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SINTESIS SENYAWA DIOKSOLAN DARI ASAM LEMAK SAWIT DISTILAT

Renni Yuliasari, Tjahjono Herawan, dan Eka Nuryanto

ABSTRAK

Asam lemak sawit distilat merupakan hasil samping proses fraksinasi minyak sawit yang jumlahnya sekitar 2,5 - 3,5 % dari jumlah minyak sawit mentah yang diolah. Asam lemak sawit distilat mengandung sekitar 50 % asam lemak sawit tidak jenuh. Asam lemak sawit tidak jenuh ini digunakan sebagai bahan baku pembuatan dioksolan. Dioksolan dapat disintesis dengan cara epoksidasi asam lemak sawit tidak jenuh, epoksi yang terbentuk selanjutnya direaksikan dengan aseton. Hasil penelitian menunjukkan bahwa reaksi dioksolanisasi epoksi metil stearat dengan aseton optimum pada perbandingan mol sebesar 1 : 1 dengan menggunakan BF3 sebagai katalis sebesar 10% (b/b). Dioksolan yang dihasilkan tersebut mempunyai oksiran oksigen sebesar 0,007%. Hasil analisis kromatografi lapis tipis menunjukkan bahwa dioksolan mempunyai nilai Rf sebesar 0,71 dan hasil analisis infra red spectroscopy menunjukkan bahwa dioksolan muncul pada puncak (peak) 1100 cm-.1. Reaksi dioksolanisasi tersebut menghasilkan dioksolan sebesar 22,69%.

Kata kunci : Minyak sawit, asam lemak sawit distilat, dioksolan, biopestisida

PENDAHULUAN

Dioksolan merupakan salah satu jenis senyawa turunan keton yang dapat dimanfaatkan sebagai bahan baku pada industri farmasi dan surfaktan. Menurut Ahmad *et al.* (1) dioksolan juga dapat dimanfaatkan sebagai bahan baku biopestisida, yaitu sebagai insektisida, fungisida, dan germisida. Dioksolan dapat disintesis, baik dari senyawa okso dengan 1,2-propanediol (1) maupun dari senyawa epoksi dengan senyawa yang mengandung gugus keton (8). Salah satu senyawa turunan dioksolan yang digunakan sebagai insektisida yaitu 2-(1,3-dioksolan-2-il) fenil metilkarbamat (7). Pada umumnya senyawa tersebut disintesis dari bahan aktif yang berbahaya bagi lingkungan sehingga residu yang dihasilkan dapat menimbulkan dampak lingkungan dan kesehatan manusia. Dioksolan merupakan salah satu bioproduk yang disintesis dari asam lemak sawit distilat (ALSD) yang bersifat ramah lingkungan.

Fraksinasi minyak sawit dapat menghasilkan ALSD sekitar 2,5-3,5% dari jumlah minyak sawit mentah (MSM) yang diolah (6, 7). Sampai saat ini pemanfaatan ALSD masih sangat terbatas, yaitu digunakan sebagai bahan baku pembuatan sabun berkualitas rendah. Sementara itu ALSD mengandung sejumlah asam lemak jenuh (ALJ) dan asam lemak tidak jenuh (ALTJ) yang sangat berpotensi sebagai bahan baku sintesis produk-produk oleokimia. ALJ dan ALTJ dapat dipisahkan dengan menggunakan metode kristalisasi pelarut (2). Asam lemak sawit jenuh dapat dimanfaatkan sebagai bahan baku pembuatan sabun, sedangkan ALTJ dapat dimanfaatkan sebagai bahan baku sintesis epoksi. Epoksi yang dihasilkan tersebut dapat digunakan sebagai bahan baku untuk sintesis dioksolan (8).

BAHAN DAN METODE

Bahan baku yang digunakan pada penelitian ini adalah ALSD yang diperoleh dari PT Pamina, Adolina. Bahan kimia yang digunakan adalah aseton, dietil eter, karbon tetraklorida, asam sulfat, asam asetat glasial, hidrogen peroksida, dan bahan kimia yang digunakan untuk analisis berasal dari Merck, Jerman.

Pembuatan senyawa dioksolan terdiri dari 2 proses, yaitu epoksidasi ALSD dan dioksolanisasi epoksi metil stearat.

Preparasi epoksi metil stearat

Tahap pertama adalah pemisahan ALJ dan ALTJ dari ALSD menggunakan metode kristalisasi dengan menggunakan pelarut (2). Kristalisasi ALSD dilakukan sebanyak tiga kali sehingga diperoleh fraksi cair yang mempunyai kandungan ALTJ yang tinggi. Hasil analisis kromatografi gas merk Shimadzu GC-14B menunjukkan bahwa fraksi cair (ALTJ) mengandung asam oleat sebesar 59,29%; asam linoleat sebesar 19,37%; dan campuran antara asam palmitat dan stearat sekitar 20%.

Tahap kedua adalah esterifikasi ALTJ dengan metanol pada suhu 80 – 100 °C selama 2 jam dengan menggunakan katalis asam. Kelebihan metanol diuapkan dengan rotari evaporator, katalis asam yang masih tertinggal di dalam produk dihilangkan dengan cara pencucian. Metil oleat (MO) yang diperoleh mempunyai bilangan asam sebesar 6,70 mg KOH/g sample; bilangan penyabunan sebesar 197,76 mg KOH/g sample; oksiran oksigen sebesar 0,02%; and bilangan iod sebesar 81,29 g/100g sampel.

Tahap ke tiga adalah epoksidasi (MO) dengan asam perasetat pada suhu 65 °C selama 7 jam dengan menggunakan asam sebagai katalis (5). Epoksi metil stearat (EMS) yang dihasilkan mempunyai oksiran oksigen sebesar 3,75% dan bilangan iod sebesar 2,43 g/100 g sample.

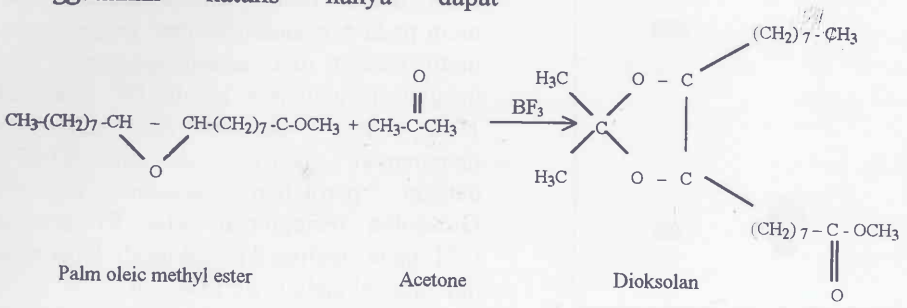
Sintesis dioksolan

Sintesis dioksolan dilakukan dengan menggunakan metode Kazimiera *et.al* (3) yang telah dimodifikasi. Dioksolanisasi EMS dengan aseton dilakukan pada suhu 100 °C dengan menggunakan CCl_4 sebagai pelarut dan 2 jenis katalis, yaitu p-TSA dan BF_3. Kedua jenis katalis tersebut dapat digunakan untuk dioksolanisasi 1,2-propanediol (1) atau epoksi asam butirat (8). Penelitian pendahuluan menunjukkan bahwa katalis BF_3 lebih efektif menurunkan oksiran oksigen dibandingkan dengan katalis p-TSA. Dengan demikian pada penelitian ini jenis katalis yang digunakan digunakan adalah BF_3. Dioksolanisasi EMS dilakukan pada berbagai perbandingan mol dan jumlah katalis yang digunakan, yaitu 1:1, 1:2, dan 2:1 mol/mol serta 5, 10, dan 15% (b/b). Peubah yang diamati ialah penurunan oksiran oksigen selama reaksi berlangsung. Dioksolanisasi dapat tercapai jika oksiran oksigen yang diperoleh kurang dari 0,1%. Dioksolan yang diperoleh selanjutnya dilakukan analisis dengan menggunakan kromatografi lapis tipis dan *infra red spectroscopy*.

HASIL DAN PEMBAHASAN

Hasil penelitian menunjukkan bahwa dioksolanisasi EMS dengan aseton pada perbandingan mol 1 : 1 dan menggunakan p-TSA sebanyak 5% (b/b) dapat menurunkan oksiran oksigen dari 3,65% menjadi 1,18%. Sedangkan dioksolanisasi

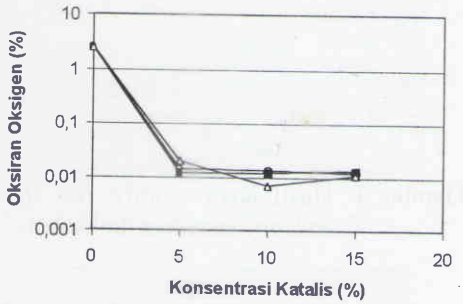
dengan menggunakan BF_3 pada kondisi yang sama dapat menurunkan oksiran oksigen hingga 0,02%. Sementara itu dioksolanisasi EMOS dan aseton tanpa menggunakan katalis hanya dapat menurunkan oksiran oksigen hingga 2,40%. Penurunan oksiran oksigen tersebut disebabkan oleh adanya reaksi hidroksilasi EMS.



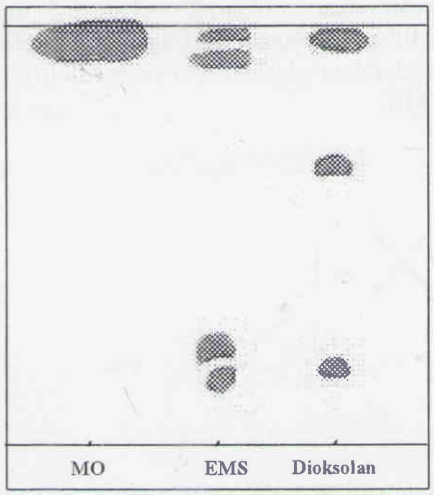
Gambar 1. Reaksi dioksolanisasi epoksi metil stearat dengan aseton

Pada Gambar 2 memperlihatkan pengaruh dari konsentrasi katalis dan perbandingan mol antara EMS dan aseton terhadap oksiran oksigen selama reaksi dioksolanisasi berlangsung. Penurunan oksiran oksigen pada perbandingan mol 2 : 1 dan 1 : 2 (MS : aseton) pada konsentrasi katalis 5, 10, dan 10% tidak menunjukkan perbedaan yang nyata, dan hanya mampu menurunkan okiran oksigen hingga 0,011 - 0,014%. Sementara itu, pada perbandingan mol 1 : 1 dan dengan menggunakan katalis BF_3 sebesar 10% dapat menurunkan oksiran oksigen hingga 0,007%. Pada akhir reaksi dioksolan yang dihasilkan hanya sebesar 22,69%.

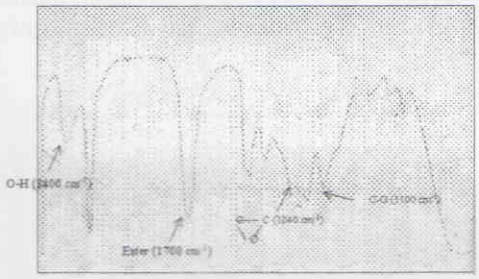
Pada Gambar 3 memperlihatkan hasil analisis kromatografi lapis tipis (KLT) MO, EMS< dan dioksolan. Metil oleat mempunyai nilai Rf sebesar 0,98; epoksi metil ester stearat menghasilkan 3 spot dengan nilai Rf masing-masing sebesar 0,26; 0,34; dan 0,95. Sementara itu, dioksolan menghasilkan 3 spot dengan nilai Rf masing-masing sebesar 0,28; 0,71; dan 0,98. Dengan demikian dioksolan mempunyai nilai Rf sebesar 0,71. Hasil analisis *infra red spectroscopy* menunjukkan bahwa dioksolan muncul pada *peak* 1100 cm^{-1} (Gambar 4). *Peak* tersebut tidak muncul pada hasil analisis *infra red spectroscopy* dari EMS (Gambar 5).



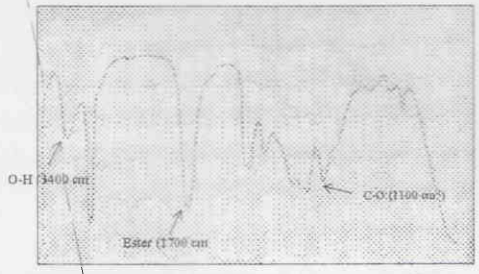
Gambar 2. Pengaruh konsentrasi katalis terhadap penurunan bilangan oksiran oksigen pada: (△) EMS/Aseton = 1/1 (mol/mol), (●) EMS/Aseton = 2/1 (mol.mol), (■) EMS/Aseton = 1/2 (mol/mol)



Gambar 3. Kromatografi lapis tipis dari metil oleat, epoksi metil oleat, dan dioksolan



Gambar 4. Hasil analisis *infra red spectroscopy* senyawa dioksolan



Gambar 5. Hasil analisis *infra red spectroscopy* epoksi metil oleat sawit

KESIMPULAN

Dioksolan dapat disintesis dari epoksidasi dan dioksolanisasi asam lemak sawit tidak jenuh. Reaksi dioksolanasasi optimum pada perbandingan mol antara epoksi metil stearat dan aseton sebesar 1 : 1 dengan menggunakan katalis BF_3 sebanyak 10% (b/b). Dioksolan yang dihasilkan mempunyai oksiran oksigen 0,007% dengan perolehan sebesar 22,69%. Dioksolan mempunyai nilai Rf sebesar 0,71 pada analisis kromatografi lapis tipis dan muncul pada *peak* 1100 cm^{-1}

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Synthesis of dioxolane from palm fatty acid distillate

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Abstract

Palm fatty acid distillate is a by-product of palm oil fractionation that is about 2.5 – 3.5 % of crude palm oil fractionated. Palm fatty acid distillate contains about 50% of unsaturated fatty acid. Unsaturated fatty acid was used as raw material of dioxolane and a kind of raw material of biopesticide. Biopesticide that produced from dioxolane is environmental friendly. Dioxolane can be synthesised by epoxydation of unsaturated fatty acid, and then epoxy was reacted by acetone. Results of the research showed that optimum condition of dioxolanation of epoxy palm oleic methyl ester by acetone was 1 : 1 mole/mole and BF_3 as catalyst was 10% (w/w). Oxyrane oxygen of dioxolane was 0.007%. Result of thin layer chromatography showed that Rf value of dioxolane was 0.71 and result of infra red spectroscopy showed that wavelength of dioxolane was 1100 cm^{-1}. Yield of dioxolanation of epoxy palm oleic methyl ester by acetone (1 : 1 mole/mole) was 22.69%.

Key words : Palm oil, palm fatty acid distillate, dioxolane, biopesticide

Introduction

Dioxolane is chemical compound derived from of ketone. Dioxolane has been used as raw material of pharmaceutical and surfactant industries. According to Ahmad *et al.* (1) it was identified as raw material of biopesticide, such as insecticide, fungicide, and germicide. Dioxolane can be synthesized from reaction of either oxo and 1,2-propanediol (1) or epoxy and ketone (8). One kind of derived of dioxolane, that was used as insecticide is 2-(1,3-dioxolane-2-yl) phenyl methylcarbamat (7). Generally, pesticide is synthesized from active material, which is hazardous to environmental and human healthy. Dioxolane which is synthesized from palm fatty acid ditillate (PFAD) is environmental friendly.

Developing of palm oil fractionation can increase a by-product, that is PFAD. Palm oil fractionation produced about 2.5 – 3.5% PFAD of crude palm oil fractionated (6, 7). At the present, using of PFAD is limited, that is used as raw material of low quality of soap making. At the same time, PFAD contains saturated fatty acid (SFA) and unsaturated fatty acid (UFA) which has potential to synthesis oleochemical products. SFA and UFA can be separated by surely of solvent and temperature (2). SFA can use as raw material of soap making and UFA can use as raw material of synthesis of epoxy. Epoxy was used as raw material of synthesis of dioxolane (8) that can be used as biopesticide. So, biopesticide that synthesized from epoxy palm fatty acid is environmental friendly.

Materials and Methods

Material

This research was done in chemical laboratory, Indonesian Oil Palm Research Institute. Materials, which are used in this research are PFAD, acetone, organic solvent, sulfuric acid, peracetic acid as oxidator, organics chemistry that have

high purity, and chemicals analysis. Materials, which are used in this research are PFAD, Acetone, organic solvent, sulfuric acid, percloric acid as oxidator, organics chemitry that have high purity, and chemicals analysis.

Methods

Two steps synthesize of dioxolane; these are preparation of raw materials and synthesis of dioxolane. Preparations of raw materials contain fractionation of PFAD, esterification, and epoxydation. Dioxolane is prepared by dioxolanation of epoxy methyl ester.

Preparation of raw materials

Preparations of raw materials contain 3 steps. The first step is crystalization of PFAD by methanol to produce SFA and UFA (2). Crystalization of PFAD was done three times until producing high UFA. Result of gas chromatography by Shimadzu GC-14B, UFA contains 59,29% oleic acid; 19,37% linoleic acid; and about 20% were mixture of palmitic and stearic acid. The second step is esterification of UFA by methanol at 80 - 100°C during 2 hours by use acid as catalyst. Rotary evaporator evaporated excess of methanol in product, residu of acid was washing completely. Oleic methyl ester had acid value was 6,70 mg KOH/g sample; saponification value was 197,76 mg KOH/g sample; oxyran oxygen was 0,02%; and iod value was 81,29 g/100g sample, respectively. The third step is epoxidation of oleic methyl ester by modification method of Sadi *et al.* (5) by add of acid as catalyst. Epoxidation of methyl ester was done by in-situ process at 65 °C during 7 hours in the reactor. Epoxy oleic methyl ester (EPOMe) had oxyrane oxygen was 3,75% and iod value was 2,43 g/100 g sample, respectively.

Synthesis of raw material of biopesticide

Synthesis of dioxolane was done by modification of Kazimiera et al. method's (3). Dioxolanation of EPOMe with acetone was done at 100°C and uses CCl_4 as a solvent and two kind of catalysts, these are p-TSA and BF_3. Ahmad et al. (1) used p-TSA was 5% and Yamamura et al. (8) used BF_3 was 5% as catalyst on epoxidation of propanediol and epoxy butiric acid. On the end of reaction, sample was added by water. Product that produced was extracted by diethyl ether. Change of oxyrane oxygen was analyzed every hour. The final product was analyzed by thin layer chromatography and infra red spectroscopy (IR).

Results and Discussion

Preparation of dioxolane used two kind of catalyst, these were p-TSA and BF_3. According to Ahmad *et al.* (1) and Yamamura *et al.* (8), dioxolane can be synthesized from propanediol and ketone, which used p-TSA as catalyst, meanwhile ethyl epoxy butirate and ketone by BF_3 as catalyst. Result of the research showed that dioxolanation of EPOMe by acetone (1 : 1 mole/mole) with p-TSA was 5% (w/w) can decrease oxyrane oxygen from 3.65% to 1.18%. At the same time, dioxolanation of EPOMe by aceton (1:1 mole/mole), which used of BF_3 as catalyst was 5% can decrease oxirane oxygen up to 0.02%. Dioxolanation of EPOMe without catalyst can decrease oxyrane oxygen was only 2.40%. Reduction of oxyrane oxygen in

control was only caused by hydroxylation of EPOMe. Thus, on this research was used BF_3 as catalyst.

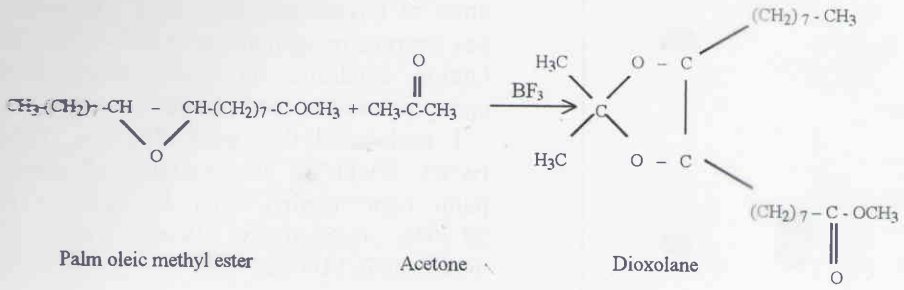

Figure 1. Dioxolanation of epoxy oleic methyl ester

Dioxolanation of EPOMe by acetone in mole ratio was 1 : 1, 1 : 2, and 2 : 1 that use BF_3 between 5 – 15% (v/v) can produce dioxolanes, which have oxyrane oxygen were 0.007 – 0.02%. Dioxolanation of EPOMe by acetone in mole ratio was 1 : 1 (mole/mole) that use BF_3 was 10% (w/w) can produce dioxolane which has a lowest oxyrane oxygen , that was 0.007%. At the same time, reactant ratio between EPOMe and acetone was 2 : 1 mole/mole and 1 : 2 mole/mole can produce dioxolanes, which have oxyrane oxygen between 0.011% until 0.014% (Fig. 2). Yield of dioxolanation EPOMe by acetone is 22.69%, respectively.

Results of thin layer chromatography by hexane-ethyl acetate (4:1 v/v) showed that Rf value of POMe was 0.98, each of Rf value of EPOMe was 0.26, 0.34, and 0.95. At the same time, each of Rf value of dioxolane was 0.28, 0.71, and 0.98 (Fig. 3). Thus, Rf value of dioxolane is 0.71. Results of infra red spectroscopy showed that wave length of EPOMe was 820 - 840 cm^{-1} and 1240 cm^{-1} (Fig. 4). After dioxolanation of EPOMe, wave leght of EPOMe moved from 820 - 840 cm^{-1} to 1100 cm^{-1} (Gambar 5). Dioxolanation of EPOMe produced a by-product, that is hydroxyl compound, which has wave length was 3400 cm^{-1}.

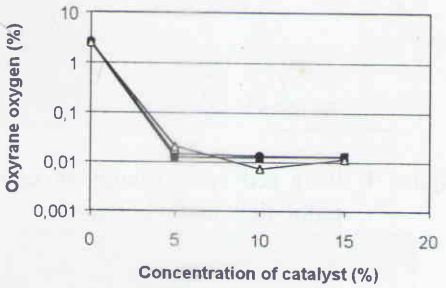

Figure 2. Influent of concentration of catalyst to oxyrane oxygen in dioxolanation;(△)EPOMe/acetone=1/1(mole/mole);(●)EPOMe/acetone=2/1(mole/mole); (□)EPOMe/acetone=1/2(mole/mole)

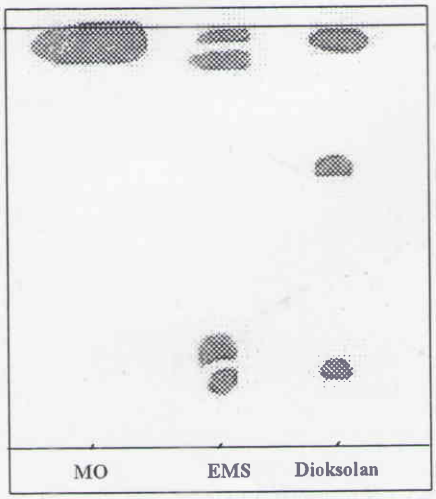

Figure 3. Thin layer chromatography of palm oleic methyl ester, epoxy palm oleic methyl ester, and dioxolane

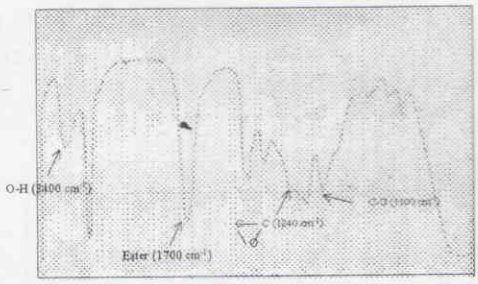

Figure 4. Infra red spectroscopy of epoxy palm oleic methyl ester

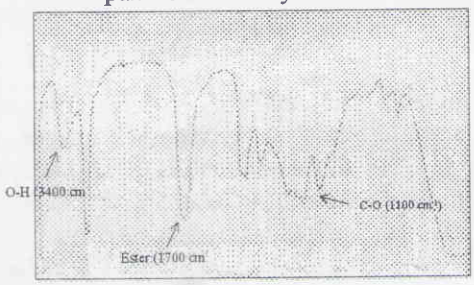

Figure 5. Infra red spectroscopy of dioxolane

Conclusions

Dioxolane can be synthesized by esterification, epoxydation, and dioxolanation of unsaturated fatty acid. Dioxolane has oxyrane oxygen about 0.007 - 0.014%. Option condition on dioxolanation was epoxy palm oleic methyl ester : acetone = 1 : 1 mole/mole that used BF_3 was 10% (w/w). Yield of dioxolanation of epoxy palm oleic methyl ester by acetone is 22.69%, respectively. Wave length of dioxolane is 1100 cm^{-1}.

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