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(54) **LUBRICANT COMPOSITIONS HAVING
ENHANCED ESTOLIDE CONTENT,
METHODS OF MAKING, AND USES
THEREOF**

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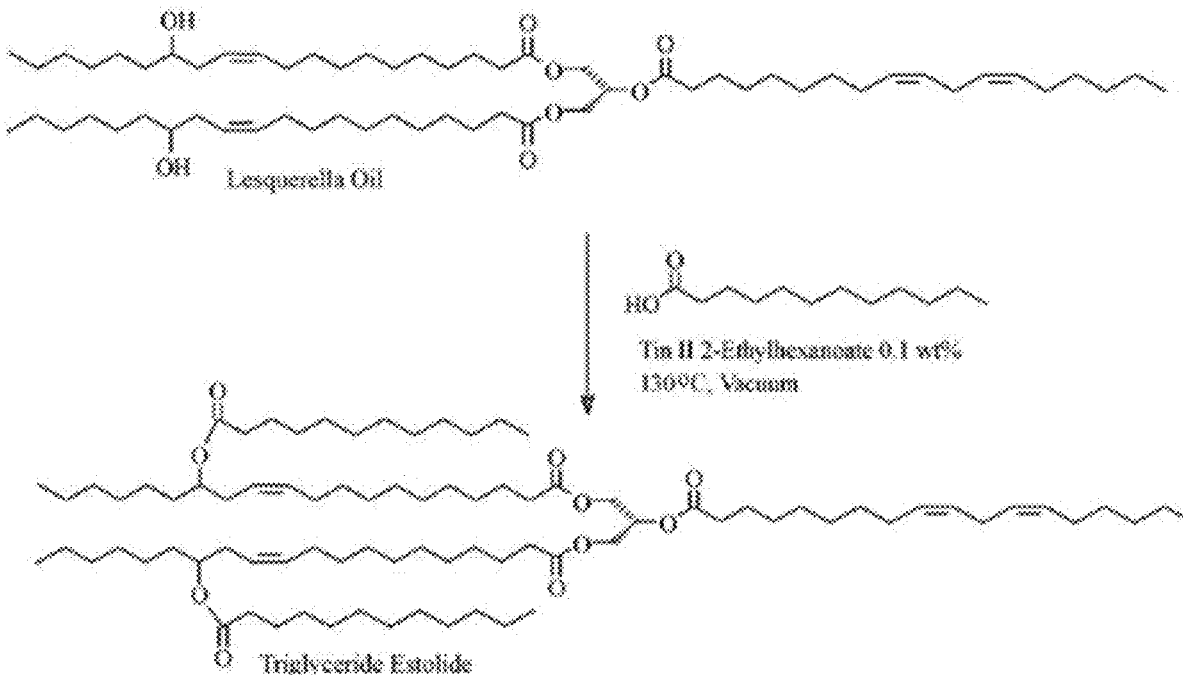
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(57) **ABSTRACT**

Various liquid and semisolid lubricant compositions are provided, in particular lubricant compositions are provided which have been chemically modified to increase a concentration of triacylglyceride estolide content. The estolides can be produced via esterification with one or more fatty acids such as palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, or a combination thereof. Both liquid and semisolid lubricant compositions are provided.



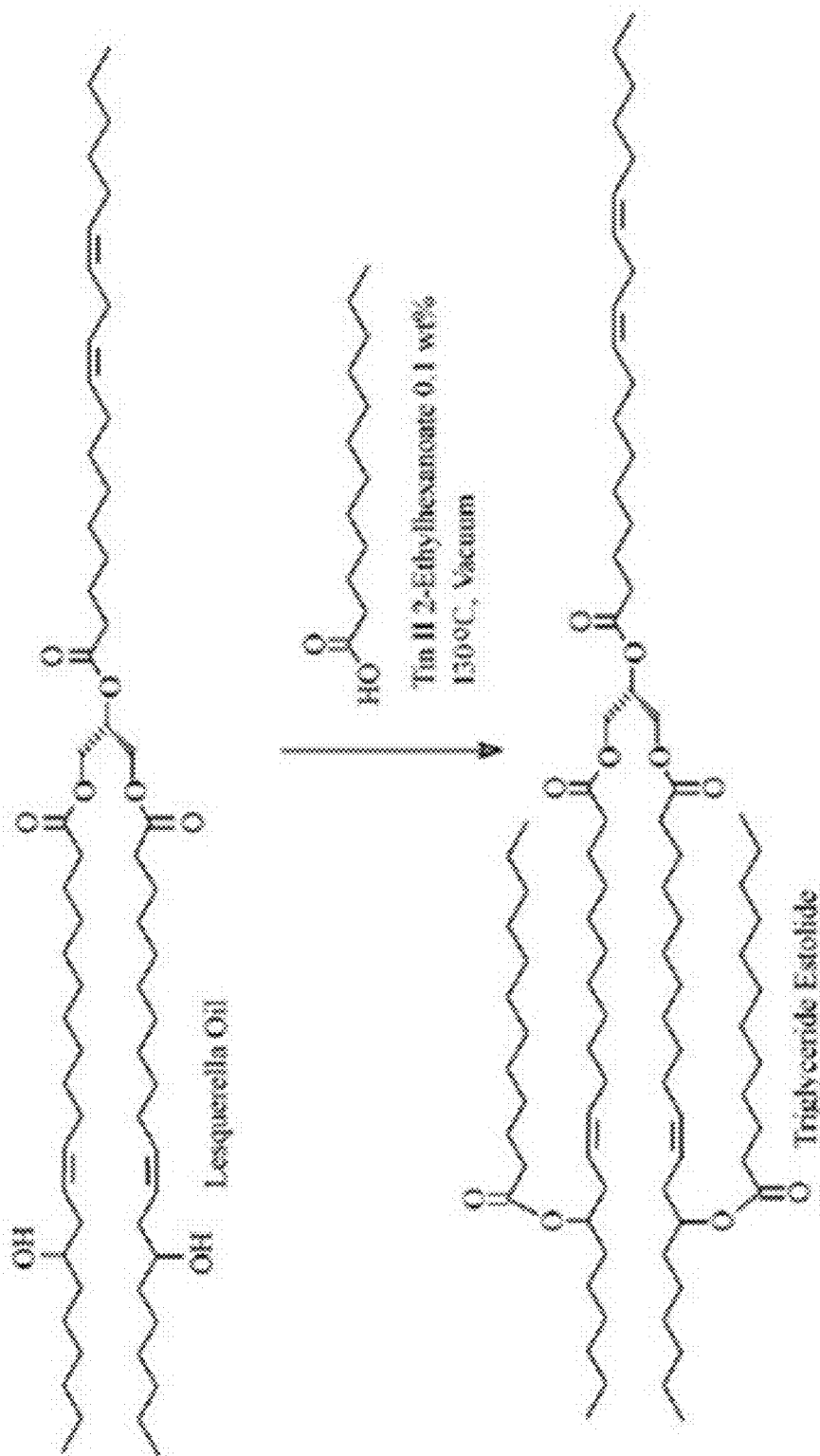


FIG. 1

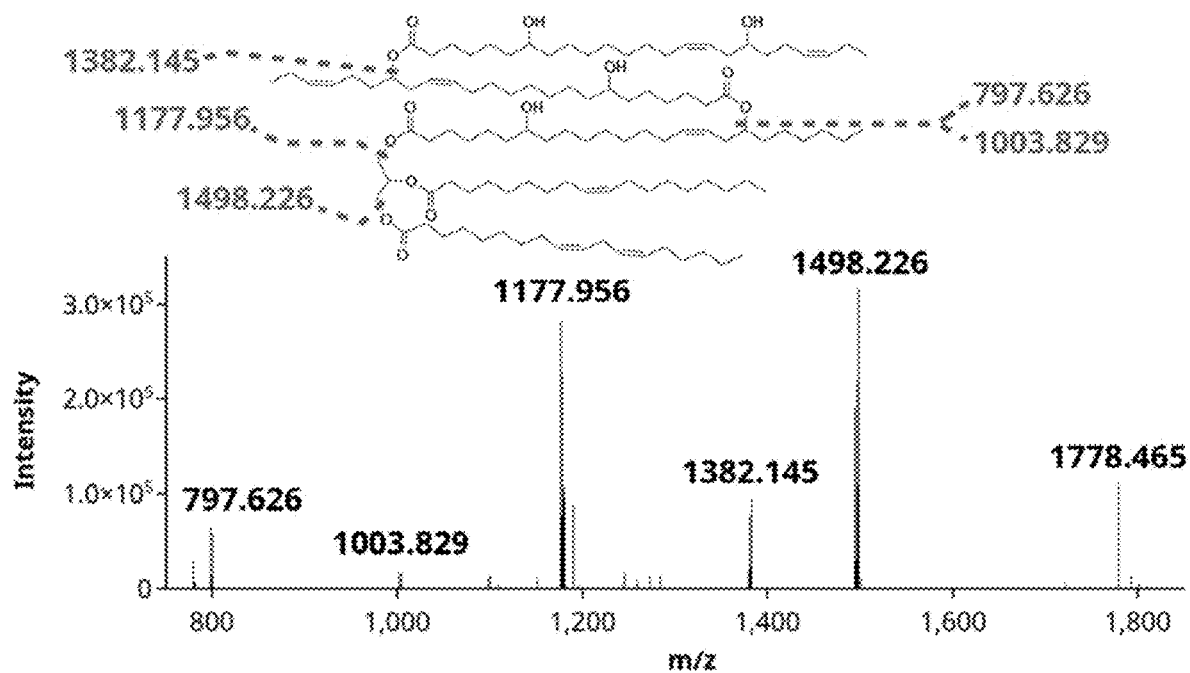


FIG. 2

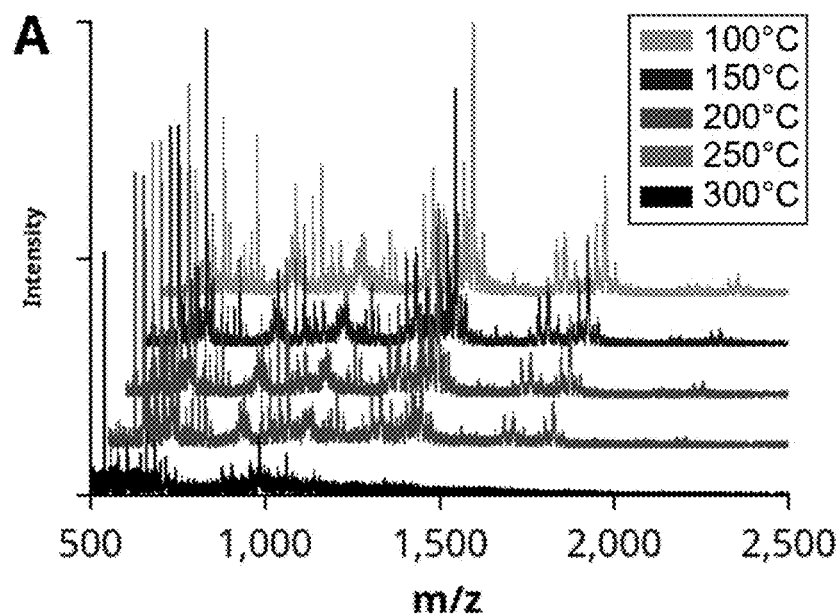


FIG. 3A

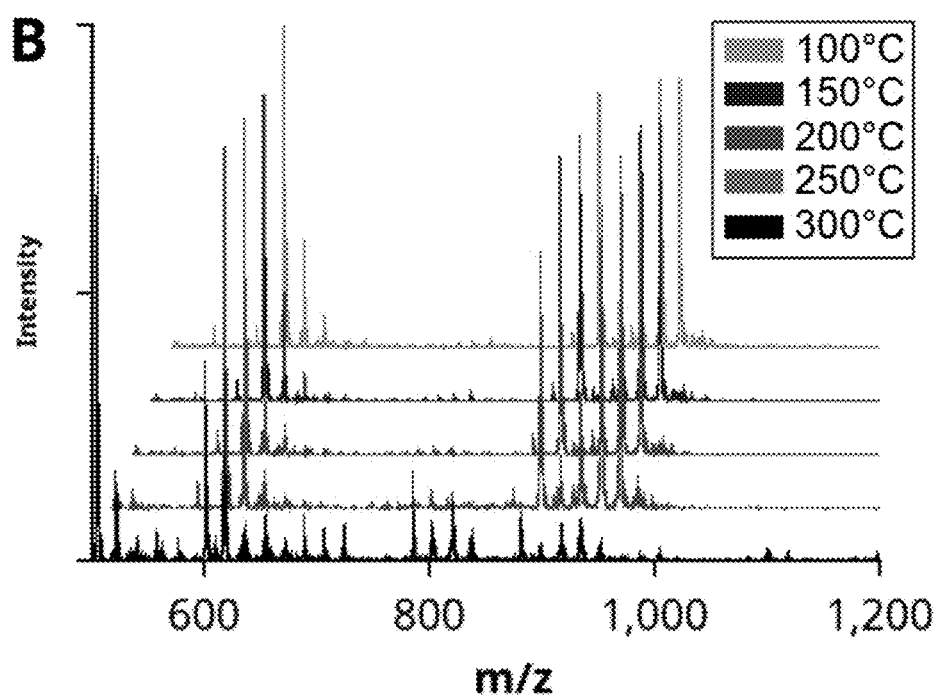


FIG. 3B

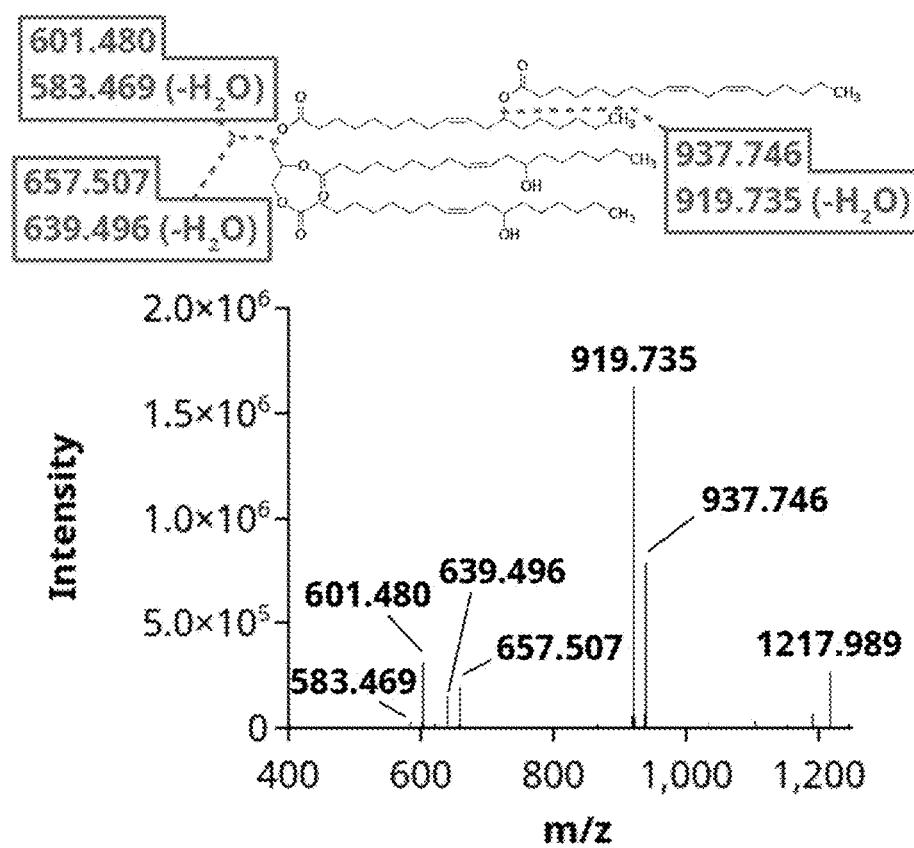


FIG. 3C

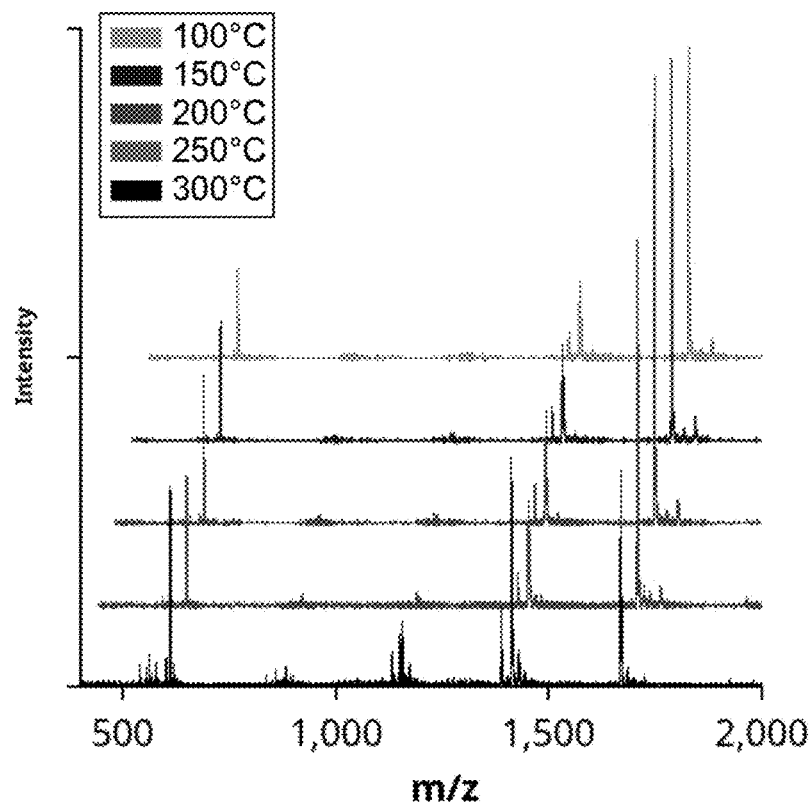


FIG. 3D

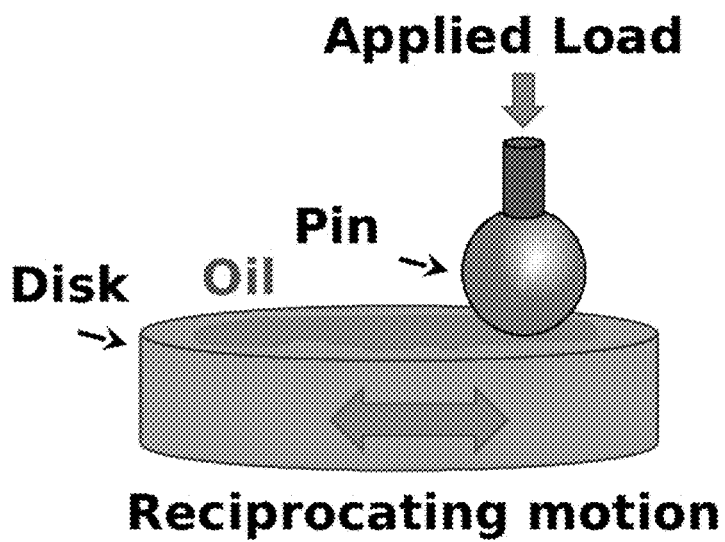


FIG. 4

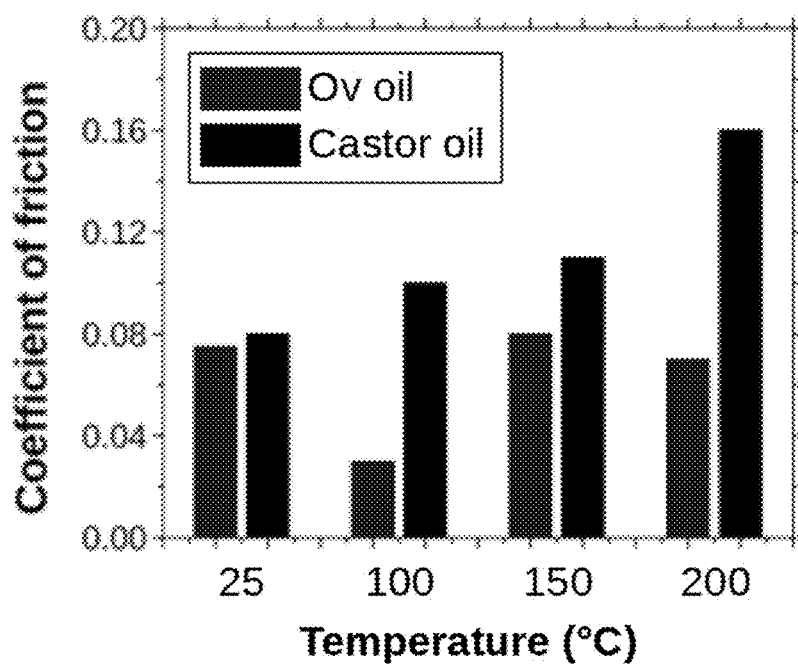


FIG. 5A

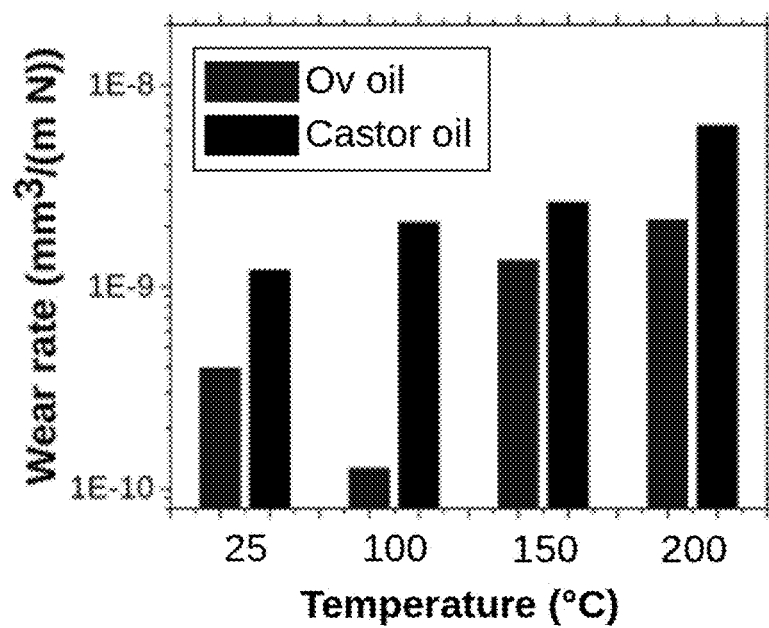


FIG. 5B

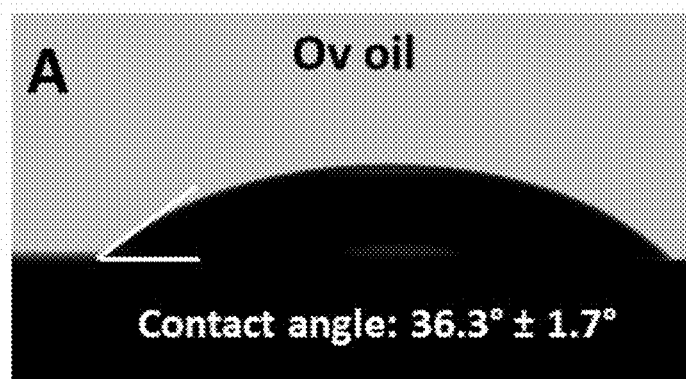


FIG. 6A

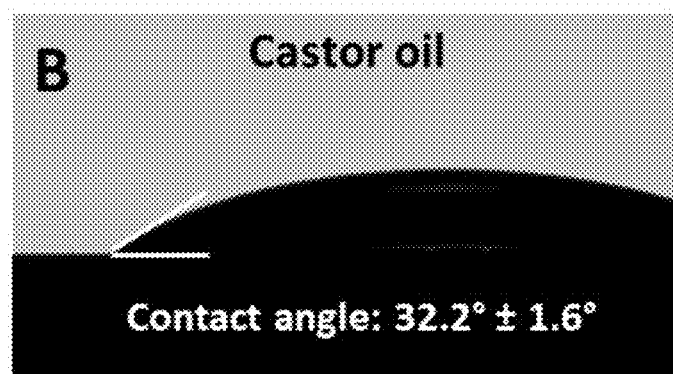


FIG. 6B

Ov oil

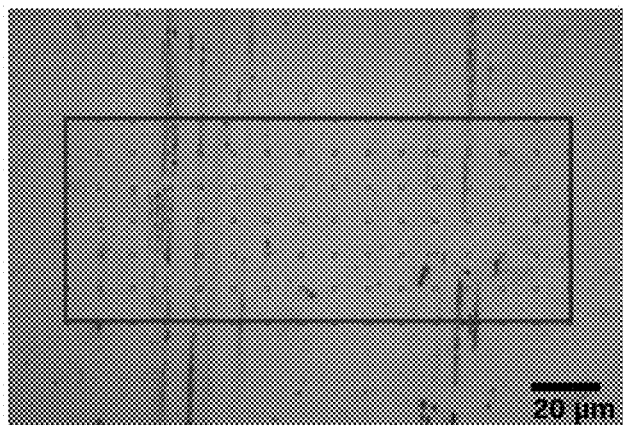


FIG. 7A

Castor oil

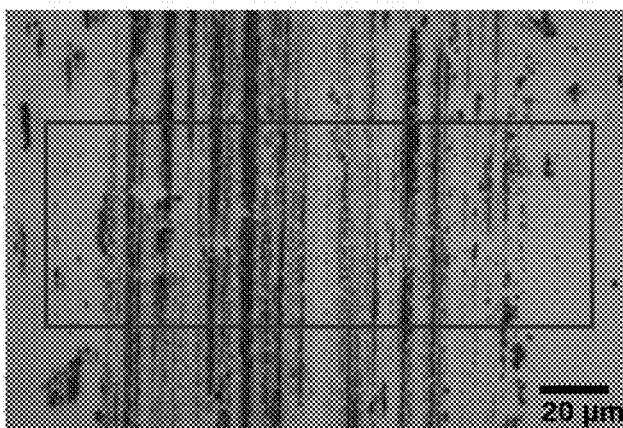


FIG. 7B

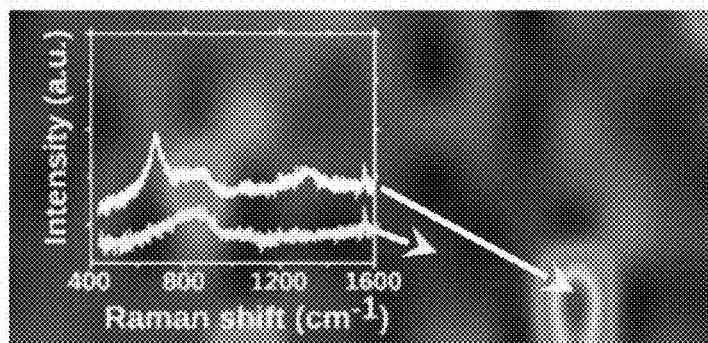


FIG. 7C

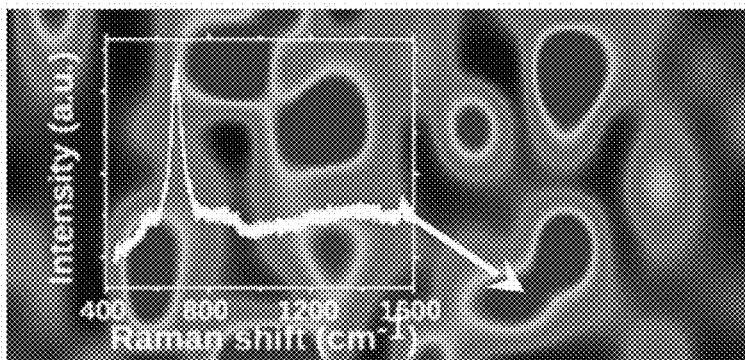


FIG. 7D

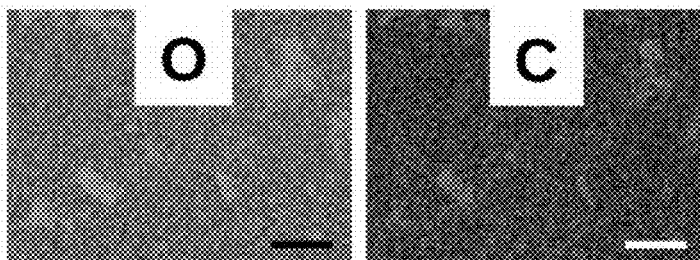


FIG. 7E

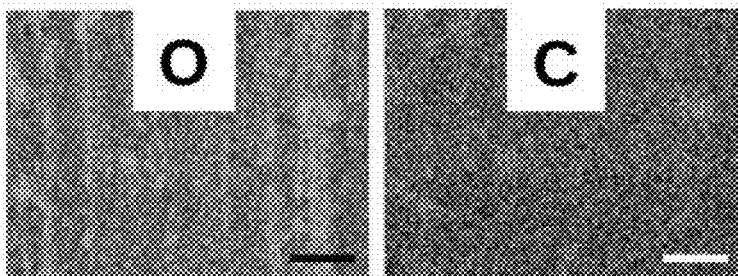


FIG. 7F

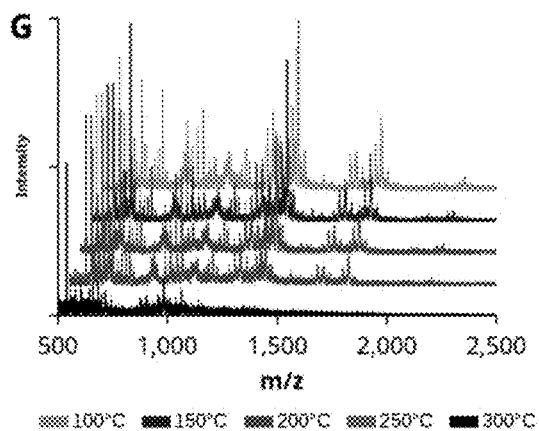


FIG. 7G

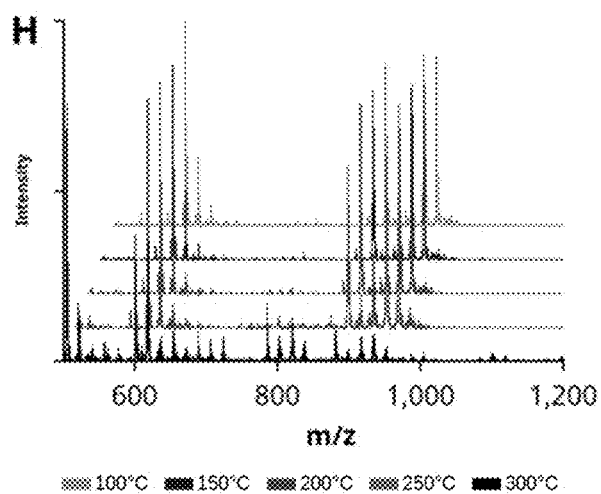


FIG. 7H

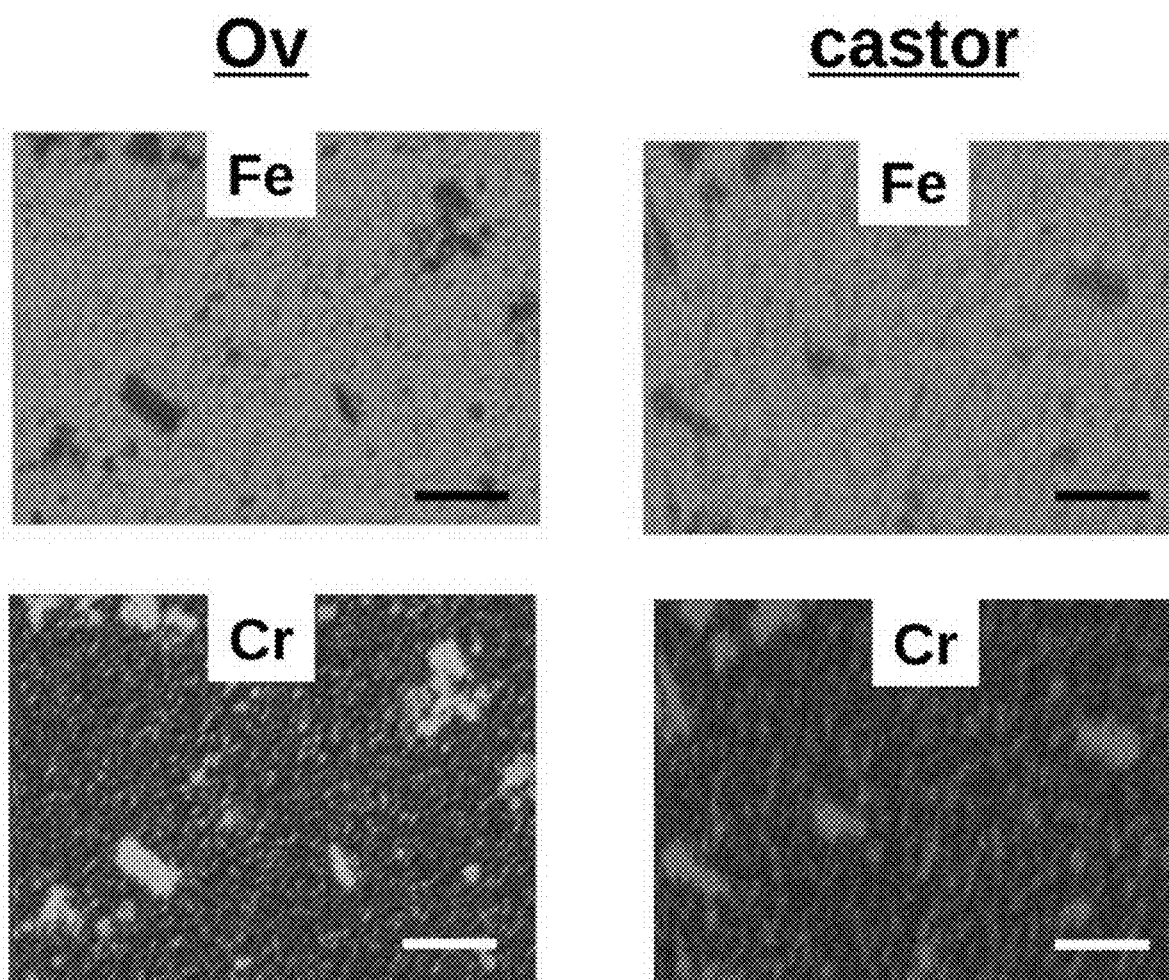


FIG. 8

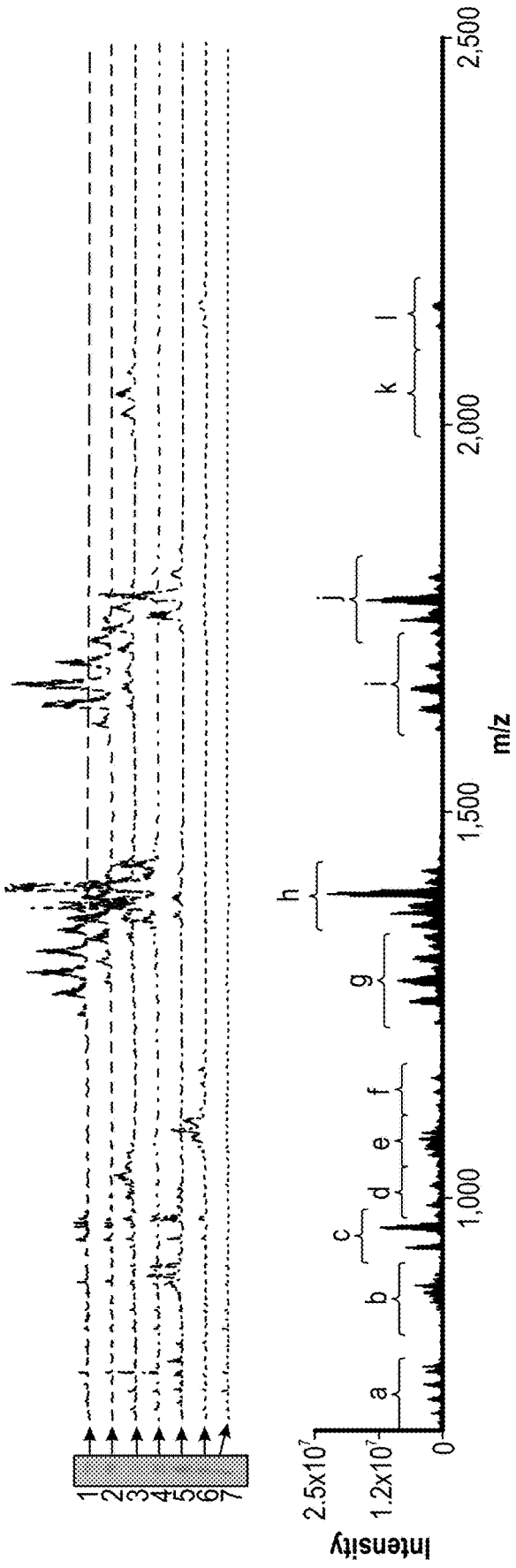


FIG. 9A

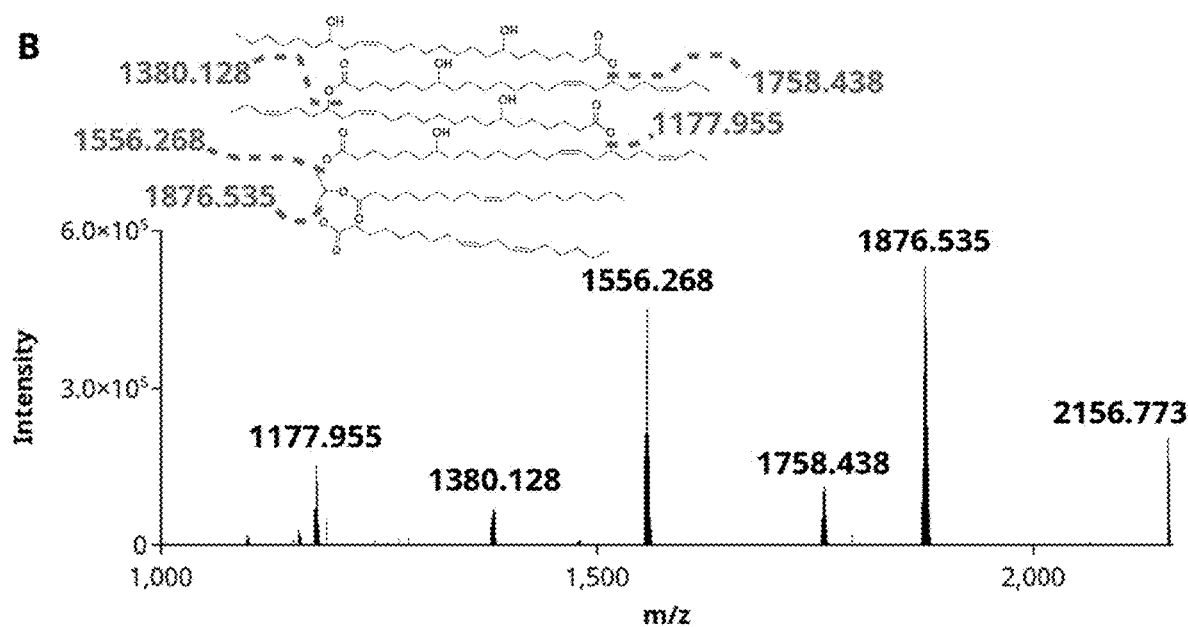


FIG. 9B

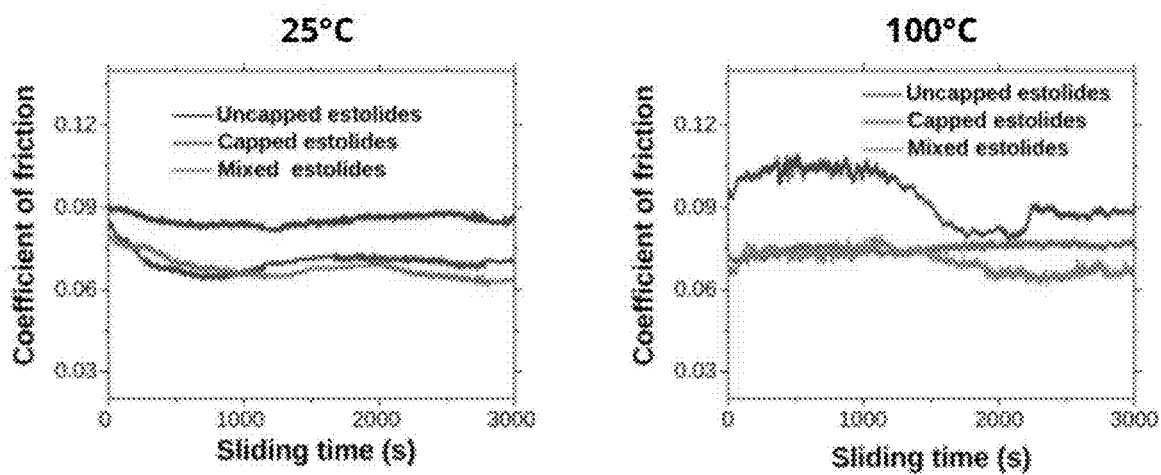


FIG. 9C

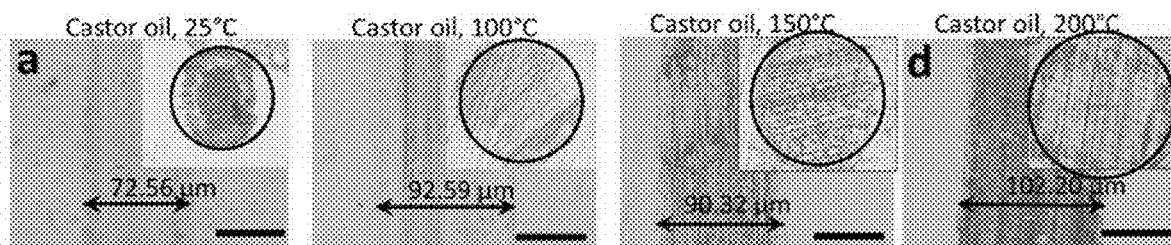


FIG. 10A

FIG. 10B

FIG. 10C

FIG. 10D

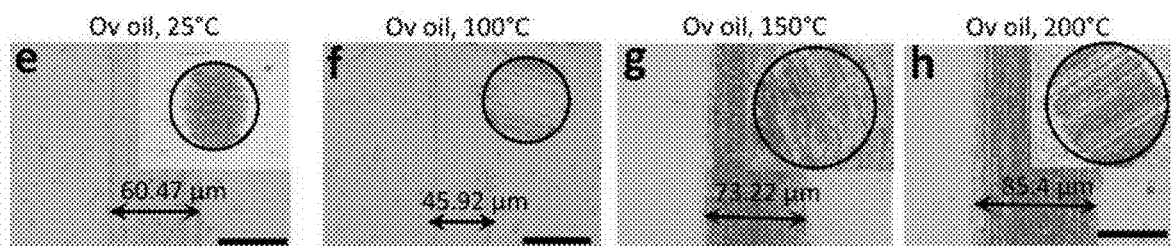


FIG. 10E

FIG. 10F

FIG. 10G

FIG. 10H

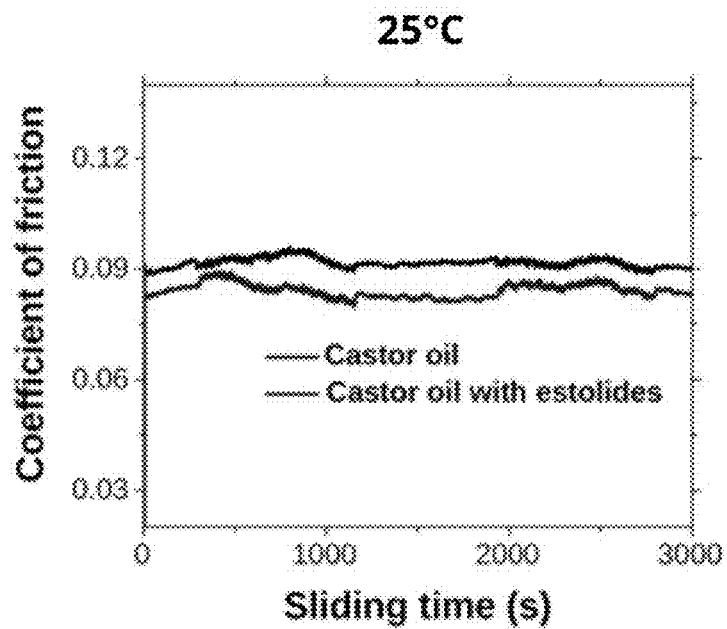
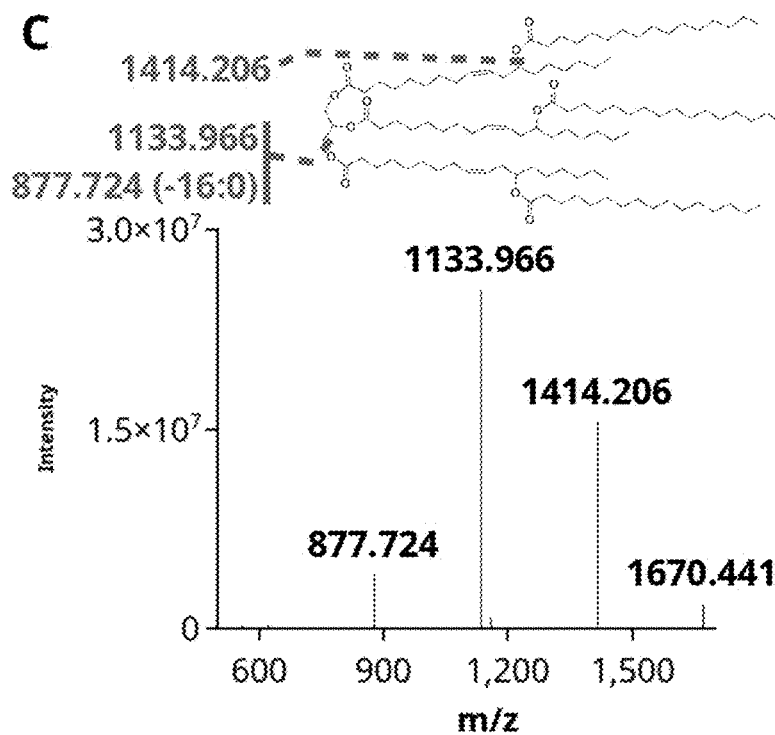
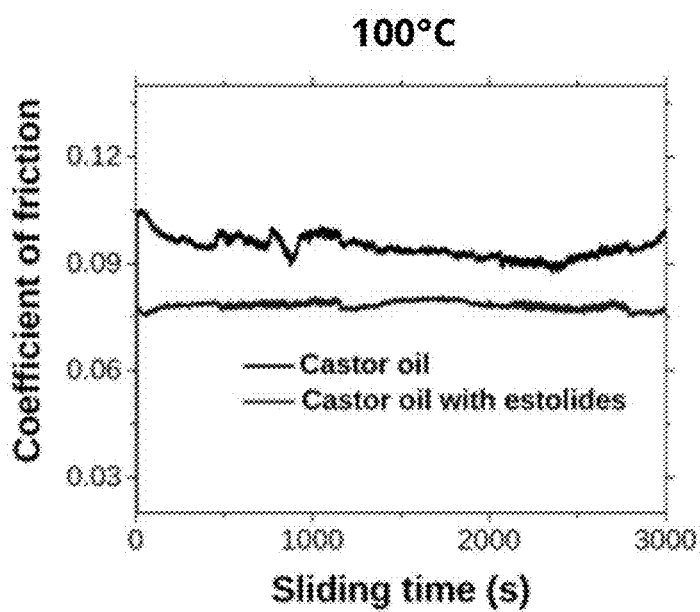


FIG. 11A



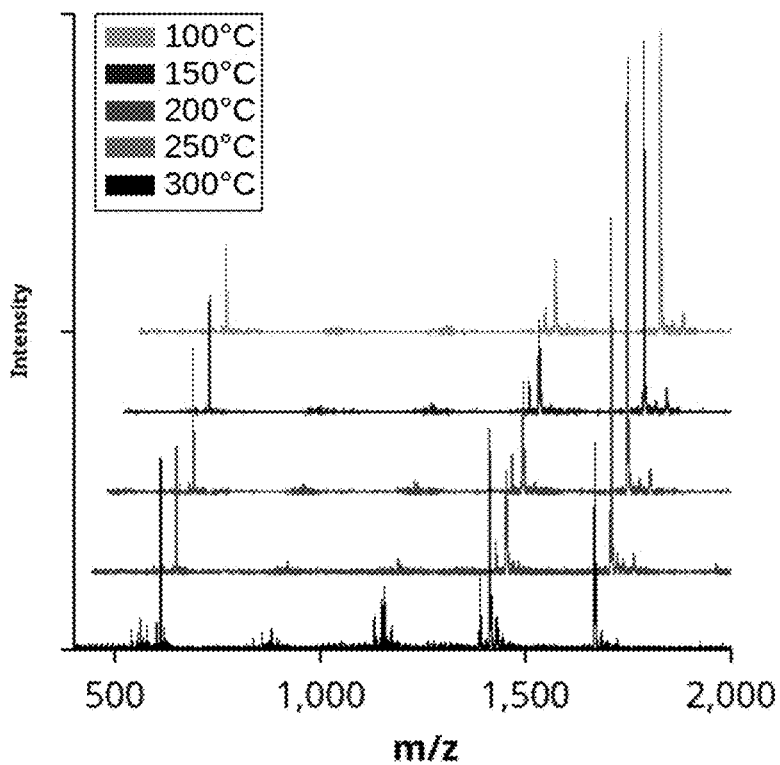


FIG. 11D

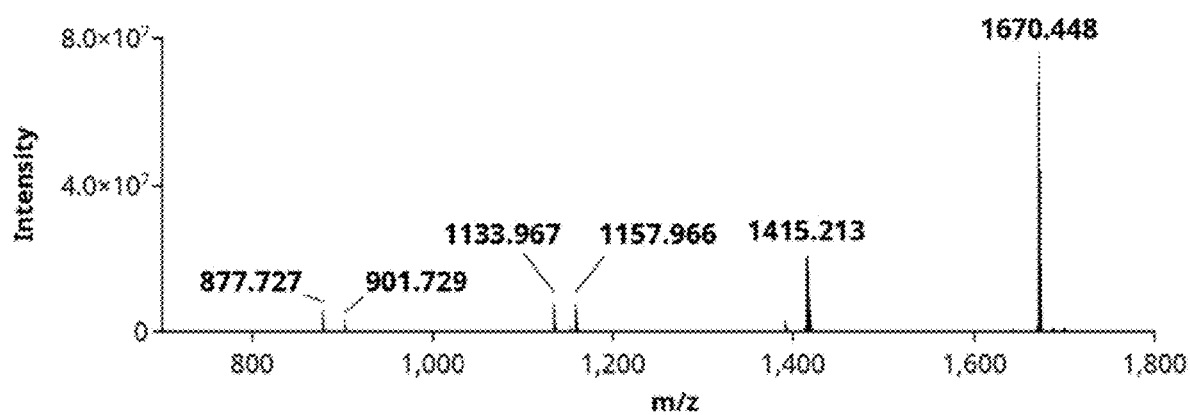


FIG. 12

Castor oil, 100°C

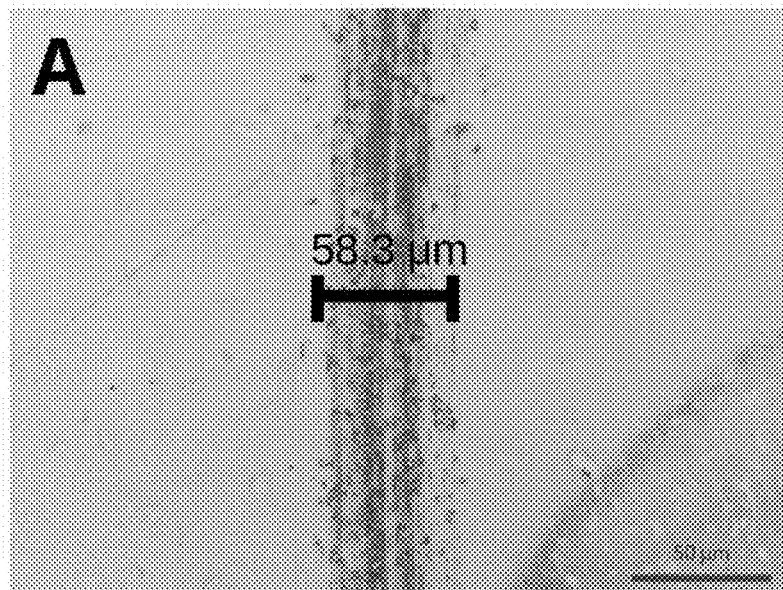


FIG. 13A

Synthetic 16:0
Castor estolides, 100°C

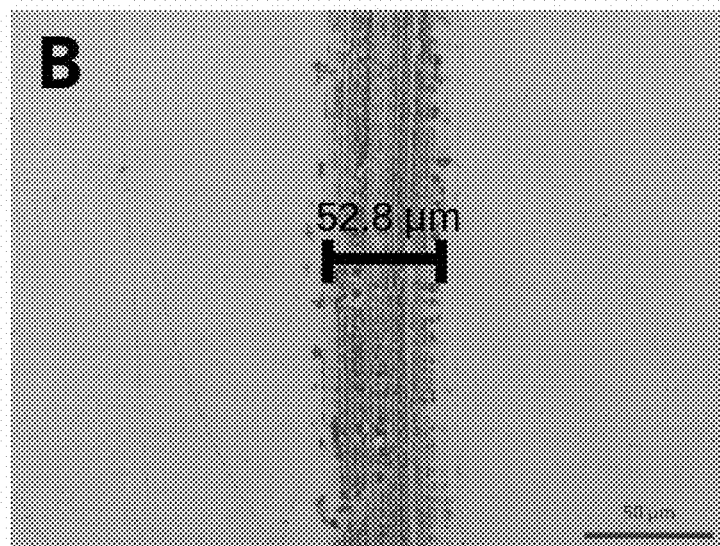


FIG. 13B

Castor oil, 100°C

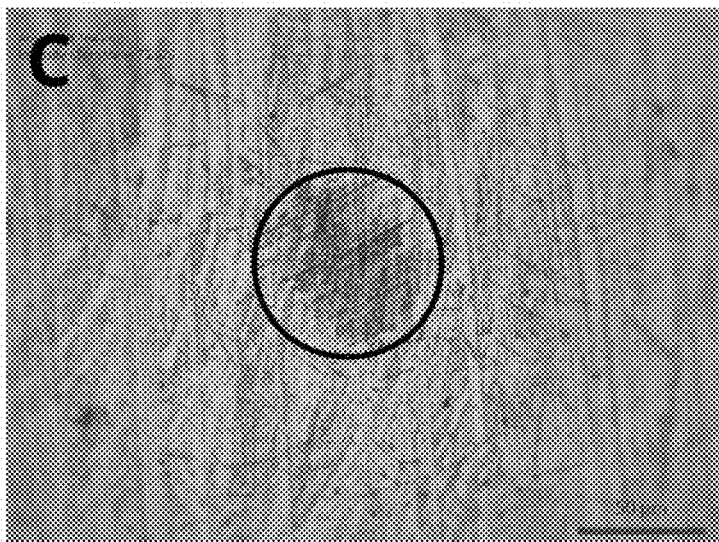


FIG. 13C

Synthetic 16:0
Castor estolides, 100°C

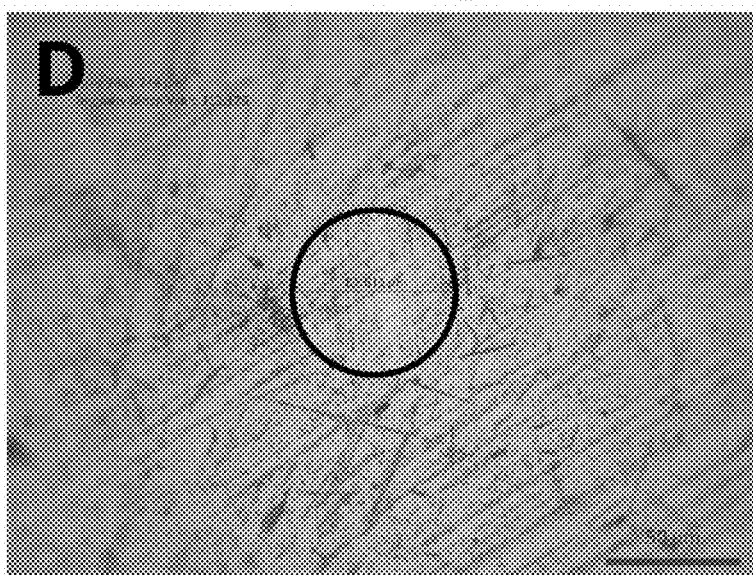


FIG. 13D

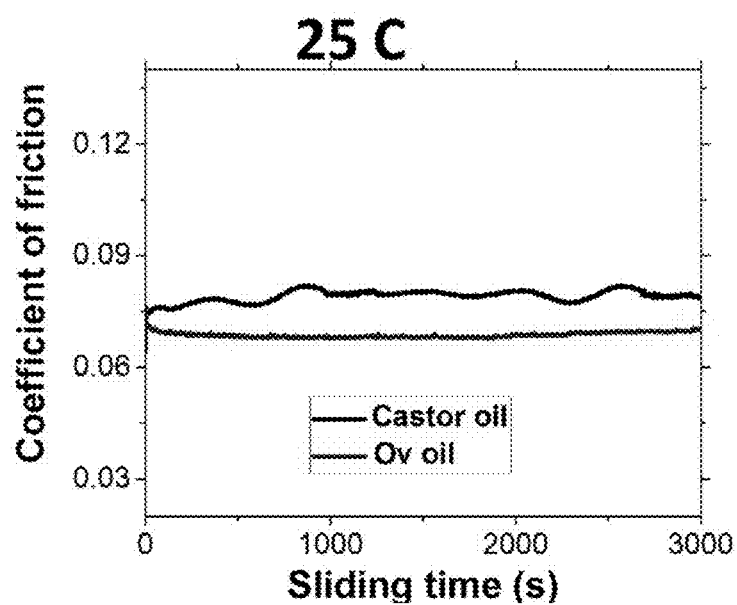


FIG. 14A

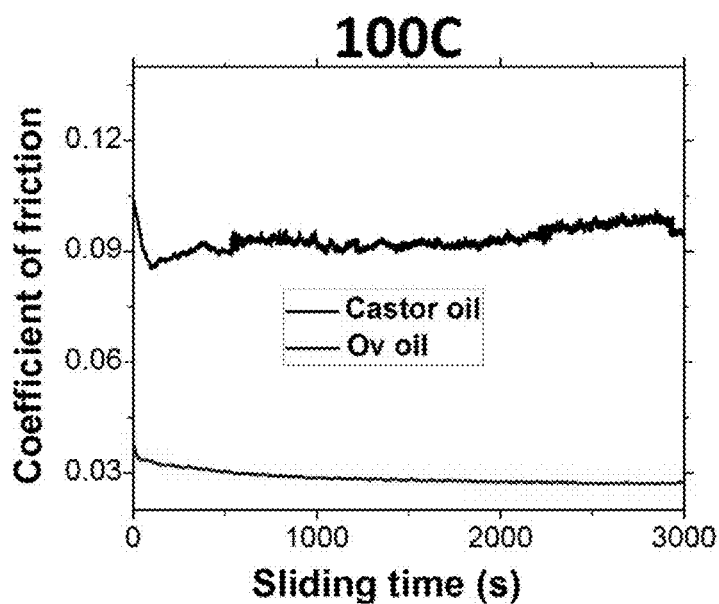


FIG. 14B

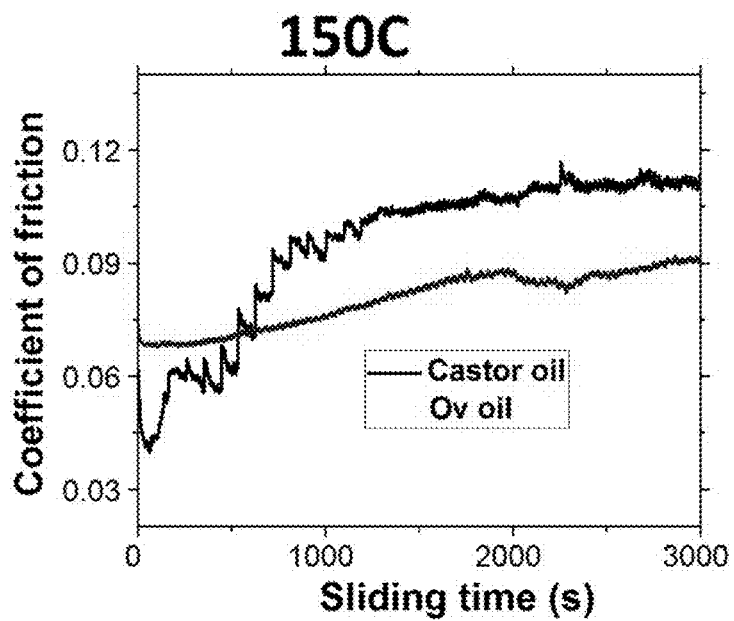


FIG. 14C

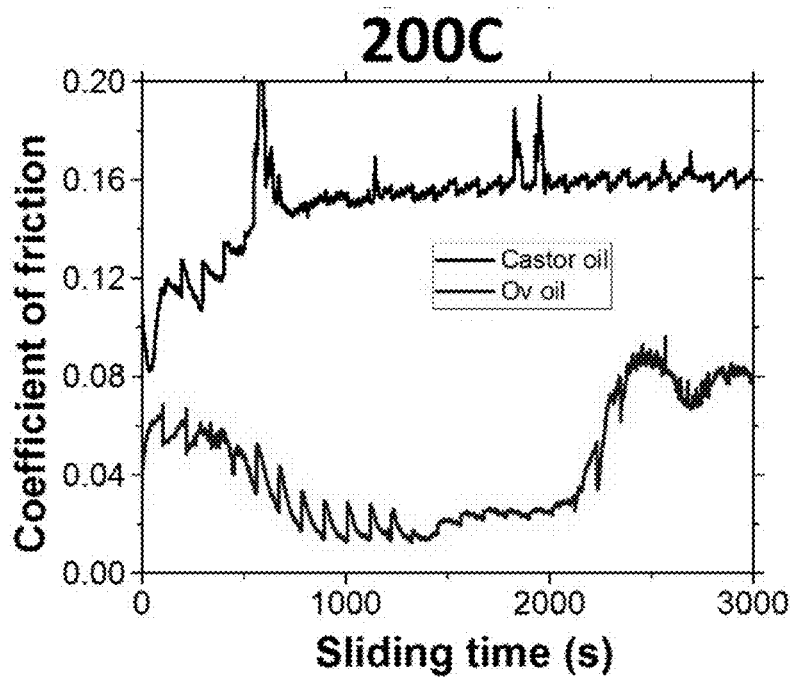


FIG. 14D

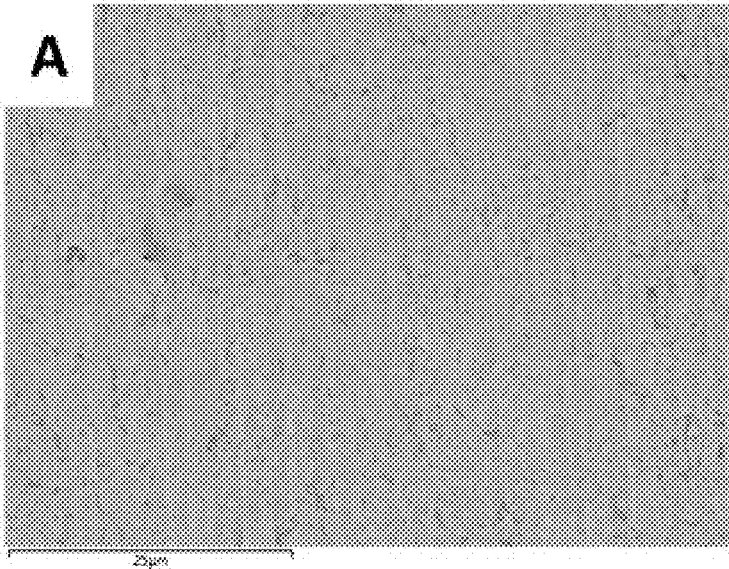


FIG. 15A

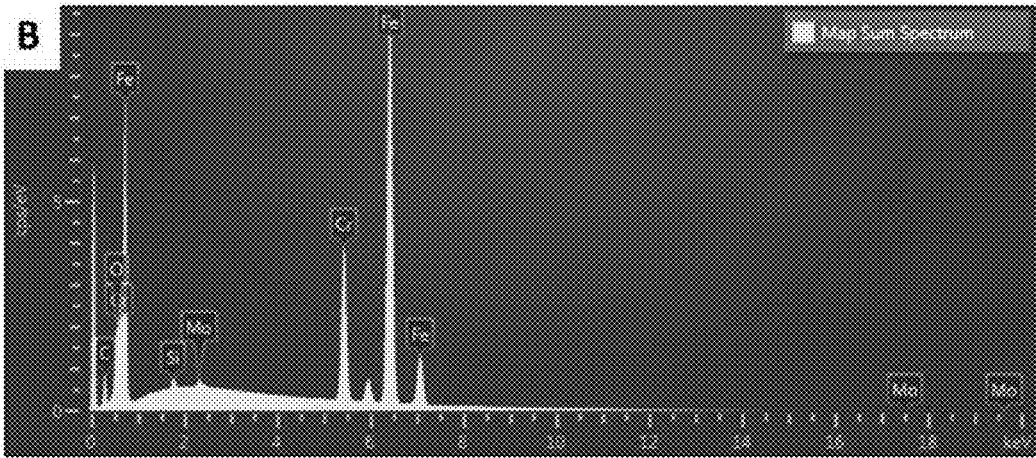


FIG. 15B

C

Element	Weight %	Atomic %
Cr	16.39	13.69
Fe	74.64	58.06
C	6.11	22.11
O	1.98	5.38
Si	0.33	0.51
Mo	0.55	0.25
Total	100.00	100.00

FIG. 15C

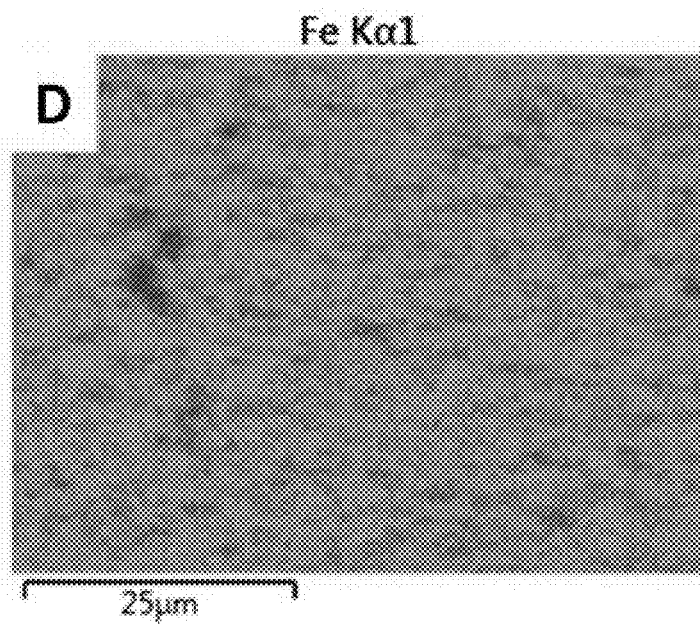


FIG. 15D

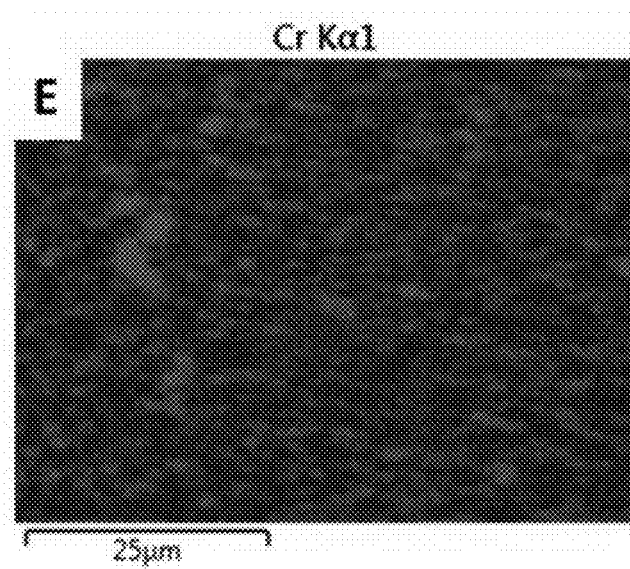


FIG. 15E

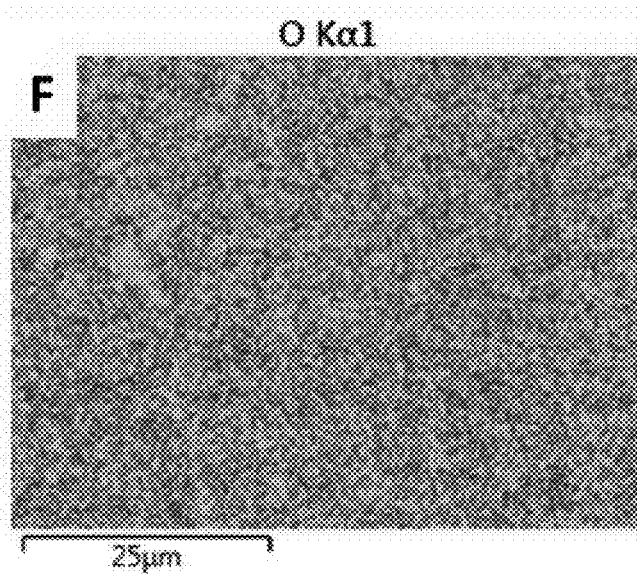


FIG. 15F

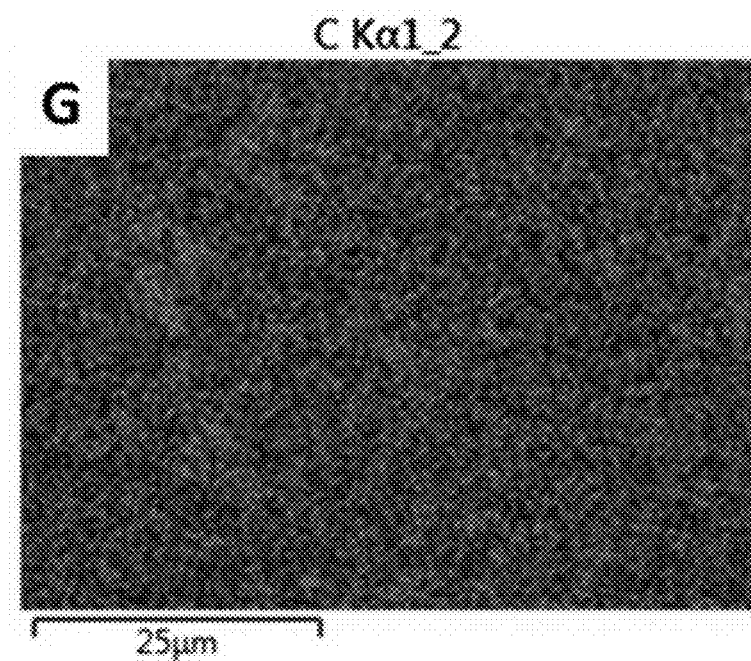


FIG. 15G

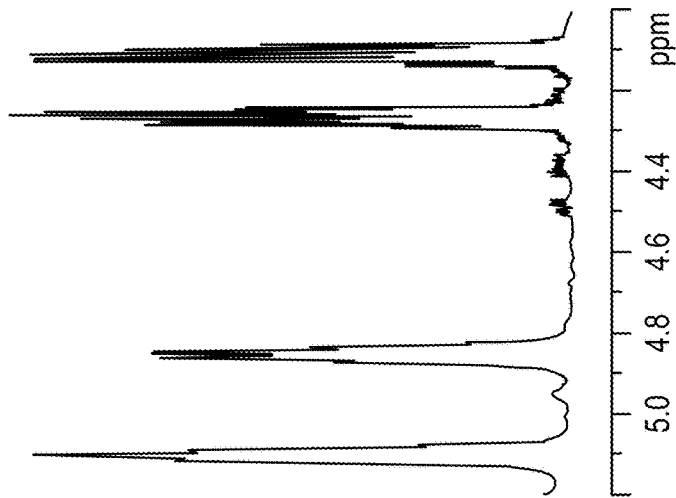


FIG. 16C

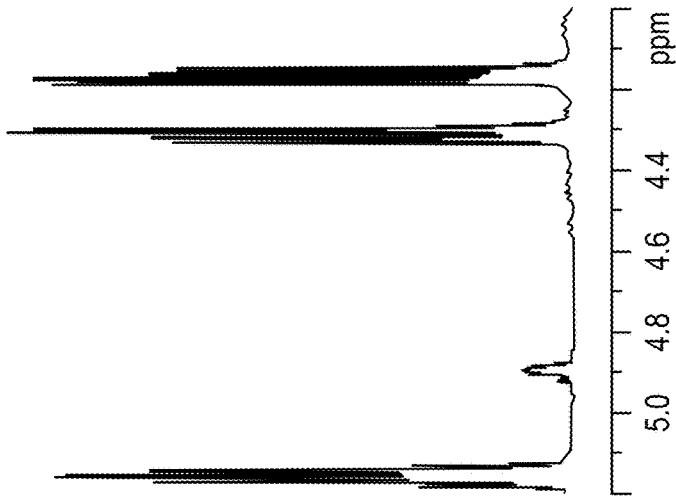


FIG. 16B

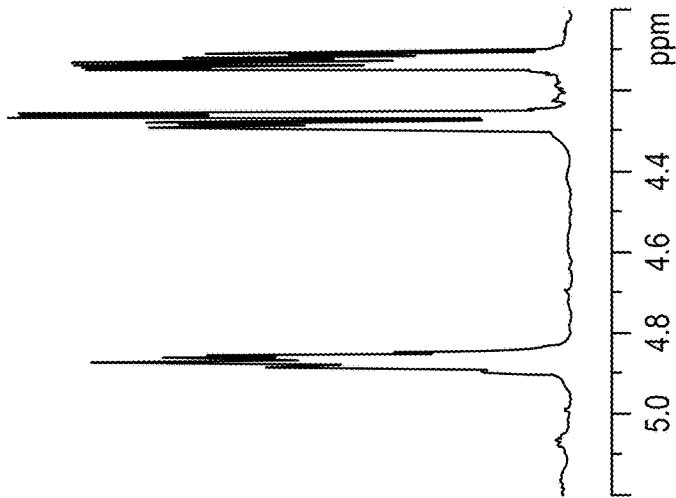


FIG. 16A

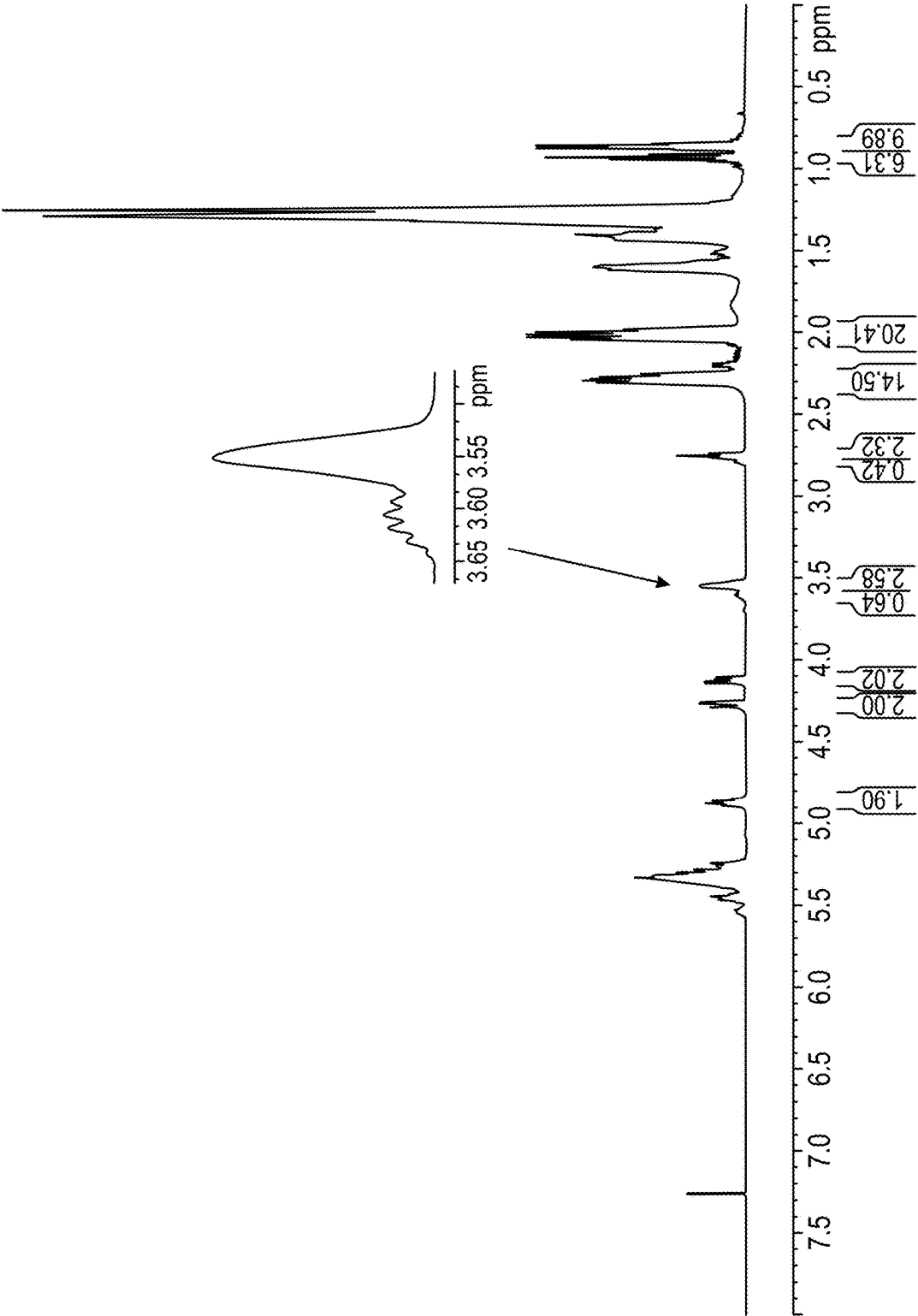


FIG. 16D

**LUBRICANT COMPOSITIONS HAVING
ENHANCED ESTOLIDE CONTENT,
METHODS OF MAKING, AND USES
THEREOF**

RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 62/924,445, filed Oct. 22, 2019, which is incorporated herein by reference in its entirety.

**STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH OR DEVELOPMENT**

[0002] This invention was made with government support under award IOS1339385 awarded by the National Science Foundation and award DE-SC0016536 awarded by the Department of Energy. The government has certain rights in the invention.

TECHNICAL FIELD

[0003] The present disclosure generally relates to lubricant compositions.

BACKGROUND

[0004] Increasing transportation and other industrial activities since the beginning of the last century have consumed much of our non-renewable energy resources (like petroleum) day by day, and a significant portion of the energy produced is spent overcoming friction in moving mechanical systems.^{4, 2} Sliding, rolling, or rotating contact interfaces in every manmade, natural or biological system generate friction. If not reduced or controlled effectively, high friction often leads to higher wear losses and, hence, shorter life and poor reliability.⁵

[0005] Consequently, friction has been one of the most active fields of study. Many researchers are still working to understand the root causes of friction and new ways to nearly eliminate it to achieve much higher efficiency and longer durability in all types of moving mechanical systems.^{6, 7}

[0006] One of the most effective ways of controlling friction is to use a lubricant in liquid, solid, and/or semisolid (grease) forms.⁸ Lubricants reduce friction by preventing sliding contact interfaces from severe or more frequent metal-to-metal contacts or by forming a low-shear, high-durability boundary film on rubbing surfaces.⁹ For example, depending on the sliding speed and other operating conditions, engine oils can effectively separate the contacting surfaces of rings and liners and, thereby, reduce the frequency of direct metal-to-metal contact and thus friction and wear.⁶

[0007] The petroleum industry offers many lubricants capable of working at customer-specified conditions. While being effective from the lubricative standpoint, synthetic oils and their derivatives are not appropriate for a range of bio-friendly applications (food and medical industry) and lead to adverse impact on the environment.¹⁰

[0008] Use of conventional oils and their products is often associated with producing hazardous waste and dangerous exhaust. While being effective from the lubricative standpoint, synthetic oils and their derivatives often are not appropriate for a range of bio-friendly applications, such as food and medical industry, and lead to adverse impact to the environment (7). Additionally, the conventional petroleum-

based oils usually gave low flash point leading to instability of oils' lubrication characteristics and their rapid degradation during thermal cycling.

[0009] There remains a need for improved lubricant compositions that overcome the aforementioned deficiencies.

SUMMARY

[0010] In some aspects, the present disclosure is directed to lubricant compositions. The lubricant compositions can be liquid or semi-solid lubricant compositions. In some aspects, the lubricant compositions include a triacylglycerol (TAG) estolide, and have been chemically modified to increase a concentration of the TAG estolide. The concentration can be increased by 2, 3, or 4 times relative to the unmodified composition. In some instances, the unmodified composition does not contain a TAG estolide or contains very little TAG estolide, and the chemical modification converts triacylglycerides in the composition to estolides.

[0011] The compositions can be chemically modified to convert a TAG to a TAG estolide. The chemical modification can include esterification of a triacylglycerol with one or more fatty acids to produce the TAG estolide. Examples of fatty acids can include palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, or a combination thereof.

[0012] Increasing the TAG estolide content has been found to improve the lubrication and temperature stability of the lubricant compositions. The TAG estolide can be capped, uncapped, or a mixture thereof. In particular aspects, the triacylglycerol (TAG) estolide includes an estolide of the triglyceride of ricinoleic acid comprising up to 3 estolide additions.

[0013] The lubricant composition can be in a semisolid form or a liquid form. In some aspects, the lubricant composition is in the form of a semisolid lubricant composition including an emulsion of (i) a thickener and (ii) an oil. The semisolid or liquid lubricant composition can include various additives such as an antioxidant, an antiwear additive, a corrosion inhibitor, a detergent, a metal deactivator, a viscosity modifier, a dispersant, or a combination thereof.

[0014] Methods of making a lubricant composition are also provided that include chemically modifying a base oil to increase a concentration of the TAG estolide relative to a reference concentration of the TAG estolide in the base oil without the chemical modification. The chemical modification can include esterification of a triacylglycerol with one or more fatty acids to produce the TAG estolide. The one or more fatty acids can be selected from the group consisting of palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, and a combination thereof.

[0015] The methods can include reacting a fatty acid with a chloride source and a dimethylformamide catalyst to produce an acyl chloride; and then reacting the acyl chloride with a triacylglyceride in the oil to produce the TAG estolide. Chloride sources can include a thionyl chloride, an oxalyl chloride, or a combination thereof.

[0016] Other systems, methods, features, and advantages of lubricant compositions will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional systems, methods, features, and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Further aspects of the present disclosure will be readily appreciated upon review of the detailed description of its various embodiments, described below, when taken in conjunction with the accompanying drawings.

[0018] FIG. 1 is a structure of estolide molecules derived from *Lesquerella* seed oil by chemical catalysis.

[0019] FIG. 2 is a MALDI-MS/MS of uncapped diacyl TAG estolide 108:8-6OH.

[0020] FIGS. 3A-3D show thermal stability of Ov and castor oils. ESI-MS showed the greatest thermal degradation occurred at 300° C. for both Ov (FIG. 3A) and castor (FIG. 3B) oil. However, castor oil showed fragmentation while m/z peaks of Ov oil decreased uniformly. Surprisingly castor oil showed the appearance of high-mass m/z peaks at 300° C. not found in lower temperatures. The peak at m/z 1217.991 from the 300° C. treated castor oil was selected for MALDI-MS/MS (FIG. 3C) and found to be an oleoyl estolide of tri-ricinolein. Analysis of synthetic castor estolides (FIG. 3D) showed similar results as for Ov and unmodified castor between 100° C. and 250° C. with few changes. At 300° C. the synthetic castor estolides showed thermal degradation by the loss of the estoylated palmitate, demonstrating the presence of estolides affects the means of thermal degradation compared to the fragmentation observed in unmodified castor oil (FIG. 3B).

[0021] FIG. 4 shows schematic of the experimental setup employed for measuring lubrication characteristics of the oil using pin-on-disk macroscale tribometer at the reciprocating mode with precise temperature control up to 450° C.

[0022] FIGS. 5A-5B show coefficient of friction (CoF) measurements (FIG. 5A) and wear rate of steel surfaces used in CoF measurements (FIG. 5B) for Ov and castor oils at 25° C., 100° C., 150° C., and 200° C.

[0023] FIGS. 6A-6B show wetting characteristics of Ov oil in comparison to castor oil. Both Ov oil (FIG. 6A) and castor oil (FIG. 6B) create low contact angle with underlying steel substrate, thus further supporting high lubricity potential.

[0024] FIGS. 7A-7H depict analysis of the wear tracks formed in castor and Ov oil. Analysis of the wear track formed after the 100° C. tribotest of sliding steel surfaces lubricated with (FIG. 7A) Ov oil and (FIG. 7B) castor oil. Raman 2D map of the iron oxide peak (at $\sim 675\text{ cm}^{-1}$) of the (FIG. 7C) Ov oil indicates very little oxidation of the steel surface during sliding in contrast to the (FIG. 7D) castor oil. Detailed EDS analysis of the wear tracks formed during lubrication with (FIG. 7E) Ov oil and (FIG. 7F) castor oil confirms this results suggesting the better oxidation resistance and protection properties of the Ov oil. FIGS. 7G and 7H show electrospray ionization mass spectrometry (ESI-MS) following exposure to temperatures ranging from 100° C. to 300° C. of Ov seed oil and castor oil, respectively.

[0025] FIG. 8 depicts SEM-EDS elemental maps of Ov and castor oil wear tracks for chromium and iron. Little difference is seen between Ov oil and castor oil lubricated surfaces for the elemental maps of iron (Fe) or chromium (Cr) (scale bar=10 μm).

[0026] FIGS. 9A-9C depict Ov TAG estolide structure characterization. ESI-MS analysis of seed oil shows peaks of high m/z values (FIG. 9A). MS/MS and calculating m/z values show presence of: a) PC and diacyl estolide fragments, b) doubly charged diacyl estolide TAG, c) hydroxyl-TAG, d) doubly charged capped triacyl estolide TAG, e)

doubly charged uncapped triacyl estolide TAG, f) triacyl estolide fragments, g) capped monoacyl estolide TAG, h) uncapped monoacyl estolide TAG, i) capped diacyl estolide TAG, j) uncapped diacyl estolide TAG, k) capped triacyl estolide TAG, and l) uncapped triacyl estolide TAG. HPTLC separation of OV seed oil separates estolide TAG by 1) capped monoacyl estolide TAG, 2) capped diacyl estolide TAG, 3) capped triacyl estolide TAG, 4) uncapped monoacyl estolide TAG, 5) uncapped estolide TAG, and 6) uncapped estolide TAG.

[0027] FIGS. 10A-10H depict wear tracks and wear marks formed on steel surfaces during tests in Ov (FIGS. 10E-10H) and castor (FIGS. 10A-10D) oils. Analysis of the wear Tracks for the tests performed OV and Castor oils at (FIG. 10A and FIG. 10E) 25° C., (FIG. 10B and FIG. 10F) 100° C., (FIG. 10C and FIG. 10G) 150° C. and (FIG. 10D and FIG. 10H) 200° C.

[0028] FIGS. 11A-11D demonstrate increased estolide content in castor oil for improving the lubrication properties of the oil. Coefficient of friction results for castor oil with increased estolides number at (FIG. 11A) RT and at (FIG. 11B) 100° C. (FIG. 11C) structure of the oil and (FIG. 11D) thermal degradation stability of the oil.

[0029] FIG. 12 depicts MALDI-MS of synthetic 16:0 castor oil estolides. MALDI-MS of synthetic castor estolides shows the presence of tripalmitoylated ricinolein (102:3-3OH) at m/z 1670.448, dipalmitoylated 18:1-1OH/18:1-1OH/18:2 (86:4-2OH) at m/z 1415.213, monopalmitoylated 18:1-1OH/18:2/18:2 (70:5-1OH) at m/z 1157.966, monopalmitoylated 18:1-1OH/16:0/18:2 (68:3-1OH) at m/z 1133.967, and hydroxy TAG 18:2/18:2/18:2 at m/z 901.729 and 18:2/18:2/16:0 at m/z 877.727.

[0030] FIGS. 13A-13D depict wear marks of unmodified Castor oil and synthetic 16:0 castor estolides. The synthetic castor estolides produced less wear during tribotests for both surface tracks (FIGS. 13A-13B) and ball tracks (FIGS. 13C-13D) (scale bar=50 μm). The surface track width for unmodified castor oil (FIG. 13A) measured 58.3 μm versus 52.8 μm for synthetic castor estolides (FIG. 13B), and the ball track diameters measured 72.2 μm for unmodified castor oil (FIG. 13C) compared to 61.6 μm for the synthetic castor estolides.

[0031] FIGS. 14A-14D depict tribological analysis of the Ov oil in comparison to castor oil. Tribology behavior of the Ov and Castor oils at (FIG. 14A) 25° C., (FIG. 14B) 100° C., (FIG. 14C) 150° C. and (FIG. 14D) 200° C.

[0032] FIGS. 15A-15G depict analysis of the wear track formed in synthetic 16:0 castor estolides. SEM EDS analysis of the (FIG. 15A) weartrack formed during the tribological test: (FIG. 15B) detailed spectra acquired from the wear track with (FIG. 15C) relative concentration of different elements. Detailed map of (FIG. 15D) iron, (FIG. 15E) chromium, (FIG. 15F) oxygen, and (FIG. 15G) carbon atoms shows almost no contrast, thus indicating efficient lubricative nature of the estolides.

[0033] FIGS. 16A-16D are a complete 500-MHz proton NMR spectrum for unfractionated Ov estolide oil in CDCl_3 at 28° C. The full spectrum (FIG. 16D), shows the estolide, glycerol methylene, and hydroxy-bearing methine resonances within the region from δ 5.24-3.5 ppm, as well as other signals corresponding to the acyl chains. FIGS. 16A-16C show an expansion of the methine on the carboxyl side of an estolide ester (δ $\sim$ 4.9) and the doublet of doublet (dd) resonances for the methylene hydrogens of the glycerol

backbone at approximately δ 4.1 and 4.3 ppm. (FIG. 16A) Expansion for Ov oil with the estolide signal at δ 4.86. Spectral data is shown for benzoylated castor oil (FIG. 16B), where the homoallylic estolide methine at C-12 is further downfield at δ 5.15 but the glycerol resonances are unperturbed. In benzoylated Ov oil (FIG. 16C), both naturally occurring and benzoyl estolides linkages are observed. Of note, signals from the glycerol backbone are more complex, altered by the proximate benzoyl ester at C-7, possibly stemming from magnetic anisotropy. In FIG. 16D, the smaller, downfield multiplet for the methine of the free C-18 alcohol and the prominent broad methine resonance at C-7 for the free hydroxyl group in Ov oil are observed, consistent with the estolides primarily occurring at C-18 on wuhanic/nebraskanic chains.

DETAILED DESCRIPTION

[0034] In various aspects, the disclosure is directed to lubricant compositions and methods of making lubricant compositions. Lubricant compositions made with oils having increased estolide content have been determined to have a variety of beneficial properties. The lubricants can include liquid and semisolid lubricants.

[0035] Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, and as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting. The skilled artisan will recognize many variants and adaptations of the embodiments described herein. These variants and adaptations are intended to be included in the teachings of this disclosure and to be encompassed by the claims herein.

[0036] All publications and patents cited in this specification are cited to disclose and describe the methods and/or materials in connection with which the publications are cited. All such publications and patents are herein incorporated by references as if each individual publication or patent were specifically and individually indicated to be incorporated by reference. Such incorporation by reference is expressly limited to the methods and/or materials described in the cited publications and patents and does not extend to any lexicographical definitions from the cited publications and patents. Any lexicographical definition in the publications and patents cited that is not also expressly repeated in the instant specification should not be treated as such and should not be read as defining any terms appearing in the accompanying claims. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present disclosure is not entitled to antedate such publication by virtue of prior disclosure. Further, the dates of publication provided could be different from the actual publication dates that may need to be independently confirmed.

[0037] Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described. Functions or constructions well-known in the art may not be described in detail for brevity and/or clarity. Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of nanotechnology, organic chemistry, material sci-

ence and engineering and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

[0038] It should be noted that ratios, concentrations, amounts, and other numerical data can be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a numerical range of “about 0.1% to about 5%” should be interpreted to include not only the explicitly recited values of about 0.1% to about 5%, but also include individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure, e.g. the phrase “x to y” includes the range from ‘x’ to ‘y’ as well as the range greater than ‘x’ and less than ‘y’. The range can also be expressed as an upper limit, e.g. ‘about x, y, z, or less’ and should be interpreted to include the specific ranges of ‘about x’, ‘about y’, and ‘about z’ as well as the ranges of ‘less than x’, ‘less than y’, and ‘less than z’. Likewise, the phrase ‘about x, y, z, or greater’ should be interpreted to include the specific ranges of ‘about x’, ‘about y’, and ‘about z’ as well as the ranges of ‘greater than x’, ‘greater than y’, and ‘greater than z’. In some embodiments, the term “about” can include traditional rounding according to significant figures of the numerical value. In addition, the phrase “about ‘x’ to ‘y’”, where ‘x’ and ‘y’ are numerical values, includes “about ‘x’ to about ‘y’”.

[0039] Reference throughout this specification to “one embodiment”, “an embodiment”, “another embodiment”, “some embodiment,” means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases “in one embodiment,” “in an embodiment,” “in another embodiment”, or “in some embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, the particular features, structures or characteristics may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments. Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention. For example, in the appended claims, any of the claimed embodiments can be used in any combination.

Definitions

[0040] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the specification and relevant art and should not be interpreted in an idealized or overly formal sense unless expressly defined herein.

[0041] The articles “a” and “an,” as used herein, mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of “a” and “an” does not limit the meaning to a single feature unless such a limit is specifically stated. The article “the” preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used.

[0042] The term “fatty acid,” as used herein, refers to a saturated or unsaturated monocarboxylic acid having an aliphatic tail, which may include from about 4 to about 32 carbon atoms. The fatty acid may be a saturated monocarboxylic acid having the general formula $C_nH_{2n+1}COOH$, wherein n is a positive integer. In one example, n may be from about 4 to about 28. The aliphatic tail of the fatty acid may have one or more hydroxyl functional groups, or the tail of the fatty acid may be free of hydroxyl functional groups. The fatty acid may occur naturally in the form of esters in fats, waxes, and essential oils or in the form of glycerides in fats and fatty oils. Examples of fatty acids can include, but are not limited to, oleic acid, myristic acid, palmitic acid, rumenic acid, vaccenic acid, myristoleic acid, palmitoleic acid, stearic acid, and alpha-linoleic acid. It may also include any other conventional fatty acids, derivatives thereof, and combinations thereof. For ease of description, fatty acids will in some aspects be described using the nomenclature “X:Y—(OH)_z” where X is the number of carbon atoms in the chain, Y is the number of double bonds in the chain, and Z is the number of hydroxyl groups. If there are no hydroxyl groups, the nomenclature is simply “X:Y”. For example, a fatty acid having 24 carbon atoms, 1 double bond, and 2 hydroxyl groups can be denoted by “24:1-(OH)₂”.

[0043] The terms “triacylglycerol” and “triacylglyceride”, as interchangeably used herein, refer to tri esters of three fatty acids (or estolides thereof) and glycerol. For ease of description, triacylglycerols will in some aspects be described by the structure of each of the fatty acids from which it is derived using the nomenclature [X:Y—(OH)_z]₁—[X:Y—(OH)_z]₂—[X:Y—(OH)_z]₃ where each occurrence “X:Y—(OH)_z” describes the structure of one of the three fatty acids in the triacylglyceride and can be the same or different. For example, [18:2]₁—[18:2]₂—[24:1-(OH)₂]₃ describes the tri ester of glycerol with three fatty acids with (i) two of them having 18 carbon atoms and 2 double bonds and (ii) the third having 24 carbon atoms, 1 double bond, and 2 hydroxyl groups.

[0044] The term “estolide,” as used herein, refers to a fatty acid or an ester thereof having a secondary ester linkage of one or more additional fatty acids to an alkyl backbone. The nomenclature of estolides will be, in some aspects, by identifying the two or more fatty acids using the nomenclature for fatty acids described above. For example, 18:2-(OH)₁-18:1(OH)₂ describes an estolide of the fatty acid 18:2-(OH)₁ having a secondary ester linkage of 18:1(OH)₂ attached thereto. The estolide nomenclature can also be combined with the nomenclature for triacylglycerols described above. In some aspects, the TAG estolides are referred to by a nomenclature with the following structure: aa:bb-nOH, where ‘aa’ refers to the number of C in the FA moieties, ‘bb’ refers to the number of unsaturations, and ‘n’ refers to the number of OH groups from the dihydroxy FAs present. For example, the uncapped diacyl TAG estolide of 108:8-6OH (FIG. 2) contains 108 C in the FAs, 8 unsatu-

rations, and 6 OH groups from the dihydroxy FAs. TAG estolides with hFAs at the terminal end of the estolide branch chain are called “uncapped”, while those TAG estolides with nonhydroxy FAs at the terminal end are “capped” TAG estolides.

[0045] The term “petroleum oil,” as used herein, refers to oils produced entirely or primarily from fossil material, such as petroleum, natural gas, coal, etc.

[0046] The term “synthetic oil,” as used herein, refers to products produced by reacting carboxylic acids with glycerol, e.g., glycerol triacetate, and the like. It will be understood that such synthetic oils can contain between about 0.1 wt % to about 20 wt. % mono- and di-glycerides, and mixtures thereof.

[0047] The term “semisolid,” as used herein, refers to compositions that at or around room temperature, e.g. at a temperature of about 15° C. to 25° C., are not free flowing in the same way as a liquid and may have a consistency of a paste, cream, or a grease.

[0048] Lubricant Compositions and Methods of Making Lubricant Compositions

[0049] In various aspects of this disclosure, lubricant compositions are provided containing oil that has been chemically modified to increase the estolide content. Previous results indicated that long chain di-hydroxy fatty acids and estolides thereof demonstrate excellent lubricant properties.

[0050] In some aspects, the present disclosure is directed to lubricant compositions. The lubricant compositions can be liquid or semi-solid lubricant compositions. In some aspects, the lubricant compositions include a triacylglycerol (TAG) estolide, and have been chemically modified to increase a concentration of the TAG estolide. The concentration can be increased by 2, 3, or 4 times relative to the unmodified composition. In some instances, the unmodified composition does not contain a TAG estolide or contains very little TAG estolide, and the chemical modification converts triacylglycerides in the composition to estolides.

[0051] The compositions can be chemically modified to convert a TAG to a TAG estolide. The chemical modification can include esterification of a triacylglycerol with one or more fatty acids to produce the TAG estolide. Examples of fatty acids can include palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, or a combination thereof.

[0052] Increasing the TAG estolide content has been found to improve the lubrication and temperature stability of the lubricant compositions. The TAG estolide can be capped, uncapped, or a mixture thereof. In particular aspects, the triacylglycerol (TAG) estolide includes an estolide of the triglyceride of ricinoleic acid comprising up to 3 estolide additions.

[0053] The lubricant composition can be in a semisolid form or a liquid form. In some aspects, the lubricant composition is in the form of a semisolid lubricant composition including an emulsion of (i) a thickener and (ii) an oil. The semisolid or liquid lubricant composition can include various additives such as an antioxidant, an antiwear additive, a corrosion inhibitor, a detergent, a metal deactivator, a viscosity modifier, a dispersant, or a combination thereof.

[0054] Methods of making a lubricant composition are also provided that include chemically modifying a base oil to increase a concentration of the TAG estolide relative to a reference concentration of the TAG estolide in the base oil

without the chemical modification. The chemical modification can include esterification of a triacylglycerol with one or more fatty acids to produce the TAG estolide. The one or more fatty acids can be selected from the group consisting of palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, and a combination thereof. In one embodiment, the base oil is a petroleum or syncrude fraction recovered from the fractionation operation.

[0055] The methods can include reacting a fatty acid with a chloride source and a dimethylformamide catalyst to produce an acyl chloride; and then reacting the acyl chloride with a triacylglyceride in the oil to produce the TAG estolide. Chloride sources can include a thionyl chloride, an oxalyl chloride, or a combination thereof.

[0056] In some aspects, the Ov oil has been processed to increase the estolide content. For example, the estolide content can be increased via esterification of a triacylglycerol. Suitable esterification reactions are described, for instance, in U.S. Pat. No. 5,427,704 to Lawate, the contents of which are incorporated by reference. In some aspects, the oil is esterified with one or more C 24:2 (OH)₂ and C24:1 (OH)₂ fatty acids. In some aspects, the estolides are capped, i.e. containing a non-hydroxylated fatty acid. In some aspects, the estolides are uncapped, i.e. containing a di-hydroxy fatty acid.

[0057] In various aspects, the lubricant compositions include one or more additives. Additives can be oil additives and/or grease additives. In various aspects, the additives are antioxidant such as (+)- α -tocopherol (TCP), propyl gallate (PG), l-ascorbic acid 6-palmitate (AP), 4,4'-methylenebis(2,6-di-tert-butylphenol) (MBP), butylated hydroxyl anisole (BHA), butylated hydroxyl toluene (BHT), propyl gallate (PG), or tert-butyl hydroquinone (TBHQ). In some aspects, the additive is an antiwear additive such as zinc dithiophosphate (ZDP), zinc dialkyl dithiophosphate (ZDDP), tricresyl phosphate (TCP), dioleoyl phosphite, bis(2-ethylhexyl) phosphate, diphenyl cresyl phosphate, triphenyl phosphorothionate, chlorinated paraffins, glycerol monooleate, or a combination thereof. The additives can include a corrosion inhibitor such as a thiadiazole, a benzotriazole, a tolutriazole, a zinc dithiophosphate, a metal phenolate, a metal sulfonate, a fatty acid, a carboxylic acid, an amine, and a combination thereof. The additive can include a detergent such as a polyisobutylene succinimide, a polyisobutylene amine succinamide, an aliphatic amine, a polyolefin maleic anhydride, or a combination thereof. Metal deactivators such as a triazole, a tolyltriazole, a thiadiazole, or a combination thereof can also be included as additives in some aspects. In some aspects, the additives include viscosity modifiers such as an ethylene-olefin co-polymer, a maleic anhydride-styrene alternating copolymer, a polymethacrylate, a hydrogenated styrene-butadiene copolymer, a hydrogenated styrene-isoprene copolymer, an ester thereof, or a combination thereof. The additives can also include dispersants such as succinimide, benzylamine, or a combination thereof.

[0058] In some aspects, semisolid lubricants are provided wherein the oil is emulsified with a thickener. For example, an oil can be emulsified with a thickener to form a semisolid lubricant. In some aspects, a mixture of triacylglycerols fatty acids and estolides thereof are emulsified with a thickener to form a semisolid lubricant. Suitable thickeners can include a soap such as calcium stearate, sodium stearate, lithium stearate, lithium 12-hydroxystearate, and a combination thereof.

[0059] Uses of Lubricant Compositions

[0060] The lubricant compositions can be used in a variety of applications, for example in engines or in other industrial applications. The lubricant compositions can replace many uses of petroleum-based lubricants and/or many uses of castor oil based lubricants. Any number of applications will be readily ascertained upon reading the present disclosure when accompanied with the below examples.

Examples

[0061] Now having described the embodiments of the present disclosure, in general, the following Examples describe some additional embodiments of the present disclosure. While embodiments of the present disclosure are described in connection with the following examples and the corresponding text and figures, there is no intent to limit embodiments of the present disclosure to this description. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

[0062] These examples unravel the origin of biolubricity of plant-based oils by analyzing the structure of *Orychophragmus violaceus* seed oil and transfer this knowledge to improve friction and wear reducing characteristics of one of a commonly used biolubricant, castor oil. The characterization analysis demonstrates that the major component contributing to excellent antioxidation and thermal stability performance of the oils is the presence of capped and uncapped estolides unleashing their full potential at specific to their structure temperature regimes. As it is shown with castor oil, extraction of estolides from Ov oil enables design of environmentally friendly thermally stable lubricants in a wide range of existing oil crops.

[0063] Materials and Methods

[0064] *Orychophragmus violaceus* Seed Oil Extraction:

[0065] Approximately 30 mg of *O. violaceus* seeds were used per extraction for oil used in MS applications. Seeds were homogenized by bead beating for 45 sec with glass beads (Biospec Mini-Bead-Beater-16, Bartlesville, Okla., USA) in 1 ml of 70° C. isopropanol with 0.01% butylated hydroxytoluene (BHT, w/v). An additional 1 ml of 70° C. isopropanol was added to wash out homogenization tubes and collected with homogenized sample. The homogenized seeds were incubated at 70° C. for 30 min to extract total lipids. Following incubation, 1 ml of CHCl₃ and 0.45 ml of distilled water were added to each extraction. Samples were left to extract overnight at 4° C. Extracted samples had an additional 2 ml of isopropanol, 1 ml CHCl₃, and 0.45 ml of water added before vortexing and centrifugation to sediment homogenized material. Supernatant was transferred to fresh tubes and then partitioned with the addition of 1 ml of CHCl₃ and 2 ml of 1 M KCl. Partitioned samples were vortexed and centrifuged. The aqueous top layer was aspirated off, and this washing was repeated two more times. Following the wash, the organic layer was evaporated to dryness under nitrogen gas. Dried extracts were resuspended in 1 ml of CHCl₃ until prepared for MS analysis.

[0066] Tribology Tests:

[0067] The Ov oil used for tribology tests was extracted directly from the seeds of Ov plants by cold pressing and filtering through a paper filter (Sigma Aldrich). The density of the Ov oil was measured to be 0.905 g/cm³. The viscosity of the Ov oil measured with Brookfield DV-II+ viscometer was 1209 centipoise. Density and viscosity of the cold

pressed castor oil used as a baseline for the comparison analysis were 0.959 g/cm³ and 612 centipoises correspondingly. The tribology tests were done using an Anton Paar macroscale pin-on-disk tribometer with the 10 μ N sensitivity of the frictional force sensor. The tests were performed at least 3 times to ensure reproducibility of the results. The tribology tests were performed in a linear reciprocating mode with 10 mm running distance and 1 Hz frequency of reciprocating motion. For the elevated temperature tests performed in the range of 25 up to 300° C. the stability of the setup, the temperature was demonstrating $\pm 1^\circ$ C. accuracy.

[0068] Testing of the lubrication efficiency of the Ov oil was performed using mirror-polished (roughness ~ 20 -30 nm) 440 C stainless steel flat and ball (6 mm in diameter) samples. The samples were heat treated to demonstrate the maximum hardness of 58 $\pm$ 2 HRC. Both the substrate and counterbody were cleaned by acetone before running the test. The samples were submerged with 1.5 ml of oil during the tribology tests. The tests were performed at a maximum contact pressure of 1.5 GPa, indicating the boundary lubrication regime.

[0069] Characterization of the Wear:

[0070] After the tests, to perform further characterization of the wear tracks formed, the excess of oil was removed and the samples were rinsed with acetone followed by isopropanol.

[0071] The wear volume of wear scar on the pin side was calculated based on the following equations

$$V = \left(\frac{\pi h}{6} \right) \left(\frac{3d^2}{4} + h^2 \right) \quad (1)$$

where d is the wear scar diameter, r is the radius of the ball, and

$$h = r - \sqrt{r^2 - \frac{d^2}{4}} \quad (2)$$

[0072] The optical images of the wear tracks were acquired using a Zeiss optical microscope. The micrographs and Energy Dispersive Spectroscopy (EDS) mapping were done by using FEI Quanta 200 Scanning Electron Microscope (SEM) equipped with EDS. The oxidation of the wear tracks was further characterized by Raman analysis performed using Nicolet Almega XR Dispersive Raman spectrometer with a green laser (wavelength of 534 nm).

[0073] HPTLC, ESI-MS, and MS/MS Analysis of Ov Oil:

[0074] Extracts used for HPTLC separation were diluted 1:10 in CHCl₃. Diluted lipid extract was spotted in a series of 2 μ l spots on to an HPTLC plate (EMD Millipore HPTLC, Ca. no. 1.51160.0001). Spotted HPTLC plates were run in a solvent system of 70:30:1 diethyl ether/heptane/acetic acid. One lane of the HPTLC plate was cut off and then charred by spraying with an aqueous solution of 10% cuprous sulfate with 8% phosphoric acid. Sprayed cut section of the HPTLC plate was charred in hot oven until dark bands were visible. The cut section of the HPTLC plate that was charred was used to guide the scraping of the bands from the uncharred portion of the HPTLC plate. Bands were scraped off the

HPTLC plate using a razor blade. Scrapings for each apparent band were collected separately and then extracted with 1 ml CHCl₃/MeOH (1:1, v/v) three times. Extracted washes were collected together and evaporated under nitrogen until dryness until prepared for ESI-MS analysis.

[0075] Extracted seed oil and extracted lipids scratched off from HPTLC plate used in ESI-MS analysis was diluted and resuspended in 1:100 in CHCl₃/MeOH/500 mM ammonium acetate (1:1:0.02, v/v/v) prior to analysis. From seed oils assayed for thermal stability and friction coefficients, 30 mg of spent seed oil was massed and then dissolved 1:100 (wt/v) in CHCl₃/MeOH (2:1, v/v) until prepared for ESI-MS analysis in which dissolved oil was diluted 1:100 further in CHCl₃/MeOH/500 mM ammonium acetate (1:1:0.02, v/v/v) prior to analysis. Samples were analyzed by direct infusion ESI-MS using an API 3000 triple quadrupole mass spectrometer (Applied Biosystems). The following parameters were set during analysis: injection rate of 20 μ l/min, source temperature of 100° C., curtain gas of 10, nebulizing gas of 12, ionspray voltage of +5500 V, declustering potential of 100 V, other parameters were left as default. Total ion scans were collected from m/z of 700 to 2500 with a scan time of 1.8 sec for extracted seed oils, and collected from m/z 200 to 700 and 700 to 2500 for spent seed oil used in thermal stability assays. Product ion scans were collected using the same set parameters with the following exceptions: collisional energy between 35 and 45 V, and collisional cell exit potential of 14 V. Samples used in product ion scans to determine OH binding of the estolide branch from the glycerol bound hydroxy FA in negative ionization mode were conducted with the same parameters described above with the following modifications: ionization mode set to negative, ionspray voltage of -4500 V, declustering potential of -60 V, collisional energy between -45 V and -60 V, collected from m/z 50 to 850 with a scan time of 1 sec. Data was collected using Analyst software (Sciex), exported as individual text files, and then analyzed.

[0076] Solid Phase Extraction Separation of Ov TAG Estolides:

[0077] To determine the individual tribological properties of capped and uncapped TAG estolides, each type was separated using solid phase extraction (SPE) on a Supelco Discovery DSC-Si 6 ml, SPE cartridge (Sigma Aldrich cat. no. 52655-U). Ov oil was extracted in the same manner described above from approximately 2 g of seed. Oil extracts were dissolved in 2 ml of hexane and divided into four portions roughly representing 500 μ l. Each divided portion was loaded on to an individual SPE cartridge and let flow through. The solvents used to elute the TAG estolides through the column include, in the order used: 6 ml of hexane/diethylether (4:1, v/v) collected in 0.5 ml fractions, 5 ml of methanol collected in 1 ml fractions, and 3 ml of chloroform collected in a single fraction. Following the collection of the fractions, 2 μ l were spotted on to an HPTLC plate to estimate the efficacy of separation. Solvent conditions and detection for TLC analysis were the same as described above. Those fractions deemed to contain only capped or only uncapped TAG estolides were combined to form one collected sample of either capped TAG estolides or uncapped TAG estolides. Fractions containing a mixture of both capped and uncapped TAG estolides were pooled into a single collected sample to be used as a comparison to the samples containing only capped or uncapped TAG estolides. Additionally, another 1 g of Ov seeds were extracted and

separated by SPE, but had all collected fractions combined as a control unseparated oil to compare to Ov oil separated into capped, uncapped, and mixed samples. In both the separated and unseparated oils a waxy, resinous material eluted during the chloroform wash and was collected but not mixed into any of the collected or pooled fractions as its identity could not be determined by TLC. On the TLC plate this fraction remained as a spot at the origin with no apparent migration. The separated TAG estolides were then used in tribological measurements to determine the properties of each kind of TAG estolides relative to the unseparated Ov oil, labeled as "mixed."

[0078] MALDI-MS and MS/MS Analysis of Ov Seed Oil:

[0079] Extracted *O. violaceus* oil was analyzed by MALDI-MS/MS using a MALDI-LTQ-Orbitrap-XL mass spectrometer (ThermoScientific) by spotting 5 μ L of 1:10 oil diluted in CHCl_3 on to a Superfrost Plus microscope slide (Fisherbrand), dried under a stream of nitrogen gas. Dried spots were coated with 2,5-dihydroxybenzoic acid (2,5-DHB) by sublimation. Mass spectrometer parameters were set as follows: laser energy of 12 μ J/pulse, 10 laser shots per step, normalized collision energy of 40, and an activation time of 35 ms. The MS/MS scan of the uncapped diacyl-estolide 108:8-6OH was selected for the sodiated parent ion of m/z 1778.50 and collected from a m/z range of 485 to 1800. The MS/MS scan of the uncapped triacyl-estolide 132:10-8OH was selected for the sodiated parent ion of m/z 2156.8 and collected from a m/z range of 590 to 2200. Data were averaged across 50 steps and exported from Xcalibur software (ThermoScientific).

[0080] Synthesis of Synthetic Palmitoylated (16:0) Estolides of Castor Oil:

[0081] In a dry 250-mL one-necked round-bottom flask equipped with a septum and mineral oil bubbler, was placed a palmitic acid (40.44 g, 0.158 mmol, 3.62 equiv), toluene (40 mL), and a football-shaped stir bar. To the suspension, *N,N*-dimethylformamide (250 μ L) was added to the suspension followed by oxalyl chloride (12.9 mL, 0.152 mol, 3.5 equiv) in five portions over one hour. During the course of the reaction, gas was rapidly evolved with very little heat production. After stirring for 4 h, a homogeneous, colorless solution resulted. Nitrogen gas was bubbled through the solution for 15 minutes to reduce the dissolved HCl content.

[0082] A second dry 250-mL one-necked round-bottom flask equipped with a dropping funnel and N_2 gas inlet was loaded with castor oil (40.34 g, estimated molecular weight 932.8 g/mol, 0.0435 mol, 1.00 equiv), toluene (30 mL), and pyridine (12.7 mL, 0.158 mol, 3.62 equiv). The dropping funnel was loaded with palmitoyl chloride solution and added over 25 min, using an ice-bath to moderate reaction temperature to $<30^\circ\text{C}$. After stirring at 20°C for 17 h, the resulting solution was extracted with toluene (20 mL) and water (75 mL). The organic phase was then washed with 50% (w/v) *N,N*-dimethylamino-2-ethanol (deanol; 3 $\times$ 25 mL) at 80°C , water (2 $\times$ 50 mL), and 1N HCl (100 mL then 50 mL). The organic phase and the upper portion of the aqueous phase were filtered through Celite to remove solids. The hazy solution was then washed with water (3 $\times$ 50 mL) and saturated brine (25 mL). After drying over MgSO_4 and vacuum filtration, the solvent was removed at 50°C using a rotary evaporator, the final yield of pale yellow estolide oil was 60.08 g (89%).

[0083] IR (KBr film, neat) 2922, 2852, 1734, 1465, 1166, 722 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.4-5.5 (m,

2.71H), 5.3 (m, 3.53H), 5.24 (m, 1H), 4.86 (m, 2.67H, estolide $\text{RR}'\text{CHO}$ palmitoyl), 4.28 (dd, 2H), 4.13 (dd, 2H), 2.3 (m 19.6H), 2.0 (m, 6.53H), 1.6 (m, 12.4H), 1.5 (m, 5.76H), 1.2-1.35 (m, 123H), 0.85 (m, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz) δ 173.5, 173.2, 132.4, 124.4, 73.6, 68.9, 62.0, 34.7, 34.1, 34.0, 33.6, 32.0, 31.9, 31.7, 29.7, 29.62, 29.58, 29.52, 29.46, 29.32, 29.27, 29.15, 29.1, 29.05, 29.01, 27.3, 25.3, 25.1, 24.83, 24.80, 22.6, 22.5, 14.05, 14.00.

[0084] Benzoylation of castor and Ov oil was accomplished using a similar procedure.

[0085] Thermal Stability of Oils

[0086] Thermal stability of Ov and castor seed oils was assessed by electrospray ionization mass spectrometry (ESI-MS) following exposure to temperatures ranging from 100°C to 300°C (FIGS. 3A-3D). Few changes were seen in either Ov or castor oils from temperatures 100°C to 250°C . At 300°C , most of the m/z peaks from Ov seed oil were reduced or absent (FIG. 3A). In contrast, castor oil showed a marked decrease in hydroxy TAG content at 300°C , from m/z 870 to 960 (FIG. 3B). Diacylglycerol m/z peaks appeared to increase in intensity from m/z 610 to 730. These observations suggest thermal degradation of castor oil occurs by fragmentation of glycerol bound FAs. Several other peaks increased in intensity just below the m/z range of hydroxy TAG from 780 to 840. Additionally, peaks between m/z of 1050 and 1250 increased. The m/z peak at 1217.991 was selected for MALDI-MS/MS to determine the identity of this novel peak present only at 300°C . treated oil but absent at lower temperatures. Fragmentation of the parent ion suggested a TAG estolide of tri-ricinolein with an additional linoleate esterified to one of the hFAs (FIG. 3C).

[0087] Synthetic castor estolides also showed greater thermal stability compared to unmodified castor oil. At 300°C , fully estoylated tri-ricinolein showed fragmentation, decreasing its intensity, and subsequently increasing the intensity of synthetic castor estolides with 0, 1, or 2 estolide acylations (FIG. 3D).

[0088] Discussion

[0089] In this examples naturally occurring TAG estolides were found to comprise the majority of the seed oil from *Orychophragmus violaceus* (Ov). Tribological analyses of Ov oil found it to have greater thermal stability, oxidative stability, and lubricity compared to Castor oil at a wide range of temperatures. At high temperatures, Castor oil was seen to degrade by fragmentation of the hydroxy TAG while the constituents of Ov oil decreased overall with the possible effect of driving polymerization of the estolide branch in TAG estolide. Electrospray ionization mass spectrometry (ESI-MS) allowed the discovery of m/z peaks well higher than predicted for hydroxy TAG molecular species containing nebraskanic or wuhanic acids. These high mass m/z peaks showed Ov oil contained capped and uncapped TAG estolides with a majority being uncapped with two FAs. Analysis of Ov oil by matrix assisted laser desorption ionization (MALDI) MS suggested minor amounts of TAG estolides can contain up to seven FAs in an estolide branch chain. Synthetic castor estolides were made to show that the presence of TAG estolides improves a seed oil's lubricity and thermal stability properties. This study revealed a structural-functional relationship from naturally occurring TAG estolides of Ov that can aid in the improvement of bio-based lubricants and as a potential chemical feedstock to other industrial bioproducts.

[0090] The seed oil from the Brassicaceae member *Orychophragmus violaceus* (Ov) has been shown to produce dihydroxy very long chain fatty acids (VLCFAs) through a discontinuous elongation pathway involving a modified fatty acid desaturase 2 (FAD2), much like the FAD2 from *Ricinus communis* (castor), and by a modified fatty acid elongase 1 (FAE1). Comparison of the Ov and castor oils at room temperature and at 100° C. revealed that lubrication characteristics of the Ov oil in reducing friction and wear of sliding steel surfaces significantly outperform the characteristics of castor oil. However, the origin of such a significant improvement step for the biolubricant class was not understood.

[0091] The structural modifications of the Ov seed oil were explored when exposed to high temperature regimes. The friction and wear of steel surfaces lubricated with Ov oil in comparison to castor oil showed lower values at all temperatures measured from 25, 100, 150, and 200° C. (FIGS. 5A-5B and FIGS. 6A-6B). In case of the Ov oil, the coefficient of friction (CoF) reduced up to three times at elevated temperatures. For all the cases, the wear rate of the lubricated steel surfaces decreased up to an order of magnitude (FIG. 5B).

[0092] The results demonstrate the largest friction and wear reduction in case of the Ov oil when the tests are performed at 100° C. (FIGS. 5A-5B). To better understand protective properties of the Ov oil, we performed further characterization of the wear track formed during the run in the Ov oil at 100° C. (FIGS. 7A-7H). Scanning electron microscopy energy dispersive x-ray spectroscopy (SEM EDS) analysis of the wear track formed on the flat sample side indicates presence of oxygen along the wear track grooves in case of castor oil, while in case of the Ov oil, no oxygen contrast is observed. These results suggest that the structure of the Ov oil enables suppression of the steel surface oxidation under high normal load and shear conditions and leads to better lubricative characteristics of the oil. Interestingly, no carbon contrast is observed inside the wear track, indicating that the Ov oil lubricity originates from the oil itself rather than from tribochemically driven formation of carbon-cased protective layers. These results suggest that the Ov oil shows very high stability to variation in the local heating induced by the applied in the wear track stresses. In case of castor oil, its degradation exposes the surface to bare metal-metal sliding leading to oxidation of the steel contact. Raman mapping of the iron oxide peak at $\sim 675\text{ cm}^{-1}$) indicates much higher corrosion of steel inside the wear track formed in castor oil (FIG. 7F). In contrast, the Ov oil demonstrates excellent protection against oxidation of the surface attributed to the degradation resistance of the oil and uniformity of the protective lubricative layer (FIG. 7E).

[0093] To gauge the thermal stability of either seed oils, samples of each were analyzed using electrospray ionization mass spectrometry (ESI-MS) following exposure to temperatures ranging from 100° C. to 300° C. to determine what oil constituents may have changed as a result of the exposure to high temperatures (FIGS. 7G-7H). Few changes were seen in either Ov or castor oils from temperatures 100° C. to 250° C. There was a slight decrease in overall intensity at 250° C. Ov oil relative to 100° C. However, at 300° C. most of the m/z peaks from Ov seed oil were absent (FIG. 7G). In contrast, castor oil at 300° C. showed a marked decrease in the hydroxy TAG content, seen from m/z of 870 and 960 (FIG. 7H). There was also a decrease in peak intensity at m/z

peaks of 599.8 and 617.9, which appeared to be protonated and ammoniated, respectively, diacylglycerols (DAG) with two linoleate FAs. However, additional DAG m/z peaks are seen to increase in intensity above these two in the castor oil treated at 300° C. This would suggest at higher temperatures, the thermal degradation of castor oil leads to the fragmentation of glycerol bound FAs. Several other peaks increased in intensity just below the m/z range of hydroxy TAG from 780 to 840. These peaks included 784.2, 801.3, 819.4, and 837.3, which appear to be fragmented hydroxy TAG. Further analysis using high resolution MALDI-MS (FIG. 8) showed the m/z masses closely resembled a fragmented ricinoleate with one and two dehydrations. Additionally, peaks above the region of hydroxy TAG between m/z of 1050 and 1250 also increased. An m/z peak at 1217.991 was selected for MALDI-MS/MS to determine the identity of this novel peak found in the castor oil treated at 300° C. but absent in oil at lower temperatures. High resolution MALDI-MS/MS suggested the novel peak was a TAG estolide of ricinolein with an additional linoleate esterified to one of the hydroxy FAs (FIG. 8). Fragment ion peaks at 919.735 and 937.746 showed a hydroxy TAG fragment ion dehydrated or hydrated, respectively, from the fragment loss of linoleate. The estolide fragment of two FAs was seen at the m/z peak of 601.480 and dehydrated to 583.469 while the DAG fragment was seen at 657.507 and dehydrated to 639.496.

[0094] In Ov seed oil, many high mass m/z peaks were observed in the seed oil even at room temperature, far higher than expected for TAG or hydroxy TAG containing nebraskanic acid or wuhanic acid moieties. As plants that are capable of synthesizing hydroxy FAs are also known to be able to produce estolides, acylated hydroxy FAs, these high mass m/z peaks were further investigated to determine their identities.

[0095] Recent evidence for the synthesis of dihydroxy very long chain fatty acids (VLCFAs) in the seed oil of the Brassicaceae member *Orychophragmus violaceus* has raised interest in determining what lipid species may contain this dihydroxy FA and its ultimate fate. Plants capable of synthesizing hydroxylated fatty acids are known to have the capacity to form estolides, lipid compounds composed of hydroxy FAs with additional FAs esterified to the OH of the hydroxy FA. One such example is triacylglycerol (TAG) estolides which have an hydroxy FA esterified to the glycerol backbone to form hydroxy-TAG with additional FAs esterified to the glycerol bound hydroxy FA. Analysis of extracted Ov seed oil by direct infusion electrospray ionization (ESI) mass spectrometry (MS) revealed a complex mixture of analytes with m/z ratios higher than what is predicted for hydroxy-TAG composed of 16 C or 18 C FAs, or simply TAG with either of the previously characterized dihydroxy VLCFAs, nebraskanic acid (7,18-(OH)₂-24:1^{A15}) or wuhanic acid (7,18-(OH)₂-24:2^{A15,21}) suggesting the presence of TAG estolides. HPTLC separated the constituents of Ov seed oil to produce six distinct bands following copper-sulfuric acid charring along with a smear from the origin and some faded spots between the darker bands (FIG. 9A). Each distinct band and the smear from the origin was scraped off from the TLC plate, extracted, and then analyzed individually by ESI-MS to determine its identity.

[0096] Product ion scans via ESI-MS/MS and MALDI-MS/MS reveal the presence of TAG estolides in Ov seed oil with the most abundant form as TAG estolide with two or

three dihydroxy VLCFAs esterified to a glycerol bound dihydroxy VLCFA (FIGS. 9A-9C). Subsequent analysis by product ion scans, as well as rationalization by detected m/z values, revealed the individual components of Ov oil. TAG estolides terminating with a non-hydroxy FA are known as capped estolides, while those terminating with an hydroxy FA are known as uncapped estolides, referring to the available OH that can be further acylated. HPTLC separated TAG estolides by capped TAG estolides preceding uncapped TAG estolides. The bands in the TLC run as: 1) capped monoacyl TAG estolide, 2) capped diacyl TAG estolide, 3) capped triacyl TAG estolide, 4) uncapped monoacyl TAG estolide, 5) uncapped diacyl TAG estolide, and 6) uncapped triacyl TAG estolide. These molecular species were also seen in the Q1 scan of the ESI-MS spectrum, and agrees with the predicted m/z for such TAG estolide molecular species. Further analysis of the Ov m/z peaks revealed individual components of the Ov oil as: a) mixture of PC, none of which was found to contain the dihydroxy VLCFAs, and, presumably, estolide fragments consisting of two dihydroxy VLCFAs linked together that are both hydroxylated and dehydrated, likely due to effects of in-source ionization, b) doubly charged diacyl TAG estolides, mostly of the uncapped form, c) TAG containing no more than one glycerol bound dihydroxy VLCFA, but as there is no distinct TLC band belonging to hydroxy-TAG, these m/z peaks may indicate in-source fragmentation from Ov estolides which would suggest Ov oil is essentially entirely TAG estolides, d) doubly charged capped triacyl TAG estolides, e) doubly charged uncapped triacyl TAG estolides, f) estolide fragments consisting of three dihydroxy VLCFAs that are hydroxylated and dehydrated due to effects of in-source ionization, g) capped monoacyl TAG estolides, h) uncapped monoacyl TAG estolides, i) capped diacyl TAG estolides, j) uncapped diacyl TAG estolides, k) capped triacyl estolides, and l) uncapped triacyl estolides.

[0097] Further analysis of Ov oil via MALDI-MS shows that higher order TAG estolide polyesters exist beyond triacyl TAG estolides, but are at much lower abundance (FIGS. 10A-10H). The m/z values of these higher order polyester TAG estolides indicated they could contain up to six acyl groups in an estolide branch chain. Fragmented estolide fragments between clusters of m/z peaks of TAG estolide molecular species indicate estolide fragments with polymers of up to nine and ten dihydroxy VLCFAs, which would indicate the presence of TAG estolides that can range up to eight or nine FAs in an estolide branch if the estolide fragment is fragmented from the glycerol backbone, or up to ten or eleven FAs in an estolide branch if the estolide fragments are fragmented from the hydroxylated FA esterified to the glycerol backbone. Analysis of these higher order polyester estolides is limited due to instrument limitations with m/z range, potential fragmentation upon ionization or post source decay, and ionizability.

[0098] Product ion scans were taken using MALDI-MS/MS and collisional induced dissociation (CID) to determine the TAG estolide structures more fully. The MS/MS spectra of the most abundant uncapped diacyl and triacyl-TAG estolide were selected for MS/MS analysis (FIG. 2). The parent ion mass of 1778.5 was selected for and then fragmented. This mass corresponded to the sodiated parent ion mass of an uncapped diacyl-TAG estolide with the composition of 108:8-6OH, where the '108' refers to the number of C in the FA moieties, '8' refers to the number of unsatura-

tions, and '6OH' refers to the number of OH groups from the dihydroxy FAs present. The theoretical m/z of a sodiated parent ion mass for an 108:8-6OH estolide TAG is 1778.5, selected by the LTQ front end of the LTQ-Orbitrap used for CID MS/MS. Strong fragment ion signals were found at m/z 1498.226, 1382.145, 1175.939, 1003.829, and 797.626 (FIGS. 10A-10H). The first fragment ion at 1498.226 indicated a loss of a linoleate ion $[M-18:2+Na]^+$. However, additional peaks differing by approximately 2 amu were also found at m/z 1496.212 and 1494.195 suggesting fragmentation of oleate $[M-18:1+Na]^+$ and stearate $[M-18:0+Na]^+$, respectively, as possible fragmentations. This would also suggest that isobaric TAG estolide molecular species are overlapping in the full ESI-MS spectrum scan as seen in FIG. 9A and highlighted by TLC separation. The fragmentation at 1382.145 indicated a loss of a wuhanic acid $[M-24:2(OH)_2+Na]^+$, but another m/z peak approximately 2 amu less at 1380.129 may indicate the loss of a nebraskanic acid moiety $[M-24:1(OH)_2+Na]^+$. The fragment ion at m/z 1175.939 had a mass corresponding most closely to that of a fragment consisting of three wuhanic acids linked together, presumably the estolide branch fragmented from the glycerol backbone. This suggested the estolide branch chain is likely from a single glycerol bound hydroxy FA rather than multiple glycerol bound hydroxy FAs considering the high ion intensity of the fragment ion at m/z 1177.956. The TAG fragment ion was seen at m/z 1003.829 resulting from the fragment loss of two wuhanic acids $[M-2(24:2(OH)_2)+Na]^+$. Additionally, a peak approximately 2 amu lower at m/z 1001.814 may indicate a fragment ion loss of one wuhanic acid and one nebraskanic acid $[M-24:2(OH)_2-24:1(OH)_2+Na]^+$. The differences in the fragmentations observed is likely to be due to overlapping isobaric TAG estolide molecular species differing in unsaturation of the estolide branch and the glycerol bound FAs. Finally, a fragment ion at m/z at 797.626 suggested an estolide branch fragment ion from the glycerol bound hydroxy FA consisting of two wuhanic FAs $[(24:2(OH)_2)_2+Na]^+$. Another peak differing by approximately 2 amu at 799.641 indicated another possible estolide branch fragment ion of one wuhanic acid and one nebraskanic acid $[(24:2(OH)_2+24:1(OH)_2)+Na]^+$. The presence of fragmentation peaks at both m/z of 797.626 and 1175.939 support a TAG estolide structure with a single glycerol bound hydroxy FA with an estolide branch chain rather than multiple hydroxy FAs bound to the glycerol backbone.

[0099] MALDI-MS/MS analysis of the parent ion mass of m/z 2156.8 indicated the sodiated uncapped triacyl-TAG estolide 132:10-8OH. Strong fragment ions were found at 1876.535, 1758.438, 1556.268, 1478.202, 1380.128, and 1177.955 (FIG. 9B). However, there were several neighboring peaks differing by approximately 2 amu, which suggested overlapping isobaric molecular species similarly to the diacyl-TAG estolide 108:8-6OH described above (FIG. 8). The description here will be for one possible TAG estolide structure, though multiple molecular species are likely present and overlapping in the spectrum. Fragmentation at m/z 1876.535 is equivalent to the loss of linoleate $[M-18:2+Na]^+$, at m/z 1758.438 from fragmentation of a nebraskanic acid $[M-24:1(OH)_2+Na]^+$, at m/z 1556.268 is the estolide branch fragment consisting of three wuhanic acid moieties and one nebraskanic acid moiety fragmented from the glycerol backbone $[((24:2(OH)_2)_3+24:1(OH)_2)+Na]^+$. A smaller m/z peak at 1478.202 resulted from the fragmentation of both linoleate and nebraskanic acid $[M-18:$

2-24:1(OH)₂+Na]⁺. The fragment ion at m/z 1380.128 resulted from the loss of a nebraskanic and a wuhanic acid [M-24:1(OH)₂-24:2(OH)₂+Na]⁺. Finally, an estolide branch fragment at m/z 1177.955 consisted of two wuhanic acids and one nebraskanic acid [((24:2(OH)₂)₂+24:1(OH)₂)+Na]⁺. Similar to the MS/MS spectrum of 108:8-6OH, the m/z peaks at 1177.955 and 1556.268 both suggest a single glycerol bound hydroxy FA with an estolide branch chain.

[0100] MS analysis of Ov seed oil revealed a complex mixture of TAG estolides not seen before in other seed oils. Ov TAG estolides varied by the number of acylations making up the polyester-like branch chain, the FA carbon length, the number of unsaturations, and whether the FAs were hydroxy or nonhydroxy. Those TAG estolides with hydroxy-FAs (i.e. nebraskanic or wuhanic acid) at the terminal end of the estolide branch chain are called here “uncapped” as they are capable of further acylation, while those TAG estolides with nonhydroxy FAs at the terminal end are “capped” TAG estolides as they are incapable of further acylation at the terminal acyl group. Considering that the presence of these free, unacylated OH groups at the terminal end may affect the tribological properties of uncapped TAG estolides relative to capped TAG estolides, separating the two types was done to determine whether significant differences exist by measuring to the CoF at 25° C. and 100° C. At 25° C. the uncapped estolides were shown to have a lower CoF relative to the capped TAG estolides (FIG. 9A). However, at 100° C. the opposite was seen, with capped TAG estolides showing a lower CoF (FIG. 9B). Consistent at both temperatures was a lower CoF for a mixture of capped and uncapped TAG estolides, suggesting that both types of TAG estolides provide the improved tribological properties observed in Ov oil at a range of temperatures, as well as potential thermal stability.

[0101] The improved lubricity properties of castor oil are attributed to the presence of hydroxy FAs compared to other seed oils lacking hydroxy FAs. However, considering that Ov oil in comparison to castor oil was shown to have a lower CoF at a range of temperatures, then the presence of TAG estolides in Ov oil may suggest another constituent that further improves lubricative and tribological properties of plant based oils. In order to determine if TAG estolides provide a further improvement to plant based oils synthetic TAG estolides were made from castor oil (FIG. 11C) and then used to measure the CoF at 25° C. and 100° C. compared to unmodified castor oil. Synthetic castor oil estolides were made by esterifying palmitate to the free OH groups found on ricinoleate in hydroxy TAG. The synthetic castor estolides produced here differed from the TAG estolides found in Ov oil in that they were completely capped with palmitate. In castor oil the predominant TAG species is ricinolein, containing three ricinoleic acid moieties. From the MS spectra of the prepared oil (FIG. 12) the presence of the TAG estolides was confirmed and shown to contain estolide acylations to each of the available OH groups for a maximum total of three estolide additions to ricinolein. This is a further difference compared to the TAG estolides of Ov where only one of the glycerol bound FAs is observed to be a hydroxy FA with a single estolide branch chain.

[0102] The synthetic 16:0 castor estolides showed a lower CoF at both temperatures relative to unmodified castor oil (FIGS. 11A-11B), further supporting the evidence that the presence of TAG estolides, and not only the presence of

hydroxy FAs, improve the lubricative and tribological properties of a plant seed oil. The wear tracks where unmodified castor oil was used as the lubricating oil measured 72.2 μm in diameter for ball tracks and 58.3 μm in width for surface tracks (FIG. 13A and FIG. 13C). Wear tracks from the synthetic 16:0 castor estolides showed a diameter of 61.6 μm for the ball track and 52.8 μm for the surface track (FIG. 13B and FIG. 13D).

[0103] The synthetic 16:0 castor estolides were also tested for their thermal stability. Similarly to what was found for both Ov and unmodified castor oil (FIGS. 7G-7H), few changes were observed between the temperatures of 100° C. to 250° C., and only at 300° C. are the more dramatic changes seen (FIG. 11D). At 300° C. the m/z intensity of the TAG estolide of ricinolein with three acylations, one per OH group, decreases in signal intensity while the m/z peaks for the TAG estolides with one and two acylations increase (FIG. 11D). The loss of estolide acylations suggests an alternate mode of thermal degradation by the loss of the estolide acyl groups rather than the fragmentation observed in unmodified castor oil as seen in FIG. 7H.

[0104] In this study the Brassicaceae member *Orychophragmus violaceus* was found to produce novel types of TAG estolides. These TAG estolides were composed of two glycerol bound 16-18C FAs and one VLCFA dihydroxy FA with an estolide branch chain located at the 18OH position. The estolide branch were found to have between one and three FAs in the most predominant forms of TAG estolide in Ov oil. High mass MALDI-MS also found evidence for larger, more polymerized estolide branch chains that could contain up to 10 FAs. Previously Ov oil used as a lubricant produced a lower CoF compared to castor oil. In this study, Ov oil was seen to produce a lower CoF at a wide range of temperatures and the question of whether this was due to the presence of TAG estolides was investigated. Analysis of the steel surfaces used in the friction tests were found to contain less oxygen and had less formation of iron oxide when Ov oil was used compared to castor oil suggesting better protection. Additionally, the wear produced on the steel surfaces during tribotests was smaller with Ov oil. Since TAG estolides were seen to be the principal component of the seed oil from Ov, and that Ov seed oil had better lubricative properties than castor oil, synthetic estolides of castor oil were made to determine if they would improve the lubricative properties of castor oil. Here synthetic 16:0 castor estolides were shown to lower the CoF of unmodified castor oil and demonstrated estolides produce lower CoFs in plant seed oils used as lubricants.

[0105] In addition to the superior lubricative properties observed in Ov oil relative to castor oil, analyzing the oils subjected to high temperatures suggested that Ov oil may also have added thermal stability properties. While few changes were observed in either oil from 100° C. to 250° C., major changes in m/z peaks were seen in oils exposed to 300° C. In Ov oil many of the m/z peaks disappeared, but it is not clear whether these peaks represent a complete degradation of the TAG estolides in the oil or if the TAG estolides were converted to something else that would not be detected using the MS methods used here. In contrast, the hydroxy TAG content of castor oil decreased while simultaneously m/z peaks lower in mass than hydroxy TAG increased suggesting fragmentation of the hydroxy TAG. Surprisingly, castor oil treated at 300° C. also resulted in the formation of a single FA TAG estolide. This unexpected

result may suggest one mechanism for the degradation of seed oils containing hydroxy FAs, such as Ov and castor. This finding is particularly germane to Ov oil which already contained TAG estolides, but also TAG estolides of a high degree of polymerization. One possible explanation for the decrease in nearly all of the m/z peaks in the 300° C. treated Ov oil is the formation of more highly polymerized TAG estolides that are less optimal for analysis by either ESI-MS or MALDI-MS.

[0106] The potential of polymerizing hydroxy FA containing oils, such as that found in Ov seed oil, for the production of polymers may yield another use for an already functional oil seen to have greater lubricative properties. To determine whether TAG estolides provide thermal stability the synthetic 16:0 castor estolides were also subject to temperatures ranging from 100° C. to 300° C. Similar to that found with Ov and unmodified castor oil, few changes were seen between 100° C. to 250° C., but at 300° C. the acylations of the synthetic 16:0 castor estolides appeared to cleave. This results in higher m/z peak intensities for TAG estolides containing only one or two acylations as opposed to the predominant TAG estolide with three acylations. Also noteworthy, however, was the lack in the appearance of m/z fragmentation peaks below the m/z peaks of hydroxy TAG as was seen in the unmodified castor oil at 300° C. It is clear that the estolide form of castor oil appears to affect the way in which it degrades at high temperatures. However, the m/z peaks in Ov oil were seen to decrease without the increase of TAG estolides with fewer acylations, e.g. a TAG estolide with an estolide branch of three FAs fragmenting to a TAG estolide with an estolide branch of two FAs.

[0107] While this study shows TAG estolides in Ov oil provide superior lubricity properties relative to castor oil, as demonstrated with the synthetic 16:0 castor estolides, the significance of the chemical properties of TAG estolides and their relation to lubricity and friction still yet remains unclear. For example, while the esterification of FAs to the free OH groups of hydroxy TAG increases lubricative properties, it is not certain whether this is a result of the 'capping' of free OH groups or if it is simply due to the addition of FAs. As shown with the separated Ov TAG estolides, the capped TAG estolides showed a greater reduction in friction relative to the uncapped TAG estolides at 100° C. However, at lower temperatures the reverse was found, and in either temperature tested the mixture of the capped and uncapped TAG estolides reduced the CoF the greatest. This suggests a much more complex interaction of the constituents of Ov oil. Other factors that may affect the quality and capability of plant seed oil in their use as a functional fluid, such as a lubricant, include: carbon length of the FA moieties, degree of unsaturation, higher degrees of estolide branch chain polymerization, estolides of TAG compared to estolides of FAs alone, and number of hydroxy FAs bonded to the glycerol sn positions in TAG and whether estolides form at the three positions rather than the one found in Ov TAG estolides.

[0108] Using Ov oil as a model to further improve castor oil was one example in designing a synthetic oil on properties derived from a naturally occurring oil. However, further improvements could also be made. The castor oil in this study was made to TAG estolides by the addition of palmitate (16:0), but it is not clear whether other moieties would have produced oils of greater or lesser value in regards to their lubricative or thermal stability properties.

Additionally, the observations of mixed capped and uncapped Ov TAG estolides suggests that different oil blends may also produce more favorable properties than relying on chemical modifications alone. Together this study revealed an unusual lipid in *Orychophragmus violaceus* formed from dihydroxy VLCFAs to TAG estolides with long polymerized estolide branch chains, and showed that the chemistry of unusual lipids from nature can provide new insights into the design and understanding of synthetic oils for improved and varied properties. This study also showed how the chemical structure of TAG and TAG estolides results in its functional properties relative to friction and possibly thermal stability. Similarly, Ov oil may offer an environmentally friendly source of plant based oil lubricants as an alternative to petroleum based oils and could offer a unique chemical feedstock, such as in synthesizing plant oil based polymers, given the high degree of estolide polymerization found in Ov oil.

[0109] The present disclosure further includes the following embodiments.

1A. A lubricant composition comprising a triacylglycerol (TAG) estolide, wherein the lubricant composition has been chemically modified to increase a concentration of the TAG estolide relative to a reference concentration of the TAG estolide in the otherwise same lubricant composition except without the chemical modification.

2A. The lubricant composition according to paragraph 1A, wherein the chemical modification comprises esterification of a triacylglycerol with one or more fatty acids to produce the TAG estolide.

3A. The lubricant composition according to paragraph 2A, wherein the one or more fatty acids are selected from the group consisting of palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, and a combination thereof.

4A. The lubricant composition according to any one of paragraphs 1A-3A, wherein the TAG estolide is capped.

5A. The lubricant composition according to any one of paragraphs 1A-3A, wherein the TAG estolide is uncapped.

6A. The lubricant composition according to any one of paragraphs 1A-5A, wherein the triacylglycerol (TAG) estolide comprises an estolide of the triglyceride of ricinoleic add comprising up to 3 estolide additions.

7A. The lubricant composition according to any one of paragraphs 1A-6A, wherein the lubricant composition is in the form of a semisolid lubricant composition comprising an emulsion of (i) a thickener and (ii) an oil.

8A. The lubricant composition according to paragraph 7A, wherein the thickener is selected from the group consisting of a soap such as calcium stearate, cellulose, sodium stearate, lithium stearate, lithium 12-hydroxystearate, and a combination thereof.

9A. The lubricant composition according to any one of paragraphs 1A-8A, further comprising one or more grease additives.

10A. The lubricant composition according to paragraph 9A, wherein the one or more grease additives are selected from the group consisting of an antioxidant, an antiwear additive, a corrosion inhibitor, a detergent, a metal deactivator, a viscosity modifier, a dispersant, and a combination thereof.

11A. The lubricant composition according to paragraph 10A, wherein the one or more grease additives comprise an antioxidant, and

[0110] wherein the antioxidant is selected from the group consisting of (+)- α -tocopherol (TCP), propyl gallate (PG), l-ascorbic acid 6-palmitate (AP), 4,4'-methylenebis(2,6-di-tert-butylphenol) (MBP), butylated hydroxyl anisole (BHA), butylated hydroxyl toluene (BHT), propyl gallate (PG), tert-butyl hydroquinone (TBHQ).

12A. The lubricant composition according to paragraph 10A, wherein the one or more grease additives comprise an antiwear additive, and

[0111] wherein the antiwear additive is selected from the group consisting of zinc dithiophosphate (ZDP), zinc dialkyl dithiophosphate (ZDDP), tricresyl phosphate (TCP), dioleoyl phosphite, bis(2-ethylhexyl) phosphate, diphenyl cresyl phosphate, triphenyl phosphorothionate, chlorinated paraffins, glycerol monooleate, and a combination thereof.

13A. The lubricant composition according to paragraph 10A, wherein the one or more grease additives comprise a corrosion inhibitor, and

[0112] wherein the corrosion inhibitor is selected from the group consisting of a thiadiazole, a benzotriazole, a toluotriazole, a zinc dithiophosphate, a metal phenolate, a metal sulfonate, a fatty acid, a carboxylic acid, an amine, and a combination thereof.

14A. The lubricant composition according to paragraph 10A, wherein the one or more grease additives comprise a detergent, and

[0113] wherein the detergent is selected from the group consisting of a polyisobutylene succinimide, a polyisobutylene amine succinamide, an aliphatic amine, a polyolefin maleic anhydrides, and a combination thereof.

15A. The lubricant composition according to paragraph 10A, wherein the one or more grease additives comprise a metal deactivator, and

[0114] wherein the metal deactivator is selected from the group consisting of a triazole, a tolyltriazole, a thiadiazole, and a combination thereof.

16A. The lubricant composition according to paragraph 10A, wherein the one or more grease additives comprise a viscosity modifier, and

[0115] wherein the viscosity modifier is selected from the group consisting of an ethylene-olefin co-polymer, a maleic anhydride-styrene alternating copolymer, a polymethacrylate, a hydrogenated styrene-butadiene copolymer, a hydrogenated styrene-isoprene copolymer, an ester thereof, and a combination thereof.

17A. The lubricant composition according to paragraph 10A, wherein the one or more grease additives comprise a dispersant, and

[0116] wherein the dispersant is selected from the group consisting of succinimide, benzylamine, and a combination thereof.

18A. The lubricant composition according to any one of paragraphs 1A-7A, wherein the lubricant composition is in the form of a liquid at standard temperature and pressure.

19A. The lubricant composition according to paragraph 18A, further comprising one or more oil additives.

20A. The lubricant composition according to paragraph 19A, wherein the one or more oil additives are selected from the group consisting of an antioxidant, an antiwear additive, a friction reduction additive, a corrosion inhibitor, a detergent, a metal deactivator, a viscosity modifier, a dispersant, and a combination thereof.

21A. The lubricant composition according to paragraph 20A, wherein the one or more oil additives comprise an antioxidant, and

[0117] wherein the antioxidant is selected from the group consisting of (+)- α -tocopherol (TCP), propyl gallate (PG), l-ascorbic acid 6-palmitate (AP), 4,4'-methylenebis(2,6-di-tert-butylphenol) (MBP), butylated hydroxyl anisole (BHA), butylated hydroxyl toluene (BHT), propyl gallate (PG), and tert-butyl hydroquinone (TBHQ).

22A. The lubricant composition according to paragraph 20A, wherein the one or more oil additives comprise an antiwear additive, and

[0118] wherein the antiwear additive is selected from the group consisting of carbon-based materials (graphene, diamond nanoparticles, bucky balls, carbon nanotubes), zinc dithiophosphate (ZDP), zinc dialkyl dithiophosphate (ZDDP), tricresyl phosphate (TCP), dioleoyl phosphite, bis(2-ethylhexyl) phosphate, diphenyl cresyl phosphate, triphenyl phosphorothionate, chlorinated paraffins, glycerol monooleate, and a combination thereof.

23A. The lubricant composition according to paragraph 20A, wherein the one or more oil additives comprise a corrosion inhibitor, and

[0119] wherein the corrosion inhibitor is selected from the group consisting of a thiadiazole, a benzotriazole, a toluotriazole, a zinc dithiophosphate, a metal phenolate, a metal sulfonate, a fatty acid, a carboxylic acid, an amine, and a combination thereof.

24A. The lubricant composition according to paragraph 20A, wherein the one or more oil additives comprise a detergent, and

[0120] wherein the detergent is selected from the group consisting of a polyisobutylene succinimide, a polyisobutylene amine succinamide, an aliphatic amine, a polyolefin maleic anhydride, and a combination thereof.

25A. The lubricant composition according to paragraph 20A, wherein the one or more oil additives comprise a metal deactivator, and

[0121] wherein the metal deactivator is selected from the group consisting of a triazole, a tolyltriazole, a thiadiazole, and a combination thereof.

26A. The lubricant composition according to paragraph 20A, wherein the one or more oil additives comprise a viscosity modifier, and

[0122] wherein the viscosity modifier is selected from the group consisting of an ethylene-olefin co-polymer, a maleic anhydride-styrene alternating copolymer, a polymethacrylate, a cellulose, a hydrogenated styrene-butadiene copolymer, a hydrogenated styrene-isoprene copolymer, an ester thereof, and a combination thereof.

27A. The lubricant composition according to paragraph 20A, wherein the one or more oil additives comprise a dispersant, and

[0123] wherein the dispersant is selected from the group consisting of succinimide, benzylamine, and a combination thereof.

28A. A method of making a lubricant composition comprising chemically modifying a base oil to increase a concentration of the TAG estolide relative to a reference concentration of the TAG estolide in the base oil without the chemical modification.

29A. The method according to paragraph 28A, wherein the chemical modification comprises esterification of a triacylglycerol with one or more fatty acids to produce the TAG estolide.

30A. The method according to paragraph 29A, wherein the one or more fatty acids are selected from the group consisting of palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, and a combination thereof.

31A. The method according to any one of paragraphs 28A-30A, wherein the TAG estolide is capped.

32A. The method according to any one of paragraphs 28A-30A, wherein the TAG estolide is uncapped.

33A. The method according to any one of paragraphs 28A-30A, wherein the triacylglycerol (TAG) estolide comprises an estolide of the triglyceride of ricinoleic acid comprising up to 3 estolide additions.

34A. The method according to any one of paragraphs 28A-30A, wherein the chemical modification comprises:

[0124] reacting a fatty acid with a chloride source and a dimethylformamide catalyst to produce an acyl chloride;

[0125] reacting the acyl chloride with a triacylglyceride in the oil to produce the TAG estolide.

35A. The method according to paragraph 34A, wherein the fatty acid is selected from the group consisting of palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, and a combination thereof.

[0126] It should be emphasized that the above-described embodiments of the present disclosure are merely possible examples of implementations, and are set forth only for a clear understanding of the principles of the disclosure. Many variations and modifications may be made to the above-described embodiments of the disclosure without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure.

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What is claimed is:

1. A lubricant composition comprising a triacylglycerol (TAG) estolide, wherein the lubricant composition has been chemically modified to increase a concentration of the TAG estolide relative to a reference concentration of the TAG estolide in the otherwise same lubricant composition except without the chemical modification.

2. The lubricant composition according to claim 1, wherein the chemical modification comprises esterification of a triacylglycerol with one or more fatty acids to produce the TAG estolide.

3. The lubricant composition according to claim 2, wherein the one or more fatty acids are selected from the group consisting of palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, and a combination thereof.

4. The lubricant composition according to claim 1, wherein the TAG estolide is capped.

5. The lubricant composition according to claim 1, wherein the TAG estolide is uncapped.

6. The lubricant composition according to claim 1, wherein the triacylglycerol (TAG) estolide comprises an estolide of the triglyceride of ricinoleic acid comprising up to 3 estolide additions.

7. The lubricant composition according to claim 1, wherein the lubricant composition is in the form of a semisolid lubricant composition comprising an emulsion of (i) a thickener and (ii) an oil.

8. The lubricant composition according to claim 7, wherein the thickener is selected from the group consisting of calcium stearate, cellulose, sodium stearate, lithium stearate, lithium 12-hydroxystearate, and a combination thereof.

9. The lubricant composition according to claim 1, further comprising one or more grease additives.

10. The lubricant composition according to claim 9, wherein the one or more grease additives are selected from the group consisting of an antioxidant, an antiwear additive, a corrosion inhibitor, a detergent, a metal deactivator, a viscosity modifier, a dispersant, and a combination thereof.

11. The lubricant composition according to claim 10, wherein the one or more grease additives comprise an antioxidant, and

wherein the antioxidant is selected from the group consisting of (+)- α -tocopherol (TCP), propyl gallate (PG), l-ascorbic acid 6-palmitate (AP), 4,4'-methylenebis(2,6-di-tert-butylphenol) (MBP), butylated hydroxyl ani-

sole (BHA), butylated hydroxyl toluene (BHT), propyl gallate (PG), and tert-butyl hydroquinone (TBHQ).

12. The lubricant composition according to claim **10**, wherein the one or more grease additives comprise an antiwear additive, and

wherein the antiwear additive is selected from the group consisting of zinc dithiophosphate (ZDP), zinc dialkyl dithiophosphate (ZDDP), tricresyl phosphate (TCP), dioleoyl phosphite, bis(2-ethylhexyl) phosphate, diphenyl cresyl phosphate, triphenyl phosphorothionate, chlorinated paraffins, glycerol monooleate, and a combination thereof.

13. The lubricant composition according to claim **10**, wherein the one or more grease additives comprise a corrosion inhibitor, and

wherein the corrosion inhibitor is selected from the group consisting of a thiadiazole, a benzotriazole, a tolutriazole, a zinc dithiophosphate, a metal phenolate, a metal sulfonate, a fatty acid, a carboxylic acid, an amine, and a combination thereof.

14. The lubricant composition according to claim **10**, wherein the one or more grease additives comprise a detergent, and

wherein the detergent is selected from the group consisting of a polyisobutylene succinimide, a polyisobutylene amine succinamide, an aliphatic amine, a polyolefin maleic anhydride, and a combination thereof.

15. The lubricant composition according to claim **10**, wherein the one or more grease additives comprise a metal deactivator, and

wherein the metal deactivator is selected from the group consisting of a triazole, a tolyltriazole, a thiadiazole, and a combination thereof.

16. The lubricant composition according to claim **10**, wherein the one or more grease additives comprise a viscosity modifier, and

wherein the viscosity modifier is selected from the group consisting of an ethylene-olefin co-polymer, a maleic anhydride-styrene alternating copolymer, a polymethacrylate, a hydrogenated styrene-butadiene copolymer, a hydrogenated styrene-isoprene copolymer, an ester thereof, and a combination thereof.

17. The lubricant composition according to claim **10**, wherein the one or more grease additives comprise a dispersant, and

wherein the dispersant is selected from the group consisting of succinimide, benzylamine, and a combination thereof.

18. A method of making a lubricant composition comprising chemically modifying a base oil to increase a concentration of the TAG estolide relative to a reference concentration of the TAG estolide in the base oil without the chemical modification.

19. The method according to claim **18**, wherein the chemical modification comprises esterification of a triacylglycerol with one or more fatty acids to produce the TAG estolide.

20. The method according to claim **19**, wherein the one or more fatty acids are selected from the group consisting of palmitoleic acid, oleic acid, linoleic acid, lauric acid, palmitic acid, stearic acid, and a combination thereof.

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