CHAPTER 3

RESULTS AND DISCUSSION

Preliminary screening using breast cancer MCF7 and small cell lung NCI-H187 cancer cell lines indicated the CH_2Cl_2 extract of the roots of *Maytenus mekongensis* possessing inhibitory activities, with IC_{50} values of 0.274 and 0.102 μg/mL, respectively. The CH_2Cl_2 extract was thus chosen for further investigation. Systematic fractionation of the CH_2Cl_2 extract led to the separation of twenty compounds. The structure elucidation of the isolated compounds were determined by spectroscopic method.

Structure Elucidation of Compound I

Compound **I** was obtained as colorless needles, mp 318-319 °C. The FTIR spectrum showed absorption band for a hydroxyl (ν_{max} 3488 cm^{-1}) and a lactone carbonyl (ν_{max} 1748 cm^{-1}) functional groups. It was assigned the molecular formula $C_{30}H_{46}O_3$ as deduced from the HRESIMS which displayed a molecular ion at *m/z* 455.3531 corresponding to $[M + H]^+$ (calcd for $C_{30}H_{47}O_3$ 455.3525).

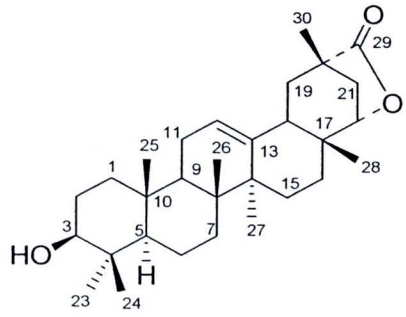
The ^{13}C NMR spectrum showed the presence of thirty two carbons comprising seven methyls, nine methylenes, six methines and eight quaternary carbons including one carbonyl and one olefinic carbons at δ_C 182.38 and 140.23, respectively.

The ^{1}H NMR spectrum showed signals for seven quaternary methyl groups at δ_H 1.18, 1.05, 0.97, 0.92, 0.91, 0.84, and 0.76. The less shielded doublet of double signal at δ_H 3.20 (J = 11.2 and 4.8 Hz) indicated the carbinolic proton at C-3. A trisubstituted olefinic group signal observed at δ_H 5.27 (1H, t, J = 3.6 Hz) and δ_C 140.2 and 124.7 indicated an olean-12-en.[48] A doublet signal at δ_H 4.13 (1H, J = 5.4 Hz) was assigned for oxymethine proton bonded to *O*COR group.

^{1}H-^{1}H COSY spectrum indicated cross-peaks between a doublet of doublet signal at δ_H 2.11 (H-18) and signals at δ_H 1.87 and 1.46 assigned to H_2-19.

The HMBC spectrum indicated long-range correlations between H-3/C-23 (δ_C 28.10) and C-24 (δ_C 15.60) indicated the presence of a hydroxyl group at C-3. The ^{3}J ^{1}H-^{13}C correlations of H_2-19/C-13 (δ_C 140.23), C-17 (δ_C 35.26), C-18 (δ_C 43.43), C-20 (δ_C 42.53), C-29 (δ_C 182.38), C-30 (δ_C 20.95) indicated the carboxyl carbonyl at C-29. The HMBC correlations between proton signal at δ_H 4.13 (H-22)/C-18, C-19, C-28, C-29 indicated a lactone bond between an oxygen atom at C-22 and C-29. The ORTEP structure of compound **I** was obtained after X-ray crystallographic analysis (Figure 2) which showed configuration at C-22 as reported.

Compound **I** was identified as abruslactone A.[49] Further use of 2D-NMR data led to full assignment of the ^{1}H and ^{13}C chemical shift (Table 1). The specific rotation of compound **I** was found to be $[\alpha]_D^{29}$ +67.41 (*c* 0.64, $CHCl_3$), which is different from that reported for abruslactone A $[\alpha]_D$ -33.4 (*c* 0.20, $CHCl_3$).[50]



Compound **I**

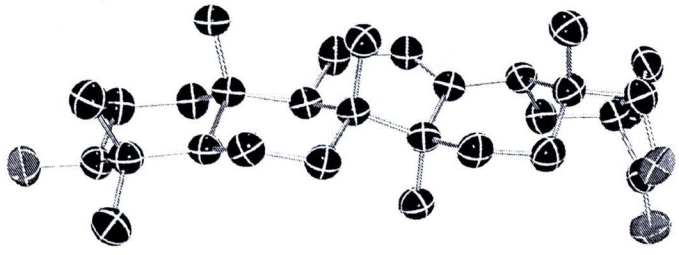


Figure 1 ORTEP drawing of compound **I**

Table 1 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **I** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	1.61	38.61 CH_2	C-2, 3, 5, 10
	0.99		
2	1.58[a]	27.19 CH_2	C-3, 5, 10
3	3.20 dd (11.2, 4.8)	78.88 CH	C-23, 24
4	-	38.75 qC	-
5	0.72 d (11.4)	55.20 CH	C-7, 9, 10, 23, 24, 25
6	1.58[a]	18.32 CH_2	C-4, 7, 8, 9
	1.38		
7	1.55	33.13 CH_2	C-5, 6, 8, 26
	1.36		

Table 1 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
8	-	39.30 qC	-
9	1.51	47.54 CH	C-5, 8, 11, 26
10	-	37.02 qC	-
11	1.87	23.48 CH_2	C- 9, 12, 13
12	5.27 t (3.6)	124.65 CH	C- 9, 11, 14
13	-	140.23 qC	-
14	-	39.51 qC	-
15	1.68 dt (13.6, 3.2)	24.33 CH_2	C-16
16		25.20 CH_2	C-14
17	-	35.26 qC	-
18	2.11 dd (12.9, 8.6)	43.43 CH	C -12, 13, 14, 16, 17, 20
19	1.87	39.85 CH_2	C-13, 17, 18, 20, 29, 30
	1.46		
20	-	42.53 qC	-
21	2.24 d (11.9)	33.83 CH_2	C-17, 19, 20, 22, 29, 30
	1.91 dd (11.9, 5.5)		
22	4.13 d (5.4)	83.10 CH	C-16, 18, 20, 21, 28, 29
23	0.97 s	28.10 CH_3	C-4, 5, 22, 24
24	0.76 s	15.60 CH_3[b]	C-3, 4, 5, 23
25	0.92 s	15.60 CH_3[b]	C-1, 9
26	0.91 s	17.00 CH_3	C-7, 14, 9
27	1.05 s	24.05 CH_3	C-8, 13, 14, 15
28	0.84 s	24.95 CH_3	C-16, 17, 18, 22
29	-	182.38 qC	-
30	1.18 s	20.95 CH_3	C-20, 21, 29

[a, b] Overlapping signal.

Structure Elucidation of Compound II

Compound **II** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption band for a hydroxyl (ν_{max} 3272 cm^{-1}) and C-H stretching of CH_2 (ν_{max} 2923 and 2855 cm^{-1}) functional groups. The high-resolution ESIMS suggested a molecular formula of $C_{30}H_{50}O_2$, as indicated from the $[M + H]^+$ ion at *m/z* 443.3881 (calcd for $C_{30}H_{51}O_2$, 443.3889).

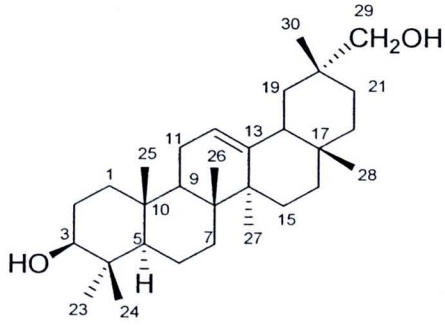
^{13}C NMR spectrum showed the presence of thirty carbons comprising seven methyls, eleven methylenes, five methines and seven quaternary carbons including one olefinic carbon at δ_C 144.80.

The ^1H NMR spectrum showed signals for seven quaternary methyl groups at δ_H 0.77, 0.83, 0.89, 0.91, 0.94, 0.97 and 1.11. A doublet of doublet signal at δ_H 3.20 (J = 11.6 and 4.9 Hz) was assigned for H-3. The signals at δ_H 5.18 (1H, t, J = 3.6 Hz), δ_C 122.15 and δ_H 3.24 (2H s), δ_C 79.03 could be assigned to olefinic and carbinolic groups, respectively. The olefinic group signals at δ_C 144.80 and 122.15 also indicated an olean-12-en.[50]

The HMBC spectrum showed long range ^1H-^{13}C correlations between H-3/C-23 (δ_C 28.32) and C-24 (δ_C 15.55) indicated the presence of a hydroxyl group at C-3. The hydroxyl group attached to C-29 was seen from the long range ^1H-^{13}C correlations between H-30 (δ_H 0.89) /C-19 (δ_C 41.00), C-20 (δ_C 36.16), C-21 (δ_C 29.00) and C-30 (δ_C 74.85).

The ^1H and ^{13}C resonances could be fully assigned by the use of ^1H-^1H-COSY, HMQC and HMBC correlation spectra (Table 2). The spectroscopic data of compound **II** was found to be similar with those reported for 3β,29-

dihydroxyolean-12-en in the literatures.[50] Compound **II** was thus concluded as 3β,29-dihydroxyolean-12-en.



Compound **II**

Table 2 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **II** in $CDCl_3$-MeOH-d_4 22:1 v/v

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	1.59	36.59 CH_2	C-2, 3, 4, 5
2	1.95 td (13.5, 4.9)[a]	26.92 CH_2	C-4
	0.76		
3	3.20 dd (11.6, 4.9)	79.03 CH	C-23
4	-	38.77 qC	-
5	0.73 dd (11.6, 1.6)	55.20 CH	C-4, 6, 7, 9, 24
6	1.54	18.36 CH_2	C-7
	1.36		
7	1.51	32.64 CH_2	C-5, 6, 8, 9, 26
	1.31		
8	-	39.80 qC	-
9	1.53	47.66 CH	C-8, 11, 26
10	-	36.95 qC	-
11	1.84 td (11.5, 3.6)	23.53 CH_2	C-8, 9, 12, 13
12	5.18 t (3.6)	122.15 CH	C-11, 14, 18

Table2 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
13	-	144.80 qC	-
14	-	41.67 qC	-
15	1.75	26.08 CH_2	C-14, 16
16	1.61	27.22 CH_2	C-15, 22
17	-	32.89 qC	-
18	1.95 td (13.5, 4.5)[a]	46.31 CH	C-12, 13, 17, 28
19	1.69 t (13.5)	41.00 CH_2	C-13, 18, 20, 21, 30
	1.00		
20	-	36.16 qC	-
21	1.41	29.00 CH_2	C-17, 19, 22
	1.06		
22	1.43	36.16 CH_2	C-17, 18, 20, 21
	1.27		
23	0.97 s	28.32 CH_3	C-3, 4, 5, 24
24	0.77 s	15.55 CH_3	C-3, 4, 5, 14
25	0.91 s	15.49 CH_3	C-1, 5
26	0.94 s	16.78 CH_3	C-7, 9, 14
27	1.11 s	26.02 CH_3	C-8, 15
28	0.83 s	28.10 CH_3	C-16, 17, 18, 22
29	3.24 s	74.85 CH_2	C-19, 20, 21, 30
30	0.89 s	18.97 CH_3	C-19, 20, 21, 29,30

[a]Overlapping signal.

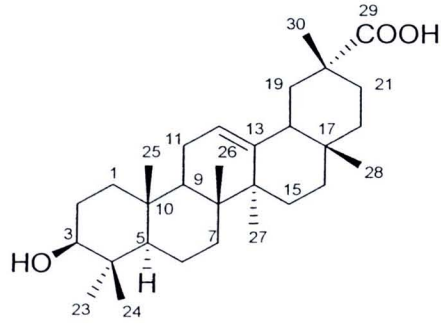
Structure Elucidation of Compound III

Compound **III** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption band for a hydroxy (ν_{max} 3368 cm^{-1}) and a carbonyl (ν_{max} 1699 cm^{-1}) functional groups. High resolution ESIMS of compound **III** gave $[M + H]^+$ ion at *m/z* 457.3676 (calcd for $C_{30}H_{49}O_3$, 457.3682) which supported the molecular formula $C_{30}H_{48}O_3$.

Most of the ^1H and ^{13}C NMR spectra of compound **III** are similar to those of compound **II**. The difference in compound **III** was that an oxygenated methylene group signals at δ_H 3.24 (2H s), δ_C 74.85 was not observed and replaced by a carboxyl group signal (δ_C 182.06).

The HMBC spectrum also showed the correlations of H-30 (δ_H 1.17) to the carboxyl carbon signal (δ_C 182.06, C-29). Full assignment of ^1H and ^{13}C NMR chemical shifts was as shown in Table 3. The ^1H and ^{13}C NMR data of compound **III** were found to be similar those reported for 3β-hydroxy-olean-12-en-29-oic acid in the literatures.[51]

Compound **III** was assigned as 3β-hydroxyolean-12-en-29-oic acid.



Compound **III**

Table 3 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **III** in $CDCl_3$-MeOH-d_4 32:1 v/v

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	1.58[a]	38.57 CH_2	C-2, 24, 25
	0.92		
2	1.98 td (13.7, 4.8)	27.20 CH_2	C-3, 5
	1.58[a]		
3	3.17 dd (10.3, 4.8)	78.89 CH	C-1, 23, 24
4	-	38.92 qC	-
5	0.68 d (11.3)	55.15 CH	C-1, 7, 24
6	1.50	18.33 CH_2	C-7
	1.37		
7	1.50	32.60 CH_2	C-5, 26
	1.26		
8	-	39.60 qC	-
9	1.51	47.59 CH	C-5, 11, 26
10	-	36.90 qC	-
11	1.92	23.51 CH_2	C-8, 9, 12, 13
	1.85		
12	5.17 t (3.5)	122.79 CH	C-11, 14, 18
13	-	144.00 qC	-
14	-	41.63 qC	-
15	1.73 td (14.0, 4.4)	25.97 CH_2	C-14, 16, 28
	0.95		
16	1.20	26.89 CH_2	C-14, 15
	1.06		
17	-	32.37 qC	-
18	1.95	46.00 CH	C-17, 16

Table 3 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
13	-	144.80 qC	-
14	-	41.67 qC	-
15	1.75	26.08 CH_2	C-14, 16
16	1.61	27.22 CH_2	C-15, 22
17	-	32.89 qC	-
18	1.95 td (13.6, 4.5)[a]	46.31 CH	C-12, 13, 17, 28
19	1.69 t (13.6)	41.00 CH_2	C-13, 18, 20, 21, 30
	1.00		
20	-	36.16 qC	-
21	1.41	29.00 CH_2	C-17, 19, 22
	1.06		
22	1.43	36.16 CH_2	C-17, 18, 20, 21
	1.27		
23	0.97 s	28.32 CH_3	C-3, 4, 5, 24
24	0.77 s	15.55 CH_3	C-3, 4, 5, 14
25	0.91 s	15.49 CH_3	C-1, 5
26	0.94 s	16.78 CH_3	C-7, 9, 14
27	1.11 s	26.02 CH_3	C-8, 15
28	0.83 s	28.10 CH_3	C-16, 17, 18, 22
29	-	74.85 CH_2	-
30	0.89 s	18.97 CH_3	C-19, 20, 21, 29

[a]Overlapping signals.

Structure Elucidation of Compound IV

Compound **IV** was obtained as a colorless amorphous solid, mp 318-319 °C. The FTIR spectrum showed absorption band for a hydroxy (ν_{max} 3400 cm^{-1}) and a carbonyl (ν_{max} 1721 cm^{-1}) functional groups. The HRESIMS suggested a molecular formula of $C_{30}H_{48}O_3$, as indicated from the $[M + Na]^+$ ion at *m/z* 479.3502 (calcd for $C_{30}H_{48}O_3Na$, 479.3501).

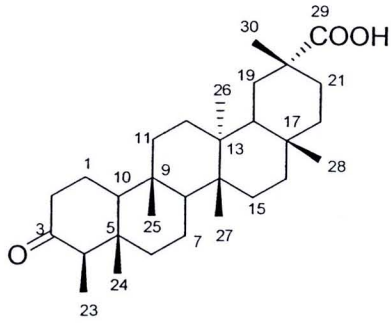
The ^{13}C NMR spectrum showed the presence of thirty carbons comprising seven methyls, eleven methylenes, four methines and eight quaternary carbons including one carbonyl carbons at δ_C 213.32 and one carboxyl carbon at δ_C 184.60.

The ^1H NMR and HMQC spectrum showed signals for seven methyl groups at δ_H 1.70, 1.24, 0.93, 0.85 × 2, 0.85 as doublet, and 0.69. The ^1H-^1H COSY spectrum indicated that proton at δ_H 2.18 (q, J = 6.9 Hz) assigned to H-4, correlated with doublet signal at δ_H 0.85 (H_3-23).

The HMBC correlations between H_3-24 (δ_H 0.69) and H_3-25 (δ_H 0.85)/C-10 (δ_C 59.85); H_3-25 and H_3-26/C-8 (δ_C 50.77) indicated a friedelane skeleton. The long range ^1H-^{13}C correlations between H_3-23 (δ_H 0.85)/C-3 (δ_C 213.32), C-4 (δ_C 58.29), C-5 (δ_C 42.06) and the HMBC correlations between H-19(δ_H 2.32)/C-13 (δ_C 39.18), C-17 (δ_C 30.12), C-18 (δ_C 44.24), C-20 (δ_C 40.46), C-29 (δ_C 184.60) and C-30 (δ_C 31.49) and between H_3-30 (δ_H 1.24)/C-29 indicated the presence of a ketone group at C-3 and carboxylic group at C-29.

Full assignment of ^1H and ^{13}C NMR chemical shifts of compound **IV** shown in Table 4. Comparison of the spectroscopic data between compound **IV** and polpunonic acid, which has been previously isolated from *Maytenus diversifolia*,[52]

it was found to be similar. Compound **IV** was thus concluded to be 3-oxofriedelan-29-oic acid, polpunonic acid.



Compound **IV**

Table 4 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **IV** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	1.96	22.27 CH_2	C-3, 10
	1.69		
2	2.38 dd (13.8, 3.4)	41.51 CH_2	C-3, 4, 10
	2.23 dd (13.8, 7.3)		
3	-	213.32 qC	-
4	2.18 q (6.9)	58.29 CH	C-3, 5, 10, 23, 24
5	-	42.06 qC	-
6	1.72	41.38 CH_2	C-7, 8, 24
	1.24[a]		
7	1.43	18.25 CH_2	C-8
	1.25[a]		
8	1.36	50.77 CH	C-10
9	-	37.45 qC	-
10	1.46	59.85 CH	C-1, 2, 4, 24

Table 4 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
11	1.46	35.33 CH_2	C-13, 25
	1.27		
12	1.54	30.27 CH_2	C-27
13	-	39.18 qC	-
14	-	39.24 qC	-
15	1.37	29.52 CH_2	C-26
	1.28		
16	1.70	36.17 CH_2	C-22, 28
	1.36		
17	-	30.12 qC	-
18	1.56	44.24 CH	C-26
19	2.32 d (13.2)	29.48 CH_2	C-13, 17, 18, 20, 27 ,29, 30
	1.54		
20	-	40.458 qC	-
21	2.14 brd (14.1)	29.42 CH_2	C-19, 20, 29
	1.55		
22	1.98 td (14.1, 4.1)	36.65 CH_2	C-18, 28
	0.93[b]		
23	0.85 d (6.9)	6.79 CH_3	C-3, 4, 5
24	0.69 s	14.66 CH_3	C-4, 5, 6
25	0.85 s	18.40 CH_3	C-8, 10, 11
26	0.85 s	16.34 CH_3	C-13, 15
27	0.93 s[b]	18.10 CH_3	C-8, 11, 14
28	1. 70 s	31.82 CH_3	C-17, 18, 22
29	-	184.60 qC	-
30	1.24 s	31.49 CH_3	C-20, 29

[a, b]Overlapping signals.

Structure Elucidation of Compound V

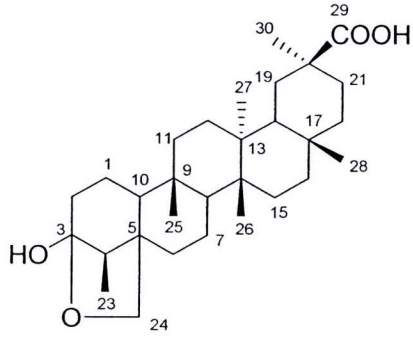
Compound **V** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption band for hydroxyl (ν_{max} 3401 cm^{-1}) and a carbonyl (ν_{max} 1742 cm^{-1}) functional groups. It was assigned the molecular formula $C_{30}H_{48}O_4$ as deduced from the HRESIMS which displayed a molecular ion at *m/z* 495.3445 corresponding to $[M + Na]^+$ (calcd for $C_{30}H_{48}O_4Na$, 493.3450).

The ^{13}C NMR spectrum showed the presence of thirty carbons comprising six methyls, twelve methylenes, four methines and eight quaternary carbons including one deoxygenated carbon at δ_C 106.24 and one carboxyl carbon at δ_C 181.68.

The ^{1}H NMR spectrum showed signals for five tertiary methyl groups at δ_H 0.82, 0.89, 1.12, 1.25, 1.42 and one secondary methyl group at δ_H 1.21 (d, J = 6.9 Hz).

Friedelane skeleton was implied from the HMBC correlations between H_3-25 (δ_H 0.89)/C-9 (δ_C 50.43), C-10 (δ_C 57.50); H_3-26 (δ_H 0.82)/C-8, C-13 (δ_C 39.73), C-15 (δ_C 29.81). The HMBC correlations between H_3-23 (δ_H 1.21)/signal at δ_C 106.24 assigned to C-3, signal at δ_C 54.10 assigned to C-4, signal at δ_C 47.30 assigned to C-5 and between signals at δ_H 4.24 and 3.71 (assigned to H_2-24)/ C-3, C-4, C-6, C-10 indicated bonding between C(3)-O to C-24 and between H-19/C-17 (δ_C 30.63), C-18 (δ_C 44.96), C-20 (δ_C 40.87), C-29 (δ_C 181.68) and C-30 (δ_C 32.48) and between H_3-30 (δ_H 1.42)/C-29 indicated the presence of a carboxyl group at C-29.

Full assignment of ^{1}H and ^{13}C NMR chemical shifts of compound **V** in Table 5. A comparison of the spectroscopic data between compound **V** and salaspermic acid, which was isolated from *Tripterygium wilfordii,*[53] indicated similarity. Compound **V** was therefore identified as salaspermic acid.



Compound **V**

Table 5 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **V** in pyridine-d_5

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	1.90 ddd (18.3, 12.3, 5.7)	20.67 CH_2	C-2, 3, 5, 10
	1.53[a]		
2	2.22 dd (12.0, 5.6)	39.20 CH_2	C-3, 4, 10
	1.93 ddd (17.4, 12.0, 6.9)		
3	-	106.24 qC	-
4	1.50	54.10 CH	C-24
	1.25		
5	-	47.30 qC	-
6	1.68	34.21 CH_2	C-4, 8, 24
	1.27		
7	1.35[b]	19.74 CH_2	C-5, 8, 9
8	1.23	50.43 CH	C-6, 10
9	-	37.79 qC	-
10	1.14	57.50 CH	C-2, 4, 24

Table 5 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
11	1.29[c]	34.96 CH_2	-
12	1.66[e]	29.67 CH_2	C-14
13	-	39.73 qC	-
14	-	39.46 qC	-
15	1.29[c, e]	29.81 CH_2	C-17, 26
16	1.35[b]	37.56 CH_2	C-28
	1.05		
17	-	30.63 qC[d]	-
18	1.53[a]	44.96 CH	C-19, 20, 22, 28
19	2.67 brd (15.0)	31.07 CH_2	C-17, 18, 20, 29, 30
	1.69		
20	-	40.87 qC	-
21	2.52 brd (13.8)	30.63 CH_2[d]	C-17, 22, 30
	1.47		
22	2.35 td (13.8, 3.8)	36.85 CH_2	C-17, 28
	1.01		
23	1.21 d (6.9)	8.70 CH_3	C-3, 4, 5
24	4.24 d (8.0)	73.22 CH_3	C-4, 6, 10
	3.71 d (8.0)		
25	0.89 s	16.87 CH_3	C-9, 10, 11
26	0.82 s	17.05 CH_3	C-8, 14, 15
27	1.25 s	18.26 CH_3	C-12, 14, 18
28	1.12 s	32.25 CH_3	C-16, 17, 16, 18
29	-	181.68 qC	-
30	1.42 s	32.48 CH_3	C-19, 20

[a-d]Overlapping signals. [e]Interchangeable signal.

Structure Elucidation of Compound VI

Compound **VI** was obtained as colorless needles. The FTIR spectrum showed absorption bands for a carbonyl (ν_{max} 1705 cm^{-1}) and an olefinic (ν_{max} 1667 cm^{-1}) functional groups. The HRESIMS spectrum suggested a molecular formula of $C_{30}H_{44}O_3$ as indicated from the $[M + Cl]^+$ ion at *m/z* 519.2894 (calcd for $C_{30}H_{44}ClO_3$, 519.2883).

The ^{13}C NMR spectrum showed the presence of thirty two carbons comprising six methyls, ten methylenes, three methines and eleven quaternary carbons including three carbonyl carbons (δ_C 195.02, 193.44, and 182.13) and two olefinic carbons (δ_C 127.47 and 146.52).

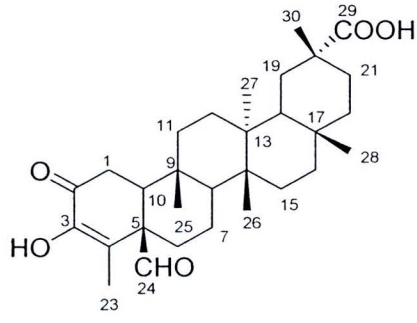
The ^1H NMR spectrum showed signals for six tertiary methyl groups at δ_H 0.80, 0.83, 0.89, 1.04, 1.19 and 1.62. The aldehyde function was observed from the low field signals at δ_H 9.59 (d, J = 1.5 Hz) and δ_C 195.02. Two sets of doublet signals at δ_H 2.83 (J = 18.2, 15.2 Hz) and 2.63 (J = 18.2, 4.8 Hz) could be assigned to methylene protons next to carbonyl group.

The ^1H-^1H COSY spectrum indicated cross-peaks between H-1 (δ_H 2.83, 2.63)/H-10 (δ_H 2.14); H-19 (δ_H 2.27 and 1.51)/H-18 (δ_H 1.50) and between H-21 (δ_H 2.10 and 1.31)/H-22 (δ_H 1.95 and 0.93).

The HMBC spectrum showing the ^3J ^1H-^{13}C correlations between H_3-25/C-8, C-10 and between H_3-26/C-8, C-13 implied a freidelane skeleton as those found in **IV**-**V**. The HMBC correlations between H-10/signal at δ_C 193.44 (C-2), δ_C 127.47 (C-4), δ_C 49.50 (C-8), δ_C 195.02 (C-24), δ_C 17.32 (C-25) indicated a keto group at C-2 and a formyl group at C-24, correlations

between H-1/C-2 (δ_C 193.44), C-3 (δ_C 146.52), C-5 (δ_C 54.70), C-9 (δ_C 36.93) and C-10 (δ_C 55.82) indicated α-hydroxy-α,β-unsaturated ketone moiety at the A-ring. Connectivity of a carboxylic group (δ_C 182.13, C-29) to C-20 was proposed from the HMBC cross-peaks between H-19/C-29 and C-30 and between H_3-30/C-29. Further use of 2D-NMR data led to full assignment of the ^1H and ^{13}C chemical shifts (Table 6).

The ^1H and ^{13}C NMR data of compound **VI** was closely related to cangoronine which had been very recently isolated from *Maytenus ilicifolia*.[23] From the above evidence compound **VI** was thus concluded to be D:A-friedooloean-24-al-3-en-3-ol-2-on-29-oic acid, cangoronine.



Compound **VI**

Table 6 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **VI** in $CDCl_3$-MeOH-d_4 15:1 v/v

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	2.83 dd (18.2, 15.2)	30.70 CH_2	C-2, 3, 5, 9, 10
	2.63 dd (18.2, 4.8)		
2	-	193.44 qC	-
3	-	146.52 qC	-
4	-	127.47 qC	-
5	-	54.70 qC	-
6	2.63 dd (18.1, 4.8)	31.39 CH_2	C-7, 8
	1.16		
7	1.55[a]	18.44 CH_2	C-6, 9, 8, 14
8	1.55[a]	49.50 CH	C-6, 25, 26
9	-	36.93 qC	-
10	2.14 dd (15.1, 4.7)	55.82 CH	C-2, 4, 5, 8, 11, 24, 25
11	1.25	33.13 CH_2	C-8, 12, 13, 25
	1.06		
12	1.29	29.59 CH_2	C-15, 18, 27
13	-	39.17 qC	-
14	-	39.11 qC	-
15	1.272	29.17 CH_2	C-16, 26
16	1.556	35.98 CH_2	C-14, 28
17	-	30.12 qC	-
18	1.50	44.21 CH	C-17, 19, 20, 22, 27
19	2.27 brd (14.6)	30.22 CH_2	C-17, 18, 20, 29, 30
	1.51		
20	-	40.21 qC	-
21	2.10 brd (11.8)	29.06 CH_2	C-20, 22, 29, 30
	1.31		

Table 6 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
22	1.95 td (14.1, 4.1)	36.47 CH_2	C-16, 17, 28
	0.93 dt (14.0, 4.1)		
23	1.62 s	10.68 CH_3	C-4, 5, 24
24	9.59 d (1.5)	195.02 CH	C-1, 5
25	0.83 s	17.32 CH_3	C-8, 9, 10, 11
26	0.80 s	16.06 CH_3	C-8, 13, 15
27	0.89 s	17.56 CH_3	C-12, 14, 18
28	1.04 s	31.76 CH_3	C-17, 18, 22
29	-	182.13 qC	-
30	1.19 s	31.67 CH_3	C-19, 20, 21, 29

[a]Overlapping signal.

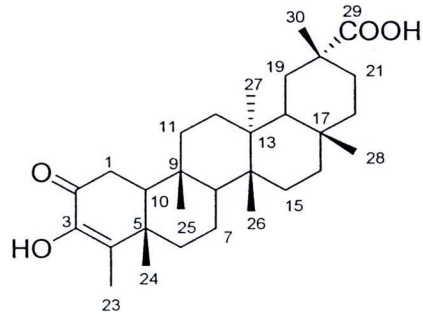
Structure Elucidation of Compound VII

Compound **VII** was afforded as colorless needles. The FTIR spectrum showed absorption bands for a carbonyl (ν_{max} 1711 cm^{-1}) and an olefinic (ν_{max} 1657 cm^{-1}) functional groups. High resolution ESIMS spectrum of compound **VII** gave $[M + Na]^+$ ion at *m/z* 493.3300 (calcd for $C_{30}H_{46}O_4Na$, 493.3282) which supported the molecular formula $C_{30}H_{46}O_4$.

Most of the ^1H and ^{13}C chemical shifts were similar to those of compound **VI**. The difference in compound **VII** was that an aldehyde group signals at around δ_H 9.59, δ_C 195.02 were not observed and replaced by the singlet signal at ca δ_H 1.01. The HMBC spectrum also showed the correlations

of methyl group signal at δ_H 1.01 (assigned to H_3-24) to C-4 (δ_C 141.73), C-5 (δ_C 39.16) and C-10 (δ_C 55.63).

The use of 2D experiments led to the assignment of ^1H and ^{13}C resonances of compound **VII** as shown in Table 7. The spectroscopic data is in good agreement with the reported data of 3-hydroxy-2-oxofriedelan-3-ene-20α-carboxylic acid isolated recently from *Tripterygium wilfordii*.[54] Compound **VII** was thus concluded to be 3-hydroxy-2-oxofriedelan-3-ene-20α-carboxylic acid.



Compound **VII**

Table 7 ^1H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **VII** in $CDCl_3$-MeOH-d_4 7:1 v/v

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	2.43 dd (13.6, 3.9)	32.43 CH_2	C-2, 4, 5, 10
	2.36 d (13.6)		
2	-	195.40 qC	-
3	-	142.50 qC	-
4	-	141.73 qC	-
5	-	39.16 qC[b]	-
6	1.79	38.25 CH_2	C- 8, 10, 24
	1.32		
7	1.49	17.86 CH_2	C-9, 14

Table 7 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
8	1.26	49.98 CH	C-14, 15, 25, 26
9	-	36.67 qC	-
10	1.71	55.63 CH	C-1, 2, 5, 8, 9, 25
11	1.60	34.21 CH_2	C-25
	1.29		
12	1.25	36.02 CH_2	C-9, 14
13	-	39.41 qC	-
14	-	39.16 qC[b]	-
15	1.20	29.17 CH_2	C-13
16	1.39	29.63 CH_2	C-14, 17, 18, 28
17	-	30.08 qC	-
18	1.49	44.29 CH	C-20, 22, 27, 28
19	2.24 d (12.3)	30.23 CH_2	C-17, 18, 20, 29
	1.46		
20	-	40.17 qC	-
21	2.05 brd (14.0)	29.00 CH_2	C-19, 22, 29, 30
	1.28		
22	1.91 td (14.0, 3.6)	36.54 CH_2	C-17, 18
23	1.74 s	10.31 CH_3	C-3, 4, 5
24	1.01 s[a]	18.73 CH_3	C-4, 5, 10
25	0.87 s	18.02 CH_3	C-8, 10, 11
26	0.80 s	16.08 CH_3	C-8, 13, 15
27	0.86 s	17.47 CH_3	C-12, 13, 18
28	1.01 s[a]	31.62 CH_3	C-17, 18, 22
29	-	181.84 qC	-
30	1.13 s	31.71 CH_3	C-19, 20, 29

[a, b]Overlapping signals.

Structure Elucidation of Compound VIII

Compound **VIII** was obtained as a reddish brown amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3368 cm^{-1}), a carbonyl (ν_{max} 1707 cm^{-1}) and an olefinic (ν_{max} 1595cm^{-1}) functional groups. The high resolution ESIMS spectrum of compound **VIII** gave $[M + H]^+$ ion at *m/z* 421.2753 (calcd for $C_{28}H_{37}O_3$, 421.2743) which supported the molecular formula $C_{28}H_{36}O_3$.

The ^{13}C NMR spectrum showed the presence of twenty eight carbons comprising six methyls, six methylenes, four methines and twelve quaternary carbons including two carbonyl carbons (δ_C 213.57 and 178.41) and five olefinic carbons (δ_C 168.69, 164.71, 146.09, 127.73 and 117.18).

The ^1H NMR spectrum showed signals for six methyl groups at δ_H 2.20, 1.43, 1.33, 1.00, 0.99 and 0.96. Olefinic proton signals were observed at δ_H 7.02, 6.53 and 6.43. The signals at δ_H 2.89 (d, J = 14.3 Hz) and 1.84 (d, J = 14.1 Hz) indicated methylene proton connecting to keto group.

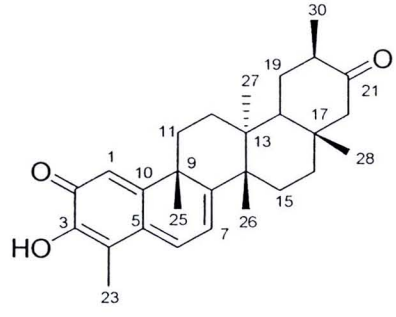
The HMBC correlation between methyl proton (δ_H 1.43, H_3-25)/olefinic carbon signals [δ_C 168.69 (C-8), 164.71 (C-10)] and between the methyl signal at δ_H 1.33 (H_3-26)/olefinic carbon signal at δ_C 168.69 (C-8), and a methelene group carbon (δ_C 28.50, C-15) indicated a friedelane with double bonds at C-1(10) and C-7(8).

The ^3J ^1H-^{13}C correlations between olefinic proton signal at δ_H 6.53 (H-1)/olefinic carbon signals at 146.09 (C-3) and 127.73 (C-5) indicated a keto group at C-2 and and enol function at C-3(4). The HMBC correlations of

proton signals at δ_H 2.89 (H-20) and 1.84 (H_2-22) with carbons signals at δ_C 32.57 (C-28), δ_C 213.57 (C-21) and of proton signal at δ_H 2.48 (H-20) with C-21, C-30 implied the presence of a keto group at C-21 and a methyl group at C-20.

The ^{1}H-^{1}H COSY spectrum also indicated cross-peaks between quintet signal at δ_H 2.48 (H-20) and signals at δ_H 2.18 and 1.74 (assigned to H_2-19) and δ_H 0.96 (d, H_3-30).

Further use of 2D-NMR data led to full assignment of the ^{1}H and ^{13}C chemical shifts (Table 8). Comparison of the spectroscopic data between compound **VIII** and tingenone, which has been previously isolated from *Kokoona ochracea*,[55] it was found to be similar. Compound **IV** was thus concluded to be tingenone.



Compound **VIII**

Table 8 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **VIII** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	6.53 s	119.79 CH	C-3, 5, 9
2	-	178.41 qC	-
3	-	146.09 qC	-
4	-	117.18 qC	-
5	-	127.73 qC	-
6	7.02 d (7.1)	133.60 CH	C-4, 8, 10
7	6.43 d (7.1)	118.15 CH	C-5, 9
8	-	168.69 qC	-
9	-	42.71 qC	-
10	-	164.71 qC	-
11	2.23	33.78 CH_2	
12	1.84	29.93 CH_2	C-9, 11
13	-	40.62 qC	-
14	-	44.64 qC	-
15	1.65[a]	28.50 CH_2	C-17
16	1.89	35.50 CH_2	C-17, 22
	1.43 brd (12.8)		
17	-	38.17 qC	-
18	1.64[a]	43.50 CH	C-12, 17, 20, 22
19	2.18	32.06 CH_2	C-17, 20, 21, 30
	1.72		
20	2.48 qint (6.4)	41.88 CH	C-21, 30
21	-	213.57 qC	-
22	2.89 d (14.3)	52.53 CH_2	C-17, 19, 21, 28
	1.84 d (14.3)		

Table 8 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
23	2.20 s	10.26 CH_3	C-3, 4, 5
24	-	-	-
25	1.43 s	39.03 CH_3	C-8, 9, 10, 11
26	1.33 s	21.55 CH_3	C-8, 13, 14, 15
27	1.00 s	19.70 CH_3	C-12, 14
28	0.99 s	32.57 CH_3	C-16, 17, 18, 22
29	-	-	-
30	0.96 d (5.2)	15.06 CH_3	C-19, 21

[a]Overlapping signal.

Structure Elucidation of Compound IX

Compound **IX** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3500 cm^{-1}) and a carbonyl (ν_{max} 1747 cm^{-1}) functional group. The HRESIMS spectrum suggested a molecular formula of $C_{38}H_{47}NO_{18}$, as indicated from the $[M + Na]^+$ ion at 828.2690 (calcd for $C_{38}H_{47}NO_{18}Na$, 828.2691).

The ^{13}C NMR spectrum showed the presence of thirty eight carbons comprising ten methyls, two methylenes, twelve methines and fourteen quaternary carbons including eight carbonyl carbons (δ_C 173.97, 170.23, 170.01, 168.92, 168.84 × 2, 168.59 and 168.46).

The ^1H NMR spectrum showed signals for six acetyl groups at δ_H 2.30, 2.19, 2.13, 2.13, 1.97 and 1.81, as well as the low-field oxymethine protons

between δ_H 7.00-4.70, and aromatic protons between δ_H 8.67-7.24, in conjunction with the ^1H-^1H COSY spectrum which showed sequential correlations from H-1 to H-3, H-5 to H-8, with two oxymethylene group signals at at δ_H 5.93 and 3.66 (both d, J = 11.5 Hz, H_2-15) and at δ_H 5.10 and 4.46 (both d, J = 13.6 Hz, H_2-11) implied the presence of a dihydro-β-agarofuran moiety commonly found in the sesquiterpene pyridine alkaloids in the *Maytenus* plants.[10]

The presence of an evoninic acid moiety[10] was implied from the ^1H-^1H COSY correlations of signals between δ_H 1.37 (d, H-9′)/4.63 (q, H-7′); 1.16 (d, H-10′)/2.55 (q, H-8′) and between pyridyl ring proton signals of H-5′/H-4′, H-6′, in addition to the ^3J ^1H-^{13}C correlations between H-7′/C-2′, C-3′, C-8′, C-9′, C-10′, C-11′, and H-4′/ C-2′, C-6′ and C-12′. Connectivities between oxygen atom at C-3 to C-11′, and oxygen atom at C-15 to C-12′ were detected from the HMBC correlations between H-3/C-11′ (δ_C 173.97), and between H_2-15 (5.93 and 3.67)/C-12′ (δ_C 168.46), respectively. Connectivities of each OAc group to a particular oxymethine carbon were also observed from HMBC correlations. Full assignment of ^1H and ^{13}C NMR chemical shifts was as shown in Table 9. Most of ^1H and ^{13}C NMR shifts are rather similar to those reported for euonymine previously isolated from *Euonymus sieboldiana*.[56] Compound **IX** was concluded to be euonymine.

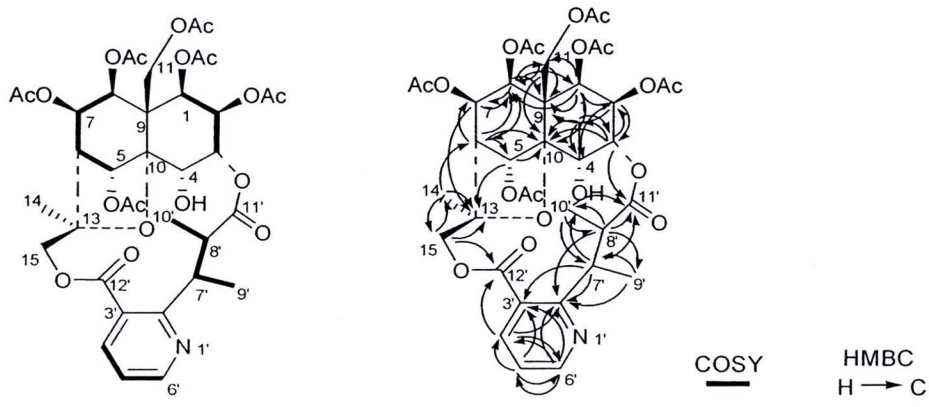
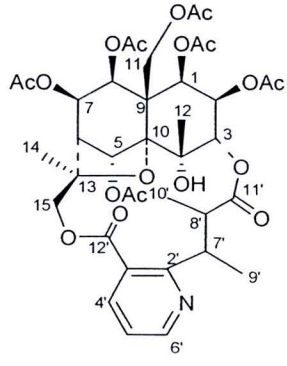


Figure 2 ^{1}H-^{1}H COSY and HMBC correlations of compound **IX**



Compound **IX**

Table 9 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **IX** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.52 d (4.0)	72.29 CH	C- 9, 10, 11, 1-O<u>C</u>OCH$_3$
2	5.21 dd (2.5, 4.0)	68.76 CH	C-3, 4, 9, 2-O<u>C</u>OCH$_3$
3	4.70 d (2.5)	75.70 CH	C-1, 2, 4, 10, 11′
4	-	70.52 qC	-
5	7.00 s	73.75 qC	C-10, 13, 5-O<u>C</u>OCH$_3$
6	2.31 d (3.1)	50.49 CH	C-5, 7, 8, 10
7	5.48 dd (6.1, 4.0)	68.96 CH	C-9, 7-O<u>C</u>OCH$_3$
8	5.33 d (6.1)	70.66 CH	C-1, 9, 11, 8-O<u>C</u>OCH$_3$
9	-	52.14 qC	-

Table 9 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
10	-	94.01 qC	-
11	5.10 d (13.6)	59.97 CH_2	C- 8, 9, 10, 11-O<u>C</u>OCH$_3$
	4.46 d (13.6)		
12	1.52 d (1.1)	22.89 CH_3	C- 3, 4, 10
13	-	84.14 qC	-
14	1.67 s	18.46 CH_3	C-6, 13, 15
15	5.93 d (11.5)	69.86 CH_2	C-13, 14, 12′
	3.67 d (11.5)		
2′	-	165.29 qC	-
3′	-	125.04 qC	-
4′	8.04 dd (7.8, 1.8)	137.72 CH	C-2′, 6′, 12′
5′	7.24 dd (7.8, 4.8)	121.08 CH	C-2′, 3′, 4′, 6′
6′	8.67 dd (4.8, 1.8)	151.47 CH	C-2′, 3′, 4′, 5′
7′	4.63 q (7.0)	36.40 CH	C-2′, 3′, 8′, 9′, 10′, 1′1
8′	2.55 q (7.0)	44.91 CH	C-2′, 7′, 9′, 10′, 11′
9′	1.37d (7.0)	11.84 CH_3	C-2′, 7′, 8′
10′	1.16 d (7.0)	9.66 CH_3	C-7′, 8′, 11′
11′	-	173.97 qC	-
12′	-	168.46 qC	-
1-OCO<u>C</u>H$_3$	1.81 s	20.39 CH_3[b]	C-1, 1-O<u>C</u>OCH$_3$
2-OCO<u>C</u>H$_3$	2.13 s	20.97 CH_3	C-2, 2-O<u>C</u>OCH$_3$
5-OCO<u>C</u>H$_3$	2.19 s	21.59 CH_3	C-5, 5-O<u>C</u>OCH$_3$
7-OCO<u>C</u>H$_3$	2.13 s	20.97 CH_3	C-7, 7-O<u>C</u>OCH$_3$
8-OCO<u>C</u>H$_3$	1.97 s	20.43 CH_3	C-8, 8-O<u>C</u>OCH$_3$
11-OCO<u>C</u>H$_3$	2.30 s	21.28 CH_3[b]	C-11, 11-O<u>C</u>OCH$_3$
1-O<u>C</u>OCH$_3$	-	168.84 qC[a]	-
2-O<u>C</u>OCH$_3$	-	168.84 qC[a]	-

Table 9 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
5-O<u>C</u>OCH$_3$	-	170.01 qC	-
7-O<u>C</u>OCH$_3$	-	168.59 qC	-
8-O<u>C</u>OCH$_3$	-	168.92 qC	-
11-O<u>C</u>OCH$_3$	-	170.23 qC	-
4-OH	5.71 brs	-	C-3, 4, 10

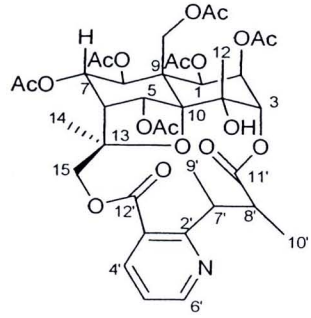
[a]Overlapping signal. [b]Interchangeable signal.

Structure Elucidation of Compound X

Compound **X** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3487 cm^{-1}) and a carbonyl (ν_{max} 1755 cm^{-1}) functional groups. It showed dark quenching spot under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{38}H_{47}NO_{18}$, as indicated from the $[M + Na]^+$ ion at 828.2685 (calcd for $C_{38}H_{47}NO_{18}Na$, 828.2691).

The ^1H and ^{13}C NMR spectra showed close resemblance to those of compound **IX**. However, the signal at δ_H 5.49 assignable for H-7 was observed as doublet of doublets with $J_{7,8}$ = 9.7 and $J_{6,7}$ = 3.3 Hz, respectively, indicated the orientation of H-7 as α.

This compound was reported previously as a chemically transformed product from evonine,[10] however no detail NMR data was given. Full assignment of ^1H and ^{13}C NMR chemical shifts was as shown in Table 10. Compound **IX** was concluded to be 7-*epi*-euonymine.



Compound **X**

Table 10 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **X** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.54 d (3.6)	72.30 CH	C- 8, 9, 11, 1-O<u>C</u>OCH$_3$
2	5.23 t (3.1)	68.47 CH	C-4, 9, 2-O<u>C</u>OCH$_3$
3	4.70 d (2.7)	75.13 CH	C-1, 2, 10, 12, 11′
4	-	70.54 qC	-
5	6.62 s	74.68 qC	C-7, 9, 10, 13, 5-O<u>C</u>OCH$_3$
6	2.45 d (3.3)	49.43 CH	C-7, 10
7	5.49 dd (9.7, 3.3)	73.57 CH	C-7, 8, 13
8	5.65 d (9.7)	73.94 CH	C-2, 9, 11, 8-O<u>C</u>OCH$_3$
9	-	51.43 qC	-
10	-	94.33 qC	-
11	4.75 d (13.2)	60.63 CH$_2$	C- 8, 9, 10, 11-O<u>C</u>OCH$_3$
	4.61 d (13.2)		
12	1.55 d (1.0)	23.82 CH$_3$	C- 3, 4, 10
13	-	85.64 qC	-
14	1.70 s	19.44 CH$_3$	C-6, 15
15	5.94 d (11.5)	69.89 CH$_2$	C-13, 14, 2′, 12′
	3.64 d (11.5)		

Table 10 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
2′	-	168.42 qC	-
3′	-	125.03 qC	-
4′	8.04 dd (7.8, 1.8)	137.70 CH	C-6′
5′	7.25 dd (7.8, 4.8)	121.06 CH	C-3′, 5′, 6′
6′	8.67 dd (4.8, 1.8)	151.51 CH	C-2′, 4′, 5′
7′	4.63 q (6.8)	36.44 CH	C-10, 2′, 8′, 9′, 10′, 11′
8′	2.57 q (6.6)	44.80 CH	C-2′, 7′, 9′, 10′, 11′
9	1.38 d (7.0)	12.02 CH_3	C-7′, 8′
10′	1.19 d (7.1)	11.48 CH_3	C-2′, 7′, 8′, 11′
11′	-	173.96 qC	-
12′	-	168.42 qC	-
1-OCO$\underline{C}H_3$	1.81 s	20.52 CH_3	C-1, 1-O$\underline{C}OCH_3$
2-OCO$\underline{C}H_3$	2.12 s	20.98 CH_3[a]	2-O$\underline{C}OCH_3$
5-OCO$\underline{C}H_3$	2.19 s	21.49 CH_3	5-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	2.00 s	20.85 CH_3[a]	C-7, 7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.96 s	20.72 CH_3	C-8, 8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.29 s	21.15 CH_3	11-O$\underline{C}OCH_3$
1-O$\underline{C}OCH_3$	-	169.03 qC	-
2-O$\underline{C}OCH_3$	-	168.55 qC	-
5-O$\underline{C}OCH_3$	-	169.66 qC	-
7-O$\underline{C}OCH_3$	-	169.81 qC	-
8-O$\underline{C}OCH_3$	-	169.60 qC	-
11-O$\underline{C}OCH_3$	-	169.97 qC	-
4-OH	4.49 d (1.25)	-	C-4, 12
5-OH	-	-	-

[a]Overlapping signal.

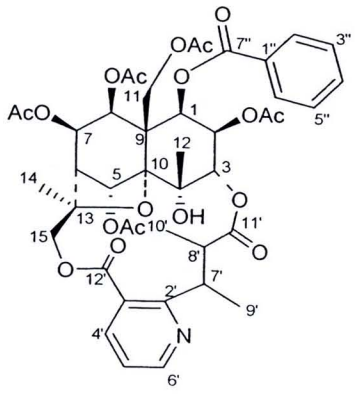
Structure Elucidation of Compound XI

Compound **XI** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3501 cm^{-1}) and a carbonyl (ν_{max} 1747 and 1732 cm^{-1}) functional group. The HRESIMS spectrum suggested a molecular formula of $C_{43}H_{49}NO_{18}$, as indicated from the $[M + H]^+$ ion at 868.3027 (calcd for $C_{43}H_{50}NO_{18}$, 868.3028).

The ^{13}C NMR spectrum showed the presence of forty three carbons comprising nine methyls, two methylenes, seventeen methines and fifteen quaternary carbons including eight carbonyl carbons (δ_C 173.98, 170.35, 169.93, 169.87, 168.86, 168.48, 168.22 and 164.52).

Compound **XI** showed rather similar patterns of ^1H and ^{13}C NMR signals as of compound **X**. However, the ^1H NMR spectrum of compound **X** showed only five acetyl groups (δ_H 2.34, 2.21, 2.20, 2.10 and 1.38), and the aromatic proton signals at δ_H 7.77 (d, J = 7.4 Hz, H-2″, 6″), 7.52 (t, J = 7.4 Hz, H-4″), 7.37 (t, J = 7.4 Hz, H-3″, 5″) indicated the presence of a benzoyl group. The long range HMBC correlations of H-1 (δ_H 5.85)/C-7″ (δ_C 164.52) indicated bonding of *O*-Bz group at C-1.

Full assignment of ^1H and ^{13}C NMR chemical shifts was as shown in Table 11 and most of ^1H and ^{13}C NMR shifts are rather similar to those reported for mayteine previously isolated from *Euonymus japonica*.[57] Compound **XI** was thus concluded to be mayteine.



Compound **XI**

Table 11 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XI** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.85 d (3.3)	73.45 CH	C-2, 8, 9, 11, 7″
2	5.33 dd (3.3, 2.4)[a]	69.17 CH	C-4, 2-O$\underline{C}$OCH$_3$
3	4.77 d (2.4)	76.62 CH	C-1, 4, 10, 11, 12
4	-	70.56 qC	-
5	7.03 s	73.81 CH	C-7, 10, 13, 5-OCO$\underline{C}$H$_3$
6	2.34 d (4.1)	50.38 CH	C-5, 7, 10, 8
7	5.50 dd (5.9, 4.1)	68.90 CH	C-1, 9, 7-O$\underline{C}$OCH$_3$
8	5.39 d (5.9)	71.32 CH	C-1, 9, 8-O$\underline{C}$OCH$_3$
9	-	52.51 qC	-
10	-	94.07 qC	-
11	5.33 d (13.5)[a]	60.01 CH$_2$	C-8, 9, 11-O$\underline{C}$OCH$_3$
	4.64 d (13.5)[b]		
12	1.56 s	22.84 CH$_3$	C-3, 4, 10
13	-	84.36 qC	-
14	1.70 s	18.40 CH$_3$	C-6, 15
15	5.95 d (11.6)	69.94 CH$_2$	C-13, 14, 12′
	3.67 d (11.6)		
2′	-	165.32 qC	-
3′	-	125.04 qC	-

Table 11 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
4′	8.06 dd (7.8, 1.9)	137.72 CH	C-2′, 6′, 12′
5′	7.26 dd (7.8, 4.7)	121.08 CH	C-3′, 6′
6′	8.69 dd (4.7, 1.9)	151.52 CH	C-2′, 4′, 5′
7′	4.65 q (6.8)[b]	36.51 CH	C-2′, 8′, 9′, 10′, 11′
8′	2.58 q (7.1)	44.77 CH	C-2′, 7′, 9′, 10′, 11′
9′	1.39 d (5.8)	11.89 CH_3	C-2′, 7′, 8′
10′	1.20 d (7.1)	9.77 CH_3	C-7′, 8′, 11′
11′	-	173.98 qC	-
12′	-	168.22 qC	-
1″	-	129.10 qC	-
2″,6″	7.77 d (7.4)	129.48 CH	C-1″, 7″
3″,5″	7.37 t (7.4)	128.48 CH	C-1″, 2″, 6″
4″	7.52 t (7.4)	133.40 CH	C-2″, 6″
7″	-	164.52 qC	-
1-OCO$\underline{C}H_3$	-	-	-
2-OCO$\underline{C}H_3$	2.21 s	20.94 CH_3	2-O$\underline{C}OCH_3$
5-OCO$\underline{C}H_3$	2.20 s[c]	21.6 CH_3	5-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	2.10 s[c]	20.86 CH_3	7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.38 s	19.85 CH_3	8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.34 s	21.33 CH_3	11-O$\underline{C}OCH_3$
1-O$\underline{C}OCH_3$	-	-	-
2-O$\underline{C}OCH_3$	-	168.86 qC[d]	-
5-O$\underline{C}OCH_3$	-	169.87 qC[e]	-
7-O$\underline{C}OCH_3$	-	169.93 qC[e]	-
8-O$\underline{C}OCH_3$	-	168.48 qC[d]	-
11-O$\underline{C}OCH_3$	-	170.35 qC	-
4-0H	4.53 brs	-	C-4, 10, 12

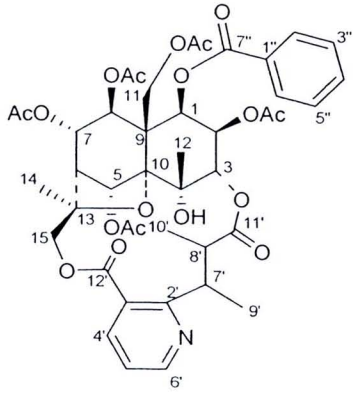
[a, b, c] Overlapping signals. [d, e] Interchangeable signals.

Structure Elucidation of Compound XII

Compound **XII** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3492 cm^{-1}) and a carbonyl (ν_{max} 1748 cm^{-1}) functional group. It showed dark quenching spot under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{43}H_{49}NO_{18}$, as indicated from the $[M+Na]^+$ ion at 890.2842 (calcd for $C_{43}H_{49}NO_{18}Na$, 890.2847).

The ^1H and ^{13}C NMR spectra showed close resemblance to those of compound **XI**. However, the signal at δ_H 5.50 (H-7) was observed as doublet of doublets with $J_{7,8}$ = 9.7 and $J_{6,7}$ = 3.2 Hz, respectively, indicated the orientation of H-7 as α.

Full assignment of ^1H and ^{13}C NMR chemical shifts was as shown in Table 12. Most of ^1H and ^{13}C NMR shifts are rather similar to those reported for 8β-acetoxy-1-*O*-benzoyl-1-*O*-deacetyl-8-deoxoevonine, 7-*epi*-mayteine previously isolated from *Maytenus vitis-idaea* and *Maytenus spinosa*.[19] Compound **XII** was concluded to be 7-*epi*-mayteine.



Compound **XII**

Table 12 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XII** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.86 d (3.7)	72.47 CH	C- 8, 9, 11, 7″
2	5.35 dd (3.7, 2.8)	68.76 CH	C-4, 9
3	4.78 d (2.8)	75.02 CH	C-2, 10, 11′
4	-	70.58 qC	-
5	6.63 s	74.74 qC	C-7, 10, 13
6	2.45 d (3.2)	49.51 CH	C-7, 10
7	5.50 dd (9.7, 3.2)	73.47 CH	C-8, 13
8	5.39 d (9.7)	74.04 CH	C-1, 7, 9, 11
9	-	51.82 qC	-
10	-	94.33 qC	-
11	4.91 d (13.2)	60.61 CH_2	C-8, 9, 10
	4.85 d (13.2)		
12	1.60 d (1.0)	23.91 CH_3	C-3, 4, 10
13	-	85.79 qC	-
14	1.74 s	19.38 CH_3	C-6, 13, 15
15	5.95 d (11.4)	69.94 CH_2	C-13, 14,
	3.67 d (11.4)		
2′	-	165.33 qC	-
3′	-	125.07 qC	-
4′	8.06 dd (7.8, 1.8)	137.90 CH	C-2′, 6′, 12′
5′	7.25 dd (7.8, 4. 8)	121.08 CH	C-3′
6′	8.69 dd (4.8, 1.8)	151.42 CH	C-4′, 5′
7′	4.65 q (7.0)	36.51 CH	C-8′, 9′, 10′
8′	2.62 q (7.0)	44.79 CH	C-7′, 9′, 10′
9′	1.39 d (7.0)	12.07 CH_3	C-7′

Table 12 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
10′	1.23 d (7.0)	9.93 CH_3	C-7′
11′	-	173.95 qC	-
12′	-	168.15 qC	-
1″	-	129.53 qC	-
2″,6″	7.76 dd (7.4, 1.2)	129.33 CH	C-1″, 4″
3″,5″	7.37 t (7.4)	128.48 CH	C-1″
4″	7.50 tt (7.4, 1.2)	133.40 CH	C-2″, 6″
7″	-	164.43 qC	-
2-OCO$\underline{C}H_3$	2.12 s	20.82 CH_3	2-O$\underline{C}OCH_3$
5-OCO$\underline{C}H_3$	2.21 s[a]	21.47 CH_3	5-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	1.93 s[a]	20.75 CH_3	7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.38 s	20.10 CH_3	8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.31 s	21.15 CH_3	11-O$\underline{C}OCH_3$
2-O$\underline{C}OCH_3$	-	168.37 qC	-
5-O$\underline{C}OCH_3$	-	169.67 qC	-
7-O$\underline{C}OCH_3$	-	169.77 qC[b]	-
8-O$\underline{C}OCH_3$	-	169.45 qC[b]	-
11-O$\underline{C}OCH_3$	-	170.35 qC	-
4-0H	4.51 d (1.2)	-	C-4, 10, 12

[a, b] Interchangeable signals.

Structure Elucidation of Compound XIII

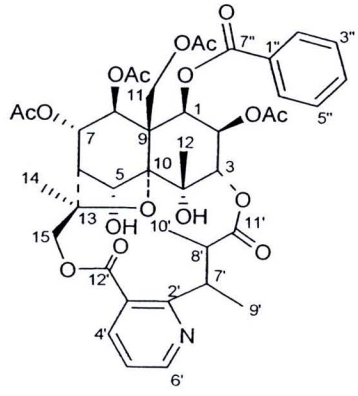
Compound **XIII** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3400 cm^{-1}) and a carbonyl (ν_{max} 1748 cm^{-1}) functional group. It showed dark quenching spot

under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{41}H_{47}NO_{17}$, as indicated from the $[M+Na]^+$ ion at 848.2736 (calcd for $C_{41}H_{47}NO_{17}Na$, 848.2742).

The ^{13}C NMR spectrum showed the presence of forty one carbons comprising eight methyls, two methylenes, sixteen methines and fifteen quaternary carbons including seven carbonyl carbons (δ_C 173.74, 170.03, 169.84, 169.46, 168.80, 168.03 and 164.43).

The ^1H NMR spectrum of compound **XIII** showed similar patterns of NMR signals as those of compound **IX**, but with four acetyl groups at (δ_H 2.24, 2.13, 1.92, and 1.36), and the signal assignable to H-5 resonated at δ_H 5.21 (d, J = 2.6 Hz), which is more shielded than those in **IX** thus indicating C-5 as a free hydroxylated carbon. The HMBC correlations between H-5/C-7 (δ_C 73.21), C-10 (δ_C 94.33) and C-13 (δ_C 86.14) were also detected.

Full assignment of ^1H and ^{13}C NMR chemical shifts was as shown in Table 13. Most of ^1H and ^{13}C NMR shifts are rather similar to those reported for euojaponine A previously isolated from *Euonymus japonica*.[57] However, the doublet of doublets assignable to H-7 at δ_H 5.47 showed a $J_{7,8}$ value of 9.8 Hz and $J_{6,7}$ of 3.0 Hz thus required the orientation of H-7 as β. The NOE difference technique which indicated interactions between H-5/H-6, H-7 and H_3-12 provided further support to the assignment. Compound **XIII** was concluded to be 7-*epi*-euojaponine A.



Compound **XIII**

Table 13 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XIII** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.84 d (3.5)	72.30 CH	C-2, 8, 9, 10, 7″
2	5.37 t (3.1)	68.43 CH	C-1?, 4, 2-O<u>C</u>OCH$_3$
3	4.77 d (2.6)[a]	74.33 CH[d]	C-1, 2, 10, 12
4	-	70.47qC	-
5	5.21 d (2.6)	76.70 qC[c]	C-7, 10, 13
6	2.54 brd (2.9)	51.37 CH[b]	C-5, 7, 8, 10, 13
7	5.47 dd (9.8, 3.1)	73.21 CH	C-6, 8, 13, 7-O<u>C</u>OCH$_3$
8	5.76 d (9.8)	74.15 CH[d]	C-1, 6, 7, 11, 8-O<u>C</u>OCH$_3$
9	-	51.37 qC[b]	-
10	-	94.33 qC	-
11	5.02 d (13.2)	60.37 CH$_2$	C-1, 8, 10, 11-O<u>C</u>OCH$_3$
	4.70 d (13.2)		
12	1.88 s	23.95 CH$_3$	C- 4, 10
13	-	86.14 qC	-
14	1.74 s	19.61 CH$_3$	C-6, 13, 15
15	6.07 d (12.0)	70.81 CH$_2$	C-13, 14, 12′
	3.66 d (12.0)		

Table 13 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
2′	-	165.85 qC	-
3′	-	125.40 qC	-
4′	8.13 dd (7.8, 1.7)	138.15 CH	C-2′, 6′, 12′
5′	7.27 dd (7.8, 4.8)	121.18 CH	C-3′, 6′
6′	8.69 dd (4.8, 1.7)	151.69 CH	C-2′, 4′, 5′
7′	4.79 q (6.7)[a]	36.14 CH	C-2′, 3′, 10′, 11′
8′	2.58 q (7.2)	45.26 CH	C-2′, 7′, 10′, 11′
9′	1.40 d (7.0)	11.55 CH_3	C-2′, 7′
10′	1.18 d (7.1)	9.742 CH_3	C-7′
11′	-	173.74 qC	-
12′	-	168.80 qC	-
1″	-	129.45 qC	-
2″,6″	7.76 d (7.7)	129.30 CH	C-1″, 4″, 7″
3″,5″	7.37 brt (7.7)	128.44 CH	C-1″, 2″, 6″
4″	7.50 brt (7.7)	133.24 CH	C-2″, 6″
7″	-	164.43 qC	-
2-OCO$\underline{C}H_3$	2.13 s	20.82 CH_3[c]	C-2, 2-O$\underline{C}OCH_3$
5-OCO$\underline{C}H_3$	-	-	-
7-OCO$\underline{C}H_3$	1.92 s	20.82 CH_3[c]	C-7, 7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.36 s	20.09 CH_3	C-8, 8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.24 s	21.34 CH_3	11-O$\underline{C}OCH_3$
2-O$\underline{C}OCH_3$	-	168.03 qC	-
7-O$\underline{C}OCH_3$	-	169.84 qC	-
8-O$\underline{C}OCH_3$	-	169.46 qC	-
11-O$\underline{C}OCH_3$	-	170.03 qC	-
4-0H	5.71 brs	-	C-4, 12
5-OH	6.12 d (2.9)	-	C-5, 6, 10

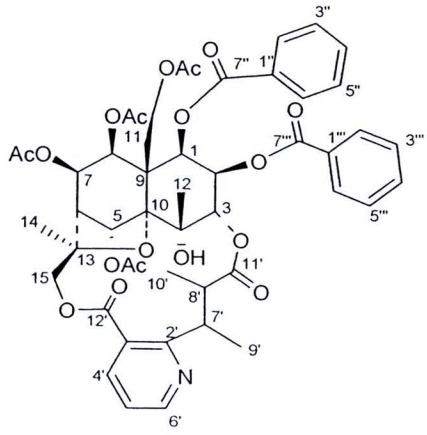
[a-c]Overlapping signals. [d]Interchangeable signal. [c]Obscured by solvent signal.

Structure Elucidation of Compound XIV

Compound **XIV** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3494 cm^{-1}) and a carbonyl (ν_{max} 1746 and 1723 cm^{-1}) functional group. It showed dark quenching spot under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{48}H_{51}NO_{18}$, as indicated from the $[M+H]^+$ ion at 930.3193 (calcd for $C_{48}H_{52}NO_{18}$, 930.3184).

The ^{13}C NMR spectrum showed the presence of forty eight carbons comprising eight methyls, two methylenes, twenty two methines and sixteen quaternary carbons including eight carbonyl carbons (δ_C 173.91, 170.48, 169.93 × 2, 168.86, 168.52, and 164.66 × 2).

The ^1H NMR spectrum of compound **XIV** showed similar patterns of NMR signals as those of compound **XI**, but with four acetyl groups (at δ_H 2.29, 2.21, 2.11, and 1.31), and signals between δ_H 8.09-7.28 revealed the presence of two benzoyl groups. The HMBC correlations between H-1 (δ_H 6.02)/the higher-field carbonyl signal at δ_C 164.66 (C-7″), and between H-2 (δ_H 5.60)/C-7‴ (δ_C 164.66) indicated that one *O*-Bz group connected to C-1 and the second group at C-2, respectively. The broad singlet at δ_H 7.04 (H-5) which showed long-range HMBC correlation with a carbonyl carbon at δ_C 169.93 implied a C(5)-OAc linkage. Most of the ^1H and ^{13}C NMR resonances are rather similar to those reported for mayteine previously isolated from *Maytenus ebenifolia*.[10] Compound **XIV** could be therefore identified as 2-*O*-benzoyl-2-deacetylmayteine.



Compound **XIV**

Table 14 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XIV** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	6.02 d (4.2)	73.30 CH	C-8, 9, 11, 7″
2	5.60 dd (4.2, 2.4)[a]	69.81 CH	C-2, 3, 9, 2-O<u>C</u>OCH$_3$
3	4.93 d (2.4)	75.61CH	C-1, 10, 12, 11′
4	-	70.50 qC	-
5	7.04 brs	73.77 qC	C-6, 7, 10, 13
6	2.37 d (4.1)	51.37 CH	C-5, 7, 8, 10
7	5.53 dd (5.9, 4.1)	68.86 CH	C-6, 8, 9, 7-O<u>C</u>OCH$_3$
8	5.45 d (5.9)	71.31 CH	C-1, 9, 11, 8-O<u>C</u>OCH$_3$
9	-	52.49 qC	-
10	-	94.09 qC	-
11	5.63 d (13.4)[a]	60.56 CH$_2$	C-8, 9, 10, 11-O<u>C</u>OCH$_3$
	4.56 d (13.4)[b]		
12	1.66 s	23.24 CH$_3$	C-3, 4, 10
13	-	84.39 qC	-
14	1.73 s	18.48 CH$_3$	C-6, 13, 15

Table 14 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
15	5.98 d (11.5)	69.95 CH_2	C-13, 14, 12′
	3.71 d (11.5)		
2′	-	165.39 qC	-
3′	-	125. 05 qC	-
4′	8.07 m[c]	137.76 CH	C-6′
5′	7.27 t (4.9)[d]	121.10 CH	C-3′, 6′
6′	8.69 dd (4.9, 1.8)	151.53 CH	C-2′, 4′, 5′
7′	4.67 q (7.0)	36.51 CH	C-2′, 3′, 8′, 9′, 10′, 11′
8′	2.64 q (7.0)	44.94 CH	C-2′, 7′, 9′, 10′, 11′
9′	1.39 d (7.0)	11.93 CH_3	C-2′, 7′, 8′
10′	1.22 d (7.1)	9.83 CH_3	C-7′, 8′, 11′
11′	-	173.91 qC	-
12′	-	168.52 qC	-
1″	-	129.52 qC[e]	-
2″,6″	8.09 m[c]	130.00 CH	C- 4″
3″,5″	7.50 brt (7.4)	128.76 CH	C-1″
4″	7.61 brt (7.4)	133.35 CH[f]	C-2″, 6 ″
7″	-	164.66 qC[g]	-
1‴	-	129.52 qC[e]	-
2‴, 6‴	7.71 dd (7.3, 1.0)	129.58 CH	C- 1‴, 4‴
3‴, 5‴	7.28 m[d]	128.39 CH	C- 1‴
4‴	7.46 brt (7.3)	133.35 CH[f]	C- 2‴, 6‴
7‴	-	164.66 qC[g]	-
5-OCO$\underline{C}H_3$	2.21 s	21.63 CH_3	C-5, 5-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	2.11 s	20.97 CH_3	C-7, 7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.31 s	19.77 CH_3	C-8, 8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.29 s	21.26 CH_3	11-O$\underline{C}OCH_3$

Table 14 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
5-O<u>C</u>OCH$_3$	-	169.93 qC	-
7-O<u>C</u>OCH$_3$	-	169.93 qC	-
8-O<u>C</u>OCH$_3$	-	168.86 qC	-
11-O<u>C</u>OCH$_3$	-	170.48 qC	-
4-0H	4.56 d (1. 0)[b]	-	C-4, 12

[a-g]Overlapping signals.

Structure Elucidation of Compound XV

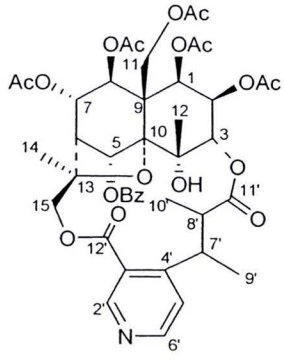
Compound **XV** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3493 cm^{-1}) and a carbonyl (ν_{max} 1748 and 1723 cm^{-1}) functional group. It showed dark quenching spot under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{43}H_{49}NO_{18}$, as indicated from the $[M+H]^+$ ion at 868.3049 (calcd for $C_{43}H_{50}NO_{18}$, 868.3028).

The ^{13}C NMR spectrum showed the presence of forty three carbons comprising nine methyls, two methylenes, seventeen methines and fifteen quaternary carbons including eight carbonyl carbons (δ_C 173.54, 170.01, 169.73, 169.65, 169.11, 168.61, 168.02 and 165.71).

The ^{1}H NMR spectrum showed five acetyl groups at δ_H 2.36, 2.13, 2.01, 1.98 and 1.83, and aromatic protons of one benzoyl group between δ_H 8.29-7.47. The ^{1}H-^{1}H COSY spectrum indicated the connectivity between protons of the dihydroagrarofuran moiety[10] and also connectivity between H-8′/H-10′

and H-7′, and between H-7′/H-9′. Signals of the pyridyl nucleus showed however a singlet at δ_H 8.95 and two doublets at δ_H 8.69 and 7.37, both with J = 5.2 Hz, which are different from those found in the evoninic acid nucleus as observed in **IX-XIV**,[10] thus indicated compound **XV** to possess an isomeric evoninic acid moiety. The HMBC spectrum showing ^3J correlations between H_2-15 and H-2′/C-12′, and between H-5′/C-7′ thus required an arrangement of the pyridyl ring as a 3,4-disubstituted.[59] The HMBC correlations between H-5, H-2″ and H-6″/carbonyl carbon (δ_C 165.71, C-7″) indicated a connection of C-5 to an *O*-benzoyl group.

Full assignment of the ^{1}H and ^{13}C NMR chemical shifts is as shown in Table 15. Compound **XV** could therefore be assigned accordingly as 7-*epi*-5-*O*-benzoyl-5-deacetylperitassine A.[58]



Compound **XV**

Table 15 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XV** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.59 d (3.5)	72.29 CH	C- 8, 9, 11, 1-O<u>C</u>OCH$_3$
2	5.27 t (3.1)	68.39 CH	C-3, 4, 9, 2-O<u>C</u>OCH$_3$
3	4.73 d (2.9)[a]	75.39 CH	C-1, 2, 4, 10, 12, 11′
4	-	70.83 qC	-
5	6.75 brs	75.75 qC	C-9, 10, 13, 7″
6	2.61 d (2.5)	49.66 CH	C-7, 8, 10, 15
7	5.69 dd (9.8, 2.9)	73.23 CH	C-8, 9, 13, 7-O<u>C</u>OCH$_3$
8	5.72 d (9.8)	74.12 CH	C-1, 7, 8-O<u>C</u>OCH$_3$
9	-	51.65 qC	-
10	-	94.11 qC	-
11	4.76 d (13.3)	60.59 CH$_2$	C- 8, 9
	4.71 d (13.3)		
12	1.57 d (1.1)	23.66 CH$_3$	C- 3, 4, 10
13	-	83.85 qC	-
14	1.75 s	19.35 CH$_3$	C-6, 13, 15
15	6.05 d (11.6)	70.21 CH$_2$	C-13, 14, 12′
	3.58 d (11.6)		
2′	8.95 s	150.86 CH	C-3′, 4′, 6′, 12′
3′	-	125.32 qC	-
4′	-	156.34 qC	-
5′	7.37 d (5.2)	121.63 CH	C-3′, 6′, 7′, 12′
6′	8.69 d (5.2)	152.83 CH	C-2′, 4′, 5′
7′	4.73 m[a]	33.24 CH	C-3′, 4′, 5′, 8′, 10′
8′	2.49 q (7.3)	45.56 CH	C-4′, 7′, 10′, 11′

Table 15 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
9′	1.39 d (7.2)	11.50 CH_3	C-4′, 7′, 8′
10′	1.10 d (7.2)	10.02 CH_3	C-7′, 8′, 11′
11′	-	173.54 qC	-
12′	-	168.02 qC	-
1″	-	129.26 qC	-
2″,6″	8.29 dd (7.3, 1.4)	130.33 CH	C-1″, 4″, 7″
3″,5″	7.47 brt (7.3)	128.84 CH	C-1″
4″	7.57 tt (7.3, 1.3)	133.66 CH	C-2″, 6″
7″	-	165.71 qC	-
1-OCO$\underline{C}H_3$	1.83 s	20.53 CH_3	C-1, 1-O$\underline{C}OCH_3$
2-OCO$\underline{C}H_3$	2.13 s	20.99 CH_3	C-2, 2-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	2.01 s[b]	20.85 CH_3	7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.98 s[b]	20.72 CH_3	C-8, 8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.36 s	21.26 CH_3	11-O$\underline{C}OCH_3$
1-O$\underline{C}OCH_3$	-	169.11 qC	-
2-O$\underline{C}OCH_3$	-	168.61 qC	-
7-O$\underline{C}OCH_3$	-	169.73 qC	-
8-O$\underline{C}OCH_3$	-	169.65 qC	-
11-O$\underline{C}OCH_3$	-	170.01 qC	-
4-OH	5.02 d (1.3)	-	C-4, 12

[a]Overlapping signal. [b]Interchangeable signal.

Structure Elucidation of Compound XVI

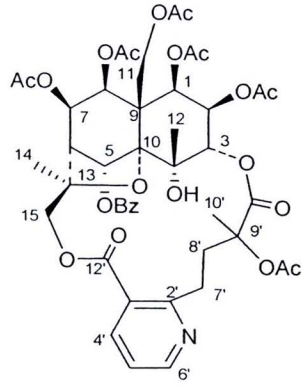
Compound **XVI** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3542 cm^{-1}) and an ester carbonyl (ν_{max} 1748 cm^{-1}) functional group. It showed dark quenching spot under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{45}H_{51}NO_{20}$ as indicated from the $[M+Na]^+$ ion at 948.2902 (calcd for $C_{45}H_{51}NO_{20}Na$, 948.2902).

The ^{13}C NMR spectrum showed the presence of forty five carbons comprising nine methyls, four methylenes, fifteen methines and seventeen quaternary carbons including nine carbonyl carbons (δ_C 171.49, 170.94, 170.15, 170.10, 168.89, 168.73, 168.32, 167.37 and 165.60).

The ^1H NMR spectrum of compound **XVI** consisted of well-spread signals of six acetyl groups at δ_H 2.27, 2.23, 2.12, 2.10, 1.98, and 1.89, as well as the low-field oxymethine protons between δ_H 5.60-5.02, and aromatic protons between δ_H 8.18-7.45. The ^1H-^1H COSY spectrum showed connectivity between protons of the dihydroagrarofuran moiety.[10] The HMBC cross-peaks between singlet at δ_H 7.01 (H-5) and *ortho*-aromatic proton at δ_H 8.18 with the higher-field carbonyl signal at δ_C 165.6 indicated bonding between an *O*-Bz group and C-5. The singlet at δ_H 1.74 (H_3-10′) and two sets of mutually coupled multiplet signals of the non-equivalent methylene protons (H_2-7′) at δ_H 3.71 and 3.01, and of H_2-8′ at δ_H 2.65 and 2.17, in addition to the HMBC correlations of H_3-10′/C-8′ (δ_C 37.74), C-9′ (δ_C 80.41) and C-11′ (δ_C 171.49) indicated the presence of an oxygenated wilfordic acid moiety in **XVI**.[59] Connectivities between C(15)-

O/C-12′, and C(3)-O/C-11′ were based on the HMBC cross-peaks of H-15, and H-4′ (δ_H 8.13)/C-12′ (δ_C 167.37), and of H-3 (δ_H 5.02), and H_2-8′/C-11′, respectively. In addition, the long-range HMBC correlation between OCOCH_3-9′/C-9′ required the presence of an OAc group at C-9′. The signal at δ_H 5.60, assigned to H-7, was observed as doublet of doublets with $J_{7,8}$ = 6.6 and $J_{6,7}$ = 3.8 Hz, respectively.

The NOE difference experiment which revealed NOE interactions between H-5/H-6 and H_3-12, and no NOE effect between H-5/H-7 implied the orientation of H-7 as α. Based on the spectroscopic data (Table 16), compound **XVI** was identified as 2,9′-di-*O*-acetyl-5-*O*-benzoyl-5-deacetylwilforidine.[59] Since this compound was not previously isolated, it was given the name mekongensine.



Compound **XVI**

Table 16 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XVI** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.59 d (3.8)[a]	72.48 CH	C- 2, 8, 11, 1-O<u>C</u>OCH$_3$
2	5.19 dd (3.8, 2.7)[b]	69.34 CH	C-1, 4, 11, 2-O<u>C</u>OCH$_3$
3	5.02 d (2.7)	77.91 CH	C-1, 2, 4, 10, 12, 11′
4	-	70.10 qC	-
5	7.01 brs	74.98 qC	C-6, 7, 10, 13
6	2.53 d (3.8)	50.94 CH	C-5, 7, 8, 10
7	5.60 dd (6.6, 3.8)[a]	68.83 CH	C-5, 8, 11, 7-O<u>C</u>OCH$_3$
8	5.39 d (6.6)	71.91 CH	C-1, 6, 8-O<u>C</u>OCH$_3$
9	-	52.36 qC	-
10	-	92.95 qC	-
11	5.20 d (13.4)[b]	60.31 CH$_2$	C- 1, 8, 9, 10, 11-O<u>C</u>OCH$_3$
	4.55 d (13.4)		
12	1.57 d (0.6)	23.05 CH$_3$	C- 3, 4, 10
13	-	83.95 qC	-
14	1.63 s	17.99 CH$_3$	C-15
15	5.41 d (12.2)	69.94 CH$_2$	C-6, 13, 14, 12′
	3.93 d (12.2)		
2′	-	160.61 qC	-
3′	-	125.71 qC	-
4′	8.13 dd (7.8, 1. 8)	139.33 CH	C-2′, 6′
5′	7.26 dd (7.8, 4.8)	121.52 CH	C-3′, 6′
6′	8.67 dd (4.8, 1.8)	151.80 CH	C-2′, 4′, 5′
7′	3.71 ddd (14.3, 12.5, 4.2)	31.01 CH$_2$	C-2′
	3.01 ddd (14.3, 12.5, 4.2)		
8′	2.65 ddd (13.9, 12.5, 4.3)	37.74 CH$_2$	C-7′, 9′, 11′
	2.17 m		

Table 16 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
9′	-	80.41 qC	-
10′	1.74 s	22.31 CH_3	C-8′, 9′, 11′
11′	-	171.49 qC	-
12′	-	167.37 qC	-
1″	-	129.16 qC	-
2″,6″	8.18 dd (7.6, 1.3)	130.26 CH	C-1″, 4″, 7″
3″,5″	7.45 t (7.6)	128.87 CH	C-1″, 7″
4"	7.56 tt (7.6, 1.3)	133.73 CH	C-2″, 6″
7"	-	165.60 qC	-
1-OCO$\underline{C}H_3$	1.98 s	20. 55 CH_3	C-1, 1-O$\underline{C}OCH_3$
2-OCO$\underline{C}H_3$	1.89 s	20. 97CH_3[c]	C-2, 2-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	2.23 s	20. 08 CH_3	C-7, 7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	2.12 s	20. 48 CH_3	C-8, 8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.27 s	21.40 CH_3[c]	C-11, 11-O$\underline{C}OCH_3$
9′-OCO$\underline{C}H_3$	2.10 s	20.08 CH_3	C-9′, 9′-O$\underline{C}OCH_3$
1-O$\underline{C}OCH_3$	-	168.73 qC	-
2-O$\underline{C}OCH_3$	-	168.32 qC	-
7-O$\underline{C}OCH_3$	-	170.15 qC	-
8-O$\underline{C}OCH_3$	-	168.89 qC	-
11-O$\underline{C}OCH_3$	-	170.10 qC	-
9'-O$\underline{C}OCH_3$	-	170.94 qC	-
4-OH	4.14 d (1.0)	-	C-4, 12, 10

[a, b]Overlapping signals. [c]Interchangeable signal.

Structure Elucidation of Compound XVII

Compound **XVII** was isolated as a colorless solid with same molecular formula as **XVI**. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3540 cm^{-1}) and an ester groups (ν_{max} 1755 and 1732 cm^{-1}). The ^{1}H and ^{13}C NMR spectra showed close resemblance to those of compound **XVI** (Table 17). However, the signal at δ_H 5.77 (H-7) was observed as doublet of doublets with $J_{7,8}$ = 9.5 and $J_{6,7}$ = 3.6 Hz, respectively, indicating different orientation at C-7 as compare to that of **XVI**. The NOE difference technique indicated interactions between H-5/H-6, H-7 and H_3-12 provided support to the assignment of H-7 as α. Compound **XVII** was accordingly proposed as a 7-epimer of compound **XVI** and given the name 7-*epi*-mekongensine.[59] The ORTEP structure of compound **XVII** was finally obtained after X-ray crystallographic analysis (Figure 3).

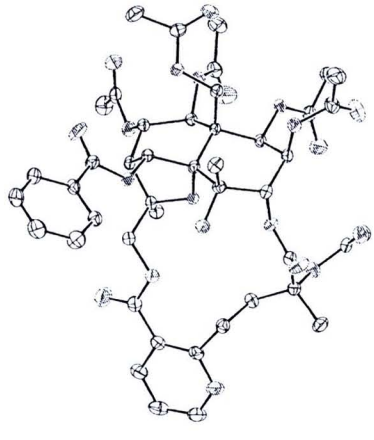
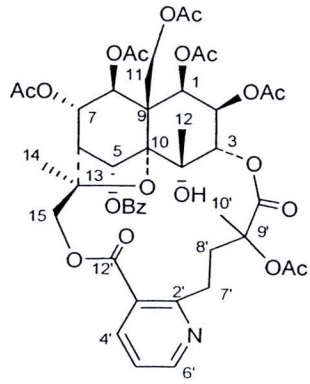


Figure 3 ORTEP drawing of compound **XVII**



Compound **XVII**

Table 17 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XVII** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.62 d (3.5)	71.65 CH	C- 2, 9, 10, 11, 1-O<u>C</u>OCH$_3$
2	5.17 dd (3.5, 2.6)	68.98 CH	C-3, 4, 9, 2-O<u>C</u>OCH$_3$
3	5.00 d (2.6)	77.30 CH	C-2, 4, 10, 12, 11′
4	-	70.29 qC	-
5	6.69 brs	75.74 qC	C-9, 10, 13
6	2.61 d (3.6)[a]	50.08 CH	C-5, 6, 8, 13, 10, 15
7	5.77 dd (9.5, 3. 6)	73.09 CH	C-6, 8, 13, 7-O<u>C</u>OCH$_3$
8	5.68 d (9.5)	74.82 CH	C-1, 9, 11, 8-O<u>C</u>OCH$_3$
9	-	51.79 qC	-
10	-	93.12 qC	-
11	4.82 d (13.3)	60.51 CH$_2$	C-1, 8, 9, 10, 11-O<u>C</u>OCH$_3$
	4.60 d (13.3)		
12	1.60 s	23.81 CH$_3$	C- 3, 10
13	-	85.47 qC	-
14	1.67 s	19.01 CH$_3$	C-6, 13
15	5.46 d (12.0)	69.95 CH$_2$	C-13, 14,12′
	3.89 d (12.0)		

Table 17 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
2′	-	160.53 qC	-
3′	-	125.99 qC	-
4′	8.13 dd (7.8, 1.7)	139.89 CH	C-2′, 6′
5′	7.28 dd (7.8, 4.9)	121.81 CH	-
6′	8.71 dd (4.8, 1.7)	151.79 CH	-
7′	3.61 dt (13.3, 4.4)	30.77 CH_2	C-2′, 8′
	3.02 dt (13.3, 4.4)		
8′	2.61 dt 13.7, 4.4)[a]	44.80 CH_2	C-7′, 9′, 10′, 11′
	2.19 m		
9′	-	80.36 qC	-
10′	1.75 s	21.80 qC	C-8′, 9′, 11′
11′	-	171.33 qC	-
12′	-	167.04 qC	-
1″	-	128.91 qC[c]	-
2″,6″	8.20 dd (7.7, 1.4)	130.32 CH	C-3″, 5″, 4″
3″,5″	7.45 t (7.7)	128.91 CH[c]	C-1″
4″	7.57 t (7.7)	133.85 CH	C-2″, 6″
7″	-	165.63 qC	-
1-OCO$\underline{C}H_3$	1.86 s	20.59 CH_3	C-1, 1-O$\underline{C}OCH_3$
2-OCO$\underline{C}H_3$	2.11 s	20.93 CH_3	C-2, 2-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	1.99 s	20.80 CH_3	C-7, 7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.97 s	20.74 CH_3[d]	C-8, 8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.36 s	21.28 CH_3[d]	C-11, 11-O$\underline{C}OCH_3$
9′-OCO$\underline{C}H_3$	2.15 s	21.21 CH_3	C-9′, 9′-O$\underline{C}OCH_3$
1-O$\underline{C}OCH_3$	-	168.49 qC	-
2-O$\underline{C}OCH_3$	-	168.29 qC	-
7-O$\underline{C}OCH_3$	-	169.99 qC	-

Table 17 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
8-O<u>C</u>OCH$_3$	-	169.70 qC[b]	-
11-O<u>C</u>OCH$_3$	-	169.70 qC[b]	-
9'-O<u>C</u>OCH$_3$	-	171.00 qC	-
4-OH	4.24 d (1.0)	-	C-4, 12, 10

[a, b] Overlapping signals. [c, d] Interchangeable signals.

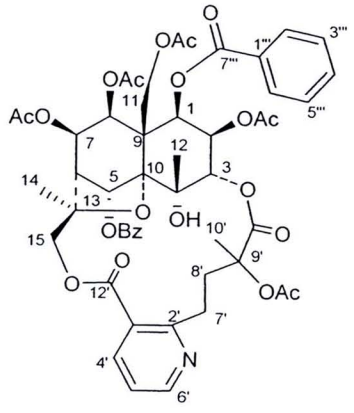
Structure Elucidation of Compound XVIII

Compound **XVIII** was obtained as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3543 cm^{-1}) and an ester carbonyl (ν_{max} 1747 and 1732 cm^{-1}) functional group. It showed dark quenching spot under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{50}H_{53}NO_{20}$ as indicated from the $[M+Na]^+$ ion at 1010.3015 (calcd for $C_{50}H_{53}NO_{20}Na$, 1010.3059).

The ^{13}C NMR spectrum showed the presence of fifty carbons comprising eight methyls, four methylenes, twenty methines and eighteen quaternary carbons including nine carbonyl carbons (δ_C 171.38, 170.93, 170.21, 170.05, 168.92, 167.99, 167.46, 165.63 and 164.58).

Compound **XVIII** showed rather similar patterns of ^1H and ^{13}C NMR signals as of compound **XVI** and **XVII**. However, the ^1H NMR spectrum of compound **XVIII** showed only five acetyl groups at δ_H 2.25, 2.19, 2.16, 2.12, and 1.34 and the aromatic proton signals between 8.20-7.45 indicated the

presence of two benzoyl groups. The long range HMBC correlations of H-1 (δ_H 5.99)/C-7‴ (δ_C 164.58), and of H-5 (δ_H 6.95)/C-7″ (δ_C 165.63) indicated bonding of one *O*-Bz group at C-1, and the *O*-Bz group at C-5. Compound **XVIII** was thus identified as 1-*O*-benzoyl-1-deacetylmekongensine.



Compound **XVIII**

Table 18 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XVIII** in $CDCl_3$

Position	δ_H (*J* in Hz)	δ_C, type	HMBC
1	5.99 d (3.7)	72.37CH	C-15, 10, 11, 7″
2	5.31 dd (3.7, 2.6)	68.84 CH	C-1, 3, 4, 2-O<u>C</u>OCH$_3$
3	5.11 d (2.6)	77.61 CH	C-1, 2, 10, 12, 11′
4	-	70.09 qC	-
5	6.95 s	75.09 qC	C-6, 7, 10, 13, 7″
6	2.58 d (3.8)	50.83 CH	C-5, 7, 8, 10, 15
7	5.64 dd (5.8, 3.8)	68.77 CH	C-1, 5, 9, 11, 7-O<u>C</u>OCH$_3$
8	5.48 d (5.8)	72.66 CH	C-9, 8-O<u>C</u>OCH$_3$
9	-	52.83 qC	-
10	-	92.96 qC	-

Table 18 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
11	5.43 d (13.2)[a]	60.62 CH_2	C-1, 8, 9, 10, 11-O<u>C</u>OCH_3
	4.70 d (13.2)		
12	1.62 s	23.07 CH_3	C- 3, 4, 10
13	-	84.06 qC	-
14	1.70 s	18.00 CH_3	C-6, 13, 15
15	5.40 d (11.9)[a]	69.98 CH_2	C-13, 14,12′
	3.97 d (11.9)		
2′	-	160.96 qC	-
3′	-	125.71 qC	-
4′	8.15 dd (7.9, 1.8)	139.39 CH	C-2′, 6′
5′	7.27 dd (7.9, 4.8)	121.44 CH	C-3′
6′	8.71 dd (4.8, 1.7)	151.88 CH	C-2′, 4′, 5′
7′	3.74 dt (14.7, 4.1)	30.06 CH_2	C-2′, 10′
	3.04 dt (14.7, 4.1)		
8′	2.72 dt (14.0, 4.1)	37.58 CH_2	C-9′, 10′, 11′
	2.20 m[b]		
9′	-	80.36 qC	-
10′	1.76 s	22.66 CH_3	C-9′, 11′
11′	-	171.38 qC	-
12′	-	167.46 qC	-
1″	-	129.27 qC	-
2″,6″	8.20 dd (7.7, 1.5)	130.26 CH	C-1″, 4″, 7″
3″,5″	7.45 t (7.7)	128.52 CH	C-1″, 7″
4″	7.56 m[c]	133.49 CH	C-2″, 6″
7″	-	165.63 qC	-
1‴	-	129.13 qC	-
2‴,6‴	7.87 dd (7.8, 14)	129.71 CH	C-1‴, 4‴, 7‴

Table 18 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
3‴,5‴	7.40 t (7.8)	128.88 CH	C-1‴, 2‴, 6‴, 7‴
4‴	7.56 m[c]	133.80 CH	-
7‴	-	164.58 qC	-
2-OCOC$\underline{H}_3$	2.16 s	20.95 CH_3	C-2, 2-OC$\underline{O}$C$\underline{H}_3$
7-OCOC$\underline{H}_3$	2.19 s[b]	21.13 CH_3	C-7, 7-OC$\underline{O}$C$\underline{H}_3$
8-OCOC$\underline{H}_3$	1.34 s	19.84 CH_3[d]	C-8, 8-OC$\underline{O}$C$\underline{H}_3$
11-OCOC$\underline{H}_3$	2.25 s	21.45 CH_3[d]	C-11, 11-OC$\underline{O}$C$\underline{H}_3$
9′-OCOC$\underline{H}_3$	2.12 s	21.03 CH_3	C-9′, 9′-OC$\underline{O}$C$\underline{H}_3$
2-OC$\underline{O}$CH$_3$	-	167.99 qC	-
7-OC$\underline{O}$CH$_3$	-	170.05 qC	-
8-OC$\underline{O}$CH$_3$	-	168.92 qC	-
11-OC$\underline{O}$CH$_3$	-	170.21 qC	-
9′-OC$\underline{O}$CH$_3$	-	170.93 qC	-
4-OH	4.16 d (0.9)	-	C-4, 12, 10

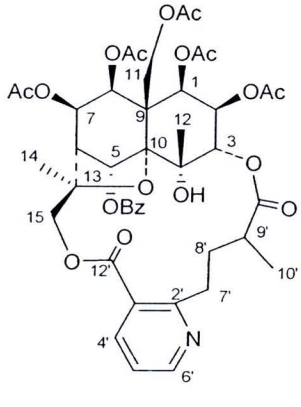
[a-c]Overlapping signals. [d]Interchangeable signal.

Structure Elucidation of Compound XIX

Compound **XIX** was isolated as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3568 cm^{-1}) and an ester carbonyl (ν_{max} 1748 and 1723 cm^{-1}) functional groups. It showed dark quenching spot under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{43}H_{49}NO_{18}$ as indicated from the $[M+Na]^+$ ion at 890.2856 (calcd for $C_{43}H_{49}NO_{18}Na$, 890.2847).

The ^{13}C NMR spectrum showed the presence of fourty three carbons comprising eight methyls, four methylenes, sixteen methines and fifteen quaternary carbons including eight carbonyl carbons (δ_C 175.05, 170.24, 170.07, 169.41, 169.00, 168.74, 166.56 and 165.77).

The ^{1}H NMR spectrum of compound **XIX** showed five acetyl groups at δ_H 2.27, 2.24, 2.12, 1.99, and 1.86 and aromatic protons of one benzoyl group (δ_H 8.25-7.46). The singlet signal at ca δ_H 1.74 of H_3-10′ in compound **XVI** was absence and replaced by the doublet at δ_H 1.20. The ^{1}H-^{1}H COSY spectrum indicated correlations of signals at δ_H 1.20 (d, H_3-10′)/ δ_H 2.40 (H-9′); H-9′/H-8′ (δ_H 2.00), and H-8′/H-7′ (δ_H 3.96, 3.03). The ^{1}H-^{1}H COSY correlations of aromatic proton H-5′/H-4′, H-6′, in addition to the ^{3}J ^{1}H-^{13}C correlations between H-7′/C-9′, C-3′ implied the presence of a wilfordic acid moiety[59] in compound **XIX**. Connectivities between C(15)-*O* to C-12″ and C(3)-*O* to C-11″ were detected from the HMBC cross-peaks of H_2-15/C-12″ and of H-3/C-11″, respectively. Compound **XIX** was finally elucidated as 9′-deacetoxymekongensine.



Compound **XIX**

Table 19 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XIX** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	5.65 d (3.6)	73.53 CH	C- 8, 9, 10, 11, 1-$\underline{C}OCH_3$
2	5.17 dd (3.6, 2.6)	69.22 CH[b]	C-1, 3, 4, 9, 2-O$\underline{C}OCH_3$
3	4.98 d (2.6)	76.12 CH	C-1, 2, 10, 12, 11′
4	-	70.05 qC	-
5	6.98 s	74.88 qC	C-3, 4, 6, 7, 10, 13, 7″
6	2.52 d (3.8)	50.99 CH	C-5, 7, 10, 15
7	5.55 dd (5.8, 3.8)	69.32 CH[b]	C-5, 8, 9, 7-O$\underline{C}OCH_3$
8	5.39 d (5.8)	71.13 CH	C-1, 9, 11, 8-O$\underline{C}OCH_3$
9	-	52.21 qC	-
10	-	93.40 qC	-
11	5.26 d (13.2)	60.29 CH_2	C-1, 8, 9, 10, 11-O$\underline{C}OCH_3$
	4.52 d (13.2)		
12	1.56 d (1.1)	22.78 CH_3	C-3, 4,10
13	-	84.37 qC	-
14	1.86 s	17.92 CH_3	C-6, 13, 15
15	5.76 d (11.9)	70.50 CH_2	C-13, 14,12′
	3.67 d (11.9)		
2′	-	163.56 qC	-
3′	-	125.01 qC	-
4′	8.30 d (7.8)	139.45 CH	C-2′, 6′
5′	7.30 dd (7.8, 4.8)	121.52 CH	-
6′	8.25 dd (4.8, 1.7)	152.25 CH	-
7′	3.96 ddd (12.8, 9.7, 6.2)	32.52 CH_2	-
	3.03 m		
8′	2.00 m[a]	33.29 CH_2	-

Table 19 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
9′	2.40 m	38.51 CH	C-10′, 11′
10′	1.20 d (6.9)	18.54 CH_3	C-8′, 9′, 11′
11′	-	175.05 qC	-
12′	-	166.56 qC	-
1″	-	129.35qC	-
2″,6″	8.25 dd (7.4, 1.4)	130.31 CH	C-1″, 4″, 7″
3″,5″	7.46 t (7.4)	128.85 CH	C-1″, 7″
4″	7.57 tt (7.4, 1.4)	133.64 CH	C-2″, 6″
7″	-	165.77 qC	-
1-OCO$\underline{C}H_3$	1.86 s	20.52 CH_3	C-1, 1-O$\underline{C}OCH_3$
2-OCO$\underline{C}H_3$	2.12 s	21.03 CH_3[c]	C-2, 2-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	2.24 s	21.08 CH_3[c]	C-7, 7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.99 s[a]	20.52 CH_3	C-8, 8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.27 s	21.36 CH_3	C-11, 11-O$\underline{C}OCH_3$
1-O$\underline{C}OCH_3$	-	169.41 qC	-
2-O$\underline{C}OCH_3$	-	168.74 qC[d]	-
7-O$\underline{C}OCH_3$	-	170.07 qC[d]	-
8-O$\underline{C}OCH_3$	-	169.00 qC	-
11-O$\underline{C}OCH_3$	-	170.24 qC	-
4-OH	5.14 d (1.0)	-	C-4, 12, 10

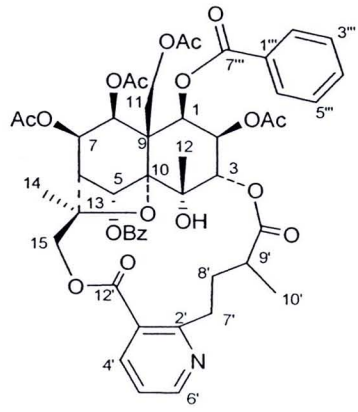
[a] Overlapping signal. [b-d] Interchangeable signals.

Structure Elucidation of Compound XX

Compound **XX** was isolated as a colorless amorphous solid. The FTIR spectrum showed absorption bands for a hydroxy (ν_{max} 3467 cm^{-1}) and an ester carbonyl (ν_{max} 1747 and 1723 cm^{-1}) functional groups. It showed dark quenching spot under UV 254 light. The HRESIMS spectrum suggested a molecular formula of $C_{48}H_{51}NO_{18}$ as indicated from the $[M+Na]^+$ ion at 952.3005 (calcd for $C_{48}H_{51}NO_{18}Na$, 952.3004).

The ^{13}C NMR spectrum showed the presence of fourty three carbons comprising nine methyls, two methylenes, seventeen methines and fifteen quaternary carbons including eight carbonyl carbons (δ_C 174.95, 170.22, 170.15, 168.99, 168.40, 165.79, 164.91 × 2).

Compound **XX** showed similar sets of ^1H and ^{13}C NMR signals as found in compound **XIX**. The ^1H NMR spectrum of compound **XX** showed only four acetyl groups at δ_H 2.310, 2.21, 2.13, and 1.42 but with aromatic proton signals between δ_H 8.26-7.39 of two benzoyl groups. The long range HMBC correlations of H-1 (δ_H 6.50)/C-7‴ (δ_C 164.91), and of H-5 (δ_H 7.03)/C-7″ (δ_C 164.91) indicated connections of one *O*-Bz group to C-1, and the second group to C-5. Full assignment of ^1H and ^{13}C NMR chemical shifts was as shown in Table 20. Compound **XX** was thus proposed as 1-*O*-benzoyl-1-deacetyl-9′-deacetoxy mekongensine.



Compound **XX**

Table 20 ^{1}H (400 MHz), ^{13}C NMR (100 MHz) data, and HMBC correlations of compound **XX** in $CDCl_3$

Position	δ_H (J in Hz)	δ_C, type	HMBC
1	6.50 d (3.8)	73.48 CH	C- 8, 9, 11, 7‴
2	5.27 dd (3.8, 2.7)	69.83 CH	C-3, 4, 9, 2-O<u>C</u>OCH$_3$
3	5.05 d (2.7)	76.09 CH	C-1, 2, 10, 12, 11′
4	-	70.84 qC	-
5	7.03 s	74.94 qC	C-6, 7, 10, 13, 7″
6	2.55 d (4.0)	50.90 CH	C-5, 7, 8, 10
7	5.56 dd (6.0, 4.0)	69.13 CH	C-5, 8, 9, 7-O<u>C</u>OCH$_3$
8	5.46 d (6.0)	71.76 CH	C-1, 9, 11, 8-O<u>C</u>OCH$_3$
9	-	52.58 qC	-
10	-	93.57 qC	-
11	5.44 d (13.4)	60.40 CH$_2$	C-8, 9, 10, 11-O<u>C</u>OCH$_3$
	4.72 d (13.4)		
12	1.60 d (1.1)	22.77 CH$_3$	C-3, 4, 10
13	-	84.55 qC	-
14	1.69 s	17.84 CH$_3$	C-6, 13, 15
15	5.78 d (11.9)	70.50 CH$_2$	C-13, 14, 12′
	3.69 d (11.9)		

Table 20 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
2′	-	163.20 qC	-
3′	-	125.44 qC	-
4′	8.31 d (7.8)	139.00 CH	C-2′, 6′
5′	7.31 dd (7.8, 4.8)	121.84 CH	
6′	8.76 dd (4.8, 1.8)	152.90 CH	
7′	3.98 ddd (13.5, 9.5, 6.5)	33.35 CH_2[b]	
	3.05 m		
8′	2.04 m	33.29 CH_2[b]	C-7′, 9′, 11′
	2.36 m[a]		
9′	2.46 m	38.51 CH	C-11′
10′	1.24 d (7.0)	18.59 qC	C-8′, 9′, 11′
11′	-	174.95 qC	-
12′	-	165.79 qC	-
1″	-	129.35 qC	-
2″,6″	8.26 dd (7.7, 1.2)	130.32 CH	C-1″, 4″, 7″
3″,5″	7.47 tt (7.7, 1.4)	128.87 CH	C-2″, 6″
4″	7.58 tt (7.7, 1.4)	133.66 CH	C-2″, 6″
7″	-	164.91 qC	-
1‴	-	129.25 qC	-
2‴,6‴	7.84 dd (7.8, 1.5)	129.53 CH	C-1‴, 4‴, 7‴
3‴,5‴	7.39 dt (7.8, 1.5)	128.50 CH	C-1‴, 2‴, 6‴
4‴	7.53 tt (7.8, 1.5)	133.48 CH	C-2‴, 6‴
7‴	-	164.91 qC	-
2-OCO$\underline{C}H_3$	2.13 s	20.91 CH_3	2-O$\underline{C}OCH_3$
7-OCO$\underline{C}H_3$	2.21 s	21.04 CH_3	7-O$\underline{C}OCH_3$
8-OCO$\underline{C}H_3$	1.42 s	19.96 CH_3	8-O$\underline{C}OCH_3$
11-OCO$\underline{C}H_3$	2.31 s[a]	21.47 CH_3	11-O$\underline{C}OCH_3$

Table 20 (continued)

Position	δ_H (J in Hz)	δ_C, type	HMBC
2-O<u>C</u>OCH$_3$	-	168.40 qC	-
7-O<u>C</u>OCH$_3$	-	170.15 qC	-
8-O<u>C</u>OCH$_3$	-	168.99 qC	-
11-O<u>C</u>OCH$_3$	-	170.22 qC	-
4-OH	5.16 d (1.3)	-	C-12

[a] Overlapping signal.

Compounds **IX, XI, XII** and **XVI-XX** were evaluated for their cytotoxic, antiplasmodial and antituberculous activity. Results are as shown in Table 21. Compounds (**XVI-XX**) with wilfordic acid moiety, either with or without a 9′-OAc group, exhibited comparable antiplasmodial activity, while compounds (**IX, XI** and **XII**) with evoninic acid moiety showed no inhibitory activity. Only compounds **XVI** and **XIX** showed very weak cytotoxic activity (IC_{50} = 28.16 and 46.67 μg/mL, respectively) against human mouth epidermal carcinoma (KB) cell line, and no inhibitory activity was observed with other cell lines. The cytotoxic activity exhibited by the CH_2Cl_2 extract may thus be due to the presence of cytotoxic triterpenes.[51,54] Compound **XVI** was evaluated for its antimycobacterial activity against *Mycobacterium tuberculosis* H37Ra and showed no activity at 200 μg/mL.

Table 21 Biological activities of some isolates[a]

Compound	Anti-TB	Antiplasmodial	Cell lines		
			KB	MCF7	NCI-H187
IX	nd	inact	inact	inact	inact
XI	nd	inact[b]	inact	inact	inact
XII	nd	inact	inact	inact	inact
XVI	Inact[c]	2.86 (3.1×10^{-3})	28.16 (3.0×10^{-2})	inact	inact
XVII	nd	3.60 (3.9×10^{-3})	inact[d]	inact	inact
XVIII	nd	3.46 (3.5×10^{-3})	inact	inact	inact
XIX	nd	2.74 (3.1×10^{-3})	46.67 (5.4×10^{-1})	inact	inact
XX	nd	2.33 (2.5×10^{-3})	inact	inact	inact
Ellipticine[e]	-	-	0.448	-	-
Doxorubicine[e]	-	-	0.249	0.573	0.035
Dihydroartemisinine[e]	-	(3.7 nM) 4.7 nM	-	-	-
kanamycin	2.5	-	-	-	-

[a] Values indicated are the IC_{50} values in μg/mL (in parentheses, mM), [b]inactive at 10 μg/mL. [c]inactive at 200 μg/mL. [d]inactive at 50 μg/mL. nd = not determined. [e]Positive control compounds.