Triterpenoids from the Stems of *Momordica charantia*

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Two new cucurbitane triterpenes, (23*E*)-7*β*-methoxycucurbita-5,23,25-trien-3*β*-ol (**1**) and 23,25-dihydroxy-5*β*,19-epoxycucurbit-6-ene-3,24-dione (**2**), and a new *D*:*C*-friedooleanane triterpene, 3*α*-[(*E*)-feruloyloxy]-*D*:*C*-friedooleana-7,9(11)-dien-29-oic acid (**3**), together with two known *D*:*C*-friedooleanane triterpenes, 3*β*-[(*E*)-feruloyloxy]-*D*:*C*-friedooleana-7,9(11)-dien-29-oic acid (**4**) and 3-oxo-*D*:*C*-friedooleana-7,9(11)-dien-29-oic acid (**5**), were isolated from the stems of *Momordica charantia*. The structures of the new compounds **1**–**3** were determined by spectroscopic methods.

1. Introduction. – *Momordica charantia* L. (Cucurbitaceae), commonly known as bitter gourd or bitter melon, is a slender-stemmed tendril climbing vegetable crop and is wildly planted in tropical areas, including Asia, East Africa, and South America. The tissues of this plant have extensively been used in folk medicine for the treatment of diabetes and detoxification in Taiwan. Various investigations have shown that the crude extracts of the fruit of *M. charantia* possess diverse biological activities [1][2] and more than sixty triterpenoids have been isolated from the fruits [3–15], seeds [16–18], roots [19], leaves, and vines [20][21] of *M. charantia*. On the basis of an interest in the discovery of secondary metabolites from Taiwanese *M. charantia*, we reported the isolation and structure elucidation of fourteen cucurbitane-type triterpenoids from the MeOH extract of the stems of this plant [22][23]. In the continuing phytochemical investigation, we further isolated two new cucurbitane triterpenes, (23*E*)-7*β*-methoxycucurbita-5,23,25-trien-3*β*-ol (**1**) and 23,25-dihydroxy-5*β*,19-epoxycucurbit-6-ene-3,24-dione (**2**), and a new *D*:*C*-friedooleanane triterpene, 3*α*-[(*E*)-feruloyloxy]-*D*:*C*-friedooleana-7,9(11)-dien-29-oic acid (**3**), along with two known *D*:*C*-friedooleanane triterpenes, 3*β*-[(*E*)-feruloyloxy]-*D*:*C*-friedooleana-7,9(11)-dien-29-oic acid (**4**) [24] and 3-oxo-*D*:*C*-friedooleana-7,9(11)-dien-29-oic acid (**5**; *Fig. 1*) [25], from the same part of *M. charantia*. Here, we describe the isolation and structure elucidation of the new compounds **1**–**3**.

2. Results and Discussion. – The HR-EI-MS of **1** gave a molecular-ion peak at *m*/*z* 454.3790 that corresponded to the molecular formula $C_{31}H_{50}O_2$, indicating seven degrees of unsaturation. The IR spectrum showed bands attributable to OH

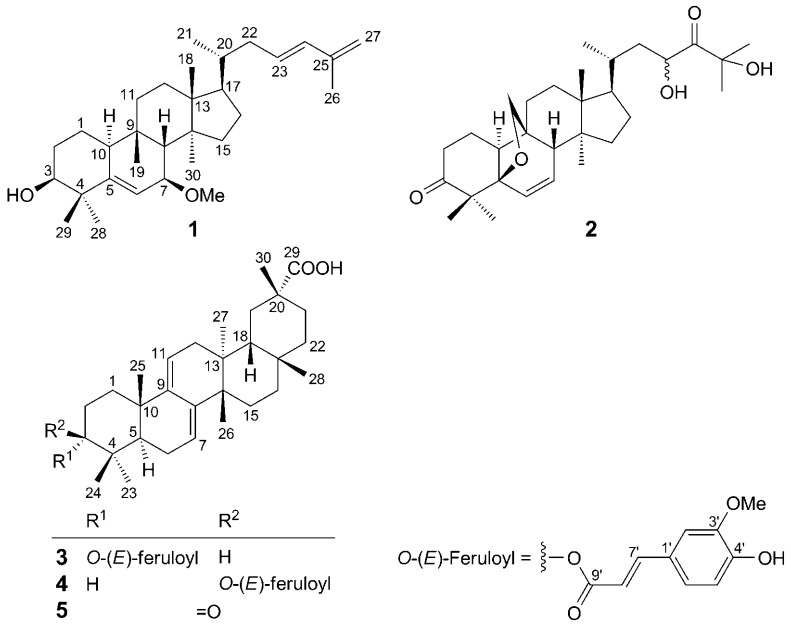

Fig. 1. *Structures of compounds* **1**–**5** *from* M. charantia

(3427 cm^{-1}), and terminal C=C bond (3060, 1654, 734 cm^{-1}) functionalities. The ^{1}H-NMR spectrum of **1** (*Table 1*) displayed signals for five tertiary Me groups (δ(H) 0.68, 0.91, 0.96, 1.02, 1.19 (5*s*)), a secondary Me group (δ(H) 0.88 (*d*, $J = 6.0$)), a vinylic Me group (δ(H) 1.82 (*s*)), a MeO group (δ(H) 3.33 (*s*)), two secondary O-bearing CH groups (δ(H) 3.41 (*d*, $J = 4.0$), 3.49 (br. *s*)), and a terminal CH_2 group (δ(H) 4.83 (br. *s*)). In addition, olefinic H-atom signals attributed to a trisubstituted C=C bond (δ(H) 5.81 (br. *d*, $J = 4.0$)) and a (*E*)-configured disubstituted C=C bond (δ(H) 6.09 (*d*, $J =$ 15.6), 5.59 (*ddd*, $J = 6.4, 8.4, 15.6$)), coupling to a neighboring CH_2 group (δ(H) 1.72–1.84 (*m*), 2.20–2.28 (*m*); δ(C) 39.8 (*t*)) were also observed. The ^{13}C-NMR spectrum of **1** (*Table 1*) exhibited 31 C-atom signals, which were resolved by DEPT experiments as signals of seven Me and seven CH_2 groups, one olefinic CH_2, four CH, two O-bearing CH, three olefinic CH groups, four quaternary C-atoms, and two quaternary olefinic and one MeO C-atom. A careful comparison of the ^{13}C-NMR data of **1** with those of (23*E*)-cucurbita-5,23,25-triene-3β,7β-diol [22] showed that the two compounds were closely similar except that the substituent at C(7) was a MeO group in **1** instead of a OH group. The MeO group was located at C(7), which was confirmed by the HMBCs between 7-MeO (δ(H) 3.33)/C(7) (δ(C) 77.2)), H–C(7) (δ(H) 3.41)/C(5) (δ(C) 146.8)), C(9) (34.0), and C(14) (47.9). The typical NMR signals of a conjugated diene functionality (δ(H) 4.83 (br. *s*, CH_2(27)), 5.59 (*ddd*, $J = 6.4, 8.4, 15.6$, H–C(23)), 6.09 (*d*, $J = 15.6$, H–C(24); δ(C) 114.1 (C(27)), 129.4 (C(23)), 134.1 (C(24)), 142.2 (C(25))) [22] and the EI-MS fragment ions at *m*/*z* 81 ([$CH_2CHCHC(CH_3)CH_2$]$^+$), 109 ([C_8H_{13} (side chain)]$^+$), and 313 ([$M - C_8H_{13} - MeOH$]$^+$) suggested that the side chain of **1** was a (23*E*)-23,25-didehydro-conjugated diene C_8 moiety. The HMBCs between

Table 1. *^{1}H- and ^{13}C-NMR Data for* **1** *and* **2**. At 400/100 MHz, respectively, in $CDCl_3$; δ in ppm, J in Hz.

Position	**1**		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
1	1.41–1.48 (*m*), 1.52–1.59 (*m*)	21.1	1.48–1.54 (*m*), 1.88–1.95 (*m*)	24.7
2	1.70–1.78 (*m*), 1.84–1.91 (*m*)	28.6	2.24–2.31 (*m*), 2.69 (*dt*, J = 6.0, 14.4)	36.1
3	3.49 (br. *s*)	76.8		214.5
4		41.7		48.4
5		146.8		89.6
6	5.81 (br. *d*, J = 4.0)	120.9	6.01 (*dd*, J = 2.0, 9.6)	131.3
7	3.41 (*d*, J = 4.0)	77.2	5.70 (*dd*, J = 3.6, 9.6)	132.2
8	2.03 (*s*)	47.9	2.37 (br. *d*, J = 2.0)	51.9
9		34.0		45.5
10	2.24–2.30 (*m*)	38.6	2.59 (*dd*, J = 5.6, 12.4)	39.1
11	1.42–1.49 (*m*), 1.58–1.65 (*m*)	32.6	1.45–1.50 (*m*), 1.66–1.72 (*m*)	23.9
12	1.46–1.54 (*m*), 1.59–1.67 (*m*)	30.0	1.48–1.56 (*m*), 1.60–1.67 (*m*)	30.8
13		46.1		45.4
14		47.9		48.7
15	1.29–1.36 (*m*)	34.7	1.28–1.37 (*m*)	33.0
16	1.28–1.36 (*m*), 1.88–1.96 (*m*)	27.7	1.84–1.92 (*m*)	28.2
17	1.46–1.54 (*m*)	50.1	1.40–1.48 (*m*)	50.8
18	0.91 (*s*)	15.4	0.89 (*s*)	15.0
19	0.96 (*s*)	28.8	3.48 (*d*, J = 8.4), 3.54 (*d*, J = 8.4)	79.8
20	1.46–1.58 (*m*)	36.7	1.82–1.91 (*m*)	32.9
21	0.88 (*d*, J = 6.0)	18.8	1.01 (*d*, J = 6.4)	17.9
22	1.72–1.84 (*m*), 2.20–2.28 (*m*)	39.8	1.38–1.44 (*m*), 1.46–1.53 (*m*)	41.3
23	5.59 (*ddd*, J = 6.4, 8.4, 15.6)	129.4	4.65–4.72 (*m*)	71.0
24	6.09 (*d*, J = 15.6)	134.1		217.1
25		142.2		77.2
26	1.82 (*s*)	18.8	1.42 (*s*)	27.7
27	4.83 (br. *s*)	114.1	1.41 (*s*)	27.8
28	1.02 (*s*)	27.8	1.11 (*s*)	24.5
29	1.19 (*s*)	25.4	1.12 (*s*)	16.7
30	0.68 (*s*)	18.0	0.92 (*s*)	20.1
7-MeO	3.33 (*s*)	56.3		
23-OH			2.98 (br. *d*, J = 8.0)	

H–C(23) (δ(H) 5.59)/C(20) (δ(C) 36.7), C(22) (39.8), and C(25) (142.2) and CH_2(27) (δ(H) 4.83)/C(24) (δ(C) 134.1), C(25), and C(26) (18.8) (*Fig. 2*) further confirmed the above proposal. The relative configurations of sterogenic C-atoms in the tetracyclic rings were determined by significant NOE correlations H–C(3) (δ(H) 3.49)/Me(28)

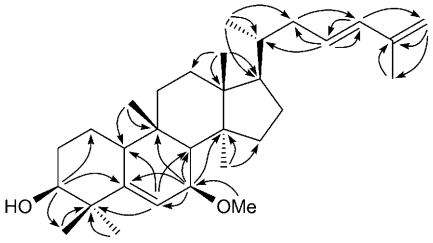

Fig. 2. *Main HMBCs of* **1**

(1.02), H–C(3)/Me(29) (1.19), H–C(7) (3.41)/Me(30) (0.68), H–C(8) (2.03)/Me(18) (0.91), H–C(8)/Me(19) (0.96), H–C(10) (2.24–2.30)/Me(28), H–C(10)/Me(30), and H–C(17) (1.46–1.54)/Me(30) in the NOESY spectrum (*Fig. 3*). The configuration of C(20) was assigned as (*R*) due to the NOESY correlations between Me(18) and H–C(20) (δ(H) 1.46–1.58); and H–C(12) (1.59–1.67) and Me(21) (0.88) (*Fig. 3*). Thus, compound **1** was determined as (23*E*)-7β-methoxycucurbita-5,23,25-trien-3β-ol.

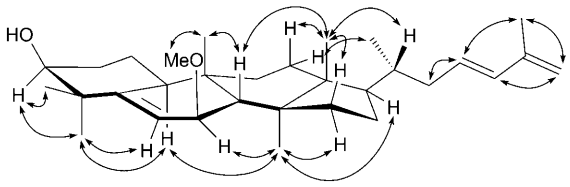

Fig. 3. *Main NOESY correlations of* **1**

Compound **2** was deduced to be a triterpenoid due to a positive *Liebermann–Burchard* test. Its HR-EI-MS showed a molecular-ion peak at *m*/*z* 486.3336, indicating the molecular formula $C_{30}H_{46}O_5$. The IR spectrum of **2** revealed the presence of OH (3393 cm^{-1}) and C=C bond (3027, 1647, and 734 cm^{-1}) functionalities. The ^{1}H- and ^{13}C-NMR data (*Table 1*) displayed signals for six tertiary Me groups (δ(H) 0.89, 0.92, 1.11, 1.12, 1.41, 1.42 (6*s*)), a secondary Me group (δ(H) 1.01 (*d*, *J* = 6.4, Me(21))), an O-bearing CH_2 group (δ(H) 3.48 (*d*, *J* = 8.4, 1 H of CH_2(19)), 3.54 (*d*, *J* = 8.4, 1 H of CH_2(19)); δ(C) 79.8 (*t*, C(19)), and an O-bearing CH group (δ(H) 4.65–4.72 (*m*, H–C(23))), coupling with a OH group (δ(H) 2.98 (br. *d*, *J* = 8.0, 23-OH); disappeared on D_2O exchange). Moreover, the NMR signals for an allylic *ABX* system of (*Z*)-oriented cyclohexene (δ(H) 6.01 (*dd*, *J* = 2.0, 9.6, H–C(6)), 5.70 (*dd*, *J* = 3.6, 9.6, H–C(7)), 2.37 (br. *d*, *J* = 2.0, H–C(8)); δ(C) 131.3 (*d*, C(6)), 132.2 (*d*, C(7)), 51.9 (*d*, C(8))) were also observed. Altogether, 30 C-atom signals were observed in the ^{13}C-NMR spectrum of **2** and were attributed by DEPT experiments to seven Me and seven CH_2 groups, one O-bearing CH_2 group, four CH groups, one O-bearing CH group, two olefinic CH groups, and four quaternary, two O-bearing quaternary, and two CO C-atoms. The ^{1}H- and ^{13}C-NMR data of the tetracyclic skeleton of **2** were similar to those of (23*E*)-5β,19-epoxycucurbita-6,23-diene-3β,25-diol [22], except for the signals of the *A*-ring atoms (C(1) to C(5), C(10)). The absence of the NMR signal of an O-bearing CH group, accompanied by the appearance of a ketone CO group signal (δ(C) 214.5), in **2** indicated that the secondary alcohol at C(3) was oxidized to a ketone functionality. The structure of the side chain of **2** was elucidated as a 24-oxo-23,25-dihydroxy C_8 moiety, which was deduced from the HMBCs between Me(21) (δ(H) 1.01)/C(17) (δ(C) 50.8)), C(20) (32.9)) and C(22) (41.3); CH_2(22) (δ(H) 1.46–1.53)/C(17)), C(20) and C(23) (δ(C) 71.0); H–C(23) (δ(H) 4.65–4.72)/C(22)), and Me(27) (δ(H) 1.41)/C(24) (δ(C) 217.1)) and C(25) (77.2). The structure of the side chain of **2** was further confirmed by the EI-MS fragment ions at *m*/*z* 428 ($[M - C_3H_7O + H]^+$), 327 ($[M - C_8H_{15}O_3$ (side chain)$]^+$), and 159 ([side chain]$^+$). The NOESY correlations Me(18) (δ(H) 0.89)/H–C(20) (1.82–1.91) and H–C(12) (1.60–1.67)/Me(21) (1.01) allowed us to assure the configuration at C(20) as (*R*). Thus, compound **2** was determined as 23,25-dihydroxy-5β,19-epoxycucurbit-6-ene-3,24-dione.

Compound **3** was isolated as a colorless amorphous solid. Its HR-EI-MS showed a molecular-ion peak at m/z 630.3946, corresponding to the molecular formula $C_{40}H_{54}O_6$, which represents 14 degrees of unsaturation. The IR spectrum of **3** indicated the existence of OH (3420 cm^{-1}), carboxylic acid (3042, 1708 cm^{-1}), conjugated ester (1698 cm^{-1}), conjugated C=C bond (1631, 1592, 812 cm^{-1}) functionalities, and of a phenyl group (1592, 1514 cm^{-1}). In the ^{1}H-NMR spectrum of **3** (*Table 2*), the singals for seven tertiary Me groups (δ(H) 0.72, 0.82, 0.86, 0.90, 0.93, 1.01, 1.16 (7*s*)), two olefinic H-atoms (δ(H) 5.18 (br. *s*), 5.40 (br. *s*)), and an O-bearing CH group in proximity to an ester group (δ(H) 4.82 (br. *s*)) were observed. The ^{1}H-NMR spectrum also revealed the presence of an (*E*)-feruloyl moiety on the basis of the signals of two coupled olefinic H-atoms (δ(H) 6.27 (*d*, $J = 16.0$) and 7.58 (*d*, $J = 16.0$)), a set of *ABX* aromatic H-atoms (δ(H) 6.87 (*d*, $J = 8.8$), 6.97 (*d*, $J = 2.0$), and 7.04 (*dd*, $J = 2.0, 8.8$)), and a MeO group (δ(H) 3.90 (*s*), showing a NOE correlation with a signal at δ(H) 7.04). The ^{13}C-NMR spectrum of **3** (*Table 2*) exhibited 40 C-atom signals, which were attributed by the DEPT experiments to seven Me, one MeO, nine CH_2, two CH, one O-bearing CH groups, six quaternary C-atoms, seven olefinic CH groups, five quaternary olefinic, one carboxylic acid, and one ester CO C-atoms. The UV absorption at λ_{max} 238 nm, as well as the ^{1}H- and ^{13}C-NMR signals for olefinic functionalities (δ(H) 5.18 (br. *s*, 1 H), 5.40 (br. *s*, 1 H); δ(C) 113.7 (*d*), 117.8 (*d*), 141.6 (*s*), 144.2(*s*)) were consistent with a 7,8,9,11-tetradehydro conjugated diene system [26], which led to the proposal that compound **3** is a *D* : *C*-friedooleana-7,9(11)-diene triterpene. The HMBCs between CH_2(6) (δ(H) 2.02 – 2.10)/C(7) (δ(C) 117.8)) and CH_2(12) (δ(H) 2.09 – 2.18)/C(11) (δ(C) 113.7)) further confirmed the conjugated diene system. Comparisons of the ^{1}H- and ^{13}C-NMR spectroscopic data of **3** with those of 3β-[(*E*)-feruloyloxy]-*D* : *C*-

Table 2. *^{1}H- and ^{13}C-NMR Data for* **3**. At 400/100 MHz, respectively, in $CDCl_3$; δ in ppm, J in Hz.

Position	δ(H)	δ(C)	Position	δ(H)	δ(C)
1	1.48 – 1.57 (*m*), 1.73 – 1.81 (*m*)	30.2	21	1.29 – 1.38 (*m*), 2.16 – 2.24 (*m*)	29.5
2	1.79 – 1.87 (*m*), 1.96 – 2.04 (*m*)	23.2	22	0.82 – 1.89 (*m*), 1.95 – 2.03 (*m*)	32.6
3	4.82 (br. *s*)	78.3	23	0.86 (*s*)	27.3
4		37.0	24	1.01 (*s*)	22.1
5	1.66 – 1.74 (*m*)	43.2	25	0.90 (*s*)	20.4
6	2.02 – 2.10 (*m*), 2.12 – 2.20 (*m*)	23.8	26	0.82 (*s*)	20.2
7	5.40 (br. *s*)	117.8	27	0.72 (*s*)	19.0
8		141.6	28	0.93 (*s*)	30.9
9		144.2	29		183.2
10		36.1	30	1.16 (*s*)	32.9
11	5.18 (br. *s*)	113.7	1′		127.2
12	1.63 – 1.72 (*m*), 2.09 – 2.18 (*m*)	38.8	2′	6.97 (*d*, $J = 2.0$)	110.3
13		37.4	3′		146.6
14		40.5	4′		147.8
15	1.23 – 1.29 (*m*), 1.47 – 1.54 (*m*)	26.8	5′	6.87 (*d*, $J = 8.8$)	114.8
16	1.33 – 1.41 (*m*), 1.66 – 1.74 (*m*)	36.9	6′	7.04 (*dd*, $J = 2.0, 8.8$)	122.7
17		31.3	7′	7.58 (*d*, $J = 16.0$)	144.8
18	1.47 – 1.53 (*m*)	45.1	8′	6.27 (*d*, $J = 16.0$)	116.2
19	1.60 – 1.69 (*m*), 2.24 – 2.33 (*m*)	30.4	9′		167.2
20		40.1	3′-MeO	3.90 (*s*)	56.3

friedooleana-7,9(11)-dien-29-oic acid [24] showed that the signal patterns of these two compounds were almost identical, except that the O-bearing CH group at C(3) was β-orientated in **3** instead of α. A broad *singlet* singal of H–C(3) at δ(H) 4.82 (br. *s*) and the HMBC between H–C(3) and C(9′) (δ(C) 167.0 (*s*)) confirmed that the (*E*)-feruloyloxy moiety was attached to C(3) in α-orientation. Hence, compound **3** was determined as 3α-[(*E*)-feruloyloxy]-*D*:*C*-friedooleana-7,9(11)-dien-29-ol.

Experimental Part

General. TLC was performed by using silica-gel *60* F_{254} plates (*Merck*). Column chromatography (CC): silica gel (SiO_2; 230–400 mesh ASTM, *Merck*). HPLC: *Lichrosorb Si 60* column (5 µm, 250 × 10 mm). Optical rotations: *JASCO DIP-180* digital spectropolarimeter. UV Spectra: *Shimadzu UV-1601PC* spectrophotometer. IR Spectra: *Nicolet 510P* FT-IR spectrometer. NMR Spectra: in $CDCl_3$ at r.t. on a *Varian Mercury plus 400* NMR spectrometer, and the solvent resonance used as internal shift reference (TMS as standard); the 2D-NMR spectra recorded by using standard pulse sequences. EI-MS and HR-EI-MS: *Finnigan TSQ-700* and *JEOL SX-102A* mass spectrometers, resp.

Plant Material. The stems of *M. charantia* were collected in Pingtung County, Taiwan (July, 2003) and identified by Prof. *Sheng-Zehn Yang*, Curator of Herbarium, National Pingtung University of Science and Technology, where a voucher specimen (No. 2013) was deposited.

Extraction and Isolation. The sliced, air-dried stems (18 kg) of *M. charantia* were exhaustively extracted with MeOH (3 × 30 l) at r.t. (7 d each). The combined MeOH extracts were evaporated under reduced pressure to obtain a black residue, which was suspended in H_2O (3 l), and then partitioned sequentially, using AcOEt and BuOH (3 × 2 l) as solvent. The AcOEt fraction (386 g) was subjected to CC (120 × 10 cm) on SiO_2 using a stepwise gradient mixture hexane/AcOEt as eluent. Eleven fractions were collected as follows: *Fr. 1* (5000 ml; hexane), *Fr. 2* (4000 ml; hexane/AcOEt 49:1), *Fr. 3* (4000 ml; hexane/AcOEt 19:1), *Fr. 4* (4000 ml; hexane/AcOEt 9:1), *Fr. 5* (4000 ml; hexane/AcOEt 17:3), *Fr. 6* (4000 ml; hexane/AcOEt 8:2), *Fr. 7* (4000 ml; hexane/AcOEt 7:3), *Fr. 8* (3000 ml; hexane/AcOEt 5:5), *Fr. 9* (3000 ml; hexane/AcOEt 4:6), *Fr. 10* (3000 ml; hexane/AcOEt 2:8), and *Fr. 11* (6000 ml; AcOEt). *Fr. 6* was further chromatographed on a SiO_2 column (5 × 45 cm), eluted with a gradient of CH_2Cl_2/AcOEt (8:1 to 0:1) to yield seven fractions (each *ca.* 700 ml), *Frs. 6A–6G. Fr. 6F* was subjected to CC (SiO_2; hexane/CH_2Cl_2/AcOEt 3:3:1) and semiprep. HPLC (hexane/AcOEt 7:3) to yield **3** (6 mg). CC of *Fr. 6G* (SiO_2; CH_2Cl_2/AcOEt gradient 100:1 to 0:1) to yield **5** (11 mg). *Fr. 7* was further chromatographed (SiO_2; (5 × 45 cm); CH_2Cl_2/AcOEt gradient 8:1 to 0:1) to give seven fractions (each *ca.* 600 ml), *Frs. 7A–7G.* HPLC of *Fr. 7F* with hexane/CH_2Cl_2/AcOEt 3:3:1 and hexane/AcOEt 7:3 yielded **4** (3 mg). *Fr. 8* was further purified by CC (SiO_2 (5 × 45 cm); CH_2Cl_2/AcOEt 7:1) to provide six fractions (each *ca.* 500 ml), *Frs. 8A–8F. Fr. 8E* was subjected to CC (SiO_2; hexane/CH_2Cl_2/AcOEt 3:3:1) and semiprep. HPLC (CH_2Cl_2/AcOEt 3:2) to yield **1** (1 mg) and **2** (5 mg).

*(23*E*)-7β-Methoxycucurbita-5,23,25-trien-3β-ol* (=(*1*S,*4*S,*7*S,*9β,23*E)*-7-Methoxy-9,10,14-trimethyl-4,9-cyclo-9,10-secocholesta-5,23,25-trien-1-ol*; **1**). Amorphous white powder. $[\alpha]_D^{25} = +70.1$ ($c = 0.07$, $CHCl_3$). IR (KBr): 3427, 3060, 2940, 2872, 1713, 1654, 1455, 1382, 1270, 1182, 1080, 977, 934, 734. ^{1}H- and ^{13}C-NMR: *Table 1.* EI-MS: 454 (58, M^+), 436 (100), 421 (65), 421 (63), 389 (30), 367 (10), 351 (23), 339 (23), 313 (5), 223 (52), 203 (38), 187 (38), 164 (38), 149 (40), 135 (40), 123 (40), 109 (53), 95 (42), 81 (45). HR-EI-MS: 454.3790 (M^+, $C_{31}H_{50}O_2^+$; calc. 454.3813).

23,25-Dihydroxy-5β,19-epoxycucurbit-6-ene-3,24-dione (=(*5*R,*8*S,*9*S,*10*S,*13*R,*14*S,*17*R*)-17-(4,6-Dihydroxy-6-methyl-5-oxoheptan-2-yl)-1,8,10,11,12,13,14,15,16,17-decahydro-4,4,13,14-tetramethyl-2*H*-5,9-(epoxymethano)cyclopenta[*a*]phenanthren-3(*4*H)-one*; **2**). Amorphous white powder. $[\alpha]_D^{25} = -82.6$ ($c = 0.12$, $CHCl_3$). IR (KBr): 3393, 3027, 2975, 2945, 2872, 1718, 1703, 1647, 1470, 1372, 1270, 1187, 1133, 1041, 973, 861, 734. ^{1}H- and ^{13}C-NMR: *Table 1.* EI-MS: 486 (2, M^+), 468 (7), 428 (100), 412 (16), 398 (18), 389 (15), 367 (14), 355 (60), 343 (49), 327 (14), 325 (22), 309 (20), 187 (43), 173 (25), 159 (30), 145 (29), 133 (23), 121 (22), 109 (16), 55 (18). HR-EI-MS: 486.3336 (M^+, $C_{30}H_{46}O_5^+$; calc. 486.3346).

*3α-[(*E*)-Feruloyloxy]*-D:C-*friedooleana-7,9(11)-dien-29-oic Acid* (=(2R,*4a*S,*6a*S,*8a*R,*10*-R,*12a*S,*14a*S,*14b*R)*-1,2,3,4,4a,5,6,6a,8,8a,9,10,11,12,12a,14,14a,14b-Octadecahydro-10-{[(2*E*)*-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoyl]oxy}-2,4a,6a,9,9,12a,14a-heptamethylpicene-2-carboxylic Acid*; **3**). Amorphous white solid. $[\alpha]_D^{25} = +54.5$ ($c = 0.16$, $CHCl_3$). UV (MeOH): 238 (4.10), 285 (4.11), 335 (4.40). IR (KBr): 3420, 3042, 2940, 2867, 1708, 1698, 1631, 1592, 1514, 1460, 1372, 1270, 1168, 1031, 982, 895, 812, 734, 705. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 630 (62, M^+), 584 (6), 454 (2), 436 (16), 421 (20), 367 (8), 253 (18), 194 (18), 177 (100), 145 (26), 107 (18). HR-EI-MS: 630.3946 (M^+, $C_{40}H_{54}O_6^+$; calc. 630.3922).

This research was supported by grants to *C.-I C.* from the *National Science Council of Taiwan* (NSC 97-2317-B-020-002 and NSC 98-2622-B-020-003-CC1). We thank Ms. *Shu-Yun Sun* for the EI-MS and HR-EI-MS experiments in the Instrumentation Center of the College of Science, National Taiwan University. We are grateful to the *National Center for High-Performance Computing* for computer time and facilities.

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Received October 29, 2009