Research Article

Chemical modifications of *Sterculia foetida* L. oil to branched ester derivatives

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An experimental study to modify *Sterculia foetida* L. oil (STO) or the corresponding methyl esters (STO FAME) to branched ester derivatives is reported. The transformations involve conversion of the cyclopropene rings in the fatty acid chains of STO through various catalytic as well as stoichiometric reactions. Full conversion of the cyclopropene rings was obtained using Diels–Alder chemistry involving cyclopentadiene in water at 40°C without the need for a catalyst. Olefin metathesis reactions were performed using a Grubbs 2nd generation catalyst and cyclopropene ring conversion was ≥99 and 54 mol% with 2,3-dimethyl-2-butene and 1-octene, respectively. Oxidation reactions were performed using established epoxidation (Sharpless) and dihydroxylation (Prilezhaev) protocols using aqueous hydrogen peroxide as the oxidant. For both reactions, full conversion of the cyclopropene rings was obtained at RT to yield the corresponding α,β-unsaturated ketone in good selectivities. Rearrangement reactions of the cyclopropene rings to the corresponding conjugated diene were successfully performed using homogeneous and heterogeneous palladium catalysts. Excellent conversions (≥99%) were obtained using homogeneous palladium catalyst in a biphasic cyclohexane–water mixture (1:1) at 90°C. Relevant cold flow properties of all products were determined and compared to crude STO and STO FAME. Best results were obtained for the metathesis products of STO with 1-octene, with a cloud point (CP) and pour point (PP) of −12°C.

Practical applications: The *S. foetida* L. tree produces a tropical oil with high potential to be converted to various oleochemical products. The oil contains cyclopropene rings in the fatty acid chains which are known to be very reactive and as such excellent starting materials for various chemical modification reactions. We here report an experimental study on the modifications of STO into novel branched ester derivatives which are prospective products for a range of applications. Examples are the use as cold-flow improvers for biodiesel or biolubricants (ester derivatives with long, aliphatic branches), as reactive building block material for resin, coatings and/or packaging application (derivatives containing unsaturated (cyclic) structures in the fatty acid chains).

Keywords: Branched ester derivatives / Chemical modifications / *Sterculia foetida* L. oil

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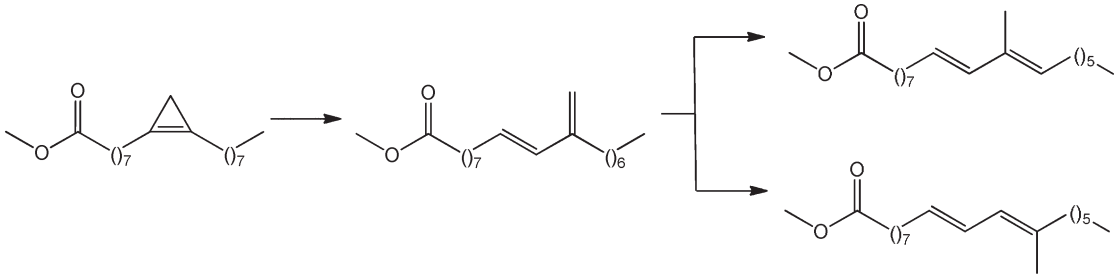
Abbreviations: APT, attached proton test; **1,** methyl esters of STO; **2,** methyl esters of Diels–Alder reaction products; **3a,** product of metathesis reaction of STO with 2,3-dimethyl-2-butene; **3b,** product of metathesis reaction of STO with 1-octene; **4a,** methyl esters of **3a**; **4b,** methyl esters of **3b**; **5,** product of epoxidation reaction; **6,** product of hydroxylation reaction; **7,** product of 1,4-addition reaction of STO with *n*-octylMgBr; **8,** methyl esters of **7**; **9,** methyl esters of rearrangement product; **CE,** cyclopropene; **CP,** cloud point; **CPEFA,** cyclopropene fatty acids; **MTO,** methyl trioxorhenium; **PP,** pour point; **STO,** *Sterculia foetida* L. oil

1 Introduction

Sterculia foetida L, belonging to the family of Sterculiaceae and the order of Malvales, is a tropical tree with oil bearing seeds. The tree is natively wide spread from east Africa to north Australia and also grows in Indonesia [1]. The shape and size of the kernels resembles that of olives and as such the tree is also known as 'Java olive'. Other trivial names include wild almond tree, hazel sterculia, and poon [1, 2]. In middle Java, the productivity of *S. foetida* L. is reported to range between 450 and 2080 kg dry seeds/tree/year. When assuming a plant population of 66 trees/ha in a plantation wise setting, the seed yield ranges between 30 and 137 tonnes dry seeds/ha/year. Typically, 60% of the seed consist of seed kernel and the oil content of the seed kernel may be as high as 50–60 wt% (dry basis). The latter values are comparable to other tropical oil seeds such as *Jatropha* and rubber (60 wt%) as well as castor and Karanja (50 wt%) [2]. With these data, an oil productivity between 10 and 50 tonnes oil/ha/year may be estimated. This is high compared to that of *Jatropha curcas* L. (up to 2 tonnes oil/ha/year) or palm (currently at 3–6 tonnes oil/ha/year) [3]. However, this is only a very rough theoretical estimate as to the best of our knowledge *Sterculia* plantations do not exist to date and yield data need to be verified using scientifically sound methods.

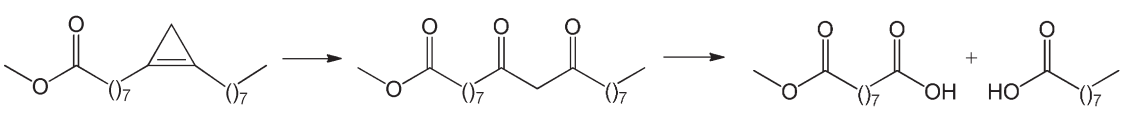
The oil from the *S. foetida* L. (STO) seeds is considered non-edible, though a recent study indicates that the oil has potential as a health supplement to reduce belly fat built up [4]. STO contains fatty acids with cyclopropene units (CPEFA), which may account up to 70 wt%, in the form of sterculic acid (9,10-methylene-9-octadecenoic acid) and malvalic acid (8,9-methylene-8-heptadecenoic acid) [5]. This amount is the highest among all other plant oils containing cyclopropene rings [6]. In plants, sterculic acid is formed from oleic acid [7, 8]. Malvalic acid is derived from sterculic acid by α-oxidation at the carboxylic end to the intermediate (R)-2-hydroxysterculic acid followed by cleavage to malvalic acid [9, 10]. Both fatty acids are found in the roots, leaves, stems and callus tissues in plants belonging to the Malvaceae family [11, 12], and are mentioned to have anti-fungal activity [13]. Sterculic acid may also be obtained by chemical synthesis by the addition of a methylene unit to stearolic acid (9-octadecynoic acid, C18:3) [14].

The cyclopropene unit is very reactive due to a high strain energy (approximately 50 kcal/mol) [15]. The presence of this reactive functional group renders STO a very interesting feedstock for the production of oleochemicals. Rearrangement and subsequent hydrogenation reactions of STO methyl ester using heterogeneous palladium and rhodium on carbon catalysts to obtain methyl branched derivatives have been reported by Pryde [16, 17]. The rearrangement reaction was performed under N_2 at 150°C for 9 h, followed by a hydrogenation reaction at RT at 40 psi H_2 pressure for 1 h. Rearrangement reactions of the cyclopropene rings in STO methyl esters were also reported to be catalysed by SiO_2 under N_2 at 160°C for 15 min [18]. Both rearrangement systems led to the formation of isomeric FAME containing methylene- and methyl-branched isomers in conjugation with a C–C double bond in the fatty acid chain (Eq. 1).



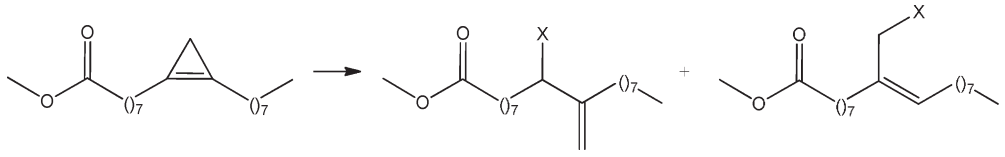
(eq. 1)

Gellerman [18] reported the hydrogenation of the cyclopropene rings in STO methyl esters to the corresponding cyclopropane rings using Pd–Pb on $CaCO_3$ as catalyst in methyl acetate as solvent at atmospheric pressure for 5 min. Oxidation of sterculic acid using potassium permanganate was reported to give an α-ketol, which was characterised as 9,11-dioxo-nonadecanoic acid, after a more detailed study using a range of analytical methods by other groups [19] (Eq. 2). This compound was also formed by oxidation using ozone in anhydrous ethyl acetate at −25°C for 30 min followed by hydrogenation using Pd/C in combination with hydrogen gas (5 h at 0°C) [20]. Oxidation of 9,11-dioxo-nonadecanoic acid by hydrogen peroxide in acetic acid under reflux conditions for 1 h gave 1,9-nonanedioic acid and nonanoic acid as the only fission products [20].



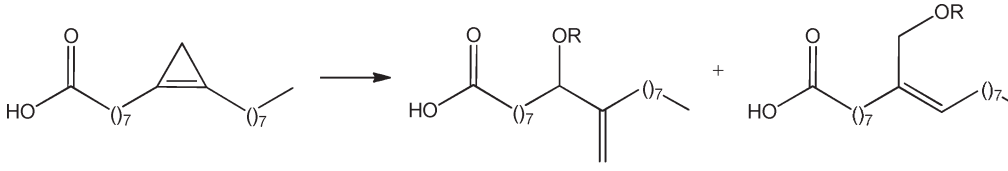
(eq. 2)

Reduction of sterculic acid with lithium hydride in ether gave sterculyl alcohol. Subsequent hydrogenation reactions of this alcohol using Pd and Pt catalysts revealed that the cyclopropene ring was kept intact during reduction [20]. Halogenation reactions of CPEFA with concentrated aqueous hydrogen halides in acetic acid for 1 h gave isomeric mono-unsaturated monohalo compounds [21] (Eq. 3).



(eq. 3)

Polymerisation of sterculic acid was reported by intermolecular addition of the carboxylic acid group to the cyclopropene unit of another fatty acid chain [22, 23] (Eq. 4, where R is a sterculic acid chain).



(eq. 4)

Branched ester derivatives of vegetable oils have interesting product properties. Ester derivatives with long, aliphatic branches on the fatty acid chains show improved flow-ability properties at low temperatures compared to the pure plant oils as the branches inhibit crystallisation [24]. Ester derivatives with unsaturated cyclic structures in the fatty acid chain, for example those resembling norbornene-like structures, may find applications as reactive building blocks in resins and/or packaging material [25, 26], as well as reactive monomers in coatings and paints [27, 28]. Ester derivatives with conjugated dienes in the fatty acid chains are of interest as reactive compounds in coating formulations [29]. Furthermore, a recent study showed that fatty acid derivatives containing α,β-unsaturated ketone units in the fatty acid chains may serve as reactive precursors for thermoset polymers [30].

We here report an experimental study to introduce branches in the fatty acid chain by modification of the cyclopropene rings of STO using both catalytic and stoichiometric chemistry. These include Diels–Alder, olefin metathesis, oxidation and rearrangement reactions (Fig. 1). The relevant

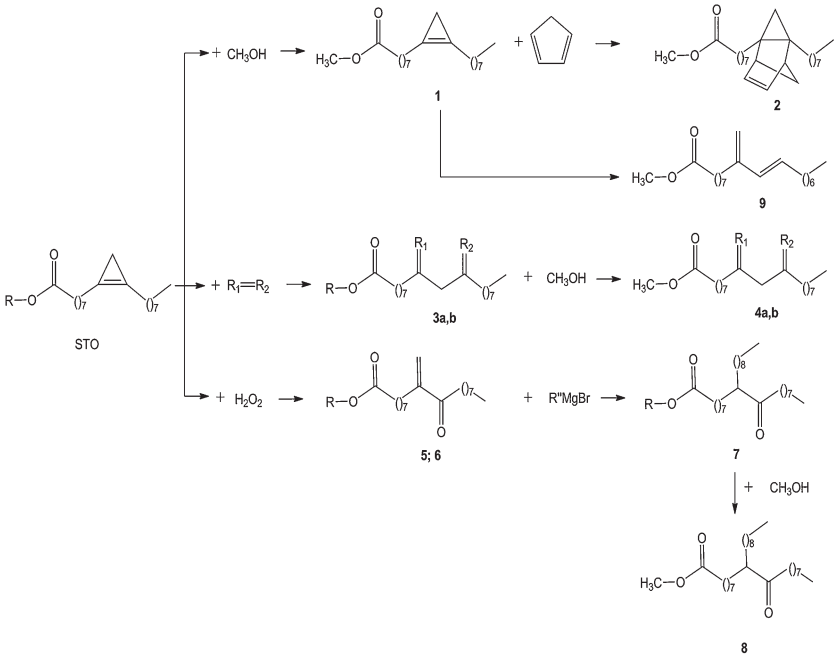


Figure 1. Chemical modifications of STO to branched ester derivatives. (R = remaining triglyceride structure, R1, R2 = substituents of the olefin, R″ = *n*-octyl).

cold flow properties of the products were determined and compared to STO and STO FAME. In addition, the storage stability of the oil was investigated.

2 Materials and methods

2.1 General

S. foetida L. oil originating from Indonesia was obtained from the Bandung Institute of Technology, Indonesia. Methanol (99.9%), diethyl ether (>99.0%), toluene (99.5%), dichloromethane (99.9%) were obtained from Lab-Scan (Gliwice, Poland). Heptane (>99%), cyclohexane (>99%), and sodium methoxide (anhydrous) were obtained from Acros Organics (Geel, Belgium). Dicyclopentadiene (93%) and 1-octene (>97%) were obtained from Merck (Darmstadt, Germany). Ammonium hydroxide solution (≥25% NH_3 in H_2O), trimethylsulphonium hydroxide (0.25 M in methanol), and tert-butylhydroperoxide solution (5.5 M in decane) were obtained from Fluka (Buchs, Switzerland). Palladium(II)acetate (98%), the tri-sodium salt of tris-(m-sulphophenyl)phosphine (Na_3TPPTS) (96%), scandium-(III)triflate (99%), copper(II)triflate (98%), Grubbs' 2nd generation catalyst ((1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene) (tricyclohexylphosphine) ruthenium), *n*-octylmagnesium bromide solution (2.0 M in diethylether), furan (98%), Al_2O_3 (basic, activated, Brockmann I, ~150 mesh, surface area 155 m^2/g), 2,3-dimethyl-2-butene (98%), 3-pyridinemethanol (98%), potassium-tert-butoxide solution (1 M in THF), tert-butyl methyl ether (98%), urea (98%), chloroform-d (99.8 atom %D), Fuller's earth (100–200 mesh), Quantofix® peroxide test sticks 1–100 mg/L, 2-amino-2-methyl-1-propanol (≥97%) and KF on alumina (40 wt% loading) were obtained from Sigma–Aldrich (Steinheim, Germany). Aqueous hydrogen peroxide (30 wt%) and sodium chloride (>99.5%) were obtained from Merck (Darmstadt, Germany). Palladium on carbon (5 wt%) was obtained from Engelhard (Rome, Italy). Methyl trioxorhenium (MTO, 98%) and OsO_4 (FibreCat™ 3003) were obtained from Alfa Aesar (Sulzbach, Germany). Magnesium sulphate (dried) was from Boom BV (Meppel, The Netherlands). All materials were used as received unless otherwise stated.

2.2 Analytical methods

The ^1H, ^{13}C, and APT NMR spectra were recorded in $CDCl_3$ at RT using a Varian AS400 or AS200 NMR Spectrometer. For ^1H NMR spectra, a total of 32 scans were performed with a relaxation delay of 1 s while 4000 scans were recorded for ^{13}C and APT NMR spectra with a relaxation delay of 5 s.

Quantification and compositional analysis of the fatty acids were performed by GC using a Shimadzu 2014 model equipped with HP1 5973 column (length 30 m, inside diameter 0.25 mm, film 0.25 μm) and an FID detector. GC–MS spectra for structural analysis were recorded on an HP 6890 model equipped with the same column as the GC–FID and with a mass selective detector. Peak identification was done using the NIST05a mass spectra library. For both GC methods, injection and detection were performed at 280°C, using oven temperature heating profiles from 175 to 280°C with an increment of 8°C/min. The STO was *trans*-methylated using trimethylsulphonium hydroxide solution prior to analysis by GC–MS and GC–FID according to a published procedure [31]. Typically, the oil (100 mg) was dissolved in methyl tert-butyl ether (5 mL). This solution (200 μL) was placed in a 2 mL vial equipped with insert and trimethylsulphonium hydroxide (100 μL) was added and mixed, and the sample was injected to the GC.

The oxidation and rearrangement products were analysed by GC–MS after a derivatisation protocol using 2-amino-2-methyl-1-propanol, as described in [32]. The sample (up to 4 mg) was charged to a 4 mL vial and 2-amino-2-methyl-1-propanol (500 μL) was added. The tube was flushed with nitrogen, capped, and heated in oven at 180°C for 18 h. After this period, the mixture was allowed to cool to RT. Dichloromethane (5 mL) and milli-Q water (2 mL) were added. The tube was shaken thoroughly and subsequently the organic and water phase were allowed to settle. The aqueous layer was removed using a pasteur pipette and the organic layer was washed again with water (2 mL). The organic layer was dried over $MgSO_4$. Dichloromethane was removed by a gentle N_2 stream. The sample was then dissolved in iso-octane and injected to the GC–MS.

The oxidation products were also analysed by GC–MS after a derivatisation protocol using pyridinemethanol, as described in ref. 33. Typically, 3-pyridinemethanol (400 μL) was mixed with potassium tert-butoxide solution (200 μL) to obtain a homogeneous solution. This mixture (500 μL) was mixed with the sample (10 mg) in dry dichloromethane (2 mL) in a 4 mL vial. The vial was closed and subsequently heated to 45°C for 45 min. Thereafter, the mixture was allowed to cool to RT and water (2 mL) and hexane (4 mL) were added and the biphasic system was intensely mixed. The phases were allowed to settle and the organic phase was taken and washed with water (2 mL) and dried over $MgSO_4$. The solvents were removed by evaporation (200 mbar, 50°C). The oily product was dissolved in hexane (1 mL) and injected to the GC–MS.

High resolution ESI-MS (HR-ESI-MS) analysis was performed using an EASY-nLC™ II HPLC apparatus from Proxeon Biosystems A/S, Denmark. The measurements were run in the positive scan mode with a sample concentration of 1 mg/mL in chloroform.

2.3 Cloud and pour point analyses

The cloud point (CP) and pour point (PP) were determined using a Mini Pour/Cloud Point tester model

MPC-102A/102L from Tanaka Scientific Limited, Tokyo, Japan, with detection interval of 1°C. The L mode was used for STO and the UH mode for the modified oils and esters.

2.4 Acid value analysis

The acid value of the products was determined using a slightly modified acid–base titration procedure reported by the National Cottonseed Products Association (Method number 28.029). The product (0.1 g) was weighed, mixed with diethyl ether and ethanol (50/50%, v/v solution, 20 mL) and then titrated with a 0.01 N KOH solution using phenolphthalein as the indicator until a faint red colour appeared and persisted for at least 30 s.

2.5 Purification of STO

For the olefin metathesis reaction, the oil was de-acidified using a procedure reported in [24(a)]. The oil was washed with aqueous NH_4OH solution at RT for 10 min. The soap was removed by centrifugation. Thereafter, the oil was washed several times with water and centrifuged (4000 rpm) until a clear oil was obtained. The neutral oil was mixed with Fuller's earth at RT for 1 h and centrifuged (4000 rpm) to remove the remaining solids. The oil was stored under nitrogen before the reaction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (m, –C***H***=C***H***–), 5.26 (m, OC***H***$(CH_2)_2$), 4.29 (dd, $\mathcal{J}$ = 11.9 Hz, 4.3 Hz, OCH(C***H***$_2)_2$), 4.14 (dd, $\mathcal{J}$ = 11.9 Hz, 6.0 Hz, OCH(C***H***$_2)_2$), 2.76 (t, $\mathcal{J}$ = 6.4 Hz, =CH–C***H***$_2$–CH=), 2.36 (t, $\mathcal{J}$ = 7.2 Hz, –C***H***$_2$COO–), 2.30 (3H, m, allylic –C***H***$_2$– of cyclopropene), 2.02 (1H, m, allylic –C***H***$_2$– of cyclopropene), 1.61 (m, –C***H***$_2$–), 1.57–1.33 (m, –C***H***$_2$–), 1.33–1.21 (m, –C***H***$_2$–), 0.87 (t, $\mathcal{J}$ = 6.8 Hz, C***H***$_3$CH$_2$), 0.76 (2H, s, –C–C***H***$_2$–C–, cyclopropene).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2–172.7 (–***C***OO–), 130.1–127.9 (***C***H=***C***H), 109.5–109.1 (–***C***–CH$_2$–***C***–, cyclopropene), 68.9 (O***C***H(CH$_2)_2$), 62.1 (OCH(***C***H$_2)_2$), 34.3–34.1 (allylic –***C***H$_2$– of cyclopropene), 31.9 (–***C***H$_2$–), 31.0–28.8 (–***C***H$_2$–), 27.5–26.9 (–***C***H$_2$–), 26.0–25.6 (–***C***H$_2$–), 24.8 (–***C***H$_2$–), 22.6 (–***C***H$_2$–), 14.1 (***C***H$_3$CH$_2$), 7.4 (–C–***C***H$_2$–C–, cyclopropene).

2.6 *Trans*-esterification of STO with methanol

The procedure for the *trans*-esterification reaction of STO with methanol was adapted from the work of Karaosmanoğlu et al. [34]. Before *trans*-esterification, the oil was purified as follows: crude oil (15 mL), diethyl ether (15 mL), and $CaCO_3$ (2 g) were mixed at RT for 10 min, centrifuged, and decanted to obtain the organic phase. $MgSO_4$ (2 g) was added to the organic phase and mixed for 5 min, centrifuged, and decanted. The organic phase was then filtered through a 0.45 μm PTFE filter. Diethyl ether was removed by evaporation in a rotary evaporator (stepwise down to 20 mbar at 40°C, few hours) and characterised by ^{1}H NMR to check the presence of remaining ether.

A pre-determined amount of purified STO (10 g, 11.2 mmol) was added to a solution of methanol (2.43 mL, 60 mmol) and sodium methoxide (0.34 mL, 30 vol% in methanol) in a flask (50 mL) at 35°C. The mixture was allowed to react overnight, thereafter, an equal volume of water was added to allow separation in a centrifuge tube. The mixture was shaken once gently, therefore shaken vigorously two times and directly centrifuged. The upper phase was decanted and dried over $MgSO_4$ to obtain the methyl esters (STO FAME). The STO FAME (**1**) was characterised by ^{1}H, ^{13}C NMR and HPLC HR-ESI-MS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (m, C***H***=CH), 3.63 (m, COOC***H***$_3$), 2.74 (t, $\mathcal{J}$ = 6.0 Hz, =CH–C***H***$_2$–CH=), 2.34 (t, $\mathcal{J}$ = 6.8 Hz, –C***H***$_2$COO–), 2.27 (4H, t, $\mathcal{J}$ = 7.0 Hz, allylic –C***H***$_2$– of cyclopropene), 2.00 (1H, m, $\mathcal{J}$ = 7.0 Hz, allylic –C***H***$_2$– of cyclopropene), 1.59 (m, –C***H***$_2$–), 1.55–1.45 (m, –C***H***$_2$–), 1.40–1.17 (m, –C***H***$_2$–), 0.85 (t, $\mathcal{J}$ = 6.4 Hz, C***H***$_3$CH$_2$), 0.73 (2H, s, –C–C***H***$_2$–C–, cyclopropene).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1 (–***C***OO–), 130.0–129.6 (***C***H=***C***H), 127.9–127.8 (***C***H=***C***H), 109.5–109.1 (–***C***–CH$_2$–***C***–, cyclopropene), 51.3 (COO***C***H$_3$), 34.0 (allylic –***C***H$_2$– of cyclopropene), 31.8 (allylic –***C***H$_2$– of cyclopropene), 29.6–28.9 (–***C***H$_2$–), 27.3–27.1 (–***C***H$_2$–), 25.9 (–***C***H$_2$–), 25.6 (–***C***H$_2$–), 24.9 (–***C***H$_2$–), 22.6 (–***C***H$_2$–), 14.0 (***C***H$_3$CH$_2$), 7.3 (–C–***C***H$_2$–C–, cyclopropene).

HR-ESI-MS: *m/z* 295.2630 [C18:2, M + H]$^+$ (calc. 295.2639), 295.2630 [C18:CE, M + H]$^+$ (calc. 295.2639), 297.2789 [C18:1, M + H]$^+$ (calc. 297.2795), 309.2789 [C19:CE, M + H]$^+$ (calc. 309.2795).

2.7 Enrichment of the cyclopropene content in STO FAME

The cyclopropene content in the STO FAME was enriched by a fractionation method using urea [35]. The procedure was as follows: urea (20 g) was added to methanol (100 mL) and the mixture was heated at reflux until all urea was dissolved. STO FAME (8.3 g) as prepared in sub-section 2.4 was added to the methanol solution, mixed, and allowed to cool to RT overnight. The resulting suspension was filtered and the remaining solids were washed twice with methanol (2.5 mL) saturated with urea. The solution was then poured into aqueous HCl (1%, 60 mL) and extracted twice, first with hexane (50 mL) then with diethyl ether (50 mL). The organic layers were combined and washed twice with water (50 mL) and subsequently dried over $MgSO_4$. The solvents were removed by evaporation in a rotary evaporator (200 mbar, 30–50°C) for 2 h. After removing the solvent, 3.0 g of methyl esters were recovered. The content of fatty acids with cyclopropene units was 81 mol% as determined by GC–MS.

2.8 Modification reactions

The modification reactions were performed either using the STO FAME (Diels–Alder and rearrangement reactions) or the purified STO (olefin metathesis and oxidation—addition reactions), see Fig. 1 for details. In the latter case, the methyl esters were obtained after the modification reaction by a subsequent *trans*-esterification reaction with methanol.

2.9 Diels–Alder reactions of STO FAME with cyclopentadiene

The Diels–Alder reactions were carried out according to a procedure published by Corey and coworkers[36]. Cyclopentadiene was obtained from dicyclopentadiene by catalytic cracking using Cu metal. Dicyclopentadiene (10 g) was charged to a distillation set-up equipped with a Vigreux column containing copper. The cyclopentadiene vapor was collected in a condenser and cooled and stored in an ice bath (0°C) to prevent dimerisation.

Typically, the Diels–Alder experiments were performed as follows: STO FAME, **1** (3 g, 10 mmol), as prepared in sub-section 2.4, were placed in an Erlenmeyer flask (100 mL) and the diene (cyclopentadiene or furan) was added at the desired mol ratio (1 or 15). Solvent (toluene, cyclohexane or water; 10 mL) and in some cases a catalyst (10 mol%), were added and the reaction was carried out at the desired temperature (22, 30 and 40°C) for 18 h. The solvent and excess diene were removed by evaporation using a rotary evaporator (100 mbar, 80°C) for 2 h. Product (**2**) was characterised by ^{1}H and ^{13}C NMR.

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.75 (2H, s, –CH–C***H***=C***H***–CH–, Diels–Alder adduct), 5.27 (m, –C***H***=C***H***–), 3.58 (s, COOC***H***$_3$), 2.69 (t, $\mathcal{J} = 5.3$ Hz, =CHC***H***$_2$CH=), 2.49 (2H, s, –C–C***H***–CH=CH–C***H***–C–, Diels–Alder adduct), 2.24 (m, –C***H***$_2$COO–), 1.95 (m, –C***H***$_2$CH=CH–), 1.70 (1H, d, $\mathcal{J} = 6.0$ Hz, CH–C***H***$_2$–CH, Diels–Alder adduct), 1.62–1.07 (m, –C***H***$_2$–), 0.79 (t, $\mathcal{J} = 5.7$ Hz, C***H***$_3$CH$_2$), 0.45 (1H, d, $\mathcal{J} = 4.8$ Hz, –C–C***H***$_2$–C, cyclopropane, Diels–Alder adduct), 0.0 (1H, m, –C–C***H***$_2$–C, cyclopropane, Diels–Alder adduct).

^{13}C NMR (50 MHz, $CDCl_3$) δ 175.5 (–***C***OO–), 133.2 (–CH–***C***H=***C***H–CH–, Diels–Alder adduct), 130.2 (***C***H=***C***H), 59.7 (CH–***C***H$_2$–CH, Diels–Alder adduct), 51.6 (COO***C***H$_3$), 47.9 (–C–***C***H–CH=CH–***C***H–C–, Diels–Alder adduct), 34.3 (–***C***H$_2$–), 32.1–31.8 (–***C***H$_2$–), 30.2–28.9 (–***C***H$_2$–), 27.9 (–***C***H$_2$–), 27.5 (–***C***H$_2$–), 25.2 (–***C***H$_2$–), 22.9 (–***C***H$_2$–), 14.3 (***C***H$_3$CH$_2$).

2.10 Olefin metathesis reactions of STO with 2,3-dimethyl-2-butene

Olefin metathesis reactions were performed using a procedure given by Mol [37]. The syntheses were carried out under nitrogen using standard Schlenk and glovebox techniques. STO (2 g, 2.23 mmol) was added to a Schlenk tube containing Grubbs' 2nd generation catalyst (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro (phenylmethylene) (tricyclohexylphosphine) ruthenium (10 mg, $1.18.10^{-5}$ mol) and the mixture was stirred at RT. The olefin (2,3-dimethyl-2-butene) was introduced (olefin to cyclopropene mol ratio of 20:1) and the resulting mixture was kept at 55°C for 6 h. Thereafter, the mixture was cooled to RT and the olefin was removed by evaporation using a rotary evaporator (100 mbar, 80°C) for 2 h. Subsequently, the mixture was added over a silica gel column to remove catalyst residues, giving product **3a**. Thereafter, a *trans*-esterification with methanol was performed under reaction conditions as described in sub-section 2.4. The reaction mixture containing **4a** was characterised using ^{1}H and ^{13}C NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (s, =C***H***$_n$), 5.54 (s, =C***H***$_n$), 5.34–5.14 (m, C***H***=C***H***), 4.84 (s, C***H***=C***H***), 4.83 (s, –C***H***=C***H***–), 4.77 (m, C***H***=C***H***), 4.60 (m, C***H***=C***H***) 3.50 (s, COOC***H***$_3$), 2.50 (t, $\mathcal{J} = 7.4$ Hz $(CH_3)_2$C=C–C***H***$_2$–C=C$(CH_3)_2$, metathesis adduct and linoleic derivatives), 2.14 (t, $\mathcal{J} = 7.4$ Hz, –C***H***$_2$COO–), 1.85 (m (***H***$_2$C–$(CH_3)_2$C–CH$_2$–C$(CH_3)_2$–C***H***$_2$, allylic, metathesis adduct and unsaturated fatty acid (derivatives)), 1.66 (m, C=(C***H***$_3$)$_2$, metathesis adduct), 1.65 (m, C=(C***H***$_3$)$_2$, metathesis adduct), 1.48 (s, C=(C***H***$_3$)$_2$, metathesis adduct), 1.46 (m, –C***H***$_2$–), 1.26–0.79 (m, –C***H***$_2$–), 0.72 (t, $\mathcal{J} = 6.6$ Hz, C***H***$_3$CH$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5–174.3 (–***C***OO–), 133.8 (***C***=***C***), 130.6–128.0 (***C***=***C***), 118.2 (***C***=***C***), 51.6 (COO***C***H$_3$), 34.3–27.2 (–***C***H$_2$–), 25.2 (–***C***H$_2$–), 22.9 (–***C***H$_2$–), 14.3 (***C***H$_3$CH$_2$).

2.11 Olefin metathesis reactions of STO with 1-octene

Olefin metathesis reaction with 1-octene to give **3b** and the subsequent *trans*-esterification to yield **4b** were performed at similar conditions as given for 2,3-dimethyl-2-butene. The reaction mixture after *trans*-esterification was analysed by ^{1}H, ^{13}C NMR, and HPLC HR-ESI-MS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (d, $\mathcal{J} = 4.4$ Hz, =C***H***$_n$), 5.64 (d, $\mathcal{J} = 6.0$ Hz, =C***H***$_2$), 5.47–5.17 (m, C***H***=C***H***), 4.94 (m, C=C***H***–, metathesis adduct), 4.86 (m, C=C***H***$_2$, metathesis adduct), 4.73–4.68 (m, C***H***=C***H***), 3.61–3.60 (m, COOC***H***$_3$), 2.61 (dd, $\mathcal{J} = 7.1$ Hz, =C–C***H***$_2$–C=, metathesis adduct or linoleic acid derivative), 2.24 (m, –C***H***$_2$COO–), 2.15–1.85 (m, allylic –C***H***$_2$–, remaining cyclopropene), 2.05–1.0 (m, –C***H***$_2$–), 0.83 (t, $\mathcal{J} = 5.6$ Hz, C***H***$_3$CH$_2$), 0.71 (m, C–C***H***$_2$–C, remaining cyclopropene).

HR-ESI-MS: *m/z* 407.3871 [C18:CE metathesis adduct, M + H]$^{+}$ (calc. 407.3891), 421.4040 [C19:CE metathesis adduct, M + H]$^{+}$ (calc. 421.4047).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5 (***C***OO–),114.3 (***C***H=***C***H), 112.6–112.4 (***C***H=***C***H), 51.6 (COO***C***H$_3$), 34.0

(allylic ***C***H_2–C= cyclopropene), 32.1–31.9 (allylic ***C***H_2–C= cyclopropene), 29.9–29.0(–***C***H_2–), 27.6–27.4 (–***C***H_2–), 26.3–26.2 (–***C***H_2–), 25.2 (–***C***H_2–), 22.9–22.8 (–***C***H_2–), 14.3 (***C***H_3CH_2), 7.6 (C–***C***H_2–C, remaining cyclopropene).

2.12 Oxidation of STO at typical epoxidation conditions using the Sharpless method [38]

Methyl trioxorhenium (4.78×10^{-2} g, 0.14 mmol), pyridine (279 μL, 3.5 mmol), STO (10 g, 28.8 mmol total C = C) and dichloromethane (5.8 mL) were placed in a three necked round bottom flask equipped with a reflux condenser. The reaction was started by the drop wise addition of aqueous hydrogen peroxide (6.0 mL, 57.6 mmol) under vigorous stirring at RT in about 10 min. The stirring was stopped after 1.5 h and subsequently diethyl ether (150 mL) and brine (100 mL) were added and both liquid phases were allowed to settle. The organic phase was passed through a basic Al_2O_3 column to remove catalyst residues, subsequently washed with brine until no peroxide was left and dried over $MgSO_4$. The solvents were removed under vacuum (150 mbar, 30°C) for 3 h. The product (**5**) was characterised using NMR (^{1}H, ^{13}C) and GC–MS after derivatisation with pyridinemethanol and 2-amino-2-methyl-1-propanol. Subsequently, **5** was *trans*-esterified with methanol and the methyl esters were characterised using APT and HPLC HR-ESI-MS.

^{1}H NMR for **5**: (201 MHz, $CDCl_3$) δ 5.93 (1H, s, O=C–C=C***H***$_2$, unsaturated ketone), 5.67 (1H, s, O=C–C=C***H***$_2$, unsaturated ketone), 5.28 (s, remaining –C***H***=C***H***–), 5.26 (m, OC***H***$(CH_2)_2$), 4.28 (dd, $\mathcal{J}$ = 12 Hz, 4.4 Hz, OCH(C***H***$_2)_2$), 4.11 (dd, $\mathcal{J}$ = 12.0 Hz, 5.8 Hz, OCH(C***H***$_2)_2$), 3.15–2.79 (m, –C***H***–O–C***H***–, epoxide), 2.63 (t, $\mathcal{J}$ = 7.4 Hz, –C***H***$_2$COO–), 2.41–2.10 (m, –C***H***$_2$–), 1.65–1.12 (m, –C***H***$_2$–), 0.85 (t, $\mathcal{J}$ = 6.2 Hz, C***H***$_3CH_2$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 202.5 (O=***C***–C=CH_2, unsaturated ketone), δ 202.4 (O=***C***–C=CH_2, unsaturated ketone), 173.2–172.8 (–***C***OO–), 149.0 (O=C–***C***=CH_2, unsaturated ketone), 148.9 (O=C–***C***=CH_2, unsaturated ketone), 123.5 (O=C–C=***C***H_2, unsaturated ketone), 123.4 (O=C–C=***C***H_2, unsaturated ketone), 68.9 (–O***C***H$(CH_2)_2$), 62.1 (OCH(***C***$H_2)_2$), 57.2 (–***C***H–O–***C***H–, –epoxide), 37.8 (–***C***H_2–), 37.7 (–***C***H_2–), 34.1–22.6 (–***C***H_2–), 14.1 (***C***H_3CH_2).

APT NMR for methyl esters of **5** (101 MHz, $CDCl_3$) δ 202.7 and 201.9 (O=***C***–C=CH_2, upward, unsaturated ketone), 174.2 and 173.9 (–***C***OO–, upward), 149.2 and 148.9 (O=C–***C***=CH_2, upward, unsaturated ketone), 123.1 and 122.8 (O=C–C=***C***H_2, upward, unsaturated ketone), 57.2–56.5 (–***C***H–O–***C***H–, downward, epoxide), 51.3 (COO***C***H3, downward), 37.7–37.6 (=***C***H_2–, upward), 34.1–33.8 (–***C***H_2–, upward), 32.0–31.7 (–***C***H_2–, upward), 30.8–30.7 (–***C***H_2–, upward), 29.9–28.1 (–***C***H_2–, upward), 27.9–25.8 (–***C***H_2–, upward), 26.8–23.7 (–***C***H_2–, upward), 22.5 (–***C***H_2–, upward), 14.1 (***C***H_3CH_2, downward).

HR-ESI-MS for methyl esters of **5**: *m*/*z* 311.2582 [C18 enone, M + H]$^+$ (calc. 311.2588), 313.2736 [epoxystearate, M + H]$^+$ (calc. 313.2744), 325.2738 [C19 enone, M + H]$^+$ (calc. 325.2744), 327.2528 [diepoxystearate, M + H]$^+$ (calc. 327.2537).

2.13 Oxidation of STO at typical dihydroxylation conditions using the Prilezhaev method [39]

S. foetida L. oil (10 g, 28.8 mmol total C=C) and formic acid (8.7 mL, 230 mmol) were placed in a three necked round bottom flask. The reaction was started by the dropwise addition of aqueous hydrogen peroxide (6.0 mL, 57.6 mmol) at RT over a period of 10 min and the mixture was allowed to react under vigorous stirring. After 24 h, stirring was ceased and diethyl ether (150 mL) and brine (100 mL) were added. After vigorous mixing, both liquid layers were allowed to settle. The organic phase was washed with brine until no residual peroxide could be detected and dried over $MgSO_4$. The solvent was removed in vacuo (300 mbar, 30°C) for 1 h. The product (**6**) was characterised using ^{1}H and ^{13}C NMR and GC–MS after derivatisation with pyridinemethanol.

^{1}H NMR (201 MHz, $CDCl_3$) δ 8.16–8.0 (m, CH–O–C***H***O, formyl branch), 5.94 (1H, s, O=C–C=C***H***$_2$, unsaturated ketone), 5.67 (1H, s, O=C–C=C***H***$_2$, unsaturated ketone), 5.24 (m, OC***H***$(CH_2)_2$), 4.68 (m, C***H***–O–CHO, formyl branch), 4.28 (dd, $\mathcal{J}$ = 11.8 Hz, 4.0 Hz, OCH(C***H***$_2)_2$), 4.12 (dd, $\mathcal{J}$ = 11.7 Hz, 5.8 Hz, OCH(C***H***$_2)_2$), 3.95–3.35 (m, HO–C***H***–C***H–***OH, dihydroxy), 2.64 (m, –C***H***$_2$COO–), 2.27 (m, –C***H***$_2$–), 1.74–1.06 (m, –C***H***$_2$–), 0.86 (t, $\mathcal{J}$ = 6.5 Hz, C***H***$_3CH_2$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 202.5 and 202.4 (O=***C***–C–CH_2, unsaturated ketone), 173.2 and 172.8 (–***C***OO–), 163.3 (CH–O–***C***HO, formyl branch), 149.0 and 148.9 (O=C–***C***–CH_2, unsaturated ketone), 123.5 and 123.4 (O=C–C–***C***H_2, unsaturated ketone), 75.4–72.0 (–***C***(H)OH–), 68.8 (–O***C***H$(CH_2)_2$), 62.0 (OCH(***C***$H_2)_2$), 57.5–56.7 (–***C***H–O epoxide), 37.8–37.7 (–***C***H_2–), 34.2–22.4 (–***C***H_2–), 14.1 (***C***H_3CH_2).

2.14 Addition reactions of 9(10)-*ene*-10(9)-oxo-octadecanoate with *n*-octylmagnesium bromide

The reaction of the 9(10)-*ene*-10(9)-oxo-octadecanoate moieties in **5** (Section 2.6.4) with *n*-octylmagnesium bromide is based on the work of Tawney [40]. Typically, *n*-octylmagnesiumbromide solution (16.5 mL, 33 mmol, 2.0 M in diethyl ether) was mixed with $CuCl_2$ (7.4×10^{-2} g, 0.55 mmol) in a three necked round bottom flask equipped with a reflux condenser at RT under N_2 for 45 min. The dispersion was cooled to 5°C and then **5** (10 g, 27.5 mmol enone) dissolved in diethyl ether (15 mL) was added stepwise in a 1 h period. Thereafter the reaction temperature was raised to 55°C and the mixture was reacted for another 3 h. The reaction mixture was allowed to stand overnight.

Chipped ice (16.5 g) and glacial acetic acid (5 mL) were added to quench the reaction. Subsequently, diethyl ether (50 mL) was added and the water phase was separated from the organic phase. The water phase was washed with an equal volume of diethyl ether and the ether phase was combined with the organic phase. The resulting organic phase was dried over $MgSO_4$. The solvents were removed in vacuo (150 mbar, 30°C for 1 h, thereafter 30 mbar and 80°C). The product (**7**) was characterised by ^{1}H and ^{13}C NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (1H, s, O=C–C=C$\boldsymbol{H}_2$, remaining unsaturated ketone), 5.68 (1H, s, O=C–C=C$\boldsymbol{H}_2$, remaining unsaturated ketone), 5.25 (m, OC$\boldsymbol{H}$(CH$_2$)$_2$), 5.03–4.9 (s, C=C$\boldsymbol{H}_2$ (1 + 2)-addition adduct), 4.28 (m, OCH(C$\boldsymbol{H}_2$)$_2$), 4.13 (dd, $\mathcal{J}$ = 11.1 Hz, 5.6 Hz, OCH(C$\boldsymbol{H}_2$)$_2$), 3.63 (m, C$\boldsymbol{H}$–OH, hydroxy), 2.64 (m, C$\boldsymbol{H}$ (1 + 4)-addition adduct), 2.31 (t, $\mathcal{J}$ = 7.4 Hz, –C$\boldsymbol{H}_2$COO–), 1.7–1.1 (m, –C$\boldsymbol{H}_2$–), 0.87 (t, $\mathcal{J}$ = 5.8 Hz, C$\boldsymbol{H}_3$CH$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216–211 (O=$\boldsymbol{C}$–CH (1 + 4)-addition adduct), 174.0–172.5 (–$\boldsymbol{C}$OO–), 152.9 (CH$_2$=$\boldsymbol{C}$–C–OH (1 + 2)-addition adduct), 108.1 ($\boldsymbol{C}$H$_2$=C–C–OH (1 + 2)-addition adduct), 78.0 ($\boldsymbol{C}$H–OH), 74.4 ($\boldsymbol{C}$H–OH), 72.9 (CH$_2$=C–$\boldsymbol{C}$–OH (1 + 2)-addition adduct), 68.8 (O$\boldsymbol{C}$H(CH$_2$)$_2$), 63.0–62.1 (OCH($\boldsymbol{C}$H$_2$)$_2$), 54.0–50.5 (CH (1 + 4)-addition adduct), 43.0–22.5 (–$\boldsymbol{C}$H$_2$–), 14.1 ($\boldsymbol{C}$H$_3$CH$_2$).

2.15 Rearrangement reactions of STO FAME

The rearrangement reaction of STO FAME (**1**) was performed using Pd-TPPTS and Pd/C in heptane or cyclohexane as solvent, according to a procedure reported by Kai and Pryde [16]. The reactions were carried out in a stirred batch stainless steel autoclave (350 mL, Buchii GmBH) under nitrogen using a stirrer speed of 1400 rpm. Typically, **1** (3 g, 10 mmol), as prepared in sub-section 2.4., were charged to the autoclave and dissolved in 100 mL of an organic solvent (heptane or cyclohexane). In the case of the homogeneous Pd-TPPTS catalyst, water was added (volume ratio of water to organic solvent was 1 or 0.5). Subsequently, the heterogeneous catalyst (Pd/C) or the homogeneous catalyst components (Pd-acetate, 0.5 wt% on ester, calculated as metal and TPPTS ligand at a molar ratio of ligand to metal precursor of 2) were added. The reactor was flushed with nitrogen, closed, and the reactor contents were heated to the pre-determined temperature (90°C for the homogeneous catalyst and 150°C for Pd/C). A typical reaction time of 6 h was applied. The reactor content was cooled to RT and the liquid phase was allowed to settle. The organic phase was collected and the solvent was removed in vacuo at elevated temperature (212 mbar, 60°C) for 2 h. The product (**9**) was characterised by ^{1}H, APT NMR and HPLC HR-ESI-MS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46–6.40 (m, C$\boldsymbol{H}$=C$\boldsymbol{H}$, rearrangement product), 6.05–5.92 (m, C$\boldsymbol{H}$=C$\boldsymbol{H}$, rearrangement product), 5.79–5.58 (m, C$\boldsymbol{H}$=C$\boldsymbol{H}$, rearrangement product), 5.39–5.24 (m, C$\boldsymbol{H}$=C$\boldsymbol{H}$, oleic and linoleic), 4.85 and 4.71 (m, =C$\boldsymbol{H}_2$, methylene branch, rearrangement product), 3.63–3.60 (s, COOC$\boldsymbol{H}_3$), 2.75 (m,=CH–C$\boldsymbol{H}_2$–CH=), 2.36–2.18 (m, –C$\boldsymbol{H}_2$COO–), 2.08–1.11 (m, –C$\boldsymbol{H}_2$–), 0.84 (t, $\mathcal{J}$ = 6.6 Hz, C$\boldsymbol{H}_3$CH$_2$).

APT NMR (101 MHz, $CDCl_3$) δ 174.6 and 174.8 (–$\boldsymbol{C}$OO–, upward), 147.0 and 146.9 (CH$_2$=$\boldsymbol{C}$–CH=CH–, upward, rearrangement product), 132.7–128.4 (CH=$\boldsymbol{C}$H, downward, rearrangement product and other unsaturated fatty acids), 113.4 and 113.3 ($\boldsymbol{C}$H$_2$=C–CH=CH–, upward, rearrangement product), 51.3 (COO$\boldsymbol{C}$H$_3$, downward), 35.0–20.3 (–$\boldsymbol{C}$H$_2$–, upward), 14.6 ($\boldsymbol{C}$H$_3$CH$_2$, downward).

HR-ESI-MS: *m/z* 295.2630 [C18:2, M + H]$^+$ (calc. 295.2639), 295.2630 [C18:2 conjugated, M + H]$^+$ (calc. 295.2639), 297.2786 [C18:1, M + H]$^+$ (calc. 297.2795), 309.2788 [C19:2 conjugated, M + H]$^+$ (calc. 309.2795).

3 Results and discussion

The modification reactions of STO in this study are primarily aimed to obtain branched ester derivatives of STO. The introduction of branches in the fatty acids chain of STO or its methyl esters (STO FAME) was performed by various modification reactions. Synthetic strategies include Diels–Alder, olefin metathesis, oxidation, addition and rearrangement reactions, as summarised in Fig. 1. As the STO contains also considerable amounts of saturated and unsaturated fatty acids (up to 33 wt%, see Table 1), the products of the modification reactions are mixtures of cyclopropene derived products and straight chain fatty acids or derivatives thereof. Product separation by conventional methods (distillation, extraction) proved very cumbersome. The product mixtures as such were therefore analysed by NMR (^{1}H, ^{13}C, APT), HPLC HR-ESI-MS and in some cases with GC–MS using suitable derivatisation strategies to determine the chemo- and regio-selectivity of the reactions involving the cyclopropene units.

3.1 Characterisation of the STO feedstock

Both the crude and purified STO were characterised using ^{1}H and ^{13}C NMR as well as GC–FID to determine the fatty acid composition and the CPEFA content of the oil. The ^{1}H and ^{13}C NMR spectra of the purified STO are shown in Fig. 2. Characteristic resonances of the cyclopropene units are present as a singlet at δ 0.76 ppm (C–C$\boldsymbol{H}_2$–C) in ^{1}H NMR spectra and at δ 7.34 ppm (C–$\boldsymbol{C}$H$_2$–C) and about 109 ppm ($\boldsymbol{C}$–CH$_2$–$\boldsymbol{C}$) in ^{13}C NMR. The conversion of the cyclopropene rings in the various reactions is easily monitored by ^{1}H NMR by considering the disappearance of the characteristic CH$_2$ resonances of the cyclopropene unit. In addition, the anticipated peaks of the glycerol backbone and fatty acid chains without cyclopropene units are present. The fatty acids composition according to GC–FID is presented in

Table 1. Fatty acids composition of STO

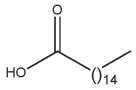
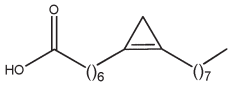
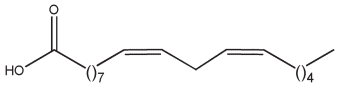
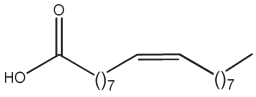
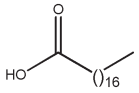
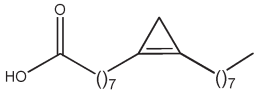
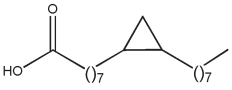
Fatty acids			This study (GC–FID, wt%)	Literature [5] (wt%)
Palmitic acid	C16:0		17.1	20.0
Malvalic acid	C18:CE		9.1	11.4
Linoleic acid	C18:2		5.6	4.12
Oleic acid	C18:1		7.4	8.3
Stearic acid	C18:0		2.1	0.54
Sterculic acid	C19:CE		58.2	55.7
Dihydrosterculic acid	C19:CA		0.5	–
Total cyclopropenoid fatty acids fraction			67.3	67.1
Total unsaturated fatty acids fraction			80.3	79.5

Table 1. The STO used in this study contains about 67 wt% of CPEFA, with sterculic acid as the main fatty acid in the triglyceride (58 wt%). Malvalic acid, the C18 derivative of sterculic acid, was present in much lower amounts (about 9 wt%). The fatty acid composition is in line with earlier literature data [5].

The acid value of the crude STO was 3.62 mg KOH/g oil. A significant reduction in the free fatty acid content was obtained by using a conventional de-acidification procedure (0.17 mg KOH/g oil). During this procedure, the cyclopropene content of the oil was not affected, an indication that the cyclopropene rings are stable in a basic environment.

The oil is easily converted to the corresponding methyl esters (FAME) by a conventional *trans*-esterification reaction with methanol at 35°C using NaOMe as the basic catalyst. An HPLC HR-ESI-MS analysis (positive mode) of the STO FAME showed product peaks with m/z values of 309.2789 and 295.2630 amu, which correspond to methyl sterculate and methyl malvalate chains, respectively.

3.2 Diels–Alder reaction of STO FAME with cyclopentadiene

Diels–Alder reactions of the STO FAME (**1**) with cyclopentadiene were investigated to produce esters derivatives of STO with relatively bulky and unsaturated substituents in the fatty acid chains (Eq. 5). The reactions were performed in an apolar organic solvent (toluene/hexane) or water in a temperature range of 20–40°C. In some cases, a typical Lewis acid catalyst like $Sc(OTf)_3$ or $Cu(OTf)_2$ was applied. An overview of the experiments is given in Table 2. Initial experiments were performed in toluene at RT with a 15-fold excess

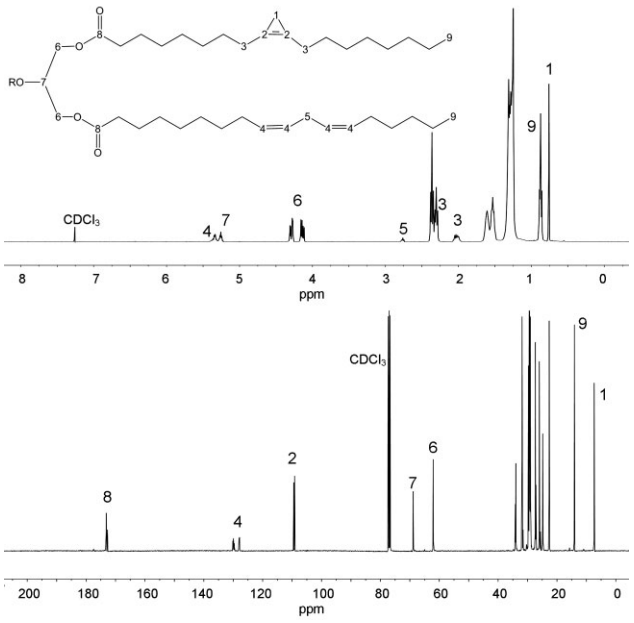
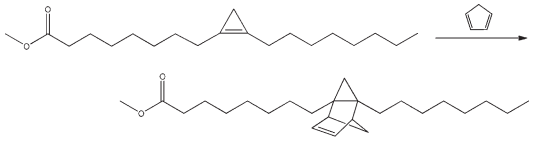


Figure 2. ^{1}H and ^{13}C NMR spectra of STO.

of cyclopentadiene on cyclopropene units for an 18 h reaction times. The cyclopropene conversion was 72 mol% in this case, and the selectivity to the anticipated Diels–Alder product was 93 mol% (Eq. 5). By products were not identified.



(eq. 5)

In a subsequent experiment, the molar ratio of the cyclopentadiene to cyclopropene units was reduced from 15 to 1 to a 1 to 1 ratio. A considerable reduction in both the conversion and selectivity were observed (Table 2). However, when increasing the temperature from 20 to 40°C, this negative effect was suppressed and a high cyclopropene conversion and product selectivity were observed (86 and 93 mol%, respectively).

To reduce reaction times, the use of Lewis acid catalysts ($Sc(OTf)_3$ and $Cu(OTf)_2$) were explored. Full conversion of the cyclopropene rings was observed, however, the corresponding cycloaddition product was not observed (NMR). So far, we have not been able to identify the reaction products. Thus, Lewis acid catalysts indeed have a positive effect on activity, though do not lead to the formation of the desired products.

Solvent effects were explored by performing also some reactions in water and cyclohexane at 40°C and a 1 to 1 mol ratio of cyclopentadiene and cyclopropene units. The results are given in Table 2. The differences in reaction performance between toluene and cyclohexane are only minor. The solubility parameter of toluene (8.9 $(cal/cm^3)^{0.5}$) and cyclohexane (8.2 $(cal/cm^3)^{0.5}$) [41] are close and as such no major differences are anticipated and this indeed proved to be the case. A reaction in water (40°C, 18 h, molar ratio of diene to dienophile = 1) gave excellent results. Essential quantitative cyclopropene conversion and selectivity to the cycloaddition product were observed (Table 3 entry 9). These findings are in line with extensive work by Breslow [42], who demonstrated that Diels–Alder reactions between non-polar compounds may proceed at much higher rates in water than in organic solvents. The reaction rate acceleration in water is probably due to favourable hydrogen bonding between water molecules and the polarised transition state [43, 44].

Table 2. Overview of the Diels–Alder reactions[a)]

Exp	Diene	T (°C)	Diene/dienophile (mol)	Solvent	Conversion (mol%)[b)]	Selectivity (mol%)[b)]
1	Cyclopentadiene	20	15	Toluene	72	93
2	Cyclopentadiene	20	1	Toluene	41	73
3	Cyclopentadiene	40	1	Toluene	86	93
4	Cyclopentadiene	20	1	Cyclohexane	46	66
5	Furan	20	15	Toluene	2	0
6	Cyclopentadiene	30	1	Toluene	70	92
7	Cyclopentadiene[c)]	40	1	Toluene	>99	0
8	Cyclopentadiene[d)]	40	1	Toluene	>99	0
9	Cyclopentadiene	40	1	Water	>99	>99

[a)] Reaction time: 18 h.
[b)] Conversion and product selectivity were calculated by ^{1}H NMR. Conversion is the cyclopropene conversion, selectivity is defined as the amount of the Diels–Alder product divided by the amount of cyclopropene rings converted.
[c)] In presence of scandium (III) triflate.
[d)] In presence of copper (II) triflate.

Table 3. Results of the olefin metathesis reactions[a)]

Exp	Olefin	Catalyst (mol%)	Temperature (°C)	Reaction time (h)	Conversion (mol%)	Selectivity (mol%)
1	2,3-Dimethyl-2-butene	0.18	40	6	78	29
2	2,3-Dimethyl-2-butene	0.18	55	6	99	32
3	1-Octene	0.18	55	6	54	47
4	CPFA methyl ester	0.18	55	6	26	–
5	CPFA methyl ester	0.9	55	170	40	–

[a)] Conversion and product selectivity were calculated by ^{1}H NMR. Conversion is the cyclopropene conversion, selectivity is defined as the amount of the metathesis products divided by the amount of cyclopropene rings converted.

A representative ^{1}H NMR spectrum of the cycloaddition product is shown in Fig. 3. Characteristic peaks of the cycloaddition products are at 0.0 and 0.45 ppm, belonging to the two diastereotopic protons of the cyclopropane CH_2 group, at 2.49 ppm (CH at the bridgehead) and 5.75 ppm (olefinic CH groups in the cycloaddition product). For comparison, ^{1}H NMR spectra of the oil of the *Litchi chinensis* plant, known to contain fatty acid chains with cyclopropane units, show resonances at δ −0.3 and 0.6 ppm for the methylene protons of the cyclopropane ring [45]. Based on the NMR data, only one of the possible geometric isomers is formed. Diels–Alder reactions are known to be concerted reactions, meaning that the new σ-bonds between the cyclopropene ring and cyclopentadiene are formed while the existing π-bonds are converted [46]. Based on this mechanism, the likely cycloaddition product is the *cis*-isomer.

Finally, also a reaction was performed with furan instead of cyclopentadiene (Table 2, entry 5). Disappointing results were obtained, a low conversion (2 mol%) and no indication for the formation of the cycloaddition product. These findings may be rationalised by considering that Diels–Alder reactions between an electron rich diene such as a furan are generally only successful with electron poor cyclopropenes, such as halo-substituted cyclopropenes [47].

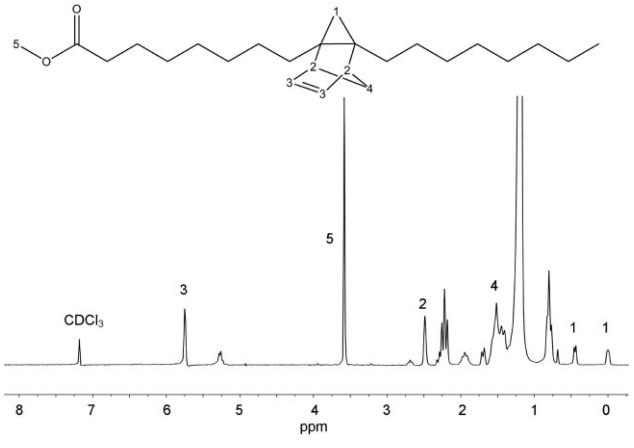
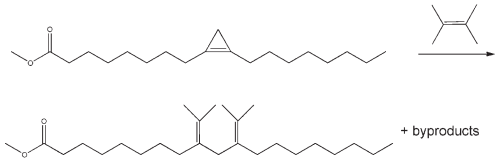


Figure 3. ^{1}H NMR spectrum of Diels–Alder product of STO FAME (**2**) with cyclopentadiene.

3.3 Olefin metathesis reactions of STO FAME with 2,3-dimethyl-2-butene or 1-octene

Cross olefin metathesis reactions of STO FAME, **1**, with aliphatic olefins (2,3-dimethyl-2-butene or 1-octene) were investigated as an alternative reaction to produce branched esters derivatives (Eq. 6). Grubbs' 2nd generation catalyst ((1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro-(phenylmethylene)(tricyclohexylphosphine) (ruthenium) was used. Typical reaction times were 6 h and reaction temperature was either 40 or 55°C. The olefin was used in excess on the cyclopropene units; the catalyst intake was 0.18 mol% on cyclopropene units.



(eq. 6)

Initially, experiments were carried out with 2,3-dimethyl-2-butene at 40°C (Eq. 6). Cyclopropene conversion was 78 mol% and the selectivity to the desired cross metathesis product was about 29 mol% (Table 3). Methyl branches of the cross metathesis products were observed by ^{1}H NMR by the appearance of sharp peaks in the regions δ 1.48–1.67 and 2.48–2.53 ppm (Fig. 4).

The selectivity of the reactions is relatively low, as the primary cross metathesis products are known to be prone to secondary or further metathesis reactions, giving rise to a broad spectrum of products [37, 48]. In addition, the STO FAME do not only contain fatty acid chains with cyclopropene units but also the conventional mono- and di-saturated fatty acids like oleic and linoleic acid (see Table 1) that are also known to be reactive in metathesis reactions.

Experiments at slightly higher temperatures (55 instead of 40°C), gave essential quantitative conversion of 2,3-dimethyl-2-butene and a selectivity to the desired branched fatty acid chains (Eq. 6) of 32 mol% (Table 3).

Subsequent experiments were performed with 1-octene (Eq. 7). At 50°C, 54 mol% cyclopropene conversion was

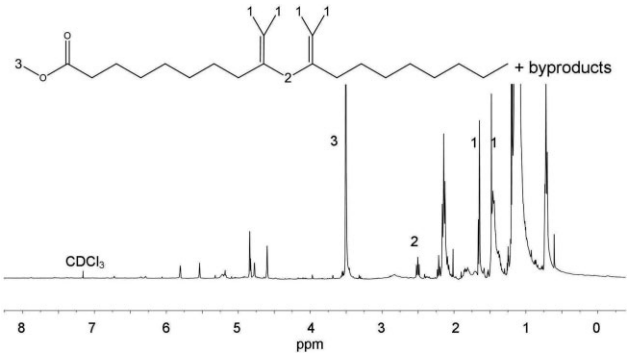
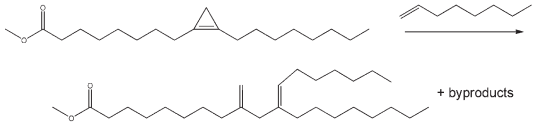


Figure 4. ^{1}H NMR spectrum of the olefin metathesis reaction product of STO with 2,3-dimethyl-2-butene after *trans*-esterification with methanol (**4a**).

observed after 6 h (Table 3). Like with 2,3-dimethyl-2-butene, the selectivity is rather low (47 mol%), likely due to consecutive reactions. For example, we also observed the formation of 10-methyl-9-undecenoic acid and 2-methyl-2-undecene (GC–MS), the reaction products of the oleic acid chains in STO with 2,3-dimethyl-2-butene. The presence of the branches was confirmed by ^{1}H NMR spectra, showing resonances of the $=CH_2$ groups of the methylidene branch at δ 4.86 ppm and at δ 4.94 ppm for the H atom of the =CHR unit of the C7 branch (Eq. 7). An HPLC HR-ESI-MS analysis (positive mode) of the metathesis product showed product peaks with *m*/*z* values of 421.4040 and 407.3871 amu, which correspond to the metathesis product of 1-octene with methyl sterculate and methyl malvalate, respectively. The formation of these products was further confirmed by an oxidative cleavage experiment using OsO_4 as the catalyst and hydrogen peroxide as the oxidant in acetonitrile. The reaction mixture was analysed by GC–MS and clearly showed the presence of methyl 9,11-dioxononadecanoate, methyl 8,10-dioxooctadecanoate, heptanal and heptanoic acid. This supports the formation of the cross-metathesis product with the C7 branch in the fatty acid chain.

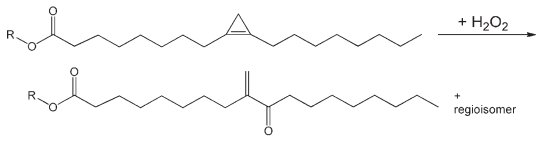


(eq. 7)

To gain insights in the reactivity of STO at metathesis conditions in the absence of external olefins, STO enriched in cyclopropene units (obtained by fractionation using urea) was subjected to a reaction with the Grubbs catalyst at 55°C. Conversion of the cyclopropene units was indeed observed (26 mol% after 6 h and 40 mol% after 170 h, see Table 3), indicating that the cyclopropene units are reactive under these conditions. ^{1}H as well as ^{13}C NMR spectra showed a large number of peaks, making identification of individual products cumbersome. However, this reaction shows that when performing cross metathesis reaction of STO with other olefins, inter molecular reactions between cyclopropene units or thermal reactions may also play a role, further complicating the chemistry and leading to a reduced selectivity of the cross-metathesis reactions.

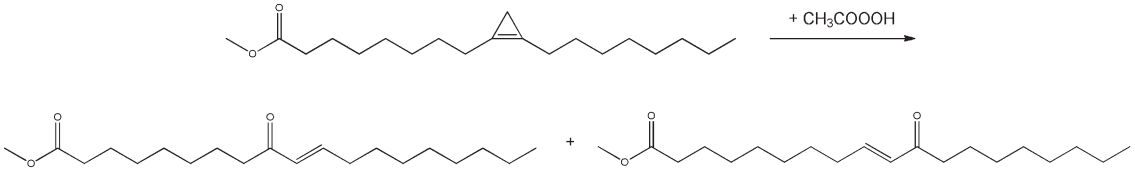
3.4 Oxidation reactions of STO using hydrogen peroxide at typical epoxidation and hydroxylation conditions

Oxidation reactions of STO with aqueous hydrogen peroxide were performed using a typical epoxidation protocol with MTO as the catalyst [38] and a dihydroxylation reaction using in situ formed performic acid [39]. For both reactions, $\geq$99% conversion of the cyclopropene rings was observed (^{1}H and ^{13}C NMR). The cyclopropene unit is converted to an α,β-unsaturated ketone (enone), as shown in Eq. (8).



(eq. 8)

HPLC HR-ESI-MS analysis of the *trans*-methylated product shows peaks with *m*/*z* values of 325.2738 and 311.2582 amu, which correspond to the enone derived from methyl sterculate and methyl malvalate, respectively. Characteristic resonances of the CH_2 moiety of the methylene branch in ^{1}H NMR were observed at δ 5.67 and 5.93 ppm. Characteristic peaks in ^{13}C NMR spectra were at about δ 123 ppm for the C=***C***H$_2$ group, at δ 149 ppm for the ***C***=CH$_2$ group and at δ 202 ppm for the carbonyl group, which is in line with literature data [49]. APT NMR of the product mixture after *trans*-methylation with methanol shows characteristic resonances of =***C***H$_2$ groups at about δ 123 ppm. ***C***H=***C***H groups are absent, indicating that the double bond is not located in the main fatty acid chain. The latter finding contradicts with literature data on the peracetic acid oxidation of sterculic acid. The authors reported the formation of a mixture of 9-oxo-nonadec-10-enoic acid and 11-oxo-nonadec-9-enoic acid (Eq. 9) [50]. However, neither mass spectra nor a rationalise for product formation are provided.



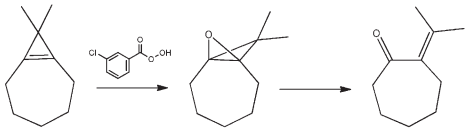
(eq. 9)

In theory, two enone regio-isomers may be formed, 9-*ene*-10-oxo-octadecanoate and 10-*ene*-9-oxo-octadecanoate. Both isomers are reported to be formed in 70% yield in equimolar amounts when oxidising STO methyl esters at ambient temperature without bubbling air for a week in the absence of catalyst [49]. We have attempted to gain insights in the ratio of the two regio-isomers by GC–MS using various derivatisation protocols (pyridinemethanol, 2-amino-2-methyl-1-propanol). Only a single peak was observed for the enone-products under the prevailing conditions. Though it is tempting to suggest that only one regio-isomer is formed, it is more likely that separation of the two regio-isomers by GC is difficult and that both are formed during reaction.

This was supported by catalytic epoxidations of the reaction mixture using KF on alumina as catalyst and *tert*-butylhydroperoxide as the oxidant in acetonitrile and subsequent analyses by GC–MS. Using this method, a single enone product peak was observed on the GC. However, the fragmentation pattern indicates the presence of two regio-isomers (Fig. 5). Besides the molecular peak at *m*/*z* of 340, four peaks at *m*/*z* 199 and 141 as well as *m*/*z* 185 and 155 are observed, which arise from the fragmentation of the epoxide of 9-*ene*-10-oxo- and 10-*ene*-9-oxo-octadecanoate, respectively. Thus, it is likely that two regio-isomeric enones are formed when oxidising the cyclopropene rings using conventional epoxidation methods.

Further proof for the formation of the two regio-isomers comes from ^{13}C NMR measurements. All characteristic peaks of the enone moiety are not observed as single peaks but always a set of two is present with essentially identical intensities. This is a clear indication that two regio-isomers are formed during the reaction.

The reaction mechanism for enone formation is not known in detail. Friedrich et al. [51] postulated that the reaction likely proceeds via an intermediate oxabicyclobutane compound, see Eq. 10 for a substituted cyclopropene such as 8,8-dimethylbicyclooct-1(7)-ene. The oxabicyclobutane subsequently rearranges to form an enone. However, Okovytyy et al. [52] concluded on the basis of theoretical calculations that the intermediate oxabicyclobutane is not formed, and that the reaction proceeds via a bi-radical intermediate which forms an enone by a fast proton transfer.



(eq. 10)

NMR spectra of the reaction product also show some characteristic resonances of epoxide fragments at δ 2.79–3.15 ppm (^{1}H NMR), see Fig. 6 for details. These are likely from the epoxidation of the straight chain fatty acids with C–C double bonds (Table 1).

A slight change of product chemoselectivity was observed when performing the reaction under dihydroxylation conditions using formic acid. At this condition, the selectivity for the enone was slightly lower (95%) and minor amounts of 1,9-nonanedioic acid and nonanoic acid were observed as well (GC–MS). The latter is indicative for the occurrence of oxidative cleavage reactions involving the cyclopropene rings. This reactivity pattern has also been observed by Ciabattoni and Kocienski [53] when using *m*-chloroperbenzoic acid as the oxidant. Nevertheless, both oxidation methods are very suitable for the selective conversion of the cyclopropene units to enones, which is an interesting functional group for further derivatisation chemistry.

3.5 Addition reactions of 9(10)-*ene*-10(9)-oxo-octadecanoate with *n*-octylmagnesium bromide

The STO derivative with an enone group in the fatty acid chains (**5**) obtained by oxidation with hydrogen peroxide,

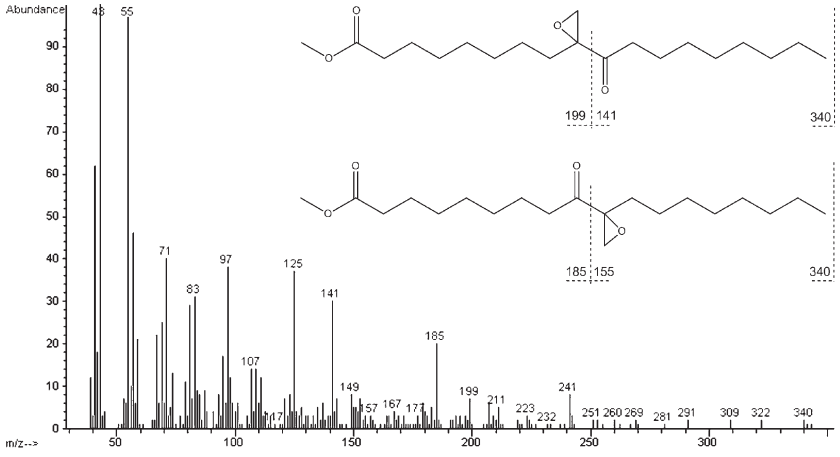


Figure 5. Mass fragmentation pattern of the epoxidised enone units in STO.

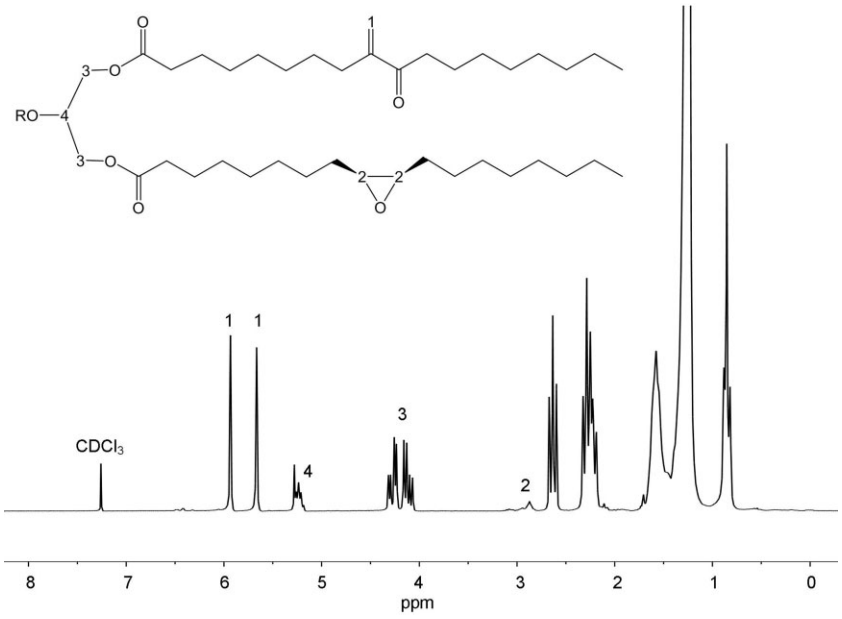
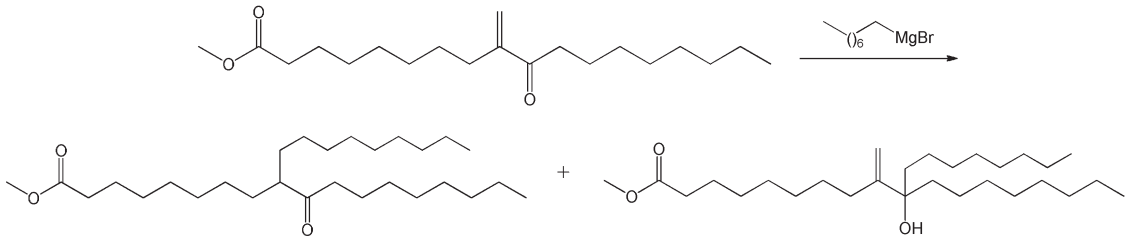


Figure 6. ^{1}H NMR spectrum of the oxidation product of STO at typical epoxidation conditions (**5**).

was subjected to a Cu-catalysed 1,4-addition reaction with *n*-octylmagnesiumbromide (Eq. 11) using a procedure provided by Tawney [40].



(eq. 11)

The reaction was carried out in diethyl ether at the boiling point of the solution for 3 h. Work-up gave the product as an orange coloured oil. The reaction was initially performed using 1 mol% of copper (II) chloride as the catalyst. A conversion of 82 mol% of the enone was obtained, with a 75 mol% selectivity to the 1,4-addition product and about 20 mol% to the 1,2-addition product.

Characteristic ^{1}H NMR resonances of the 1,4-addition product are at δ 2.64 ppm, from the CH group next to the carbonyl group. The 1,2-addition product shows clear peaks of the olefinic $=CH_2$ protons at δ 4.89 and 5.03 ppm. In ^{13}C NMR, the carbonyl group of the 1,4-addition product is present at δ 211–216 ppm. The CH group next to the carbonyl group of the 1,4-addition product is observed at δ 50.5–54.0 ppm. Meanwhile, the 1,2-addition product shows resonances of the $C=CH_2$ carbons at δ 108 and 153 ppm. The presence of the 1,2-addition product is likely due to the un-catalysed addition reaction between the reactant with octylmagnesium bromide [40]. Therefore, a reaction with 2 mol% of catalyst instead of the original 1 mol% under otherwise similar reaction conditions was employed. Improved results were obtained and the conversion of the enone was increased to 94 mol% with a selectivity of 92 mol% to the 1,4-addition product.

3.6 Rearrangement reactions of STO FAME to a conjugated diene with a methylene branch using homogeneous Pd catalysts

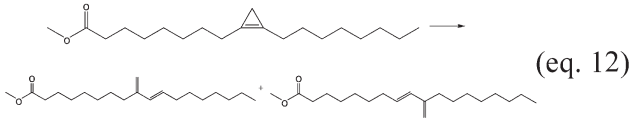
The ring opening of the cyclopropene unit in STO or derivatives to a conjugated diene with a methylene branch is an interesting reaction as the products are attractive starting material for further chemistry (Eq. 12). Rearrangement reactions of STO FAME were conducted under a nitrogen atmosphere using a homogeneous palladium catalyst in a biphasic liquid–liquid system. The biphasic system consists of water and the STO FAME dissolved in a hydrocarbon solvent (heptane or cyclohexane). A water-soluble Pd catalyst (Pd-TPPTS) was used, which allows for recycle of the catalyst after the reaction by a simple phase separation. The catalyst was made in situ from the catalyst components $(Pd(OAc)_2$

Table 4. Results of the rearrangement reactions[a)]

Exp	Catalyst	Solvent	Temperature (°C)	Water/solvent (v/v)	Conversion[b)] (mol%)	Selectivity[b)] (mol%)
1	Pd-TPPTS	Heptane	90	1	>99	90
2	Pd-TPPTS	Cyclohexane	90	1	>99	>99
3	Pd/C 5%	Heptane	150	–	75	94

[a)] Reaction time: 6 h.
[b)] Conversion and product selectivity were calculated by ^{1}H NMR. Conversion is the cyclopropene conversion, selectivity is defined as the amount of rearrangement product divided by the amount of cyclopropene rings converted.

and Na_3TPPTS). The reactions were carried out at 90°C with 0.5 wt% catalyst to the ester. Catalyst performance was compared with a typical heterogeneous Pd catalyst (Pd/C 5%). The rearrangement reaction of STO FAME using a homogeneous catalyst in a biphasic solvent system has never been studied before and is an absolute novelty of this paper.


(eq. 12)

The results of the rearrangement reaction with Pd-TPPTS are given in Table 4. After 6 h, quantitative conversion of cyclopropene units was observed in both organic solvents (cyclohexane and heptane). The selectivity towards the desired product (Eq. 12) was >90 mol% for both cases and slightly higher in cyclohexane than in heptane.

The reaction products were primarily characterised by ^{1}H, ^{13}C, and APT NMR. The characteristic peaks of the methylene branch (C=C***H***$_2$) appeared at δ 4.71–4.85 ppm in ^{1}H NMR, which is in line with literature data [16]. Meanwhile, characteristic peaks of the conjugated diene were present at around δ 113.3 (***C***H$_2$=C–CH=CH–), 133–128 ppm (–CH=***C***H–), and 147 ppm (CH$_2$=***C***–CH=CH–) in APT NMR measurements. The reaction is expected to lead to the formation of two regio-isomers, methyl 9-methylene-octadec-10-enoate and methyl 10-methylene-octadec-8-enoate. Analyses of the reaction mixture by GC–MS after various derivatisation reactions only showed a single peak. However, as the two regio-isomers are expected to have very similar physical properties, this is not conclusive evidence for the formation of a single regio-isomer. ^{13}C NMR is more informative and all characteristic peaks for the conjugated diene moiety are not observed as single peaks but double peaks with equal intensities. This is a clear indication that both regio-isomers are formed in essentially similar amounts.

A possible byproduct is a conjugated diene with a methyl branch by a subsequent rearrangement reaction (Eq. 1). However, this structural unit was not detected by NMR when applying the homogeneous catalysts under the prevailing reaction conditions.

To confirm the presence of a conjugated diene with a methylene branch, the reaction product was hydrogenated using palladium on carbon catalyst (10 wt%) at a H_2 pressure of 40 bar and a temperature of 80°C for 20 h. After reaction, the presence of the methyl peak of the new –***C***H$_3$ (methyl) group was observed at δ 19.7 ppm and the ***C***H group was present at δ 32.7 ppm in APT NMR spectra. Thus, it can be concluded that the rearrangement product indeed contains a conjugated diene moiety with a methylene branch. HPLC HR-ESI-MS analysis of the reaction product shows two clear peaks with *m*/*z* values of 309.2788 and 295.2630 amu, which indicates that the reaction is not associated with molecular weight changes, in line with the occurrence of a rearrangement reaction.

For reference, the rearrangement reaction was also performed with Pd on C at 150°C [16]. In this case, the reaction was carried out in heptane as the solvent. Despite the elevated temperature used for this reaction compared to the reaction with the homogeneous catalyst (90°C), the cyclopropene conversion is less than quantitative (75 mol%), though selectivity is similar to the homogeneous system. Therefore, the biphasic catalysis system using Pd-TPPTS as the catalyst appears as an attractive catalyst for these rearrangements reactions.

3.7 Cold flow properties

The cold flow properties of the STO and derivatives were determined using CP and PP analyses. The results of the measurements are given in Fig. 7. Modification reactions in general resulted in a reduction of the PP and CP when compared to STO FAME (**1**). The purified/de-acidified STO has a CP and PP of −3 and −5°C, respectively, which is in line with literature data [54]. The PP and CP for STO FAME (**1**) were both −1°C, which is slightly higher than for STO. Despite various literature reports on the preparation of STO FAME, CP and PP values have not been reported. It is well known that the cold flow properties of methyl esters of vegetable oils highly depend on the composition of the fatty acid chain in the oil. For example, the PP of methyl esters of rapeseed oil is −9°C, due to a large fraction of unsaturated

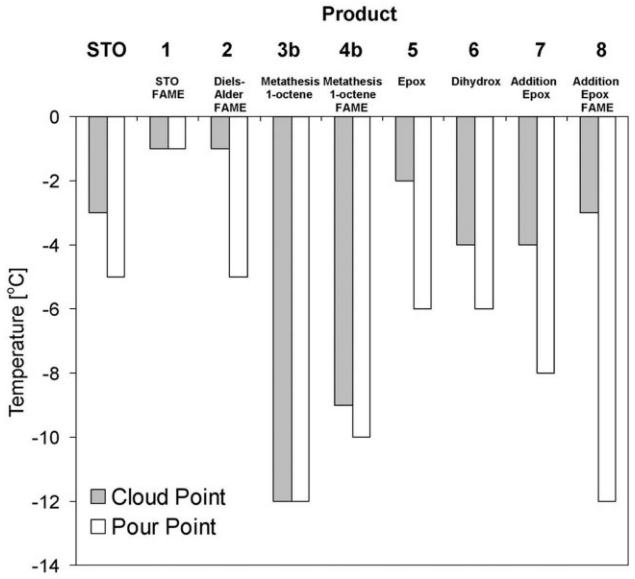


Figure 7. Cold-flow properties of STO and derivatives.

C18:1 and C22:1 fatty acids in the oil [55]. In contrast, both methyl esters of palm and tallow oil have a PP of 15°C, as they contain a large fraction of saturated C16:0 fatty acids.

The methyl ester derivative of Diels–Alder reaction (**2**) has a CP and PP of −1 and −5°C, which is close to that of STO but better than STO FAME (**1**). A related product containing this functional group is not reported in the literature, making comparison with literature data impossible. The product from the metathesis of 1-octene with STO (**3b**) showed a CP and PP value of −12°C. After *trans*-esterification with methanol, the CP and PP were −9 and −10°C (**4b**).

The epoxidation and dihydroxylation products (**5** and **6**) have similar CP and PP values of −3 and −6°C, which is not surprising considering a similar chemoselectivity for both reactions to the enone. The values are close to those for the STO feed. Cold flow properties of enones derived from methyl sterculate and methyl malvalate are not available in the literature [49]. A structurally related fatty acid with an enone moiety has been prepared by Cádiz and coworkers [30], to be used as a novel reactive building block in polymer synthesis. However, the cold flow properties of this compound are also not reported. The addition product, **7**, has a CP and PP of −4 and −8°C, respectively. Structurally related compounds have been prepared, for example, by the alkoxylation of the olefinic groups in unsaturated methyl esters and triglycerides [56–59]. However, the cold flow properties of these branched fatty acid derivatives were not provided, making a comparison cumbersome.

Further improvements in cold-flow properties of the derivatives are likely possible by using fractionated STO enriched in cyclopropene units for the modification reactions. By this procedure, the amount of the fatty acids without cyclopropene rings in the products is reduced considerably. Particularly a reduction of the amount of saturated fatty acids (cf Table 1, 17 wt% palmitic acid) in crude STO is expected to have a positive effect on PP and CP of the products, as these acids are known to have a high PP and CP. These studies using fractionated STO are in progress and will be reported in due course.

3.8 Stability of STO during storage

The modification reactions reported here indicate that STO is an interesting starting material for the synthesis of derivatives due to the presence of highly reactive cyclopropene rings. However, this high reactivity may also lead to reactions during storage (e.g. polymerisation) and as such the storage stability may be limited. For instance, Nunn reported that sterculic acid polymerises rapidly at 96°C in a N_2 atmosphere [20] as was observed by an increase in the molecular weight (five times the original value after 230 min). Therefore, the chemical composition of the oil upon storage at 6°C was investigated by ^{1}H NMR and GC analysis. The results showed that significant cyclopropene rings conversion was not observed for storage period of at least 8 months at this temperature.

4 Conclusions

An experimental study on the chemical modifications of STO and STO FAME to prepare branched ester derivatives is reported. Excellent conversions of the cyclopropene rings under mild reaction conditions were obtained for almost all reactions performed in this study. The cold flow properties of some relevant branched oil and ester derivatives were determined and are similar or better compared to STO FAME. The high reactivity combined with a good storage stability at 6°C, makes STO a very attractive feedstock for the production of various oleo-chemical derivatives.

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The authors have declared no conflict of interest.

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