Constituents of the Seeds of *Swietenia mahagoni* JACQ. II.[1] Structures of Swietemahonin A, B, C, D, E, F, and G and Swietemahonolide[2]

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Eight new tetranortriterpenoids, swietemahonin A—G and swietemahonolide, were isolated from the cotyledons of seeds of *Swietenia mahagoni*. The structures 1—8 are proposed for these compounds, respectively, based mainly on detailed analyses of the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra by the use of two-dimensional NMR techniques (^{1}H–^{1}H chemical shift correlation spectroscopy (COSY), ^{1}H–^{13}C COSY, and ^{1}H–^{13}C long-range COSY).

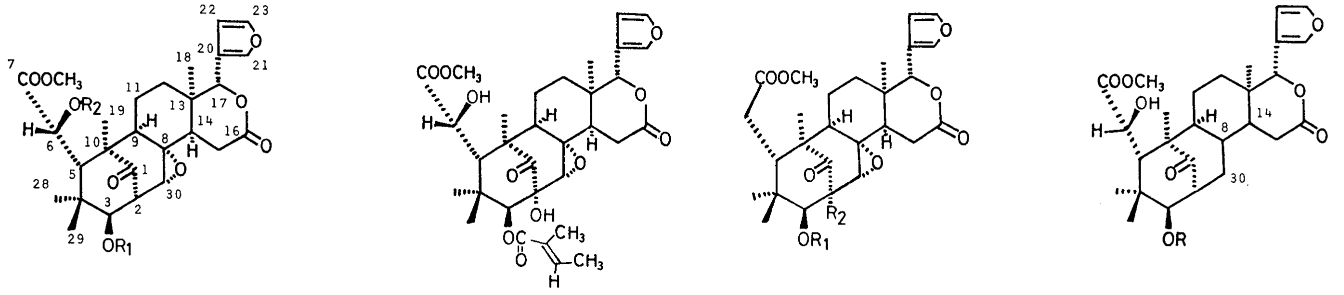
Keywords *Swietenia mahagoni*; swietemahonin A; swietemahonin B; swietemahonin C; swietemahonin D; swietemahonin E; swietemahonin F; swietemahonin G; swietemahonolide; tetranortriterpenoid; 2D-NMR

In the preceding paper,[1] we reported the isolation of eighteen new tetranortriterpenoids together with ten known compounds from the seeds of *Swietenia mahagoni* JACQ., a valuable timber tree of the family Meliaceae, the seeds of which are used as a folk medicine for treatment of hypertension, diabetes, and malaria in Indonesia. We also reported the structures of eight new compounds, swietenins B—F, 3-*O*-acetylswietenolide, 6-*O*-acetylswietenolide, and 3-*O*-tigloyl-6-*O*-acetylswietenolide.[1] In this paper we wish to describe in detail the structure elucidation of eight other compounds named swietemahonin A (**1**), swietemahonin B (**2**), swietemahonin C (**3**), swietemahonin D (**4**), swietemahonin E (**5**), swietemahonin F (**6**), and swietemahonin G (**7**) and swietemahonolide (**8**), by the use of two-dimensional nuclear magnetic resonance (2D-NMR) spectral techniques.

The ether extract of the cotyledon part of seeds of *S. mahagoni* was roughly separated by silica gel column chromatography and the fractions were carefully separated by repeated preparative thin layer chromatography (TLC) to give **1**—**8** along with swietenins B—F, 3-*O*-acetylswietenolide, 6-*O*-acetylswietenolide, and 3-*O*-tigloyl-6-*O*-acetylswietenolide and ten known tetranortriterpenoids.[1]

Swietemahonin A (**1**) was obtained as colorless needles, mp 174—174.5 °C, $[\alpha]_D$ $-12.2°$ ($CHCl_3$), and has the molecular formula $C_{30}H_{38}O_{10}$ (M^+ 558.2478, Calcd 558.2464). In the infrared (IR) spectrum, it showed absorptions at 3500 (OH), 1735 (lactone), 1725 (ester), 1710 (ketone), 1500 and 880 (furan) cm^{-1}. The ^{1}H-NMR spectrum of **1**, which was fully analyzed by the application of ^{1}H–^{1}H chemical shift correlation spectroscopy (COSY)[3] (Fig. 1), indicated the presence of a methyl ester (δ 3.92), a propionyl group (δ 1.24 and 2.50), a lactone (δ 5.12), a β-substituted furan (δ 6.39, 7.43, and 7.44), a hydroxy-bearing methine (δ 4.46), and four *tert*-methyl groups (δ 0.88, 1.05, 1.11, and 1.34). Also it showed a signal (δ 4.94) which could be assigned to a proton geminal to an *O*-acyl grouping (Table I). On the other hand, the ^{13}C-NMR spectrum of **1** exhibited signals due to a ketone (δ 213.51) and three ester carbonyls (δ 171.20, 173.14, and 175.62) (Table II). The above spectral data, compared with those of swietenine (**9**)[1,4] and swietenolide (**10**)[1,5] (ref. Tables I and II), suggested that compound **1** is a member of the tetranortriterpenoids having a structure similar to **9** or **10**.

In the ^{1}H–^{1}H COSY (Fig. 1), the signal due to the acyloxy-bearing methine proton at δ 4.94 (3-H, d, J= 9.5 Hz) showed a correlation with the methine proton at δ 3.54 (2-H, dd, J=9.5, 2.5 Hz), which, in turn, was cor-



1: $R_1=\overset{1'}{C}O\overset{2'}{C}H_2\overset{3'}{C}H_3$, R_2=H

2: R_1=$COCH_2CH_3$, R_2=$COCH_3$

3: $R_1=\overset{1'}{C}O\underset{CH_3}{\overset{2'}{C}H}\overset{3'}{C}H_3$, R_2=$COCH_3$

4: R_1=$COCH_3$, R_2=H

5: $R_1=\overset{1'}{C}O\text{-}\underset{CH_3}{\overset{2'}{C}}=\underset{CH_3}{\overset{3'}{C}H}$, R_2=H

6: $R_1=CO\text{-}\underset{CH_3}{C}=\underset{CH_3}{CH}$, R_2=$COCH_3$

7

8: $R_1=\overset{1'}{C}O\text{-}\underset{CH_3}{\overset{2'}{C}}=\underset{CH_3}{\overset{3'}{C}H}$, R_2=H

11: R_1=$COCH_3$, R_2=H

12: $R_1=CO\underset{CH_3}{CH}CH_3$, R_2=OH

9: $\Delta^{8,30}$, $R=CO\text{-}\underset{CH_3}{C}=\underset{CH_3}{CH}$

10: $\Delta^{8,14}$, R=H

Chart 1

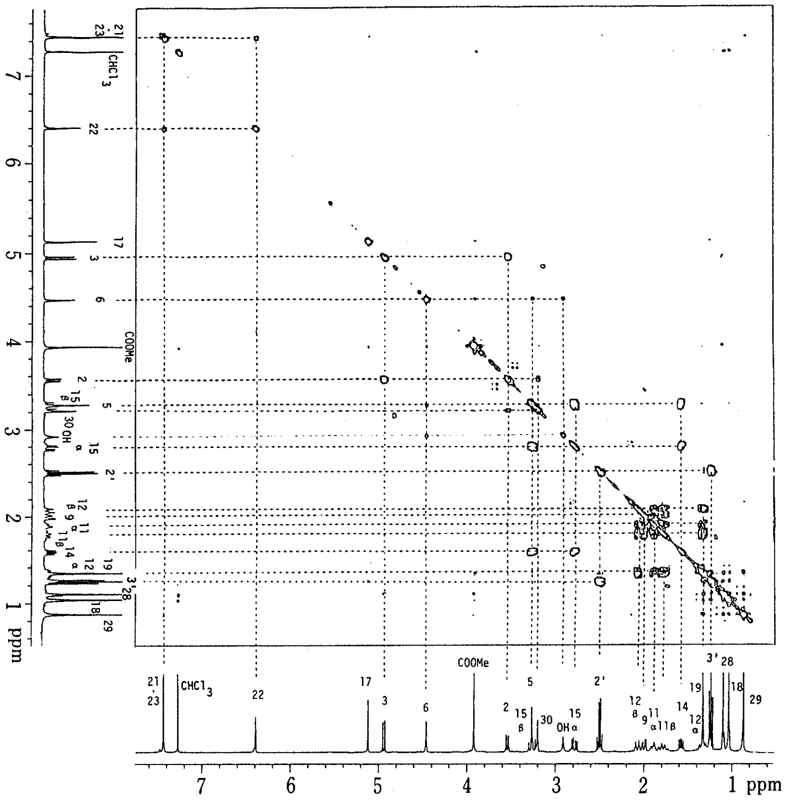


Fig. 1. Contour Map of the ^{1}H–^{1}H COSY Spectrum of Swietemahonin A (**1**) in CDCl$_3$

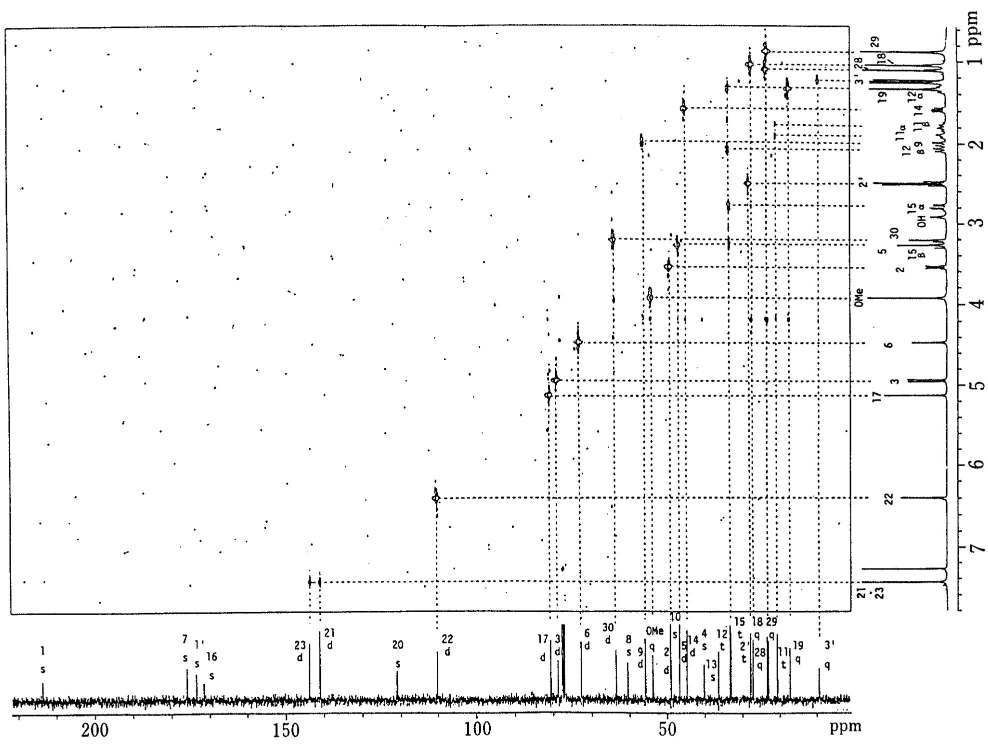


Fig. 2. Contour Map of the ^{1}H–^{13}C COSY Spectrum of Swietemahonin A (**1**) in CDCl$_3$

The multiplicities of carbon signals were determined by means of distortionless enhancement by palarization transfer (DEPT) and are indicated as, s, d, t, and q.

related with the proton at δ 3.20 (30-H, d, $J=2.5$ Hz). The last signal could be ascribed to an oxygenated methine proton, because the ^{13}C-signal correlated with this proton in the ^{1}H–^{13}C COSY (Fig. 2) had the chemical shift value of δ 63.23. Furthermore, this methine was believed to form an epoxide ring in view of the molecular formula and the similarity of the ^{1}H- and ^{13}C-NMR data to those recorded for xylocarpin (**11**) (δ_H 3.30, d, $J=3.0$ Hz; δ_C 63.3).[6] These findings led us to suppose that the structure of swietemahonin A might be **1**.

At this stage, we measured the ^{1}H–^{13}C long-range COSY of **1** in order to confirm the assumed structure **1**. As shown

TABLE I. ^{1}H-NMR Spectral Data for Swietemahonins A (**1**), B (**2**), C (**3**), D (**4**), E (**5**), F (**6**), and G (**7**), Swietemahonolide (**8**), Swietenine (**9**), and Swietenolide (**10**) from *Swietenia mahagoni*

^{1}H	**1**[b]	**2**[b]	**3**[b]	**4**[b]	**5**[b]	**6**[b]	**7**[b]	**8**[b]	**9**[b]	**10**[b]
2	3.54 dd (9.5, 2.5)	3.56 dd (9.5, 2.5)	3.57 dd (9.5, 2.5)	3.54 dd (9.5, 2.5)	3.61 dd (9.5, 2.5)	3.63 dd (9.5, 2.5)	—	3.64 dd (9.5, 2.5)	3.52 ddd (9, 8, 1.5)	3.04 ddd (10, 5.5, 2.5)
3	4.94 d (9.5)	5.01 d (9.5)	5.00 d (9.5)	4.93 d (9.5)	4.84 d (9.5)	4.92 d (9.5)	4.93 s	5.05 d (9.5)	4.64 d (9)	3.58 d (10)
5	3.26 s	3.44 s	3.45 s	3.27 s	3.36 s	3.54 s	3.28 s	3.31 dd (8.5, 3)	3.50 br s	3.25 br s
6	4.46 s	5.49 s	5.49 s	4.46 s	4.46 s	5.51 s	4.44 s	2.34 dd (17, 3) 2.39 dd (17, 8.5)	4.56 br s	4.54 br s
9	2.00 dd (13.5, 4.5)	1.96 d (6.5)	1.96 m	2.00 dd (14, 4.5)	2.01 dd (14, 4.5)	1.93 m	1.98 dd (14, 4)	1.87 m	2.30 ddd (13, 4, 1.5)	2.07 br s
11	1.78 qd (13.5, 4) 1.89 dtd (13.5, 4.5, 3)	1.92 m	1.92 m	1.78 qd (14, 4) 1.89 dtd (14, 4.5, 3)	1.77 qd (14, 4.5) 1.92 m	1.93 m	1.78 qd (12.5, 4) 1.94 m	1.79 m	1.81 m 2.05 qd (13, 4)	1.14 m 1.73 m
12	1.34 ddd (15, 13.5, 4) 2.07 dt (15, 3.5)	1.23 m 2.02 dt (15, 3)	1.24 m 2.04 m	1.32 m 2.07 dt (14, 3)	1.38 m 2.10 ddd (15, 4, 3)	1.26 ddd (15, 13, 4) 2.05 dt (15, 3)	1.43 m 2.15 ddd (14.5, 4.5, 2.5)	1.21 m 1.91 m	1.46 ddd (17, 11, 4) 1.77 m	1.78 ddd (15, 9, 3) 1.86 ddd (15, 6, 3)
14	1.58 dd (12.5, 7)	1.57 dd (14, 5)	1.57 dd (14, 5.5)	1.58 dd (12.5, 6.5)	1.54 dd (12, 7.5)	1.53 dd (13.5, 6)	1.58 dd (11, 8)	1.55 dd (16, 5)	2.23 ddd (5, 2, 1.5)	—
15	2.79 dd (17, 7) 3.27 dd (17, 12.5)	2.75 dd (16, 5) 3.47 dd (16, 14)	2.78 dd (16, 5.5) 3.48 dd (16, 14)	2.78 dd (17, 6.5) 3.26 dd (17, 12.5)	2.71 dd (17.5, 7.5) 3.16 dd (17.5, 12)	2.70 dd (16.5, 6) 3.36 dd (16.5, 13.5)	2.78 dd (18, 8) 3.11 dd (18, 11)	2.74 dd (16, 5) 3.57 t (16)	2.83 dd (18, 5) 2.76 dd (18, 2)	3.46 dt (21, 2.5) 4.03 dt (21, 1)
17	5.12 s	5.16 s	5.15 s	5.12 s	5.08 s	5.12 s	5.10 s	5.15 s	5.54 s	5.47 s
21	7.43 dd (1.8, 0.8)	7.50 dd (1.8, 0.8)	7.49 dd (1.8, 1)	7.43 dd (1.8, 1)	7.40 dd (1.8, 0.8)	7.47 dd (1.8, 1)	7.40 dd (1.8, 0.8)	7.47 dd (1.8, 0.8)	7.56 dd (1.8, 1)	7.48 dd (1.8, 0.8)
22	6.39 dd (1.8, 0.8)	6.46 dd (1.8, 0.8)	6.45 dd (1.8, 1)	6.40 dd (1.8, 1)	6.35 dd (1.8, 0.8)	6.42 dd (1.8, 1)	6.33 dd (1.8, 0.8)	6.44 dd (1.8, 0.8)	6.38 dd (1.8, 1)	6.40 dd (1.8, 0.8)
23	7.44 t (1.8)	7.44 t (1.8)	7.44 t (1.8)	7.44 t (1.8)	7.43 t (1.8)	7.43 t (1.8)	7.44 t (1.8)	7.42 t (1.8)	7.45 t (1.8)	7.41 t (1.8)
18[a]	1.05 s	1.02 s	1.03 s	1.04 s	1.04 s	1.01 s	1.05 s	1.00 s	0.97 s	0.99 s
19[a]	1.34 s	1.08 s	1.09 s	1.33 s	1.35 s	1.10 s	1.44 s	1.08 s	1.45 s	1.40 s
28[a]	1.11 s	1.09 s	1.09 s	1.11 s	1.12 s	1.11 s	1.08 s	0.83 s	1.12 s	1.00 s
29[a]	0.88 s	0.94 s	0.95 s	0.88 s	0.92 s	0.99 s	0.88 s	0.84 s	0.89 s	0.88 s
30	3.20 d (2.5)	3.25 d (2.5)	3.26 d (2.5)	3.20 d (2.5)	3.10 d (2.5)	3.16 d (2.5)	3.31 s	3.22 d (2.5)	5.34 dt (8, 1.5)	2.01 ddd (14.5, 5.5, 2.5) 3.19 dd (14.5, 2.5)
COOMe	3.92 s	3.80 s	3.80 s	3.92 s	3.95 s	3.83 s	3.96 s	3.75 s	3.76 s	3.82 s
6-OCOCH$_3$	—	2.18 s	2.19 s	—	—	2.19 s	—	—	—	—
3-*O*-Acyl										
2′	2.50 q (7.5)	2.53 q (7.0)	2.76 septet (7.0)	2.23 s	—	—	—	—	—	—
2′-Me	—	—	1.27 d (7)	—	1.94 br s	1.94 br s	1.97 br s	1.94 br s	1.82 br s	—
3′	1.24 t (7.5)	1.24 t (7)	1.29 t (7)	—	7.01 qq (6, 1.5)	7.01 qq (7, 1.5)	7.02 qq (7, 1)	7.03 qq (7, 1)	6.87 qq (7, 1.5)	—
3′-Me	—	—	—	—	1.93 d (6)	1.94 br s	1.93 dd (7, 1)	1.93 br d (7)	1.74 br d (7)	—

δ Values in CDCl$_3$. Values in parentheses are coupling constants (Hz). *a*) Assignments were confirmed by NOE experiments. *b*) ^{1}H–^{1}H Correlation spectra were measured.

in Fig. 3, the carbonyl ^{13}C-signals at δ 213.51 (C-1) and δ 175.62 (C-7) showed long-range correlations with the ^{1}H-signals at δ 1.34 (19-H$_3$), 3.20 (30-H), and 3.54 (2-H) and at δ 3.26 (5-H), 3.92 (COOCH$_3$), and 4.46 (6-H), respectively, while the ^{13}C-signals at δ 173.14 (C-1′) and δ 171.20 (C-16) were correlated with the ^{1}H-signals at δ 1.24 (3′-H$_3$), 2.50 (2′-H$_2$), and 4.94 (3-H) and at δ 2.79, 3.27 (15-H$_2$), and 5.12 (17-H), respectively. On the other hand, the oxygenated quaternary carbon at δ 60.17 (C-8) showed long-range correlations with the protons at δ 3.54 (2-H) and 2.00 (9-H). Some other significant long-range correlations observed are shown by arrows in the formula in Fig. 3. Thus the planar structure of **1** was verified.

The relative stereochemistry of **1** was determined on the basis of the coupling constants of each proton (Table I) and the results of nuclear Overhauser effect (NOE) experiments. As shown in Fig. 4, irradiation at 29-H$_3$ and 18-H$_3$ increased the signal intensity of 28-, 2′-, 5-, ester methyl, and 3-protons and the 14-, 21-, and 22- protons, respectively, and irradiation at 28-H$_3$ and 19-H$_3$ enhanced the signal intensity of the 19- and 3-protons and the 28-, 9-, and 6-protons, respectively. The configuration of epoxy ring in

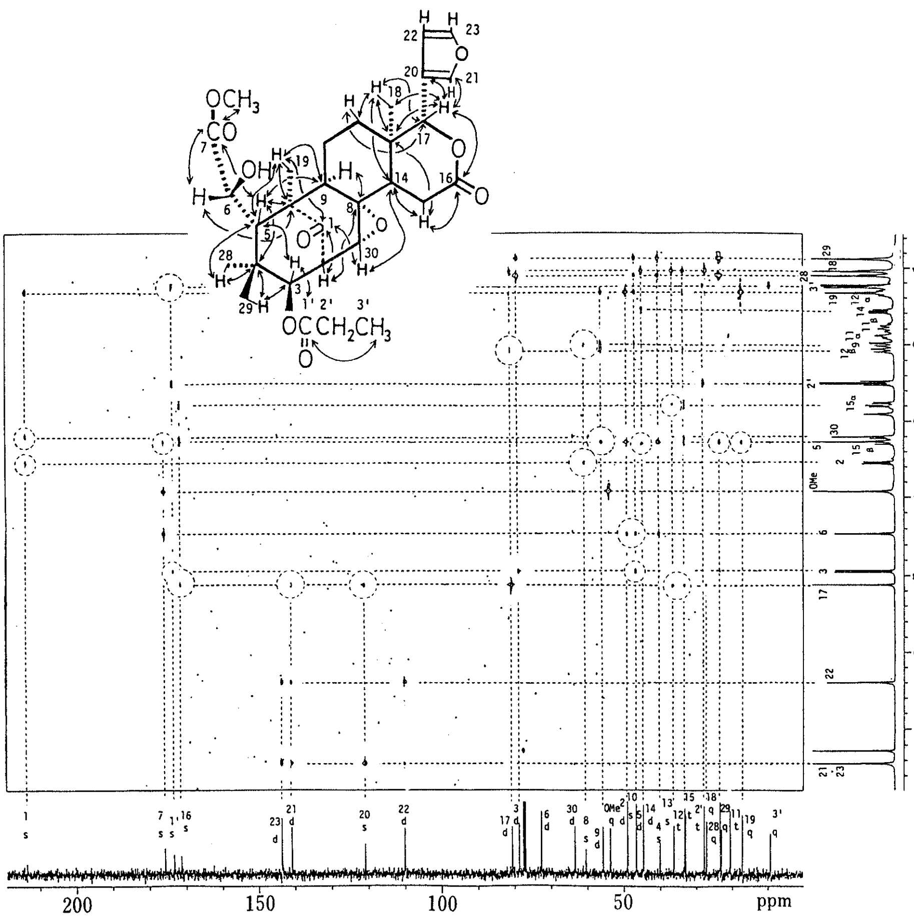


Fig. 3. Contour Map of the ^1H–^{13}C Long-Range COSY Spectrum of Swietemahonin A (**1**) in $CDCl_3$ ($J_{CH}=10\,Hz$)

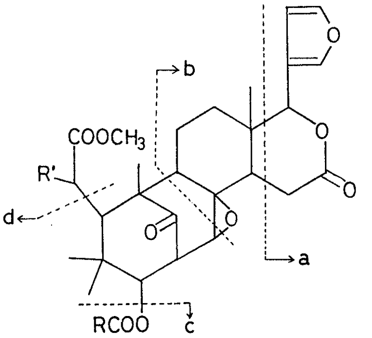


Chart 2

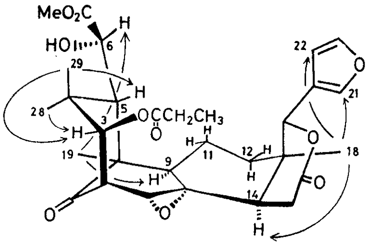
1 is determined to be α in view of the ^1H-coupling constant ($J_{2,30}=2.5\,Hz$).[6] Thus, the structure of swietemahonin A was proved to be **1**. In accordance with this conclusion, the mass spectra (MS) of **1** revealed fragment ion peaks at m/z 540 (M^+-H_2O), 484 (M^+-c-H), 466 ($M^+-c-H-H_2O$), 420 (M^+-a), 395 ($M^+-c-H-d$), 346 ($M^+-a-c-H$), 311 (M^+-b), and 237 ($M^+-b-c-H$) (base peak), which may be interpreted in terms of the fragmentations shown in Chart 2.

Swietemahonin B (**2**), colorless needles, mp 286—287 °C, $[\alpha]_D$ −6.8 ° ($CHCl_3$), has the molecular formula $C_{32}H_{40}O_{11}$ (M^+ 600.2580, Calcd 600.2571) and its IR spectrum showed strong carbonyl absorptions (1750—1710 cm^{-1}) and medium absorptions due to a furan (1500 and 880 cm^{-1}). The ^1H-NMR spectrum was closely similar to that of swietemahonin A (**1**) except for the appearance of a new signal due to an acetyl methyl (δ 2.18) and a remarkable down-field shift of a proton singlet (δ5.49) assignable to 6-H (Table I). Next, the ^{13}C-NMR spectrum of **2** was examined and the assignments of ^{13}C-signals were performed by the use of 2D-NMR spectroscopy as shown in Table II.

Acetylation of **1** with acetic anhydride–pyridine gave an acetate, which was found to be identical with swietemahonin B (**2**). Therefore, swietemahonin B (**2**) was determined to be the acetate of swietemahonin A (**1**).

Swietemahonin C (**3**) is a very minor component obtained as colorless needles, mp 309—310 °C, $[\alpha]_D$ −10.8 ° ($CHCl_3$), and has the molecular formula $C_{33}H_{42}O_{11}$ (M^+ 614.2726, Calcd 614.2726). The MS of **3** exhibited the molecular ion peak at m/z 614 and fragment ion peaks at m/z 476 (M^+-a), 367 (M^+-b), 279 ($M^+-b-c-H$) (base peak), and 219 ($M^+-b-c-H-AcOH$), and its IR spectrum showed strong carbonyl bands (1750—1720 cm^{-1}) and furan bands (1510 and 880 cm^{-1}). The ^1H- and ^{13}C-NMR spectra were almost identical with those of **2** except for the appearance of signals ascribable to an isobutyryl residue (see Tables I and II). From these comparisons of the ^1H- and ^{13}C-NMR data, it was concluded that the structure of swietemahonin C is represented by the formula **3** having an isobutyryl residue at C-3 instead of the propionyl residue in **2**.

Swietemahonin D (**4**), colorless needles, mp 191—192 °C, $[\alpha]_D$ −44.7 ° ($CHCl_3$), is also a very minor component and the molecular formula $C_{29}H_{36}O_{10}$ was established by MS and high-resolution MS. It showed IR, ^1H- and ^{13}C-NMR spectra closely similar to those of swietemahonin A (**1**)



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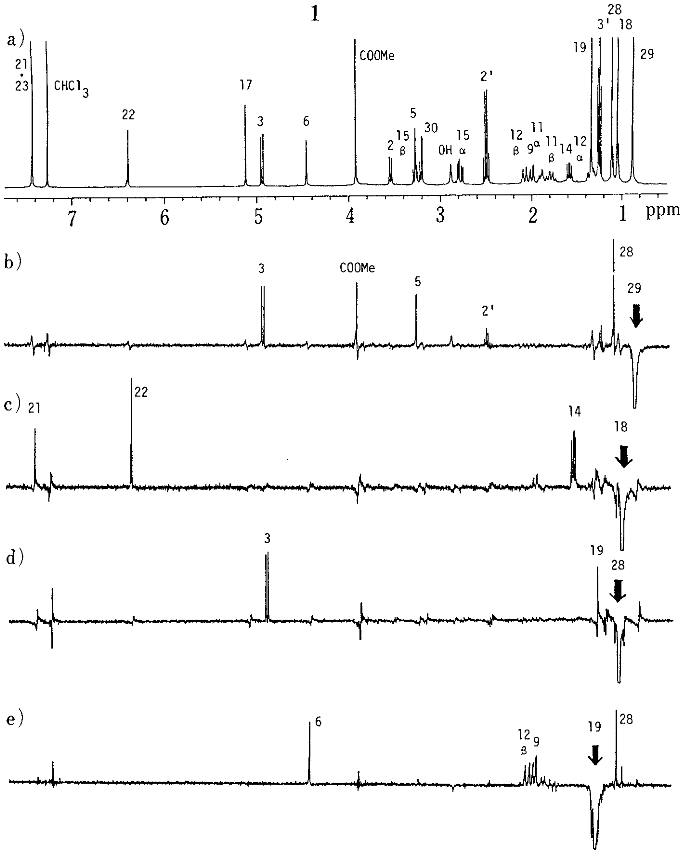

Fig. 4. ^{1}H-NMR (Normal and NOE) Spectra of Swietemahonin A (**1**)

a) Normal spectrum. b—e) NOE difference spectra on irradiation at δ 0.88, 1.05, 1.11, and 1.34, respectively.

except for the appearance of the NMR signals due to an acetyl residue (δ_H 2.23; δ_C 171.25 and 20.76) instead of the signals due to the propionyl residue in **1** (Tables I and II). Based on these spectral data, swietemahonin D was determined to be **4**.

Swietemahonin E (**5**), colorless needles, mp 151—152 °C, $[\alpha]_D$ −20.7° (CHCl$_3$), has the molecular formula $C_{32}H_{40}O_{10}$ (M$^+$ 584.2605, Calcd 584.2620) and it showed an IR spectrum very similar to that of swietemahonin A (**1**). The ^{1}H- and ^{13}C-NMR spectra are almost identical with those of **1** except for the appearance of the signals ascribable to a tigloyl residue instead of the signals due to the propionyl residue in **1** (Tables I and II). From these comparisons of ^{1}H- and ^{13}C-NMR data, it was concluded that swietemahonin E has the structure **5** carrying a tigloyl residue at C-3.

Swietemahonin F (**6**), colorless needles, mp 278—280°C, $[\alpha]_D$ −11.1° (CHCl$_3$), has the molecular formula $C_{34}H_{42}O_{11}$ (M$^+$ 626.2685, Calcd 626.2726) and it showed an IR spectrum closely similar to that of **5**. The ^{1}H-NMR spectrum is also closely similar to that of **5** except for the down-field shift of a proton singlet (δ 5.51) assignable to 6-H and the appearance of a new signal (δ 2.19) due to an acetyl methyl group (Table I). Acetylation of **5** with acetic anhydride in pyridine yielded an acetate (**6**), mp 277—278 °C, which was identical with swietemahonin F. Therefore, swietemahonin F is determined to be the 6-*O*-acetate of swietemahonin E (**5**). The ^{13}C-NMR data of this compound (**6**), analyzed with the aid of ^{1}H–^{13}C and ^{1}H–^{13}C long-range COSY, also supported the structure **6** (Table II).

It should be noted here that Taylor and Taylor$^{7)}$ have reported the isolation of an amorphous compound having the structure **6** from *Swietenia macrophylla*. However, there were some discrepancies between swietemahonin F and their compound in the methyl group regions of the ^{1}H- and ^{13}C-NMR data.$^{7)}$

Swietemahonin G (**7**) is also a minor component obtained as colorless needles, mp 135—137 °C, and showed $[\alpha]_D$ −15.9° (CHCl$_3$) and IR ν_{max} cm^{-1}: 3500, 1740, 1735, 1720, 1710, 1500, and 880. In the MS, it gave the molecular ion peak at m/z 600 corresponding to the formula $C_{32}H_{40}O_{11}$, which was established by high-resolution MS. The ^{1}H-NMR spectrum of **7** was very similar to that of swietemahonin E (**5**), but it was characteristic that both the signals assignable to 3-H (δ 4.93) and 30-H (δ 3.31) appeared as sharp singlets (Table I), suggesting that C-2 is fully substituted. From the molecular formula of **7**, which has one more oxygen atom than **5**, it is reasonable to deduce that C-2 is substituted by a hydroxyl group.

This was supported by the ^{13}C-NMR spectrum of **7**, which was fully analyzed by the application of ^{1}H–^{13}C and ^{1}H–^{13}C long-range COSY. As can be seen in Table II, it closely resembled that of **5**, but it revealed a marked down-field shift of the C-2 signal (δ 78.20, s) and slight down-field shifts of the C-3 and C-30 signals (δ 86.41 and δ 69.09, respectively).

On the basis of these spectral data, the structure of swietemahonin G was assigned as the formula **7**.

Swietemahonolide (**8**), colorless needles, mp 212—213 °C, $[\alpha]_D$ −20.2° (CHCl$_3$), has the molecular formula $C_{32}H_{40}O_9$ (M$^+$ 568.2663, Calcd 568.2672) and showed IR absorptions at 1735 (lactone), 1720 (ester), 1710 (ketone), 1500 and 880 cm^{-1} (furan). The ^{1}H-NMR spectrum of **8**, analyzed with the aid of ^{1}H–^{1}H COSY, indicated the presence of a furan (δ7.47, 6.44, and 7.42), a lactone (δ 5.15), an ester methyl (δ 3.75), an epoxide (δ 3.22), and a tigloyl (δ 7.03, 1.94, and 1.93) along with four *tert*-methyl groups (δ 1.00, 1.08, 0.83, and 0.84) (Table I). The spectral pattern was similar to that of swietemahonin E (**5**), but a pair of double doublets due to methylene protons appeared newly at δ 2.34 (J=17.0, 3.0 Hz) and 2.39 (J=17.0, 8.5 Hz), instead of the signal due to 6-H in **5**. Moreover, the singlet signal due to 5-H (δ 3.36) in **5** was changed to a double doublet (δ 3.31, J= 8.5, 3.0 Hz) in **8**.

The ^{13}C-NMR spectrum of **8**, analyzed with the aid of ^{1}H–^{13}C COSY, exhibited a signal at δ 33.21 arising from a methylene group which corresponds to the ^{1}H-signals at δ 2.34 and 2.39. It also indicated the presence of a ketone (δ 214.39), a methyl ester (δ 174.24 and 52.35), a lactone (δ 171.73 and 78.79), a furan (δ 120.25, 140.95, 110.30, and 143.10), an epoxide (δ 60.67 and 63.43), a tigloyl (δ 166.88, 127.64, 140.10, 12.43, and 14.80), and four *tert*-methyl groups (δ 26.39, 15.97, 21.08, and 22.86) (Table II).

These spectral data suggested that the structure of swietemahonolide might be **8**.

Table II. ^{13}C-NMR Spectral Data for Swietemahonins A (**1**), B (**2**), C (**3**), D (**4**), E (**5**), F (**6**), and G (**7**), Swietemahonolide (**8**), Swietenine (**9**), and Swietenolide (**10**) from *Swietenia mahagoni*

^{13}C	**1**$^{a)}$	**2**$^{a)}$	**3**$^{a)}$	**4**$^{a)}$	**5**$^{a)}$	**6**$^{a)}$	**7**$^{a)}$	**8**$^{a)}$	**9**$^{a)}$	**10**$^{a)}$
1	213.51 (s)	212.87 (s)	212.97 (s)	213.35 (s)	213.70 (s)	213.14 (s)	212.49 (s)	214.39 (s)	216.53 (s)	219.80 (s)
2	48.68 (d)	48.54 (d)	48.71 (d)	48.54 (d)	49.01 (d)	48.92 (d)	78.20 (s)	49.01 (d)	48.95 (d)	49.99 (d)
3	78.44 (d)	77.88 (d)	77.80 (d)	78.67 (d)	79.13 (d)	78.59 (d)	86.41 (d)	77.44 (d)	78.41 (d)	78.50 (d)
4	39.78 (s)	39.81 (s)	39.95 (s)	39.69 (s)	40.05 (s)	40.08 (s)	40.71 (s)	39.52 (s)	39.04 (s)	39.66 (s)
5	46.26 (d)	45.50 (d)	45.50 (d)	46.29 (d)	46.16 (d)	45.37 (d)	46.02 (d)	42.51 (d)	45.47 (d)	44.00 (d)
6	72.40 (d)	72.25 (d)	72.23 (d)	72.48 (d)	72.39 (d)	72.31 (d)	72.13 (d)	33.21 (t)	72.87 (d)	73.57 (d)
7	175.62 (s)	171.16 (s)	171.10 (s)	175.56 (s)	175.85 (s)	171.08 (s)	175.65 (s)	174.24 (s)	175.97 (s)	175.83 (s)
8	60.17 (s)	60.11 (s)	60.26 (s)	60.11 (s)	60.30 (s)	60.29 (s)	62.79 (s)	60.67 (s)	138.28 (s)	129.05 (s)
9	55.45 (d)	56.13 (d)	56.04 (d)	55.51 (d)	55.08 (d)	55.89 (d)	54.20 (d)	55.84 (d)	57.56 (d)	52.96 (d)
10	48.54 (s)	48.48 (s)	48.55 (s)	48.54 (s)	48.65 (s)	48.62 (s)	49.33 (s)	48.30 (s)	50.39 (s)	53.99 (s)
11	20.38 (t)	19.78 (t)	19.87 (t)	20.35 (t)	20.63 (t)	20.00 (t)	20.67 (t)	19.47 (t)	21.28 (t)	29.08 (t)
12	32.91 (t)	33.39 (t)	33.33 (t)	32.98 (t)	32.59 (t)	33.09 (t)	32.27 (t)	33.41 (t)	34.64 (t)	18.74 (t)
13	35.19 (s)	36.32 (s)	36.27 (s)	35.97 (s)	35.65 (s)	36.11 (s)	35.52 (s)	36.35 (s)	36.73 (s)	37.81 (s)
14	44.30 (d)	45.50 (d)	45.34 (d)	44.46 (d)	43.52 (d)	44.84 (d)	42.92 (d)	45.64 (d)	45.09 (d)	130.75 (s)
15	32.65 (t)	33.51 (t)	33.53 (t)	32.68 (t)	32.50 (t)	33.35 (t)	32.16 (t)	33.88 (t)	29.57 (t)	33.15 (t)
16	171.20 (s)	171.76 (s)	171.60 (s)	169.67 (s)	170.78 (s)	171.31 (s)	170.32 (s)	171.73 (s)	168.45 (s)	171.43 (s)
17	80.37 (d)	79.14 (d)	79.31 (d)	80.29 (d)	80.86 (d)	79.47 (d)	81.27 (d)	78.79 (d)	76.71 (d)	80.51 (d)
20	120.62 (s)	120.08 (s)	120.12 (s)	120.61 (s)	120.93 (s)	120.35 (s)	121.03 (s)	120.25 (s)	121.38 (s)	120.81 (s)
21	140.69 (d)	141.03 (d)	140.99 (d)	140.72 (d)	140.63 (d)	140.93 (d)	140.60 (d)	140.95 (d)	140.54 (d)	141.06 (d)
22	109.89 (d)	110.21 (d)	110.18 (d)	109.91 (d)	109.82 (d)	110.14 (d)	109.64 (d)	110.30 (d)	109.24 (d)	109.80 (d)
23	143.44 (d)	143.21 (d)	143.26 (d)	143.45 (d)	143.48 (d)	143.26 (d)	143.64 (d)	143.10 (d)	143.20 (d)	142.88 (d)
18	26.86 (q)	26.50 (q)	26.59 (q)	26.80 (q)	27.06 (q)	26.64 (q)	27.14 (q)	26.39 (q)	21.28 (q)	17.91 (q)
19	17.01 (q)	15.95 (q)	15.93 (q)	17.03 (q)	17.07 (q)	16.01 (q)	17.21 (q)	15.97 (q)	16.53 (q)	17.91 (q)
28	23.10 (q)	23.18 (q)	23.33 (q)	23.04 (q)	23.24 (q)	23.40 (q)	22.48 (q)	21.08 (q)	22.80 (q)	23.22 (q)
29	22.72 (q)	22.54 (q)	22.52 (q)	22.74 (q)	23.24 (q)	23.01 (q)	22.48 (q)	22.86 (q)	23.05 (q)	23.63 (q)
30	63.23 (d)	63.40 (d)	63.25 (d)	63.31 (d)	63.04 (d)	63.23 (d)	67.09 (d)	63.43 (d)	123.66 (d)	33.80 (t)
$\mathrm{COO\underline{C}H_3}$	53.50 (q)	53.34 (q)	53.34 (q)	53.53 (q)	53.47 (q)	53.31 (q)	53.62 (q)	52.35 (q)	53.28 (q)	53.23 (q)
$\mathrm{6\text{-}O\underline{C}OCH_3}$	—	169.62 (s)	169.67 (s)	—	—	169.68 (s)	—	—	—	—
$\mathrm{6\text{-}OCO\underline{C}H_3}$	—	20.93 (q)	20.94 (q)	—	—	20.94 (q)	—	—	—	—
$\mathrm{3\text{-}OCOR_1}$										
1′	173.14 (s)	173.28 (s)	175.95 (s)	171.25 (s)	166.77 (s)	166.84 (s)	166.54 (s)	166.88 (s)	166.92 (s)	—
2′	27.52 (t)	27.44 (t)	34.18 (d)	20.76 (q)	127.88 (s)	127.65 (s)	128.18 (s)	127.64 (s)	127.77 (s)	—
3′	9.24 (q)	9.18 (q)	—	—	139.54 (d)	140.16 (d)	139.05 (d)	140.10 (d)	139.02 (d)	—
$\mathrm{2'\text{-}\underline{C}H_3}$	—	—	18.82 (q) 19.50 (q)	—	12.34 (q)	12.38 (q)	12.57 (q)	12.43 (q)	11.75 (q)	—
$\mathrm{3'\text{-}\underline{C}H_3}$	—	—	—	—	14.70 (q)	14.78 (q)	14.64 (q)	14.80 (q)	14.64 (q)	—

δ Values in $CDCl_3$. Multiplicities of carbon signals were determined by the distortionless enhancement by palarization transfer (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.

Then, the ^{1}H–^{13}C long-range COSY of **8** was examined to confirm the assumed structure **8** (Fig. 5). As expected, the ^{13}C-signals at δ 214.39 (C-1) and at δ 174.24 (C-7) showed long-range correlations with the ^{1}H-signals at δ 1.08 (19-H_3) and 3.22 (30-H) and at δ 2.34 (6-H) and 3.75 ($COOCH_3$), respectively. In turn, the ^{13}C-signal at δ 171.73 (C-16) was correlated with the ^{1}H-signals at δ 2.74 (15α-H) and 3.57 (15β-H), and the signal at δ 166.88 (C-1′) with the ^{1}H-signals at δ 1.94 (2′-CH_3) and 5.05 (3-H). Some other significant long-range correlations are also shown by arrows in the formula in Fig. 5.

The relative stereochemistry of **8** was determined on the basis of the coupling constants of each proton (Table I) and the result of NOE experiments. Irradiation at 28-H_3 and 29-H_3 caused an increase of the signal intensity of the 19-, 6-, and 3-protons and the 6-, 5-, ester methyl, 3-, and 3′-protons, respectively. On the other hand, irradiation at 18-H_3 and 19-H_3 enhanced the signal intensity of the 14-, 21-, and 22-protons and the 28-, 9-, and 6-protons, respectively. Therefore, the structure of swietemahonolide was proved to be **8**.

The absolute stereochemistry of swietemahonins A—G (**1**—**7**) and swietemahonolide (**8**) was determined to be the same as that of swietenine (**9**)[8] based on the negative Cotton effect at around 300 nm in the circular dichroism (CD) spectra. As to naturally occurring 8,30-oxides of swietenine-type tetranortriterpenoids, xylocarpin (**11**) from *Xylocarpus granatum*[6] and humilin B (**12**) from *Swietenia humilis*[9] have hitherto been reported. The 8,30α-oxide (**6**) of swietenine acetate has also been claimed to occur in *Swietenia macrophylla*.[7] Our present results provide additional examples of this class of compounds in Meliaceous plants.

It is noteworthy that all the compounds reported in the present paper have an inhibitory effect on rabbit blood-platelet aggregation. Details of this biological activity will be reported in a forthcoming paper.

Experimental

Melting points were determined with a Kofler-type apparatus and are uncorrected. Optical rotations were measured in chloroform solutions on a JASCO DIP-4 automatic polarimeter at 20—22 °C. CD spectra were recorded on a JASCO J-500C spectropolarimeter in chloroform solutions. IR spectra were taken with a JASCO IRA-2 spectrometer in chloroform solutions. ^{1}H- and ^{13}C-NMR spectra were taken on a JEOL-GX 400 spectrometer with tetramethylsilane as an internal standard, and chemical shifts are recorded in δ values. ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, and ^{1}H–^{13}C long-range COSY were measured under the same conditions as described in a previous paper.[1] MS and high-resolution MS were obtained with a JEOL JMS-D 300 spectrometer (ionization voltage, 70 eV; accelerating

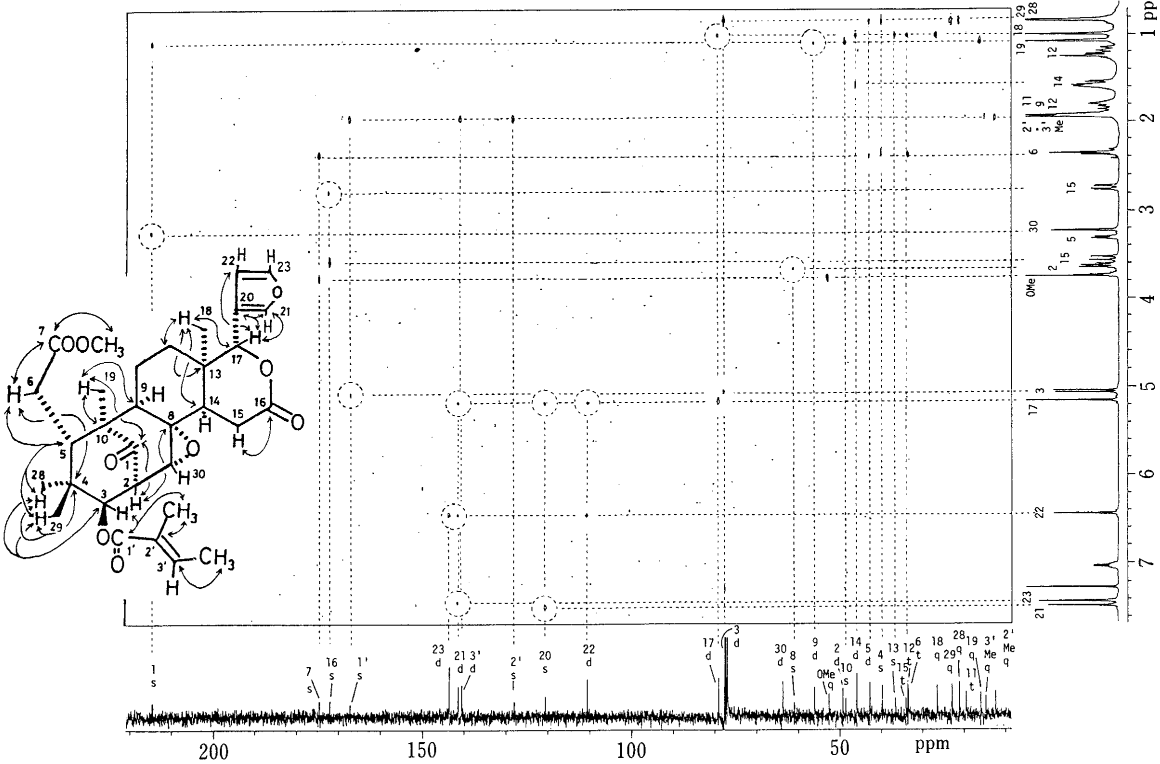

Fig. 5. Contour Map of the ^{1}H–^{13}C Long-Range COSY Spectrum of Swietemahonolide (**8**) in CDCl$_3$ (J_{CH}=10 Hz)

voltage, 3 kV) using a direct inlet system. Preparative TLC was carried out on Merck Kieselgel GF$_{254}$ plates and the plates were examined under ultraviolet (UV) light. Extraction of substances from silica gel was done with MeOH–CH$_2$Cl$_2$ (1:9 or 3:7) and solutions were concentrated *in vacuo*. TLC analyses were done on Merck Kieselgel GF$_{254}$ plates; developed plates were examined under UV light.

Isolation and Properties of Tetranortriterpenoids from the Cotyledons of *Swietenia mahagoni* Details of the extraction and isolation of tetranortriterpenoids from the cotyledon part (700 g) of seeds (1.8 kg) of *Swietenia mahagoni* were described in the preceding paper.[1] A portion (100 g) of the oily fraction (327 g) of the ether extract was separated by a combination of silica gel column chromatography and preparative TLC to give swietemahonin A (**1**) (59 mg), swietemahonin B (**2**) (33 mg), swietemahonin C (**3**) (8 mg), swietemahonin D (**4**) (2.7 mg), swietemahonin E (**5**) (44 mg), swietemahonin F (**6**) (33 mg), swietemahonin G (**7**) (6 mg), and swietemahonolide (**8**) (6 mg) together with other tetranortriterpenoids.

Swietemahonin A (**1**): Colorless needles (from AcOEt–isopropyl ether), mp 174—174.5 °C, $[\alpha]_D$ −12.2° (c=0.88). IR ν_{max} cm^{-1}: 3500, 1735, 1725, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. CD (c=1.8×10^{-4}, CHCl$_3$) $[\theta]$ (nm): −3.07×10^4 (293), −3.04×10^4 (300), −1.88×10^4 (310). MS m/z: 558 (M$^+$), 540 (M$^+$−H$_2$O), 484 (M$^+$−c−H), 466 (M$^+$−c−H−H$_2$O), 420 (M$^+$−a), 395 (M$^+$−c−H−d), 346 (M$^+$−a−c−H), 311 (M$^+$−b), 237 (M$^+$−b−c−H) (base peak). High-resolution MS m/z: Found 558.2478, Calcd for $C_{30}H_{38}O_{10}$ (M$^+$) 558.2464; Found 420.2169, Calcd for $C_{23}H_{32}O_7$ 420.2148; Found 395.1843, Calcd for $C_{24}H_{27}O_5$ 395.1858; Found 346.1735, Calcd for $C_{20}H_{26}O_5$ 346.1779; Found 311.1496, Calcd for $C_{16}H_{23}O_6$ 311.1495.

Swietemahonin B (**2**): Colorless needles (from AcOEt–isopropyl ether), mp 286—287 °C, $[\alpha]_D$ −6.8° (c=1.48). IR ν_{max} cm^{-1}: 1750, 1740, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. CD (c=3.9×10^{-4}, CHCl$_3$) $[\theta]$ (nm): −1.78×10^4 (293), −1.75×10^4 (300), −1.03×10^4 (310). MS m/z: 600 (M$^+$), 540 (M$^+$−AcOH), 462 (M$^+$−a), 353 (M$^+$−b), 279 (M$^+$−b−c−H) (base peak), 219 (M$^+$−b−c−H−AcOH). High-resolution MS m/z: Found 600.2580, Calcd for $C_{32}H_{40}O_{11}$ (M$^+$) 600.2571; Found 540.2391, Calcd for $C_{30}H_{36}O_9$ 540.2360; Found 462.2232, Calcd for $C_{25}H_{34}O_8$ 462.2252; Found 353.1569, Calcd for $C_{18}H_{25}O_7$ 353.1599; Found 279.1233, Calcd for $C_{15}H_{19}O_5$ 279.1233.

Swietemahonin C (**3**): Colorless needles (from AcOEt–isopropyl ether), mp 309—310 °C, $[\alpha]_D$ −10.8° (c=0.93). IR ν_{max} cm^{-1}: 1750, 1740, 1720, 1500, 880. ^{1}H-NMR and ^{13}C-NMR: Tables I and II. CD (c=1.6×10^{-3}, CHCl$_3$) $[\theta]$ (nm): −1.51×10^4 (293), −1.51×10^4 (301), −9.08×10^3 (310). MS m/z: 614 (M$^+$), 596 (M$^+$−H$_2$O), 476 (M$^+$−a), 367 (M$^+$−b), 279 (M$^+$−b−c−H) (base peak), 219 (M$^+$−b−c−H−AcOH). High-resolution MS m/z: Found 614.2726, Calcd for $C_{33}H_{42}O_{11}$ (M$^+$) 614.2726; Found 476.2417, Calcd for $C_{26}H_{36}O_8$ 476.2410; Found 367.1806, Calcd for $C_{19}H_{27}O_7$ 367.1757; Found 279.1227, Calcd for $C_{15}H_{19}O_5$ 279.1232.

Swietemahonin D (**4**): Colorless needles (from AcOEt–isopropyl ether), mp 191—192 °C, $[\alpha]_D$ −44.7° (c=0.21). IR ν_{max} cm^{-1}: 3500, 1740, 1730, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. CD (c=3.7×10^{-4}, CHCl$_3$) $[\theta]$ (nm): −1.11×10^4 (292), −1.09×10^4 (300), −6.79×10^3 (310). MS m/z: 544 (M$^+$), 484 (M$^+$−c−H), 466 (M$^+$−c−H−H$_2$O), 406 (M$^+$−a), 395 (M$^+$−c−H−d), 346 (M$^+$−a−c−H), 297 (M$^+$−b), 237 (M$^+$−b−c−H) (base peak). High-resolution MS m/z: Found 544.2325, Calcd for $C_{29}H_{36}O_{10}$ (M$^+$) 544.2309; Found 484.2128, Calcd for $C_{27}H_{32}O_8$ 484.2097; Found 466.2021, Calcd for $C_{27}H_{30}O_7$ 466.1991; Found 406.1952, Calcd for $C_{22}H_{30}O_7$ 406.1991; Found 395.1882, Calcd for $C_{24}H_{27}O_5$ 395.1859; Found 297.1311, Calcd for $C_{15}H_{21}O_6$ 297.1338; Found 237.1108, Calcd for $C_{13}H_{17}O_4$ 237.1126.

Swietemahonin E (**5**): Colorless needles (from AcOEt–isopropyl ether), mp 151—152 °C, $[\alpha]_D$ −20.7° (c=0.58). IR ν_{max} cm^{-1}: 3550, 1735, 1720, 1710, 1510, 875. ^{1}H- and ^{13}C-NMR: Tables I and II. CD (c=4.0×10^{-4}, CHCl$_3$) $[\theta]$ (nm): −2.19×10^4 (293), −2.11×10^4 (301), −1.25×10^4 (310). MS m/z: 584 (M$^+$), 485 (M$^+$−c), 467 (M$^+$−c−H$_2$O), 446 (M$^+$−a), 396 (M$^+$−c−d), 346 (M$^+$−a−c−H), 337 (M$^+$−b), 237 (M$^+$−b−c−H). High-resolution MS m/z: Found 584.2605, Calcd for $C_{32}H_{40}O_{10}$ (M$^+$) 584.2620; Found 337.1611, Calcd for $C_{18}H_{25}O_6$ 337.1650.

Swietemahonin F (**6**): Colorless needles (from AcOEt–isopropyl ether), mp 278—280 °C, $[\alpha]_D$ −11.1° (c=0.8). IR ν_{max} cm^{-1}: 1750, 1730, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. CD (c=2.1×10^{-4}, CHCl$_3$) $[\theta]$ (nm): −3.80×10^4 (293), −3.76×10^4 (300), −2.16×10^4 (310). MS m/z: 626 (M$^+$), 608 (M$^+$−H$_2$O), 527 (M$^+$−c), 488 (M$^+$−a), 379 (M$^+$−b), 279 (M$^+$−b−c−H), 219 (M$^+$−b−c−H−AcOH), 83 (C_4H_7-CO$^+$, base peak). High-resolution MS m/z: Found 626.2685, Calcd for $C_{34}H_{42}O_{11}$ (M$^+$) 626.2726; Found 608.2571, Calcd for $C_{34}H_{40}O_{10}$ 608.2620; Found 488.2388, Calcd for $C_{27}H_{36}O_8$ 488.2409; Found 279.1193, Calcd for $C_{15}H_{19}O_5$ 279.1232.

Swietemahonin G (**7**): Colorless needles (from AcOEt–isopropyl ether), mp 135—137 °C, $[\alpha]_D$ −15.9° (c=0.57). IR ν_{max} cm^{-1}: 3500, 1740, 1735, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. CD (c=5.6×10^{-5}, CHCl$_3$) $[\theta]$ (nm): −9.73×10^4 (287), −8.11×10^4 (295). MS m/z: 600 (M$^+$), 544 (M$^+$−C_4H_8), 500 (M$^+$−c−H), 483 (M$^+$−c−H$_2$O), 455 (M$^+$−C_4H_8−d), 406 (M$^+$−C_4H_8−a), 297 (M$^+$−C_4H_8−b), 237 (M$^+$−C_4H_8−b−CO$_3$). High-resolution MS m/z: Found 600.2604, Calcd for $C_{32}H_{40}O_{11}$ (M$^+$) 600.2570; Found 544.1959, Calcd for $C_{28}H_{32}O_{11}$

544.1945; Found 500.2055, Calcd for $C_{27}H_{32}O_9$ 500.2047; Found 483.2006, Calcd for $C_{27}H_{31}O_8$ 483.2018; Found 455.1662, Calcd for $C_{25}H_{27}O_8$ 455.1705; Found 297.0956, Calcd for $C_{14}H_{17}O_7$ 297.0973; Found 237.1162, Calcd for $C_{13}H_{17}O_4$ 237.1127.

Swietemahonolide (**8**): Colorless needles (from AcOEt–isopropyl ether), mp 212—213 °C, $[\alpha]_D$ −20.2° (c=0.55). IR ν_{max} cm^{-1}: 1735, 1720, 1710, 1500, 880. ^{1}H- and ^{13}C-NMR: Tables I and II. CD ($c=5.3\times10^{-4}$, $CHCl_3$) $[\theta]$ (nm): -6.82×10^3 (293), -6.82×10^3 (302), -4.17×10^3 (311). MS m/z: 568 (M^+), 550 (M^+-H_2O), 469 (M^+-c), 468 (M^+-c-H), 451 (M^+-H_2O-c), 450 (M^+-H_2O-c-H), 430 (M^+-a), 391 ($M^+-H_2O-c-H-COOCH_3$), 377 ($M^+-H_2O-c-H-d$), 321 (M^+-b), 221 ($M^+-b-c-H$), 83 ($C_5H_7O^+$, base peak). High-resolution MS m/z: Found 568.2663, Calcd for $C_{32}H_{40}O_9$ (M^+) 568.2672; Found 550.2528, Calcd for $C_{32}H_{38}O_8$ 550.2566; Found 469.2184, Calcd for $C_{27}H_{33}O_7$ 469.2226; Found 450.2054, Calcd for $C_{27}H_{30}O_6$ 450.2043; Found 430.2393, Calcd for $C_{25}H_{34}O_6$ 430.2356; Found 391.1872, Calcd for $C_{25}H_{27}O_4$ 391.1908; Found 377.1729, Calcd for $C_{24}H_{25}O_4$ 377.1752; Found 321.1716, Calcd for $C_{18}H_{25}O_5$ 321.1702.

Acetylation of Swietemahonin A (1) Swietemahonin A (**1**) (10 mg) was treated with acetic anhydride (0.5 ml) and pyridine (0.5 ml) at room temperature for 2 d. The reaction mixture was worked up in the usual manner and the product was purified by preparative TLC with AcOEt–benzene (10 : 90) to give an acetate (**2**) (8.0 mg), mp 285—286 °C, which was identical with swietemahonin B (**2**) on TLC and ^{1}H-NMR comparisons.

Acetylation of Swietemahonin E (5) Swietemahonin E (**5**) (3 mg) was mixed with acetic anhydride (0.2 ml) and pyridine (0.2 ml) and the mixture was allowed to stand overnight at room temperature. Then, the reaction mixture was worked up in the usual manner and the product was subjected to preparative TLC with MeOH–$CHCl_3$ (1 : 99) to give an acetate (**6**) (2.0 mg), mp 277—278 °C, which was identical with swietemahonin F (**6**) on TLC and ^{1}H-NMR comparisons.

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References and Notes

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