Flavone Glycosides from *Strobilanthes formosanus*

Kuo-Ching Kao[a] (高國清), Yu-Ling Ho[b] (何玉鈴), I-Hsin Lin[c] (林宜信), Li-Kang Ho[d] (何禮剛) and Yuan-Shiun Chang[a]* (張永勳)

[a]*Institute of Chinese Pharmaceutical Sciences, China Medical University, Taichung 404, Taiwan, R.O.C.*

[b]*Nursing Department, HungKuang University, Shalu, Taichung Shien 433, Taiwan, R.O.C.*

[c]*Institute of Chinese Medical Sciences, China Medical University, Taichung 404, Taiwan, R.O.C.*

[d]*Department of Pharmacology, National Yang-Ming University, Taipei 112, Taiwan, R.O.C.*

Two new flavone glycosides, 3′-hydroxy-5,7-dimethoxyflavone 4′-*O*-β-D-apiofuranoside (**1**), and 5,7-dimethoxyflavone 4′-*O*-[β-D-apiofuranosyl(1→5)-β-D-glucopyranoside] (**2**) along with four known compounds, 4′-hydroxy-5,7-dimethoxyflavone (**3**), 2,6-dimethoxy-1,4-benzoquinone (**4**), lupeol (**5**) and betulin (**6**) were isolated from the stem and roots of *Strobilanthes formosanus*. Their structures were elucidated on the basis of their spectroscopic evidence.

Key words: *Strobilanthes formosanus*; Acanthaceae; Flavone glycosides; 3′-hydroxy-5,7-dimethoxyflavone 4′-*O*-β-D-apiofuranoside; 5,7-dimethoxyflavone 4′-*O*-[β-D-apiofuranosyl(1→5)-β-D-glucopyranoside].

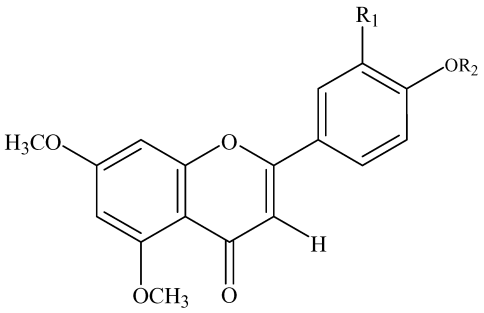
INTRODUCTION

As a part of our continuing studies on bioactive compounds from medicinal plants, we investigated the constituents of *Strobilanthes formosanus* Moore (Acanthaceae), which is a perennial herb endemic to Taiwan.[1] It has been used in Chinese folk medicine for the treatment of cough, fever, mumps, pharyngitis, hepatitis, and trauma.[2] This plant species was hitherto uninvestigated and herein we report the isolation and structural elucidation of two new flavone glycosides, 3′-hydroxy-5,7-dimethoxyflavone 4′-*O*-β-D-apiofuranoside (**1**), and 5,7-dimethoxyflavone 4′-*O*-[β-D-apiofuranosyl(1→5)-β-D-glucopyranoside] (**2**) along with four other known compounds 4′-hydroxy-5,7-dimethoxyflavone (**3**),[3] 2,6-dimethoxy-1,4-benzoquinone (**4**),[4] lupeol (**5**)[5] and betulin (**6**)[6] from the methanol extract of stem and roots of *S. formosanus*. The structures of the new compounds were elucidated based on their spectroscopic data. The known compounds were identified by comparison with literature data and authentic samples.

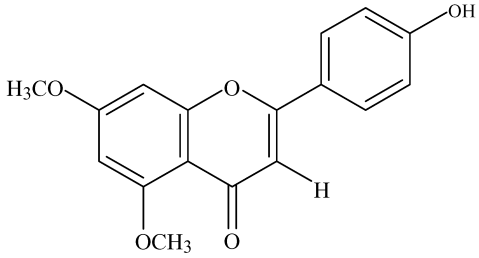
RESULTS AND DISCUSSION

Compound **1** was obtained as colourless amorphous powder. The molecular formula of **1** was obtained as $C_{22}H_{22}O_{10}$ by HRFABMS, and supported by ^{13}C NMR and DEPT analysis. Positive ion FABMS of **1** showed a pseudo-molecular ion $[M+H]^+$ peak at *m/z* 447, and a fragment ion peak at *m/z* 315 $[M+H-132]^+$ indicated the loss of a pentose moiety from the molecular ion. The UV spectrum showed characteristic flavone absorptions at 265 and 330 nm. The presence of three spin-coupling systems in the ^1H-^1H COSY spectrum of **1** indicated that the structure had 5, 7, 3′, and 4′ substituents. The ^1H NMR spectrum showed the *meta*-related subsitution of A ring of a flavone unit [δ 6.51 (1H, d, *J* = 2.0 Hz, H-6), 6.80 (1H, d, *J* = 2.0 Hz, H-8), 6.54 (1H, s, H-3)]. Ring B showed an ABX system of protondoublets [δ 7.46 (1H, d, *J* = 1.8 Hz, H-2′), 7.10 (1H, d, *J* = 9.0 Hz, H-5′), 7.46 (1H, dd, *J* = 9.0, 1.8 Hz, H-6′)]. The ^1H NMR spectrum showed a D_2O exchangeable singlet at δ 9.42, which correlated in HMBC spectrum to C-2′, C-3′ and C-4′, indicating that C-3′ was hydroxylated. The ^1H NMR signals at δ 3.83 (3H, s) and 3.90 (3H, s) were correlated to the ^{13}C NMR signals at δ 161.0 and 164.7, respectively, in its HMBC spectrum, suggesting that these methoxyl groups were located at C-5 and C-7. For the sugar moiety, the apiosyl anomeric carbon C-1″ showed a signal at δ 107.9, along with the signals of one quaternary carbon at δ 79.5 (C-3″), an oxymethine at δ 76.9 (C-2″), and two oxymethylenes at 75.0 (C-4″) and 63.1 (C-5″). An anomeric proton signal in the ^1H NMR at δ 5.56 (1H, d, *J* = 3.6 Hz) was assigned to a β-apiofuranosyl (Api) unit by 2D NMR experi-

* Corresponding author. Tel: +886-4-2203-0380; fax: +886-4-2208-3362; e-mail: yschang@mail.cmu.edu.tw



	R_1	R_2
1	OH	-β-D-apiofuranoside
2	H	-[β-D-apiofuranosyl(1→5)-β-D-glucopyranoside]



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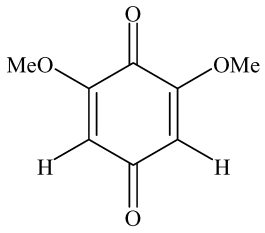

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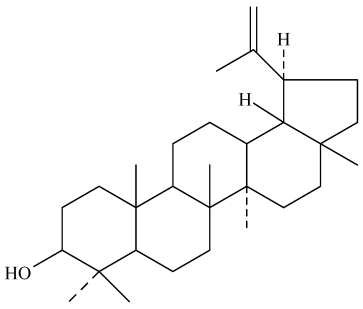

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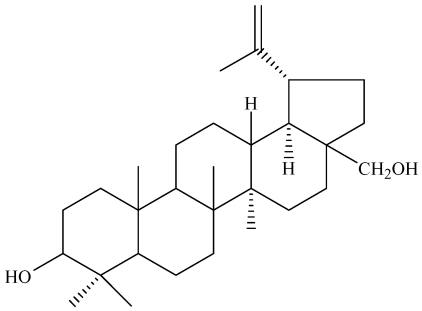

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ments (^{1}H-^{1}H COSY, NOESY, HMQC and HMBC) and coupling con stant mea sure ments (Ta bles 1 and 2).[3] There fore, **1** was elu ci dated as 3′-hydroxy-5,7-dimethoxyflavone 4′-*O*-β-D-apiofuranoside.

Com pound **2** was ob tained as colour less amor phous pow der. Its HRFABMS ex hib ited a mo lec u lar ion peak at *m/z* 592 con sis tent with the mo lec u lar for mula $C_{28}H_{32}O_{14}$ which is also sup ported by ^{13}C NMR anal y sis. FABMS in the pos itive ion mode gave a pseudo-molecular ion peak $[M+H]^+$ at *m/z* 593 and frag ment ion peak at *m/z* 460 [M+H-133], in dicat ing the loss of apiose moi ety and a peak at *m/z* 299 [M+H-132-162]$^+$ was due to the ad di tional loss of glu cose moi ety from the mo lec u lar ion. The ^{13}C and DEPT NMR spec tra showed the pres ence of two methoxyl, three meth y lene, thirteen methine and ten quarternary car bons. The UV ab sorptions at 265 and 320 nm and the typ i cal ^{1}H NMR sig nal at δ 6.68 (1H, s, H-3) re vealed the pres ence of a flavone skel e ton. ^{1}H NMR showed two meta cou pled pro ton sig nals at δ 6.51 (1H, d, *J* = 2.0 Hz, H-6) and 6.86 (1H, d, *J* = 2.0 Hz, H-8) sugges tive of methoxyl groups at C-5 and C-7 of A ring. The posi tions of methoxyl groups were con firmed by long range ^{1}H-^{13}C cor re la tions from the methoxyl pro tons at δ 3.83 (3H, s) to C-5 (δ 56.7) and 3.90 (3H, s) to C-7 (δ 56.6) in the HMBC spec trum. ^{1}H NMR spec trum also showed sig nals for

Table 1. ^{1}H NMR Data of Compounds **1** and **2** in DMSO-d_6 (600 MHz)

Protons	**1**		**2**	
	^{1}H, δ (no. of H, mult., *J*)	NOESY	^{1}H, δ (no. of H, mult., *J*)	NOESY
3	6.54 (1H, s)	H-6′	6.68 (1H, s)	H-6′
5-OCH_3	3.83 (3H, s)	---	3.83 (3H, s)	H-6
6	6.51 (1H, d, *J* = 2.0 Hz)	---	6.51 (1H, d, *J* = 2.0 Hz)	OCH_3-5
7-OCH_3	3.90 (3H, s)	---	3.90 (3H, s)	H-8
8	6.80 (1H, d, *J* = 2.0 Hz)	---	6.86 (1H, d, *J* = 2.0 Hz)	OCH_3-7
2′	7.46 (1H, d, *J* = 1.80 Hz)	---	8.01 (1H, d, *J* = 9.0 Hz)	H-3′
3′	---	---	7.14 (1H, d, *J* = 9.0 Hz)	H-2′
3′-OH	9.42 (1H, s)	---	---	---
5′	7.10 (1H, d, *J* = 9.0 Hz)	H-6′, H-1″	7.14 (1H, d, *J* = 9.0 Hz)	H-6′, H-1″
6′	7.46 (1H, dd, *J* = 9.0, 1.80 Hz)	H-5′, H-3	8.01 (1H, d, *J* = 9.0 Hz)	H-5′, H-3
1″	5.56 (1H, d, *J* = 3.6 Hz)	H-5′	5.60 (1H, d, *J* = 3.6 Hz)	H-5′, H-2″
2″	4.24 (1H, dd, *J* = 3.6, 6.6 Hz)	---	4.23 (1H, dd, *J* = 3.6, 6.6 Hz)	OH-2″, H-1″, H-5″a, H-5″b, H-1‴
2″-OH	5.39 (1H, d, *J* = 6.6 Hz)	OH-5″	5.52 (1H, d, *J* = 6.6 Hz)	H-2″, OH-3″, OH-2‴, OH-3‴, OH-4‴, OH-6‴
3″-OH	4.74 (1H, s)	---	4.98 (1H, s)	OH-3″, OH-5″, OH-2‴, OH-4‴, OH-6‴
4″a	3.75 (1H, d, *J* = 10.0 Hz)	---	3.80 (1H, d, *J* = 9.0 Hz)	H-4″b
4″b	4.06 (1H, d, *J* = 10.0 Hz)		4.11 (1H, d, *J* = 9.0 Hz)	H-4″a
5″a	3.50 (1H, m)	---	3.53 (1H, d, *J* = 10.0 Hz)	H-5″b, H-2″, H-1‴
5″b	3.50 (1H, m)		3.77 (1H, d, *J* = 10.0 Hz)	H-5″a, H-2″, H-1‴
5″-OH	4.92 (1H, t)	OH-2″	---	---
1‴	---	---	4.19 (1H, d, *J* = 7.8 Hz)	H-5″a, H-5‴, H-5″b, H-2″
2‴	---	---	3.00 (1H, m)	---
2‴-OH	---	---	5.11 (1H, d, *J* = 4.8 Hz)	OH-2″, OH-3″, OH-3‴, OH-4‴, OH-6‴
3‴	---	---	3.12-3.17 (1H, m)	---
3‴-OH	---	---	4.95 (1H, d, *J* = 5.4 Hz)	OH-2″, OH-3″, OH-2‴, OH-4‴, OH-6‴
4‴	---	---	3.04 (1H, m)	---
4‴-OH	---	---	4.98 (1H, d, *J* = 5.4 Hz)	OH-2″, OH-3″, OH-2‴, OH-3‴, OH-6‴
5‴	---	---	3.09-3.16 (1H, m)	---
6‴a	---	---	3.68 (1H, ddd, *J* = 11.1, 5.4, 1.8 Hz)	H-6‴b
6‴b			3.44 (1H, q, *J* = 11.1, 5.4 Hz)	H-6‴a
6‴-OH	---	---	4.55 (1H, t, *J* = 5.4 Hz)	OH-2″, OH-3″, OH-2‴, OH-3‴, OH-4‴

H-2′, 6′ and H-3′, 5′ at δ 8.01 (2H, d, *J* = 9.0 Hz) and 7.14 (2H, d, *J* = 9.0 Hz), re spec tively in ferred a para-substituted B ring. Ad di tionally, the ^{1}H NMR spec trum showed two anomeric pro ton sig nals at δ 5.60 (1H, d, *J* = 3.6 Hz), 4.19 (1H, d, *J* = 7.8 Hz), in di cat ing the pres ence of two sugar moi eties. The sugar moi eties were iden ti fied as apiose and glu cose by the 2D NMR ex per i ments (^{1}H-^{1}H COSY, NOESY, HMQC and HMBC) and cou pling con stant mea sure ments, which were in agreement with pub lished data.[7] In the HMBC spectrum, cross-peaks were ob served be tween the ter mi nal glucosyl anomeric pro ton and an in ner apiosyl C-5″ at 70.6 in ferred the 1→5 interlinkage of sugar moi eties. In the NOESY spectrum cross-peaks were ob served be tween the in ner apiosyl anomeric pro ton and C-4′ con firmed the place ment of a sugar unit at C-4′. Thus, com pound **2** was de ter mined to be 5,7-di-methoxyflavone 4′-*O*-[β-D-apiofuranosyl(1→2)-β-D-glu co-pyranoside] (**2**).

EXPERIMENTAL SECTION

Instrumentation

Melting points were de ter mined with a Yanaco MP-500 micromelting point apparatus and were uncorrected. UV

Table 2. ^{13}C NMR and HMBC Correlation Data of Compounds **1** and **2** in DMSO-d_6 (600 MHz)

No.	**1**		**2**	
	$^{\delta}C$, δ*	HMBC (C→H)	$^{\delta}C$, δ*	HMBC (C→H)
2	160.1 (s)	H-2′, H-6′, H-3	160.1 (s)	H-2′, H-6′, H-3
3	107.3 (d)	H-3	107.3 (d)	H-3
4	177.4 (s)	---	177.4 (s)	H-3
5	161.0 (s)	H-6, OCH_3-5	160.8 (s)	H-6, OCH_3-5
5-OCH_3	56.7 (q)	---	56.7 (q)	---
6	96.8 (d)	H-8	96.8 (d)	H-8
7	164.7 (s)	H-8, H-6, OCH_3-7	164.7 (s)	H-8, H-6, OCH_3-7
7-OCH_3	56.6 (q)	---	56.6 (q)	---
8	93.9 (d)	H-6	93.9 (d)	H-6
9	159.9 (s)	H-8	159.8 (s)	H-8
10	108.5 (s)	H-8, H-3	108.5 (s)	H-8, H-3, H-6
1′	125.1 (s)	H-5′, H-3	124.6 (s)	H-5′, H-3′, H-3
2′	113.8 (d)	H-6′, OH-3′	128.5 (d)	H-6′
3′	147.9 (s)	OH-3′, H-2′, H-5′	117.2 (s)	H-2′, H-3′, H-5′
4′	148.5 (s)	OH-3′, H-2′, H-6′, H-5′	160.1 (s)	H-2′, H-6′, H-3′, H-5′, H-1″
5′	117.0 (d)	H-6′	117.2 (d)	H-3′
6′	118.7 (d)	H-2′	128.5 (d)	H-2′
1″	107.9 (d)	OH-2″, H-4″a	107.0 (d)	OH-2″, H-2″, H-4″a
2″	76.9 (d)	OH-2″, OH-3″, H-4″a, H-5″	76.9 (d)	OH-2″, H-4″a, OH-3″
3″	79.5 (s)	OH-2″, OH-5″, OH-3″, H-4″a, H-5″	78.3 (s)	H-4″a, H-5″a, H-5″b, OH-2″, OH-3″
4″	75.0 (t)	OH-3″, H-5″	75.0 (t)	H-1″, OH-3″, H-4″a, H-5″a, H-5″b
5″	63.1 (t)	OH-5″	70.6 (t)	OH-3″, H-3, H-1‴
1‴	---	---	103.8 (d)	OH-2‴, H-5″a, H-5″b
2‴	---	---	74.0 (d)	OH-2‴, OH-4‴, H-3‴
3‴	---	---	77.2 (d)	OH-2‴, OH-3‴, OH-4‴
4‴	---	---	70.8 (d)	OH-3‴, OH-4‴
5‴	---	---	77.3 (d)	OH-6‴, OH-4‴, H-6‴b, H-5‴
6‴	---	---	61.6 (t)	OH-6‴

*Multiplicities were determined by DEPT experiment.

spectra were obtained on a Shimadzu UV-160A-visible Spectrophotometer. IR spectra were recorded in KBr using a Nicolet Impact 400 FT-IR Spectrometer. NMR (^1H, ^{13}C, DEPT, COSY, NOESY, HMQC and HMBC) spectra were obtained with Varian VXR-600 FT-NMR and Bruker DPX-200 FT-NMR spectrophotometers. EI-MS was recorded on a VG Platform II Mass Spectrometer, FABMS on a JOEL JMS-SX/SX 102A Tandem Mass Spectrometer and HRFABMS were obtained in the positive ion mode on a Finnigan/Thermo Quest MAT 95XL Mass Spectrometer.

Plant Material

The roots of *S. formosanus* Moore were collected from Nantou County of central Taiwan in August 1999, and authenticated by Dr. Chun-Chuan Chen, Associate Professor of Pharmacognosy, Institute of Chinese Pharmaceutical Sciences, China Medical University. A voucher specimen (No. ICPS-98003) has been deposited in the Herbarium of the Institute of Chinese Pharmaceutical Sciences, China Medical University, Taichung, Taiwan.

Extraction and Isolation

The air-dried roots of *S. formosanus* (3.1 Kg) was extracted exhaustively with methanol (60 L × 5) at room temperature. The extract was filtered and concentrated under reduced pressure to give 248.1 g of the residue. The crude extract was partitioned in succession between H_2O and *n*-Hexane, followed by $CHCl_3$, EtOAc and *n*-BuOH, yielding 175.5, 32.8, 5.5, 3.0, 14.8 g extracts, respectively. The *n*-BuOH extract (14.8 g) was subjected to column chromatography using Diaion HP-20 with a stepwise gradient of MeOH in $CHCl_3$ to give 5 fractions. Fraction 2 was rechromatographed over silica gel with $CHCl_3$-MeOH as eluent and finally purified by sephadex to yield compound **1** (21 mg) and **2** (45 mg). Fraction 1 was subjected to column chromatography on sephadex LH-20 eluted with MeOH to give **3** (5 mg). The

$CHCl_3$ extract (5.54 g) was directly chromatographed on silica gel eluting with $CHCl_3$ to afford 33 fractions. Fr. 3-5 was subjected to repeated column chromatography over silica gel using *n*-hexane-$CHCl_3$ (1:4) as eluent to yield **5** (21 mg). Similarly, Fr. 6-8 was rechromatographed on silica gel and eluted with *n*-hexane-$CHCl_3$ (1:4) to give **4** (3 mg) and **6** (35 mg).

3′-Hydroxy-5,7-dimethoxyflavone 4′-*O*-β-D-apiofuranoside (1)

Colourless amorphous powder; mp 198-201 °C; R_f = 0.30 ($CHCl_3$:MeOH = 7:1); UV λ_{max} (MeOH) (log ε): 265 (4.53), 330 (4.58) nm; IR (KBr) ν_{max}: 3311 (OH), 2678, 1713 (C=O), 1644, 1605 (aromatic), 1493, 1458, 1351, 1266, 1119, 1034, 996, 826 cm^{-1}; HRFABMS *m/z*: 447.1300 $[M+H]^+$ (Calcd. for $C_{22}H_{23}O_{10}$, 447.1300); FABMS *m/z* (rel. int. %): 447 $[M+H]^+$ (43.6), 315 $[M+H-132]^+$ (38); ^1H NMR: see Table 1; ^{13}C NMR: see Table 2.

5,7-Dimethoxyflavone 4′-*O*-[β-D-apiofuranosyl(1→5)-β-D-glucopyranoside] (2)

Colourless amorphous powder; mp 230.1-233.6 °C; R_f = 0.39 ($CHCl_3$:MeOH = 4:1); UV λ_{max} (MeOH) (log ε): 265 (3.98), 320 (3.98) nm; IR (KBr) ν_{max}: 3442, 3357 (OH), 2686, 1729 (C=O), 1644, 1580 (aromatic), 1598, 1513, 1466, 1428, 1351, 1243, 1158, 1113, 1065, 1003, 849 cm^{-1}; HRFABMS *m/z*: 593.1867 $[M+H]^+$ (Calcd. for $C_{28}H_{33}O_{14}$, 593.1867); FABMS *m/z* (rel. int. %): 593 $[M+H]^+$ (6.7), 299 $[M+H-132-162]^+$ (20); ^1H NMR: see Table 1; ^{13}C NMR: see Table 2.

4′-Hydroxy-5,7-dimethoxyflavone (3)

Colourless needles (MeOH); mp 289-290 °C; R_f = 0.53 ($CHCl_3$:MeOH = 12:1); EI-MS (70 eV) *m/z* (rel. int. %): 298 $[M]^+$ (68), 269 (32), 252 (27), 225 (21), 151 (26), 121 (33), 118 (57), 89 (58), 69 (100); ^1H NMR (600 MHz, DMSO-d_6): δ 7.88 (2H, d, *J* = 9.0 Hz, H-2′, H-6′), 6.90 (2H, d, *J* = 9.0 Hz, H-3′, H-5′), 6.83 (1H, d, *J* = 2.0 Hz, H-8), 6.58 (1H, s, H-3), 6.49 (1H, d, *J* = 2.0 Hz, H-6); ^{13}C-NMR (125 MHz, DMSO-d_6): δ 175.6 (s, C-4), 163.6 (s, C-7), 160.5 (s, C-5), 160.2 (s, C-2), 160.0 (s, C-4′), 159.1 (s, C-9), 127.8 (d, C-2′, 6′), 121.3 (d, C-1′), 115.8 (d, C-3′, 5′), 108.2 (s, C-10), 106.1 (d, C-3), 96.1 (d, C-6), 93.3 (d, C-8), 56.0 (q, OCH_3-5), 55.9 (q, OCH_3-7).

2,6-Dimethoxy-1,4-benzoquinone (4)

Golden yellow needles; mp: 189 °C; R_f = 0.39 ($CHCl_3$); EI-MS (70 eV) *m/z* (rel. int. %): 168 $[M]^+$ (7), 138 (2), 125 (3), 97 (5), 80 (10), 69 (100), 53 (27); ^1H NMR (200 MHz, $CDCl_3$): δ 5.86 (2H, s, H-3, H-5), 3.83 (6H, s, 2, 6-OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 186.7 (s, C-4), 176.4 (s, C-1), 157.1 (s, C-2), 107.2 (t, C-3, 5), 56.3 (d, C-2, 6-OCH_3).

Lupeol (5)

White needles; mp: 214~215 °C; R_f = 0.58 ($CHCl_3$); IR (KBr) ν_{max}: 3326 (OH), 2948 (CH), 1459 (CH_2), 1382 (CH_3), 1042 (C-O) cm^{-1}; EI-MS (70 eV) *m/z* (rel. int. %): 426 $[M]^+$ (100), 411 (17), 315 (13), 234 (11), 218 (47), 219 (14), 207 (44), 189 (41), 125 (39), 121 (39), 109 (40); ^1H NMR (200 MHz, $CDCl_3$): δ 4.69 (1H, dd, *J* = 2.4, 1.4 Hz, H-29), 4.57 (1H, d, *J* = 2.4 Hz, H-29), 3.19 (1H, m, H-3), 2.38 (1H, ddd, *J* = 11.0, 11.0, 5.5 Hz, H-19), 1.68 (3H, s, H-30), 0.76, 0.79, 0.83, 0.95, 0.97, 1.03 (3H each, s, 6 × CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 150.8 (s, C-20), 109.1 (t, C-29), 78.8 (d, C-3), 55.1 (d, C-5), 50.2 (d, C-9), 48.1 (d, C-19), 47.8 (d, C-18), 42.8 (s, C-17), 42.6 (s, C-14), 40.6 (s, C-8), 39.7 (t, C-22), 38.6 (s, C-4), 38.5 (t, C-1), 37.8 (d, C-13), 36.9 (s, C-10), 35.4 (t, C-16), 34.0 (t, C-7), 29.6 (t, C-21), 27.8 (q, C-23), 27.2 (t, C-15), 27.2 (t, C-2), 24.9 (t, C-12), 20.7 (t, C-11), 19.1 (q, C-30).

Betulin (6)

White needles; mp: 218~220 °C; R_f = 0.5 ($CHCl_3$:EtOAc, 8:1); IR (KBr) ν_{max}: 3300~3600 (OH), 2944 (CH_2), 1458, 1374, 1038 (C-O) cm^{-1}; EI-MS (70 eV) *m/z* (rel. int. %): 442 $[M]^+$ (11), 424 (4), 411 (25), 234 (17), 220 (11), 207 (41), 203 (40), 189 (53), 135 (50), 121 (53), 107 (59), 95 (83), 79 (57), 55 (100); ^1H NMR (200 MHz, $CDCl_3$): δ 4.68 (1H, br. s, H-29), 4.58 (1H, br. s, H-29), 3.80 (1H, d, *J* = 10.7 Hz, H-28), 3.33 (1H, d, *J* = 10.7 Hz, H-28), 3.14 (1H, dd, *J* = 10.4, 5.2 Hz, H-3), 1.66 (3H, s, H-30), 0.76, 0.82, 0.97, 0.98, 1.02 (3H each, s, 5 × CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.3 (s, C-20), 109.5 (t, C-29), 78.8 (d, C-3), 60.3 (t, C-28), 55.0 (d, C-5), 50.1 (d, C-9), 48.5 (d, C-18), 47.6 (d, C-19), 47.6 (s, C-17), 42.5 (s, C-14), 40.7 (s, C-8), 38.6 (s, C-4), 38.4 (t, C-1), 37.1 (d, C-13), 36.9 (s, C-10), 34.0 (t, C-7), 33.7 (t, C-22), 29.5 (t, C-21), 28.9 (t, C-16), 27.8 (q, C-23), 27.1 (t, C-2), 26.8 (t, C-15), 24.9 (t, C-12), 20.6 (t, C-11), 18.8 (q, C-30), 18.1 (t, C-6), 15.9 (q, C-26), 15.7 (q, C-25), 15.1 (q, C-24), 14.5 (q, C-27).

ACKNOWLEDGEMENTS

The authors are grateful to the National Science Council, Republic of China and China Medical University, Taichung, Taiwan, for support of this research under Grant NSC 90-2323-B-039-001 and CMC90-P-02.

Received February 26, 2003.

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