

CHAPTER IV

RESULT AND DISCUSSION

The hexane crude extract of the stem bark of *C. oblongifolius* was separated by silica gel column chromatography using a hexane-ethyl acetate gradient system to obtain six compounds and a mixture as shown in Table 4.

Table 4 The results of separation of hexane crude extract of *C. oblongifolius* by column chromatography

Compounds	Physical appearance	Weight (g)
1	colorless needle crystal	0.05
2	white solid	13.21
3	white solid	0.08
4	white solid	0.06
Mixture 5	white needle crystal	1.73
6	white solid	8.38
7	viscous transparent oil	0.11

4.1 Structure elucidation of the isolated compounds from the stem barks of *Croton oblongifolius* Roxb.

4.1.1 Structure elucidation of Compound 1

The IR spectrum of Compound 1 is shown in Fig.11 and the absorption peaks are assigned as shown in Table 5. Its IR spectrum showed the presence of a carboxylic group according to the broad absorption band between 3421 to 2626 cm^{-1} and the strong absorption band at 1707 cm^{-1} due to the carboxylic acid carbonyl stretching.

Table 5 The IR absorption bands assignment of Compound 1

Wave number (cm^{-1})	Intensity	Tentative Assignment
3421-2626	Broad	O-H stretching vibration of acid
2946	Strong	C-H stretching vibration of $-\text{CH}_3$, $-\text{CH}_2$
1707	Strong	C=O stretching vibration of acid
1654, 1652	Medium	C=C stretching vibration

The $^1\text{H-NMR}$ spectrum of Compound 1 (Fig.12) indicated that it possesses three methyl groups attaching to quaternary carbons at 0.88, 0.86 and 0.82 ppm, one olefinic methyl group at 1.67 ppm and five olefinic protons at 6.90, 6.31, 5.47, 5.00 and 4.84 ppm.

The $^{13}\text{C-NMR}$ spectrum (Fig.13, Table 6) showed 20 signals which the carbonyl group of carboxylic acid corresponding to the signal at 174.3 ppm. The six signals of olefinic carbons appeared at 141.8, 140.6, 133.6, 133.5, 133.1 and 110.0 ppm.

DEPT-90 spectrum (Fig.14) indicated the presence of three sp^2 methine carbons at 141.8, 133.6 and 133.1 ppm and two saturated methines at 49.9 and 49.3 ppm.

DEPT-135 spectrum (Fig.14) showed six methylene carbons at 110.0, 41.9, 40.1, 26.0, 24.0 and 18.6 ppm and four methyl carbons at 33.3, 22.2, 14.8 and 11.7 ppm which indicated that the carbon signals at 133.6, 133.1, 36.9 and 32.8 ppm were quaternary.

Compound 1 showed a molecular ion with m/z 302 ($C_{20}H_{30}O_2$) which indicated degree of unsaturation of six. Compound 1 must consist of 2 rings in addition to the three double bonds and a carboxyl group. These data indicated that Compound 1 could be labdane diterpenoid. It could be concluded that Compound 1 exhibited the ^{13}C -NMR chemical shifts similar to those of labda-7,12(*E*),14-triene-17-oic acid [2].

The ^{13}C -NMR chemical shift of Compound 1 and labda-7,12(*E*),14-triene-17-oic acid were compared in Table 6.

Table 6 ^{13}C -NMR chemical shifts of Compound 1 and Labda-7,12(*E*),14-triene-17-oic acid

Carbon position	Chemical shifts (ppm)	
	Compound 1	Labda-7,12(<i>E</i>),14-triene-17-oic acid
1	40.1t	40.1t
2	18.6t	18.6t
3	41.9t	41.9t
4	32.8s	32.8s
5	49.3d	49.3d
6	24.0t	23.9t
7	140.6d	140.5d
8	133.6s	133.6s
9	49.9d	49.9d
10	36.9s	36.9s
11	26.0t	26.0t
12	133.5d	133.4d
13	133.1s	133.1s
14	141.8d	141.8d
15	110.0t	109.9t
16	11.7q	11.7q
17	174.3s	174.1s
18	33.3q	33.3q
19	22.2q	22.2q
20	14.8q	14.8q

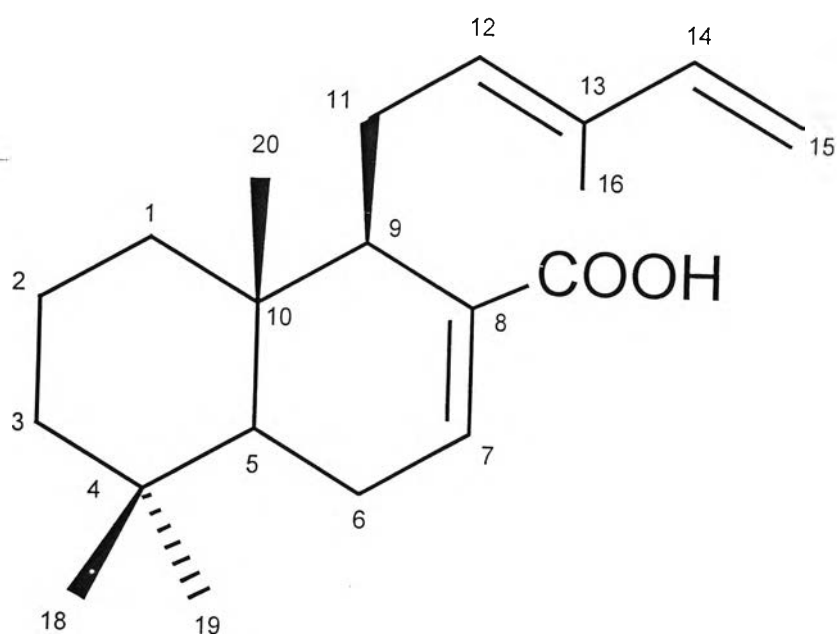


Figure 4 The structure of Compound 1



4.1.2 Structure elucidation of Compound 2

The IR spectrum of Compound 2 is shown in Fig 16 and the absorption peaks are assigned as shown in Table 7. Its IR spectrum showed important absorption bands at 3400-3600 cm^{-1} (O-H stretching vibration of alcohol), 2960, 2930 and 2868 cm^{-1} (C-H stretching vibration), 1675 cm^{-1} (C=O stretching vibration of carbonyl group) and 1634 cm^{-1} (C=C stretching vibration of alkene).

Table 7 The IR absorption bands assignment of Compound 2

Wave number (cm^{-1})	Intensity	Tentative Assignment
3600-3400	Broad	O-H stretching vibration of acid
2960, 2930, 2868	Strong	C-H stretching vibration of $-\text{CH}_3$, $-\text{CH}_2$
1675	Strong	C=O stretching vibration of carbonyl group
1634	Medium	C=C stretching vibration of alkene

The $^1\text{H-NMR}$ spectrum of Compound 2 (Fig.17) indicated that it possesses three methyl groups at 0.76, 0.84 and 1.26 ppm, three olefinic protons of furanoid group at 7.33, 7.19 and 6.26 ppm and one vinylic proton at 6.85 ppm.

The $^{13}\text{C-NMR}$, DEPT-90 and DEPT-135 spectrum (Fig.19) showed 20 signals. Six signals of olefinic carbons appeared at δ 142.7, 141.5, 140.4, 138.4, 125.6 and 110.9 ppm. The signal at 173.1 ppm should be the carbonyl of carboxylic acid. There were thirteen sp^3 carbon signals at δ 46.7(d), 38.8(s), 38.6(t), 37.6(s), 36.2(d), 35.8(t), 27.5(t), 27.3(t), 20.5(q), 18.3(q), 18.2(t), 17.4(t) and 16.0(q) ppm.

Its molecular formula was established as $C_{20}H_{28}O_3$, which was confirmed by observing the molecular ion at m/z 316 (Fig.20). The molecular formula, $C_{20}H_{28}O_3$, of Compound 2 defined degree of unsaturation of seven, therefore, Compound 2 must consist of one ring of furan (DBE = 3) in addition to one double bond, two rings and one carbonyl group of carboxylic acid. Compound 2 exhibited the ^{13}C -NMR chemical shifts identical to (-)-hardwickiic acid [28]. These data indicated that Compound 2 was (-)-hardwickiic acid.

The spectroscopic and physical data of Compound 2 was identical to those reported for (-)-hardwickiic acid obtained from *Croton californicus*[7], *Hardwickia pinnata* [29], *Solidago juncea* [30], *Solidago arguta* [31], *Crangaea maderaspatana* [32], *Baccharis macraei* [33], and *Clerodendrum neriifolium* [34].

A comparison of the ^{13}C -NMR chemical shifts of Compound 2 and (-)-hardwickiic acid is shown in Table 8.

Table 8 ^{13}C -NMR chemical shifts of Compound 2 and (-)-Hardwickiic acid

Carbon position	Chemical shifts (ppm)	
	Compound 2	(-)-Hardwickiic acid
1	35.8t	35.8t
2	18.2t	18.2t
3	140.4d	140.3d
4	141.5s	141.5s
5	37.6s	37.6s
6	38.6t	38.7t
7	27.3t	27.3t
8	36.2d	36.3d
9	38.8s	38.8s
10	46.7d	46.7d
11	17.4t	17.5t
12	27.5t	27.5t
13	125.6s	125.6s
14	110.9d	110.0d
15	142.7d	142.7d
16	138.4d	138.4d
17	16.0q	15.9q
18	173.1s	172.6s
19	20.5q	20.5q
20	18.3q	18.3q

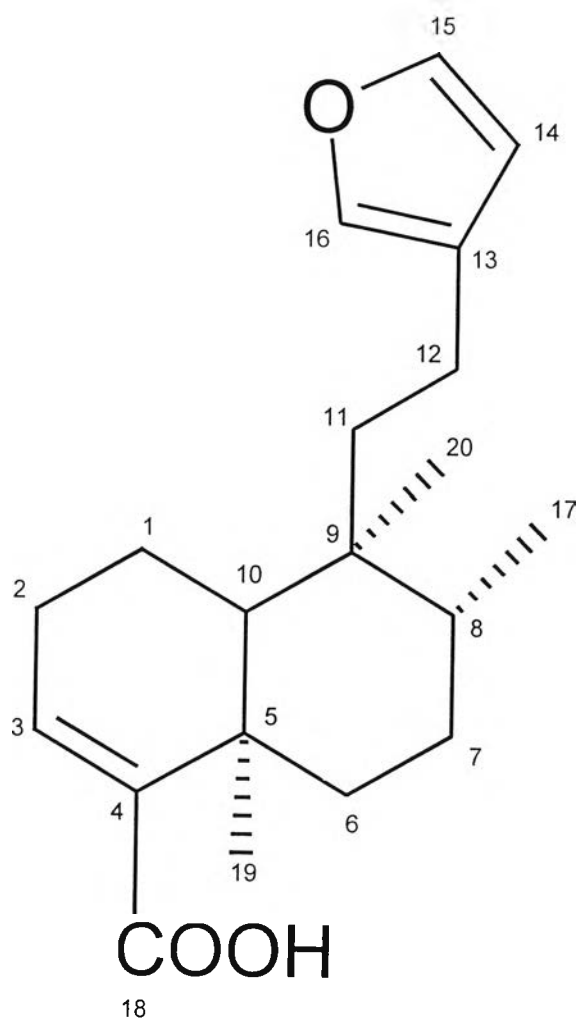
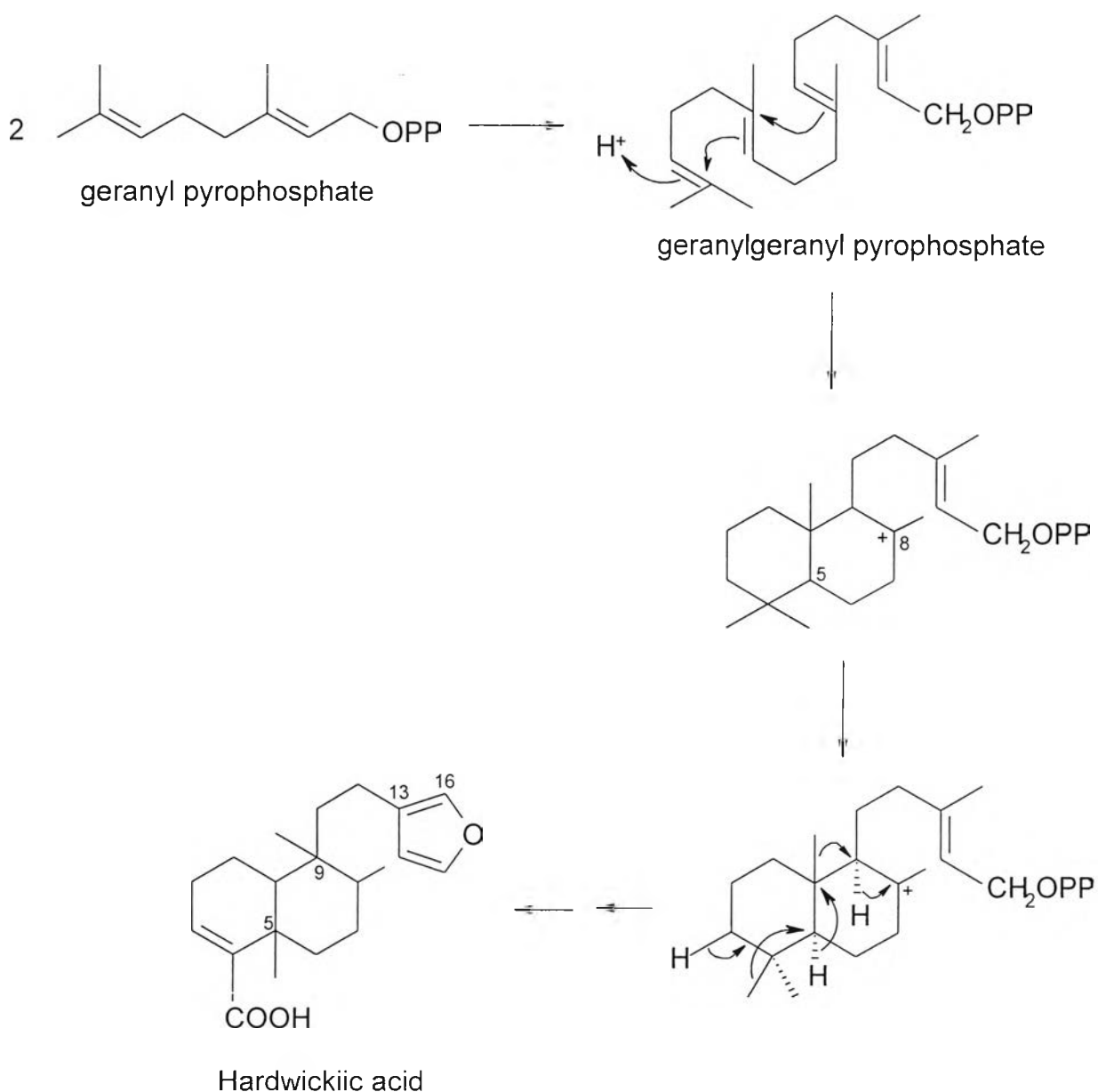


Figure 5 The structure of Compound 2

The study of other *Croton* genus have led to the isolation of diterpenes belong to the labdane and isopimarane diterpene which are biogenetically related to clerodane such as hardwickiic acid.

Biogenetic pathway of hardwickiic acid was shown below [35].



4.1.3 Structure elucidation of Compound 3

The IR spectrum of Compound 3 is shown in Fig.21 and the absorption peaks are assigned as shown in Table 9. Its IR spectrum showed important absorption bands at 3645 cm^{-1} (O-H stretching vibration of alcohol), 2974 , 2940 and 2863 cm^{-1} (C-H stretching vibration), 1722 cm^{-1} (C=O stretching vibration) and 1639 cm^{-1} (C=C stretching vibration of alkene).

Table 9 The IR absorption bands assignment of Compound 3

Wave Number (cm^{-1})	Intensity	Tentative assignment
3465	Medium	O-H stretching vibration of alcohol
2982, 2940, 2862	Strong	C-H stretching vibration of $-\text{CH}_2$, $-\text{CH}_3$
1730	Strong	C=O stretching vibration
1642	Medium	C=C stretching vibration
1441	Medium	$-\text{CH}_2$, $-\text{CH}_3$ bending
1252	Medium	C-O stretching vibration

The $^1\text{H-NMR}$ spectrum of compound 3 (Fig.22) showed four methyl groups attaching to quaternary carbons at 0.84, 0.86, 1.06 and 2.10 ppm, one olefinic methyl groups at 1.75 ppm, six olefinic protons at 6.30, 5.35, 5.06, 4.90, 4.88 and 4.46 ppm and a double doublet at 6.31 ppm.

The $^{13}\text{C-NMR}$ spectrum (Fig.23) showed 22 signals, which the carbonyl group of acetate corresponding to the signal at 171.6 ppm.

The DEPT-90 spectrum (Fig.24) indicated the presence of two sp^2 methine carbons at 141.4 and 133.1 ppm and four saturated methine carbons at 80.4, 73.2, 56.6 and 54.4 ppm.

The DEPT-135 spectrum (Fig.24) showed six methylene carbons at 110.1, 108.8, 42.3, 37.6, 23.5 and 23.4 ppm and five methyl carbons at 28.7, 21.4, 16.5, 15.2 and 11.9 ppm which indicated that the carbon signals at 171.6, 146.9, 133.7, 40.1 and 39.9 ppm were quaternary.

Compound 3 showed a molecular ion with m/z 346 ($C_{22}H_{34}O_3$) (Fig.25) which indicated the degree of unsaturation of seven. Compound 3 must consist of two rings in addition to the three double bonds and one carbonyl group. These data indicated that Compound 3 could be labdane diterpenoid. It could be concluded that the Compound 3 exhibited the ^{13}C -NMR chemical shifts similar to 2-acetoxy-labda-8(17),12(*E*),14-triene-3-ol [4].

The ^{13}C -NMR chemical shifts of Compound 3 and 2-acetoxy-labda-8(17),12(*E*),14-triene-2-ol were compared in Table 10.

Table 10 ^{13}C -NMR chemical shifts of Compound 3 and 2-acetoxy-labda-8(17),12(*E*),14-triene-3-ol

Carbon position	Chemical shifts (ppm)	
	Compound 3	2-acetoxy-labda-8(17),12(<i>E</i>),14-triene-3-ol
1	42.3t	42.3t
2	73.2d	73.2d
3	80.4d	80.5d
4	39.9s	39.9s
5	54.4d	54.4d
6	23.5t	23.5t
7	37.6t	37.6t
8	146.9s	146.3s
9	56.6d	56.6d
10	40.1s	40.2s
11	23.4t	23.4t
12	133.1d	133.1d
13	133.7s	133.7s
14	141.4d	141.4d
15	110.1t	110.1t
16	11.9q	11.9q
17	108.8t	108.8t
18	28.7q	28.7q
19	16.5q	16.5q
20	15.2q	15.2q
C=O	171.6s	171.6s
CH ₃ CO	21.4q	21.4q

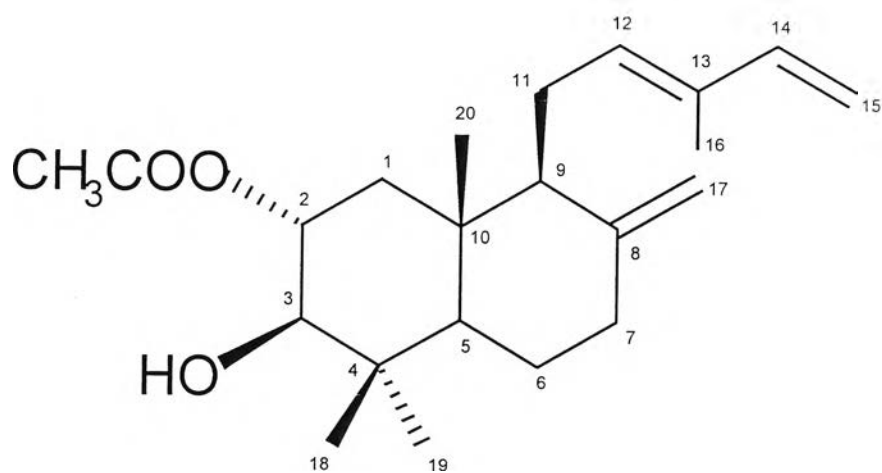


Figure 6 The structure of Compound 3

4.1.4 Structure elucidation of Compound 4

The IR spectrum of Compound 4 is shown in Fig.26 and the absorption peak are assigned as shown in Table 11. Its IR spectrum showed important absorption bands at 3439 cm^{-1} (O-H stretching vibration of alcohol), 2940 and 2848 cm^{-1} (C-H stretching vibration), 1722 cm^{-1} (C=O stretching vibration) and 1644 cm^{-1} (C=C stretching vibration of alkene).

Table 11 The IR absorption bands assignment of Compound 4

Wave Number (cm^{-1})	Intensity	Tentative assignment
3439	Medium	O-H stretching vibration of alcohol
2940, 2848	Strong	C-H stretching vibration of $-\text{CH}_2$, $-\text{CH}_3$
1723	Strong	C=O stretching vibration
1644	Medium	C=C stretching vibration
1460, 1373	Medium	$-\text{CH}_2$, $-\text{CH}_3$ bending
1250	Medium	C-O stretching vibration

The ^1H and ^{13}C -NMR spectrum of compound 4 (Fig.27, 28) were similar to those of compound 3.

The ^{13}C -NMR, DEPT-90 and DEPT-135 spectrum (Fig.29) showed 22 signals, which the carbonyl group of acetate corresponding to the signal at 172.4 ppm and oxygen bearing methine carbon at 67.8 ppm.

Compound 4 showed a molecular ion at m/z 346 ($\text{C}_{22}\text{H}_{34}\text{O}_3$) (Fig.30) which indicated the degree of unsaturation of seven. Compound 4 must consist of two rings in addition to the three double bonds and one carbonyl group. These data indicated that Compound 4 could be labdane diterpenoid. It could be concluded that Compound 4 was 3-acetoxy-labdane-8(17),12(E),14-triene-2-ol [4].

The ^{13}C -NMR chemical shifts of Compound 4 and 3-acetoxy-labda-8(17),12(*E*),14-triene-2-ol were compared in Table 12.

Table 12 ^{13}C -NMR chemical shifts of Compound 4 and 3-acetoxy-labda-8(17),12(*E*),14-triene-2-ol

Carbon	Chemical shifts (μm)	
	Compound 4	3-acetoxy-labda-8(17),12(<i>E</i>),14-triene-2-ol
1	46.3t	46.3t
2	67.8d	67.8d
3	84.5d	84.5d
4	39.3s	39.4s
5	54.4d	54.4d
6	23.5t	23.5t
7	37.6t	37.6t
8	146.9t	146.9t
9	56.6d	56.6d
10	40.0s	40.1s
11	23.3t	23.3t
12	133.0d	133.0d
13	133.8s	133.8s
14	141.4d	141.5d
15	110.1t	110.2t
16	11.9q	11.9q
17	108.8t	108.8t
18	28.7q	28.7q
19	17.5q	17.5q
20	15.4q	15.4q
C=O	172.4s	172.4s
CH_3CO	21.1q	21.2q

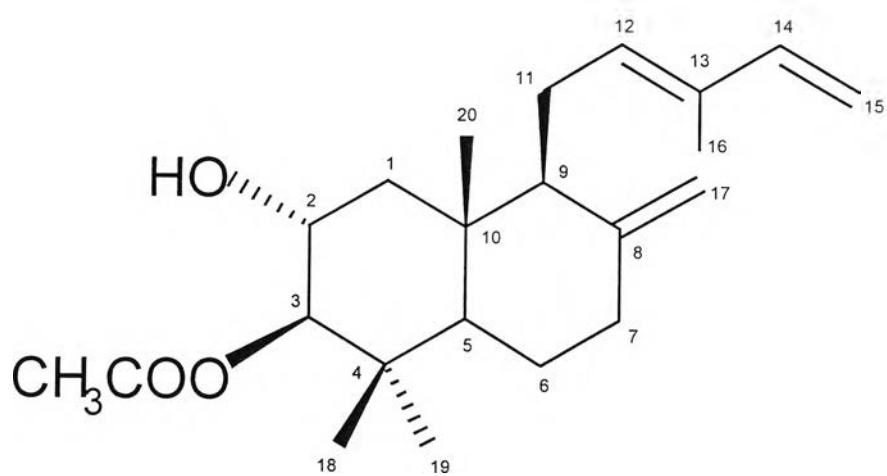


Figure 7 The structure of Compound 4

4.1.5 Structure elucidation of Mixture 5

The IR spectrum of Mixture 5 is shown in Fig.31 and is summarized in Table 13. From the IR spectrum, important absorption bands are shown at 3430 cm^{-1} (O-H stretching vibration), 1059 cm^{-1} (C-O stretching vibration of alcohol), 1670-1630 cm^{-1} (C=C stretching vibration of olefinic) and 840 and 800 cm^{-1} (C-H out of plane bending vibration) cm^{-1} . The absorption peak at 1380 cm^{-1} corresponded to C-H symmetric bending vibration mode of CH_3 group.

Table 13 The IR absorption bands assignment of Mixture 5

Wave Number (cm-1)	Intensity	Tentative Assignment
3500-3200	Broad	O-H Stretching vibration
2937-2868	Strong	C-H Stretching vibration of $-\text{CH}_3$, $-\text{CH}_2$
1641	Weak	C=C Stretching vibration
1464	Medium	C-H Bending vibration of $-\text{CH}_3$, $-\text{CH}_2$
1381	Medium	C-H in plane bending vibration
1059	Medium	C-O Stretching vibration

The $^1\text{H-NMR}$ spectrum (CDCl_3) of Mixture 5 (Fig.32) showed signals at 0.68-2.26 ppm, which were the signals of methyl, methylene and methine groups of steroids ($-\text{CH}_3$, $-\text{CH}_2$, $-\text{CH}$ respectively). The proton adjacent to the hydroxy group ($-\text{CH-OH}$) was shown as the multiplet signal at 3.50 ppm. While the multiplet signal at 5.09 ppm was due to the disubstituted vinylic protons ($-\text{CH}=\text{CH}-$). The most downfield signal at 5.35 ppm was the signal of trisubstituted vinylic proton ($-\text{CH}=\text{C}-$).

The ^{13}C -NMR spectrum in CDCl_3 (Fig.33) showed the carbon signals at 11.9-56.9 ppm which are CH_3 , CH_2 and CH of steroid. The olefinic carbon signals were observed at 121.7, 129.4, 138.3 and 140.8 ppm, while the signal at 71.8 ppm are characteristic for the carbon adjacent to the hydroxy group. The ^{13}C -NMR chemical shift assignments of Mixture 5 are presented in Table 14.

Table 14 ^{13}C -NMR chemical shift of β -sitosterol, Stigmasterol and Mixture 5

Carbon position	Chemical shift (ppm)		
	β -sitosterol	Stigmasterol	Mixture 5
1	37.1	37.4	37.3
2	31.8	31.7	31.7
3	71.9	71.8	71.8
4	42.4	42.4	42.4
5	140.9	140.0	140.8
6	121.8	121.7	121.7
7	32.0	31.9	32.0
8	32.0	31.9	32.0
9	50.3	50.3	50.2
10	36.6	36.6	36.6
11	21.1	21.1	21.1
12	39.9	39.8	39.8
13	42.4	42.4	42.4
14	56.8	57.0	56.9
15	24.3	24.4	24.3
16	28.2	28.9	28.2, 28.9
17	56.2	56.0	56.0
18	11.9	12.2	11.9, 12.2
19	19.4	19.4	19.3
20	36.2	40.5	36.2, 40.5
21	19.1	21.1	19.0, 21.1
22	34.0	138.4	33.9, 138.3
23	29.3	129.4	29.2, 129.4
24	50.3	51.3	51.3
25	26.2	31.9	26.2, 32.0
26	18.8	19.0	19.0
27	19.8	21.1	19.7, 21.1
28	23.1	25.4	23.0, 25.4
29	11.9	12.0	11.9, 12.0

The ^{13}C -NMR signals of campesterol were superimposed on those of β -sitosterol.

The IR and NMR spectra suggested that Mixture 5 could be a steroidal compound [36].

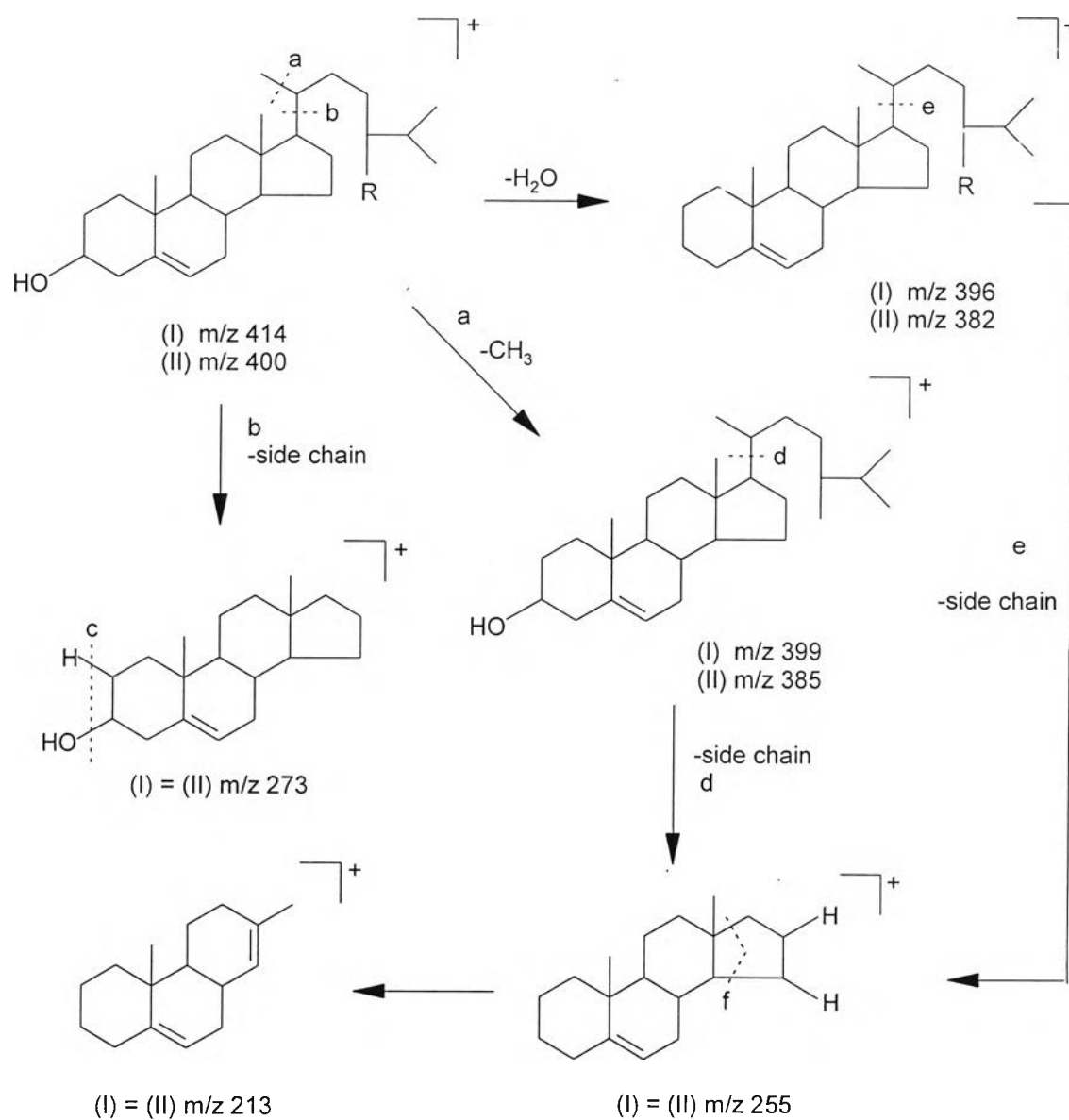
The mass spectrum (Fig.34) showed a molecular ion peak corresponding to campesterol, stigmasterol and β -sitosterol at m/z 400 ($C_{28}H_{48}O$), 412 ($C_{29}H_{48}O$) and 414 ($C_{29}H_{50}O$), respectively. The fragmentation pattern ion mass spectrum pattern of this compound indicated that this compound was a mixture of steroids generally found in most plants. However, this mixture could not be separated even though the absorbent of the column and the developing solvent system were varied. The possible mass fragmentation of Mixture 5 is shown in Scheme 4.

The presence of β -sitosterol in plants is frequently accompanied by one or more steroids such as stigmasterol and campesterol. When comparing the GC-MS chromatogram data of Mixture 5 (Fig.35) with those of the authentic cholesterol, campesterol, stigmasterol and β -sitosterol, it was clear that Mixture 5 was a mixture of campesterol, stigmasterol and β -sitosterol as in Table 15.

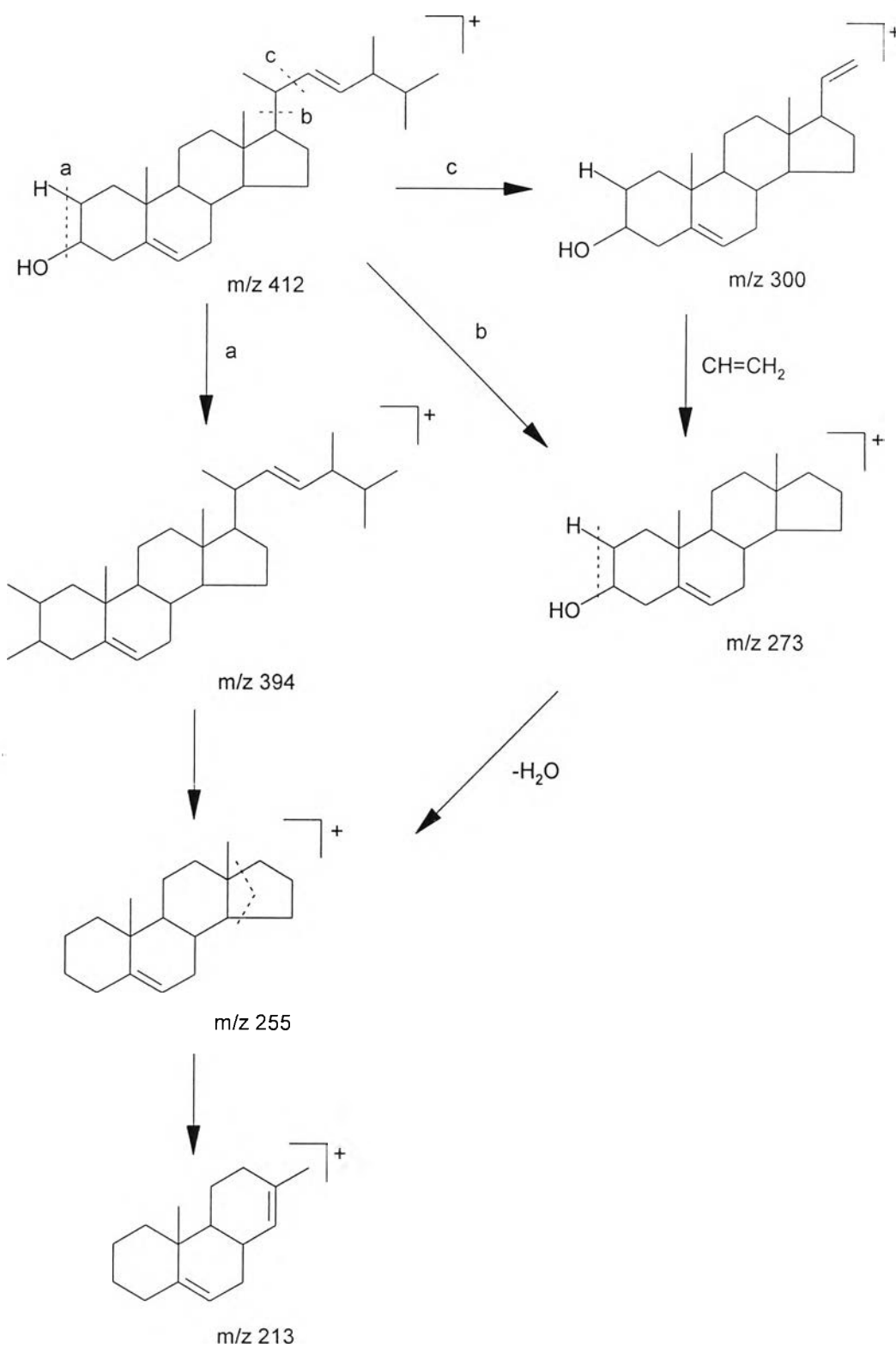
Table 15 The comparison of retention time between Mixture 5 and authentic steroids.

Name of substances	Retention time (min)	
	Standard steroid	Mixture 5
Campesterol	19.77	20.12
Stigmasterol	20.91	21.00
β -sitosterol	24.15	23.96

DB-1 capillary column, column temperature isothermal 290°C, injection temperature 250°C, Mass detector, Flow rate of He 50 cm³/sec

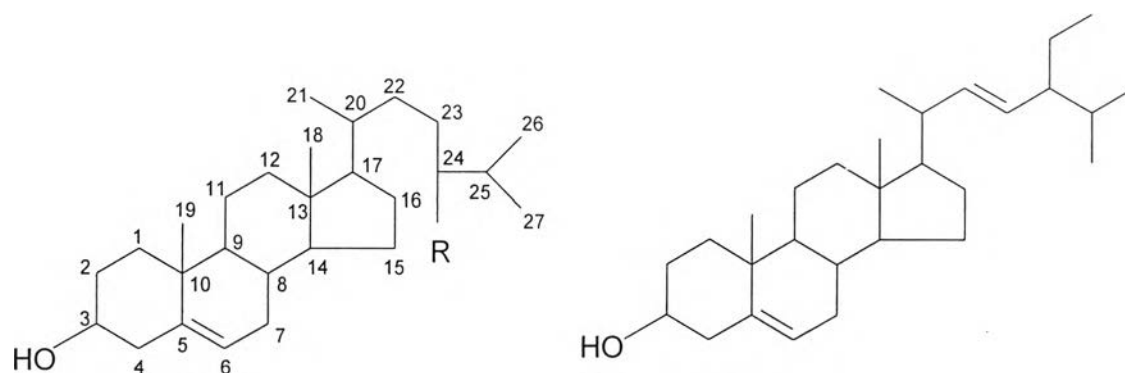


Scheme 4 The possible mass fragmentation pattern of Mixture 5 for β -sitosterol
 (I, $R = C_2H_5$) and Campesterol (II, $R = CH_3$)



Scheme 5 The possible mass fragmentation of Mixture 5 for Stigmasterol

From these results, it indicated that Mixture 5 was a mixture of campesterol, stigmasterol and β -sitosterol. The structure of these three steroids are shown below:



R = Et, β -sitosterol MW = 414

Stigmasterol MW = 412

R = Me, campesterol MW = 400

Figure 8 The structure of Mixture 5

4.1.6 Structure elucidation of Compound 6

The IR spectrum of Compound 6 is shown in Fig.36 and the absorption peaks are assigned as shown in Table 16. Its IR spectrum showed important absorption bands at 3374 cm^{-1} (O-H stretching vibration of alcohol), 2975 to 2854 cm^{-1} (C-H stretching vibration), 1645 and 1610 cm^{-1} (C=C stretching vibration of alkene) and 1218 cm^{-1} (C-O stretching vibration).

Table 16 The IR absorption bands assignment of Compound 6

Wave Number (cm^{-1})	Intensity	Tentative assignment
3374	Strong	O-H stretching vibration of alcohol
2975, 2945, 2854	Strong	C-H stretching vibration of $-\text{CH}_2$, $-\text{CH}_3$
1645, 1610	Medium	C=C stretching vibration
1446, 1388	Medium	$-\text{CH}_2$, $-\text{CH}_3$ bending
1218	Medium	C-O stretching vibration

The ^1H and ^{13}C -NMR data of Compound 6 were similar to those of Compound 3 and 4 except the absence of acetyl group. Thus, the structure of Compound 6 was proposed to be labda-8(17),12(*E*),14-triene-2,3-diol as shown in Figure 8. It showed a molecular ion with m/z 304 ($\text{C}_{20}\text{H}_{32}\text{O}_2$) (Fig.40) which indicated the degree of unsaturation of five.

The ^{13}C -NMR chemical shifts of Compound 6 and labda-8(17),12(*E*),14-triene-2,3-diol were compared in Table 17.

Table 17 ^{13}C -NMR chemical shifts of Compound 6 and labda-8(17),12(*E*),14-triene-2,3-diol.

Carbon position	Chemical shifts (ppm)	
	Compound 6	labda-8(17),12(<i>E</i>),14-triene-2,3-diol
1	45.0t	45.0t
2	69.1d	69.1d
3	83.5d	83.5d
4	39.4s	39.3s
5	54.6d	54.5d
6	23.6t	23.6t
7	37.7t	37.7t
8	147.2s	147.2s
9	56.7d	56.7d
10	40.1s	40.1s
11	23.3t	23.3t
12	133.2d	133.2d
13	133.7s	133.7s
14	141.5d	141.5d
15	110.1t	110.1t
16	11.9q	11.9q
17	108.6t	108.6t
18	28.8q	28.8q
19	16.6q	16.6q
20	15.4q	15.5q

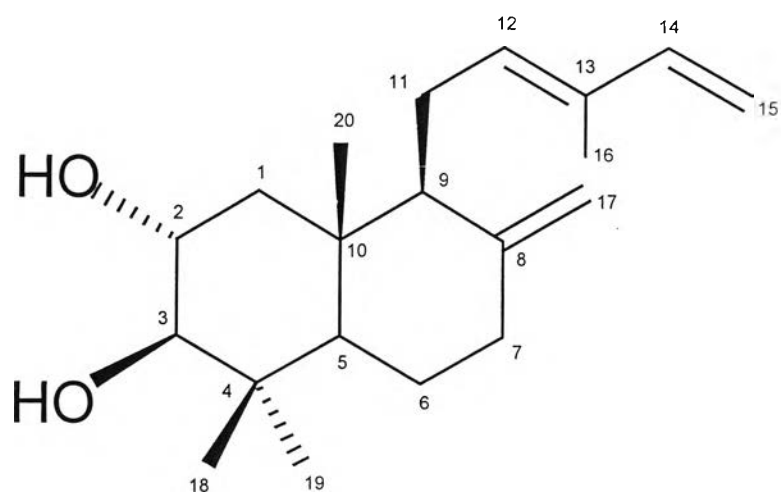


Figure 9 The structure of Compound 6

4.1.7 Structure elucidation of Compound 7

The IR spectrum of Compound 7 is shown in Fig.41 and assigned as shown in Table 18. Its IR spectrum showed the presence of a carboxylic group according to the broad absorption band between 3500 to 3100 cm^{-1} and the strong absorption band at 1718 cm^{-1} due to the carboxylic acid carbonyl stretching.

Table 18 The IR absorption bands assignment of Compound 7

Wave number (cm^{-1})	Intensity	Tentative Assignment
3500-3100	Broad	O-H stretching vibration of acid
2955	Strong	C-H stretching vibration of $-\text{CH}_3$, $-\text{CH}_2$
1718, 1675	Strong	C=O stretching vibration of acid
1630	Medium	C=C stretching vibration
1243	Medium	C-O stretching vibration

The ^1H and ^{13}C -NMR data of Compound 7 were similar to those of Compound 2 except for the downfield positions of C-20 at δ_{C} 68.3 ppm when compared to that of Compound 2 at δ_{C} 18.2 ppm. Its ^1H -NMR spectrum (Fig.42) showed two doublet signals at δ_{H} 4.30 and δ_{H} 4.50 ppm of 2H-20.

Compound 7 showed a molecular ion with m/z 436 ($\text{C}_{27}\text{H}_{32}\text{O}_5$) (Fig.45) which indicated degree of unsaturation of twelve. Compound 7 must consist of one ring of furan (DBE = 3) in addition to one double bond, two rings, one carbonyl group of carboxylic acid and one benzoyl group (DBE = 5).

Comparison of spectral data including ^1H -NMR, ^{13}C -NMR, DEPT-90 and DEPT-135 of this compound with those of Compound 2 demonstrated that

Compound 7 differed from Compound 2 only in having a benzoyl ester group attached at C-20. These data indicated that Compound 7 was (-)-20-benzyloxyhardwickiic acid [5].

The ^{13}C -NMR chemical shifts of Compound 7 and (-)-20-benzyloxyhardwickiic acid were compared in Table 19.

Table 19 ^{13}C -NMR chemical shifts of Compound 7 and (-)-20-benzyloxyhardwickiic acid

Carbon position	Chemical shifts (ppm)	
	Compound 7	(-)-20-benzyloxyhardwickiic acid
1	19.7t	19.2t
2	28.6t	28.1t
3	141.0d	140.5d
4	141.5s	140.9s
5	38.2s	37.7s
6	36.5t	36.0t
7	27.7t	27.2t
8	36.8d	36.3d
9	42.8s	42.3s
10	47.9d	47.4d
11	32.9t	32.4t
12	18.4t	17.9t
13	125.7s	125.1s
14	111.5d	110.9d
15	143.4d	142.9d
16	139.0d	138.5d
17	17.5q	16.9q
18	173.0s	172.0s
19	20.7q	20.2q
20	68.3t	67.7t
21	167.4s	166.8s
22	130.9s	130.4s
23	130.0d	129.5d
24	129.0d	128.5d
25	133.5d	132.9d
26	129.0d	128.5d
27	130.0d	129.5d

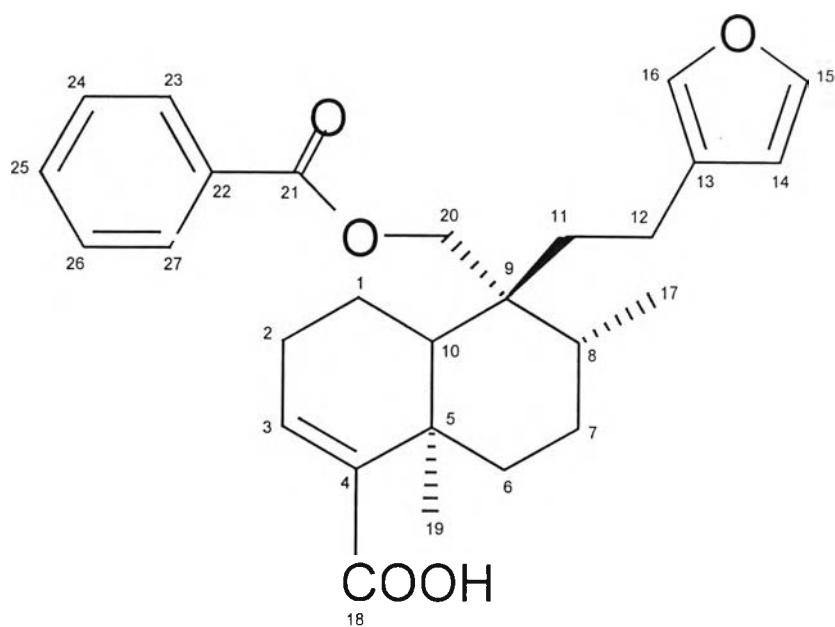


Figure 10 The structure of Compound 7