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Swietenialides, novel ring D opened phragmalin limonoid orthoesters from *Swietenia mahogani* JACQ.

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Abstract—Three novel ring D opened limonoids corresponding to the phragmalin 8,9,14-orthoacetate with the addition of methyl 2,30-orthoacetate or a propionate, swietenialides A, B, and C and two ring-D opened phragmalin-type 1,8,9-orthoacetates, swietenialides D and E, were isolated together with one known mexicanolide, 2-hydroxyswietenin, from the ether extract of the stem bark of *Swietenia mahogani* JACQ. (Meliaceae). The structure of these unique compounds was elucidated by spectroscopic means.

1. Introduction

Meliaceae plants are attracting considerable interest, because of their significant biological activities. We have reported many limonoid antifeedants from Meliaceae plants of *Trichilia roka*,[1] *Melia azedarach*,[2] *M. toosendan*[3] and *Khaya senegalensis*.[4] *Swietenia mahogani* JACQ. is a large meliaceous mahogany 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.[5] Limonoids have been classified on the basis of which of the four rings, designated as A, B, C, and D in the intact triterpene nucleus have been oxidized. Ever since two rings B,D-seco limonoids of methyl angolensate (**1**) and its 6-hydroxy derivative (**2**) were isolated by Taylor,[6] many mexicanolide-type compounds of rings B,D-seco limonoid having a bicyclo[3,3,1]-ring system such as swietenin (**3**)[7] have been reported from *S. mahogani*.[8,9]

During our study on limonoid antifeedants from Meliaceae plants, we have found out the ether extract of the stem bark of *S. mahogany* collected at Alexandria, Egypt to have potent activity against *Spodoptera* insects. We studied the limonoid constituents of the ether extract and isolated six new limonoids of three ring D opened phragmalin-type limonoids possessing two orthoester groups, named swietenialides A (**4**), B (**5**), and C (**6**) and two ring-D opened phragmalin limonoids orthoacetates, named swietenialides D (**7**) and E (**8**), together with one known mexicanolide, 2-hydroxyswietemin (**9**).[10] This is the first isolation of limonoid diorthoesters in nature. All of the isolated compounds showed antifeedant activity against *S. littoralis* (Boisduval). Herein we report the structure elucidation of these phragmalin limonoids.

2. Results and discussion

Column chromatography of the methylene chloride soluble part of the extract (6 g) on silica, followed by a combination use of TLC separation and reversed phase HPLC purification, gave three ring D opened phragmalin-type limonoid diorthoesters, swietenialides A (**4**, 18 mg), B (**5**, 6 mg), and C (**6**, 7.5 mg) and two ring-D opened phragmalin limonoid orthoacetates, swietenialides D (**7**, 9 mg), and E (**8**, 2 mg) and one mexicanolide, 2-hydroxyswietenin (**9**, 8 mg).

Swietenialide A (**4**) was isolated as amorphous powder, $[\alpha]_D=-26°$, and it was shown to have the molecular formula $C_{40}H_{52}O_{17}$ (degree of unsaturations: 15) by accurate mass measurement (HRFAB-MS: *m/z* 805.3268 $[M+1]^+$; Δ −1.5 mmu) and ^{13}C NMR data. The UV maximum at 212 nm and the IR absorption at 3600–3200, 2985 and 1740–1715 cm^{-1} showed the presence of carbon–carbon double bond and hydroxyl and several types carbonyl groups. From the ^1H and ^{13}C NMR data (Tables 1 and 2), it was evident that seven of the elements of unsaturation were present as double bonds: three carbon–carbon (one furan ring) and four CO (as esters). Thus, the molecule is octacyclic. The NMR data also revealed that

Keywords: swietenialides A–E; ring D opened phrogmalin limonoids; 8,9,14- and 1,8,9-orthoacetyl groups; methoxy,2,30-orthoacetate; diorthoester compounds; antifeedant activity; *Swietenia mahogany* JACQ., Meliaceae.
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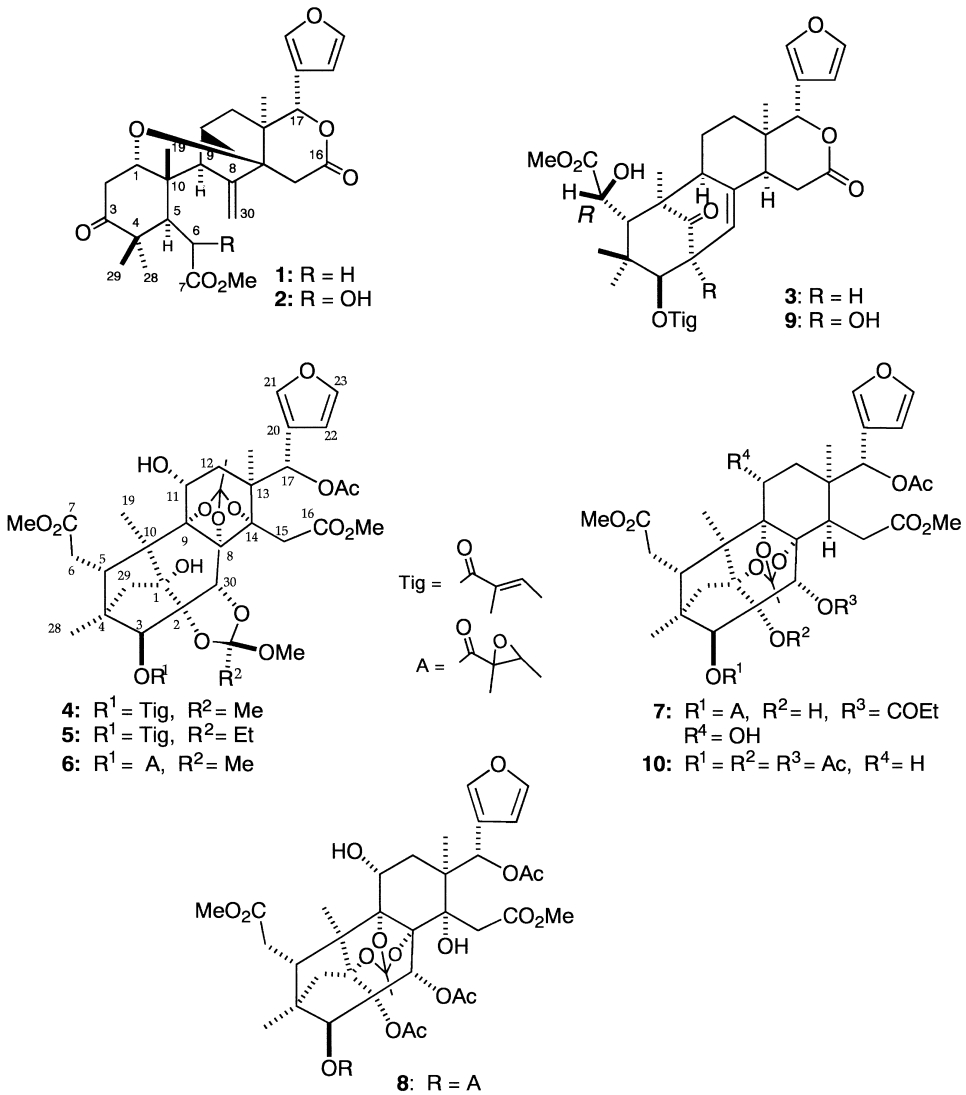

compound **4** had eleven tertiary methyls (one acetyl and three methoxy), four methylenes, nine methines (four olefinic), sixteen carbons (two olefinic) not bonded to hydrogen. From the NMR data, the presence of each one of β-furyl moiety (δ_H 6.54, 7.44 and 7.69, each 1H) and acetyl group (δ_H 2.09) was recognized. The presence of one tigloyl and two orthoester groups was also assumed from the characteristic signals of 2′ and 3′Me and 3′H in tigloyl at δ_H 1.69 (3H, br d, J=7.0 Hz), 1.95 (3H, br s) and 7.10 (1H, qq, J=1.3, 7.0 Hz) and of two orthoester carbons at δ_C 119.4 s and 122.1 s. Three methoxy (one etheric: δ_H 3.12, and two esteric: 2×δ_H 3.65) and two hydroxyl groups (δ_H 1.42 and 3.92) were also observed.

All protons directly bonded with carbon atoms were assigned by the HMQC spectrum. From decouplings and the subsequent 2D NMR studies using the ^{1}H–^{1}H COSY, HMBC (Fig. 1) and NOESY (Fig. 2) spectra, it was strongly suggested that **3** was a unique ring D opened phragmalin-type compound derived from a mexicanolide by oxidation of the C-29 methyl. Thus, H_2-6 methylene protons at δ 2.28 and 3.12 attached to a carbon adjacent to an ester carbonyl were coupled with the H-5 broad doublet proton at δ 2.88, and the presence of this moiety and a characteristic low-field H-17 proton at δ 6.14 (s) strongly suggested that **4** was a rings B,D-seco limonoid. In addition to this knowledge, the absence of one tertiary methyl signal at 8β (C-30) in the basic limonoid skeleton and the presence of 29-methylene signals (δ 1.72 and 2.15, each 1H, d, J=11.3 Hz) supported that **4** was a phragmalin-type limonoid having the tricyclo[3.3.1.^{2,10}1^{1,4}]decane ring system.

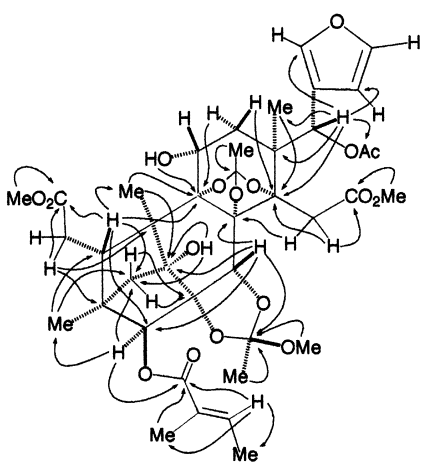

Figure 1. Significant HMBC correlations in **4**.

Table 1. ^{1}H NMR spectral data for swietenialides A–E (**4**–**8**)

No	4	5	6	7	8
3	5.34 s	5.35 s	5.30 s	4.75 s	5.26 s
5	2.88 br d (10.6)	2.89 br d (10.6)	2.84 br d (10.6)	2.65 dd (2.0, 11.3)	2.71 br d (9.1)
6	2.28 dd (10.6, 16.6)	2.23 dd (10.5, 16.5)	2.24 dd (10.6, 16.4)	2.36 dd (9.2, 15.6)	2.36 dd (9.1, 15.8)
	3.12 br d (16.0)	3.12 br d (16.5)	3.09 br d (16.4)	2.16 dd (2.1, 15.6)	2.21 br d (15.8)
11β	4.34 ddd (4.8, 9.3, 12.2)	4.36 ddd (4.8, 9.4, 12.4)	4.35 m	4.15 br d (4.1)	4.02 ddd (11.7, 3.8, 3.2)
12α	1.99 dd (12.2, 13.4)	1.98 dd (12.4, 13.4)	1.99 dd (12.6, 13.5)	1.61 dd (4.1, 15.5)	1.59 dd (3.8, 15.4)
12β	1.30 dd (4.8, 13.4)	1.30 dd (4.8, 13.4)	1.31 dd (3.7, 13.5)	1.37 br d (15.5)	1.39 dd (3.2, 15.4)
14				2.97 dd (6.5, 7.2)	
15	2.76 d (14.8)	2.78 d (14.6)	2.78 d (14.8)	2.44 dd (6.3, 15.3)	2.51 d (14.1)
	3.16 d (14.8)	3.12 d (14.6)	3.17 d (14.8)	2.87 dd (7.2, 15.3)	2.65 d (14.1)
17	6.14 s	6.15 s	6.26 s	5.70 s	5.63 s
18	1.27 s	1.26 s	1.29 s	1.45 s	1.51 s
19	1.21 s	1.21 s	1.21 s	1.11 s	1.17 s
21	7.69 br s	7.68 br s	7.74 br s	7.83 br s	7.86 br s
22	6.54 br s	6.54 br d (0.9)	6.53 br s	6.48 br s	6.54 br d (1.3)
23	7.44 br t (1.4)	7.43 br t (1.5)	7.35 br s	7.35 br s	7.37 br t (1.3)
28	0.82 s	0.82 s	0.85 s	0.92 s	0.90 s
$29_{pro\text{-}R}$	2.15 d (11.3)	2.13 d (11.3)	2.14 d (11.4)	1.86 d (10.8)	1.95 d (12.9)
$29_{pro\text{-}S}$	1.72 d (11.3)	1.75 d (11.3)	1.71 d (11.4)	1.73 d (10.8)	1.66 d (12.9)
30	5.25 s	5.23 s	5.25 s	5.57 s	6.02 s
2-OAc					2.09 s
17-OAc	2.09 s	2.10 s	2.11 s	1.99 s	1.95 s
30-OAc					2.08 s
7-OMe	3.65 s	3.66 s	3.69 s	3.68 s	3.53 s
16-OMe	3.65 s	3.65 s	3.64 s	3.60 s	3.75 s
Propanoyl					
2′				2.42 m	
3′				1.18 t (7.4)	
1-OH	3.92 s	3.87 s	3.90 s		
2-OH				2.56 s	
11-OH	1.42 d (9.3)	1.43 d (9.4)	1.44 d (9.3)	2.50 s	4.94 d (11.7)
14-OH					5.79 s
Orthoesters					
2′	1.79 s	1.78 s	1.79 s	1.67 s	1.67 s
2″	1.61 s	1.92, 1.94 dq (15.1,7.4)	1.62 s		
3″		0.99 t (7.4)			
1″-OMe	3.12 s	3.10 s	3.16 s		
Tigloyl					
3′	7.10 qq (1.3, 7.0)	7.09 qq (1.4, 7.0)			
4′	1.69 br d (7.0)	1.68 dq (7.0, 0.9)			
2′-Me	1.95 br s	1.95 br s			
2′,3′-Epoxy-2′-methylbutyryl					
3′			3.26 q (5.4)	3.27 q (5.4)	3.15 q (5.4)
4′			1.34 d (5.4)	1.41 d (5.4)	1.49 d (5.4)
2′-Me			1.70 s	1.71 s	1.78 s

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

On the other hand, long range $^1H-^{13}C$ correlations of the H-17 signal with an acetoxy carbonyl carbon signal at δ 168.8 and one of carbomethoxy signals at δ 3.65 with the 16-ester carbonyl carbon signal at δ 171.4 clarified that **4** was a ring D opened phragmalin limonoid like pseudorelone C (**10**)[11] and procerin (**11**)[12] from *Pseudocedrela kotschyii* and *Corapa procera*. The presence of orthoester group in **4** was presumed from that almost all of the phragmalin groups isolated so far contained an orthoacetate group and the characteristic orthoacetate carbon resonance was observed at δ 119.4. The presence of the 3-tigloyloxy and 1,11-dihydroxyl groups was also elucidated by the HMBC correlations of the 3-H signal at δ 5.34 with the tigloyl carbonyl carbon signal at δ 167.2 and two OH signals at δ 3.92 and 1.42 with the C-1 and C-11 signals at δ 81.8 and 67.1 (Table 1). Especially, the presence of 1-OH group located one orthoacetate group at positions 8, 9 and 14, since the group had been observed either at positions 8, 9, 14 or at 1, 8, 9 in phragmalins. Finally, the remaining second orthoacetate group possessing a methoxy group was located to C-2 and C-30 from singlet signals due to H-3 (δ 5.34) and H-30 (δ 5.25) and the HMBC correlations of the H-30 and one methoxy methyl (2″-OMe) signals at δ 3.12 with the second orthoacetate carbon signal at δ 122.1 (C-1″).

The structure of **4** including the stereochemistry appears to fully explain the NMR data on swietenialide A by the consideration using of a molecular model and the NOESY spectrum. Significant NOE correlations between the H-30 signal and H-5 and H-17 signals, the $H_{pro\text{-}S}$ signal of the 29-methylene at δ 2.33 and the 10-Me(19) signal at δ 1.21, and the other $H_{pro\text{-}R}$ signal at δ 2.11 and the H-3 signal clarified relative stereochemistry between these protons in the tricyclo[3.3.1.1]decane ring system. As the absolute structure of a mexicanolide swietenin (**3**) isolated from the same species has been determined by X-ray analysis, absolute stereochemistry of the protons attributable to the

Table 2. ^{13}C NMR spectral data for swietenialides A–D (**4**–**8**)

No	4	5	6	7	8	No	4	5	6	7	8
1	81.8 s	82.0 s	81.8 s	85.5 s	84.7 s	2-OAc					21.5 q
2	86.1 s	85.8 s	85.7 s	79.6 s	86.1 s						169.9 s
3	85.4 d	85.5 d	86.4 d	84.3 d	82.2 d	17-OAc	21.0 q	21.1 q	21.1 q	21.2 q	21.4 q
4	43.4 s	43.5 s	43.4 s	45.5 s	45.9 s		168.8 s	168.6 s	169.0 s	169.2 s	169.0 s
5	40.4 d	40.5 d	40.4 d	36.8 d	36.6 d	30-OAc					21.4 q
6	32.4 t	32.6 t	32.4 t	34.2 t	34.0 t						168.1 s
7	174.9 s	174.7 s	174.9 s	172.7 s	172.2 s	7-OMe	51.3 q	51.8 q	51.3 q	51.9 q	51.8 q
8	90.3 s	90.5 s	90.2 s	87.2 s	88.9 s	16-OMe	51.7 q	51.4 q	51.8 q	51.5 q	52.1 q
9	87.1 s	87.2 s	87.1 d	86.4 d	87.5 d	Propanoyl					
10	52.1 s	52.2 s	52.0 s	45.2 s	46.9 s	1′				171.7 s	
11	67.1 d	67.2 d	67.1 d	66.8 d	66.3 d	2′				27.7 t	
12	38.1 t	38.2 t	39.0 t	37.0 t	38.6 t	3′				8.4 q	
13	43.8 s	43.9 s	43.8 s	38.5 s	43.2 s	Orthoesters					
14	87.8 s	87.8 s	87.8 s	45.7 d	80.4 d	1′	119.4 s	119.2 s	119.4 s	119.0 s	119.4 s
15	38.7 t	39.0 t	38.7 t	30.4 t	36.5 t	2′	16.3 q	16.5 q	16.3 q	13.3 q	20.4 q
16	171.4 s	171.3 s	171.3 s	175.1 s	174.6 s	1″	122.1 s	123.3 s	122.3 s		
17	68.7 d	68.8 d	68.6 d	70.6 d	70.2 d	2″	19.7 q	25.6 q	19.6 q		
18	17.7 q	17.9 q	17.8 q	23.6 q	20.3 q	3″		8.0 s			
19	14.6 q	14.8 q	14.8 q	16.3 q	17.0 q	1″-OMe	51.3 q	50.3 q	50.8 q		
20	122.3 s	122.2 s	122.1 s	122.5 s	121.6 s	Tiglate					
21	141.2 d	141.0 d	141.6 d	142.6 d	143.0 d	1′	167.2 s	166.9 s			
22	109.6 d	109.6 d	109.8 d	109.7 d	109.5 d	2′	127.8 s	127.7 s			
23	143.5 d	143.3 d	143.4 d	142.8 d	142.8 d	3′	138.6 d	138.3 d			
28	14.4 q	14.6 q	14.5 q	14.4 q	14.4 q	4′	14.6 q	14.4 q			
29	41.7 t	41.8 t	41.5 t	39.8 t	39.8 t	2′-Me	12.2 q	12.4 q			
30	71.4 d	71.1 d	71.2 d	70.6 d	67.7 d	2′,3′-Epoxy-2′-methylbutyryl					
2-OAc					21.5 q	1′			171.0 s	172.1 s	170.6 s
					169.9 s	2′			58.0 s	58.3 s	58.9 s
17-OAc	21.0 q	21.1 q	21.1 q	21.2 q	21.4 q	3′			58.8 d	59.0 d	58.8 d
	168.8 s	168.6 s	169.0 s	169.2 s	169.0 s	4′			13.4 q	13.3 q	13.5 q
30-Oac					21.4 q	2′-Me			13.5 q	13.5 q	13.9 q
					168.1 s						

Measured in $CDCl_3$ at 150 MHz. Chemical shift values are in ppm from TMS.

rings A and B of basic limonoid skeleton was assigned such as in the structure **4**. An NOE correlation between the H-30 and the 2″-OMe signals, therefore, elucidated *R* configuration of the second orthoacetate carbon (C-1″). On the other hand, the stereochemistry at C-17 was also presumed to be the same *R* as that in **9** as supported in the following manner. The ring C should be fixed in a chair form by the formation of 8,9,14-orthoacetate, which was clear from the large coupling (J=12.2 Hz) of the H-11β signal at δ 4.34 with H-12α at δ 1.99 and a remarkable NOE correlation between the H-11 and H-5 signals. Next, a large upfield shift of the H-12β signal to δ 1.30 was observed. As this shift could be account for by the ring current of the furan ring, **4** should have a preferential conformer such as in Figure 2(a). Taking into account this conformation, the observed remarkable NOE correlations of the H-17 signal with the H-11 and H-30 signals and the furan proton (H-21 and H-22) signals with the 13α-Me (C-18) and 11-H signals could be well explained.

Swietenialide B (**5**), $C_{41}H_{54}O_{17}$, $[\alpha]_D$=−33°, showed very similar IR and NMR (^1H–^1H COSY, HMQC, HMBC and NOESY) spectra to those of **4**, including all the functional groups in **4**, except for the change of the second orthoacetate group in **4** to orthopropionate (δ_H 0.99, 3H, t, J=7.4 Hz, 1.92 and 1.94, each 1H, dq, J=15.1, 7.4 Hz; δ_C 19.7 q and 123.3 s) in **5**. As the presence of 8,9,14-orthoacetate and 1-OH group was elucidated by the chemical shift of C-1′ (δ 119.2) and strong HMBC correlations of the OH signal at δ 3.87 with C-1 and C-28 signals at δ 82.0 and 41.8, the second orthoacetate was assigned to C-2 and C-30. An NOE correlation observed between the H-30 (δ 5.23) and I″-OMe (δ 3.10) signals confirmed the same *R* configuration of C-1″ as that in **4** (Fig. 3). NOE studies elucidated all other stereochemistry in **5** to be the same as those in **4**.

The ^1H and ^{13}C NMR data of Swietenialide C (**6**), $C_{40}H_{52}O_{18}$, $[\alpha]_D$=−6.3°, were also very close to those of compound **1** including the presence of methyl 2,30-orthoacetate group (C″-1: δ 122,3) to indicate **6** also having the same carbon skeleton as **4** and **5**. However, a sharp carbonyl band at 1740 cm^{-1} in the IR spectrum suggested the lack of conjugate enone system in **6**. The NMR studies including the HMBC and NOE correlations elucidated that **6** differed from **4** only in the change to 2′,3′-epoxy-2′-methylbutyryl (δ_H 1.34, 3H, d, J=5.4 Hz, 1.70, 3H, s, and 3.26, 1H, q, J=5.4 Hz; δ_C 19.7 q and 122.1 s) of the tigloyl group in **4**. As this group must be derived from tigloyl, it should have *cis*-configuration, which was confirmed by a pronounced NOE correlation between 2′ and 3′-Methyl groups. Although we could not determine the absolute stereochemistry, the absolute configurations of C-2′ and C-3′ were assumed to be *S* and *R* in analogy with those in a similar phragmalin-type utilin isolated from *Entandophragma utile*,[13] the absolute structure of which had been determined by X-ray analysis.[14]

Swietenialide D (**7**), $[\alpha]_D$=−26°, has the same molecular formula $C_{40}H_{52}O_{17}$ as that of **4** and the UV and IR spectra showed similar absorptions with those of **6** at 210 nm and at 3600–3250 and 1740 cm^{-1}. However, the NMR spectrum showed the presence of only one orthoacetate group (δ_H

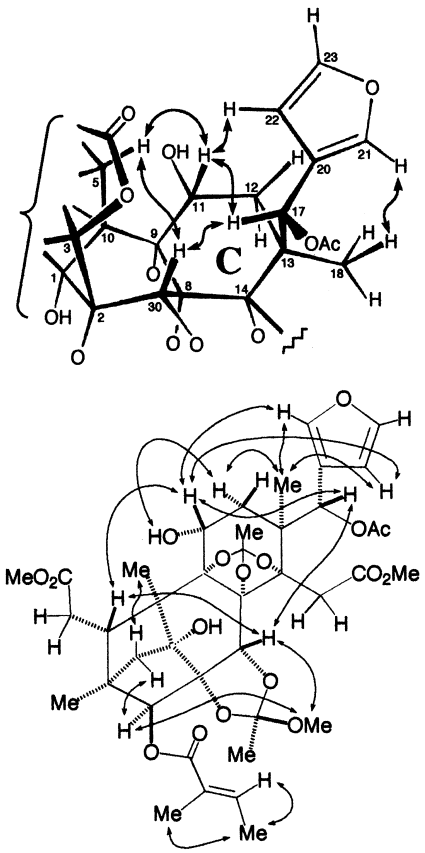

Figure 2. Selected NOE correlations in **4**. Preferential conformation and NOE correlations around the ring C in **4**.

1.67, 3H, s; δ_C 13.3 q and 119.0 s) and 2′,3′-epoxy-2′-methylbutyryl group together with additional signals due to a propanoyl group (δ_H 1.18, 3H, t, J=7.4 Hz and 2.41 and 2.43, each 1H, dq, H=14.8 and 7.4 Hz; δ_C 13.3 q, 27.7 t and 171.7 s) different from the compound **6**. From the ^{1}H and ^{13}C NMR data (Tables 1 and 2), it was evident that **7** was octacyclic and its heptaunsaturations were present as double bonds: two carbon–carbon (as a furan ring) and five CO (as esters). The NMR data also revealed that compound **7** had ten tertiary methyls (one acetyl and two methoxy), five methylenes, ten methines (three olefinic), fifteen carbons (one olefinic) not bonded to hydrogen and two hydroxyl groups. A β-furyl moiety and one acetyl and two methoxy groups were also observed from the NMR data.

Although the chemical shifts of many signals due to the limonoid skeleton in **7** were somewhat different from those of **4**–**6**, the HMQC assignment of all the proton and carbon signals indicated **7** to be also a ring-D opened phragmalin limonoid. The ^{1}H NMR spectrum showed the presence of the characteristic H-17 singlet at δ 5.70, two 29-methylene doublet at δ 1.73 and 1,86 (each J=10.8 Hz) and two carbomethoxy groups assigned to 7- and 16-OMe at δ 3.60 and 3.65. Although the position of the orthoacetate group could not determined directly by the HMBC spectrum, it was located to the position 1, 8 and 9 because of the correlations of two hydroxyl proton signals at δ 2.56 and 2.50 with the C-2 and C-11 signals at δ 79.6 and 66.8, respectively (Fig. 3). The presence of 3-(2′,3′-epoxy-2′-methyl)butyryl and 30-propanoyl ester moieties were also elucidated by HMBC correlations of the H-3 and H-30 signals at δ 5.75 and 3.06 with the carbonyl carbon signals at δ 172.1 and 171.7. The configuration of these protons were assigned as α and β on the basis of the NOE correlations (Fig. 4), in which the H-3 signal showed a similar correlation to that in **6**, but the H-30 signal obtained a new correlation with the H-12β signal, not with the H-11β signal, together with the H-5 and H-17 signals. The H-5 signal also showed a new NOE correlation with the H-12β signal. These findings suggested strongly a conformation change of the ring C in **7** from that in **4**–**6**, and the conformational change accounted nicely for the chemical shift deviation of many NMR signals in **7** from those of **4**–**6**.

Swietenialide E (**8**), $[\alpha]_D$=−24°; molecular formula $C_{41}H_{52}O_{19}$, showed similar ^{1}H and ^{13}C NMR data to those of **7** except for an introduction of one hydroxyl group and the change of some substituents, and extensive NMR studies using HMQC, HMBC and NOESY spectra suggested that **8** was also a 1,8,9-orthoacetate having the same carbon skeleton of the ring-D opened phragmalin as **7**. Although **8** also had two hydroxyl groups, they were elucidated to be at C-11 and C-14 by the HMBC correlations of the hydroxyl protons at δ 4.94 and 5.70 with the C-11 and C-14 carbons at δ 66.3 and 80.4, respectively. The presence of 3β-(2′,3′-epoxy-2′-methyl)butyryl and 30-acetoxy groups were

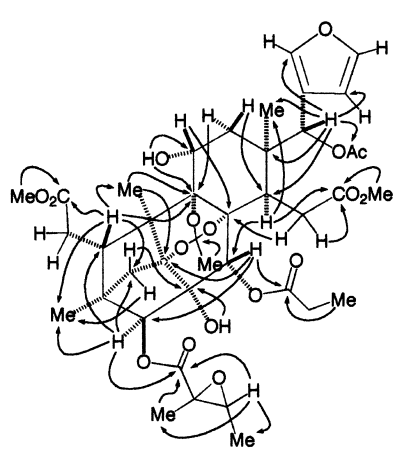

Figure 3. Significant HMBC correlations in **7**.

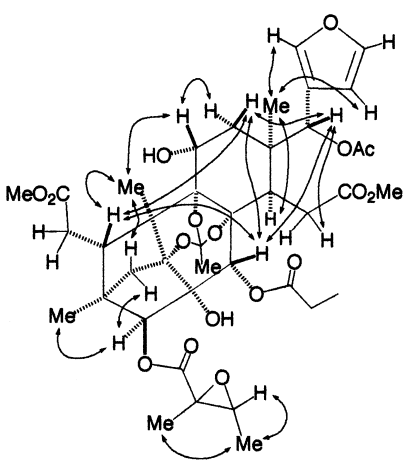

Figure 4. Selected NOE correlations in **7**.

elucidated by HMBC correlations of the H-3 and H-30 signals at δ 5.26 and 6.02 with the carbonyl carbon signals at δ 170.6 and 168.1, which were correlated with the H-2′ and acetyl methyl signals at δ 3.15 and 2.08, respectively. The large difference in the chemical shifts of the H-3 and H-30 signals in **8** from those in **7** may be attributable to the dissolution of a 7-membered hydrogen bonding between the 2-OH and 30-propanoyl carbonyl groups in **7**, followed by a conformation change of the bridged decane ring. Finally, the position of the orthoacetate group to be 1, 8 and 9 same as in **7** was determined from the NOE observation between the methyl signal at δ 1.78 and the proton signal of the 14-OH group and the consideration of a molecular model.

Many phragmalin limonoids have been reported from several Meliaceae plants,[15] but this is the first isolation from *S. mahogani*. The isolated compounds **4**–**8** showed the antifeedant activity at 1000 ppm concentration against the third-instar larvae of *S. littoralis* (Boisduval).

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were measured at 600 and 150 MHz at 27°C in $CDCl_3$ on a JEOL FX-600 spectrometer. IR (KBr) and UV (MeOH) spectra were recorded on JASCO FT/IR 5300 and Shimadzu UV-210A spectrophotometers. Optical and CD spectra were measured in MeOH at 22° using JASCO DIP-370S and JASCO J-720 spectropolarimeters. HPLC was performed on Waters μBondapak C_{18} column by using 25–45% H_2O–MeOH and 50–55% H_2O–CH_3CN as solvents. Kieselgel 60F_{254} plates (0.2 mm thick, Merck) were used for prep. TLC.

3.2. Plant material

The stem bark was collected in April 2001 at Alexandria in Egypt.

3.3. Extraction and isolation

After defatting with hexane, the dried stem bark (950 g) was extracted with Et_2O (3 l) to yield 13 g of material, 10 g of which was dissolved in 1 l of MeOH–H_2O (2:1) and then extracted with CH_2Cl_2 (3×600 ml). The CH_2Cl_2 layer (6 g) was fractionated by column chromatography on silica gel using a CH_2Cl_2–MeOH solvent system. A limonoid fraction (600 mg) eluted with 1% MeOH–CH_2Cl_2 was separated two fractions by HPLC with 25% H_2O–MeOH. From the first fraction, a mexicanolide-type compound was isolated and the second fraction was further fractionated using 50% H_2O–CH_3CN as solvent to give three fractions (fr 2: 42 mg, fr 3: 35 mg and fr 4: 21 mg). Fractions 3 and 4 were purified by prep. TLC to give **4** (18 mg) and **5** (6 mg) using 20% acetone–benzene and 25% AcOEt–CH_2Cl_2 as solvents, respectively. On the other hand, fr 2 was separated to two fractions by prep. TLC with 50% AcOEt–hexane, one of which was followed by further TLC separation with 10% acetone–CH_2Cl_2 to give **6** (7.5 mg) and **7** (9 mg), and the other was purified by HPLC with 55% H_2O–CH_3CN to give **8** (2 mg).

3.3.1. Swietenialide A (4). White amorphous powder; HRFABMS *m/z*: 805.3268 $[M+1]^+$, calcd for $C_{40}H_{53}O_{17}$, 805.3283; $[\alpha]_D=-26°$ (c 0.75); IR (KBr) ν_{max} cm^{-1}: 3600–3200, 2985, 1740–1715, 1655, 1261, 1160, 1045 and 906; UV (MeOH) λ_{max} nm (ϵ): 212 (8,800).

3.3.2. Swietenialide B (5). White amorphous powder; HRFABMS *m/z*: 819.3424 $[M+1]^+$, calcd for $C_{41}H_{55}O_{18}$, 819.3439; $[\alpha]_D=-33°$ (c 0.16); IR (KBr) ν_{max} cm^{-1}: 3600–3200, 2990, 1740–1715, 1655, 1230, 1165, 1045 and 908; UV (MeOH) λ_{max} nm (ϵ): 215 (12,000).

3.3.3. Swietenialide C (6). White amorphous powder; HRFABMS *m/z*: 821.3231 $[M+1]^+$, calcd for $C_{40}H_{53}O_{18}$, 821.3232; $[\alpha]_D=-6°$ (c 0.19); IR (KBr) ν_{max} cm^{-1}: 3580–3300, 3050, 1740, 1715, 1655, 1230, 1165, 1045 and 908; UV (MeOH) λ_{max} nm (ϵ): 209 (5,100).

3.3.4. Swietenialide D (7). White amorphous powder; HRFABMS *m/z*: 805.3278 $[M+1]^+$, calcd for $C_{40}H_{53}O_{17}$, 805.3283; $[\alpha]_D=-26°$ (c 0.21); IR (KBr) ν_{max} cm^{-1}: 3600–3300, 3000, 1739, 1277, 1236, 1178, 1045 and 893; UV (MeOH) λ_{max} nm (ϵ): 215 (5,500).

3.3.5. Swietenialide E (8). White amorphous powder; HRFABMS *m/z*: 849.3181 $[M+1]^+$, calcd for $C_{41}H_{53}O_{19}$, 849.3181; $[\alpha]_D=-24°$ (c 0.16); IR (KBr) ν_{max} cm^{-1}: 3600–3200, 2970, 1740–1720, 1655, 1261, 1160, 1045 and 906; UV (MeOH) λ_{max} nm (ϵ): 212 (7,500).

3.4. Antifeedant test

The antifeeding activity of the isolated compounds was tested at 1000 ppm concentration by a conventional leaf disk method[16] using Chinese cabbage (*Brassica campestris* L. var *chinensis*) against the third-instar larvae of *S. littoralis* (Boisduval).

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