

## CHAPTER III

### DISCUSSION

#### Structural Elucidation of the Isolated Compounds from the stem barks of *Croton oblongifolius* Roxb.

##### 1. Structure Elucidation of compound 1

The IR spectrum of compound 1 (Fig.22) was summarized in Table 2.

**Table 2** The IR absorption band assignment of compound 1

Wave number (cm <sup>-1</sup> )	Intensity	Tentative Assignment
2924,2867	strong	C-H stretching vibration of -CH <sub>2</sub> , -CH <sub>3</sub>
1672,1645	strong	C=C stretching vibration
1453,1384	medium	-CH <sub>2</sub> , -CH <sub>3</sub> bending

The <sup>1</sup>H-NMR spectrum (Fig.23, table3) of compound 1 showed a three methyl groups attaching to quaternary carbons (0.88,0.86 and 0.79 ppm) and two olefinic methyl groups (1.74 and 1.60 ppm) and five olefinic protons (6.35,5.51,5.40,5.04 and 4.80 ppm) and a double doublet at 6.35 ppm.

The <sup>13</sup>C-NMR spectrum (Fig.24, table3) showed 20 lines. Six signals of olefinic carbons appeared at 141.74,135.91,135.00,132.42,122.62 and 109.79 ppm.

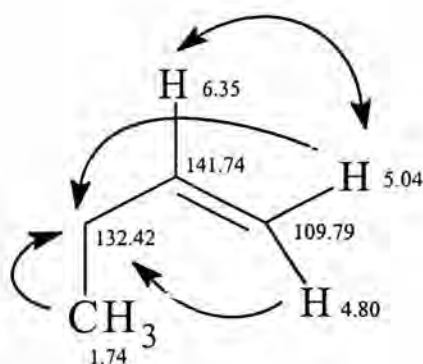
DEPT 90 Experiments (Fig.25), indicated the presence of three sp<sup>2</sup> methine carbons at 141.74,135.91 and 122.62 ppm and two saturated methines at 55.22 and 50.20 ppm. The DEPT-135 spectrum (Fig.25) showed six methylene carbons at 109.79,42.26,39.74,26.28,23.75 and 18.89 ppm and five methyl carbons at

33.27,22.46,21.97,14.03 and 11.85 ppm (Table4) which indicated that the carbon signals at 135.00,132.42,36.81 and 32.98 ppm were quaternary.

Compound 1 showed a molecular ion with  $m/z$  272 ( $C_{20}H_{32}$ ) which indicated DBE of 5. The information from 2D-NMR techniques, COSY correlations (Fig.29, table4), HMQC correlations (Fig.27, table3), HMBC correlations (Fig.28, table4) were used to assist the interpretation the structure of compound 1.

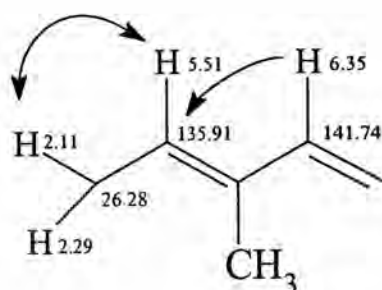
Two dimensional NMR techniques were used for assisting the structure assignment. The protons directly attached to carbons in compound 1 were assigned by HMBC spectra (Fig.28, table4).

Crucial long-range  $^1H$ - $^{13}C$  correlations were obtained by HMBC correlations (Fig.5), the proton at 5.04 and 4.80 ppm was coupled with carbon at 132.42 ppm and the proton of methyl (1.74 ppm) was coupled with carbon at 132.42 ppm. The COSY spectrum (Fig.4) showed that the proton at 5.04 ppm was coupled with the proton at 6.35 ppm (see Scheme 1).



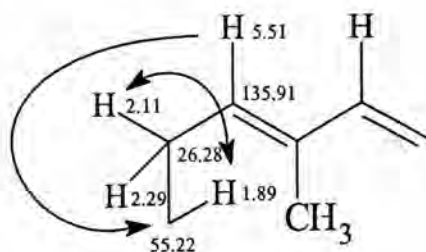
**Scheme 1**

The HMBC spectrum showed that the proton at 6.35 ppm was coupled with the carbon at 135.91 ppm and the proton at 5.51 ppm was coupled with the proton at 2.11 ppm according to COSY spectrum (see Scheme 2).



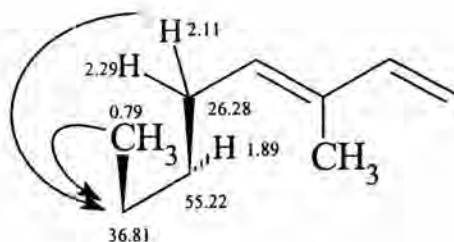
Scheme 2

HMBC spectrum showed that the proton at 5.51 ppm was coupled with the carbon at 55.22 ppm and the proton at 2.11 ppm was coupled with proton at 1.89 ppm according to COSY spectrum (see Scheme 3).



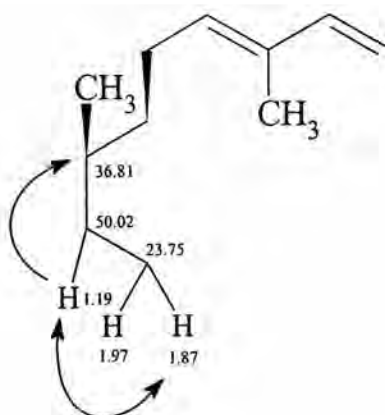
Scheme 3

HMBC spectrum showed that the proton at 2.11 ppm was coupled with the carbon at 36.81 ppm and the proton at methyl (0.79 ppm) was coupled with the carbon at 36.81 ppm. Moreover, *cis*-conformation was assigned by NOESY spectrum (Fig.30) coupling between the proton at 1.89 ppm and the protons of methyl (0.79 ppm) were not appereced (see Scheme 4).



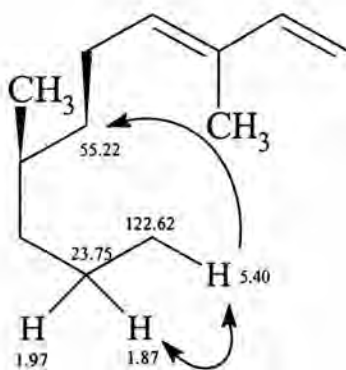
Scheme 4

The proton at 1.19 ppm was coupled with the carbon at 36.81 ppm according to HMBC spectrum and coupled with the proton at 1.86 ppm according to COSY spectrum (see Scheme 5).



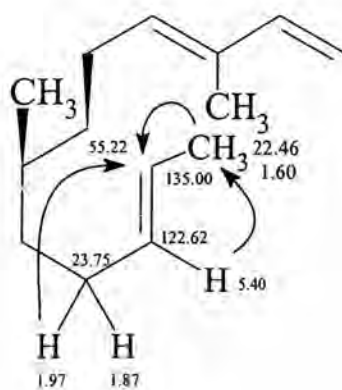
Scheme 5

The proton at 5.40 ppm was coupled with the proton at 1.86 ppm according to COSY spectrum and coupled with the carbon at 55.22 ppm in HMBC spectrum (see Scheme 6).



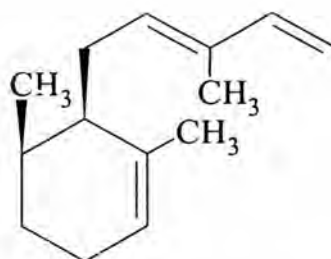
Scheme 6

The HMBC spectrum showed that the proton at 1.97 ppm and the proton of methyl (1.60 ppm) were coupled with the carbon at 135.00 ppm (see Scheme 7).



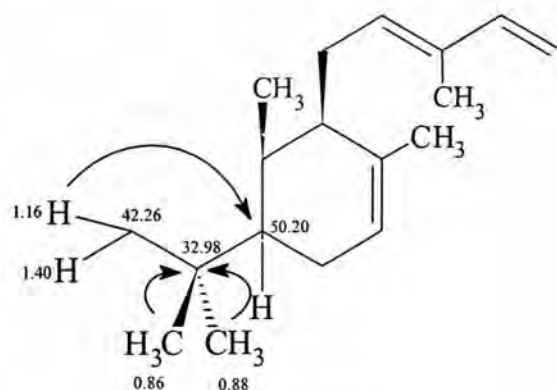
Scheme 7

Connecting one bond between the carbon at 55.22 and 135.00 ppm which was shown in Scheme 8.



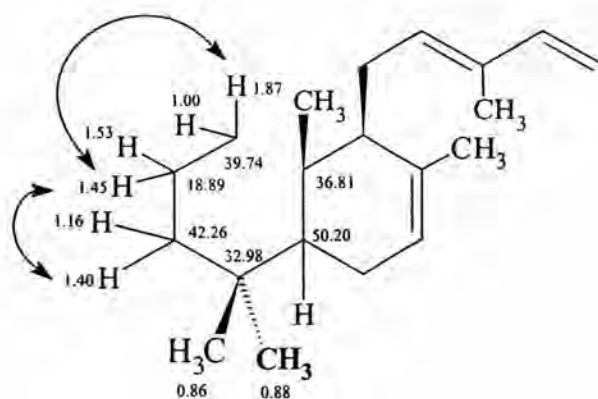
Scheme 8

The proton at 1.16 ppm was coupled with the carbon at 50.20 ppm and the proton of two methyl (0.86 and 0.88 ppm) and the proton at 1.19 ppm coupled with the carbon at 32.98 ppm (see Scheme 9).



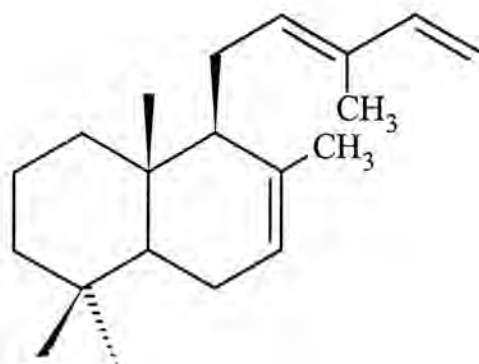
Scheme 9

Moreover, the proton at 1.45 ppm was coupled with the proton at 1.40 ppm and coupled with the proton at 1.87 ppm according to COSY spectrum (see Scheme 10).



Scheme 10

Connecting one bond between the carbon at 39.74 ppm with the carbon at 36.81 ppm. Thus, the structure of compound 1 was proposed to be labda-7,12-14-triene as shown in figure 3. The COSY correlations and long-range C-H correlations by HMBC spectrum were summarized in figure 4 and 5 respectively.

Figure 3 The structure of compound 1

**Table 3** The HMQC spectral data of compound **1**

<sup>13</sup> C-NMR (ppm)	<sup>1</sup> H-NMR (ppm), coupling constant (Hz)
11.85q	1.74s
14.03q	0.79s
18.89t	1.53m, 1.45m
21.97q	0.88s
22.46q	1.60s
23.75t	1.86m, 1.97d( <i>J</i> =17.0)
26.28t	2.11m, 2.29d( <i>J</i> =14.4)
32.98s	-
33.27q	0.86s
36.81s	-
39.74t	1.00dt( <i>J</i> =3.4, 13.4), 1.87m
42.26t	1.16dd( <i>J</i> =3.4, 13.1), 1.40d( <i>J</i> =11.9)
50.20d	1.19dd( <i>J</i> =4.9, 11.5)
55.22d	1.89m
109.79t	4.80d( <i>J</i> =11.9), 5.04d( <i>J</i> =16.9)
122.62d	5.40dt( <i>J</i> =2.1, 6.1)
132.42s	-
135.00s	-
135.91d	5.51t( <i>J</i> =6.7)
141.74d	6.35dd( <i>J</i> =10.7, 17.4)



**Table 4** The HMQC, HMBC and COSY spectral data of compound **1**

position	$\delta_c^a$	$\delta_H$	HMBC (H to C)	COSY
1	39.74(t)	1.00dt( $J=3.4,13.4$ ), 1.87m	C-3,C-2,C-20	H-2(1.53), H-2(1.45)
2	18.89(t)	1.45m, 1.53m	C-3	H-1(1.87),H-3(1.16) H-1(1.00),H-3(1.40)
3	42.26(t)	1.16dd( $J=3.4,13.1$ ), 1.40d( $J=11.9$ )	C-1,C-2,C-4,C-10,C-18,C-19	H-2(1.45) H-2(1.53)
4	32.98(s)	-	-	-
5	50.20(d)	1.19dd( $J=4.9,11.5$ )	C-4,C-6,C-9,C-10,C-18, C-19,C-20	H-6(1.87,1.97)
6	23.75(t)	1.86m, 1.97d( $J=17.0$ )	C-7,C-8C-10	H-5(1.19),H-7(5.40) H-5(1.19)
7	122.62(d)	5.40dt( $J=2.1,6.1$ )	C-5,C-6,C-9,C-17	H-6(1.87)
8	135.00(s)	-	-	-
9	55.22(d)	1.89m	C-5,C-12	H-11(2.11,2.29)
10	36.81(s)	-	-	-
11	26.28(t)	2.11m 2.29d( $J=14.4$ )	C-8,C-9,C-10,C-12,C-13, C-14	H-9(1.89),H-12(5.5) H-9(5.51)
12	135.91(d)	5.51t( $J=6.7$ )	C-9,C-11,C-14	H-11(2.11,2.29)
13	132.42(s)	-	-	-
14	141.74(d)	6.35dd( $J=10.7,17.4$ )	C-12,C-13	H-15(5.04,4.80)
15	109.79(t)	4.80d( $J=10.7$ ), 5.04d( $J=16.9$ )	C-13,C-14,C-16	H-14(6.35) H-14(6.35)
16	11.85(q)	1.74s	C-13,C-14,C-15	
17	22.46(q)	1.60s	C-7,C-8	
18	33.27(q)	0.86s	C-3,C-4,C-5	
19	21.97(q)	0.88s	C-3,C-4,C-5	
20	14.03(q)	0.79s	C-1,C-9,C-10	

<sup>a</sup> Carbon type as determined by DEPT experiments spectra : s = singlet, d = doublet, t = triplet, q = quartet.

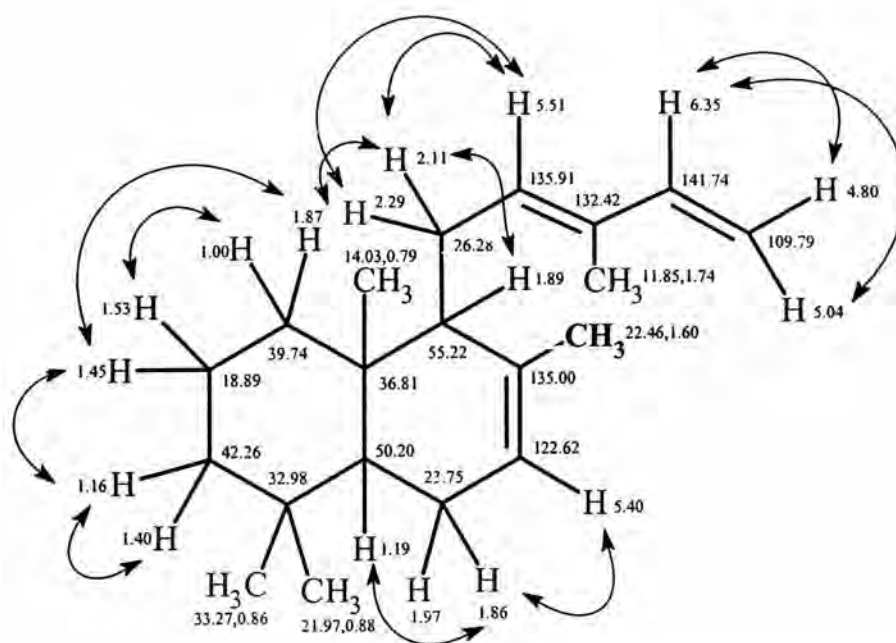


Figure 4 The COSY correlations of compound 1

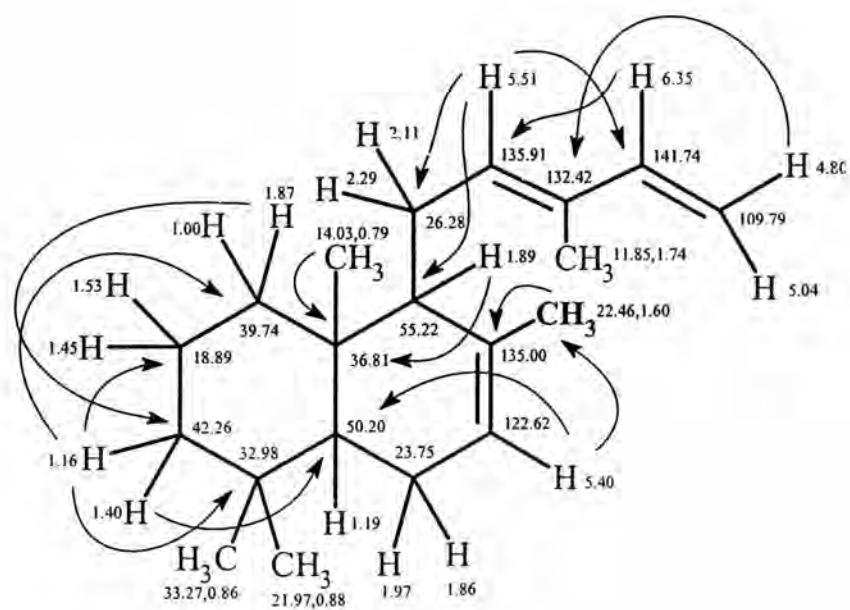


Figure 5 The HMBC correlations of compound 1

<sup>13</sup>C-NMR spectrum of compound 1 was compared with labda-7,12(Z),14-triene (Fig.6B) that and this showed that they have similar structure (Table5).

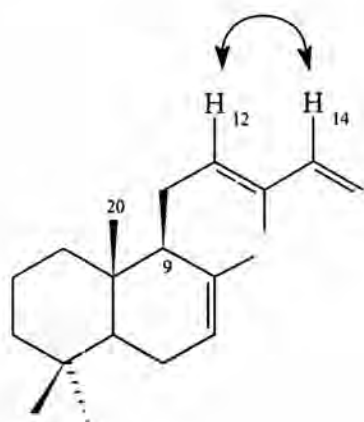
**Table 5** <sup>13</sup>C-NMR data of compound 1 and labda-7,12(Z),14-triene (125 MHz, CDCl<sub>3</sub>).

position	compound <u>1</u>	labda-7,12(Z),14-triene
1	39.74	39.77
2	18.89	18.95
3	42.26	42.30
4	32.98	33.06
5	50.20	50.23
6	23.75	23.80
7	122.62	122.66
8	135.00	135.26
9	55.22	55.41
10	36.81	36.92
11	26.28	25.40
12	135.91	134.04
13	132.42	130.59
14	141.74	133.77
15	109.79	113.23
16	11.85	19.90
*17	22.46	22.79
18	33.27	33.37
19	21.97	22.06
20	14.03	14.11

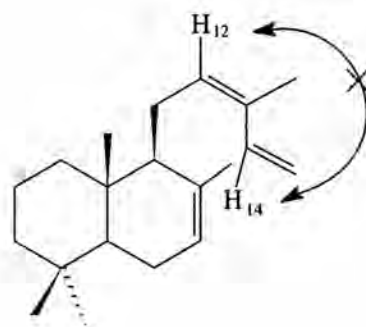
\*The chemical shift of  $\delta_{\text{C-17}}$  represented the functional group of compound 1

Comparison of  $^{13}\text{C}$ -NMR spectrum of compound 1 and labda-7,12(*Z*),14-triene (Fig.6B) suggested that the stereochemistry of the side-chain double bond are different and this was confirmed by NOESY correlations (Fig.6A and 6B). So, stereochemistry of  $\Delta^{12}$  in 1 possessed an *E* configuration and the  $\Delta^{12,14}$  were conjugated diene system and compound 1 was assigned to labda-7,12(*E*),14-triene.

The stereochemistry of the main structure of compound 1 had similar structure to labda-7,12(*Z*),14-triene and confirmed by NOESY correlations that the proton at H-9 (1.89 ppm) and the protons of methyl (H-20) were not appeared. So, relative stereochemistry of compound 1 was determined on the basis of NOESY spectra, Key NOE correlations in compound 1 are shown in figure 7.

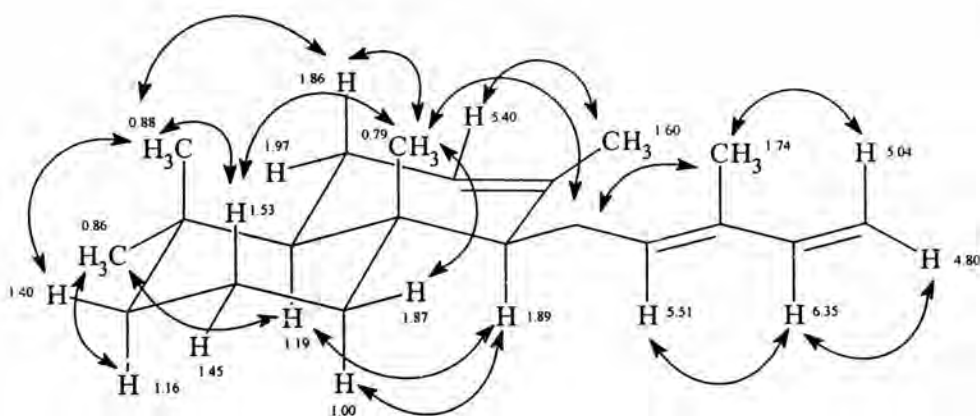


6A



6B

The above structure was shown by the NOESY correlations of compound 1 (6A) and labda-7-12*Z*, 14-triene (6B).



**Figure 7** The NOESY correlations of compound 1

## 2. Structure Elucidation of Compound 2

The IR spectrum of compound 2 (Fig.31) showed the presence of an aldehyde group according to at 2852 and 2710  $\text{cm}^{-1}$ .

**Table 6** The IR absorption band assignment of compound 2

Wave number ( $\text{cm}^{-1}$ )	Intensity	Tentative Assignment
2954,2923	strong	C-H stretching vibration of $-\text{CH}_2-$ , $-\text{CH}_3$
2852,2710	strong, medium	C-H stretching vibration of aldehyde
1690	strong	C=O stretching vibration
1636, 1607	medium	C=C stretching vibration
1460,1389	medium	$-\text{CH}_2-$ , $-\text{CH}_3$ bending

The  $^1\text{H-NMR}$  spectrum (Fig.32, table7) indicated that compound 2 possessed three a methyl groups attaching to quaternary carbons (0.79,0.86 and 0.91 ppm) and one olefinic methyl group (1.70 ppm) and five olefinic protons (6.83,6.29,5.44,5.00 and 4.84 ppm) and one proton for the aldehyde functional group (9.37 ppm).

The  $^{13}\text{C}$ -NMR spectrum (Fig.33, table7) showed the carbonyl group of aldehyde corresponding to the signal at 194.31 ppm. The signals of olefinic carbons appeared at 151.80,143.40,141.77,133.77,132.56 and 109.79 ppm.

From DEPT 90 Experiments (Fig.34) showed six methine carbons at 194.31 ppm (aldehyde), 151.80,141.77,133.77,49.41 and 49.38 ppm. The DEPT-135 (Fig.34) indicated six methylene carbons at 109.79,41.86,39.87,24.90, 24.75 and 18.50 ppm and four methyl carbons at 33.22,22.07,14.73 and 11.76 ppm.

Moreover, There were four quaternary carbons at 43.40,132.56, 36.71 and 32.85 ppm according DEPT-135 spectrum.

Compound 2 showed a molecular ion with  $m/z$  286 ( $\text{C}_{20}\text{H}_{30}\text{O}$ ) and Elemental analysis which indicated DBE of 6.

Comparison of spectral data (Table15) of this compound with that of 1, indicated that compound 2 differed from compound 1 only in having the aldehyde group in place of one methyl of compound 1 at C-17. The information of 2D-NMR including COSY correlations (Fig.38, table8), NOESY correlations (Fig.39), HMQC correlations (Fig.36, table7) and HMBC correlations (Fig.37, table8) supported that structural elucidation of 2. The above data indicated that compound 2 was  $\lambda$ -7,12 (*E*),14-triene-17-al (Fig.8)

**Table 7** The HMQC spectral data of compound 2

<sup>13</sup> C-NMR (ppm)	<sup>1</sup> H-NMR (ppm), coupling constant (Hz)
11.76q	1.70s
14.73q	0.79s
18.50t	1.40d( <i>J</i> =3.6),1.50m
22.07q	0.91s
24.75t	2.48d( <i>J</i> =16.8),2.62m
24.90t	2.34m,2.18m
32.85s	-
33.22q	0.86s
36.71s	-
39.87t	1.00dt( <i>J</i> =3.7,13.1),1.90dd( <i>J</i> =2.1,12.8)
41.86t	1.43dd( <i>J</i> =3.4,6.1),1.16t( <i>J</i> =4.3)
49.38d	1.13dd( <i>J</i> =4.3,12.5)
49.41d	2.30d( <i>J</i> =5.8)
109.79t	4.84d( <i>J</i> =10.7),5.00d( <i>J</i> =17.4)
132.56s	-
133.77d	5.44t( <i>J</i> =6.7)
141.77d	6.29dd( <i>J</i> =11.0,17.4)
143.40s	-
151.80d	6.83dt( <i>J</i> =2.1,5.8)
194.31d	9.37s

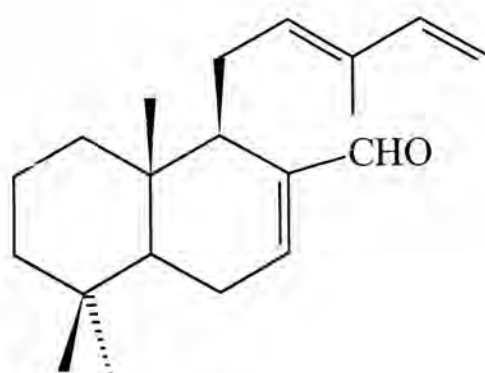
**Table 8** The HMQC, HMBC and COSY spectral data of compound 2

position	$\delta_c^a$	$\delta_H$	HMBC (H to C)	COSY
1	39.87(t)	1.00dt( $J=3.7,13.1$ ), 1.90dd( $J=2.1,12.8$ )	C-3,C-9	H-2(1.40) H-2(1.50,1.40)
2	18.50(t)	1.40d( $J=3.1$ ), 1.50m	C-1,C-5,C-9	H-1(1.00),H-3(1.43) H-1(1.90)
3	41.86(t)	1.14t( $J=4.3$ ), 1.43dd( $J=3.4,6.1$ )	C-1,C-2,C-4,C-5	H-2(1.40) H-2(1.40)
4	32.85(s)	-	-	-
5	49.38(d)	1.12dd( $J=4.3,12.5$ )	C-4,C-6,C-7, C-9,C-10,C-19, C-20	H-6(2.18,2.34)
6	24.90(t)	2.18m, 2.34m	C-5,C-7,C-8,C-10	H-5(2.18) H-5(2.18),H-7(6.83)
7	151.80(d)	6.83dt( $J=2.1,5.8$ )	C-5,C-6,C-9,C-17	H-6(2.34)
8	143.40(s)	-	-	-
9	49.41(d)	2.30d( $J=5.8$ )	C-5,C-8,C-10	H-11(2.48)
10	36.71(s)	-	-	-
11	24.75(t)	2.48d( $J=16.8$ ), 2.62m	C-8,C-9,C-10, C-12,C-13,C-14	H-9(2.30),H-12(5.44) H-12(5.44)
12	133.77(d)	5.44t( $J=6.7$ )	C-9,C-11,C-14,C-16	H-11(2.48,2.62)
13	132.56(s)	-	-	-
14	141.77(d)	6.29dd( $J=11.0,17.4$ )	C-11,C-12,C-13,C-16	H-15(5.00,4.84)
15	109.79(t)	4.84d( $J=16.8$ ), 5.00d( $J=17.39$ )	C-13,C-14	H-14(6.29) H-14(6.29)
16	11.76(q)	1.70s	C-12,C-13,C-14	
17	194.31(d)	9.37s	C-7,C-3,C-9	
18	33.22(q)	0.86s	C-3,C-4,C-5,C-19	
19	22.07(q)	0.91s	C-3,C-4,C-5	
20	14.73(q)	0.79s	C-1,C-9,C-10,C-11	

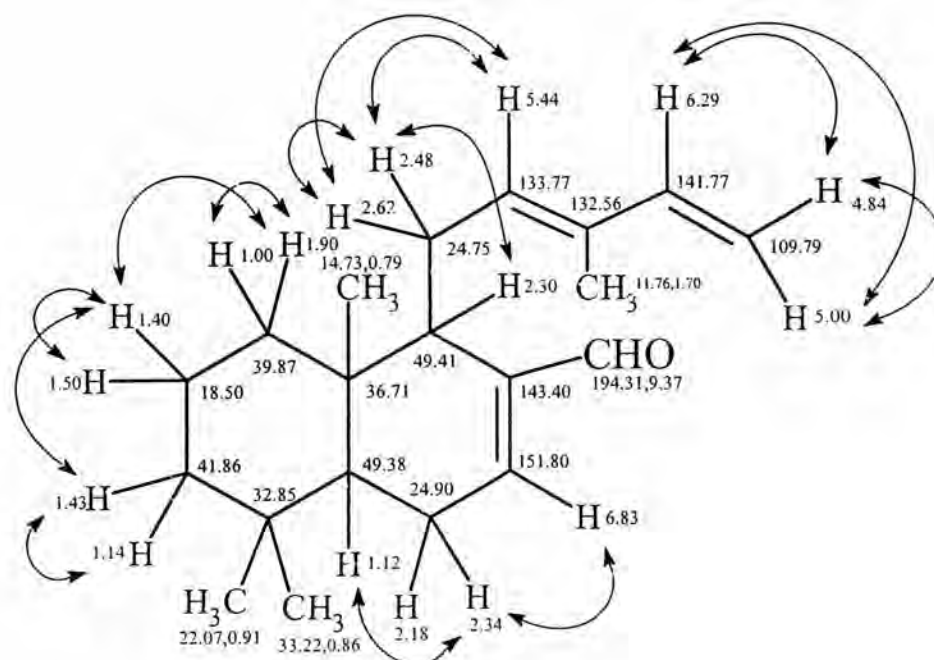
<sup>a</sup> Carbon type as determined by DEPT experiment : s = singlet, d = doublet,

t = triplet, q = quartet

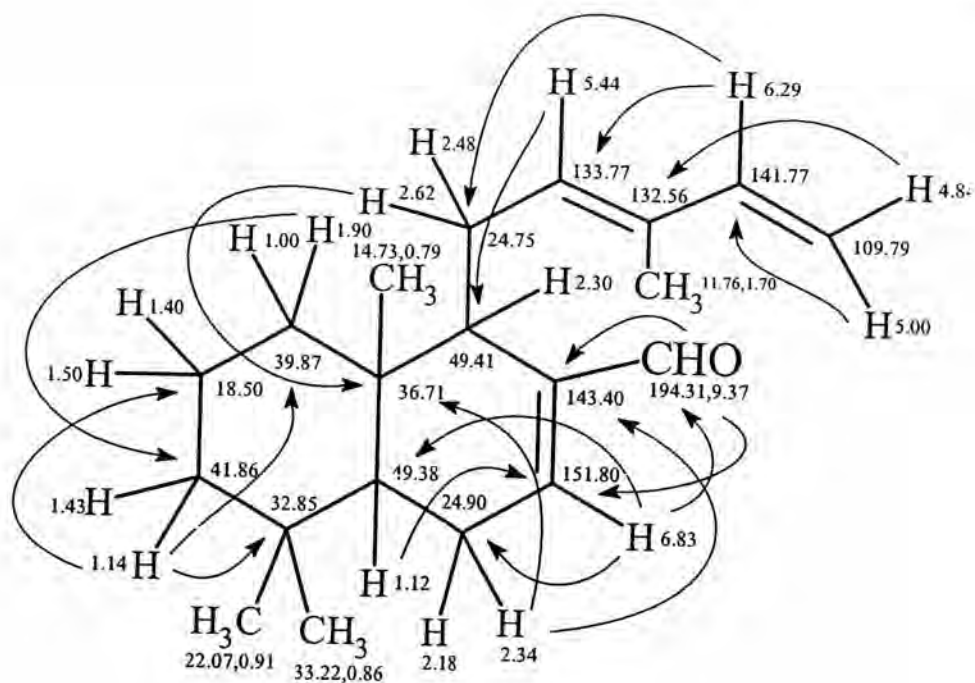




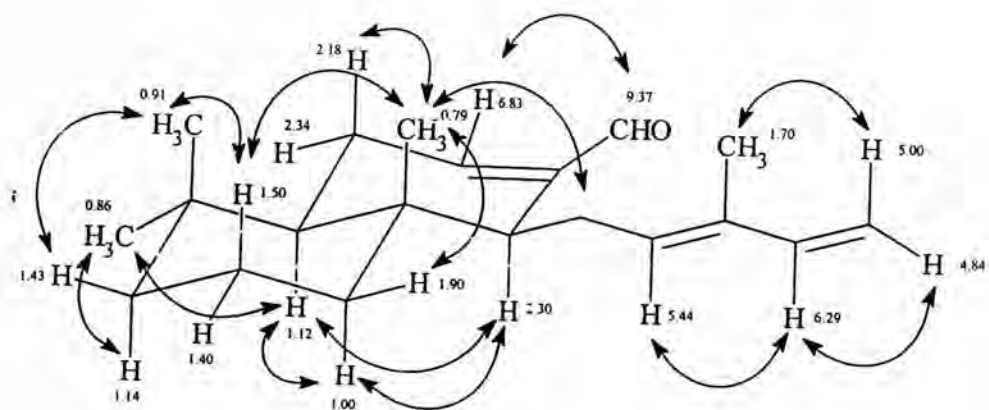
**Figure 8** The structure of compound 2



**Figure 9** The COSY correlations of compound 2



**Figure 10** The HMBC correlations of compound 2



**Figure 11** The NOESY correlations of compound 2

Relative stereochemistry of compounds 2 was determined on the basis of NOESY spectra. Key NOE correlations in compound 2 are shown in Figure 11.

### 3. Structure Elucidation of Compound 3

The IR spectrum of compound 3 (Fig.40) showed the presence of a hydroxy group according to the broad absorption band between 3242 to 3163  $\text{cm}^{-1}$ .

**Table 9** The IR absorption band assignment of compound 3

wavenumber ( $\text{cm}^{-1}$ )	intensity	tentative assignment
3242-3163	broad	O-H stretching vibration of alcohol
2919,2815	strong	C-H stretching vibration of $-\text{CH}_2-$ , $-\text{CH}_3$
1640,1607	medium	C=C stretching vibration
1441,1388	midium	$-\text{CH}_3$ , $-\text{CH}_2-$ bending

The molecular formular of compound 3 was assigned to be  $\text{C}_{20}\text{H}_{32}\text{O}$  according to microanalysis and EI MS [ $\text{M}^+$ ] ( $m/z$  288) which indicated of 6 DBE. The  $^{13}\text{C}$ -NMR spectrum (Fig.45, table10) of compound 3 was similar to that of compound 1 except for the downfields position of C-17 (65.97 ppm), compared with that of compound 1 (22.5 ppm). It's DEPT spectrum (Fig.43) showed two double doublet signals ( $\delta_{\text{H}}$  3.9,  $J = 12.8$  and  $\delta_{\text{H}}$  4.0,  $J = 12.8$ ) of 2H-17. Comparison of spectral data including  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR including DEPT analysis, NOESY correlations, COSY correlations, HMQC correlations and HMBC correlatiions of this compound with of that compound 1 demonstrated that compound 3 differed from 1 only in having a hydroxy group attached to C-17. Based on the spectral data discussed above and shown below, the structure of compound 3 was assigned to be labda-7,12(E),14-triene-17-ol (Fig.12).

**Table 10** The HMQC spectral data of compound **3**

<sup>13</sup> C-NMR (ppm)	<sup>1</sup> H-NMR (ppm),coupling constant (Hz)
11.94q	1.75s
13.99q	0.77s
18.83t	1.53m,1.45t( <i>J</i> =3.7)
21.96q	0.87s
23.55t	2.04d( <i>J</i> =5.8),1.90m
25.85t	2.33d( <i>J</i> =15.0),2.15m
32.96s	-
33.19q	0.85s
36.66s	-
39.57t	1.91m,1.01dt( <i>J</i> =3.8,13.1)
42.15t	1.39m,1.16dt( <i>J</i> =3.1,12.9)
49.84d	1.23dd( <i>J</i> =4.9,13.0)
52.23d	2.07m
65.98d	4.04d( <i>J</i> =12.7),3.9d( <i>J</i> =12.8)
110.67t	5.06d( <i>J</i> =17.0),4.91d( <i>J</i> =10.7)
125.40s	5.75m
133.54d	-
134.70s	5.55t( <i>J</i> =6.7)
138.57d	-
141.27d	6.34dd( <i>J</i> =10.7,17.4)

**Table 11** The HMQC, HMBC and COSY spectral data of compound 3

position	$\delta_c^a$	$\delta_H$	HMBC (H to C)	COSY
1	39.57(t)	1.01dt( $J=3.8,13.1$ ) 1.19m	C-3,C-2,C-20	H-2(1.45) H-2(1.45)
2	18.83(t)	1.45t( $J=3.7$ ), 1.53m	C-1,C-3	H-1(1.01,1.91),H-3(1.16) H-3(1.16)
3	42.15(t)	1.16dt( $J=3.1,12.8$ ), 1.39m	C-1,C-2,C-4,	H-2(1.45,1.53)
4	32.96(s)	-	-	-
5	49.84(d)	1.23dd( $J=4.9,13.0$ )	C-3,C-4,C-7,C-9, C-10,C-18,C-20	H-6(1.90,2.04)
6	23.55(t)	2.04d( $J=5.8$ ), 1.90m	C-7,C-8,C-10	H-5(1.23),H-7(5.75) H-5(1.23),H-7(5.75)
7	125.40(d)	5.75m	C-5,C-6,C-9,C-17	H-6(2.04,1.90)
8	138.57(s)	-	-	-
9	52.23(d)	2.07m	C-5,C-7,C-12	H-11(2.15)
10	36.66(s)	-	-	-
11	25.85(t)	2.33d( $J=15.0$ ), 2.15m	C-8,C-9,C-12,C-13	H-12(5.55) H-9(2.07),H-12(5.55)
12	134.78(d)	5.55t( $J=6.7$ )	C-9,C-11,C-14	H-11(2.33,2.15)
13	133.54(s)	-	-	-
14	141.27(d)	6.34dd, $J=10.7,17.4$ )	C-12,C-13,C-16	H-15(5.06,4.91)
15	110.67(t)	4.91d( $J=10.7$ ), 5.06d( $J=17.0$ )	C-13,C-14,	H-14(6.34) H-14(6.34)
16	11.93(q)	1.75s	C-12,C-13,C-14	
17	65.97(t)	3.86d( $J=12.8$ ), 4.04d( $J=12.7$ )	C-7,C-8	
18	33.19(q)	0.85s	C-3,C-4,C-5,C-19	
19	21.95(q)	0.87s	C-3,C-4,C-5	
20	13.99(q)	0.77s	C-1,C-5,C-9,C-10	

<sup>a</sup> Carbon type as determined by DEPT experiments : s = singlet, d = doublet,  
t = triplet, q = quartet

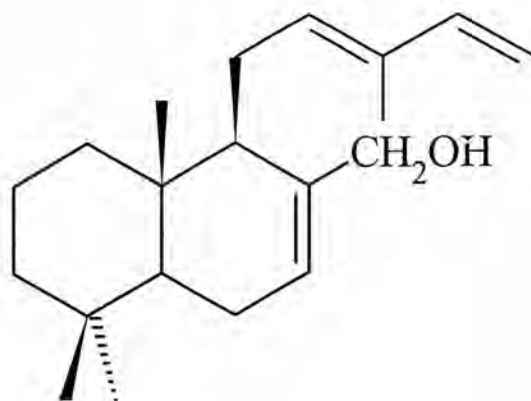


Figure 12 The structure of compound 3

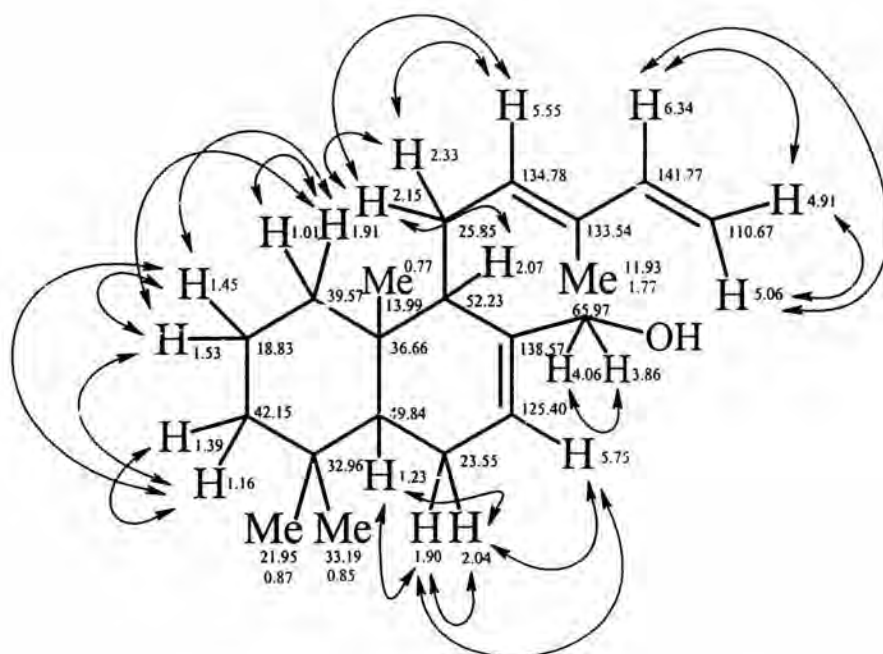
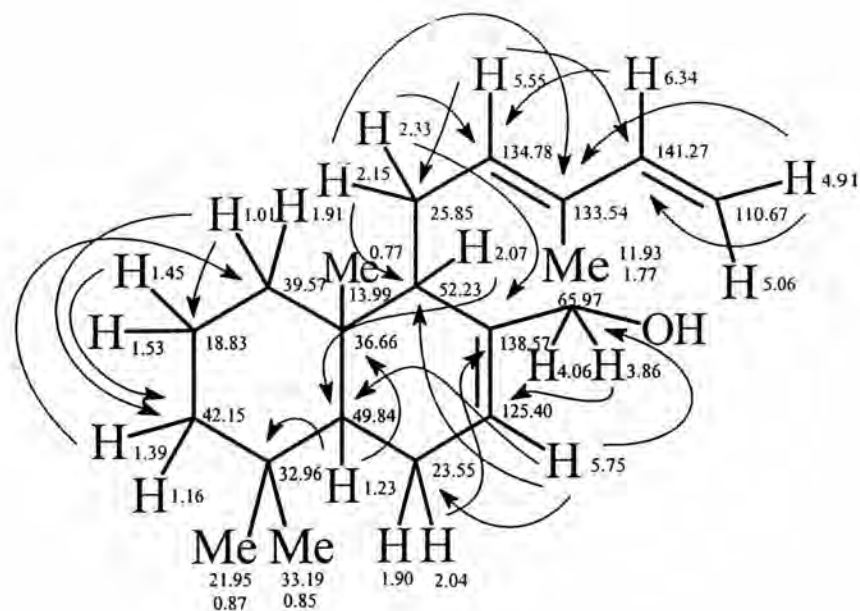
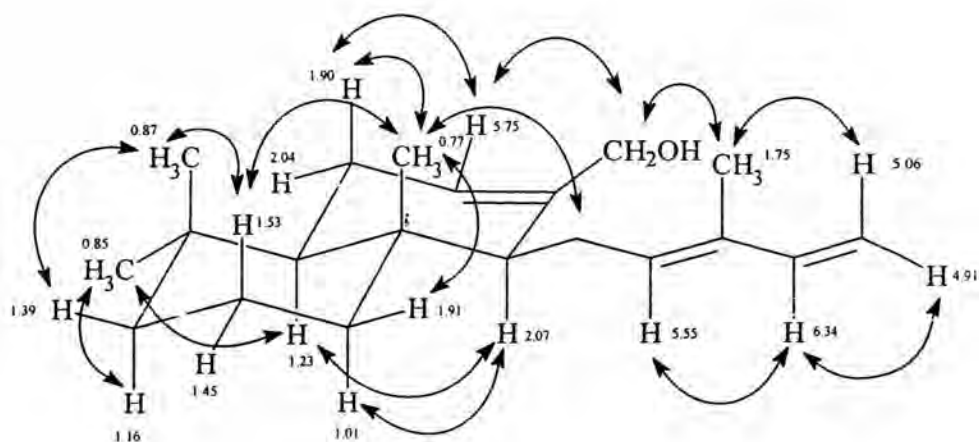


Figure 13 The COSY correlations of compound 3



**Figure 14** The HMBC correlations of compound 3



**Figure 15** The NOESY correlations of compound 3

Relative stereochemistry of compounds 3 was determined on the basis of NOESY spectra. Key NOE correlations in compound 3 are shown in Figure 15.

#### 4. Structural Elucidation of Compound 4

The IR spectrum of compound **4** (Fig.49) showed the presence of a carboxylic group according to the broad absorption band between 3421 to 2626  $\text{cm}^{-1}$  and the strong absorption band at 1707  $\text{cm}^{-1}$  due to the carboxylic acid carbonyl stretching.

**Table 12** The IR absorption band assignments of compound **4**

Wavenumber ( $\text{cm}^{-1}$ )	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 molecular formula of compound **4** was proposed to be  $\text{C}_{20}\text{H}_{30}\text{O}_2$ , based on microanalysis and EI MS [ $\text{M}^+$ ] ( $m/z$  302) which indicated DBE of 6. The presence of carboxylic moiety was supported by  $^{13}\text{C}$  resonance at  $\delta_{\text{C}}$  174.11. The  $^{13}\text{C}$ -NMR spectral data (Table13) were similar to that of compound **1**, **2** and **3** except for the functional group of this compound at C-17 because a carboxylic acid. Thus, the structure of compound **4** was proposed to be labda-7,12(*E*),14-triene-17-oic acid (Fig.16) and the proposed structure was further conformed from 2D-NMR analysis.



**Table 13** The HMQC spectral data of Compound 4

<sup>13</sup> C-NMR (ppm)	<sup>1</sup> H-NMR (ppm),coupling constant(Hz)
11.72q	1.67s
14.78 q	0.82s
18.57t	1.4d( <i>J</i> =2.5),1.5m
22.15q	0.89s
23.98t	2.03m,2.19m
26.03t	2.32dd( <i>J</i> =6.1,16.8),2.58m
32.80s	-
33.31q	0.86s
36.88s	-
40.08t	1.01dt( <i>J</i> =3.4,13.1),1.87m
41.93t	1.15d( <i>J</i> =4.0),1.42m
49.34d	1.18d( <i>J</i> =4.3)
49.95d	2.37m
109.94t	4.84d( <i>J</i> =11.0),5.0d( <i>J</i> =17.4)
133.08s	-
133.44d	5.47t( <i>J</i> =6.7)
133.64s	-
140.52d	6.90dt( <i>J</i> =2.1,6.2)
141.77d	6.31dd( <i>J</i> =10.7,17.4)
174.11s	-

**Table 14** The HMBC, HMQC and COSY spectral data of compound **4**

position	$\delta_c^a$	$\delta_H$	HMBC (H to C)	COSY
1	40.08(t)	1.01dt( $J=3.4,13.1$ ), 1.87m	C-3,C-2,C-20	H-2(1.40) H-2(1.40,1.50)
2	18.57(t)	1.4d( $J=2.5$ ), 1.5m	C-3	H-1(1.01,1.87),H-3 H-1,H-3(1.15)
3	41.93(t)	1.15d( $J=4.0$ ), 1.42m	C-1,C-2,C-4,C-10,C-18, C-19	H-2(1.50) H-2(1.40)
4	32.80(s)	-	-	-
5	49.34(d)	1.18d( $J=4.3$ )	C-4,C-6,C-9, C-10,C-18, C-19,C-20	H-6(2.19,2.03)
6	23.98(t)	2.03m, 2.19m	C-7,C-8,C-10	H-5(1.18),H-7(6.90) H-5(1.18)
7	140.52(d)	6.90dt( $J=2.1,6.2$ )	C-5,C-6,C-9,C-17	H-6(2.19,2.03)
8	133.64(s)	-	-	-
9	49.95(d)	2.37m	C-5,C-12	H-11(2.58)
10	36.88(s)	-	-	-
11	26.03(t)	2.32dd( $J=6.1,16.8$ ), 2.58m	C-8,C-9,C-10,C-12, C-13,C-14	H-12(5.47) H-9(2.37),H-12(5.47)
12	133.44(d)	5.47t( $J=6.72$ )	C-9,C-11,C-14	H-11(2.32,2.58)
13	133.08(s)	-	-	-
14	141.77(d)	6.31dd( $J=10.7,17.4$ ) 4.84d( $J=11.0$ ),	C-12,C-13	H-15(5.0,4.84)
15	109.94(t)	5.00d( $J=17.4$ )	C-13,C-14,C-16	H-14(6.31) H-14(6.31)
16	11.72(q)	1.67s	C-13,C-14,C-15	
17	174.11(s)	-	-	
18	33.31(q)	0.86s	C-3,C-4,C-5	
19	22.15(q)	0.89s	C-3,C-4,C-5	
20	14.78(q)	0.82s	C-1,C-9,C-10	

<sup>a</sup>Carbon type as determined by DEPT experiments : s = singlet, d = doublet,  
t = triplet, q = quartet

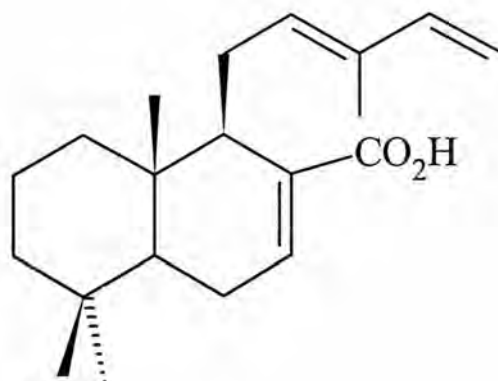


Figure 16 Structure of compound 4

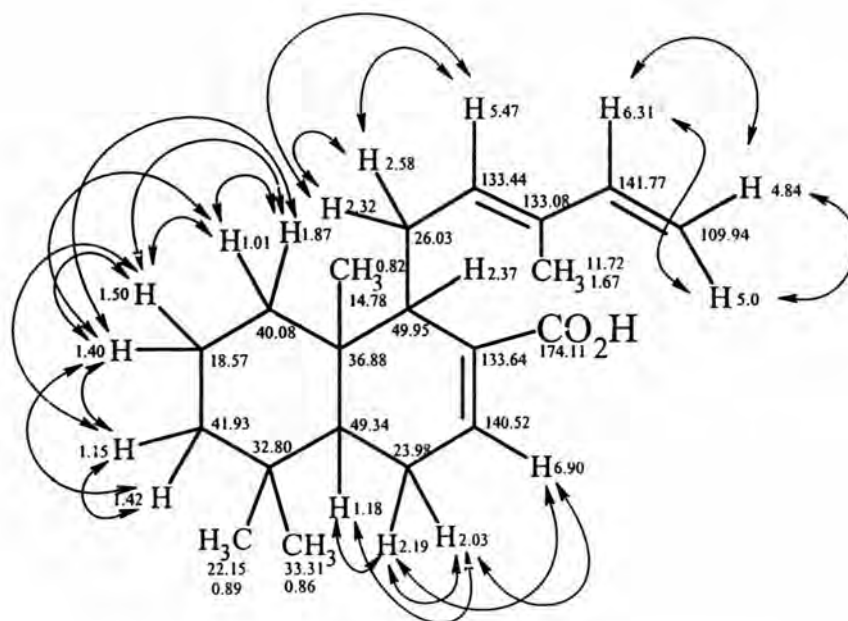
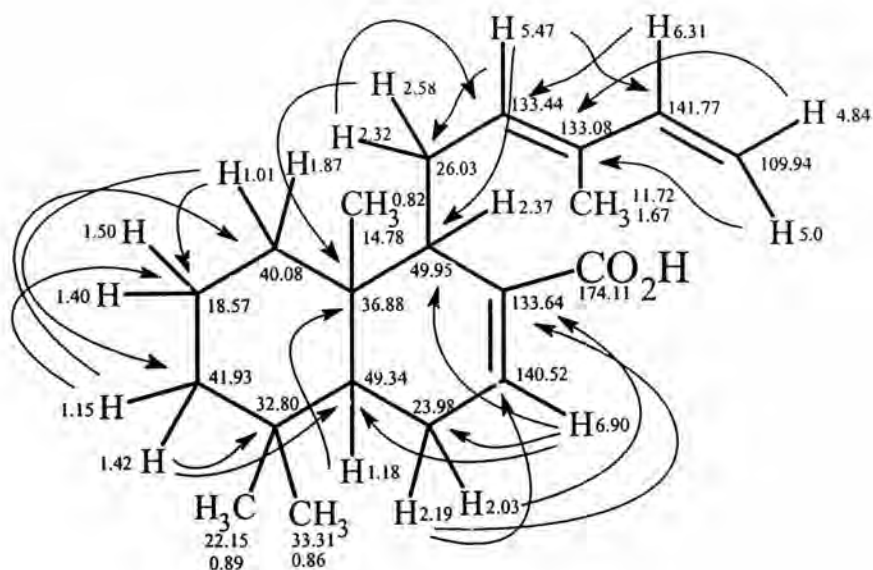
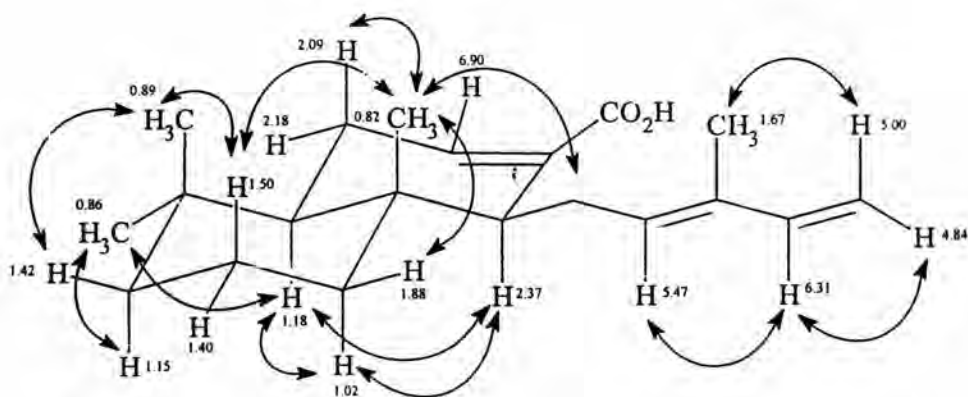


Figure 17 The COSY correlations of compound 4



**Figure 18** The HMBC correlations of compound 4

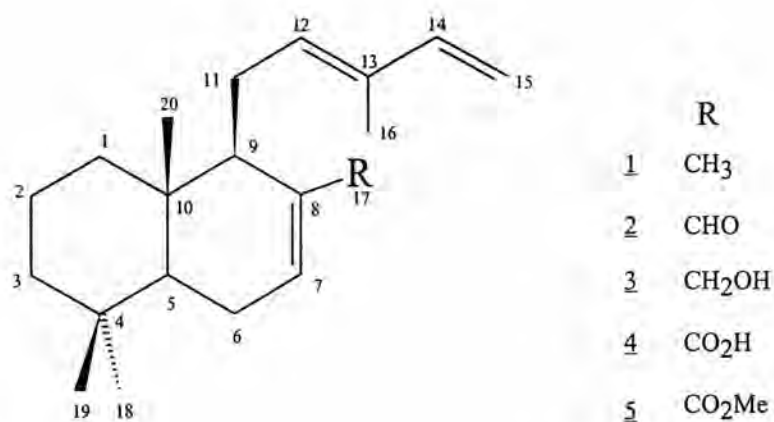


**Figure 19** The NOESY correlations of compound 4

Relative stereochemistry of compounds 4 was determined on the basis of NOESY spectra. Key NOE correlations in compound 4 are shown in Figure 19.

Compound 5 was a methyl ester of compound 4 which was generated by treatment of 4 with diazomethane in ether. The molecular formula of compound 5 was indicated  $C_{21}H_{34}O_2$  and showed molecular ion at  $m/z$  316. The  $^{13}C$ -NMR spectrum was similar to that of compound 4 except for the moving upfield position of C-17 carboxylate ester ( $\delta_C$  169.54), compared with of compound 4 ( $\delta_C$  174.11).

The structure of compound 1-5 (Fig.20) were assigned to same skeleton structure and differed about functional group at  $\delta_C$ -17.



**Figure 20** The structure of compound 1-5

The  $^{13}C$  and  $^1H$ -NMR of compound 1-5 were presented on table 15 and 16 respectively.

**Table 15**  $^{13}\text{C}$ -NMR spectral data of compound 1-5 (125 MHz,  $\text{CDCl}_3$ ) ppm

position	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
1	39.74	39.87	39.57	40.08	39.92
2	18.89	18.50	18.83	18.57	18.57
3	42.26	41.86	42.15	41.93	41.95
4	32.98	32.85	32.96	32.80	33.28
5	50.20	49.38	49.84	49.34	49.39
6	23.75	24.90	23.55	23.98	23.71
7	122.62	151.80	125.40	140.52	137.04
8	135.00	143.40	138.57	133.64	134.52
9	55.22	49.41	52.23	49.95	50.33
10	36.81	36.71	36.66	36.88	36.78
11	26.28	24.75	25.85	26.03	26.23
12	135.91	133.77	134.78	133.44	133.62
13	132.42	132.56	133.54	133.08	133.06
14	141.74	141.77	141.27	141.77	141.72
15	109.79	109.79	110.67	109.94	109.96
16	11.85	11.76	11.93	11.72	11.73
*17	22.46	194.31	65.97	174.11	169.54
18	33.27	33.22	33.19	33.31	32.80
19	21.97	22.07	21.95	22.15	22.13
20	14.03	14.73	13.99	14.78	14.51
$\text{CH}_3\text{O-}$					51.32

\*The chemical shift of  $\delta_{\text{C-17}}$  represented the functional group of compound 1-5

**Table 16**  $^1\text{H-NMR}$  spectral data of compound 1-4 and coupling constant  
(500 MHz,  $\text{CDCl}_3$ )

position	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
1	1.00dt( $J=3.4,13.4$ ), 1.87m	1.00dt( $J=3.7,13.1$ ), 1.90dd( $J=2.1,12.8$ )	1.01dt( $J=3.8,13.1$ ) 1.19m	1.01dt( $J=3.4,13.1$ ), 1.87m
2	1.45m,1.53m	1.40d( $J=3.1$ ),1.50m	1.45t( $J=3.7$ ),1.53m	1.4d( $J=2.5$ ),1.5m
3	1.16dd( $J=3.4,13.1$ ), 1.40d( $J=11.9$ )	1.16t( $J=4.3$ ), 1.43dd( $J=3.4,6.1$ )	1.16dt( $J=3.1,12.8$ ), 1.39m	1.15d( $J=4.0$ ), 1.42m
4	-	-	-	-
5	1.19dd( $J=4.9,11.5$ )	1.13dd( $J=4.3,12.5$ )	1.23dd( $J=4.9,13.0$ )	1.18d( $J=4.3$ )
6	1.87m,1.97d( $J=17.0$ )	2.18m,2.34m	2.04d( $J=5.8$ ),1.90m	2.03m,2.19m
7	5.40dt( $J=2.1,6.1$ )	6.83dt( $J=2.1,5.8$ )	5.75m	6.90dt( $J=2.1,6.2$ )
8	-	-	-	-
9	1.89m	2.30d( $J=5.8$ )	2.07m	2.37m
10	-	-	-	-
11	2.11m 2.29d( $J=14.4$ )	2.48d( $J=16.8$ ), 2.62m	2.33d( $J=15.0$ ), 2.15m	2.32dd( $J=6.1,16.8$ ), 2.58m
12	5.51t( $J=6.7$ )	5.44t( $J=6.7$ )	5.55t( $J=6.7$ )	5.47t( $J=6.7$ )
13	-	-	-	-
14	6.35dd( $J=10.7,17.4$ )	6.29dd( $J=11.0,17.4$ )	6.34dd( $J=10.7,17.4$ )	6.31dd( $J=10.7,17.4$ )
15	4.80d( $J=10.7$ ), 5.04d( $J=16.9$ )	4.84d( $J=10.7$ ), 5.00d( $J=17.4$ )	4.91d( $J=10.7$ ), 5.06d( $J=17.0$ )	4.84d( $J=11.0$ ), 5.00d( $J=17.4$ )
16	1.74s	1.70s	1.75s	1.67s
*17	1.60s	9.37s	3.86d( $J=12.8$ ),4.04d ( $J=12.7$ )	-
18	0.86s	0.86s	0.85s	0.86s
19	0.88s	0.91s	0.87s	0.89s
20	0.79s	0.79s	0.77s	0.82s

\*The chemical shift of  $\delta_{\text{H-17}}$  represented the functional group of compound 1-4

Compounds 1-4 were isolated from stem bark of *Croton oblongifolius* Roxb., using chromatographic technique and were identified as the labdane diterpenoids. The structure of these four compounds were established by spectral data including UV, IR, MS,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR and elemental analysis data. The structural search from TIAC in Thailand indicated that compound 1-4 were new labdane diterpenoids.