

Esters of petroselinic acid containing *Trachyspermum copticum* seed oil: Potential industrial lubricant base stocks

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Received 2 August 2018; accepted (revised) 26 July 2019

Trachyspermum copticum seed oil contains volatile oil rich in thymol, which is distilled out and used for medicinal and aromatic formulations. The seed powder after removal of the volatiles loses its importance. However, the fixed oil being rich in unsaturation with petroselinic acid (18:1, Δ_6 ; 68.3%) and linoleic acid (18:2; 25.3%) is used for preparing biolubricant base stocks. Methyl, isopropyl and 2-ethyl hexyl esters of the oil have been converted to epoxides, followed by *in situ* hydroxylation and acylation using hexanoic and butyric anhydrides. The acylated products have been evaluated for lubricant properties, and are found to exhibit density (0.91-0.97 g/cc); viscosity of 23.5-27.3 cSt at 40°C and 4.85-5.33 cSt at 100°C. The values are comparable to jatropha acylated products. The products exhibited good copper corrosion resistance value of '1a' and high flash points of 230-242°C. The acylated esters with good weld load behavior, and lower wear and pour point values and viscosity indices, 128.84-138.94, can be potential base stocks belonging to group III category lubricants with ISO VG Grade about 22. These products can be further explored for the preparation of hydraulic, metal working and other industrial fluid formulations.

Keywords: *Trachyspermum copticum*, seed oil, acylated products, biolubricant base stocks

Worldwide vegetable oils production is estimated to be 125 MMTs, and it is expected to reach 175 MMTs by 2020. Olive oil based lubricants have been used as early as 1650 BC. Lubricant formulations prepared from vegetable oils namely olive, rapeseed, castor, palm and the animal fats from the sperm whale, lard, and grease from wools were known since 50 AD (Emmanuel *et al.* 2009; Honary, 2004)^{1,2}. Vegetable oils are being investigated as a potential source of environment-friendly lubricants due to their biodegradability, renewability and excellent lubrication properties. A large number of vegetable oils were screened for their potentiality for industrial applications like biodiesel, lubricants, foaming agents and other minor uses, apart from their traditional food applications. Vegetable oils with superior lubricity and emulsifying characteristics enhance their potentiality as additives and compete with the cheaper mineral oil-based lubricants (Honary, 2004)². Masjuki *et al.* (1999)³ reported that palm oil-based lubricants reduced the hydrocarbon and carbon monoxide emission levels to a greater extent than mineral oil-based lubricants.

The disadvantages like lower oxidative stability and pour points of vegetable oils can be overcome by chemical modifications such as epoxidation, hydroxylation, acetylation at the double bond position, estolide formation, and transesterification of plant oils with polyols, and preparation of acyloxy oils/derivatives (Sharma *et al.* 2006)⁴. Incorporation of antioxidants, detergents, dispersants, viscosity modifiers, pour point depressants, antiwear agents, rust and corrosion inhibitors, emulsifiers, foam inhibitors, thickeners, friction modifiers, dyes, and biocides into base fluid help in improving their lubricant performance (Rafael *et al.* 2011)⁵. Formation of epoxide on the double bond is an addition reaction, which can be useful for further conversion to various compounds by reaction with a variety of nucleophiles (Campanella *et al.* 2008)⁶.

Epoxidation reactions have been carried out industrially to obtain a variety of commercially important products. Epoxidation of unsaturated fatty acids of soybean (Sinadinovic-Fiser *et al.* 2001; Vlcek and Petrovic, 2006)^{7,8} and other plant oils like canola (Mungroo *et al.* 2008)⁹, rapeseed (Milchert *et al.*

2010)¹⁰, and linseed (Tellez *et al.* 2009)¹¹ were carried out. Non-traditional oils like mahua (Goud *et al.* 2006)¹², cottonseed (Dinda *et al.* 2008)¹³, Rubber seed (Okieimen *et al.* 2002)¹⁴, Karanja (Goud *et al.* 2006)¹², and Jatropha (Goud *et al.* 2007; Goud *et al.* 2010; Meyer *et al.* 2008; Rios *et al.* 2005; Daniel *et al.* 2011)¹⁵⁻¹⁹ were also epoxidized. These base stocks exhibited low pour points with wide viscosity ranges. During recent times, *Jatropha curcus L* oil, a non-edible oil has been widely explored for the production of biodiesel and biolubricant base stocks, and was found to be a promising raw material (Sammaiah *et al.* 2014)²⁰. Biolubricant base stocks such as fatty acid methyl, butyl, 2-methyl-1-propyl, and 2-ethylhexyl esters of epoxidized Karanja (*Pongamia glabra*) oil with excellent lubricant properties were also synthesized (Padmaja *et al.* 2012; Geethanjali *et al.* 2013)^{21,22}.

These products exhibited broad viscosity ranges which with suitable additives such as antioxidants and pour point depressants can be used for metal working and hydraulic fluid formulations. However, the epoxides being less stable and further to improve oxidation stability and pour points, the epoxy functionality is converted to hydroxyl followed by acylation with various acid anhydrides. Acyloxy stearic acid products with 2-ethylhexanol, 2-ethylhexyl-10,12-dihydroxy-9-acyloxystearate were prepared from ricinoleic acid (Salimon *et al.* 2012)²³ and these products with wide viscosity indices, flash points, pour points (PP), and oxidative stabilities were found to be potential for use as bio-based industrial materials in biolubricants, surfactants, or fuel. Triesters of epoxidised Karanja oil were prepared using behenic acid and *p*-toluenesulfonic acid (*p*-TSA). The epoxide ring was opened and converted into diesters of octanol and 2-ethylhexanol to improve the oxidation and flow characteristics (Prerna Singh and Chhibber, 2013)²⁴. The products exhibited improved viscosity index, pour point and flash points of 194 cp, -36°C and 307°C respectively, when compared to 172cp, -179°C and 212°C, respectively for the pre-modified oil. The modified products can find applications such as metalworking, hydraulic fluid turbine oil, refrigeration, and as food processing lubricants. Acylation of derivatives of polyhydroxy triglycerides of milkweed (*Asclepias syriaca L.*) seed oil was carried out using C₂-C₅ anhydrides by Harry-O'kuru *et al.* (2011)²⁵. The products exhibited high viscosity ranges and good moisturizing properties.

Propanoylated, butanoylated, and hexanoylated karanja oil and its fatty acid methyl esters were synthesized and evaluated for lubricant properties (Padmaja *et al.* 2012, Geethanjali *et al.* 2013)^{21,22}. Based on the study, propanoylated and butanoylated esters of karanja fatty acid methyl esters were categorized under ISO VG 46 and ISO VG 68 categories of hydraulic fluids, respectively as per IS: 3098.

With the above background, in the present study, the petroselinic acid (18:1 Δ 6, 68.3%) containing *Trachyspermum copticum* seed oil (Prabhakara Rao *et al.* 2015)²⁶ was exploited for the preparation of biolubricant base stocks. The seed after distillation of essential oil is of less importance. Hence there is a need to look for alternative applications. As the importance of vegetable oil-based lubricants is growing day-by-day and the fact that coriander seed oil containing petroselinic acid (18:1 Δ 6, 74%) was earlier exploited by Cermak *et al.* (2011)²⁷ for lubricant base stock preparation as estolide 2-ethylhexyl (2-EH) esters. These esters were found to possess very good lubricant properties such as kinematic viscosities (53 - 75 cSt at 40°C and 9.1 to 14.6 cSt at 100°C) and viscosity index (VI) (151-165). The caprylic (C8) acid capped coriander estolide 2-EH ester showed the lowest pour point of -33°C and cloud point -33°C. These are high viscous fluids, while most of the industrial applications demand low viscosity grades such as VG 22 and 32. Hence, an attempt was made to utilize *Trachyspermum copticum* fatty acids for the preparation of lubricant base stocks with the desired viscosity range. The fatty acids were subjected to a two-step synthesis for the preparation of acylated products, and these products were evaluated for lubricant properties.

Materials and Methods

Trachyspermum copticum (Ajwain) seed was procured from Kurnool district, Andhra Pradesh, India. Sodium hydroxide, potassium hydrogen phthalate, hydrochloric acid, sulphuric acid, glacial acetic acid, sodium bicarbonate, hydrogen bromide, crystal violet indicator, methanol, hexane, ethyl acetate, 2-ethyl hexane 1-ol, 2-methyl propane-1-ol (isobutyl alcohol), *p*-toluenesulphonic acid (*p*-TSA), 4-dimethylaminopyridine (DMAP), aqueous hydrogen peroxide (30%), formic acid (85%), xylene, toluene, anhydrous sodium sulphate and phenolphthalein indicator were purchased from M/s S.d. Fine Chem Ltd., Mumbai, India. Butyric and hexanoic anhydrides were procured from M/s Sigma Aldrich

(St. Louis MO, USA). Analytical grade reagents and distilled solvents were used in the study.

Distillation of essential oil

The essential oil from the seed powder was recovered using hydro-steam distillation in a modified Clevenger apparatus in batches of 5 kg and the after the process the materials was dried in a cabinet tray dryer to about 10% moisture.

Extraction of oil

The dry material after essential oil recovery was coarsely ground and extracted at 10 kg scale using hexane (1:5 wt./vol.) by packing the material in 1 kg cloth bags in an all glass soxhlet apparatus. Hexane was removed from the oil using rotary evaporator followed by drying under reduced pressure. Four batches were carried out to obtain 5 kg of oil amounting to an average yield of 12.5%.

Preparation of *Trachyspermum copticum* oil fatty acids (TFA)

Trachyspermum copticum oil (500 g, 0.57 mol) and sodium hydroxide (91.2 g, 2.28 mol) were taken into a 1000 mL of distilled water and stirred mechanically for six hours in a 2 L, 4-necked flask with a provision for mechanical stirrer maintaining the temperature at 90°C. The reaction was monitored by TLC eluted with a solvent mixture (hexane:ethyl acetate, 90:10 v/v). After the completion of hydrolysis, the reaction mixture was neutralized using HCl solution, extracted with ethyl acetate, washed with water to remove excess acid, passed through anhydrous sodium sulfate and the solvent was distilled out. The product was further dried under reduced pressure to obtain *Ajwain* fatty acids (AFA, 467 g; 95% yield).

Preparation of *Trachyspermum copticum* fatty acid alkyl esters

Alkyl esters of *Trachyspermum copticum* fatty acids were prepared using methanol, 2-ethyl-1-hexanol and isobutyl alcohol (Salimon *et al.* 2011²⁸; Salimon *et al.* 2012²³). *Ajwain* fatty acids (TFAs; 600 g, 2.74 mol), alcohol (1.5 equivalents, 4.19 mol), *p*-TSA (1% on the weight of AFA), and 1200 mL of xylene (2 vol) were stirred at reflux under nitrogen atmosphere. A Dean and Stark apparatus was fixed to the reflux condenser and the reaction was conducted until a theoretical amount of water was collected. The crude esters mixture was distilled at 60–150°C and 5 mm Hg to remove excess alcohol and xylene. The ester product in hexane was thoroughly mixed with NaHCO₃ solution, dried over a bed of anhydrous

Na₂SO₄, concentrated and dried applying vacuum. The yields of *Ajwain* fatty acid alkyl esters were 90, 92 and 95%, for methyl, 2-ethyl hexyl and isobutyl esters respectively. Two batches of esterification were carried out for each ester to collect about 1 kg of the alkyl esters. The esters were passed through basic alumina column eluted with hexane to obtain the above esters with an acid value <0.5.

Analysis of esters

The esters were analysed for their fatty acid composition using GC employing a DB 225 (capillary column (30 m × 0.25 mm, 0.25 μm of film thickness). The GC-MS was conducted using a HP-5 MS capillary column (30 m × 0.25 mm i.d.) coupled with an Agilent 5973 mass spectrometer (Christie, 2003)²⁹. A Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) 6850 series) equipped with an FID detector was used. A temperature programming (160°C - 2 min, 5°C/min - 220°C -10 min at 220°C) was used for resolving the fatty acid methyl esters. Nitrogen at a flow rate of 1.5 mL/min was used as the carrier gas. The injector temperature was 230°C, detector 250°C and the split ratio of 50:1 was maintained. Standard fatty acid methyl esters were used for identification. The mass spectrometer (70 eV; m/z 50 – 550, EI mode; source temperature 230°C and a quadruple temperature 150°C) was used for confirmation. The column temperature programming was 200°C (2 min.) - 4°C/min - 300°C (20 min.). Helium (carrier gas) was used at a flow rate of 1.0 mL/min. The inlet temperature was 300°C and split ratio of 50:1 was maintained. Mass spectrometric fragmentation, comparison of retention times of standard reference compounds and Wiley and NIST libraries were utilized for structural interpretation.

Hydroxylation of *Trachyspermum copticum* fatty acid alkyl esters

Alkyl esters (500 g; 2.15 mol of methyl, 1.51 mol of 2-ethyl hexyl, and 1.82 mol of isobutyl esters) were epoxidised using 30% hydrogen peroxide (724.3 g, 6.45 mol; 508.7 g, 4.53 mol; 612.5 g, 5.45 mol, respectively). Formic acid (148 g, 3.22 mol; 104.2 g, 2.26 mol; 125 g, 2.72 mol) was used to form performic acid which reacts with the double bond. *Trachyspermum copticum* fatty acid alkyl esters, concentrated sulfuric acid and hydrogen peroxide was mixed in a three-necked round-bottom flask, and the temperature was reduced to 10°C using an ice bath (Hwang and Erhan, 2001; Hwang and Erhan, 2006)²⁸⁻³⁰. Hydrogen peroxide solution (30%) was added slowly

over a period of 1 hr to the reaction mixture continuously stirring at 10°C. After the addition, the temperature of the contents was gradually increased to 60°C, and the stirring was continued for 6 h. Sample aliquots were collected at hourly intervals to monitor the course of the reaction. The samples were extracted with ethyl acetate and analyzed for oxirane by titrating with standard HBr solution using crystal violet as the indicator (Cd. 9-57)³¹. The time required for obtaining maximum oxirane value (4.89) against a theoretical value (5.0) was recorded. Hydroxylation was initiated by raising the reaction mixture temperature to 90°C for a period of 12 h. The final product was extracted with ethyl acetate and washed with water until it was free of acid (Cd 13-60)³¹. The structure of the proposed hydroxylated product was confirmed by IR, and ¹H NMR. GC and GC-MS of the silylated hydroxy product were carried out.

Acylation of hydroxy fatty acid alkyl esters

The dihydroxy Ajwain fatty acid methyl esters (500 g each, 1.8 mol, 1.4 mol and 1.8 mol, respectively) were further converted to their respective acyl derivatives. Butyric anhydride (853 g, 5.4 mol; 663 g, 4.2 mol; 853 g, 5.4 mol) and hexanoic anhydrides (1156 g, 5.4 mol; 899 g, 4.2 mol; 1156 g, 5.4 mol) were used along with DMAP (0.1%) as catalyst and xylene as the reaction medium. Hydroxylated *Ajwain* fatty acid alkyl esters, three equivalents of anhydride, DMAP, and xylene were stirred in a three-necked round-bottom flask maintained at 140–150°C for 6–10 hr. TLC of the reaction mixture was conducted using a solvent mixture of hexane:ethyl acetate (90:10 v/v) and IR were used to determine the completion of the reaction. The excess anhydride and xylene were removed from the products by distillation at 140°C under 5 mm Hg vacuum. The product in ethyl acetate was washed free of acid using water, dried over a bed of anhydrous sodium sulphate and concentrated under vacuum. The product was passed through a column of basic alumina to eliminate fatty acid residues to <0.1 (acid value) to yield diacyl fatty acid alkyl esters in 85% yield. The acylated derivatives appeared as dark, viscous liquids and were analyzed by FTIR and ¹H NMR spectral data to confirm their structures (Akintayo *et al.* 2002)³².

Spectral analysis

¹H NMR spectroscopy of the acyl derivatives was conducted using a Bruker AR X 400 Spectrometer (500, 300 MHz). Tetramethyl silane was used as the

internal standard. Infrared spectra of the derivatives dissolved in chloroform, were obtained using a Perkin-Elmer (Norwalk, CT, USA) Model Spectrum BX FTIR spectrometer neat as a thin film in absorbance mode.

Physico-chemical and Lubricant Properties

All the products were characterized as per the standard American Oil Chemical Society (AOCS, 1997)³¹ and Standard test methods of ASTM (2002)³³ for various physico-chemical properties. Various parameters such as density, viscosity, acid value (AOCS Cd 3d-63), oxirane value (Cd 9-57)³¹, hydroxyl value (Cd 13-60)³¹, flash point (D-93)³³, copper corrosion test (D-130)³³, weld load (IP-239)³³, and wear (D-4172)³³ were evaluated.

The density of the products was determined by using an Anton Paar DMA 4500 M density meter at 15°C as per ASTM method D-4052³³. The measurements were carried out thrice and the results reported are average of the three determinations.

The viscosity of the acyl derivatives was determined at two temperatures of 40°C and 100°C in Cannon-Fenske Viscometer tubes maintained at constant temperature bath (Cannon Instrument Co., State College, PA). Viscosity and viscosity indices (VI) were computed as per ASTM D 445³³ and ASTM D 2270³³ standard methods, respectively. All the measurements were carried out in duplicate, and the mean values were presented.

ASTM D 130 method was used for evaluating the corrosiveness of the derivative in a Koehler Inc. apparatus. The sample liquid (30 mL) is heated to 100°C and the polished copper strip is dipped in it for 3 h and it thoroughly washed. The color and the extent of tarnish was compared with ASTM copper strip corrosion standard.

Flash points of the acylated derivatives were measured in a Koehler Inc. apparatus following the standard ASTM D 93³³ procedure. The minimum temperature at which the the vapor of the sample gets ignited at atmospheric conditions is noted.

Weld load of the base stocks was measured according to the ASTM IP 239 method developed by Stanhope Seta, U.K. Three stainless steel balls were placed in the ball cup assembly and the fourth ball is placed into a ball chuck placed above. The spindle is attached to the above ball and the load is increased gradually up to 10 kg and observed for 1 min. The minimum weight required for fusing the balls together is noted as the weld load of the liquid derivatives.

ASTM D 4172³³ method was applied for determining wear for the lubricant base stocks. Four Ball Tester (Stanhope Seta, UK.) was used in the determination, and steel balls present in the lubricant (3 stationery balls) were brought into contact interface by a steel ball (rotating, 12.7 mm diameter) with load. The scar diameter is measured to assess the anti wear properties of test lubricant base stocks.

The pour point is defined as the lowest temperature at which the sample flows. The standard ASTM D5949³³ was used for measuring the pour point values. Model PSA-70 S (Hammersmith Gate, Richmond, B.C., Canada) a phase Technology Analyzer was utilized for the measurements. Triplicate determinations conducted for each sample with a resolution of 1°C increment and average values (rounded off to whole degree) are presented.

Results and Discussion

Trachyspermum copticum oil after distillation to remove the volatile oil (7%) was subjected to Soxhlet extraction using hexane. The oil with petroselinic acid (68%) was hydrolysed to obtain fatty acids. The fatty acid composition of the oil is presented in Table I. The fatty acids were esterified with different alcohols, namely, methanol, 2-methylpropan-1-ol, and 2-ethylhexan-1-ol to yield corresponding esters in 90, 92 and 95%, respectively. The fatty acid esters were epoxidized using formic acid and hydrogen peroxide. The extent of epoxidation was monitored by oxirane value (Table II). Hydroxylated products were further acylated using butyric and hexanoic anhydrides to prepare their corresponding acylated products. The yields noted were butyloxy methyl ester 87%, butyloxy 2-ethyl hexyl ester 85%, butyloxy isobutyl ester, hexyloxy methyl ester 89%, hexyloxy 2-ethyl hexyl ester and hexyloxy isobutyl ester 85%. The reaction pathway is presented in Scheme I.

Spectral analysis of hydroxylated and acylated esters

The formation of the hydroxyl group was observed in the FTIR at 3445-3463 cm^{-1} . The absence of double bond at 3004 cm^{-1} further confirmed the hydroxylation. ¹H NMR spectral data of products exhibited 3.2–3.4 (–CH–OH), 2.25 (–CH₂–C=O), 1.60–1.2(–CH₂–), and δ 0.85–0.93 (CH₃). Later, hydroxy alkyl esters were acylated with butyric and hexanoic anhydrides.

The absence of hydroxy bands at 3447 cm^{-1} and a corresponding peak at 1739 cm^{-1} in the FTIR spectra of the acylated products confirmed ester structures in

Table I — Fatty acid composition (wt. %) of total lipid of *trachyspermum copticum* seeds

Fatty acid	Total lipid
16:0	4.5 ± 0.05
18:0	0.9 ± 0.08
Saturated	5.4
18:1 Δ 6	68.3 ± 2.46
Monounsaturated	68.3
18:2	25.3 ± 0.70
18:3	1.0 ± 0.06
Polyunsaturated	26.3

Values are mean of triplicate analyses ± Standard deviation

Table II — Oxirane values of epoxides formed during the course of reaction

Time (h)	Methyl ester	2-Ethyl hexyl ester	Isobutyl ester
1	2.08	1.38	3.83
2	2.25	2.78	4.05
3	3.76	3.24	4.87
4	3.82	4.87	4.89
5	3.85	4.87	4.89
6	3.86	4.88	4.89

Values are mean of duplicate analyses

the products. Methylene asymmetric stretching in the FTIR spectra of all the compounds (2928 and 2856 cm^{-1}), methylene bending (1465 cm^{-1}), methyl symmetrical bending vibration (1372 cm^{-1}), and methylene rocking (722 cm^{-1}) and C–O stretching resulted in 1234, 1174, and 1106 cm^{-1} in esters. Acylated products were confirmed by the increase in ratio of peak intensities of 1465:1372 cm^{-1} . In the ¹H NMR spectra, the presence of additional peaks in acylated products at δ 2.07 is due to methyl protons of the –COCH₃ which confirmed the formation of the acyloxy groups. The absence of peaks at δ 3.2–3.4 for hydroxy products in the acylated derivatives also confirmed their conversion. The spectral data is summarized in Table III.

Lubricant properties of acylated products

The acylated products were evaluated for lubricant properties namely density, viscosity, viscosity indices, copper corrosion test and flash points using ASTM standard methods (Table IV) and compared with acylated derivatives of soybean and jatropha oils rich in unsaturation. The products were found to exhibit densities in the range 0.9100-0.9724. The acylated derivatives were exhibiting viscosity in the range of 23.50–27.31cSt at 40°C and 4.85–5.43 cSt at 100°C (Table IV). The viscosity of the acylated derivatives was matching with those of ISO VG 22 which is much lower compared to petroselinic acid-based

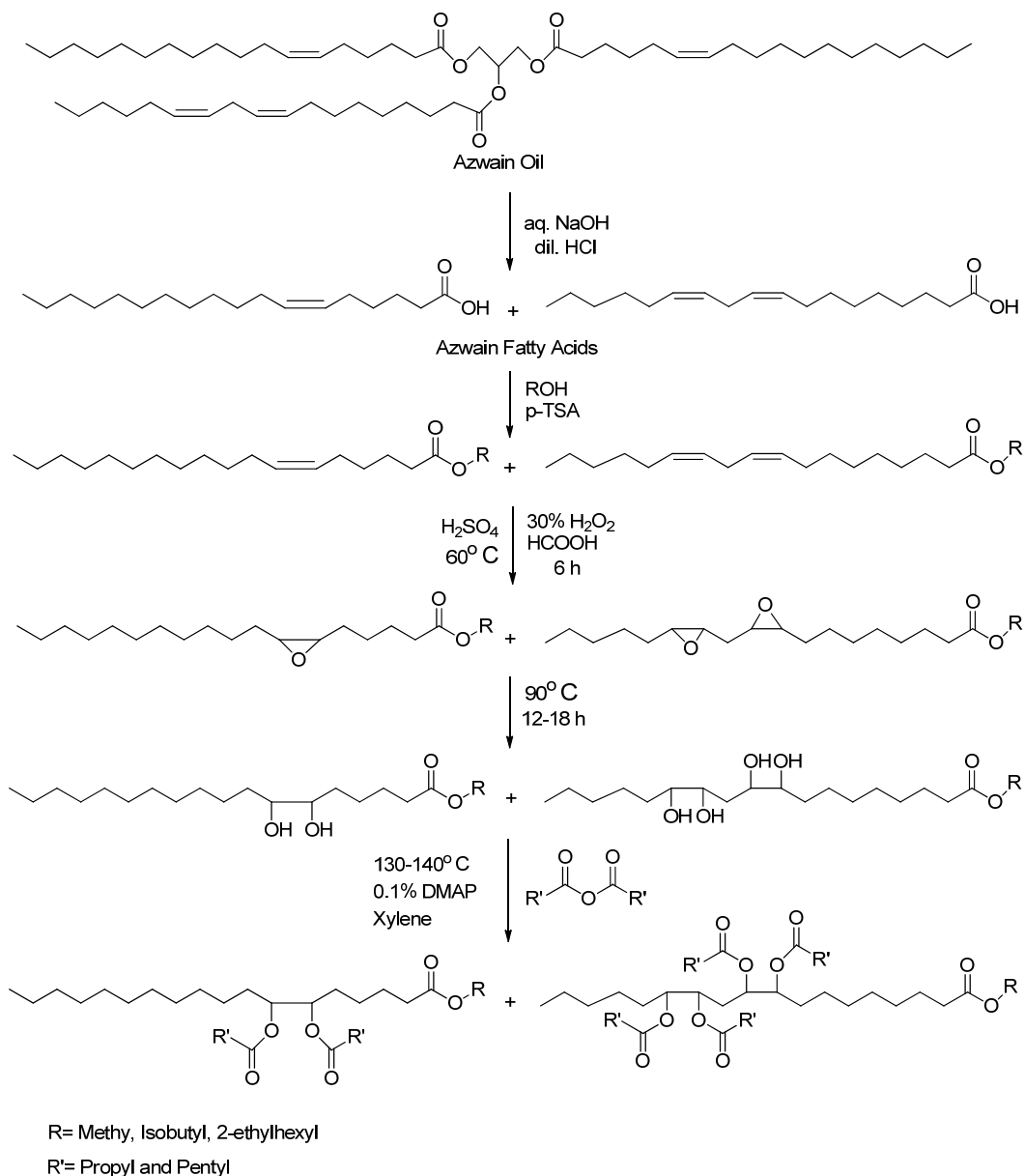

 Scheme I — Scheme of synthesis of acylated derivatives of *azwain* fatty acid esters

 Table III — ^1H NMR and FT-IR spectral data of the acylated *ajwain* (*Trachyspermum copticum*) fatty acid esters

Base stock compound	Chemical shift (^1H NMR in CDCl_3)	Assignment	IR (neat, cm^{-1})	Assignment
<i>Butanoylated Esters of Azwain Fatty Acid Methyl Esters (BOAFAME):</i>				
	δ (ppm)		Wave number cm^{-1}	
	0.88 (t)	$-\text{CH}_2-\text{CH}_3$	2928	C-H
	0.96 (t)	$-\text{CO}-(\text{CH}_2)_2-\text{CH}_3$	1735	C=O
	1.24-1.35 (m)	$-\text{CH}_2-\text{CH}_3$	1176	C-C (=O)-O
	1.44-1.65 (m)	$-\text{CH}_2-\text{CH}_2-\text{CO}-$		
	2.26 (t)	$-\text{CH}_2-\text{C}=\text{O}$		
	3.64 (s)	$-\text{O}-\text{CH}_3$		
	4.92-4.96 (m)	$-\text{CH}-\text{O}-\text{C}=\text{O}$		

(Contd.)

Table III — ¹ H NMR and FT-IR spectral data of the acylated ajwain (<i>Trachyspermum copticum</i>) fatty acid esters (Contd.)				
Base stock compound	Chemical shift (¹ H NMR in CDCl ₃)	Assignment	IR (neat, cm ⁻¹)	Assignment
<i>Hexanoylated Esters of Azwain Fatty Acid Methyl Esters (HOAFAME)</i>				
	0.88 (t)	-CH ₂ -CH ₃	2928	(C-H),
	0.90 (t)	-CO-(CH ₂) ₄ -CH ₃	1740	(C=O),
	1.2-1.36 (m)	-CH ₂ -CH ₃ ,	1171	C-C (=O)-O
	1.42-1.64 (m)	-CH ₂ -CH ₂ -CO-		
	2.28 (t)	-CH ₂ -C=O		
	3.64 (s)	-O-CH ₃		
	4.91-4.96 (m)	-CH-O-C=O		
<i>Butanoylated Esters of Azwain Fatty Acid 2-Methyl-1-propyl Esters (BOAFaiBE)</i>				
	0.88 (t)	-CH ₂ -CH ₃	2929	(C-H),
	0.93 (d)	-CH-(CH ₃) ₂	1736	C=O
	0.96 (d)	-CO-(CH ₂) ₂ -CH ₃	1178	C-C (=O)-O
	1.24-1.5 (m)	-CH ₂ -CH ₃		
	1.56-1.65 (m)	-CH ₂ -CH ₂ -CO-		
	1.93 (m)	-CH-(CH ₃) ₂		
	2.24-2.27 (m)	-CH ₂ -C=O		
	3.82 (d)	-CH ₂ O- C=O		
	4.92-4.98 (m)	-CH-O-C=O		
<i>Hexanoylated Esters of Azwain Fatty Acid 2-Methyl-1-propyl Esters (HOAFaiBE)</i>				
	0.88 (t)	-CH ₂ -CH ₃	2929	C-H
	0.90 (t)	-CO-(CH ₂) ₄ -CH ₃	1738	C=O
	0.93 (d)	-CH-(CH ₃) ₂	1171	C-C (=O)-O
	1.24-1.5 (m)	-CH ₂ -CH ₃		
	1.56-1.65 (m)	-CH ₂ -CH ₂ -CO-		
	1.93 (m)	-CH-(CH ₃) ₂		
	2.24-2.32 (m)	-CH ₂ -C=O		
	3.82 (d)	-CH ₂ O- C=O		
	4.92-4.98 (m)	-CH-O-C=O		
<i>Butanoylated Esters of Azwain Fatty Acid 2-Ethyl-1-hexyl Esters (BOFAEHE)</i>				
	0.89 (t)	-CH ₂ -CH ₃		
	0.96 (t)	-CO-(CH ₂) ₂ -CH ₃		
	1.2-1.38 (m)	-CH ₂ -CH ₃		
	1.40-1.68 (m)	-CH ₂ -CH ₂ -CO-		
	2.23-2.34 (m)	-CH ₂ -C=O		
	3.95 (d)	-CH ₂ -O-C=O		
	4.93-4.98 (m)	-CH-O-C=O		
<i>Hexanoylated Esters of Azwain Fatty Acid 2-Ethyl-1-hexyl Esters (HOFAEHE):</i>				
	0.90 (t)	-CH ₂ -CH ₃	2930	C-H
	1.24-1.38 (m)	-CH-CH ₃	1729	C=O
	1.43-1.65 (m)	-CH ₂ -CH ₂ -CO-	1174	C-C (=O)-O
	2.24-2.35 (m)	-CH ₂ -C=O		
	3.95 (d)	-CH ₂ -O-C=O		
	4.92-4.98 (m)	-CH-O-C=O		

estolide esters (Cermak *et al.* 2011)²⁷. Hwang *et al.* (2003)³⁴ reported acetyl and hexanoyl derivatives of 2-ethylhexyl esters of epoxidised soybean oil with viscosities of 57.2 and 41.1 cSt at 40°C and viscosity index in the range 127 and 159, respectively. Salimon and Salih (2010)³⁵ used epoxidised oleic acid and prepared ring opened products with behenic acid.

The resultant acylated products were esterified using octanol and 2-ethyl hexanol and further, the free hydroxyl group was reacted with oleic and stearic acids to form triesters with improved pour points, viscosity and flash points. The viscosities and viscosity indices of the acylated *Trachyspermum copticum* alkyl esters were found comparable to

Table IV — Lubricant properties of acyloxy derivatives of *Trachyspermum copticum* fatty acid alkyl esters

Product	Density (g/cc)	Viscosity cSt	Viscosity index	Cu corrosion test	Flash point (°C)	Weld load (kg)	Wear (mm)	Pour point (°C)	
		40°C	100°C						
Butyloxy methyl ester	0.96224	24.23	5.01	137.28	1a	220	110	0.73	3
Hexyloxy methyl ester	0.97236	27.31	5.43	138.56	1a	232	130	0.69	0
Butyloxy isobutyl ester	0.95210	24.01	4.97	136.36	1a	236	130	0.70	-3
Hexyloxy isobutyl ester	0.94200	26.19	5.33	138.94	1a	244	130	0.72	-6
Butyloxy 2-ethylhexyl ester	0.92310	23.50	4.85	131.85	1a	256	110	0.71	-15
Hexyloxy2-ethylhexyl ester	0.91000	25.80	5.10	128.84	1a	264	120	0.70	-18

Values are mean of duplicate analyses

jatropha acylated products and lower compared to the above reports. These viscosities lie within the hydraulic base fluids specification.

Among the alkyl acylated derivatives, hexanoylated 2-ethylhexyl esters showed higher viscosities compared to other products which can be attributed to longer chain lengths. However, the increase in viscosities was lower with an increase in number of alkyl chains which may be attributed to branching. Similar effects of branching on the viscosities were reported in other vegetable oil-based branched polysaccharides (Johnson, 1999)³⁶, branched polymers (Wood –Adams, 2011)³⁷ and estolides of petroselinic acid (Cermak *et al.* 2011)²⁷.

The viscosity indices were in the range 128.84-138.94. The VI of acylated products also increased with increasing chain length of the acyl group. Similar results were reported by Yao *et al.* (2010)³⁸ for acylated products of ricinoleic acid. The VI values for the acylated derivatives are comparable to those of synthetic and mineral oils (Rudnick, 2006)³⁹. Based on the viscosity indices (128.84-138.94), the acyloxy ester derivatives belonged to group III category lubricants, which can be further explored for the preparation of hydraulic and metal working and other industrial fluids applications. Flash point measurement indicates the degree of volatility and resistance of the lubricants towards fire. The flash point of acylated products was found to be in the range of 220–264°C (Table IV). The flash points increased with increasing chain length of the end-chain ester group and the acyl group. All of the

acylated products with flash point ≥ 165 °C lie well within the range of hydraulic oils (Talis *et al.* 2009)⁴⁰. The high flash point is desirable for lubricants for safety in the handling and storage of the products. The flash points of acylated *Trachyspermum* fatty acid esters were found comparable to the corresponding acylated jatropha fatty acid esters (202-254°C) (Sammaiah *et al.* 2014)²⁰. The copper corrosion test of all acylated *Trachyspermum copticum* esters showed slight tarnishing with the value of '1a' indicating better corrosion resistance of the products. The load bearing capacity of the lubricant base stocks can be assessed from weld load. It was observed that the weld load ranged between 110-130 kg and lowest for butyloxy methyl ester and highest for hexanoyloxy 2-ethyl hexyl ester of *Ajwain* oil. The higher weld load value for hexyloxy-2-ethylhexyl ester may be attributed to longer side chain length, higher molecular weight and reduced unsaturation (Adhvaryu and Erhan, 2002)⁴¹. However, all the products exhibited weld load of about 130 kg, which indicates their suitability for metal working operations. Wear was measured by noting the scar diameter in the four ball wear test. It was noted that the wear was in the range of 0.69-0.73 mm. Lower values were seen for hexyloxy2-ethyl hexyl ester (0.70 mm) and butyloxy2-ethyl hexyl ester (0.71 mm) and butyloxy methyl ester (0.73 mm). Slightly higher values were recorded for hexyloxy methyl ester (0.75 mm), butyloxyisobutyl ester (0.73 mm) and hexyloxy isobutyl esters (0.72 mm). However, the values were found lower compared to acylated polyol

esters of castor oil (Kamalakar *et al.* 2015)⁴². The property indicated the ability of the flow of the lubricant at lower temperatures. The pour point of the acylated *Trachyspermum copticum* alkyl esters ranged between 3 to -18°C . The value decreased with branching as observed in 2-ethyl hexyl and isoalkyl esters hexanoylated and butanoylated products. While, the pour point of straight chain esters such as butanoyloxy and hexanoyloxy methyl esters were higher and these esters can be used in high temperature applications (Salimon *et al.* 2012)²³.

Conclusions

Trachyspermum copticum which loses its importance after distillation of the essential oil was exploited for the production of lubricant base stocks. The lubricant properties of acylated products of *Trachyspermum copticum* fatty acid alkyl esters were comparable to *jatropha* acylated products. The products showed good copper corrosion resistance value of '1a' and high flash points of 220-264°C. Good weld load behavior, and lower wear values and high viscosity indices, 132-149, makes the acyloxy ester derivatives attractive for many industrial applications. The values show that these base stocks belong to group III category lubricants, which can be further explored for the preparation of hydraulic, metal working and other industrial fluids applications.

Acknowledgments

The authors thank the Director, CSIR-CFTRI, Mysuru for his support.

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