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

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Eleven new phragmalin-type limonoids, swietenitins N—X (1—11), together with a known one, epoxyfebrinin B (12), were isolated from the twigs of *Swietenia macrophylla*. The structures of the new compounds were established on the basis of spectroscopic methods, and that of compound 1 was confirmed by single-crystal X-ray diffraction. The stereochemistry of epoxyfebrinin B (12) was fully assigned in this study.

Key words *Swietenia macrophylla*; limonoid; Meliaceae; X-ray diffraction; structure elucidation

Swietenia species of family Meliaceae are mainly found in Malaysia, India and Southeast Asia, and many of them have been applied in traditional medicine.[1—6] Recently, we reported the isolation and characterization of sixteen D-ring opened phragmalin-type limonoid orthoesters from the twigs and leaves of *Swietenia macrophylla* which were collected in Hainan Province of People's Republic of China.[7] In a continuation, eleven new phragmalin-type limonoid orthoesters, swietenitins N—X (**1**—**11**), as well as a known one epoxyfebrinin B (**12**), were further isolated from the same plant sample. The stereochemistry of epoxyfebrinin B (**12**) was completely assigned in the current study. The antimicrobial activities of these isolates against a small panel of microbes were evaluated, but none of them were active. Herein, we report the isolation and structure elucidation of **1**—**12**.

Results and Discussion

Swietenitins N—Q (1—4) and Epoxyfebrinin B (12) Swietenitin N (**1**), a colorless crystal, had the molecular formula $C_{39}H_{48}O_{15}$ as determined by high resolution-electron ionization-mass spectra (HR-EI-MS) at *m*/*z* 756.2970 $[M]^+$ (Calcd 756.2993), which was supported by the protonated and sodiated molecular ions at *m*/*z* 756 $[M+H]^+$ and 779 $[M+Na]^+$ in the positive mode of electrospray ionization (ESI)-MS, respectively. The IR absorption peaks at 3537 and 1743 cm^{-1} implied the presence of hydroxyl and ester carbonyl groups. ^{13}C-NMR and distortionless enhancement by polarization transfer (DEPT) spectra displayed 39 carbon resonances comprising nine methyl (one methoxyl), six methylenes, six sp^3 methines (four oxygenated), nine sp^3 quaternary carbons (six oxygenated), five carbonyl and two double bonds. Furthermore, a combined analysis of its ^{1}H- and ^{13}C-NMR data (Tables 1, 2) revealed the presence of one acetyl, an orthoacetate group, a β-furyl ring, a propionyloxy group and an 2,3-epoxy-2-methyl-butyryl moiety. There are sixteen unsaturations in the molecule of **1**, of which, nine degrees are occupied by five ester carbonyls, 2,3-epoxy-2-methyl-butyryl moiety and the β-furyl ring, and the remaining seven degrees required **1** being heptacyclic at the central core. The aforementioned data suggested that **1** was a phragmalin-type limonoid orthoester.

Extensive analysis of 2D-NMR spectra, especially heteronuclear multiple bond correlation (HMBC), allowed the assignment of the most functional groups to the limonoid core and confirmed the framework of a phragmalin-type limonoid for **1**. In the HMBC (Fig. 1A), the key correlations of H_2-29/C-1, C-2, C-4, C-28 and C-10, and H-30/C-3, C-2, C-8 and C-9 revealed **1** being a B-*seco* phragmalin-type limonoid. The carbon resonances at δ 170.4 and 78.8 were assignable to C-16 and C-17 by the HMBC correlations between H_2-15 and C-16, and between H_3-18 and C-17, respectively, indicating the existence of the ring D of a six-membered lactone.[8] The quaternary carbon at δ 118.8 (C-31) correlating with a methyl at δ 1.67 (s) revealed the presence of a typical orthoacetate moiety. The HMBC correlations from H-19 and H-29 to C-1, from H-3 and H-29 to C-2, from H-15 and H-30 to C-8, and from H-11 and H-12 to C-9 allowed the assignments of four oxygenated quaternary carbons of C-1, C-2, C-8 and C-9, respectively. For the phragmalin-type limonoids, an 1,8,9-[9] or 8,9,14-[9] or 8,9,30-orthoacetate[10] was usually found, and the presence of an 1,8,9-orthoacetate in **1** was thus tentatively assigned. Furthermore, the strong HMBC correlation between H-3 and C-1′ of 2,3-epoxy-2-methyl-butyryl group indicated that it was located at C-3. The key HMBC correlation between H-30 and the carbonyl of propionyl at δ 171.8 located the propionyloxy group at C-30. The remaining acetoxyl was then posited at C-2 by comparing its NMR data with those of limonoids possessing the same substituted pattern reported.[11] The planar structure of **1** was thus elucidated.

The relative configuration of **1** was assigned by a single crystal X-ray diffraction (Fig. 1B), which also confirmed its planar structure. In its NMR spectrum, the H-3′ of **1** resonated at δ 3.93 (q, J=5.4 Hz) indicated that the 2,3-epoxy-2-methyl-butyryl group at C-3 took a 2*R*,3*S*-configuration.[7]

Swietenitin O (**2**) was obtained along with epoxyfebrinin B (**12**) from an uneasy-separated mixture by semi-preparative HPLC, and both compounds shared the same molecular formula $C_{38}H_{46}O_{15}$. The IR and MS spectra of **2** and **12** were almost identical, and their ^{1}H- and ^{13}C-NMR data (Tables 1, 2) also showed high similarity with the only obvious difference being the chemical shift of H-3′ at δ 3.90 (q, J=5.6 Hz) for **2** and at δ 3.13 (q, J=5.5 Hz) for **12**, suggesting that they are a pair of 2′,3′-epimers. According to the chemical shifts of H-3′,[7] the absolute configuration of 2,3-epoxy-2-methyl-butyryl in **2** and **12** were assigned as 2*R*, 3*S* and 2*S*, 3*R*, respectively. This was confirmed by rotating frame Overhauser effect spectroscopy (ROESY) experiments (Fig. 2), in which,

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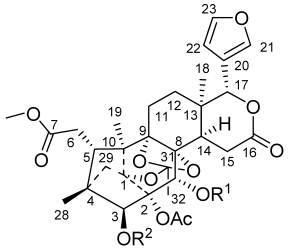
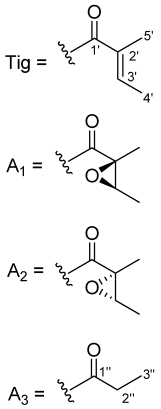
Table 1. [1]H-NMR Spectroscopic Data for Compounds **1**—**5**, **12**[a)]

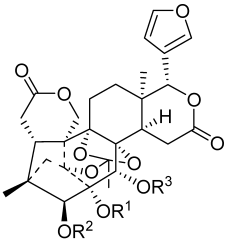
No.	1	2	12	3	4	5
3	5.16 (s)	5.18 (s)	5.17 (s)	5.28 (s)	5.32 (s)	4.69 (s)
5	2.85 (d, 8.8)	2.85 (dd, 9.2, 1.8)	2.94 (d, 9.4)	2.98 (dd, 9.1, 2.6)	2.28 (br d, 9.3)	2.72 (m)
6	2.27 (m)	2.25 (dd, 15.9, 1.8)	2.26 (dd, 16.1, 1.6)	2.28 (dd, 15.9, 2.6)	2.38 (m)	2.48 (dd, 17.0, 4.8)
	2.45 (dd, 15.8, 8.8)	2.44 (dd, 15.9, 9.2)	2.49 (dd, 16.1, 9.4)	2.46 (dd, 15.9, 9.1)		2.60 (m)
11α	1.67 (m)	1.67 (m)	1.64 (m)	1.66 (m)	1.98 (m)	1.81 (m)
11β	2.11 (m)	2.10 (m)	2.08 (m)	2.08 (m)	2.23 (dd, 14.7, 4.4)	2.26 (m)
12α	1.34 (m)	1.37 (m)	1.28 (m)	1.30 (m)	—	1.33 (m)
12β	1.64 (m)	1.67 (m)	1.62 (m)	1.64 (m)	3.92 (dt, 12.3, 2.7)	1.39 (m)
14	2.08 (m)	2.07 (d, 10.8)	2.06 (d, 10.8)	2.07 (d, 11.1)	—	2.01 (d, 9.5)
15	2.71 (dd, 20.4, 10.9)	2.71 (dd, 10.8, 20.4)	2.72 (dd, 10.8, 20.1)	2.71(dd, 20.3, 11.1)	6.37 (s)	2.69 (m)
	3.28 (d, 20.4)	3.28 (d, 20.4)		3.28 (d, 20.1)	3.28 (d, 20.3)	3.22 (d, 19.8)
17	5.54 (s)	5.54 (s)	5.55 (s)	5.59 (s)	5.85 (s)	5.32 (s)
18	1.04 (s)	1.04 (s)	1.07 (s)	1.04 (s)	1.46 (s)	1.18 (s)
19	1.15 (s)	1.15 (s)	1.17 (s)	1.17 (s)	1.34 (s)	4.37 (d, 13.7)
						4.78 (d, 13.7)
21	7.58 (s)	7.57 (s)	7.52 (s)	7.53 (br d, 0.8)	7.69 (s)	7.76 (s)
22	6.52 (s)	6.52 (s)	6.46 (s)	6.49 (s)	6.64 (br d, 1.1)	6.45(br d, 1.3)
23	7.45 (br d, 1.4)	7.41 (br t, 1.7)	7.42 (s)	7.42 (br t, 1.7)	7.54 (br t, 1.7)	7.43 (br t, 1.6)
28	0.88 (s)	0.89 (s)	0.94 (s)	0.90 (s)	0.73 (s)	0.98 (s)
29a	1.99 (d, 11.1)	1.99 (d, 10.7)	2.00 (d, 10.9)	1.99 (d, 11.1)	1.98 (d, 11.4)	2.25 (d, 11.3)
29b	1.68 (d, 11.1)	1.68 (d, 10.7)	1.70 (d, 10.9)	1.71 (d, 11.1)	1.75 (d, 11.4)	1.81 (d, 11.3)
30	6.20 (s)	6.15 (s)	6.23 (s)	6.29 (s)	5.45 (s)	5.64 (s)
32	1.67 (s)	1.67 (s)	1.78 (s)	1.67 (s)	1.70 (s)	1.69 (s)
7-OMe	3.74 (s)	3.74 (s)	3.70 (s)	3.65 (s)	3.72 (s)	—
2-Ac	2.15 (s)	2.16 (s)	2.14 (s)	2.15 (s)	2.20 (s)	—
30-Ac		1.94 (s)	1.92 (s)	—	—	—
3′	3.93 (q, 5.4)	3.90 (q, 5.6)	3.13 (q, 5.5)	7.07 (qd, 7.2, 1.3)	6.58 (qd, 7.0, 1.4)	3.12 (q, 5.5)
4′	1.33 (d, 5.4)	1.32 (d, 5.6)	1.38 (d, 5.5)	1.82 (dd, 7.2, 1.3)	1.70 (d, 7.0)	1.41 (d, 5.5)
5′	1.67 (s)	1.59 (s)	1.67 (s)	1.67 (s)	1.86 (s)	1.61 (s)
2″	2.10 (q, 7.4)	—	—	2.15 (q, 7.3)	—	2.38 (qd, 7.5, 2.6)
3″	1.04 (t, 7.4)	—	—	0.97 (t, 7.3)	—	1.09 (t, 7.5)

a) Recorded in $CDCl_3$ at 400 MHz. δ in ppm and *J* in Hz are in the parentheses.

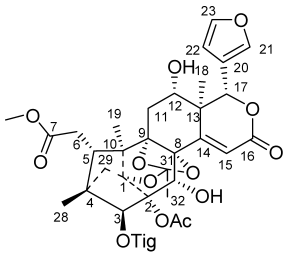


	R^1	R^2
1	A_3	A_2
2	Ac	A_2
3	A_3	Tig
12	Ac	A_1





	R^1	R^2	R^3
5	H	A_1	A_3
6	Ac	A_1	A_3
7	H	Tig	A_3
8	H	Tig	Ac



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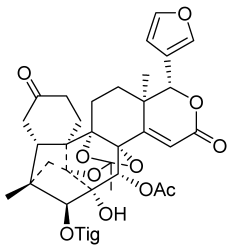

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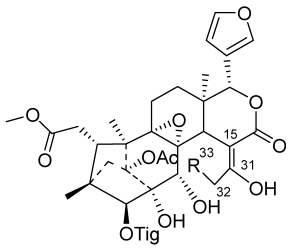

	R
10	H
11	CH_3

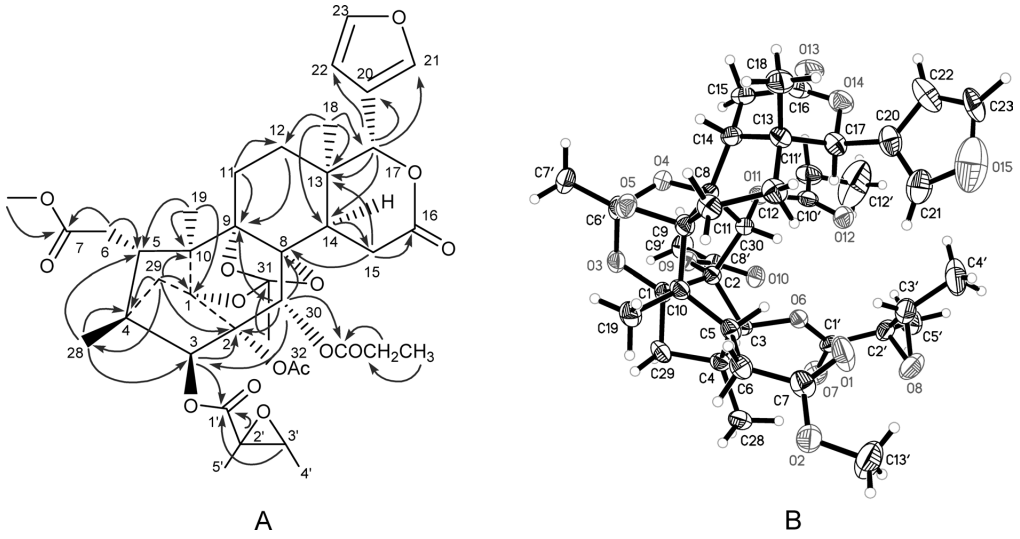

Fig. 1. (A) Selected HMBC Correlations (H→C) of **1**; (B) Single-Crystal X-Ray Structure of **1**

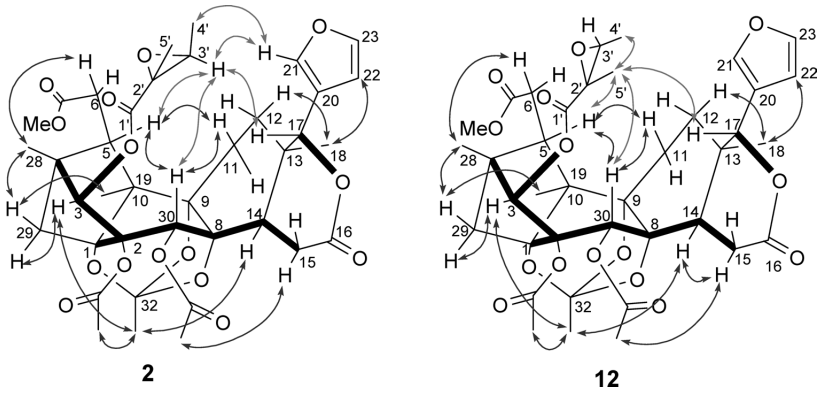

Fig. 2. Key ROESY Correlations (H↔H) of **2** and **12**

key ROESY correlations from H-3′ at δ 3.90 to H-5, H-21 and H-30, and from Me-4′ to H-21 for a typical 2*R*,3*S*-epoxy-2-methyl-butyryl moiety were observed in **2**; and the strong ROESY correlations from Me-5′ to H-5, H-17 and H-30 for a 2*S*,3*R*-epoxy-2-methyl-butyryl moiety were detected in **12**.[7] The structures of the new limonoid **2** and the known limonoid epoxyfebrinin B (**12**) were therefore completely assigned.

Swietenitin P (**3**), a white amorphous powder, had a molecular formula of $C_{39}H_{48}O_{14}$ as determined by the HR-EI-MS at *m*/*z* 740.3025 $[M]^+$ (Calcd 740.3044). In comparison with compound **1**, the molecular formula of **3** showed 16 mass units less consistent with the loss of an oxygen atom. The NMR (Tables 1, 2) data showed that the structure of **3** is closely related to that of **1**. The only structural difference was the presence of a tigloyloxy group[10] (δ 7.07, 1H, qd, J=7.2, 1.3 Hz, δ 1.67, 3H, s, and δ 1.82, 3H, dd, J=7.2, 1.3 Hz; δ 166.8, δ 128.0, δ 138.6, δ 12.0 and δ 14.7) at C-3 of **3**, replacing the 2,3-epoxy-2-methyl-butyryloxyl group of **1**.

Swietenitin Q (**4**) was obtained as a white amorphous powder. Its HR-EI-MS ion at *m*/*z* 698.2567 $[M]^+$ (Calcd 698.2574) corresponds to the molecular formula of $C_{36}H_{42}O_{14}$, in conjunction with the ^{1}H- and ^{13}C-NMR data, which requires sixteen degree of unsaturations. The IR spectrum showed the presence of hydroxyl (3446 cm^{-1}) and ester (1728 cm^{-1}) groups. Comparison of the ^{1}H- and ^{13}C-NMR data of **4** with those of compound **3** showed many similarities with several changes being the presence of a Δ^{14} double bond and the substituting groups at C-12 and C-30. A Δ^{14} double carbon bond was assigned on the basis of chemical shift of H-15 at δ 6.37 (s), and the chemical shifts of C-14 at δ 150.9 and C-15 at δ 124.6. This was confirmed by the HMBC correlations from H-15 to C-8, C-13, C-14 and C-16. The presence of a hydroxyl group at C-30 of **4** was assigned on basis of chemical shift of H-30 at δ 5.45, which was obviously upfield shifted as compared with that of compound **3** at δ 6.29 due to the absence of the acylation effect. In addition, a hydroxyl group was attached to C-12 on the ground of chemical shifts of H-12 at δ 3.92 (dt, 12.3, 2.7 Hz) and C-12 at δ 66.8, and this was verified by the mutual HMBC correlations of H-12/C-17, H-12/C-18, H_2-11/C-13, and H_2-11/C-8. The relative configuration of **4** was established by ROESY spectrum, in which, the key correlations from H-12 to H-17, H-5, H-6 and H-11 indicated that the OH-12 was an α-configuration.

Swietenitins R—V (5—9) Swietenitin R (**5**) was obtained as a white amorphous powder, showing a molecular formula of $C_{36}H_{42}O_{14}$ (HR-EI-MS at *m*/*z* 698.2590 $[M]^+$, Calcd 698.2575), which was supported by the sodiated ion at *m*/*z* 721 $[M+Na]^+$ and the protonated ion at *m*/*z* 699 $[M+H]^+$ in the positive-mode of ESI-MS. The IR absorption

Table 2. ^{13}C-NMR Spectroscopic Data of Compounds **1**—**12**[a)]

No.	**1**	**2**	**12**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
1	86.7	86.8	86.8	86.8	84.4	85.7	85.3	85.5	85.6	84.8	83.3	83.3
2	85.3	85.2	85.2	85.5	83.8	79.4	85.0	78.3	78.6	78.3	73.1	73.2
3	82.1	82.1	82.3	81.3	84.6	83.4	81.4	84.2	84.1	85.1	85.9	85.9
4	45.8	45.9	45.9	46.0	44.7	45.5	46.3	45.4	45.5	45.4	44.2	44.2
5	36.2	36.3	36.0	36.2	40.0	33.4	32.9	34.0	34.0	35.0	40.5	40.5
6	33.3	33.3	33.3	33.5	33.7	31.0	30.8	31.0	31.0	31.6	33.6	33.6
7	173.0	173.0	172.7	172.9	174.2	171.1	170.8	171.1	171.1	171.1	173.5	173.5
8	85.4	85.4	85.4	85.6	83.8	86.4	86.0	86.4	86.3	83.5	65.4	65.5
9	85.4	85.3	85.3	85.6	86.1	86.3	85.6	86.3	86.3	84.5	70.2	70.3
10	46.1	46.2	46.1	46.4	48.1	44.6	45.1	44.7	44.7	46.6	45.4	45.4
11	25.2	25.3	25.4	25.4	34.6	25.5	25.7	25.7	25.7	25.5	20.0	20.0
12	29.0	29.2	29.2	29.1	66.8	29.4	29.4	26.3	26.3	26.2	28.7	28.7
13	34.3	34.2	34.2	34.5	44.7	34.3	34.2	34.4	34.3	37.5	33.2	33.2
14	42.9	43.0	43.0	43.0	150.9	42.8	43.0	42.8	42.8	160.0	48.6	48.0
15	26.3	26.4	26.4	26.4	124.6	26.4	26.3	29.5	29.6	120.2	93.5	92.1
16	170.4	170.2	170.3	170.4	162.7	170.0	170.1	169.8	169.8	163.0	170.5	170.7
17	78.8	79.0	79.0	78.7	78.2	78.2	78.4	79.6	79.3	80.1	75.1	75.0
18	19.5	19.5	19.5	19.5	12.8	20.0	20.8	20.0	20.0	18.3	21.4	21.6
19	16.6	16.7	16.9	16.8	15.5	68.7	68.7	68.8	68.8	68.5	15.8	15.8
20	121.2	121.2	121.1	121.3	121.6	120.4	120.7	120.8	120.9	119.4	120.5	120.6
21	140.5	140.5	140.5	140.6	142.2	142.0	141.0	140.7	140.6	141.4	141.8	141.8
22	109.5	109.5	109.7	109.7	109.7	109.7	109.6	109.5	109.4	109.7	109.7	109.8
23	142.9	143.0	143.0	142.8	144.9	143.3	143.4	143.3	143.4	143.2	143.3	143.3
28	13.5	13.6	13.5	14.4	13.9	13.4	13.5	13.7	13.7	14.1	15.6	15.6
29	40.0	40.0	40.1	40.0	39.5	38.1	38.7	38.2	38.2	38.5	38.8	38.8
30	69.0	69.1	69.2	69.0	73.9	70.2	68.4	70.0	70.4	69.1	67.3	67.3
31	118.8	118.9	119.0	118.9	119.5	119.6	119.5	119.6	119.6	120.1	177.5	182.3
32	20.9	21.0	21.0	21.0	16.5	20.9	21.6	21.0	21.0	21.0	19.4	26.1
2-Ac	21.6	21.6	21.7	21.7	21.9		20.8			1-Ac	21.0	C-33 11.7
	169.7	168.4	168.2	170.2	169.9		169.3				169.4	
30-Ac		21.5	21.5						21.0	21.0		1-Ac 21.0
		170.2	170.3						169.1	170.8		169.4
7-OMe	52.3	52.3	52.2	52.0	52.3						52.1	52.1
1′	170.1	169.7	169.7	166.8	167.5	170.7	169.7	167.0	167.0	167.0	167.8	167.8
2′	58.1	58.0	58.5	128.0	131.0	58.2	58.0	128.8	128.6	127.4	128.1	128.1
3′	58.8	58.7	59.3	138.6	135.6	58.5	58.9	137.6	137.9	139.6	138.9	138.9
4′	13.2	13.2	13.3	12.0	13.0	13.4	13.7	12.3	12.4	12.0	12.4	12.5
5′	14.3	14.4	14.5	14.7	13.6	13.8	13.9	14.5	14.5	14.6	14.2	14.2
1″	171.8			171.5		172.5	172.1	172.5				
2″	27.6			26.4		27.5	27.7	27.7				
3″	8.16			8.23		8.65	8.38	8.60				

a) Recorded in $CDCl_3$ at 100 MHz.

bands at 1749 cm^{-1} implied the presence of ester groups.[12)] ^{1}H- and ^{13}C-NMR analysis indicated that compound **5** was a structural congener of **3**. Compared the ^{13}C-NMR data of **5** with those of compound **3**, the C-2 of **5** was upfield shifted to δ 79.4 ($\Delta\delta$ *ca.* 6) indicating that a hydroxyl group was located at the C-2 of **5**, which subsequently caused a obvious downfield shift of C-3 at δ 83.4 in the ^{13}C-NMR, and upfield shift of H-3 at δ 4.69 in ^{1}H-NMR. Furthermore, in the HMBC spectrum (Fig. 3A), the key correlations of H_2-6/C-5 and C-7, and H_2-19/C-1, C-5, C-7 and C-10 revealed the presence of a six-membered γ-lactone. A propionyloxy group was located at C-30 by the HMBC correlation between the H-30 and its carbonyl carbon at δ 172.5. The strong HMBC correlation between H-3 and C-1′ of 2,3-epoxy-2-methyl-butyryl group indicated that it was located at C-3. In addition, the H-3′ was resonated at δ 3.12 (q, J=5.5 Hz) in the ^{1}H-NMR spectrum, indicating that the absolute stereochemistry of 2,3-epoxy-2-methyl-butyryl group was 2*S*,3*R*,[7)] which was verified by the ROESY correlations (Fig. 3B).

Swietenitin S (**6**), a white amorphous powder, showed the molecular formula of $C_{38}H_{44}O_{15}$, as determined by HR-EI-MS at *m*/*z* 740.2665 $[M]^+$ (Calcd 740.2680). Comparison of the ^{1}H- and ^{13}C-NMR data of **6** with those of **5** showed high similarity, except for the presence of two additional carbon resonances at δ 20.8 and 169.3 in the ^{13}C-NMR of **6** being assignable to an acetyl group, indicating that compound **6** was an acetylated analogue of **5**. By comparing with **5**, the down field shifted proton resonances of H-3 at δ 5.23 and H-30 at δ 6.06 in **6** indicated that the acetoxyl group was located at C-2 replacing the OH-2 of **5**. The down field shifted proton resonances of H-3 and H-30 could be rationalized as the deshielding effect of OAc-2. The structure of **6** was further confirmed by HMBC and ROESY spectra. The H-3′ resonated at δ 3.11 (q, J=5.4 Hz) in the ^{1}H-NMR spectrum, indicated a 2*S*,3*R*-configuration for 2,3-epoxy-2-methyl-butyryl group at the C-3 of **6**.[7)]

Swietenitin T (**7**) was yielded as a white amorphous powder, and had a molecular formula of $C_{36}H_{42}O_{13}$ as established from the HR-EI-MS ion at *m*/*z* 682.2608 $[M]^+$ (Calcd 682.2626), which was supported by the protonated ion at *m*/*z* 683 $[M+H]^+$ and sodiated ion at *m*/*z* 705 $[M+Na]^+$ in the positive-mode of ESI-MS. Compared with compound **5**, its

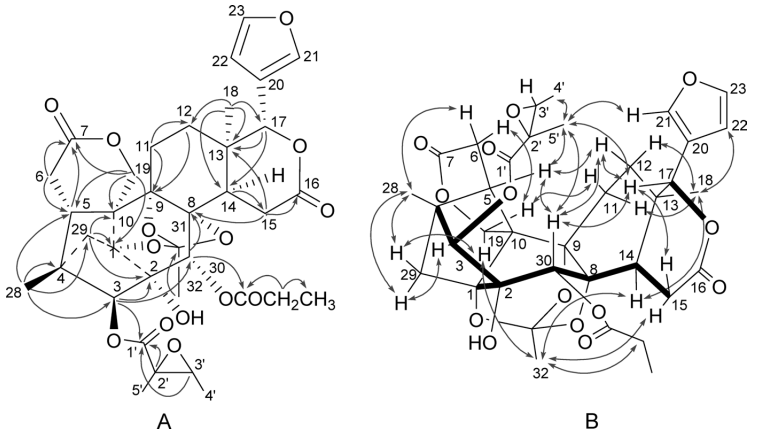

Fig. 3. (A) Key HMBC (H→C) Correlations of **5**; (B) Key ROESY (H↔H) Correlations of **5**

Table 3. ^{1}H-NMR Spectroscopic Data for Compounds **6**—**11**[a)]

No.	**6**	**7**	**8**	**9**	**10**	**11**
3	5.23 (s)	4.69 (s)	4.73 (s)	4.68 (s)	4.87 (s)	4.87 (s)
5	2.68 (m)	2.75 (m)	2.74 (m)	2.80 (m)	2.93 (br d, 10.6)	2.96 (br d, 10.3)
6	2.50 (dd, 16.9, 4.9)	2.51 (dd, 17.0, 4.9)	2.50 (dd, 17.0, 4.5)	2.65 (m)	2.37 (dd, 16.0, 11.4)	2.37 (dd, 16.1, 11.4)
	2.60 (dd, 16.9, 3.0)	2.66 (dd, 17.0, 3.3)	2.65 (dd, 17.0, 3.0)		2.49 (m)	2.49 (dd, 16.1, 3.4)
11α	1.86 (m)	1.86 (m)	1.82 (m)	2.20 (dd, 15.3, 5.3)	1.95 (m)	1.93 (m)
11β	2.25 (m)	2.30 (m)	2.24 (m)	2.27 (dd, 12.4, 5.3)	2.14 (m)	2.13 (m)
12α	1.40 (m)	1.34 (br d, 14.4)	1.35 (br d, 13.7)	1.48 (dt, 13.4, 2.8)	1.32 (m)	1.32 (m)
12β	1.44 (m)	1.48 (br dt, 11.1, 3.3)	1.50 (dt, 14.7, 3.3)	1.66 (dd, 14.1, 5.3)	1.40 (m)	1.43 (m)
14	2.03 (d, 10.7)	2.02 (dd, 9.1, 2.8)	2.03 (m)	—	2.64 (m)	2.63 (s)
15	2.73 (m)	2.72 (m)	2.70 (m)	6.04 (s)	—	—
	3.26 (br d, 18.7)	3.22 (d, 19.5)	3.22 (d, 19.1)			
17	5.33 (s)	5.35 (s)	5.32 (s)	5.11 (s)	5.50 (s)	5.50 (s)
18	1.14 (s)	1.11 (s)	1.11 (s)	1.12 (s)	0.86 (s)	0.87 (s)
19	4.39 (d, 14.0)	4.40 (d, 13.8)	4.39 (d, 13.6)	4.37 (d, 13.8)	1.24 (s)	1.24 (s)
	4.79 (d, 14.0)	4.79 (d, 13.8)	4.79 (d, 13.6)	4.89 (d,13.8)		
21	7.55 (s)	7.43 (d, 1.6)	7.44 (s)	7.51 (s)	7.88 (br s)	7.88 (br s)
22	6.39 (s)	6.37 (d, 1.0)	6.36 (s)	6.43 (s)	6.49 (dd, 2, 0.8)	6.49 (br s)
23	7.44 (br t, 1.5)	7.41 (s)	7.40 (s)	7.44 (s)	7.45 (d, 1.7)	7.45 (br s)
28	0.98 (s)	1.01 (s)	1.00 (s)	1.06 (s)	0.87 (s)	0.88 (s)
29a	2.35 (d, 11.6)	2.26 (d, 11.2)	2.27 (d, 11.2)	2.35 (d, 11.4)	1.85 (dd, 10.8, 1.7)	1.85 (d, 11.5)
29b	1.75 (d, 11.6)	1.83 (m)	1.86 (d, 11.2)	1.89 (d, 11.4)	1.75 (d, 10.8)	1.75 (d, 11.5)
30	6.06 (s)	5.68 (s)	5.63 (s)	5.38 (s)	5.26 (s)	5.28 (s)
32	1.70 (s)	1.70 (s)	1.70 (s)	1.71 (s)	7-OMe	7-OMe
					3.74 (s)	3.74 (s)
1-Ac	—	—	—	—	2.15 (s)	2.13 (s)
2-Ac	2.16 (s)	—	30-Ac 2.06 (s)	30-Ac 1.99 (s)	2-OH 3.00 (s)	2-OH 2.95 (s)
3′	3.11 (q, 5.4)	6.84 (qd, 7.1, 1.6)	6.85 (qd, 7.1, 1.1)	6.85 (qd, 7.0, 1.4)	6.90 (qd, 7.0, 1.2)	6.90 (q, 6.4)
4′	1.44 (d, 5.4)	1.88 (d, 7.1)	1.84 (d, 7.1)	1.83 (d, 7.0)	1.43 (dd, 7.0, 1.2)	1.43 (d, 6.4)
5′	1.70 (s)	1.94 (s)	1.91 (s)	1.81 (s)	1.88 (br t, 1.3)	1.88 (s)
2″	2.17 (m)	2.35 (m)	—	—	Enol-	—
3″	1.04 (t, 7.1)	1.04 (t, 7.4)	—	—	34 2.07 (s)	2.13 (m)
						2.60 (m)
	—	—	—	—	35	1.14 (t, 7.7)

a) Recorded in $CDCl_3$ at 400 MHz. δ in ppm and J in Hz are in the parentheses.

molecular formula showed 16 mass units less that is consistent with the loss of an oxygen atom. The NMR (Tables 2, 3) data showed that the structure of **7** was closely related to that of **5**. The only difference was the presence of a tigloyloxyl group at the C-3 of **7** replacing the 2,3-epoxy-2-methylbutyryl group in **5**. The tigloyloxyl moiety in **7** was identified by the NMR data (δ 6.84, 1H, qd, J=7.1, 1.6 Hz, δ 1.94, 3H, s, and δ 1.88, 3H, d, J=7.1 Hz; δ 167.0, δ 128.8, δ 137.6, δ 12.3 and δ 14.5).

Swietenitin U (**8**), a white amorphous powder, had a molecular formula of $C_{35}H_{38}O_{12}$ as determined by the HR-EI-MS at m/z 650.2345 $[M-H_2O]^+$ (Calcd 650.2363). The NMR spectra of **8** showed high similarity to those of **7** except for the absence of one –CH_2– unit, and this was supported by its molecular formula, which showed 14 mass units less than that of **7**. A detail analysis of its NMR data further revealed that an acetoxyl group was attached at the C-30 of **8** instead of the propionyloxyl group of **7**. The structure of **8** was fi-

nally confirmed by HMBC and ROESY spectra.

Swietenitin V (**9**), a white amorphous powder, gave a molecular formula of $C_{35}H_{38}O_{13}$, as established on the basis of HR-EI-MS at *m*/*z* 666.2319 $[M]^+$ (Calcd 666.2313). The IR spectrum implied the functionalities of **9** being similar to those of **8**. Extensive analysis of its EI-MS and NMR data suggested that it is a structural congener of **8** with the only change being the presence of a Δ^{14} double bond, which resulted in the H-15 resonated at δ 6.04 (s), and the C-14, C-15 appeared at δ 160.0 and δ 120.2, respectively, in the ^{1}H- and ^{13}C-NMR of **9**. The structural assignment of **9** was finally confirmed by HMBC spectrum, in which the key correlations from H-15 to C-16 (δ 163.0), C-14 (δ 160.0), C-8 (δ 83.5) and C-13 (δ 37.5) were observed. Therefore, the structure of **9** was elucidated.

Swietenitin W (10) and Swietenitin X (11) Swietenitin W (**10**), a white amorphous powder, possessed a molecular formula of $C_{36}H_{42}O_{12}$, as determined by the HR-EI-MS at *m*/*z* 666.2680 $[M-H_2O]^+$ (Calcd 666.2676) requiring fifteen degrees of unsaturation, and this was supported by the sodiated molecular ion at *m*/*z* 707 $[M+Na]^+$ in the positive mode of ESI-MS. The IR absorptions showed the presence of hydroxyl (3600—3200 cm^{-1}) and ester (1724—1715 cm^{-1}) groups. Its NMR data (Tables 2, 3) in combination with the DEPT experiments revealed that **10** possessed one secondary methyl, seven tertiary methyls (one from acetyl and one from methoxy), six methylenes, eight methines (three olefinic) and fourteen quaternary carbons. The presence of a β-furan ring (δ 7.88, δ 6.49 and δ 7.45, each 1H) and a tigloyl group were identified by the analysis of its ^{1}H-NMR data. Comprehensive analysis of its NMR data (Tables 2, 3) indicated that **10** is a phragmalin-type limonoid bearing biosynthetically extended C2 unit at C-15 and forming enol moiety between C-15 and C-31, which is similar to the case of neobeguin.[13] This was confirmed by the HMBC correlations from H-14 to C-13, C-15, C-16 and C-31, and from Me-32 to C-31 and C-15. The tigloyloxyl group was located at C-3 by HMBC correlation between H-3 and C-1′. A proton resonance at δ 3.00 was distinguished to be O<u>H</u>-2 by ^{1}H-detected heteronuclear multiple quantum coherence (HMQC) spectrum, and was confirmed by the HMBC correlations from O<u>H</u>-2 to C-1, C-2 and C-30 (Fig. 4A). The NMR analysis also revealed the absence of orthoester group in compound **10**. Two oxygenated quaternary carbon resonances up-field shifted at δ 65.4 and δ 70.2, were tentatively assigned to the presence of an 8,9-epoxy group, which was confirmed by the HMBC correlations of H-11/C-8, C-9 and C-12, and H-14/C-8 and C-9. The oxygenated tertiary carbon resonance at δ 67.3 was assigned to C-30 bearing a hydroxyl by the HMBC correlations from H-30 to C-8 and C-2, and this was supported by the relatively up-field shifted H-30 at δ 5.26 (s). The remaining acetoxyl group was thus only assignable to the quaternary C-1 at δ 83.3, which showed multiple HMBC correlations with Me-19, H-3, H_2-29 and OH-2. The presence of a C-1-OAc was confirmed by the key ROESY correlations from the methyl of Ac to H-29 and CH_3-19 (Fig. 4B).

The relative configuration of **10** was established by ROESY spectrum (Fig. 4B), in which, the ROESY cross-peaks from H-17β to H-5, H-11 and H-21, and from Me-28 with OMe-7 and H-6 indicated that H-5, H-11, H-21 and Me-28 were cofacial and arbitrarily assigned as a β-orientation. The ROESY correlations of H-3/H-29, CH_3-19/<u>C</u>H$_3$CO-1 and H-29/<u>C</u>H$_3$CO-1 revealed that CH_3-19, CH_2-29 and OAc-1 were α-oriented. The key correlation between H-3′ and H-5 showed that the tigloyloxyl group at C-3 took a β-orientation. Furthermore, the ROESY correlations of H-14/Me-18 and H-14/Me-32 showed that Me-18 was in a α-configuration, and the $\Delta^{15(31)}$ double bond took a *Z*-geometry. Although there were no direct ROESY correlations available to assign the relative configuration of C-8, C-9 and C-30, the 8, 9-epoxy group and OH-30 could be assigned in an α-configuration on the basis of biogenetic reasoning and stereo specific requirement for a phragmalin-type limonoid.

Swietenitin X (**11**), a white amorphous powder, showed a molecular formula of $C_{37}H_{44}O_{12}$ as determined by HR-EI-MS at *m*/*z* 680.2819 $[M-H_2O]^+$ (Calcd 680.2833). The NMR spectra of **11** showed high similarity to those of **10** except for the presence of one additional $-CH_2-$ unit, and this was supported by its EI-MS. A detail analysis of the NMR data of **11** further revealed that an ethyl group was linked at C-31 instead of a methyl in **10**. This was confirmed by the key HMBC correlations from Me-33 and H-14 to C-31, and from H-32 to C-15. Therefore, the structure of **11** was elucidated.

Compounds **1**—**12** were evaluated for antimicrobial activity against a small penal of microbes, including Gram-positive and Gram-negative bacteria, and fungi by microdilution assay,[14,15] unfortunately, the results showed that all the compounds were inactive.

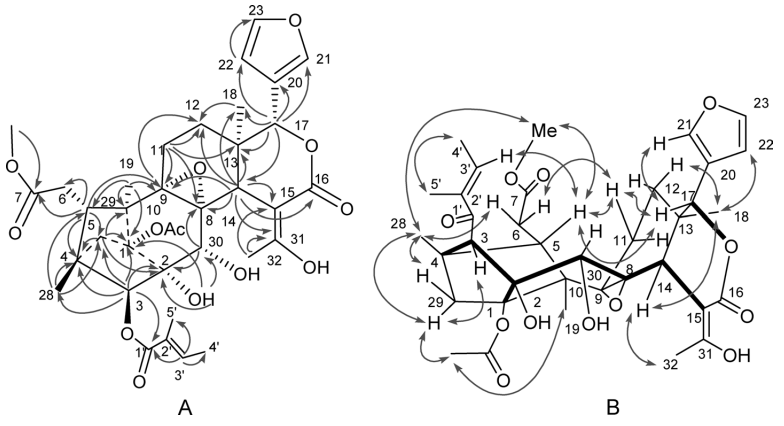

Fig. 4. (A) Key HMBC (H→C) Correlations of **10**; (B) Key ROESY (H↔H) Correlations of **10**

Experimental

General Experimental Procedures Optical rotations were measured on a Perkin-Elmer 341 polarimeter. Melting points were measured with an SGW X-4 melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer 577 spectrometer in KBr discs. NMR spectra were recorded on a Bruker AM-400 spectrometer. EI-MS (70 eV) and HR-EI-MS were measured on a Finnigan MAT-95 mass spectrometer in *m/z* (rel. %), and ESI-MS was carried out on a Finnigan LC Q^{DECA} instrument. Semi-preparative HPLC was performed on a Waters 515 pump equipped 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 Plant, Shanghai, People's Republic of China). Silica gel (200—300 mesh), silica gel H60, Sephadex LH-20 (Amersham Biosciences, U.S.A.), reversed-phase C_{18} silica gel (150—200 mesh, Merck, Germany), and MCI gel (CHP20P, 75—150 μm, Mitsubishi Chemical Industries Ltd., Japan) were used for column chromatography. Pre-coated silica gel GF_{254} plates (Qingdao Haiyang Chemical Co., Ltd., Qingdao, People's Republic of China) were used for TLC.

Plant Material The plant material of *Swietenia macrophylla* King was collected from Hainan Island of China and was authenticated by Professor S. M. Huang of Department of Biology, Hainan University. A voucher specimen (accession number: SMt-2006-1Y) has been deposited in the Shanghai Institute of Materia Medica.

Extraction and Isolation The dried powder of twigs of *S. macrophylla* (10 kg) was percolated with 95% EtOH for 3 times. 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 a silica gel column eluted in gradient with petroleum ether/acetone (10 : 1 to 0 : 1) to afford eight fractions A—H. Fraction F (3.2 g) was then subjected to a column of high porous polymer (MCI) gel (MeOH/H_2O, 50 : 50 to 90 : 10; v/v) to obtain four subfractions F1—F5. Fraction F2 (502 mg) was separated over a silica gel column eluted in gradient with petroleum ether/ethyl acetate (6 : 1 to 0 : 1, v/v), to afford four fractions F2a—F2d (102, 54, 78, 65 mg). Fraction F2a was purified on a semi-preparative HPLC with 60% methanol in water to yield compound **1** (20 mg), **12** (5 mg) and **2** (15 mg). By using the same purification procedures, fraction F2b gave **6** (5 mg); fractions F2c yielded **8** (3 mg) and **5** (5 mg); fraction F2d afforded **7** (10 mg) and **9** (5 mg). Fraction G (5.0 g) was then subjected passage over a column of MCI gel eluted with MeOH/H_2O (50 : 50 to 90 : 10; v/v) to obtain four subfractions G1—G4. Fraction G3 (2.31 g) was chromatographed on a silica gel column eluted with petroleum ether/ethyl acetate (4 : 1 to 0 : 1) to give three fractions G3a—G3c. Fraction G3b (105 mg) was separated on a column of Sephadex LH-20 gel to collect two major components, each of which was then purified by semi-preparative HPLC and 55% acetonitrile in water was used as the mobile phase to yield **3** (5 mg) and **4** (3 mg), respectively. By using the same purification procedures, fraction G4 yielded **10** (2 mg) and **11** (2 mg).

Swietenitin N (**1**): Colorless crystal; $[\alpha]_D^{20}$ −49.0 (c=0.100, MeOH), mp 240—242 °C; IR (KBr) ν_{max} 3622, 3537, 2962, 1743, 1385, 1242, 1167, 1049 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; EI-MS 70 eV *m/z* (relative intensity) 756 $[M]^+$ (22), 682 (17), 641 (9), 563 (91), 481 (39), 465 (42), 447 (24), 405 (29), 182 (30), 95 (100), 83 (65), 57 (62); HR-EI-MS *m/z* 756.2970 $[M]^+$ (Calcd for $C_{39}H_{48}O_{15}$, 756.2993).

Swietenitin O (**2**): White amorphous powder; $[\alpha]_D^{20}$ −54.0 (c=0.100, MeOH); IR (KBr) ν_{max} 3629, 3446, 2968, 1743, 1371, 1240, 1049, 876 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; EI-MS 70 eV *m/z* (relative intensity) 742 $[M]^+$ (30), 682 (22), 563 (100), 481 (39), 447 (21), 405 (25), 327 (16), 229 (14), 182 (21), 121 (29), 95 (70), 83 (21); HR-EI-MS *m/z* 742.2857 $[M]^+$ (Calcd for $C_{38}H_{46}O_{15}$, 742.2836).

Swietenitin P (**3**): White amorphous powder; $[\alpha]_D^{20}$ +40.0 (c=0.055, MeOH); IR (KBr) ν_{max} 3437, 2955, 1740, 1460, 1387, 1240, 1151, 1088 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; EI-MS 70 eV *m/z* (relative intensity) 740 $[M]^+$ (5), 728 (1), 681 (2), 639 (22), 607 (2), 547 (61), 481 (28), 465 (11), 405 (7), 301 (8), 182 (9), 121 (8), 95 (11), 83 (100), 55 (20); HR-EI-MS *m/z* 740.3025 $[M]^+$ (Calcd for $C_{39}H_{48}O_{14}$, 740.3044).

Swietenitin Q (**4**): White amorphous powder; $[\alpha]_D^{20}$ +240.0 (c=0.005, MeOH); IR (KBr) ν_{max} 3446, 2929, 1728, 1628, 1381, 1238, 1117, 1024 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; EI-MS 70 eV *m/z* (relative intensity) 698 $[M]^+$ (2), 674 (2), 638 (18), 609 (7), 514 (8), 482 (12), 383 (11), 315 (9), 180 (17), 121 (20), 95 (19), 83 (100), 55 (26); HR-EI-MS *m/z* 698.2567 $[M]^+$ (Calcd for $C_{36}H_{42}O_{14}$, 698.2574).

Swietenitin R (**5**): White amorphous powder; $[\alpha]_D^{20}$ −39.0 (c=0.095, MeOH); IR (KBr) ν_{max} 3622, 3548, 2964, 1749, 1630, 1460, 1367, 1298, 1225, 1180, 1047 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; EI-MS 70 eV *m/z* (relative intensity) 698 $[M]^+$ (5), 680 (7), 639 (10), 624 (5), 582 (23), 565 (16), 465 (12), 449 (22), 301 (38), 95 (100), 83 (82), 57 (67); HR-EI-MS *m/z* 698.2590 $[M]^+$ (Calcd for $C_{36}H_{42}O_{14}$, 698.2575).

Swietenitin S (**6**): White amorphous powder; $[\alpha]_D^{20}$ −64 (c=0.001, MeOH); IR (KBr) ν_{max} 3446, 2920, 1757, 1639, 1369, 1238, 1049, 876 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 2 and 3; EI-MS 70 eV *m/z* (relative intensity) 740 $[M]^+$ (21), 681 (34), 625 (20), 583 (15), 547 (86), 465 (50), 449 (57), 389 (20), 327 (12), 121 (34), 95 (100), 57 (70); HR-EI-MS *m/z* 740.2665 $[M]^+$ (Calcd for $C_{38}H_{44}O_{15}$, 740.2680).

Swietenitin T (**7**): White amorphous powder; $[\alpha]_D^{20}$ −33.0 (c=0.040, MeOH); IR (KBr) ν_{max} 3448, 2974, 1751, 1651, 1460, 1273, 1086 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 2 and 3; EI-MS 70 eV *m/z* (relative intensity) 682 $[M]^+$ (7), 623 (5), 566 (5), 549 (8), 465 (8), 449 (8), 301 (9), 121 (5), 95 (12), 83 (100), 55 (20); HR-EI-MS *m/z* 682.2608 $[M]^+$ (Calcd for $C_{36}H_{42}O_{13}$, 682.2626).

Swietenitin U (**8**): White amorphous powder; $[\alpha]_D^{20}$ −8.0 (c=0.025, MeOH); IR (KBr) ν_{max} 3448, 2920, 1753, 1651, 1458, 1371, 1272, 1148, 1053 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 2 and 3; EI-MS 70 eV *m/z* (relative intensity) 650 $[M-H_2O]^+$ (1), 609 (2), 566 (2), 549 (3), 465 (5), 437 (2), 369 (5), 301 (6), 121 (8), 95 (16), 83 (100), 55 (29); HR-EI-MS *m/z* $[M-H_2O]^+$ 650.2345 (Calcd for $C_{35}H_{38}O_{12}$, 650.2363).

Swietenitin V (**9**): White amorphous powder; $[\alpha]_D^{20}$ +33.0 (c=0.040, MeOH); IR (KBr) ν_{max} 3467, 2956, 1728, 1649, 1402, 1259, 1223, 1055, 876 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 2 and 3; EI-MS 70 eV *m/z* (relative intensity) 666 $[M]^+$ (1), 624 (6), 564 (10), 509 (6), 468 (17), 421 (3), 386 (3), 368 (9), 299 (3), 201 (2), 121 (3), 95 (10), 83 (100), 55 (29); HR-EI-MS *m/z* 666.2319 (Calcd for $C_{35}H_{38}O_{13}$, 666.2313).

Swietenitin W (**10**): White amorphous powder; $[\alpha]_D^{20}$ +17.0 (c=0.150, MeOH); IR (KBr) ν_{max} 3440, 2926, 1730, 1641, 1381, 1252, 1121, 1028 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 2 and 3; EI-MS 70 eV *m/z* (relative intensity) 666 $[M-H_2O]^+$ (10), 606 (5), 523 (4), 464 (4), 427 (5), 299 (3), 219 (4), 121 (10), 95 (8), 83 (100), 55 (33); HR-EI-MS *m/z* 666.2680 $[M-H_2O]^+$ (Calcd for $C_{36}H_{42}O_{12}$, 666.2676).

Swietenitin X (**11**): White amorphous powder; $[\alpha]_D^{20}$ +31.0 (c=0.085, MeOH); IR (KBr) ν_{max} 3435, 2928, 1732, 1639, 1373, 1232, 1121, 1028 cm^{-1}; ^{1}H-NMR data, ^{1}H- and ^{13}C-NMR data, see Tables 2 and 3; EI-MS 70 eV *m/z* (relative intensity) 680 $[M-H_2O]^+$ (4), 647 (1), 620 (2), 564 (2), 520 (2), 464 (5), 422 (2), 343 (2), 313 (2), 189 (3), 121 (11), 83 (100), 55 (39); HR-EI-MS *m/z* 680.2819 $[M-H_2O]^+$ (Calcd for $C_{37}H_{44}O_{12}$, 680.2833).

Epoxyfebrinin B (**12**): White amorphous powder; $[\alpha]_D^{20}$ +7.0 (c=0.030, MeOH); IR (KBr) ν_{max}3448, 2956, 1741, 1628, 1371, 1242, 1049 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Tables 1 and 2; EI-MS 70 eV *m/z* (relative intensity) 742 $[M]^+$ (16), 682 (20), 563 (57), 480 (47), 465 (27), 405 (23), 327 (16), 182 (29), 121 (37), 95 (100), 83 (59); HR-EI-MS *m/z* 742.2842 $[M]^+$ (Calcd for $C_{38}H_{46}0O_{15}$, 742.2837).

X-Ray Crystallographic Analysis of 1 Colorless crystals of **1** were obtained in a mixture of solvents (90% MeOH in water). Crystal data were obtained on a Bruker SMART charge coupled device (CCD) detector employing graphite monochromated Mo-$K\alpha$ radiation (λ=0.71073 Å) at 293 K and operating in the ϕ–ω scan mode. The structure was solved by direct methods SHELXS-97[16] and refined with full-matrix least-squares calculations on F^2 using SHELX-97.[17] 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** has been deposited at the Cambridge Crystallographic Data Centre (deposition number CCDC-722594). 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, U.K. [fax: (+44) 1223–336–033; or email: deposit@ccdc.cam.ac.uk].

Crystal data for **1**: $C_{39}H_{50}O_{16}$; M_r=774.79; orthorhombic crystalline system; space group: $P2_12_12_1$; a=13.5869(9) Å, b=16.5391(10) Å, c=17.2334(11) Å; V=3872.6(4) $Å^3$; Z=4; d=1.329 mg m^3; crystal dimensions 0.323×0.285×0.167 mm^3; the final indices were R_1=0.0508, wR_2=0.1205.

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