D-Ring-Opened Phragmalin-Type Limonoid Orthoesters from the Twigs of *Swietenia macrophylla*

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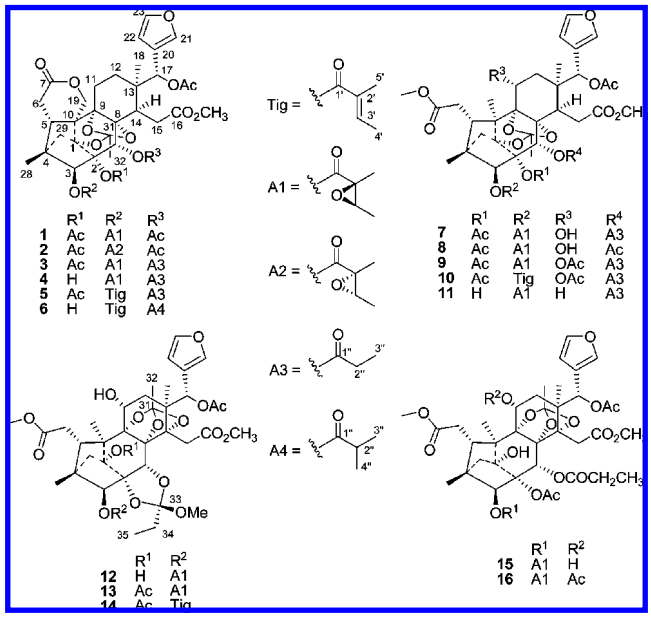
Sixteen new D-ring-opened phragmalin limonoid orthoesters, swietenitins A−M (**1**−**6**, **8**, **10**, **12**−**16**), 2-acetoxyswietenialide D (**7**), 2,11-diacetoxyswietenialide D (**9**), and 11-deoxyswietenialide D (**11**), and four known compounds were isolated from the twigs of *Swietenia macrophylla*. The structures of **1**−**16** were established on the basis of spectroscopic methods, and **1** and **2** were confirmed by single-crystal X-ray diffraction. The ^{1}H NMR-based conformational analysis on the epimeric compounds **1** and **2** provided a general approach to determine the absolute configuration of the 2,3-epoxy-2-methylbutyryloxy unit at C-3 borne by a large group of the known phragmalin-type limonoid orthoesters.

Swietenia macrophylla King (Meliaceae), a timber tree, grows in tropical areas of Asia, such as India, Malaysia, and southern mainland China.[1] This plant has traditional applications for the treatment of hypertension.[2] Previous chemical investigations on the genus *Swietenia* have led to the isolation of an array of structurally diverse limonoids exhibiting a wide range of biological activities, such as antihypertensive,[2] insect antifeeding,[3] anti-PAF,[4] antidiabetes,[4] antimalarial,[4,5b] and antifungal effects.[5a] These structurally diverse and biologically interesting metabolites have stimulated the continuing chemical study of this genus.[6] In the current investigation, which was conducted as a part of a continuing project of the investigation of the constituents of plants of the Meliaceae family, 16 new D-ring-opened phragmalin limonoid orthoesters, swietenitins A−M (**1**−**6**, **8**, **10**, **12**−**16**), 2-acetoxyswietenialide D (**7**), 2,11-diacetoxyswietenialide D (**9**), and 11-deoxyswietenialide D (**11**), together with four known compounds, were isolated from an ethanol extract of the twigs of *S. macrophylla*. The structures of **1**−**16** were established on the basis of spectroscopic methods, and two were confirmed by single-crystal X-ray diffraction. A ^{1}H NMR-based conformational analysis was developed to determine the absolute configuration of the 2,3-epoxy-2-methylbutyryloxy substituent at C-3 of phragmalin-type limonoid orthoesters, corroborating with the single-crystal X-ray diffraction of **1** and **2**.



Results and Discussion

Swietenitin A (**1**), obtained as colorless crystals, gave the molecular formula $C_{40}H_{48}O_{17}$, as determined by HREIMS at *m/z* 800.2875 $[M]^+$ (calcd 800.2891), which was supported by the sodiated and protonated molecular ion peaks at *m/z* 823 $[M + Na]^+$ and *m/z* 801 $[M + H]^+$ in the positive ESIMS. The IR absorptions at 1763 and 1740 cm^{-1} implied the presence of six-membered γ-lactone and ester groups, respectively.[6c] The ^{13}C NMR spectrum displayed 40 carbon resonances including nine methyls (one methoxy), six methylenes (one oxygenated), nine methines (three olefinic and four oxygenated), and 16 quaternary carbons (one olefinic and six oxygenated). Furthermore, a combined analysis of its ^{1}H and ^{13}C NMR data (Tables 1 and 2) revealed the presence of three acetyls, an orthoacetate group, a β-furyl ring, and a 2,3-epoxy-2-methylbutyryl moiety. There were 17 unsaturations in the molecule of **1**, of which nine degrees were occupied by six ester carbonyls and the β-furyl ring, and the remaining eight degrees required **1** to be octacyclic at the central core. The aforementioned data suggested that **1** is a phragmalin-type limonoid orthoester.[7]

Extensive analysis of 2D NMR spectra, especially the HMBC data, allowed the assignment of most functional groups to the limonoid core and confirmed the framework of a ring-D-*seco* phragmalin-type limonoid for **1**. In the HMBC spectrum (Figure 1), the key correlations of H_2-6/C-5 and C-7 and of H_2-19/C-1, C-5, C-7, and C-10 revealed the presence of a six-membered γ-lactone. The correlation between H-17 and the carbonyl of an acetyl at δ 169.7 and the correlations from H_2-15 and OMe to C-16 at δ 174.1 showed that the OMe and an OAc group are attached to C-16 and C-17, respectively, indicating that **1** is a ring-D-*seco* limonoid. The strong HMBC correlation between H-3 and C-1′ of the epoxytiglate unit indicated its location at C-3. The HMBC correlation between H-30 and the carbonyl of one acetyl at δ 168.7 showed the presence of an acetoxy at C-30. The quaternary carbon at δ 119.4 (C-31) correlating with the methyl at δ 1.65 (s) revealed the presence of a typical orthoacetate moiety. Furthermore, the mutual HMBC correlations of C-1/H-19 and H-29, C-2/H-3 and H-29, C-8/H-15 and H-30, and C-9/H-11 and H-12 allowed the assignments of four oxygenated quaternary carbons to C-1, C-2, C-8, and C-9, respectively. For the phragmalin-type limonoids isolated from this genus, a 1,8,9-,[8a] 8,9,14-,[8a] or 8,9,30-orthoacetate[8b] is usually found. The presence of an 1,8,9-orthoacetate in **1** was assigned tentatively, and the remaining OAc was thus located at C-2 by comparing its NMR data with those of limonoids possessing the same substituted pattern reported.[9]

The relative configuration of **1** was assigned by a ROESY experiment (Figure 2a), in which strong cross-peaks from H-17β to H-30 and H-15 indicated that H-30 and CH_2-15 are cofacial, and these were arbitrarily assigned with a β-orientation. The

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Table 1. ^{1}H NMR Spectroscopic Data of **1**−**6**[a]

proton	1	2	3	4	5	6
3	5.25 (s)	5.30 (s)	5.25 (s)	4.66 (s)	5.36 (s)	4.71 (s)
5	2.61 (dd, 4.7, 3.0)	2.57 (m)	2.61 (dd, 4.7, 3.1)	2.63 (dd, 4.7, 3.1)	2.68 (dd, 4.5, 2.7)	2.66 (dd, 4.8, 3.2)
6	2.43 (dd, 17.1, 4.7)	2.38 (dd, 16.5, 3.8)	2.43 (dd, 16.8, 4.7)	2.40 (dd, 16.9, 4.7)	2.43 (dd, 16.8, 4.5)	2.43 (dd, 16.8, 4.8)
	2.52 (dd, 17.1, 3.0)	2.55 (m)	2.52 (dd, 16.8, 3.1)	2.54 (dd, 16.9, 3.1)	2.53 (dd, 16.8, 2.7)	2.57 (dd, 16.8, 3.2)
11α	1.90 (m)	1.86 (m)	1.89 (m)	1.88 (m)	1.89 (m)	1.89 (m)
11*β*	2.16 (m)	2.12 (m)	2.16 (m)	2.11 (m)	2.18 (m)	2.13 (m)
12α	1.12 (m)	1.08 (m)	1.15 (m)	1.07 (m)	1.05 (m)	1.07 (m)
12*β*	1.16 (m)	1.15 (m)	1.15 (m)	1.14 (m)	1.19 (m)	1.16 (m)
14	2.31 (m)	2.32 (dd, 9.2, 4.0)	2.38 (m)	2.31 (m)	2.32 (m)	2.28 (m)
15	2.24 (m)	2.25 (dd, 15.8, 9.2)	2.23 (m)	2.31 (m)	2.20 (m)	2.28 (m)
	2.86 (dd, 15.1, 3.7)	2.84 (dd, 15.8, 4.0)	2.86 (dd, 15.8, 3.8)	2.82 (dd, 18.7, 8.9)	2.85 (dd, 15.9, 3.6)	2.80 (dd, 19.6, 9.1)
17	5.68 (s)	5.70 (s)	5.61 (s)	5.65 (s)	5.69 (s)	5.66 (s)
18	1.26 (s)	1.23 (s)	1.25 (s)	1.24 (s)	1.24 (s)	1.24 (s)
19	4.35 (d, 14.0)	4.32 (d, 13.8)	4.34 (d, 14.1)	4.33 (d, 13.9)	4.35 (d, 13.9)	4.34 (d, 13.7)
	4.77 (d, 14.0)	4.75 (d, 13.8)	4.78 (d, 14.1)	4.75 (d, 13.9)	4.78 (d, 13.9)	4.76 (d, 13.7)
21	7.76 (brs)	7.70 (brs)	7.75 (brd, 0.7)	7.92 (brs)	7.66 (brs)	7.59 (brs)
22	6.41 (brd, 1.9)	6.41 (brs)	6.40 (brd, 1.7)	6.41 (brd, 1.6)	6.40 (brs)	6.36 (brd, 1.2)
23	7.38 (brt, 1.6)	7.39 (brs)	7.37 (brt, 1.7)	7.37 (brt, 1.6)	7.39 (brs)	7.37 (brt, 1.2)
28	0.94 (s)	0.89 (s)	0.94 (s)	0.94 (s)	0.90 (s)	0.96 (s)
29_a	2.30 (m)	2.27 (d, 11.5)	2.32 (d (11.2)	2.20 (d, 11.2)	2.29 (d, 11.6)	2.20 (d, 10.8)
29_b	1.70 (m)	1.68 (d, 11.5)	1.70 (d, 11.2)	1.75 (d, 11.2)	1.73 (d, 11.6)	1.74 (d, 10.8)
30	5.95 (s)	5.83 (s)	5.97 (s)	5.53 (s)	6.05 (s)	5.61 (s)
32	1.65 (s)	1.58 (s)	1.65 (s)	1.63 (s)	1.66 (s)	1.64 (s)
OMe-16	3.69 (s)	3.68 (s)	3.68 (s)	3.69 (s)	3.68 (s)	3.68 (s)
Ac-2	1.96 (s)	1.97 (s)	1.95 (s)		1.98 (s)	
Ac-17	2.13 (s)	2.15 (s)	2.12 (s)	1.97 (s)	2.14 (s)	1.93 (s)
Ac-30	2.06 (s)	2.06 (s)				
3′	3.14 (q, 5.5)	4.13 (q, 5.4)	3.16 (q, 5.5)	3.17 (q, 5.5)	6.89 (q, 6.9)	6.76 (dq, 6.8, 1.3)
4′	1.52 (d, 5.5)	1.48 (d (5.4)	1.55 (d, 5.5)	1.45 (d, 5.5)	1.95 (d, 6.9)	1.94 (d, 6.8)
5′	1.69 (s)	1.65 (s)	1.69 (s)	1.67 (s)	1.66 (s)	1.64 (s)
2″			2.22 (q, 7.5)	2.47 (q, 7.5)	2.25 (q, 7.4)	2.66 (m)
3″			1.19 (t, 7.5)	1.22 (t, 7.5)	1.10 (t, 7.4)	1.22 (d, 7.0)
4″						1.25 (d, 7.0)

[a] Data were measured in $CDCl_3$ at 400 MHz; chemical shifts are expressed in ppm; the spin coupling (*J*) is given in parentheses (Hz).

ROESY correlations of H-3 with H-29 and of Me-5′ with H-5 and H-21 revealed that the 2,3-epoxy-2-methylbutyryl substituent is *β*-directed. The key correlation between Me-18 and H-14 indicated that H-14 is α-oriented. The Me-32, correlating with the methyl of OAc-2 and H-14, implied that the OAc-2 and the 1,8,9-orthoacetate motif are α-oriented. The mutual ROESY correlations of H-29a/Me-28 and H-19, and H-29b/H-3 and Me-28, were observed to distinguish two protons at C-29 (Figure 2a). The strong correlation between Me-4′ and Me-5′ indicated that two methyls of 2,3-epoxy-2-methylbutyryl are *cis*-configured. A single-crystal X-ray diffraction analysis (Figure 2b) was used to confirm the structure of **1**.

Swietenitin B (**2**), obtained along with **1** from a mixture by semipreparative HPLC, shared the same molecular formula, $C_{40}H_{48}O_{17}$, as **1**, as determined by HREIMS at *m*/*z* 800.2904 $[M]^+$ (calcd 800.2891). The IR and mass spectra of **1** and **2** were almost identical, and their ^{1}H and ^{13}C NMR data (Table 1) also showed a high similarity with the only difference being the chemical shift of H-3′ at *δ* 3.14 for **1** and at *δ* 4.13 for **2**, suggesting that **2** is probably the 2′,3′-epimer of **1**. In its ROESY spectrum (Figure 3a), the strong correlation between Me-4′ and Me-5′ indicated that two methyls of the 2,3-epoxy-2-methylbutyryl unit are also *cis*-configured. The key ROESY correlations from H-3′ at *δ* 4.13 to H-21 and H-30 and from Me-4′ to H-21 suggested that the absolute configuration of the 2,3-epoxy-2-methylbutyryl substituent of **2** is enantiomeric to that of **1**. To verify this deduction, the single-crystal X-ray diffraction of **2** was also performed (Figure 3b), which was fully consistent with the results established by spectroscopic analysis.

Observation of the ^{1}H NMR data of compounds **1** and **2** indicated the presence of significant steric hindrance between the bulky 2,3-epoxy-2-methylbutyryl group and the limonoid core, making one stable conformation predominant for each of the compounds in solution. The 2,3-epoxy-2-methylbutyryl group at C-3 in **1** and **2** showed noticeable differences in the ^{1}H NMR spectrum, in particular, H-3′ at *δ* 3.14 for **1** and at *δ* 4.13 for **2**. The H-3′ signal of **2** was shifted downfield about Δ*δ* 1.0 due largely to the strong deshielding effect of the *β*-furyl ring. On biogenetic grounds and since all limonoid derivatives isolated hitherto have the same absolute configuration in the limonoid core, the absolute configurations of **1** and **2** were assumed as depicted. The absolute configurations of the 2,3-epoxy-2-methylbutyryl unit in **1** and **2** could be assigned by ROESY spectra (Figures 2a and 3a) as 2*S*, 3*R* and 2*R*, 3*S*, respectively.

Furthermore, ^{1}H NMR-based conformational analysis (Figures 2a and 3a) combined with the corroboration of the single-crystal X-ray diffraction of swietenitins A (**1**) and B (**2**) (Figures 2b and 3b) have enabled the proposal of guidelines to determine the absolute configuration of the 2,3-epoxy-2-methylbutyryl unit at C-3 of phragmalin-type limonoid orthoesters. These can be summarized as follows: (1) For compound **1**, with a 2*S*,3*R*-epoxy-2-methylbutyryl moiety at C-3, the H-3′ signal resonated at *δ* 3.14 (Table 1), and ROESY correlations from Me-5′ to H-5 and H-21 were observed (Figure 2a); (2) for compound **2**, with a 2*R*,3*S*-configuration, H-3′ was downfield shifted to *δ* 4.13 due to the deshielding effect of the *β*-furyl ring, and ROESY correlations from H-3′ to H-21 and H-30 and from Me-4′ to H-21 were evident (Figure 3a).

Swietenitin C (**3**), a white amorphous powder, gave a molecular formula of $C_{41}H_{50}O_{17}$, as determined by the HREIMS at *m*/*z* 814.3061 $[M]^+$ (calcd 814.3048). The NMR spectra of **3** showed many similarities to those of **1** except for the presence of one additional $-CH_2-$ unit, and this was supported by its EIMS. A detailed analysis of the NMR data of **3** further revealed the presence of a propionyloxy group at C-30 instead of the acetoxy group in **1**. The H-3′ signal of compound **3** resonated at *δ* 3.16 (q, $J = 5.5$ Hz) and was indicative of the presence of a 2*S*,3*R*-epoxy-2-methylbutyryl group at C-3.

Swietenitin D (**4**), a white amorphous powder, gave a molecular formula of $C_{39}H_{48}O_{16}$, as established from the HREIMS at *m*/*z* 772.2925 $[M]^+$ (calcd 772.2943). This assignment was supported

Table 2. ^{13}C NMR Spectroscopic Data for **1**−**8**[a]

carbon	1	2	3	4	5	6	7	8
1	85.3	85.0	85.5	85.6	85.4	85.6	85.9	85.8
2	85.5	85.2	85.4	80.0	85.6	80.4	85.6	85.7
3	81.8	82.6	81.8	84.3	81.3	83.9	82.0	82.2
4	46.0	46.2	46.1	45.0	46.4	45.2	46.1	46.2
5	33.2	32.6	33.1	33.7	33.3	34.0	36.2	36.3
6	30.9	30.7	31.0	31.1	31.0	31.2	33.9	33.9
7	171.1	171.1	171.1	171.4	171.3	171.5	172.2	172.2
8	86.2	86.1	86.4	87.1	86.5	87.4	86.1	86.0
9	85.9	85.7	85.9	86.4	86.0	86.5	85.1	85.0
10	45.2	45.0	45.2	44.6	45.3	44.7	46.1	46.0
11	25.8	25.6	25.9	25.6	25.9	25.8	66.7	66.7
12	31.6	31.4	31.7	31.5	31.7	31.6	37.3	37.2
13	38.9	38.7	38.9	38.8	38.7	38.8	38.7	38.7
14	47.7	47.5	47.6	47.0	47.7	47.2	46.5	46.7
15	30.3	30.1	30.5	30.0	30.5	30.2	30.8	30.6
16	174.1	173.9	174.2	174.3	174.2	174.3	174.6	174.5
17	69.8	69.9	69.8	69.7	69.9	69.9	71.1	70.7
18	21.2	21.2	21.4	21.0	21.3	21.3	23.9	23.9
19	68.7	68.6	68.8	68.8	68.9	68.9	16.8	16.8
20	121.8	121.8	121.8	121.6	122.1	122.2	122.6	122.6
21	142.7	142.1	142.8	143.0	142.4	142.5	141.9	142.0
22	109.0	108.9	109.0	108.9	109.1	109.0	109.7	109.6
23	143.2	143.0	143.2	143.2	143.1	143.2	142.6	142.7
28	13.6	13.5	13.6	13.6	13.6	13.6	14.5	14.5
29	38.6	38.3	38.9	38.1	38.9	38.2	39.9	40.0
30	68.6	68.2	68.5	70.0	68.5	69.7	68.1	68.3
31	119.4	119.1	119.4	119.4	119.3	119.5	118.8	118.8
32	20.6	20.4	20.7	20.5	20.7	20.6	20.7	20.8
OMe-7							51.9	51.9
OMe-16	51.5	51.3	51.6	51.6	51.5	51.6	51.5	51.5
Ac-2	169.5	169.2	169.4		169.3		169.9	169.0
	21.5	21.3	22.2		21.2		21.3	21.4
Ac-17	169.7	170.0	169.5	169.3	169.8	169.1	168.7	167.9
	21.4	21.2	21.6	21.4	21.6	21.2	21.6	21.6
Ac-30	168.7	168.5						170.7
	21.5	21.3						21.4
1′	170.1	170.7	171.3	171.3	166.4	166.9	170.5	170.0
2′	58.4	58.2	58.3	58.3	128.4	129.7	58.6	58.7
3′	58.7	58.5	58.6	58.6	137.3	136.3	59.2	59.1
4′	13.4	13.4	13.6	13.6	12.6	12.6	13.5	13.6
5′	14.0	13.8	13.7	13.7	14.3	14.4	13.8	13.7
1″			172.0	172.2	171.7	174.2	170.9	
2″			28.0	27.8	27.7	34.6	27.9	
3″			8.3	8.5	8.1	18.6	8.4	
4″						18.1		

[a] Data were measured in $CDCl_3$ at 100 MHz; chemical shift values are in ppm from TMS.

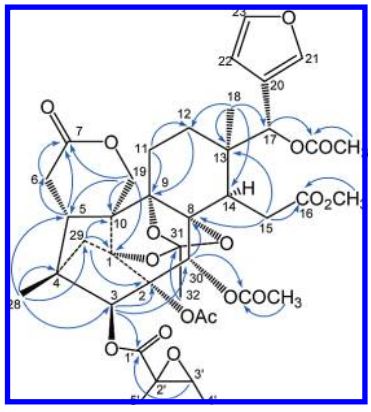

Figure 1. Key HMBC (H → C) correlations of **1**.

by the sodiated molecular ion peak at *m*/*z* 795 $[M + Na]^+$ in the positive-mode ESIMS. From the molecular formula, 16 unsaturations in compound **4** were calculated. The ^1H and ^{13}C NMR data of **4** indicated its structure to be closely related to that of **3**, with the only difference being the presence of a hydroxy group at C-2 in **4** replacing the acetoxy of **3**, which led to the chemical shifts of H-30 and H-3 of **4** being shifted upfield as compared with those of **3** due to the absence of shielded effects of acetyl group. The structure of **4** was thus elucidated as shown.

Swietenitin E (**5**), a white amorphous powder, showed a HREIMS ion at *m*/*z* 798.3098 $[M]^+$ (calcd 798.3099), corresponding to the molecular formula $C_{41}H_{50}O_{16}$, which was supported by the pseudomolecular ion peaks at *m*/*z* 799 $[M + H]^+$ and 821 $[M + Na]^+$ in the positive-mode ESIMS. Compared with compound **3**, its molecular formula was 16 mass units less, consistent with the loss of an oxygen atom. The NMR data (Tables 1 and 2) showed that the structure of **5** is closely related to that of **3**. The only difference was the presence of a tiglyl group (δ 6.89, 1H, q, J = 6.9 Hz, 1.66, 3H, s, and 1.95, 3H, d, J = 6.9 Hz; δ 166.4, 128.4, 137.3, 12.6, and 14.3) at C-3 of **5**, replacing the 2,3-epoxy-2-methylbutyryl group in **3**.

Swietenitin F (**6**) was obtained as a white amorphous powder with a molecular formula of $C_{40}H_{50}O_{15}$ (HREIMS *m*/*z* 770.3156 $[M]^+$, calcd 770.3150). ^1H and ^{13}C NMR analysis indicated that compound **6** is a structurally related congener of **5**. On comparing the ^{13}C NMR data with those of compound **5**, the C-2 signal of **6** was shifted upfield to δ 80.4 ($\Delta\delta$ ca. 5), indicating that a hydroxy group is located at this position, which subsequently caused a downfield shift of C-3 to δ 83.9 in the ^{13}C NMR spectrum and an upfield shift of H-3 at δ 4.71 in the ^1H NMR spectrum. Furthermore, ^1H and ^{13}C NMR analysis also showed the presence of an isobutyryl

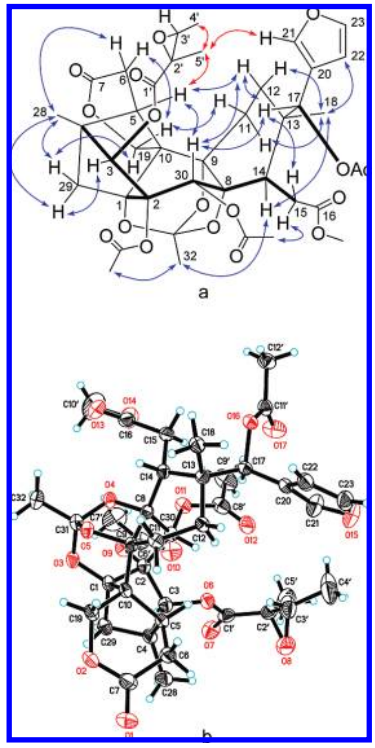

Figure 2. (a) Key ROESY correlations (H ↔ H) of **1**. (b) X-ray structure of **1**.

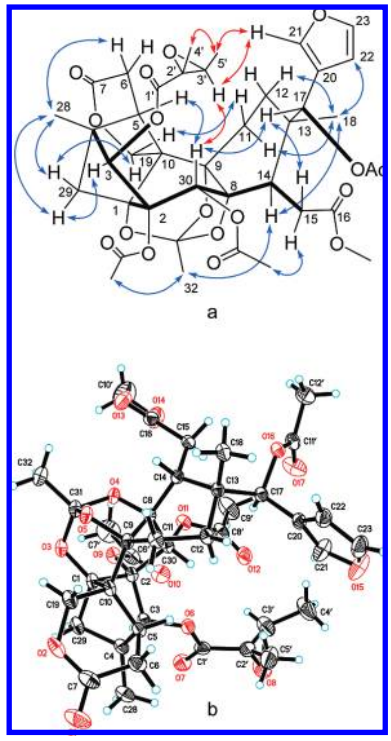

Figure 3. (a) Key ROESY correlations (H ↔ H) of **2**. (b) X-ray structure of **2**.

moiety (δ 2.66, 1H, m; 1.22, 3H, d, J = 7.0 Hz; 1.25, 3H, d, J = 7.0 Hz; δ 174.2, 34.6, 18.6 and 18.1). The isobutyryloxy was located at C-30 by the HMBC correlation between the carbonyl resonance at δ 174.2 and H-30 at δ 5.61.

2-Acetoxyswietenialide D (**7**), a white amorphous powder, gave the molecular formula $C_{42}H_{54}O_{18}$, as determined by HREIMS at m/z 846.3307 $[M]^+$ (calcd 846.3310). Comparison of the ^1H and ^{13}C NMR data of **7** with those of swietenialide D[8a] showed a high

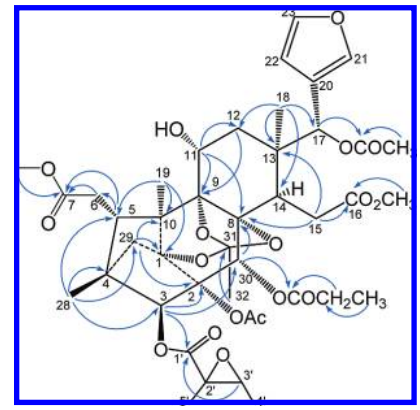

Figure 4. Key HMBC (H → C) correlations of **7**.

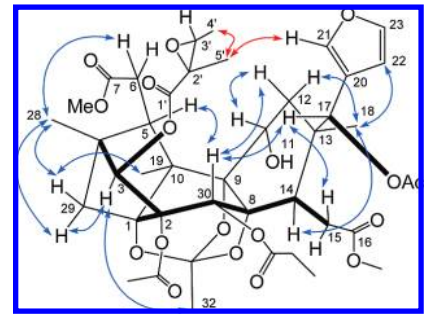

Figure 5. Key ROESY (H ↔ H) correlations of **7**.

similarity, with the additional carbon resonances at δ 21.3 and 169.9 in the ^{13}C NMR being assignable to an acetyl group, indicating that compound **7** is an acetylated analogue of swietenialide D. In this comparison, the chemical shifts of the H-3 at δ 5.22 and H-30 at δ 6.08 in **7** indicated that an acetoxy is located at C-2 replacing OH-2 of swietenialide D. The downfield-shifted proton resonances of H-3 and H-30 were rationalized as the deshielding effect of OAc-2. The structure of **7** was confirmed by HMBC and ROESY spectra (Supporting Information, Figures S41 and S42). The H-3′ proton resonated at δ 3.16 (q, J = 5.3 Hz) in the ^1H NMR spectrum, indicating that the absolute stereochemistry of the 2,3-epoxy-2-methylbutyryl group is in the 2*S*,3*R*-configuration, as compared with compound **1**.

Swietenitin G (**8**) was afforded as a white amorphous powder having a molecular formula of $C_{41}H_{52}O_{18}$, as established from the HREIMS ion at m/z 832.3134 $[M]^+$ (calcd 832.3154). The ^1H and ^{13}C NMR data of **8** also showed high similarities to those of **7**, with the only difference being assignable to the presence of an acetoxy unit (δ 170.7, 21.4; δ 2.01, s) at C-30 of **8** in place of a propionyloxy in **7** (Tables 2 and 3).

2,11-Diacetoxyswietenialide D (**9**) was obtained as a white amorphous powder with a molecular formula of $C_{44}H_{56}O_{19}$, as established on the basis of HREIMS at m/z 888.3424 $[M]^+$ (calcd 888.3416). Comparison of its EIMS and ^1H and ^{13}C NMR data with those of **7** suggested that compound **9** is also a ring-B,D-*seco* phragmalin-type limonoid bearing an 1,8,9-orthoacetate, with the only structural difference being the presence of an OAc group at the C-11 of **9** replacing the 11-OH of **7**. This structural change obviously caused a downfield shift of H-11 to δ 5.36 (brs) in the ^1H NMR spectrum of **9** due to an acetylation effect.

Swietenitin H (**10**), a white amorphous powder, gave a molecular formula of $C_{44}H_{56}O_{18}$, as established on the basis of the HREIMS at m/z 872.3439 $[M]^+$ (calcd 872.3467). This assignment was supported by the sodiated molecular ion at m/z 895 $[M + Na]^+$ in the positive-mode ESIMS. Analysis of the MS and NMR data of **10** suggested that its structure is closely related to compound **9**, with the only change being the substituent group at C-3. A

Table 3. ^{1}H NMR Spectroscopic Data of **7**−**11**[a]

proton	7	8	9	10	11
3	5.22 (s)	5.21 (s)	5.20 (s)	5.30 (s)	4.69 (s)
5	2.72 (brd, 9.0)	2.73 (dd, 9.3 (2.4)	2.75 (brd, 9.2)	2.81 (m)	2.77 (dd, 9.4, 2.8)
6	2.16 (m)	2.16 (m)	2.20 (m)	2.21 (m)	2.23 (dd, 11.6, 2.8)
	2.39 (m)	2.35 (m)	2.37 (m)	2.35 (m)	2.39 (dd,11.6 (9.4)
11α					1.80 (m)
11*β*	4.16 (brd, 1.9)	4.15 (brd, 2.5)	5.36 (brs)	5.37 (brs)	2.05 (m)
12α	1.33 (brd, 5.5)	1.32 (m)	1.45 (m)	1.43 (m)	1.03 (m)
12*β*	1.58 (dd, 15.5, 4.1)	1.59 (m)	1.59 (m)	1.53 (m)	1.18 (m)
14	2.83 (m)	2.81 (m)	2.88 (m)	2.87 (m)	2.44 (m)
15	2.34 (m)	2.36 (m)	2.44 (m)	2.38 (m)	2.44 (m)
	2.84 (m)	2.82 (m)	2.90 (m)	2.92 (m)	2.85 (dd, 19.3, 9.5)
17	5.62 (s)	5.68 (s)	5.66 (s)	5.73 (s)	5.71 (s)
18	1.43 (s)	1.43 (s)	1.35 (s)	1.36 (s)	1.25 (s)
19	1.15 (s)	1.14 (s)	1.21 (s)	1.19 (s)	1.10 (s)
21	7.67 (brs)	7.69 (brs)	7.67 (brs)	7.66 (s)	7.84 (s)
22	6.46 (brs)	6.47 (brd, 1.7)	6.41 (brs)	6.42 (brd, 1.5)	6.44 (s)
23	7.35 (brs)	7.36 (brt, 1.7)	7.34 (brs)	7.35 (brt, 1.5)	7.34 (s)
28	0.91 (s)	0.91 (s)	0.91 (s)	0.86 (s)	0.93 (s)
29_a	1.94 (m)	1.96 (d, 11.1)	2.01 (m)	1.96 (m)	1.87 (d, 11.0)
29_b	1.68 (m)	1.68 (m)	1.66 (m)	1.69 (m)	1.69 (m)
30	6.08 (s)	6.07 (s)	6.09 (s)	6.15 (s)	5.64 (s)
32	1.70 (s)	1.70 (s)	1.65 (s)	1.67 (s)	1.70 (s)
OMe-7	3.56 (s)	3.56 (s)	3.59 (s)	3.56 (s)	3.57 (s)
OMe-16	3.69 (s)	3.69 (s)	3.70 (s)	3.69 (s)	3.68 (s)
Ac-2	2.10 (s)	2.11 (s)	2.10 (s)	2.12 (s)	
Ac-11			2.13 (s)	2.13 (s)	
Ac-17	1.98 (s)	1.99 (s)	1.99 (s)	1.97 (s)	1.98 (s)
Ac-30		2.01 (s)			
3′	3.16 (q, 5.3)	3.15 (q, 5.5)	3.15 (q, 5.4)	7.08 (q, 5.9)	3.24 (q, 5.5)
4′	1.53 (d, 5.3)	1.50 (d, 5.5)	1.52 (d, 5.4)	1.92 (d, 5.9)	1.43 (d, 5.5)
5′	1.84 (s)	1.82 (s)	1.84 (s)	1.60 (s)	1.60 (s)
2″	2.26 (q, 7.4)		2.28 (q, 6.9)	2.30 (q, 7.5)	2.35 (q, 7.6)
3″	1.15 (t, 7.4)		1.12 (t, 6.9)	1.09 (t, 7.5)	1.20 (t, 7.6)

[a] Data were measured in $CDCl_3$ at 400 MHz; chemical shifts are expressed in ppm; the spin coupling (*J*) is given in parentheses (Hz).

tigloyloxy group with *E*-geometry at C-3 was evident from the NMR data (*δ* 7.08, 1H, q, *J* = 5.9 Hz, 1.92, 3H, d, *J* = 5.9 Hz and 1.60, 3H, s; *δ* 170.8, 128.3, 137.7, 14.2, and 14.3), as in swietenialide A.[8a] Therefore, the structure of **10** was elucidated as shown.

11-Deoxyswietenialide D (**11**), a white amorphous powder, gave a molecular formula of $C_{40}H_{52}O_{16}$, as established from HREIMS at *m*/*z* 788.3253 $[M]^+$ (calcd 788.3255). Detailed analysis of the spectroscopic data of **11** indicated that it is the 11-dehydroxy derivative of swietenialide D.[8a] Thus, the C-11 signal of **11** resonated at *δ* 25.6 in the ^{13}C NMR spectrum, and the H_2-11 of **11** appeared at *δ* 1.80 (m) and 2.05 (m) in the ^{1}H NMR spectrum and fully substantiated this structural assignment.

Swietenitin I (**12**) was obtained as a white amorphous powder possessing a molecular formula of $C_{41}H_{54}O_{18}$, as determined by the HREIMS at *m*/*z* 834.3283 $[M]^+$ (calcd 834.3285), representing 15 degrees of unsaturation. Its NMR data (Tables 4 and 5) revealed the presence of a primary methyl, a secondary methyl, nine tertiary methyls (one from acetyl and three methoxy), five methylenes, nine methines (three olefinic), and 16 quaternary carbons. The presence of a *β*-furan ring (*δ* 7.74, 6.53, and 7.42, each 1H), a 2,3-epoxy-2-methylbutyryl, and two orthoester groups (*δ* 123.4 and 119.1) was determined from the ^{1}H and ^{13}C NMR spectrum. These data suggested that compound **12** is a ring-B,D-*seco* phragmalin-type limonoid bearing two orthoesters, with a structure closely related to swietenialide B.[8a] Comparison of the spectroscopic data of **12** with those of swietenialide B indicated that the only structural difference is the presence of an 2,3-epoxy-2-methylbutyryl ester (Tables 4 and 5) at the C-3 of **12** instead of the tigloyloxy group in swietenialide B. This was verified by the key HMBC correlation between H-3 and C-1′. The H-3′ signal resonated at *δ* 3.28 (q, *J* = 5.4 Hz) in the ^{1}H NMR spectrum and suggested that the 2,3-epoxy-2-methylbutyryl unit of **12** is in a 2*S*,3*R*-configuration, by analogy with compound **1**. The structure of **12** was confirmed from its HMBC and ROESY spectra (Figures 6 and 7).

Swietenitin J (**13**), a white amorphous powder, was found to possess a molecular formula of $C_{43}H_{56}O_{19}$, as established from the HREIMS at *m*/*z* 876.3392 $[M]^+$ (calcd 876.3415), indicating 16 degrees of unsaturation. The ^{1}H and ^{13}C NMR data of **13** resembled those of **12**, with the only changes being due to the presence of one more acetyl group. Compared to compound **12**, the C-1 signal of **13** resonated downfield at *δ* 85.5 (Δ*δ* 3.5), and there were also small changes of the proton and carbon resonances around C-1 (Tables 4 and 5) due to the deshielding effects of an acetyl group, suggesting that an acetate group was located at C-1. The structure of **13** was thus established and confirmed from the HMBC and ROESY spectra (Supporting Information, Figures S77 and S78).

Swietenitin K (**14**) was afforded as a white amorphous powder, possessing a molecular formula of $C_{42}H_{52}O_{17}$, as assigned by the HREIMS (*m*/*z* 828.3214 $[M - CH_3OH]^+$, calcd 828.3205). The ^{1}H and ^{13}C NMR data of **14** shared close similarities to those of **13**, except for the presence of a tigloyl group (*δ* 7.09, 1H, qd, *J* = 7.0, 1.3 Hz, 1.65, 3H, d, *J* = 7.0 Hz and 1.91, 3H, s; *δ* 167.1, 127.6, 138.4, 12.4, and 14.6) replacing the 2,3-epoxy-2-methylbutyryl group of **13**. This ester group was located at C-3 by the key HMBC correlation between H-3 and C-1′ (Supporting Information, Figure S84).

Swietenitin L (**15**) was obtained as a white amorphous powder with a molecular formula of $C_{42}H_{54}O_{19}$, as determined by the HREIMS at *m*/*z* 862.3227 $[M]^+$ (calcd 862.3260). The ^{1}H and ^{13}C NMR data of compound **15** showed similarities to those of **12**, with the differences being due to the presence of additional acetyl (*δ* 2.13, s; *δ* 170.2, 21.7) and propionyl (*δ* 2.22, 2H, q, *J* = 7.5 Hz, and 1.09, 3H, t, *J* = 7.5 Hz; *δ* 171.6, 27.6 and 8.6) groups, with the concomitant absence of a 2,30-orthoester moiety. The proton resonance at *δ* 4.05 of a hydroxy group as distinguished by the HMQC spectrum was assigned to HO-1 by the HMBC correlation from this signal to C-1 and C-29 (Figure 8). A propionyloxy group was located at C-30 by a key HMBC correlation between H-30 at *δ* 6.53 and the carbonyl resonance at *δ* 171.6 of the propionyl group

Table 4. ^{1}H NMR Spectroscopic Data of **12**−**16**[a]

proton	12	13	14	15	16
3	5.32 (s)	5.38 (s)	5.38 (s)	5.27 (s)	5.30 (s)
5	2.84 (brd, 10.8)	2.78 (brd, 10.8)	2.84 (brd, 10.8)	2.90 (brd, 10.6)	2.85 (brd, 10.0)
6	2.24 (dd, 16.4, 10.8)	2.21 (dd, 16.4, 10.8)	2.21 (dd, 16.4, 10.8)	2.27 (dd, 16.6, 10.6)	2.18 (m)
	3.08 (brd, 16.4)	3.13 (brd, 16.4)	3.15 (brd, 16.4)	3.22 (brd, 16.6)	2.30 (m)
11β	4.37 (m)	4.39 (m)	4.39 (m)	4.35 (m)	5.21 (dd, 12.0, 4.9)
12α	1.26 (m)	1.26 (m)	1.28 (m)	1.24 (m)	1.53 (m)
12β	2.01 (m)	2.00 (m)	2.04 (m)	1.90 (m)	1.90 (m)
15	2.80 (d, 14.6)	2.71 (d, 14.5)	2.70 (d, 14.6)	2.70 (d, 13.4)	2.78 (d, 13.4)
	3.22 (d, 14.6)	3.24 (d (14.5)	3.23 (d, 14.6)	2.97 (d (13.4)	2.98 (d, 13.4)
17	6.26 (s)	6.28 (s)	6.16 (s)	5.63 (s)	5.70 (s)
18	1.27 (s)	1.26 (s)	1.24 (s)	1.21 (s)	1.26 (s)
19	1.20 (s)	1.15 (s)	1.15 (s)	1.27 (s)	1.22 (s)
21	7.74 (brs)	7.75 (brs)	7.70 (brs)	7.63 (brs)	7.80 (s)
22	6.53 (brs)	6.54 (brs)	6.55 (brs)	6.47 (brs)	6.37 (s)
23	7.42 (brs)	7.42 (brs)	7.44 (brs)	7.42 (brs)	7.37 (s)
28	0.85 (s)	0.82 (s)	0.84 (s)	0.86 (s)	0.84 (s)
29_a	2.14 (d, 11.7)	2.91 (d, 12.1)	2.91 (d, 12.0)	2.18 (d, 11.7)	2.08 (m)
29_b	1.73 (d, 11.7)	2.42 (d, 12.1)	2.41 (d, 12.0)	1.58 (d, 11.7)	1.60 (m)
30	5.22 (s)	5.27 (s)	5.25 (s)	6.53 (s)	6.54 (s)
32	1.78 (s)	1.77 (s)	1.78 (s)	1.85 (s)	1.88 (s)
33	1.93 (q, 7.4)	1.90 (q, 7.5)	1.90 (q, 7.5)		
34	0.98 (t, 7.4)	0.92 (t, 7.5)	0.92 (t, 7.5)		
OMe-7	3.68 (s)	3.69 (s)	3.66 (s)	3.71 (s)	3.70 (s)
OMe-16	3.67 (s)	3.67 (s)	3.66 (s)	3.69 (s)	3.69 (s)
OMe-33	3.13 (s)	3.09 (s)	3.09 (s)		
OH-1	3.89 (s)			4.05 (s)	
Ac-1		2.04 (s)	2.04 (s)		
Ac-2				2.13 (s)	2.14 (s)
Ac-11					1.99 (s)
Ac-17	2.12 (s)	2.13 (s)	2.10 (s)	2.00 (s)	2.00 (s)
3′	3.28 (q, 5.4)	3.22 (q, 5.2)	7.09 (dq, 7.0, 1.3)	3.07 (q, 5.4)	3.13 (q, 5.4)
4′	1.33 (d, 5.4)	1.31 (d, 5.2)	1.65 (d, 7.0)	1.48 (d, 5.4)	1.49 (d, 5.4)
5′	1.70 (s)	1.67 (s)	1.91 (s)	1.92 (s)	1.97 (s)
2″				2.22 (q, 7.5)	2.23 (q, 7.4)
3″				1.09 (t, 7.5)	1.10 (t, 7.4)

[a] Data were measured in $CDCl_3$ at 400 MHz; chemical shifts are expressed in ppm; the spin coupling (*J*) is given in parentheses (Hz).

(Figure 8). This was supported by the downfield-shifted proton resonance of H-30 ($\Delta\delta$ 1.3) as compared with that of **12**, due to an acetylation effect. The acetoxy group was thus attached to C-2 and confirmed by the ROESY correlation between CH_3CO-2 and H-32 (Figure 9). The configuration of **15** was confirmed by a ROESY experiment (Figure 9). In addition, H-3′ resonated at δ 3.07 (q, J = 5.4 Hz) and indicated that the 2,3-epoxy-2-methylbutyryl group was in a 2*S*,3*R*-configuration, as compared with compound **1**.

Swietenitin M (**16**), a white amorphous powder, showed a molecular formula of $C_{44}H_{56}O_{20}$, as determined by HREIMS at *m*/*z* 904.3389 $[M]^+$ (calcd 904.3365). The ^{1}H and ^{13}C NMR data of **16** resembled those of **15**, except for the presence of one more acetyl group, which was located at C-11 by the HMBC correlation between its carbonyl resonance at δ 168.4 and H-11. The H-11 signal of **16** was downfield shifted $\Delta\delta$ 0.86 as compared with that of compound **15** due to an acetylation effect. The configuration of **16** was confirmed by the ROESY spectrum (Supporting Information, Figure S99) as being identical to that of compound **15**, and the C-3 unit of **15** was assigned as a 2*S*,3*R*-epoxy-2-methylbutyryl group, on the basis of the H-3′ resonance at δ 3.13 (q, 5.4 Hz).

Four known compounds were identified as swietenialide D,[8a] roxburghiadiol A,[10] secomahoganin,[4d] and 7-deacetoxy-7-oxogedunin,[11] on the basis of comparison of their ^{1}H and ^{13}C NMR spectra and ESIMS data with literature values.

Experimental Section

General Experimental Procedures. Melting points were measured on a SGW X-4 melting instrument and are uncorrected. Optical rotations were determined on a Perkin-Elmer 341 polarimeter. IR spectra were recorded on a Perkin-Elmer 577 spectrometer. NMR spectra were measured on a Bruker AM-400 spectrometer with TMS as internal standard. EIMS (70 eV) and HREIMS were carried out on a Finnigan MAT 95 mass spectrometer. Semipreparative HPLC was performed on a Waters 515 pump with a Waters 2487 detector (254 nm) and a YMC-Pack ODS-A column (250 × 10 mm, S-5 μm, 12 nm). All solvents used were of analytical grade (Shanghai Chemical Reagents Company, Ltd.). Silica gel (200−300 mesh, Qingdao Haiyang Chemical Co., Ltd.) and Sephadex LH-20 gel (Pharmacia Biotech, Sweden) were used for column chromatography.

Plant Material. The twigs of *Swietenia macrophylla* were collected from Sanya of Hainan Island, People's Republic of China, and authenticated by Professor S. M. Huang of the Department of Biology, Hainan University. A voucher specimen (accession number SMt-2006-1Y) has been deposited at the Shanghai Institute of Materia Medica.

Extraction and Isolation. The dried, powdered twigs of *S. macrophylla* (10 kg) were percolated three times with 95% EtOH. After removal of the solvent under reduced pressure, the EtOH extract (1.5 kg) was partitioned between H_2O and EtOAc to give an EtOAc-soluble fraction (700 g), which was subjected to silica gel column chromatography eluted with a gradient of petroleum ether−acetone (10:1 to 0:1) to afford eight fractions, A−H. Fraction C (5.7 g) was then subjected to passage over a column of MCI gel (MeOH−H_2O, 50:50 to 90:10) to obtain four subfractions, C1−C4. Fraction C2 (215 mg) was subjected to silica gel column chromatography eluted with a gradient of petroleum ether−isopropyl alcohol (20:1 to 5:1), to afford four fractions, C2a−2d (35, 27, 45, and 20 mg). Fraction C2a was purified by a semipreparative HPLC with 70% methanol in water to yield compound **10** (3 mg). By using the same purification procedures, fraction C2b gave **9** (12 mg); fractions C2c yielded **5** (7 mg), **6** (5 mg), and secomahoganin (12 mg); and fraction C2d afforded **14** (3 mg) and **11** (2 mg). Fraction D (13.9 g) was then subjected to passage over a column of MCI gel eluted with MeOH−H_2O (50:50 to 90:10) to obtain eight subfractions, D1−D8. Fraction D5 (3.39 g) was chromatographed on a silica gel column, eluted with petroleum ether−ethyl acetate (4:1 to 1:1), to give five subfractions, D5a−5e. Fraction D5d (215 mg) was separated on a column of Sephadex LH-20 gel to purify the major component, which was further separated by semipreparative HPLC with 55% acetonitrile in water as the mobile phase, to yield **2** (3 mg). Fraction E (27.1 g)

Table 5. ^{13}C NMR Spectroscopic Data for **9**−**16**[a]

carbon	9	10	11	12	13	14	15	16
1	85.8	85.9	85.6	82.0	85.5	85.9	84.2	84.3
2	85.6	85.8	79.9	85.3	86.3	86.3	84.4	84.3
3	82.2	81.3	84.6	86.4	86.0	85.0	83.2	82.8
4	46.1	46.3	45.0	43.5	43.7	43.7	43.8	43.8
5	36.4	36.5	33.7	40.4	38.5	38.5	39.9	38.5
6	33.8	33.9	31.5	32.6	32.4	32.5	32.4	29.7
7	172.5	172.5	171.8	174.7	174.5	174.6	174.4	172.1
8	86.0	86.1	87.0	90.2	88.8	89.0	90.5	90.6
9	85.1	85.2	87.0	87.2	86.8	86.9	87.4	86.6
10	46.1	46.1	45.0	52.1	53.1	53.2	51.0	51.0
11	66.6	66.7	25.6	67.1	67.5	67.5	66.7	70.5
12	37.8	36.8	31.5	38.0	38.2	38.3	37.8	32.7
13	38.7	38.7	39.0	43.8	43.8	43.9	44.4	44.8
14	46.8	47.0	47.3	87.7	87.6	87.6	89.2	89.3
15	30.9	30.8	30.0	39.0	39.1	39.0	39.1	39.4
16	174.6	174.6	174.6	171.2	171.7	171.7	170.6	170.6
17	71.3	70.9	70.5	68.7	68.8	68.9	71.5	71.4
18	23.7	23.7	20.7	18.0	18.1	18.0	18.0	19.2
19	16.6	16.5	16.5	15.0	15.5	15.4	14.8	14.9
20	122.5	122.5	122.2	122.0	122.0	122.3	122.9	121.0
21	141.9	142.0	142.5	141.4	141.4	141.0	140.4	142.3
22	109.6	109.5	109.4	109.8	109.9	109.7	109.4	109.4
23	142.7	142.7	142.7	143.1	143.0	143.2	143.1	142.7
28	14.5	14.5	13.5	14.7	14.6	14.6	14.6	14.6
29	40.1	40.0	39.0	41.5	40.0	40.1	41.6	41.4
30	68.2	68.2	70.9	70.8	71.2	71.5	62.0	61.6
31	118.9	118.9	118.8	119.1	118.9	118.9	119.2	119.3
32	20.8	20.8	20.7	16.4	16.5	16.5	16.5	16.4
33				123.4	124.0	124.0		
34				25.5	26.7	26.9		
35				8.0	8.0	8.0		
OMe-7	52.0	51.8	51.8	51.9	51.4	51.8	51.6	51.6
OMe-16	51.5	51.4	51.6	51.4	50.9	51.3	52.0	52.2
OMe-33				50.5	50.9	49.6		
Ac-1					169.5	169.5		
					22.3	22.3		
Ac-2	169.9	169.7					170.2	170.3
	21.3	21.3					21.7	21.7
Ac-11	169.5	169.5						168.4
	21.1	21.1						21.4
Ac-17	168.4	168.5	169.2	168.7	168.8	168.7	167.3	167.2
	21.6	21.7	20.7	21.2	21.2	21.1	21.2	21.4
1′	170.5	170.8	172.0	170.8	170.9	167.1	170.2	170.1
2′	58.6	128.3	58.3	58.0	58.0	127.6	58.5	58.4
3′	59.2	137.7	59.1	58.8	58.9	138.4	59.3	59.3
4′	13.6	14.2	13.5	13.6	13.6	12.4	13.4	13.5
5′	13.8	14.3	13.5	13.6	13.7	14.6	13.7	13.6
1″	170.9	170.8	172.7				171.6	171.4
2″	27.9	27.8	27.9				27.6	27.6
3″	8.4	8.3	8.7				8.6	8.6

[a] Data were measured in $CDCl_3$ at 100 MHz; chemical shift values are in ppm from TMS.

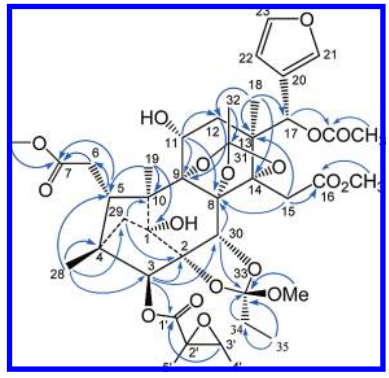

Figure 6. Key HMBC (H → C) correlations of **12**.

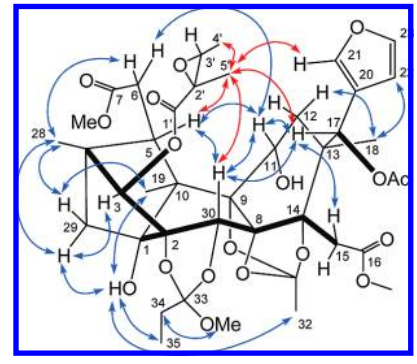

Figure 7. Key ROESY (H ↔ H) correlations of **12**.

was chromatographed on a column of MCI gel (MeOH−H_2O, 50:50 to 90:10) to obtain six subfractions, E1−E6. Fraction E3 (9.45 g) was separated on a silica gel column (petroleum ether−ethyl acetate, 4:1 to 0:1) to obtain five fractions, E3a−E3e. Fraction E3a (767 mg) was subjected to a column of reversed-phase silica gel (MeOH−H_2O, 50:50 to 100:0) to obtain seven subfractions, E3a1−E3a7, and then E3a5 (121 mg) was separated on a silica gel column (petroleum ether−ethyl acetate, 4:1 to 0:1) to obtain **12** (12 mg), **13** (10 mg), and roxburghiadiol A (15 mg). By using the same purification procedures,

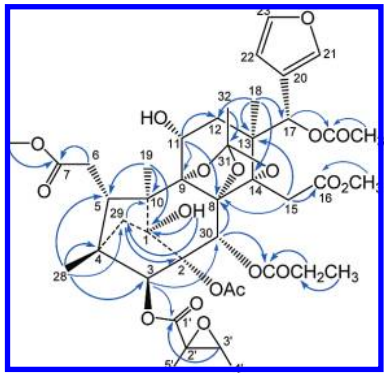

Figure 8. Key HMBC (H → C) correlations of **15**.

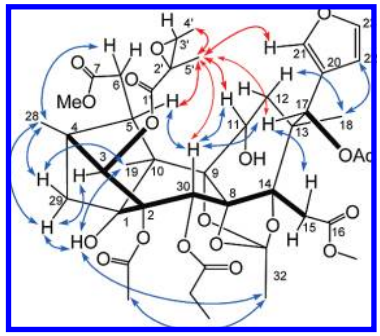

Figure 9. Key ROESY (H ↔ H) correlations of **15**.

fraction E2 yielded **4** (25 mg) and **3** (30 mg); fraction E3 gave **1** (35 mg), **7** (7 mg), 7-deacetoxy-7-oxogedunin (25 mg), and swietenialide D (30 mg); fraction E4 produced **8** (34 mg); and fractions E5 and E6 afforded **15** (8 mg) and **16** (4 mg), respectively.

Swietenitin A (1): colorless crystals; mp 240−242 °C; $[\alpha]^{20}_D$ −28.9 (*c* 0.97, CH_3OH); IR (KBr) ν_{max} 3464, 2953, 1763, 1381, 1240, 1108, 1051 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 800 (28), 757 (100), 667 (7), 631 (15), 579 (2), 481 (3), 431 (4), 383 (12), 323 (12), 95 (30), 83 (12); HREIMS *m/z* 800.2875 ($[M]^+$, calcd for $C_{40}H_{48}O_{17}$, 800.2891).

Swietenitin B (2): colorless crystals; mp 250−251 °C; $[\alpha]^{20}_D$ +18 (*c* 0.04, $CHCl_3$); IR (KBr) ν_{max} 3448, 2955, 1762, 1371, 1244, 1051 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 800 (14), 757 (64), 667 (4), 631 (4), 579 (2), 461 (12), 401 (12), 383 (16), 323 (16), 219 (16), 121 (24), 95 (76), 83 (100); HREIMS *m/z* 800.2904 ($[M]^+$, calcd for $C_{40}H_{48}O_{17}$, 800.2891).

Swietenitin C (3): white powder; $[\alpha]^{20}_D$ −11 (*c* 0.15, CH_3OH); IR (KBr) ν_{max} 3442, 2955, 1761, 1636, 1458, 1381, 1240, 1047 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 814 (31), 771 (100), 755 (6), 645 (18), 579 (6), 499 (6), 383 (24), 323 (18), 219 (18), 173 (6), 121 (18), 95 (40), 83 (15), 57 (35); HREIMS *m/z* 814.3061 ($[M]^+$, calcd for $C_{41}H_{50}O_{17}$, 814.3048).

Swietenitin D (4): white powder; $[\alpha]^{20}_D$ −27.3 (*c* 0.55, CH_3OH); IR (KBr) ν_{max} 3414, 2970, 1736, 1414, 1363, 1237, 1174, 1058 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 772 (25), 754 (12.3), 715 (8), 698 (26), 639 (22), 596 (43), 578 (39), 522 (13), 490 (58), 462 (51), 375 (57), 315 (100), 301 (20), 121 (35), 95 (70), 83 (25), 57 (66); HREIMS *m/z* 772.2925 ($[M]^+$, calcd for $C_{39}H_{48}0_{16}$, 772.2943).

Swietenitin E (5): white powder; $[\alpha]^{20}_D$ −15 (*c* 0.56, CH_3OH); IR (KBr) ν_{max} 3467, 2953, 1751, 1653, 1458, 1369, 1240, 1024 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 798 (7), 755 (47), 696 (1), 563 (3), 544 (3), 462 (6), 401 (3), 383 (10), 219 (7), 149 (12), 121 (3), 95 (12), 83 (100), 55 (16); HREIMS *m/z* 798.3098 ($[M]^+$, calcd for $C_{41}H_{50}O_{16}$, 798.3099).

Swietenitin F (6): white powder; $[\alpha]^{20}_D$ −30 (*c* 0.25, CH_3OH); IR (KBr) ν_{max} 3437, 2953, 1747, 1651, 1437, 1385, 1236, 1148, 1024 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 770 (2), 752 (8), 682 (4), 623 (3), 580 (5), 462 (6), 375 (15), 315 (21), 283 (4), 95 (10), 83 (100), 55 (20); HREIMS *m/z* 770.3156 ($[M]^+$, calcd for $C_{40}H_{50}O_{15}$, 770.3150).

2-Acetoxyswietenialide D (7): white powder; $[\alpha]^{20}_D$ −45 (*c* 1.2, CH_3OH); IR (KBr) ν_{max} 3496, 2991, 2953, 1740, 1439, 1371, 1242, 1088, 1026 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 2; EIMS *m/z* 846 (50), 803 (100), 768 (8), 699 (12), 633 (23), 592 (22), 499 (23), 383 (20), 355 (20), 182 (20), 121 (28), 95 (62), 55 (68); HREIMS *m/z* 846.3307 ($[M]^+$, calcd for $C_{42}H_{54}O_{18}$, 846.3310).

Swietenitin G (8): white powder; $[\alpha]^{20}_D$ −42 (*c* 0.29, CH_3OH); IR (KBr) ν_{max} 3487, 2953, 1740, 1439, 1371, 1244, 1049 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 2; EIMS *m/z* 832 (29), 789 (75), 699 (15), 663 (37), 592 (30), 531 (25), 499 (34), 415 (27), 383 (34), 182 (36), 121 (47), 95 (100), 83 (60); HREIMS *m/z* 832.3134 ($[M]^+$, calcd for $C_{41}H_{52}O_{18}$, 832.3154).

2,11-Diacetoxyswietenialide D (9): white, amorphous powder; $[\alpha]^{20}_D$ −25 (*c* 0.12, CH_3OH); IR (KBr) ν_{max} 3440, 2953, 1743, 1630, 1439, 1369, 1236, 1149, 1024 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 5; EIMS *m/z* 888 (21), 845 (100), 773 (16), 719 (12), 575 (8), 463 (13), 383 (15), 295 (14), 182 (17), 121 (20), 95 (50), 83 (47), 55 (34); HREIMS *m/z* 888.3424 ($[M]^+$, calcd for $C_{44}H_{56}O_{19}$, 888.3416).

Swietenitin H (10): white, amorphous powder; $[\alpha]^{20}_D$ −20 (*c* 1.5, CH_3OH); IR (KBr) ν_{max} 3437, 2953, 2924, 1743, 1653, 1437, 1370, 1234, 1149, 1024 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 5; EIMS *m/z* 872 (2), 829 (49), 771 (1), 619 (1), 576 (10), 494 (5), 383 (6), 313 (3), 231 (3), 182 (6), 121 (6), 95 (11), 83 (100), 55 (16); HREIMS *m/z* 872.3439 ($[M]^+$, calcd for $C_{44}H_{56}O_{18}$, 872.3467).

11-Deoxyswietenialide D (11): white, amorphous powder; $[\alpha]^{20}_D$ +60 (*c* 0.01, CH_3OH); IR (KBr) ν_{max} 3435, 2922, 2852, 1740, 1639, 1464, 1236, 1178, 908 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 5; EIMS *m/z* 788 (10), 770 (14), 694 (4), 613 (8), 559 (4), 515 (4), 473 (34), 429 (19), 375 (84), 315 (61), 224 (38), 182 (75), 121 (25), 95 (54), 83 (100), 57 (58); HREIMS *m/z* 788.3253 ($[M]^+$, calcd for $C_{40}H_{52}O_{16}$, 788.3255).

Swietenitin I (12): white, amorphous powder; $[\alpha]^{20}_D$ −9.1 (*c* 0.12, CH_3OH); IR (KBr) ν_{max} 3442, 2950, 2850, 1740, 1630, 1462, 1437, 1380, 1232, 1180, 1045 cm^{-1}; ^1H NMR, see Table 4; ^{13}C NMR, see Table 5; EIMS *m/z* 834 (12), 803 (41), 775 (43), 743 (18), 653 (11), 626 (35), 547 (26), 507 (55), 383 (37), 323 (25), 209 (31), 180 (63), 121 (100), 83 (63), 57 (45); HREIMS *m/z* 834.3283 ($[M]^+$, calcd for $C_{41}H_{54}O_{18}$, 834.3285).

Swietenitin M (13): white, amorphous powder; $[\alpha]^{20}_D$ +5.3 (*c* 0.47, CH_3OH); IR (KBr) ν_{max} 3477, 2953, 1736, 1417, 1367, 1232, 1182, 1014 cm^{-1}; ^1H NMR, see Table 4; ^{13}C NMR, see Table 5; EIMS *m/z* 876 (6), 844 (70), 817 (33), 786 (10), 668 (12), 609 (27), 567 (16), 507 (31), 414 (25), 355 (19), 251 (17), 180 (45), 121 (67), 83 (100), 57 (28); HREIMS *m/z* 876.3392 ($[M]^+$, calcd for $C_{43}H_{56}O_{19}$, 876.3415).

Swietenitin J (14): white, amorphous powder; $[\alpha]^{20}_D$ +23 (*c* 0.04, CH_3OH); IR (KBr) ν_{max} 3481, 2951, 1730, 1437, 1417, 1367, 1230, 1121, 1065 cm^{-1}; ^1H NMR, see Table 4; ^{13}C NMR, see Table 5; EIMS *m/z* 828 (15), 796 (21), 769 (33), 726 (2), 657 (2), 593 (2), 561 (2), 514 (2), 461 (2), 389 (4), 251 (1), 182 (1), 121 (7), 83 (100), 55 (18); HREIMS *m/z* 828.3214 ($[M - CH_3OH]^+$, calcd for $C_{42}H_{52}O_{17}$, 828.3205).

Swietenitin K (15): white, amorphous powder; $[\alpha]^{20}_D$ +10 (*c* 0.28, CH_3OH); IR (KBr) ν_{max} 3446, 2951, 1763, 1628, 1460, 1371, 1236, 1026 cm^{-1}; ^1H NMR, see Table 4; ^{13}C NMR, see Table 5; EIMS *m/z* 862 (25), 844 (100), 803 (31), 742 (10), 668 (9), 609 (21), 567 (12), 507 (20), 415 (27), 383 (25), 251 (17), 180 (87), 121 (98), 83 (82), 57 (85); HREIMS *m/z* 862.3227 ($[M]^+$, calcd for $C_{42}H_{54}O_{19}$, 862.3260).

Swietenitin L (16): white, amorphous powder; $[\alpha]^{20}_D$ +11 (*c* 0.15, CH_3OH); IR (KBr) ν_{max} 3433, 2925, 1747, 1628, 1459, 1371, 1229, 1047 cm^{-1}; ^1H NMR, see Table 4; ^{13}C NMR, see Table 5; EIMS *m/z* 904 (14), 886 (25), 845 (20), 802 (8), 784 (14), 729 (4), 679 (7), 629 (7), 591 (8), 530 (10), 415 (15), 355 (15), 180 (58), 149 (100), 121 (58), 83 (61), 57 (45); HREIMS *m/z* 904.3389 ($[M]^+$, calcd for $C_{44}H_{56}O_{20}$, 904.3365).

X-ray Crystallographic Data for 1: formula $C_{40}H_{48}O_{17}$; M_r = 800.78; orthorhombic crystalline system; space group $P2_12_12_1$; a = 11.3136(6) Å, b = 15.2891(9) Å, c = 22.5337(13) Å; V = 3897.8(4) $Å^3$; Z = 4; d = 1.365 mg m^3; crystal dimensions 0.458 × 0.411 × 0.327 mm^3; the final indices were R_1 = 0.0425, wR_2 = 0.1037.

X-ray Crystallographic Data for 2: formula $C_{40}H_{48}O_{17}$; M_r = 800.78; orthorhombic crystalline system; space group $P2_12_12_1$; a = 11.1609(6) Å, b = 15.3050(9) Å, c = 23.1138(13) Å; V = 3948.2(4)

Å^3; $Z = 4$; $d = 1.347$ mg m^3; crystal dimensions 0.467 × 0.410 × 0.326 mm^3; the final indices were $R_1 = 0.0425$, $wR_2 = 0.1033$.

Colorless crystals of **1** and **2** were obtained in a mixed solvent of MeOH−H_2O. Crystal data were obtained on a Bruker SMART CCD detector employing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K and operating in the $\phi-\omega$ scan mode. The structure was solved by direct methods with SHELXS-97[12] and refined with full-matrix least-squares calculations on F^2 using SHELX-97.[13] All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms. Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers CCDC-714940 and CCDC-714941). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK [fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: X-ray single-crystal structure refinement data of **1** and **2**, NMR, MS, and IR spectra of swietenitins A−M (**1**−**6**, **8**, **10**, **12**−**16**), 2-acetoxyswietenialide D (**7**), 2,11-diacetoxyswietenialide D (**9**), and 11-deoxyswietenialide D (**11**). This material is available free of charge via the Internet at http://pubs.acs.org.

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