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Rings B,D-seco limonoids from the leaves of *Swietenia mahogani*

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Abstract

Seven phragmalin limonoids of swietephragmins A-G, and two other different types of 2-hydroxy-3-*O*-tigloylswietenolide and deacetylsecomahoganin, were isolated along with three known limonoids from the leaves of *Swietenia mahogani* (Meliaceae). Their structures were determined by spectroscopic methods.

Keywords: *Swietenia mahogani*; Meliaceae; Phragmalins; Swietephragmins A-G; Mexicanolide; 2-Hydroxy-3-*O*-tigloylswietenolide; Rings B,D-seco limonoid; Deacetylsecomahoganin

1. Introduction

Swietenia mohogani JACQ. is a valuable meliaceous timber tree closely related to the African genus *Khaya* and one of the most popular traditional medicines in Africa. The decoction of the bark of these mahoganies is extensively used as febrifuge, which could be associated with its use as an antimalarial drug (Nagalakshmi et al., 2001). This genus is one of the main sources of rings B,D-seco limonoids of mexicanolides and phragmalins. Ever since a mexicanolide was isolated (Adeoye and Bekoe, 1965), many limonoids having bicyclo[3,3,1] and tricyclo[3.3.1.1] ring systems have been reported (Taylor, 1984).

In our continuing search for limonoid antifeedants from the family Meliaceae, we have reported the isolation of ring D opened phragmalin-type limonoids from the stem bark of *Swietenia mahogani*, collected at Alexandria, Egypt (Saad et al., 2003). A subsequent study of the leaves isolated seven new phragmalins possessing an orthoester group at 8,9,30-position, named swietephragmins A (**1**)–F (**6**) and G (**9**), together with two new different type rings B,D-seco limonoids, 2-hydroxy-3-*O*-tigloylswietenolide (**7**) and deacetylsecomahoganin (**8**), along with three known limonoids of methyl 6-hydroxyangolensate (**10**) (Adesogan and Taylor, 1968), swietemahonin G (**11**) (Kadota et al., 1990b) and 7-deacetoxy-7-oxogedunin (**12**) (Kadota et al., 1990a). We describe herein the isolation, and structural elucidation of these new limonoids. The antifeedant activity of the isolated compounds was also described briefly.

2. Results and discussion

After partition with hexane and methylene chloride of the ether extract of the leaves dissolved in H_2O–MeOH (1:1), the methylene chloride layer was subjected to chromatographic separation using SiO_2 with MeOH–CH_2Cl_2 as an eluant system, with the resulting limonoid fraction divided into four fractions by S_iO_2 rechromatography with hexane–AcOEt (1:1) for elution. The first limonoid fraction was purified by a combination of TLC and reversed phase HPLC to give nine new compounds, **1**–**9**, and three known compounds, **10**–**12**.

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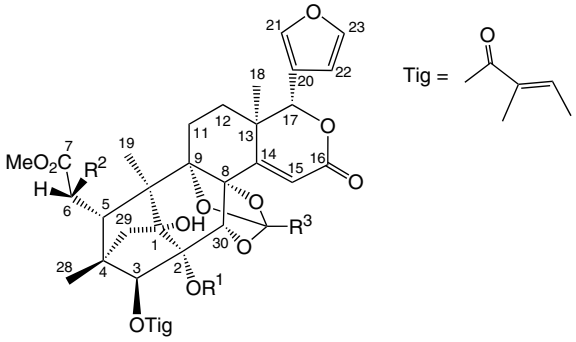
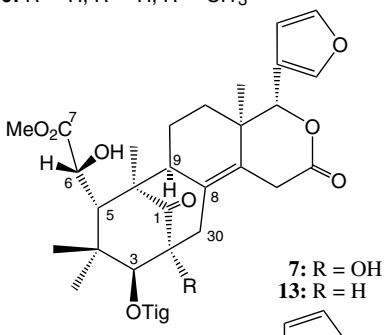
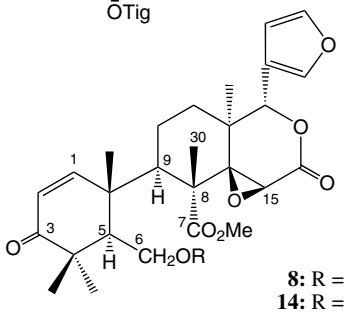


1: R^1 = Ac, R^2= H, R^3= $CH(CH_3)_2$
2: R^1 = Ac, R^2= H, R^3= $CH(CH_3)CH_2CH_3$
3: R^1 = H, R^2= H, R^3= $CH(CH_3)CH_2CH_3$
4: R^1 = H, R^2= H, R^3= $CH(CH_3)_2$
5: R^1 = H, R^2= OH, R^3= $CH(CH_3)CH_2CH_3$
6: R^1 = H, R^2= H, R^3= CH_2CH_3
9: R^1 = H, R^2= H, R^3= CH_3



7: R = OH
13: R = H



8: R = H
14: R = Ac
15: R= β-D-glu

Swietephragmin A (**1**) was found to possess a molecular formula of $C_{38}H_{46}O_{13}$ (16 unsaturations) as determined from the HRFAB-MS (*m/z:* 711.3009$[M+1]^+$, Δ −0.8 mmu) and ^{13}C NMR spectrum. The IR spectrum revealed absorption bands for hydroxyl (3600–3200 cm^{-1}) saturated (1740 cm^{-1}) and unsaturated ester carbonyl (1724 and 1715 *sh* cm^{-1}) groups. The UV spectrum also indicated the presence of an α,β-unsaturated ester group at 215 nm. From the ^1H and ^{13}C NMR spectra, it was clear that eight of the elements of unsaturation were present as double bonds: four carbon–carbon double bonds (one furan ring) and four CO (as esters). Therefore, the molecule is octacyclic. The presence of a β-furyl group was recognized together with each one of acetyl, tigloyl, methoxy and hydroxyl groups.

All protons directly bonded with carbon atoms were assigned by analysis of the HMQC spectrum. From the subsequent 2D NMR spectroscopic studies of the ^1H–^1H COSY, HMBC and NOESY spectra, it was strongly suggested that **1** was a phragmalin limonoid (Tables 1 and 2). Thus, a characteristic low-field singlet at δ 5.71 due to H-17 was observed and the H_2-6 protons at δ 2.34 (*dd*, $J = 16.4$ and 11.7 Hz) and 2.40 (*br d*, $J = 16.4$ Hz), attached to a methylene carbon adjacent to an ester carbonyl, were coupled with the H-5 broad doublet proton at δ 2.48 (*br d*, $J = 11.7$ Hz). These observations strongly suggested that **1** was a rings B,D-seco limonoid. In addition to this knowledge, the absence of two tertiary methyl signals due to 4β̃-Me (Me-29) and 8β-Me (Me-30) groups in the basic limonoid skeleton, and the presence of two proton resonances at δ 1.73 and 1.94 (each d, $J = 11.5$ Hz) assigned to the 29-methylene group, strongly supported that **1** had a tricyclo $[3.3.1^{2,10}.1^{1,4}]$ decane ring system. The presence of an orthoester group in **1** was also presumed from the characteristic orthocarbon resonance of δ 122.9. Almost all of the phragmalins isolated so far have been reported to be 1,8,9- or 8,9,14-orthoacetates except for some exceptions (Olmo et al., 1997; Nakatani et al., 2001; Saad et al., 2004), and their orthocarbon signals have been observed around δ 119 (Taylor, 1984).

The ^1H and ^{13}C NMR spectra due to the tricyclodecane ring of **1** were similar to those of swietenialide A (Saad et al., 2003) isolated from the stem bark of the same plant. All of the carbons due to the ring system, including Me-19 and 28 were, respectively, assigned by long-range C–H correlations (Fig. 1) of a broad doublet ($J = 11.7$ Hz, H-5) and two methine singlets at δ 5.34 (H-3) and 5.44 (H-30) with the corresponding carbon signals. A W-type long range coupling between the H-5 signal and one (*Pro-S*) of 29-methylene signals observed at δ 1.73 and the NOE correlation of the other H-29 signal at δ 1.94 (*Pro-R*) with the 10α-Me (Me-19), confirmed the ring structure and their relative stereochemistry. The presence of 3-tigloyl and 1-OH groups was elucidated by HMBC correlations of the H-3 and OH signals with the tigloyl carbonyl carbon and C-1 signals, respectively. On the other hand, compound **1** showed the presence of one trisubstituted double bond at δ_C151.8 (*s*, C-14) and 123.4 (*d*, C-15) conjugated with a lactone carbonyl. An olefinic proton at δ 6.32 (*s*, H-15) correlating to the carbon at 163.6 (C-16) in the HMBC spectrum, showed additional correlations with two quaternary carbons of C-8 and C-13. In the HMBC correlations (Fig. 1), the H_2-11, H_2-12 and H-17 signals correlated with C-8, C-9 and C-11–C-17 resonances, and characterized the second fragment of C and D rings including 13-Me (Me-18) and a furan ring. Finally, the orthoester moiety, identified as an isobutylate group, was located at the positions 8,9,30 by the HMBC correlation of the H-30 resonance with the orthocarbon signal at δ 122.9 and a consideration of the molecular model. This was supported further by the NOEs of the acetyl signal of 2-OAc with the H-3 and H-30 signals.

Stereochemistry of **1** was elucidated by the consideration of NOE correlations (Fig. 2) using a molecular model. Strong cross-peaks of H-5 with H-12β and H-17, and

Table 1
^{1}H NMR spectroscopic data for swietephragmins A–F (**1**–**6**) and G (**9**)

No.	**1**	**2**	**3**	**4**	**5**	**6**	**9**
3	5.34 *s*	5.30 *s*	4.83 *s*	4.83 *s*	4.73 *s*	4.83 *s*	4.83 *s*
5	2.48 *br d* (11.7)	2.48 *br d* (11.5)	2.55 *br d* (11.5)	2.55 *br d* (11.6)	2.63 *br s*	2.55 *br d* (11.5)	2.54 *br d* (11.4)
6	2.34 *dd* (16.4, 11.7)	2.34 *dd* (16.5, 11.7)	2.38 *dd* (16.6, 11.5)	2.38 *dd* (16.6, 11.6)	4.57 *br s*	2.38 *dd* (16.5, 11.5)	2.38 *dd* (16.6, 11.4)
	2.40 *br d* (16.4)	2.40 *br d* (16.3)	2.43 *dd* (16.6, 2.0)	2.44 *dd* (16.6, 1.8)		2.43 *br d* (16.5)	2.43 *br d* (16.6)
11α	1.87 *ddd* (15.8, 15.0, 4.0)	1.87 *dt* (4.2, 15.4)	1.86 *m*	1.85 *dt* (3.9, 14.9)	1.89 *dt* (3.9, 15.5)	1.89 *dt* (3.7, 14.7)	1.91 *dt* (3.6, 14.7)
11β	2.17 *dt* (15.0, 3.5)	2.11 *dt* (15.0, 3.0)	2.08 *dt* (14.9, 3.2)	2.08 *dt* (14.9, 3.4)	2.21 *dt* (14.9, 3.2)	2.09 *dt* (14.9, 1.9)	2.10 *dt* (14.9, 2.0)
12α	1.16 *dt* (14.1, 3.5)	1.16 *dt* (14.1, 3.7)	1.22 *dt* (14.3, 3.6)	1.13 *dt* (14.5, 3.7)	1.21 *dt* (13.8, 3.3)	1.13 *ddd* (14.3, 3.7, 1.9)	1.13 *dt* (14.3, 3.0)
12β	1.57 *ddd* (15.8, 14.1, 3.2)	1.56 *dt* (3.7, 14.1)	1.51 *br dt* (2.7, 14.7)	1.51 *br dt* (3.6, 14.8)	1.58 *br dt* (2.9, 14.5)	1.50 *br dt* (2.0, 14.5)	1.50 *br t* (14.5)
15α	6.32 *s*	6.39 *s*	5.97 *s*	5.97 *s*	5.94 *s*	5.97 *s*	5.97 *s*
17	5.71 *s*	5.71 *s*	5.68 *s*	5.68 *s*	5.52 *s*	5.69 *s*	5.69 *s*
18	1.36 *s*	1.35 *s*	1.33 *s*	1.33 *s*	1.29 *s*	1.34 *s*	1.35 *s*
19	1.30 *s*	1.29 *s*	1.28 *s*	1.29 *s*	1.54 *s*	1.28 *s*	1.28 *s*
21	7.48 *br s*	7.48 *br s*	7.47 *br s*	7.47 *br s*	7.47 *br s*	7.47 *br s*	7.47 *br s*
22	6.46 *br d* (1.1)	6.46 *br d* (1.1)	6.44 *br d* (1.4)	6.44 *br d* (1.1)	6.40 *br s*	6.44 *br s*	6.44 *br s*
23	7.42 *br t* (1.5)	7.42 *br t* (1.3)	7.42 *t* (1.5)	7.41 *t* (1.5)	7.43 *br s*	7.41 *br s*	7.41 *br s*
28	0.68 *s*	0.73 *s*	0.82 *s*	0.82 *s*	0.95 *s*	0.82 *s*	0.82 *s*
$29_{pro\text{-}R}$	1.94 *d* (11.5)	1.94 *d* (11.6)	1.82 *d* (11.4)	1.83 *d* (11.1)	2.27 *d* (10.7)	1.83 *d* (11.3)	1.83 *d* (11.5)
$29_{pro\text{-}S}$	1.73 *br d* (11.5)	1.72 *br d* (11.6)	1.78 *br d* (11.4)	1.78 *br d* (11.1)	1.73 *d* (10.7)	1.78 *br d* (11.3)	1.78 *br d* (11.5)
30	5.44 *s*	5.43 *s*	4.49 *s*	4.50 *s*	4.47 *s*	4.51 *s*	4.51 *s*
OMe	3.68 *s*	3.68 *s*	3.72 *s*	3.72 *s*	3.85 *s*	3.72 *s*	3.72 *s*
2-OAc	2.19 *s*	2.19 *s*			2.17 *s*		
1-OH	3.44 *s*	3.45 *s*	3.49 *s*	3.49 *s*	3.53 *s*	3.50 *s*	3.50 *s*
2-OH			3.55 *s*	3.56 *s*	3.57 *s*	3.56 *s*	3.56 *s*
6-OH					2.80 *s*		
Tigloyl							
3′	6.62 *qq* (6.9, 1.4)	6.62 *qq* (6.9, 1.4)	6.91 *qq* (7.1, 1.2)	6.91 *qq* (7.0, 1.3)	6.75 *br q* (7.0)	6.91 *br q* (7.0)	6.91 *br q* (6.8)
4′	1.71 *br d* (6.9)	1.71 *br d* (7.0)	1.75 *br d* (7.1)	1.75 *dq* (7.0, 0.9)	1.74 *br d* (6.9)	1.75 *br d* (7.0)	1.75 *br d* (6.8)
2′-Me	1.87 *br s*	1.87 *br s*	1.85 *br s*	1.85 *br s*	1.85 *br s*	1.85 *br s*	1.85 *br s*
Orthoesters							
2′′	2.19 quint (6.9)	1.94 *m*	1.92 *m*	2.17 quint (7.0)	1.93 *m*	1.96 *dq* (14.5, 7.6)	1.67 *s*
						1.93 *dq* (14.5, 7.6)	
3′′-a	1.04 *d* (6.9)	1.24 *m*	1.22 *dq* (9.6, 7.5)	1.04 *d* (7.0)	1.23 *m*	1.03 *t* (7.6)	
3′′-b		1.68 *m*	1.71 *m*		1.71 *m*		
4′′		0.93 *t* (7.5)	0.93 *t* (7.5)		0.93 *t* (7.5)		
2′′-Me	1.04 *d* (6.9)	1.02 *d* (6.9)	1.02 *d* (6.9)	1.04 *d* (7.0)	1.02 *d* (6.9)		

All spectra were measured in $CDCl_3$ at 600 MHz. Chemical shifts are expressed in ppm. *J* values in parentheses are in Hz.

Table 2
^{13}C NMR spectroscopic data for swietephragmis A–F (**1**–**6**) and G (**9**)

No.	1	2	3	4	5	6	9
1	84.7	84.6	84.6	84.6	84.6	84.7	84.6
2	84.0	84.0	75.7	75.7	75.6	75.7	75.7
3	84.8	84.7	86.6	86.6	87.5	86.7	86.7
4	44.7	44.7	43.7	43.7	43.4	43.7	43.8
5	39.6	39.6	40.1	40.1	45.5	40.1	40.2
6	33.7	33.7	33.7	33.7	71.6	33.7	33.8
7	173.9	173.9	173.9	173.9	174.5	173.9	173.6
8	83.9	83.7	83.6	83.8	83.6	83.8	84.0
9	85.7	85.7	86.6	86.7	87.0	86.9	87.2
10	48.1	48.0	47.2	47.2	48.4	47.3	47.3
11	26.9	26.0	25.7	25.7	25.6	25.9	26.2
12	29.3	29.3	29.0	29.0	29.4	29.0	29.2
13	37.7	37.7	37.7	37.7	37.8	37.7	37.9
14	151.8	151.8	153.1	153.0	153.1	153.0	152.7
15	123.4	123.4	122.5	122.5	122.1	122.6	122.5
16	163.6	163.6	163.2	163.2	162.7	163.1	162.8
17	79.8	79.8	79.7	79.7	80.0	79.7	79.7
18	19.2	19.2	19.8	19.8	19.8	19.8	20.1
19	15.4	15.4	15.5	15.4	17.4	15.4	15.6
20	119.9	119.9	119.8	119.8	119.6	119.8	119.4
21	142.0	142.0	142.0	142.0	141.4	142.1	141.9
22	110.2	110.2	110.1	110.1	109.8	110.1	110.0
23	143.3	143.2	143.2	143.2	143.2	143.2	143.1
28	13.8	13.8	14.4	14.4	15.6	14.4	14.6
29	39.0	39.0	38.5	38.5	39.8	38.6	38.7
30	73.9	73.7	77.9	78.0	77.7	78.1	78.1
OMe	52.1	52.1	52.1	52.1	52.3	52.1	52.2
OAc	170.3	170.2					
	21.8	21.8					
Tiglate							
1′	167.9	167.9	168.1	168.2	167.7	168.2	167.9
2′	130.8	130.8	130.0	130.0	130.2	130.1	129.9
3′	136.1	136.1	139.9	139.9	139.0	139.9	139.8
4′	13.5	13.5	14.2	14.2	14.4	14.2	14.4
2′-Me	12.9	12.8	12.3	12.3	12.5	12.3	12.4
Orthoester							
1″	122.9	123.0	122.9	122.8	122.5	121.3	119.7
2″	28.9	35.4	35.5	28.9	35.5	23.2	16.6
3″	16.6	23.6	23.6	16.6	23.7	7.6	
4″		13.5	11.4		11.6		
2″-Me	16.6	12.8	13.1	16.6	13.3		

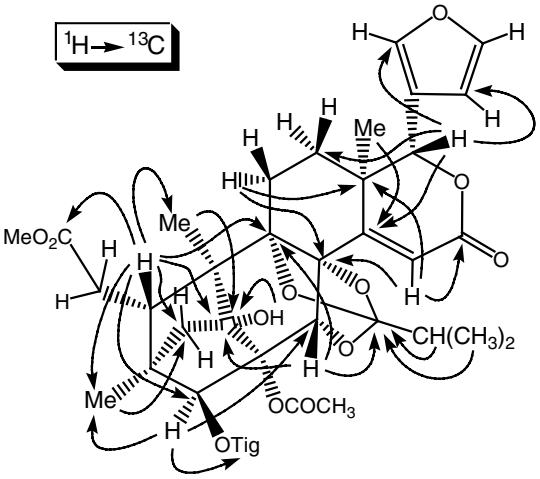


Fig. 1. Selected HMBC correlations in **1**.

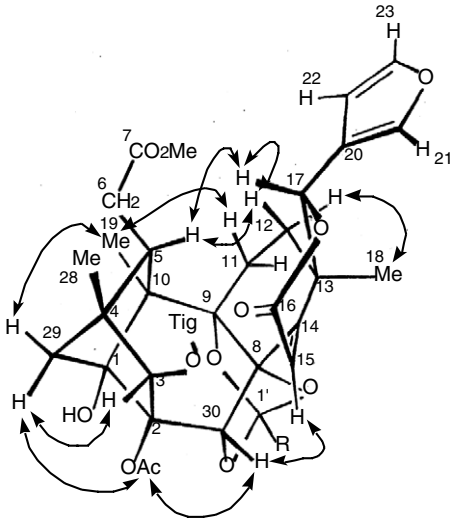


Fig. 2. Significant NOE correlations in **1**.

H-12β with H-17 in the NOESY spectrum indicated a β orientation for these three protons. In addition to a cross-peak between H-30 and H-15, a NOE correlation of H-11β with H_3-19 (10α-Me) indicated that **1** was present in a folded conformation containing a quasi chair C ring as shown in Fig. 2. The NOE observation of 2-OAc with H-3 and H-30 also supported this structure assignment. Thus, swietephragmin A was identified as the 8,9,30-*ortho*-isobutylate (**1**) of methyl 2-acetoxy-3β-tigloyloxy-1,8,9,30-tetrahydroxy-[3.3. $1^{2,10}$. $1^{1,4}$]-tricyclomeliac-16,17-lactonic-14(15)-en-7-oate.

Swietephragmin B (**2**) was obtained as a white amorphous powder. The molecular formula ($C_{39}H_{48}O_{13}$) was determined by the HRFAB-MS (*m/z:* 725.3154 $[M+1]^+$, Δ −1.9 mmu) and NMR spectra, which suggested the presence of one additional –CH_2– unit in **2** compared to **1**. The IR and NMR (Tables 1 and 2) spectroscopic data of **2** were extremely similar to those of **1**, with the only difference being observed in the change of the orthoester group to a 2-methylbutanoate moiety in **2**. The 8,9,30-orthoester bonding in **2** was also confirmed by both the similar HMBC correlation between the H-30 signal and the orthoester carbon resonance observed at δ 123.0, as well as the NOEs of the 2-OAc signal with the 1-OH and H-3 resonances.

Swietephragmin C (**3**) exhibited the molecular formula of $C_{37}H_{46}O_{12}$ by HRFAB-MS (*m/z:* 683.3059 $[M+1]^+$, Δ −0.8 mmu) and NMR spectroscopic data. The NMR spectra were similar to those of **2** including the presence of tigloyl and 2-methylbutanoyl orthoester groups, except for the change of an acetoxy group to a hydroxyl group. In the HMBC spectrum, two OH groups were correlated to C-1, C-2 and C-29 and to C-1, C-2 and C-3, respectively, to elucidate clearly the structure having the 8,9,30-orthoester group. Although the NOE correlations in **3** resembled those in **1** and **2** to suggest not so large conformation change in **3**, the H-30 signal was observed

at a high-field of δ 4.49 compared to δ 5.44 and 5.43 in **1** and **2**. This high-field shift was attributed to an anisotropic effect of the carbon–oxygen double bond of the 3-tigloyl group fixed by a seven membered hydrogen bonding with the 2-OH group.

The molecular formula of swietephragmin D (**4**) was determined as $C_{36}H_{44}O_{12}$ by HRFAB-MS (*m/z:* 669.2914 $[M+1]^+$, Δ +0.3 mmu) and NMR data. The ^1H and ^{13}C NMR spectroscopic data (Tables 1 and 2) were extremely similar to those of **3** except for the replacement of 2-methylbutanoyl orthoester in **3** by 2-methylpropanoate in **4**.

Swietephragmin E (**5**) was shown to have the molecular formula $C_{37}H_{46}O_{13}$ by HRFAB-MS (*m/z:* 699.3021 $[M+1]^+$, Δ +0.6 mmu). Although the NMR spectra of **5** were also similar to those of **3** and **4**, it showed the presence of an additional hydroxyl group. The structure of **5** as a 6-hydroxyl derivative of **3** was readily elucidated from that of a hydroxymethine signal at δ 4.57 (H-6) weakly coupled to an OH resonance at δ 2.80 and showed a HMBC correlation with an ester carbonyl carbon at δ 174.5 (C-7). The *R* configuration at C-6 was inferred from that of some mexicanolides, swietenins and swietemahonins (Connolly et al., 1965; Kadota et al., 1990a,b; Saad et al., 2004) isolated from the same plant *S. mahogani*. This was supported by the NOE correlations observed between the H-6 signal and the H-5, H-12β and 10-Me (Me-19) resonances, the 6-OH signal and the H-28$_{Pro\text{-}S}$ and 4α-Me (Me-28) resonances, and the 7-carboxymethyl signal and the H-17 and tigloyl 3′-H and 3′-Me resonances. The latter implied that the 7-CO_2Me group was oriented to the same β-side as H-17 and 3-tigloyl of the molecule. The H-28$_{Pro\text{-}S}$ signal showed a W-type long range coupling with the H-5 signal and a strong NOE with the H-3α resonance, which also accounted well for the stereochemistry of **5**.

The structure of swietephragmin F (**6**), $C_{35}H_{42}O_{12}$; HRFAB-MS (*m/z:* 655.2736$[M+1]^+$, Δ −1.9 mmu) was readily deduced from the spectroscopic data. The ^1H and ^{13}C NMR spectra were very similar to those of compounds **3** and **4** except for the change of the orthoester groups to an orthopropyonate moiety in **6**.

The molecular formula of **7** (2-hydroxy-3-*O*-tigloylswietenolide) was determined to be $C_{32}H_{40}O_{10}$ by HRFAB-MS (*m/z:* 585.2673 $[M+1]^+$, Δ −2.6 mmu). The UV and IR spectra showed similar absorption bands to those of the phragmalins, **(1)–(6)**, and the NMR spectra (Table 3) suggested a mexicanolide structure for **7**. Thus the presence of four tertiary methyls, due to the basic limonoid skeleton, and one methyl ester moiety was observed along with each keto and lactonic carbonyl and tigloyl groups and two hydroxyl groups. The ^1H NMR spectrum resembled 3-*O*-tigloylswietenolide (**13**) isolated from the same species (Kadota et al., 1990) except for the presence of an additional hydroxyl group in **7**. The presence of C-8/C-14 double bond was elucidated by HMBC correlations of the H-15β and H-30 signals with the C-8 and C-14 resonances. An additional OH group at δ 4.14 was located in C-2 by HMBC correlations of the OH signal with the C-1, C-2 and C-3 resonances at δ 217.2, 77.9 (*s*) and 87.5 (*d*). Significant NOE correlations of the H-5 signal with the 4β-Me (28) and the two tigloyl methyl signals and the 10α-Me (19) signal with the H-6 and H-9 resonances clarified the relative stereochemistry of these protons in the dicyclo[3.3.1]nonane ring system. Finally, the configuration at C-6 was assumed to be the same *R* as that of known mexicanolides (Taylor, 1969; Kadota et al., 1990a,b) from the same specimen.

The molecular formula of compound **8**, 6-*O*-deacetoxysecomahoganin, was determined to be $C_{27}H_{34}O_8$ by HRFAB-MS (*m/z:* 487.2327 $[M+1]^+$, Δ −0.5 mmu). Compound **8** showed UV and IR absorptions due to a conjugated enone system at λ_{max} 230 nm and ν_{max} 1680 cm^{-1}

Table 3
^1H and ^{13}C NMR spectroscopic data for compounds **7** and **8**

No.	**7**		**8**	
	δ_H	δ_C	δ_H	δ_C
1		217.2	6.67 *d* (10.6)	152.6
2		77.9	5.93 *d* (10.6)	126.5
3	4.78 *s*	87.5		203.6
4		39.7		44.9
5	3.30 *br s*	45.0	1.94 *br t* (4.7)	51.5
6	4.54 *br s*	73.1	3.94 *m*, 4.11 *m*	61.1
7		175.3		176.7
8		126.4		43.1
9	2.10 *m*	53.0	3.32 *d* (11.1)	43.1
10		52.5		50.8
11α	1.80 *m*	18.8	1.57 *m*	21.5
11β	1.90 *m*		1.42 *m*	
12α	1.19 *ddd* (15.0, 10.3, 3.1)	29.6	1.45 *m*	32.5
12β	1.74 *dd* (15.0, 3.1)		1.77 *m*	
13		38.2		37.8
14		132.8		68.2
15α	3.26 *br d* (21.3)	33.2	3.67 *s*	51.4
15β	3.60 *d* (21.3)			
16		169.0		166.9
17	5.41 *s*	80.9	5.42 *s*	78.4
18	0.99 *s*	17.7	1.22 *s*	19.3
19	1.53 *s*	17.7	1.19 *s*	18.2
20		120.7		120.0
21	6.40 *br s*	141.1	7.38 *s*	141.2
22	7.41 *br s*	109.7	6.33 *br s*	109.9
23	7.43 *br t* (1.4)	143.2	7.38 *s*	143.3
28	0.84 *s*	23.3	1.26 *s*	24.2
29	1.05 *s*	22.2	1.07 *s*	23.2
30α	1.76 *br d* (14.8)	44.7	1.25 *s*	15.1
30β	3.04 *d* (14.8)			
OMe	3.86 *s*	53.2	3.80 *s*	53.3
2-OH	4.14 *br s*			
6-OH	2.81 *s*		2.16 *br s*	
Tig				
1′		167.0		
2′		129.2		
3′	6.91 *br q* (7.0)	138.7		
4′	1.82 *br d* (7.0)	14.5		
2′-Me	1.90 *br s*	12.4		

All spectra were measured in $CDCl_3$ at 600 MHz. Chemical shifts are expressed in ppm. *J* value in parentheses are in Hz.

different from the above compounds, and the NMR spectrum (Tables 3) also revealed several differences. The ^{1}H and ^{13}C NMR spectroscopic data showed the presence of six methyls (five tertiary and one methoxy), three methylenes, nine methines (five olefinic), and nine quaternary carbons (one olefinic and one keto and two ester carbonyls). Thus **9** is tetracyclic. The ^{1}H NMR spectrum showed a characteristic H-15 epoxide proton as a singlet at 3.67 and five methyls due to the basic limonoid skeleton at δ 1.07, 1.19, 1.22, 1.25 and 1.26. The presence of the lactonic D ring was also confirmed by the characteristic H-17 singlet at δ 5.42. A conjugated enone system at δ_H 6.67 and 5.93 (each *d*, $J = 10.6$ Hz); δ_C152.6 (*d*), 126.5 (*d*) and 203.6, was assigned to ring A by analysis of the HMBC correlations. The H-1 signal at δ 6.67 showed correlations with the C-3, C-5, C-10 and C-19 signals. On the other hand, the HMBC and NOESY spectra clarified that ring B was opened at C_6–C_7. Thus, the HMBC correlations of the H-9 signal with the C-1, C-5, C-7, C-19 and C-30 resonances, and the NOE correlations of the H-9 signal with the H-5 and H-19 resonances, the H-1 signal with the H-11β and Me-30 resonances, and the H-5 signal with the H-11α resonance, suggested that rings A and C in the molecule were twisted about 90° through the C_9–C_{10} bonding in a preferential conformer. These data clarified **9** to have the same aglycone moiety as secomahoganin (**12**) (Kadota et al., 1990b) and khayanoside (**13**) (Nakatani et al., 2002).

The structure of the last compound, swietephragmin G (**9**), $C_{34}H_{40}O_{12}$; HRFAB-MS (*m/z*: 641.2604 $[M+1]^+$, Δ 0.6 mmu) was readily elucidated from analysis of the spectroscopic data. The ^{1}H and ^{13}C NMR spectra were very similar to those of compounds **4, 5** and **7** except for the orthoester group being orthoacetate in **9**.

The antifeedant activity of the isolated compounds (**1**–**12**) was tested by a conventional leaf disk method (Wada and Munakata, 1968) against the third-instar larvae of *Spodoptera littoralis* (Boisd.). All of the compounds except for 7-deacetoxy-7-oxogedunin (**12**) were active at 1000 ppm, corresponding to a concentration of ca. 20 μg/leaf-cm^2, in which swiemahonin G (11) was most active and swietephragmins **1**–**6** and **9**, showed moderate activities. Details will be reported together with another biological activities of cytotoxity and antiviral activity against HIV-1 replication in the near future.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were measured at 600 and 150 MHz in $CDCl_3$ on JEOL FX-600 spectrophotometer. IR (KBr) and UV (MeOH) spectra were recorded on JASCO FT/IR 5300 and Shimadzu UV-210A spectrophotometers. HPLC were performed on Waters μBondapak C_{18} column by using 35–65% H_2O/MeOH as solvent.

3.2. Plant material

The leaves of *S. mahogani* were collected in April 2001 at Alexandria in Egypt. The plant material was identified by Dr. Khaleil Darweish of Alexandria University and a voucher specimen is deposited in the Faculty of Agriculture, Alexandria University.

3.3. Extraction and isolation of compounds *1–6*

Air-dried leaves of *S. mahogani* (1.9 kg) were extracted with Et_2O (15 l) at room temperature for four weeks to give a crude extract (102.2 g). The Et_2O extract was suspended in 1 l of H_2O–MeOH (1:2), fractionated successfully with hexane (3 × 500 ml) and CH_2Cl_2(3 × 500 ml) to give hexane (67.7 g) and CH_2Cl_2 (32.3 g) extract. The CH_2Cl_2 extract (10 g) was subjected to SiO_2 (500 g) cc with a 0–10% MeOH/CH_2Cl_2 gradient eluent to give 50 fractions. The limonoid fractions of 18–41 eluted with 2.5% MeOH/CH_2Cl_2 were further applied to SiO_2 (150 g) with hexane/AcOEt (1:1) to give 50 fractions, which were combined as needed to give three limonoid and two non-limonoid fractions. The first fraction (1.4 g) was roughly separated into 13 fractions through HPLC with 25% H_2O/MeOH as solvent, followed by TLC separation with 3% MeOH/CH_2Cl_2 and HPLC purification with 20–30% H_2O/MeOH to give **1** (31.5 mg), **2** (40 mg), **3** (16 mg), **4** (12.5 mg), **5** (14.5 mg), **6** (9.5 mg), **7** (5 mg), **8** (5.5 mg), **9** (6 mg), **10** (15 mg), **11** (12 mg) and **12** (0.5 mg).

3.3.1. Swietephragmin A (*1*)

White amorphous powder; $C_{38}H_{46}O_{13}$; HRFAB-MS *m/z:* 711.3009 $[M+1]^+$ (calc. 711.3017); UV λ_{max} nm (ε): 215 (16,000); IR ν_{max} cm^{-1}: 3600–3200, 1740, 1724, 1715 *sh*, 1635; for ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

3.3.2. Swietephragmin B (*2*)

White amorphous powder; $C_{39}H_{48}O_{13}$;HRFAB-MS *m/z:* 725.3154 $[M+1]^+$ (calc. 725.3173); UV λ_{max} nm (ε): 215 (14,000); IR ν_{max} cm^{-1}: 3600–3300, 1740–1710; for ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

3.3.3. Swietephragmin C (*3*)

White amorphous powder; $C_{37}H_{46}O_{12}$;HRFAB-MS *m/z:* 683.3059 $[M+1]^+$ (calc. 683.3067); UV λ_{max} nm (ε): 215 (14,000); IR ν_{max} cm^{-1}: 3550–3200, 1735–1710; for ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

3.3.4. Swietephragmin D (*4*)

White amorphous powder; $C_{36}H_{44}O_{12}$;HRFAB-MS *m/z*: 669.2914 $[M+1]^+$ (calc. 669.2911); UV λ_{max} nm (ε): 215 (14,000); IR ν_{max} cm^{-1}: 3500–3200, 1735–1710; for ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

*3.3.5. Swietephragmin E (**5**)*

White amorphous powder; $C_{37}H_{46}O_{13}$;HRFAB-MS *m/z:* 669.3021 $[M+1]^+$ (calc. 669.3015); UV λ_{max} nm (ε): 215 (16,000); IR ν_{max} cm^{-1}: 3600–3200, 1740–1710; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

*3.3.6. Swietephragmin F (**6**)*

White amorphous powder; $C_{35}H_{42}O_{12}$; HRFAB-MS *m/z:* 655.2736 $[M+1]^+$ (calc. 655.2755); UV λ_{max} nm (ε): 215 (16,000); IR ν_{max} cm^{-1}: 3600–3300, 1740–1710; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

*3.3.7. 3-O-Tigloylswietenolide (**7**)*

White amorphous powder; $C_{32}H_{40}O_{10}$;HRFAB-MS *m/z:* 585.2673 $[M+1]^+$ (calc. 585.2699); UV λ_{max} nm (ε): 215 (12,000); IR ν_{max} cm^{-1}: 3500–3200, 1745–1710; for ^1H and ^{13}C NMR spectroscopic data, see Tables 3.

*3.3.8. 6-O-Deacetylsecomahoganin (**8**)*

White amorphous powder; $C_{27}H_{34}O_8$;HRFAB-MS *m/z:* 487.2327 $[M+1]^+$ (calc. 487.2332); UV λ_{max} nm (ε): 230 (12,000); IR ν_{max} cm^{-1}: 3500–3300, 1740, 1720, 1680; for ^1H and ^{13}C NMR spectroscopic data, see Tables 3.

*3.3.9. Swietephragmin G (**9**)*

White amorphous powder; $C_{34}H_{40}O_{12}$;HRFAB-MS *m/z:* 641.2604 $[M+1]^+$ (calc. 641.2598); UV λ_{max} nm (ε): 215 (16,000); IR ν_{max} cm^{-1}: 3600–3300, 1740–1710; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

3.4. Antifeedant test

The antifeeding potential of the isolated compounds was tested three times by a conventional leaf disk method against thrid-instar larvae of *S. littoralis*. Five leaf disks (diameter 1.2 cm) of Chinese cabbage (*Brassica campestris* var. *chinensis*) were immersed in an acetone solution of the sample for 2 s. The treated disks were arranged alternatively with another five control disks (immersed only in acetone) close to the wall of a Petri dish. Ten larvae were placed in the centre of each Petri dish. The eaten areas of treated and untreated leaf disks were evaluated at appropriate intervals for 3–10 h. The experiment was terminated after the larvae had eaten approximately 50% of one of the disks.

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References

Adeoye, S.A., Bekoe, D.A., 1965. The molecular structure of *Cedrela odorata* substance. Biol. J. Chem. Soc. Commun., 301–302.

Adesogan, E.K., Taylor, D.A.H., 1968. Extractives from *Khaya senegalensis* (Desr.) A. Juss.. J. Chem. Soc. (C), 1974–1981.

Connolly, J.D., Henderson, R., McCrindle, R., Overton, K.H., Bacca, N.S., 1965. Tetranortriterpenoids Part I. The constitution of swietenine. J. Chem. Soc., 6935–6939.

Kadota, S., Marpaung, L., Kikuchi, T., Ekimoto, H., 1990a. Constituents of the seeds of *Swietenia mahogani* JACQ.I. Isolation, structures, and ^1H- and ^{13}C-nuclear magnetic resonance signal assignments of new tetranortriterpenoids related to swietenine and swietenolides. Chem. Pharm. Bull. 38, 639–651.

Kadota, S., Marpaung, L., Kikuchi, T., Ekimoto, H., 1990b. Constituents of the seeds of *Swietenia mahogani* JACQ. II. Structures of swietemahoganin A, B, C, D, E, F, and G and swietemahonolide. Chem. Pharm. Bull. 38, 894–901.

Nagalakshmi, M.A.H., Thangadurai, D., Muralidara, D., Pullaiah, R.T., 2001. Phytochemical and antimicrobial study of *Chukrasia tabularis* leaves. Fitoterapia 72, 62–64.

Nakatani, M., Abdelgaleil, S.A.M., Kurawaki, J., Okamura, H., Iwagawa, T., Doe, M., 2001. Antifeedant rings B and D opened limonoids from *Khaya senegalensis*. J. Nat. Prod. 64, 1261–1265.

Nakatani, M., Abdelgaleil, S.A.M., Kassem, Sh.M.I., Takezaki, K., Okamura, H., Iwagawa, T., Doe, M., 2002. Three new modified limonoids from *Khaya senegalensis*. J. Nat. Prod. 65, 1219–1221.

Olmo, L.R.V., da Silva, M.F.G.F., Fo, E.R., Vieira, P.C., Fernandes, J.B., Pinheiro, A.L., Vilela, E.F., 1997. Limonoids from the leaves of *Khaya senegalensis*. Phytochemistry 44, 1157–1165.

Saad, M.M.G., Iwagawa, T., Doe, M., Nakatani, M., 2003. Swietenialides, novel ring D opened phragmalin limonoid orthoesters from *Swietenia mahogani* JACQ. Tetrahedron 59, 8027–8033.

Saad, M.M.G., Iwagawa, T., Okamura, H., Doe, M., Nakatani, M., 2004. Three new mexicanolides from the stem bark of *Swietenia mahogani* JACQ. Heterocycles 63, 389–399.

Taylor, D.A.H., 1969. Extractives from *Swietenia mahogani* (L) Jacq. J. Chem. Soc. Chem. Commun., 58–59.

Taylor, D.A.H., 1984. In: Herz, W., Grisebach, H., Kirby, G.W. (Eds.), Progress in the Chemistry of Organic Natural Products. Springer, New York, pp. 1–102.

Wada, K., Munakata, K., 1968. Naturally occurring insect control chemicals. J. Agr. Food Chem. 16, 471–474.