CHAPTER IV

RESULTS AND DISCUSSION

Palm oil and its free fatty acids (e.g. oleic acid, stearic acid and palmitic acid) were used as raw materials through out this research. The ^{13}C-NMR spectrum of palm oil, oleic acid, stearic acid and palmitic acid are shown in Figure A1, A2, A3, and A4 respectively.

Figure A1, ^{13}C-NMR spectrum, shows the important signals of the triglyceride of palm oil at 62.1 and 68.9 ppm, and the signal of C=O (ester group) appears at 173.9 ppm. In addition, Figure A1 also shows signals of alkenes at between 126 and 130 ppm.

Figure A2, A3, A4, ^{13}C-NMR spectrum, show the same important signal of C=O (carboxylic group) appears at 180 ppm. In addition, Figure A2 also shows signals of alkenes at between 126 and 130 ppm.

This research was studied in two reaction methods. The first method was consisted of two distinct process : transesterification and re-transesterification of palm oil. The second method was esterification of fatty acid of palm oil (e.g. oleic acid, stearic acid and palmitic acid)

4.1 Transesterification

Transesterification was carried out to give the methyl ester from palm oil and methanol. The ^{13}C-NMR spectrum of methanol is shown in Figure A5. The results of methyl ester formation at optimum condition are shown by ^{13}C-NMR, and GC-MS spectrum in Figure A11, C1 and D1 to D2 respectively.

Figure A11, ^{13}C-NMR, when reaction temperature was 80 °C and reaction time was 6 hours, shows that the peaks of triglyceride of palm oil at 62.1 and 68.9 ppm disappeared and the important peaks of CH_3-O- and C=O of methyl ester product appeared at 51.1 and 173.9 ppm, respectively. In addition, Figure A11 also shows the peaks due to alkenes at between 127 and 130 ppm.

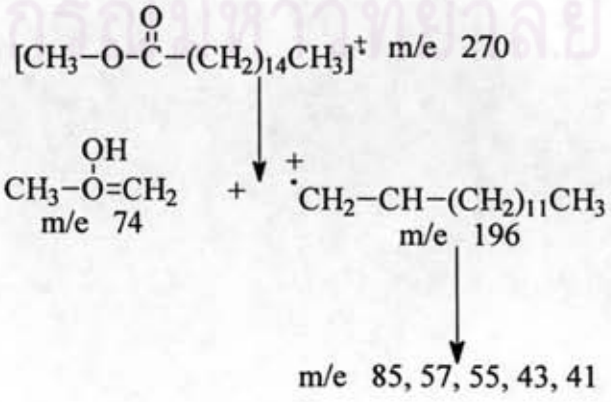
These experimental results indicate that the transesterification reaction of palm oil with methanol was completed with a reaction temperature of 80 °C and a reaction time of 6 hours. In this study, the yield of the resulting product was 85.67 %.

The composition of methyl ester product was determined by GC-MS The GC-MS which was performed on DB-1 capillary column. The GC-MS chromatogram is shown in Figure C1 and mass spectrum of each peak is shown in Figure D1 to D2.

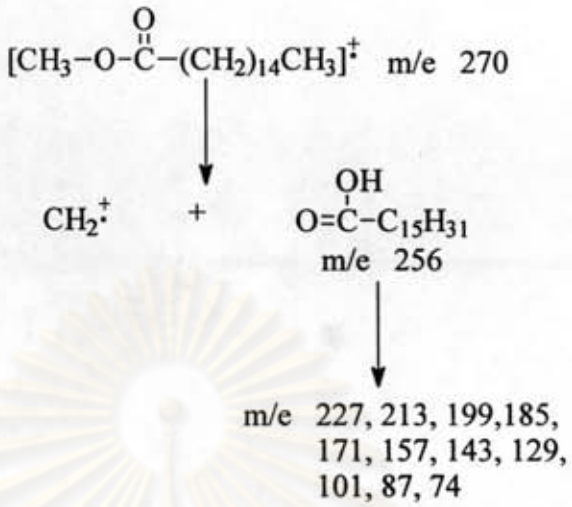
Figure C1, indicates that the methyl ester product is composed of a mixture of the methyl esters of long chain fatty acid. The main components are methyl palmitate and methyl oleate, at retention times 9.085 and 10.396 min, respectively.

The Mass-spectrum of methyl palmitate (MW 270), at retention time 9.085 min in Figure D1 shows a base peak at 74 due to fragmentation as shown in the following equation :

Equation I

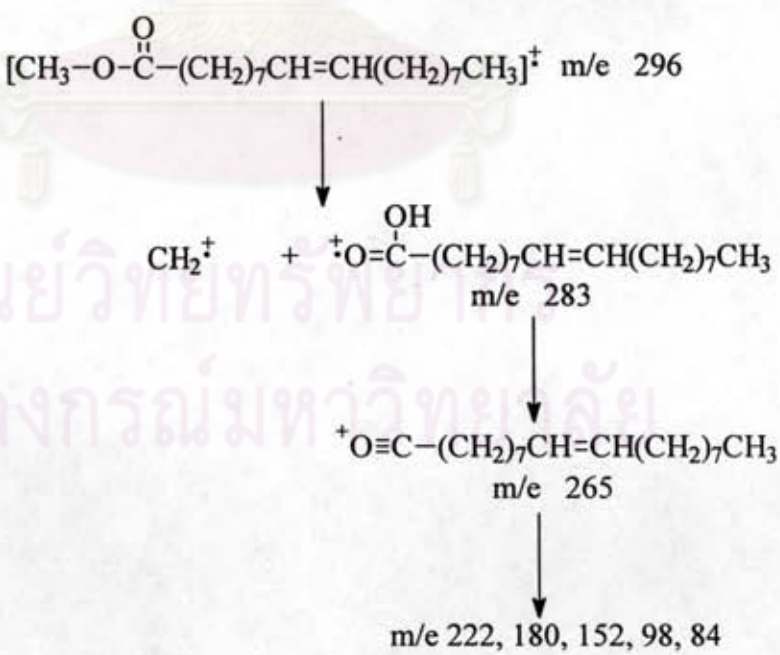


Equation II



The Mass-spectrum of methyl palmitate (MW 296), at retention time 10.396 min in Figure D2 shows a base peak at 55 due to fragmentation as shown in the following equation :

Equation I



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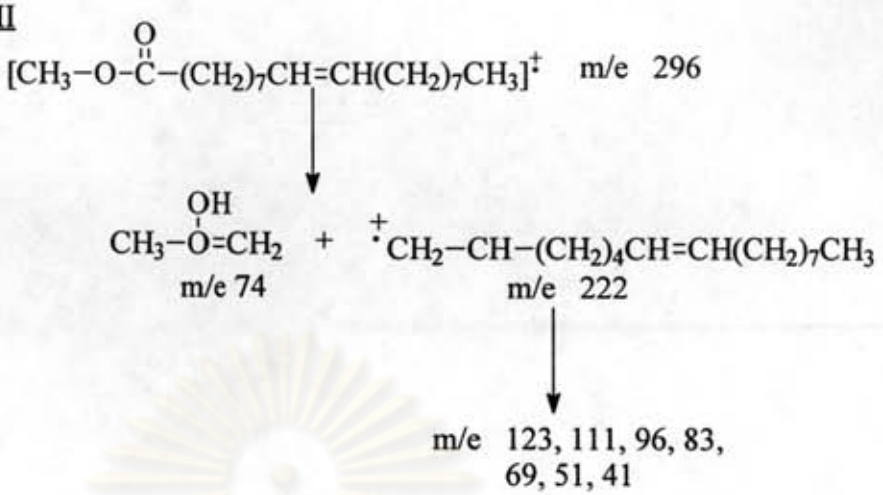
Equation II



The physical and chemical properties of the methyl ester product, are shown in Table 4.1. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E1 (palm oil) and Figure E2 (methyl ester).

Table 4.1 : The physical and chemical properties of palm oil and methyl ester of palm oil

Properties	Palm Oil	Methyl Ester Product
Color, ASTM	1.0	1.5
Kinematic Viscosity		
@ 40 °C, cSt	40.26	5.78
@ 100 °C, cSt	8.37	2.03
Viscosity Index	190.48	169.33
Pour Point, °C	+12	-3
Flash Point, °C	314	178
Oxidation Point, °C	428	360
Oxidation Compounds, %wt	14.54	10.96

4.2 Re-transesterification of methyl ester with diols

Re-transesterification was carried out to give diesters from the methyl ester of palm oil, by reaction with the diols using concentrated sulfuric acid as a catalyst.

The optimum conditions for re-transesterification with each diol was obtained by varing reaction temperature and reaction time. In this study, the reaction temperature was varied between 70, 80, and 90 °C. While the reaction was performed at various temperature, the reaction time was varied between 3 and 6 hours.

Characteristics of diester products were determined by ^{13}C-NMR and GC-MS.

The ^{13}C-NMR spectrum of 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol, and 2-ethyl-1,3-hexanediol are shown in Figures A6, A7, A8, A9, and A10, respectively.

4.2.1 Re-transesterification of the methyl ester of palm oil with 1,3-propanediol

The results of 1,3-propanediester from re-transesterification at optimum condition are shown by ^{13}C-NMR and GC-MS spectrum in Figure A12, C2, and D3 to D4 respectively.

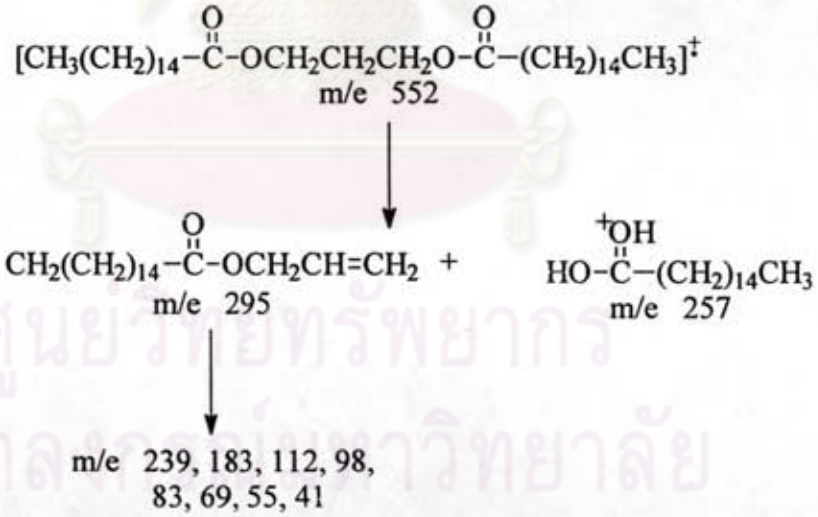
Figure A12,^{13}C-NMR, when the reaction temperature was 80 °C and the reaction time was 3 hours, the peak of CH_3-O- at 50.9 ppm disappeared and the peak of -CH_2-O- appeared at 60.9 ppm. In addition, Figure A12 also shows the peak of C=O (ester group) at 173.9 ppm and the peaks of alkenes at between 127 and 130 ppm.

These experimental results indicate that the re-transesterification reaction of methyl ester of palm oil with 1,3-propanediol was completed with a reaction temperature of 80 °C and reaction time of 3 hours. In this study, the yield of the resulting product was 89.56 %.

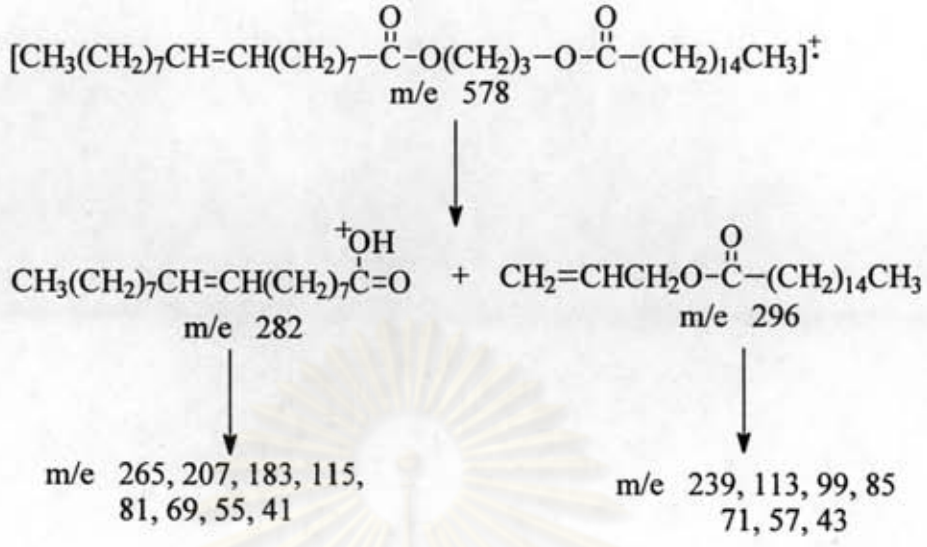
The composition of the 1,3-propanediester product was determined by GC-MS which was performed on a DB-1 capillary column. The GC-MS chromatograms are shown in Figures C2 and D3 to D4.

Figure C2, indicates that the 1,3-propanediester product is composed of a mixture of 1,3-propanediesters having long chain fatty acid groups. The main components are 1,3-propanedipalmitate and 1,3-propanepalmitate-oleate, at retention times 10.594 and 12.392 min, respectively.

The Mass-spectrum of 1,3-propanedipalmitate (MW 552) at retention time 10.594 min in Figure D3, fragmentation could occur as the following equation :



The Mass-spectrum of 1,3-propanepalmitate-oleate (MW 578) at retention time 12.392 min in Figure D4, fragmentation could occur as the following equation :



The 1,3-propanediester product from the methyl ester of the palm oil was a semisolid, and the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were determined and the results are shown in Figure E3.

The results from Figure E3 indicate that the oxidation point is 463 °C and the oxidative compounds are 1.98 %wt.

4.2.2 Re-transesterification of the methyl ester of palm oil with 1,4-butanediol

The results of 1,4-butanediester from re-transesterification under optimum condition are shown by ^{13}C-NMR and GC-MS spectrum in Figure A13, C3, and D5 to D6 respectively.

Figure A13, ^{13}C-NMR spectrum, when the reaction temperature was 80 °C and the reaction time was 3 hours, the peak of CH_3-O- at 51.1 ppm disappeared and the peak of -CH_2-O- appeared at 64 ppm. In addition,

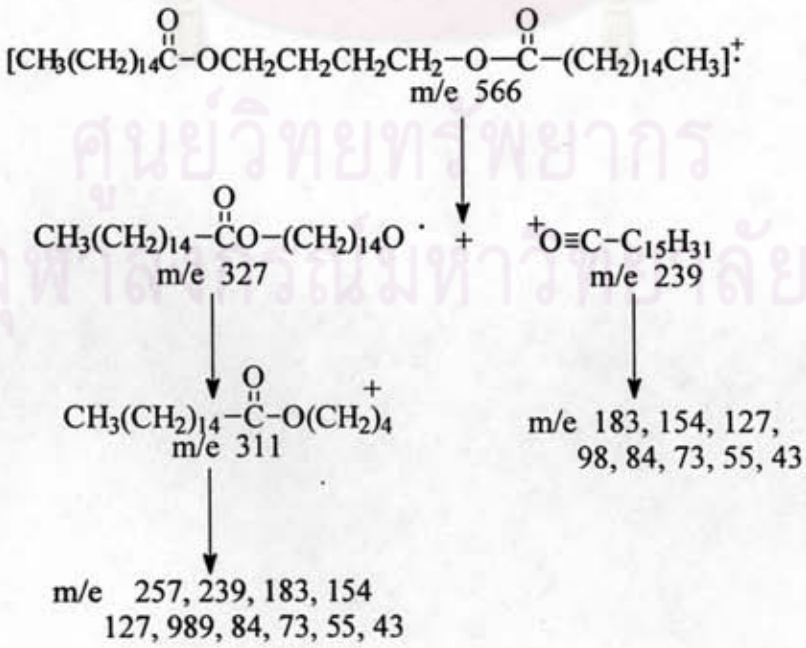
Figure A13 also shows peak of C=O (ester group) at 173.9 ppm and the peaks of alkenes at between 126 and 130 ppm.

These experimental results indicate that the re-transesterification reaction of methyl ester of palm oil with 1,4-butanediol was completed with a reaction temperature of 80 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 92.15 %.

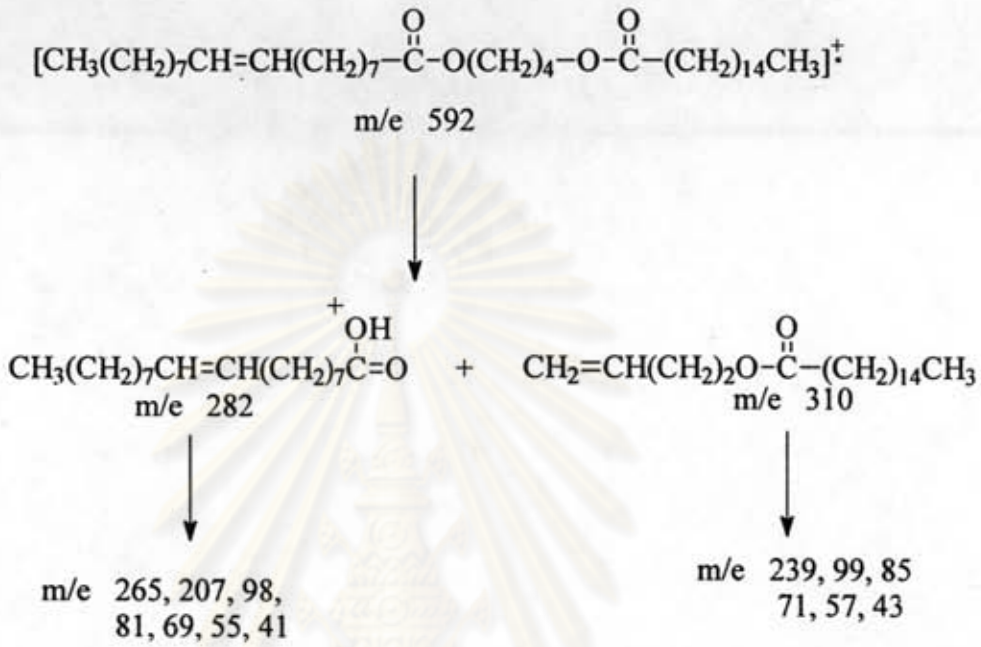
The composition of 1,4-butanediester product was determined by GC-MS which was performed on a DB-1 capillary column. The GC-MS chromatogram is shown in Figure C3 and D5 to D6.

Figure C3, indicates that the 1,4-butanediester product is composed of a mixture of 1,4-butanediester of long chain fatty acid. The main components are 1,4-butanedipalmitate and 1,4-butaneoleate-palmitate, at retention times 11.016 and 12.547 min, respectively.

The Mass-spectrum of 1,4-butanedipalmitate (MW 566) at retention time 11.016 min in Figure D5, fragmentation could occur as the following equation :



The Mass-spectrum of 1,4-butaneoleate-palmitate (MW 592) at retention time 12.547 min in Figure D6, fragmentation could occur as the following equaticn :



The 1,4-butanediester product from the methyl ester of palm oil was a semisolid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E4.

The results from Figure E4 indicate that the oxidation point 478 °C and the oxidative compounds are 1.70 %wt.

4.2.3 Re-transesterification of the methyl ester of palm oil with 1,5-pentanediol

The results of 1,5-pentanediester from re-transesterification under optimum condition are shown by ^{13}C-NMR and GC-MS spectrum in Figure A14, C4, and D7 to D8 respectively.

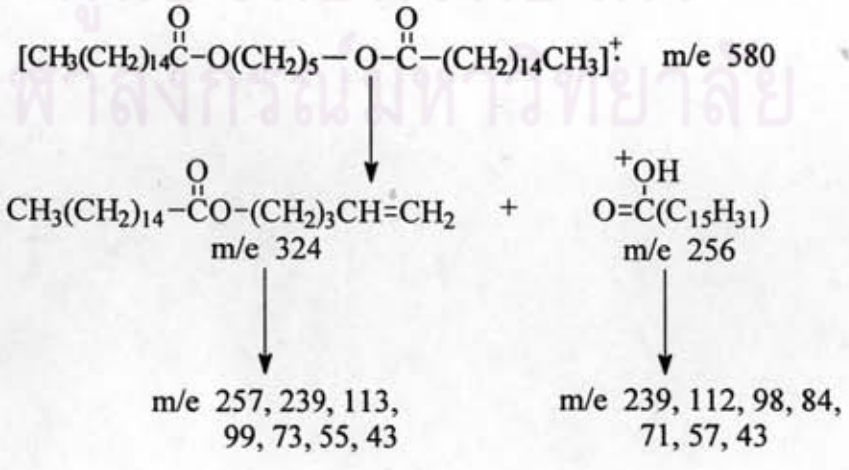
Figure A14, ^{13}C-NMR spectrum, when the reaction temperature was 80 °C and the reaction time was 3 hours, the peak of CH_3-O- at 51.1 ppm disappeared and the peak of -CH_2-O- appeared at 64.2 ppm. In addition, Figure A14 also shows the peak of C=O (ester group) at 173.9 ppm and the peaks of alkenes at between 126 and 130 ppm.

These experimental results indicate that the re-transesterification reaction of methyl ester of palm oil with 1,5-pentanediol was completed with a reaction temperature of 80 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 87.83 %.

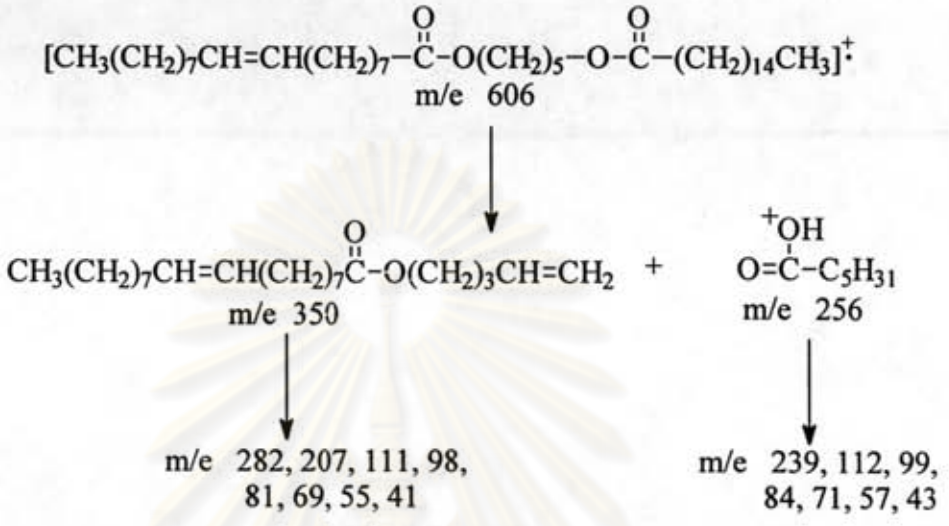
The composition of 1,5-pentaediester product was determined by GC-MS which was performed on a DB-1 capillary column. The GC-MS chromatogram is shown in Figure C4 and D7 to D8.

Figure C34, indicates that the 1,5-pentanediester product is composed of a mixture of 1,5-pentanediester of long chain fatty acid. The main components are 1,5-pentanedipalmitate and 1,5-pentanepalmitate-oleate, at retention times 11.412 and 13.049 min, respectively.

The Mass-spectrum of 1,5-pentanedipalmitate (MW 580) at retention time 11.412 min in Figure D7, fragmentation could occur as the following equation :



The Mass-spectrum of 1,5-pentaneoleate-palmitate (MW 606) at retention time 13.049 min in Figure D8, fragmentation could occur as the following equation :



The 1,5-pentanediester product from the methyl ester of palm oil was a semisolid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E5.

The results from Figure E5 indicate that the oxidation point 463 °C and the oxidative compounds are 1.47 %wt.

4.2.4 Re-transesterification of the methyl ester of palm oil with 2,2-dimethyl-1,3-propanediol

The results of 2,2-dimethyl-1,3-propanediester from re-transesterification under optimum condition are shown by ^{13}C-NMR and GC-MS spectrum in Figure A15, C5, and D9 to D10 respectively.

Figure A15, ^{13}C-NMR spectrum, when the reaction temperature was 80 °C and the reaction time was 3 hours, the peak of CH_3-O- at 51.1 ppm

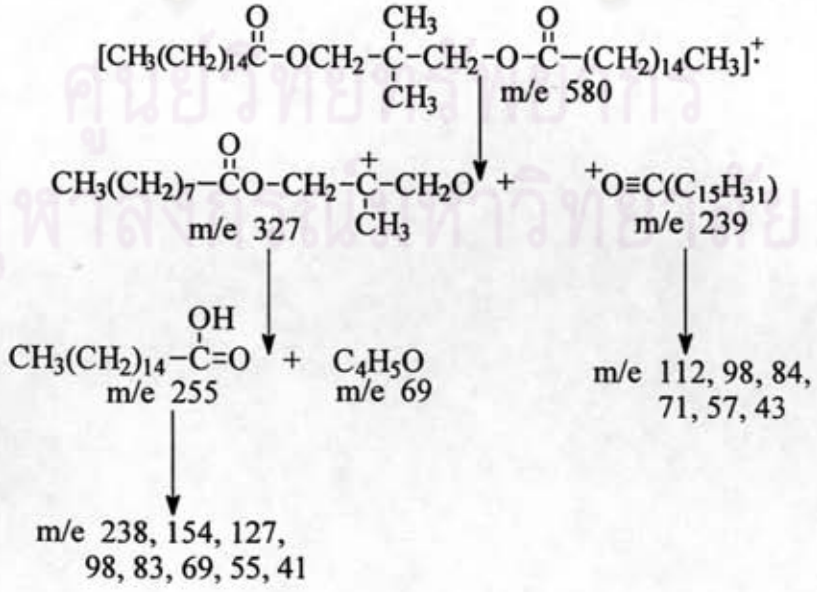
disappeared and the peak of -CH_2-O- appeared at 68.5 ppm. In addition, Figure A15 also shows the peak of C=O (ester group) at 173.9 ppm and the peaks of alkenes at between 126 and 130 ppm.

These experimental results indicate that the re-transesterification reaction of the methyl ester of palm oil with 2,2-dimethyl-1,3-propanediol was completed with a reaction temperature of 80 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 85.67 %.

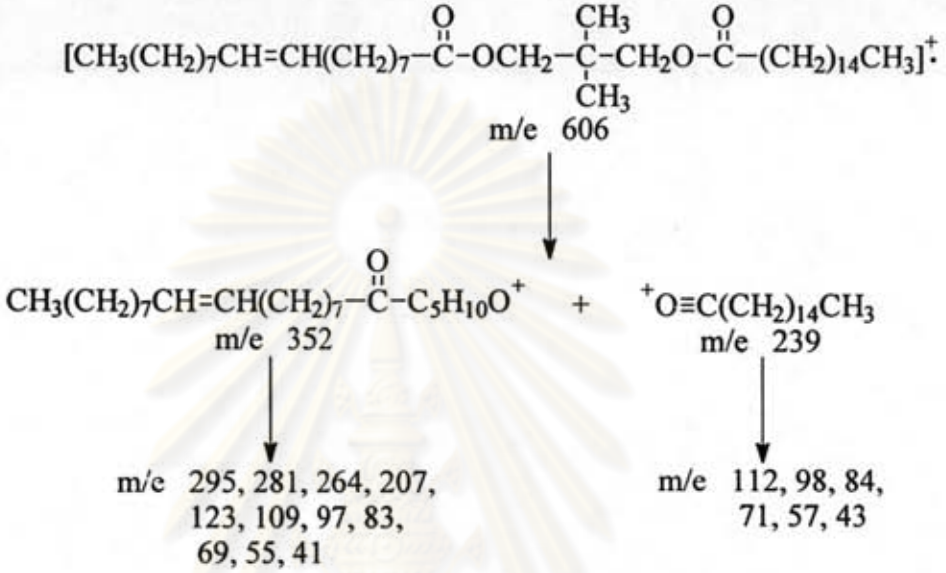
The composition of 2,2-dimethyl-1,3-propanediester product was determined by GC-MS which was performed on a DB-1 capillary column. The GC-MS chromatogram is shown in Figure C5 and D9 to D10.

Figure C5, indicates that the 2,2-dimethyl-1,3-propanediester product is composed of a mixture of 2,2-dimethyl-1,3-propanediester of long chain fatty acid. The main components are 2,2-dimethyl-1,3-propanedipalmitate and 2,2-dimethyl-1,3-propaneoleate-palmitate, at retention times 12.342 and 14.244 min, respectively.

The Mass-spectrum of 2,2-dimethyl-1,3-propanedipalmitate (MW 580) at retention time 12.342 min in Figure D9, fragmentation could occur as the following equation :



The Mass-spectrum of 2,2-dimethyl-1,3-propaneoleate-palmitate (MW 606) at retention time 14.244 min in Figure D10, fragmentation could occur as the following equation :



The following physical and chemical properties, as shown in Table 4.2, were studied : color, pour point, kinematic viscosity at 40 and 100 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E1 (palm oil) and Figure E6 (2,2-dimethyl-1,3-propanediester product).

Table 4.2 : The physical and chemical properties of palm oil and 2,2-dimethyl-1,3-propanediester product

Properties	Palm Oil	2,2-dimethyl-1,3-propanediester product
Color, ASTM	1.0	1.5
Kinematic Viscosity		
@ 40 °C, cSt	40.26	15.36
@ 100 °C, cSt	8.37	4.07
Viscosity Index	190.48	178.08
Pour Point, °C	+12	-3
Flash Point, °C	314	206
Oxidation Point, °C	428	500
Oxidation Compounds, %wt	14.54	1.42

4.2.5 Re-transesterification of the methyl ester of palm oil with 2-ethyl-1,3-hexanediol

The results of 2-ethyl-1,3-hexanediester from re-transesterification under optimum condition are shown by ^{13}C-NMR and GC-MS spectrum in Figure A16, C6, and D11 to D12, respectively.

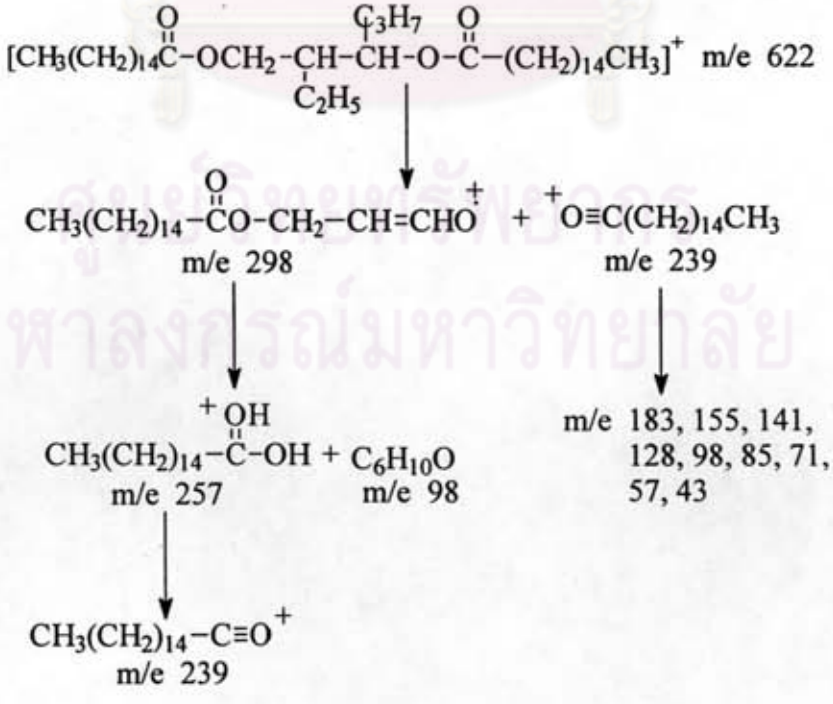
Figure A16, ^{13}C-NMR spectrum, when reaction temperature was 80 °C and reaction time was 3 hours, the peak of CH_3-O- at 51.1 ppm disappeared, the peak of -CH_2-O- appeared at 63.5 ppm and the peak of -CH-O- appeared at 73.5 ppm. In addition, Figure A16 also shows the peaks of C=O (ester group) at 173 and 173.5 ppm and the peaks of alkenes at between 126 and 130 ppm.

These experimental results indicate that the re-transesterification reaction of the methyl ester of palm oil with 2-ethyl-1,3-hexanediol was completed with a reaction temperature of 80 °C and reaction time of 3 hours. In this study, the yield of the resulting product was 88.72 %.

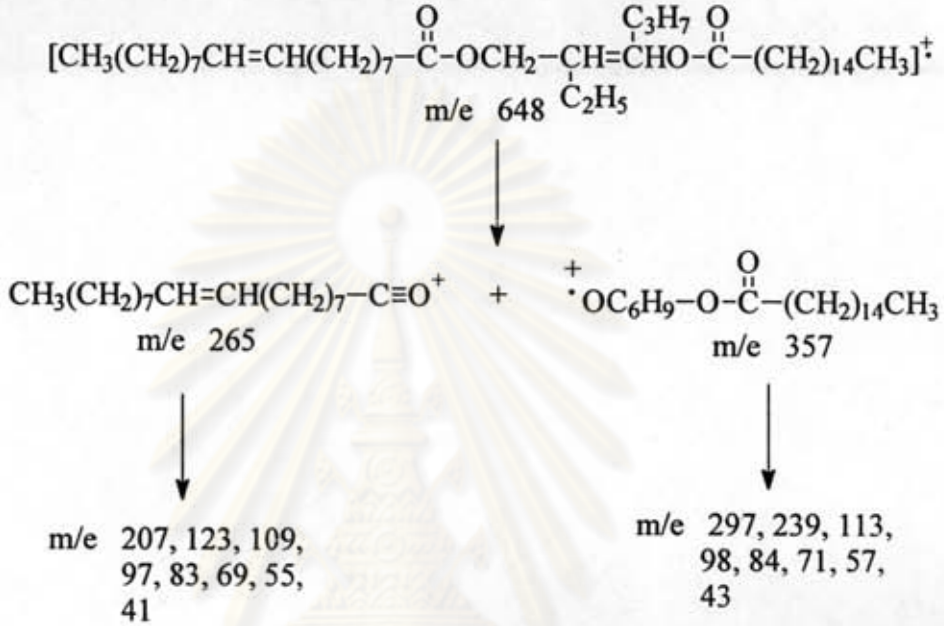
The composition of 2-ethyl-1,3-hexanediester product was determined by GC-MS which was performed on a DB-1 capillary column. The GC-MS chromatogram is shown in Figure C6 and D11 to D12.

Figure C6, indicates that the 2-ethyl-1,3-hexanediester product is composed of a mixture of 2-ethyl-1,3-hexanediester of long chain fatty acid. The main components are 2-ethyl-1,3-hexanedipalmitate and 2-ethyl-1,3-hexaneoleate-palmitate, at retention times 10.724 and 12.125 min, respectively.

The Mass-spectrum of 2-ethyl-1,3-hexanedipalmitate (MW 622) at retention time 10.724 min in Figure D11, fragmentation could occur as the following equation :



The Mass-spectrum of 2-ethyl-1,3-hexaneoleate-palmitate (MW 648) at retention time 12.125 min in Figure D12, fragmentation could occur as the following equation :



The following physical and chemical properties, as shown in Table 4.3, were studied : color, pour point, kinematic viscosity at 40 and 100 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E1 (palm oil) and Figure E7 (2-ethyl-1,3-hexanediester product).

Table 4.3 : The physical and chemical properties of palm oil and 2-ethyl-1,3-hexanediester product

Properties	Palm Oil	2-ethyl-1,3-hexanediester product
Color, ASTM	1.0	2.0
Kinematic Viscosity		
@ 40 °C, cSt	40.26	22.95
@ 100 °C, cSt	8.37	5.24
Viscosity Index	190.48	170.83
Pour Point, °C	+12	-9
Flash Point, °C	314	208
Oxidation Point, °C	428	488
Oxidation Compounds, %wt	14.54	2.01

4.3 Esterification of fatty acids with diols

Esterification process was carried out to give diesters from fatty acids (e.g. oleic acid, stearic acid and palmitic acid) by reacting with the diols (e.g. 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol and 2-ethyl-1,3-hexanediol) in toluene (azeotroping agent) and using concentrated sulfuric acid as a catalyst.

The optimum condition for esterification with each fatty acid and each diol were obtained by varying reaction temperature and reaction time. In this study, the reaction temperature was varied from 110 to 150 °C. While the reaction was performed at various temperature, the reaction time was varied between 3 and 6 hours.

Characteristics of the diester products were determine by ^{13}C-NMR, FTIR and GC-MS.

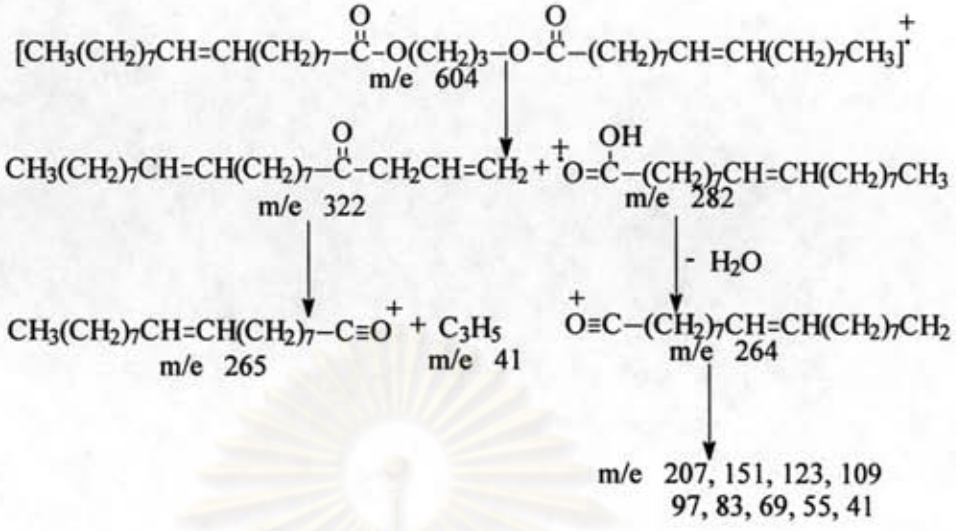
4.3.1 Esterification of oleic acid with 1,3-propanediol

The results of 1,3-propanedioleate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A17, B17, C7, and D13, respectively.

Figure A17, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and -CH_2-O- of diester product appeared at 173.9 and 61 ppm, respectively. In addition, Figure A17 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B17, FTIR spectrum at this condition demonstrate that the peak of C=O (carbonyl group) shifted from 1,701 cm^{-1} (carboxylic acid) to 1,741 cm^{-1} (ester) and the peak of -C-O- shows at 1,173 cm^{-1} (ester).

These experimental results indicate that the esterification of oleic acid with 1,3-propanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 87.35 %.

Figure C7, GC-chromatogram, indicates that 1,3-propanedioleate is shown at retention time 13.953 min. The Mass-spectrum is shown in Figure D13, fragmentation could occur as the following equation :



The following physical and chemical properties, as shown in Table 4.4, were studied : color, pour point, kinematic viscosity at 40 and 10 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E8.

Table 4.4 : The physical and chemical properties of 1,3-propane-dioleate

Properties	1,3-propanedioleate
Color, ASTM	1.5
Kinematic Viscosity	
@ 40 °C, cSt	20.82
@ 100 °C, cSt	5.38
Viscosity Index	213.86
Pour Point, °C	-9
Flash Point, °C	206
Oxidation Point, °C	463
Oxidation Compounds, %wt	4.90

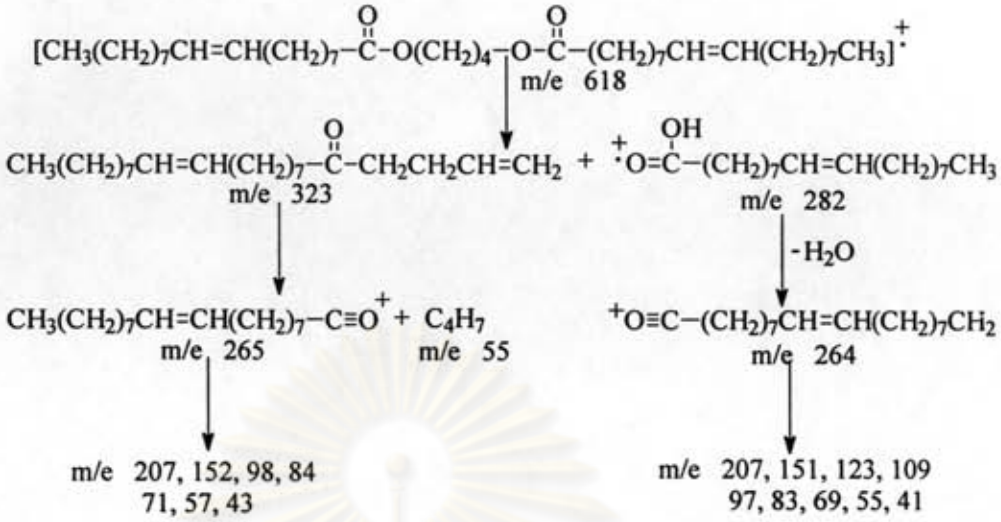
4.3.2 Esterification of oleic acid with 1,4-butanediol

The results of 1,4-butanedioleate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A18, B18, C8, and D14, respectively.

Figure A18, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and -CH_2-O- of diester product appeared at 173.9 and 64 ppm, respectively. In addition, Figure A18 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B18, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,701 cm^{-1} (carboxylic acid) to 1,736 cm^{-1} (ester), and peak of -C-O- at 1,168 cm^{-1} (ester).

These experimental results indicate that the esterification of oleic acid with 1,4-butanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 88.25 %.

Figure C8, GC-chromatogram, indicates that 1,4-butanedioleate is shown at retention time 15.382 min. The Mass-spectrum is shown in Figure D14, fragmentation could occur as the following equation :



The following physical and chemical properties, as shown in Table 4.5, were studied : color, pour point, kinematic viscosity at 40 and 10 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E9.

Table 4.4 : The physical and chemical properties of 1,4-butanedioleate

Properties	1,4-butanedioleate
Color, ASTM	1.5
Kinematic Viscosity	
@ 40 °C, cSt	21.56
@ 100 °C, cSt	5.53
Viscosity Index	214.61
Pour Point, °C	-9
Flash Point, °C	212
Oxidation Point, °C	475
Oxidation Compounds, %wt	3.47

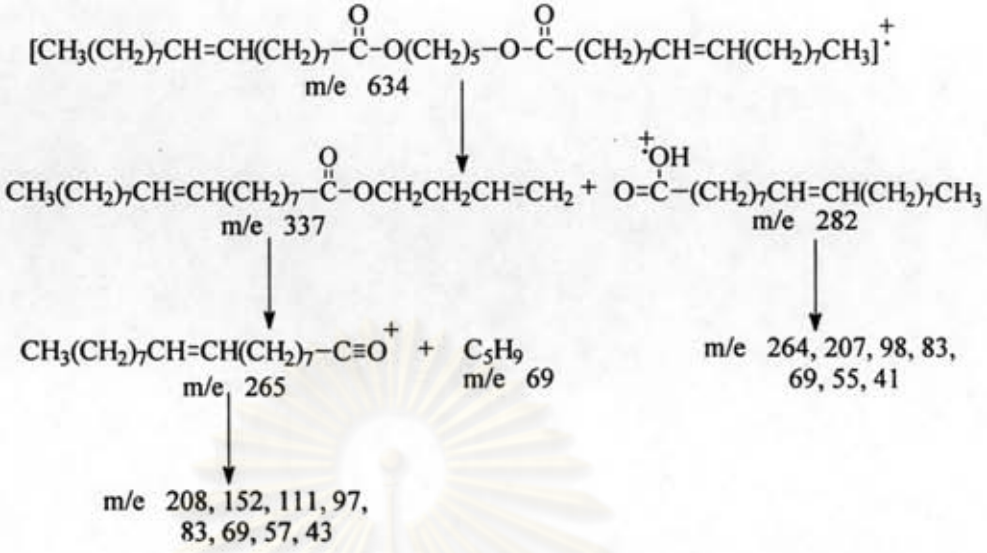
4.3.3 Esterification of oleic acid with 1,5-pentanediol

The results of 1,5-pentanedioleate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A19, B19, C9, and D15, respectively.

Figure A19, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and -CH_2-O- of diester product appeared at 173.9 and 64 ppm, respectively. In addition, Figure A19 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B19, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,701 cm^{-1} (carboxylic acid) to 1,741 cm^{-1} (ester) and shows the peak of -C-O- at 1,173 cm^{-1} (ester).

These experimental results indicate that the esterification of oleic acid with 1,5-pentanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 89.17 %.

Figure C9, GC-chromatogram, indicates that 1,5-pentanedioleate is shown at retention time 16.898 min. The Mass-spectrum is shown in Figure D15, fragmentation could occur as the following equation :



The following physical and chemical properties, as shown in Table 4.6, were studied : color, pour point, kinematic viscosity at 40 and 10 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E10.

Table 4.6 : The physical and chemical properties of 1,5-pentane-dioleate

Properties	1,5-pentanedioleate
Color, ASTM	1.5
Kinematic Viscosity	
@ 40 °C, cSt	23.21
@ 100 °C, cSt	5.88
Viscosity Index	216.86
Pour Point, °C	-9
Flash Point, °C	234
Oxidation Point, °C	438
Oxidation Compounds, %wt	3.29

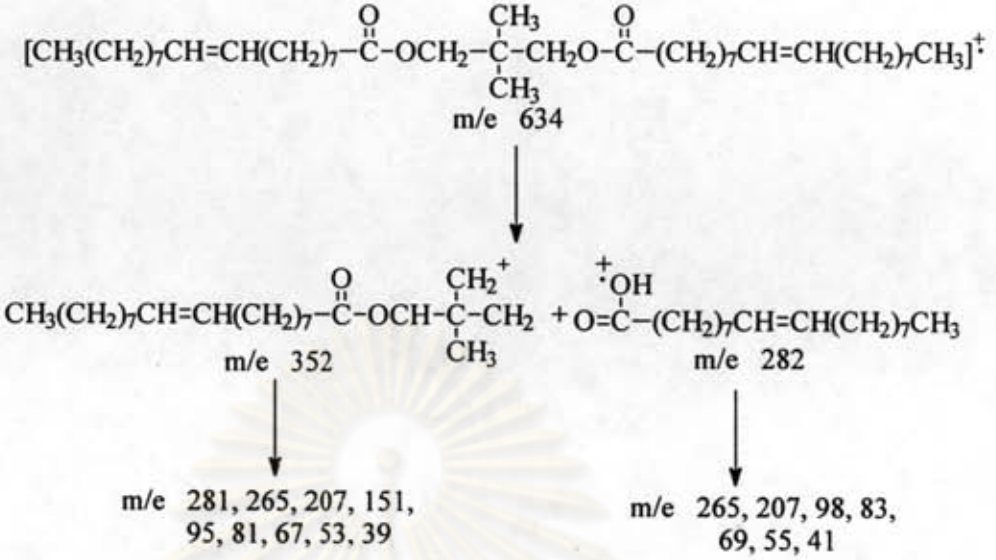
4.3.4 Esterification of oleic acid with 2,2-dimethyl-1,3-propanediol

The results of 2,2-dimethyl-1,3-propanedioleate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A20, B20, C10, and D16, respectively.

Figure A20, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxy group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and -CH_2-O- of diester product appeared at 173 and 68.5 ppm, respectively. In addition, Figure A20 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B17, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,701 cm^{-1} (carboxylic acid) to 1,741 cm^{-1} (ester) and peak of -C-O- at 1,173 cm^{-1} (ester).

These experimental results indicate that the esterification of oleic acid with 2,2-dimethyl-1,3-propanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 89.56 %.

Figure C10, GC-chromatogram, indicates that 2,2-dimethyl-1,3-propanedioleate is shown at retention time 14.427 min. The Mass-spectrum is shown in Figure D16, fragmentation could occur as the following equation :



The following physical and chemical properties, as shown in Table 4.7, were studied : color, pour point, kinematic viscosity at 40 and 10 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E11.

Table 4.7 : The physical and chemical properties of 2,2-dimethyl-1,3-propanedioleate

Properties	2,2-dimethyl-1,3-propanedioleate
Color, ASTM	1.5
Kinematic Viscosity	
@ 40 °C, cSt	18.72
@ 100 °C, cSt	4.81
Viscosity Index	195.07
Pour Point, °C	-12
Flash Point, °C	208
Oxidation Point, °C	463
Oxidation Compounds, %wt	1.15

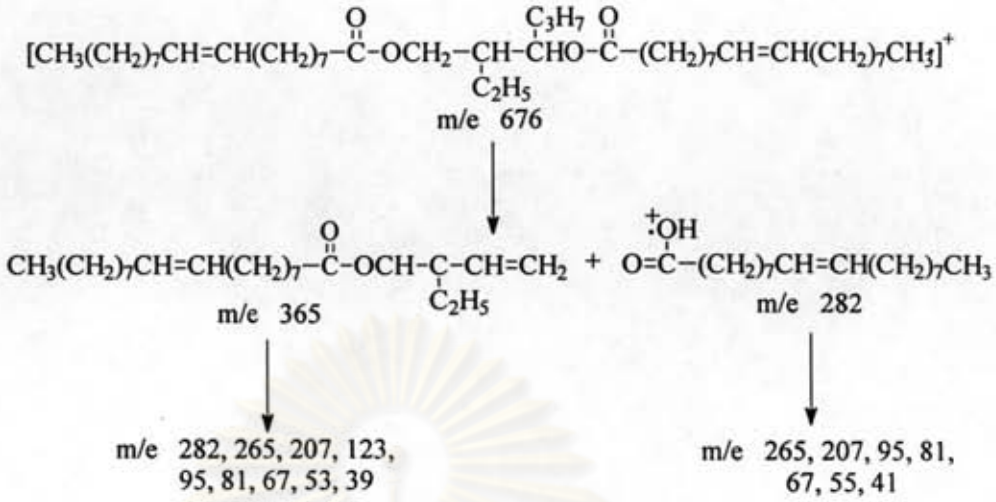
4.3.5 Esterification of oleic acid with 2-ethyl-1,3-hexanediol

The results of 2-ethyl-1,3-hexanedioleate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A21, B21, C11, and D17, respectively.

Figure A21, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) appeared at 173 and 173.5 ppm peak of -CH-O-, and peak of $-CH_2-O-$ diester product appeared at 73 and 63 ppm, respectively. In addition, Figure A21 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B21, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,701 cm^{-1} (carboxylic acid) to 1,741 cm^{-1} (ester) and the peak of -C-O shows at 1,168 cm^{-1} (ester).

These experimental results indicate that the esterification of oleic acid with 2-ethyl-1,3-hexanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 86.78 %.

Figure C11, indicates that 2-ethyl-1,3-hexanedioleate is shown at retention time 16.713 min. The Mass-spectrum is shown in Figure D17, fragmentation could occur as the following equation :



The following physical and chemical properties, as shown in Table 4.8, were studied : color, pour point, kinematic viscosity at 40 and 10 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E12.

Table 4.8 : The physical and chemical properties of 2-ethyl-1,3-hexanedioleate

Properties	2-ethyl-1,3-hexanedioleate
Color, ASTM	2.0
Kinematic Viscosity	
@ 40 °C, cSt	21.52
@ 100 °C, cSt	5.15
Viscosity Index	182.62
Pour Point, °C	-15
Flash Point, °C	212
Oxidation Point, °C	488
Oxidation Compounds, %wt	2.50

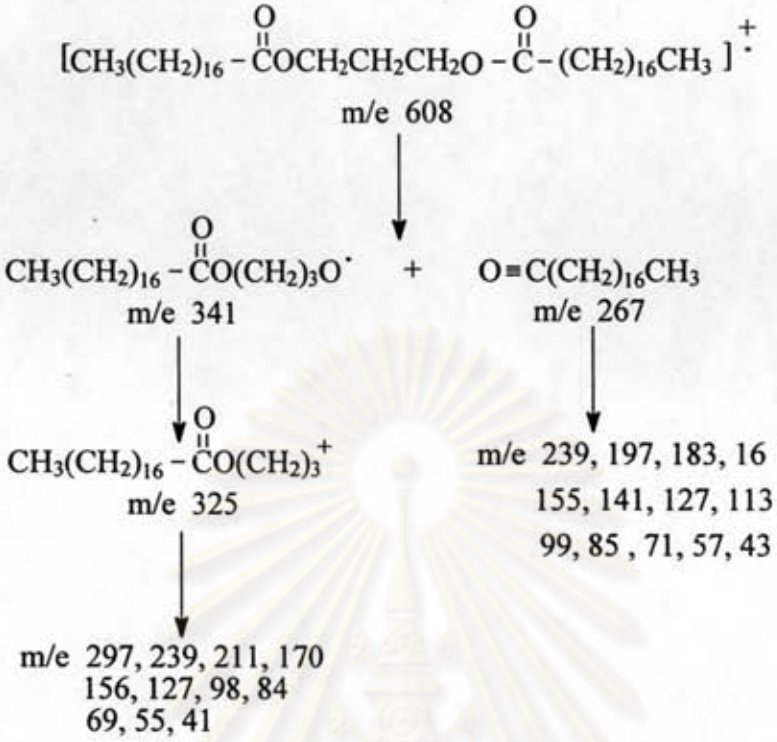
4.3.6 Esterification of stearic acid with 1,3-propanediol

The results of 1,3-propanedistearate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A22, B22, C12, and D18, respectively.

Figure A22, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and peak of -CH_2-O- of diester product appeared at 173.9 and 61 ppm, respectively. In addition, Figure A22 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B22, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,707 cm^{-1} (carboxylic acid) to 1,729 cm^{-1} (ester) and the peak of -C-O- shows at 1,180 cm^{-1} (ester).

These experimental results indicate that the esterification of stearic acid with 1,3-propanediol was completed with a reaction temperature of 130 °C and reaction time of 3 hours. In this study, the yield of the resulting product was 89.15 %.

Figure C12, GC-chromatogram, indicates that 1,3-propanedistearate is shown at retention time 10.727 min. The Mass-spectrum is shown in Figure D18, fragmentation could occur as the following equation :



The 1,3-propanedistearate was a solid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E13.

The results from Figure E13 indicate that the oxidation point 488 °C and the oxidative compounds are 3.59 %wt.

4.3.7 Esterification of stearic acid with 1,4-butanediol

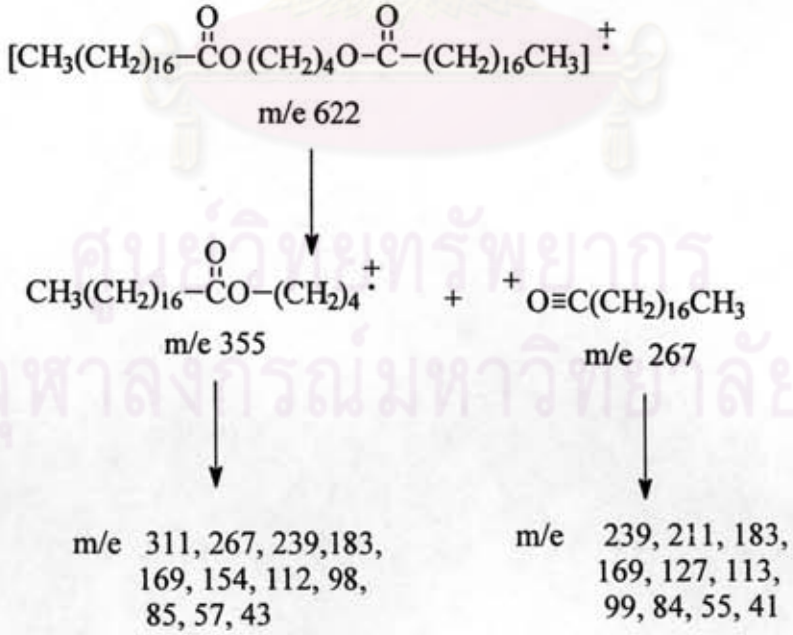
The results of 1,4-butanedistearate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A23, B23, C13, and D19, respectively.

Figure A23, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group)

and peak of -CH_2-O-of diester product appeared at 173.9 and 64 ppm, respectively. In addition, Figure A23 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B23, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,707 cm^{-1} (carboxylic acid) to 1,739 cm^{-1} (ester) and appears the peak of -C-O- at 1,180 cm^{-1} (ester).

These experimental results indicate that the esterification of stearic acid with 1,4-butanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 92.43 %.

Figure C13, GC-chromatogram, indicates that 1,4-butanedistearate is shown at retention time 11.467 min. The Mass-spectrum is shown in Figure D19, fragmentation could occur as the following equation :



The 1,4-butanedistearate was a solid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E14.

The results from Figure E14 indicate that the oxidation point 490 °C and the oxidative compounds are 3.10 %wt.

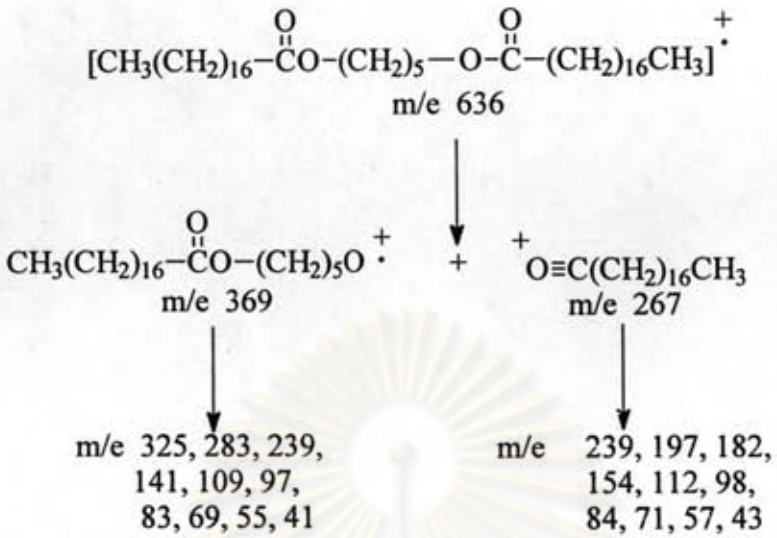
4.3.8 Esterification of stearic acid with 1,5-pentanediol

The results of 1,5-pentanedistearate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A24, B24, C14, and D20, respectively.

Figure A24, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and peak of -CH_2-O- of diester product appeared at 173.5 and 64 ppm, respectively. In addition, Figure A24 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B24, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,707 cm^{-1} (carboxylic acid) to 1,739 cm^{-1} (ester) and appears the peak of -C-O- at 1,180 cm^{-1} (ester).

These experimental results indicate that the esterification of stearic acid with 1,5-pentanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 93.78 %.

Figure C14, GC-chromatogram, indicates that 1,5-pentanedistearate is shown at retention time 12.367 min. The Mass-spectrum is shown in Figure D20, fragmentation could occur as the following equation :



The 1,5-pentanedistearate was a solid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E15.

The results from Figure E15 indicate that the oxidation point 490 °C and the oxidative compounds are 2.69 %wt.

4.3.9 Esterification of stearic acid with 2,2-dimethyl-1,3-propanediol

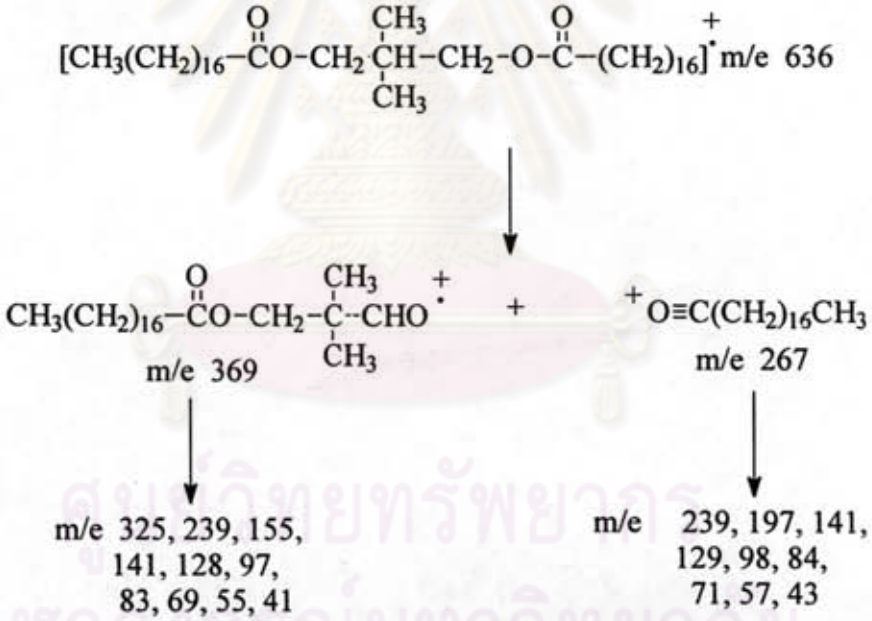
The results of 2,2-dimethyl-1,3-propanedistearate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A25, B25, C15, and D21, respectively.

Figure A25, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and peak of -CH_2-O- of diester product appeared at 173.9 and 69 ppm, respectively. In addition, Figure A25 also shows the peak of alkenes at between 126 and 130 ppm. Figure B25, FTIR spectrum at this condition

demonstrated that the peak of C=O (carbonyl group) shifted from 1,707 cm^{-1} (carboxylic acid) to 1,734 cm^{-1} (ester) and appears the peak of -C-O- at 1,180 cm^{-1} (ester).

These experimental results indicate that the esterification of stearic acid with 2,2-dimethyl-1,3-propanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 91.89 %.

Figure C15, GC-chromatogram, indicates that 2,2-dimethyl-1,3-propanedistearate is shown at retention time 11.116 min. The Mass-spectrum is shown in Figure D21, fragmentation could occur as the following equation :



The 2,2-dimethyl-1,3-propanedistearate was a solid, the physical properties could not be detrermined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E16.

The results from Figure E16 indicate that the oxidation point 480 °C and the oxidative compounds are 1.09 %wt.

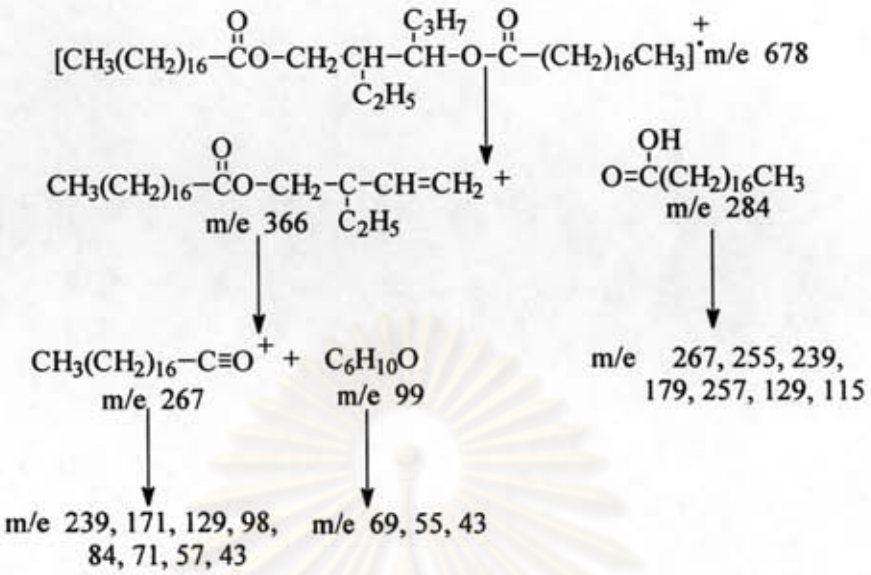
4.3.10 Esterification of stearic acid with 2-ethyl-1,3-hexanediol

The results of 2-ethyl-1,3-hexanedistearate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A26, B26, C16, and D22, respectively.

Figure A26, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) appeared at 173 and 173.5, peak of -CH-O-, and peak of -CH_2-O- of diester product appeared at 73.5 and. 63 ppm, respectively. In addition, Figure A26 also shows the peaks of alkenes at between 126 and 130 ppm. For Figure B26, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,707 cm^{-1} (carboxylic acid) to 1,745 cm^{-1} (ester) and appears the peak of-C-O- at 1,180 cm^{-1} (ester).

These experimental results indicate that the esterification of stearic acid with 2-ethyl-1,3-hexanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product is 92.55 %.

Figure C15, GC-chromatogram, indicates that 2-ethyl-1,3-hexanedistearate is shown at retention time 12.335 min. The Mass-spectrum is shown in Figure D22, fragmentation could occur as the following equation :



The following physical and chemical properties, as shown in Table 4.9, were studied : color, pour point, kinematic viscosity at 40 and 100 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E10.

Table 4.9 : The physical and chemical properties of 2-ethyl-1,3-hexanedistearate

Properties	2-ethyl-1,3-hexanedistearate
Color, ASTM	1.0
Kinematic Viscosity	
@ 40 °C, cSt	24.40
@ 100 °C, cSt	5.45
Viscosity Index	169.61
Pour Point, °C	+9
Flash Point, °C	182
Oxidation Point, °C	470
Oxidation Compounds, %wt	2.17

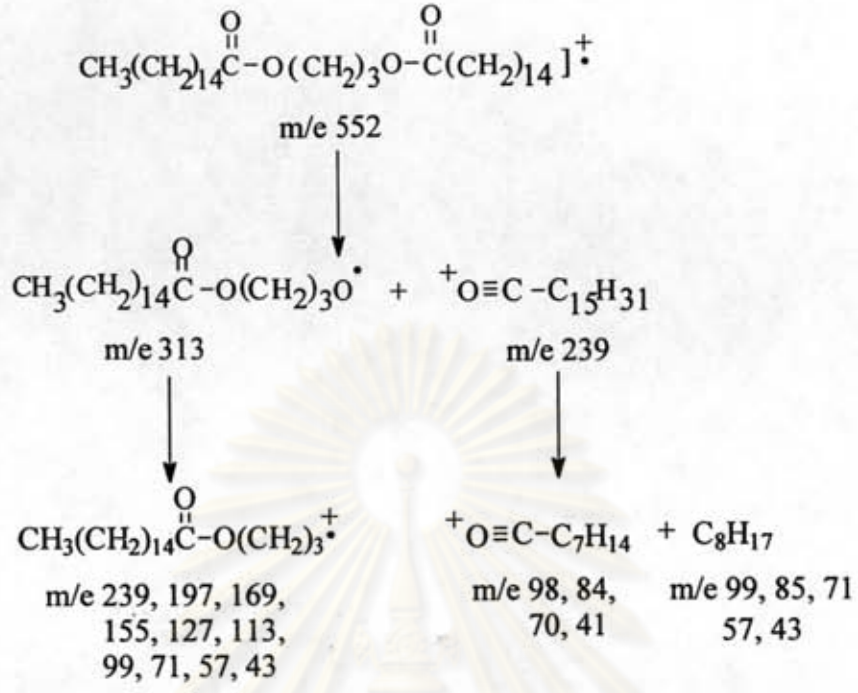
4.3.11 Esterification of palmitic acid with 1,3-propanediol

The results of 1,3-propanedioleate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A27, B27, C17, and D23, respectively.

Figure A27, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the result demonstrated that the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and peak of -CH_2-O- of diester product appeared at 173.5 and 61 ppm, respectively. In addition, Figure A27 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B27, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,702 cm^{-1} (carboxylic acid) to 1,731 cm^{-1} (ester) and appears the peak of -C-O- at 1,183 cm^{-1} (ester).

These experimental results indicate that the esterification of a palmitic acid with 1,3-propanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 92.47 %.

Figure C17, GC-chromatogram, indicates that 1,3-propanedipalmitate is shown at retention time 10.825 min. The Mass-spectrum is shown in Figure D23, fragmentation could occur as the following equation :



The 1,3-propanedipalmitate was a solid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E18.

The results from Figure E18 indicate that the oxidation point 478 °C and the oxidative compounds are 3.52 %wt.

4.3.12 Esterification of palmitic acid with 1,4-butanediol

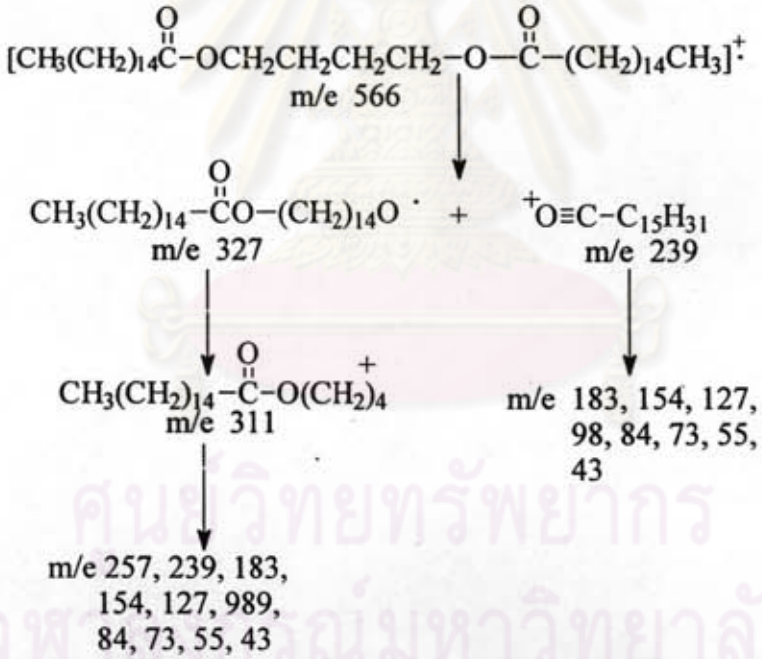
The results of 1,4-butanedipalmitate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A28, B28, C19, and D24, respectively.

Figure A28, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the result demonstrated that the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and peaks of -CH_2-O- of diester product appeared at 173.9 and 64 ppm, respectively. In addition, Figure A28

also shows the peaks of alkenes at between 126 and 130 ppm. For Figure B28, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,702 cm^{-1} (carboxylic acid) to 1,741 cm^{-1} (ester) and shows the peak of -C-O- at 1,183 cm^{-1} (ester).

These experimental results indicate that the esterification of palmitic acid with 1,4-butanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 93.32 %.

Figure C18, GC-chromatogram, indicates that 1,4-butanedipalmitate is shown at retention time 11.611 min. The Mass-spectrum is shown in Figure D24, fragmentation could occur as the following equation :



The 1,4-butanedipalmitae was a solid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E19.

The results from Figure E19 indicate that the oxidation point 390 °C and the oxidative compounds are 2.99 %wt.

4.3.13 Esterification of palmitic acid with 1,5-pentanediol

The results of 1,5-pentanedipalmitate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A29, B29, C19, and D25, respectively.

Figure A29, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) and peak of -CH_2-O- of diester product appeared at 173.9 and 64.5 ppm, respectively. In addition, Figure A29 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B29, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,702 cm^{-1} (carboxylic acid) to 1,731 cm^{-1} (ester) and shows the peak of -C-O- at 1,178 cm^{-1} (ester).

These experimental results indicate that the esterification of palmitic acid with 1,5-pentanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 91.58 %.

Figure C19, GC-chromatogram, indicates that 1,5-pentanedipalmitate is shown at retention time 12.639 min. The Mass-spectrum is shown in Figure D29, fragmentation could occur as the following equation :

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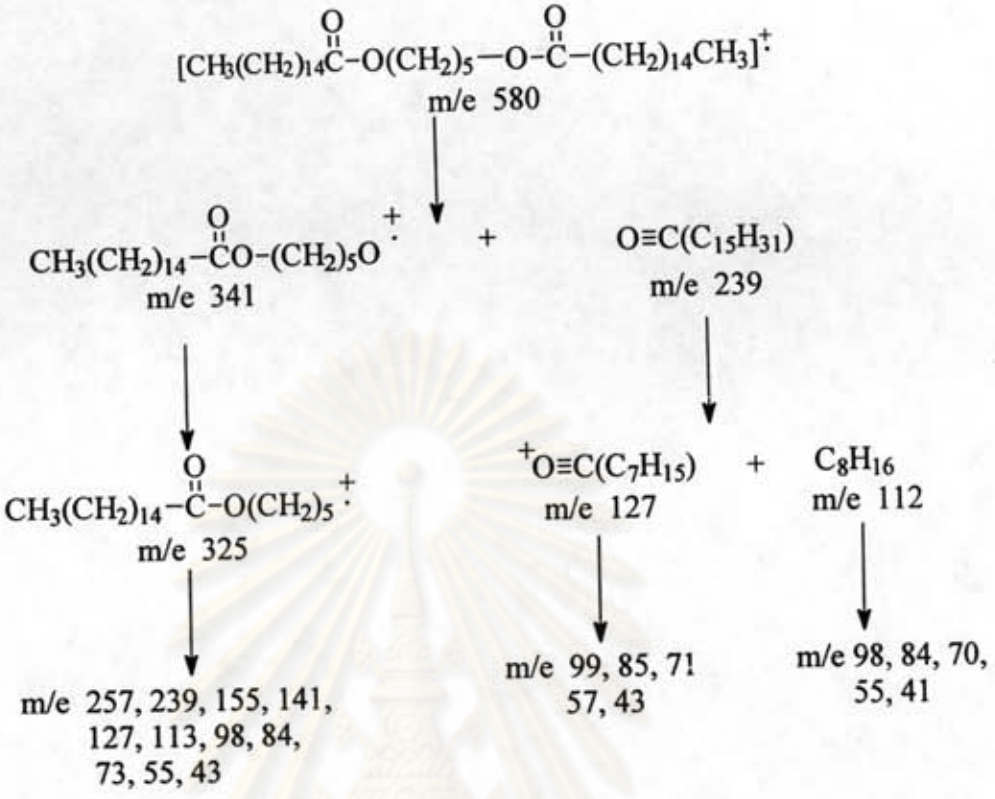


The 1,5-pentanedipalmitate was a solid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E20.

The results from Figure E20 indicate that the oxidation point 490 °C and the oxidative compounds are 2.00 %wt.

4.3.14 Esterification of palmitic acid with 2,2-dimethyl-1,3-propanediol

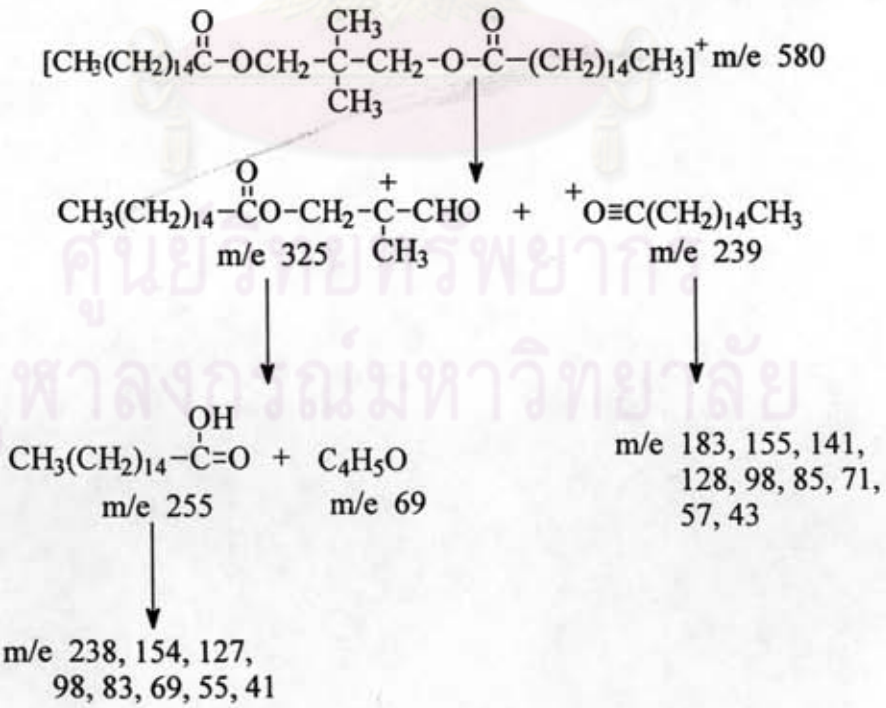
The result of 2,2-dimethyl-1,3-propanedipalmitate from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A30, B30, C20, and D26, respectively.

Figure A30, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester

group) and peak of $-CH_2-O-$ of diester product appeared at 173.9 and 59 ppm, respectively. In addition, Figure A30 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B30, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,702 cm^{-1} (carboxylic acid) to 1,736 cm^{-1} (ester) and shows the peak of -C-O- at 1,178 cm^{-1} (ester).

These experimental results indicate that the esterification of palmitic acid with 2,2-dimethyl-1,3-propanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 89.95 %.

Figure C20, GC-chromatogram, indicates that 2,2-dimethyl-1,3-propanedipalmitate is shown at retention time 11.089 min. The Mass-spectrum is shown in Figure D26, fragmentation could occur as the following equation :



The 2,2-dimethyl-1,3-propanedipalmitate was a solid, the physical properties could not be determined. The chemical properties, oxidation and thermal stability, were analyzed by TGA analyzer and the results are shown in Figure E21.

The results from Figure E21 indicate that the oxidation point 488 °C and the oxidative compounds are 1.43 %wt.

4.3.15 Esterification of palmitic acid with 2-ethyl-1,3-hexanediol

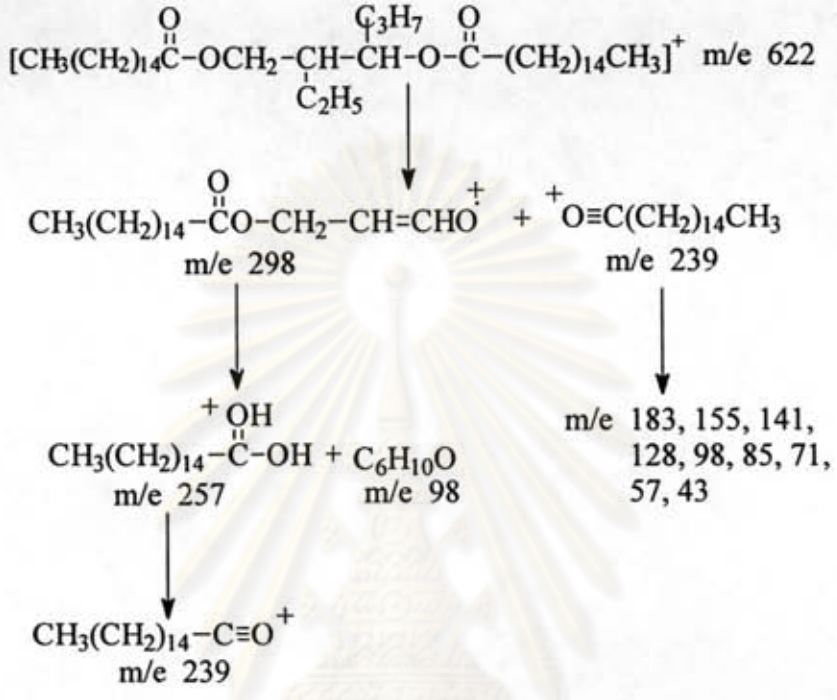
The results of 2-ethyl-1,3-hexanedipalmitic from esterification under optimum condition are shown by ^{13}C-NMR, FTIR and GC-MS spectrum in Figure A31, B31, C21, and D27, respectively.

Figure A31, ^{13}C-NMR spectrum, when the reaction temperature was 130 °C and the reaction time was 3 hours, the peak of carboxylic group of fatty acid at 180 ppm disappeared and the important peak of C=O (ester group) at 173 and 173.5 peak of -CH-O-, and peak of -CH_2-O- of diester product appeared at 73 and 63 ppm, respectively. In addition, Figure A31 also shows the peaks of alkenes at between 126 and 130 ppm. Figure B31, FTIR spectrum at this condition demonstrated that the peak of C=O (carbonyl group) shifted from 1,702 cm^{-1} (carboxylic acid) to 1,736 cm^{-1} (ester) and shows the peak of -C-O- at 1,173 cm^{-1} (ester).

These experimental results indicate that the esterification of palmitic acid with 2-ethyl-1,3-hexanediol was completed with a reaction temperature of 130 °C and a reaction time of 3 hours. In this study, the yield of the resulting product was 91.18 %.

Figure C21, GC-chromatogram, indicates that 2-ethyl-1,3-hexanedipalmitate is shown at retention time 12.597 min. The Mass-

spectrum is shown in Figure D27, fragmentation could occur as the following equation :



The following physical and chemical properties of 2-ethyl-1,3-hexane-dipalmitate, as shown in Table 4.10, were studied : color, pour point, kinematic viscosity at 40 and 100 °C, viscosity index, flash point, and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the results are shown in Figure E22.

Table 4.10 : The physical and chemical properties of 2-ethyl-1,3-hexanedipalmitate

Properties	2-ethyl-1,3-hexanedipalmitate
Color, ASTM	1.0
Kinematic Viscosity	
@ 40 °C, cSt	23.46
@ 100 °C, cSt	5.25
Viscosity Index	165.29
Pour Point, °C	-3
Flash Point, °C	206
Oxidation Point, °C	468
Oxidation Compounds, %wt	1.54

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย