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Synthesis and characterization of new esters of oleic acid and glycerol analogues as potential lubricants

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ABSTRACT

A series of noncommercial polyols which do not contain β-hydrogen were used to synthesize new oleic acid based esters as potential thermally stable biolubricants. Commercial trimethylolpropane (TMP) was used to synthesize TMP trioleate as a reference polyol ester. The esters were purified by column chromatography and their structures were confirmed by ^1H and ^{13}C NMR and HRMS. The evaluated properties were kinematic viscosity, thermo-oxidative stability (by TGA) and melting point (m.p., by DSC). All the esters showed high viscosity indices (160–200) and similar thermo-oxidative stability (T_{onset} of triesters around 330 °C), but a small change in the structure of the triols could generate esters of different viscosity grades (ISO VG 46 and 68) and different m.p. (ranging from −15 to −35 °C). Two of the polyols generated triesters with virtually the same properties of TMP trioleate: pentaerythritil monoethyl ether (PEET) and pentaerythritil monobutyl ether (PEBUT). Two polyols must be highlighted: pentaerythritil monophenyl ether (PEPH) and trimethyloltoluene (TMT). PEPH generated an ISO VG 68 lubricant with a m.p. of −19 °C, relatively low for this class, and TMT generated an ISO VG 68 lubricant with no defined melting peak, suggesting it has better cold temperature flow properties than TMP trioleate.

1. Introduction

The search for environmental-friendly materials has led to evaluation of vegetable oil based lubricants, also named as biolubricants. The advantages of using biolubricants are their renewability, low toxicity, good biodegradability and some tribological properties like higher lubricity, higher viscosity index, higher detergency and low volatility.

Due to the presence of hydrogens in the beta position of glycerol backbone in triglycerides, vegetable oils are thermally sensitive, undergoing elimination at high temperatures (see Fig. 1), and so they generally are not appropriate for many lubricant purposes that require heat resistance. One of the ways to overcome this instability in natural oils is to modify these esters substituting glycerol for polyols that do not contain the β-hydrogen (Gryglewicz et al., 2003; Nagendramma, 2011). Among the polyols mostly used for this purpose there are neopentyl glycol (NPG), trimethylolpropane (TMP), and pentaerythritol (PE), also known as neopentyl polyols (da Silva et al., 2013; Gryglewicz et al., 2003; Oh et al., 2013; Åkerman et al., 2011a).

Only a few examples in the biolubricant field are known where non-commercial polyols as the backbone structure for fatty acid esters were examined. For example, Kawasaki synthesized polyesters of fatty acids using polyols with the general formula ($HO{-}CH_2CR^1R^2CH_2{-}O{-}(CH_2CR^1R^2CH_2{-}O)_n{-}H$) where R^1 and R^2 are independent C1-6 alkyl chains or methylol (CH_2OH), and n is an integer between 0 and 4 (Kawasaki, 2005).

Among the fatty acids frequently used to produce biolubricants, oleic acid (**1**) is by far the most abundant monoenoic acid of animal and vegetable tissues (Christie, 2014), and it is an abundant fatty acid of commercial vegetable oils like olive oil (about 80%), canola oil (60–80%), high oleic sunflower oil (more than 80%), palm oil (about 50%), corn oil (16–44%) (Neff et al., 1994; Gryglewicz et al., 2003; Yunus et al., 2005; White et al., 2007; Quinchia et al.,

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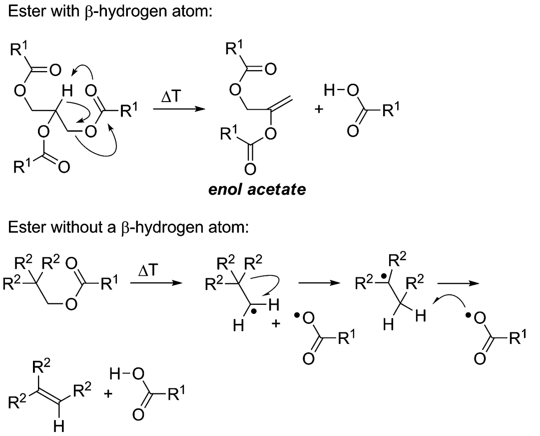

Fig. 1. Thermal destruction pathway of esters with β-hydrogen atoms on the alcohol part in comparison to esters without β-hydrogen atoms.

2014). Oleic acid is also abundant in non-edible oils promising for biodiesel production: *Jatropha curcas* L. oil (26–44%), *Pongamia pinnata* or Karanja oil (44–71%), *Madhuca indica* or Mahuca oil (41–51%), *Azadirachta indica* or Neem oil (44%) and *Calophyllum inophyllum* L. oil (38–43%) (Atabani et al., 2013).

Many works report the study of oleic acid based esters as lubricants (García-Zapateiro et al., 2014; Quinchia et al., 2014). As an unsaturated fatty acid, oleic acid displays lower oxidative stability than saturated fatty acids. On the other hand, it presents better cold flow properties, which make it interesting for the synthesis of liquid lubricants and for applications in cold climates, due to its lower pour point. For example, TMP trioleate is recommended to be used as a fire resistant hydraulic fluid in machines where the maximum reservoir temperature is between 60 and 100 °C, since temperatures above this would cause a rapid degradation because of its unsaturations (Clariant International Ltd, 2010; Eastwood et al., 2005).

The aim of this work was to synthesize esters of oleic acid with novel glycerol analogues that do not contain a central β-hydrogen, with the purpose to investigate the influence of the polyol structure on their physical–chemical properties and to evaluate their potential as lubricant base stocks. The glycerol analogues synthesized in this work were either derived from pentaerythritol (PE) and short chain alcohols/phenol or from formaldehyde and phenylacetaldehyde, an aromatic compound either found in buckwheat (Janeš et al., 2009) or synthesized from styrene oxide (Bhatia et al., 2001; Paparatto and Gregorio, 1988).

2. Materials and methods

2.1. Materials

Oleic acid (90%) was obtained from Sigma–Aldrich and Alfa Aesar, pentaerythritol (98%), sodium methoxide (95%) and potassium hydroxide (85%) from Merck, phenylacetaldehyde (98%) from Acros, paraformaldehyde (90–92%) from Janssen Chimica, 2-ethyl-2-hydroxymethyl-1,3-propanediol (trimethylolpropane or TMP, 98%) from Alfa Aesar. Diethyl carbonate was 99%. The methyl oleate (**2**) used in this work was prepared by Fischer esterification of oleic acid with methanol (molar ratio of oleic acid/methanol 1:10) using sulfuric acid as catalyst and a reaction time of 3 h at 65 °C (Lucena et al., 2008). The product was purified by vacuum distillation (b.p. 128 °C at 0.2 mm Hg) yielding a colorless liquid with an acid value varying from 1.0 to 2.2 mg KOH g^{-1}.

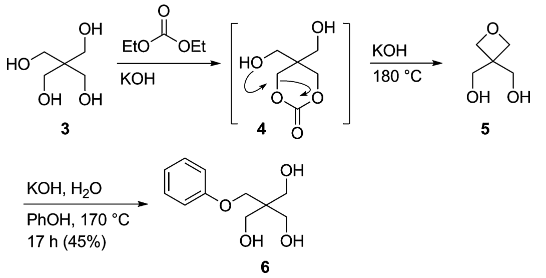

Fig. 2. Synthesis of 3,3-bis(hydroxymethyl)-oxetane (**5**, OX) and its reaction with phenolate to give the triol **6** (PEPH).

2.2. Synthesis and characterization of glycerol analogues

2.2.1. Synthesis of 2-hydroxymethyl-2-phenoxymethyl-propan-1,3-diol (pentaerythritil monophenyl ether, 6, PEPH)

The synthesis of PEPH (**6**) was performed following a procedure adapted from literatures (Pattison, 1957; Chen et al., 2002; Sangermano et al., 2009). Fig. 2 shows the reaction sequence. Thus, pentaerythritol (**3**) was converted to the cyclic carbonate **4** with diethyl carbonate followed by base induced formation of the oxetane with concomitant release of carbon dioxide (Morita et al., 2004). In a subsequent step, the oxetane ring of the resulting 3,3-bis(hydroxymethyl)-oxetane (OX, **5**) was opened with phenolate to give triol **6**.

*2.2.1.1. Synthesis of 3,3-bis(hydroxymethyl)-oxetane (OX, **5**).* To a 500 mL round bottom flask were added pentaerythritol (**3**) (102.0 g, 0.734 mol), diethyl carbonate (116 mL, 0.944 mol) and potassium hydroxide (0.236 g, 3.58 mmol), dissolved in absolute ethanol (13.0 mL). This mixture was refluxed for 4 h using an oil bath at 110–120 °C. After that the reflux condenser was removed, and additional potassium hydroxide (0.236 g) was added to the mixture. Then, a Vigreux column with a distillation system was attached to the flask and the mixture was stirred during 4 h and heated (oil bath at 140–150 °C) to remove the formed ethanol. Finally, the bath temperature was increased to 180 °C, allowing the removal of the excess of diethyl carbonate. When this temperature was reached, the Vigreux column was removed and the system was connected to a vacuum pump (0.3 mbar) to induce the decarboxylation of the carbonate. The product 3,3-bis(hydroxymethyl)-oxetane (**5**, OX) distilled at 145 °C (0.5 mbar) and was obtained as an amorphous colorless solid. R_f (CH_2Cl_2/MeOH 10:1) 0.19. R_f is the retention factor on thin layer chromatography (TLC).

*2.2.1.2. Synthesis of hydroxymethyl-2-phenoxymethyl-propan-1,3-diol (**6**) starting from OX.* The procedure below is a protocol adapted from two previous works (Cheymol et al., 1959; Cornia et al., 2008). See Fig. 2 for reaction scheme.

Potassium hydroxide (2.37 g, 0.036 mol) and phenol (7.26 g, 0.077 mol) were dissolved in water (10 mL) in a steel reactor. Thereafter, OX (**4**) (4.25 g, 0.036 mol) dissolved in water (12 mL) was added and the reactor was sealed and heated at 170 °C for 17 h. Water (10 mL) was added to the cooled reaction mixture, which was then acidified with concentrated HCl until formation of two phases. The organic phase was separated and the aqueous phase was saturated with NaCl and extracted with chloroform (3 × 75 mL) to remove the residual product from the aqueous phase (a pale red powder, 0.68 g, was collected during this step and identified by ^{1}H NMR as **6**). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuum. The crude product was purified by flash chromatography (CH_2Cl_2/MeOH, 10:1, R_f = 0.36) to give triol **6** (2.79 g, 36.5%) as a pale brown/red solid.