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Adewale Adewuyi
Industrial Unit, Department of Chemistry, University of Ibadan, Ibadan, Oyo State 200284, Nigeria, walexy62@yahoo.com

Rotimi A. Oderinde
Industrial Unit, Department of Chemistry, University of Ibadan, Ibadan, Oyo State 200284, Nigeria

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Synthesis of Epoxy Monoethanolamide from *Bauhinia monandra* Seed Oil

Adewale Adewuyi* and Rotimi A. Oderinde

Industrial Unit, Department of Chemistry, University of Ibadan, Ibadan, Oyo State 200284, Nigeria

*e-mail: walexy62@yahoo.com

Abstract

In this study, we synthesized epoxidised monoethanolamide (EMA) from *Bauhinia monandra* seed oil (BMO) via a simple reaction route. In this process, BMO was transesterified to obtain a mixture of methyl esters, which was subjected to a urea adduct complexation reaction. The unsaturated methyl esters (BME) from the urea adduct complexation reaction were then epoxidised using performic acid produced *in situ* in a one-pot reaction system. The epoxidised methyl esters were converted to EMA by reacting them with monoethanolamine (1:10). The progression of the reaction was monitored using Fourier transform infrared spectroscopy and proton nuclear magnetic resonance spectroscopy, and the fatty acid composition was determined by gas chromatography. The results indicate that the most abundant fatty acid in BMO is C18:1 (25.70% ± 0.20%), with a degree of unsaturation of 49.00% ± 0.50%. After the urea adduct complexation reaction, the degree of unsaturation increased to 95.20% ± 0.10% with C18:2 (75.00% ± 0.10%) becoming the most dominant fatty acid. The oxirane oxygen content was found to be 5.50% ± 0.50%. The results of this study suggest that the urea adduct complexation reaction offers a potential means for increasing the unsaturation of fatty methyl esters. In addition, our findings show that EMA can be produced at low or room temperature.

Abstrak

Sintesis Epoxy Monoethanolamide dari Minyak Biji *Bauhinia monandra*. Dalam studi ini, kami mensintesis epoxidised monoethanolamide (EMA) dari minyak biji *Bauhinia monandra* (BMO) melalui rute reaksi yang sederhana. Dalam proses ini, BMO ditransesterifikasi untuk menghasilkan campuran metil ester, yang selanjutnya digunakan untuk reaksi kompleksasi urea. Metil ester tak jenuh (BME) hasil dari reaksi kompleksasi urea kemudian di epoksidasi menggunakan asam performat yang diproduksi secara *in situ* dalam sistem reaksi *one-pot*. Metil ester terepoksidasi kemudian dikonversi menjadi EMA dengan menggunakan monoetanolamina (1:10). *Fourier Transform Infrared* (FTIR) dan *Proton Nuclear Magnetic Resonance* (NMR) digunakan untuk memonitor reaksi, sedangkan kromatografi gas (GC) digunakan untuk menentukan komposisi dari asam lemak. Hasil penelitian menunjukkan bahwa asam lemak yang paling banyak terdapat dalam BMO adalah C18: 1 (25,70% ± 0,20%), dengan tingkat ketidakjenuhan 49,00% ± 0,50%. Setelah reaksi kompleksasi urea, tingkat ketidakjenuhan meningkat menjadi 95,20% ± 0,10% dengan C18: 2 (75,00% ± 0,10%) menjadi asam lemak yang paling dominan. Kandungan *oxirane oxygen* yang dihasilkan sebesar 5,50% ± 0,50%. Hasil penelitian ini menunjukkan bahwa reaksi kompleksasi urea merupakan cara yang potensial untuk meningkatkan ketidakjenuhan dari metal ester. Selain itu, hasil dari penelitian ini menunjukkan bahwa EMA dapat disintesis pada suhu rendah atau suhu kamar.

Keywords: Bauhinia monandra, epoxidation, epoxy monoethanolamide, fatty acids, urea adduct complexation reaction

1. Introduction

Seed oils are important sources of fatty acids that play important role in the synthesis of surfactants and other oleochemicals [1], [2]. Surfactants are used in several domestic and industrial applications, some of which include detergents, dispersants, stabilizers, emulsifiers, softeners, and wetting agents [3]. Previous reports have also noted their use as important components in formulations of agrochemicals, corrosion inhibitors, cosmetics, detergents, lubricants, polymers, and textile finishes [4], [5]. Several surfactants from seed oil have been reported, but the one of importance in this study is alkanolamide.

Fatty acid alkanolamides are organic molecules with unique properties that qualify them as surfactants. Given these properties, they have found application in cosmetics, toiletries, and pharmaceuticals [6]-[8]. They can be synthesized via an amidation reaction in which esters react with amines. They are nonionic and have excellent foam properties. Over the years, alkanolamides have been synthesized from petroleum-based feedstock, which is nonrenewable and yields products with low biodegradability as well as toxic by-products [9]. This has given rise to a demand for feedstock that is renewable, biodegradable, environmentally friendly, and cost effective. Due to the negative impact of some chemical petroleum-based products on human health and the environment, a strong desire has also emerged to identify a replacement for petroleum-based surfactants [10], [11]. This has directed research attention toward the use of seed oil as a possible feedstock from renewable sources for the biodegradable, environmentally friendly, and cost-effective production of alkanolamide.

Efforts have been made to use modified alkanolamides that have improved properties. Such modifications could promote a wider application of alkanolamides as surfactants. Although some work has been reported, these efforts must be improved and intensified. Although the use of hydroxyl methylated oil has been reported in the synthesis of alkanolamide polyols to increase the number of hydroxyl groups and improve their distribution [12], to the best of our knowledge there is scant information on the use of fatty epoxidised methyl esters as feedstock for the production of alkanolamide. In this study, we prepared epoxidised monoethanolamide (EMA) from epoxidised methyl esters (EBB). The aim of the work is to produce EMA from an underutilized seed oil by a urea adduct complexation reaction as a potential means of increasing the degree of unsaturation in a mixture of methyl esters.

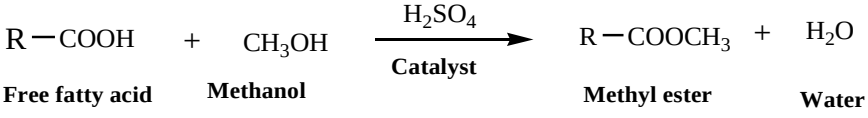
2. Experimental

Materials. The mature seeds of *Bauhinia monandra* were collected from a garden in the north campus of The Polytechnic of Ibadan, Ibadan, Oyo state, Nigeria. Formic acid (100%) and hydrogen peroxide (30%) were purchased from Merck, Darmstadt, Germany. All the solvents and chemicals used in this study were of analytical grade and were purchased from S.D. Fine Chemicals, Mumbai, India. The seeds of *Bauhinia monandra* were air dried, grinded, and then extracted with n-hexane in a Soxhlet extractor for 10 h to obtain Bauhinia monandra seed oil (BMO) [14].

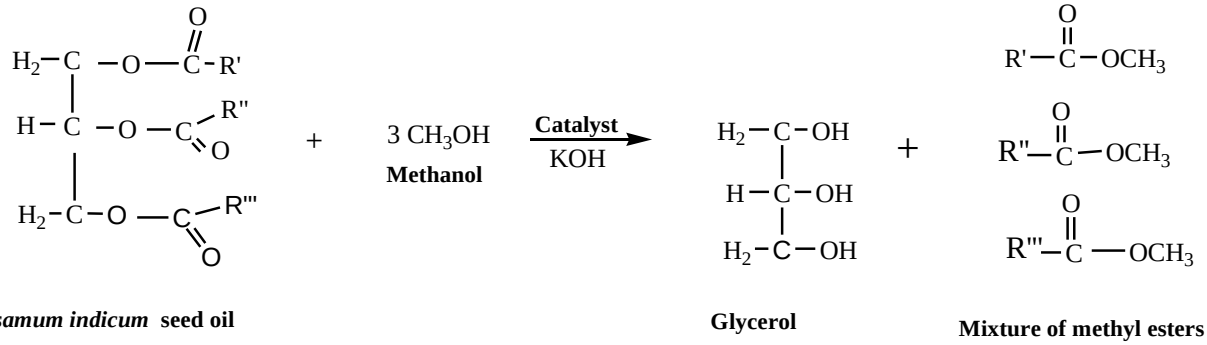
Preparation of methyl esters from BMO. To convert BMO to methyl esters, first, an esterification reaction was generated using 2% sulphuric acid in methanol at 70 °C for 2 h to convert the free fatty acid content to methyl esters. This was followed by a transesterification reaction [15] using 1% KOH in methanol at 70 °C for 4 h. The obtained product was then extracted with ethyl acetate, washed with distilled water until free of KOH, and passed over sodium sulphate. The ethyl acetate was then removed using a rotary evaporator to obtain the *Bauhinia monandra* methyl esters. This procedure is shown in Scheme 1.

Urea adduct complexation reaction of Bauhinia monandra methyl esters. The mixture of *Bauhinia monandra* methyl esters (100 g) and urea–methanol solution (200 g/L) was homogenized by continuous stirring and gentle warming [16]. The mixture was then cooled to room temperature and refrigerated at 5 °C for 8 h. The urea complexes were removed by filtration,

I: Esterification of free fatty acid in BMO *with 2% H_2SO_4 / MeOH*



II: Transesterification of BMO to methyl esters using 1% KOH / MeOH



Scheme 1. Preparation of Methyl Esters from BMO

washed twice with methanol saturated with urea, and the obtained filtrate was poured into 1% hydrochloric acid (600 mL) and extracted alternatively with hexane and diethyl ether. The successive organic layers were washed with distilled water, passed over anhydrous sodium sulfate, and later concentrated using a rotary evaporator. This reaction was repeated changing the ratio of the fatty methyl esters to urea from 1:2 to 2:1 to further increase the degree of unsaturation of the fatty methyl esters, as previously described by Adewuyi *et al*. [17]. The resulting fatty methyl esters (BME) were then analyzed for their fatty acid composition using gas chromatography, as described below.

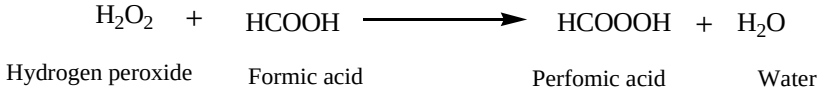
Physicochemical analysis of BMO and BME. BMO and BME were analyzed to determine their iodine, saponification, and free fatty acid contents using the method described by the Association of Official Analytical Chemists [18].

Fatty acid compositions of BMO and BME. To ensure that the fatty acid compositions of BMO and BME comprised fatty acid methyl esters, we used the method described by Adewuyi *et al*. [16]. To do so, we used an Agilent 6890 N series gas chromatograph equipped with an FID detector on a split injector. The detector (250 °C), injector (230 °C), and carrier gas (nitrogen at a flow rate of 1.5 mL/min) were appropriately programmed and a fused silica capillary column (DB-225, 30 x 0.32 m i.d., J & W Scientifics, USA) was used. The oven temperature was set to 160 °C for 2 min and was gradually increased to 230 °C at a rate of 4 °C/min. The area percentages were recorded by a standard Chemstation Data System.

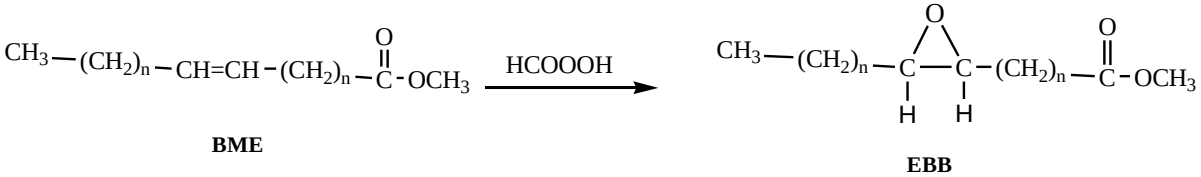
Epoxidation of BME. The epoxidation of BME was performed using performic acid in a 150-mL three-necked round-bottom flask, as reported in a previous study [4]. Briefly, a mixture of 40.43 g (0.0482 mol) of BME and 4.9 g (0.106 mol) of 100% formic acid was cooled to 15 °C while stirring. This was followed by the dropwise addition of 46.1 g (0.407 mol) of hydrogen peroxide with continuous stirring for about 30 min. The temperature was later increased to 70 °C and maintained for 3 h with aliquots taken at 30-min intervals for analysis by Fourier transform infrared spectroscopy (FTIR). After the formation of epoxide, the mixture was cooled to room temperature and EBB was extracted with ethyl acetate, washed with distilled water until free of acid, and passed over sodium sulfate. This was later concentrated using a rotary evaporator. This reaction is shown in Scheme 2. The percentage oxirane value of EBB was determined using the method approved by the American Oil Chemist's Society [18].

Synthesis of EMA. EMA was synthesized by agitating monoethanolamine/EBB (10:1) and sodium methoxide (2% by weight of monoethanolamine/EBB) in a 50-mL round-bottom flask at room temperature for 2 h. We then added diethyl ether, transferred the mixture into a separating funnel, and washed it with 10 mL of 5% aqueous hydrochloric acid. The diethyl ether phase was then separated, washed with distilled water, and passed over sodium sulfate. The resulting product was later concentrated using a rotary evaporator to obtain EMA. This reaction mechanism is presented in Scheme 3.

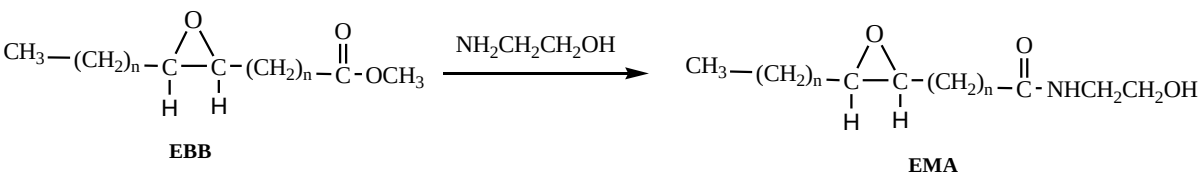
First step: Formation of performic acid



Second step: Epoxidation reaction



Scheme 2. Epoxidation of BME



Scheme 3. Synthesis of EMA

Characterization. The FTIR spectra of BMO, BME, EBB, and EMA were recorded using a Perkin Elmer FTIR system spectrum BX LR64912C. The samples were spread over NaCl cells, and their spectra were recorded in the range of 4000–400 cm^{-1}. The proton nuclear magnetic resonance (^{1}HNMR) spectra of BMO, BME, EBB and EMA were obtained using a 300 MHZ Brucker NMR spectrophotometer in $CDCL_3$ containing some amount of TMS as an internal standard.

3. Results and Discussion

Physicochemical properties and fatty acid composition of BMO and BME. The physicochemical properties and fatty acid composition of BMO have been previously reported [19]. Table 1 presents the results for BMO and BME. The free fatty acid was found to comprise 4.07% ± 0.10% of BMO, which was reduced to 0.05% ± 0.01% in BME. This may be due to the treatment of the oil with 2% H_2SO_4 which may have converted the free fatty acids to esters. Moreover, the urea from the adduct complexation reaction may have also formed a complex with some of the saturated free fatty acids. The saponification value was 185.00 ± 0.50 mgKOH/g in BMO and 190.20 ± 0.70 mgKOH/g in BME. The iodine value of BMO was found to be 107.26 ± 1.00 g iodine/100 g but after the urea adduct complexation reaction, this value increased to 191.01 ± 0.80 g iodine/100 g in BME. Table 2 shows the fatty acid compositions of BMO and BME. C18:1, the major fatty acid present in BMO, was found to comprise 25.70% ± 0.20%. C18:2, the second most predominant fatty acid in BMO, was found to comprise 17.90% ± 0.70%. C18:3 and C18:0 were found to comprise 4.30% ± 0.20% and 7.50% ± 0.50%, respectively. C16:0 was determined to comprise 16.50% ± 0.20% of BMO. Long chain fatty acids like C22:0 (16.10% ± 0.20%) and C24:0 (9.60% ± 0.30%) were also present in BMO, but not in BME.

After the urea complexation reaction, the fatty acid profile had changed. The saturated fatty acid methyl esters were separated from the unsaturated fatty acid methyl esters, with the predominant fatty acid in BME being C18:2 (75.00% ± 0.10%). The first treatment given to the fatty acid methyl esters of BMO at a ratio of 1:2 (BMO to urea) increased the amount of C18:2 fatty acid in BMO from 17.90% ± 0.70% to 72.60% ± 0.50%, and the second treatment at a ratio of 2:1 (BMO to urea) increased this amount from 72.60% ± 0.50% to 75.00% ± 0.10% in BME. The long chain fatty acids, especially C24:0, C22:0, and C20:0, formed complexes with urea more readily than the short chain C16:0. In the C18 carbon chain moiety, C18:0 and C18:1 were reduced as C18:2 increased. A reduction in the percentage composition of C18:3 was also observed, which may be due to the environment and interactions with this fatty acid moiety. The degree of unsaturation of the methyl esters was increased from 49.00% to 95.20%, with a percentage yield of 50.30%. This remarkable increase in C18:2 from 17.90% ± 0.70% in BMO to 75.00% ± 0.10% in BME and the total degree of unsaturation of the methyl esters demonstrate the promise of urea complexation as a method for modifying the unsaturation of a mixture of methyl esters.

Tabel 1. Physicochemical Characterization of BMO and BME

Parameter	BMO[a]	BME
Free fatty acid (%)	4.07 ± 0.10	0.05 ± 0.01
Saponification value (mgKOH/g)	185.00 ± 0.50	190.20 ± 0.70
Iodine value (g iodine/100g)	107.26 ± 1.00	191.01 ± 0.80
State at room temperature	Liquid	Liquid

Values are mean ± standard deviation of triplicate determinations.
a = Adewuyi and Oderinde (2011).

Tabel 2. Fatty Acid Composition (wt%) of BMO and BME

Fatty acids	BMO[a]	BME
16:0	16.50 ± 0.20	3.80 ± 0.50
18:0	7.50 ± 0.50	1.00 ± 0.20
18:1	25.70 ± 0.20	20.10 ± 0.10
18:2	17.90 ± 0.70	75.00 ± 0.10
18:3	4.30 ± 0.20	0.10 ± 0.10
20:0	1.30 ± 0.50	ND
20:1	1.10 ± 0.30	ND
22:0	16.10± 0.20	ND
24:0	9.60 ± 0.30	ND
Unsaturated	49.00 ± 0.50	95.20 ± 0.10
Saturated	51.00 ± 0.30	4.80 ± 0.30

Values are mean ± standard deviation of triplicate determinations.
a = Adewuyi and Oderinde (2011).

Epoxidation of BME. The epoxidation of BME was achieved by the generation of performic acid *in situ* in a one-pot reaction system. The high degree of unsaturation of 95.20% of BME makes it suitable for this reaction. The presence of unsaturated double bonds in the BME was confirmed by FTIR and HNMR, as shown in Figures 1 and 2. *In situ* epoxidation was performed using formic acid and hydrogen peroxide. This reaction is characterized by two main steps involving the formation of peroxoacid (peroxoformic acid) and the formation of epoxides. The first step is the acid-catalyzed formation of peroxoformic acid from formic acid, and the second step is the uncatalyzed epoxidation of BME with peroxoformic acid. The reaction was monitored using FTIR. To check the progress of the reaction, aliquots were taken at intervals of 30 min. Based on the FTIR analysis, the optimum yield was obtained after 3 h at a reaction temperature of

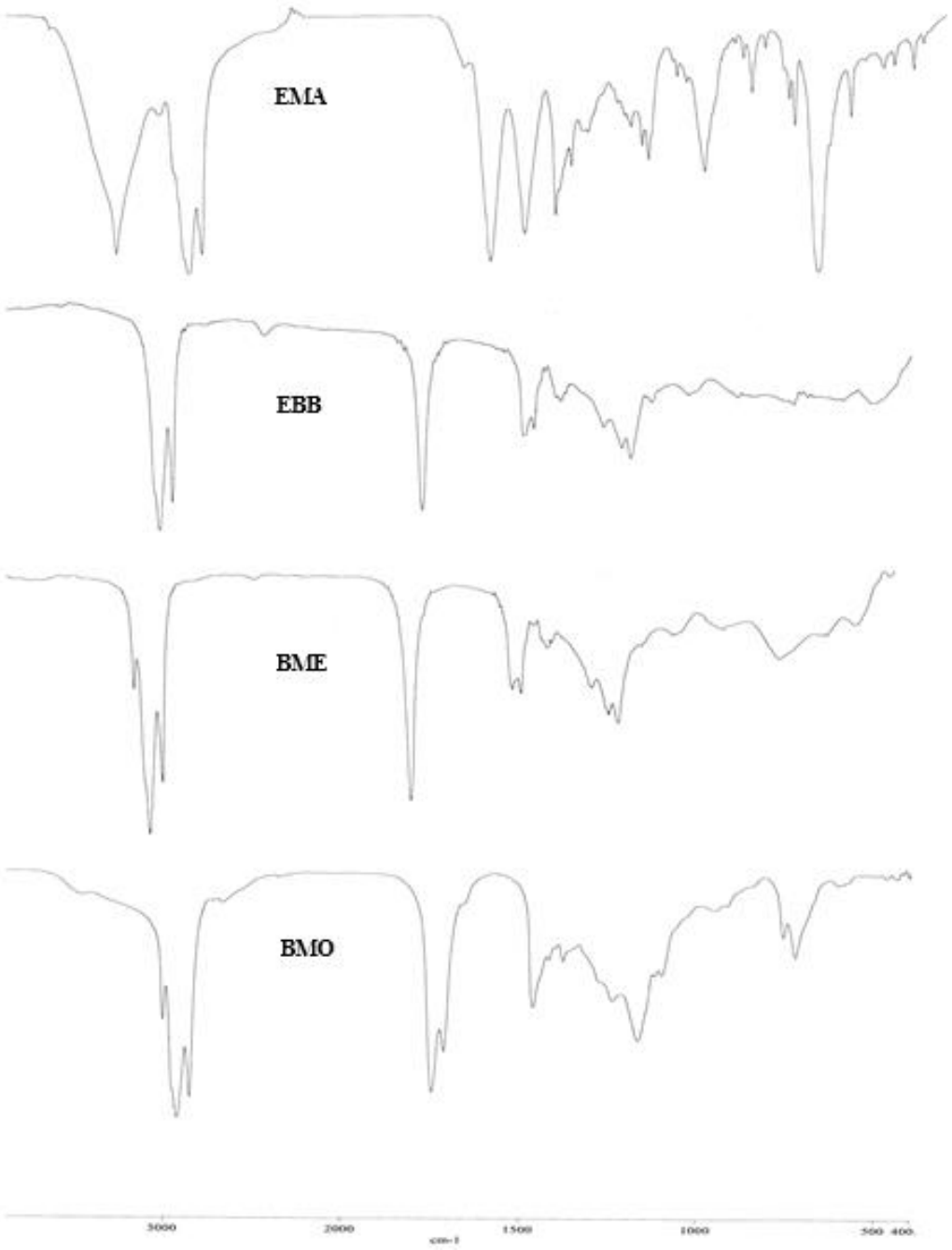


Figure 1. FTIR Spectra of BMO, BME, EBB, and EMA

70 °C without any detectable ring opening of the epoxides. The percentage oxirane oxygen content of the EBB was determined to be 5.50% ± 0.50%.

Synthesis of MEA. MEA was synthesized by reacting EBB with monoethanolamine at room temperature. The monoethanolamine served as a reagent and solvent for EBB and MEA. Sodium methoxide was added as a base catalyst to shorten the reaction time. The reaction was completed after 2 h with a percentage yield of 95.20%. This procedure was conducted at room temperature for a better yield than those of previously reported procedures, which required high temperature and had lower yields [20-22]. The use of sodium methoxide as a catalyst may account for this result. In Figure 1, the characteristic peak at 3006.70 cm^{-1} in BMO and BME was attributed to the C-H stretching of -C=C-H, which suggests the presence of unsaturated bonds. This band at 3006.70 cm^{-1} was not observed in EBB or EMA, which indicates that the double bonds had been epoxidised. A peak at 2927 cm^{-1} was also common in all the spectra, which may be accounted for by the C-H stretching of–CH_3.

The values 1458 cm^{-1} and 1169 cm^{-1}, which are common to the spectra of BMO and EBB, can be assigned to the C-H bending frequency of saturated alkane and the C-O stretching frequency of ester; respectively. The vibrational frequency at 1743 cm^{-1} was only observed in BMO, EBB, and EMA, which was attributed to the C=O stretching frequency of ester. This C=O stretching frequency of the ester functional group at 1743 cm^{-1} was not observed in EMB, which suggests the conversion of the ester functional group to amide. The presence of a peak at 834 cm^{-1} in EBB and EMA suggests the formation of epoxides. This peak was considered to be due to the symmetric in-plane deformation of the epoxy group, whereas the peak at 1246 cm^{-1} may also be attributed to the symmetric ring stretching of the epoxy group in both spectra. The band at 3317 cm^{-1} was observed only in EMA and may be attributed to the frequency of vibration of the OH groups contributed by the monoethanolamine. A peak at 1645 cm^{-1} was also observed only in EMA and appeared as the C=O frequency (1743 cm^{-1}) of esters disappeared in EBB, which can be attributed to the C=O frequency of amide.

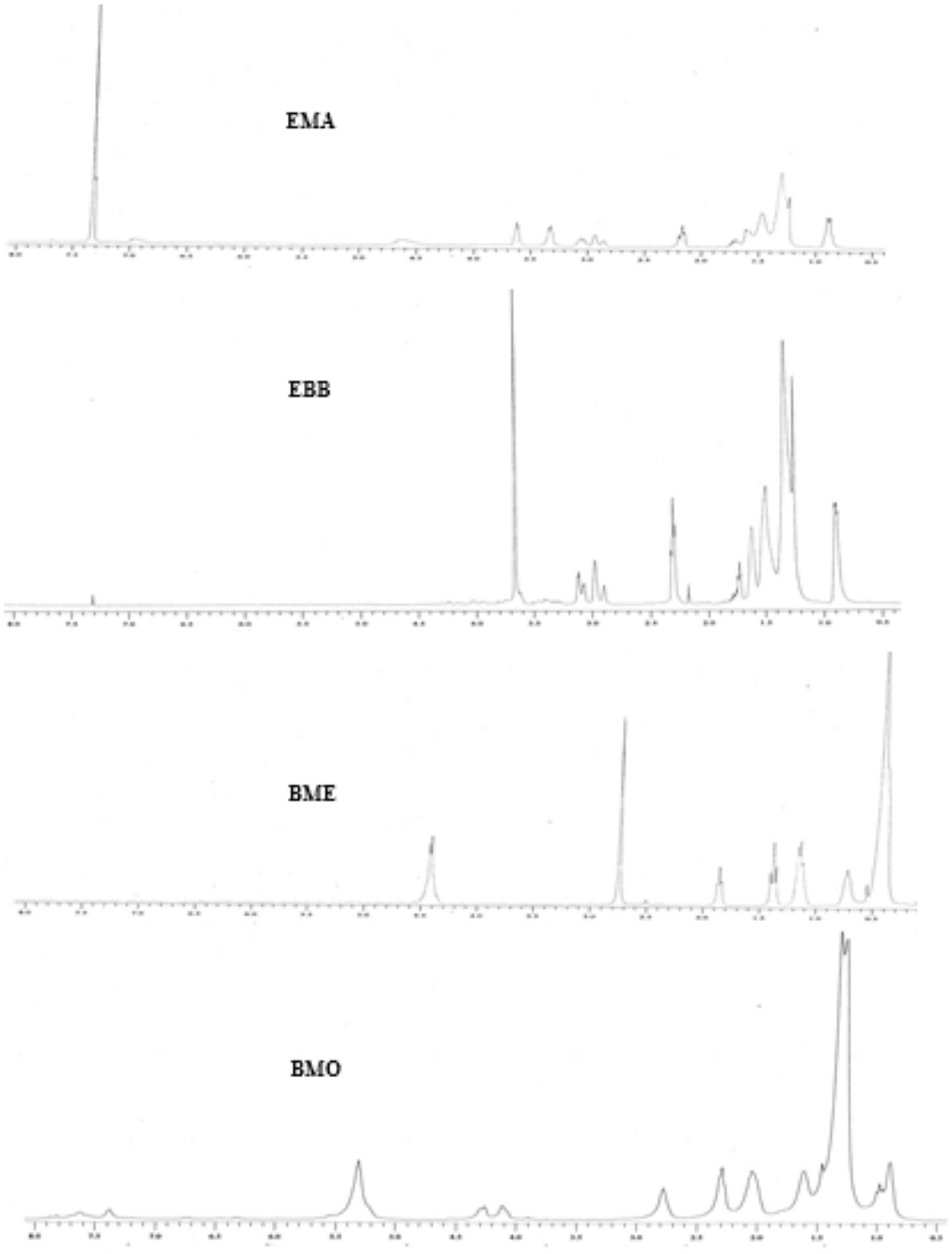


Figure 2. ^{1}HNMR Results for BMO, BME, EBB, and EMA

Figure 2 shows the ^{1}HNMR spectra of BMO, BME, EBB and EMA, in which we can see that ethylene protons appeared at 5.1–5.5 ppm in BMO and at 4.3–4.6 ppm in BME. This signal was not observed in EBB or EMA, which confirms the presence of unsaturation only in BMO and BME. The glycerol backbone of triglyceride was observed at 4.1–4.3 ppm in BMO, but no such peak was observed in BME, EBB, or EMA, which indicates the conversion of BMO to methyl esters. The methoxy groups of the esters in BME and EBB were observed at 2.7 ppm and 3.6 ppm, respectively. This chemical shift from the methoxy group of the esters was not observed in EMA, which indicates the conversion of ester to amide. The terminal methyl groups exhibited a chemical shift between 0.5 ppm and 1.0 ppm in BMO, BME, EBB, and EMA. Epoxy protons were observed at 2.9–3.1 ppm in EBB and EMA. The signal that appeared at 3.7 ppm in EMA was attributed to the contribution of the hydroxyl group it contains. The chemical shift at 7.3 ppm in EMA confirms the formation of amide.

4. Conclusion

The results of this study confirmed the preparation of EMA at room temperature within 2 h with a yield of 95.2% using the unsaturated methyl ester product from the urea complexation reaction. This finding also shows that urea adduct complexation can be used to increase the unsaturation of fatty methyl esters.

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