 (CO_2CH_3), 43.5 (**C**HCO_2), 34.1–22.7 (19 CH_2), 14.1 (CH_2CH_3). IR ν(cm^{-1}): 3499 (O–H), 2929 (C–H), 2856 (C–H), 1732 (C=O), 1452 (C–H).

METHYL 9(10)-BENZOYLOXY-10(9)-HYDROXYSTEARATE 2B

HRMS ESI+ (*m/z*) 457.29245 calculated for $C_{26}H_{42}O_5Na^+$, found 457.29253. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09–8.00 (m, 2H, Ar–**H**), 7.61–7.50 (m, 1H, Ar–**H**), 7.49–7.38 (m, 2H, Ar–**H**), 5.14–5.01 (m, 1H, CO_2CH), 3.76–3.67 (m, 1H, C**H**OH), 3.63(7) (s, 1.5 H, CH_3CO_2), 3.64(3), (s, 1.5 H, CH_3CO_2), 2.26 (m, 2H, CH_2CO_2), 1.98–1.12 (m, 27H), 0.91–0.78 (m, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 174.4 (**C**O_2CH_3), 166.5 (**C**O_2CH), 133.1 (CH), 130.4 (**C**CO_2), 129.8 (CH), 128.5 (CH), 77.5 (CH), 77.4 (CH), 72.8 (CH), 51.5 (CO_2CH_3), 34.2–22.7 (14 CH_2), 14.2 (CH_2CH_3). IR ν(cm^{-1}): 3502 (O–H), 3064 (C–H aromatic), 2927 (C–H), 2856 (C–H), 1740 (C=O), 1717 (C=O), 1453 (C–H).

CYCLOHEXYL 9(10)-METHOXY-10(9)-HYDROXYSTEARATE 3A

HRMS ESI+ (*m/z*) 435.34448 calculated for $C_{25}H_{48}O_4Na^+$, found 435.34449. ^1H NMR (300 MHz, $CDCl_3$) δ 4.76–4.65 (m, 1H, CO_2CH), 3.43 (s, 1H, C**H**OH), 3.36 (s, 3H, CH_3O), 2.98–2.90 (m, 1H, C**H**OCH_3), 2.38 (bs, 1H, O**H**), 2.22 (t, J = 7.4 Hz, 2H, CH_2CO_2), 1.85–1.13 (m, 40H), 0.83 (t, J = 6.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3 (**C**O_2), 84.4 (CH), 72.6(CH), 72.3(CH), 58.1 (O**C**H_3), 34.8–22.7 (19 CH_2), 14.13 (CH_2CH_3). IR ν(cm–1): 3468 (O–H), 2930 (C–H), 2856 (C–H), 1732 (C=O), 1455 (C–H).

CYCLOHEXANEMETHYL 9(10)-METHOXY-10(9)-HYDROXY-STEARATE 3B

HRMS ESI+ (*m/z*) 449.36013 calculated for $C_{26}H_{50}O_4Na^+$, found 449.36009. 1H NMR (300 MHz, $CDCl_3$) δ 3.84 (d, J = 6.4 Hz, 2H, CO_2CH_2), 3.44 (s, 1H, CHO**H**), 3.37 (s, 3H, O**C**H_3), 2.96 (q, J = 5.5 Hz, 1H, C**H**OCH_3), 2.36 (s, 1H, O**H**), 2.30–2.22 (m, 2H, CH_2CO_2), 1.76–1.02 (m, 33H), 1.02–0.77 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0 (**C**O_2), 84.4(2) (CH), 84.3(8) (CH), 72.7 (CH), 69.5 (**C**H_2O), 58.19 (**C**H_3O),

37.2 (**C**HCH$_2$O), 34.4–22.7 (19 CH$_2$), 14.16 (CH$_2$**C**H$_3$). IR ν(cm^{-1}): 3468 (O–H), 2927 (C–H), 2854 (C–H), 1738 (C=O), 1452 (C–H).

BENZYL 9(10)-METHOXY-10(9)-HYDROXYSTEARATE 3C

HRMS ESI+ (*m/z*) 443.31318 calculated for $C_{26}H_{44}O_4Na^+$, found 443.31316. 1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5H, Ar–H), 5.10 (s, 2H, C**H$_2$**–Ph), 3.47 (s, 1H, C**H**OH), 3.40 (s, 1.5 H, OC**H$_3$**), 3.39 (s, 1.5 H, OC**H$_3$**), 2.98 (m,C**H**OCH$_3$), 2.45 (s, 1H, CHO**H**), 2.34 (t, J = 7.5 Hz, 2H, C**H$_2$**CO$_2$), 1.73–1.00 (m, 26H), 0.92–0.83 (m, 3H, CH$_2$C**H$_3$**). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6 (**C**O$_2$), 136.20 (**C**CH$_2$O), 128.53 (CH), 128.15 (CH), 84.3(8) (CH), 84.3(4) (CH), 72.6 (CH), 66.0 (**C**H$_2$Ph), 58.13 (O**C**H$_3$), 34.3–22.7 (14 CH$_2$), 14.1 (CH$_2$**C**H$_3$). IR ν(cm^{-1}): 3468 (O–H), 3066 (C–H aromatic), 3034 (C–H aromatic), 2928 (C–H), 2855 (C–H), 1738 (C=O), 1608 (C=C aromatic), 1587 (C=C aromatic), 1498 (C=C aromatic), 1457 (C–H).

METHYL 9(10)-BENZYLOXYSTEARATE 4

HRMS ESI+ (*m/z*) 427.31827 calculated for $C_{26}H_{44}O_3Na^+$, found 427.31813. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3–7.20 (m, 5H, Ar–**H**), 4.49 (s, 2H, C**H$_2$**Ph), 3.66 (s, 3H, CO$_2$C**H$_3$**), 3.42–3.29 (m, 1H, C**H**OBn), 2.29 (t, *J* = 7.5 Hz, 2H, C**H$_2$**CO$_2$), 1.71–1.14 (m, 28H), 0.88 (t, *J* = 6.6 Hz, 3H, CH$_2$C**H$_3$**). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 174.4 (**C**O$_2$), 139.4 (**C**CH$_2$O), 128.4 (CH), 127.8 (CH), 127.5 (CH), 79.1(6) (CH), 79.1(9) (CH), 70.9 (**C**H$_2$Ph), 51.5 (CO$_2$C**H$_3$**), 34.2–22.8 (15 CH$_2$), 14.2 (CH$_2$**C**H$_3$). IR ν(cm^{-1}): 3089, 3065 (C–H aromatic), 3030, 2927 (C–H), 2855 (C–H), 1742 (C=O), 1456 (C–H).

METHYL 9(10)-CYCLOHEXANECARBOXYSTEARATE 5A

HRMS ESI+ (*m/z*) 447.34448 calculated for $C_{26}H_{48}O_4Na^+$, found 447.34455. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.82 (app. quin. *J* = 6.2 Hz, 1H, CO$_2$C**H**), 3.63 (s, 3H, CO$_2$C**H$_3$**), 2.30–2.17 (m, 3H, C**H$_2$**CO$_2$, C**H**CO$_2$), 1.91–1.13 (m, 38H), 0.84 (t, *J* = 6.6 Hz, 3H, CH$_2$C**H$_3$**). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 175.9 (CH**C**O$_2$), 174.3 (**C**O$_2$CH$_3$), 73.6(7) (CH), 73.7(0) (CH), 51.4 (CO$_2$**C**H$_3$), 43.6 (CH), 34.3–22.8 (20 CH$_2$), 14.1 (CH$_2$**C**H$_3$). IR ν(cm^{-1}): 2929 (C–H), 2856 (C–H), 1743 (C=O), 1452 (C–H).

METHYL 9(10)-BENZOYLOXYSTEARATE 5B

HRMS ESI+ (*m/z*) 441.29753 calculated for $C_{26}H_{42}O_4Na^+$, found 441.29759. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07–8.00 (m, 2H, Ar–**H**), 7.56–7.49 (m, 1H, Ar–**H**), 7.46–7.37 (m, 2H, Ar–**H**), 5.18–5.06 (m, 1H, C**H**OBn), 3.64 (s, 1.5 H, CO$_2$C**H$_3$**), 3.63 (s, 1.5H, CO$_2$C**H$_3$**), 2.26 (t, *J* = 7.5 Hz, 2H, C**H$_2$**CO$_2$), 1.76–1.14 (m, 28H), 0.85 (t, *J* = 6.2 Hz, 3H, CH$_2$C**H$_3$**). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 174.3 (**C**O$_2$CH$_3$), 166.4 (**C**O$_2$CH), 132.7 (CH), 131.0 (**C**CO$_2$), 129.6 (CH), 128.4 (CH), 75.1(1) (CH), 75.0(8) (CH), 51.4 (CO$_2$**C**H$_3$), 34.3–22.7 (15CH$_2$), 14.1 (CH$_2$**C**H$_3$). IR ν(cm^{-1}): 3063 (C–H aromatic), 2928 (C–H), 2856 (C–H), 1741 (C=O), 1717 (C=O), 1452 (C–H).

METHYL 9(10)-CYCLOHEXYLOXY-10(9)-METHOXYSTEARATE 6A

HRMS ESI+ (*m/z*) 449.36013 calculated for $C_{26}H_{50}O_4Na+$, found 449.36013. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 3H, CO$_2$C**H$_3$**), 3.39–3.32 (m, 4H, CHOC**H$_3$**,CH), 3.28–3.17 (m, 1H, Cyc–C**H**), 3.07 (dt, J = 7.4, 3.7 Hz, 1H, CH), 2.27 (t, J = 7.5 Hz, 2H, C**H$_2$**CO$_2$), 1.91–1.09 (m, 36H), 0.85 (t, J = 6.7 Hz, 3H, CH$_2$C**H$_3$**). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2 (**C**O$_2$), 82.9 (CH), 77.3 (CH), 58.4 (CHO**C**H$_3$), 51.34 (CO$_2$**C**H$_3$), 34.1–22.6 (19 CH$_2$), 14.1 (CH$_2$**C**H$_3$). IR ν(cm^{-1}): 2929 (C–H), 2856 (C–H), 1743 (C=O), 1452 (C–H).

METHYL 9(10)-CYCLOHEXANEMETHOXY-10(9)-METHOXY-STEARATE 6B

HRMS ESI+ (*m/z*) 463.37578 calculated for $C_{27}H_{52}O_4Na^+$, found 463.37565. 1H NMR (300 MHz, $CDCl_3$) δ 3.64 (s, 3H, CO$_2$C**H$_3$**), 3.37 (s, 3H, COC**H$_3$**), 3.32–3.08 (m, 4H, CHOC**H$_2$**Cy, C**H**OCH$_3$), 2.28 (t, J = 7.5 Hz, 2H, C**H$_2$**CO$_2$), 1.82–0.79 (m, 40H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4 (**C**O$_2$), 82.4 (CH), 80.6 (CH), 77.0 (OC**H$_2$**), 58.5 (CHO**C**H$_3$), 51.5 (CO$_2$**C**H$_3$), 38.7 (**C**H), 34.2-22.8 (19 CH$_2$), 14.2 (CH$_2$**C**H$_3$). IR *ν*(cm^{-1}): 2925 (C–H), 2854 (C–H), 1744 (C=O), 1451 (C–H).

METHYL 9(10)-BENZYLOXY-10(9)-METHOXYSTEARATE 6C

HRMS ESI+ (m/z) 457.32883 calculated for $C_{27}H_{46}O_4Na^+$, found 457.32880. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.21 (m, 5H, Ar–**H**), 4.66–4.51 (m, 2H, C**H$_2$**Ph), 3.66 (s, 3H, CO$_2$C**H$_3$**), 3.49–3.30 (m, 4H, C**H$_3$**O, C**H**OBn), 3.23–3.14 (m, 1H, C**H**OCH$_3$), 2.30 (t, *J* = 7.5 Hz, 2H C**H$_2$**CO$_2$), 1.69–1.17 (m, 26H), 0.89 (t, *J* = 6.6 Hz, 1H, CH$_2$C**H$_3$**). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 174.3 (**C**O$_2$CH$_3$), 139.1 (OCH$_2$**C**), 128.3 (CH), 128.0 (CH), 127.6 (CH), 82.6 (CH), 80.0 (CH), 72.7 (O**C**H$_2$), 58.6 (CHO**C**H$_3$), 51.4 (CO$_2$**C**H$_3$), 34.1–22.7 (14 CH$_2$), 14.2 (CH$_2$**C**H$_3$). IR ν(cm^{-1}): 3088, 3064, 3030, 2927 (C–H), 2856 (C–H), 1742 (C=O), 1456 (C–H).

METHYL 9(10)-CYCLOHEXANECARBOXY-10(9)-METHOXY-STEARATE 7A

HRMS ESI+ (*m/z*) 477.35505 calculated for $C_{27}H_{50}O_5Na^+$, found 477.35527. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.93 (dt, *J* = 8.6, 4.4 Hz, 1H, CO$_2$C**H**), 3.61 (s, 3H, CO$_2$C**H$_3$**), 3.36 (s, 3H, CHOC**H$_3$**), 3.15–3.06 (m, 1H, C**H**OCH$_3$), 2.33–2.20 (m, 3H, C**H$_2$**CO$_2$, C**H**CO$_2$), 1.91–1.11 (m, 36H), 0.83 (t, *J* = 6.5 Hz, 3H, CH$_2$C**H$_3$**). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 175.8 (CH**C**O$_2$), 174.2 (**C**O$_2$CH$_3$), 81.6 (CH), 73.4(2) (CH), 73.3(9) (CH), 58.4 (CHO**C**H$_3$), 51.40 (CO$_2$**C**H$_3$), 43.4 (**C**HCO$_2$), 34.1–22.7 (19 CH$_2$), 14.12 (CH$_2$**C**H$_3$). IR ν(cm^{-1}): 2929 (C–H), 2856 (C–H), 1733 (C=O), 1453 (C–H).

METHYL 9(10)-BENZOYLOXY-10(9)-METHOXYSTEARATE 7B

HRMS ESI+ (m/z) 471.30810 calculated for $C_{27}H_{44}O_5Na^+$, found 471.30832. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 2H, Ar–**H**), 7.53 (t, *J* = 7.3 Hz, 1H, Ar–**H**), 7.42 (t, *J* = 7.6 Hz, 2H, Ar–**H**), 5.27–5.18 (m, 1H, CO$_2$C**H**), 3.62(4) (s, 1.5H, CO$_2$C**H$_3$**), 3.61(9) (s, 1.5H, CO$_2$C**H$_3$**), 3.43 (s, 3H, CHOC**H$_3$**), 3.33–3.25 (m, 1H, C**H**OCH$_3$), 2.25 (t, *J* = 7.5 Hz, 2H, C**H$_2$**CO$_2$), 1.75–1.13 (m, 26H), 0.83 (t, *J* = 6.6 Hz, 3H, CH$_2$C**H$_3$**). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 174.2 (**C**O$_2$CH$_3$), 166.3 (Ph**C**O$_2$), 132.9 (CH), 130.6 (**C**CO$_2$), 129.7 (CH), 128.3 (CH), 81.7(1) (CH), 81.6(9) (CH), 74.8(8) (CH), 78.8(5) (CH), 58.6 (CHO**C**H$_3$), 51.4 (CO$_2$**C**H$_3$), 34.1–22.7 (13CH$_2$), 14.1 (CH$_2$**C**H$_3$).). IR ν(cm^{-1}): 3063 (C–H aromatic), 2928 (C–H), 2856 (C–H), 1741 (C=O), 1719 (C=O), 1452 (C–H).

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Notes and references

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† Electronic Supplementary Information (ESI) available: viscometry methods, viscosity calculations, DSC data for pure compounds, DSC data for additive tests, example DSC curves and byproduct characterisation See DOI: 10.1039/b000000x/

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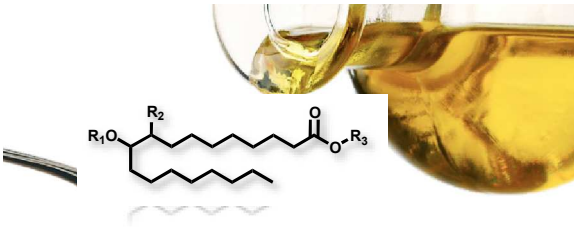

The effect of molecular structure on commercially relevant lubrication properties is elucidated in a set of 16 renewable oleate derivatives.