

Synthesis of Dioxo-Dioxane and Dioxo-Dioxepane Ethyl Oleate Derivatives as Bio-Lubricant Base Stocks

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Abstract: In this study, two novel compounds, i.e., ethyl 8-(3-octyl-5,6-dioxo-1,4-dioxan-2-yl)octanoate and ethyl 8-(3-octyl-5,7-dioxo-1,4-dioxepan-2-yl)octanoate were prepared from oleic acid as the starting material. Both compounds were obtained from the esterification of the ethyl 9,10-dihydroxyoctadecanoate with dicarboxylic acids in the presence of *p*-toluenesulfonic acid as a catalyst. The chemical structures of the synthesized products were confirmed by FTIR, ¹H-NMR, and MS spectrometers. The bio-lubricant properties of the products, such as density, total acid number, total base number, and iodine value, were determined and the effect of the dioxane and dioxepane heterocyclic rings to their bio-lubricant properties was discussed. The esterification of ethyl 9,10-dihydroxyoctadecanoate with oxalic acid gave ethyl 8-(3-octyl-5,6-dioxo-1,4-dioxan-2-yl)octanoate compound in 93.9% yield, while the esterification of ethyl 9,10-dihydroxyoctadecanoate with malonic acid gave ethyl 8-(3-octyl-5,7-dioxo-1,4-dioxepan-2-yl)octanoate compound in 89.6% yield. The density and total base number of the products were close to the standard commercial lubricant values. Meanwhile, the total acid number and the iodine value of the ethyl 8-(3-octyl-5,6-dioxo-1,4-dioxan-2-yl)octanoate were smaller than the standard commercial lubricant, showing that this compound is a promising bio-lubricant in a real application.

Keywords: synthesis; dioxane; dioxepane; bio-lubricant; oleic acid

■ INTRODUCTION

Researches concerning bioenergy and biomaterial are increasing rapidly over the past several years [1-3]. Among them, bio-lubricant is gaining great interest because of the depleting oil-based lubricant reserves [4-5]. Bio-lubricant is an environmentally friendly product because it is biodegradable and does not contain either sulfur or harmful aromatic compounds [6-7]. Many researchers reported the availability to prepare bio-lubricant from vegetable oil, such as jatropha oil [8], canola oil [9], seed oil [10], and so on. However, the vegetable oil-derived bio-lubricant has several drawbacks, such as high acidic property caused by free fatty acids present and poor oxidation stability due to unsaturated fatty acids contained [11-13]. Therefore, many efforts are based on the chemical modification of vegetable oil to

improve their physicochemical properties as bio-lubricants [14-15].

Madankar et al. modified fatty acids in canola oil through epoxidation, followed by ring-opening reaction with alcohols [9]. Furthermore, they also reported that the lubricant thermal stability increased by employing a longer carbon chain of the alkoxy ether substituent. Even though some chemical modifications of the vegetable oils were reported, ester-based lubricants were mostly developed due to the high yield obtained and the simple reaction process. Abdullah et al. prepared some polyesters of linoleic acid [16], while Salih et al. synthesized some triesters of oleic acid as bio-lubricant base stocks [17]. It was reported that polyester based lubricant performed a high viscosity index, a low pour point, a low volatility, and a high onset temperature.

However, the polyester-based lubricant is easily hydrolyzed at high temperatures; therefore, their total acid numbers (TAN) are quite high. Sammaiah et al. reported that the TAN of the hydroxy of jatropha fatty acid alkyl ester for methyl, *n*-butyl, isopropyl, isobutyl, and 2-ethylhexyl as alkyl groups were 220.13; 224.46; 220.46; 222.52; and 195.37 mg KOH/g, respectively [8], which is unfavorable.

In our previous works, we reported a wide application of oleic acid to prepare bio-lubricants and bio-greases [18-20]. The structure of the synthesized products in our previous work are shown in Fig. 1. The carboxylic acid functional group was modified to be an ester functional group to decrease the acidity property, and the unsaturated double bond was transformed into various heterocyclic rings to increase the oxidation stability [18]. Because of these chemical modifications, the TAN of the synthesized products were 14.53, 1.71, 11.00, and 5.46 mg

KOH/g for ketal, acetal, D[4.4] and D[4.5] compounds, respectively, which are much lower than the Sammaiah et al. reports [8]. The other physicochemical properties are satisfying enough. However, the D[4.4] and D[4.5] compounds are less stable due to the presence of the bicyclic functional group.

In the present work, the other heterocyclic rings, i.e., dioxo-dioxane and dioxo-dioxepane, were evaluated for their bio-lubricant physicochemical properties. The ethyl 8-(3-octyl-5,6-dioxo-1,4-dioxan-2-yl)octanoate (abbreviated as Cyclic-6) and ethyl 8-(3-octyl-5,7-dioxo-1,4-dioxepan-2-yl)octanoate (abbreviated as Cyclic-7) were prepared through esterification between ethyl 9,10-dihydroxyoctadecanoate (EtDHO) and dicarboxylic acids. The physicochemical properties of the products as bio-lubricants were examined, and the effect of the heterocyclic rings was discussed.

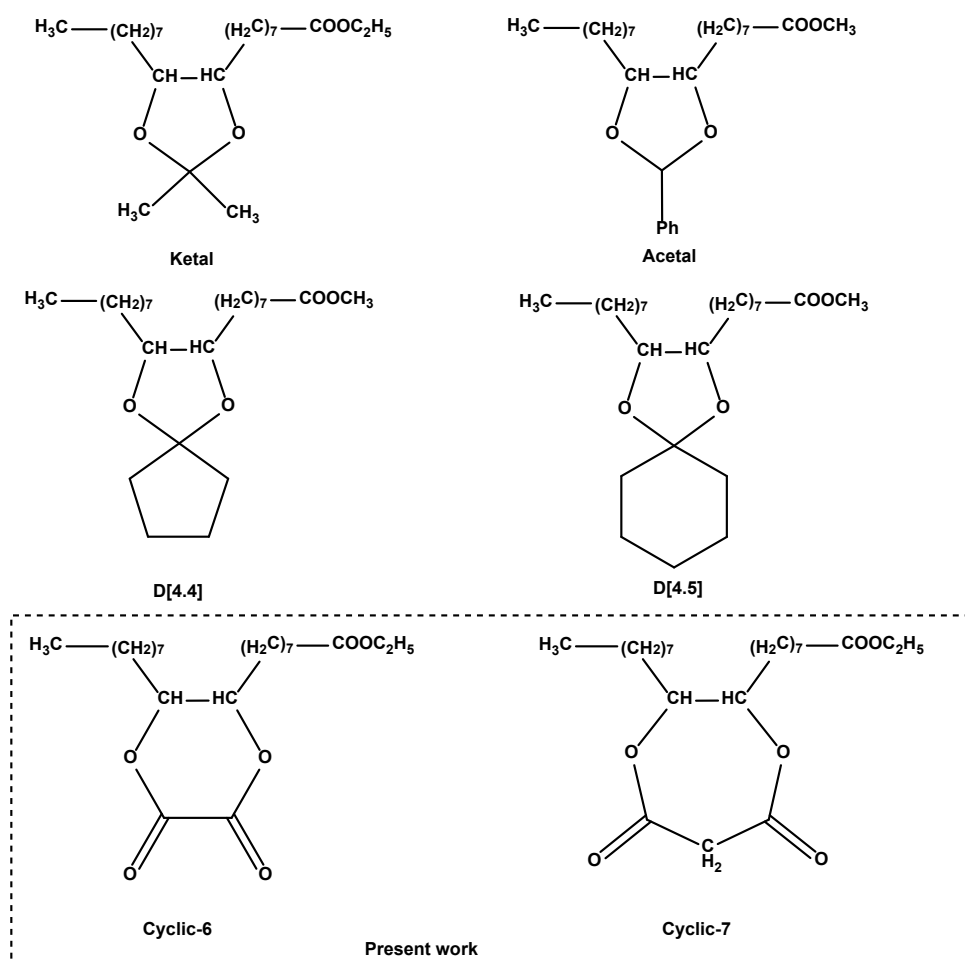


Fig 1. Prepared heterocyclic compounds derived from oleic acid in previous and present works

■ EXPERIMENTAL SECTION

Materials

Oleic acid was obtained from Sigma Aldrich, while other chemicals, such as oxalic acid dihydrate, malonic acid, *p*-toluenesulfonic acid monohydrate (*p*TSA), sodium bicarbonate, anhydrous sodium sulfate, acetonitrile, dichloromethane, and chloroform were in pro analysis grade and purchased from Merck. The 9,10-dihydroxyoctadecanoic acid (DHOA) and ethyl 9,10-dihydrooctadecanoate (EtDHO) were prepared as previously described [18]. Commercial lubricant, Pertamina Mesran Super 20W-50, was purchased and used as a standard for the lubricants' physicochemical properties test.

Instrumentation

The Fourier Transform Infrared (FTIR) spectra of the synthesized compounds were recorded on a Shimadzu Prestige-21 FTIR spectrophotometer, while the mass spectra (MS) of the synthesized products were recorded on a Shimadzu QP 2010S with Agilent GC Type 6890-MS Type 5973. The Proton Nuclear Magnetic resonance (¹H-NMR) spectra were recorded on a JEOL-MY500 NMR Spectrometer. Density, total acid number (TAN), total base number (TBN), and iodine value (IV) were determined by titration method according to American Society for Testing and Material (ASTM) in a similar manner as previously reported [18].

Procedure

Synthesis of ethyl 8-(3-octyl-5,6-dioxo-1,4-dioxan-2-yl)octanoate (Cyclic-6)

The EtDHO (0.68 g, 2.0 mmol) was dissolved into 25 mL of acetonitrile. The *p*TSA (0.10 g, 0.5 mmol) and oxalic acid dihydrate (1.01 g, 8.0 mmol) were added to the solution, and the mixture was refluxed for 5 h. The solvent was evaporated, and the residue was extracted with chloroform. The organic layer was washed twice with NaHCO₃ 10% (w/v) and then three times with distilled water. The organic layer was dried with anhydrous Na₂SO₄, and the solvent was evaporated to obtain the desired product as a light-yellow viscous liquid in a 93.9% yield. FTIR (KBr pellet, cm⁻¹): 2924 (C-H sp³), 1721, and

1697 (C=O ester), 1458 (CH₂), and 1265 (C-O ester). ¹H-NMR (CDCl₃, ppm): 0.83 (t, 3H, -CH₃), 1.17–1.58 (m, 29H, -CH₂- and -CH₂COOCH₂CH₃), 2.23 (t, 2H, -CH₂COOCH₂CH₃), 3.56 (m, 2H, -CH-O), 4.10 (q, 2H, -CH₂COOCH₂CH₃). MS: 397 (M⁺-H), 368 (M⁺-H-C₂H₅), 355 (M⁺-C₃H₇), 281, 263, 155, 69, 55, 43 (base peak).

Synthesis of ethyl 8-(3-octyl-5,6-dioxo-1,4-dioxepan-2-yl)octanoate (Cyclic-7)

The EtDHO (0.68 g, 2.0 mmol) was dissolved into 25 mL of acetonitrile. The *p*TSA (0.10 g, 0.5 mmol) and malonic acid (0.832 g, 8.0 mmol) were added to the solution, and the mixture was refluxed for 5 h. The solvent was evaporated, and the residue was extracted with dichloromethane. The organic layer was washed 3 times with NaHCO₃ 10% (w/v) and then 4 times with distilled water. The organic layer was dried with anhydrous Na₂SO₄, and the solvent was evaporated to obtain the desired product as a light-yellow viscous liquid in 89.6% yield. FTIR (KBr pellet, cm⁻¹): 2940 (C-H sp³), 1713, and 1680 (C=O ester), 1427 (CH₂), and 1250 (C-O ester). ¹H-NMR (CDCl₃, ppm): 0.84 (t, 3H, -CH₃), 1.22–1.58 (m, 29H, -CH₂- and -CH₂COOCH₂CH₃), 2.25 (t, 2H, -CH₂COOCH₂CH₃), 3.55 (m, 2H, -CH-O), 3.98 (d, 2H, CO-CH₂-CO), 4.09 (q, 2H, -CH₂COOCH₂CH₃). MS: 410 (M⁺-2H), 367 (M⁺-2H-C₃H₇), 263, 155, 137, 69, 55 (base peak), 43.

■ RESULTS AND DISCUSSION

Synthesis of Cyclic-6 and Cyclic-7

The synthesis scheme of Cyclic-6 and Cyclic-7 compounds from oleic acid as the starting material is shown in Fig. 2. The first reaction is a hydroxylation by using potassium permanganate as the oxidation agent in an alkaline condition to give 9,10-dihydroxyoctadecanoic acid (DHOA) compound. Afterward, the carboxylic acid of DHOA was esterified with ethanol in the presence of montmorillonite KSF as an acid catalyst to form EtDHO compound. Finally, the desired compounds were obtained by cyclization through the esterification between the diol functional group of the EtDHO compound with a dicarboxylic acid. Cyclization of EtDHO with oxalic acid produced dioxane heterocyclic ring in the Cyclic-6 compound, while cyclization of EtDHO with malonic acid

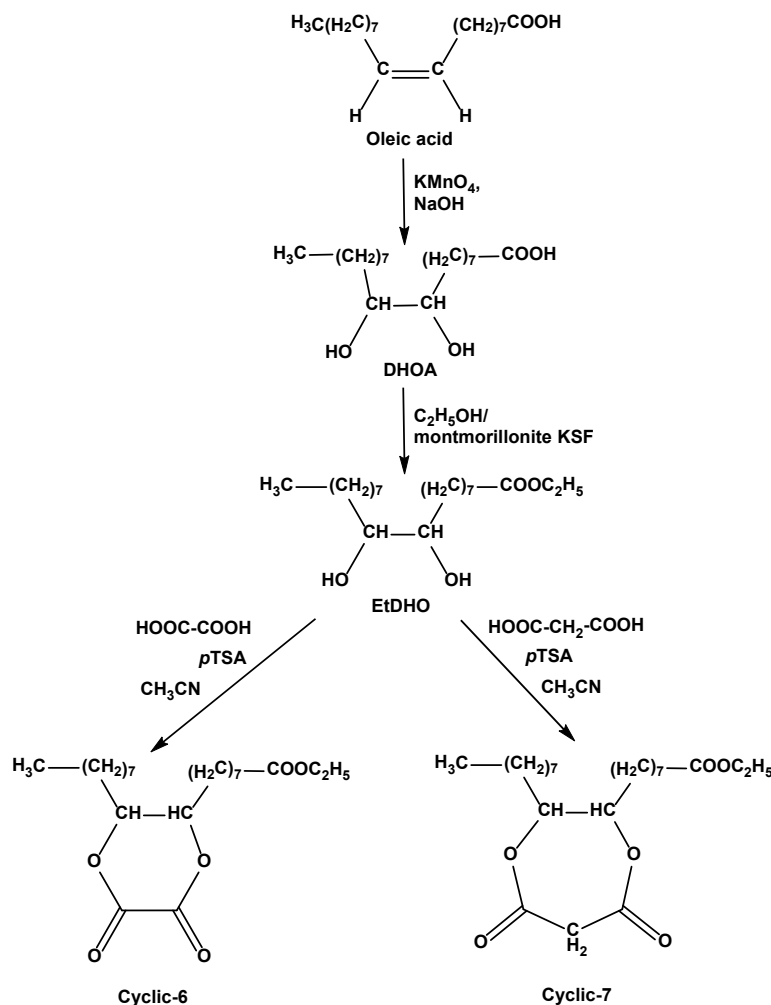


Fig 2. Synthesis scheme of Cyclic-6 and Cyclic-7 compounds from oleic acid

produced a dioxepane heterocyclic ring in the Cyclic-7 compound. The Cyclic-6 and Cyclic-7 were obtained in high yield, i.e., 93.9 and 89.6%, respectively, which is remarkable. Furthermore, both are novel compounds, which have never been reported before to the best of our knowledge.

The chemical structures of both products were confirmed by FTIR and ¹H-NMR analysis. The FTIR spectra of Cyclic-6 and Cyclic-7 compounds are shown in Fig. 3. The absence of a broad peak around 3000–3500 cm⁻¹ showed that the hydroxyl (-OH) groups were completely esterified. The presence of two strong peaks at 1680–1725 cm⁻¹ emphasized that each of the synthesized compounds has two C=O ester groups, which are chemically nonequivalent. The absorption peak of the methylene (-CH₂-) functional groups showed at 1458 and

1427 cm⁻¹ for Cyclic-6 and Cyclic-7, respectively. Meanwhile, the absorption peak of the C-O ester functional groups was found at 1265 and 1250 cm⁻¹ for Cyclic-6 and Cyclic-7, respectively.

The chemical structure of the Cyclic-6 was elucidated by ¹H-NMR spectra (data not shown). A triplet peak at 1.29 ppm and a quartet peak at 4.10 ppm confirmed that ethyl ester was formed. However, the dioxane heterocyclic ring could not be proven by using ¹H-NMR spectra because there is no additional proton after the esterification with oxalic acid. The ¹H-NMR spectrum of the Cyclic-7 product is shown in Fig. 4. The ethoxy functional group in Cyclic-7 was confirmed by the presence of triplet peak at 1.29 ppm (3H, overlapped with other peaks) and quartet peak at 4.09 ppm (2H). Furthermore, the methylene group from the malonic acid

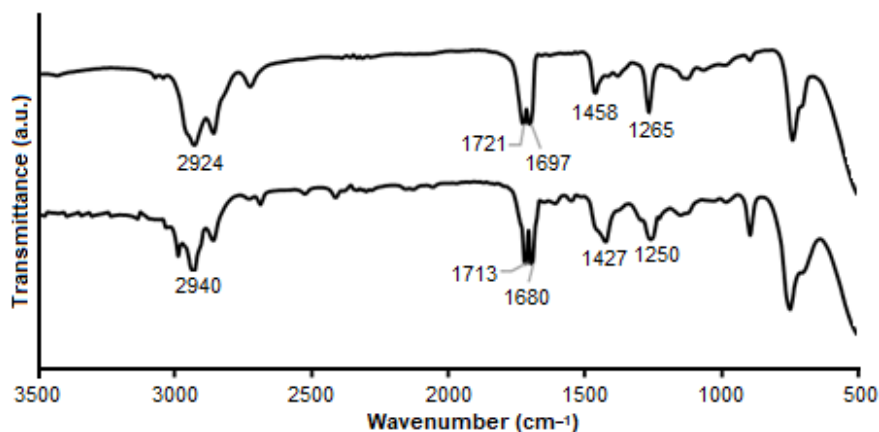


Fig 3. FTIR spectra of (a) Cyclic-6 and (b) Cyclic-7 compounds

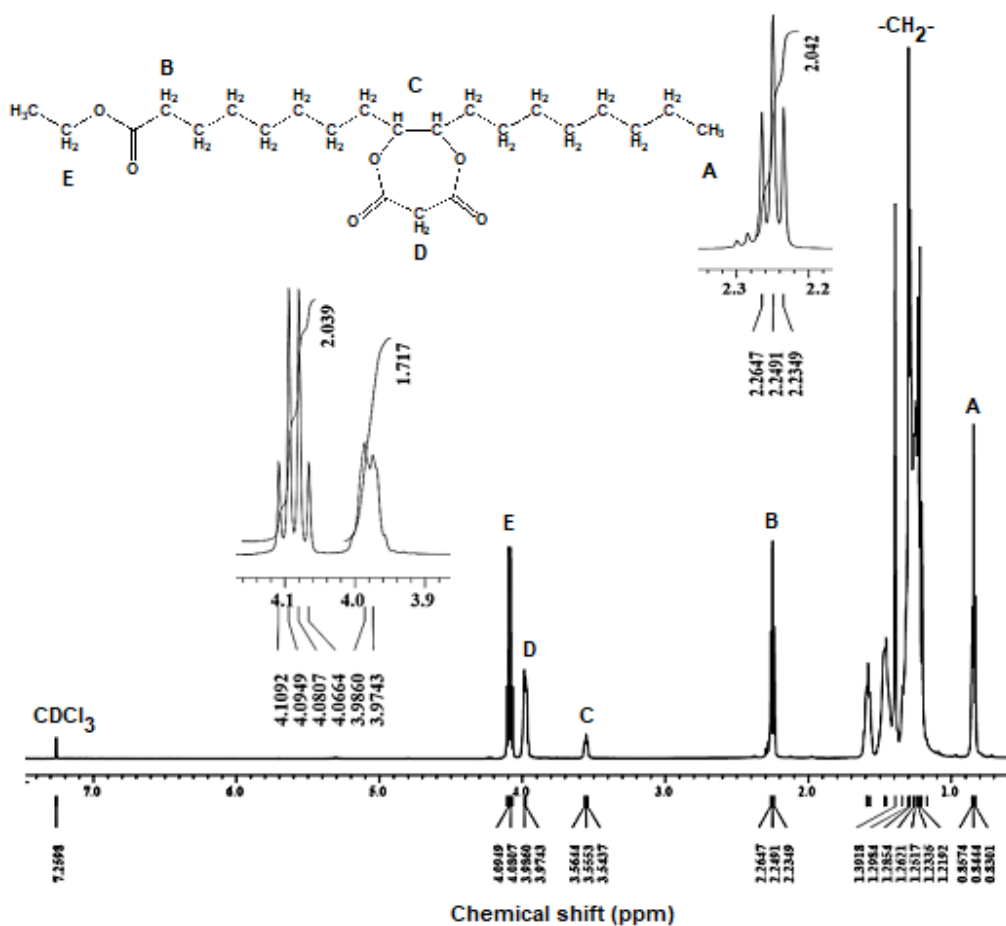


Fig 4. $^1\text{H-NMR}$ spectra of Cyclic-7 compound

appeared as a doublet at 3.98 ppm (2H) due to the geminal coupling. The other protons also appeared and were assigned, as shown in Fig. 3. Both FTIR and $^1\text{H-NMR}$ spectra confirmed that Cyclic-6 and Cyclic-7 compounds had been successfully prepared.

The Physicochemical Properties of Cyclic-6 and Cyclic-7 as Bio-lubricants

The physicochemical properties of Cyclic-6 and Cyclic-7 are shown in Table 1. The density of Cyclic-6 and Cyclic-7 are both higher than ketal, acetal, D[4.4],

Table 1. Bio-lubricant physicochemical properties of the products

No	Compounds	Physicochemical properties				Ref.
		Density (g/mL)	TAN (mg KOH/g)	TBN (mg KOH/g)	IV (mg I ₂ /g)	
1	Ketal	0.824	14.53	48.95	0.76	[19]
2	Acetal	-	1.71	14.12	0.25	[20]
3	D[4.4]	0.916	11.00	24.24	21.28	[18]
4	D[4.5]	0.913	5.46	14.04	17.73	[18]
5	Cyclic-6	1.045	1.37	3.53	0.72	This work
6	Cyclic-7	0.939	2.89	6.61	0.69	This work
7	Oleic acid	0.985	196.80	0.54	89.90	This work
8	Commercial lubricant	0.893	85.37	5.36	31.73	This work

and D[4.5] compounds. The higher density of Cyclic-6 and Cyclic-7 are probably caused by stronger intermolecular hydrophobic interaction. The density of Cyclic-6 was the highest due to the highest stability of the dioxane ring amongst all rings. It is well known that a six-membered ring is more stable and well-arranged than the seven-membered ring; therefore, it is in agreement with the measured density property [18].

The TAN value represents a possible corrosion level to the engine caused by using the lubricant. Compared to the hydroxy fatty acid alkyl ester of jatropha [8], the TAN values of the synthesized products decrease significantly by the formation of dioxane and dioxepane heterocyclic rings. It means that a cyclic ester functional group is preferable than polyester substituents. From Table 1, it is shown that the TAN values of Cyclic-6 and Cyclic-7 are lower than others, demonstrating that both compounds are preferable due to low corrosion level to the engine. The low TAN of Cyclic-6 and Cyclic-7 were caused by their stability against the acid hydrolysis process. The TAN value of Cyclic-6 is the lowest because of a stable six-member heterocyclic ring. Similar to the TAN results, the TBN value of the Cyclic-6 is the lowest, demonstrating that the Cyclic-6 compound is very stable to acid hydrolysis as well as the alkaline hydrolysis process.

The IV value represents the stability of the compound towards oxidation. Unsaturated fatty acid, such as oleic acid, has a high IV value due to the presence of the C=C double bond. Through chemical modifications of oleic acid, the IV significantly decreased, as shown in Table 1. The IV values of Cyclic-6 and Cyclic-7 compounds are less

than 1.00 mg I₂/g, showing that they are stable against the oxidation process. Compared to the commercial lubricant, Cyclic-6 and Cyclic 7 are better because their TAN and IV values are lower. Therefore, Cyclic-6 and Cyclic-7 are promising bio-lubricant candidates because of the shown excellent lubricant properties.

■ CONCLUSION

The Cyclic-6 and Cyclic-7 compounds were successfully synthesized from the esterification between EtDHO and oxalic acid and malonic acid, respectively. From the results, Cyclic-6 bio-lubricant gave lower TAN, demonstrating that Cyclic-6 is more stable than Cyclic-7 for acid hydrolysis. The density and TBN of the Cyclic-6 bio-lubricant are similar to the commercial lubricant. These findings are useful for the chemical design of fatty acids to improve the physicochemical properties of the bio-lubricant derived from vegetable oils.

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