Synthesis of Epoxy from Unsaturated Fatty Acids of Castor Oil (Ricinus *communis Linn*)

Marham Sitorus[1*], Ramlan Silaban[1], Retno Dwi Suyanti[1] and Trilita Halasson Sihite[2]

1. Department of Chemistry, State University of Medan – INDONESIA

2. Chemistry Department Students, State University of Medan - INDONESIA

*** Corresponding Author: Tel. 062 82167726315; E-mail: marham@unimed.ac.id**

ABSTRACT: Fatty acid epoxy or oxirane compounds are intermediates that are reactive to polar reagents. The purpose of reacting them with polar reagents is to obtain compounds that increase the polarity of the hydrocarbon part so that they are more effective when used as surfactants. In this study, epoxy was synthesized from unsaturated fatty acids of castor oil. The epoxy reagent used was performic acid which was synthesized in situ from formic acid and hydrogen peroxide using sulfuric acid as a catalyst at a temperature of 70 ^{o}C and a time of 90 minutes. Based on analysis with an FTIR Spectrophotometer, it was confirmed that fatty acid epoxy compounds had been formed, namely by the appearance of C-O-C epoxy absorption at 1015 cm^{-1} for stretching and 856 cm^{-1} for bending. Furthermore, based on the results of analysis with GC-MS, the epoxy results were: epoxy hexadecanoate (0.96%), epoxy hexadecanoate (1.02%) and epoxy risnoleate 0.34 %. The epoxidation reaction performed is still not optimal, but it can be used as a reference for refining subsequent epoxidation reactions.

***Keywords**: epoxy; castor oil; peroxyformic acid; surfactant*

INTRODUCTION

Castor oil is obtained from the flesh of the seeds of the castor plant (Ricinus *communis Linn*) as in figure 1, which is isolated by soxhlet extraction with n-hexane or petroleum solvent, which in this study used n-hexane [1]

[a] **[b]** **[c]**

Figure 1: Castor seeds [a], peeled castor beans, [b] castor oil extracted by soxhlet extraction of castor seeds with n-hexane solvent.

The main component of castor oil is ricinoleate (18:1 (9), 12-OH), which can reach 80–90%. Other components include hexadecanoate, 9,12-Octadecanoate, 9-Octadecanoate, and other trace components [2]. Castor oil is a non-edible oil, so various methods are used to transform it into more useful derivatives [3, 4, and 5].

In this study, the unsaturated fatty acids of castor oil were transformed into epoxy (oxirane) compounds through an epoxidation reaction [6]. Castor oil is obtained from castor seeds and isolated by shocklation. Epoxy fatty acids are intermediates that are reactive to polar reagents through a ring-opening reaction [7]. Epoxy derivatives are widely used as effective surfactants because they increase the hydrophilic properties of the hydrocarbon portion [8]. If the per-carboxylic acid reagent is not available, an alternative synthesis can be made in situ by reacting the carboxylic acid with hydrogen peroxide [9].

The epoxidation reaction of unsaturated fatty acids in castor oil is carried out with a performic acid reagent made in situ from formic acid and hydrogen peroxide with a sulfuric acid catalyst [10] with a general reaction equation as shown in Figure 2. Epoxidation is carried out by optimizing the temperature (T) and time (t) based on the change in the iodine number with the highest decrease [11]. The resulting epoxy is analyzed using an FTIR spectrometer to confirm functional groups and a GC-MS tool to identify the epoxy formed.

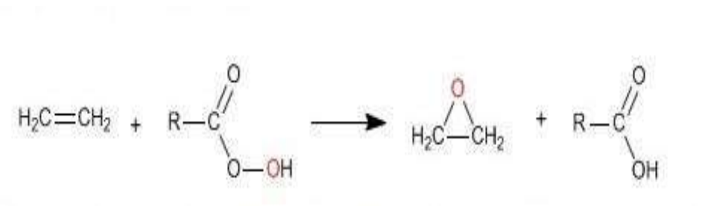


Figure 2: General equation of the epoxidation reaction of alkenes with percarboxylic acids

EXPERIMENTAL

Equipment and Chemicals

The equipment used included various glassware, a shock absorber, a Buchi R 80 evaporator, and a reflux apparatus. A Bruker Invenio S FTIR spectrometer was used to record functional groups. A Shimadzu QP010S GC-MS (Agilent DB-5MSUI column, 30 meters long, 0.25 mm ID, 0.25 µm film, helium as carrier gas, and ionizer: EI 70 ev) was used to identify castor oil components and epoxidation products. The consumable chemicals included castor bean samples from Deliserdang Regency, North Sumatra, n-hexane, Wijs reagent (iodine monochloride), potassium chlorate, sodium hydroxide, sulfuric acid, methanol, formic acid, and hydrogen peroxide, all of which were brand-specific.

Isolation, FTIR, and GC-MS Analysis of Castor Oil

Castor seeds were peeled, chopped, and air-dried until free of moisture. The chopped, water-free pulp was then wrapped in filter paper, suitable for the size of a shock absorber reactor. It was placed in a 100 mL three-necked flask containing n-hexane, set up with the reactor, and connected to a cooler. Shakletation was performed by evaporating the solvent through repeated circulation until no significant color change occurred in the extractor. The solvent was then evaporated using an evaporator to obtain pure castor oil. This was then analyzed by using FTIR spectroscopy and its components identified using GS-MS.

Optimization of Temperature (T) and Time (t) Epoxidation of Castor Oil Fatty Acids with Performic Acid.

Epoxidation was carried out by reacting hydrogen peroxide with formic acid in a volume ratio of 2:1. A total of 0.6 ml of formic acid (CH_2O_2) was placed in a three-necked flask equipped with a thermometer and a stopper on the other neck. Let stand for 5 minutes, then added 1.2 mL of 30% Hydrogen Peroxide (H_2O_2) for 5-6 minutes dropwise. The mixture was stirred with a magnetic stirrer at 200 rpm while adding 1 drop of sulfuric acid (H_2SO_4) catalyst. After being closed, heat the hot plate while continuing to stir. Then, after reaching the specified temperature, 10 ml of castor oil was added, the flask was closed again, and the speed was increased to 480 rpm, with temperature variations of 60 ºC, 65 ºC, and 70 ºC for 60 minutes starting from when the specified temperature was reached. Furthermore, time variations were carried out at 60, 75, and 90 minutes at 60 ºC.

Determination of the iodine number of castor oil and epoxidation results with variations in temperature (T) and time (t)

A total of 1.0 g of castor oil and the epoxidation results at various temperatures and times were put into an Erlenmeyer flask, then 10 mL of chloroform and 25 mL of Wijs reagent were added. Left for 30 minutes in a dark room while shaking, then 5 mL of 15% KI was added and shaken, then diluted to 100 mL of distilled water and titrated with 0.1 N $Na_2S_2O_3$ until a pale yellow color was obtained. After that, 2% starch indicator was added and titration was continued until the blue color disappeared. Iodine number is determined by the following equation.

$$Iodine\ Number = \frac{(mL\ blank - mL\ Thyo)\ x\ N\ Thyo\ x\ 12{,}7}{Sample\ Weight}$$

Then the epoxidation of castor oil fatty acids was carried out at the Optimal Temperature (T) and Time (t). Epoxidation was carried out with a volume ratio of formic acid and Hydrogen peroxide (2: 1) 0.6 mL formic acid, 1.2 mL Hydrogen peroxide, one drop of acid catalyst and 10 mL castor oil. Next, the organic phase was taken and rinsed with water approximately 2x 15 mL. Then dried with anhydrous Na_2SO_3. The dried results were analyzed for functional groups by FTIR and composition by GC-MS[12]

RESULT AND DUSCUSSION

Isolation, FTIR, and GC-MS Analysis of Castor Oil

Isolation was performed by soxhlet extraction with n-hexane solvent, circulating until the solvent color no longer changed significantly, indicating optimal extraction of the castor oil [13]. The chromatogram from the GC-MS analysis is shown in Figure 3, and the spectra from the FTIR analysis are shown in Figure 4, paralleling the FTIR spectra from the epoxidation results..

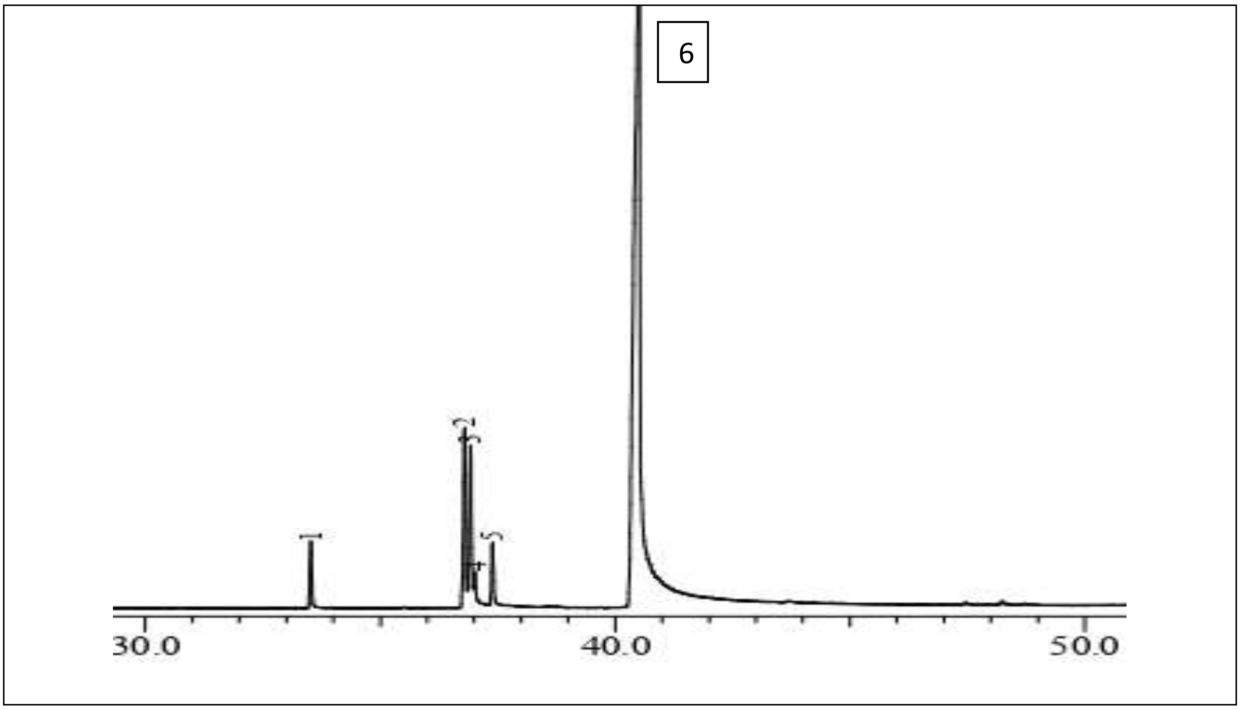


Figure 3. GC-MS spectra of castor oil isolated using soxhlet extraction **with n-hexane as a solvent.**

GC – MS analysis was carried out in the form of castor oil fatty acid methyl ester so that the boiling point of the castor oil fatty acid component corresponds to the GC-MS analysis temperature [14]. Based on the interpretation of Library chromatogram data, the chemical composition of the isolated castor oil is as in table 1.

Table 1. Chemical composition of castor oil isolated using soxhlet extraction with n-hexane as a solvent.

Peak Number	t_R (minute)	Composition (%)	SI (Similarity Index)	Component
1	33,523	2,53	97	Palmitate
2	36,797	7,58	96	2,9-Hexadecanoate
3	36,922	6,88	94	9-Octadecanoate
4	37,010	1,46	96	13-Octadecanoate
5	37,390	2,44	96	Octadecanoate
6	40,505	79,2	91	Ricinoleic (18: 1(9) 12-OH)

Based on table 1, the main component of castor oil is ricinolate, which is 79.2% and is an unsaturated fatty acid at C_9. Other saturated fatty acids are 2,9-hexadecanoate (7.58%), 9-Octadecanoate (6.88%) and 13-Octadecanoate (1.46%). These four unsaturated fatty acids are expected to produce epoxy through an epoxidation reaction with a performic acid epoxidizing agent made in situ using a sulfuric acid catalyst [15].

Optimization of Temperature (T) and Time (t) Epoxidation of Fatty Acids in Castor Oil with Performic Acid and Epoxidation at Optimal Conditions

The bond angle distortion of epoxy (oxirane) is very high so it is susceptible to polar reagents and high temperatures, so the temperature variation used is moderate. On the other hand, the reaction time will have implications for reversible reactions if the reaction time is too long. The continuation of the reaction is monitored by measuring the Iodine number, where the optimal conditions are the temperature and time with the highest decrease in Iodine Number. [16]. The results of the optimization of temperature (T) and epoxidation time are as in table 2.

Table 2. Iodine number resulting from epoxidation with temperature variations at 60 minutes [a] and time variations at 70 °C [b]

[a]. Temperature variation at 60 minutes

Temperature (°C)	mL blank	mL thiosulfate	Iodine Number (mg/g)
Castor Oil	74.4	19.4	69.8
60	74,4	19.5	69,7
65	74.4	22,5	65.9
70	74,4	24.0	64.01

[b]. Time variation at 70°C

Time (minute)	mL blank	mL thiosulfate	Iodine Number (mg/g)
Castor oil	74.4	19.4	69.8
60	74,4	20.8	68.07
75	74.4	21.5	67.2
90	74,4	24.0	64.0

An example of iodine calculation for castor oil based on titration data in table 2 is as follows.

$$Iodine\ Number = \frac{(74{,}4 - 19{,}4)\ x\ 0{,}1\ x\ 12{,}7}{1{,}0}$$

$$= 69{,}8\ mg/g$$

Based on Table 2, the optimal conditions for castor oil epoxidation are 70°C and 90 minutes. Optimization of the epoxidation conditions was discontinued because the iodine value did not decrease significantly after the initial reaction temperature and time. Besides that, the most common reaction for oils or fats is around 90 minutes at a temperature and an hour at a time. Epoxidation was then carried out under these optimal condition, with the results of FTIR spectroscopy analysis compared with castor oil, as shown in Figure 4.

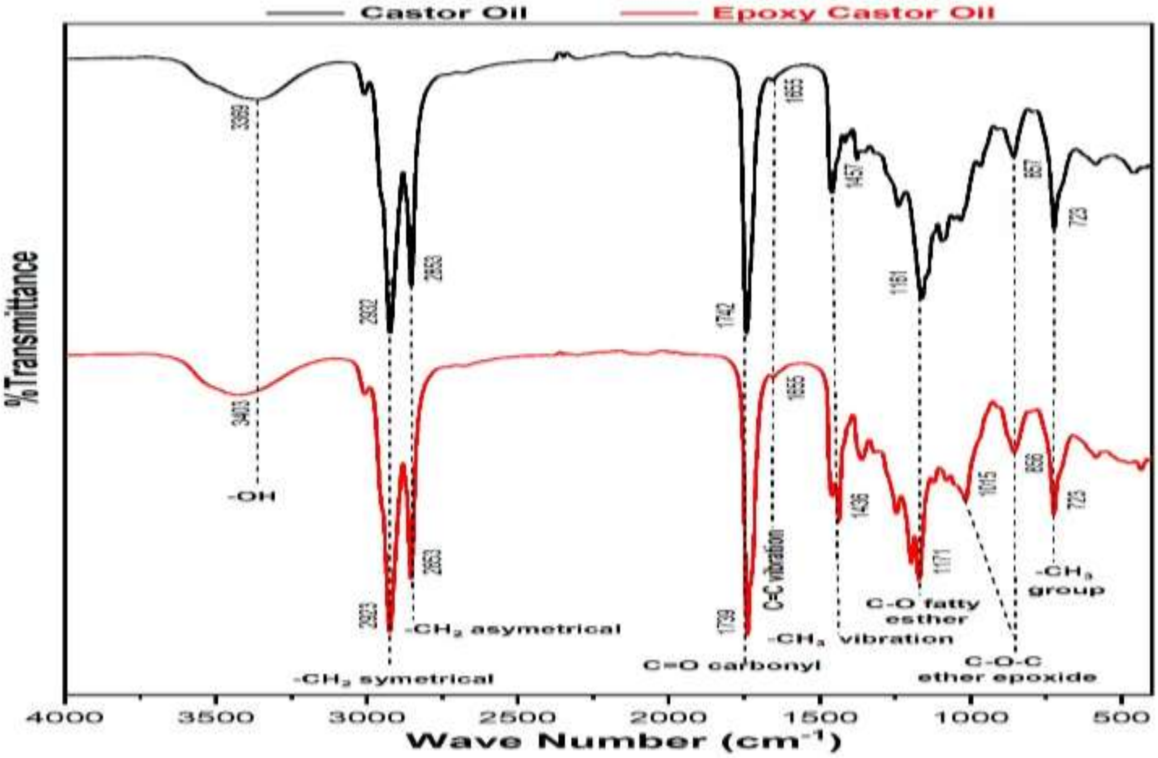


Figure 3. FTIR spectra of castor oil (black) and fatty acid epoxy results of castor oil (red)

The epoxidation reaction of unsaturated fatty acids in castor oil is the transformation of alkene functional groups into epoxy (oxirane). The carbonyl (C = O) absorption in castor oil is at 1742 cm-1, while in castor oil epoxy it is at 1739 cm$^{-1.}$ Meanwhile, the alkene (C = C) absorption is at 1655 cm^{-1} in both castor oil and the epoxidation product. The change in alkene absorption intensity was not seen significantly, but the formation of epoxy products was clearly visible from the FTIR spectrum of castor oil epoxy, namely the appearance of C - O - C absorption (epoxy ether) at 1015 cm^{-1} for stretching and 858 cm^{-1} for bending [17]. The conformation of alkenes that had changed to epoxy was also supported by a significant decrease in the iodine number, as shown in Table 2. Analysis of the chemical composition of the oil epoxidation results was carried out using GC-MS, with chromatogram shown in Figure 4

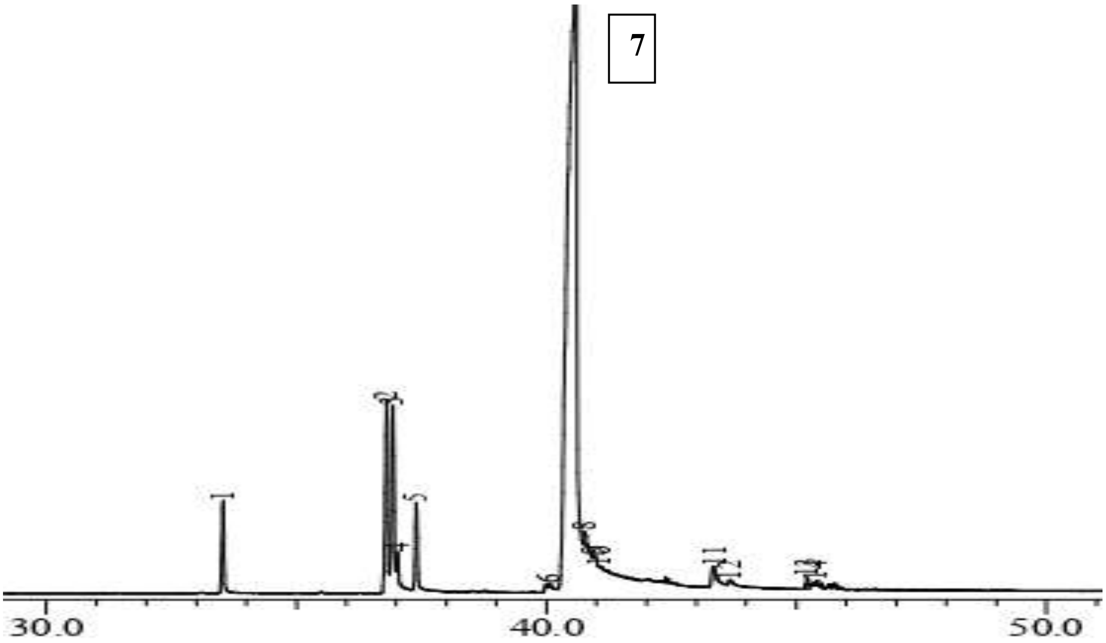


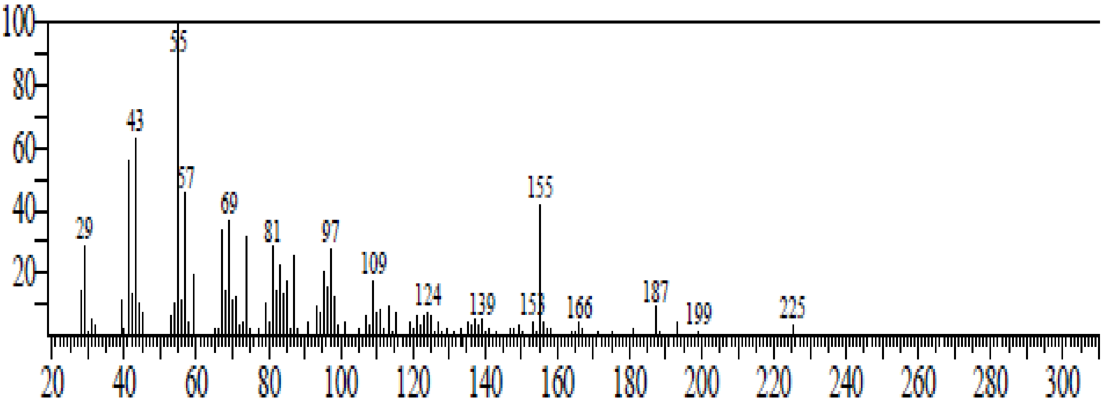
Figure 4. GC-MS chromatogram of castor oil epoxidation with performic acid and sulfuric acid as catalyst.

The chemical composition of castor oil epoxy based on interpretation of the GC-MS library chromatogram is as shown in table 3.

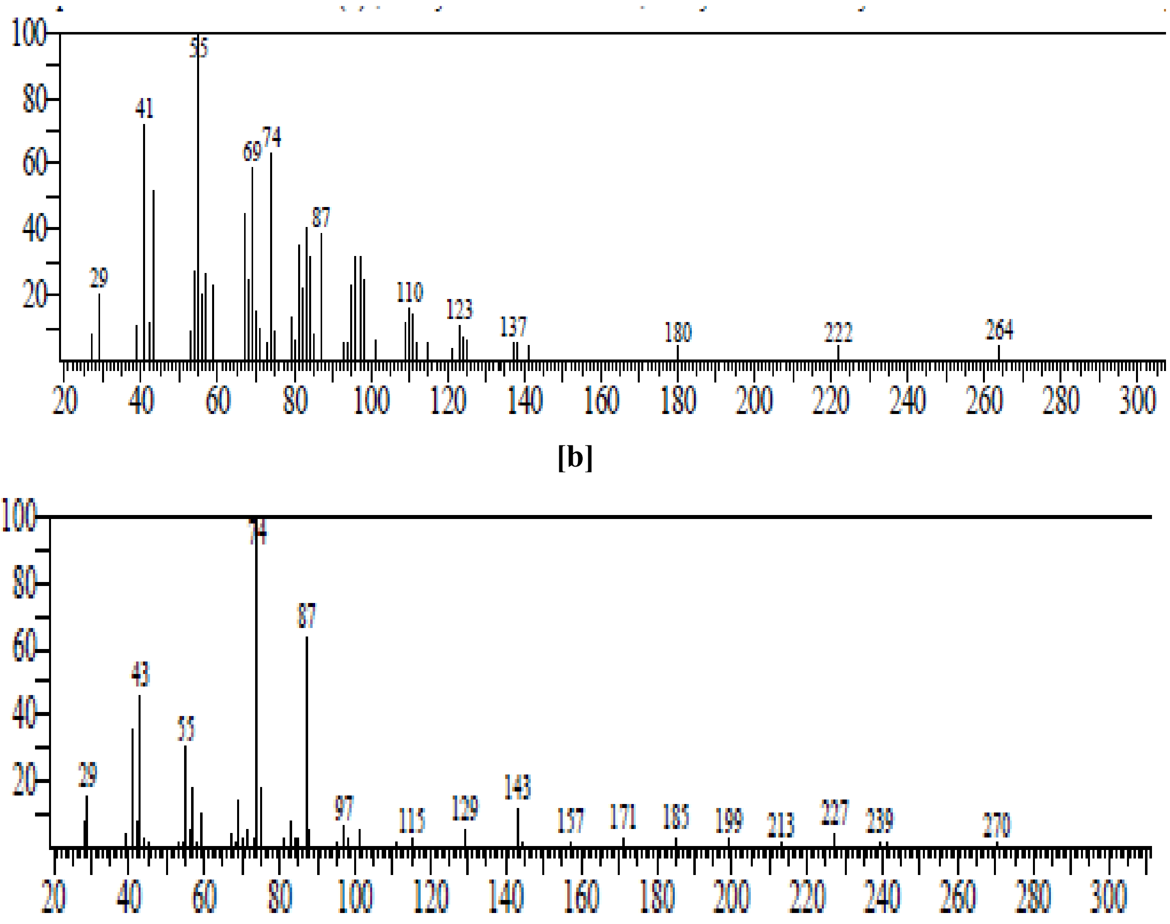
Table 3. Composition of castor oil epoxidation with performic acid and sulfuric acid as catalyst.

Peak Number	retention time (minute)	Composition (%)	SI (Similarity Index)	Component
1	33,523	2,60	97	Hexadecanoate
2	36,810	6,32	96	9,12- Hexadecanoate
3	36.934	5,90	95	9(Z)- Hexadecanoate
4	37,019	1.61	96	19 – Octadecanoate
5	37,399	2,57	90	Octadecanoate
6	40,070	0,30	91	9 (Z), 12 (Z) Octadecanoate
7	40,597	73,01	86	Ricinoleic residue
8	40,766	3,55	82	10 – Octadecanoate
9	40,958	0,96	81	**Epoxyhexadecanoate**
10	41,067	0,59	86	9,15- Octadecanoate
11	43,348	1.62	86	**Eoxy octadecanoate**
12	43,675	0,34	86	**Epoxy ricinoleic**
13	45,422	0,43	36	Not confirmed (SI<50)
14	45,422	0,41	35	Not confirmed (SI<50)

Based on the data in table 3 interpreted from the MS library data, the chromatogram of the castor oil epoxidation results is shown in Figure 2. From the epoxidation results, three epoxies were formed, peak number 9 with retention time = 40.958 minutes is epoxy hexadecanoate (0.96%), peak number 11 with retention time = 43.675 minutes is epoxy decanoate (1.62%) and peak number 12 retention time = 43.675 minutes is epoxy ricinoleate (0.34%), with the MS fragmentation spectra as in Figure 5 [18].



[a]



[b]

[c]

Figure 5: MS fragmentation spectra of epoxy hexadecanoate [a], epoxy octadecanoate [b] and epoxy ricinoleate [c]

The molecular weight of epoxymethyl ester hexanoate is 284 g/mol, epoxymethyl ester hexadecanoate 308 g/mol, and epoxyricinoleate 324 g/mol. In the MS spectra of Figure 5, the Molecular Weight (M^+) does not appear because fatty acids are relatively less stable molecules and are difficult to fragment [19]. Although the M^+ peak does not appear, data supporting the formation of conformational epoxy is a high Similarity Index (SI) of 80% and above, with SI of 81, 80, and 86%, respectively [20-21]. The epoxy yield obtained is not optimal but provides useful initial data for carrying out subsequent, better epoxidation reactions. One possible cause is the reversible reaction, which reverts to fatty acids due to the influence of the sulfuric acid catalyst, which can cause ring opening before the organic phase and the water phase are separated with a separating funnel [22-23]. Another possible cause is the formation of performic acid in situ which is not optimal, because the reaction is carried out in a one-pot reaction. Furthermore, for further research, percarboxylic acid will be directly tested, namely m-CPBA (metacholoroperoxybenzoic acid) as a peracid commonly used for epoxidation reactions [24-25].

CONCLUTION

Epoxy synthesis from unsaturated fatty acids of castor oil was carried out with performic acid reagent synthesized in situ from formic acid and hydrogen peroxide with sulfuric acid catalyst. The reaction was carried out under optimal conditions, namely at a temperature of 70 ºC and a time of 90 minutes. Based on analysis with an FTIR Spectrophotometer, it was confirmed that the fatty acid epoxy compound had been formed, namely by the appearance of C-O-C epoxy (oxirane) absorption at 1015 cm^{-1} for stretching and 856 cm^{-1} for bending. The occurrence of the epoxidation reaction was also supported by data on a significant decrease in the Iodine number from 59.9 mg/g for castor oil to 19.5 mg/g at temperature optimization and 20.8 mg/g for time optimization. Furthermore, based on the results of the analysis using GC-MS, the epoxy results obtained were: epoxy hexadecanoate (0.96%), epoxy hexadecanoate (1.02 %) and epoxy risnoleate 0.34 %. The epoxidation reaction carried out was still not optimal, but it can be used as a reference to perfect the next epoxidation reaction.

ACKNOWLEDGEMENTS

Thanks are extended to LPPM Unimed which funded the Research through BOPTN funds for the 2025 Fiscal Year Applied Product Research scheme with Research Contract No: 0045/UN33.8/PPKM/PPT/2025. Thanks are also extended to Apt Nora Susanti, S.Si, M.Sc who helped record the FITR spectra data. Furthermore, thanks are extended to Prof. Dr. Tutik Dwi Wahyuningsih, M. Sc and Timur Setyawan, heads of the Organic Chemistry Laboratory and operators in recording GC-MS Spectroscopy data.

CONFLICT OF INTEREST

The author declare that ther is no conflict of interest regarding the publication of this article.

REFRENCES

1. J. M .Danlami, A.B. Arsad, and M.A.A. Zaini; *J. Taiwan Inst. Chem. Eng.*; 47: 99-104; (2015); DOI:10.1016/j.jtice.2014.10.012
2. H. Kheyrodin; *Int. J. Clin. Chem. Lab. Med.* ; 10(1): 8 – 11; (2025); DOI: https://doi.org/10.20431/2455-7153.1001002.
3. F.O. Nitbai, P.J.P. Tjitda, H.E. Wogo, and A.I.R. Detha; *J. Oleo.Sci*; 71(6):781-783; (2022); doi : 10.5650/jos.ess21226.
4. M. Sitorus, S. Ibrahim, H. Nurdin, D. Darwis; *Indones. J. Chem.* ; 9(2): 278-284; (2009); https://doi.org/10.22146/ijc.21543.
5. Z. Yoping, H. Yong, and F. Yuming, *Green Chem.*; 111: 71-77; (2022); **DOI: 10.1039/c6gc00942e.**
6. G. Lewandowski, M. Musik, K. Malarczyk-Martusik, L. Salacinski, and E. Milchrtt; *Mini Reviews in Organic Chemistry;* 16 (4): 1-11; (2019); DOI:10.2174/1570193X16666190430154319
7. A. Brandolese, F.D. Monica, M.A. Pericas and A. W. Kleij; *Macromolecules*; 55 (7): 2566 – 2577; (2022); doi: 10.1021/acs.macromol.2c00321
8. C. Morissean, S.D. Kodani, S.G. Kamita, Y. Yung, K.S. Stephan Lee, B,D. Hamoch, and M. Battimo, *Int. J. Mol Sci*; 22 (9); 44993-45009; (2021); doi: 10.3390/ijms22094993
9. T. Cogliano, V. Russo, R. Turco, E. Santacesaria, M. Di Serio, T. Salmi, and R. Tesser; *Chem. Eng. Sci*; 251: 117488; (2022); https://doi.org/10.1016/j.ces.2022.117488
10. S. Bagagnan, My D. Jeselme, V. Alphonse, and S. Guerin- Rechdaomi; *Environmental Science and Pollution Research;* 31 (48): 58252-58262; (2024); DOI:10.1007/s11356-024-34958-4
11. M. B. Mahadi, N. Z. Abbas; I. M. Rasib, and M. A. Rahman; *IOP Conference Series Material Science and Engineering;* 1251 (1): 012017; (2022); DOI:10.1088/1757-899X/1257/1/012017.
12. N. Panchal and V. M. Vaghela; *Orient. J. Chem*; 40(4): 997 – 1016; (2024); http://dx.doi.org/10.13005/ojc/400410
13. K. Patel, N. Panchal, and P. Ingle; *IJARCS*; 6(3): 6-21; (2019); DOI: http://dx.doi.org/10.20431/2349-0403.0603002
14. J. Ecker, M. Scherer, G. Schmitz, and G. Liebishch; *J. Chromatogr. B*; 897: 98 – 104; (2012), https://doi.org/10.1016/j.jchromb.2012.04.015
15. A. L. Mihai, N. Mioara, and M. Belc; *Rom. Biotechnol. Lett*; 24(6): 973-985; (2019); http://dx.doi.org/10.25083/rbl/24.6/973.985
16. A. Babu, N. R. Mathew, and R. Ashwini; *International Journal of Research Publication and Reviews*; 4(10): 1342-1345; (2023); Journal homepage: www.ijrpr.com

17. G. F. Faturachman, A. J. Kamanda, S. Maharani, L.A. Latif, G. A. Belo, and S.G. Ayubi; *Indonesian Journal of Pharmaceutical Education*; 5(1): 27-33; (2025); DOI: 10.37311/ijpe.v5i1.23309
18. A. Dekebo, S. Youl-Kwon, C. Jung, and D. Hokim; *J. Apic. Res*; 33(2):117-128; (2018); http://dx.doi.org/10.17519/apiculture.2018.06.33.2.117
19. A. Nugraha and A. Nandyanto; *IJoMR*; 1(2): 171-206; (2021); http://dx.doi.org/10.17509/ijomr.v1i2.35191
20. M. R. L. Himabindu. S. A. Parameswari, and C. Gopinath; *IJPQA*; 4(3): 42-51; (2013);
21. D. Tsikhas; *J. Clin. Med* 4(3): 42-51; (2024); **https://doi.org/10.3390/jcm13237276**
22. D. Kotnarowsko; *Progress in Organic Coatings*; 67(3): 324 – 328; (2010); https://doi.org/10.1016/j.porgcoat.2009.10.026
23. D. Kotnarowsko, O. Kobus, Y. Kolomiiets, and A. Aleinikova; *IOP Cooference Series Material Science and Engineering*; 70(1): 012081; (2019); http://dx.doi.org/10.1088/1757-899X/708/1/012081
24. A. Horn and U. Kazmaier; *Eur. J. Org.Chem*; 218(20-21): 2531-2536; (2018), https://doi.org/10.1002/ejoc.201701645
25. H. Harrasi, I. R. Green, I. Ahmed, and A. Al – Harrasi; *RSC Advances*; 4(31): 12882 – 12917, (2014), http://dx.doi.org/10.1002/chin.201431229