CHAPTER 3

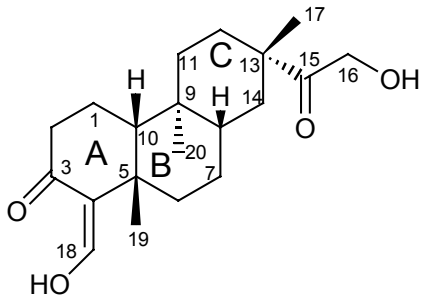
RESULTS, DISCUSSION AND CONCLUSION

3.1 Structure elucidation of compounds from the bark of C. tagal

The air-dried and crushed stem bark of *C. tagal* (4.8 kg) was extracted with methylene chloride and concentrated in vacuo to give residue (17.4 g) which was subjected to quick column chromatography and/or crystallization to give 13 new diterpenoids of dolabranes: **TD1-TD3, TD6-TD7** and **TD10,** nor-dolabranes: **TD19-TD24** and pimaranes: **TD25-TD26** together with 15 known diterpenoids of dolabranes: **TD1-TD18** and kauranes: **TD27-TD28.**

Their structures were elucidated mainly by 1D and 2D NMR spectroscopic data such as ^{1}H, ^{13}C NMR, DEPT 135°, DEPT 90°, HMQC, HMBC, ^{1}H-^{1}H COSY and 2D NOESY. Mass spectral data were determined for new compounds. In addition X-ray cryctallographic structures were reported for compounds **TD1, TD5, TD13, TD25** and **TD28.** The known compounds were compared with the reported NMR data and/or other physical data of those compounds.

3.1.1 Compound **TD1**



TD1 was obtained as a colorless plate crystal (methylene chloride /Hexane), mp 122-123°C, $[\alpha]_D^{27}$: -24.0° (*c* = 1.96, $CHCl_3$). IR absorptions at 3453 and 1697 cm^{-1} (**Figure 9**) suggested the presence of hydroxyl and enone functionalities, which was supported by λ_{max} 243 nm (weak) and 295 nm (medium) in UV spectrum (**Figure 8**). X-ray crystallographic analysis of **TD1** was carried out and gave ORTEP drawing as shown in **Figure 2.** The structure of **TD1** enabled assignment of a dolabrane

diterpene with a molecular formula $C_{20}H_{30}O_4$ by HREIMS. Its structure was clarified by ^1H and ^{13}C NMR spectra (**Table 1**, **Figure 10** and **11**).

The ^{13}C NMR spectrum of **TD1** showed 20 spectral lines which were sorted by DEPT experiments as three methines (including an sp^2 oxy-methine), eight methylenes, three methyls, and six quaternary carbons. A closer analysis of the ^{13}C NMR data allowed the identification of two carbonyl groups whose signals appeared at δ 215.2 (C-15) identified for a ketone and at δ 199.3 (C-3). The downfield chemical shift of the latter together with signals of a double bond at δ 116.4 (C-4) and 171.4 (C-18) indicated a carbonyl conjugated with a double bond. A hydroxy methylene carbon which connected to keto carbonyl carbon appeared at δ 63.9 (C-16). All other signals indicated non-functionalized, saturated carbons. The ^1H NMR spectrum clearly exhibited three singlet quaternary methyl groups at δ 0.72 (H_3-20), 1.17 (H_3-19), and 1.22 (H_3-17), a downfield olefinic proton at δ 7.94 (*d*, *J* = 7.8 Hz, H-18), a chelated hydroxy proton at δ 15.43 (*d*, *J* = 7.8 Hz, OH-18), a hydroxy methylene protons at δ 4.38 (d, J = 3.9 Hz, H_2-16), along with hydroxy proton at δ 3.26 (*br t*, *J* = 3.9 Hz, OH-16).

The important HMBC correlations were noticed between hydroxy methylene protons, H_2-16 (δ 4.38)/C-13 (δ 45.4), and C-15 (δ 215.2) and between a chelated hydroxyl proton, 18-OH (δ 15.43)/C-3 (δ 199.3), C-4 (δ 116.4), and C-18 (δ 171.4). The X-ray cryatallographic analysis of **TD1** together with the reported dolabrane structures from the same plant (Zhang et al., 2005) enabled assignment of *cis*-A/B and *trans*-B/C ring junctions. Therefore, compound **TD1** was established as *ent*-5α, 3,15-dioxodolabr-4(18)-ene-16,18-diol, a new compound designated as ceriotagalsin A.

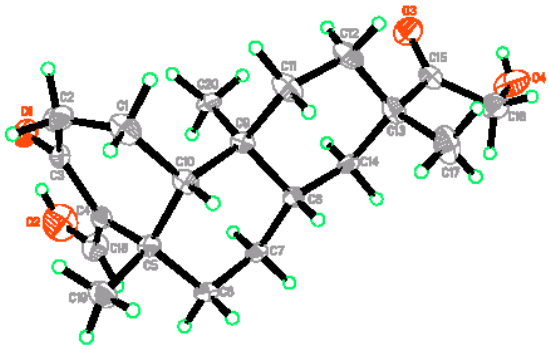
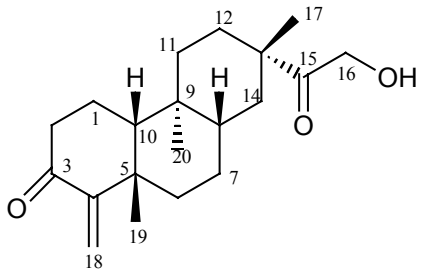


Figure 2 X-ray ORTEP diagram of compound **TD1**

Table 1 The ^{1}H, ^{13}C and HMBC spectral data of compound **TD1**

Position	Type of C	δ_C /ppm	δ_H /ppm, multiplicity (*J*/Hz)	HMBC/$^{1}H \rightarrow ^{13}C$
1	CH_2	16.1		
2	CH_2	31.4	2.49, *dd* (9.3, 6.3)	1, 3, 4, 10
3	C	199.3		
4	C	116.4		
5	C	36.2		
6	CH_2	36.5	2.16, *m*; 1.42, *m*	
7	CH_2	25.3		
8	CH	41.9	1.46, *m*	
9	C	37.6		
10	CH	51.7	1.25, *m*	
11	CH_2	34.9		
12	CH_2	27.7		
13	C	45.4		
14	CH_2	34.4		
15	C	215.2		
16	CH_2	63.9	4.38, *d* (3.9)	13, 15
17	CH_3	20.6	1.22, *s*	12, 13, 15
18	CH	171.4	7.94, *d* (7.8)	2, 3, 4, 5, 19
19	CH_3	35.8	1.17, *s*	4, 5, 6, 10
20	CH_3	12.6	0.72, *s*	8, 9, 10, 11
	OH-16		3.26, *br t* (3.9)	
	OH-18		15.43, *d* (7.8)	3, 4, 18

3.1.2 Compound **TD2**



TD2 was isolated as a colorless oil, $[\alpha]_D^{28}$: +2.0° (*c* = 2.58, $CHCl_3$). The IR and UV spectra were closely similar to spectra of **TD1**. Its molecular formula $C_{20}H_{30}O_3$ established from HREIMS which was 16 mass units less than that of **TD1**, suggesting the loss of one oxygen atom.

The ^1H and ^{13}C NMR spectra of **TD2** (**Table 2, Figures 12** and **13**) were similar to those of **TD1**. The difference was found in ring A, where the exo-methylene protons at δ 5.26 (*s*, H-18a) and 5.95 (*s*, H-18b) replaced signals of an oxy-olefinic proton and a chelated hydroxy proton in **TD1**. The two olefinic protons H_2-18 showed HMBC correlations with C-3 (δ 202.9), C-4 (δ 151.9), C-5 (40.8) and C-19 (δ 33.4). Therefore, compound **TD2** was deduced to be *ent*-5α,3,15-dioxodolabr-4(18)-ene-16-ol, a new compound designated as ceriotagalsin B.

Table 2 The ^1H, ^{13}C and HMBC spectral data of compounds **TD2** and **TD1**

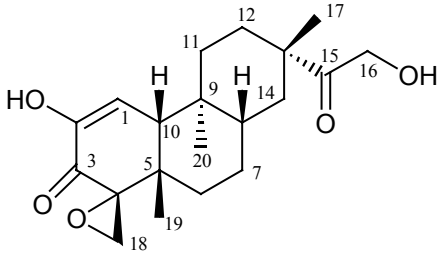
Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD2**) $^1H \rightarrow ^{13}C$
		TD1	**TD2**	**TD2**	**TD1**	
1	CH_2	16.1	17.6			
2	CH_2	31.4	36.3	2.53, *dd* (9.1, 6.3)	2.49, *dd* (9.3, 6.3)	1, 3, 4, 10
3	C	199.3	202.9			
4	C	116.4	151.9			
5	C	36.2	40.8			
6	CH_2	36.5	37.2	2.12, *m*; 1.45, *m*	2.16, *m*; 1.42, *m*	
7	CH_2	25.3	25.3			
8	CH	41.9	41.7	1.44, *m*	1.46, *m*	
9	C	37.6	38.0			
10	CH	51.7	52.1	1.33, *m*	1.25, *m*	
11	CH_2	34.9	35.0			
12	CH_2	27.7	27.9			
13	C	45.4	45.5			
14	CH_2	34.4	34.6			
15	C	215.2	215.2			
16	CH_2	63.9	63.8	4.39, *br s*	4.38, *d* (3.9)	13, 15
17	CH_3	20.6	20.5	1.23, *s*	1.22, *s*	12, 13, 15
18	CH_2	171.4	116.5	5.26, *s* (Ha); 5.95, *s* (Hb)	7.94, *d* (7.8)	3, 4, 5, 19

Table 2 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD2**) $^1H \rightarrow ^{13}C$
		TD1	**TD2**	**TD2**	**TD1**	
19	CH_3	35.8	33.4	1.11, *s*	1.17, *s*	4, 5, 6, 10
20	CH_3	12.6	13.5	0.81, *s*	0.72, *s*	8, 9, 10, 11
	OH-16				3.26, *br t* (3.9)	
	OH-18				15.43, *d* (7.8)	

* For **TD2**

3.1.3 Compound **TD3**



TD3 came as a colorless oil, $[\alpha]_D^{28}$: +109.0° (*c* = 0.98, $CHCl_3$) and its molecular formula was assigned as $C_{20}H_{28}O_5$ from HREIMS. In IR spectrum, hydroxyl (3440 cm^{-1}) and enone (1697 cm^{-1}) absorptions were displayed.

The ^1H and ^{13}C NMR spectra of **TD3** (**Table 3, Figures 14** and **15**) were similar to those of **TD1**, except for a difference in the signals for ring A. In place of signals for an oxy-olefinic, a chelated hydroxy and four methylene protons in **TD1**, an olefinic and epoxidic geminal proton signals were present in **TD3**. The olefinic proton at δ 6.27 (*d*, *J* = 6.6 Hz, H-1) showed a correlation with proton at δ 2.22 (*d*, *J* = 6.6 Hz, H-10) in ^1H-^1H COSY, suggesting that vinyl carbons of an enone were located at C-1 and C-2 of ring A. A strong hydrogen bond of an hydroxy proton at C-2 with the carbonyl group at C-3 was defined by the appearance of a broaden ^1H NMR signal at δ 6.00 and ^{13}C NMR signals of an enone at δ 118.1 (C-1), 147.6 (C-2), and 191.9 (C-3). The ^{13}C NMR downfield chemical shift at δ 147.6 (C-2) indicated that the double bond carried a hydroxyl group. The chemical shift of two epoxidic geminal protons at δ 3.10 (*d*, *J* = 6.3 Hz) and 3.12 (*d*, *J* = 6.3 Hz) indicated a β-orientation, the same as reported for tagalsin B (Zhang et al., 2005) and oxidopanamensin (Koike et al., 1980). NOE correlation between H_2-18 and H_3-19 supported the assignment. Thus, compound **TD3** was identified

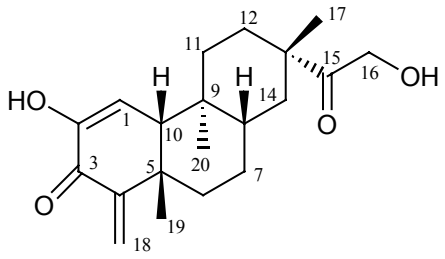
as *ent*-5α,18β,3,15-dioxodolabr-4,18-epoxy-1-ene-2,16-diol, a new compound designated as ceriotagalsin C.

Table 3 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD3** and **TD1**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD3**)
		TD1	**TD3**	**TD3**	**TD1**	$^{1}H \rightarrow ^{13}C$
1	CH	16.1	118.1	6.27, *d* (6.6)		2, 3, 5, 10
2	C	31.4	147.6		2.49, *dd* (9.3, 6.3)	
3	C	199.3	191.9			
4	C	116.4	61.2			
5	C	36.2	37.2			
6	CH_2	36.5	32.1	1.64, *m*; 1.25, *m*	2.16, *m*; 1.42, *m*	
7	CH_2	25.3	27.1			
8	CH	41.9	39.6	1.55, *m*	1.46, *m*	
9	C	37.6	39.2			
10	CH	51.7	54.7	2.22, *d* (6.6)	1.25, *m*	1, 2, 5, 9, 20
11	CH_2	34.9	34.0			
12	CH_2	27.7	27.9			
13	C	45.4	45.5			
14	CH_2	34.4	35.4			
15	C	215.2	214.9			
16	CH_2	63.9	63.9	4.40, *br s*	4.38, *d* (3.9)	13, 15
17	CH_3	20.6	20.3	1.27, *s*	1.22, *s*	12, 13, 15
18	CH_2	171.4	55.7	3.10, *d* (6.3); 3.12, *d* (6.3)	7.94, *d* (7.8)	3, 4, 5
19	CH_3	35.8	29.4	1.22, *s*	1.17, *s*	4, 5, 6, 10
20	CH_3	12.6	13.1	0.76, *s*	0.72, *s*	9, 10, 11
	OH-2			6.00, *br s*		1, 2, 3
	OH-16				3.26, *br t* (3.9)	
	OH-18				15.43, *d* (7.8)	

* For **TD3**

3.1.4 Compound **TD4**



TD4 was isolated as a colorless oil, $[\alpha]_D^{28}$: +235.4° (*c* = 4.58, $CHCl_3$). The ^1H and ^{13}C NMR spectra of **TD4** (**Table 4, Figures 16** and **17**) were similar to those of **TD3**, except for a difference in the signal for ring A. In place of the epoxidic geminal signals in **TD3**, the exocyclic olefinic protons were present in **TD4**. It showed the hydroxy methylene protons at δ 4.39 (*s*, H_2-16), an olefinic proton, H-1 at δ 6.17 (*d*, *J* = 6.9 Hz) and hydroxy proton, OH-2 at δ 6.33 (*br s*) in **TD3**. The exocyclic olefinic protons, δ 6.25 (*s*, H-18a) and 5.41 (*s*, H-18b) showed correlation with C-2 (δ 147.4), C-3 (δ 185.0), C-4 (δ 149.2) and C-5 (δ 41.1) in HMBC. By comparison of the ^{13}C NMR spectral data with the previously reported data (Kijjoa et al., 1994) (**Table 4**), compound **TD4** was identified as *ent*-5α,3,15-dioxodolabr-1,4(18)-diene-2,16-diol.

Table 4 The ^1H, ^{13}C and HMBC spectral data of compounds **TD4, TD3** and *ent*-5α,3,15-dioxodolabr-1,4(18)-diene-2,16-diol (**R**)

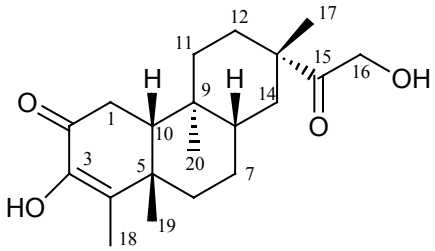
Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD4**)
tion	of C*	**R**	**TD4**	**TD3**	**TD4**	**TD3**	$^1H \rightarrow ^{13}C$
1	CH	117.1	117.2	118.1	6.17, *d* (6.9)	6.27, *d* (6.6)	2, 3, 5, 10
2	C	148.6	147.4	147.6			
3	C	185.0	185.0	191.9			
4	C	147.4	149.2	61.2			
5	C	41.1	41.1	37.2			
6	CH_2	36.4	36.3	32.1	2.20, *m*; 1.48, *m*	1.64, *m*; 1.25, *m*	
7	CH_2	25.2	25.2	27.1			
8	CH	40.2	40.1	39.6	1.47, *m*	1.55, *m*	
9	C	40.4	40.4	39.2			
10	CH	55.2	55.1	54.7	2.02, *d* (6.9)	2.22, *d* (6.6)	5, 19, 20

Table 4 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD4**)
		R	**TD4**	**TD3**	**TD4**	**TD3**	$^1H \rightarrow ^{13}C$
11	CH_2	35.5	35.4	34.0			
12	CH_2	27.7	27.6	27.9			
13	C	45.6	45.6	45.5			
14	CH_2	34.9	34.2	35.4			
15	C	214.8	215.0	214.9			
16	CH_2	63.8	63.8	63.9	4.39, *s*	4.40, *br s*	13, 15
17	CH_3	20.4	20.4	20.3	1.26, *s*	1.27, *s*	12, 13
18	CH_2	119.0	119.1	55.7	6.25, *s*;	3.10, *d* (6.3);	2, 3, 4, 5
					5.41, *s*	3.12, *d* (6.3)	
19	CH_3	33.8	33.8	29.4	1.13, *s*	1.22, *s*	5, 6, 10
20	CH_3	11.9	11.9	13.1	0.62, *s*	0.76, *s*	9, 10
	OH-2				6.33, *br s*	6.00, *br s*	

* For **TD4**

3.1.5 Compound **TD5**



TD5 was isolated as a colorless plate crystals ($CHCl_3$), mp 153-154°C, $[\alpha]_D^{28}$: +66.4° (*c* = 2.29, $CHCl_3$). The ^1H and ^{13}C NMR spectra of **TD5** (**Table 5**, **Figures 18** and **19**) were very similar to those of **TD4**, except for a difference in the signals for ring A which were displayed as 3-hydroxy-4-methyl-2-enone cyclohexane, whose ^1H NMR spectrum showed the signals of allylic methyl at δ 1.87 (*s*, H_3-18) and a broad singlet signal of a hydroxy proton at δ 6.11 (*br s*, OH-3). ^{13}C NMR spectrum displayed the signals of an enone functionality at δ 193.0 (C-2), 144.5 (C-3) and 135.3 (C-4). The important HMBC correlations between allylic methyl protons, H_3-18/C-3, C-4, C-5 (δ 38.9), and C-19 (δ 31.6) and between H-1 (δ 2.86, 2.71)/C-2, C-3, and C-10 (δ 54.2) were displayed. By comparison of the ^{13}C NMR

spectral data with the previously reported data (Kijjoa et al., 1994) (**Table 5**), compound **TD5** was established as *ent*-5α,2,15-dioxodolabr-3-ene-3,16-diol, whose structure was supported by X-ray crystallographic analysis (**Figure 3**).

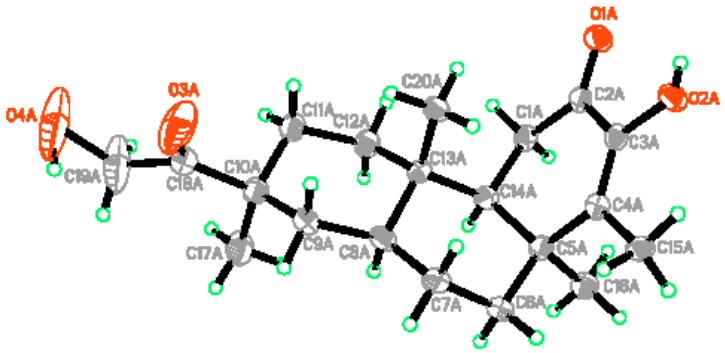


Figure 3 X-ray ORTEP diagram of compound **TD5**

Table 5 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD5**, **TD4** and *ent*-5α,2,15-dioxodolabr-3-ene-3,16-diol (**R**)

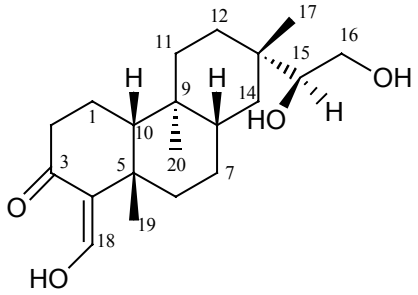
Posi-tion	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD5**)
		R	**TD5**	**TD4**	**TD5**	**TD4**	^{1}H→^{13}C
1	CH_2	37.4	33.1	117.2	2.86, *dd* (18.6, 6.2); 2.71, *d* (18.6)	6.17, *d* (6.9)	2, 3, 10
2	C	192.5	193.0	147.4			
3	C	144.3	144.5	185.0			
4	C	135.2	135.3	149.2			
5	C	38.6	38.9	41.1			
6	CH_2	34.6	37.7	36.3	2.19, *m*; 1.24, *m*	2.20, *m*; 1.48, *m*	
7	CH_2	26.2	26.4	25.2			
8	CH	40.5	41.1	40.1	1.42, *m*	1.47, *m*	
9	C	37.5	37.8	40.4			
10	CH	53.8	54.2	55.1	1.67, *m*	2.02, *d* (6.9)	2, 4, 5, 19
11	CH_2	32.9	33.4	35.4			
12	CH_2	27.3	27.6	27.6			
13	C	45.0	45.3	45.6			
14	CH_2	32.9	34.9	34.2			
15	C	214.8	215.0	215.0			

Table 5 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD5**)
		R	**TD5**	**TD4**	**TD5**	**TD4**	$^1H \rightarrow ^{13}C$
16	CH_2	63.6	63.8	63.8	4.33, *s*	4.39, *s*	13, 15, 17
17	CH_3	20.3	20.6	20.4	1.23, *s*	1.26, *s*	12, 13, 15
18	CH_3	12.3	13.6	119.1	1.87, *s*	6.25, *s*; 5.41, *s*	3, 4, 5, 19
19	CH_3	31.3	31.6	33.8	1.24, *s*	1.13, *s*	6, 10
20	CH_3	11.3	11.6	11.9	0.63, *s*	0.62, *s*	8, 9, 10, 11
	OH-2					6.33, *br s*	
	OH-3				6.11, *br s*		

* For **TD5**

3.1.6 Compound **TD6**



TD6 was isolated as a colorless oil, $[\alpha]_D^{28}$: -31.1° (*c* = 1.15, $CHCl_3$). The ^1H and ^{13}C NMR spectra (**Table 6, Figures 20** and **21**) of **TD6** indicated that it contained a hydroxy enone of a dolabrane backbone as in **TD1**, but the molecular formula of **TD6** was $C_{20}H_{32}O_4$ as indicated by HREIMS, differing from **TD1** by an additional two hydrogen atoms.

The ^1H NMR spectrum showed the signals for three AB_2 system of 1,2-hydroxyethyl side-chain at δ 3.74 (*dd*, *J* = 10.8, 2.4 Hz, H-16a), 3.52 (*dd*, *J* = 10.8, 9.3 Hz, H-16b), and 3.32 (*dd*, *J* = 9.3, 2.4 Hz, H-15) instead of a hydroxy methylene protons in **TD1**. The ^{13}C NMR signal of ketone carbonyl carbon at δ 215.2 in **TD1** was replaced by a signal of an oxy-methine carbon at δ 81.1 (C-15) in **TD6**. This was confirmed by HMBC correlation observed between H-17 (δ 0.92, *s*)/C-12 (δ 28.6), C-13 (δ 36.2), C-14 (δ 36.3), and C-15. The configuration at C-15 of a 1,2-dihydroxyethyl side-chain may be assigned on the basis of the carbon chemical shifts

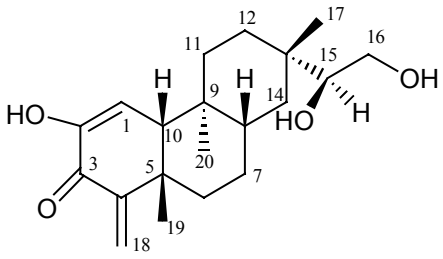
around C-13. The two epimers of *ent*-dolabr-4(18)-ene-7α,15*S*/*R*,16-diol showed different ^{1}H NMR chemical shifts at C-12 and C-14 (Ansell et al., 1993). In case of compound **TD6**, the chemical shifts at C-12 and C-14 were displayed at δ 28.6 and 36.3, respectively, comparable to those of an *ent*-dolabr-4(18)-ene-15*S*,16-diol at δ28.5 (C-12) and 36.1 (C-14) (Ansell et al., 1993). Hence, compound **TD6** could be deduced as *ent*-5α,15*S*,3-oxodolabr-4(18)-ene-15,16,18-triol, a new compound designated as ceriotagalsin D.

Table 6 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD6** and **TD1**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD6**)
		TD1	**TD6**	**TD6**	**TD1**	^{1}H→^{13}C
1	CH_2	16.1	16.1			
2	CH_2	31.4	31.5	2.49, *m*	2.49, *dd* (9.3, 6.3)	1, 3, 4, 10
3	C	199.3	199.5			
4	C	116.4	116.6			
5	C	36.2	36.5			
6	CH_2	36.5	36.7	2.16, *m*; 1.36, *m*	2.16, *m*; 1.42, *m*	
7	CH_2	25.3	25.6			
8	CH	41.9	42.1	1.37, *m*	1.46, *m*	
9	C	37.6	37.7			
10	CH	51.7	51.8	1.23, *m*	1.25, *m*	
11	CH_2	34.9	34.9			
12	CH_2	27.7	28.6			
13	C	45.4	36.2			
14	CH_2	34.4	36.3			
15	CH	215.2	81.1	3.32, *dd* (9.3, 2.4)		16
16	CH_2	63.9	62.6	3.74, *dd* (10.8, 2.4); 3.52, *dd* (10.8, 9.3)	4.38, *d* (3.9)	15
17	CH_3	20.6	19.0	0.92, *s*	1.22, *s*	12, 13, 14, 15
18	CH	171.4	171.4	7.93, *d* (7.5)	7.94, *d* (7.8)	2, 3, 5
19	CH_3	35.8	35.8	1.51, *s*	1.17, *s*	4, 5, 6, 10
20	CH_3	12.6	12.6	0.69, *s*	0.72, *s*	8, 9, 10, 11
	OH-18			15.42, *d* (7.5)	15.43, *d* (7.8)	2, 3, 4, 18

* For **TD6**

3.1.7 Compound **TD7**



TD7 was isolated as a colorless oil, $[\alpha]_D^{28}$: +120° (*c* = 0.33, $CHCl_3$) and analyzed for $C_{20}H_{30}O_4$ as indicated by HREIMS. The ^1H and ^{13}C NMR spectra of **TD7** (**Table 7**, **Figures 22** and **23**) showed dolabrane backbone with 1,2-dihydroxyethyl group side-chain connected to ring C as in **TD6**. The resonances assigned for ring A were identical to those of tagalsin C (Zhang et al., 2005) and *ent*-5α,3,15-dioxodolabr-1,4(18)-diene-2,16-diol (Kijjoa et al., 1994). The exo-methylene protons at δ 5.41 (*s*, H-18a), and 6.24 (*s*, H-18b) and the olefinic proton at δ 6.19 (*d*, *J* = 6.6 Hz, H-1) were observed. The latter proton showed HMBC correlations with C-2 (δ 147.3), C-3 (δ 185.2), C-5 (δ 41.2), and C-10 (δ 55.4). The ^{13}C NMR spectrum indicated hydroxy enone at δ 185.2 (C-3), 147.3 (C-2), and 118.0 (C-1) and exo-methylene group at δ 148.8 (C-4), and 119.0 (C-18). Therefore, compound **TD7** was deduced to be *ent*-5α,15*S*,3-oxodolabr-1,4(18)-diene-2,15,16-triol, a new compound designated as ceriotagalsin E.

Table 7 The ^1H, ^{13}C and HMBC spectral data of compounds **TD7** and **TD6**

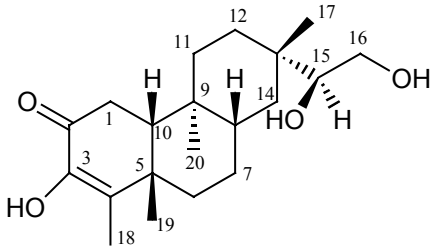
Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD7**)
		TD6	**TD7**	**TD7**	**TD6**	$^1H \rightarrow ^{13}C$
1	CH	16.1	118.0	6.19, *d* (6.6)		2, 3, 5, 10
2	C	31.5	147.3		2.49, *m*	
3	C	199.5	185.2			
4	C	116.6	148.8			
5	C	36.5	41.2			
6	CH_2	36.7	36.5	2.20, *m*; 1.40, *m*	2.16, *m*; 1.36, *m*	
7	CH_2	25.6	25.5			
8	CH	42.1	40.4	1.43, *m*	1.37, *m*	
9	C	37.7	40.7			

Table 7 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD7**) $^1H \rightarrow ^{13}C$
		TD6	**TD7**	**TD7**	**TD6**	
10	CH	51.8	55.4	2.03, *d* (6.6)	1.23, *m*	1, 2, 4, 5, 9, 20
11	CH_2	34.9	34.8			
12	CH_2	28.6	28.3			
13	C	36.2	36.8			
14	CH_2	36.3	36.8			
15	CH	81.1	81.0	3.32, *dd* (9.3, 2.7)	3.32, *dd* (9.3, 2.4)	12, 13, 16, 17
16	CH_2	62.6	62.5	3.52, *dd* (10.8, 9.3); 3.74, *dd* (10.8, 2.7)	3.74, *dd* (10.8, 2.4); 3.52, *dd* (10.8, 9.3)	13, 15
17	CH_3	19.0	19.0	0.96, *s*	0.92, *s*	12, 15
18	CH_2	171.4	119.0	5.41, *s*; 6.24 *s*	7.93, *d* (7.5)	3, 4, 5, 19
19	CH_3	35.8	33.8	1.12, *s*	1.51, *s*	4, 5, 6, 10
20	CH_3	12.6	12.0	0.60, *s*	0.69, *s*	8, 9, 10, 11

* For **TD7**

3.1.8 Compound **TD8**



TD8 was isolated as a white solid, mp 126-128°C, $[\alpha]_D^{28}$: -17.8° (*c* = 1.33, $CHCl_3$). The ^1H and ^{13}C NMR spectra of **TD8** (**Table 8**, **Figures 24** and **25**) were similar to those of **TD6**, except for a difference in the signals for ring A which were displayed as 3-hydroxy-4-methyl-2-enone cyclohexane whose ^1H NMR spectrum showed the signals of an allylic methyl at δ 1.87 (*s*, H_3-18) and a broad singlet signal of a hydroxy proton at δ 6.16 (*br s*, OH-3). ^{13}C NMR spectrum displayed the signals of an enone functionality at δ 193.1 (C-2), 144.6 (C-3) and 135.6 (C-4). The important HMBC correlations between allylic methyl protons H_3-18/C-3, C-4, C-5 (δ 39.0) and C-19 (δ 31.7) and between H-1 (δ 2.84 and 2.71)/C-2, C-3, C-5, C-9 (δ 38.0),

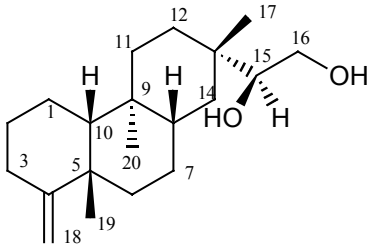
and C-10 (δ 54.3) were displayed. By comparison of the ^{13}C NMR spectral data with the previously reported data (Kijjoa et al., 1995) (**Table 8**), compound **TD8** was established as *ent*-5α,15S,2-oxodolabr-3-ene-3,15,16-triol.

Table 8 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD8, TD6** and *ent*-5α,2-oxodolabr-3-ene-3,15,16-triol (**R**)

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD8**)
		R	**TD8**	**TD6**	**TD8**	**R**	^{1}H→^{13}C
1	CH_2	38.0	33.2	16.1	2.84, *dd* (18.6, 6.3) ; 2.71, *d* (18.6)	2.81, *dd* (18.5, 6.5) ; 2.69, *d* (18.5)	2, 3, 5, 9, 10
2	C	193.0	193.1	31.5			
3	C	144.6	144.6	199.5			
4	C	135.3	135.6	116.6			
5	C	39.0	39.0	36.5			
6	CH_2	36.4	37.8	36.7	2.17, *m*; 1.25, *m*	2.13, *m*; 1.24, *m*	
7	CH_2	26.9	26.8	25.6			
8	CH	41.3	41.2	42.1	1.37, *m*	1.38, *m*	
9	C	38.1	38.0	37.7			
10	CH	54.5	54.3	51.8	1.64, *m*	1.62, *m*	
11	CH_2	33.9	33.7	34.9			
12	CH_2	28.4	28.4	28.6			
13	C	36.5	36.4	36.2			
14	CH_2	33.2	36.3	36.3			
15	CH	81.0	81.0	81.1	3.31, *dd* (9.6, 2.4)	3.29, *dd* (10, 2)	13, 16
16	CH_2	62.6	69.5	62.6	3.73, *dd* (10.5, 2.4); 3.08, *dd* (10.5, 9.6)	3.70, *br d* (10, 2); 3.49, *br d* (10, 10)	15
17	CH_3	19.2	19.0	19.0	0.92, *s*	0.91, *s*	12, 13, 14, 15
18	CH_3	13.6	13.6	171.4	1.87, *s*	1.85, *s*	3, 4, 5, 19
19	CH_3	31.7	31.7	35.8	1.23, *s*	1.20, *s*	4, 5, 9
20	CH_3	11.5	11.6	12.6	0.59, *s*	0.57, *s*	8, 9, 10, 11
	OH-3				6.16, *br s*	6.09, *br s*	1, 2, 3

* For **TD8**

3.1.9 Compound **TD9**



TD9 was isolated as a colorless oil, $[\alpha]_D^{28}$: +69.3° (*c* = 0.50, $CHCl_3$). The ^1H and ^{13}C NMR spectra of **TD9** (**Table 9**, **Figures 26** and **27**) showed dolabrane backbone with 1,2-dihydroxyethyl group side-chain connected to ring C as in **TD6**, but the resonances assigned for ring A showed the exo-methylene protons at δ 4.73 (*s*, H-18a) and 4.71 (*s*, H-18b) which replaced the hydroxyl enone of **TD6**. The ^{13}C NMR spectrum indicated the exocyclic olefinic group at δ 154.0 (C-4), and 105.7 (C-18). By comparison of the ^{13}C NMR spectral data with the previously reported data (Ansel et al., 1993) (**Table 9**), compound **TD9** was deduced to be *ent*-5α-dolabr-4(18)-ene-15*S*,16-diol.

Table 9 The ^1H, ^{13}C and HMBC spectral data of compounds **TD9**, **TD6** and *ent*-5α-dolabr-4(18)-ene-15*S*,16-diol (**R**)

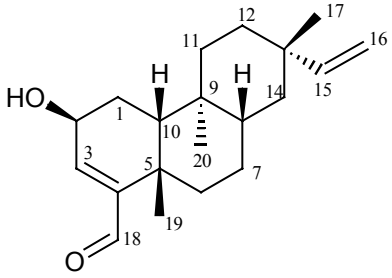
Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (TD9)
tion	of C*	R	**TD9**	**TD6**	**TD9**	**TD6**	$^1H \rightarrow ^{13}C$
1	CH_2	20.7	20.6	16.1			
2	CH_2	24.1	24.1	31.5		2.49, *m*	
3	CH_2	38.6	31.9	199.5	3.15, *m*		
4	C	153.9	154.0	116.6			
5	C	40.0	39.9	36.5			
6	CH_2	36.0	38.4	36.7	2.22, *m*; 1.31, *m*	2.16, *m*; 1.36, *m*	
7	CH_2	26.3	26.2	25.6			
8	CH	42.4	42.3	42.1	1.30, *m*	1.37, *m*	
9	C	38.6	36.0	37.7			
10	CH	54.6	54.4	51.8	1.17, *m*	1.23, *m*	
11	CH_2	32.0	35.8	34.9			
12	CH_2	28.5	28.9	28.6			
13	C	35.5	36.6	36.2			

Table 9 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (TD9)
		R	**TD9**	**TD6**	**TD9**	**TD6**	$^1H \rightarrow ^{13}C$
14	CH_2	36.1	36.5	36.3			
15	CH	85.0	81.4	81.1	3.32, *d* 99.0, 3.0)	3.32, *dd* (9.3, 2.4)	12, 13, 14, 16, 17
16	CH_2	64.7	62.6	62.6	3.74, *dd* (12.0, 9.0) ; 3.52, *dd* (9.0, 3.0)	3.74, *dd* (10.8, 2.4); 3.52, *dd* (10.8, 9.3)	13, 15
17	CH_3	19.3	18.8	19.0	0.91, *s*	0.92, *s*	12, 13, 14
18	CH_2	105.8	105.7	171.4	4.73, *s*; 4.71, *s*	7.93, *d* (7.5)	
19	CH_3	32.9	32.0	35.8	1.25, *s*	1.51, *s*	3, 4, 5, 10
20	CH_3	15.6	15.5	12.6	0.86, *s*	0.69, *s*	8, 9, 10

* For **TD9**

3.1.10 Compound **TD10**



TD10 was isolated as a colorless oil, $[\alpha]_D^{28}$: +37.0° (*c* = 0.16, $CHCl_3$), and assigned the molecular formula of $C_{20}H_{30}O_4$ as indicated by HREIMS. Comparison of its NMR spectra (**Table 10, Figures 28 a**nd **29**) with **TD1** showed that **TD10** was also a tricyclic diterpenoid.

The ^1H NMR spectrum of **TD10** exhibited three singlet methyl groups at δ 0.74 (H_3-20), 1.02 (H_3-17), and 1.29 (H_3-19), an olefinic proton at δ 6.54 (*d*, *J* = 3.0 Hz, H-3) and a terminal vinylic group at δ 4.84 (*dd*, *J* = 10.8, 1.2 Hz, H-16a), 4.91 (*dd*, *J* = 17.4, 1.2 Hz, H-16b), and 5.79 (*dd*, *J* = 17.4, 10.8 Hz, H-15), an oxy-methine proton at δ 4.72 (*ddd*, *J* = 9.3, 8.1, 3.0 Hz, H-2), along with a singlet signal of a formyl proton at δ 9.47 (H-18). Its ^{13}C NMR spectrum displayed conjugated enone system at δ 159.6 (C-3), 149.0 (C-4), and 194.7 (C-18), a monosubstituted

double bond at δ 151.1 (C-15), and 108.8 (C-16), and an oxy-methine carbon at δ 65.6 (C-2).

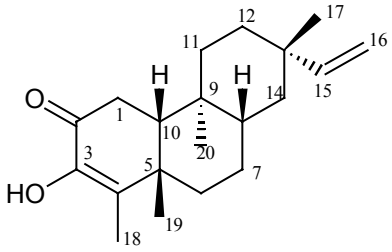
The HMBC correlation between a formyl proton H-18/C-3, C-4, and C-5 (δ 37.3) supported the connection of the formyl group at C-18. The ^{1}H-^{1}H COSY cross peak of an oxy-methine proton H-2 with an olefinic proton H-3 confirmed that C-2 carried a hydroxyl group. The oxy-methine proton H-2 was assigned as an axial proton (α-orientation) due to the spin coupling of this proton at δ 4.72 (*ddd*, *J* = 9.3, 8.1, 3.0 Hz, H-2). Thus, compound **TD10** could be deduced as *ent*-5α,18-oxodolabr-3,15-diene-2β-ol, a new compound designated as ceriotagalsin F.

Table 10 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD10** and **TD1**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD10**) $^{1}H \rightarrow {}^{13}C$
		TD1	**TD10**	**TD10**	**TD1**	
1	CH_2	16.1	35.4			
2	CH	31.4	65.6	4.72, *ddd* (9.3, 8.1, 3.0)	2.49, *dd* (9.3, 6.3)	1, 5
3	CH	199.3	159.6	6.54, *d* (3.0)		
4	C	116.4	149.0			
5	C	36.2	37.3			
6	CH_2	36.5	28.4	3.17, *m*; 1.72, *m*	2.16, *m*; 1.42, *m*	
7	CH_2	25.3	27.0			
8	CH	41.9	41.7	1.38, *m*	1.46, *m*	
9	C	37.6	37.6			
10	CH	51.7	56.3	1.43, *m*	1.25, *m*	
11	CH_2	34.9	35.7			
12	CH_2	27.7	31.7			
13	C	45.4	36.2			
14	CH_2	34.4	38.9			
15	CH	215.2	151.1	5.79, *dd* (17.4, 10.8)		12, 13, 14, 17
16	CH_2	63.9	108.8	4.91, *dd* (17.4, 1.2); 4.84, *dd* (10.8, 1.2)	4.38, *d* (3.9)	13, 15
17	CH_3	20.6	23.0	1.02, *s*	1.22, *s*	12, 13, 14
18	CH	171.4	194.7	9.47, *s*	7.94, *d* (7.8)	3, 4, 5
19	CH_3	35.8	34.4	1.29, *s*	1.17, *s*	4, 5, 6, 10
20	CH_3	12.6	14.1	0.74, *s*	0.72, *s*	8, 9, 10 11

* For **TD10**

3.1.11 Compound **TD11**



TD11 was isolated as a white solid, mp 90-91°C, $[\alpha]_D^{28}$: +17.6° (*c* = 2.38, $CHCl_3$). The ^1H and ^{13}C NMR spectra of **TD11** (**Table 11**, **Figures 30** and **31**) were very similar to those of **TD10**, except for a difference in the signal for ring A which were displayed as 3-hydroxy-4-methyl-2-enone cyclohexane, whose ^1H NMR spectrum showed the signals of allylic methyl at δ 1.87 (*s*, H_3-18) and a broad singlet signal of a hydroxy proton at δ 6.12 (*br s*, OH-3). ^{13}C NMR spectrum displayed the signals of an enone functionality at δ 193.1 (C-2), 144.5 (C-3) and 135.5 (C-4). The important HMBC correlations between allylic methyl protons, H_3-18/C-3, C-4 and C-19 (δ 31.7) and between H-1 (δ 2.83 and 2.73)/C-2, C-3, C-5 (δ 38.9), C-9 (δ 38.1) and C-10 (δ 54.5) were displayed. By comparison of the ^{13}C NMR spectral data with the previously reported data of tagalsin G (Zhang et al., 2005) (**Table 11**), compound **TD11** was established as *ent*-5α,2-oxodolabr-3,15-diene-3-ol.

Table 11 The ^1H, ^{13}C and HMBC spectral data of compounds **TD11**, **TD10** and tagalsin G (**R**)

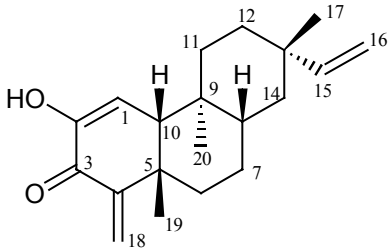
Posi-tion	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD11**)
		R	**TD11**	**TD10**	**TD11**	**TD10**	$^1H \rightarrow ^{13}C$
1	CH_2	33.2	33.2	35.4	2.83, *dd* (18.6, 6.3) ; 2.73, *br d* (18.6)		2, 3, 5, 9, 10
2	C	193.1	193.1	65.6		4.72, ddd (9.3, 8.1, 3.0)	
3	C	144.5	144.5	159.6		6.54, d (3.0)	
4	C	135.5	135.5	149.0			
5	C	39.0	38.9	37.3			
6	CH_2	38.0	38.0	28.4	2.17, *m*; 1.38, *m*	3.17, *m*; 1.72, *m*	

Table 11 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD11**)
		R	**TD11**	**TD10**	**TD11**	**TD10**	$^1H \rightarrow ^{13}C$
7	CH_2	26.7	26.7	27.0			
8	CH	41.6	41.6	41.7	1.39, *m*	1.38, *m*	
9	C	38.1	38.1	37.6			
10	CH	54.5	54.5	56.3	1.67, *m*	1.43, *m*	
11	CH_2	34.2	34.1	35.7			
12	CH_2	31.7	31.6	31.7			
13	C	36.2	36.2	36.2			
14	CH_2	38.9	38.8	38.9			
15	CH	150.9	150.9	151.1	5.78, *dd* (17.4, 10.5)	5.79, *dd* (17.4, 10.8)	12, 13, 14, 17
16	CH_2	108.9	108.9	108.8	4.90, *dd* (17.4, 1.5); 4.84, *dd* (10.5, 1.5)	4.91, *dd* (17.4, 1.2); 4.84, *dd* (10.8, 1.2)	13, 15
17	CH_3	23.1	23.1	23.0	1.02, *s*	1.02, *s*	12, 13, 14, 15
18	CH_3	11.6	11.6	194.7	1.87, *s*	9.47, *s*	3, 4, 19
19	CH_3	31.6	31.7	34.4	1.24, *s*	1.29, *s*	4, 5, 10
20	CH_3	13.7	13.7	14.1	0.60, *s*	0.74, *s*	8, 9, 10
	OH-3				6.12, *br s*		

* For **TD11**

3.1.12 Compound **TD12**



TD12 was isolated as a pale yellow oil, $[\alpha]_D^{28}$: +92.3° (*c* = 0.05, $CHCl_3$). Comparison of ^1H and ^{13}C NMR spectra of **TD12** and **TD11** (**Table 12**, **Figures 32** and **33**) revealed that signals assigned to rings B and C were similar, while the signals for ring A were almost identical to those of **TD4**. An exocyclic olefinic protons, δ

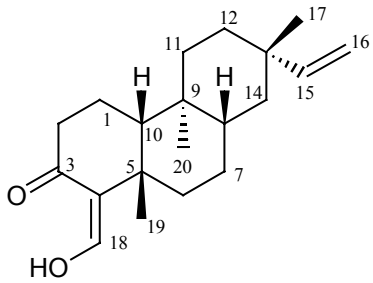
6.24 (*s*, H-18a) and 5.41 (*s*, H-18b) and an olefinic proton H-1 at δ 6.20 (*d*, *J* = 6.6 Hz) of **TD12** replaced the 3-hydroxy-4-methyl-2-enone cyclohexane group of **TD11**. The important HMBC correlations between olefinic protons, H_3-18/C-3 (δ 185.3), C-4 (δ 148.9), C-5 (δ 41.2), and C-19 (δ 33.9) and between H-1/C-3, C-5 and C-10 (δ 55.5) were displayed. By comparison of the ^{13}C NMR spectral data with the previously reported data of tagalsin C (Zhang et al., 2005) (**Table 12**), compound **TD12** was established as *ent*-5α,2-oxodolabr-1,4(18),15-triene-2-ol.

Table 12 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD12**, **TD11** and tagalsin C (**R**)

Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD12**)
tion	of C*	**R**	**TD12**	**TD11**	**TD12**	**R**	^{1}H→^{13}C
1	CH	118.2	118.1	33.2	6.20, *d* (6.6)	6.22, *d* (6.7)	3, 5, 10
2	C	147.2	147.2	193.1			
3	C	185.3	185.3	144.5			
4	C	148.8	148.9	135.5			
5	C	41.2	41.2	38.9			
6	CH_2	36.6	36.6	38.0	2.19, *m*; 1.51, *m*	2.20, *m*; 1.48, *m*	
7	CH_2	25.4	25.5	26.7			
8	CH	40.8	40.9	41.6	1.46, *m*	1.48, *m*	
9	C	40.8	40.8	38.1			
10	CH	55.5	55.5	54.5	2.06, *d* (6.6)	2.08, *d* (6.7)	1, 2, 8, 11, 20
11	CH_2	35.2	35.3	34.1			
12	CH_2	31.6	31.6	31.6			
13	C	36.5	36.5	36.2			
14	CH_2	39.4	39.4	38.8			
15	CH	150.8	150.9	150.9	5.79, *dd* (17.4, 10.8)	5.80, *dd* (17.5, 10.8)	12, 13, 14, 17
16	CH_2	108.9	108.9	108.9	4.94, *dd* (17.5, 1.5); 4.85, *dd* (10.8, 1.5)	4.90, *d* (17.5); 4.87, *d* (10.8)	13, 14, 15
17	CH_3	22.9	22.9	23.1	1.06, *s*	1.05, *s*	12, 13, 14
18	CH_2	118.9	118.9	11.6	6.24, *s*; 5.41, *s*	6.26, *s*; 5.43, *s*	3, 4, 5, 19
19	CH_3	33.9	33.9	31.7	1.12, *s*	1.14, *s*	4, 5, 6, 10
20	CH_3	12.0	12.1	13.7	0.60, *s*	0.64, *s*	8, 9, 10 ,11

* For **TD12**

3.1.13 Compound **TD13**



TD13 was isolated as a colorless plate crystal ($CHCl_3$), mp 101-102°C, $[\alpha]_D^{28}$: +37.8° (*c* = 2.05, $CHCl_3$). Comparison of ^1H and ^{13}C NMR spectra of **TD13** and **TD11** (**Table 13**, **Figures 34** and **35**) revealed that signals assigned to rings B and C were similar, while the signal for ring A were almost identical to those of **TD1. A**n olefinic proton, H-18 at δ 7.93 (*d*, *J* = 7.5 Hz) and a chelated □ydroxyl proton, OH-18 at δ 15.43 (*d*, *J* = 7.5 Hz) of **TD12** replaced the 3-hydroxy-4-methyl-2-enone cyclohexane group of **TD11.** The important HMBC correlations between olefinic proton, H-18/C-2 (δ 31.5), C-3 (δ 199.6), C-4 (δ 116.8), and C-10 (δ 51.9) were displayed. By comparison of the ^{13}C NMR spectral data with the previously reported data of tagalsin F (Zhang et al., 2005) (**Table 13**), compound **TD1** was established as *ent*-5α,2-oxodolabr-4(18),15-diene-18-ol. The X-ray crystallographic structure of **TD1** was also displayed (**Figure 4**).

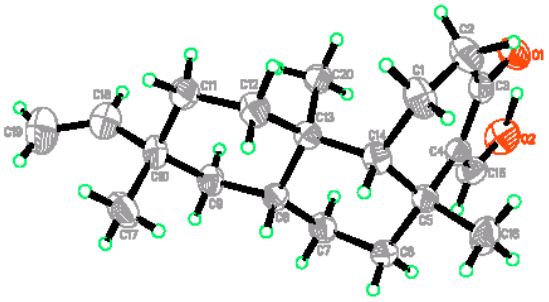


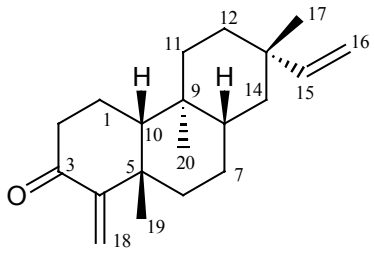
Figure 4 X-ray ORTEP diagram of compound **TD13**

Table 13 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD13, TD11** and tagalsin F (**R**)

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (J/Hz)		HMBC (TD13)
		R	**TD13**	**TD11**	**TD13**	**R**	$^{1}H \rightarrow ^{13}C$
1	CH_2	16.1	16.1	33.2	2.04, *m*; 1.96, *m*	2.04, *m*; 1.97, *m*	
2	CH_2	31.5	31.5	193.1	2.48, *m*	2.46, *m*; 2.45, *m*	
3	C	199.6	199.6	144.5			
4	C	116.7	116.8	135.5			
5	C	36.3	36.3	38.9			
6	CH_2	36.7	36.7	38.0	2.16, *m; 1.45*, *m*	2.13, *m;* 1.42, *m*	
7	CH_2	25.5	25.5	26.7			
8	CH	42.5	42.6	41.6			
9	C	37.7	37.8	38.1			
10	CH	51.8	51.9	54.5	1.26, *m*	1.24, *m*	
11	CH_2	35.2	35.3	34.1			
12	CH_2	31.7	31.7	31.6			
13	C	36.1	36.2	36.2			
14	CH_2	38.8	38.9	38.8			
15	CH	150.9	151.0	150.9	5.79, *dd* (17.4, 10.5)	5.78, *dd* (17.5, 10.7)	12, 13, 14, 17
16	CH_2	108.8	108.8	108.9	4.91, *dd* (17.4, 1.5); 4.87, *dd* (10.5, 1.5)	4.88, *d* (17.5); 4.84, *d* (10.7)	13
17	CH_3	23.0	23.1	23.1	1.02, *s*	1.01, *s*	12, 13, 14, 15
18	CH	171.2	171.3	11.6	7.93, *d* (7.5)	7.90, *d* (7.8)	2, 3, 4, 10
19	CH_3	35.8	35.9	31.7	1.16, *s*	1.15, *s*	4, 5, 9, 10
20	CH_3	12.7	12.7	13.7	0.70, *s*	0.69, *s*	8, 9, 10. 11
	OH-18				15.43, *d* (7.5)	15.46, *d* (7.8)	3, 4, 18

* For **TD13**

3.1.14 Compound **TD14**



TD14 was isolated as a pale yellow oil, $[\alpha]_D^{28}$: -8.39° (*c* = 1.00, $CHCl_3$). Comparison of IR, ^1H and ^{13}C NMR spectroscopic data of **TD14** and **TD13** (**Table 14, Figures 36** and **37**) revealed that signals assigned to rings B and C were very similar, while the signals for ring A were almost identical to those of **TD2.** Two singlet olefinic protons at δ 5.93 (H-18a) and 5.33 (H-18b) of **TD14** replaced an olefinic and chelated □ydroxyl protons of **TD13.** By comparison of the ^{13}C NMR spectral data with the previously reported data of tagalsin E (Zhang et al., 2005) (**Table 14**), compound **TD14** was established as *ent*-5α,2-oxodolabr-4(18),15-diene.

Table 14 The ^1H and ^{13}C spectral data of compounds **TD14, TD13** and tagalsin E (**R**)

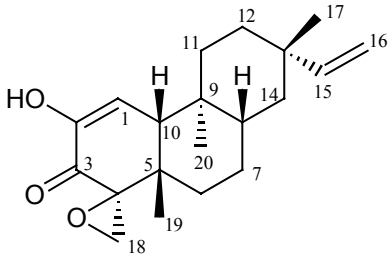
Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)	
tion	of C*	**R**	**TD14**	**TD13**	**TD14**	**R**
1	CH_2	18.0	17.7	16.1		
2	CH_2	36.7	36.5	31.5	2.57, *m*; 2.53, *m*	
3	C	203.7	203.5	199.6		
4	C	152.5	152.3	116.8		
5	C	41.2	41.0	36.3		
6	CH_2	37.6	37.4	36.7		
7	CH_2	25.8	25.6	25.5		
8	CH	42.7	42.5	42.6		
9	C	38.4	38.2	37.8		
10	CH	52.6	52.4	51.9		
11	CH_2	35.8	35.6	35.3		
12	CH_2	32.1	31.9	31.7		
13	C	36.6	36.3	36.2		
14	CH_2	39.2	39.0	38.9		
15	CH	151.2	151.0	151.0	5.80, *dd* (17.4, 10.8)	5.79, *dd*(17.5, 10.8)

Table 14 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)	
		R	**TD14**	**TD13**	**TD14**	**R**
16	CH_2	109.1	108.8	108.8	4.93, *dd* (17.4, 1.2); 4.85, *dd* (10.8, 1.2)	4.92, *d* (17.5); 4.84, *d* (10.8)
17	CH_3	93.2	23.0	23.1	1.03, *s*	1.02, *s*
18	CH_2	116.5	116.3	171.3	5.93, *s*; 5.33, *s*	5.92, *s*; 5.24, *s*
19	CH_3	33.8	33.6	35.9	1.10, *s*	1.08, *s*
20	CH_3	13.9	13.6	12.7	0.79, *s*	0.78, *s*

* For **TD14**

3.1.15 Compound **TD15**



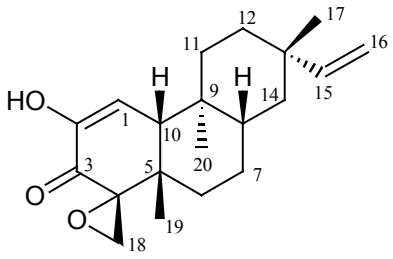
TD15 was isolated as a white solid, mp 68-69°C, $[\alpha]_D^{28}$: +120.0° (*c* = 0.75, $CHCl_3$). Comparison of IR, ^1H and ^{13}C NMR spectroscopic data of **TD15** and **TD12** (**Table 15**, **Figures 38** and **39**) revealed that signals assigned to rings B and C were very similar, while the signals for ring A were similar to those of **TD3**. The two geminal epoxidic protons, H_2-18 at δ 3.45 (*d*, *J* = 6.3 Hz) and 2.98 (*d*, *J* = 6.3 Hz) of **TD15** replaced the two olefinic signals of **TD12**. The important HMBC correlations between epoxidic protons, H_2-18/C-3 (δ 191.2), C-4 (δ 60.1), and C-5 (δ 35.7), along with H-1 (δ 6.34)/C-2 (δ 147.7), C-3 and C-10 (δ 54.4) were displayed. The configuration of the epoxidic group at C-4 (δ 60.1) was assigned as α-orientation, due to the chemical shifts of protons at C-18, which differed from the chemical shift of β-orientation at δ 3.12 (*d*, *J* = 6.3 Hz, H-18a) and 3.10 (*d*, *J* = 6.3 Hz, H-18b) in **TD3**. By comparison of the ^{13}C NMR spectral data with the previously reported data of tagalsin A (Zhang et al., 2005) (**Table 15**), compound **TD15** was established as *ent*-5α,18α,3-oxodolabr-4,18-epoxy-1,15-diene-2-ol.

Table 15 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD15, TD12** and tagalsin A (**R**)

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD15**)
		R	**TD15**	**TD12**	**TD15**	**R**	$^{1}H \rightarrow ^{13}C$
1	CH	120.6	120.3	118.1	6.34, *d* (6.9)	6.34, *d* (6.8)	2, 3, 10
2	C	147.7	147.7	147.2			
3	C	191.2	191.2	185.3			
4	C	60.1	60.1	148.9			
5	C	35.6	35.7	41.2			
6	CH_2	34.2	34.3	36.6			
7	CH_2	27.2	27.2	25.5			
8	CH	40.8	40.9	40.9			
9	C	39.7	39.8	40.8			
10	CH	54.3	54.4	55.5	2.14, *d* (6.9)	2.14, *d* (6.8)	4, 5, 9, 19, 20
11	CH_2	35.0	35.1	35.3			
12	CH_2	31.7	31.8	31.6			
13	C	36.4	36.4	36.5			
14	CH_2	39.4	39.4	39.4			
15	CH	150.8	150.9	150.9	5.80, *dd* (17.4, 10.8)	5.79, *dd* (17.5, 10.7)	12, 13, 14
16	CH_2	108.9	109.0	108.9	4.91, *dd* (17.4, 1.5); 4.85, *dd* (10.8, 1.5)	4.92, *br d* (17.5); 4.85, *br d* (10.7)	13
17	CH_3	22.9	22.9	22.9	1.06, *s*	1.05, *s*	12, 13, 14, 15
18	CH_2	50.6	50.6	118.9	3.45, *d* (6.3); 2.98, *d* (6.3)	3.44, *d* (6.1); 2.96, *d* (6.1)	3, 4, 5
19	CH_3	31.6	31.7	33.9	1.20, *s*	1.18, *s*	4, 5, 6, 10
20	CH_3	12.1	12.1	12.1	0.78, *s*	0.77, *s*	9, 10, 11
	OH-2				5.90, *br s*	6.15, *br s*	1, 2, 3

* For **TD15**

3.1.16 Compound **TD16**



TD16 was isolated as a white solid, mp 83-84°C, $[\alpha]_D^{28}$: +86.1° (*c* = 2.25, $CHCl_3$). The IR, ^1H and ^{13}C NMR spectroscopic data of **TD16** were almost identical to those of **TD15** (**Table 16**, **Figures 40** and **41**), except for the signals of the epoxidic protons, where H_2-18 at δ 3.14 (*d*, *J* = 6.3 Hz) and 3.11 (*d*, *J* = 6.3 Hz) of **TD16** replaced H_2-18 of **TD15**. By comparison of the ^{13}C NMR spectral data with the previously reported data of tagalsin B (Zhang et al., 2005) (**Table 16**), compound **TD16** was established as *ent*-5α,18β,3-oxodolabr-4,18-epoxy-1,15-diene-2-ol, a C-18 epimer of **TD15**.

Table 16 The ^1H and ^{13}C spectral data of compounds **TD16**, **TD15** and tagalsin B (**R**)

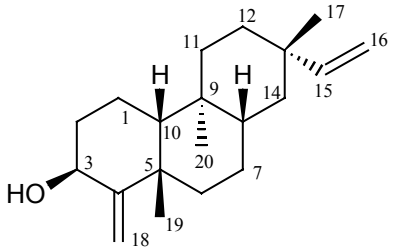
Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)	
tion	of C*	**R**	**TD16**	**TD15**	**TD16**	**R**
1	CH	119.0	119.1	120.3	6.32, *d* (6.6)	6.30, *d* (6.7)
2	C	147.2	147.5	147.7		
3	C	191.9	191.2	191.2		
4	C	61.1	61.3	60.1		
5	C	36.9	37.2	35.7		
6	CH_2	32.0	32.2	34.3		
7	CH_2	27.1	27.3	27.2		
8	CH	40.0	40.3	40.9		
9	C	39.1	39.5	39.8		
10	CH	54.7	55.0	54.4	2.24, *d* (6.6)	2.21, *d* (6.7)
11	CH_2	34.6	34.9	35.1		
12	CH_2	31.5	31.8	31.8		
13	C	36.1	36.3	36.4		
14	CH_2	39.2	39.4	39.4		
15	CH	105.4	105.6	150.9	5.81, *dd* (17.4, 10.8)	5.88, *dd* (17.5, 10.8)

Table 16 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)	
		R	**TD16**	**TD15**	**TD16**	**R**
16	CH_2	108.9	109.1	109.0	4.93, *dd* (17.4, 1.2); 4.88, *dd* (10.8, 1.2)	4.91, *d* (17.8); 4.86, *d* (10.8)
17	CH_3	22.6	22.8	22.9	1.08, *s*	1.06, *s*
18	CH_2	55.5	55.7	50.6	3.14, *d* (6.3); 3.11, *d* (6.3)	3.13, *d* (6.2); 3.11, *d* (6.2)
19	CH_3	29.2	29.4	31.7	1.23, *s*	1.21, *s*
20	CH_3	12.9	13.1	12.1	0.75, *s*	0.73, *s*

* For **TD16**

3.1.17 Compound **TD17**



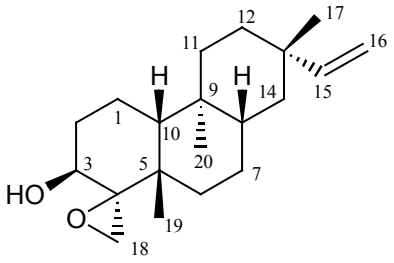
TD17 was isolated as a pale yellow oil, $[\alpha]_D^{28}$: +40.8° (*c* = 0.25, $CHCl_3$). Comparison of IR, ^1H and ^{13}C NMR spectroscopic data of **TD17** and **TD14** (**Table 17, Figures 42** and **43**) revealed that signals assigned to rings B and C were very identical. The difference was shown in ring A, where an oxymethine proton H-3 at δ 4.43 (*dd*, *J* = 4.2, 2.1 Hz) in **TD17** replaced the carbonyl group in **TD14.** The important HMBC correlations between oxymethine proton H-3/C-1 (δ 16.5), C-2 (δ 29.8), and C-18 (δ 112.2), along with olefinic protons H_2-18 (δ 5.05 and 5.02)/C-3 (δ 74.1), C-4 (δ 155.0), C-5 (δ 39.2) and C-19 (δ 34.9) were displayed. The oxymethine proton at C-3 was assigned as equatorial position (α-orientation), due to the small coupling constants of this proton (*dd*, *J* = 4.2, 2.1 Hz). Therefore, compound **TD17** was established as *ent*-5α-dolabr-4(18),15-diene-3α-ol, the same as previously reported (Krebs et al. 2004).

Table 17 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD17** and **TD14**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD17**)
		TD14	**TD17**	**TD17**	**TD14**	$^{1}H \rightarrow ^{13}C$
1	CH_2	17.7	16.5	2.15, *m*; 1.78, *m*		
2	CH_2	36.5	29.8	2.13, *m*; 1.75, *m*		
3	CH	203.5	74.1	4.43, *dd* (4.2, 2.1)		1, 2, 18
4	C	152.3	155.0			
5	C	41.0	39.2			
6	CH_2	37.4	39.3	2.27, *m*; 1.31, *m*		
7	CH_2	25.6	26.0			
8	CH	42.5	42.8	1.35, *m*		
9	C	38.2	38.2			
10	CH	52.4	54.1	1.24, *m*		
11	CH_2	35.6	36.2			
12	CH_2	31.9	31.9			
13	C	36.3	36.4			
14	CH_2	39.0	39.0			
15	CH	151.0	151.4	5.80, *dd* (17.4, 10.8)	5.80, *dd* (17.4, 10.8)	12, 13, 14, 17
16	CH_2	108.8	108.6	4.90, *dd* (17.4, 1.5); 4.84, *dd* (10.8, 1.5)	4.93, *dd* (17.4, 1.2); 4.85, *dd* (10.8, 1.2)	13, 15
17	CH_3	23.0	22.9	1.01, *s*	1.03, *s*	12, 13, 14, 15
18	CH_2	116.3	112.2	5.05, *s*; 5.02, *s*	5.93, *s*; 5.33, *s*	3, 4, 5, 19
19	CH_3	33.6	34.9	1.45, *s*	1.10, *s*	4, 5, 6
20	CH_3	13.6	15.3	0.79, *s*	0.79, *s*	8, 9, 10, 11

* For **TD17**

3.1.18 Compound **TD18**



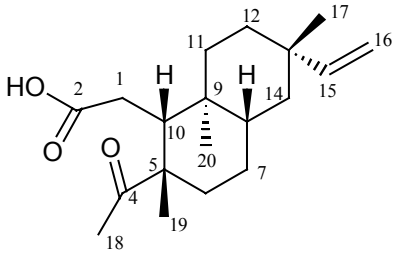
TD18 was isolated as a white solid, mp 87-88°C, $[\alpha]_D^{28}$: +38.4° (*c* = 2.64, $CHCl_3$). The IR, ^1H and ^{13}C NMR spectroscopic data of **TD18** were almost identical to those of **TD17** (**Table 18**, **Figures 44** and **45**), except for the signals of the epoxidic protons in ring A, where H_2-18 at δ 3.07 (*d*, *J* = 4.8 Hz) and 2.71 (*d*, *J* = 4.8 Hz) of **TD18** replaced the two olefinic protons of **TD17**. Due to chemical shifts of two epoxidic protons, C-18 carbon was assigned as 18α, the same as in **TD15**. By comparison of the ^{13}C NMR spectral data with the previously reported data of tagalsin D (Zhang et al., 2005) (**Table 18**), compound **TD18** was established as *ent*-5α,18α,-dolabr-4,18-epoxy-15-ene-3α-ol.

Table 18 The ^1H and ^{13}C spectral data of compounds **TD18**, **TD17** and tagalsin **D** (**R**)

Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)	
tion	of C*	**R**	**TD18**	**TD17**	**TD18**	**R**
1	CH_2	15.7	15.7	16.5		
2	CH_2	29.1	29.0	39.3		
3	CH	73.4	73.4	74.1	3.45, *dd* (2.0, 1.5)	3.45, *dd* (2.0, 1.5)
4	C	62.3	62.3	155.0		
5	C	35.9	35.9	39.2		
6	CH_2	34.4	34.4	26.0		
7	CH_2	27.9	27.8	29.8		
8	CH	41.8	41.2	42.8		
9	C	37.4	37.4	38.2		
10	CH	54.7	54.7	54.1		
11	CH_2	35.9	35.9	36.2		
12	CH_2	32.1	32.1	31.9		
13	C	36.2	36.2	36.4		
14	CH_2	38.9	38.9	39.0		
15	CH	151.2	151.2	151.4	5.80, *dd* (17.4, 10.8)	5.80, *dd*(17.5, 10.8)
16	CH_2	108.8	108.7	108.6	4.91, *dd* (17.4, 1.5);	4.90, *d* (17.5);
					4.85, *dd* (10.8, 1.5)	4.84, *d* (10.8)
17	CH_3	22.8	22.8	22.9	1.01, *s*	1.01, *s*
18	CH_2	56.5	56.5	112.2	3.07, *d* (4.8);	3.08, *d* (4.6);
					2.71, *d* (4.8)	2.70, *d* (4.6)
19	CH_3	30.8	30.8	34.9	1.38, *s*	1.39, *s*
20	CH_3	16.8	16.9	15.3	0.87, *s*	0.87, *s*

* For **TD18**

3.1.19 Compound **TD19**



TD19 was isolated as a white solid, mp 87-88°C, $[\alpha]_D^{28}$: -4.53° (*c* = 1.50, $CHCl_3$). The IR absorptions at 1701 and 1636 cm^{-1} suggested the presence of a carbonyl and a vinyl groups. The ^{13}C NMR spectrum (**Table 19**, **Figure 47**) showed nineteen carbons and the ^{1}H NMR spectrum (**Table 19**, **Figure 46**) displayed four singlet methyl groups at δ 0.57 (H_3-20), 1.02 (H_3-17), 1.14 (H_3-19), and 2.19 (H_3-18) and the terminal vinylic protons at δ 4.85 (*d*, *J* = 10.5 Hz, H-16a), 4.89 (*d*, *J* = 17.4 Hz, H-16b), and 5.77 (*dd*, *J* = 17.4, 10.5 Hz, H-15). Comparison with **TD18** revealed that signals for rings B and C were identical. The ^{1}H NMR signals for ring A in **TD18** were replaced by signals of downfield methylene protons H_2-1 at δ 3.11 (*dd*, *J* = 18.3, 1.2 Hz) and 2.63 (*dd*, *J* = 18.3, 6.9 Hz) and a methyl ketone at δ 2.19 (H_3-18). The ^{13}C NMR signals of carboxyl and carbonyl were displayed at δ 180.6 and 214.6, respectively. These data indicated that ring A was broken. By comparison of the ^{13}C NMR spectral data with the previously reported data of tagalsin H (Zhang et al., 2005) (**Table 19**), compound **TD19** was established as *ent*-2-*seco*-3-nor-5α,4-oxodolabr-15-ene-2-oic acid.

Table 19 The ^{1}H and ^{13}C spectral data of compounds **TD19**, **TD18** and tagalsin H (**R**)

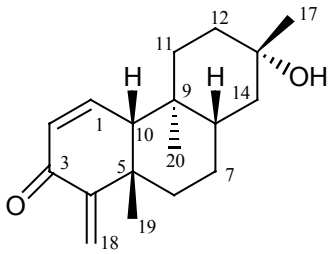
Posi-tion	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)	
		R	**TD19**	**TD18**	**TD19**	**R**
1	CH_2	31.1	31.4	15.7	3.11, *dd* (18.3, 1.2; 2.63, *dd* (18.3, 6.9)	3.15, *dd* (18.0, 2.0; 2.66, *dd* (18.0, 7.0)
2	C	179.5	180.6	29.0		
3	-	-	-	73.4		
4	C	214.7	214.6	62.3		
5	C	50.4	50.4	35.9		
6	CH_2	38.7	38.7	34.4		

Table 19 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)	
		R	**TD19**	**TD18**	**TD19**	**R**
7	CH_2	27.3	27.3	27.8		
8	CH	42.1	42.1	41.2		
9	C	38.6	38.6	37.4		
10	CH	54.3	54.3	54.7	1.87, *m*	1.89, *m*
11	CH_2	33.0	33.0	35.9		
12	CH_2	31.8	31.8	32.1		
13	C	36.2	36.2	36.2		
14	CH_2	39.1	39.1	38.9		
15	CH	150.9	150.9	151.2	5.77, *dd* (17.4, 10.5)	5.78, *dd* (17.5, 10.5)
16	CH_2	108.9	108.9	108.7	4.89, *d* (17.4);	4.88, *d* (17.5);
					4.85, *d* (10.5)	4.84, *d* (10.5)
17	CH_3	23.1	23.1	22.8	1.02 *s*	1.04, *s*
18	CH_3	27.6	27.6	56.5	2.19 *s*	2.22, *s*
19	CH_3	28.4	28.4	30.8	1.14 *s*	1.17, *s*
20	CH_3	12.3	12.2	16.9	0.57 *s*	0.58, *s*

* For **TD19**

3.1.20 Compound **TD20**



TD20 showed eighteen carbons in ^{13}C NMR spectrum (**Table 20, Figure 49**) and its molecular formula was established as $C_{18}H_{26}O_2$ on the basis of HREIMS. The ^1H NMR spectrum of **TD20** (**Table 20, Figure 48**) showed three singlet methyl signals at δ 0.70 (H_3-20), 1.10 (H_3-19), and 1.30 (H_3-17). The ^{13}C NMR resonances indicated methyl signals at δ 12.3 (C-20), and 33.5 (C-19) which was related to A/B *cis*-ring junction of dolabrane skeleton as in **TD1**. The two olefinic units were conjugated with a carbonyl group (δ 191.1, C-3) as displayed at δ 130.4 (C-1), and 149.7 (C-2) for

endo-conjugation and δ 150.0 (C-4), and 117.5 (C-18) for *exo*-conjugation in ^{13}C NMR spectrum, while the proton signals of these functions displayed a disubstituted olefinic protons at δ 6.96 (*dd*, *J* = 10.2, 6.0 Hz, H-1), and 6.29 (*d*, *J* = 10.2 Hz, H-2) and exocyclic ones at δ 5.33 (*s*, H-18a), and 6.15 (*s*, H-18b). The conjugated enone system was located at ring A by the HMBC correlations observed between H-1/C-3, C-5 (δ 40.6), and C-10 (δ 57.4), between H-2/C-1, C-3, and C-10 and between H_2-18/C-3, and C-5. In addition, the HMBC correlations were further observed between H_3-17/C-12 (δ 35.6), C-14 (δ 43.2), and oxy-quaternary carbon C-13 (δ 71.2) indicating that **TD20** was 15,16 nordolabrane diterpene. The stereochemistry of the hydroxyl group at C-13 was determined by NOESY experiment which revealed correlations from H_3-20 (δ 0.70) to H-11equatorial (δ 1.64), H-7axial (δ 1.44), H-12axial (δ 1.55), H-14axial (δ 1.49) and no correlations from H-12axial and H-14axial to H_3-17 (δ 1.30). These results established the hydroxyl group as 13β. Thus, compound **TD20** was deduced as *ent*-5α,3-oxo-15,16-nordolabr-1,4(18)-diene-13β-ol, a new compound designated as ceriotagalsin G.

Table 20 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD20** and **TD1**

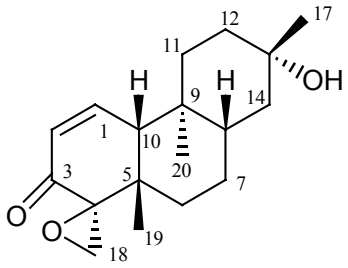
Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD20**)
		TD1	**TD20**	**TD20**	**TD1**	$^{1}H \rightarrow ^{13}C$
1	CH	16.1	149.7	6.96, *dd* (10.2, 6.0)		3, 5, 10
2	CH	31.4	130.4	6.29, *d* (10.2)	2.49, *dd* (9.3, 6.3)	1, 3, 10
3	C	199.3	191.1			
4	C	116.4	150.0			
5	C	36.2	40.6			
6	CH_2	36.5	36.3	2.23, *m*; 1.45, *m*	2.16, *m*; 1.42, *m*	
7	CH_2	25.3	25.3	1.44, *m*; 1.24, *m*		
8	CH	41.9	44.0	1.31, *m*	1.46, *m*	
9	C	37.6	39.8			
10	CH	51.7	57.4	1.99, *d* (6.0)	1.25, *m*	1, 2, 8, 20
11	CH_2	34.9	37.3	1.64, *m*; 1.26, *m*		
12	CH_2	27.7	35.6	1.60, *m*; 1.55, *m*		
13	C	45.4	71.2			
14	CH_2	34.4	43.2	1.49, m; 1.42, *m*		

Table 20 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD20**) $^1H \rightarrow ^{13}C$
		TD1	**TD20**	**TD20**	**TD1**	
15		215.2				
16		63.9			4.38, *d* (3.9)	
17	CH_3	20.6	26.8	1.30, *s*	1.22, *s*	12, 13, 14
18	CH_2	171.4	117.5	5.33, *s*; 6.15, *s*	7.94, *d* (7.8)	3, 5
19	CH_3	35.8	33.5	1.10, *s*	1.17, *s*	4, 5, 6, 10
20	CH_3	12.6	12.3	0.70, *s*	0.72, *s*	8, 9, 10, 11

* For **TD20**

3.1.21 Compound **TD21**



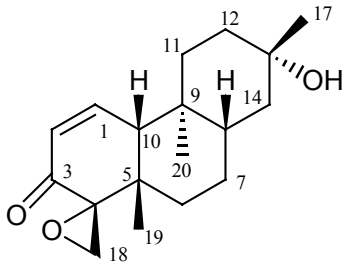
The ^{13}C NMR spectrum of **TD21** showed eighteen signals, suggesting $C_{18}H_{26}O_3$ as confirmed by HREIMS. The ^1H and ^{13}C NMR spectra of **TD21** (**Table 21**, **Figures 50** and **51**) exhibited signals similar to those of **TD20** except that the exocyclic olefinic protons in **TD20** were replaced by a pair of separated epoxidic geminal signals at δ 2.88 (*d*, *J* = 6.5 Hz, H-18a), and 3.36 (*d*, *J* = 6.5 Hz, H-18b). Furthermore, ^{13}C NMR signals of **TD21** at δ 60.3 (C-4) and 50.5 (C-18) were observed instead of the signals of an olefinic group for **TD20**. The configuration of the epoxide group was the same as found for tagalsin A (Zhang et al., 2005). The important HMBC showed the correlation between epoxidic protons H_2-18 with C-4, and C-5 (δ 35.5). Therefore, compound **TD21** was determined as *ent*-5α,18α,3-oxo-15,16-nordolabr-4,18-epoxy-1-ene-13β-ol, a new compound designated as ceriotagalsin H.

Table 21 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD21** and **TD20**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD21**) $^{1}H \rightarrow ^{13}C$
		TD20	**TD21**	**TD21**	**TD20**	
1	CH	130.4	151.2	7.11, *dd* (10.5, 6.5)	6.96, *dd* (10.2, 6.0)	3, 5, 10
2	CH	149.7	130.4	6.33, *d* (10.5)	6.29, *d* (10.2)	4, 10
3	C	191.1	194.3			
4	C	150.0	60.3			
5	C	40.6	35.5			
6	CH_2	36.3	33.9			
7	CH_2	25.3	27.2			
8	CH	44.0	43.8			
9	C	39.8	39.2			
10	CH	57.4	56.4	2.08, *d* (6.5)	1.99, *d* (6.0)	4, 5, 9, 19, 20
11	CH_2	37.3	37.3			
12	CH_2	35.6	35.7			
13	C	71.2	71.4			
14	CH_2	43.2	43.2			
17	CH_3	26.8	26.7	1.30, *s*	1.30, *s*	12, 13, 14
18	CH_2	117.5	50.5	2.88, *d* (6.5); 3.36, *d* (6.5)	5.33, *s*; 6.15, *s*	4, 5
19	CH_3	33.5	31.4	1.17, *s*	1.10, *s*	4, 5, 6, 10
20	CH_3	12.3	12.2	0.86, *s*	0.70, *s*	8, 9, 10, 11

* For **TD21**

3.1.22 Compound **TD22**



The molecular formula of **TD22** was identical to that of **TD21** on the basis of HREIMS. The ^{1}H and ^{13}C NMR spectra of **TD22** (**Table 22, Figures 52** and **53**)

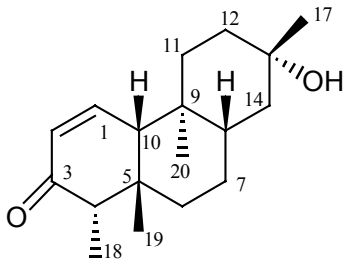
resembled those of **TD21** except for the signals of epoxidic group (H_2-18) which were shifted to δ 3.04 (*d*, *J* = 6.6 Hz), and 3.07 (*d*, *J* = 6.6 Hz) and the chemical shift of C-18 which resonated at δ 55.2 in **TD22** in contrast to δ 50.5 in **TD21**. By the same comparison as for tagalsin A, and B (Zhang et al., 2005) and oxidopanamensin (Koike et al., 1980), compound **TD22** was assigned to be an epimer of **TD21** at epoxidic C-18. Thus, this compound was elucidated as *ent*-5α,18β,3-oxo-15,16-nordolabr-4,18-epoxy-1-ene-13-ol, a new compound designated as ceriotagalsin I.

Table 22 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD22** and **TD21**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD22**)
		TD21	**TD22**	**TD22**	**TD21**	$^{1}H \rightarrow ^{13}C$
1	CH	151.2	150.3	7.07, *dd* (10.2, 6.0)	7.11, *dd* (10.5, 6.5)	3, 9, 10
2	CH	130.4	130.5	6.30, *d* (10.2)	6.33, *d* (10.5)	4, 10
3	C	194.3	195.1			
4	C	60.3	61.2			
5	C	35.5	36.8			
6	CH_2	33.9	31.9	1.71, *m*; 1.66, *m*		
7	CH_2	27.2	27.3			
8	CH	43.8	43.2	1.47, *m*		
9	C	39.2	38.8			
10	CH	56.4	58.0	2.19, *d* (2.0)	2.08, *d* (6.5)	2, 5, 9, 19, 20
11	CH_2	37.3	37.1			
12	CH_2	35.7	35.7			
13	C	71.4	70.9			
14	CH_2	43.2	43.1			
17	CH_3	26.7	26.7	1.31, *s*	1.30, *s*	8, 12, 13
18	CH_2	50.5	55.2	3.07, *d* (6.6); 3.04, *d* (6.6)	2.88, *d* (6.5); 3.36, *d* (6.5)	
19	CH_3	31.4	29.2	1.19, *s*	1.17, *s*	4, 5, 6, 10
20	CH_3	12.2	13.3	0.83, *s*	0.86, *s*	8, 9, 10, 11

* For **TD22**

3.1.23 Compound **TD23**



The ^{13}C NMR spectrum (**Table 23, Figure 55**) of **TD23** indicated that it contained eighteen carbons of a nordolabrane backbone as in **TD20**–**TD22**. The molecular formula $C_{18}H_{28}O_2$ of **TD23** was indicated by HREIMS. It differed from **TD20** by an additional two hydrogen atoms. The ^{1}H NMR spectrum (**Table 23, Figure 54**) of **TD23** exhibited disubstituted olefinic protons at δ 6.14 (*d*, *J* = 10.2 Hz, H-2), and 6.84 (*dd*, *J* = 10.2, 5.7 Hz, H-1) with similarity to those of **TD20**–**TD22**. The difference was shown in ring A, of which the exocyclic olefinic protons in **TD20** were replaced by the signals of a methyl doublet at δ 1.04 (*d*, *J* = 6.6 Hz, H_3-18) and a methine proton at δ 2.83 (*q*, *J* = 6.6 Hz, H-4) in **TD23**. The HMBC correlations were observed between H-4/C-3 (δ 202.6), C-5 (δ 39.3), C-18 (δ 8.0), and C-19 (δ 26.3) and between H_3-18/C-3, C-4 (δ 45.0) and C-5, which confirmed an attachment of a doublet methyl at C-4. The methyl group at C-18 could be assigned as α-orientation by NOESY experiment which revealed correlations from H_3-20 (δ 0.87) to H_3-18 (δ 1.04) but no correlations from H_3-20 to H-4 (δ 2.83). Therefore, compound **TD23** was deduced to be *ent*-5α,18β,3-oxo-15,16-nordolabr-1-ene-13-ol, a new compound designated as ceriotagalsin J.

Table 23 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD23** and **TD20**

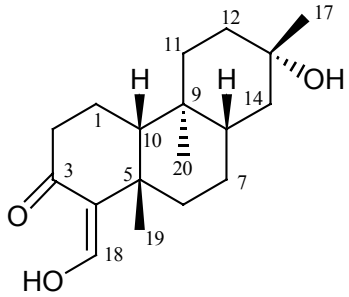
Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD23**)
		TD20	**TD23**	**TD23**	**TD20**	^{1}H→^{13}C
1	CH	130.4	148.0	6.84, *dd* (10.2, 5.7)	6.96, *dd* (10.2, 6.0)	3, 5, 10
2	CH	149.7	130.2	6.14, *d* (10.2)	6.29, *d* (10.2)	4, 10
3	C	191.1	202.6			
4	CH	150.0	45.0	2.83, *q* (6.6)		3, 5, 18, 19
5	C	40.6	39.3			

Table 23 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD23**) $^1H \rightarrow ^{13}C$
		TD20	**TD23**	**TD23**	**TD20**	
6	CH_2	36.3	37.5	1.97, *m*; 1.27, *m*	2.23, *m*; 1.45, *m*	
7	CH_2	25.3	25.3			
8	CH	44.0	44.5	1.30, *m*	1.31, *m*	
9	C	39.8	39.0			
10	CH	57.4	57.4	1.88, *d* (5.7)	1.99, *d* (6.0)	1, 5, 9, 19, 20
11	CH_2	37.3	37.4			
12	CH_2	35.6	35.6			
13	C	71.2	71.1			
14	CH_2	43.2	43.0			
17	CH_3	26.8	27.0	1.32, *s*	1.30, *s*	12, 13, 14
18	CH_3	117.5	8.0	1.04, *d* (6.6)	5.33, *s*; 6.15, *s*	3, 4, 5
19	CH_3	33.5	26.3	0.87, *s*	1.10, *s*	4, 5, 6, 10
20	CH_3	12.3	13.5	0.92, *s*	0.70, *s*	8, 9, 10, 11

* For **TD23**

3.1.24 Compound **TD24**



TD24 was isolated as a white solid, mp 147-148°C, $[\alpha]_D^{28}$: -56.3° (*c* = 0.25, $CHCl_3$). **TD24** showed eighteen carbons in ^{13}C NMR spectrum (**Table 2, Figure 55**) and its molecular formula was established as $C_{18}H_{28}O_3$ on the basis of HREIMS. The ^1H and ^{13}C NMR spectra (**Tables 24, Figures 56** and **57**) of **TD24** showed the signals similar to those of **TD20** with the exception of the signals for ring A, where an olefinic proton at δ 7.94 (*d*, *J* = 7.0 Hz, H-18) and a chelated hydroxy proton at δ 15.43 (*d*, *J* = 7.0 Hz, 18-OH) were observed, instead of the two olefinic protons as in **TD20**. The important HMBC showed the correlations between olefinic proton H-18/C-2 (δ 31.5),

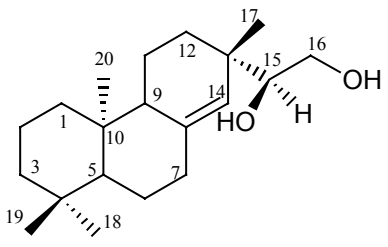
C-3 (δ 199.3), C-4 (δ 116.6), and C-5 (δ 36.2) and between H_3-17/C-12 (δ 35.6), C-13 (δ 71.2), and C-14 (δ 42.7). Therefore, compound **TD24** was determined as *ent*-5α,3-oxo-15,16-nordolabr-4(18)-ene-13,18-diol, a new compound designated as ceriotagalsin K.

Table 24 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD24** and **TD20**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD24**) $^{1}H \rightarrow ^{13}C$
		TD20	**TD24**	**TD24**	**TD20**	
1	CH_2	130.4	16.5		6.96, *dd* (10.2, 6.0)	
2	CH_2	149.7	31.5	2.49, *m*	6.29, *d* (10.2)	1, 3, 4, 10
3	C	191.1	199.3			
4	C	150.0	116.6			
5	C	40.6	36.2			
6	CH_2	36.3	36.8	2.17, *m*; 1.78, *m*	2.23, *m*; 1.45, *m*	
7	CH_2	25.3	25.1			
8	CH	44.0	45.3	1.31, *m*	1.31, *m*	
9	C	39.8	37.7			
10	CH	57.4	51.9	1.23, *m*	1.99, *d* (6.0)	
11	CH_2	37.3	37.5			
12	CH_2	35.6	35.6			
13	C	71.2	71.2			
14	CH_2	43.2	42.7			
17	CH_3	26.8	16.9	1.25, *s*	1.30 *s*	12, 13, 14
18	CH	117.5	171.5	7.94, *d* (7.0)	6.15, *s*; 5.33, *s*	2, 3, 4, 5
19	CH_3	33.5	35.7	1.16, *s*	1.10, *s*	5, 10
20	CH_3	12.3	12.9	0.77, *s*	0.70, *s*	8, 9, 10, 11
	OH-18			15.43, *d* (7.0)		2, 3, 4, 8

* For **TD24**

3.1.25 Compound **TD25**



TD25 was obtained as a colorless plate crystal (acetone), mp 104-105° C, $[\alpha]_D^{28}$: -17.7° (*c* = 1.93, $CHCl_3$). X-ray crystallographic analysis of **TD25** was carried out and gave ORTEP drawing as shown in **Figure 5**, whose structure enabled assignment of a pimarane diterpene with a molecular formula $C_{20}H_{34}O_2$ by HREIMS. Its ^1H NMR spectrum (**Table 25, Figure 58**) showed the signals for trisubstituted olefinic proton at δ 5.27 (*s*, H-14), for AB_2 system of 1,2-hydroxyethyl side-chain at δ 3.61 (*dd*, *J* = 9.3, 2.1 Hz, H-16a), 3.51 (*dd*, *J* = 10.5, 9.3 Hz, H-16b) and 3.70 (*dd*, *J* = 10.5, 2.1 Hz, H-15), and four singlet quaternary methyl groups at δ 0.90 (H_3-17), 0.88 (H_3-19), 0.84 (H_3-18) and 0.78 (H_3-20). The important HMBC correlations were noticed between a hydroxy methine proton H-15/C-12 (δ 32.4), C-13 (δ 36.3), C-14 (δ 126.9), C-16 (δ 63.3) and C-17 (δ 23.7). The ^1H and ^{13}C NMR spectra (**Table 25, Figures 56 and 59**) of **TD25** were in agreement with those of flavidusin A (Zhao et al., 1998) except for the signals of C-8 (δ 140.1), C-12 (δ 32.4), C-13 (δ 36.3), C-14 (δ 126.9) and C-15 (δ 78.8) which differed from the signals of flavidusin A (isoprima-8(14)-ene-15,16-diol) of C-8 (δ 137.6), C-12 (δ 31.1), C-13 (δ 38.4), C-14 (δ 129.1) and C-15 (δ 79.8). X-ray crystallographic analysis of **TD25** enabled assignment of 1,2-hydroxyethyl side-chain as axial-orientation and *S* configuration for C-15. Thus, compound **TD25** was elucidated as *ent*-15*S*-prima-8(14)-ene-15,16-diol, a new compound designated as ceriotagalsin L.

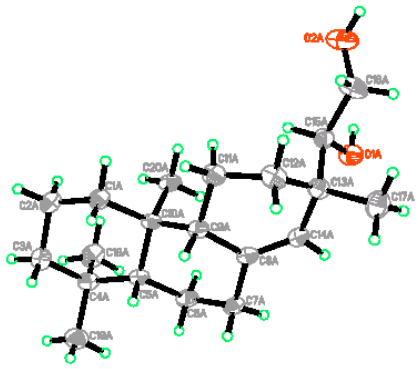


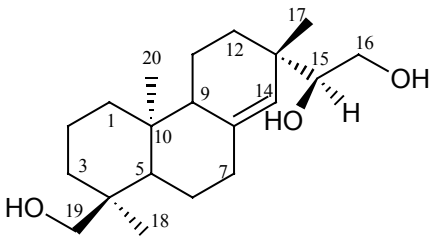
Figure 5 X-ray ORTEP diagram of compound **TD25**

Table 25 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD25** and flavidusin A (**R**)

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD25**) $^{1}H \rightarrow ^{13}C$
		R	**TD25**	**TD25**	**R**	
1	CH_2	40.0	39.2			
2	CH_2	19.0	18.9			
3	CH_2	42.4	42.1			
4	C	33.4	33.3			
5	CH	51.3	54.9	1.05, *m*		
6	CH_2	22.9	22.6			
7	CH_2	36.6	36.3	2.31, *m*; 2.06, *m*		
8	C	137.6	140.1			
9	CH	54.4	50.4	1.72, *m*		
10	C	38.5	38.5			
11	CH_2	19.4	19.0			
12	CH_2	31.1	32.4			
13	C	38.4	36.3			
14	CH	129.1	126.9	5.27, *s*	5.67, *s*	7, 12, 13, 17
15	CH	79.8	78.8	3.70, *dd* (10.5, 2.1)	3.85, *dd* (8.8, 2.4)	12, 13, 15, 16, 17
16	CH_2	63.5	63.3	3.61, *dd* (9.3, 2.1); 3.51, *dd* (10.5, 9.3)	4.17, *dd* (10.7, 2.4); 3.92, *dd* (10.7, 8.8)	9, 12, 13, 17
17	CH_3	22.3	23.7	0.90 *s*	1.24, *s*	12, 13, 14, 15
18	CH_3	33.9	33.7	0.84, *s*	0.78, *s*	3, 4, 5
19	CH_3	23.3	22.1	0.88, *s*	0.82, *s*	3, 4, 5
20	CH_3	15.1	15.0	0.78, *s*	0.82, *s*	1, 5, 9, 10

* For **TD25**

3.1.26 Compound **TD26**



TD26 was isolated as a white solid, mp 119-120°C, $[\alpha]_D^{28}$: -17.8° (*c* = 1.33, $CHCl_3$), its molecular formula was established as $C_{20}H_{34}O_3$ from HREIMS which was 16 mass units more than that of **TD25**, suggesting the addition of one oxygen atom. The ^1H and ^{13}C NMR spectra (**Tables 26**, **Figures 60** and **61**) of **TD26** were comparable to those of **TD25** and a synthetic compound, isoprima-8(14)-ene-15,16,18-triol (Wenkert et al., 1979) except for the hydroxy methylene protons at C-19 (δ 65.2) and methyl group at δ 27.1 (C-18) in **TD26** replaced the hydroxy methylene protons at C-18 (δ 70.8) and methyl group at δ 17.3 (C-19) in the latter compound. By comparison of the ^{13}C NMR spectral data with the previously reported data of isoprima-8(14)-ene-15,16,18-triol, compound **TD26** was assigned as *ent*-15*S*-prima-8(14)-ene-15,16,19-triol, a new compound designated as ceriotagalsin M.

Table 26 The ^1H, ^{13}C and HMBC spectral data of compounds **TD26**, **TD 25** and isoprima-8(14)-ene-15,16,18-triol (**R**)

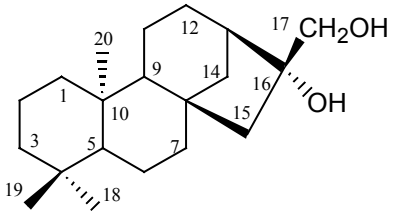
Posi-tion	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD26**)
		R	**TD26**	**TD25**	**TD26**	**TD25**	$^1H \rightarrow ^{13}C$
1	CH_2	38.2	39.1	39.2			
2	CH_2	17.8	18.6	18.9			
3	CH_2	35.3	35.4	42.1			
4	C	37.2	38.6	33.3			
5	CH	47.2	55.9	54.9	1.26, *m*	1.05, *m*	
6	CH_2	22.0	22.6	22.6			
7	CH_2	34.9	36.6	36.3	2.33, *m*; 2.06, *m*	2.31, *m*; 2.06, *m*	
8	C	138.6	139.6	140.1			
9	CH	50.3	50.5	50.4	1.75, *m*	1.72, *m*	
10	C	36.6	38.4	38.5			
11	CH_2	17.8	19.0	19.0			
12	CH_2	31.5	32.4	32.4			
13	C	37.4	37.1	36.3			
14	CH	127.0	127.2	126.9	5.27 *s*	5.27 *s*	7, 9, 12, 17
15	CH	75.5	78.7	78.8	3.60, *dd* (9.0, 1.5)	3.70, *dd* (10.5, 2.1)	16, 17

Table 26 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD26**)
		R	**TD26**	**TD25**	**TD26**	**TD25**	$^1H \rightarrow ^{13}C$
16	CH_2	62.7	63.3	63.3	3.70, *dd* (9.0, 1.5); 3.49, *dd* (10.5, 9.0)	3.61, *dd* (9.3, 2.1); 3.51, *dd* (10.5, 9.3)	14, 15
17	CH_3	21.8	23.6	23.7	0.90, *s*	0.90, *s*	12, 13, 14, 15
18	CH_3	70.8	27.1	33.7	0.99, *s*	0.84, *s*	3, 4, 5, 19
19	CH_2	17.3	65.2	22.1	3.43, *d* (11.1); 3.82, *d* (11.1)	0.88, *s*	3, 4, 5, 19
20	CH_3	14.7	16.1	15.0	0.76, *s*	0.78, *s*	5, 9, 10

* For **TD26**

3.1.27 Compound **TD27**



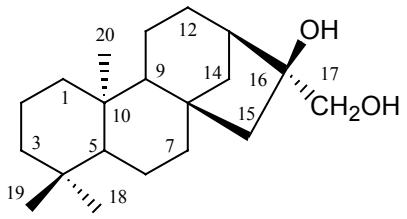
TD27 was obtained as a white solid, mp 174-175°C, $[\alpha]_D^{28}$: -9.2° (*c* = 2.25, $CHCl_3$). The ^1H and ^{13}C NMR spectral data (**Table 27, Figures 62** and **63**) of **TD27** were suggestive of a kaurane diterpenoid. The ^1H NMR spectrum showed three singlet methyl groups at δ 0.86 (H_3-18), 0.82 (H_3-19), and 1.03 (H_3-20) and two oxy-methylene protons at δ 3.80 (d, *J* = 11.1 Hz), and 3.68 (*d*, *J* = 11.1 Hz). Its ^{13}C NMR spectrum displayed the signals of an oxy-methylene carbon at δ 66.4 (C-17) and oxyquaternary carbon at δ 81.9 (C-16). The important HMBC correlations were noticed between two oxy-methylene protons, H_2-17/C-13 (δ 45.5), C-15 (δ 53.4) and C-16, between H_3-18 and H_3-19/C-3, and C-5 and between H_3-20/C-1(δ 42.0), C-5, and C-9 (δ 56.7). By comparison of the ^{13}C NMR spectral data with the previously reported data (Kitajima et al., 1982), compound **TD27** was assigned as *ent*-kauran-16β,17-diol.

Table 27 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TD27** and *ent*-kauran-16β,17-diol (**R**)

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TD27**) $^{1}H \rightarrow ^{13}C$
		R**	**TD27**	**TD27**	**R****	
1	CH_2	42.0	42.0			
2	CH_2	18.2	18.3			
3	CH_2	42.0	42.0			
4	C	33.4	33.3			
5	CH	56.1	56.1	0.80, *m*		
6	CH_2	20.5	20.4			
7	CH_2	37.2	37.3	1.98, *m*; 1.58, *m*		
8	C	44.6	44.7			
9	CH	56.7	56.7	1.01, *m*		
10	C	39.4	39.4			
11	CH_2	18.3	18.6			
12	CH_2	26.3	26.3			
13	C	45.5	45.5	2.05, *m*		
14	CH_2	40.4	40.3			
15	CH_2	53.4	53.4			
16	C	81.6	81.9			
17	CH_2	66.2	66.4	3.80, *d* (11.1); 3.68, *d* (11.1)	3.80, *d* (11); 3.65, *d* (11)	13, 15, 16
18	CH_3	33.4	33.6	0.86, *s*	0.84, *s*	3, 5
19	CH_3	21.5	21.5	0.82, *s*	0.80, *s*	3, 5, 18
20	CH_3	17.7	17.8	1.03, *s*	1.02, *s*	1, 5, 9

* For **TD27** **In pyridine

3.1.28 Compound **TD28**



TD28 was isolated as a white solid, mp 134-135°C, $[\alpha]_D^{28}$: -37.5° (*c* = 0.30, $CHCl_3$). The ^1H and ^{13}C NMR spectra of **TD28** (**Table 28**, **Figures 64** and **65**) resembled those of **TD27** except for the signals of two oxy-methylene protons that displayed at δ 3.47 (*d*, *J* = 9.0 Hz), and 3.39 (*d*, *J* = 9.0 Hz) and the chemical shift of C-17 which resonated at δ 69.9 in **TD28** in contrast to δ 66.4 in **TD27**. The structure of **TD28** was assigned to be an epimer of **TD27** at C-16. By comparison of the ^{13}C NMR spectral data with the previously reported data (Kitajima et al., 1982) (**Table 28**), compound **TD28** was established as *ent*-kauran-16α,17-diol, whose structure was supported by X-ray crystallographic analysis (**Figure 6**) (Chantrapromma et al. 2006).

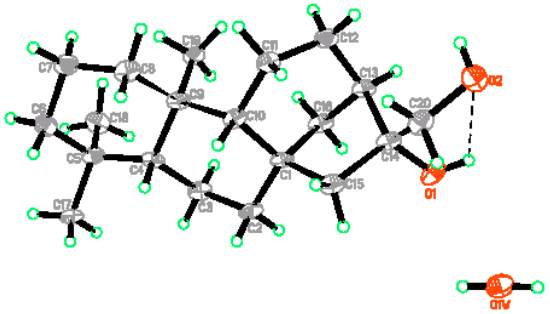


Figure 6 X-ray ORTEP diagram of compound **TD28**

Table 28 The ^1H, ^{13}C and HMBC spectral data of compounds **TD28**, **TD27** and *ent*-kauran-16α,17-diol (**R**)

Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC *
tion	of C*	**R**	**TD28**	**TD27**	**TD28**	**TD27**	$^1H \rightarrow ^{13}C$
1	CH_2	41.9	41.9	42.0			
2	CH_2	18.7	18.8	18.3			
3	CH_2	42.0	42.1	42.0			
4	C	33.2	33.2	33.3			
5	CH	56.1	56.2	56.1	0.81, *m*	0.80, *m*	
6	CH_2	20.0	21.6	20.4			
7	CH_2	38.2	38.3	37.3	2.03, *m*; 1.02, *m*	1.98, *m*; 1.58, *m*	
8	C	43.5	43.5	44.7			
9	CH	56.9	57.0	56.7	1.14, *m*	1.01, *m*	
10	C	39.3	39.4	39.4			
11	CH_2	18.6	18.6	18.6			

Table 28 Continued

Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC *
tion	of C*	**R**	**TD28**	**TD27**	**TD28**	**TD27**	$^1H \rightarrow ^{13}C$
12	CH_2	26.7	26.7	26.3			
13	C	52.6	40.8	45.5	2.09, *m*	2.05, *m*	
14	CH_2	40.4	40.4	40.3			
15	CH_2	56.1	52.8	53.4			
16	C	79.7	79.8	81.9			
17	CH_2	69.7	69.9	66.4	3.47, *d* (9.0);	3.80, *d* (11.1);	13, 15,
					3.39, *d* (9.0)	3.68, *d* (11.1)	16
18	CH_3	33.6	33.6	33.6	0.84, *s*	0.86, *s*	3, 5, 19
19	CH_3	21.5	21.6	21.5	0.80, *s*	0.82, *s*	3, 5, 18
20	CH_3	17.6	17.6	17.8	1.03, *s*	1.03, *s*	9, 10

* For **TD28**

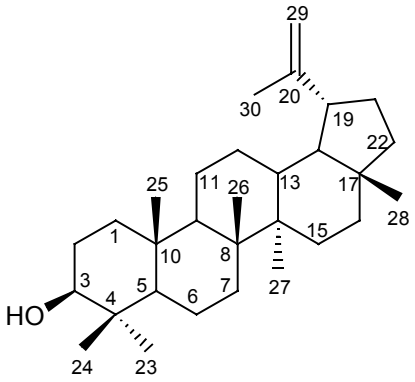
3.2 Structure elucidation of compounds from the hypocotyls and fruits of C. tagal

Dried milled hypocotyls of *C. tagal* (5.3 kg) were extracted with hexane and methylene chloride, successively. The crude hexane extract was subjected to chromatography and/or crystallization to give triterpenoids of three known lupanes: **TL6**, **TL7** and **TL11**. The crude methylene chloride extract was purified by chromatography and/or crystallization to yield triterpenoids of three new dammaranes: **TM7-TM9**, ten known lupanes: **TL1-TL5**, **TL8-TL10**, **TL12** and **TL13**, and a mixture of two known steroids: **TS1** and **TS2**.

Dried milled fruits of *C. tagal* (574.0 g) were extracted with hexane and methylene chloride, successively. The combined dried crude hexane (6.0 g) and methylene chloride (6.1 g) extracts were subjected to chromatography and/or crystallization to give triterpenoids of two new dammaranes: **TM1-TM6**, four known dammaranes: **TM1-TM6** and one known oleanane: **TO1**.

Their structures were elucidated mainly by 1D and 2D NMR spectroscopic data such as ^1H, ^{13}C NMR, DEPT 135°, DEPT 90°, HMQC, HMBC, ^1H-^1H COSY and 2D NOESY. Mass spectral data were determined for new compounds. In addition X-ray crystallographic structure was reported for compound **TL7**.

3.2.1 Compound **TL1**



Compound **TL1** was obtained as a white solid, mp 193-194°C, $[\alpha]_D^{28}$: +25.0° (*c* = 0.20, MeOH). The IR spectrum (**Figure 66**) showed absorption bands for hydroxyl group at 3343 cm^{-1} and double bond at 1638 cm^{-1}. It gave a purple vanillin-sulfuric acid test indicating a triterpene.

The ^{13}C NMR spectral data (**Table 29, Figure 69**) showed 30 signals for 30 carbons. Analysis of DEPT-90° and DEPT-135° spectra of this compound suggested the presence of seven methyls (δ 14.6, 15.4, 16.0, 16.1, 18.0, 19.3 and 28.0), eleven methylenes (δ18.3, 20.9, 25.2, 27.4, 27.5, 29.9, 34.3, 35.6, 38.7, 40.0 and 109.3), six methines (δ 38.1, 48.0, 48.3, 50.5, 55.3 and 79.0) and six quaternary carbons (δ 37.2, 38.9, 40.8, 42.8, 43.0 and 151.0).

The ^{1}H NMR spectral data (**Table 29, Figure 68**) showed characteristic of lupane triterpenoids as seven methyl singlet signals at δ 0.76, 0.79, 0.83, 0.94, 0.97 and 1.03 including one vinylic methy at δ 1.68, two protons of an isopropenyl moiety at δ 4.68 (*d*, *J* = 2.1 Hz, H-29a) and 4.56 (*m*, H-29b) and a typical lupane H_β-19 proton at δ 2.38 (*m*). An oxymethine proton was shown at δ 3.19 (1H, *dd*, *J* = 10.8, 5.1 Hz, H-3) whose doublet of doublet splitting pattern together with a large coupling constant with *Jax-ax* = 10.8 Hz and *Jax-eq* = 5.1 Hz indicated its axial (α) orientation.

The position of the hydroxyl group at C-3 was determined through an HMBC experiment in which the oxymethine proton at δ3.19 (H-3) showed correlations with C-1 (δ 38.7) and C-4 (δ 38.9), C-23 (δ 28.0) and C-24 (δ 15.4). And the position of a methine proton at C-19 was determined from HMBC correlation of H-19 (δ2.38) with C-18 (δ48.3), C-20 (δ151.0), C-21 (δ29.9), C-29 (δ109.3) and

C-30 (δ 19.3). Thus, on the basis of its spectroscopic data and comparison of the ^{1}H and ^{13}C NMR spectral data (**Table 29**) with the previously reported data (Reynolds et al., 1986), compound **TL1** was assigned as lupeol.

Table 29 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TL1** and lupeol

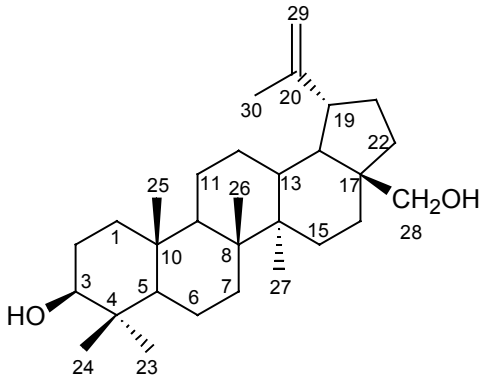
Posi-tion	Type of C*	δ_C /ppm)		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL1**)
		lupeol	**TL1**	lupeol	**TL1***	$^{1}H \rightarrow ^{13}C$
1	CH_2	38.7	38.7	0.91, *m*	0.91,*t* ; 1.68, *d*	
2	CH_2	27.4	27.4	1.56, *m*	1.54, *q*; 1.61 *d*	
3	CH	79.0	79.0	3.19, *dd* (10.8, 5.1)	3.18, *dd*	1, 4, 23, 24
4	C	38.8	38.9			
5	CH	55.3	55.3	0.69, *m*	0.69, *d*	
6	CH_2	18.3	18.3	1.40, *m*; 1.55, *m*	1.39, *q*; 1.54 *d*	
7	CH_2	34.2	34.3	1.40, *m*	1.41, *m*	
8	C	40.8	40.8			
9	CH	50.4	50.5	1.28, *m*	1.28, *d*	
10	C	37.1	37.2			
11	CH_2	20.9	20.9	1.22, *m*; 1.45, *m*	1.25, *q*; 1.42, *d*	
12	CH_2	25.1	25.2	1.08, *m*	1.07, *q*; 1.68, *d*	
13	CH	38.0	38.1	1.67, *m*	1.67, *t*	
14	C	42.8	42.8			
15	CH_2	27.4	27.5	1.56, *m*	1.01, *d*; 1.71, *t*	
16	CH_2	35.5	35.6	1.51, *m*	1.38, *t*; 1.49, *d*	
17	C	43.0	43.0			
18	CH	48.2	48.3	1.38, *m*	1.37, *t*	
19	CH	47.9	48.0	2.38, *m*	2.39, *m*	13, 18, 20, 21, 29, 30
20	C	150.9	151.0			
21	CH_2	29.8	29.9	1.94, *m*	1.33, *m*; 1.93, *m*	
22	CH_2	40.0	40.0	1.20, *m*; 1.40, *m*	1.20, *m*; 1.42, *m*	
23	CH_3	28.0	28.0	0.97, *s*	0.98, *s*	3, 4, 5, 24
24	CH_3	15.4	15.4	0.76, *s*	0.77, *s*	3, 4, 5, 23
25	CH_3	16.1	16.1	0.83, *s*	0.84, *s*	1, 5, 9

Table 29 Continued

Position	Type of C*	δ_C /ppm)		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL1**)
		lupeol	**TL1**	lupeol	**TL1***	$^1H \rightarrow ^{13}C$
26	CH_3	16.0	16.0	1.03, *s*	1.04, *s*	7, 8, 9, 14
27	CH_3	14.5	14.6	0.94, *s*	0.97, *s*	8, 14, 15
28	CH_3	18.0	18.0	0.79, *s*	0.79, *s*	16, 17, 18, 22
29	CH_2	109.3	109.3	4.68, *d* (2.1); 4.56, *m*	4.56, *m;* 4.69, *m*	19, 30
30	CH_3	19.3	19.3	1.68, *s*	1.69, *s*	19, 20, 29

* Deduced from HMQC experiment

3.2.2 Compound **TL2**



Compound **TL2** was obtained as a white solid, mp 230-231°C, $[\alpha]_D^{28}$: +16.7° (*c* = 0.15, MeOH). It gave a purple vanillin-sulfuric acid test indicating a triterpene. The IR spectrum showed similar characteristic bands to those of **TL1**.

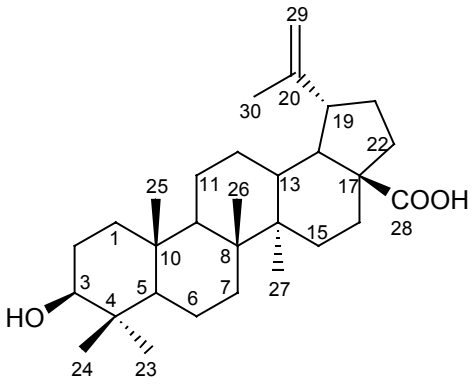
Comparison of ^1H and ^{13}C NMR spectral data (**Table 30**, **Figures 70** and **71**) of compounds **TL2** and **TL1** revealed close structural similarity. Difference in the spectrum of **TL2** was shown as only six singlet signals of methyl groups at δ 0.76, 0.82, 0.97, 0.98, 1.02 and 1.68. In addition, AB system of oxy-methylene protons was shown at δ 3.80 (*dd*, *J* = 10.8, 1.5 Hz, H-28a) and 3.33 (*d*, *J* = 10.8 Hz, H-28b) which was not observed in **TL1**. On the basis of HMBC experiment, the oxy-methylene protons H_2-28 showed long-range correlation with C-16 (δ 29.2), C-17 (δ 47.5) and C-22 (δ 34.0), thus the oxy-methylene protons were located at C-28 (δ 60.6). This compound was established as betulin by comparison of its spectral data with those reported in the literature (Tinto et al., 1992) (**Table 30**). Compound **TL2** was assigned as betulin.

Table 30 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL2**, **TL1** and betulin (**R**)

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL2**)
		R	**TL2**	**TL1**	**TL2****	**TL1****	$^{1}H \rightarrow ^{13}C$
1	CH_2	38.8	38.7	38.7	0.90, *m*; 1.70, *m*	0.91, *m*	
2	CH_2	27.2	27.4	27.4	1.59, *m*	1.56, *m*	
3	CH	78.9	79.0	79.0	3.19, *dd* (10.8, 5.1)	3.19, *dd* (10.8, 5.1)	1, 4, 23, 24
4	C	38.9	38.9	38.9			
5	CH	55.3	55.3	55.3	0.68, *m*	0.69, *m*	
6	CH_2	18.3	18.3	18.3	1.41, *m*	1.40, *m*; 1.55, *m*	
7	CH_2	34.3	34.2	34.3	1.04, *m*; 1.40, *m*	1.40, *m*	
8	C	40.9	40.9	40.8			
9	CH	50.4	50.4	50.5	1.27, *m*	1.28, *m*	
10	C	37.2	37.2	37.2			
11	CH_2	20.9	20.8	20.9	1.28, *m*; 1.46, *m*	1.22, *m*; 1.45, *m*	
12	CH_2	25.3	25.2	25.2	1.68, *m*	1.08, *m*	
13	CH	27.3	37.3	38.1	1.67, *m*	1.67, *m*	
14	C	42.7	42.7	42.8			
15	CH_2	27.0	27.0	27.5	1.11, *m*; 1.66, *m*	1.56, *m*	
16	CH_2	29.2	29.2	35.6	1.20, *m*; 1.98, *m*	1.51, *m*	
17	C	47.8	47.5	43.0			
18	CH	48.8	48.8	48.3	1.60, *m*	1.38, *m*	
19	CH	47.8	47.5	48.0	2.38, *m*	2.38, *m*	13, 18, 20, 21, 29, 30
20	C	150.6	150.5	151.0			
21	CH_2	29.8	29.8	29.9	1.91, *m*	1.94, *m*	
22	CH_2	34.0	34.0	40.0	1.80, *m*; 1.88, *m*	1.20, *m*; 1.40, *m*	
23	CH_3	28.0	28.0	28.0	0.97, *s*	0.97, *s*	3, 4, 5, 24
24	CH_3	15.4	15.4	15.4	0.76, *s*	0.76, *s*	3, 4, 5, 23
25	CH_3	16.1	16.1	16.1	0.82, *s*	0.83, *s*	1, 5, 9
26	CH_3	16.0	16.0	16.0	1.02, *s*	1.03, *s*	7, 8, 9, 14
27	CH_3	14.8	14.8	14.6	0.98, *s*	0.94, *s*	8, 13, 14, 15
28	CH_2	60.2	60.6	18.0	3.33, *d* (10.8); 3.80, *dd* (10.8, 1.5)	0.79, *s*	16, 17, 22
29	CH_2	109.6	109.7	109.3	4.68, *d* (2.1);4.58, *m*	4.68, *d*(2.1);4.56, *m*	19, 20, 30
30	CH_3	19.1	19.1	19.3	1.68, *s*	1.68, *s*	19, 20, 29

* For **TL3** and betulin ** Deduced from HMQC experiment

3.2.3 Compound **TL3**



Compound **TL3** was obtained as a white solid, mp 279-280°C, $[\alpha]_D^{28}$: +15.0° (*c* = 0.10, MeOH). It gave a purple vanillin-sulfuric acid test indicating a triterpene. The IR spectrum (**Figure 67**) showed absorption bands of a hydroxyl group at 3415 cm^{-1} and a carbonyl group at 1686 cm^{-1}.

The ^1H and ^{13}C NMR spectral data of **TL3** (**Table 31, Figures 72** and **73**) were similar to those of **TL2**. The difference in the spectrum of **TL3** was shown as disappearance of an oxy-methylene protons at δ 3.80 (1H, *dd*, *J* = 10.8, 1.5 Hz) and 3.33 (1H, *d*, *J* = 10.8 Hz) in the ^1H NMR spectrum and the ^{13}C NMR spectrum displayed a signal of a carboxyl carbon at δ 179.6 instead of an oxy-methylene carbon at δ 60.6, thus suggesting a carboxylic functionality at C-28. The location of the carboxyl group was confirmed by HMBC experiment in which the methylene proton signals at δ 1.83 (1H, *m*, H-22a) and 1.41 (1H, *m*, H-22b) showed correlations with C-17 (δ 55.3), C-18 (δ 48.3) and C-28 (δ 179.6). Thus on the basis of its spectroscopic data and comparison of the NMR chemical shifts with those reported in the literature (Kitajima et al., 1990), (**Table 31**), compound **TL3** was assigned as betulinic acid.

Table 31 ^1H, ^{13}C and HMBC spectral data of compounds **TL3**, **TL2** and betulinic acid (**R**)

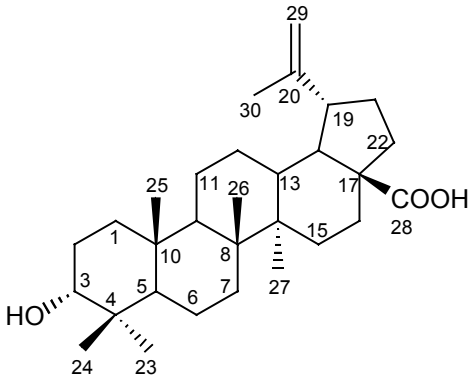
Posi-tion	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL3**)
		R	**TL3**	**TL2**	**TL3****	**TL2****	$^1H \rightarrow ^{13}C$
1	CH_2	38.5	37.7	38.7	0.87, *m*; 1.64, *m*	0.90, *m*; 1.70, *m*	
2	CH_2	28.2	26.4	27.4	1.55, *m*	1.59, *m*	

Table 31 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL3**)
		R	**TL3**	**TL2**	**TL3****	**TL2****	$^1H \rightarrow ^{13}C$
3	CH	78.1	78.0	79.0	3.19, *dd* (10.8, 5.4)	3.19, *dd* (10.8, 5.1)	4, 23, 24
4	C	39.4	37.9	38.9			
5	CH	55.9	54.4	55.3	0.69, *m*	0.68, *m*	4, 6, 7, 9
6	CH_2	18.7	17.3	18.3	1.35, *m; 1.*48, *m*	1.41, *m*	
7	CH_2	34.7	33.3	34.2	1.35, *m*	1.04, *m*; 1.40, *m*	
8	C	41.0	39.7	40.9			
9	CH	50.9	49.5	50.4	1.20, *m*	1.27, *m*	
10	C	37.5	36.2	37.2			
11	CH_2	21.1	19.8	20.8	1.41, *m*	1.28, *m*; 1.46, *m*	
12	CH_2	26.0	24.5	25.2	1.67, *m*	1.68, *m*	
13	CH	39.2	37.4	37.3	2.20, *m*	1.67, *m*	
14	C	42.8	41.4	42.7			
15	CH_2	30.2	28.7	27.0	1.14, *m;* 1.23, *m*	1.11, *m*; 1.66, *m*	
16	CH_2	32.8	31.2	29.2	2.22, *m*	1.20, *m*; 1.98, *m*	
17	C	56.6	55.3	47.5			
18	CH	49.7	48.3	48.8	1.55, *m*	1.60, *m*	
19	CH	47.7	45.9	47.5	3.00, *m*	2.38, *m*	18, 20, 21, 29, 30
20	C	151.4	149.4	150.5			
21	CH_2	31.1	29.6	29.8	1.89, *m*	1.91, *m*	
22	CH_2	37.4	36.0	34.0	1.40, *m*; 1.93, *m*	1.80, *m*; 1.88, *m*	17, 18, 28
23	CH_3	28.5	27.0	28.0	0.97, *s*	0.97, *s*	3, 4, 5, 24
24	CH_3	16.2	14.3	15.4	0.75, *s*	0.76, *s*	3, 4, 5, 23
25	CH_3	16.3	15.1	16.1	0.82, *s*	0.82, *s*	1, 3, 9, 10
26	CH_3	16.2	15.0	16.0	0.94, *s*	1.02, *s*	7, 8, 9, 14
27	CH_3	14.8	13.7	14.8	0.98, *s*	0.98, *s*	8, 13, 14, 15
28	C	179.0	179.6	60.6		3.33, *d* (10.8); 3.80, *dd* (10.8, 1.5)	
29	CH_2	110.0	108.7	109.7	4.74, *br s;* 4.61, *br s*	4.68, *d* (2.1); 4.58, *m*	19, 30
30	CH_3	19.4	18.4	19.1	1.69, *s*	1.68, *s*	19, 20, 29

* For **TL4** and betulinic acid ** Deduced from HMQC experiment

3.2.4 Compound **TL4**



Compound **TL4** was obtained as a white solid, mp 257-259°C, $[\alpha]_D^{28}$: -10.0° (*c* = 0.05, MeOH). It gave a positive vanillin-sulfuric acid test indicating a triterpene. The IR spectrum showed absorption bands similar to those of compound **TL3**.

The ^{1}H and ^{13}C NMR spectral data (**Table 32, Figures 74** and **75**) of compound **TL4** were similar to those of compound **TL3**, except that the splitting pattern of H-3 in **TL4** at δ 3.38 was a triplet (*J* = 2.7 Hz) instead of a doublet of doublet (*J* = 10.8, 5.4 Hz) of **TL3**. The difference in the multiplicity with a small coupling constant of H-3 in compound **TL4** was in agreement with the respective coupling pattern (equatorial-equatorial and equatorial-axial) of H-3 and H-2, indicating that H-3 is situated in an equatorial position. The location of a hydroxyl group at C-3 was determined through an HMBC experiment in which the oxymethine proton signal at δ 3.38 (H-3) showed long-range correlations with C-1 (δ 33.2) and C-5 (δ 49.0). Thus on the basis of its spectroscopic data and comparison of NMR chemical shifts from the previous report (Kitajima et al., 1990) (**Table 32**), compound **TL4** was assigned as 3-*epi*-betulinic acid, an epimer of betulinic acid.

Table 32 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL4**, **TL3** and 3-*epi*-betulinic acid (**R**)

Posi	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL4**)
tion	of C*	**R**	**TL4**	**TL3**	**TL4****	**TL3****	^{1}H→^{13}C
1	CH_2	37.7	33.2	78.0	1.18, *m*	0.87, *m*; 1.64, *m*	
2	CH_2	26.4	25.5	37.9	1.02, *m*; 1.68, *m*	1.55, *m*	
3	CH	78.0	76.2	54.4	3.38, *t* (2.7)	3.19, *dd* (10.8, 5.4)	1, 5

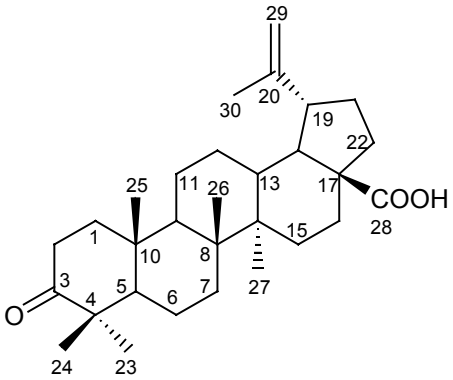
Table 32 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL4**)
		R	**TL4**	**TL3**	**TL4****	**TL3****	$^1H \rightarrow ^{13}C$
4	C	37.9	37.5	17.3			
5	CH	54.4	49.0	33.3	1.18, *m*	0.69, *m*	
6	CH_2	17.3	18.2	39.7	1.34, *m;* 1.38, *m*	1.35, *m;* 1.48, *m*	
7	CH_2	33.3	34.1	49.5	1.30, *m*	1.35, *m*	
8	C	39.7	40.8	36.2			
9	CH	49.5	50.3	19.8	1.40, *m*	1.20, *m*	
10	C	36.2	37.3	24.5			
11	CH_2	19.8	20.7	37.4	1.42, *m*	1.41, *m*	
12	CH_2	24.5	25.3	41.4	1.52, *m;* 1.82, *m*	1.67, *m*	
13	CH	37.4	38.2	28.7	2.21, *m*	2.20, *m*	26, 27
14	C	41.4	42.5	31.2			
15	CH_2	28.7	29.6	55.3	1.14, *m*	1.14, *m;* 1.23, *m*	
16	CH_2	31.2	32.2	48.3	2.24, *m*	2.22, *m*	
17	C	55.3	56.2	45.9			
18	CH	48.3	49.2	149.4	1.57, *m*	1.55, *m*	
19	CH	45.9	47.0	29.6	3.00, *m*	3.00, *m*	
20	C	149.4	150.7	36.0			
21	CH_2	29.6	30.6	27.0	1.93, *m*	1.89, *m*	17, 18, 19, 28
22	CH_2	36.0	37.1	14.3	1.95, *m*	1.40, *m*; 1.93, *m*	17, 18, 28
23	CH_3	27.0	28.2	15.1	0.93, *s*	0.97, *s*	3, 4, 5, 24
24	CH_3	14.3	22.1	15.0	0.82, *s*	0.75, *s*	3, 4, 5, 23
25	CH_3	15.1	15.9	13.7	0.94, *s*	0.82, *s*	1, 5, 9
26	CH_3	15.0	15.9	179.6	0.83, *s*	0.94, *s*	7, 8, 9, 14
27	CH_3	13.7	14.7	108.7	0.99, *s*	0.98, *s*	8, 13, 14, 15
28	C	179.6	179.2	18.4			
29	CH_2	108.7	109.5		4.73, *d* (1.8); 4.60, *m*	4.74, *br s*; 4.61, *br s*	19, 30
30	CH_3	18.4	19.3		1.69, *s*	1.69, *s*	19, 20, 29

* For **TL4** and 3-*epi*-betulinic acid

** Deduced from HMQC experiment

3.2.5 Compound **TL5**



Compound **TL5** was obtained as a white solid, mp 250-254°C, $[\alpha]_D^{28}$: +32.0° (*c* = 0.37, MeOH). The IR spectrum exhibited absorption band of a carbonyl group at 1704 cm^{-1}. It gave a purple vanillin- sulfuric acid test indicating a triterpene.

The ^1H and ^{13}C NMR spectral data of **TL5** (**Table 33**, **Figures 76** and **77**) were closely related to compound **TL3**, except the oxymethine proton (H-3) at δ 3.19 (*dd*, *J* = 10.8, 5.4 Hz) disappeared and the methylene protons (H_2-2) were shifted downfield to δ 2.45 (*m*) as compared to that of **TL3** at δ 1.55 (*m*). The ^{13}C NMR spectral data of compound **TL5** displayed a signal of a carbonyl group at δ 218.3 which was assigned to C-3 and no signal of oxy-methine carbon as observed in **TL3**. The location of the carbonyl group was confirmed by HMBC experiment in which both H_3-24 (δ 1.02) and H_3-23 (δ 1.07) showed long-range correlation with C-3 (δ 218.3), C-4 (δ 47.3) and C-5 (δ 54.9). By comparison of the physical and spectral data with the previously reported data (Gonzalez et al., 1983) (**Table 33**), compound **TL5** was assigned as betulonic acid.

Table 33 ^1H, ^{13}C and HMBC spectral data of compounds **TL5** and **TL3**

Posi-	Type	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL5**)
tion	of C*	**TL3**	**TL5**	**TL5****	**TL3****	$^1H \rightarrow ^{13}C$
1	CH_2	37.7	39.6		0.87, *m*; 1.64, *m*	
2	CH_2	26.4	34.1	2.45, m	1.55, *m*	
3	C	78.0	218.3		3.19, *dd* (10.8, 5.4)	
4	C	37.9	47.3			
5	CH	54.4	54.9	1.24, m	0.69, *m*	

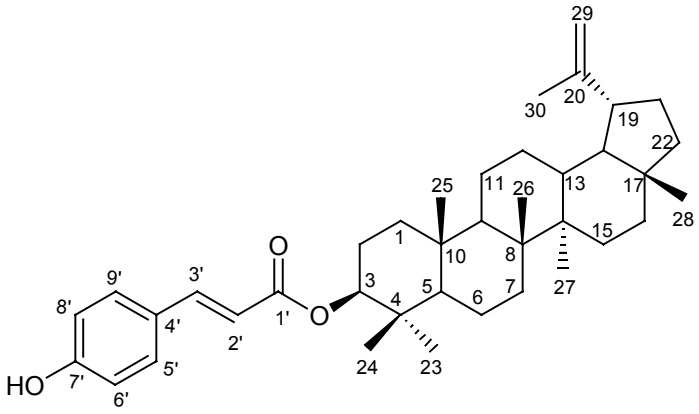
Table 33 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL5**)
		TL3	**TL5**	**TL5****	**TL3****	$^1H \rightarrow ^{13}C$
6	CH_2	17.3	19.6		1.35, *m*; 1.48, *m*	
7	CH_2	33.3	33.6		1.35, *m*	
8	C	39.7	40.6			
9	CH	49.5	49.8	1.35, m	1.20, *m*	
10	C	36.2	36.9			
11	CH_2	19.8	21.4		1.41, *m*	
12	CH_2	24.5	25.5		1.67, *m*	
13	CH	37.4	38.5	2.20, m	2.20, *m*	
14	C	41.4	42.5			
15	CH_2	28.7	30.6		1.14, *m*; 1.23, *m*	
16	CH_2	31.2	32.1		2.22, *m*	
17	C	55.3	56.4			
18	CH	48.3	49.2	1.62, m	1.55, *m*	
19	CH	45.9	46.9	3.01, m	3.00, *m*	18, 20, 21, 30
20	C	149.4	150.3			
21	CH_2	29.6	29.7		1.89, *m*	
22	CH_2	36.0	37.0		1.40, *m*; 1.93, *m*	
23	CH_3	27.0	26.6	1.07, *s*	0.97, *s*	3, 4, 5, 24
24	CH_3	14.3	21.0	1.02, *s*	0.75, *s*	3, 4, 5, 23
25	CH_3	15.1	16.0	0.93, *s*	0.82, *s*	1, 5, 9, 10
26	CH_3	15.0	15.8	0.98, *s*	0.94, *s*	7, 8, 9, 14
27	CH_3	13.7	14.6	0.99, *s*	0.98, *s*	8, 13, 14, 15
28	C	179.6	182.2			
29	CH_2	108.7	109.8	4.62, *br s*; 4.75, *br s*	4.61, *br s*; 4.74, *br s*	19, 20, 30
30	CH_3	18.4	19.4	1.70, *s*	1.69, *s*	19, 29, 30

* For **TL5**

** Deduced from HMQC experiment

3.2.6 Compound **TL6**



Compoud **TL6** was isolated as a white solid, mp 166-167°C, $[\alpha]_D^{28}$: +20.0° (*c* = 0.05, MeOH). The IR spectrum suggested hydroxyl (3397 cm^{-1}), conjugated ester (1726 cm^{-1}) and double bond (1602 cm^{-1}) functionalities. The UV absorption maxima at 227 and 313 nm, again suggested the presence of conjugation in the molecule. It gave a purple vanillin-sulfuric acid test indicating a triterpene.

The ^{1}H and ^{13}C NMR spectral data (**Table 34, Figures 78** and **79**) of compounds **TL6** and **TL1** exhibited the same pattern. The difference was shown in **TL6** which displayed additional signals due to the presence of *trans*-coumaroyl substituent as two *para*-disubstituted aromatic protons at δ 7.41 and 6.85 (each *d*, *J* = 8.7 Hz, H-5′, H-9′ and H-6′, H-8′, respectively) and two *trans* olefinic protons at δ 7.61 (H-3′) and 6.29 (H-2′) as a doublet with coupling constant 15.9 Hz. The oxy-methine proton (H-3) was shown to be shifted more downfield than compound **TL1** at δ 4.62 (*m*) as a result of the ester substituent at C-3. The ^{13}C NMR spectral data of compound **TL6** suggested the presence of an ester group as a signal at δ 167.8, which was confirmed by HMBC experiment in which the oxy-methine H-3 showed long-range correlation with C-1′ (δ 167.8) and C-4 (δ 38.1), C-23 (δ 28.0) and C-24 (δ 16.2). Thus compound **TL6** was identified as 3β-*E*-coumaroyllupeol by comparison of its spectral data with those reported data (Kuo et al., 1997).

Table 34 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL6**, **TL1** and 3β-*E*-coumaroyllupeol (**R**)

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL6**)
		R	**TL6**	**TL1**	**TL6****	**TL1****	$^1H \rightarrow ^{13}C$
1	CH_2	38.5	38.4	38.7	1.70, *m*	0.91, *m*	
2	CH_2	23.9	23.9	27.4	1.70, *m*	1.56, *m*	
3	CH	80.9	81.2	79.0	4.62, *m*	3.19, *dd* (10.8, 5.1)	1′, 4, 23, 24
4	C	38.1	38.1	38.8			
5	CH	55.5	55.4	55.3	0.82, *m*	0.69, *m*	
6	CH_2	18.3	18.2	18.3	1.42, *m*; 1.55, *m*	1.40, *m*; 1.55, *m*	
7	CH_2	34.3	34.2	34.2	1.42, *m*	1.40, *m*	
8	C	40.9	40.9	40.8			
9	CH	50.4	50.4	50.4	1.31, *m*	1.28, *m*	
10	C	37.2	37.1	37.1			
11	CH_2	21.0	21.0	20.9	1.47, *m*	1.22, *m*; 1.45, *m*	
12	CH_2	25.2	25.1	25.1	1.71, *m*	1.08, *m*	
13	CH	38.1	38.1	38.0	1.63, *m*	1.67, *m*	
14	C	42.9	42.9	42.8			
15	CH_2	27.5	27.5	27.4	1.04, *m*	1.56, *m*	
16	CH_2	35.6	35.6	35.5	1.48, *m*; 1.53, *m*	1.51, *m*	
17	C	43.0	43.0	43.0			
18	CH	48.3	48.3	48.2	1.38, *m*	1.38, *m*	
19	CH	48.0	48.0	47.9	2.38, *m*	2.38, *m*	20, 29, 30
20	C	151.0	151.0	150.9			
21	CH_2	29.9	29.9	29.8	1.89, *m*; 1.95, *m*	1.94, *m*	19, 30
22	CH_2	40.0	40.0	40.0	1.20, *m*; 1.41, *m*	1.20, *m*; 1.40, *m*	
23	CH_3	28.0	28.0	28.0	0.89, *s*	0.97, *s*	3, 4, 5, 24
24	CH_3	16.0	16.2	15.4	0.88, *s*	0.76, *s*	3, 4, 5, 23
25	CH_3	16.7	16.7	16.1	0.92, *s*	0.83, *s*	1, 5, 9
26	CH_3	16.2	16.0	16.0	1.04, *s*	1.03, *s*	7, 8, 9, 14
27	CH_3	14.6	14.6	14.5	0.95, *s*	0.94, *s*	8, 13, 14, 15
28	CH_3	18.0	18.0	18.0	0.79, *s*	0.79, *s*	16, 17, 18, 22
29	CH_2	109.4	109.4	109.3	4.69, *d* (2.1); 4.58, *m*	4.68, *d* (2.1); 4.56, *m*	19, 30
30	CH_3	19.3	19.3	19.3	1.69, *s*	1.68, *s*	19, 20, 29

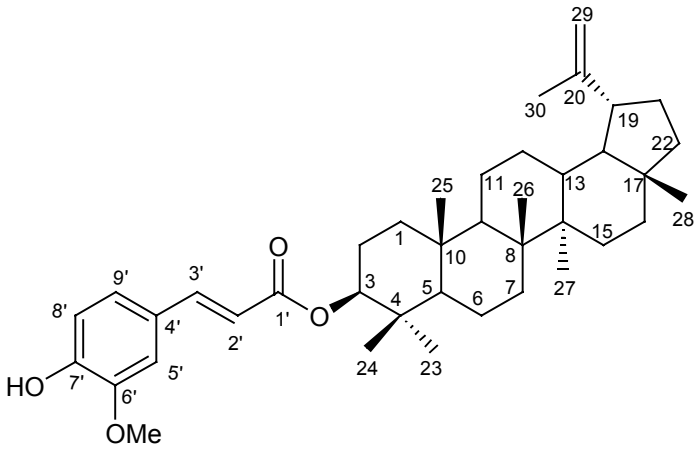
Table 34 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL6**)
		R	**TL6**	**TL1**	**TL6****	**TL1****	$^1H \rightarrow ^{13}C$
1′	C	167.2	167.8				
2′	CH	116.5	115.9		6.29, *d* (15.9)		1′, 3′, 4′
3′	CH	143.8	144.4		7.61, *d* (15.9)		1′, 5′, 9′
4′	C	127.6	127.0				
5′, 9′	CH	129.9	130.0		7.41, *d* (8.7)		3′, 5′, 9′, 7′
6′, 8′	CH	115.8	116.0		6.85, *d* (8.7)		4′, 6′, 8′, 7′
7′	C	157.4	158.1				

* For **TL6** and 3β-*E*-coumaroyllupeol

** Deduced from HMQC experiment

3.2.7 Compound **TL7**



Compound **TL7** was obtained as a white solid, mp 167-169°C, $[\alpha]_D^{28}$: +140.0° (c = 0.03, MeOH). Its ESITOFMS mass spectrum showed the $[M-H]^-$ ion peak at m/z 601.4244, corresponding to the molecular formula $C_{40}H_{58}O_4$. The IR spectrum (**Figure 80**) suggested hydroxyl (3534 cm^{-1}), double bond (1635, 1604 cm^{-1}), and conjugated ester (1703 cm^{-1}) functionalities. This compound exhibited UV absorption (**Figure 81**) maxima at 234, 298, and 325 nm, again suggesting the presence of conjugation in the molecule. It gave a purple vanillin-sulfuric acid test indicating a triterpene.

The ^1H and ^{13}C NMR spectra (**Table 35, Figures 82** and **83**) of **TL7** and **TL6** exhibited the same pattern. The difference was shown in the ^1H NMR spectra of a

substituent group which supported the presence of a *trans*-feruloyl as three 1,2,4-trisubstituted aromatic protons at δ 6.91 (1H, *d*, *J* = 8.1 Hz, H-8′), 7.03 (1H, *d*, *J* = 1.8 Hz, H-5′), and 7.07 (1H, *dd*, *J* = 8.1, 1.8 Hz, H-9′), two *trans*-oriented vinyl protons at δ 6.29 and 7.59 (each *d*, *J* = 15.9 Hz, H-2′, H-3′, respectively), and aromatic methoxy protons at δ 3.93 (3H, s). A signal of a hydroxy proton (disappeared on D_2O exchange) was shown at δ 5.85 (1H, s). A cross peak between H-5′ and the aromatic OMe in the NOESY spectrum located the latter at position C-6′. Lupane triterpenoid skeleton was evident from the following ^{1}H NMR signals: six methyls at δ 0.79, 0.88, 0.89, 0.92, 0.95, 1.04 (3H, *s*, each), an isopropenyl group [δ 1.69 (3H, *s*), 4.60 (1H, *m*), 4.69 (1H, *d*, *J* = 2.1 Hz], and a typical lupane Hβ-19 proton at δ 2.37 (1H, *m*). An oxymethine proton in proximity to an ester moiety was shown at δ 4.62 (*dd*, *J* = 9.0, 5.4 Hz, H-3). The doublet of doublet splitting pattern together with large coupling constants of H-3 with *Jax-ax* = 9.0 Hz and *Jax-eq* = 5.4 Hz indicated an axial (α) orientation of H-3. The ester carbonyl was also confirmed by ^{13}C NMR signal at δ 167.1. The ester substituent was placed at C-3 as a result of downfield shift observed for H-3 and C-3 in the proton and ^{13}C NMR spectra, respectively, compared with an analogous data of lupeol, and from the correlations between H-3 (δ 4.62) and C-23 (δ 28.0), C-24 (δ 16.2), and C-1′ (δ 167.1) observed in the HMBC spectrum. The ^{13}C NMR signals for sp^2 methine carbons were shown at δ 116.3 (C-2′), 144.3 (C-3′), 109.3 (C-5′), 114.7 (C-8′), and 123.1 (C-9′), and one olefinic methylene carbon at δ 109.4 (C-29). Therefore, compound **TL7** was assigned as 3β-*E*-feruloyllupeol, the same as a compound isolated from *Ceriops decandra* (Ponglimanont and Thongdeeying, 2005) whose X-ray crystallographic structure was also displayed (Pakhathirathien et al., 2005) (**Figure 7**).

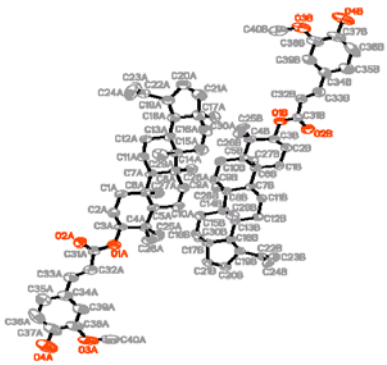


Figure 7 X-ray ORTEP diagram of compound **TL7**

Table 35 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL7** and **TL6**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL7**)
		TL7	**TL6**	**TL7****	**TL6****	$^{1}H \rightarrow ^{13}C$
1	CH_2	38.5	38.4		1.70, *m*	
2	CH_2	23.9	23.9		1.70, *m*	
3	CH	80.9	81.2	4.62, *dd* (9.0, 5.4)	4.62, *m*	1′, 23, 24
4	C	38.1	38.1			
5	CH	55.5	55.4		0.82, *m*	
6	CH_2	18.3	18.2		1.42, *m*; 1.55, *m*	
7	CH_2	34.3	34.2		1.42, *m*	
8	C	40.9	40.9			
9	CH	50.4	50.4		1.31, *m*	
10	C	37.2	37.1			
11	CH_2	21.0	21.0		1.47, *m*	
12	CH_2	25.2	25.1		1.71, *m*	
13	CH	38.1	38.1		1.63, *m*	
14	C	42.9	42.9			
15	CH_2	27.5	27.5		1.04, *m*	
16	CH_2	35.6	35.6		1.48, *m*; 1.53, *m*	
17	C	43.0	43.0			
18	CH	48.3	48.3		1.38, *m*	
19	CH	48.0	48.0	2.37, *m*	2.38, *m*	20, 30, 29, 21
20	C	151.0	151.0			
21	CH_2	29.9	29.9		1.89, *m*; 1.95, *m*	
22	CH_2	40.0	40.0		1.20, *m*; 1.41, *m*	

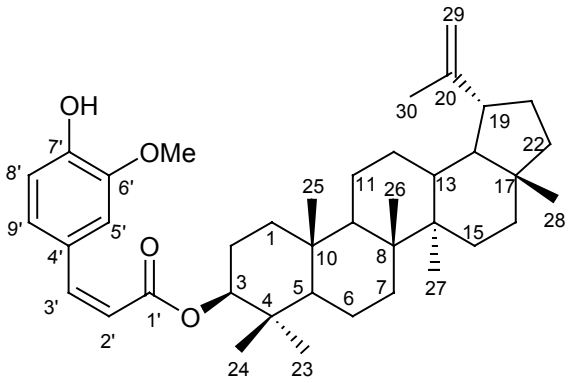
Table 35 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL7**)
		TL7	**TL6**	**TL7****	**TL6****	$^{1}H \rightarrow ^{13}C$
23	CH_3	28.0	28.0	0.88, *s*	0.89, *s*	5, 3, 4, 24
24	CH_3	16.2	16.2	0.89, *s*	0.88, *s*	3, 4, 5, 23
25	CH_3	16.7	16.7	0.92, *s*	0.92, *s*	1, 9, 5
26	CH_3	16.0	16.0	1.04, *s*	1.04, *s*	7, 8 , 9, 14

Posi-	Type	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL7**)
tion	of C*	**TL7**	**TL6**	**TL7****	**TL6****	$^1H \rightarrow ^{13}C$
27	CH_3	14.6	14.6	0.95, *s*	0.95, *s*	8, 14, 13, 15
28	CH_3	18.0	18.0	0.79, *s*	0.79, *s*	16, 17, 18, 22
29	CH_2	109.4	109.4	4.69, *d* (2.1);	4.69, *d* (2.1);	18, 30
				4.60, *m*	4.58, *m*	
30	CH_3	19.3	19.3	1.69, *s*	1.69, *s*	19, 20, 29
1′	C	167.1	167.8			
2′	CH	116.3	115.9	6.29, *d* (15.9)	6.29, *d* (15.9)	1′, 4′
3′	CH	144.3	144.4	7.59, *d* (15.9)	7.61 *d* (15.9)	1′, 2′, 4′, 5′, 9′
4′	C	127.2	127.0			
5′	CH	109.3	130.0	7.03, *d* (1.8)	7.41, *d* (8.7)	3′, 4′, 7′, 9′
6′	C	146.8	116.0		6.85, *d* (8.7)	
7′	C	147.8	158.1			
8′	CH	114.7	116.0	6.91, *d* (8.1)	6.85, *d* (8.7)	4′, 6′
9′	CH	123.1	130.0	7.07, *dd* (8.1, 1.8)	7.41, *d* (8.7)	3′, 5′, 7′
	OMe	56.0		3.93, *s*		6′
	OH			5.85, br *s*		

* For **TL7** ** Deduced from HMQC experiment

3.2.8 Compound **TL8**



Compound **TL8** was obtained as a white solid, mp 195-197°C, $[\alpha]_D^{28}$: +41.7° (*c* = 0.06, MeOH). Its ESITOFMS mass spectrum showed the $[M-H]^-$ ion peak at m/z 601.4260, corresponding to the molecular formula $C_{40}H_{58}O_4$. The IR and UV spectrum showed absorption bands similar to those of **TL7**.

The ^{1}H and ^{13}C NMR spectral data (**Table 36, Figures 84** and **85**) were closely related to those of **TL7**, except for the olefinic proton signals at δ 5.81 (1H, *d*, *J* = 12.9 Hz) and 6.77 (1H, *d*, *J* = 12.9 Hz) assignable, respectively to H-2′ and H-3′ on the feruloyl group. Judging from the small *J* value (12.9 Hz), the double bond should have a *Z* geometry. These spectral data implied a lupeol bearing a *Z*-feruloyl group. On the basis of HMBC, the *Z*-feruloyl moiety was located at C-3 by correlation of H-3 signal (δ 4.54) with C-1′ (δ 166.4), C-23 (δ 28.0), and C-24 (δ 16.2). The coupling constant and splitting pattern of H-3 (*dd*, *J* = 11.1, 5.4 Hz) indicated a β-orientation of H-3. Thus compound **TL8** was assigned as 3β-*Z*-feruloyllupeol, the same as a compound isolated from *Ceriops decandra* (Ponglimanont and Thongdeeying, 2005).

Table 36 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL8** and **TL7**

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL8**)
		TL8	**TL7**	**TL8****	**TL7****	$^{1}H \rightarrow ^{13}C$
1	CH_2	38.5	38.5			
2	CH_2	23.9	23.9			
3	CH	80.9	80.9	4.54, *dd* (11.1, 5.4)	4.62, *dd* (9.0, 5.4)	1′, 23, 24
4	C	38.1	38.1			
5	CH	55.5	55.5			
6	CH_2	18.3	18.3			
7	CH_2	34.3	34.3			
8	C	40.9	40.9			
9	CH	50.4	50.4			
10	C	37.2	37.2			
11	CH_2	21.0	21.0			
12	CH_2	25.2	25.2			
13	CH	38.1	38.1			
14	C	42.9	42.9			
15	CH_2	27.5	27.5			

Table 36 Continued

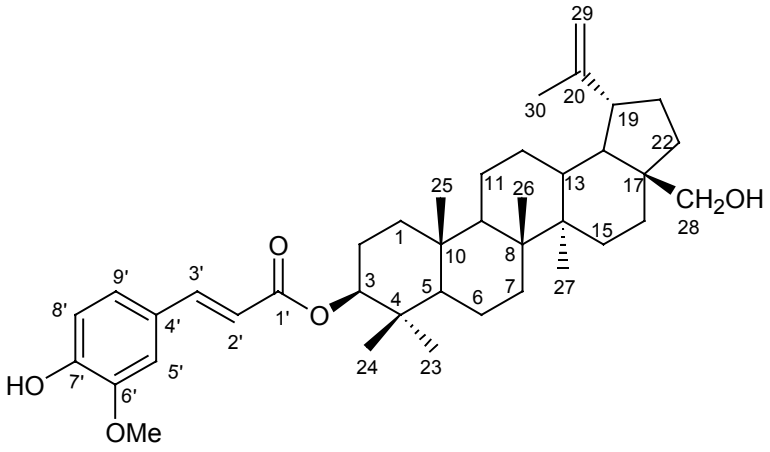
Position	Type	δ_C /ppm	δ_H /ppm, multiplicity (*J*/Hz)	HMBC (**TL8**)

tion	of C*	**TL8**	**TL7**	**TL8****	**TL7****	$^{1}H \rightarrow ^{13}C$
16	CH_2	35.6	35.6			
17	C	43.0	43.0			
18	CH	48.3	48.3			
19	CH	48.0	48.0	2.38, *m*	2.37, *m*	13, 20, 21, 29, 30
20	C	151.0	151.0			
21	CH_2	29.9	29.9			
22	CH_2	40.0	40.0			
23	CH_3	28.0	28.0	0.86, *s*	0.88, *s*	3, 5, 24
24	CH_3	16.2	16.2	0.81, *s*	0.89, *s*	3, 5, 23
25	CH_3	16.7	16.7	0.86, *s*	0.92, *s*	1, 5, 9
26	CH_3	16.0	16.0	1.03, *s*	1.04, *s*	7, 8, 9, 14
27	CH_3	14.5	14.6	0.94, *s*	0.95, *s*	8, 13, 14, 15
28	CH_3	18.0	18.0	0.79, *s*	0.79, *s*	16, 17, 18, 22
29	CH_2	109.4	109.4	4.69, *d* (2.1): 4.57, *m*	4.69, *d* (2.1); 4.60, *m*	19, 20, 30
30	CH_3	19.4	19.3	1.69, *s*	1.69, *s*	19, 20, 29
1′	C	166.4	167.1			
2′	CH	117.4	116.3	5.81, *d* (12.9)	6.29, *d* (15.9)	1′, 3′, 4′
3′	CH	143.5	144.3	6.77, *d* (12.9)	7.59, *d* (15.9)	1′, 2′, 5′, 9′
4′	C	127.3	127.2			
5′	CH	112.9	109.3	7.78, *d* (1.8)	7.03, *d* (1.8)	3′, 4′, 6′, 7′, 9′
6′	C	146.0	146.8			
7′	C	147.0	147.8			
8′	CH	113.9	114.7	6.87, *d* (8.4)	6.91, *d* (8.1)	4′, 6′, 7′
9′	CH	125.6	123.1	7.10, *dd* (8.4, 1.8)	7.07, *dd* (8.1, 1.8)	3′, 5′, 7′, 8′
	OMe	56.0	56.0	3.91, *s*	3.93, *s*	
	OH			5.88, br *s*	5.85, br *s*	6′

* For **TL8**

** Deduced from HMQC experiment

3.2.9 Compound **TL9**



Compound **TL9** was isolated as a white solid, mp 152-154°C. $[\alpha]_D^{28}$: +16.2° (c = 0.40, MeOH). Its IR and UV spectra showed absorption bands similar to compound **TL7**.

The ^{1}H and ^{13}C NMR spectral data of compound **TL9** (**Table 37**, **Figures 86** and **87**) and **TL7** exhibited the same pattern, except that compound **TL9** displayed only six singlet methyl signals (δ 0.88, 0.90, 0.92, 0.99, 1.04 and 1.71). It appeared that a singlet signal of H_3-28 was replaced with the AB system of oxymethylene protons at δ 3.80 and 3.33 (each *d*, *J* = 10.5 Hz). The parent triterpene structure was identified as betulin by a combination of HMQC and HMBC experiments. Thus on the basis of its spectroscopic data and comparison of the NMR spectral data with previously reported data (Kuo et al., 1997) (**Table 37**), compound **TL9** was assigned as 3β-*E*-feruloylbetulin.

Table 37 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL9**, **TL7** and 3β-*E*-feruloylbetulin (**R**)

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL9**)
		R	**TL9**	**TL7**	**TL9****	**TL7****	^{1}H→^{13}C
1	CH_2	38.4	38.4	38.5			
2	CH_2	23.7	23.8	23.9			
3	CH	80.8	80.8	80.9	4.62, *m*	4.62, *dd* (9.0, 5.4)	1′, 23, 24
4	C	38.1	38.1	38.1			
5	CH	55.4	55.4	55.5			
6	CH_2	18.2	18.2	18.3			

Table 37 Continued

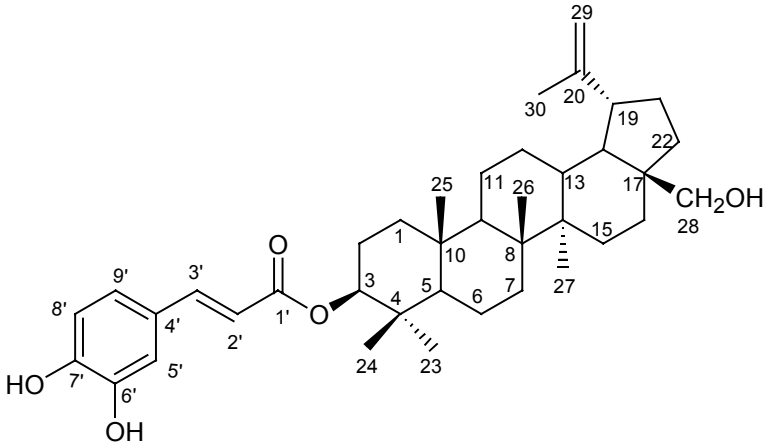
Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL9**)
		R	**TL9**	**TL7**	**TL9****	**TL7****	$^1H \rightarrow ^{13}C$
7	CH_2	34.0	34.0	34.3			
8	C	40.9	41.0	40.9			
9	CH	50.3	50.3	50.4			
10	C	37.1	37.1	37.2			
11	CH_2	20.9	20.9	21.0			
12	CH_2	25.2	25.2	25.2			
13	CH	37.3	37.3	38.1			
14	C	42.7	42.7	42.9			
15	CH_2	27.0	27.1	27.5			
16	CH_2	29.2	29.2	35.6			
17	C	47.8	47.8	43.0			
18	CH	48.7	48.8	48.3			
19	CH	47.8	47.8	48.0	2.39, *m*	2.37, *m*	18, 21
20	C	150.5	150.5	151.0			
21	CH_2	29.7	29.8	29.9			
22	CH_2	34.2	34.2	40.0			
23	CH_3	28.0	28.0	28.0	0.90, *s*	0.88, *s*	3, 4, 5, 24
24	CH_3	16.0	16.7	16.2	0.88, *s*	0.89, *s*	3, 4, 5, 23
25	CH_3	16.2	16.2	16.7	0.92, *s*	0.92, *s*	1, 5, 9
26	CH_3	16.6	16.0	16.0	1.04, *s*	1.04, *s*	7, 8, 9, 14
27	CH_3	14.7	14.7	14.6	0.99, *s*	0.95, *s*	8, 13, 14, 15
28	CH_2	60.7	60.6	18.0	3.80,*d* (10.5); 3.33, *d* (10.5)	0.79, *s*	21, 22
29	CH_2	109.7	109.7	109.4	4.68, *d* (1.8); 4.59, *m*	4.69, *d* (2.1); 4.60, *m*	19, 30
30	CH_3	19.1	19.1	19.3	1.71, *s*	1.69, *s*	19, 20, 29
1′	C	167.1	167.1	167.1			
2′	CH	114.6	116.3	116.3	6.28, *d* (15.9)	6.29, *d* (15.9)	1′, 3′, 4′
3′	CH	144.3	144.3	144.3	7.59, *d* (15.9)	7.59, *d* (15.9)	1′, 2′, 4′, 5′, 9′
4′	C	127.1	127.2	127.2			
5′	CH	109.2	109.3	109.3	7.03, *d* (1.5)	7.03, *d* (1.8)	3′, 6′, 9′
6′	C	146.7	146.8	146.8			
7′	C	147.8	147.8	147.8			

Table 37 Continued

Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL9**)
tion	of C*	**R**	**TL9**	**TL7**	**TL9****	**TL7****	$^1H \rightarrow ^{13}C$
8′	CH	116.2	114.7	114.7	6.91, *d* (8.1)	6.91, *d* (8.1)	4′,6′
9′	CH	123.0	123.0	123.1	7.07, *dd* (8.1, 1.5)	7.07, *dd* (8.1, 1.8)	3′, 5′, 7′
	OMe	56.0	56.0	56.0	3.85, (*s*)	3.93, *s*	
	OH				5.89, (br s)	5.85, br s	

* For **TL9** and 3β-*E*-feruloylbetulin ** Deduced from HMQC experiment

3.2.10 Compound **TL10**



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Compound **TL10** was isolated as a white solid, mp 160-163°C, $[\alpha]_D^{28}$: +47.0° (c = 1.00, MeOH). Its IR spectrum suggested hydroxyl (3413 cm^{-1}), conjugated ester (1726 cm^{-1}) and double bond (1605 cm^{-1}) functionalities. This compound exhibited UV absorption similar to compound **TL9**.

Comparison of the ^1H and ^{13}C NMR spectral data (**Table 38, Figures 88** and **89**) of compounds **TL10** and **TL9** revealed close structural similarity. The difference was shown in the absence of the aromatic methoxy protons at δ 3.85 (3H, *s*, OMe-6′) which was confirmed by HMBC experiment in which H-8′ [δ 6.87 (*d*, *J* = 8.1 Hz)] showed correlation with C-4′ (δ 127.5), C-6′ (δ 144.0), C-7′ (δ 146.5) and C-9′ (δ 122.3). Thus, on the basis of its spectroscopic data and comparison with previously reported data (Chen et al., 1999) (**Table 38**), compound **TL10** was assigned as 3β-*E*-caffeoylbetulin.

Table 38 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL10**, **TL9** and 3β-*E*-caffeoylbetulin (**R**)

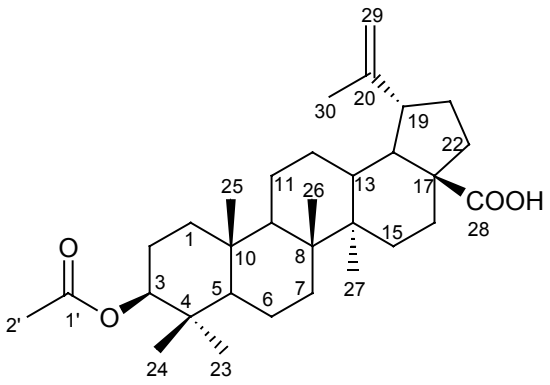
Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL10**)
		R	**TL10**	**TL9**	**TL10**	**TL9**	$^{1}H \rightarrow ^{13}C$
1	CH_2	38.4	38.4	38.4			
2	CH_2	23.8	23.8	23.8			
3	CH	81.3	81.2	80.8	4.59, *dd* (8.7, 7.2)	4.62, *m*	1′, 2, 4, 24
4	C	38.1	38.1	38.1			
5	CH	55.5	55.4	55.4			
6	CH_2	18.2	18.2	18.2			
7	CH_2	34.2	34.2	34.0			
8	C	41.0	40.9	41.0			
9	CH	50.3	50.3	50.3			
10	C	37.1	37.1	37.1			
11	CH_2	27.0	20.8	20.9			
12	CH_2	25.2	25.2	25.2			
13	CH	37.3	37.3	37.3			
14	C	42.7	42.7	42.7			
15	CH_2	20.9	27.0	27.1			
16	CH_2	29.2	29.2	29.2			
17	C	47.8	47.8	47.8			
18	CH	48.8	48.7	48.8			
19	CH	47.8	47.8	47.8	2.38, *m*	2.39, *m*	13, 18, 21
20	C	150.4	150.4	150.5			
21	CH_2	29.7	29.7	29.8			
22	CH_2	34.0	34.0	34.2			
23	CH_3	28.0	28.0	28.0	0.88, *s*	0.90, *s*	3, 4, 5, 24
24	CH_3	16.7	16.7	16.7	0.91, *s*	0.88, *s*	3, 4, 5, 23
25	CH_3	16.2	16.2	16.2	0.87, *s*	0.92, *s*	1, 5, 9, 10
26	CH_3	16.0	15.8	16.0	1.03, *s*	1.04, *s*	7, 8, 9, 14
27	CH_3	14.8	14.8	14.7	0.99, *s*	0.99, *s*	8, 13, 14, 15
28	CH_2	60.7	60.7	60.6	3.36, *d* (10.5); 3.82, *d* (10.5)	3.33, *d* (10.5); 3.80, *d* (10.5)	16, 17, 22
29	CH_2	109.8	109.8	109.7	4.59, *m*; 4.68, *d* (1.5)	4.59, *m*; 4.68, *d* (1.8)	19, 30

Table 38 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL10**)
		R	**TL10**	**TL9**	**TL10**	**TL9**	$^1H \rightarrow ^{13}C$
30	CH_3	19.1	19.1	19.1	1.69, *s*	1.71, *s*	19, 20, 29
1′	C	168.0	167.7	167.1			
2′	CH	115.9	116.1	116.3	7.55, *d* (15.9);	6.28, *d* (15.9)	1′, 4′
3′	CH	144.9	144.7	144.3	6.26, *d* (15.9)	7.59, *d* (15.9)	1′, 2′, 4′, 5′, 9′
4′	C	127.4	127.5	127.2			
5′	CH	115.4	114.3	109.3	7.10, *d* (1.5)	7.03, *d* (1.5)	3′, 6′, 9′
6′	C	144.1	144.0	146.8			
7′	C	146.6	146.5	147.8			
8′	CH	114.3	115.4	114.7	6.87, *d* (8.1)	6.91, *d* (8.1)	4′,6′, 7′, 9′
9′	CH	122.3	122.3	123.0	7.00, *dd* (8.1, 1.5)	7.07, *dd* (8.1, 1.5)	3′, 5′, 7′
	OMe			56.0		3.85, (*s*)	
	OH					5.89, (*br s*)	

* For **TL9** and 3β-*E*-caffeoylbetulin

3.2.11 Compound **TL11**



Compoud **TL11** was isolated as a white solid, mp 269-271°C, $[\alpha]_D^{28}$: +8.0° (*c* = 0.05, MeOH). The IR spectrum suggested conjugated ester (1740 cm^{-1}), carboxy carbonyl (1704 cm^{-1}) functionalities. It gave a purple vanillin-sulfuric acid test indicating a triterpene.

The ^1H and ^{13}C NMR spectral data (**Table 39**, **Figures 90** and **91**) of compounds **TL11** and **TL3** exhibited the same pattern. The difference was shown in the

compound **TL11** which displayed additional signals due to the presence of acetyl substituent as singlet methyl protons at δ 2.08. The oxymethine proton (H-3) was shown to be shifted more downfield than compound **TL3** at δ 4.62 (*m*) as a result of the ester substituent at C-3. The ^{13}C NMR spectral data of compound **TL11** suggested the presence of an ester group as a signal at δ 170.9, which was confirmed by HMBC experiment in which the oxymethine H-3 showed long-range correlation with C-1′ (δ 170.9), C-4 (δ 37.1), C-23 (δ 27.8) and C-24 (δ 21.7). Thus, compound **TL11** was identified as 3β-acetylbetulinic acid by comparison of its physical data with those reported data (Tiwari et al., 1980).

Table 39 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL11** and **TL3**

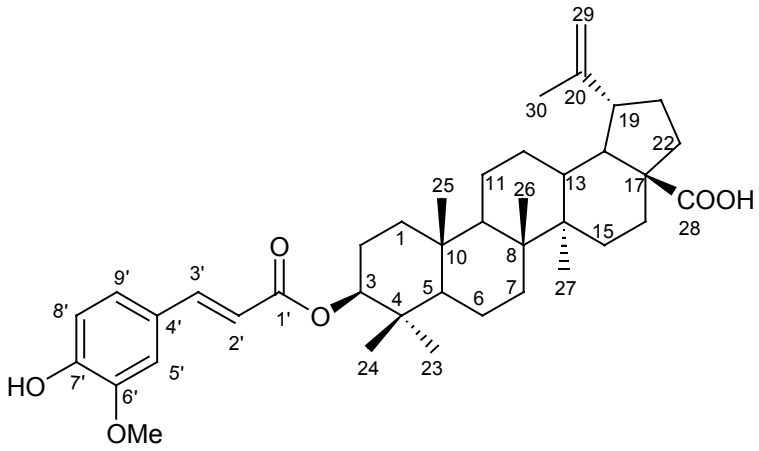
Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL11**)
		TL11	**TL3**	**TL11****	**TL3****	^{1}H→^{13}C
1	CH_2	36.7	37.7		0.87, *m*; 1.64, *m*	
2	CH_2	25.5	26.4		1.55, *m*	
3	CH	78.4	78.0	4.62, *br s*	3.19, *dd* (10.8, 5.4)	1′, 4, 23, 24
4	C	37.1	37.9			
5	CH	50.3	54.4	1.17, *m*	0.69, *m*	
6	CH_2	18.1	17.3		1.35, *m*; 1.48, *m*	
7	CH_2	33.9	33.3		1.35, *m*	
8	C	40.9	39.7			
9	CH	50.2	49.5	1.41, *m*	1.20, *m*	
10	C	37.2	36.2			
11	CH_2	20.7	19.8		1.41, *m*	
12	CH_2	22.9	24.5		1.67, *m*	
13	CH	38.4	37.4	2.19, *m*	2.20, *m*	
14	C	42.5	41.4			
15	CH_2	29.7	28.7		1.14, *m*; 1.23, *m*	
16	CH_2	32.2	31.2		2.22, *m*	
17	C	56.5	55.3			
18	CH	49.3	48.3	1.63, *m*	1.55, *m*	
19	CH	46.4	45.9	3.02, *m*	3.00, *m*	18, 20, 21, 29, 30
20	C	150.4	149.4			
21	CH_2	30.6	29.6		1.89, *m*	

Table 39 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL11**)
		TL11	**TL3**	**TL11****	**TL3****	$^1H \rightarrow ^{13}C$
22	CH_2	34.1	36.0		1.40, *m*; 1.93, *m*	
23	CH_3	27.8	27.0	0.83, *s*	0.97, *s*	4, 5, 24
24	CH_3	21.7	14.3	0.86, *s*	0.75, *s*	4, 5, 23
25	CH_3	15.9	15.1	0.85, *s*	0.82, *s*	1, 5, 9, 10
26	CH_3	16.1	15.0	0.95, *s*	0.94, *s*	7, 8, 9, 14
27	CH_3	14.9	13.7	1.03, *s*	0.98, *s*	8, 13, 14, 15
28	C	182.6	179.6			
29	CH_2	109.7	108.7	4.62, *br s*; 4.74, *br s*	4.61, *br s*; 4.74, *br s*	19, 20, 30
30	CH_3	19.4	18.4	1.70, *s*	1.69, *s*	19, 20, 29
1′	C	170.9				
2′	CH_3	21.4		2.08, *s*		1′, 3

* For **TL11** ** Deduced from HMQC experiment

3.2.12 Compound **TL12**



Compound **TL12** was isolated as a white solid, mp 224-225°C, $[\alpha]_D^{28}$: +7.8° (*c* = 0.76, MeOH). Its IR and UV spectra showed absorption bands similar to compound **TL7**.

The ^1H and ^{13}C NMR spectral data of compounds **TL12** and **TL7** (**Table 40, Figures 92** and **93**) exhibited the same pattern except that **TL12** displayed only six singlet methyls (δ 0.88, 0.89, 0.92, 0.96, 0.99 and 1.69). The ^{13}C NMR spectrum

displayed a signal of a carboxyl carbon C-18 at δ181.4 instead of a methyl carbon at δ 18.0 in **TL7**. On the basis of its spectroscopic data and comparison of the NMR chemical shifts of those reported in the literature (Siddiqui et al., 2001) (**Table 40**), compound **TL12** was assigned as 3β-*E*-feruloylbetulinic acid.

Table 40 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL12**, **TL7** and 3β-*E*-feruloylbetulinic acid (**R**)

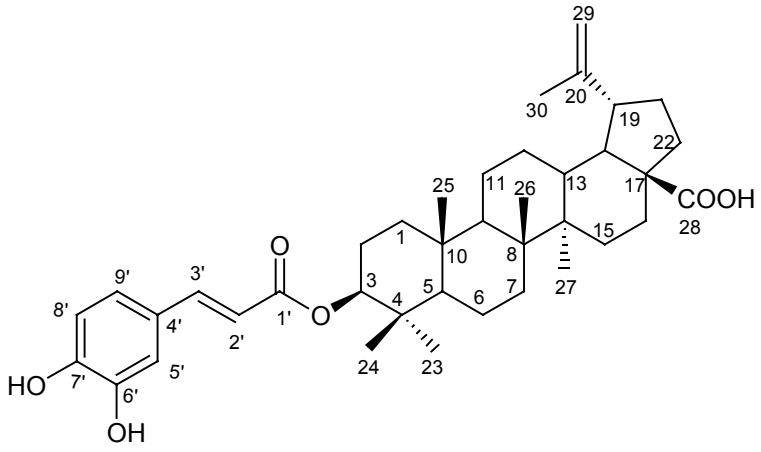
Posi-tion	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL12**)
		R	**TL12**	**TL7**	**TL12**	**TL7**	^{1}H→^{13}C
1	CH_2	38.3	38.4	38.5			
2	CH_2	26.2	23.8	23.9			
3	CH	79.7	80.8	80.9	4.89, dd (11.6, 4.7)	4.62, *dd* (9.0, 5.4)	1′, 2, 4, 23, 24
4	C	38.8	38.1	38.1			
5	CH	47.8	49.3	55.5			
6	CH_2	16.9	18.2	18.3			
7	CH_2	23.2	30.6	34.3			
8	C	42.9	40.7	40.9			
9	CH	52.2	50.4	50.4			
10	C	37.2	37.2	37.2			
11	CH_2	21.2	20.9	21.0			
12	CH_2	23.8	25.5	25.2			
13	CH	38.5	38.4	38.1			
14	C	43	42.4	42.9			
15	CH_2	30.3	32.2	27.5			
16	CH_2	31.3	34.3	35.6			
17	C	55.8	56.4	43.0			
18	CH	46.7	49.3	48.3			
19	CH	49.8	46.9	48.0	3.02, m	2.37, *m*	18, 21
20	C	147.8	150.4	151.0			
21	CH_2	29.7	29.7	29.9			
22	CH_2	37.3	37.0	40.0			
23	CH_3	28.1	28.0	28.0	0.89, s	0.88, *s*	3, 4, 5, 24
24	CH_3	16.3	16.0	16.2	0.92, s	0.89, *s*	3, 4, 5, 23

Table 40 Continued

Posi-	Type	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL12**)
tion	of C*	**R**	**TL12**	**TL7**	**TL12**	**TL7**	$^1H \rightarrow ^{13}C$
25	CH_3	16.3	16.2	16.7	0.88, s	0.92, *s*	1, 5, 9
26	CH_3	16.4	16.7	16.0	0.96, s	1.04, *s*	7, 8, 9, 14
27	CH_3	14.9	14.7	14.6	0.99, s	0.95, *s*	8, 13, 14, 15
28	C	179.2	181.4	18.0		0.79, *s*	21, 22
29	CH_2	110.6	109.8	109.4	4.64, br s;	4.69, *d* (2.1);	19, 30
					4.57, br s	4.60, *m*	
30	CH_3	19.5	19.3	19.3	1.69, s	1.69, *s*	19, 20, 29
1′	C	167.5	167.2	167.1			
2′	CH	115.0	116.2	116.3	6.30, d (15.9)	6.29, *d* (15.9)	1′, 3′, 4′
3′	CH	145.6	144.4	144.3	7.59, d (15.9)	7.59, *d* (15.9)	1′, 2′, 4′, 5′, 9′
4′	C	127.0	127.1	127.2			
5′	CH	109.5	109.3	109.3	7.03, *d* (1.6)	7.03, *d* (1.8)	3′, 6′, 9′
6′	C	146.0	146.7	146.8			
7′	C	147.2	147.8	147.8			
8′	CH	114.6	114.7	114.7	6.91, *d* (8.1)	6.91, *d* (8.1)	4′,6′
9′	CH	123.0	123.0	123.1	7.06, *dd*(8.1, 1.6)	7.07, *dd* (8.1, 1.8)	3′, 4′, 5′, 7′
	OMe	55.5	56.0	56.0	3.94, s	3.93, *s*	
	OH				5.88, br s	5.85, br s	

* For **TL11** and 3β-*E*-feruloylbetulinic acid

3.2.13 Compound **TL13**



Compound **TL13** was isolated as a white solid, mp 254-256°C, $[\alpha]_D^{28}$: +10.6° (c = 0.05, MeOH). Its IR spectrum suggested hydroxyl (3426 cm^{-1}), conjugated ester (1723 cm^{-1}) and double bond (1607 cm^{-1}) functionalities. This compound exhibited UV absorption similar to compound **TL12**.

Comparison of the ^{1}H and ^{13}C NMR spectral data (**Table 41**, **Figures 94** and **95**) of compounds **TL13** and **TL12** revealed close structural similarity. The difference was shown in the absence of the aromatic methoxy protons at δ 3.94 (3H, *s*, OMe-6′) which was confirmed by HMBC experiment in which H-8′ [δ 6.82 (d, *J* = 8.1 Hz)] showed correlation with C-4′ (δ 126.9), C-6′ (δ 144.8), C-7′ (δ 147.2) and C-9′ (δ 121.9). Thus, on the basis of its spectroscopic data and comparison with previously reported data (Chen et al., 1999), (**Table 41**), compound **TL13** was assigned as 3β-*E*-caffeoylbetulinic acid.

Table 41 ^{1}H, ^{13}C and HMBC spectral data of compounds **TL13**, **TL12** and 3β-*E*-caffeoylbetulinic acid (**R**)

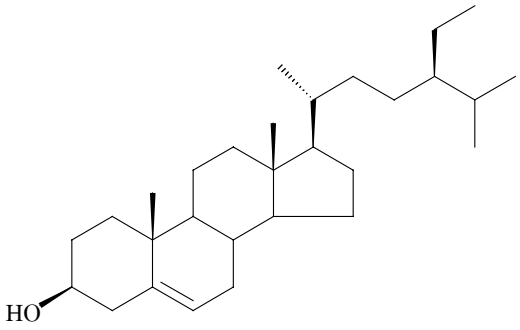
Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL13**)
		R	**TL13**	**TL12**	**TL13**	**TL12**	$^{1}H \rightarrow ^{13}C$
1	CH_2	38.9	38.4	38.4			
2	CH_2	24.6	23.8	23.8			
3	CH	80.8	81.0	80.8	4.58, *m*	4.89,, dd (11.6, 4.7)	1′, 24
4	C	38.6	38.0	38.1			
5	CH	56.0	55.4	49.3			
6	CH_2	18.8	18.2	18.2			
7	CH_2	34.9	34.2	30.6			
8	C	41.4	40.7	40.7			
9	CH	51.0	50.4	50.4			
10	C	37.6	37.1	37.2			
11	CH_2	30.5	20.9	20.9			
12	CH_2	26.3	25.4	25.5			
13	CH	38.9	38.4	38.4			
14	C	43.2	42.4	42.4			
15	CH_2	21.5	29.7	32.2			
16	CH_2	33.1	32.2	34.3			

Table 41 Continued

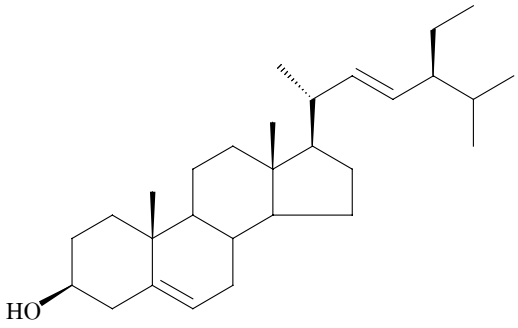
Position	Type of C*	δ_C /ppm			δ_H /ppm, multiplicity (*J*/Hz)		HMBC (**TL13**)
		R	**TL13**	**TL12**	**TL13**	**TL12**	$^1H \rightarrow ^{13}C$
17	C	56.9	56.4	56.4			
18	CH	50.5	49.3	49.3			
19	CH	48.1	47.0	46.9	3.02, m	3.02, m	18, 21
20	C	151.6	150.7	150.4			
21	CH_2	31.5	30.6	29.7			
22	CH_2	37.9	37.2	37.0			
23	CH_3	28.4	28.0	28.0	0.88, s	0.89, s	3, 4, 5, 24
24	CH_3	16.6	16.1	16.0	0.94, s	0.92, s	3, 4, 5, 23
25	CH_3	17.2	16.7	16.2	0.92, s	0.88, s	1, 5, 9
26	CH_3	16.7	16.2	16.7	0.98, s	0.96, s	7, 8, 9, 14
27	CH_3	15.2	14.7	14.7	1.05, s	0.99, s	8, 13, 14, 15
28	C	179.2	179.2	181.4			21, 22
29	CH_2	110.3	109.4	109.8	4.73, br s; 4.59, br s	4.64, br s; 4.57, br s	19, 30
30	CH_3	19.8	19.4	19.3	1.71, s	1.69, s	19, 20, 29
1′	C	167.7	167.9	167.2			
2′	CH	116.1	115.3	116.2	6.23, d (15.9)	6.30, d (15.9)	1′, 3′, 4′
3′	CH	144.7	144.9	144.4	7.53, d (15.9)	7.59, d (15.9)	1′, 2′, 4′, 5′, 9′
4′	C	127.5	126.9	127.1			
5′	CH	114.3	114.0	109.3	7.05, d (1.8)	7.03, *d* (1.6)	3′, 6′, 9′
6′	C	144.0	144.8	146.7			
7′	C	146.5	147.2	147.8			
8′	CH	115.4	115.2	114.7	6.82, d (8.1)	6.91, *d* (8.1)	4′,6′, 7′, 9′
9′	CH	122.3	121.9	123.0	6.95, dd (8.1, 1.8)	7.06, *dd* (8.1, 1.6)	3′, 5′, 7′
	OMe			56.0		3.94, s	
	OH					5.88, br s	

* For **TL11** and 3β-*E*-caffeoylbetulinic acid

3.2.14 Compound **TS1** and **TS2**



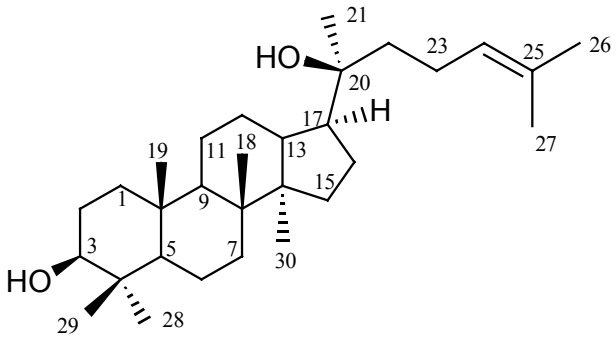
TS1



TS2

The mixture of **TS1** and **TS2** was isolated as a white solid. Its IR spectrum showed absorption bands at 3425 (hydroxy) and 1642 cm^{-1} (double bond). The ^{1}H NMR spectral data (**Figure 96**) contained an oxymethine protons at δ 3.57-3.47 (*m*), three olefinic protons at δ 5.36-5.34 (*d*, *J* = 5.1 Hz), 5.16 (*dd*, *J* = 15.1, 8.4 Hz) and 5.01 (*dd*, *J* = 15.1, 8.4 Hz). The ^{1}H NMR data was corresponded to previous reported data (Cheenpracha, 2004). Thus, this mixture was identified as β-sitosterol and stigmasterol.

3.2.15 Compound **TM1**



Compound **TM1** was obtained as a colorless oil, $[\alpha]_D^{28}$: +31.8° (*c* = 0.30, MeOH). The IR spectrum (**Figure 97**) showed absorption bands at 3440 and 1642 cm^{-1} for hydroxyl and double bond functionalities, respectively.

In the ^{13}C NMR spectrum (**Table 42**, **Figure 99**), compound **TM1** showed 30 carbon resonances. Characteristic for a tetracyclic dammarane as five methyl singlets at δ 0.77 (H_3-29), 0.84 (H_3-19), 0.88 (H_3-30), 0.96 (H_3-18) and 0.97

(H_3-28) appeared in the ^{1}H NMR spectrum of **TM1** (**Table 42**, **Figure 98**). The oxy-methine proton (H-3) resonated at δ 3.19 (*dd*, *J* = 10.5, 5.1 Hz) showing *J* values consistent with axial orientation. The ^{13}C NMR spectrum and DEPT experiments revealed the side chain (C-20 to C-27) as having three methyls (δ 17.7, 25.3 and 25.7), two methylenes (δ 22.5 and 40.5), one olefinic methine carbon (δ 124.8), and two quaternary carbons (δ 75.4, 131.5). The olefinic methine proton at δ 5.12 (*tt*, *J* = 7.2, 1.2 Hz) at C-24 (δ 124.8) showed the HMBC correlations with two vinyl methyl carbons C-26 (δ 25.7), and C-27 (δ 17.7), olefinic carbon C-25 (δ 131.5), and C-23 (δ 22.5). An oxy-methine proton at δ 3.91 (H-3) showed HMBC correlations with C-4 (δ 39.0), C-28 (δ 28.0), and C-29 (δ 15.4) and methyl protons at δ 0.88 (H_3-30) showed HMBC correlations with C-8 (δ 40.3), C-13 (δ 42.3), C-15 (δ 31.2), and C-17 (δ 49.8). Thus on the basis of its spectroscopic data and comparison of the ^{1}H and ^{13}C NMR spectral data with the previously reported data (**Table 42**) (Asakawa et al., 1977), compound **TM1** was assigned as dammarenediol II.

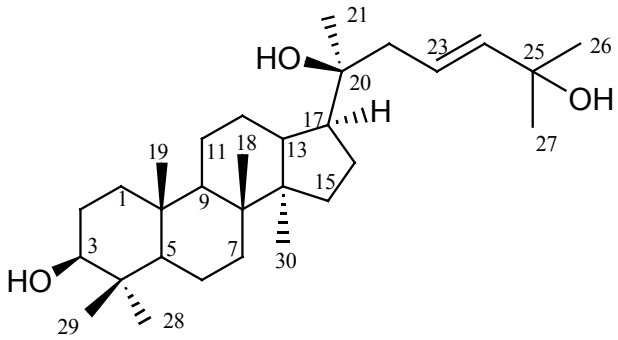
Table 42 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TM1** and dammarenediol II (**R**)

Posi-tion	Type of C*	δ_C /ppm)		δ_H /ppm (multiplicity; *J*/Hz)	HMBC (**TM1**)
		R	**TM1**	**TM1**	^{1}H$\rightarrow$^{13}C
1	CH_2	39.0	39.1		
2	CH_2	27.4	27.4		
3	CH	78.9	78.9	3.19, *dd* (10.5, 5.1)	4, 28, 29
4	C	39.1	39.0		
5	CH	55.9	55.9	0.71, *m*	
6	CH_2	18.3	18.3		
7	CH_2	35.2	35.2		
8	C	40.4	40.3		
9	CH	50.6	50.6	1.24, *m*	
10	C	37.1	37.1		
11	CH_2	21.5	21.5		
12	CH_2	25.4	24.8		
13	CH	42.3	42.3	1.61 *m*	
14	C	50.3	50.3		
15	CH_2	31.2	31.2		

Table 42 Continued

Posi-tion	Type of C*	δ_C /ppm)		δ_H /ppm (multiplicity; *J*/Hz)	HMBC (**TM1**)
		R	**TM1**	**TM1**	$^1H \rightarrow ^{13}C$
16	CH_2	27.6	27.5		
17	CH	49.9	49.8	1.72, *m*	
18	CH_3	15.5	15.5	0.96, *s*	7, 8, 9, 14
19	CH_3	16.2	16.2	0.84, *s*	1, 5, 9, 10
20	C	75.4	75.4		
21	CH_3	24.8	25.3	1.34, *s*	17, 20, 22
22	CH_2	40.5	40.5		
23	CH_2	22.6	22.5	2.04, *m*	20, 22, 24, 25
24	CH	124.7	124.8	5.12, *tt* (7.2, 1.2)	22, 23, 25, 26, 27
25	C	131.6	131.5		
26	CH_3	25.7	25.7	1.69, *s*	24, 25, 27
27	CH_3	17.7	17.7	1.62, *s*	24, 25, 26
28	CH_3	28.0	28.0	0.97, *s*	3, 4, 5, 29
29	CH_3	15.4	15.4	0.77, *s*	3, 4, 5, 28
30	CH_3	16.5	16.5	0.88, *s*	8, 13, 15, 17

3.2.16 Compound **TM2**



Compound **TM2** was obtained as a white solid, mp 128-129°C, $[\alpha]_D^{28}$: +24.0° (*c* = 0.20, MeOH). The IR spectrum showed absorption bands at 3304 and 1643 cm^{-1} for hydroxyl and double bond functionalities, respectively.

The ^1H and ^{13}C NMR spectra for the tetracyclic moiety of **TM2** (**Table 43, Figures 100** and **101**) were similar to those of **TM1**. The difference was in the side chain (C-20 to C-27). Two olefinic methine protons in **TM2** with the same chemical

shift at δ 5.70 (*m*) on the sp^2 carbons at C-23 (δ 122.4) and C-24 (δ 142.0) replaced an olefinic methine proton and two sp^2 carbons at C-24 and C-25 in **TM1**. Three singlet methyl signals were shown at δ_H 1.13, 1.33 (2 x CH_3): δ_C 25.7, 30.0 and 29.9, respectively. These results were also confirmed by the HMBC correlation as follows: the H_3-26 and H_3-27 (each, δ 1.33) showed correlation with C-25 (δ 70.8) and C-24 (δ 142.0), and H-23 (δ 5.70) with C-25 (δ 70.8), C-24 and C-22 (δ 43.4). The NMR spectroscopic data of the side chain (C-20 to C-27) agreed well with those of isofouquierol (Butruille and Dominguez, 1974) and isofouquierone (Waterman and Ampofo, 1985). Thus, compound **TM2** was identified as isofouquierol.

Table 43 ^1H, ^{13}C and HMBC spectral data of compounds **TM2** and **TM1**

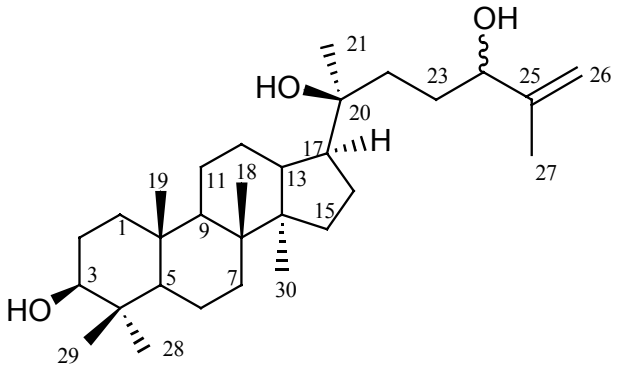
Position	Type of C*	δ_C /ppm		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM2**)
		TM1	**TM2**	**TM2**	**TM1**	$^1H \rightarrow ^{13}C$
1	CH_2	39.1	39.0			
2	CH_2	27.4	27.5			
3	CH	78.9	79.0	3.20, *dd* (10.8, 5.4)	3.19, *dd* (10.5, 5.1)	4, 28, 29
4	C	39.0	39.0			
5	CH	55.9	55.9	0.77, *m*	0.71, *m*	
6	CH_2	18.3	18.3			
7	CH_2	35.2	35.2			
8	C	40.3	40.4			
9	CH	50.6	50.6	1.34, *m*	1.24, *m*	
10	C	37.1	37.1			
11	CH_2	21.5	21.5			
12	CH_2	24.8	24.9			
13	CH	42.3	42.4	1.73, *m*	1.61, *m*	
14	C	50.3	50.3			
15	CH_2	31.2	31.1			
16	CH_2	27.5	27.4			
17	CH	49.8	50.1	1.74, *m*	1.72, *m*	
18	CH_3	15.5	15.5	0.96, *s*	0.96, *s*	7, 8, 9, 14
19	CH_3	16.2	16.2	0.85, *s*	0.84, *s*	1, 5, 9, 10
20	C	75.4	75.1			
21	CH_3	25.3	25.7	1.13, *s*	1.34, *s*	17, 20, 22
22	CH_2	40.5	43.4	2.20, *m*		

Table 43 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM2**)
		TM1	**TM2**	**TM2**	**TM1**	$^1H \rightarrow ^{13}C$
23	CH	22.5	122.4	5.70, *m***	2.04, *m*	22, 24, 25
24	CH	124.8	142.0	5.70, *m***	5.12, *tt* (7.2, 1.2)	22, 23, 25
25	C	131.5	70.8			
26	CH_3	25.7	30.0	1.33, *s****	1.69, *s*	25, 24
27	CH_3	17.7	29.9	1.33, *s****	1.62, *s*	25, 24
28	CH_3	28.0	28.0	0.97, *s*	0.97, *s*	3, 4, 5, 29
29	CH_3	15.4	15.4	0.77, *s*	0.77, *s*	3, 4, 5, 28
30	CH_3	16.5	16.4	0.87, *s*	0.88, *s*	8, 13, 14, 15

* For **TM2** ** Deduced from HMQC *** Six proton integration

3.2.17 Compound **TM3**



Compound **TM3** was obtained as a white solid, mp 156-158°C, $[\alpha]_D^{28}$: +38.4° (*c* = 0.10, MeOH). The IR spectrum showed absorption bands at 3414 and 1610 cm^{-1} for hydroxyl and double bond functionalities, respectively.

The ^1H and ^{13}C NMR spectra for the tetracyclic moiety of **TM3** (**Table 44**, **Figures 102** and **103**) were similar to those of **TM1**. The difference was in the side chain (C-20 to C-27). The oxy-methine proton at δ 4.09 (H-24) on the carbon at δ 75.9 and two terminal methylene protons δ 4.98 (*br s*, H-26a), and δ 4.86 (*m*, H-26b) and carbons at δ 147.6 (C-25), and δ 110.8 (C-26) of **TM3** replaced an olefinic methine proton and two sp^2 carbons (C-24 and C-25) of **TM1**. Two singlet methyl signals were shown at δ_H 1.16 and 1.75: δ_C 25.3 and 18.0, respectively. These results were also confirmed by the HMBC correlation as follows: the H_3-27 showed correlation

with C-24 (δ 75.9), C-25 (δ 147.6), and C-26 (δ 110.8) and H-24 (δ 4.09) with C-23 (δ 29.7), C-25, C-26 and C-27 (δ 18.0). The NMR spectroscopic data of the side chain (C-20 to C-27) agreed well with those of fouquierol (Butruille and Dominguez, 1974). Thus, compound **TM3** was identified as fouquierol.

Table 44 ^{1}H, ^{13}C and HMBC spectral data of compounds **TM3** and **TM1**

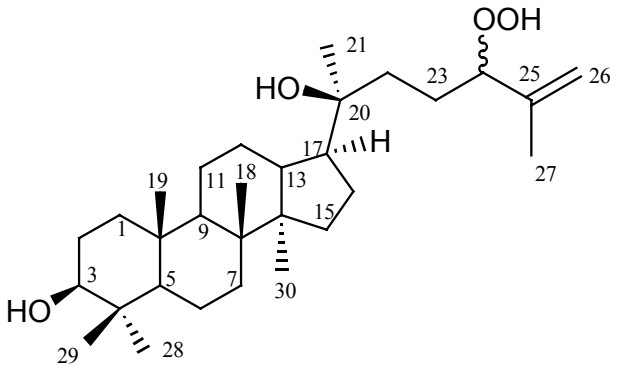
Position	Type of C*	δ_C /ppm		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM3**)
		TM1	**TM3**	**TM3**	**TM1**	$^{1}H \rightarrow ^{13}C$
1	CH_2	39.1	39.0			
2	CH_2	27.4	27.5			
3	CH	78.9	79.0	3.21, *dd* (10.8, 5.1)	3.19, *dd* (10.5, 5.1)	4, 28, 29
4	C	39.0	39.0			
5	CH	55.9	55.9	0.75, *m*	0.71, *m*	
6	CH_2	18.3	18.3			
7	CH_2	35.2	35.2			
8	C	40.3	40.4			
9	CH	50.6	50.6	1.28, *m*	1.24, *m*	
10	C	37.1	37.1			
11	CH_2	21.5	21.5			
12	CH_2	24.8	24.8			
13	CH	42.3	42.4	1.65, *m*	1.61, *m*	
14	C	50.3	50.3			
15	CH_2	31.2	31.2			
16	CH_2	27.5	27.4			
17	CH	49.8	50.1	1.77, *m*	1.72, *m*	
18	CH_3	15.5	15.5	0.97, *s*	0.96, *s*	7, 8, 14
19	CH_3	16.2	16.2	0.86, *s*	0.84, *s*	1, 5, 9, 10
20	C	35.4	75.2			
21	CH_3	25.3	25.3	1.16, *s*	1.34, *s*	17, 20, 22
22	CH_2	40.5	36.0			
23	CH_3	22.5	29.7		2.04 *m*	
24	CH	124.8	75.9	4.09, *m*	5.12, *tt* (7.2, 1.2)	23, 25, 26, 27
25	C	131.5	147.6			
26	CH_2	25.7	110.8	4.98, *br s*; 4.86, *m*	1.69, *s*	24, 25, 27
27	CH_3	17.7	18.0	1.75, *s*	1.62, *s*	24, 25, 26

Table 44 Continued

Position	Type of C*	δ_C /ppm		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM3**)
		TM1	**TM3**	**TM3**	**TM1**	$^1H \rightarrow ^{13}C$
28	CH_3	28.0	28.0	0.99, *s*	0.97, *s*	3, 4, 5, 29
29	CH_3	15.4	15.4	0.79, *s*	0.77, *s*	3, 4, 5, 28
30	CH_3	16.5	16.5	0.89, *s*	0.88, *s*	8, 13, 14, 15

* For **TM3**

3.2.18 Compound **TM4**



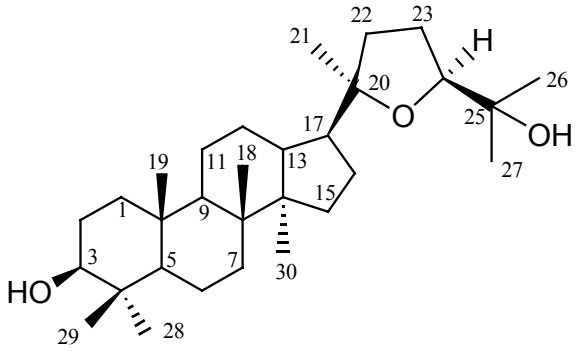
Compound **TM4** was obtained as a white solid, mp 183-185°C, $[\alpha]_D^{28}$: +54.1° (*c* = 0.04, MeOH). In the ^{13}C NMR spectrum, signals were displayed for three oxygenated carbons at δ 75.1, 78.8, and 89.5. Comparison of ^1H and ^{13}C NMR spectra (**Table 45, Figures 104** and **105**) of **TM3** and **TM4** revealed that an oxy-methine proton (H-24) at δ 4.31 (*t*, *J* = 6.31 Hz) and carbon (C-24) at δ 89.5 were shifted downfield while the signals in **TM3** displayed at δ_H 4.09 and δ_C 75.9, indicating that C-24 is connected to a hydroperoxy group. The presence of a hydroperoxy group at C-24 was supported by the molecular formula $C_{30}H_{52}O_4$, a broad downfield signal of a hydroperoxy proton at δ_H 8.08, and the downfield chemical shift of the oxygenated carbon C-24 at δ_C 89.5. The terminal olefinic methylene protons at δ 5.02 (m, H_2-26) showed the HMBC correlations with vinyl methyl carbon C-27 (δ 17.1), olefinic carbon C-25 (δ 144.1), and C-24 (δ 89.5). An oxy-methine proton at δ 4.31 (*t*, *J* = 6.3 Hz, H-24) with C-23 (δ 24.6), C-27 (δ 17.1) and C-26 (δ 113.7). Thus, compound **TM4** was determined as 20(*S*)-3β,20-dihydroxy-24-perhydroxydammar-25-ene, a new compound designated as cereotagaloperoxide (Pakhathirathien et al., 2005).

Table 45 ^{1}H, ^{13}C and HMBC spectral data of compounds **TM4** and **TM3**

Posi-tion	Type of C*	δ_C /ppm)		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM4**)
		TM3	**TM4**	**TM4**	**TM3**	$^{1}H \rightarrow ^{13}C$
1	CH_2	39.0	39.0			
2	CH_2	27.5	27.0			
3	CH	79.0	78.8	3.20, *dd* (11.1, 5.7)	3.21, dd (10.8, 5.1)	2, 4, 28, 29
4	C	39.0	38.9			
5	CH	55.9	55.8	0.73, *m*	0.75, m	
6	CH_2	18.3	18.2			
7	CH_2	35.2	35.2			
8	C	40.4	40.3			
9	CH	50.6	50.6	1.33, *m*	1.28, *m*	
10	C	37.1	37.0			
11	CH_2	21.5	21.5			
12	CH_2	24.8	24.8			
13	CH	42.4	42.3	1.63, *m*	1.65, *m*	
14	C	50.3	50.3			
15	CH_2	31.2	31.1			
16	CH_2	27.4	27.4			
17	CH	50.1	49.6	1.72, *m*	1.77, *m*	
18	CH_3	15.5	15.3	0.96, *s*	0.97, *s*	7, 8, 9, 14
19	CH_3	16.2	16.1	0.85, *s*	0.86, *s*	1, 5, 9, 10
20	C	75.2	75.1			
21	CH_3	25.3	24.6	1.13, *s*	1.16, *s*	17, 20, 22
22	CH_2	36.0	36.5			
23	CH_2	29.7	24.6			
24	CH	75.9	89.5	4.31, *t* (6.3)	4.09, *m*	23, 25
25	C	147.6	144.1			
26	CH_2	110.8	113.7	5.02, *m*	4.98, *br s*; 4.86, *m*	24, 25, 27
27	CH_3	18.0	17.1	1.75, *s*	1.75, *s*	24, 25, 26
28	CH_3	28.0	27.8	0.97, *s*	0.99, *s*	3, 4, 5, 29
29	CH_3	15.4	15.3	0.78, *s*	0.79, *s*	3, 4, 5, 28
30	CH_3	16.5	16.4	0.87, *s*	0.89, *s*	8, 13, 14, 15
	OOH			8.08,, br s		

* For **TM4**

3.2.19 Compound **TM5**



Compound **TM5** was obtained as a white solid, mp 205-207°C, $[\alpha]_D^{28}$: +19.3° (*c* = 0.05, MeOH). Comparison of ^{1}H and ^{13}C NMR spectra (**Table 46, Figures 106** and **107**) of **TM3** and **TM5** revealed similar signals for tetracyclic moiety.

The ^{13}C NMR spectrum analysed by the aid of DEPT experiment, indicated the presence of eight methyls, four sp^3 quaternary carbons and four oxygenated carbons: C-25 (δ 71.4), C-3 (δ 79.0), C-24 (δ 83.3) and C-20 (δ 86.3). The two oxygenated downfield signals (C-20 and C-24) indicated that one tertiary hydroxyl group must be attached to the terminal isopropyl unit and one oxygen formed an ether linkage between C-20 and C-24. This was indeed supported by the HMBC correlations between H_3-21 (δ 1.13)/C-17 (δ 49.6), C-20, and C-22 (δ 35.7) and between H_3-26 (δ 1.12) and H_3-27 (δ 1.21)/C-24, C-25 and C-26. As for the configuration at C-20 and C-24 of the side chain, both were assigned as *S* by comparing the chemical shifts of H-24 (δ 3.73, *t*, *J* = 6.9 Hz), H_3-26 and H_3-27 of **TM5** with those reported data (Tanaka et al., 1993). Thus, compound **TM5** was determined as ocotillol II.

Table 46 ^{1}H, ^{13}C and HMBC spectral data of compounds **TM5**, **TM3** and octotillol-II (**R**)

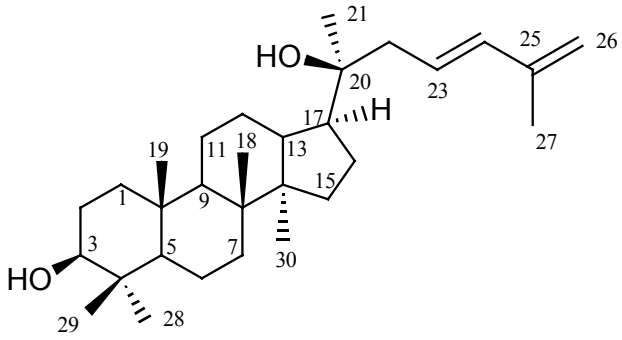
Posi-	Type	δ_C /ppm			δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM5**)
tion	of C*	**R**	**TM5**	**TM3**	**TM5**	**TM3**	^{1}H→^{13}C
1	CH_2	39.1	39.1	39.0			
2	CH_2	27.4	27.4	27.5			
3	CH	79.0	79.0	79.0	3.20, *dd* (10.8,5.7)	3.21, *dd* (10.8,5.1)	4, 28, 29
4	C	39.0	39.0	39.0			
5	CH	55.9	55.9	55.9	0.71,, *m*	0.75, *m*	

Table 46 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM5**)
		R	**TM5**	**TM3**	**TM5**	**TM3**	$^1H \rightarrow ^{13}C$
6	CH_2	18.3	18.3	18.3			
7	CH_2	35.3	35.3	35.2			
8	C	40.4	40.4	40.4			
9	CH	50.8	50.8	50.6	1.31, *m*	1.28, *m*	
10	C	37.2	37.2	37.1			
11	CH_2	21.6	21.6	21.5			
12	CH_2	25.7	25.7	24.8			
13	CH	43.0	43.0	42.4	1.53, *m*	1.65, *m*	
14	C	50.1	49.9	50.3			
15	CH_2	31.5	31.5	31.2			
16	CH_2	27.4	27.4	27.4			
17	CH	49.5	49.6	50.1	1.78, *m*	1.77, *m*	
18	CH_3	15.5	15.4	15.5	0.95, *s*	0.97, *s*	7, 8, 14
19	CH_3	16.3	16.2	16.2	0.84, *s*	0.86, *s*	1, 5, 9, 10
20	C	86.4	86.3	75.2			
21	CH_3	23.6	23.5	25.3	1.13, *s*	1.16, *s*	17, 20, 22
22	CH_2	35.7	35.7	36.0			
23	CH_2	26.1	25.7	29.7			
24	CH	83.3	83.3	75.9	3.73, *t* (6.9)	4.09, *m*	
25	C	71.4	71.4	147.6			
26	CH_3	24.3	24.3	110.8	1.12, *s*	4.98, *br s*; 4.86, *m*	24, 25, 27
27	CH_3	27.4	27.4	18.0	1.21, *s*	1.75, *s*	24, 25, 26
28	CH_3	28.0	28.0	28.0	0.97, *s*	0.99, *s*	3, 4, 5, 29
29	CH_3	15.3	15.3	15.4	0.77, *s*	0.79, *s*	3, 4, 5, 28
30	CH_3	16.5	16.5	16.5	0.87, *s*	0.89, *s*	8, 13, 14, 15

* For **TM5**

3.2.20 Compound **TM6**



Compound **TM6** was obtained as a colorless oil, $[\alpha]_D^{28}$: +62.5° (*c* = 0.03, MeOH). The ^{13}C NMR spectral data of compound **TM6** (**Table 47**, **Figure 109**) revealed 30 carbon signals which were sorted by DEPT as seven methyl, ten methylene, seven methine and six quaternary carbons. The ^{1}H NMR spectrum (**Table 47**, **Figure 108**) showed the signals of six singlet methyls (δ 0.78, 0.85, 0.88, 0.96, 0.98, 1.14), a vinylic methyl (δ 1.86, H_3-27). The hydroxymethine proton appeared at δ 3.20 (*dd*, *J* = 10.8, 5.4 Hz, H-3), two olefinic proton signals were observed at δ 5.71 (*dt*, 15.6, 7.8 Hz, H-23) and 6.20 (*d*, *J* = 15.6 Hz), and *exo*-methylene protons at δ 4.91 (*br s*, H-26). The ^{13}C NMR signals showed a conjugated diene carbons at δ 125.8 (C-23), 136.5 (C-24), 141.9 (C-25), 115.2 (C-26), an oxygenated quaternary carbon at δ 75.3 (C-20), and one hydroxy methine carbon at δ 79.0 (C-3). The chemical shifts of tetracyclic part of the triterpene skeleton at C-1 to C-19 and C-28 to C-30 were closely related to those of **TM1**. HMBC correlations between H-24 (δ 6.20) and C-22 (δ 43.9), C-25 (δ 141.9), C-26 (δ 115.2) and C-27 (δ 18.7) confirmed the structure of **TM6**. Thus, compound **TM6** was postulated to be 20(S)-3β, 20-dihydroxydammar-23, 25-diene, a new compound designated as ceriotagalol C.

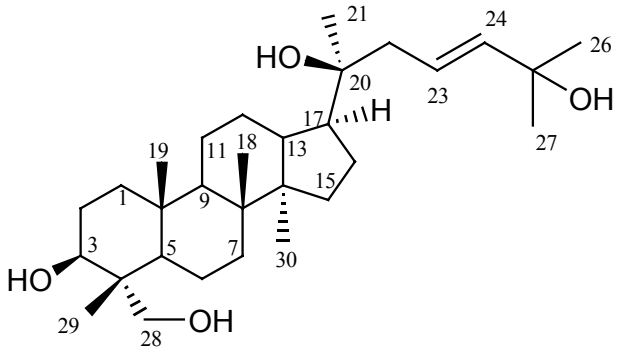
Under mildly acidic condition in $CDCl_3$, an allylic hydroxyl group of fouquierol (**TM3**) isolated from this plant was completely transformed to a conjugated diene within a few days, resulting in a more stable product of compound **TM6**.

Table 47 ^{1}H, ^{13}C and HMBC spectral data of compounds **TM6** and **TM1**

Posi-tion	Type of C*	δ_C /ppm)		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM6**)
		TM1	**TM6**	**TM6**	**TM1**	$^1H \rightarrow ^{13}C$
1	CH_2	39.1	39.0			
2	CH_2	27.4	27.5			
3	CH	78.9	79.0	3.20, *dd* (10.8, 5.4)	3.19, *dd* (10.5, 5.1)	4, 28, 29
4	C	39.0	39.0			
5	CH	55.9	55.9	0.72, *m*	0.71, *m*	
6	CH_2	18.3	18.3			
7	CH_2	35.2	35.2			
8	C	40.3	40.4			
9	CH	50.6	50.6	1.31, *m*	1.24, *m*	
10	C	37.1	37.1			
11	CH_2	21.5	21.5			
12	CH_2	24.8	24.9			
13	CH	42.3	42.4	1.74, *m*	1.61, *m*	
14	C	50.3	50.3			
15	CH_2	31.2	31.1			
16	CH_2	27.5	27.4			
17	CH	49.8	50.1	1.72, *s*	1.72, *s*	
18	CH_3	15.5	15.5	0.96, *s*	0.96, *s*	7, 8, 9, 14
19	CH_3	16.2	16.2	0.85, *s*	0.84, *s*	1, 5, 9, 10
20	C	75.4	75.3			
21	CH_3	25.3	26.0	1.14, *s*	1.34, *s*	17, 20, 22
22	CH_2	40.5	43.9	2.28, *m*		17, 21, 20, 23, 24
23	CH	22.5	125.8	5.71, *dt* (15.6, 7.8)	2.04, *m*	25
24	CH	124.8	136.5	6.20, *d* (15.6)	5.12, *tt* (7.2, 1.2)	22, 25, 26, 27
25	C	131.5	141.9			
26	CH_2	25.7	115.2	4.91, *br s*	1.69, *s*	24, 25, 27
27	CH_3	17.7	18.7	1.86, *s*	1.62, *s*	24, 25, 26
28	CH_3	28.0	28.0	0.98, *s*	0.97, *s*	3, 4, 5, 29
29	CH_3	15.4	15.3	0.78, *s*	0.77, *s*	3, 4, 5, 28
30	CH_3	16.5	16.4	0.88, *s*	0.88, *s*	8, 13, 14, 15

* For **TM6**

3.2.21 Compound **TM7**



Compound **TM7** was obtained as a colorless oil, $[\alpha]_D^{28}$: +55.6° (*c* = 0.02, MeOH). The ESITOFMS showed a pseudomolecular ion peak $[M+Na]^+$ at *m/z* 499.3754, indicating a molecular formula of $C_{30}H_{52}O_4$ (calcd for $C_{30}H_{52}O_4Na$ *m/z* 499.3763). The IR spectrum showed the same pattern as that of **TM2**.

In the ^{13}C NMR spectrum, signals were displayed for four oxygenated carbons at δ 70.8, 71.9, 75.1, and 76.6. Comparison of ^{1}H and ^{13}C NMR spectra (**Table 48**, **Figures 110** and **111**) of **TM2** and **TM7** revealed that the latter compound has one more hydroxy methylene group than **TM2**. The ^{13}C NMR spectra suggested that **TM7** and **TM2** have similar side-chain, therefore, the additional hydroxy methylene group should be at the tetracyclic moiety. This was assigned at C-28 (δ 71.9) due to HMBC correlations of H_2-28 (δ 3.72, 3.42; each, *d*, *J* = 10.5 Hz) with C-3 (δ 76.6), C-4 (δ 42.0), C-5 (δ 50.6) and C-29 (δ 11.3). ^{13}C NMR spectroscopic data of the side chain (C-20 to C-27) of **TM7** agreed well with those of **TM2** (**Table 48**). Thus, compound **TM7** was identified as 20(*S*)-3β,20,25,28-tetrahydroxydammar-23-ene, a new compound designated as cereotagalol B (Pakhathirathien et al., 2005).

Table 48 ^{1}H, ^{13}C and HMBC spectral data of compounds **TM7** and **TM2**

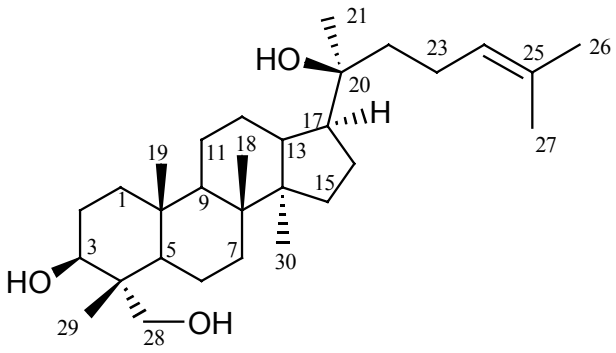
Posi-	Type	δ_C /ppm)		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM7**)
tion	of C*	**TM2**	**TM7**	**TM7**	**TM2**	$^{1}H \rightarrow ^{13}C$
1	CH_2	39.0	38.7			
2	CH_2	27.5	27.0			
3	CH	79.0	76.6	3.64, *dd* (8.4, 7.8)	3.20, *dd* (10.8, 5.4)	2, 28, 29

Table 48 Continued

Posi-tion	Type of C*	δ_C /ppm)		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM7**)
		TM2	**TM7**	**TM7**	**TM2**	$^1H \rightarrow ^{13}C$
4	C	39.0	42.0			
5	CH	55.9	50.6	1.35, *m*	0.77, *m*	
6	CH_2	18.3	18.4			
7	CH_2	35.2	35.0			
8	C	40.4	40.4			
9	CH	50.6	50.4	0.88, *m*	1.34, *m*	
10	C	37.1	37.0			
11	CH_2	21.5	21.5			
12	CH_2	24.9	24.8			
13	CH	42.4	42.4	1.69, *m*	1.73, *m*	
14	C	50.3	50.3			
15	CH_2	31.1	31.1			
16	CH_2	27.4	27.5			
17	CH	50.1	49.9	1.74, *m*	1.74, *m*	
18	CH_3	15.5	15.5	0.97, *s*	0.96, *s*	7, 8, 9, 14
19	CH_3	16.2	16.6	0.90, *s*	0.85, *s*	1, 5, 9, 10
20	C	75.1	75.1			
21	CH_3	25.7	25.8	1.13, *s*	1.13, *s*	17, 20, 22
22	CH_2	43.4	43.4	2.19, *m*	2.20, *m*	20, 23, 24
23	CH_2	122.4	122.4	5.69, *m*	5.70, *m*	22, 25
24	CH	142.0	142.1	5.69, *m*	5.70, *m*	22, 23, 25
25	C	70.8	70.8			
26	CH_3	30.0	30.0	1.33, *s*	1.33, *s*	24, 25, 27
27	CH_3	29.9	29.9	1.33, *s*	1.33, *s*	24, 25, 26
28	CH_2	28.0	71.9	3.72, *d* (10.2); 3.43, *d* (10.2)	0.97, *s*	3, 4, 5, 29
29	CH_3	15.4	11.3	0.88, *s*	0.77, *s*	3, 4, 5, 28
30	CH_3	16.4	16.5	0. 87, *s*	0.87, *s*	8, 13, 14, 15

* For **TM7**

3.2.22 Compound **TM8**



Compound **TM8** was obtained as a colorless oil, $[\alpha]_D^{28}$: +50.0° (*c* = 0.02, MeOH). The ^{1}H and ^{13}C NMR spectra for the tetracyclic moiety of **TM8** (**Table 49**, **Figures 112** and **113**) were similar to those of **TM7**, with signals for the hydroxy methylene group at δ_H 3.72, 3.42 and δ_C 71.9. The difference was in the side-chain (C-20 to C-27) where three methyls (δ 17.7, 25.4 and 25.7), two methylenes (δ 22.5 and 40.5), one olefinic methine carbon (δ 124.7), and two quaternary carbons (δ 75.4, 131.6) were displayed in **TM8**. The olefinic methine proton at δ 5.20 (m) at C-24 (δ 124.8) showed the HMBC correlations with two vinyl methyl carbons C-26 (δ 25.7), and C-27 (δ 17.7), C-25 olefinic carbon (δ 131.6), C-23 (δ 22.5) and C-22 (δ 40.5). The NMR spectroscopic data of the side-chain (C-20 to C-27) agreed well with those of **TM1**. Thus, compound **TM8** was postulated to be 20(*S*)-3β,20,28-trihydroxydammar-24-ene, a new compound designated as ceriotagalol D.

Table 49 ^{1}H, ^{13}C and HMBC spectral data of compounds **TM8**, **TM7** and **TM1**

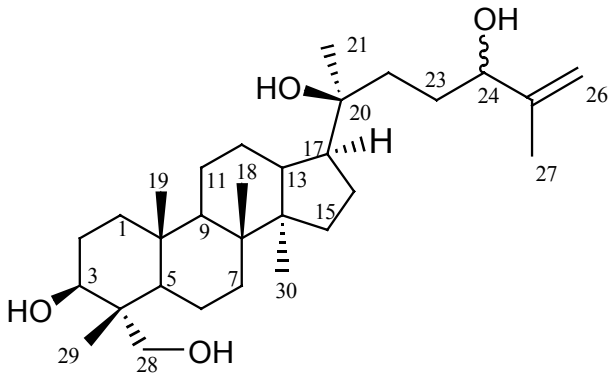
Posi-	Type	δ_C /ppm			δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM8**)
tion	of C*	**TM7**	**TM8**	**TM1**	**TM8**	**TM7**	^{1}H→^{13}C
1	CH_2	38.7	38.7	39.1			
2	CH_2	27.0	27.0	27.4			
3	CH	76.6	76.6	78.9	3.63, *dd* (7.1, 6.9)	3.64, *dd* (8.4, 7.8)	2, 4, 28, 29
4	C	42.0	42.0	39.0			
5	CH	50.6	50.6	55.9	1.30, *m*	1.35, *m*	
6	CH_2	18.4	18.4	18.3			

Table 49 Continued

Posi-	Type	δ_C /ppm			δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM8**)
tion	of C*	**TM7**	**TM8**	**TM1**	**TM8**	**TM7**	$^1H \rightarrow ^{13}C$
7	CH_2	35.0	35.0	35.2			
8	C	40.4	40.3	40.3			
9	CH	50.4	50.4	50.6	0.89, *m*	0.88, *m*	
10	C	37.0	37.0	37.1			
11	CH_2	21.5	21.5	21.5			
12	CH_2	24.8	24.8	24.8			
13	CH	42.4	42.2	42.3	1.64, *m*	1.69, *m*	
14	C	50.3	50.3	50.3			
15	CH_2	31.1	31.2	31.2			
16	CH_2	27.5	27.5	27.5			
17	CH	49.9	49.8	49.8	1.75, *m*	1.74, *m*	
18	CH_3	15.5	15.5	15.5	0.96, *s*	0.97, *s*	7, 8, 9, 14
19	CH_3	16.6	16.5	16.2	0.89, *s*	0.90, *s*	1, 5, 9, 10
20	C	75.1	75.4	75.4			
21	CH_3	25.8	25.4	25.3	1.14, *s*	1.13, *s*	17, 20, 22
22	CH_2	43.4	40.5	40.5	1.49, *m*	2.19, *m*	
23	CH	122.4	22.5	22.5		5.69, *m*	
24	CH	142.1	124.7	124.8	5.20, *m*	5.69, *m*	22, 23, 25, 26, 27
25	C	70.8	131.6	131.5			
26	CH_3	30.0	25.7	25.7	1.69, *s*	1.33, *s*	24, 25, 27
27	CH_3	29.9	17.7	17.7	1.62, *s*	1.33, *s*	24, 25, 26
28	CH_2	71.9	71.9	28.0	3.72, *d* (11.2); 3.42, *d* (11.2)	3.72, *d* (10.2); 3.43, *d* (10.2)	3, 4, 5, 29
29	CH_3	11.3	11.3	15.4	0.88, *s*	0.88, *s*	3, 4, 5, 28
30	CH_3	16.5	16.5	16.5	0.87, *s*	0.87, *s*	8, 13, 14, 15

* For **TM8**

3.2.23 Compound **TM9**



Compound **TM9** was obtained as a colorless oil, $[\alpha]_D^{28}$: +52.6° (*c* = 0.02, MeOH). This compound also exhibited a pseudomolecular ion peak $[M+Na]^+$ at *m/z* 499.3776 in the ESITOFMS, indicating a molecular formula of $C_{30}H_{52}O_4$.

The ^1H and ^{13}C NMR spectra for the tetracyclic moiety of **TM9** (**Table 50, Figures 114** and **115**) were similar to those of **TM7**. The difference was in the side- chain (C-20 to C-27). The oxymethine proton at δ 4.04 (H-24) on the carbon at δ 76.5 and two terminal methylene protons δ 4.96, and δ 4.84 (H_2-26) and carbons at δ 147.6 (C-25), and δ 110.9 (C-26) in **TM9** replaced an olefinic methine proton and two sp^2 carbons at C-24 and C-25 in **TM7**. Two singlet methyl signals were shown at δ_H 1.15 and 1.74: δ_C 25.4 and 17.8, respectively. These results were also confirmed by the HMBC correlation as follows: the H_3-27 showed correlations with C-24 (δ 76.5), C-25 (δ 147.6), and C-26 (δ 110.9) and H-24 with C-22 (δ 36.6) and C-26. The NMR spectroscopic data of the side-chain (C-20 to C-27) agreed well with those of **TM3**. Thus, compound **TM9** was identified as 20(*S*)-3β,20,24,28-tetrahydroxy-dammar-25-ene, a new compound designated as cereotagalol A(Pakhathirathien et al., 2005).

Table 50 ^1H, ^{13}C and HMBC spectral data of compounds **TM9**, **TM7** and **TM3**

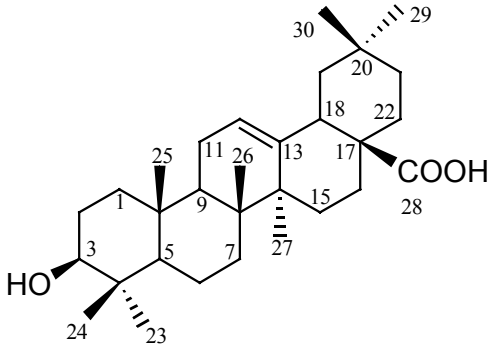
Posi-	Type	δ_C /ppm			δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM9**)
tion	of C*	**TM7**	**TM9**	**TM3**	**TM9**	**TM7**	$^1H \rightarrow ^{13}C$
1	CH_2	38.7	38.7	39.0			
2	CH_2	27.0	27.0	27.5			

Table 50 Continued

Position	Type of C*	δ_C /ppm			δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TM9**)
		TM7	**TM9**	**TM3**	**TM9**	**TM7**	$^1H \rightarrow ^{13}C$
3	CH	76.6	76.6	79.0	3.64, *t* (8.1)	3.64, *dd* (8.4, 7.8)	2, 4, 28, 29
4	C	42.0	42.0	39.0			
5	CH	50.6	50.6	55.9	1.36, *m*	1.36, *m*	
6	CH_2	18.4	18.4	18.3			
7	CH_2	35.0	35.0	35.2			
8	C	40.3	40.4	40.4			
9	CH	50.4	50.4	50.6	0.89, *m*	0.89, *m*	
10	C	37.0	37.0	37.1			
11	CH_2	21.5	21.5	21.5			
12	CH_2	24.8	24.9	24.8			
13	CH	42.2	42.3	42.4	1.62, *m*	1.62, *m*	
14	C	50.3	50.3	50.3			
15	CH_2	31.2	31.2	31.2			
16	CH_2	27.5	27.5	27.4			
17	CH	49.8	50.1	50.1	1.75, *m*	1.75, *m*	
18	CH_3	15.5	15.5	15.5	0.96, *s*	0.96, *s*	7, 8, 9, 14
19	CH_3	16.5	16.5	16.2	0.89, *s*	0.89, *s*	1, 5, 9, 10
20	C	75.4	75.1	75.2			
21	CH_3	25.4	25.4	25.3	1.15, *s*	1.15, *s*	17, 20, 22
22	CH_2	40.5	36.6	36.0			
23	CH_2	22.5	29.3	29.7			
24	CH	124.7	76.5	75.9	4.04, *m*	4.04, *m*	22, 26
25	C	131.6	147.6	147.6			
26	CH_2	25.7	110.9	110.8	4.96, m; 4.84, *m*	4.96, *br s*; 4.84, *m*	24, 25, 27
27	CH_3	17.7	17.8	18.0	1.74, *s*	1.74, *s*	24, 25, 26
28	CH_2	71.9	71.9	28.0	3.72, *d* (10.5); 3.42, *d* (10.5)	3.72, *d* (10.5); 3.42, *d* (10.5)	3, 4, 5, 29
29	CH_3	11.3	11.3	15.4	0.88, *s*	0.88, *s*	3, 4, 5, 28
30	CH_3	16.5	16.5	16.5	0.87, *s*	0.87, *s*	8, 13, 14, 15

* For **TM9**

3.2.24 Compound **TO1**



Compound **TO1** was obtained as a white solid, mp 275-276°C, $[\alpha]_D^{28}$: +82.0° (*c* = 0.10, MeOH). The IR spectrum showed absorption bands for hydroxyl group at 3456 cm^{-1} and double bond at 1690 cm^{-1}. It gave a purple vanillin-sulfuric acid test indicating a triterpene.

The ^{13}C NMR spectral data (**Table 51, Figure 117**) showed 30 signals for 30 carbons. Analysis of DEPT-90° and DEPT-135° spectra of this compound suggested the presence of seven methyls (δ 15.6, 16.5, 17.5, 23.8, 26.2, 28.8 and 33.4), eleven methylenes (δ 18.8, 23.8, 23.7, 23.8, 28.1, 28.4, 33.2, 33.4, 34.3, 39.0, 46.6 and 122.6), five methines (δ 42.1, 48.2, 55.9, 78.2 and 144.8) and seven quaternary carbons (δ 31.0, 37.4, 39.4, 39.8, 42.2, 46.7 and 180.0).

The ^{1}H NMR spectral data (**Table 51, Figure 116**) showed characteristic of olenane triterpenoid as seven methyl singlet signals at δ 0.76, 0.78, 0.90, 0.91, 0.93, 0.99 and 1.13. One methyl group was oxidized to carboxyl group which was displayed at δ_C 180.0 and an olefinic proton signal was displayed at δ 5.28 (*t*, *J* = 3.3 Hz, H-12). An oxy-methine proton was shown at δ 3.22 (1H, *dd*, *J* = 10.8, 4.5 Hz, H-3) with a doublet of doublet splitting pattern together with a large coupling constant with *Jax-ax* = 10.8 Hz and *Jax-eq* = 4.5 Hz indicating its axial (α) orientation.

The position of the hydroxyl group at C-3 was determined through an HMBC experiment in which the oxy-methine proton H-3 (δ 3.22) showed correlations with C-1 (δ 38.3), C-2 (δ 26.6), C-4 (δ 38.5), C-23 (δ 27.8), and C-24 (δ 15.3) and methyl protons H_3-29 (δ 0.90) with C-19 (δ 45.8), C-20 (δ 30.5), and C-30 (δ 23.3) and olefinic methine proton H-12 (δ 5.28) with C-9 (δ 47.5), C-11 (δ 23.2), C-14 (δ 41.5), and C-18 (δ 41.0). Thus on the basis of its spectroscopic data and comparison of the ^{1}H and ^{13}C NMR spectral data (**Table 51**) with the previously reported data (Seebacher et al., 2003), compound **TO1** was assigned as oleanolic acid.

Table 51 The ^{1}H, ^{13}C and HMBC spectral data of compounds **TO1** and oleanolic acid (**R**)

Position	Type of C*	δ_C /ppm)		δ_H /ppm (multiplicity; *J*/Hz)		HMBC (**TO1**)
		R**	**TO1**	**TO1**	**R****	$^1H \rightarrow ^{13}C$
1	CH_2	39.0	38.3			
2	CH_2	28.1	26.6			
3	CH	78.2	78.7	3.22, *dd* (10.8, 4.5)	3.44	1, 2, 4, 23, 24
4	C	39.4	38.5			
5	CH	55.9	55.1			
6	CH_2	18.8	18.1			
7	CH_2	33.4	32.5			
8	C	39.8	39.1			
9	CH	48.2	47.5			
10	C	37.4	36.8			
11	CH_2	23.7	23.2			
12	CH	122.6	122.1	5.28, *t* (3.3)	5.49	9, 11, 14, 18
13	C	144.8	143.7			
14	C	42.2	41.5			
15	CH_2	28.4	27.5			
16	CH_2	23.8	22.8			
17	C	46.7	46.2			
18	CH	42.1	41.0	2.82, *dd* (14.4, 3.9)	3.30	12, 13, 14, 16, 17, 18, 19, 28
19	CH_2	46.6	45.8			
20	C	31.0	30.5			
21	CH_2	34.3	33.7			
22	CH_2	33.2	32.4			
23	CH_3	28.8	27.8	0.99, *s*	1.24	3, 4, 5, 24
24	CH_3	16.5	15.3	0.76, *s*	1.02	3, 4, 5, 23
25	CH_3	15.6	15.0	0.93, *s*	0.93	1, 5, 9, 10
26	CH_3	17.5	16.6	0.78, *s*	1.04	8, 9, 14
27	CH_3	26.2	25.6	1.13, *s*	1.30	8, 13, 14, 15
28	C	180.0	180.9			
29	CH_3	33.4	32.8	0.90, *s*	0.97	19, 20, 30
30	CH_3	23.8	23.3	0.91, *s*	1.02	19, 20, 29

* For **TO1**

**In pyridine, not assigned multiplicity

3.3 Biological activities of the pure compounds from *C. tagal*

The biological activities of the pure compounds (**TL1-TL13** and **TM1-TM9**) from *C. tagal* were tested against KB, BC and NCI-H187 cell lines as shown in **Table 52.** The crude methylene chloride extract from the hypocotyls exhibited antituberculous (25 μg/mL) and cytotoxic activity (ED_{50} 9.91 μg/mL for KB cell 2.68 μg/mL for BC cell and 6.30 μg/ml for NCI-H187 cell) but the crude hexane extract showed only antituberculous activity (100 μg/ml). Compound **TL12** exhibited strong activity in both cell lines, while compounds **TL6** and **TL11** exhibited strong activity in BC and NCI-H187 cell lines, respectively, compound **TL9** exhibited moderate activity in both cell lines, while compounds **TL6** exhibited moderate activity in KB cell line, compound **TL11** exhibited weak activity in KB and BC cell lines, and compounds **TL3-TL5**, **TL10** and **TL13** exhibited strong to moderate activity only in NCI-H187 cell lines.

Table 52 Cytotoxic activity of compounds **TL3-6** and **TL9-TL13** in IC_{50} (μg/mL)

Compounds	KB	BC	NCI-H187
TL3	-	-	2.90
TL4	-	-	8.48
TL5	-	-	4.80
TL6	8.40	3.71	5.76
TL9	6.38	8.53	6.12
TL10	-	-	6.20
TL11	14.46	11.65	3.55
TL12	3.75	3.04	1.75
TL13	-	-	4.96

IC_{50} (μg/mL) value	Level of activity
> 20	Inactive
10 - 20	Weakly active
5 - 10	Moderately active
< 5	Strongly active
-	No investigation

The biological activities of the pure compounds (**TD1-TD28**) from *C. tagal* were also tested for antimalarial activity, according to established protocols (Trager

and Jensen 1967, Desjardins et al. 1979). Compounds **TD2**, **TD3**, **TD4**, **TD6**, **TD12**, **TD14**, **TD16**, **TD26** and **TD27** showed activity at 1.55, 2.16, 2.87, 2.81, 3.21, 2.20, 2.72, 7.43 and 6.65 μg/mL, respectively, whereas the rest of the pure compounds showed no activity. The positive control compound was artemisinin (IC_{50} 3.3–3.9 nM).

3.4 Conclusion

The investigation of the fruits, hypocotyls and bark of *Ceriops tagal* have led to the isolation of eighteen new compounds, including thirteen diterpenoids (**TD1**-**TD3**, **TD6**-**TD7**, **TD10** and **TD20**-**TD26**) and five dammarane triterpenoids (**TM4** and **TM6**-**TM9**) together with thirty five known compounds, including fifteen diterpenoids (**TD4**-**TD5**, **TD8**-**TD9**, **TD11**-**TD19** and **TD27**-T**D28**), eight triterpenoid esters (**TL6**-**TL13**), ten triterpenoids (**TL1**-**TL5**, **TM1**-**TM3**, **TM5** and **TO1**) and a mixture of two steroids (**TS1**-**TS2**). Compounds isolated from the bark were diterpenes: dolabranes (**TD1**-**TD24**); pimaranes (**TD25**-**TD26**) and kauranes (**TD27**-**TD28**). Those isolated from the hypocotyls were triterpenoids: lupanes (**TL1**-**TL13**) and dammaranes (**TM7**-**TM9**). A mixture of two steroids (**TS1** and **TS2**) was also isolated from the hypocotyls. Compounds isolated from the fruits were also dammarane triterpenoids (**TM1**-**TM6**). In addition an oleanane triterpene (**TO1**) was also isolated from the fruits.

Most of triterpenes were tested for cytotoxic activity (KB, BC and NCI-H187 cell lines), whereas diterpenes were tested for antimalarial activity. For the cytotoxicity test, the presence of CH_2OH and COOH groups at C-28 of lupane triterpenoids seem to be crucial for the activity, especially against NCI-H187 cell lines. 3β-*E*-Feruloylbetulinic acid (**TL12**) was the only compound which exhibited strong activity against all three cell lines. Some dolabrane diterpenoids showed weak antimalarial activity (**TD2**, **TD3**, **TD4**, **TD6**, **TD12**, **TD14**, **TD16**, **TD26** and **TD27**), but this was not enough information to specify the crucial functional group responsible for their activity.

X-ray crystallographic structures of compounds **TD1**, **TD5**, **TD13**, **TD25**, **TD28** and **TL7** were shown which supported the proposed structures of those compounds.