

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Synthesis of Nitrate Compounds from Vegetable Oils

Trans-esterification of vegetable oil with methanol using sulfuric acid as a catalyst to give methyl ester product. Epoxidation of methyl ester product with peroxy acid gave an epoxide product. Then hydrolysis of epoxide product with hydrochloric acid gave diol compound. Nitrate compound could be prepared from the nitration of diol compound with concentrated nitric acid and concentrated sulfuric acid. The conditions of nitration reaction were varied which shown in Table 4.1.

**Table 4.1** Variation condition of nitration reaction of vegetable oil diol.

Conditions	Temperature(°C)			Reaction time (hrs.)			
	-20	-10	0	1	3	5	7
Mole ratio (diol:HNO <sub>3</sub> :H <sub>2</sub> SO <sub>4</sub> )							
1:1:2	-	*	*	*	*	*	*
1:2:4	-	*	*	*	*	*	*
1:3:6	-	*	+	*	*	+	+

Note; (-) = no reaction  
(\* ) = incomplete reaction  
(+) = complete reaction

From Table 4.1, the optimum condition of nitration reaction was performed at temperature 0°C, mole ratio 1:3:6 and reaction time 5 hours, due to the reaction was completed. Some of the spectra of no reaction and incomplete reaction as compare with starting diol compound (Figure A41) were shown in Figure A42 and A 43, respectively.

## 4.2 Characterization of Synthesized Compounds

### 4.2.1 Palm Oil Methyl Ester

The IR spectra of palm oil and palm oil methyl ester were shown in Figures A1 and A2, respectively. The important absorption bands of palm oil and palm oil methyl ester were listed in Table 4.2.

**Table 4.2** The absorption assignments of palm oil and palm oil methyl ester.

Wave number (cm <sup>-1</sup> )		Assignments
Palm oil	Palm oil methyl ester	
3002	3002	=C-H Stretching
2854	2854	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
1654	1654	C=C Stretching
1460	1460	C-H Bending, Aliphatic
1161	1169	C-O Stretching

The IR spectrum of palm oil methyl ester (Figure A2) and the palm oil spectrum (Figure A1) could not be distinguished. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.

The  $^1\text{H-NMR}$  spectra of palm oil and palm oil methyl ester were shown in Figures A3 and A4, respectively. The important signals of palm oil and palm oil methyl ester were shown in Table 4.3.

**Table 4.3** The assignments of  $^1\text{H-NMR}$  spectra of palm oil and palm oil methyl ester.

Position of Proton	Multiplicity	Chemical Shift ( $\delta$ ,ppm)	
		Palm oil	Palm oil methyl ester
a	m	0.77-0.83	0.74-0.81
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.15-1.95	1.12-1.92
q	t	2.19-2.26	2.15-2.22
s	s	-	3.54
t,u,v	m	4.01-4.27	-
i,j	m	5.19-5.28	5.20-5.25

From the  $^1\text{H-NMR}$  spectrum of palm oil methyl ester (Figure A4) as comparing with palm oil (Figure A3), it could be observed that the signal between  $\delta_{\text{H}}$  4.01 ppm to  $\delta_{\text{H}}$  4.27 ppm belonged to the protons of glycerol moiety of triglyceride were absent, due to the formation of methyl ester. The signal at  $\delta_{\text{H}}$  3.54 ppm was belonged to the protons of methoxy group of methyl ester.

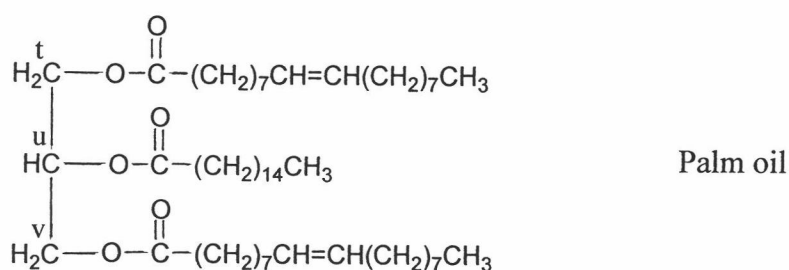
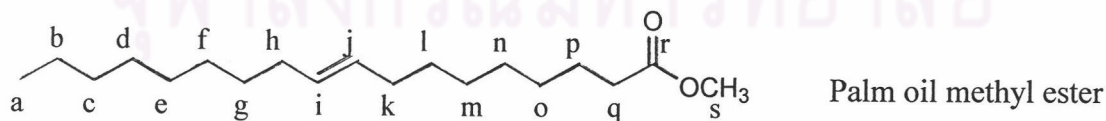
The  $^{13}\text{C-NMR}$  spectra of palm oil and palm oil methyl ester were shown in Figures A5 and A6, respectively. The important signals of palm oil and palm oil methyl ester were shown in Table 4.4.

**Table 4.4** The assignments of  $^{13}\text{C}$ -NMR spectra of palm oil and palm oil methyl ester.

Position of Carbon	Chemical Shift ( $\delta$ ,ppm)	
	Palm oil	Palm oil methyl ester
a	14.05	14.00
b,c,d,e,f,g,h,k,l,m,n,o,p	22.55-33.94	22.61-31.86
q	34.09	33.90
s	-	51.12
t,v	62.00	-
u	68.86	-
i,j	127.83-130.01	127.79-129.93
r	172.60-173.01	173.90

From the  $^{13}\text{C}$ -NMR spectrum of palm oil methyl ester (Figure A6) as comparing with palm oil (Figure A5), it was clearly seen that the signal at  $\delta_c$  62.00 ppm and  $\delta_c$  68.86 ppm belonged to the carbons of glycerol moiety of triglyceride were absent, and the signal at  $\delta_c$  51.12 ppm belonged to the carbon of methoxy group of methyl ester were shown instead.

From the results of these spectral data, it could be concluded that the product was palm oil methyl ester and its structure was as follows:



### 4.2.2 Palm Oil Epoxide

The IR spectrum of palm oil epoxide was shown in Figure A7. The important absorption bands of palm oil epoxide were listed in Table 4.5.

**Table 4.5** The absorption assignments of palm oil epoxide.

Wave number (cm <sup>-1</sup> )		Assignments
Palm oil methyl ester	Palm oil epoxide	
-	3464	O-H Stretching
3002	-	=C-H Stretching
2854	2854	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
1654	-	C=C Stretching
1460	1460	C-H Bending, Aliphatic
1169	1173	C-O Stretching

From the IR spectrum of palm oil epoxide (Figure A7) as comparing with palm oil methyl ester (Figure A2), it could be observed that the absorption bands at 3002 cm<sup>-1</sup> and 1654 cm<sup>-1</sup> were observed in the spectrum of palm oil methyl ester due to the presence of double bond in fatty acid chain, while they could not be observed in spectrum of palm oil epoxide. The characteristic absorption band of OH stretching at 3456 cm<sup>-1</sup> was likely to be dihydroxy product. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.

The <sup>1</sup>H-NMR spectrum of palm oil epoxide was shown in Figure A8. The important signals of palm oil epoxide were shown in Table 4.6.

**Table 4.6** The assignments of  $^1\text{H-NMR}$  spectrum of palm oil epoxide.

Position of Proton	Multiplicity	Chemical Shift ( $\delta$ ,ppm)
a	m	0.71-0.77
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.09-1.51
q	t	2.11-2.19
i,j	m	2.68-2.76
s	s	3.54

From the  $^1\text{H-NMR}$  spectrum of palm oil epoxide (Figure A8) as comparing with palm oil methyl ester (Figure A4), it could be observed that the signal between  $\delta_{\text{H}}$  5.20 ppm to  $\delta_{\text{H}}$  5.25 ppm belonged to the alkene protons of long chain fatty acid were absent, due to the formation of epoxide product. The signal at  $\delta_{\text{H}}$  2.68 to 2.76 ppm belonged to the proton in epoxide group.

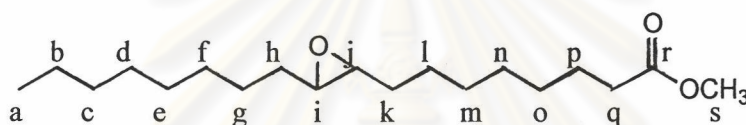
The  $^{13}\text{C-NMR}$  spectrum of palm oil epoxide was shown in Figure A9. The important signals of palm oil epoxide were shown in Table 4.7.

**Table 4.7** The assignments of  $^{13}\text{C-NMR}$  spectrum of palm oil epoxide.

Position of Carbon	Chemical Shift ( $\delta$ ,ppm)
a	14.02
b,c,d,e,f,g,h,k,l,m,n,o,p	22.62-31.86
q	34.00
s	51.32
i,j	57.13-57.17
r	174.23

From the  $^{13}\text{C}$ -NMR spectrum of palm oil epoxide (Figure A9) as comparing with palm oil methyl ester (Figure A6), it could be observed that the signals of olefinic carbon ( $-\text{C}=\text{C}-$ ) at  $\delta_c$  127.79 to 129.93 ppm were absent, due to the formation of epoxide product. The signal at  $\delta_c$  57.13 to 57.17 ppm belonged to the carbons in epoxide group.

From the results of these spectral data, it could be concluded that the product was palm oil epoxide and its structure was as follow:



#### 4.2.3 Palm Oil Diol

The IR spectrum of palm oil diol was shown in Figure A10. The important absorption bands of palm oil diol were listed in Table 4.8.

**Table 4.8** The absorption assignments of palm oil diol.

Wave number ( $\text{cm}^{-1}$ )		Assignments
Palm oil epoxide	Palm oil diol	
3464	3464	O-H Stretching
2854	2854	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
1460	1460	C-H Bending, Aliphatic
1173	1173	C-O Stretching

From the IR spectrum of palm oil diol (Figure A10), it showed the characteristic absorption broad band of OH stretching at  $3464\text{ cm}^{-1}$ , due to the formation of dihydroxy product was completed, while it could be observed the small OH band at this wave number in palm oil epoxide spectrum. The result was confirmed by using  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra.

The  $^1\text{H-NMR}$  spectrum of palm oil diol was shown in Figure A11. The important signals of palm oil diol were shown in Table 4.9.

**Table 4.9** The assignments of  $^1\text{H-NMR}$  spectrum of palm oil diol.

Position of Proton	Multiplicity	Chemical Shift ( $\delta$ ,ppm)
a	m	0.70-0.75
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.07-1.49
q	t	2.07-2.17
i,j	m	3.18-3.26
s	s	3.49

From the  $^1\text{H-NMR}$  spectrum of palm oil diol (Figure A11) as comparing with palm oil epoxide (Figure A8), it could be observed that the signal at  $\delta_{\text{H}}$  2.68 to 2.76 ppm belonged to the protons in epoxide group were absent, due to the formation of dihydroxy product. The signal at  $\delta_{\text{H}}$  3.18 to 3.26 ppm belonged to the protons of carbon that connected hydroxy group.

The  $^{13}\text{C-NMR}$  spectrum of palm oil diol was shown in Figure A12. The important signals of palm oil diol were shown in Table 4.10.

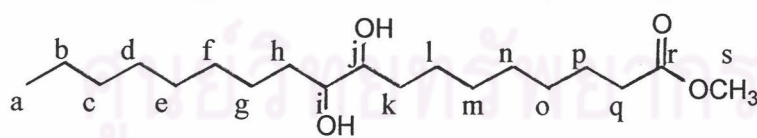


**Table 4.10** The assignments of  $^{13}\text{C}$ -NMR spectrum of palm oil diol.

Position of Carbon	Chemical Shift ( $\delta$ ,ppm)
a	13.88
b,c,d,e,f,g,h,k,l,m,n,o,p	22.55-33.79
q	33.82
s	51.09
i,j	74.19-74.24
r	173.97

From the  $^{13}\text{C}$ -NMR spectrum of palm oil diol (Figure A12) as comparing with palm oil epoxide (Figure A9), it could be observed that the signals of the carbons in epoxide group at  $\delta_c$  57.13 to 57.17 ppm were absent, due to the formation of dihydroxy product. The signal at  $\delta_c$  74.19 to 74.24 ppm belonged to the carbons connected the hydroxy group.

From the results of these spectral data, it could be concluded that the product was palm oil diol and its structure was as follows:



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#### 4.2.4 Palm Oil Nitrate

The IR spectrum of palm oil nitrate was shown in Figure A13. The important absorption bands of palm oil nitrate were listed in Table 4.11.

**Table 4.11** The absorption assignments of palm oil nitrate.

Wave number (cm <sup>-1</sup> )		Assignments
Palm oil diol	Palm oil nitrate	
3464	-	O-H Stretching
2854	2854	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
-	1639	NO <sub>2</sub> Asymmetric Stretching
1460	1460	C-H Bending, Aliphatic
-	1274	NO <sub>2</sub> Symmetric Stretching
1173	1173	C-O Stretching
-	854	N-O Stretching Vibration

From the IR spectrum of palm oil nitrate (Figure A13) as comparing with palm oil diol (Figure A10), it could be observed that there was no absorption band of OH stretching at 3464 cm<sup>-1</sup> but the absorption bands of NO<sub>2</sub> (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1639, 1274 and 854 cm<sup>-1</sup>, respectively. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.

The <sup>1</sup>H-NMR spectrum of palm oil nitrate was shown in Figure A14. The important signals of palm oil nitrate were shown in Table 4.12.

**Table 4.12** The assignments of  $^1\text{H-NMR}$  spectrum of palm oil nitrate.

Position of Proton	Multiplicity	Chemical Shift ( $\delta$ ,ppm)
a	m	0.75-0.81
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.12-1.59
q	t	2.26-2.24
s	s	3.56
i,j	m	5.06-5.16

From the  $^1\text{H-NMR}$  spectrum of palm oil nitrate (Figure A14) as comparing with palm oil diol (Figure A11), it could be observed that the signals at  $\delta_{\text{H}}$  3.18 to 3.26 ppm belonged to the protons of carbon that connected hydroxy group were absent, due to the formation of nitrate product. The signals at  $\delta_{\text{H}}$  5.06 ppm to  $\delta_{\text{H}}$  5.16 ppm belonged to the protons of carbon that connected nitrate group.

The  $^{13}\text{C-NMR}$  spectrum of palm oil nitrate was shown in Figure A15. The important signals of palm oil nitrate were shown in Table 4.13.

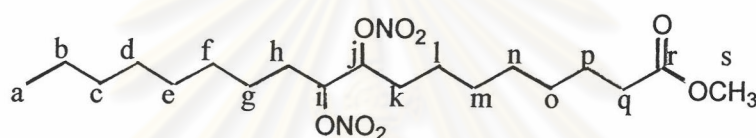
**Table 4.13** The assignments of  $^{13}\text{C-NMR}$  spectrum of palm oil nitrate.

Position of Carbon	Chemical Shift ( $\delta$ ,ppm)	Carbon Type*
a	13.79	$\text{CH}_3$
b,c,d,e,f,g,h,k,l,m,n,o,p	22.34-31.84	$\text{CH}_2$
q	33.92	$\text{CH}_2$
s	51.19	$\text{CH}_3$
i,j	81.62-81.67	CH
r	174.06	-

\* It was determined by DEPT spectra as shown in Figure A16.

From the  $^{13}\text{C}$ -NMR spectrum of palm oil nitrate (Figure A15) as comparing with palm oil diol (Figure A12), it could be observed that the signals of the carbons connected the hydroxy group at  $\delta_c$  74.19 to 74.24 ppm were absent, due to the formation of nitrate product. The signals at  $\delta_c$  81.62 to 81.67 ppm belonged to the carbons connected to the nitrate group.

From the results of the spectral data, it could be concluded that the product was palm oil nitrate and its structure was as follows:



#### 4.2.5 Soybean Oil Methyl Ester

The IR spectra of soybean oil and soybean oil methyl ester were shown in Figures A17 and A18, respectively. The important absorption bands of soybean oil and soybean oil methyl ester were listed in Table 4.14.

**Table 4.14** The absorption assignments of soybean oil and soybean oil methyl ester.

Wave number ( $\text{cm}^{-1}$ )		Assignments
Soybean oil	Soybean oil methyl ester	
3002	3002	=C-H Stretching
2854	2854	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
1654	1654	C=C Stretching
1460	1460	C-H Bending, Aliphatic
1161	1169	C-O Stretching

The IR spectrum of soybean oil methyl ester (Figure A18) and soybean oil spectrum (Figure A17) could not be distinguished. The result was confirmed by using  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra.

The  $^1\text{H-NMR}$  spectra of soybean oil and soybean oil methyl ester were shown in Figures A19 and A20, respectively. The important signals of soybean oil and soybean oil methyl ester were shown in Table 4.15.

**Table 4.15** The assignments of  $^1\text{H-NMR}$  spectra of soybean oil and soybean oil methyl ester.

Position of Proton	Multiplicity	Chemical Shift ( $\delta$ ,ppm)	
		Soybean oil	Soybean oil methyl ester
a	m	0.81-0.87	0.75-0.81
b,c,d,e,k,l,m,n,o,p	m	1.18-2.02	1.12-1.96
q	t	2.23-2.30	2.15-2.22
h	m	2.69-2.75	2.63-2.69
s	s	-	3.54
t,u,v	m	4.05-4.30	-
f,g,i,j	m	5.22-5.34	5.14-5.29

From the  $^1\text{H-NMR}$  spectrum of soybean oil methyl ester (Figure A20) as comparing with soybean oil (Figure A19), it could be observed that the signal between  $\delta_{\text{H}}$  4.05 ppm to  $\delta_{\text{H}}$  4.30 ppm belonged to the protons of glycerol moiety of triglyceride were absent, due to the formation of methyl ester. The signal at  $\delta_{\text{H}}$  3.54 ppm was belonged to the protons of methoxy group of methyl ester.

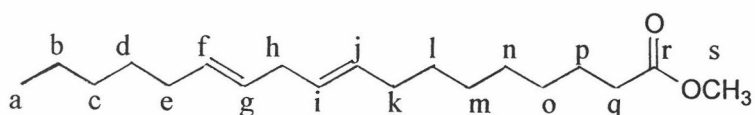
The  $^{13}\text{C}$ -NMR spectra of soybean oil and soybean oil methyl ester were shown in Figures A21 and A22, respectively. The important signals of soybean oil and soybean oil methyl ester were shown in Table 4.16.

**Table 4.16** The assignments of  $^{13}\text{C}$ -NMR spectra of soybean oil and soybean oil methyl ester.

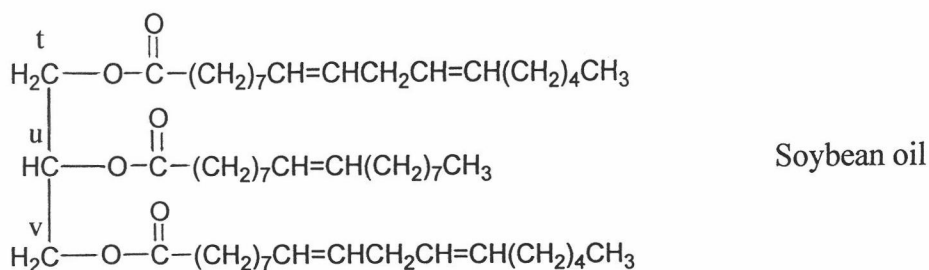
Position of Carbon	Chemical Shift ( $\delta$ ,ppm)	
	Soybean oil	Soybean oil methyl ester
a	14.03	13.95
b,c,d,e,h,k,l,m,n,o,p,q	22.55-34.10	22.51-33.93
s	-	51.18
t,v	62.02	-
u	68.87	-
f,g,i,j	127.07-131.79	127.03-131.73
r	172.63-173.03	173.95

From the  $^{13}\text{C}$ -NMR spectrum of soybean oil methyl ester (Figure A22) as comparing with soybean oil (Figure A21), it was clearly seen that the signals at  $\delta_c$  62.02 ppm and  $\delta_c$  68.87 ppm belonged to the carbons of glycerol moiety of triglyceride were absent, and the signal at  $\delta_c$  51.18 ppm belonged to the carbon of methoxy group of methyl ester was shown instead.

From the results of these spectral data, it could be concluded that the product was soybean oil methyl ester and its structure was as follows:



Soybean oil methyl ester



#### 4.2.6 Soybean Oil Epoxide

The IR spectrum of soybean oil epoxide was shown in Figure A23. The important absorption bands of soybean oil epoxide were listed in Table 4.17.

**Table 4.17** The absorption assignments of soybean oil epoxide.

Wave number (cm <sup>-1</sup> )		Assignments
Soybean oil methyl ester	Soybean oil epoxide	
-	3456	O-H Stretching
3002	-	=C-H Stretching
2854	2854	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
1654	-	C=C Stretching
1460	1460	C-H Bending, Aliphatic
1169	1169	C-O Stretching

From the IR spectrum of palm oil epoxide (Figure A23) as comparing with soybean oil methyl ester (Figure A18), it could be observed that the absorption bands at 3002 cm<sup>-1</sup> and 1654 cm<sup>-1</sup> were observed in the spectrum of soybean oil methyl ester due to the presence of double bond in fatty acid chain, while they could not be observed in the spectrum of soybean oil epoxide. It also showed the characteristic

absorption band of OH stretching at  $3456\text{ cm}^{-1}$  which was likely to be dihydroxy product. The result was confirmed by using  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra.

The  $^1\text{H-NMR}$  spectrum of soybean oil epoxide was shown in Figure A24. The important signals of soybean oil epoxide were shown in Table 4.18.

**Table 4.18** The assignments of  $^1\text{H-NMR}$  spectrum of soybean oil epoxide.

Position of Proton	Multiplicity	Chemical Shift ( $\delta$ ,ppm)
a	m	0.77-0.81
b,c,d,e,h,k,l,m,n,o,p	m	1.14-1.54
q	t	2.15-2.26
f,g,i,j	m	3.29-3.50
s	s	3.55

From the  $^1\text{H-NMR}$  spectrum of soybean oil epoxide (Figure A24) as comparing with soybean oil methyl ester (Figure A20), it could be observed that the signal between  $\delta_{\text{H}} 5.14\text{ ppm}$  to  $\delta_{\text{H}} 5.29\text{ ppm}$  belonged to the alkene protons of long chain fatty acid were absent, and the signals at  $\delta_{\text{H}} 3.29$  to  $3.50\text{ ppm}$  belonged to the protons of carbon that connected to a hydroxy group (likely from ring opening of dihydroxy product) were shown instead.

The  $^{13}\text{C-NMR}$  spectrum of soybean oil epoxide was shown in Figure A25. The important signals of soybean oil epoxide were shown in Table 4.19.

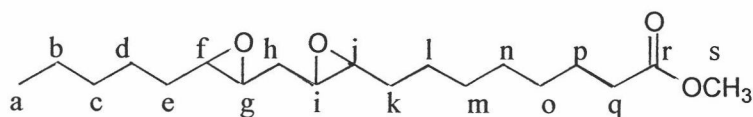


**Table 4.19** The assignments of  $^{13}\text{C}$ -NMR spectrum of soybean oil epoxide

Position of Carbon	Chemical Shift ( $\delta$ ,ppm)
a	13.97
b,c,d,e,h,k,l,m,n,o,p,q	22.55-33.92
s	51.28
f,g,i,j	56.47-57.13
r	174.19

The  $^{13}\text{C}$ -NMR spectrum of soybean oil epoxide (Figure A25) showed the difference from that of palm oil epoxide spectrum (Figure A9). That was because in soybean oil had linoleic acid (49%) more than palm oil (10%). Thus the influence of linoleic acid make the spectrum different. When comparing the  $^{13}\text{C}$ -NMR spectrum of soybean oil epoxide with that of soybean oil methyl ester (Figure A22), it could be observed that the signals of olefinic carbon ( $-\text{C}=\text{C}-$ ) at  $\delta_{\text{c}}$  127.03 to 131.73 ppm were absent, due to the formation of epoxide product. The signals at  $\delta_{\text{c}}$  56.47 to 57.13 ppm were belonged to the carbons in epoxide group. In addition, it could be observed the signals at  $\delta_{\text{c}}$  71.29 to 84.03 ppm which resulting from the ring opening hydroxy product.

From the results of these spectral data, it could be concluded that the product was soybean oil epoxide and its structure was as follows:



#### 4.2.7 Soybean Oil Diol

The IR spectrum of soybean oil diol was shown in Figure A26. The important absorption bands of palm oil diol were listed in Table 4.20.

**Table 4.20** The absorption assignments of soybean oil diol.

Wave number (cm <sup>-1</sup> )		Assignments
Soybean oil epoxide	Soybean oil diol	
3456	3456	O-H Stretching
2854	2854	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
1460	1460	C-H Bending, Aliphatic
1169	1169	C-O Stretching

From the IR spectrum of soybean oil diol (Figure A26), it showed the characteristic absorption band of OH stretching at 3456 cm<sup>-1</sup> which was larger than in soybean oil epoxide spectrum (Figure A23) due to ring opening dihydroxy product was completed. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.

The <sup>1</sup>H-NMR spectrum of soybean oil diol was shown in Figure A27. The important signals of soybean oil diol were shown in Table 4.21.

**Table 4.21** The assignments of the  $^1\text{H}$ -NMR spectrum of soybean oil diol.

Position of Proton	Multiplicity	Chemical Shift ( $\delta$ ,ppm)
a	m	0.77-0.84
b,c,d,e,h,k,l,m,n,o,p	m	1.14-1.54
q	t	2.19-2.27
f,g,i,j	m	3.30-3.51
s	s	3.55

From the  $^1\text{H}$ -NMR spectrum of soybean oil diol (Figure A27), it showed the same spectrum as that of the soybean oil epoxide (Figure A24). The formation of dihydroxy product was completed, and the signals at  $\delta_{\text{H}}$  3.30 to 3.51 ppm were belonged to the protons of carbon that connected to a hydroxy group. The result was confirmed by  $^{13}\text{C}$ -NMR spectrum.

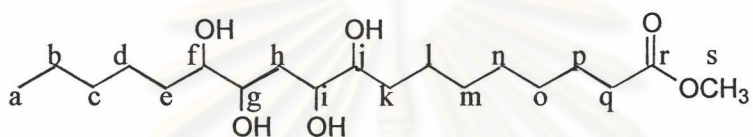
The  $^{13}\text{C}$ -NMR spectrum of soybean oil diol was shown in Figure A28. The important signals of soybean oil diol were shown in Table 4.22.

**Table 4.22** The assignments of the  $^{13}\text{C}$ -NMR spectrum of soybean oil diol.

Position of Carbon	Chemical Shift ( $\delta$ ,ppm)
a	13.96
b,c,d,e,h,k,l,m,n,o,p,q	22.63-33.88
s	51.25
f,g,i,j	71.22-83.97
r	174.15

From the  $^{13}\text{C}$ -NMR spectrum of soybean oil diol (Figure A28) as comparing with soybean oil epoxide (Figure A25), it could be observed that the signals of the carbon in epoxide group at  $\delta_c$  56.47 to 57.13 ppm were absent, due to the formation of dihydroxy product. The signal at  $\delta_c$  71.22 to 83.97 ppm belonged to the carbon connected to the hydroxy group.

From the results of these spectral data, it could be concluded that the product was soybean oil diol and its structure was as follows:



#### 4.2.8 Soybean Oil Nitrate

The IR spectrum of soybean oil nitrate was shown in Figure A29. The important absorption bands of soybean oil nitrate were listed in Table 4.23.

**Table 4.23** The absorption assignments of soybean oil nitrate.

Wave number ( $\text{cm}^{-1}$ )		Assignments
Palm oil diol	Palm oil nitrate	
3456	-	O-H Stretching
2854	2854	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
-	1639	$\text{NO}_2$ Asymmetric Stretching
1460	1460	C-H Bending, Aliphatic
-	1274	$\text{NO}_2$ Symmetric Stretching
1169	1173	C-O Stretching
-	854	N-O Stretching Vibration

From the IR spectrum of soybean oil nitrate (Figure A29) as comparing with soybean oil diol (Figure A26), it could be observed that there was no absorption band of OH stretching  $3456\text{ cm}^{-1}$  but the absorption bands of  $\text{NO}_2$  (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1639, 1274 and  $854\text{ cm}^{-1}$  respectively. The result was confirmed by using  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra.

The  $^1\text{H-NMR}$  spectrum of soybean oil nitrate was shown in Figure A30. The important signals of soybean oil nitrate were shown in Table 4.24.

**Table 4.24** The assignments of  $^1\text{H-NMR}$  spectrum of soybean oil nitrate.

Position of Proton	Multiplicity	Chemical Shift ( $\delta$ ,ppm)
a	m	0.75-0.79
b,c,d,e,h,k,l,m,n,o,p	m	1.16-1.55
q	t	2.16-2.24
s	s	3.56
f,g,i,j	m	5.08-5.14

From the  $^1\text{H-NMR}$  spectrum of soybean oil nitrate (Figure A30) as comparing with soybean oil diol (Figure A27), it could be observed that the signal at  $\delta_{\text{H}}$  3.30 to 3.51 ppm belonged to the protons of carbon that connected to a hydroxy group were absent, due to formation of nitrate product. The signals at  $\delta_{\text{H}}$  5.08 ppm to  $\delta_{\text{H}}$  5.14 ppm belonged to the proton of carbon that connected to a nitrate group.

The  $^{13}\text{C-NMR}$  spectrum of soybean oil nitrate was shown in Figure A31. The important signals of soybean oil nitrate were shown in Table 4.25.

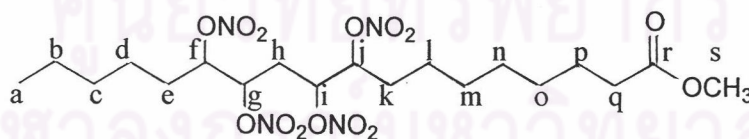
**Table 4.25** The assignments of  $^{13}\text{C}$ -NMR spectrum of soybean oil nitrate.

Position of Carbon	Chemical Shift ( $\delta$ ,ppm)	Carbon Type*
a	13.83	$\text{CH}_3$
b,c,d,e,h,k,l,m,n,o,p,q	22.31-34.35	$\text{CH}_2$
s	51.31	$\text{CH}_3$
f,g,i,j	77.13-84.20	CH
r	174.09	-

\* It was determined by DEPT spectra as shown in Figure A32.

From the  $^{13}\text{C}$ -NMR spectrum of soybean oil nitrate (Figure A31) as comparing with soybean oil diol (Figure A28), it could be observed that the signals of the carbons connected to the hydroxy group at  $\delta_c$  71.22 to 83.97 ppm were absent. due to the formation of nitrate product. The signal at  $\delta_c$  77.13 to 84.20 ppm belonged to the carbon connected to the nitrate group.

From the results of these spectral data, it could be concluded that the product was soybean oil nitrate and its structure was as follows:



### 4.3 Characterization of 2-Ethylhexyl Nitrate

The IR spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A33 and A34, respectively. The important absorption bands of 2-ethylhexyl nitrate were listed in Table 4.26.

**Table 4.26** The absorption assignments of 2-ethylhexyl nitrate.

Wave number (cm <sup>-1</sup> )	Assignment
2868	C-H Stretching, Aliphatic
1634	NO <sub>2</sub> Asymmetric Stretching
1465, 1383	C-H Bending, Aliphatic
1275	NO <sub>2</sub> Symmetric Stretching
978	C-O Stretching
866	O-N Stretching Vibration

From the IR spectrum of 2-ethylhexyl nitrate (Figure A34) comparing with of 2-ethyl-1-hexanol (Figure A33), it could be observed that there was no absorption band of OH stretching at 3200-3500 cm<sup>-1</sup>, the absorption bands of NO<sub>2</sub> (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1634, 1280 and 866 cm<sup>-1</sup> respectively. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.

The <sup>1</sup>H-NMR spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A35 and A36, respectively. The important signals of 2-ethylhexyl nitrate were shown in Table 4.27.

**Table 4.27** The assignments of  $^1\text{H-NMR}$  spectrum of 2-ethylhexyl nitrate.

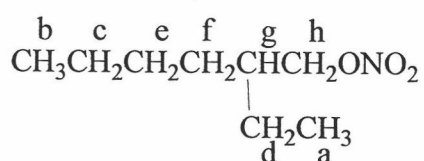
Chemical Shift ( $\delta$ ,ppm)	Multiplicity	Position of Proton	Number of Protons
0.85-0.92	<i>m</i>	a, b	6
1.27-1.48	<i>m</i>	c, d, e, f	8
1.60-1.78	<i>m</i>	g	1
4.38	<i>d</i>	h	2

The  $^{13}\text{C-NMR}$  spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A37 and A38, respectively. The important signals of 2-ethylhexyl nitrate were shown in Table 4.28.

**Table 4.28** The assignments of  $^{13}\text{C-NMR}$  spectrum of 2-ethylhexyl nitrate.

Position of Carbon	Carbon Type	Chemical Shift of Nitrate( $\delta$ ,ppm)	Chemical Shift of Alcohol( $\delta$ ,ppm)
a	$\text{CH}_3$	11.14	11.20
b	$\text{CH}_3$	14.25	14.14
c	$\text{CH}_2$	23.43	23.42
d	$\text{CH}_2$	23.10	23.73
e	CH	28.34	29.58
f	$\text{CH}_2$	29.21	30.59
g	$\text{CH}_2$	41.21	42.31
h	$\text{CH}_2$	78.19	65.20

From the results of the spectral data, it could be concluded that the product was 2-ethylhexyl nitrate and its structure was as follows:





#### 4.4 Determination of Cetane Number of Synthesized Nitrate Compounds in Base Diesel Fuel.

The cetane numbers of the blend of synthesized nitrate compounds with base diesel fuel at concentration of 0.05 to 2.00 %weight were shown in Table 4.29.

**Table 4.29** Cetane number of synthesized nitrate compounds blended with base diesel fuel.

Concentration (%weight)	Cetane Number					
	Base+POME	Base+PON	Base+PPON	Base+SOM	Base+SON	Base+EHN
0.05	52.7	53.0	53.2	52.6	53.0	54.2
0.10	52.7	53.4	53.8	52.6	53.6	56.0
0.15	-	-	-	-	-	57.0
0.20	-	-	-	-	-	58.3
0.25	52.8	54.2	55.2	52.6	54.8	-
0.50	52.8	55.4	56.9	52.5	56.5	-
0.75	52.8	56.4	58.5	52.5	58.0	-
1.00	52.9	57.3	59.7	52.5	59.3	-
1.25	52.9	58.3	-	-	-	-
1.50	52.9	59.0	-	-	-	-
1.75	52.9	59.7	-	-	-	-
2.00	52.9	60.2	-	-	-	-

Note: Base = Base Diesel Fuel

SOME = Soybean Oil Methyl Ester

POME = Palm Oil Methyl Ester

SON = Soybean Oil Nitrate

PON = Palm Oil Nitrate

EHN = 2-Ethylhexyl Nitrate

PPON = Purified Palm Oil Nitrate\*

\*Column chromatography was used to separate purified palm oil diol from palm oil diol. Purified palm oil diol was nitrated by using the same procedure nitration of palm

oil diol to give a product as purified palm oil nitrate. The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of purified palm oil nitrate were shown in Figures A39 and A40, respectively.

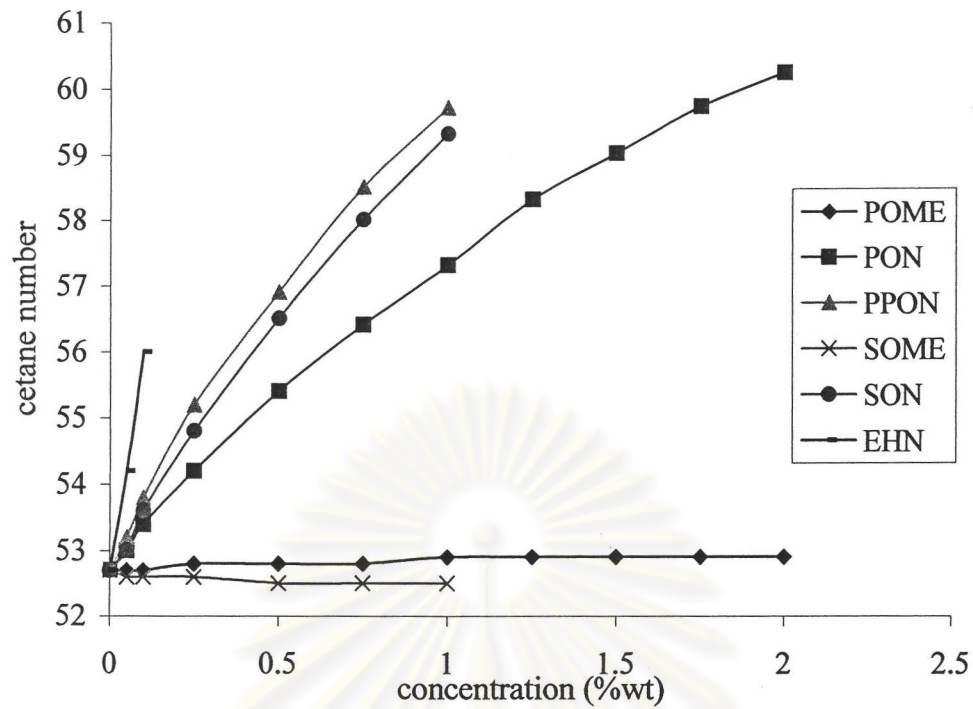
The physical properties of synthesized nitrate compounds blended with base diesel fuel at concentration were shown in Table 4.30.

**Table 4.30** Physical properties of base diesel fuel blended with synthesized nitrate compounds

Properties	Base	Base + 1.00% PON	Base + 1.00% PPON	Base + 1.00% SON
Mid-Boiling Point (°F)	554.78	557.96	557.60	557.60
API Gravity@ 60 °F	38.90	38.61	38.60	38.58
Viscosity	3.311	3.383	3.379	3.392
Pour Point (°C)	1	1	2	2
Flash Point (°C)	63	64	64	64
Cetane Index	58.24	57.98	57.93	57.90
Cetane Number	52.7	57.3	59.7	59.3

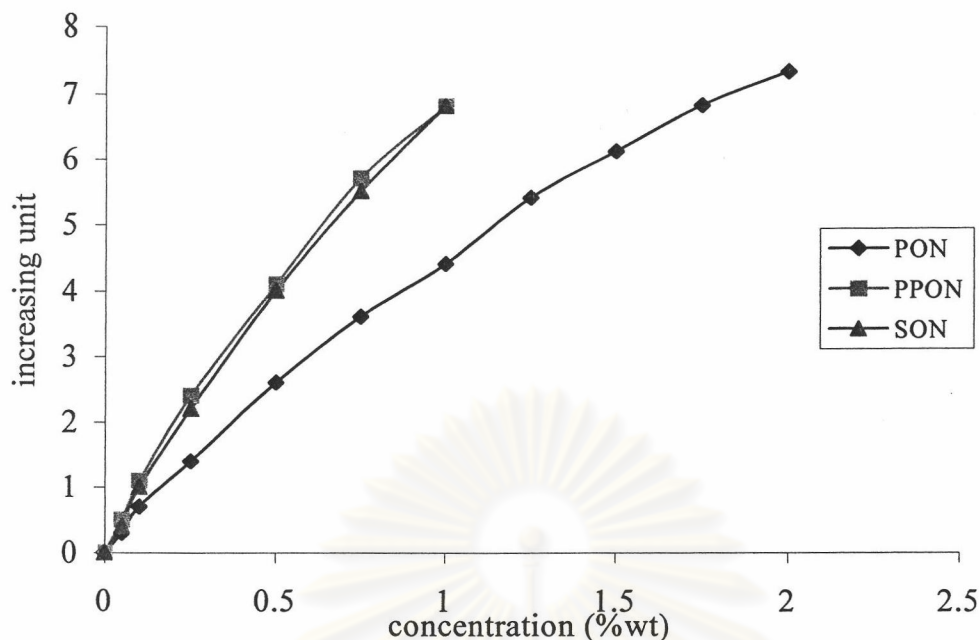
The synthesized nitrate compounds were easily soluble in base diesel fuel that did not change their physical properties within the specification of diesel fuel at the concentration of 0.05% to 1.00% by weight.

In Figure 4.1, it showed the relationship between the cetane number with concentration (%wt) of synthesized nitrate compounds in base diesel fuel.



**Figure 4.1** Relationship between the cetane number of synthesized nitrate compounds in base diesel fuel with concentration (%wt).

From the relationship between the cetane number with concentration (%wt) of synthesized nitrate compounds in base diesel fuel. It could be seen that palm oil methyl ester did not show any sign of cetane improver while palm oil nitrate and purified palm oil nitrate gave an improvement of cetane number. In addition, the cetane number of soybean oil nitrate was increased when increasing concentration of soybean oil nitrate. Thus, it could be concluded that these nitrate compounds could be raised the cetane number in diesel fuel.



**Figure 4.2** Increasing units of the synthesized nitrate compounds.

From Figure 4.2, it could be described that the cetane numbers of all samples were increased when increasing the concentration in base diesel fuel. Purified palm oil nitrate and soybean oil nitrate could be raised the cetane number up to 6.8 units at the same concentration of 1.0% by weight, whereas palm oil nitrate could be raised only 4.4 units at this concentration and increased up to 6.8 units at the concentration of 1.75% by weight.

From Figure 4.1, it could be seen that 2-ethylhexyl nitrate (EHN) gave the highest cetane number at low concentration as compare with the others. Although the cetane increasing capabilities of nitrate compounds from vegetable oils were low, but they have a potential performance advantage:

- Potentially lower feedstock costs
- Use the renewable feedstock
- Improved biodegradability
- Reduce nitrogen content (6.7%) as compared to 2-ethylhexyl nitrate (8.0%).