Full Papers

Structurally Diverse Limonoids from the Fruits of *Swietenia mahagoni*

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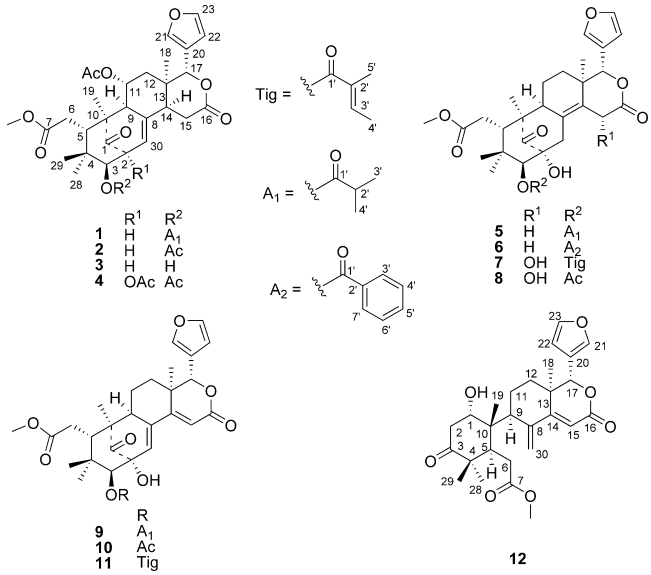
Eleven new mexicanolide-type limonoids, swietmanins A−I (**1**−**4**, **7**−**11**), 2-hydroxy-3-*O*-isobutyrylproceranolide (**5**), 2-hydroxy-3-*O*-benzoylproceranolide (**6**), and a new andirobin-type limonoid, swietmanin J (**12**), together with 19 known compounds were isolated from the fruits of *Swietenia mahagoni*. Their structures were established on the basis of spectroscopic methods. These compounds were evaluated against a small panel of microorganisms.

Swietenia mahagoni, a valuable timber tree (Meliaceae), grows mainly in tropical areas of Asia, such as India, Malaysia, and southern mainland China.[1] Its seeds have been used for the treatment of hypertension,[2] malaria,[3] and diabetes[3] in Indonesia. Chemical investigations conducted previously on the genus of *Swietenia* have led to the isolation of an array of structurally diverse limonoids with a wide range of biological activities.[2−4] In the current study, 11 new mexicanolide-type limonoids, swietmanins A−I (**1**−**4**, **7**−**11**), 2-hydroxy-3-*O*-isobutyrylproceranolide (**5**), 2-hydroxy-3-*O*-benzoylproceranolide (**6**), and a new andirobin-type limonoid, swietmanin J (**12**), as well as 19 known compounds, were isolated from the fruits of *S. mahagoni*. The structures of compounds **1**−**12** were established on the basis of spectroscopic methods. We describe herein the isolation and structural elucidation of these new isolates and the antimicrobial evaluation of all substances obtained in the investigation.



	R^1	R^2
1	H	A_1
2	H	Ac
3	H	H
4	OAc	Ac

	R^1	R^2
5	H	A_1
6	H	A_2
7	OH	Tig
8	OH	Ac

	R
9	A_1
10	Ac
11	Tig

12

Results and Discussion

Swietmanin A (**1**), a white, amorphous powder, gave a molecular formula of $C_{33}H_{42}O_{10}$, as determined by HREIMS at *m/z* 598.2765 $[M]^+$ (calcd 598.2778), which was supported by the sodiated molecular ion at *m/z* 621 $[M + Na]^+$ in the positive-mode ESIMS. The IR absorptions at 3439 and 1730 cm^{-1} implied the presence of hydroxy and carbonyl groups, respectively. The ^{13}C NMR spectrum displayed 33 carbon resonances assignable to eight methyls (one methoxy), three methylenes, 12 methines (four olefinic and two oxygenated), and 10 quaternary carbons (two olefinic and five carbonyls). The ^1H and ^{13}C NMR spectroscopic data (Tables 1 and 2) also revealed the presence of an acetyl unit and a β-furyl ring moiety. There were 13 degrees of unsaturation evident in the molecule of **1**, of which nine were represented by five carbonyls, one double bond, and a β-furyl ring, and the remaining four degrees of unsaturation required **1** to have a tetracyclic core ring system. The aforementioned data suggested that **1** is a mexicanolide-type limonoid.[5]

Analysis of the 2D NMR spectra, especially the HMBC data, confirmed **1** being a mexicanolide-type limonoid and allowed the assignment of most of the functional groups. In the HMBC spectrum (Figure 1), the key correlations between OMe/C-7 and H_2-6/C-5 and C-7 enabled the methoxy group to be placed at C-7 and a typical C-6 and C-7 appendage of a mexicanolide-type limonoid to be linked at C-5. The HMBC correlations from H-3 to C-1′, C-30, C-2, and C-4 and from Me-3′ (Me-4′) to C-1′ and C-2′ indicated the presence of an isobutyryloxy group at C-3. The $\Delta^{8(30)}$ double bond was fixed by the HMBC correlations from H-30 to C-9 and C-14 and from H-2 to C-1, C-8, and C-30. The HMBC correlations from H-2 and H_3-19 to C-1 indicated the presence of a ketone group at C-1. An acetoxy group was assigned at C-11 by the HMBC correlation between H-11 and the ester carbonyl of the acetyl unit at δ 169.8. The relative configuration of **1** was assigned by the ROESY spectrum (Figure 2). The strong cross-peaks from H-17β to H-5 and H-11 indicated that H-5 and H-11 are cofacial, and these were arbitrarily assigned in a β-orientation. In consequence, the ROESY correlations of H-2/H-3 and H-30, H-3/Me-28, and H-9/H-14 revealed that they are α-oriented. Accordingly, the structure of swietmanin A (**1**) was established as shown.

Swietmanin B (**2**), obtained as a white, amorphous powder, displayed a molecular formula of $C_{31}H_{38}O_{10}$, as determined by HREIMS at *m/z* 570.2457 $[M]^+$ (calcd 570.2465). The IR absorptions at 3439 and 1732 cm^{-1} were indicative of the presence of hydroxy and carbonyl groups, respectively. The ^1H and ^{13}C NMR data of **2** indicated its structure to be closely related to that of **1**, with the only difference being the presence of an acetoxy group at C-3 in **2** replacing the isobutyryloxy moiety of **1**. This conclusion

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

proton	1	2	3	4	5	6
2	3.55 (m)	3.55 (m)	3.42 (m)			
3	4.79 (d, 9.5)	4.77 (d, 9.2)	3.80 (d, 9.5)	5.53 (s)	5.06 (s)	5.17 (s)
5	3.47 (d, 9.7)	3.42 (d, 10.1)	3.38 (d, 10.2)	3.32 (d, 9.6)	3.15 (dd, 9.2, 3.6)	3.47 (d, 10.3)
6	2.16 (m)	2.19 (m)	2.18 (m)	2.16 (m)	2.36 (m)	2.42 (m)
	2.36 (m)	2.36 (m)	2.36 (m)	2.39 (m)		
9	2.57 (d, 10.1)	2.59 (d, 9.8)	2.56 (d, 10.2)	2.63 (d, 9.9)	2.05 (brs)	2.02 (brs)
11α					1.80 (m)	1.86 (m)
11*β*	5.46 (ddd, 10.6, 10.6, 5.4)	5.48 (m)	5.46 (m)	5.46 (ddd, 10.8, 10.8, 5.5)	1.23 (m)	1.23 (m)
12α	1.33 (dd, 13.7, 10.8)	1.33 (dd, 13.7, 11.2)	1.32 (m)	1.35 (m)	1.76 (m)	1.80 (m)
12*β*	2.13 (m)	2.14 (m)	2.12 (m)	2.16 (m)	1.12 (m)	1.10 (m)
14	2.34 (m)	2.34 (m)	2.36 (m)	2.42 (m)		
15	2.81 (d, 18.6)	2.82 (d, 18.5)	2.91 (m)	2.90 (dd, 18.3, 2.0)	3.48 (dt, 21.0, 2.9)	3.03 (m)
	2.92 (dd, 18.6, 6.1)	2.94 (dd, 18.5, 5.7)		2.99 (dd, 18.3, 5.6)	3.85 (d, 21.0)	3.19 (d, 21.6)
17	5.61 (s)	5.64 (s)	5.65 (s)	5.68 (s)	5.67 (s)	5.58 (s)
18	1.00 (s)	1.00 (s)	1.00 (s)	0.73 (s)	1.07 (s)	0.97 (s)
19	1.27 (s)	1.27 (s)	1.24 (s)	1.34 (s)	1.26 (s)	1.30 (s)
21	7.81 (brt, 0.7)	7.81 (s)	7.78 (s)	7.80 (brd, 0.4)	7.55 (s)	7.61 (s)
22	6.60 (brt, 1.0)	6.61 (brd, 1.2)	6.61 (brd, 1.4)	6.60 (brd, 1.6)	6.47 (dd, 1.8, 0.7)	6.50 (s)
23	7.42 (brt, 1.6)	7.42 (brt, 1.6)	7.41 (brt, 1.6)	7.43 (brt, 1.7)	7.42 (brt, 1.7)	7.44 (s)
28	0.80 (s)	0.80 (s)	0.81 (s)	1.01 (s)	0.77 (s)	0.85 (s)
29	0.78 (s)	0.78 (s)	0.72 (s)	0.97 (s)	0.70 (s)	0.84 (s)
30	5.50 (dt, 7.3, 2.3)	5.50 (m)	5.83 (dt, 7.0, 2.0)	5.52 (m)	3.25 (d, 14.6)	3.07 (m)
					1.78 (m)	1.80 (m)
OH-2					4.18 (s)	
OMe-7	3.71 (s)	3.72 (s)	3.68 (s)	3.72 (s)	3.70 (s)	3.76 (s)
Ac-2				2.14 (s)		
Ac-3		2.12 (s)		2.12 (s)		
Ac-11	2.08 (s)	2.10 (s)	2.07 (s)	2.08 (s)		
2′	2.64 (m)				2.66 (m)	
3′	1.16 (d, 7.1)				1.24 (m)	8.09 (dd, 7.5, 0.9)
4′	1.17 (d, 7.1)				1.24 (m)	7.51 (t, 7.5)
5′						7.61 (m)
6′						7.51 (t, 7.5)
7′						8.09 (dd, 7.5, 0.9)

[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).

was further confirmed by the HMBC correlation of H-3 to the carbon resonance at 170.9, being assignable to the carbonyl of the C-3 acetyl group (Supporting Information, Figure S11). Therefore, the structure of swietmanin B (**2**) was established as shown.

Swietmanin C (**3**), a white, amorphous powder, was assigned a molecular formula of $C_{29}H_{36}O_9$, as established from the HREIMS at *m*/*z* 528.2363 $[M]^+$ (calcd 528.2359). This was supported by the sodiated molecular ion peak at *m*/*z* 551 $[M + Na]^+$ in the positive-mode ESIMS. Analysis of ^{1}H and ^{13}C NMR data of **3** indicated its structure to show a close similarity to that of **2**, with the only change being due to the presence of a hydroxy group at C-3 in **3** instead of the acetoxy group in **2**. This structural variation resulted in the resonances of H-2 and H-3 of **3** being shifted upfield as compared with those of **2**. The structural assignment of **3** was further confirmed from the HMBC spectrum (Supporting Information, Figure S17). Thus, the structure of swietmanin C (**3**) was thus elucidated as shown.

Swietmanin D (**4**), a white, amorphous powder, showed a molecular ion at *m*/*z* 628.2501 $[M]^+$ (calcd 628.2520) in the HREIMS, corresponding to the molecular formula $C_{33}H_{40}O_{12}$, which was supported by the sodiated molecular ion at *m*/*z* 651 $[M + Na]^+$ in the positive-mode ESIMS. The NMR data (Tables 1 and 2) of **4** showed close similarities to those of **2**. The only structural difference between these compounds is the presence of an additional acetoxy group (δ 2.14, 3H, s; δ 169.8, 21.4) in **4**, which was located at C-2 by the changes of chemical shifts close to the carbon, for which the chemical shift resonated at δ 84.2. When compared with compound **2**, the chemical shift of C-1 in **4** was shifted upfield about $\Delta\delta$ 9 due largely to the γ-gauche effect of the C-2 acetyl group, and those of the C-3 and C-30 signals were shifted slightly downfield. The presence of an acetyl group at C-2 was confirmed by HMBC correlations from H-30 to C-2 (δ 84.2), C-3, C-9, and C-14 (Supporting Information, Figure S23). For a mexicanolide-type limonoid, the fusion of rings A and B requires stereospecifically that the OAc-2 group is α-oriented, which was confirmed by comparing the NMR data of **4** with compounds having the same substitution pattern for this type of limonoid.[6] Accordingly, swietmanin D was assigned as **4**.

2-Hydroxy-3-*O*-isobutyrylproceranolide (**5**) was obtained as a white, amorphous powder with a molecular formula of $C_{31}H_{40}O_9$ (HREIMS at *m*/*z* 556.2670 $[M]^+$, calcd 556.2672). Analysis of its ^{1}H and ^{13}C NMR spectra indicated that compound **5** is a congener of proceranolide.[5] A downfield resonance at δ 78.1 was shown by a HMBC correlation with the proton resonance at δ 4.18 of a hydroxy group, as distinguished by HMQC spectrum, suggesting that a hydroxy group is located at C-2 (Figure 3). The hydroxy group at C-2 also correlated in the HMBC spectrum with C-1 and C-3, to support this assignment. Furthermore, the analysis of the ^{1}H and ^{13}C NMR data of **5** (Tables 1 and 2) revealed the presence of an isobutyryl moiety (δ 2.66, 1H, m; δ 1.24, 3H, m; δ 1.24, 3H, m; and δ 176.1, 34.4, 19.9, and 18.5), which was located at C-3 by the HMBC correlation between the carbonyl of the isobutyryl group at δ 176.1 and H-3 at δ 5.06. The presence of an isobutyryloxy moiety at C-3 caused a downfield shift of C-3 to δ 85.2 in the ^{13}C NMR spectrum and a downfield shift of H-3 to δ 5.06 in the ^{1}H NMR spectrum, as compared with analogous data for proceranolide.[5] The relative configuration of **5** was determined by a ROESY experiment (Figure 4). Thus, the structure of **5** was proposed as 2-hydroxy-3-*O*-isobutyrylproceranolide.

2-Hydroxy-3-*O*-benzoylproceranolide (**6**), a white, amorphous powder, gave a molecular formula of $C_{34}H_{38}O_9$, as determined by the HREIMS at *m*/*z* 590.2518 $[M]^+$ (calcd 590.2516). Comparison of the ^{1}H and ^{13}C NMR data of **6** with those of **5** showed many similarities, with the only difference being assignable to the presence of a benzoyloxy group at C-3 of **6** instead of an isobutyryloxy at this position in **5** (see Tables 1 and 2). This assignment was confirmed by the HMBC spectrum (Supporting Information, Figure S40), in which the correlation between H-3 at δ 5.17 and C-1′ at

Table 2. ^{13}C NMR Spectroscopic Data for **1**−**12**[a]

carbon	1	2	3	4	5	6	7	8	9	10	11	12
1	215.9	215.7	217.4	206.6	217.4	217.5	216.9	216.9	212.6	212.6	212.4	71.9
2	48.6	48.3	51.0	84.2	78.1	78.2	78.3	78.3	77.2	77.0	77.7	44.0
3	76.8	77.2	76.2	78.0	85.2	86.6	86.4	85.7	85.5	85.7	85.9	214.2
4	38.7	38.2	39.8	39.7	39.1	39.4	39.3	39.0	39.6	39.4	39.6	48.3
5	40.8	41.0	39.9	41.2	40.6	40.4	40.4	40.7	40.6	40.7	40.4	42.3
6	32.4	32.4	32.7	32.2	33.2	33.0	33.1	33.1	32.7	32.6	32.6	31.1
7	173.4	173.4	173.6	173.7	173.9	174.1	174.2	174.1	173.4	173.5	173.4	174.4
8	136.4	136.4	135.6	135.4	125.8	125.3	133.2	132.8	134.1	134.3	134.2	144.8
9	59.6	59.5	59.7	59.1	52.0	51.6	51.5	51.4	53.7	53.9	54.1	50.6
10	49.9	50.0	50.2	50.9	52.0	52.4	52.4	52.4	52.5	52.5	52.6	43.7
11	68.8	68.7	68.8	68.4	18.7	18.7	18.6	18.5	21.5	22.0	21.7	21.1
12	39.8	39.8	39.8	40.0	29.0	28.7	28.3	28.0	32.4	32.5	32.6	30.1
13	36.9	36.9	36.9	36.9	38.2	38.4	38.7	38.9	37.5	37.4	37.4	39.8
14	44.8	44.8	44.8	44.7	132.9	133.6	136.0	135.9	160.0	160.0	160.2	169.8
15	30.0	30.2	30.1	30.3	33.2	33.2	65.2	65.7	113.1	113.3	113.2	110.9
16	168.9	169.1	169.7	169.1	169.5	169.0	174.4	174.4	164.6	164.7	164.6	166.4
17	77.6	77.8	77.8	79.2	80.6	80.6	81.6	81.1	79.7	79.6	79.6	80.0
18	21.5	21.6	21.5	20.9	17.7	16.8	16.8	16.9	21.9	22.6	22.2	19.5
19	17.9	18.0	17.9	17.8	16.7	16.7	16.5	16.7	15.6	15.5	15.6	21.7
20	120.4	120.5	120.5	120.4	120.5	120.7	120.4	120.1	120.0	120.0	120.0	120.0
21	141.7	141.6	141.6	141.6	141.7	141.6	141.9	142.0	141.4	141.4	141.4	142.5
22	109.6	109.6	109.6	109.6	109.8	110.0	109.9	109.9	110.1	110.1	110.1	109.9
23	142.7	142.7	142.7	142.7	142.8	142.9	143.0	142.9	143.2	143.2	143.2	144.8
28	22.2	22.2	22.2	21.7	22.5	23.4	23.3	22.7	21.5	21.5	21.7	26.0
29	20.7	20.5	20.8	20.4	19.9	19.5	19.5	19.8	20.7	20.6	20.4	23.1
30	125.7	125.8	126.9	128.3	43.9	44.3	45.2	44.8	132.9	132.8	133.3	119.7
Me-7	52.4	52.4	52.4	52.4	52.1	52.2	52.2	52.2	52.1	52.1	52.1	51.9
Ac-2				169.8								
				21.4								
Ac-3		170.9		170.2				169.6		170.2		
		20.4		21.8				21.2		20.8		
Ac-11	169.8 21.5	169.8 21.5	169.8 21.5	169.8 21.4								
1′	176.6				176.1	165.9	167.1		176.1		167.1	
2′	33.8				34.4	129.4	129.4		34.3		127.8	
3′	19.1				19.9	129.4	138.4		19.2		139.6	
4′	18.4				18.5	129.2	12.5		19.1		12.2	
5′						134.1	14.5				14.8	
6′						129.2						
7′						129.4						

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

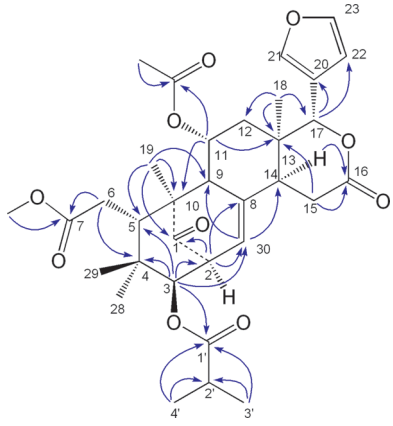

Figure 1. Key HMBC (H → C) correlations of **1**.

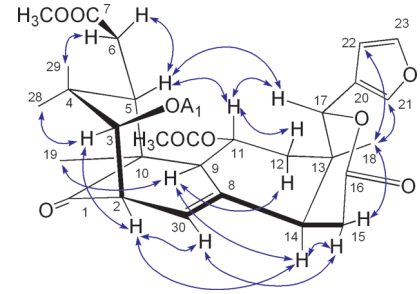

Figure 2. Key ROESY correlations (H ↔ H) of **1**.

δ 165.9 gave evidence of the benzoyloxy group being attached at C-3. Therefore, the structure of **6** was elucidated as 2-hydroxy-3-*O*-benzoylproceranolide.

Swietmanin E (**7**), a white, amorphous powder, showed a molecular formula of $C_{32}H_{40}O_{10}$, as established from the HREIMS at *m*/*z* 584.2622 $[M]^+$ (calcd 584.2622). This assignment was supported by the protonated molecular ion at *m*/*z* 585 $[M + H]^+$ in the positive-mode ESIMS. An analysis of the NMR data of **7** (Tables 2 and 3) revealed its structure to be closely related to that of **6**, with the structural changes being in the ester appendage at C-3 and the presence of an additional hydroxy group at C-15 in **7**. On the basis of the key HMBC correlation between H-3 and C-1′, a tigloyloxy unit with *E*-geometry at C-3 was evident from the NMR data (δ 6.90, 1H, qd, J = 7.1, 1.5 Hz; δ 1.80, 3H, dd, J = 7.1, 1.0 Hz; δ 1.91, 3H, t, J = 1.5 Hz; and δ 167.1, 129.4, 138.4, 12.5, and 14.5). The HMBC correlations from H-15 to C-8, C-13, C-14, and C-16 and from OH-15 to C-14, C-15, and C-16 supported the location of a hydroxy group at C-15 (Supporting Information, Figure S47). The relative configuration of **7** was assigned by the ROESY experiment, in which key cross-peaks between H-15/H-17β, H-15/H-3′, and H-17β/H-3′ indicated H-15 and H-3′ to be β-oriented (Supporting Information, Figure S48). Thus, the structure of swietmanin E was determined as **7**.

Swietmanin F (**8**) was afforded as a white, amorphous powder, having a molecular formula of $C_{29}H_{36}O_{10}$, as established on the basis of HREIMS at *m*/*z* 544.2314 $[M]^+$ (calcd 544.2308). The ^1H and ^{13}C NMR data revealed **8** to be a structural congener of **7**, with the only difference being the presence of an acetoxy unit (δ

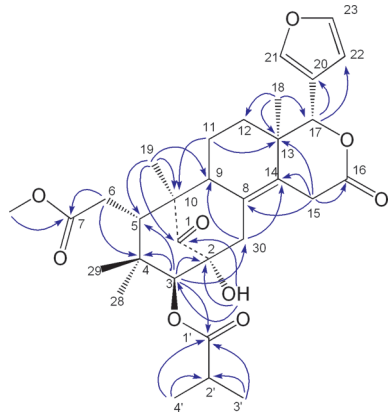

Figure 3. Key HMBC (H → C) correlations of **5**.

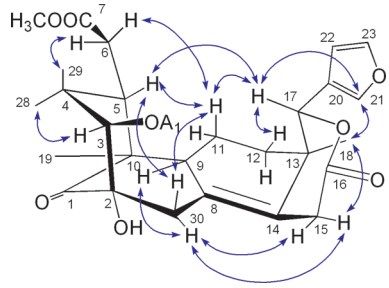

Figure 4. Key ROESY (H ↔ H) correlations of **5**.

169.6, 21.2; δ 2.18, s) at C-3 of **8** in place of the tigloyloxy group of **7** (see Tables 2 and 3). This was confirmed by the HMBC correlation between H-3 at δ 5.07 and the carbonyl signal of the acetyl at δ 169.6 (Supporting Information, Figure S55). The structure of swietmanin F was thus elucidated as **8**.

Swietmanin G (**9**) was obtained as a white, amorphous powder, with the molecular formula $C_{31}H_{38}O_9$, as determined by HREIMS at *m/z* 554.2511 $[M]^+$ (calcd 554.2516), representing 13 degrees of unsaturation. The IR absorptions at 3446 and 1734 cm^{-1} showed the presence of hydroxy and carbonyl groups, respectively. Its NMR data (Tables 2 and 3) revealed that **9** has two secondary methyls, five tertiary methyls (one methoxy), three methylenes, 10 methines (five olefinic), and 11 quaternary carbons (four carbonyls). The presence of a β-furan unit (δ 7.51, 6.48, and 7.44, each 1H) and an isobutyryl group was determined from the ^1H and ^{13}C NMR spectra. Nine of 13 double-bond equivalents were represented by a ketone group, three ester carbonyls, two double bonds, and a β-furyl ring, and the remaining four degrees of unsaturation required **9** to be tetracyclic in its central core structure. The aforementioned data were supportive of **9** being a mexicanolide-type limonoid.

Analysis of 2D NMR spectra, especially the HMBC data, confirmed the carbon framework of **9** and allowed the assignment of most of the functional groups. In the HMBC spectrum (Figure 5), the correlations of OMe/C-7 and H_2-6/C-5 and C-7 suggested a typical appendage of a mexicanolide at C-5. The HMBC correlations from H-3 to C-1′, C-2, C-4, and C-30 supported the location of the isobutyryloxy unit at C-3. The presence of a $\Delta^{8(30)}$ double bond was indicated by the HMBC correlations from H-30 to C-9 and C-14. The olefinic proton of H-15 showed strong HMBC correlations with C-13, C-14, and C-15, being indicative of the presence of a Δ^{14} double bond. The ^1H NMR resonances of H-15 at δ 6.32 (s) and H-30 at δ 6.31 (s) were shifted downfield due to the presence of the conjugated diene lactone system. A hydroxy at C-2 was assigned by the HMBC correlations from OH-2 to C-1, C-2, C-3, and C-30. The relative configuration of **9**, which bears a resemblance to its structural congener of erythrocarpine A,[7] was determined by the ROESY spectrum (Figure 6). Accordingly, the structure of swietmanin G was established as **9**.

Swietmanin H (**10**), a white, amorphous powder, gave a molecular formula of $C_{29}H_{34}O_9$, as established on the basis of the HREIMS at *m/z* 526.2210 $[M]^+$ (calcd 526.2203). This assignment was supported by the protonated and sodiated molecular ions at *m/z* 527 $[M + H]^+$ and 549 $[M + Na]^+$ in the positive-mode ESIMS. Analysis of the MS and NMR data of **10** indicated that its structure is closely related to that of compound **9**, with the only change being the presence of an acetyl group at C-3 of **10** replacing the isobutyryl unit of **9**. The attachment of the acetoxy at C-3 of **10** was confirmed by the HMBC correlation between H-3 and the carbonyl resonance of the acetyl group (Supporting Information, Figure S71). Thus, the structure of swietmanin H was proposed as **10**.

Swietmanin I (**11**), a white, amorphous powder, showed the molecular formula $C_{32}H_{38}O_9$, as determined by the HREIMS at *m/z* 566.2512 $[M]^+$ (calcd 566.2515). Analysis of the spectroscopic data of **11** indicated that it is a congener of compounds **9** and **10** with a tigloyloxy group (δ 167.1, 127.8, 139.6, 12.2, 14.8 and δ 7.04, 1H, q, J = 7.1 Hz; δ 1.91, 3H, d, J = 7.1 Hz; δ 1.94, 3H, s) at C-3 of **11** (see Tables 2 and 3). This was confirmed by the HMBC correlation between H-3 at δ 5.00 and the carbonyl signal of the tigloyl unit at δ 167.1 (Supporting Information, Figure S79). Therefore, the structure of swietmanin I was determined as **11**.

Swietmanin J (**12**) was obtained as a white, amorphous powder possessing a molecular formula of $C_{27}H_{34}O_7$, as determined by the HREIMS at *m/z* 470.2312 $[M]^+$ (calcd 470.2304), with 11 degrees of unsaturation. The IR absorptions at 3435 and 1713 cm^{-1} showed the presence of hydroxy and carbonyl groups, respectively. Its NMR data (Tables 2 and 3) revealed that **12** contains five tertiary methyls (one a methoxy), five methylenes (one olefinic), eight methines (four olefinic and two oxygenated), and nine quaternary carbons (three olefinic and three carbonyls). The presence of a β-furan ring (δ 7.34, 6.33, and 7.22, each 1H), a ketone carbonyl (δ 214.2), two ester carbonyls (δ 174.4 and 166.4), and two double bonds (δ 144.8, 119.7, 169.8, and 110.9) was determined also from the ^1H and ^{13}C NMR spectra. These functional groups accounted for eight degrees of unsaturation, and the remaining three degrees of unsaturation required **12** to be tricyclic in its central core structure, suggesting that it is an andirobin-type limonoid, with a structure that is closely related to that of methyl angolensate.[8] Comparison of the spectroscopic data of **12** with those of the latter compound suggested that the oxygen bridge between C-1 and C-14 was cleaved to give compound **12**, bearing a hydroxy unit at C-1 and a Δ^{14} double bond. This was verified from the HMBC spectrum, in which the proton resonance at δ 3.65 of the hydroxy group at C-1 correlated to C-1, C-2, and C-10, and H-15 correlated to C-8, C-13, C-14, and C-16 (Figure 7). The relative configuration of **12** was established by a ROESY experiment (Figure 8). In the ROESY spectrum, the correlations of Me-18/H-11α, Me-18/H-30, Me-18/H-22, H-30/H-9, and H-9/H-11α indicated that these functionalities are cofacial, and Me-18, H-11α, and H-9 were assigned arbitrarily an α-orientation. The ROESY cross-peaks of H-17/H-12β, H-12β/H-5, H-5/Me-28, and H-1/H-15 showed that the planes of rings A and C are vertically arranged in space, suggesting that H-5 and Me-28 are toward the back of ring A and are α-oriented. The ROESY correlation between Me-19 and Me-29 indicated that they are β-configured. Furthermore, the key ROESY correlation between H-1 and Me-19 revealed that H-1 is β-oriented. Accordingly, the structure of swietmanin J was elucidated as **12**.

Nineteen known limonoids comprising three structural classes were isolated as (a) andirobin-type: methyl angolensate[8] and methyl 6-hydroxyangolensate;[8] (b) gedunin-type: 3-deacetylkhivorin,[8] 3,7-dideacetylkhivorin,[8] 1,3,7-trideacetylkhivorin,[8] 7-deacetoxy-7-oxogedunin,[8] khivorin,[10] 7-deacetylkhivorin,[12] and 1-deacetylkhivorin;[12] and (c) mexicanolide-type: khayasin T,[6] mexicanolide,[9] 3,8-hemiketalcarapin,[9] 8α-hydroxycarapin,[9] fissinolide,[9] 2-hydroxyfissinolide,[10] 2,3-dihydroxy-3-deoxymexicanolide,[11] 2-hydroxy-6-deoxyswietenolide tiglate,[13] seneganolide A,[14] and 2-hydroxyfissi-

Table 3. ^{1}H NMR Spectroscopic Data of **7**−**12**[a]

proton	7	8	9	10	11	12
1						3.83 (s)
2						2.37 (m)
3	4.97 (s)	5.07 (s)	4.98 (s)	4.99 (s)	5.00 (s)	
5	3.29 (dd, 10.9, 2.2)	3.15 (dd, 11.1, 1.9)	3.20 (dd, 9.5, 2.2)	3.16 (dd, 9.6, 2.2)	3.23 (d, 9.4)	2.89 (d, 12.9)
6	2.35 (dd, 16.7, 2.2)	2.33 (dd, 16.5, 1.9)	2.32 (dd, 16.9, 2.2)	2.31 (dd, 16.8, 2.2)	2.30 (dd, 16.8, 3.2)	2.34 (m)
	2.43 (dd, 16.7, 10.9)	2.41 (dd, 16.5, 11.1)	2.38 (dd, 16.9, 9.5)	2.38 (dd, 16.8, 9.6)	2.39 (dd, 16.8, 9.4)	2.52 (m)
9	2.09 (brd, 5.1)	2.08 (brd, 4.5)	2.56 (dt, 12.4, 3.2)	2.27 (dt, 12.4, 3.2)	2.26 (m)	2.58 (m)
11α	1.87 (m)	1.88 (m)	1.78 (m)	1.76 (ddd, 14.4, 4.9, 3.2)	1.78 (m)	2.38 (m)
11*β*	1.80 (m)	1.80 (m)	1.53 (ddd, 24.9, 12.4, 5.3)	1.53 (ddd, 24.8, 12.4, 4.9)	1.51 (ddd, 25.3, 12.6, 5.1)	1.66 (m)
12α	1.06 (m)	1.12 (m)	1.25 (m)	1.26 (m)	1.34 (m)	1.01 (m)
12*β*	1.81 (m)	1.78 (m)	1.93 (m)	1.95 (td, 14.4, 4.9)	1.95 (m)	1.96 (m)
15	5.03 (s)	5.02 (s)	6.32 (s)	6.33 (s)	6.26 (s)	5.80 (s)
17	5.53 (s)	5.60 (s)	5.17 (s)	5.17 (s)	5.17 (s)	5.26 (s)
18	1.04 (s)	1.06 (s)	1.06 (s)	1.06 (s)	1.05 (s)	0.94 (s)
19	1.29 (s)	1.27 (s)	1.28 (s)	1.28 (s)	1.29 (s)	1.15 (s)
21	7.63 (brt, 0.7)	7.62 (brd, 0.6)	7.51 (brd, 0.8)	7.51 (brt, 0.8)	7.51 (s)	7.34 (s)
22	6.52 (dd, 1.8, 0.7)	6.51 (brt, 0.9)	6.48 (brt, 1.0)	6.48 (brt, 1.0)	6.48 (s)	6.33 (s)
23	7.43 (brt, 1.8)	7.42 (brt, 1.6)	7.44 (brt, 1.6)	7.44 (brt, 1.6)	7.44 (s)	7.22 (s)
28	0.79 (s)	0.78 (s)	0.81 (s)	0.81 (s)	0.83 (s)	1.08 (s)
29	0.74 (s)	0.69 (s)	0.73 (s)	0.74 (s)	0.75 (s)	1.19 (s)
30	3.41 (d, 15.3)	3.67 (d, 15.2)	6.31 (s)	6.32 (s)	6.28 (brd, 2.5)	5.10 (brs)
	2.00 (d, 15.3)	1.99 (d, 15.2)				5.32 (brs)
OH-1						3.65 (d, 2.4)
OH-2	4.18 (s)	4.15 (s)	4.05 (s)	4.05 (s)	4.19 (s)	
OH-15	3.23 (s)	3.49 (s)				
OMe-7	3.74 (s)	3.72 (s)	3.69 (s)	3.69 (s)	3.69 (s)	3.69 (s)
Ac-3		2.18 (s)		2.23 (s)		
2′			2.75 (q, 7.0)			
3′	6.90 (qd, 7.1, 1.5)		1.30 (d, 7.0)		7.04 (q, 7.1)	
4′	1.80 (dd, 7.1, 1.0)		1.28 (d, 7.0)		1.91 (dd, 7.1)	
5′	1.91 (t, 1.5)				1.94 (s)	

[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).

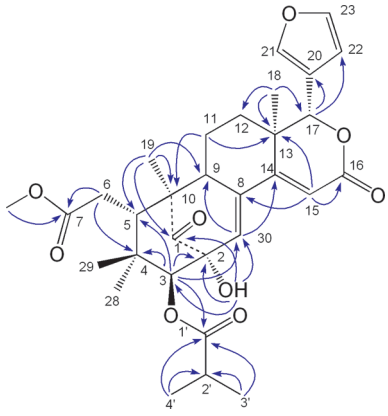

Figure 5. Key HMBC (H → C) correlations of **9**.

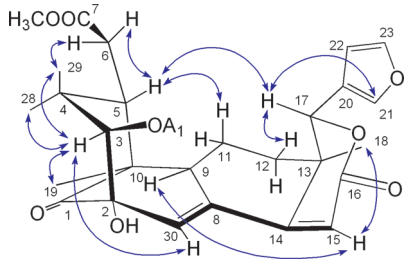

Figure 6. Key ROESY (H ↔ H) correlations of **9**.

nolid.[15] The structures of these known limonoids were identified by comparison of their spectroscopic data with those reported in the literature.

All of the isolates obtained were tested for antimicrobial activity against 11 microbes (seven bacteria and four fungi) in vitro, and compound **5** and 2-hydroxyfissinolid exhibited activity against

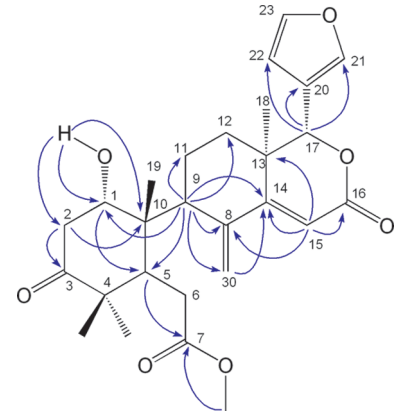

Figure 7. Key HMBC (H → C) correlations of **12**.

Micrococcus luteus ATCC 9341 with MIC values of 50 and 12.5 *μ*g/mL, respectively, and all other compounds were inactive. In this test, ofloxacin was applied as the positive control, showing a MIC value of 1.56 *μ*g/mL against *M. luteus* ATCC 9341.

Experimental Section

General Experimental Procedures. Specific 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 and HREIMS (70 eV) were carried out on a Finnigan MAT 95 mass spectrometer, and ESIMS was conducted on a Finnigan LC Q^{DECA} instrument. Semipreparative HPLC was carried out on a Waters 515 pump with a Waters 2487 detector (254 nm) and an YMC-Pack ODS-A column (250 × 10 mm, S-5 *μ*m, 12 nm). All solvents used were of analytical grade (Shanghai Chemical Reagents Company, Ltd.). Silica gel (200−300 mesh, Qingdao Haiyang Chemical Co., Ltd.), C_{18} reversed-phase silica gel (250 mesh, Merck), and Sephadex LH-20 gel (Pharmacia Biotech, Sweden) were used for column chromatography.

Plant Material. The fruits of *Swietenia mahagoni* were collected from the Xishuangbanna Tropical Botanical Garden, Mengla County,

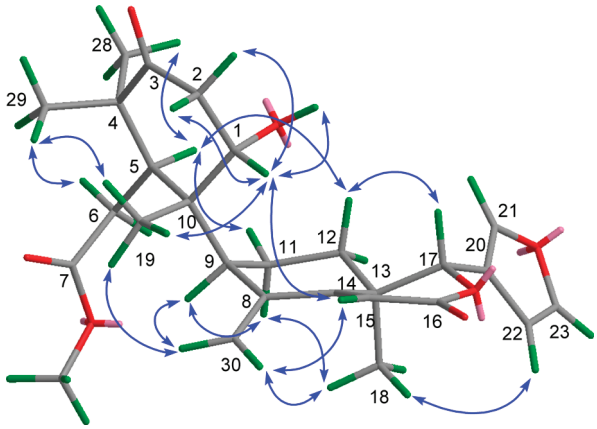

Figure 8. Key ROESY (H ↔ H) correlations of **12**.

Yunnan Province, People's Republic of China, in December 2007, and were authenticated by Professor You-Kai Xu of Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences. A voucher specimen (accession number SMt-2006-1Y) representing this collection has been deposited in the Shanghai Institute of Materia Medica.

Extraction and Isolation. The dried, powdered fruits of *S. mahagoni* (6 kg) were percolated three times with 95% EtOH. After removal of the solvent under reduced pressure, the EtOH extract (270 g) was partitioned between H_2O and EtOAc to give an EtOAc-soluble fraction (170 g), which was subjected to passage over a column of MCI gel (MeOH−H_2O, 50:50 to 90:10), to obtain five fractions, A−E. Fraction C (16.7 g) was then subjected to silica gel column chromatography eluted with a gradient of petroleum ether−ethyl acetate (3:1 to 0:1) to afford eight subfractions, C1−C8. Fraction C3 (5.1 g) was chromatographed over a column of reversed-phase silica gel (MeOH−H_2O, 50:50 to 100:0) to yield five further fractions, C3a−C3e. Fraction C3a (101 mg) was separated via semipreparative HPLC, with 70% methanol in water as the mobile phase, to produce compounds **5** (30 mg) and **6** (5 mg) and khayasin T (25 mg). Using similar purification procedures, fraction C3b afforded **7** (5 mg), mexicanolide (30 mg), 3,8-hemiketalcarapin (18 mg), 8α-hydroxycarapin (15 mg), and fissinolide (10 mg); fraction C3c furnished **8** (3 mg), khivorin (25 mg), and 2-hydroxyfissinolide (23 mg); and fraction C3d yielded 2,3-dihydroxy-3-deoxymexicanolide (20 mg) and 2-hydroxyfissinolid (1 g). Fraction D (15.2 g) was subjected to passage over a column of MCI gel eluted with MeOH−H_2O (50:50 to 90:10) to obtain four subfractions, D1−D4. Fraction D3 (3.2 g) was chromatographed on a silica gel column, eluted with petroleum ether−ethyl acetate (4:1 to 0:1), to produce four fractions, D3a−3d. Fraction D3b (198 mg) was separated on a column of Sephadex LH-20 gel to give two major components, and each of these was separated by semipreparative HPLC with 75% methanol in water as the mobile phase to yield **1** (3 mg) and **3** (5 mg), respectively. Fraction D3c (250 mg) was passed over a column of reversed-phase silica gel (MeOH−H_2O, 60:40 to 100:0) to obtain four fractions, D3c1−D3c4. Fraction D3c2 (540 mg) was separated by semipreparative HPLC, with 75% methanol in water, to yield compounds **2** (200 mg) and **4** (5 mg), methyl angolensate (10 mg), 6-hydroxyangolensate (30 mg), and 3-deacetylkhivorin (14 mg). Using the same purification procedures, fraction D3c3 yielded **10** (15 mg), 3,7-dideacetylkhivorin (17 mg), 1,3,7-trideacetylkhivorin (20 mg), and 7-deacetoxy-7-oxogedunin (10 mg), and C3c4 yielded **9** (10 mg), 7-deacetylkhivorin (23 mg), and 1-deacetylkhivorin (30 mg). Fraction D5 (5.0 g) was purified by silica gel column chromatography, eluted with petroleum ether−ethyl acetate (4:1 to 0:1), to give five subfractions, D5a−5e. Fraction D5c (276 mg) was subjected to reversed-phase silica gel column chromatography (MeOH−H_2O, 50:50 to 100:0) to obtain three subfractions, D5c1−D5c3. Fraction D5c2 (104 mg) was separated on Sephadex LH-20 gel to yield **11** (20 mg) and **12** (3 mg). Using the same purification procedures, fraction D5d yielded 2-hydroxy-6-deoxyswietenolide tiglate (15 mg) and seneganolide A (10 mg).

Swietmanin A (1): white, amorphous powder; $[\alpha]^{20}_D$ −168 (*c* 0.15, $CHCl_3$); IR (KBr) ν_{max} 3439, 2949, 1730, 1439, 1377, 1232, 1149, 1026 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 598 (27), 556 (39), 538 (26), 450 (70), 435 (26), 390 (34), 377 (61), 312 (31), 173 (61), 95 (100), 71 (66); HREIMS *m/z* 598.2765 ($[M]^+$, calcd for $C_{33}H_{42}O_{10}$, 598.2778).

Swietmanin B (2): white, amorphous powder; $[\alpha]^{20}_D$ −87.4 (*c* 0.35, CH_3OH); IR (KBr) ν_{max} 3439, 2972, 1732, 1435, 1377, 1232, 1024 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 570 (29), 510 (61), 450 (54), 435 (25), 377 (60), 312 (41), 297 (26), 239 (25),173 (61), 95 (100), 81 (22); HREIMS *m/z* 570. 2457 ($[M]^+$, calcd for $C_{31}H_{38}O_{10}$, 570.2465).

Swietmanin C (3): white, amorphous powder; $[\alpha]^{20}_D$ −101 (*c* 0.15, $CHCl_3$); IR (KBr) ν_{max} 3439, 2951, 1730, 1437, 1373, 1229, 1026 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 528 (54), 468 (40), 450 (4), 397 (20), 311 (100), 269 (25), 173 (74), 157 (50), 121 (37), 95 (89), 81 (19), 55 (8); HREIMS *m/z* 528.2363 ($[M]^+$, calcd for $C_{29}H_{36}O_9$, 528.2359).

Swietmanin D (4): white, amorphous powder; $[\alpha]^{20}_D$ −66 (*c* 0.10, CH_3OH); IR (KBr) ν_{max} 3435, 2920, 1736, 1639, 1375, 1232, 1026 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 628 (3), 586 (31), 568 (44), 526 (25), 508 (11), 466 (100), 451 (38), 380 (43), 369 (57), 338 (90), 327 (53), 310 (35), 189 (48), 95 (72), 81 (16), 55 (8); HREIMS *m/z* 628.2501 ($[M]^+$, calcd for $C_{33}H_{40}O_{12}$, 628.2520).

2-Hydroxy-3-*O*-isobutyrylproceranolide (5): white, amorphous powder; $[\alpha]^{20}_D$ −40 (*c* 0.10, CH_3OH); IR (KBr) ν_{max} 3478, 2970, 1736, 1460, 1385, 1248, 1024 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 556 (7), 460 (80), 432 (100), 414 (30), 372 (36), 344 (57), 275 (43), 243 (17), 226 (33), 207 (50), 189 (66), 95 (25), 71 (71), 55 (10); HREIMS *m/z* 556.2670 ($[M]^+$, calcd for $C_{31}H_{40}O_9$, 556.2672).

2-Hydroxy-3-*O*-benzoylproceranolide (6): white, amorphous powder; $[\alpha]^{20}_D$ −94.3 (*c* 0.35, CH_3OH); IR (KBr) ν_{max} 3437, 2918, 2850, 1728, 1628, 1452, 1381, 1269, 1026 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 590 (7), 572 (1), 494 (13), 466 (20), 450 (4), 377 (4), 344 (6), 309 (6), 283 (6), 225 (5), 207 (16), 105 (100), 77 (15), 55 (3); HREIMS *m/z* 590.2518 ($[M]^+$, calcd for $C_{34}H_{38}O_9$, 590.2516).

Swietmanin E (7): white, amorphous powder; $[\alpha]^{20}_D$ −281 (*c* 0.10, $CHCl_3$); IR (KBr) ν_{max} 3435, 2924, 1726, 1645, 1383, 1263, 1200, 1057 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 2; EIMS *m/z* 584 (5), 566 (10), 501 (8), 466 (8), 442 (9), 342 (25), 325 (26), 269 (12), 225 (30), 196 (11), 165 (13), 83 (100), 55 (30); HREIMS *m/z* 584.2622 ($[M]^+$, calcd for $C_{32}H_{40}O_{10}$, 584.2622).

Swietmanin F (8): white, amorphous powder; $[\alpha]^{20}_D$ −80 (*c* 0.05, CH_3OH); IR (KBr) ν_{max} 3433, 2922, 1728, 1637, 1437, 1377, 1234, 1057 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 2; EIMS *m/z* 544 (7), 484 (7), 468 (26), 420 (20), 402 (70), 360 (43), 342 (98), 327 (19), 311 (31), 285 (68), 269 (37), 243 (78), 225 (100), 197 (50), 165 (66), 137 (50), 95 (43), 83 (20); HREIMS *m/z* 544.2314 ($[M]^+$, calcd for $C_{29}H_{36}O_{10}$, 544.2308).

Swietmanin G (9): white, amorphous powder; $[\alpha]^{20}_D$ +306 (*c* 0.20, CH_3OH); IR (KBr) ν_{max} 3446, 2974, 1734, 1460, 1385, 1257, 1155, 1026 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 2; EIMS *m/z* 554 (14), 484 (100), 413 (48), 395 (7), 327 (33), 231 (11), 196 (35), 147 (34), 137 (23), 95 (22), 71 (25); HREIMS *m/z* 554.2511 ($[M]^+$, calcd for $C_{31}H_{38}O_9$, 554.2516).

Swietmanin H (10): white, amorphous powder; $[\alpha]^{20}_D$ +422 (*c* 0.30, $CHCl_3$); IR (KBr) ν_{max} 3448, 2918, 2850, 1732, 1458, 1375, 1234, 1030 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 2; EIMS *m/z* 526 (69), 484 (65), 451 (20), 438 (25), 413 (39), 377 (52), 327 (65), 309 (7), 231 (41), 196 (94), 147 (100), 137 (14), 95 (20), 55 (16); HREIMS *m/z* 526.2210 ($[M]^+$, calcd for $C_{29}H_{34}O_9$, 526.2203).

Swietmanin I (11): white, amorphous powder; $[\alpha]^{20}_D$ +176 (*c* 0.45, CH_3OH); IR (KBr) ν_{max} 3442, 2951, 1720, 1649, 1458, 1257, 1157, 1028 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 2; EIMS *m/z*: 566 (8), 528 (3), 484 (23), 466 (7), 327 (16), 230 (4), 196 (8), 95 (8), 83 (100), 55 (25); HREIMS *m/z* 566.2512 ($[M]^+$, calcd for $C_{32}H_{38}O_9$, 566.2515).

Swietmanin J (12): white, amorphous powder; $[\alpha]^{20}_D$ +345.5 (*c* 0.55, CH_3OH); IR (KBr) ν_{max} 3435, 2976, 1713, 1458, 1383, 1256, 1171, 1026 cm^{-1}; ^1H NMR, see Table 3; ^{13}C NMR, see Table 2; EIMS *m/z* 470 (59), 374 (43), 359 (9), 331 (6), 260 (13), 245 (20), 227 (12), 210 (18), 177 (14), 147 (100), 121 (17), 105 (17), 95 (21), 55 (6); HREIMS *m/z* 470.2312 ($[M]^+$, calcd for $C_{27}H_{34}O_7$, 470.2304).

Antimicrobial Testing. The in vitro antibacterial activities against *Staphylococcus aureus* ATCC 25923, *Staphylococcus epidermidis* ATCC 12228, *Micrococcus luteus luteus* ATCC 9341, *Escherichia coli*

ATCC 25922, *Shigella flexneri* ATCC 12022, *Pseudomonas aeruginosa* ATCC 14502, and *Bacillus subtilis* ATCC 6633 were conducted by following the procedures described previously.[16] The microbial cells were suspended in Mueller-Hinton broth to form a final density of $5 \times 10^{-5}-10^{-6}$ cfu/mL and incubated at 37 °C for 18 h under aerobic conditions with the test compounds, which were dissolved in DMSO. The blank controls of microbial culture were incubated with DMSO under the same conditions. The amount of DMSO was limited so as not to be toxic under the experimental conditions. The MIC was defined as the lowest concentration of the tested samples at which the visible growth was completely inhibited. In this test, ofloxacin was applied as the positive control.

The in vitro antifungal activity against *Candida albicans* ATCC 1600, *Saccharomyces sake* ATCC 26421, *Microsporum gypseum* ATCC 14683, and *Trichophyton rubrum* ATCC 10218 was performed according to the protocols described previously.[17] The fungi were incubated in Sabouraud dextrose broth at 37 °C for 48 h with the respective compounds, and the positive control was dissolved in DMSO. The blank controls of fungi cultures were incubated with a limited amount of DMSO under the same conditions. In this test, amphotericin B was applied as the positive control.

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Supporting Information Available: NMR, MS, and IR spectra of swietmanins A−J (**1**−**4**, **7**−**12**), 2-hydroxy-3-*O*-isobutyrylproceranolide (**5**), and 2-hydroxy-3-*O*-benzoylproceranolide (**6**). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Chen, S. K.; Chen, B. Y.; Li, H. In *Flora Republicae Popularis Sinicae (Zhongguo Zhiwu Zhi*); Science Press: Beijing, 1997; Vol. 43, pp 44−46.

(2) (a) Chan, K. C.; Tang, T. S.; Toh, H. T. *Phytochemistry* **1976**, *15*, 429–430. (b) Kojima, K.; Isaka, K.; Ogihara, Y. *Chem. Pharm. Bull.* **1998**, *46*, 523–525.

(3) (a) Kadota, S.; Marpaung, L.; Kikuchi, T.; Ekimoto, H. *Tetrahedron Lett.* **1989**, *30*, 1111–1114. (b) Kadota, S.; Marpaung, L.; Kikuchi, T.; Ekimoto, H. *Chem. Pharm. Bull.* **1990**, *38*, 894–901. (c) Kadota, S.; Marpaung, L.; Kikuchi, T.; Ekimoto, H. *Chem. Pharm. Bull.* **1990**, *38*, 1495–1500. (d) Ekimoto, H.; Irie, Y.; Araki, Y.; Han, G. Q.; Kadota, S.; Kikuchi, T. *Planta Med.* **1991**, *57*, 56–58. (e) Munoz, V.; Sauvain, M.; Bourdy, G.; Callapa, J.; Rojas, I.; Vargas, L.; Tae, A.; Deharo, E. *J. Ethnopharmacol.* **2000**, *69*, 139–155.

(4) (a) Taylor, A. R. H.; Taylor, D. A. H. *Phytochemistry* **1983**, *22*, 2870–2871. (b) Chen, Y. Y.; Wang, X. N.; Fan, C. Q.; Yin, S.; Yue, J. M. *Tetrahedron Lett.* **2007**, *48*, 7480–7484. (c) da Silva, M. N.; Arruda, M. S. P.; Castro, K. C. F.; da Silva, M. F. das G. F.; Fernandes, J. B.; Vieira, P. C. *J. Nat. Prod.* **2008**, *71*, 1983–1987. (d) Falah, S.; Suzuki, T.; Katayama, T. P. *J. Biol. Sci.* **2008**, *11*, 2007–2012.

(5) Kadota, S.; Marpaung, L.; Kikuchi, T.; Ekimoto, H. *Chem. Pharm. Bull.* **1990**, *38*, 639–651.

(6) Segura-Correa, R.; Mata, R.; Anaya, A. L.; Hernandez-Bautista, B.; Villena, R.; Soriano-Garcia, M.; Bye, R.; Linares, E. *J. Nat. Prod.* **1993**, *56*, 1567–1574.

(7) Awang, K.; Lim, C. S.; Mohamad, K.; Morita, H.; Hirasawa, Y.; Takeya, K.; Thoison, O.; Hadi, A. H. A. *Bioorg. Med. Chem.* **2007**, *15*, 5997–6002.

(8) Abdelgaleil, S. A. M.; Hashinaga, F.; Nakatani, M. *Pest Manag. Sci.* **2005**, *61*, 186–190.

(9) Adesogan, E. K.; Maclachlan, L. K.; Taylor, D. A. H. *S. Afr. J. Chem.* **1987**, *40*, 25–29.

(10) Taylor, D. A. H. *Phytochemistry* **1977**, *16*, 1847–1849.

(11) Govindachari, T. R.; Kumari, G. N. K. *Phytochemistry* **1998**, *47*, 1423–1425.

(12) Bickii, J.; Njifutie, N.; Foyere, J. A.; Basco, L. K.; Ringwald, P. *J. Ethnopharmacol.* **2000**, *69*, 27–33.

(13) Mulholland, D. A.; Taylor, D. A. H. *Phytochemistry* **1988**, *27*, 1741–1743.

(14) Abdelgaleil, S. A. M.; Iwagawa, T.; Doe, M.; Nakatani, M. *Fitoterapia* **2004**, *75*, 566–572.

(15) Adesogan, E. K.; Taylor, D. A. H. *J. Chem. Soc. (C)* **1970**, 1710–1714.

(16) Yin, S.; Fan, C. Q.; Wang, Y.; Dong, L.; Yue, J. M. *Bioorg. Med. Chem.* **2004**, *12*, 4387–4392.

(17) Yang, S. P.; Dong, L.; Wang, Y.; Wu, Y.; Yue, J. M. *Bioorg. Med. Chem.* **2003**, *11*, 4577–4584.

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