Synthesis of 1,4-Dioxaspiro[4.4] and 1,4-Dioxaspiro[4.5] Novel Compounds from Oleic Acid as Potential Biolubricant

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Received May 9, 2017; Accepted July 27, 2017

ABSTRACT

Two 1,4-dioxaspiro novel compounds which derivated from methyl 9,10-dihydroxyoctadecanoate (MDHO) with cyclopentanone and cyclohexanone had been synthesized by a sonochemical method in the presence of montmorillonite KSF catalyst. The MDHO compound had been prepared from 9,10-dihydroxyoctadecanoic acid (DHOA) and methanol. Meanwhile, DHOA was synthesized by hydroxylation of oleic acid with the solution of 1% $KMnO_4$ under basic condition. The structures of the products were confirmed by FTIR, GC-MS, ^{1}H-NMR, and ^{13}C-NMR spectrometers. Hydroxylation reaction of oleic acid gave DHOA as a white solid powder in 46.52% yield (m.p. 131-132 °C). On the other side, esterification reaction via sonochemical method between DHOA and methanol gave MDHO as a white powder in 93.80% yield (m.p. 80-81 °C). The use of cyclopentanone in 45 min sonochemical method gave methyl 8-(3-octyl-1,4-dioxaspiro[4.4]nonan-2-yl)octanoate as a yellow viscous liquid in 50.51% yield. The other compound, methyl 8-(3-octyl-1,4-dioxaspiro[4.5]decan-2-yl)octanoate as yellow viscous liquid had been synthesized by similar method with cyclohexanone via the sonochemical method in 45.12% yield. From physicochemical properties, i.e. density, total acid number, total base number, and iodine value, gave the conclusion that these novel compounds are potential biolubricant candidates to be developed.

***Keywords**: 1,4-dioxaspiro; biolubricant; oleic acid; sonochemical method*

ABSTRAK

Dua senyawa baru 1,4-dioksaspiro yang berasal dari metil 9,10-dihidroksioktadekanoat (MDHO) dengan siklopentanon dan sikloheksanon telah disintesis melalui metode sonokimia menggunakan katalis monmorilonit KSF. Senyawa MDHO disintesis dari asam 9,10-dihidroksioktadekanoat (DHOA) dan metanol. Sementara itu, DHOA diperoleh dari hidroksilasi asam oleat dengan larutan $KMnO_4$ 1% dalam suasana basa. Struktur produk telah dikonfirmasi melalui spektrometer FTIR, GC-MS, ^{1}H-NMR, dan ^{13}C-NMR. Reaksi hidroksilasi asam oleat menghasilkan padatan putih DHOA dengan rendemen 46,52% (titik lebur 131-132 °C). Sementara itu, reaksi esterifikasi antara DHOA dan metanol menghasilkan padatan putih MDHO dengan rendemen 93,80% (titik lebur 80-81 °C). Penggunaan siklopentanon pada metode sonokimia selama 45 menit menghasilkan cairan kental berwarna kuning metil 8-(3-oktil-1,4-dioksaspiro[4.4]nonan-il)oktanoat dengan rendemen 50,51%. Senyawa lain, metil 8-(3-oktil-1,4-dioksaspiro[4.5]dekan-il)oktanoat sebagai cairan kental berwarna kuning juga telah berhasil disintesis dengan metode serupa menggunakan sikloheksanon melalui metode sonokimia dengan rendemen 45,12%. Berdasarkan sifat-sifat fisikokimia yaitu densitas, angka asam total, angka basa total, dan angka iodin dari kedua senyawa baru tersebut merupakan kandidat biopelumas yang potensial untuk dikembangkan lebih lanjut.

***Kata Kunci**: 1,4-dioksaspiro; asam oleat; biopelumas; metode sonokimia*

INTRODUCTION

Renewable raw materials can significantly contribute to a sustainable development in the age of depleting petroleum reserves and increasing emission of greenhouse gasses [1]. It is obvious that the utilizations of renewable raw material in any sectors are one necessary step to improve sustainable development [2]. Some of the most widely applied renewable raw materials in the chemical industry for non-fuel applications are plant oils. Nowadays plant oils are the most important renewable raw material for the chemical industry and are heavily used as raw materials for surfactants, cosmetic products, and lubricants [3]. Plant oils are triacylglycerides with varying composition of fatty acids depending on the plant, the crop, the season, and the growing conditions [4]. The word 'oil' hereby refers to triglycerides that are liquid at room

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DOI: 10.22146/ijc.24891

Table 1. Oleic acid composition on plants oil [7-10]

Plants oil	Oleic acid percentage (%)
Palm	39.2
Sunflower	28.0
Olive	66.4
Sesame	41.5
Almond	67.2
Corn	30.1
Peanut	71.1

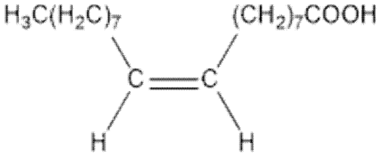

Fig 1. Structure of oleic acid

temperature.

Biolubricants derived from pure plant oils have a low stability to heat, oxidation, and hydrolysis as well as a poor performance at low temperatures [5]. Moreover, plant oils have a high total acid number and iodine value that may cause the machine to be susceptible to corrosion and reduces the engine work performance [6]. Table 1 summarizes the oleic acid (Fig. 1) percentage of some industrially important plant oils [7-10].

Due to their availability in nature are highly abundant, many researchers are interested in modifying the structure of oleic acid to improve the quality of oleic acid based biolubricants. Madankar et al. [11] had modified the structure of oleic acid by epoxidation and epoxide ring opening reaction using some variation of alcohols. The ether derivates show high-temperature stability but low viscosity index as biolubricant. Sammaiah et al. [12] have synthesized triester derivatives of oleic acid by hydroxylation and acylation reaction with acid anhydride compounds. It has high viscosity index but high total acid value due to the acidic functional group can be released from hydrolysis in such condition.

In our previous study, the synthesis of some dioxolane compounds from acetalization reaction with aromatic aldehydes was done to obtain a viscous gel for biogrease application [13]. In our present work, a new chemical modification from oleic acid to 1,4-dioxaspiro[4.4] and [4.5] novel compounds through several steps, i.e. hydroxylation, esterification, and ketalization was done. First, oleic acid was hydroxylated by potassium permanganate under basic condition to obtain 9,10-dihydroxyoctadecanoic acid (DHOA). The esterification reaction was also carried out by reacting DHOA with methanol to produce methyl 9,10-dihydroxyoctadecanoate (MDHO). Ketalization reactions with desired cyclic ketone, i.e. cyclopentanone and cyclohexanone to form the dioxaspiro ring. The effect of 1,4-dioxaspiro heterocyclic groups to physicochemical properties as biolubricant was also investigated.

EXPERIMENTAL SECTION

Materials

Oleic acid and montmorillonite KSF were purchased from Sigma-Aldrich while cyclopentanone and cyclohexanone were obtained from Merck in pro analysis specification. The other chemicals were also purchased from Merck. Hydrochloric acid was purchased from Mallinckrodt, and Pertamina Mesran Super 20W-50 as a commercial lubricant was obtained from PT Pertamina.

Instrumentation

The melting point was obtained by an Electrothermal 9100 Model Digital Melting Point apparatus. FTIR spectra were recorded on a Shimadzu Prestige-21 FTIR spectrophotometer with KBr pellets method. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained in the designated solvent ($CDCl_3$) on a JEOL-MY500 proton and carbon Nuclear Magnetic Resonance Spectrometer. GC chromatogram and MS spectra were recorded on a Shimadzu QP-2010S, Gas Chromatography-Mass Spectrometer. Density measurement was carried out by using pycnometer (Pyrex, 10 mL), meanwhile, total acid number (TAN), total base number (TBN), and iodine value (IV) were determined by titration according to American Society for Testing and Material (ASTM) methods.

Procedure

Synthesis of DHOA

As much as 3.14 g (10 mmol) of oleic acid was added to a solution of 3.14 g NaOH in 320 mL of distilled water then heated to obtain a clear solution. The system temperature was set at 0-10 °C then 250 mL of $KMnO_4$ 1% (w/v) was slowly added to the solution. Excess of $KMnO_4$ was reduced with the addition of 7 g of Na_2SO_3 then the solution was acidified by addition of concentrated HCl solution to a pH of 1. The precipitate formed was recrystallized from ethanol and washed with petroleum ether until the filtrate was clear.

Synthesis of MDHO

A total of 0.316 g (1 mmol) DHOA, 30 mL of methanol, and 0.66 g of montmorillonite KSF put in a 100 mL Erlenmeyer and sonicated at a frequency of 42 kHz for 10 min. As much as 5 mL of distilled water added to the solution and then MDHO products formed as a precipitate.

Synthesis of methyl 8-(3-octyl-1,4-dioxaspiro[4.4] nonan-2-yl)octanoate and methyl 8-(3-octyl-1,4-dioxaspiro[4.5]decan-2-yl)octanoate

As much as 0.66 g (2 mmol) MDHO was added into a 100 mL Erlenmeyer flask containing 25 mL of dichloromethane and 0.10 g of montmorillonite KSF. The solution was added with 0.17 g (2 mmol) of cyclopentanone to synthesize methyl 8-(3-octyl-1,4-dioxaspiro[4.4]nonan-2-yl)octanoate (D[4.4]) and 0.20 g (2 mmol) cyclohexanone to synthesize methyl 8-(3-octyl-1,4-dioxaspiro[4.5] decan-2-yl)octanoate (D[4.5]). The mixture was reacted in the sonicator for 45 min with water as a media. The product solution in dichloromethane was extracted with 5 mL of brine, followed by extraction with 5 mL of $NaHCO_3$ 3% (w/v). The organic layer was separated, dried with anhydrous Na_2SO_4, and the solvent was evaporated to obtain a 1,4-dioxaspiro product as a viscous liquid.

Biolubricant physicochemical properties

The density of these novel compounds was determined by ASTM D1481 method. Other physicochemical properties, such as TAN, TBN, and IV were determined by ASTM D964, ASTM D974, and ASTM D2078 methods, respectively [14-17].

RESULT AND DISCUSSION

Synthesis of DHOA

Synthesis of DHOA was carried out by hydroxylation of oleic acid with $KMnO_4$ under basic solution at 0-10 °C. The excess of $KMnO_4$ was reduced by Na_2SO_3 and followed by adding concentrated HCl. The product was washed with petroleum ether and recrystallized with ethanol to yield 1.473 g of DHOA as a white solid powder having m.p. 131-132 °C in 46.52% yield. The purity of the product was confirmed by the disappearance of the oleic acid as starting material in thin layer chromatography (TLC) plate with ethyl acetate as eluent. The retardation factor (R_f) of the product was 0.66 meanwhile the R_f of the oleic acid was 0.87.

Structural analysis based on FTIR spectra (Fig. 3) shows disappearing absorption band at 3006 cm^{-1} from C-H sp^2 and appearing band at 3279 cm^{-1} from the alcohol hydroxyl group (OH) indicating that the hydroxylation was a success. The existence of hydroxyl carboxylic acid is showed at 3202 cm^{-1} (OH stretching), C-H sp^3 at 2916 and 2855 cm^{-1}, C=O carboxylic acid at 1697 cm^{-1}, methylene group at 1435 cm^{-1} and a methyl group at 1375 cm^{-1}. MS spectra (Fig. 4) doesn't show the M^+ value of DHOA at m/z = 316 but the molecule undergoes α cleavage at C_9 to give fragment with m/z = 173. Further fragmentation gives m/z = 155 (base peak), 139, 69, 55 and 41. Based on FTIR and MS analysis and melting point measurement, it can be concluded that the DHOA was successfully produced.

Synthesis of MDHO

Esterification of DHOA was performed using methanol and montmorillonite KSF as heterogenous catalyst to give MDHO. The esterification reaction is shown schematically in Fig. 2. The result of MDHO is presented in Table 2. FTIR spectra (Fig. 3) of the resulted product shows that the absorption band at

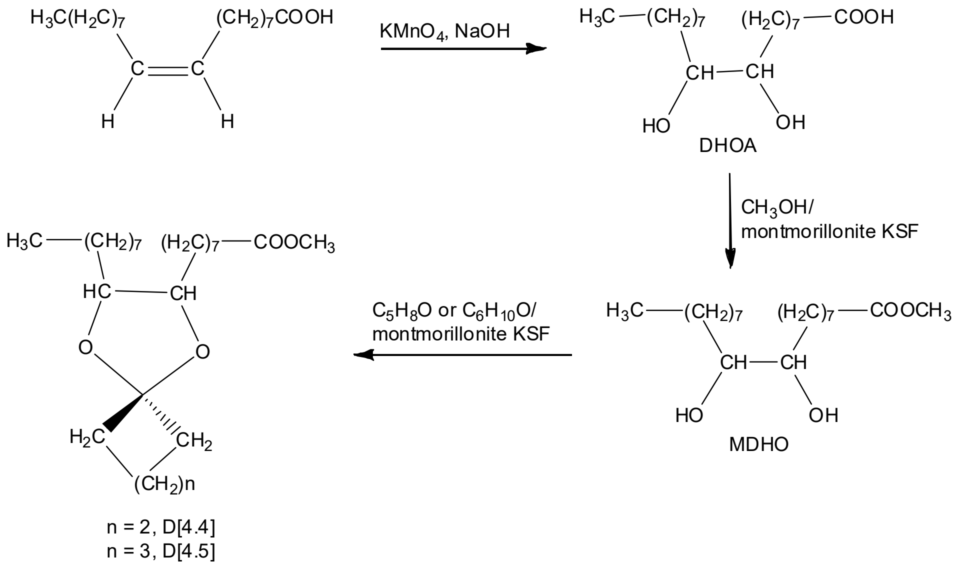

Fig 2. Scheme of synthesis of D[4.4] and D[4.5] compounds from oleic acid

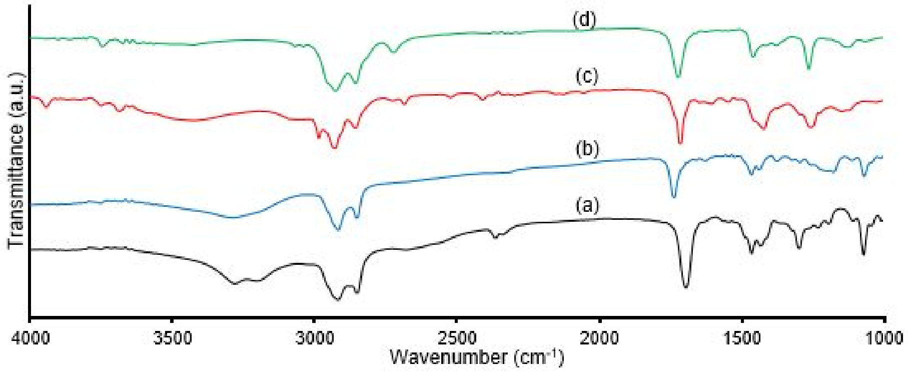

Fig 3. FTIR spectra of (a) DHOA, (b) MDHO, (c) D[4.4] and (d) D[4.5]

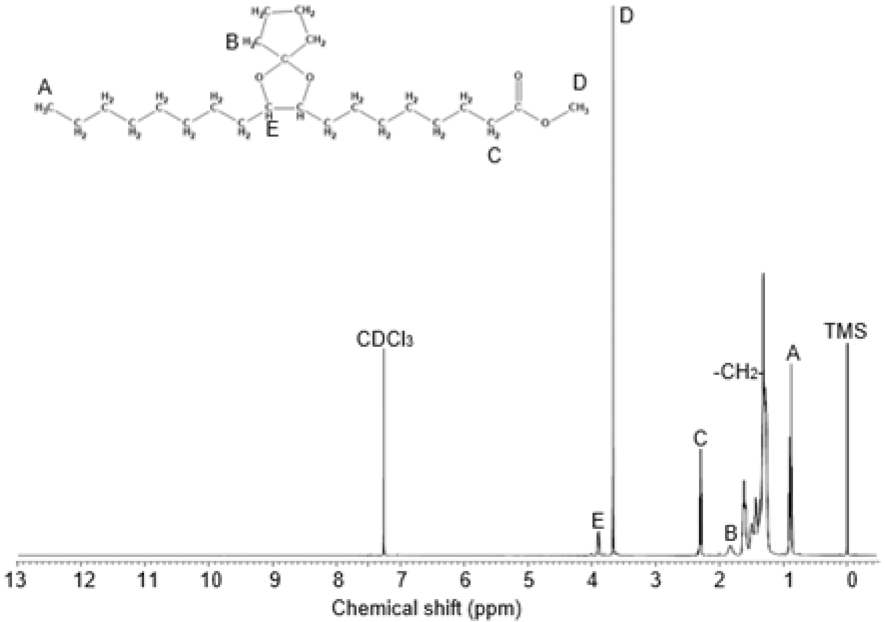

Fig 4. ^{1}H-NMR spectra of D[4.4]

Table 2. Results of the synthesized products

Compounds	Results			
	m.p. (°C)	Color	Shape	Yield (%)
DHOA	131-132	white	solid	46.52
MDHO	80-81	white	solid	93.80
D[4.4]	-	yellow	liquid	50.51
D[4.5]	-	yellow	liquid	45.12

3202 cm^{-1} has been disappeared indicating that the esterification reaction has taken place. Another strong evidence for the success of the reaction is the appearance of the strong absorption band at 1735 cm^{-1} from a carbonyl group (-C=O) and 1180 cm^{-1} which are characteristic for C-O-C ester. The next analysis was done using GC-MS spectrometer. The GC chromatogram shows 1 peak at retention time (R_t) = 34.97 min. The MS spectra doesn't show the M$^+$ value of MDHO at m/z = 330 but the molecule undergoes dehydration at C_9 to give fragment with m/z = 312. Further fragmentation gives m/z = 312, 281, 187, 155, 139, 74 (Mc Lafferty rearrangement), 69, 55, 43 (base peak) and 41.

Synthesis of D[4.4] and D[4.5]

The 1,4-dioxaspiro[4.4] ring formation from MDHO and cyclopentanone was carried out at room temperature for 45 min in the presence of montmorillonite KSF. The obtained product was extracted with brine and $NaHCO_3$ 3% solution to give D[4.4] as a yellow viscous liquid. The result of 1,4-dioxaspiro[4.4] is presented in Table 2. The FTIR spectra (Fig. 3) shows that the absorption band at 3279 cm^{-1} of alcohol hydroxyl group disappeared indicating that the ketalization reaction has taken place. This fact was strengthened by the appearance of the absorption band at 1072 cm^{-1} which is characteristic for

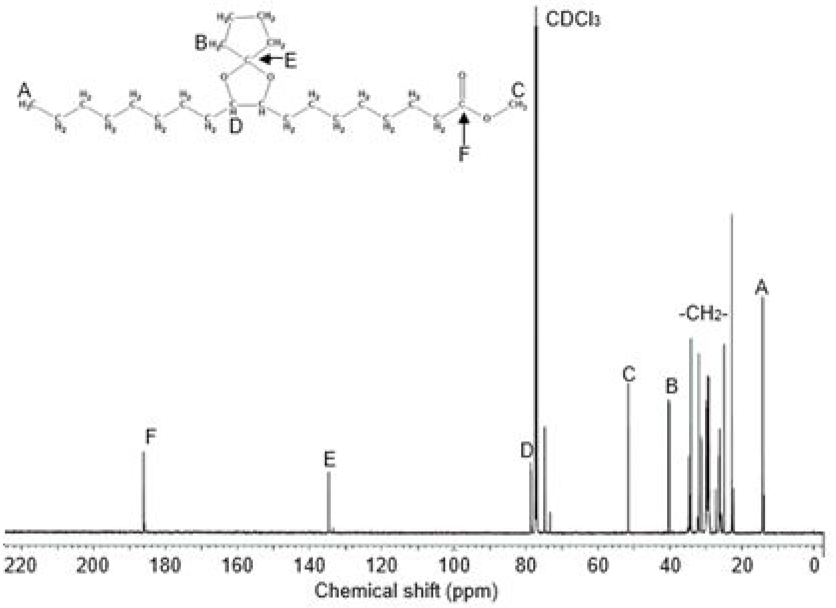

Fig 5. ^{13}C-NMR spectra of D[4.4]

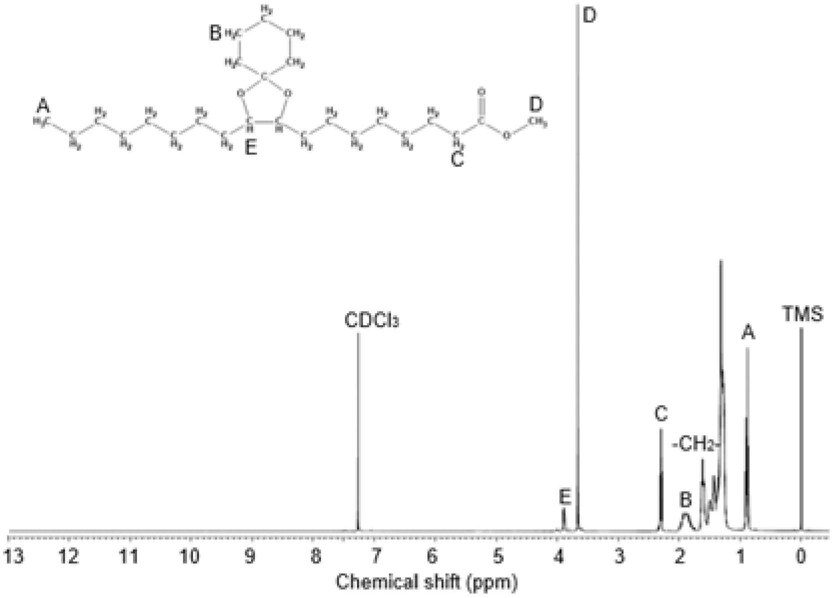

Fig 6. ^{1}H-NMR spectra of D[4.5]

C-O-C ester. The GC chromatogram shows 1 peak at Rt = 50.08 min. The MS spectra doesn't show the M^+ value of D[4.4] at m/z = 396 but the molecule undergoes methyl cleavage at ester group to give m/z = 381. Further fragmentation gives m/z = 325, 297, 265, 74 (Mc Lafferty rearrangement), 55, 43 (base peak) and 28.

The structure of D[4.4] compound was also proved by the ^{1}H-NMR and ^{13}C-NMR spectra. From ^{1}H-NMR spectra (Fig. 4) shows a signal at δ = 1.72-1.89 ppm refer to $-CH_2-$ protons and signal at δ = 3.80-3.91 ppm refer to -CH- protons which are both at 1,4-dioxaspiro[4.4] ring. Methyl ester group was identified by singlet at δ = 3.66 ppm refers to $-OCH_3$ protons and triplet signal at δ = 2.28-2.31 ppm refer to $-CH_2-CO-$ protons. The other signals refer to specific aliphatic protons as example δ = 0.88-0.90 ppm (t, 6, $-CH_3$) and δ = 1.27-1.62 ppm (m, 30, $-CH_2-$). Meanwhile, the ^{13}C-NMR spectra of D[4.4] showed in Fig. 5. It's showed 22 signals depicting 22 different types of carbons. Signals at δ = 34.04-34.12 ppm, δ = 78.58-78.66 ppm and δ = 134.61 ppm refer to carbons at 1,4-dioxaspiro[4.4] ring. The methyl ester group confirmed by signals at δ = 51.56 ppm from $-OCH_3$ and δ = 186.49 ppm from –C=O. Regarding FTIR, GC-MS, ^{1}H-NMR and ^{13}C-NMR analysis, it can be concluded that the synthesis of D[4.4] compound has been done.

On other hand, 1,4-dioxaspiro[4.5] ring formation from MDHO and cyclohexanone was carried out at room temperature for 45 min in the presence of montmorillonite KSF. The obtained product was then extracted with brine and $NaHCO_3$ 3% solution to give D[4.5] as a yellow viscous liquid. The result of D[4.5] is presented in Table 2. FTIR spectra show that the absorption band at 3279 cm^{-1} of the hydroxyl group from alcohol disappeared indicating that the ketalization reaction has taken place. Another strong evidence for the success reaction is the appearance of the absorption band at 1072 cm^{-1} which is characteristic for C-O-C ester. The GC chromatogram shows 1 peak at Rt = 47.09 min. The MS spectra shows the M^+ value of D[4.5] at m/z = 410 and further fragmentations gives m/z = 381, 367, 311, 279, 155, 74 (Mc Lafferty rearrangement), 55, 43 (base peak) and 28.

The next analysis was done using ^{1}H-NMR and ^{13}C-NMR spectrometers. The ^{1}H-NMR spectrum of the product was showed in Fig. 6. As expected, the existence of 1,4-dioxaspiro[4.5] ring protons signal which resonates at δ = 1.71-2.01 ppm ($-CH_2-$) and 3.79-3.89 ppm (-CH-) appeared, indicating the product has been acquired. Methyl ester group was identified by singlet at δ = 3.67 ppm refers to $-OCH_3$ protons and triplet signal at δ = 2.27-2.30 ppm refer to $-CH_2$-CO- protons. The other signals refer to specific aliphatic protons as example δ = 0.88-0.90 ppm (t, 6, $-CH_3$) and δ = 1.26-1.64 ppm (m, 32, $-CH_2-$). Meanwhile, the ^{13}C-NMR spectra of D[4.5] (Fig. 7) show 23 signals depicting 23 different types of carbons. Signals at δ = 33.87-34.15 ppm, δ = 78.43-78.36 ppm and δ = 134.51 ppm refer to carbons at 1,4-dioxaspiro[4.5] ring while the methyl ester group confirmed by signals at δ = 51.57 ppm from $-OCH_3$ and δ = 186.48 ppm from -C=O. Based on FTIR, GC-MS, ^{1}H-NMR and ^{13}C-NMR analysis, it can be concluded that the synthesis of D[4.5] was successfully produced.

Biolubricant Physicochemical Properties

According to ASTM as the standard method, some physicochemical properties of the D[4.4] and D[4.5] biolubricants, oleic acid as starting material, and commercial lubricant as a comparison such as density, TAN, TBN, and IV was determined. The result is presented in Table 3.

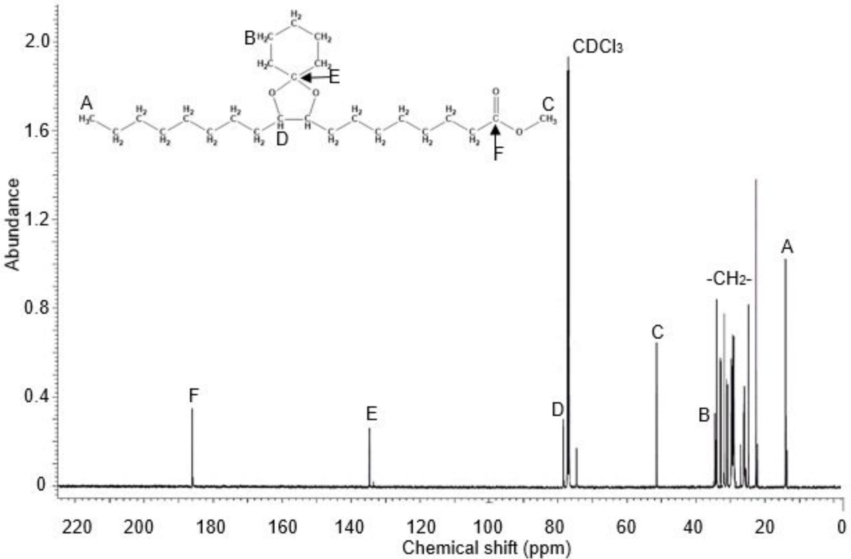

Fig 7. ^{13}C-NMR spectra of D[4.5]

Table 3. Results of the physicochemical properties of synthesized products

Compounds	Physicochemical properties			
	density (g/mL)	TAN (mg KOH/g)	TBN (mg KOH/g)	IV (mg I_2/g)
D[4.4]	0.916	11.000	24.244	21.28
D[4.5]	0.913	5.463	14.039	17.73
Oleic acid	0.985	196.800	0.540	89.90
Commercial lubricant	0.893	85.370	5.360	31.73

From the result, the density value of oleic acid is the highest, since its structure contains carboxylic acid groups that can form hydrogen bonds. Meanwhile, the low-density value of the commercial lubricant is caused by it is mostly composed of C_{20}-C_{30} hydrocarbons thus the intermolecular force that occurs is the van der Waals forces that are relatively weak. In the other hand, in D[4.4] and D[4.5] compound, there is a heterocyclic 1,4-dioxaspiro ring that relatively more polar than hydrocarbons. A good lubricant is a lubricant that has a density value between 0.7 to 0.95 g/mL [18] because, beyond that range, the lubricant has a potential to erode the metal surfaces in the engine when they rub against each other.

The TAN is a chemical parameter that expresses the degree of engine corrosion due to the use of lubricants. In Table 3, oleic acid has the highest TAN while D[4.5] compound have the lowest TAN. The high value of TAN on oleic acid is caused by a carboxylic acid group which can be ionized into carboxylate anion and hydronium cation, while on D[4.4] and D[4.5] compounds, the carboxylic group has been converted into ester groups thus the TAN value is sharply declined. The TAN value of D[4.5] compound is lower than D[4.4] due to the higher stability of six-membered ring than five membered ring for basic hydrolysis. The TAN value of the commercial lubricant is higher than the D[4.4] and D[4.5] compound because commercial lubricants are crude oil-based lubricants that may still contain nitrogen oxides and sulfur contaminants which are acidic.

The TBN is a chemical parameter that indicates the ability of the lubricant to neutralize the acids derived from fuel combustion processes and prevents dirt from sticking on the engine components. The higher the TBN of a lubricant, the better the detergency property of the lubricant. In Table 3, oleic acid shows the lowest TBN while D[4.4] compound shows the highest TBN. The TBN value of D[4.4] compound is the highest due to the low stability of five-membered heterocyclic ring to acid hydrolysis. Nevertheless, it is profitable because the detergency property of D[4.4] compound becomes larger.

The IV is a chemical parameter that states oxidative stability of a lubricant. Lubricants with high IV have many double bond unsaturated groups that are readily oxidized by air into alcohol groups which are able to form hydrogen bonds with water. Yet the water content in the lubricant is made as small as possible so that the machine is not susceptible to corrosion. In Table 3, oleic acid shows the highest number of iodine for their double bond in the C_9-C_{10} while the D[4.5] compound shows a low IV because of the double bond was converted into a heterocyclic 1,4-dioxaspiro ring.

CONCLUSION

This result describes a systematic approach to chemically modify oleic acid to yield 1,4-dioxaspiro novel compounds. Based on FTIR, GC-MS, ^{1}H-NMR, and ^{13}C-NMR analyses as described above, it was concluded that both D[4.4] and D[4.5] compounds were successfully synthesized and obtained as yellow viscous liquids. These compounds have higher density and TBN while lower TAN and IV than oleic acid and the commercial lubricant because of the carboxylic acid and alkene functional group modification. These parameters show that the quality of D[4.4] and D[4.5] based lubricants are not inferior to commercial lubricants. From these results, both 1,4-dioxaspiro compounds are potential biolubricant candidates to be developed.

ACKNOWLEDGEMENT

This research was funded by Student Creativity Program-Research from Directorate General of Higher Education, Ministry of Research, Technology and Higher Education of the Republic of Indonesia.

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