# CHAPTER III

RESULTS AND DISCUSSION

3.1 SYNTHETIC ACIDS

In the first step, acids were prepared by ozonolysis a solution of palm oil by cleavage of alkene to zwitterion and a carbonyl compound. The zwitterion was reacted with methanol to give methoxy hydroperoxide. A mixture of formic acid and hydrogen peroxide was used to decompose methoxy hydroperoxide to carboxylic acid. The crude acids were obtained in high yield.
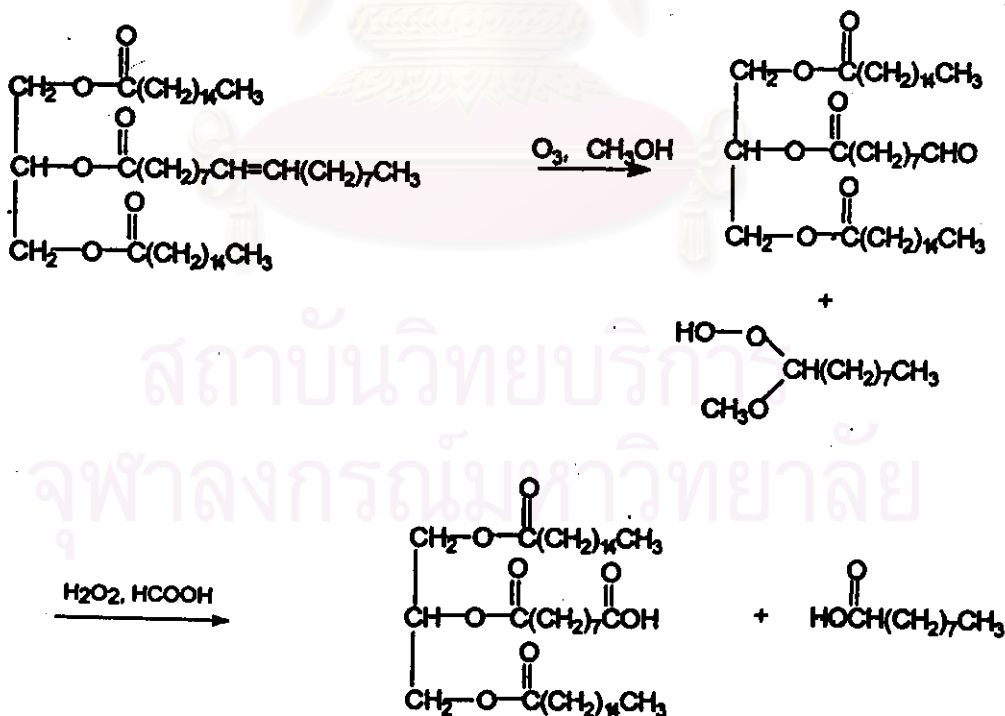
The product was characterized by ^{13}C-NMR spectrum (Fig. 3) which displayed a signal of COOH at 180.5 ppm. The signals at 130.0 and 128.5 ppm of olefinic carbons (of palm oil in Fig.1) were disappeared. Thus indicated a complete clevage of olefinic bonds.

3.2 SYNTHETIC ESTERS

The esterification (and transesterification) was prepared with five alcohols. The percentage yields and boiling point of mixed esters compounds were shown in Table 5.

Table 5 The reaction time and yield of mixed ester compounds from different alcohols

Alcohols	Reaction time (hours)	Yield (%)	boiling range ester compounds (^{o}C)
Methanol	4	86	80-170
Ethanol	4	82	120-190
Isopropanol	2	75	130-220
n-Buthanol	6	91	150-250
2-Ethyl-1-hexanol	8	88	180-250

The esterification of carboxylic acid and alcohol was a well known method for preparation of esters. The carboxylic acid were reacted with alcohol the present of in the present of sulfuric acid at room temperature, then

refluxed for 4-8 hours (see Table 5). The percentage yield of mixture ester compounds were 75 to 91 %.

3.2.1 Characterization of ester compounds

The FT-IR spectra of compound 1-15 showed the same pattern. Example, the absorption band of C-H stretching of aliphatic at 2923 and 2853 cm^{-1}, absorption band of O=C stretching at 1739 cm^{-1} and O-C stretching at 1100 cm^{-1}, as shown in Table 6.

Table 6 Assignment of the FT-IR of compound 1-15

Wave number(cm^{-1})	Intensity	Tentative assignment
2923, 2853	strong	C-H stretching vibration of CH_3-, CH_2-
1739	moderate	O=C stretching vibration
1470,1373	weak	C-H bending vibration of CH_3-, CH_2-
1230-1100	moderate	C-O stretching vibration

The ^{13}C- NMR sprectrum of compound 1-3 indicated the signal at δ 51.42 ppm which belonged to carbon atom of of methyl (OCH$_3$) (Fig. 5,10,14). The ^{1}H-NMR spectrum the siglet signal at δ 3.63 ppm indicated proton of methyl group connected oxygen (O-CH$_3$) of methyl ester (Fig. 6,11,15).

Table 7 The ^{1}H-NMR and ^{13}C-NMR data of compound 1-3

Structures and their chemical shift(ppm)
compound **1** CH_3O - CO - CH_2 - CH_2 - $(CH_2)_{10}$ - CH_2 - CH_2 - CH_3
^{1}H-NMR   δ 3.63s   2.27t 1.58p   1.15-1.38m   0.85t
^{13}C-NMR   δ 51.42   174.28 34.02 25.01   29.02   32.01   22.82 14.00
compound **2** $(CH_3O$ - CO - CH_2 - CH_2 -$CH_2)_2$ - (CH_2)
^{1}H-NMR   δ 3.59s   2.23t 1.55p 1.25m 1.18m
^{13}C-NMR   δ 51.20   174.24 34.01 24.82 28.80   22.80
compound **3** CH_3O - CO - CH_2 - CH_2 - $(CH_2)_2$ - CH_2 - CH_2 - CH_3
^{1}H-NMR   δ 3.61s   2.25t 1.56p   1.15-1.35m   0.83t
^{13}C-NMR   δ 51.20   174.02 34.00 25.02   29.20   31.90   22.45 14.01

Mass spectrum of compound 1- 3 (Fig. 8,12,16) indicated α-cleavage of M^{+}-OCH_3 at 239, 185, 141, repectively and β-cleavage ($CH_3COH=CH_2$) at 74.

The ^{13}C- NMR sprectrum of compound **4-6** indicated the signal at δ 60.01 ppm which belong to carbon atom of methylene (OCH_2CH_3) (Fig. 18, 23, 27). The ^{1}H-NMR spectrum, the quartet signal at δ 4.05 ppm indicated proton of methylene group connected to oxygen (O-CH_2CH_3) of ethyl ester (Fig. 19, 24, 28).

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Table 8 The ^{1}H-NMR and ^{13}C-NMR data of compound 4-6

Structures and their chemical shift(ppm)
compound 4 $CH_3 - CH_2 O - CO - CH_2 - CH_2 - (CH_2)_{10} - CH_2 - CH_2 - CH_3$
^{1}H-NMR   δ 1.25m 4.05q   2.25t 1.58p 1.23m 1.26m 1.19m 0.85t
^{13}C-NMR   δ 14.02 60.01 174.01 34.25 25.02 29.20 31.98 22.84 14.00
compound 5 $(CH_3 - CH_2O - CO - CH_2 - CH_2 - CH_2)_2 - (CH_2)$
^{1}H-NMR   δ 1.26t 4.10q   2.32t 1.62p 1.23m   1.19m
^{13}C-NMR   δ 14.24 60.05 173.82 34.84 24.92 29.02   29.02
compound 6 $CH_3 - CH_2 O - CO - CH_2 - CH_2 - (CH_2)_2 - CH_2 - CH_2 - CH_3$
^{1}H-NMR   δ 1.25t 4.05q   2.26t 1.57p 1.23m 1.26m 1.19m 0.85t
^{13}C-NMR   δ 14.01 60.02 174.02 34.01 25.01 29.02   32.01 22.78 14.01

Mass spectrum of compound 4- 6 (Fig. 21, 25, 29), indicated α-cleavage of M^+-OCH_2CH_3 at 239, 199, 141, repectively and β-cleavage ($CH_3CH_2COH=CH_2$) at 88.

The ^{13}C- NMR sprectrum of compound 7-9 indicated the signal at δ 67.81 ppm which belong to carbon atom of methine ($O\underline{C}H(CH_3)_2$) (Fig. 31, 36, 40). The ^{1}H-NMR spectrum, the heptet signal at δ 4.97 ppm indicated proton of methine group connected to oxygen (O-$C\underline{H}(CH_3)_2$) of isopropyl ester (Fig. 32, 37, 41).

Table 9 The ^{1}H-NMR and ^{13}C-NMR data of compound 7-9

Structures and their chemical shift(ppm)
compound 7 $(CH_3)_2$ - CHO - CO - CH_2 - CH_2 - $(CH_2)_{10}$ - CH_2 - CH_2 - CH_3
^{1}H-NMR   δ 1.20d   4.97h   2.23t   1.58p   1.15-1.38m   0.85t
^{13}C-NMR   δ 22.24   67.81   173.82 34.82 25.01 29.20   32.01   22.82   14.01
compound 8 $((CH_3)_2$ - CHO - CO - CH_2 - CH_2 - CH_2 $)_2$ - (CH_2)
^{1}H-NMR   δ 1.23m   4.92h   2.31t 1.82p 1.23m   1.19m
^{13}C-NMR   δ 22.02   67.81   174.02   34.54 25.40 29.18   29.18
compound 9 $(CH_3)_2$ - CHO - CO - CH_2 - CH_2 - $(CH_2)_2$ - CH_2 - CH_2 - CH_3
^{1}H-NMR   δ   1.22d   4.95h   2.22t   1.57p   1.23m   1.18m   1.17m 0.84t
^{13}C-NMR   δ   21.97 67.63 174.01 34.83   25.32   29.20   32.01   22.82   14.10

Mass spectrum of compound 7- 9 (Fig. 34, 38, 42) indicated α-cleavage of M^+-OCH(CH$_3$)$_2$ at 239, 213, 141, repectively and β-cleavage ((CH$_3$)$_2$CHCOH=CH$_2$) at 102.

The ^{13}C- NMR sprectrum of compound 10-12 indicated the signal at δ 63.92 ppm which belong to carbon atom of methylene (OC$\underline{H}_2$(CH$_2$)$_2$CH$_3$) (Fig. 44, 49, 53). The ^{1}H-NMR spectrum, the heptet signal at δ 4.03 ppm indicated proton of methyl group connected to oxygen (OC$\underline{H}_2$(CH$_2$)$_2$CH$_3$) of butyl ester (Fig. 45, 50, 54).

Table 10 The ^{1}H-NMR and ^{13}C-NMR data of compound 10-12

Structures and their chemical shift(ppm)
compound **10** CH$_3$ - CH$_2$ - CH$_2$ - CH$_2$O - CO - CH$_2$ - CH$_2$ - (CH$_2$)$_{10}$ - CH$_2$ - CH$_2$ - CH$_3$
^{1}H-NMR   0.89t 1.28m 1.54m 4.02t   2.24t 1.58p   1.15-1.38m   0.84t
^{13}C-NMR   δ 13.82 19.22 30.81 63.92 173.67 34.82 25.02 29.02   32.25 22.82 14.01
compound **11**   (CH$_3$ - CH$_2$ - CH$_2$ - CH$_2$O - CO - CH$_2$ - CH$_2$ - CH$_2$)$_2$ - (CH$_2$)
^{1}H-NMR   δ   0.88t   1.27m 1.53m 4.02t   2.28t 1.56p 1.25m 1.18m
^{13}C-NMR   δ   13.86   19.03   30.81   64.02 174.02 34.20 25.01 28.92 28.92
compound **12** CH$_3$ - CH$_2$ - CH$_2$ - CH$_2$O - CO - CH$_2$ - CH$_2$ - (CH$_2$)$_3$ - CH$_2$ - CH$_2$ - CH$_3$
^{1}H-NMR   δ 0.89t 1.28m 1.54m 4.03t   2.25t 1.58p   1.15-1.23m   0.85t
^{13}C-NMR   δ 13.81 19.20 30.21 63.94 174.02 34.24 25.03 29.01 31.85 22.82 14.02

Mass spectrum of compound 10- 12 (Fig. 47, 51, 55) indicated α-cleavage of M$^+$-OCH$_2$(CH$_2$)$_2$CH$_3$)$_2$ at 239, 227, 141, repectively and β-cleavage (CH$_3$(CH$_2$)$_2$CH$_2$COH=CH$_2$) at 116.

The ^{13}C-NMR sprectrum of compound 13-15 indicated the signal at δ 66.72 ppm which belong to carbon atom of of methylene (OCH$_2$CH(CH$_2$CH$_3$)CH2CH$_2$CH$_2$CH3) (Fig. 57 , 62, 66). The ^{1}H-NMR spectrum, the doublet signal at δ 3.95 ppm indicated proton of methyl group connected to oxygen (OCH$_2$CH(CH$_2$CH$_3$)CH2CH$_2$CH$_2$CH3) of 2-ethyl-1-hexyl ester (Fig. 58, 63, 67).

Table 11 The ^{1}H-NMR and ^{13}C-NMR data of compound 13-15

Structures and their chemical shift(ppm)
compound **13** CH$_3$ - CH$_2$ - CH$_2$ - CH$_2$(CH$_3$ - CH$_2$)-CH - CH$_2$O - CO - CH$_2$ - CH$_2$ - (CH$_2$)$_{10}$ - CH$_2$ - CH$_2$ - CH$_3$
^{1}H-NMR δ 0.87t 1.15-1.38m 1.31q 0.87t 1.31q 1.35h 3.94d 2.26t 1.58p 1.15-1.38m 0.85t
^{13}C-NMR δ 13.85 23.98 30.20 29.84 11.03 23.01 39.02 66.72 173.88 34.22 25.02 29.02 31.82 22.82 14.01
compound **14** (CH$_3$ - CH$_2$ - CH$_2$ - CH$_2$(CH$_3$ - CH$_2$)-CH - CH$_2$O - CO - CH$_2$ - CH$_2$)$_2$ - (CH$_2$)$_3$
^{1}H-NMR δ 0.87t 1.26m 1.30m 0.84t 1.30m 1.34h 3.93d 2.23t 1.57p 1.23m
^{13}C-NMR δ 13.85 23.96 30.22 29.87 11.01 23.01 39.01 66.64 174.02 34.20 25.02 29.03
compound **15** CH$_3$ - CH$_2$ - CH$_2$ - CH$_2$(CH$_3$ - CH$_2$)-CH - CH$_2$O - CO - CH$_2$ - CH$_2$ - (CH$_2$)$_2$ - CH$_2$ - CH$_2$ - CH$_3$
^{1}H-NMR δ 0.88t 1.27m 1.32q 0.88t 1.31q 1.35h 3.95d 2.27t 1.58p 1.15-1.38m 0.85t
^{13}C-NMR δ 13.86 23.98 30.22 29.92 11.05 23.02 39.42 66.74 174.02 34.25 25.30 29.04 32.02 23.01 14.02

Mass spectrum of compound 13- 15 (Fig. 60, 64, 68) indicated α-cleavage of M$^+$-OCH$_2$CH(CH$_2$CH$_3$)CH2CH$_2$CH$_2$CH$_3$ at 283, 239, 141, repectively and β-cleavage ((CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$)CHCH$_2$COH=CH$_2$) at 171.

From all the data above, it was concluded that compounds 1-15 shown in Table 12 were obtained.

Table 12 Ester compounds (compound 1-15)

Compound no.	Structure formula	Name
1	$CH_3O-CO-(CH_2)_{14}CH_3$	methyl hexadecanoate
2	$CH_3O-CO-(CH_2)_7-CO-OCH_3$	1, 9-dimethyl hexadecanoate
3	$CH_3O-CO-(CH_2)_7CH_3$	methyl nonanoate
4	$C_2H_5O-CO-(CH_2)_{14}CH_3$	ethyl hexadecanoate
5	$C_2H_5O-CO-(CH_2)_7-CO-OC_2H_5$	1, 9-diethyl hexadecanoate
6	$C_2H_5O-CO-(CH_2)_7CH_3$	ethyl nonanoate
7	$C_3H_7O-CO-(CH_2)_{14}CH_3$	isopropyl hexadecanoate
8	$C_3H_7O-CO-(CH_2)_7-CO-OC_3H_7$	1, 9-diisopropyl hexadecanoate
9	$C_3H_7O-CO-(CH_2)_7CH_3$	isopropyl nonanoate
10	$C_4H_9O-CO-(CH_2)_{14}CH_3$	butyl hexadecanoate
11	$C_4H_9-CO-(CH_2)_7-CO-OC_4H_9$	1,9-dibutyl hexadecanoate
12	$C_4H_9O-CO-(CH_2)_7CH_3$	butyl nonanoate
13	$C_8H_{17}O-CO-(CH_2)_{14}CH_3$	2-ethyl-1-hexyl hexadecanoate
14	$C_8H_{17}O-CO-(CH_2)_7-CO-OC_8H_{17}$	bis-(2-ethyl-1-hexyl) decanoate
15	$C_8H_{17}O-CO-(CH_2)_7CH_3$	2-ethyl-1-hexyl nonanoate

3.3 ESTER COMPOUNDS AS MARKER IN DIESEL FUEL

3.3.1 Test of ester compounds as marker in diesel fuel

The mixed ester compounds was blended with diesel fuel and presence of ester group was tested by the reaction hydroxylamine and ferric ion to give violet-colored complex. The minimum concentrations of mixed ester in diesel fuel that can be visually detected in field test were presented in Table 13.

Table 13 The minimum concentration of ester compounds in diesel fuel that could be visually detected in field test

Type of ester compounds	Concentration (ppm)
Methyl	400
Ethyl	400
Isopropyl	400
n-Butyl	500
2-ethyl-1-hexyl	450
Methyl*	1000

* From palm oil

From Table 5, methyl ester derived directly from palm oil could be visualized at concentration of 1000 ppm in diesel fuel using the reaction with hydroxylamine and ferric ion. Thus the minimum treat rate was 1000 ppm which was quite high. This was due to the low number of ester group per mole of sample. It was anticipated that if the number of ester group per mole increased, the detection limit should be increased. The number of ester group was increased by clevage of

double bond in fatty acid, followed by oxidation and esterification. It could be clearly seen that the methyl esters from such reaction could enhance the visual to just 400 ppm in diesel. No significant improvement of detection limit was observed by changing the alcohol part. Therefore, the limit of visual detection for these ester markers was the number of ester group per mole of ester.

3.3.2 Detection of ester compounds in diesel fuel by GC

Attemps were made to quantitatively detected ester compounds in diesel fuel. The GC chromatogram of mixed ester revealed unique profile of each mixed ester which could be used as finger print for the marker. Unfortunately, the retention time of most ester (Fig. 69-74) fall in the range to those of diesel hydrocarbons. Moreover, the small amount of esters (400-500 ppm) added to diesel fuel them very difficult to detect. At 10000 ppm of butyl ester gave weak singal out of intense signal from diesel fuel. Therefore, quantitative determination of this type of ester markers by GC was not practical. Infrared detection of C=O stretching was also attempted. Again, interference from lange amount of diesel fuel hydrocarbons prevented detection of the these esters.