Research Article

Synthesis and properties of highly branched *Jatropha curcas* L. oil derivatives

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The synthesis and properties of a number of novel branched *Jatropha curcas* L. oil (JO) derivatives containing vicinal di-ester units in the fatty acid chains are reported. Both the length (acetyl *vs*. hexanoyl) and the stereochemistry of the vicinal di-ester units (*cis vs. trans*) were varied. The compounds were prepared by two different synthetic approaches using catalytic chemistry. The first approach involves epoxidation of JO using a Sharpless epoxidation with methyltrioxorhenium as the catalyst to give epoxidized JO (**1**), followed by an esterification reaction with the corresponding anhydrides using ammonium-12-molybdophosphate (AMP) as catalyst to give *trans*-di-esters of JO (**4a**, **4b**). The second approach is based on the dihydroxylation of JO using either the Prilezhaev method, resulting in *trans*-diols of JO (**2**), or the Upjohn method using osmium tetroxide as catalyst to give *cis*-diols of JO (**3**). In subsequent steps, the diols were esterified with acetic- or hexanoic anhydride using dimethylaminopyridine as catalyst to produce the corresponding *cis*- and *trans*-di-esters of JO (**5a**, **5b**, **6**). The best cold flow properties (lowest pour- and cloud point, crystallization and melting temperature) were obtained for JO with hexanoyl branches in a *trans* orientation (**5b**, pour point of −14°C, melting point of −5°C, and crystallization temperature of −25°C) and these values are considerably better than for the JO source.

Practical applications: *Jatropha curcas* L. oil (JO) is a toxic oil with potential applications not only as a green biodiesel but also as a feedstock for the oleochemical industry. The toxicity prohibits the use in food products but does not interfere with technical applications. Here we report studies on the synthesis of interesting JO derivatives (epoxidized, dihydroxylated, and branched compounds) that could be useful starting materials for a range of derivatives with a broad application perspective. The branched JO derivatives with vicinal di-ester units in the fatty acid chains have cold flow properties (pour- and cloud point, melting point and crystallization temperature) considerably better than the original JO. In addition, the oxidative stability was also improved significantly. These novel branched JO derivatives may have interesting applications as cold-flow improvers for biodiesel or as biolubricants.

Keywords: Branched derivatives / Dihydroxylation / Esterification / Epoxidation / *Jatropha curcas* L. oil

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1 Introduction

The last decade, *Jatropha curcas* L. oil (JO) has attracted considerable attention from academics, companies, and policy makers throughout the world. The main driver is the use of the oil as a replacement for diesel fuel in stationary and instationary internal combustion engines, particularly as the majority of the oils from several varieties is toxic and as such does not compete directly with the food sector. However, the oil also has high potential to be used as input

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Abbreviations: AMP, ammonium-12-molybdophosphate; **DMAP,** 4-dimethylaminopyridine; **GPC,** gel permeation chromatography; **HMW,** higher molecular weight; **JO,** *Jatropha curcas* L. oil; **MTO,** methyltrioxorhenium for the oleochemical industry [1], a global business with a volume of about 18 million tonnes (2004) [2].

Pure plant oil derivatives with branches in the fatty acid chains have interesting properties. Branched fatty acids and esters can be applied in a number of products, including surfactants, fabric conditioners, textile auxiliaries, fiber treating agents, hair treating agents, cosmetics, lubricants, additives for fuels and lubricants, rolling and drawing oils, and also as solvents for printing inks [3–11]. Advantages of branched derivatives compared to linear ones are a lower melting point, distinctly reduced pour points, better oxidative stability due to a lower content of carbon–carbon double bonds, and improved lubrication ability. Applications areas are for instance the use as biolubricants or additives in biodiesel to improve the cold flow properties. Available synthetic methodology for the introduction of branches is, among others, epoxidation or dihydroxylation of the carbon–carbon double bonds in the triglyceride structure followed by esterification or etherification with alcohols, short chain carboxylic acids, or acid anhydrides [12–19].

We here report the synthesis of novel branched JO derivatives. The cold flow properties and oxidative stability of the derivatives were determined and compared to virgin JO. Structure–performance relations and particularly the effect of the lengths of the branch and the stereochemistry on cold flow properties were determined. The synthetic methodology involves epoxidized and dihydroxylated JO. As such, the latter two are also interesting reactive building blocks for applications like stabilizers and plasticizers in polymers, as additives in lubricants, as components in plastics and urethane foams, and in general as intermediates for a large number of commodities [3, 20, 21]. Limited information is available on the catalytic epoxidation and dihydroxylation reactions of JO. The epoxidation of JO with peroxyorganic acids catalyzed by acidic ion exchange resins including a kinetic study has been described recently by Goud *et al.* [20, 21].

2 Materials and methods

2.1 General

Jatropha oil (JO) originating from Indonesia was obtained from the Bandung Institute of Technology (Bandung, Indonesia) and purified by degumming, neutralization, bleaching, and deodorization (*vide infra*). Aqueous hydrogen peroxide (30-wt%), ethyl acetate (≥99.0%), acetic anhydride (≥98.0%), sodium chloride (≥99.5%), and activated carbon, were obtained from Merck (Darmstadt, Germany). Methyl tert-butyl ether (98.0%), 4-dimethylaminopyridine (DMAP, 99.0%), hexanoic anhydride (97.0%), 4-methylmorpholine *N*-oxide (97.0%), ammonium-12-molybdophosphate hydrate, Al_2O_3 (basic, activated, Brockmann I, ~150 mesh, surface area 155 m^2/g), citric acid (99.5%), Quantofix® peroxide test sticks 1–100 mg/L, chloroform-d (99.8 atom %D), Fuller's earth (100-200 mesh), and *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide with trimethylchlorosilane (99.0%, 1% TMCS) were obtained from Aldrich (Steinheim, Germany). Osmium tetroxide (≥99.9%), Celite® 545, ammonium hydroxide solution (≥25% NH_3 in H_2O), and trimethylsulfonium hydroxide (0.25 M in methanol) were obtained from Fluka (Buchs, Switzerland). Methyltrioxorhenium (MTO, 98.0%) was obtained from Alfa Aesar (Sulzbach, Germany). Diethyl ether (>99.0%), dichloromethane (99.9%), pyridine (≥99.0%), and methanol (99.9%) were from Lab-Scan (Gliwice, Poland). Magnesium sulfate (dried) was from Boom BV (Meppel, The Netherlands). All chemicals were used as received.

2.2 Analytical methods

The ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ as the solvent at RT using a Varian AS400 NMR Spectrometer. For ^{1}H NMR spectra, a total of 64 scans was performed, 4000 scans were recorded for ^{13}C NMR spectra with a relaxation delay of 5 s.

The quantification and compositional analysis of the fatty acids were performed by GC using an HP 5890 model equipped with an HP5 solgel-1MS column (length 30 m, inside diameter 0.25 mm, film 0.25 μm) and an FID detector. GC-MS spectra for structural analysis of the products were recorded on an HP 6890 equipped with an HP1 5973 column (length 30 m, inside diameter 0.25 mm, film 0.25 μm) and a mass selective detector. For both GC's, injection and detection were performed at 275°C and the column temperature was set at 180°C. Before analyses, the products were transmethylated according to a published procedure [22] using trimethylsulfonium hydroxide (0.25 M in methanol). A typical product (100 mg) was dissolved in methyl tert-butyl ether (5 mL). A sample (130 μL) was taken, placed in a 2 mL autosampler vial with insert, and trimethylsulfonium hydroxide (70 μL) was added. The vial was capped and hand-shaken for around 30 s and subsequently 1 μL of the sample was injected into the GC.

Hydroxylated JO samples were silylated before GC analyses to determine the structure and position of the OH groups according to a published procedure [23]. The samples were first transmethylated according to the procedure given above. Subsequently, the solvent was removed by passing a nitrogen flow over the samples. The transmethylated samples (1–5 mg) were placed in a 1 mL vial and pyridine (100 μL) and the silylating reagent (*N*,*O*-bis(trimethylsilyl)trifluoroacetamide) (100 μL) were added. The vial was capped and heated to 60°C for 20 min and the sample was subsequently analyzed by GC.

Gel permeation chromatography (GPC) was performed on an Agilent HPLC 1100 system. Three columns (mixed E, length 300 mm, inside diameter of 7.5 mm) were used. Polystyrene samples with different molecular weights were used for calibration purposes. In a typical analysis, the product (20 mg) was dissolved in THF (2 mL), filtered using a PTFE filter (0.2 μm pores size) and injected.

The cloud and pour point 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 virgin JO and the UH mode for modified oils.

DSC analysis was conducted using a DSC 2920 from TA Instrument with a heating rate of 10°C/min and a cooling rate of 2°C/min. The crystallization temperature was defined as the temperature at the minimum of the exothermic peak, while the melting point was taken as the temperature at the maximum of the endothermic peak. Since JO and its modified products contain a range of different fatty acid chains, at least two melting and crystallization temperatures were observed [24]. The melting points and crystallization temperatures of the products provided in this paper are those of the largest peak.

The oxidative stability of the products was determined using an 873 Biodiesel Rancimat from Metrohm Ion Analysis, Herisau, Switzerland, using air and an operating temperature of 110°C.

The oxirane number of epoxidized JO was determined with a non-aqueous titration method according to a procedure reported by Jay [25].

The acid value of the products was determined using a slightly modified 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.

The peroxide content was determined by a titration method. The oil sample (5 g) was dissolved in chloroform-acetic acid solution (30 mL, 50/50%-v/v). Saturated KI solution (0.5 mL) was added and the biphasic system was mixed by occasional swirling for 1 min. Water (30 mL) was added and the mixture was titrated directly with a 0.01 N $Na_2S_2O_3$ solution until the yellow color turned almost colorless. A starch indicator solution (two drops) was added and the titration was continued until the blue color disappeared.

The viscosity of JO was determined using a cone-and-plate viscometer of the type rheometer AR1000-N from TA Instrument with a cone diameter of 40 mm and a 2° angle. The viscosity measurements were conducted at 40°C with a shear rate of 15 s^{-1}.

The density of JO was measured at RT using a standard laboratory liquid pycnometer.

2.3 Purification of JO

Crude JO was first degummed using a slightly modified procedure as given in ref. 26. Crude JO (6 L) was heated to 70°C and an aqueous citric acid solution (600 mL, 3-wt% citric acid) was added to the oil. The mixture was stirred thoroughly at this temperature for 10 min. Thereafter, the solution was cooled to RT and centrifuged at 6000 rpm for 1 h. The degummed oil was mixed with an ammonium hydroxide solution ($\geq$25% NH_3 in H_2O, 600 mL) and stirred thoroughly at RT for 1 h, then kept undisturbed for 6 h to precipitate the soap. The solution was then centrifuged at 6000 rpm for 1 h. Water (2.5 L) was added to the centrifuged oil to remove the remaining soap. This washing step was repeated three times. The oil was then centrifuged again at 6000 rpm for 1 h to separate the remaining water and impurities. Subsequently, the oil was bleached. For this purpose, the neutralized oil was heated to 70°C and Fuller's earth (10-wt%) was added to the solution. The suspension was stirred thoroughly at this temperature for 10 min and then cooled to RT and centrifuged at 6000 rpm for 1 h. Deodorization was performed using a method adapted from ref. 27. The bleached oil was heated up to 100°C for 1 h under vacuum (5 mm Hg). The volatile impurities were condensed and removed as distillate. The deodorized oil was cooled down, stored under nitrogen, and analyzed by a variety of techniques (Tables 1, 2, and 3). Elemental analysis, calculated: C 77.3%, H 11.7%. Found: C 77.1%, H 11.8%.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H(ppm) = 0.83–0.87 ($C\boldsymbol{H}_3CH_2$), 1.18–1.58 ($–C\boldsymbol{H}_2–$), 1.96–2.05 ($–C\boldsymbol{H}_2CH{=}CH–$), 2.26–2.31 ($–C\boldsymbol{H}_2COO–$), 2.73–2.76($–CHC\boldsymbol{H}_2CH–$), 4.09–4.29($OC\boldsymbol{H}_2CH$), 5.24–5.30 ($OC\boldsymbol{H}(CH_2)_2$), 5.31–5.36 ($–C\boldsymbol{H}–C\boldsymbol{H}–$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C(ppm) = 14.3–14.4 ($\boldsymbol{C}H_3CH_2$), 22.8–34.4 ($–\boldsymbol{C}H_2–$), 62.2 ($–\boldsymbol{C}H_2COO–$), 69.1 ($–O\boldsymbol{C}H_2CH$), 128–130 ($O\boldsymbol{C}H(CH_2)_2$), 173.0 ($–\boldsymbol{C}OO–$).

2.4 Catalytic reactions

2.4.1 Synthesis of epoxidized JO (1)

JO (105 g, 392 mmol C=C), MTO (0.5 g, 0.5-mol% ratio to C=C), dichloromethane (79 mL, 5 M of C=C in dichloromethane), and pyridine (4 mL, 12-mol% to C=C) were placed in a three necked round bottom flask and stirred thoroughly at RT. The reaction was initiated by the dropwise addition of aqueous H_2O_2 (30-wt%, 80 mL, 785 mmol). Samples were taken periodically and analyzed using ^{1}H- and ^{13}C NMR to monitor the conversion. After complete conversion of the carbon–carbon double bonds (1.5 h), dichloromethane (100 mL) was added and the mixture was centrifuged to separate the aqueous and organic layer. The organic phase was passed through an Al_2O_3 column to remove the catalyst. The remaining peroxide was extracted using a brine solution until no peroxide was left in the mixture (peroxide test paper as indicator) and dried over $MgSO_4$. The dichloromethane was removed by vacuum distillation (35°C, 100 mbar). The isolated yield of the resulting colorless oil (**1**) was 107 g (96 wt% of theoretical yield). Elemental analysis, calculated: C 73.0%, H 11.0%. Found: C 73.8, H 11.3%. Oxirane number: 5.1%.

Table 1. Fatty acid composition of JO

Fatty acid		Composition (mol%), GC-FID	Composition (%) Literature data [28]
Myristic acid	14:0	–	0–0.1
Palmitic acid	16:0	13.7	14.1–15.3
Palmitoleic acid	16:1	–	0–1.3
Stearic acid	18:0	7.1	3.7–9.8
Oleic acid	18:1	50.3	34.4–45.8
Linoleic acid	18:2	28.9	29.0–44.2
Linolenic acid	18:3	–	0–0.3
Arachidic acid	20:0	–	0–0.3
Behenic acid	22:0	–	0–0.2
Total unsaturated acids fraction		**79.2**	**63.4–91.6**

Table 2. Quantitative comparison between ^{1}H NMR and GC-FID result for JO

Parameter	^{1}H NMR	GC-FID
Average number of double bonds in a fatty acid chain	1.13	1.08
Fraction of di-unsaturation in unsaturated C18 fraction	0.39	0.37[a]
Fraction of unsaturated fatty acids	0.78	0.79
Average carbon length of fatty acid chain	17.3	17.7

[a] Mole fraction of linoleic acid compared to the mole fraction of all C18 unsaturated fatty acids in JO.

^{1}H NMR (400 MHz, CDCl$_3$): δ_H(ppm) = 0.83–0.89 ($C\boldsymbol{H}_3CH_2$), 1.22–1.58 ($–C\boldsymbol{H}_2–$), 1.68–1.73 ($–CHOCHC\boldsymbol{H}_2$-CHOCH–), 2.26–2.31 ($–C\boldsymbol{H}_2COO–$), 2.86–3.09 ($–C\boldsymbol{H}OC\boldsymbol{H}–$), 4.09–4.28 ($OC\boldsymbol{H}_2CH$), 5.23 ($OC\boldsymbol{H}(CH_2)_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C(ppm) = 11.5–11.6 ($\boldsymbol{C}H_3CH_2$), 22.3–54.8 ($–\boldsymbol{C}H_2–$), 59.6–66.4 ($–C\boldsymbol{H}O\boldsymbol{C}H–$), 171 ($–\boldsymbol{C}OO–$).

2.4.2 Synthesis of *trans*-hydroxylated JO (2)

JO (25 g, 93 mmol C=C) was reacted with a mixture of formic acid (28.2 mL, 747 mmol) and aqueous H_2O_2 (30-wt%, 19 mL, 187 mmol) in a three-necked round bottom flask equipped with a magnetic stirrer at RT for 24 h. Subsequently, the organic phase was extracted with diethyl ether (150 mL) and washed several times with brine solution until no peroxide was left in the mixture (peroxide test paper as indicator). The organic layer was centrifuged to remove the remaining water and dried over $MgSO_4$. Diethyl ether was removed by vacuum distillation using a rotary evaporator ($T = 30°C$, $p = 200$ mbar). Isolated yield: 25.4 g (87 wt% of theoretical yield). Elemental analysis, calculated: C 67.3%, H 11.2%. Found: C 68.2%, H 10.6%.

^{1}H NMR (400 MHz, CDCl$_3$): δ_H(ppm) = 0.81–0.84 ($C\boldsymbol{H}_3CH_2$), 1.20–1.55 ($–C\boldsymbol{H}_2–$), 1.99–2.01 ($–CHOHC\boldsymbol{H}_2$-CHOH), 2.24–2.31 ($–C\boldsymbol{H}_2COO–$), 3.33–3.97 ($–C\boldsymbol{H}OH$), 4.07–4.25($OC\boldsymbol{H}_2CH$), 5.20 ($OC\boldsymbol{H}(CH_2)_2$), 8.00–8.31 ($\mathbf{H}COOCH–$). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C(ppm) = 14.9–15.1 ($\boldsymbol{C}H_3CH_2$), 23.5–39.6 ($–\boldsymbol{C}H_2$), 63.1 ($–\boldsymbol{C}H_2COO–$), 69.9 ($–O\boldsymbol{C}H_2CH$), 72.5–84.5 ($–\boldsymbol{C}HOH$), 161–163 ($\mathbf{C}HOOCH$), 173–174 ($–\boldsymbol{C}OO–$).

Table 3. Physical and chemical properties of JO used in this study

Properties	Crude JO	Purified JO	Unit
Acid value	4.6	0.19	mg KOH/g
Peroxide value	5.3	1.82	meq/kg
Density at rt	[a]	0.88	g/mL
Viscosity at 40°C	[a]	42	cSt

[a] n.d. not determined.

2.4.3 Synthesis of *cis*-hydroxylated JO (3)

JO (15.5 g, 58.0 mmol C=C), osmium tetroxide (167 mg, 0.58 mmol), 4-methylmorpholine *N*-oxide (10 g, 85 mmol), H_2O (50 mL), and tert-butanol (150 mL) were mixed at 60°C for 18 h under vigorous stirring. After 18 h, the reaction mixture was filtered through a Celite 545 column. The column was washed with brine (100 mL) and diethyl ether (100 mL). The combined liquids were separated by centrifugation. The organic layer was washed ten times with brine (100 mL each), and dried over $MgSO_4$. Diethyl ether was removed by vacuum distillation using a rotary evaporator ($T = 30°C$, $p = 200$ mbar and then at $T = 75°C$, $p = 100$ mbar). Isolated yield: 8.36 g (48 wt% of theoretical yield). Elemental analysis, calculated: C 68.6%, H 11.0%. Found: C 69.0%, H 11.1%.

^1H NMR (400 MHz, $CDCl_3$): δ_H(ppm) = 0.77–1.00 ($C\boldsymbol{H}_3CH_2$), 1.20–1.75 ($–C\boldsymbol{H}_2–$), 2.25–2.55 ($–C\boldsymbol{H}_2COO–$), 3.45–3.85 ($–C\boldsymbol{H}OH$), 4.10–4.38 ($OC\boldsymbol{H}_2CH$), 5.20–5.30 ($OC\boldsymbol{H}(CH_2)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C(ppm) = 13.8–14.2 ($\boldsymbol{C}H_3CH_2$), 22.5–34.6 ($–\boldsymbol{C}H_2$), 62.0–63.1 ($–\boldsymbol{C}H_2COO–$), 69.0 ($–O\boldsymbol{C}H_2CH$), 73.5–75.5 ($–\boldsymbol{C}HOH$), 172–174 ($–\boldsymbol{C}OO–$).

2.4.4 Synthesis of *trans*-di-esters from epoxidized JO (4a and 4b)

1 (40 g, 141 mmol of epoxide) was allowed to react under vigorous stirring with acetic anhydride (67 mL, fivefold molar excess of anhydride to epoxide) or hexanoic anhydride (168 mL), catalyzed by ammonium-12-molybdophosphate (AMP, 26.5 g, 14.1 mmol) at 75°C, with ethyl acetate (400 mL) as the solvent. The color of the reaction mixture changed from yellow to light green to dark green-blue. ^1H NMR analysis revealed that the reaction was complete after the last color change. The typical reaction time was 12 h for acetylation and 48 h for hexanoylation. The reaction mixture was then cooled to RT before purification.

For **4a**, a mixture of water and ethyl acetate (200 mL, 50/50%-v/v) was added slowly under vigorous stirring at 15°C. The catalyst and the water were separated by centrifugation. Activated carbon black (10 g) was added to the organic layer and stirred for 30 min. The mixture was then centrifuged, the organic layer was decanted and washed four times with brine (100 mL each) to extract the excess of acetic acid and subsequently dried using $MgSO_4$. Ethyl acetate was removed by vacuum distillation using a rotary evaporator ($T = 70°C$, $p = 100$ mbar). Isolated yield: 5.7 g (10.0 wt% of theoretical yield).

For **4b**, ethyl acetate (100 mL) and activated carbon black (10 g) were added and the suspension was mixed for 30 min. Thereafter, the suspension was centrifuged and the liquid phase was separated by decantation. Ethyl acetate was removed by vacuum distillation using a rotary evaporator ($T = 70°C$, $p = 200$ mbar). Methanol was added in a large excess to precipitate the product. This step was repeated several times until no hexanoic anhydride was left in the precipitate (monitored by ^1H NMR). The remaining solvents were then removed by vacuum distillation using a rotary evaporator ($T = 60°C$, $p = 30$ mbar). Isolated yield: 8.6 g (7.9 wt% of theoretical yield). Elemental analysis, calculated: C 71.1%, H 10.8%. Found: C 71.0%, H 10.7%.

2.4.5 Synthesis of di-esters from *trans*-hydroxylated JO (5a and 5b)

2 (10 g, 48 mmol of hydroxyl groups) was placed in a 100 mL three necked round bottom flask containing DMAP (70 mg, 0.6 mmol) as catalyst. Then acetic anhydride (5.6 mL, 60 mmol) or hexanoic anhydride (14.2 mL, 60 mmol) and pyridine (4.8 mL, 60 mmol) were introduced to the mixture. The reaction mixture was thoroughly stirred at RT for 7 h, then 4 h at 50°C, 4 h at 80°C, and 4 h at 100°C. Thereafter, the reaction mixture was cooled to RT.

For **5a**, a mixture of water and ethyl acetate (50 mL, 50/50%-v/v) was added slowly under vigorous stirring at 15°C. The organic layer was separated from the mixture by centrifugation and then washed several times with brine to extract the excess of acetic acid. Ethyl acetate was then removed by vacuum distillation using a rotary evaporator ($T = 70°C$, $p = 200$ mbar). Isolated yield: 5.73 g (43 wt% of theoretical yield).

^1H NMR (400 MHz, $CDCl_3$): δ_H(ppm) = 0.73–0.75 ($C\boldsymbol{H}_3CH_2$), 1.14–1.48 ($–C\boldsymbol{H}_2$), 1.96–2.02 ($–OCOC\boldsymbol{H}_3$, acetate branch), 2.19–2.22 ($–C\boldsymbol{H}_2COO–$), 3.99–4.19 ($OC\boldsymbol{H}_2CH$), 4.87–4.98 ($CH_3COOC\boldsymbol{H}–$), 5.14 ($OC\boldsymbol{H}(CH_2)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C(ppm) = 14.2–14.3 ($\boldsymbol{C}H_3CH_2$), 21.1–35.6 ($–\boldsymbol{C}H_2$), 62.2 $\boldsymbol{C}H_2COO–$), 69.0 ($–O\boldsymbol{C}H_2CH$), 73.4–81.8 ($CH_3COO\boldsymbol{C}H–$), 170–171 ($CH_3\boldsymbol{C}OOCH–$), 173 ($–\boldsymbol{C}OO–$).

For **5b**, a large excess of methanol was added to precipitate the product. The liquid phase was then removed by decantation. The precipitate was washed several times with methanol until all hexanoic anhydride was removed (monitored by ^1H NMR). The excess of methanol was then removed by vacuum distillation using a rotary evaporator ($T = 60°C$, $p = 200$ mbar). Isolated yield: 7.84 g (45 wt% of theoretical yield). Elemental analysis, calculated: C 70.7%, H 10.7%. Found: C 69.8%, H 10.6%.

^1H NMR (400 MHz, $CDCl_3$): δ_H(ppm) = 0.78–0.92 ($C\boldsymbol{H}_3CH_2$), 1.19–1.62 ($–C\boldsymbol{H}_2$), 2.25–2.40 ($–C\boldsymbol{H}_2COO–$), 4.02–4.32 ($OC\boldsymbol{H}_2CH$), 4.86–5.11 ($CH_3(CH_2)_4COOC\boldsymbol{H}–$), 5.19–5.25 ($OC\boldsymbol{H}(CH_2)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C(ppm) = 14.1 ($\boldsymbol{C}H_3–$), 22.5–35.7 ($–\boldsymbol{C}H_2$), 62.3 ($OCH(\boldsymbol{C}H_2)_2–$), 69.1 ($–O\boldsymbol{C}H(CH_2)_2–$), 73.9–78.0 ($CH_3(CH_2)_4COO\boldsymbol{C}H–$), 173–174 ($–\boldsymbol{C}OO–$).

2.4.6 Synthesis of a di-esters from *cis*-hydroxylated JO (6)

6 was prepared from **3** using the same reaction condition as for the preparation of **5b**. **3** (7.25 g, 43.2 mmol of hydroxyl groups) was reacted with hexanoic anhydride (10.3 mL, 43.2 mmol) catalyzed by DMAP (52.8 mg, 0.43 mmol) and pyridine (3.5 mL, 43.2 mmol). The reaction was performed at 80°C for 4 h. The purification method was the same as for **5b**. Isolated yield: 6.8 g (43 wt% of theoretical yield). Elemental analysis, calculated: C 70.5%, H 10.7%. Found: C 71.3%, H 11.0%.

3 Results and discussion

The branched Jatropha oil derivatives described in this paper contain vicinal ester groups in the fatty acid chains of the triglyceride. The length of the ester branches (methyl and *n*-pentyl) as well as the stereochemistry of the vicinal ester groups (*cis* or *trans*) were varied. The branched compounds were synthesized according to a number of catalytic steps involving epoxides and vicinal diols as the intermediate products (Fig. 1). In the following, the synthetic procedures, including optimization studies to improve yields and reduce by-products, will be reported. The products were characterized with a variety of techniques (*e.g.*, ^{1}H- and ^{13}C NMR, GC-MS, and GPC analysis) and relevant features will be reported. Finally, relevant product properties and particularly cold flow properties and oxidative stability will be discussed.

3.1 Characterization of the Jatropha oil feedstock

The Jatropha oil used in this investigation was obtained from Indonesia and purified before use by a four step procedure. Relevant oil properties are given in Tables 1–3. The composition of the fatty acid chains was determined by GC (Table 1) and the oil was shown to have a high level of unsaturation (79.2-mol%). The fatty acid profile is in general within the broad range for JO reported in the literature [28]. With this data available, relevant data like the number of carbon–carbon double bonds and the average molecular weight of the triglyceride can be calculated (Table 2). This information was used to determine catalysts and reagents intakes for the subsequent catalytic modification reactions. These characteristics were also determined from ^{1}H NMR measurements (Table 2) and compared with the GC-FID data. Good agreement between both methods was observed. A typical ^{1}H NMR spectra of JO is depicted in Fig. 2(a), showing the presence of the H-atoms attached to the carbon–carbon double bonds (peaks in the region of δ 5.3–5.4 ppm) and in the range of δ 2.6–2.8 ppm for the allylic $-CH_2-$ moiety between two adjacent carbon–carbon double bonds.

Relevant physical and chemical properties of the crude and purified JO are given in Table 3. The peroxide value of the purified oil was 1.82 meq/kg and the acid value was 0.19 mg KOH/g. These values are considerably lower than found for the crude JO (acid value of 4.6 mg KOH/g and a peroxide value of 5.3 meq/kg), a clear indication that the purification procedure was successful. Typical literature values for JO are an acid value of 4.5 mg KOH/g and a peroxide value of 1.93 meq/kg [29].

3.2 Synthesis of epoxidized JO (1)

1 was prepared using a well-known selective epoxidation route developed by Sharpless and coworkers [30] using MTO as the catalyst and hydrogen peroxide as the oxidant. **1** was obtained as a transparent colorless liquid in essentially quantitative yields

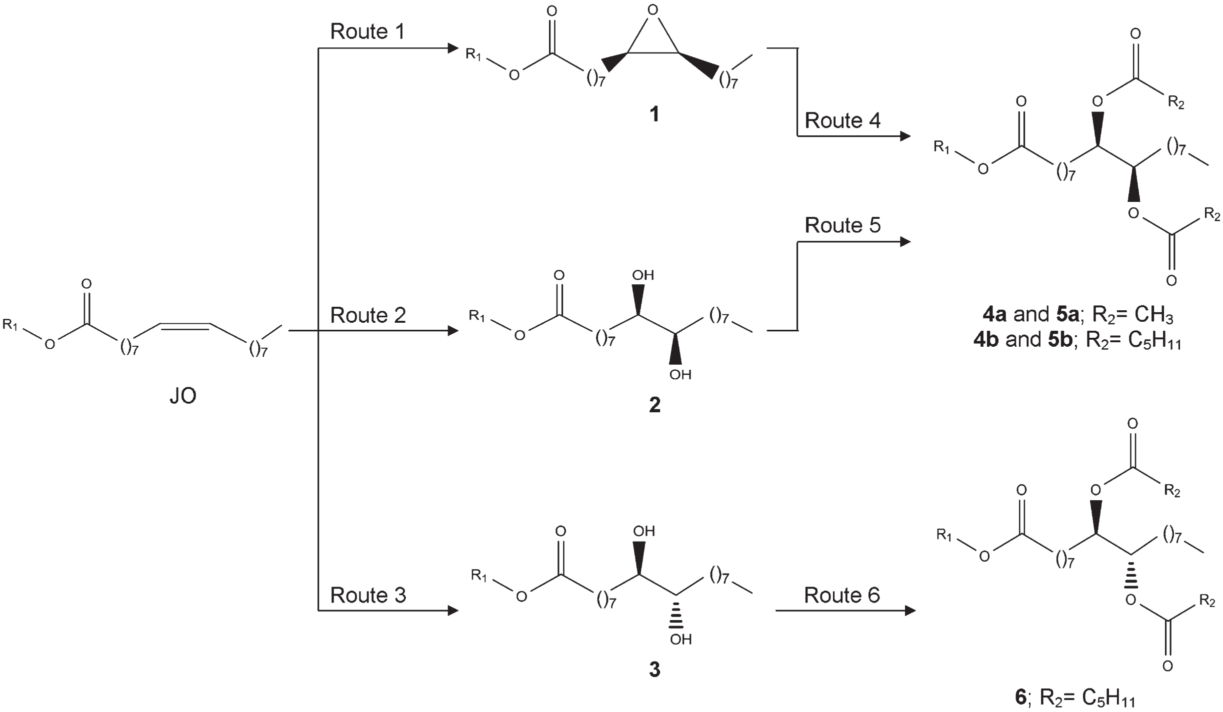

Figure 1. Overview of JO modification chemistry. R_1 = remaining triglyceride structure. (JO is a triglyceride consisting of different saturated and unsaturated fatty acids, see Table 1, and for brevity, only a mono-unsaturated fatty acids is given. Also only one representative compound of the racemic mixture is shown for each step).

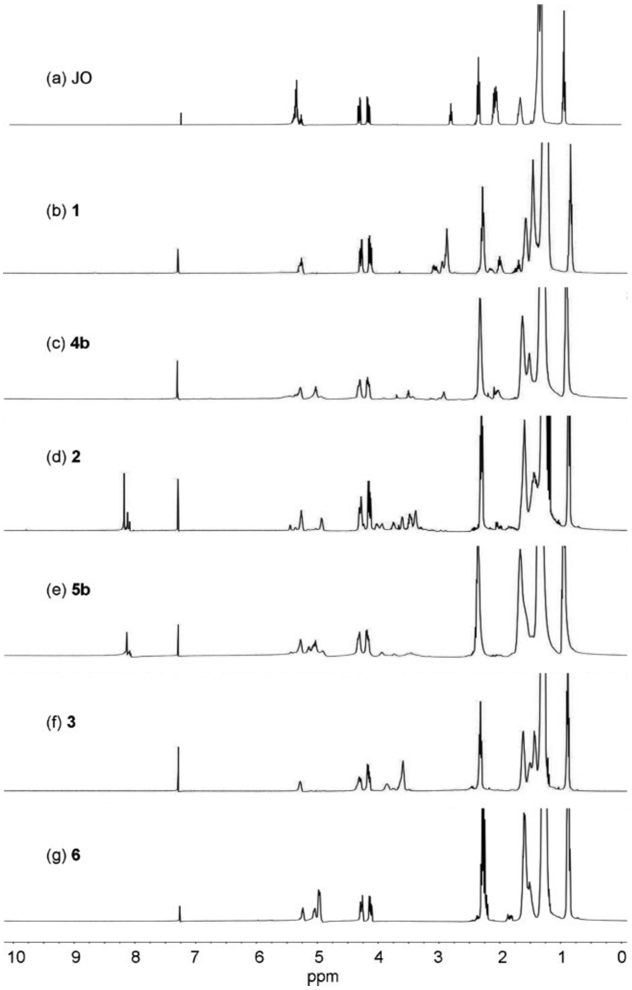

Figure 2. Typical ^{1}H NMR spectra (CDCl$_3$) of JO and derivatives.

(96 wt%) and characterized by ^{1}H- and ^{13}C NMR as well as GC-MS analysis. The oxirane number as determined by titration was 5.1%, which is below the commercial specification for epoxidized oils (6.5%) [31] and is as expected lower than the maximum value for **1** (5.4%) predicted by Meyer *et al.* [32]. A typical ^{1}H NMR spectrum is given in Fig. 2(b). Complete conversion of the carbon–carbon double bonds is observed and the characteristic peaks of olefinic and allylic hydrogen atoms at δ 5.3–5.4 and 2.6–2.8 ppm are absent. New peaks from the hydrogen atoms on the epoxide unit are present in the region of δ 2.8–3.1 ppm. Hydrolysis and the formation of diols do not occur under these conditions, as is evident from the absence of new peaks in the range 3.3–4.0 ppm.

GC-MS analysis shows the presence of both mono- and di-epoxides in the products, from the epoxidation of the oleate and linoleate fatty acid chains, respectively [33]. The stereochemistry of the epoxide units was not established. However, the Sharpless epoxidation route is known to provide epoxides in the *cis–cis* configuration [34] and this is expected to be the case for JO as well.

3.3 Synthesis of *trans*-hydroxylated JO (2) and *cis*-hydroxylated JO (3)

For the synthesis of hydroxylated JO, two well-known methods were explored, *i.e.*, a Prilezhaev dihydroxylation using performic acid [35] and an Upjohn dihydroxylation using osmium tetroxide as catalyst and 4-methylmorpholine *N*-oxide as the oxidant [36, 37]. These methods result in different product stereochemistry, *i.e.*, the *trans*-vicinal diol (**2**) from the Prilezhaev hydroxylation and the *cis*-vicinal diol (**3**) from the Upjohn hydroxylation.

The Prilezhaev method using *in situ* generated performic acid from hydrogen peroxide and formic acid gave **2**, as colorless oil in 87% yield. ^{1}H NMR showed that the carbon–carbon double bond conversion was essentially quantitative (96 mol%, see Fig. 2(d) for details). Resonances of the –C*H*–OH units appear in the region of δ 3.33–3.97 ppm. Interestingly, also some peaks are present in the region δ 8.0–8.3 ppm. These are typical for formyl branches [38], known to be formed when the intermediate epoxide is reacting with formic acid instead of water. Based on peak areas, the selectivity to diols is about 80 and 20% for formyl branches.

cis-Dihydroxylation of JO was performed using osmium tetroxide as the catalyst and 4-methylmorpholine *N*-oxide as the oxidant at 60°C for a 18 h reaction time. The solid product (**3**) was isolated in 48% yield. According to ^{1}H NMR, full conversion of the carbon–carbon double bonds to diols was achieved (Fig. 2(f)). Characteristic resonances from the *cis*-diols appear in the region δ 3.45–3.85 ppm.

Both the *trans*- and *cis*-diols were also characterized using GC-MS after methylation (of the glycerol unit) and silylation of the –OH groups on the fatty acid chains with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide. Clear GC peaks with characteristic mass fragmentation patterns were observed for 9,10-dihydroxystearate and 9,10;12,13-tetrahydroxystearate units, the result of a single dihydroxylation of oleic and a double dihydroxylation of linoleic units in the JO, respectively [39].

3.4 Synthesis of branched vicinal di-esters from epoxidized and hydroxylated JO (4a, 4b, 5a, 5b, 6)

The introduction of the ester groups on the fatty acid chains of the triglyceride was performed by reaction of either the epoxide groups of **1** or hydroxyl groups of the dihydroxylated compounds with anhydrides. To gain insights in the length of the ester branch on relevant product properties, acetic- and hexanoic anhydride were used.

3.4.1 Epoxide ring opening with anhydrides (Fig. 1, route 4)

For the ring opening of **1** with anhydrides, a published procedure was used involving AMP as the catalyst [40]. This catalyst has so far only been used for small epoxides such as styrene oxide, cyclopentane oxide, and cyclohexane oxide,

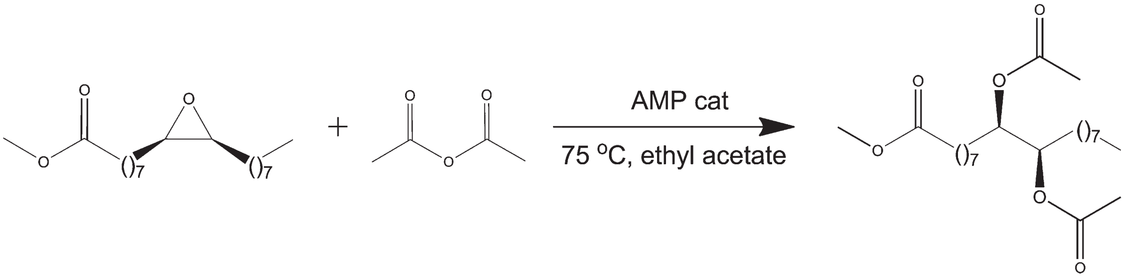

Figure 3. Model reaction for epoxide ring opening with acetic anhydride.

and also not for the esterifications using anhydrides with chain lengths longer than acetic anhydride. The use for triglycerides is a novelty of this paper. The synthetic methodology is known to result in vicinal di-esters in a *trans* configuration. Initially, experiments with JO and acetic anhydride were performed at RT, as described in the literature for small epoxides [40]. However, after 1.5 h reaction time, no conversion was observed.

To gain insights in the reaction rates, model studies were performed using epoxidized methyl oleate and acetic anhydride (Fig. 3). At RT, reactions for 23 days only resulted in 75% conversion of the epoxide. Higher reaction rates were observed at elevated temperatures and at 50, 100, 125, and 140°C, the reactions were finished within 48 h, 1.5 h, 45 min, and 10 min, respectively. The products were analyzed using NMR and GPC. Particularly, GPC analysis is very informative and reveals the formation of higher molecular weight (HMW) products besides the epoxide ring opening reaction to produce the di-esters (Fig. 4). Such HMW products are likely formed by cross-linking reactions or self polymerization reactions of the epoxide groups [16]. Even at the lowest temperature in the range (20°C), the HMW products were already formed. Such HMW products are expected to have a negative effect on product properties and some experiments were performed to reduce their formation. The stepwise addition of the epoxide to the reaction mixture gave the best results and the amount of products with molecular weights higher than 1000 Da was considerably, though not quantitatively, reduced (Fig. 4).

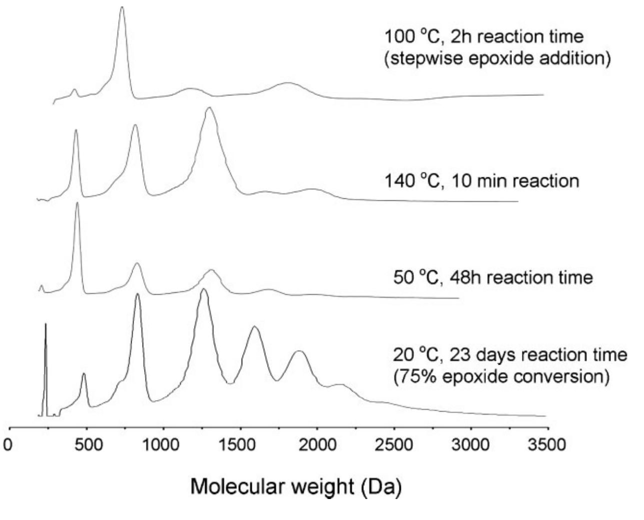

Figure 4. GPC measurements for reaction products of epoxidized methyl-oleate with acetic anhydride using AMP as the catalyst at different reaction times and temperatures (solvent free).

Further improvements were obtained using ethyl acetate as the solvent and an excess of anhydride. At 5–10 wt% intake of epoxidized methyl oleate and the use of a large excess of anhydride on epoxide, the amount of HMW products was reduced further, though not suppressed completely (Fig. 5). We therefore conclude that epoxide ring opening with AMP always leads to the formation of HMW components, the exact amount being a function of temperature, reaction time, dilution level, and molar ratios of reactants.

1 was esterified with hexanoic anhydride using the optimized conditions for the model reaction between epoxidized methyl oleate and acetic anhydride. The product (**4b**) was obtained as a yellow liquid product. Figure 2(c) shows a typical ^{1}H NMR spectrum of the product. Characteristic resonances of the di-ester branches are present in the region of δ 4.9–5.2 ppm (–C***H***–O–(C=O)–). The presence of some remaining cross-linked products is evident from resonances in the region of δ 3.3–3.7 and 4.6–4.9 ppm. This identification is based on peak intensities of samples with various levels of cross linking (as determined by GPC).

In general, the isolated yields of the reaction of **1** with anhydrides were low (<10%). This is due to a tedious work-up procedure involving multiple extraction and adsorption step to remove the excess of anhydride used in the reaction. Further optimization studies will be required to optimize the isolated yields.

3.4.2 Esterification of dihydroxylated JO derivatives with anhydrides (Fig. 1, route 5 and 6)

The *trans*-hydroxylated JO derivative was esterified with acetic and hexanoic anhydride, while the *cis*-hydroxylated JO was esterified with hexanoic anhydride to obtain the corresponding *cis*- and *trans*-vicinal di-esters. The esterification reactions of **2** (Fig. 1, route 5) were performed with DMAP as the catalyst, a molar ratio of **2** to anhydride of 1 to 1 and in the

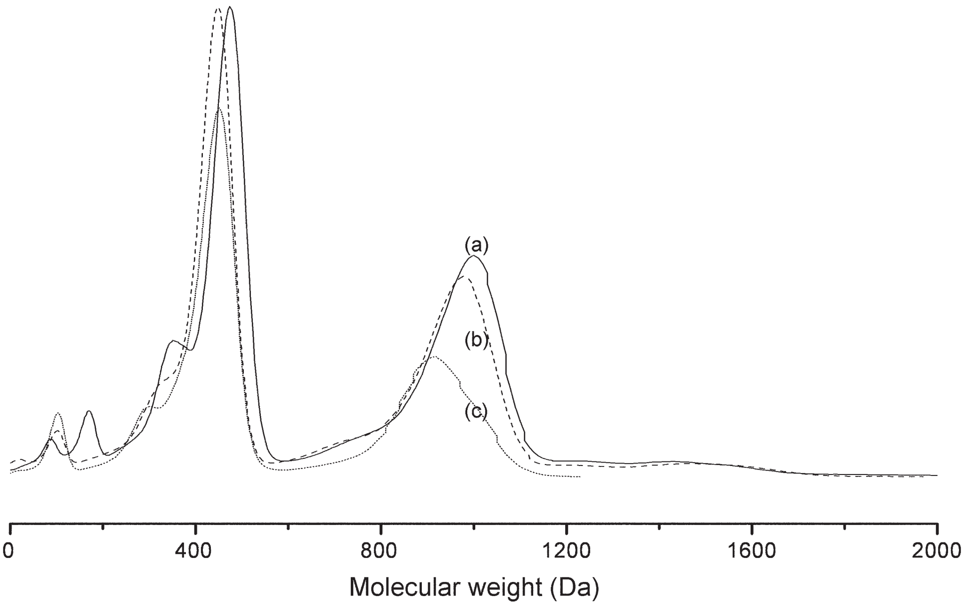

Figure 5. GPC measurements for reaction products of epoxidized methyl-oleate with acetic anhydride using AMP as catalyst at different solvent intakes and mol ratio's of reactants at 75°C. Specific reaction conditions: (a) 1 g of epoxide in 10 mL ethyl acetate, reaction time 18 h, epoxide to anhydride ratio 1:5; (b) 1 g of epoxide in 20 mL ethyl acetate, reaction time 20 h, epoxide to anhydride ratio 1:5; (c) 1 g of epoxide in 10 mL ethyl acetate, epoxide to anhydride ratio 1:65, reaction time 6 h.

absence of a solvent. The products were obtained as yellow-to-orange liquids in isolated yields of 43–45%. The effect of temperature (20, 50, 80, and 100°C) on the hydroxyl group conversion at a fixed reaction time of 4 h was determined by ^{1}H NMR and the results are given in Fig. 6. The highest conversions (>80%) were observed at 80°C. Increasing the temperature to 100°C gave a lower hydroxyl group conversion. Extending the reaction time at 100°C also did not lead to higher conversions. Thus, it is possible that the reaction is an equilibrium reaction and that full conversion of the hydroxyl groups is not possible because of thermodynamic considerations [41]. An alternative explanation is catalyst deactivation at elevated temperatures.

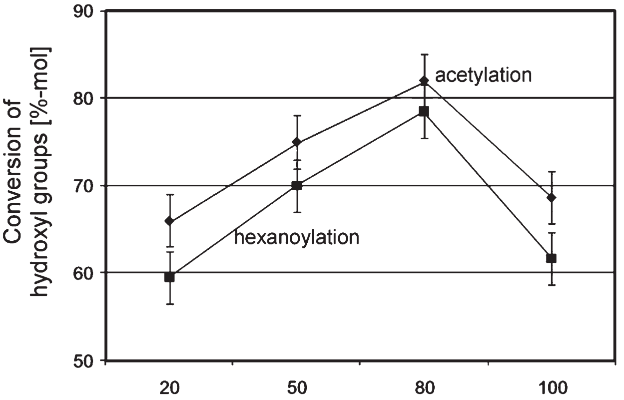

Figure 6. Hydroxyl group conversion for the reaction of **2** with acetic- and hexanoic anhydride as a function of the temperature (reaction time 4 h, anhydride to **2** molar ratio of 1:1)

Figure 2(e) shows a typical ^{1}H NMR spectrum for **5b** and particularly the product of the reaction between the **2** with hexanoic anhydride at 80°C. Clearly visible are the remaining hydroxyl groups in the region of δ 3.3–4.0 ppm, whereas protons ((–C***H***–O–(C=O)–) of the hexanoic ester branch are in the region of δ 4.8–5.2 ppm. In addition, the formyl branches are also still present in the product (8.0–8.3 ppm), an indication that exchange of formyl branches with hexanoic acid branches does not occur under the prevailing conditions. Based on the ^{1}H NMR data it may be concluded that the product **5b** contains both hexanoyl and formyl branches as well as some unconverted –OH groups.

The esterification reaction of **3**, with hexanoic anhydride (Fig. 1, route 6) was performed using the same synthetic methodology system as for **2** (DMAP catalyst, 80°C, 4 h reaction time). The product was obtained as a liquid in 43% isolated yield. Full conversion of the hydroxyl groups was accomplished (^{1}H NMR, see Fig. 2(g)), in contrast with **2**, which has a maximum hydroxyl group conversion of about 80%. This implies that the reaction is likely not an equilibrium reaction and that the experimentally observed incomplete conversions for the *trans*-analog (*vide supra*, Fig. 6) are kinetic in origin. It also suggests that the reaction of anhydrides with vicinal diols in the *cis*-configuration is much faster than for the *trans*-configuration. This conclusion is in line with literature data for the esterification of *cis*- and *trans*-vicinal diols [42–44]. For instance, the esterification reaction of a mixture of *cis*- and *trans*-1-ethyl-1,2-cyclobutanediols with methylboronic acid (at RT) gave solely esters of the *cis*-diols, while the *trans*-diols remained unreacted [42].

3.5 Product properties

3.5.1 Cold flow properties

The cold flow properties of the modified JO products were determined using cloud- and pour point analyses and by DSC (melting and crystallization temperature). The results of the measurements are given in Fig. 7. The JO feed shows a cloud point of −2°C and a pour point of −4°C. These values are in line with literature data, which reported a pour point of −3°C for JO [45]. The cold flow properties of the JO derivatives are found within a broad range. For instance, the pour points range from −14°C (for **5b**) to −3°C (for **5a**) whereas the spread in melting points (DSC) is even larger (−10°C for **1**, *vs.* 43°C for **3**). The lowest pour point in combination with lowest crystallization temperature was found for **5b** (pour point of −14°C, crystallization temperature of −25°C). Thus, considerable improvements in cold-flow properties for JO are possible by the introduction of branches in the fatty acid chains.

Comparison between the cold flow properties of **5b**, with hexanoyl branch, and the related **5a**, with acetyl branch, makes it possible to draw conclusions with respect to the length of the branch. The cloud point, pour point and melting point for **5b**, are lower than for **5a**. A similar trend was observed when comparing the data for **4a** and **4b**. This implies that longer branches lead to improved cold flow properties, which is in line with literature data [14, 16, 46, 47]. For instance, Moser determined the low temperature properties of a range of di-esters derived from oleic acid [46]. The compounds contain and α-hydroxy-ester group in the chain and a terminal ester group. Increasing chain length of the α-hydroxy-ester group was shown to result in improved low temperature properties. It was hypothesized that long chain ester more effectively disrupt crystallization.

The cold flow properties of the *trans* products obtained by the epoxidation route, **4a** and **4b**, and those of the hydroxylation route, **5a** and **5b**, differ somewhat (Fig. 7). For instance, the crystallization temperature of **4b** is −18°C while it is −25°C for **5b**. The chemical structure of the product is in principle similar, however, the products from the epoxidation route contain some cross-linked products (*vide supra*) and these may be responsible for the differences.

Of interest are also the cold-flow properties of **1**, and particularly the low crystallization temperature of −27°C is worth mentioning. This value is close to that of two literature values for epoxidized soybean oil, being −20 and −25°C [48, 49]. Apparently, crystallization is seriously inhibited when epoxide groups are present.

Clear differences in product properties are observed as a function of the stereochemistry of the vicinal diols/ester units. For instance, the cold flow properties of the **5b**, are considerably better than the *cis* analog, **6**, in all respects (Fig. 7). Apparently, the *trans* structure is favored for improved cold-flow properties. This is also supported by comparing the data for **2** and **3**, the dihydroxylated JO derivatives with vicinal diols structure element. The *cis*-diols, **3**, is solid at RT, with a melting point of 43°C and a crystallization temperature of 25°C (DSC). The *trans* analog, **2**, is a liquid at RT with a melting and crystallization temperature of 6 and −1°C,

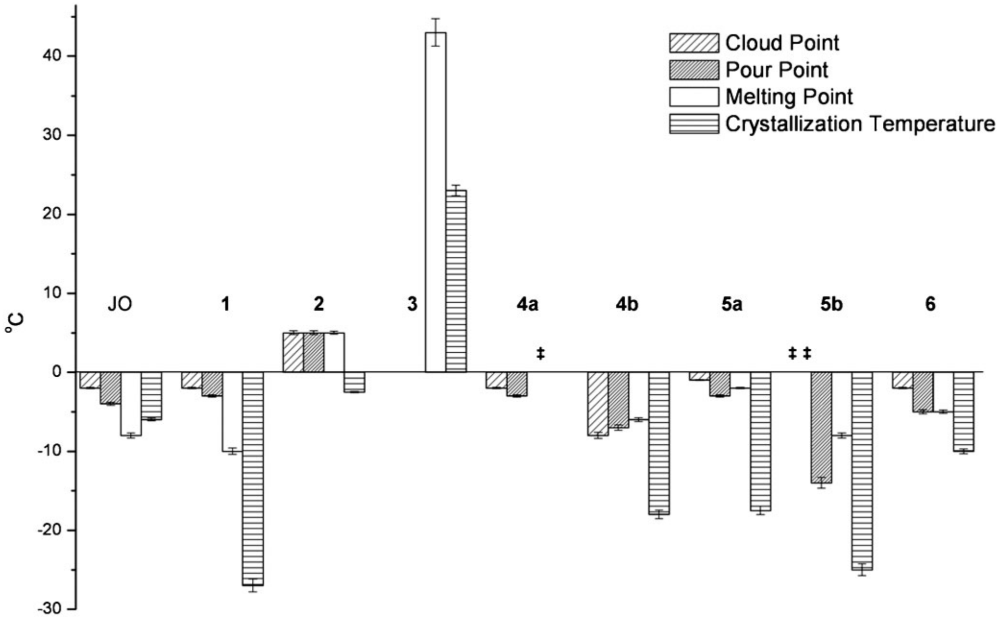

Figure 7. Summary of cold flow properties of JO and a number of derivatives. ‡ Melting point and crystallization temperature for **4a** were not determined. ‡‡ No CP was detected.

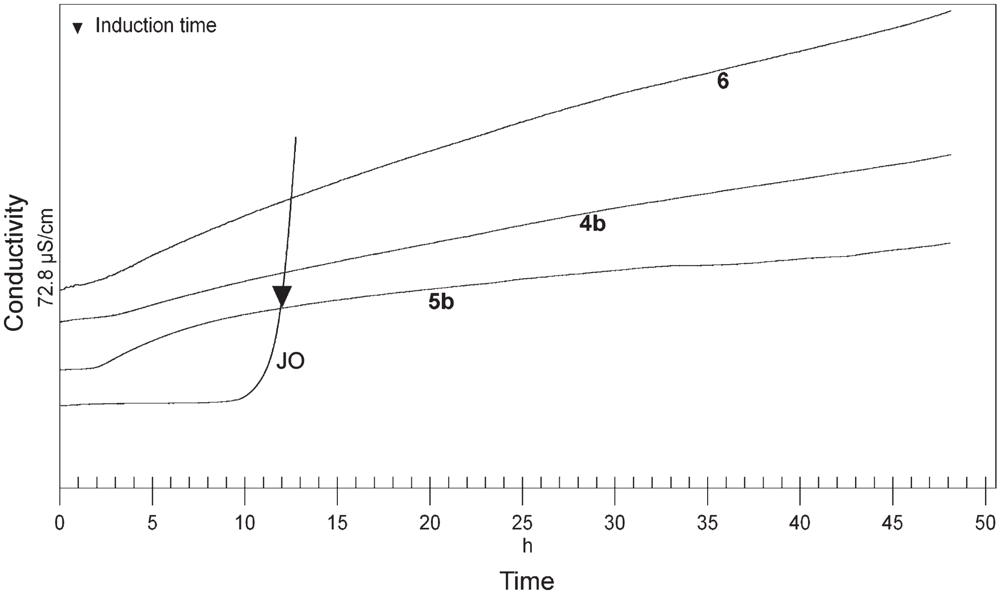

Figure 8. Oxidative stability of JO and the various hexanoylated derivatives.

respectively. Apparently, in the *cis* orientation, crystallization is more facile, presumably by improved inter- and/or intramolecular hydrogen bonding. These differences in properties are in line with available literature data. For instance, a study on *cis*- and *trans*-1,2-cyclohexanediols properties revealed that the *cis*-diols tends to solidify and has a higher melting point than the *trans*-counterpart [50].

3.5.2 Oxidative stability

The oxidative stability of the products was determined by a standard protocol using a Rancimat device with ambient air as the carrier gas at an operating temperature of 110°C. Figure 8 shows the oxidative stability of the hexanoylated products, **4b**, **5b**, and **6**, and JO as the reference. The purified JO has an oxidative stability time of 12 h (Fig. 8, indicated as induction time) after which the conductivity increases rapidly.

For all modified products, the oxidative stability is much better than for JO. The initial conductivity of the modified products is somewhat higher than the original JO, which could be due to the presence of traces of volatile organics (*e.g.*, acid residues). Though speculative, the slow increase in the conductivity in time may be caused by the formation of traces of free acids by hydrolysis of the ester branches.

The improved oxidative properties are in line with expectations as the modified products contain virtually no residual carbon–carbon double bonds, which are the prime cause for the oxidative decay of plant oils and derivatives.

4 Conclusions

The synthesis of a number of branched JO derivatives containing vicinal di-ester units in the fatty acid chains is reported. The cold flow properties (pour- and cloud point, melting point and crystallization temperature) were determined and shown to be a function of the length of the branches (acetyl *vs*. hexanoyl) and the stereochemistry of the vicinal di-ester units (*cis vs. trans*). The best cold flow properties (lowest pour and cloud points, crystallization and melting temperature) were obtained for the longest branch in a *trans* orientation, and were also considerably better than the JO source. The cold flow properties of the corresponding *cis* components were considerable less, an indication that the stereochemistry is of prime importance and should be taken into account when developing cold-flow improvers or biolubricants. The oxidative properties of the branched products are considerably better than for the JO feed, as a result of the reduced number of carbon–carbon double bonds in the structure.

In general, the final products have improved cold flow properties and better oxidative stability compared to that of virgin JO and as such could have interesting industrial applications, for example as biolubricant and cold-flow improvers.

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The authors have declared no conflict of interest.

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