Constituents of the Seeds of *Swietenia mahagoni* JACQ. I. Isolation, Structures, and ^{1}H- and ^{13}C-Nuclear Magnetic Resonance Signal Assignments of New Tetranortriterpenoids Related to Swietenine and Swietenolide[1)]

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Eighteen new tetranortriterpenoids were isolated from the cotyledons of *Swietenia mahagoni* (Meliaceae) along with ten known tetranortriterpenoids. Among them, the structures of eight new compounds, swietenins B, C, D, E, and F, 3-*O*-acetylswietenolide, 6-*O*-acetylswietenolide, and 3-*O*-tigloyl-6-*O*-acetylswietenolide, were determined by the use of two-dimensional nuclear magnetic resonance (2D NMR) techniques. Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra of the ten known compounds were also performed.

Keywords *Swietenia mahagoni*; swietenin B; swietenin C; swietenin D; swietenin E; swietenin F; 3-*O*-acetylswietenolide; 6-*O*-acetylswietenolide; 3-*O*-tigloyl-6-*O*-acetylswietenolide; tetranortriterpenoid; 2D NMR

Swietenia mahagoni JACQ.[2)] (Meliaceae) is a valuable timber tree native to the West Indies (common name: West Indian mahogany) and cultivated in tropical countries. The seeds of this plant are used for treatment of hypertension, diabetes, and malaria as a folk medicine in Indonesia. Chemical investigation of this plant has been done by Taylor,[3)] who reported the isolation of two tetranortriterpenoids, methyl angolensate (**16**) and methyl 6-hydroxyangolensate. In the course of our search for biologically significant substances from medicinal plants in Indonesia, we have isolated eighteen new tetranortriterpenoids (**1**—**8** and **19**—**28**) together with ten known ones (**9**—**18**) from the cotyledon part of seeds of this plant. Among these, several new compounds, named 3-*O*-acetylswietenolide (**6**) and swietemahonin A—G (**19**—**25**) were found to have an antagonistic effect on platelet-activating factor (PAF).[1,4)] In this paper, we wish to present full details of the isolation of these new tetranortriterpenoids and the structure elucidation of new compounds designated as swietenin B (**1**), swietenin C (**2**), swietenin D (**3**), swietenin E (**4**), swietenin F (**5**), 3-*O*-acetylswietenolide (**6**), 6-*O*-acetylswietenolide (**7**), and 3-*O*-tigloyl-6-*O*-acetylswietenolide (**8**).[5)]

The seeds of *S. mahagoni*, collected at Medan (North Sumatra, Indonesia) in August, 1987, were divided into the seed coat and cotyledon parts. The seed coat part was extracted with hot methanol, while the cotyledon part was extracted with ether at room temperature and then with boiling methanol.

The combined ether extracts from the cotyledon part were concentrated to yield a crystalline substance, which was identified as swietenine (**9**).[6)] The ethereal mother

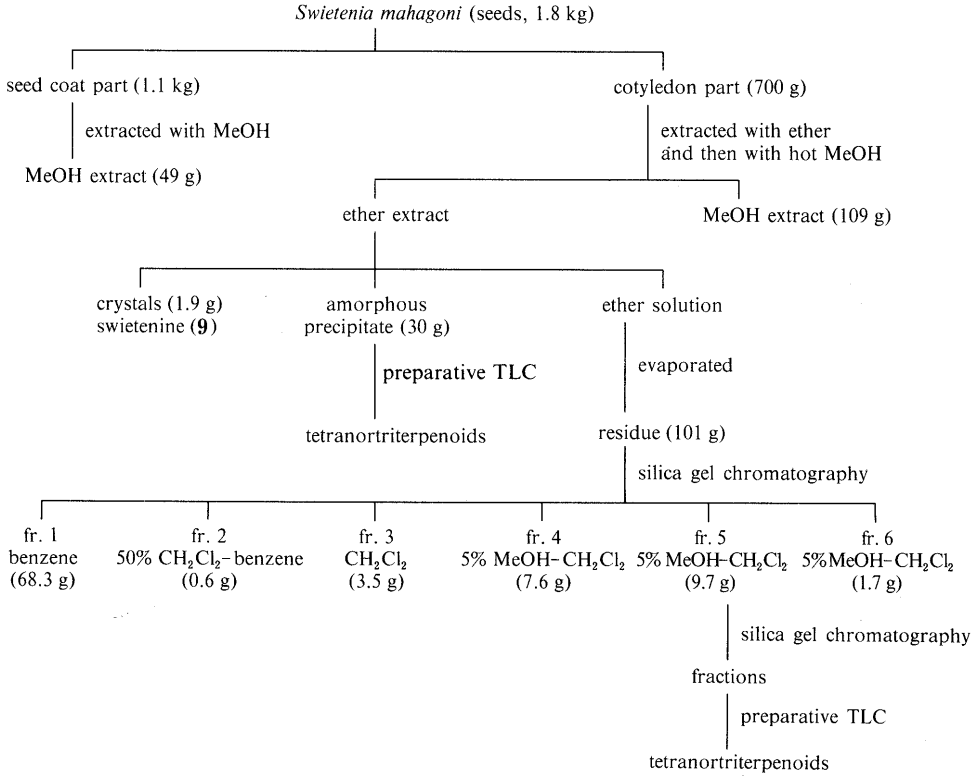
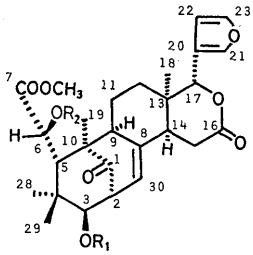
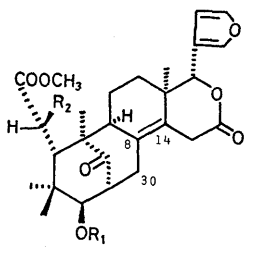


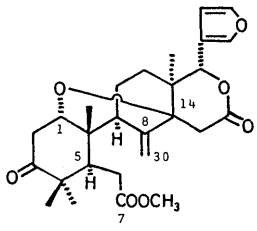
Chart 1



1 : R_1=$COCH_2CH_3$, R_2=H
2 : R_1=$COCH(CH_3)CH_3$, R_2=H
3 : R_1=$CO-C(CH_3)=CH_2$, R_2=H
4 : R_1=$CO-CH(CH_3)-CH_2CH_3$, R_2=H
5 : R_1=COC_6H_5, R_2=H
9 : R_1=$CO-C(CH_3)=CH(CH_3)$, R_2=H
10 : R_1=$CO-C(CH_3)=CH(CH_3)$, R_2=$COCH_3$



6 : R_1=$COCH_3$, R_2=OH
7 : R_1=H, R_2=$OCOCH_3$
8 : R_1=$CO-C(CH_3)=CH(CH_3)$, R_2=$OCOCH_3$
11 : R_1=H, R_2=OH
12 : R_1=$COCH_3$, R_2=$OCOCH_3$
13 : R_1=$CO-C(CH_3)=CH(CH_3)$, R_2=OH
14 : R_1=$CO-C(CH_3)=CH(CH_3)$, R_2=H
15 : R_1=H, R_2=H



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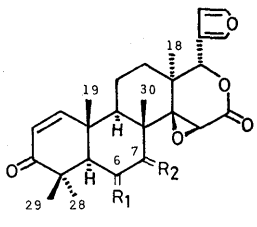
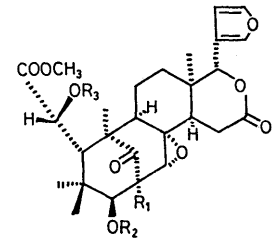
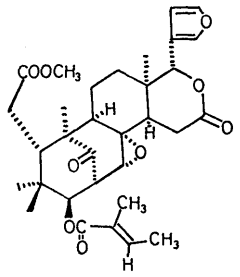


17 : R_1=H_2, R_2=O
18 : R_1=$\overset{H}{\diagup\!\!\!\diagdown}OCOCH_3$, R_2=$\overset{H}{\diagup\!\!\!\diagdown}OCOCH_3$



19 : R_1=H, R_2=$COCH_2CH_3$, R_3=H
20 : R_1=H, R_2=$COCH_2CH_3$, R_3=$COCH_3$
21 : R_1=H, R_2=$COCH(CH_3)_2$, R_3=$COCH_3$
22 : R_1=H, R_2=$COCH_3$, R_3=H
23 : R_1=H, R_2=$CO-C(CH_3)=CH(CH_3)$, R_3=H
24 : R_1=H, R_2=$CO-C(CH_3)=CH(CH_3)$, R_3=$COCH_3$
25 : R_1=OH, R_2=$CO-C(CH_3)=CH(CH_3)$, R_3=H



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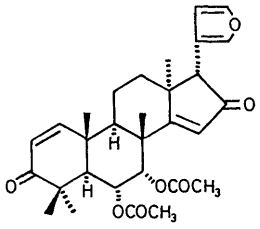

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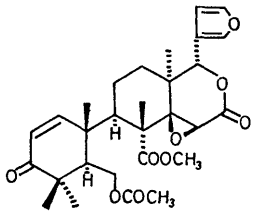

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Chart 2

liquor, on standing, yielded an amorphous precipitate, which was separated by decantation. As shown in Chart 1, the ether-soluble fraction was separated repeatedly by a combination of silica gel column chromatography and preparative thin layer chromatography (TLC) to give eighteen new tetranortriterpenoids (**1**—**8** and **19**—**28**, see Experimental) together with ten known compounds: swietenine (**9**),[6] swietenine acetate (**10**),[7] swietenolide (**11**),[8] 3,6-*O*,*O*-diacetylswietenolide (**12**),[9] 3-*O*-tigloylswietenolide (**13**),[10] khayasin T (**14**),[11] proceranolide (**15**),[12] methyl angolensate (**16**),[13] 7-deacetoxy-7-oxogedunin (**17**),[14] 6α-acetoxygedunin (**18**).[15] On the other hand, the amorphous mass, obtained from the ether extract, was repeatedly separated by preparative TLC to afford 3-*O*-acetylswietenolide (**6**), 3-*O*-tigloyl-6-*O*-acetylswietenolide (**8**), **9**, **10**, **11**, **12**, **13**, **16**, **17**, swietemahonin A (**19**), swietemahonin E (**23**), and swietemahonin F (**24**) (see Experimental).

Prior to analyzing the structures of the new compounds **1**—**8**, we carried out a re-examination of the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra of the known compounds (**9**—**18**) by means of two-dimensional (2D) NMR techniques, such as ^{1}H–^{1}H shift-correlated spectroscopy (COSY),[16] ^{1}H–^{13}C COSY, and ^{1}H–^{13}C long-range COSY. For example, detailed analysis of the ^{1}H-NMR spectrum of swietenine (**9**) with the aid of ^{1}H–^{1}H COSY allowed us to assign most of the ^{1}H-signals as illustrated in Fig. 1.

Assignments of the 18-, 19-, 28-, 29-methyl signals were done by measurements of the nuclear Overhauser effect (NOE) difference spectra (Fig. 2); *i.e.*, irradiation of the signals at δ 0.89 (29-H_3) and δ 1.12 (28-H_3) enhanced the signal intensities at δ 4.64 (3-H), 3.50 (5-H), and 3.76 ($COOCH_3$) and at δ 4.64 (3-H) and 1.45 (19-H_3), respectively. On the other hand, irradiation at δ 0.97 (18-H_3) and 1.45 (19-H_3) enhanced the signal intensities at δ 7.56 (21-H), 6.38 (22-H), 2.83 (15α-H), and 2.23 (14-H) and at δ 4.56 (6-H), 2.30 (9-H), 1.81 (11α-H), and 1.12 (28-H_3), respectively. Thus, the signals of four *tert*-methyl groups were assigned unambiguously (Table I). It should be noted here that ring A in **9** has a boat conformation.[6]

Next, the ^{1}H–^{13}C COSY of **9** (Fig. 3) led readily to

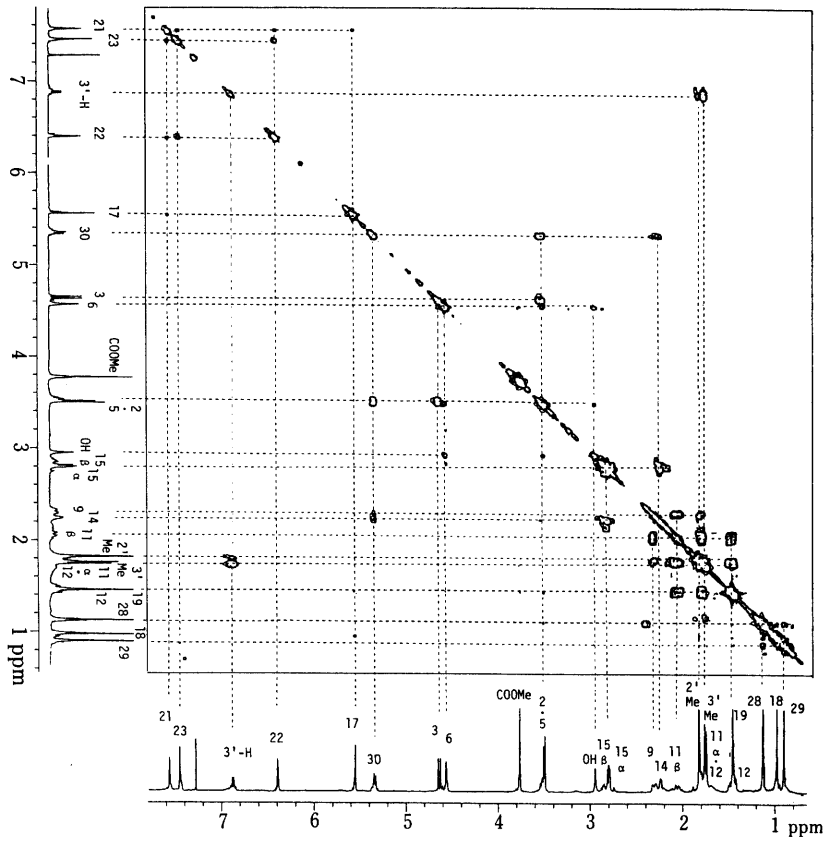

Fig. 1. Contour Map of the ^1H–^1H COSY Spectrum of Swietenine (**9**) in $CDCl_3$

precise assignments of the signals due to primary, secondary, and tertiary carbons (Table II), but the signal assignments of the quaternary ones were done by the use of ^1H–^{13}C long-range COSY. As shown in Fig. 4, the carbon atoms corresponding to the signals at δ 216.53 (C-1) and at δ 166.92 (C-1′) are correlated with the protons corresponding to the signals at δ 1.44 (19-H_3) and at δ 1.82 (2′-CH_3) and 4.64 (3-H), respectively. Similarly, quaternary carbons corresponding to the signals at δ 39.04 (C-4), 175.97 (C-7), 138.28 (C-8), 50.39 (C-10), 36.73 (C-13), 168.45 (C-16), 121.38 (C-20), and 127.77 (C-2′) can be correlated with the protons indicated by arrows in the formula (Fig. 4).

The ^1H- and ^{13}C-NMR spectra of other known compounds (**10**—**18**) were also fully analyzed in the same manner and the results are summarized in Tables I and II.

Swietenin B (**1**) was isolated as colorless needles, mp 113—115 °C, $[\alpha]_D$ −11.5° ($CHCl_3$) and has the molecular formula $C_{30}H_{38}O_9$ (M^+ 542.2477, Calcd 542.2515). In the infrared (IR) spectrum, it showed a strong absorption at 1740—1710 cm^{-1} (ketone and ester) and a moderate absorption at 880 cm^{-1} (furan). The ^1H-NMR spectrum of **1** exhibited signals due to a β-substituted furan (δ 7.55, 6.38, and 7.44), a lactone (δ 5.60), a trisubstituted olefine (δ 5.36), an acyloxyl-bearing methine (δ 4.59), a hydroxyl-bearing methine (δ 4.55), and a methyl ester (δ 3.75) along with four *tert*-methyl groups (δ 0.99, 1.44, 1.11, and 0.86) (Table III). The spectral pattern closely resembled that of swietenine (**9**), but it was characterized by the appearance of signals assignable to a propionyl group at δ 1.12 (3H, t, J=7.0 Hz) and 2.38 (2H, q, J=7.0 Hz) instead of the signals of the tigloyl group in **9** (Table III). The ^{13}C-NMR spectrum of **1** showed four carbonyl carbon signals (δ 216.25, 175.88, 173.75, and 169.20) and the spectral pattern was also similar to that of **9**, except for the signals due to the propionyl group (Table IV). Detailed analyses of the ^1H- and ^{13}C-NMR spectra with the aid of ^1H–^1H COSY, difference NOE experiments, ^1H–^{13}C COSY, and ^1H–^{13}C long-range COSY enabled us to make complete assignments of the ^1H- and ^{13}C-signals, which are shown in Tables III and IV, respectively.

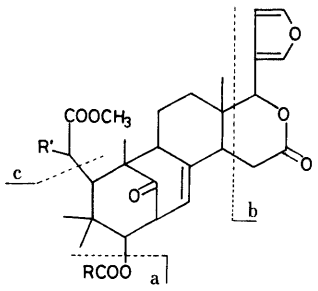

Chart 3

The mass spectrum (MS) of **1** exhibited the molecular ion peak at m/z 542 (base peak) and characteristic fragment ion peaks at m/z 468 (M^+ − a − H), 404 (M^+ − b), 379 (M^+ − a − H − c), and 330 (M^+ − a − H − b), which may be interpreted by the fragmentations shown in Chart 3.

Comparison of these ^1H- and ^{13}C-NMR and MS data with those of **9** led us to conclude that the structure of swietenin B is **1**.

Swietenin C (**2**), mp 238—239 °C, $[\alpha]_D$ −14.9° ($CHCl_3$), showed a hydroxyl band (3500 cm^{-1}) and a strong carbonyl band (1735—1710 cm^{-1}) along with a moderate band due to a furan (880 cm^{-1}) in the IR spectrum. The MS of **2**

TABLE I. ^{1}H-NMR Spectral Data for Swietenine (**9**), Swietenine Acetate (**10**), Swietenolide (**11**), 3,6-*O*,*O*-Diacetylswietenolide (**12**), 3-*O*-Tigloylswietenolide (**13**), Khayasin T (**14**), Proceranolide (**15**), Methyl Angolensate (**16**), 7-Deacetoxy-7-oxogedunin (**17**), and 6α-Acetoxygedunin (**18**) from *S. mahagoni*

^{1}H	**9**[b]	**10**[b]	**11**[b]	**12**[b]	**13**[b]	**14**[b]	**15**[b]	**16**[b]	**17**[b]	**18**[b]
1	—	—	—	—	—	—	—	3.52 dd (6.5, 4)	7.10 dd (10)	7.07 d (10)
2	3.52 ddd (9, 8, 1.5)	3.53 ddd (9, 7.5, 1.5)	3.04 ddd (10, 5.5, 2.5)	3.14 ddd (10, 5.5, 2)	3.21 ddd (10, 6, 2)	3.23 ddd (9.5, 5.5, 2.5)	3.04 ddd (9.5, 5.5, 2.5)	2.51 dd (14.5, 4) 2.90 dd (14.5, 6)	5.93 d (10)	5.95 d (10)
3	4.64 d (9)	4.70 d (9)	3.58 d (10)	4.86 d (10)	4.71 d (10)	4.85 d (9.5)	3.74 d (9.5)	—	—	—
5	3.50 br s	3.71 br s	3.25 br s	3.40 br s	3.38 br s	3.37 dd (9.5, 3.5)	3.24 dd (10.5, 3)	2.88 d (10.5)	2.18 dd (14, 3.5)	2.53 d (12.5)
6	4.56 br s	5.58 br s	4.54 br s	5.46 br s	4.56 br s	2.37 dd (16.5, 3.5) 2.42 dd (16.5, 9.5)	2.34 dd (16, 3) 2.40 dd (16, 10.5)	2.25 d (16.5) 2.61 dd (16.5, 10.5)	2.41 dd (14, 3.5) 2.93 t (14)	5.28 dd (12.5, 2.5)
7	—	—	—	—	—	—	—	—	—	4.89 d (2.5)
9	2.30 ddd (13, 4, 1.5)	2.28 ddd (13, 4, 1.5)	2.07 br s	2.08 m	2.11 m	2.01 m	1.98 m	2.17 dd (5, 1.5)	2.22 dd (11, 1.5)	2.54 dd (12.5, 5)
11	1.81 m 2.05 qd (13, 4)	1.81 m 2.19 m	1.14 m 1.73 m	1.16 m 1.81 m	1.76 m 1.88 m	1.73 m 1.84 m	1.72 m 1.80 m	1.57 tt (14, 5) 2.20 m	1.79 m 1.99 m	1.85 m 1.98 m
12	1.46 ddd (17, 11, 4) 1.77 m	1.43 ddd (17, 12, 4) 1.75 m	1.78 ddd (15, 9, 3) 1.86 ddd (15, 6, 3)	1.76 m 1.89 m	1.17 m 1.74 m	1.10 m 1.83 m	1.03 m 1.79 m	1.14 ddd (14, 6, 1.5) 1.90 td (14, 5)	1.48 m 1.85 m	1.59 m 1.74 m
14	2.23 ddd (5, 2, 1.5)	2.22 m	—	—	—	—	—	—	—	—
15	2.83 dd (18, 5) 2.76 dd (18, 2)	2.83 dd (19, 6) 2.75 dd (19, 1.5)	3.46 dt (21, 2.5) 4.03 dt (21, 1)	3.44 dt (16, 3) 3.68 d (16)	3.25 dt (20.5, 3) 3.54 dt (20.5, 1.5)	3.23 dt (21, 3) 3.61 dt (21, 1.5)	3.46 dt (21, 2.5) 4.08 dt (21, 1.2)	2.91 d (18) 2.58 d (18)	3.87 s	3.62 s
17	5.54 s	5.56 s	5.47 s	5.60 s	5.43 s	5.55 s	5.59 s	5.67 s	5.47 s	5.62 s
21	7.56 dd (1.8, 1)	7.71 dd (1.8, 0.8)	7.48 dd (1.8, 0.8)	7.52 dd (1.8, 1.0)	7.48 dd (1.8, 0.8)	7.57 dd (1.5, 0.8)	7.57 dd (1.5, 0.8)	7.44 dd (1.5, 0.8)	7.42 dd (1.8, 1)	7.42 dd (1.8, 1)
22	6.38 dd (1.8, 1)	6.45 dd (1.8, 0.8)	6.40 dd (1.8, 0.8)	6.45 dd (1.8, 1.0)	6.40 dd (1.8, 0.8)	6.48 dd (1.5, 0.8)	6.49 dd (1.5, 0.8)	6.39 dd (1.5, 0.8)	6.37 dd (1.8, 1)	6.33 dd (1.8, 1)
23	7.45 t (1.8)	7.44 t (1.8)	7.41 t (1.8)	7.43 t (1.8)	7.43 t (1.8)	7.42 t (1.5)	7.39 t (1.5)	7.38 t (1.5)	7.40 t (1.8)	7.42 t (1.8)
18[a]	0.97 s	1.03 s	0.99 s	1.04 s	0.99 s	1.03 s	1.03 s	0.84 s	1.14 s	1.24 s
19[a]	1.45 s	1.19 s	1.40 s	1.15 s	1.43 s	1.17 s	1.13 s	0.95 s	1.36 s	1.22 s
28[a]	1.12 s	1.11 s	1.00 s	1.07 s	1.10 s	0.82 s	0.72 s	1.05 s	1.16 s	1.26 s
29[a]	0.89 s	0.97 s	0.88 s	0.85 s	0.86 s	0.77 s	0.81 s	1.19 s	1.14 s	1.17 s
30	5.34 dt (8, 1.5)	5.33 dt (7.5, 1.5)	2.01 ddd (14.5, 5.5, 2.5) 3.19 dd (14.5, 2.5)	2.13 ddd (15.5, 5.5, 3) 2.79 dd (15, 2.5)	2.12 m	2.08 ddd (15.5, 5.5, 3) 2.66 dd (15.5, 2.5)	1.97 m 3.19 dd (14, 2.5)	4.90 s 5.15 s	1.22 s[a]	1.27 s[a]
COOMe	3.76 s	3.74 s	3.82 s	3.74 s	3.86 s	3.74 s	3.70 s	3.72 s	—	—
6-OAc	—	2.20 s	—	2.16 s	—	—	—	—	—	2.04 s
7-OAc	—	—	—	—	—	—	—	—	—	2.15 s
3-*O*-Acyl										
2′	—	—	—	2.15 s	—	—	—	—	—	—
2′-Me	1.82 br s	1.82 d (1)	—	—	1.89 t (1)	1.89 d (1.5)	—	—	—	—
3′	6.87 qq (7, 1.5)	6.90 qq (7, 1)	—	—	6.93 qq (7, 1)	6.96 qq (7, 1.5)	—	—	—	—
3′-Me	1.74 br d (7)	1.73 dd (7, 1)	—	—	1.83 dd (7, 1)	1.83 dd (7, 1.5)	—	—	—	—

δ values in $CDCl_3$. Values in parentheses are coupling constants (Hz). *a*) Assignments were confirmed by NOE experiments. *b*) ^{1}H-^{1}H COSY was measured.

exhibited the molecular ion peak at *m/z* 556 (base peak) and its molecular formula, $C_{31}H_{40}O_9$, was confirmed by high-resolution MS measurement.

The ^{1}H- and ^{13}C-NMR spectra of **2** were closely similar to those of swietenin B (**1**) except for the appearance of the signals due to an isobutyryl residue instead of the signals due to the propionyl residue in **1** (see Tables III and IV). From these ^{1}H- and ^{13}C-NMR comparisons, it was concluded that the structure of swietenin C is represented by the formula **2**, which has a 3-*O*-isobutyryl residue instead of the 3-*O*-propionyl residue in **1**.

Swietenin D (**3**), a minor component, showed mp 234—235 °C, $[\alpha]_D$ −33.0° ($CHCl_3$), IR ν_{max} cm^{-1}: 1735, 1700 (br), 880. In the MS, it gave the molecular ion peak at *m/z*

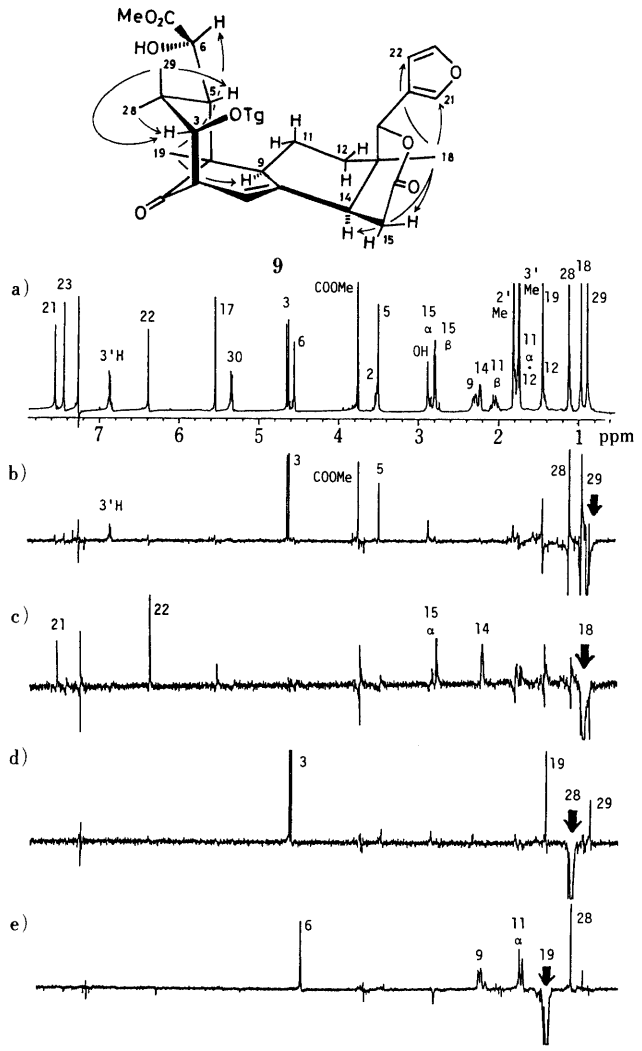

Fig. 2. ^{1}H-NMR (Normal and NOE) Spectra of Swietenine (**9**)

a) Normal ^{1}H-NMR spectrum. b—e) NOE difference spectra on irradiation at δ 0.89, 0.97, 1.12, and 1.45, respectively.

554 (base peak), corresponding to the formula $C_{31}H_{38}O_9$, and fragment ion peaks at *m/z* 468 (M^+-a-H), 416 (M^+-b), 379 ($M^+-a-H-c$), and 330 ($M^+-a-H-b$). The ^{1}H- and ^{13}C-NMR spectra were closely similar to those of **1** except for the appearance of the signals assignable to a methacryl residue instead of the signals due to the propionyl residue in **1** (see Tables III and IV). Thus, the structure of swietenin D was assigned as the formula **3**.

Swietenin E (**4**), mp 222—224 °C, $[\alpha]_D$ −31.5° ($CHCl_3$), is also a very minor constituent of the cotyledons. It has the molecular formula $C_{32}H_{42}O_9$ (M^+ 570.2791, Calcd 570.2828) and showed IR absorptions at 1735 (lactone), 1720 (ester), and 880 cm^{-1} (furan). The ^{1}H- and ^{13}C-NMR spectra resembled those of **1** except for the appearance of the signals attributable to an α-methylbutyryl residue instead of the signals due to the propionyl residue in **1** (see Tables III and IV). Based on these spectral data, swietenin E was determined to be **4**.

Swietenin F (**5**), a minor component, showed mp 120—122 °C, $[\alpha]_D$ −56.2° ($CHCl_3$), and IR ν_{max} cm^{-1}: 3500, 1735, 1720, 1700, 1600, 880. In the MS, it gave the molecular ion peak at *m/z* 590, corresponding to the formula $C_{34}H_{38}O_9$, and fragment ion peaks at *m/z* 468

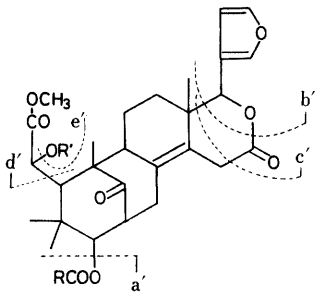

Chart 4

(M^+-a-H), 452 (M^+-b), 379 ($M^+-a-H-c$), 330 ($M^+-a-H-b$), and 105 ($C_6H_5CO^+$, base peak). The ^{1}H- and ^{13}C-NMR spectra were similar to those of **1** except for the appearance of the signals due to a benzoyl residue instead of the signals due to the propionyl residue in **1** (see Tables III and IV). Thus, the structure of swietenin F was determined to be as represented by the formula **5**.

The absolute stereochemistry of swietenins B—F (**1**—**5**) was determined to be the same as that of swietenine (**9**)[17] based on the negative Cotton effect at around 292 nm in the circular dichroism (CD) spectra, except for the absolute configuration of the α-methylbutyryl residue in **4**, which remained uncertain.

3-*O*-Acetylswietenolide (**6**) was obtained as colorless needles, mp 136—138 °C, $[\alpha]_D$ −17.8° ($CHCl_3$), and has the molecular formula $C_{29}H_{36}O_9$ (M^+ 528.2371, Calcd 528.2358). Its IR spectrum showed a hydroxyl absorption at 3500 cm^{-1} and a very strong carbonyl absorption at 1735—1710 cm^{-1} (lactone, ester, and ketone) together with medium absorptions at 1500 and 880 cm^{-1} arising from a furan ring. The ^{1}H-NMR spectrum of **6** was closely similar to that of swietenolide (**11**),[8] but a three-proton singlet due to an acetyl group appeared newly at δ 2.15 and a one-proton doublet assignable to 3-H showed a downfield shift to δ 4.82 (Table III). The MS of **6** exhibited the molecular ion peak at *m/z* 528 along with significant fragment ion peaks at *m/z* 468 ($M^+-a'-H$), 439 (M^+-d'), 432 (M^+-b'), 404 (M^+-c'), 386 ($M^+-c'-H_2O$), 343 ($M^+-b'-d'$), 315 ($M^+-c'-d'$), 301, 283 ($M^+-a'-H-b'-d'$), and 255 ($M^+-a'-H-c'-d'$), which were reasonably explained by the fragmentations shown in Chart 4.

At this stage, acetylation of **6** was carried out to give a diacetate (**12**). This product was found to be identical with 3,6-*O*,*O*-diacetylswietenolide (**12**)[9] by comparing the spectral data with those reported in the literature. Therefore, **6** was determined to be the 3-*O*-acetyl derivative of swietenolide (**11**).

6-*O*-Acetylswietenolide (**7**), mp 212—215 °C, $[\alpha]_D$ −6.5° ($CHCl_3$), has the same molecular formula $C_{29}H_{36}O_9$ as **6**. The IR spectrum of **7** showed strong carbonyl bands (1740—1710 cm^{-1}), and its spectral pattern was similar to that of **6**. Also, the ^{1}H-NMR spectrum showed a signal due to an acetyl methyl and the spectral pattern resembled that of swietenolide (**11**), but it was characterized by the downfield shift of a singlet (δ 5.45) assignable to 6-H (Table III).

Acetylation of **7** with acetic anhydride–pyridine gave a diacetate (**12**), which was identified as 3,6-*O*,*O*-diacetylswietenolide.[9] Therefore, **7** was proved to be the 6-*O*-acetyl derivative of swietenolide (**11**).

TABLE II. ^{13}C-NMR Spectral Data for Swietenine (**9**), Swietenine Acetate (**10**), Swietenolide (**11**), 3,6-*O*,*O*-Diacetylswietenolide (**12**), 3-*O*-Tigloylswietenolide (**13**), Khayasin T (**14**), Proceranolide (**15**), Methyl Angolensate (**16**), 7-Deacetoxy-7-oxogedunin (**17**), and 6α-Acetoxygedunin (**18**) from *S. mahagoni*

^{1}H	**9**[a]	**10**[a]	**11**[a]	**12**[a]	**13**[a]	**14**[a]	**15**[a]	**16**[a]	**17**[a]	**18**[a]
1	216.53 (s)	215.95 (s)	219.80 (s)	216.86 (s)	217.95 (s)	218.41 (s)	220.08 (s)	77.21 (d)	155.92 (d)	156.17 (d)
2	48.95 (d)	48.77 (d)	49.99 (d)	47.86 (d)	48.14 (d)	48.30 (d)	50.15 (d)	39.45 (t)	126.47 (d)	126.67 (d)
3	78.41 (d)	77.88 (d)	78.50 (d)	79.49 (d)	80.57 (d)	79.28 (d)	77.23 (d)	212.55 (s)	203.24 (s)	204.08 (s)
4	39.04 (s)	38.99 (s)	39.66 (s)	38.84 (s)	39.17 (s)	38.73 (s)	39.30 (s)	48.04 (s)	45.25 (s)	44.99 (s)
5	45.47 (d)	44.55 (d)	44.00 (d)	44.40 (d)	45.08 (d)	40.51 (d)	39.30 (d)	42.94 (d)[b]	54.60 (d)	38.45 (d)
6	72.87 (d)	72.78 (d)	73.57 (d)	73.05 (d)	73.36 (d)	33.42 (t)	33.54 (t)	32.54 (t)	36.71 (t)	69.67 (d)
7	175.97 (s)	171.14 (s)	175.83 (s)	171.26 (s)	175.63 (s)	174.28 (s)	174.39 (s)	173.81 (s)	208.16 (s)	72.64 (d)
8	138.28 (s)	138.44 (s)	129.05 (s)	127.61 (s)	128.52 (s)	127.80 (s)	128.27 (s)	145.91 (s)	53.44 (s)	43.12 (s)
9	57.56 (d)	57.48 (d)	52.96 (d)	53.14 (d)	53.55 (d)	52.23 (d)	51.76 (d)	49.98 (d)[b]	47.63 (d)	47.86 (d)
10	50.39 (s)	50.13 (s)	53.99 (s)	53.35 (s)	53.43 (s)	53.18 (s)	53.61 (s)	44.06 (s)	39.61 (s)	40.63 (s)
11	21.28 (t)	21.11 (t)	29.08 (t)	29.40 (t)	18.94 (t)	18.77 (t)	18.74 (t)	23.78 (t)	17.21 (t)	15.07 (t)
12	34.64 (t)	34.50 (t)	18.74 (t)	18.71 (t)	29.79 (t)	29.16 (t)	28.56 (t)	29.34 (t)	32.24 (t)	25.92 (t)
13	36.73 (s)	36.78 (s)	37.81 (s)	38.17 (s)	38.13 (s)	38.11 (s)	37.88 (s)	41.48 (s)	37.73 (s)	38.81 (s)
14	45.09 (d)	45.18 (d)	130.75 (s)	132.34 (s)	131.61 (s)	131.93 (s)	131.20 (s)	80.22 (s)	65.59 (s)	47.86 (s)
15	29.57 (t)	29.55 (t)	33.15 (t)	33.47 (t)	33.16 (t)	32.95 (t)	33.06 (t)	33.80 (t)	53.62 (d)	56.27 (d)
16	168.45 (s)	168.59 (s)	171.43 (s)	169.53 (s)	169.23 (s)	169.74 (s)	171.73 (s)	169.90 (s)	166.84 (s)	167.12 (s)
17	76.71 (d)	76.70 (d)	80.51 (d)	80.83 (d)	81.11 (d)	80.92 (d)	80.25 (d)	79.55 (d)	78.00 (d)	78.14 (d)
20	121.38 (s)	120.96 (s)	120.81 (s)	120.53 (s)	120.87 (s)	120.81 (s)	120.78 (s)	120.87 (s)	120.20 (s)	120.37 (s)
21	140.54 (d)	141.24 (d)	141.06 (d)	141.57 (d)	141.06 (d)	141.69 (d)	141.71 (d)	140.78 (d)	141.04 (d)	141.25 (d)
22	109.24 (d)	109.48 (d)	109.80 (d)	109.88 (d)	109.76 (d)	109.98 (d)	110.09 (d)	109.94 (d)	109.80 (d)	109.86 (d)
23	143.20 (d)	143.12 (d)	142.88 (d)	143.00 (d)	143.12 (d)	142.83 (d)	142.62 (d)	142.73 (d)	143.14 (d)	143.15 (d)
18	21.28 (q)	21.48 (q)	17.91 (q)	18.04 (q)	17.79 (q)	17.29 (q)	17.54 (q)	13.76 (q)	20.94 (q)	17.91 (q)
19	16.53 (q)	15.68 (q)	17.91 (q)	16.71 (q)	17.65 (q)	16.72 (q)	16.92 (q)	21.66 (q)	19.85 (q)	21.44 (q)
28	22.80 (q)	22.75 (q)	23.22 (q)	23.36 (q)	23.11 (q)	20.28 (q)	20.17 (q)	25.97 (q)	27.00 (q)	31.71 (q)
29	23.05 (q)	22.87 (q)	23.63 (q)	23.02 (q)	23.75 (q)	23.86 (q)	23.90 (q)	21.48 (q)	20.67 (q)	20.31 (q)
30	123.66 (d)	123.21 (d)	33.80 (t)	33.71 (t)	34.07 (t)	33.63 (t)	33.33 (t)	111.49 (t)	17.41 (q)	18.17 (q)
$COOCH_3$	53.28 (q)	53.14 (q)	53.23 (q)	53.35 (q)	53.14 (q)	52.09 (q)	51.97 (q)	52.05 (q)	—	—
6-$OCOCH_3$	—	169.71 (s)	—	169.71 (s)	—	—	—	—	—	170.12 (s)
6-$OCOCH_3$	—	20.96 (q)	—	20.93 (q)	—	—	—	—	—	21.00 (q)
7-$OCOCH_3$	—	—	—	—	—	—	—	—	—	170.05 (s)
7-$OCOCH_3$	—	—	—	—	—	—	—	—	—	21.26 (q)
3-$OCOR_1$										
1′	166.92 (s)	166.89 (s)	—	170.23 (s)	167.21 (s)	167.41 (s)	—	—	—	—
2′	127.77 (s)	127.55 (s)	—	21.20 (q)	129.06 (s)	128.91 (s)	—	—	—	—
3′	139.02 (d)	139.45 (d)	—	—	138.98 (d)	139.42 (d)	—	—	—	—
2′-CH_3	11.75 (q)	11.73 (q)	—	—	12.31 (q)	12.40 (q)	—	—	—	—
3′-CH_3	14.64 (q)	14.64 (q)	—	—	14.60 (q)	14.66 (q)				

δ values in $CDCl_3$. Multiplicities of carbon signals were determined by the DEPT method and are indicated as, s, d, t, and q, *a*) ^{1}H–^{13}C and ^{1}H–^{13}C long-range COSY spectra were measured. *d*) Previous assignments were revised (see ref. 18).

3-*O*-Tigloyl-6-*O*-acetylswietenolide (**8**) was obtained as colorless needles, mp 156—158 °C, $[\alpha]_D$ −7.3° ($CHCl_3$). The MS of **8** exhibited the M^+ peak at *m/z* 610 and its molecular formula was determined to be $C_{34}H_{42}O_{10}$ by high-resolution MS measurement. It showed IR absorptions at 1735 cm^{-1} (lactone), 1720 cm^{-1} (ester), 1710 cm^{-1} (carbonyl), 1500, and 880 cm^{-1} (furan).

The ^{1}H- and ^{13}C-NMR of **8**, analyzed with the aid of ^{1}H–^{1}H COSY (Fig. 5) and ^{1}H–^{13}C COSY (Fig. 6), indicated the presence of a ketone (δ_C 217.32), a methyl ester (δ_H 3.77; δ_C 171.41 and 53.14), an acetyl (δ_H 2.19; δ_C 20.99 and 169.80), a lactone (δ_H 5.48; δ_C 81.01 and 169.38), a tigloyl (δ_H 1.88, 1.82, and 6.94; δ_C 167.25, 128.97, 12.34, 14.61, and 139.39), a furan (δ_H 7.54, 6.46, and 7.44; δ_C 120.75, 141.48, 109.94, and 143.03), two acyloxy-bearing methines (δ_H 4.76 and 5.50; δ_C 80.10 and 73.14), a tetrasubstituted olefin (δ_C 127.67 and 132.49), four *tert*-methyl groups (δ_H 1.01, 1.18, 1.09, and 0.92; δ_C 17.50, 16.80, 23.14, and 23.66), and three quaternary sp^3 carbons (δ_C 39.30, 53.56, and 38.17) (see Tables III and IV). Further, the MS showed significant fragment peaks at *m/z* 550 (M^+ −e′−H), 514 (M^+ −b′), 486 (M^+ −c′), 479 (M^+ −d′), 283 (M^+ −a′−H−b′−d′), 255 (M^+ −a′−H−c′−d′), and 83 ($C_4H_7CO^+$, base peak), which may be explained by the fragmentations shown in Chart 4.

The above data led us to suppose that compound **8** might be 3-*O*-tigloyl-6-*O*-acetylswietenolide. This was supported by the ^{1}H–^{13}C long-range COSY spectrum. As shown in Fig. 7, the carbons at δ 217.32 (C-1), at δ 169.80 (6-$OCOCH_3$), and at δ 167.25 (C-1′) are correlated with the protons at δ 1.18 (19-H_3) and 2.67 (30-H), at δ 2.19 (6-$OCOCH_3$) and 5.50 (6-H), and at δ 1.88 (2′-Me) and 4.76 (3-H), respectively. On the other hand, the carbonyl carbons at δ 171.41 (C-7) and 169.38 (C-16) are correlated with the protons at δ 3.77 (OCH_3) and 5.50 (6-H) and at δ 3.24 (15-H), respectively. Similarly, quaternary carbons corresponding to the signals at δ 38.17 (C-13), 39.30 (C-4), 53.56 (C-10), 127.67 (C-8), and 132.49 (C-14) can be correlated with the protons indicated by arrows in the formula in Fig. 7. Also, some of the significant ^{1}H–^{13}C long-range correlations observed are shown here by arrows.

The relative stereochemistry of **8** was determined on the basis of coupling constants of the protons and the result of NOE experiments. As shown in Fig. 8, irradiation at the 29-

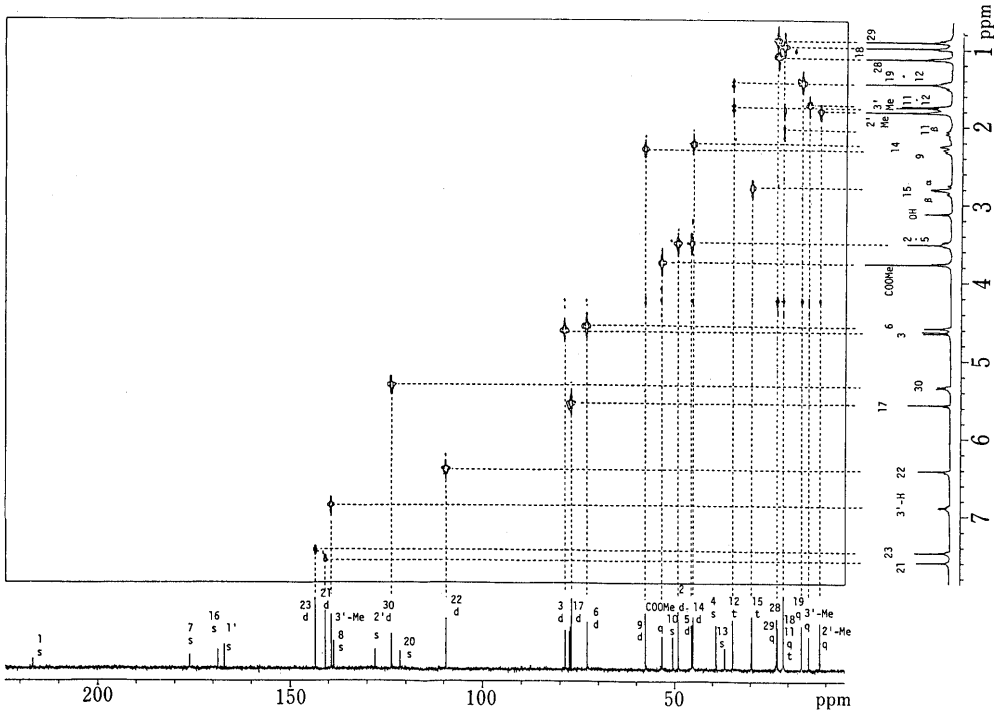

Fig. 3. Contour Map of the ^{1}H–^{13}C COSY Spectrum of Swietenine (**9**) in $CDCl_3$

The multiplicities of carbon signals were determined by means of DEPT and are indicated as s, d, t, and q.

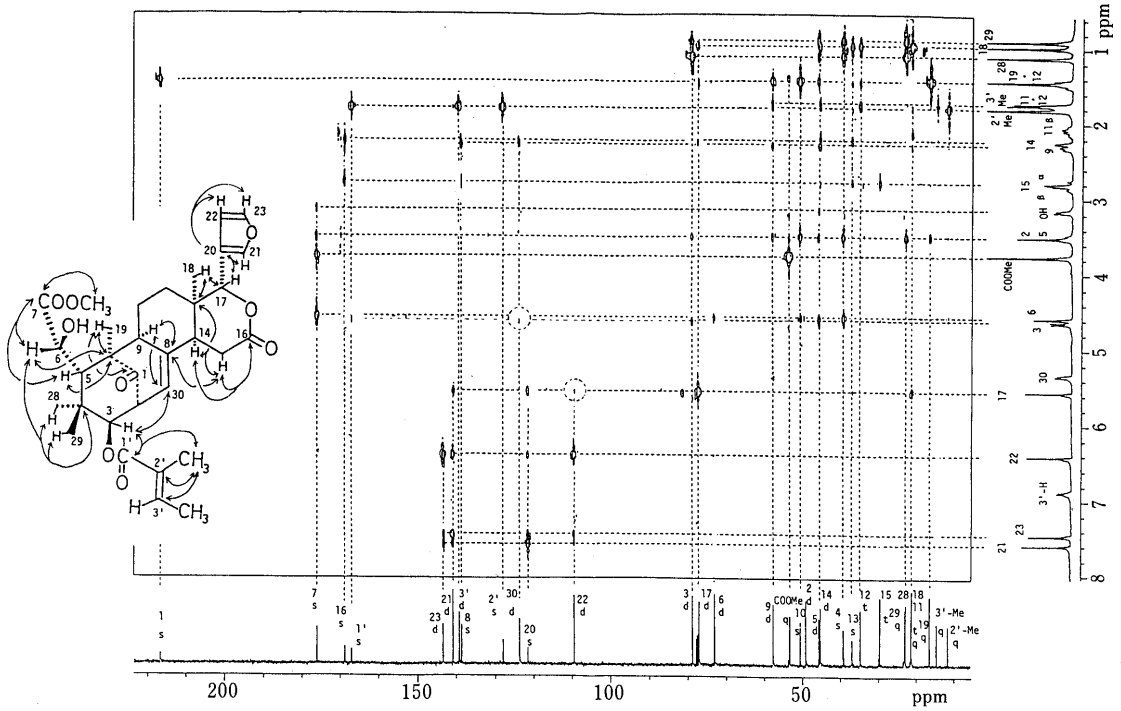

Fig. 4. Contour Map of the ^{1}H–^{13}C Long-Range COSY Spectrum of Swietenine (**9**) in $CDCl_3$ (J_{CH} = 10 Hz)

H_3 and 18-H_3 increased the signal intensities of the 5-, ester methyl, 3-, and 3′-protons and the 12α-, 15α-, 22-, and 21-protons, respectively, and irradiation at the 28-H_3 and 19-H_3 enhanced the signal intensity of the acetyl methyl and 3-protons and the 9- and 6-protons, respectively. Therefore the structure of this tetranortriterpenoid was proved to be **8**.

The absolute stereochemistry of **6**, **7**, and **8** is confirmed by the CD spectra which show negative Cotton effects at around 300 nm, similar to that of swietenolide (**11**).[8]

Throughout the structure elucidation of these tetranortriterpenoids, 2D NMR methods were effectively used. The anti-PAF activities of these compounds will be reported elsewhere.

Experimental

Melting points were determined with a Kofler-type apparatus and are uncorrected. Optical rotations were measured in chloroform solutions on a

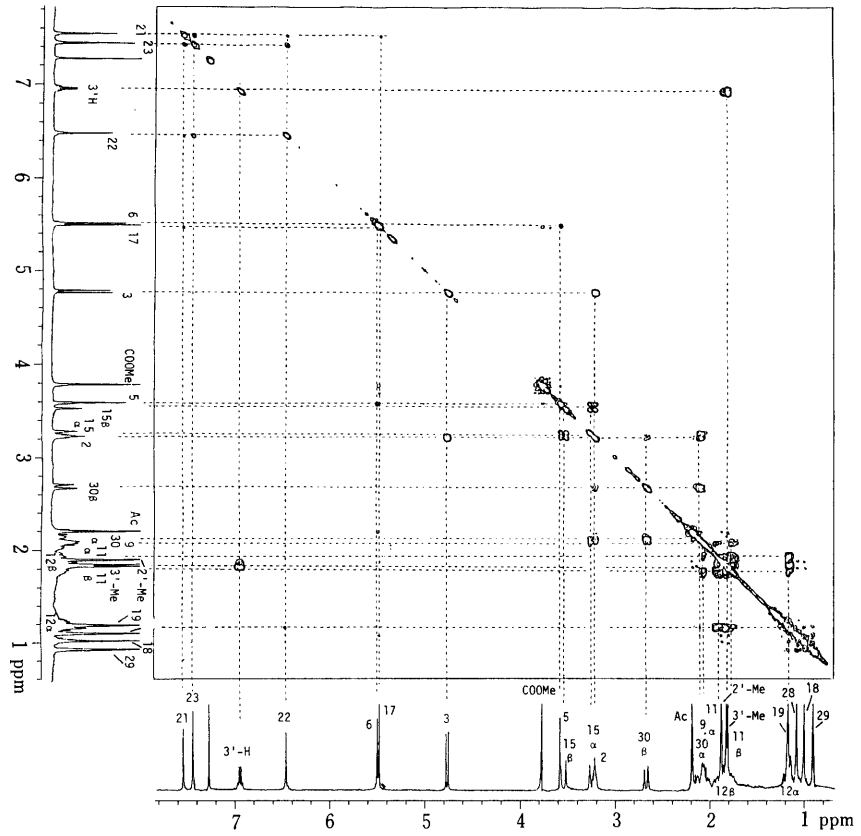

Fig. 5. Contour Map of the ^1H–^1H COSY Spectrum of 3-*O*-Tigloyl-6-*O*-acetylswietenolide (**8**) in $CDCl_3$

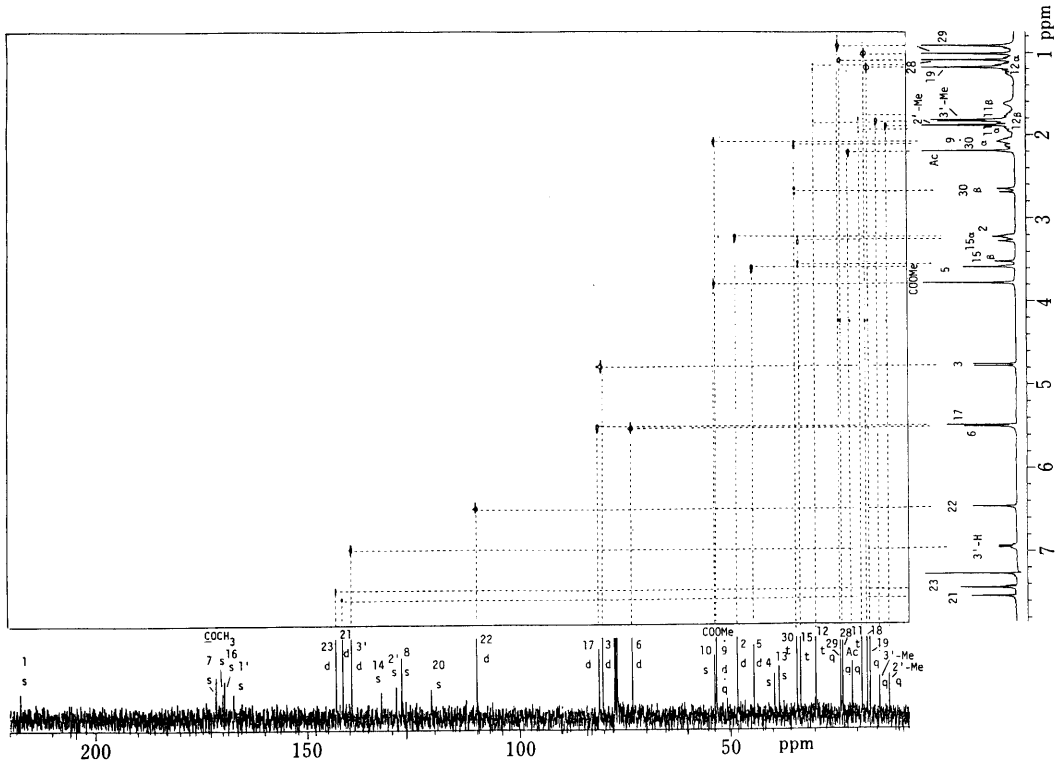

Fig. 6. Contour Map of the ^1H–^{13}C COSY Spectrum of 3-*O*-Tigloyl-6-*O*-acetylswietenolide (**8**) in $CDCl_3$

JASCO DIP-4 automatic polarimeter at 20—22 °C. CD spectra were recorded on a JASCO J-500C spectropolarimeter in chloroform ($CHCl_3$) solutions. IR spectra were taken with a JASCO IRA-2 spectrometer in $CHCl_3$ solutions. ^1H- and ^{13}C-NMR spectra were taken on a JEOL-GX 400 spectrometer in $CDCl_3$ solutions with tetramethylsilane as an internal standard, and chemical shifts are recorded in δ values. ^1H–^1H COSY, ^1H–^{13}C COSY, and ^1H–^{13}C long-range COSY were obtained with the usual pulse sequense and data processing was performed with the standard

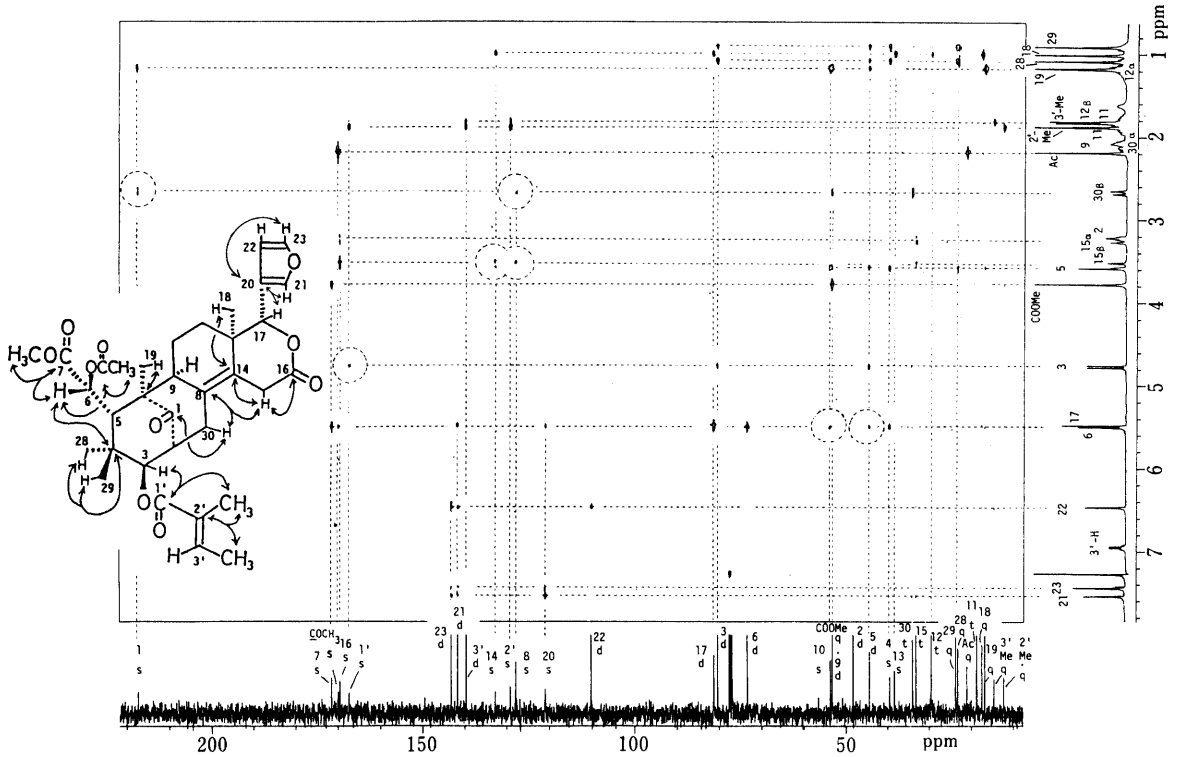

Fig. 7. Contour Map of the ^{1}H–^{13}C Long-Range COSY Spectrum of 3-*O*-Tigloyl-6-*O*-acetylswietenolide (**8**) in $CDCl_3$ ($J_{CH}=10$ Hz)

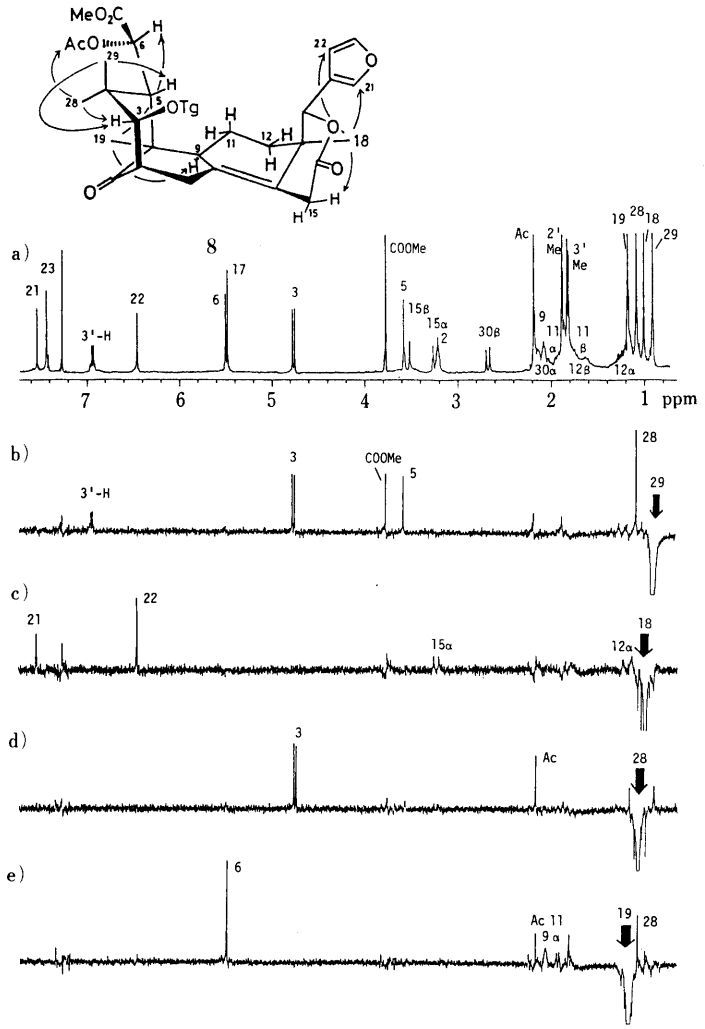

Fig. 8. ^{1}H-NMR (Normal and NOE) Spectra of 3-*O*-Tigloyl-6-*O*-acetylswietenolide (**8**)

a) Normal ^{1}H-NMR spectrum. b—e) NOE difference spectra on irradiation at δ 0.92, 1.01, 1.09, and 1.18, respectively.

TABLE III. ^{1}H-NMR Spectral Data for Swietenins B (**1**), C (**2**), D (**3**), E (**4**), and F (**5**), 3-*O*-Acetylswietenolide (**6**), 6-*O*-Acetylswietenolide (**7**), and 3-*O*-Tigloyl-6-*O*-acetylswietenolide (**8**) from *S. mahagoni*

^{1}H	**1**[b]	**2**[b]	**3**[b]	**4**[b]	**5**[b]	**6**[b]	**7**[b]	**8**[b]
2	3.50 ddd (9.5, 7, 1.5)	3.49 ddd (9, 7, 1)	3.54 ddd (9.5, 7.5, 2.5)	3.49 ddd (9, 7, 1.5)	3.58 ddd (9.5, 7, 1.5)	3.15 ddd (10, 6, 2.5)	3.05 ddd (10, 6, 2.5)	3.22 ddd (9.5, 5.5, 2.5)
3	4.59 d (9.5)	4.61 d (9)	4.64 d (9.5)	4.63 d (9)	4.96 d (9.5)	4.82 d (10)	3.62 d (10)	4.76 d (9.5)
5	3.40 br s	3.43 br s	3.50 br s	3.44 br s	3.65 br s	3.22 br s	3.45 br s	3.58 br s
6	4.55 br s	4.55 br s	4.56 br s	4.55 br s	4.61 br s	4.55 br s	5.45 br s	5.50 br s
9	2.32 ddd (14, 4, 1.5)	2.31 m	2.31 dd (13.5, 5.5)	2.31 dd (13, 4)	2.34 dd (13, 5)	2.15 m	2.02 m	2.07 mm
11	1.79 m 20.4 td (14, 4)	1.79 m 2.04 qd (13, 4)	1.77 m 2.04 qd (13, 4)	1.79 m 2.03 qd (13, 3.5)	1.79 m 2.11 qd (13, 4)	1.19 m 1.74 m	1.76 m 1.89 m	1.78 m 1.94 m
12	1.44 m 1.76 m	1.45 m 1.79 m	1.46 m 1.78 m	1.48 m 1.79 m	1.47 m 1.81 m	1.78 m 1.85 m	1.15 m 1.84 m	1.17 m 1.86 m
14	2.26 ddd (5.5, 2, 1.5)	2.26 ddd (5, 5.2, 1.5)	2.24 ddd (6, 2, 1.5)	2.27 ddd (5.5, 2.5, 1.5)	2.23 ddd (6, 2, 1.5)	—	—	—
15	2.88 dd (19, 5.5) 2.82 dd (19, 2)	2.89 dd (18, 5.5) 2.83 dd (18, 2)	2.84 dd (18, 6) 2.78 dd (18, 2)	2.88 dd (18, 5.5) 2.83 dd (18, 2.5)	2.67 dd (18, 6) 2.64 dd (18, 2)	3.47 dt (21, 3) 3.69 dt (21, 1.5)	3.45 dt (21, 2) 4.01 dt (21, 1.5)	3.24 dt (21, 3) 3.54 dt (21, 1.5)
17	5.60 s	5.60 s	5.55 s	5.60 s	5.63 s	5.56 s	5.53 s	5.48 s
21	7.55 dd (1.8, 1)	7.53 dd (1.8, 1)	7.54 dd (1.8, 1)	7.54 dd (1.8, 1)	7.59 dd (1.8, 1)	7.48 dd (1.8, 1)	7.54 dd (1.8, 1)	7.54 dd (1.5, 0.8)
22	6.38 dd (1.8, 1)	6.38 dd (1.8, 1)	6.38 dd (1.8, 1)	6.38 dd (1.8, 1)	6.40 dd (1.8, 1)	6.41 dd (1.8, 1)	6.47 dd (1.8, 1)	6.46 dd (1.5, 0.8)
23	7.44 t (1.8)	7.44 t (1.8)	7.44 t (1.8)	7.44 t (1.8)	7.47 t (1.8)	7.43 t (1.8)	7.41 t (1.8)	7.44 t (1.5)
18[a]	0.99 s	1.00 s	0.98 s	1.00 s	0.95 s	1.03 s	1.01 s	1.01 s
19[a]	1.44 s	1.44 s	1.45 s	1.44 s	1.48 s	1.42 s	1.15 s	1.18 s
28[a]	1.11 s	1.11 s	1.13 s	1.11 s	1.18 s	1.09 s	0.99 s	1.09 s
29[a]	0.86 s	0.87 s	0.90 s	0.86 s	0.94 s	0.80 s	0.94 s	0.92 s
30	5.36 dt (7, 1.5)	5.38 dt (7, 1.5)	5.36 dt (7.5, 1.5)	5.38 dt (6.5, 1.5)	5.46 dt (7, 1.5)	2.15 m 2.81 dd (15.5, 2.5)	2.00 m 3.17 dd (14.5, 2.5)	2.11 dd (15.5, 5.5) 2.67 dd (15.5, 2.5)
COOMe	3.75 s	3.74 s	3.76 s	3.74 s	3.77 s	3.84 s	3.74 s	3.77 s
6-OCOCH$_3$	—	—	—	—	—	—	2.17 s	2.19 s
3-*O*-Acyl								
2′	2.38 q (7)	2.62 septet (7)	—	2.45 sextet (6)	—	2.15 s	—	—
2′-Me	—	1.16 d (7)	1.94 br s	1.12 d (6)	—	—	—	1.88 d (1)
3′	1.12 t (7)	1.17 d (7)	5.64 q (1.5)	1.47 ddd (12.5, 6.5, 6) 1.70 ddd (12.5, 6.5, 6)	—	—	—	6.94 qq (7, 1)
3′-Me	—	—	—	0.92 t (6.5)	—	—	—	1.82 dd (7, 1)
Aromatic H	—	—	—	—	7.38 t (8) 7.55 tt (8, 1) 7.98 dd (8, 1)	—	—	—

δ values in $CDCl_3$. Values in parentheses are coupling constants (Hz). *a*) Assignments were confirmed by NOE experiments. *b*) ^{1}H–^{1}H COSY was measured.

JEOL software. MS and high-resolution MS were obtained with a JEOL JMS-D 300 spectrometer (ionization voltage, 70 eV; accelerating voltage, 3 kV) using a direct inlet system. Column chromatography was done with Mallinckrodt silica gel. Preparative TLC was carried out on Merck Kieselgel GF_{254} plates developed with MeOH–$CHCl_3$ (2:98 or 5:95) or MeOH–benzene (10:90; 15:85; 20:80; and 30:70) and spots were detected by the use of 1%$Ce(SO_4)_2$–aqueous H_2SO_4 (10%) reagent. For drying organic solvents, anhydrous $MgSO_4$ was employed.

Extraction and Separation of Constituents of the Seeds of *S. mahagoni* JACQ The seeds (1.8 kg) of *S. mahagoni*, collected at Medan (North Sumatra, Indonesia) in August, 1987, were divided into the seed coat and cotyledon parts. The seed coat part was pulverized and extracted with boiling MeOH to give a methanolic extract (49 g). The cotyledon part was also pulverized and extracted three times (1 d each) with ether (3 l × 3) at room temperature, and the plant material was further extracted with boiling MeOH (3 l × 3) to give a methanolic extract (109 g).

The above ether solutions were combined and concentrated (about 400 ml) on a water bath to yield a white crystalline substance, which was collected by filtration to give swietenine (**9**) (1.9 g). On standing, the ethereal filtrate yielded an amorphous precipitate (*ca.* 30 g), which was collected by decantation and washed with ether. The mother liquor was concentrated to afford a yellow oily residue (*ca.* 328 g). A portion (101 g) of this oily substance was chromatographed on a silica gel (2 kg) column. The column was eluted successively with benzene (3 l), benzene–CH_2Cl_2 (1:1, 2 l), CH_2Cl_2 (4 l), and MeOH–CH_2Cl_2 (5:95, 2 l) with monitoring by TLC and the eluates were separated into six fractions (frs.): fr. 1, benzene eluate

TABLE IV. ^{13}C-NMR Spectral Data for Swietenins B (**1**), C (**2**), D (**3**), E (**4**), and F (**5**), 3-*O*-Acetylswietenolide (**6**), 6-*O*-Acetylswietenolide (**7**), and 3-*O*-Tigloyl-6-*O*-acetylswietenolide (**8**) from *S. mahagoni*

^{13}C	**1**[a]	**2**[a]	**3**[b]	**4**[b]	**5**[b]	**6**[a]	**7**[a]	**8**[a]
1	216.25 (s)	216.50 (s)	216.39 (s)	216.47 (s)	216.24 (s)	217.59 (s)	218.83 (s)	217.32 (s)
2	48.68 (d)	48.83 (d)	48.83 (d)	48.93 (d)	48.95 (d)	47.86 (d)	49.95 (d)	48.16 (d)
3	78.58 (d)	78.37 (d)	78.84 (d)	78.23 (d)	78.49 (d)	79.94 (d)	78.37 (d)	80.10 (d)
4	38.78 (s)	39.08 (s)	39.02 (s)	39.14 (s)	39.36 (s)	38.72 (s)	39.84 (s)	39.30 (s)
5	45.64 (d)	45.52 (d)	45.46 (d)	45.53 (d)	45.50 (d)	45.22 (d)	43.09 (d)	44.21 (d)
6	72.84 (d)	72.78 (d)	72.84 (d)	72.77 (d)	72.90 (d)	73.33 (d)	73.60 (d)	73.14 (d)
7	175.88 (s)	175.97 (s)	175.89 (s)	176.00 (s)[c]	175.88 (s)	175.45 (s)	171.35 (s)	171.41 (s)
8	138.14 (s)	138.19 (s)	138.51 (s)	138.17 (s)	138.52 (s)	128.52 (s)	128.15 (s)	127.67 (s)
9	57.30 (d)	57.45 (d)	57.51 (d)	57.53 (d)	57.63 (d)	53.59 (d)	52.68 (d)	53.14 (d)
10	50.41 (s)	50.41 (s)	50.41 (s)	50.42 (s)	50.45 (s)	53.23 (s)	54.11 (s)	53.56 (s)
11	21.08 (t)	21.20 (t)	21.23 (t)	21.23 (t)	21.35 (t)	29.76 (t)	18.62 (t)	18.71 (t)
12	34.59 (t)	34.59 (t)	34.61 (t)	34.62 (t)	34.64 (t)	18.96 (t)	28.85 (t)	29.46 (t)
13	36.56 (s)	36.61 (s)	36.64 (s)	36.67 (s)	36.79 (s)	38.08 (s)	37.96 (s)	38.17 (s)
14	45.14 (d)	45.12 (d)	45.09 (d)	45.12 (d)	45.08 (d)	131.46 (s)	131.77 (s)	132.49 (s)
15	29.88 (t)	29.75 (t)	29.60 (t)	29.66 (t)	29.52 (t)	33.59 (t)	33.16 (t)	33.07 (t)
16	169.20 (s)	169.21 (s)	168.68 (s)	169.09 (s)	168.12 (s)	169.44 (s)	171.35 (s)	169.38 (s)
17	77.23 (d)	77.17 (d)	77.23 (d)	77.17 (d)	77.24 (d)	80.92 (d)	80.37 (d)	81.01 (d)
20	121.26 (s)	121.20 (s)	121.20 (s)	121.22 (s)	121.37 (s)	120.72 (s)	120.81 (s)	120.75 (s)
21	140.57 (d)	140.54 (d)	140.57 (d)	140.54 (d)	140.66 (d)	141.12 (d)	141.54 (d)	141.48 (d)
22	109.27 (d)	109.24 (d)	109.27 (d)	109.24 (d)	109.32 (d)	109.70 (d)	110.03 (d)	109.94 (d)
23	143.12 (d)	143.17 (d)	143.15 (d)	143.17 (d)	143.18 (d)	143.09 (d)	142.82 (d)	143.03 (d)
18	21.60 (q)	21.46 (q)	21.38 (q)	21.40 (q)	21.26 (q)	18.41 (q)	17.74 (q)	17.50 (q)
19	16.47 (q)	16.47 (q)	17.90 (q)	16.45 (q)	16.53 (q)	17.53 (q)	17.04 (q)	16.80 (q)
28	22.99 (q)	23.01 (q)	22.93 (q)[c]	23.08 (q)	22.89 (q)[c]	23.33 (q)	23.21 (q)	23.14 (q)
29	22.78 (q)	22.75 (q)	22.89 (q)[c]	22.77 (q)	22.83 (q)[c]	23.08 (q)	23.60 (q)	23.66 (q)
30	123.51 (d)	123.42 (d)	123.39 (d)	123.46 (d)	123.57 (d)	33.89 (t)	33.65 (t)	33.92 (t)
$COO\underline{C}H_3$	53.35 (q)	53.38 (q)	53.37 (q)	53.40 (q)	53.40 (q)	53.17 (q)	53.05 (q)	53.14 (q)
6-$O\underline{C}OCH_3$	—	—	—	—	—	—	170.26 (s)	169.80 (s)
6-$OCO\underline{C}H_3$	—	—	—	—	—	—	20.99 (q)	20.99 (q)
3-$OCOR_1$								
1′	173.75 (s)	176.20 (s)	166.47 (s)	175.65 (s)[c]	165.55 (s)	170.29 (s)	—	167.25 (s)
2′	27.18 (t)	33.88 (d)	135.35 (s)	40.69 (d)	—	21.14 (q)	—	128.97 (s)
3′	8.82 (q)	18.44 (q)	126.73 (t)	26.21 (t)	—	—	—	139.39 (d)
2′-$\underline{C}H_3$	—	18.89 (q)	16.48 (q)	15.98 (q)	—	—	—	12.34 (q)
3′-$\underline{C}H_3$	—	—	—	11.40 (q)	—	—	—	14.61 (q)
Aromatic C	—	—	—	—	128.72 (d)	—	—	—
					129.08 (s)			
					129.47 (d)			
					133.51 (d)			

δ values in $CDCl_3$. Multiplicities of carbon signals were determined by the DEPT method and are indicated as, s, d, t, and q, *a*) ^{1}H–^{13}C and ^{1}H–^{13}C long-range COSY spectra were measured. *b*) Signal assignments are based on the comparisons of the chemical shift values with those of **1** and **2**. *c*) Assignments may be interchanged in each compound.

(68.32 g); fr. 2, CH_2Cl_2–benzene (1 : 1) eluate (0.55 g); fr. 3, CH_2Cl_2 eluate (3.46 g); fr. 4, MeOH–CH_2Cl_2 (5 : 95) eluate (7.57 g); fr. 5, MeOH–CH_2Cl_2 (5 : 95) eluate (9.68 g); fr. 6, MeOH–CH_2Cl_2 (5 : 95) eluate (1.65 g).

Frs. 1, 2, and 3 were characterized as mixtures of fatty acids and their esters by IR and ^{1}H-NMR spectra, while frs. 4, 5, and 6 were characterized as complex mixtures of terpenoid compounds. Among these, fr. 5 (9.68 g) was again separated by chromatography on silica gel (180 g) with MeOH–CH_2Cl_2 (1 : 99; 2 l) as the eluent to give the following fractions: frs. 1—11 (150 mg) (mixture of fatty acids and their esters), frs. 12—14 (630 mg), frs. 15, 16 (330 mg), frs. 17—19 (385 mg), frs. 20—41 (1.76 g), frs. 42—46 (555 mg), frs. 47—51 (360 mg), frs. 52—54 (205 mg), frs. 55, 56 (215 mg), frs. 57—68 (300 mg), frs. 69—73 (195 mg), frs. 74—88 (3.36 g), and frs. 89—91 (770 mg).

Treatment of Frs. 12—14 Fractions 12—14 were combined and subjected to preparative TLC with MeOH–$CHCl_3$ (1 : 99) to give two fractions, the less polar one of which was subjected repeatedly to preparative TLC with AcOEt–benzene (10 : 90) and separated into four bands. The most mobile band gave secomahoganin (**28**) (10 mg) as a colorless oil. The next most mobile band gave swietemahonin F (**24**) (25 mg), colorless needles (AcOEt–isopropyl ether), mp 278—280 °C. The third most mobile band gave swietemahonolide (**26**) (6 mg), colorless needles (AcOEt–isopropyl ether), mp 212—213 °C. The least mobile band gave swietemahonin C (**21**) (8.2 mg), colorless needles (AcOEt–isopropyl ether), mp 309—310 °C.

On the other hand, the more polar fraction was separated by preparative TLC with AcOEt–benzene (10 : 90) to afford five compounds: 3-*O*-tigloyl-6-*O*-acetylswietenolide (**8**) (2.2 mg), 6α-acetoxygedunin (**18**) (4.2 mg), 7-deacetoxy-7-oxogedunin (**17**) (5 mg), methyl angolensate (**16**) (10 mg), and swietemahonin B (**20**) (16.2 mg), colorless needles (from AcOEt–isopropyl ether), mp 286—287 °C, in the order of increasing polarity.

3-*O*-Tigloyl-6-*O*-acetylswietenolide (**8**): Colorless needles (from AcOEt–isopropyl ether), mp 156—158 °C, $[\alpha]_D$ −7.3° (c=1.32). IR ν_{max} cm^{-1}: 1735, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables III and IV. CD ($c=1.64\times10^{-4}$, $CHCl_3$) [θ] (nm): -4.02×10^3 (293), -4.40×10^3 (298), -2.20×10^3 (310). MS *m/z*: 610 (M^+), 550 ($M^+-e'-H$), 514 (M^+-b'), 486 (M^+-c'), 479 (M^+-d'), 426 ($M^+-c'-e'-H$), 414 ($M^+-a'-H-b'$), 386 ($M^+-a'-H-c'$), 379 ($M^+-a'-H-d'$), 355 ($M^+-c'-d'$), 326 ($M^+-a'-H-c'-e'$), 283 ($M^+-a'-H-b'-d'$), 255 ($M^+-a'-H-c'-d'$), 83 (base peak). High-resolution MS *m/z*: Found 610.2761, Calcd for $C_{34}H_{42}O_{10}$ (M^+) 610.2777; Found 550.2517, Calcd for $C_{32}H_{38}O_8$ 550.2566; Found 514.2556, Calcd for $C_{29}H_{38}O_8$ 514.2566; Found 486.2615, Calcd for $C_{28}H_{38}O_7$ 486.2616; Found 386.2091, Calcd for $C_{23}H_{30}O_5$ 386.2092; Found 379.1863, Calcd for $C_{24}H_{27}O_4$ 379.1909; Found 326.1894, Calcd for $C_{21}H_{26}O_3$ 326.1882; Found 283.1720, Calcd for $C_{19}H_{23}O_2$ 283.1698; Found 255.1778, Calcd for $C_{18}H_{23}O$ 255.1749.

6α-Acetoxygedunin (**18**): Colorless needles (from AcOEt–isopropyl ether), mp 290—291.5 °C, $[\alpha]_D$ +24.4° (c=0.46). IR ν_{max} cm^{-1}: 1740, 1720, 1610, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. MS *m/z*: 540 (M^+), 417, 386, 357, 315, 297, 279. High-resolution MS *m/z*: Found 540.2369, Calcd for $C_{30}H_{36}O_9$ (M^+) 540.2359. The identity of **18** was established by comparison of the ^{1}H-NMR spectrum with the reported

data.[15]

7-Deacetoxy-7-oxogedunin (**17**): Colorless needles (from AcOEt–isopropyl ether), mp 264—266 °C, $[\alpha]_D$ −11.4° (c=0.94). IR ν_{max} cm^{-1}: 1740, 1720, 1670, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 438 (M^+), 423, 392, 381, 326, 315 (base peak). High-resolution MS m/z: Found 438.2034, Calcd for $C_{26}H_{30}O_6$ (M^+) 438.2041. Identity was confirmed by comparison of the ^{1}H-NMR data with the published data.[14]

Methyl angolensate (**16**): Colorless needles (from AcOEt–isopropyl ether), mp 191—193 °C, $[\alpha]_D$ −4.2° (c=2.14). IR ν_{max} cm^{-1}: 1740, 1720, 1710, 1510, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 470 (M^+), 374, 359, 332, 210. High-resolution MS m/z: Found 470.2346, Calcd for $C_{27}H_{34}O_7$ (M^+) 470.2342. The identity of **16** was confirmed by comparisons of the ^{1}H- and ^{13}C-NMR spectra and MS with the reported data.[13]

Treatment of Frs. 15, 16 Fractions 15, 16 were separated by preparative TLC with AcOEt–benzene (15:85) to give swietenine acetate (**10**) (7.6 mg), 3-*O*-tigloyl-6-*O*-acetylswietenolide (**8**) (11.2 mg), 6α-acetoxygedunin (**18**) (4.6 mg), swietemahonin B (**20**) (19 mg), 7-deacetoxy-7-oxogedunin (**17**) (3.2 mg), methyl angolensate (**16**) (27.2 mg), and 3,6-*O*,*O*-diacetylswietenolide (**12**) (27 mg) in the order of increasing polarity.

Swietenine Acetate (**10**): Colorless needles (from AcOEt–isopropyl ether), mp 129—131 °C, $[\alpha]_D$ −14.2° (c=0.70). IR ν_{max} cm^{-1}: 1740, 1730, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 610 (M^+), 510 (M^+−a−H), 468, 379 (M^+−a−H−c), 83 ($C_4H_7CO^+$). High-resolution MS m/z: Found 610.2815, Calcd for $C_{34}H_{42}O_{10}$ (M^+) 610.2777. Its identity was confirmed by comparing the spectral data with those of the acetate (**10**) obtained by acetylation of **9**.

3,6-*O*,*O*-Diacetylswietenolide (**12**): Colorless needles (from AcOEt–isopropyl ether), mp 154—155 °C, $[\alpha]_D$ −13.7° (c=0.62). IR ν_{max} cm^{-1}: 1730, 1715, 1705, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 570 (M^+), 510 (M^+−a′−H), 474 (M^+−b′), 446 (M^+−c′), 439 (M^+−d′), 414 (M^+−b′−e′−H), 386 (M^+−c′−e′−H), 354 (M^+−a′−H−b′−e′−H), 343 (M^+−b′−d′), 326 (M^+−a′−H−c′−e′−H), 315 (M^+−c′−d′), 301, 283 (M^+−a′−H−b′−d′), 255 (M^+−a′−H−c′−d′). High-resolution MS m/z: Found 570.2449, Calcd for $C_{31}H_{38}O_{10}$ (M^+) 570.2464. The identity of **12** was confirmed by comparing the spectral data with those of the acetate (**12**) obtained by acetylation of **11**.

Treatment of Frs. 17—19 Combined fractions 17—19 were subjected repeatedly to preparative TLC with MeOH–$CHCl_3$ (2:98) as the eluent and separated into three bands. The most mobile band gave khayasin T (**14**) (11.7 mg). The middle band gave 3-*O*-tigloyl-6-*O*-acetylswietenolide (**8**) (13 mg). The least mobile band gave 3,6-*O*,*O*-diacetylswietenolide (**12**) (51.6 mg).

Khayasin T (**14**): Colorless needles (from AcOEt–isopropyl ether), mp 161—163 °C, $[\alpha]_D$ −7.3° (c=1.02). IR ν_{max} cm^{-1}: 1735, 1720, 1705, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 552 (M^+), 456 (M^+−b′), 428 (M^+−c′), 356 (M^+−a′−H−b′), 328 (M^+−a′−H−c′), 313 (M^+−a′−H−c′−CH_3), 83 ($C_4H_7CO^+$, base peak). High-resolution MS m/z: Found 552.2708, Calcd for $C_{32}H_{40}O_8$ (M^+) 552.2722. The identity of **14** was confirmed by comparisons of the ^{1}H-NMR and MS with the literature values.[11]

Treatment of Frs. 20—41 A portion (200 mg) of combined fractions 20—41 was separated by preparative TLC with AcOEt–benzene (20:80) to give swietenine acetate (**10**) (45.8 mg), 3,6-*O*,*O*-diacetylswietenolide (**12**) (62.8 mg), swietemahonin E (**23**) (13 mg), colorless needles (from AcOEt–isopropyl ether), mp 151—152 °C, and swietemahonin A (**19**) (4.4 mg), colorless needles (from AcOEt–isopropyl ether), mp 174—174.5 °C, in the order of increasing polarity.

Treatment of Frs. 42—46 A portion (200 mg) of frs. 42—46 was separated by preparative TLC with AcOEt–benzene (20:80) into three bands. The most mobile band gave swietenine acetate (**10**) (81 mg). The middle band gave swietenine (**9**) (85 mg). The least mobile band gave swietemahonin E (**23**) (21 mg).

Swietenine (**9**): Colorless needles (from AcOEt–isopropyl ether), mp 276—277.5 °C, $[\alpha]_D$ −19.4° (c=0.50). IR ν_{max} cm^{-1}: 3550, 1730, 1710, 1650, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. CD (c=2.0×10^{-3}, $CHCl_3$) [θ] (nm): −1.00×10^{-4} (292). MS m/z: 568 (M^+), 468 (M^+−a−H), 379 (M^+−a−H−c), 330 (M^+−a−H−b), 83 (base peak). High-resolution MS m/z: Found 568.2664, Calcd for $C_{32}H_{40}O_9$ (M^+) 568.2671. Identity of **9** was confirmed by comparisons of the ^{1}H- and ^{13}C-NMR spectra with those reported in the literature.[6]

Treatment of Frs. 47—51 Fractions 47—51 were subjected to preparative TLC with AcOEt–benzene (15:85) to give four fractions. The first fraction gave swietenine acetate (**10**) (23.8 mg). The second fraction was further purified by preparative TLC with hexane–ether (50:50), and the more polar band afforded 3-*O*-tigloylswietenolide (**13**) (7.0 mg), while the less polar band gave swietenin E (**4**) (2.5 mg). The third fraction was also separated by preparative TLC using hexane–ether (50:50) as the eluent into three bands. The most mobile band gave swietenin C (**2**) (9.6 mg). The next most mobile band gave swietenin D (**3**) (2.0 mg). The least mobile band gave swietenin F (**5**) (2.6 mg). The fourth fraction was purified repeatedly by preparative TLC with MeOH–benzene (2:98), giving 3-*O*-acetylswietenolide (**6**) (16.1 mg) from the less polar band and swietemahonin A (**19**) (33 mg) from the more polar band.

3-*O*-Tigloylswietenolide (**13**): Colorless needles (from AcOEt–isopropyl ether), mp 208—209 °C, $[\alpha]_D$ −12.4° (c=0.63). IR ν_{max} cm^{-1}: 3500, 1730, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 568 (M^+), 550 (M^+−H_2O), 479 (M^+−d′), 472 (M^+−b′), 468 (M^+−a′−H), 444, 426, 383 (M^+−b′−d′), 355 (M^+−c′−d′), 283, 255 (M^+−a′−H−c′−d′), and 83 ($C_4H_7CO^+$, base peak). High-resolution MS m/z: Found 568.2656, Calcd for $C_{32}H_{40}O_9$ (M^+) 568.2671. This compound was identified as **13** by spectral comparisons with the published values.[10]

3-*O*-Acetylswietenolide (**6**): Colorless needles (from AcOEt–isopropyl ether), mp 136—138 °C, $[\alpha]_D$ −17.8° (c=0.49). IR ν_{max} cm^{-1}: 3550, 1735, 1720, 1710, 1510, 880. ^{1}H- and ^{13}C-NMR: Tables III and IV. CD (c=6.3×10^{-5}, $CHCl_3$) [θ] (nm): −3.65×10^4 (293), −3.57×10^4 (298), −1.98×10^4 (309). MS m/z: 528 (M^+), 468 (M^+−a′−H), 439 (M^+−d′), 432 (M^+−b′), 404 (M^+−c′), 386 (M^+−c′−H_2O), 343 (M^+−b′−d′), 301 (base peak), 283 (M^+−a′−H−b′−d′), 255 (M^+−a′−H−c′−d′). High-resolution MS m/z: Found 528.2371, Calcd for $C_{29}H_{36}O_9$ (M^+) 528.2358; Found 439.2140, Calcd for $C_{26}H_{31}O_6$ 439.2121; Found 432.2142, Calcd for $C_{24}H_{32}O_7$ 432.2147; Found 404.2213, Calcd for $C_{23}H_{32}O_6$ 404.2199; Found 343.1915, Calcd for $C_{21}H_{27}O_4$ 343.1910; Found 283.1696, Calcd for $C_{19}H_{23}O_2$ 283.1698; Found 255.1736, Calcd for $C_{18}H_{23}O$ 255.1748.

Swietenin C (**2**): Colorless needles (from AcOEt–isopropyl ether), mp 238—239 °C, $[\alpha]_D$ −14.9° (c=0.63). IR ν_{max} cm^{-1}: 3500, 1735, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables III and IV. CD (c=2.2×10^{-3}, $CHCl_3$) [θ] (nm): −9.50×10^3 (293). MS m/z: 556 (M^+, base peak), 468 (M^+−a−H), 418 (M^+−b), 379 (M^+−a−H−c), 330 (M^+−a−H−b). High-resolution MS m/z: Found 556.2683, Calcd for $C_{31}H_{40}O_9$ (M^+) 556.2673; Found 468.2135, Calcd for $C_{27}H_{32}O_7$ 468.2148; Found 379.1924, Calcd for $C_{24}H_{27}O_4$ 379.1909; Found 330.1784, Calcd for $C_{20}H_{26}O_4$ 330.1830.

Swietenin D (**3**): Colorless needles (from AcOEt–isopropyl ether), mp 234—235 °C, $[\alpha]_D$ −33.0° (c=0.23). IR ν_{max} cm^{-1}: 3500, 1735, 1720, 1700, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables III and IV. CD (c=3.0×10^{-4}, $CHCl_3$) [θ] (nm): −1.57×10^4 (293). MS m/z: 554 (M^+, base peak), 468 (M^+−a−H), 416 (M^+−b), 379 (M^+−a−H−c), 330 (M^+−a−H−b). High-resolution MS m/z: Found 554.2496, Calcd for $C_{31}H_{38}O_9$ (M^+) 554.2515; Found 468.2147, Calcd for $C_{27}H_{32}O_7$ 468.2147; Found 379.1911, Calcd for $C_{24}H_{27}O_4$ 379.1910; Found 330.1830, Calcd for $C_{20}H_{26}O_4$ 330.1831.

Swietenin E (**4**): Colorless needles (from AcOEt–isopropyl ether), mp 222—224 °C, $[\alpha]_D$ −31.5° (c=0.26). IR ν_{max} cm^{-1}: 3500, 1735, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables III and IV. CD (c=9.4×10^{-4}, $CHCl_3$) [θ] (nm): −1.11×10^4 (293). MS m/z: 570 (M^+, base peak), 468 (M^+−a−H), 432 (M^+−b), 379 (M^+−a−H−c), 330 (M^+−a−H−b). High-resolution MS m/z: Found 570.2791, Calcd for $C_{32}H_{42}O_9$ (M^+) 570.2828; Found 468.2170, Calcd for $C_{27}H_{32}O_7$ 468.2148; Found 432.2507, Calcd for $C_{25}H_{36}O_6$ 432.2511; Found 379.1879, Calcd for $C_{24}H_{27}O_4$ 379.1909; Found 330.1835, Calcd for $C_{20}H_{26}O_4$ 330.1831.

Swietenin F (**5**): Colorless needles (from AcOEt–isopropyl ether), mp 120—122 °C, $[\alpha]_D$ −56.2° (c=0.16). IR ν_{max} cm^{-1}: 3500, 1735, 1720, 1700, 1600, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables III and IV. CD (c=2.3×10^{-4}, $CHCl_3$) [θ] (nm): −1.91×10^4 (292). MS m/z: 590 (M^+), 468 (M^+−a−H), 452 (M^+−b), 379 (M^+−a−H−c), 330 (M^+−a−H−b), 105 ($C_6H_5CO^+$, base peak). High-resolution MS m/z: Found 590.2506, Calcd for $C_{34}H_{38}O_9$ (M^+) 590.2514; Found 468.2152, Calcd for $C_{27}H_{32}O_7$ 468.2148; Found 330.1786, Calcd for $C_{20}H_{26}O_4$ 330.1830.

Treatment of Frs. 52—54 Fractions 52—54 were subjected to preparative TLC with AcOEt–benzene (20:80) to give four fractions. The first fraction was again separated by preparative TLC with MeOH–benzene (3:97), giving mahonin (**27**) (5.0 mg), colorless needles, mp 148—150 °C, from the less polar band and swietenine (**9**) (9.0 mg) from the more polar band. The second fraction was recrystallized from MeOH–isopropyl ether to give swietenine (**9**) (51.2 mg). The third fraction was recrystallized from AcOEt–isopropyl ether to give swietenin B (**1**) (10.0 mg). The fourth

fraction was recrystallized from AcOEt–isopropyl ether to give swietenolide (**11**) (46.6 mg).

Swietenin B (**1**): Colorless needles (from AcOEt–isopropyl ether), mp 113—115 °C, $[\alpha]_D$ −11.5° (c=0.92). IR ν_{max} cm^{-1}: 3500, 1735, 1720, 1700, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables III and IV. CD ($c=2.7\times10^{-3}$, $CHCl_3$) [θ] (nm): -6.67×10^3 (293). MS m/z: 542 (M^+, base peak), 468 (M^+-a-H), 404 (M^+-b), 379 ($M^+-a-H-c$), 330 ($M^+-a-H-b$). High-resolution MS m/z: Found 542.2477, Calcd for $C_{30}H_{38}O_9$ (M^+) 542.2515; Found 468.2166, Calcd for $C_{27}H_{32}O_7$ 468.2148; Found 404.2174, Calcd for $C_{23}H_{32}O_6$ 404.2199; Found 379.1921, Calcd for $C_{24}H_{27}O_4$ 379.1909; Found 330.1792, Calcd for $C_{20}H_{26}O_4$ 330.1830.

Swietenolide (**11**): Colorless needles (from AcOEt–isopropyl ether), mp 174—175 °C, $[\alpha]_D$ −19.6° (c=0.50). IR ν_{max} cm^{-1}: 3550, 1730, 1720, 1510, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. CD ($c=1.37\times10^{-3}$, $CHCl_3$) [θ] (nm): -3.43×10^3 (295), -4.05×10^3 (301), -2.55×10^3 (310). MS m/z: 486 (M^+), 397 (M^+-d'), 390 (M^+-b'), 362 (M^+-c'), 301 ($M^+-c'-d'$), 283 ($M^+-c'-d'-H_2O$), 273 ($M^+-c'-d'$), 255. High-resolution MS m/z: Found 486.2248, Calcd for $C_{27}H_{34}O_8$ (M^+) 486.2235; Found 397.1969, Calcd for $C_{24}H_{29}O_5$ 397.2014; Found 390.2026, Calcd for $C_{22}H_{30}O_6$ 390.2041; Found 362.2095, Calcd for $C_{21}H_{30}O_5$ 362.2093; Found 301.1787, Calcd for $C_{19}H_{25}O_3$ 301.1802; Found 283.1670, Calcd for $C_{19}H_{23}O_2$ 283.1697; Found 273.1878, Calcd for $C_{18}H_{25}O_2$ 273.1854.

Treatment of Frs. 55, 56 Fractions 55 and 56 were combined and subjected to preparative TLC with AcOEt–benzene (20 : 80) as the eluent. The more mobile band afforded swietenine (**9**) (98 mg), and the less mobile band gave a mixture, which was again separated by preparative TLC with AcOEt–benzene (20 : 80) to give 3-*O*-acetylswietenolide (**6**) (40.0 mg) from the less polar band and swietemahonin D (**22**) (2.7 mg), colorless needles (from AcOEt–isopropyl ether), mp 191—192 °C, from the more polar band.

Treatment of Frs. 57—73 Combined frs. 57—73 were subjected to preparative TLC with AcOEt–benzene (20 : 80). The more mobile band gave swietenine (**9**) (142 mg), while the less mobile band gave a mixture, which was purified repeatedly by preparative TLC with AcOEt–benzene (20 : 80) to afford swietenine (**9**) (6.3 mg) and swietemahonin G (**25**) (6.1 mg), colorless needles (from AcOEt–isopropyl ether), mp 135—137 °C.

Treatment of Frs. 74—88 A portion (150 mg) of frs. 74—88 was separated by preparative TLC with AcOEt–benzene (20 : 80) into three bands. The most mobile band gave proceranolide (**15**) (20 mg). The middle band gave 6-*O*-acetylswietenolide (**7**) (18.4 mg). The least mobile band gave swietenolide (**11**) (84 mg).

Proceranolide (**15**): Colorless needles (from AcOEt–isopropyl ether), mp 185—188 °C, $[\alpha]_D$ −20.8° (c=0.53). IR ν_{max} cm^{-1}: 3500, 1730, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. MS m/z: 470 (M^+), 452, 374, 346, and 328. High-resolution MS m/z: Found 470.2299, Calcd for $C_{27}H_{34}O_7$ (M^+) 470.2303. Its identity was confirmed by comparing the ^{1}H- and ^{13}C-NMR data with the reported values.[12]

6-*O*-Acetylswietenolide (**7**): Colorless needles (from AcOEt–isopropyl ether), mp 212—215 °C, $[\alpha]_D$ −6.5° (c=1.82). IR ν_{max} cm^{-1}: 3500, 1740, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables III and IV. CD ($c=8.8\times10^{-4}$, $CHCl_3$) [θ] (nm): -2.73×10^3 (293), -2.95×10^3 (299), -1.99×10^3 (308). MS m/z: 528 (M^+), 510 (M^+-H_2O), 468 ($M^+-e'-H$), 432 (M^+-b'), 404 (M^+-c'), 397 (M^+-d'), 372 ($M^+-b'-e'-H$), 344 ($M^+-c'-e'-H$), 326 ($M^+-a'-H-c'-e'-H$), 301 ($M^+-b'-d'$, base peak), 283 ($M^+-a'-H-c'-d'$), 273 ($M^+-c'-d'$), 255 ($M^+-a'-H-c'-d'$). High-resolution MS m/z: Found 528.2334, Calcd for $C_{29}H_{36}O_9$ (M^+) 528.2358; Found 432.2118, Calcd for $C_{24}H_{32}O_7$ 432.2147; Found 404.2155, Calcd for $C_{23}H_{32}O_6$ 404.2199; Found 397.1987, Calcd for $C_{24}H_{29}O_5$ 397.2014; Found 344.1977, Calcd for $C_{21}H_{28}O_4$ 344.1987; Found 326.1835, Calcd for $C_{21}H_{26}O_3$ 326.1882; Found 301.1774, Calcd for $C_{19}H_{25}O_3$ 301.1803; Found 283.1678, Calcd for $C_{19}H_{23}O_2$ 283.1697; Found 273.1840, Calcd for $C_{18}H_{25}O_2$ 273.1854; Found 255.1725, Calcd for $C_{18}H_{23}O$ 255.1748.

Treatment of Frs. 89—91 Combined fractions 89—91 were separated further by preparative TLC with AcOEt–benzene (30 : 70), giving two bands. The less polar band afforded swietenolide (**11**) (158 mg), while the more polar band gave a small amount of swietemahonin A (**19**) (12 mg), colorless needles (from AcOEt–isopropyl ether), mp 174—174.5 °C.

Treatment of the Amorphous Precipitate from the Ether Extract A portion (500 mg) of the amorphous precipitate was subjected to preparative TLC with AcOEt–benzene (20 : 80) to give four fractions. The first fraction was further separated by preparative TLC with AcOEt–benzene (20 : 80). The most mobile band gave swietemahonin F (**24**) (6.2 mg). The next most mobile band gave 3-*O*-tigloyl-6-*O*-acetylswietenolide (**8**) (8.0 mg). The third most mobile band gave swietenine acetate (**10**) (34 mg). The least mobile band gave 7-deacetoxy-7-oxogedunin (**17**) (3.0 mg). The second fraction was further separated by preparative TLC with MeOH–benzene (5 : 95) and separated into four bands. The most mobile band gave 3,6-*O*,*O*-diacetylswietenolide (**12**) (32.4 mg). The next most mobile band gave methyl angolensate (**16**) (8.2 mg). The third most mobile band gave 3-*O*-tigloylswietenolide (**13**) (2.6 mg). The least mobile band gave swietenine (**9**) (20 mg). The third fraction was separated by preparative TLC with MeOH–benzene (5 : 95) into three bands. The most mobile band gave swietemahonin E (**23**) (10.8 mg). The middle band gave 3-*O*-acetylswietenolide (**6**) (15.7 mg). The least mobile band gave swietemahonin A (**19**) (6.0 mg). The least fraction was recrystallized from AcOEt–isopropyl ether to give an additional crop of swietenolide (**11**) (76.3 mg).

Acetylation of 3-*O*-Acetylswietenolide (6) 3-*O*-Acetylswietenolide (**6**) (0.5 mg) was treated with acetic anhydride (0.1 ml) and pyridine (0.1 ml) at room temperature for 1 d. Then, the reaction mixture was worked up in the usual manner and the product was subjected to preparative TLC with AcOEt–benzene (15 : 85) to give a diacetate (**12**) (0.3 mg), which was identified as 3,6-*O*,*O*-diacetylswietenolide (**12**) by TLC and ^{1}H-NMR comparisons.

Acetylation of 6-*O*-Acetylswietenolide (7) 6-*O*-Acetylswietenolide (**7**) (1.2 mg) was treated with acetic anhydride (0.1 ml) and pyridine (0.1 ml) at room temperature for 1 d. The reaction mixture was worked up in the usual manner and the product was subjected to preparative TLC with AcOEt–benzene (15 : 85) to give a diacetate (**12**) (0.5 mg), which was identified as 3,6-*O*,*O*-diacetylswietenolide (**12**) by TLC and ^{1}H-NMR comparisons.

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References and Notes

1) A part of this work was reported in our preliminary communications: *a*) S. Kadota, L. Marpaung, T. Kikuchi, and H. Ekimoto, *Tetrahedron Lett.*, **30**, 1111 (1989); *b*) S. Kadota, L. Marpaung, T. Kikuchi, and H. Ekimoto, *Chem. Pharm. Bull.*, **37**, 1419 (1989).
2) J. D. Hooker and B. D. Jackson (ed.), "Index Kewensis, an Enumeration of the Genera and Species of Flowering Plants," Vol. II, Oxford University Press, London, 1895, p. 1020. The scientific name of this plant is occasionally noted as *Swietenia mahogani* (L.) JACQ, but, in this paper, we used the name *Swietenia mahagoni* JACQ. according to the Index Kewensis.
3) D. A. H. Taylor, *J. Chem. Soc., Chem. Commun.*, **1969**, 58.
4) E. J. Corey, C.-P. Chen, and M. J. Parry, *Tetrahedron Lett.*, **29**, 2899 (1988); D. Hosford, J. M. Mencia-Huerta, C. Page, and P. Braquet, *Phytotherapy Research*, **2**, 1 (1988).
5) Structure elucidation of the other new compounds will be reported in detail in forthcoming papers.
6) J. D. Connolly, R. Henderson, R. McCrindle, K. H. Overton, and N. S. Bhacca, *J. Chem. Soc.*, **1965**, 6935.
7) A. R. H. Taylor and D. A. H. Taylor, *Phytochemistry*, **22**, 2870 (1983).
8) J. D. Connolly, R. McCrindle, K. H. Overton, and W. D. C. Warnock, *Tetrahedron*, **24**, 1507 (1968).
9) K. C. Chan, T. S. Tang, and H. T. Toh, *Phytochemistry*, **15**, 429 (1976).
10) E. K. Adesogan and D. A. H. Taylor, *J. Chem. Soc.*, (*C*), **1970**, 1710.
11) E. K. Adesogan and D. A. H. Taylor, *J. Chem. Soc.*, (*C*), **1968**, 1974.
12) B. L. Sondengan, C. S. Kamga, and J. D. Connolly, *Phytochemistry*, **19**, 2488 (1980).
13) C. W. L. Bevan, J. D. Powell, D. A. H. Taylor, T. G. Halsall, P. Toft, and M. Welfold, *J. Chem. Soc.*, (*C*), **1967**, 163; W. R. Chan, K. E. Magnus, and B. S. Mootoo, *ibid.*, **1967**, 171.
14) W. D. Ollis, A. D. Ward, H. Meirelles De Oliveira, and R. Zelnik, *Tetrahedron*, **26**, 1637 (1970).
15) D. Lavie, E. C. Levy, and R. Zelnik, *Bioorganic Chemistry*, **2**, 59 (1972).
16) A. Bax and R. Freeman, *J. Mag. Reson.*, **44**, 542 (1981).
17) A. T. McPhail and G. A. Sim, *Tetrahedron Lett.*, **1964**, 2599. The optical rotatory dispersion curve of swietenine shows a negative Cotton effect, see ref. 6.
18) D. A. H. Taylor, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 437.