

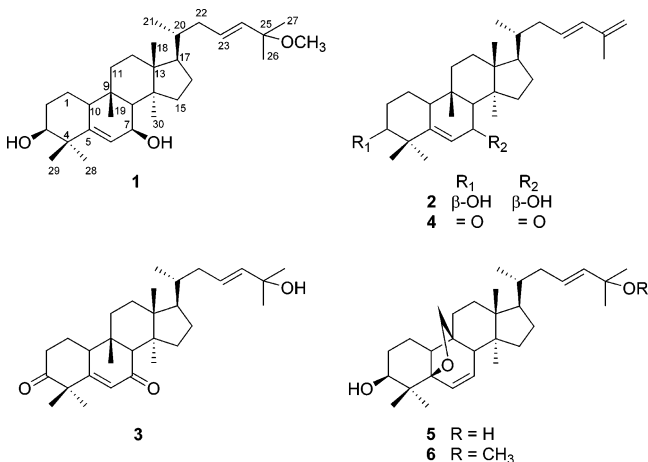
Cucurbitane-Type Triterpenoids from *Momordica charantia*Chi-I Chang,[†] Chiy-Rong Chen,[‡] Yun-Wen Liao,[†] Hsueh-Ling Cheng,[†] Yo-Chia Chen,[†] and Chang-Hung Chou^{*,§}

Graduate Institute of Biotechnology, National Pingtung University of Science and Technology, Pingtung 912, Taiwan, Republic of China, Institute of Molecular Biology, National Chung Hsing University, Taichung 402, Taiwan, Republic of China, and Department of Tropical Agriculture and International Cooperation, National Pingtung University of Science and Technology, Pingtung 912, Taiwan, Republic of China

Received March 13, 2006

Five new cucurbitane-type triterpenes, (23*E*)-25-methoxycucurbit-23-ene-3 β ,7 β -diol (**1**), (23*E*)-cucurbita-5,23,25-triene-3 β ,7 β -diol (**2**), (23*E*)-25-hydroxycucurbita-5,23-diene-3,7-dione (**3**), (23*E*)-cucurbita-5,23,25-triene-3,7-dione (**4**), and (23*E*)-5 β ,19-epoxycucurbita-6,23-diene-3 β ,25-diol (**5**), together with one known triterpene, (23*E*)-5 β ,19-epoxy-25-methoxycucurbita-6,23-dien-3 β -ol (**6**), have been isolated from the methanol extract of the stems of *Momordica charantia*. The structures of the new compounds were elucidated by spectroscopic methods.

Momordica charantia L. (Cucurbitaceae), a slender-stemmed tendril climber, is widely cultivated as a vegetable crop and has been used extensively in folk medicine as a remedy for diabetes in Asia. Previous investigations have shown that crude extracts of the fruit of *M. charantia* possess antidiabetic activity,^{1,2} and many cucurbitane-type triterpenoids have been isolated from the fruits,^{3–9} seeds,^{10–12} and leaves and vines¹³ of *M. charantia*. On the basis of an interest in the discovery of bioactive natural products, we have continued with our efforts to elucidate the antidiabetic components from Taiwanese *M. charantia*. We have examined the methanolic extract of the stems of this plant and have isolated five new cucurbitane-type triterpenoids (compounds **1–5**), together with one known cucurbitane-type triterpene (compound **6**).¹⁴ In this paper, we report the extraction, isolation, purification, and structural elucidation of those new constituents based on spectroscopic analysis.



Results and Discussion

Compound **1** gave a positive Liebermann-Burchard test. The HREIMS of the ion peak at m/z 472.3916 [M]⁺ was consistent with the molecular formula C₃₁H₅₂O₃. The IR spectrum showed the presence of hydroxyl (3360 cm⁻¹) and double-bond (1625 and 700 cm⁻¹) functionalities. The ¹H and ¹³C NMR spectra of **1** (Table 1)

indicated the presence of seven tertiary methyls [δ_H 0.69, 0.89, 1.01, 1.04, 1.19 (3H each, s), 1.23 (3H \times 2, s)], one secondary methyl [δ_H 0.87 (3H, d, J = 6.6 Hz)], a methoxyl [δ_H 3.12 (3H, s)], and two oxymethines [δ_H 3.52 (1 H, br s), 3.92 (1H, d, J = 5.6 Hz)]. In addition, olefinic NMR signals of a trisubstituted double bond [δ_H 5.80 (1H, d, J = 5.6 Hz); δ_C 122.6 (d), 146.8 (s)] and a *trans*-oriented disubstituted double bond [δ_H 5.36 (1H, d, J = 15.6 Hz), 5.48 (1H, ddd, J = 15.6, 8.4, 5.6 Hz); δ_C 128.5 (d), 136.7 (d)] coupling to a neighboring methylene [δ_H 1.76 m, 2.16 m; δ_C 39.4 (t)] were also found. The ¹³C NMR spectrum of **1** revealed 31 carbon signals, which were assigned by DEPT experiments as nine methyls, seven methylenes, four methines, five quaternary carbons, four olefinic carbons, and two oxygenated carbons. By comparison of the ¹H and ¹³C NMR data with the known compound (23*E*)-3 β -hydroxy-7 β ,25-dimethoxycucurbita-5,23-dien-19-al,⁹ compound **1** was considered as a cucurbitane-type triterpene with a Δ^{23} -unsaturated C-8 side-chain moiety. The downfield shift of H-7 [δ_H 3.92 (1H, d, J = 5.6 Hz)] in **1** indicated the presence of a hydroxyl group at C-7 instead of 7 β -methoxy group. Moreover, the disappearance of the aldehyde signal of C-19, along with the presence of one additional methyl carbon signal (δ_C 29.5), led to the proposal that the aldehyde group of (23*E*)-3 β -hydroxy-7 β ,25-dimethoxycucurbita-5,23-dien-19-al was reduced to a methyl group in **1**. The HMBC spectrum of **1** showed long-range correlations between H-3 (δ_H 3.52) and C-1 (δ_C 20.9) and C-5 (δ_C 146.8) and between H-7 (δ_H 3.92) and C-5 (δ_C 146.8), C-6 (δ_C 122.6), C-8 (δ_C 53.2), and C-9 (δ_C 33.9), and this suggested that two hydroxyl groups were located at C-3 and C-7, respectively. The olefinic proton H-6 (δ_H 5.80) also exhibited HMBC correlations with C-4 (δ_C 41.5), C-7 (δ_C 68.2), C-8 (δ_C 53.2), and C-10 (δ_C 38.5). Furthermore, the α -orientation of H-7 was determined by the cross-peaks between H-7 (δ_H 3.92) and H-30 (δ_H 0.69) observed in the NOESY spectrum of **1**. From the above evidence, compound **1** was characterized as (23*E*)-25-methoxycucurbit-23-ene-3 β ,7 β -diol. Complete ¹H–¹H COSY, HMQC, HMBC, and NOESY spectra.

The HREIMS of **2** showed a molecular ion peak at m/z 440.3625, corresponding to the molecular formula C₃₀H₄₈O₂ and indicating seven degrees of unsaturation. The IR spectrum displayed absorptions for hydroxyl (3350 cm⁻¹) and terminal double-bond (3080, 1650, 875 cm⁻¹) functionalities. The ¹H NMR spectrum of **2** (Table 1) showed resonances for five tertiary methyls [δ_H 0.69, 0.90, 1.03, 1.06, 1.20 (3H each, s)], a secondary methyl [δ_H 0.89 (3H, d, J = 6.4 Hz)], a vinylic methyl [δ_H 1.83 (3H, s)], two secondary oxygenated methines [δ_H 3.52 (1 H, t, J = 2.4 Hz), 3.92 (1H, d, J = 5.6 Hz)], and a terminal methylene [δ_H 4.83 (2H, br s)]. Olefinic proton signals attributed to a trisubstituted double bond [δ_H 5.80 (1H, d, J = 5.6 Hz)] and a *trans*-oriented disubstituted double bond

* To whom correspondence should be addressed. Tel: 886-8-770-3660. Fax: 886-8-770-2226. E-mail: choumasa@mail.npust.edu.tw.

[†] Graduate Institute of Biotechnology, National Pingtung University of Science and Technology.

[‡] National Chung Hsing University.

[§] Department of Tropical Agriculture and International Cooperation, National Pingtung University of Science and Technology.

Table 1. ^1H NMR Data for **1–5** (400 MHz in CDCl_3)

position	1	2	3	4	5
1	1.48 m, 1.56 m	1.50 m, 1.60 m	1.62 m, 2.10 m	1.63 m, 2.10 m	1.45 m
2	1.86 m, 1.72 m	1.72 m, 1.88 m	2.50 m, 2.58 m	2.51 m, 2.59 m	1.82 m
3	3.52 br s	3.52 t (2.4)			3.36 m
6	5.80 d (5.6)	5.80 d (5.6)	6.14 d (2.4)	6.14 d (2.4)	6.02 dd (1.6, 9.6)
7	3.92 d (5.6)	3.92 d (5.6)			5.61 dd (9.6, 3.6)
8	1.98 br s	2.00 br s	2.41 s	2.41 s	2.32 br s
10	2.28 m	2.29 m	2.89 m	2.90 m	2.24 dd (2.8)
11	1.42 m, 1.62 m	1.46 m, 1.62 m	1.54 m, 1.77 m	1.56 m, 1.78 m	1.46 m, 1.80 m
12	1.47 m, 1.64 m	1.48 m, 1.62 m	1.60 m, 1.74 m	1.62 m, 1.78 m	1.64 m
15	1.28 m, 1.32 m	1.28 m, 1.33 m	1.08 m, 1.55 m	1.10 m, 1.56 m	1.35 m
16	1.32 m, 1.88 m	1.40 m, 1.90 m	1.38 m, 1.86 m	1.42 m, 1.90 m	1.42 m, 2.00 m
17	1.44 m	1.46 m	1.42 m	1.50 m	1.48 m
18	0.89 s	0.90 s	0.87 s	0.88 s	0.84 s
19	1.04 s	1.06 s	0.93 s	0.92 s	3.50 d (8.4), 3.65 d (8.4)
20	1.48 m	1.32 m	1.54 m	1.52 m	1.45 m
21	0.87 d (6.6)	0.89 d (6.4)	0.88 d (6.6)	0.89 d (6.6)	0.87 d (6.6)
22	1.76 m, 2.16 m	1.79 m, 2.22 m	1.72 m, 2.12 m	1.78 m, 2.21 m	1.80 m, 2.14 m
23	5.48 ddd (15.6, 8.4, 5.6)	5.60 ddd (15.6, 7.2, 7.2)	5.57 m	5.59 m	5.57 m
24	5.36 d (15.6)	6.08 d (15.6)	5.57 m	6.09 d (15.6)	5.57 m
26	1.23 s	1.83 s	1.28 s	1.81 s	1.29 s
27	1.23 s	4.83, br s	1.28 s	4.83 br s	1.29 s
28	1.19 s	1.20 s	1.33 s	1.33 s	1.18 s
29	1.01 s	1.03 s	1.31 s	1.31 s	0.87 s
30	0.69 s	0.69 s	0.86 s	0.86 s	0.84 s
OCH ₃	3.12 s				
OH					3.98 d (9.6)

$[\delta_{\text{H}} 6.08 (1\text{H}, d, J = 15.6 \text{ Hz}), 5.60 (1\text{H}, \text{ddd}, J = 15.6, 7.2, 7.2 \text{ Hz})]$ coupling to a neighboring methylene [$\delta_{\text{H}} 1.79 \text{ m}, 2.22 \text{ m}; \delta_{\text{C}} 39.7 (t)$] were also observed. Altogether, 30 carbon signals were observed in the ^{13}C NMR spectrum of **2** and were sorted into seven methyls, seven methylenes, four methines, four quaternary carbons, six olefinic carbons, and two secondary oxygenated carbons. The ^{13}C NMR data were very similar to those of **1**, except for the signals of C-17–C-23 of the side chain. A (23*E*)- $\Delta^{23,25}$ -conjugated diene C-8 moiety as the side chain of **2** was suggested by both the NMR data [$\delta_{\text{H}} 4.83 (2\text{H}, \text{br s}, \text{H-27}), 5.60 (1\text{H}, \text{ddd}, J = 15.6, 7.2, 7.2 \text{ Hz}), 6.08 (1\text{H}, d, J = 15.6 \text{ Hz}); \delta_{\text{C}} 114.0 (C-27), 129.4 (C-23), 134.1 (C-24), 142.2 (C-25)]$ and the fragment ions in the EIMS at $m/z 81 [\text{CH}_2\text{CHCHC}(\text{CH}_3)\text{CH}_2]^+$, $m/z 109 [\text{side chain}]^+$, $m/z 331 [\text{M} - \text{side chain}]^+$. In a HMBC experiment, correlations between H-23 ($\delta_{\text{H}} 5.60$) and C-20 ($\delta_{\text{C}} 36.6$), C-22 ($\delta_{\text{C}} 39.7$), and C-25 ($\delta_{\text{C}} 142.2$) and between H-27 ($\delta_{\text{H}} 4.83$) and C-23 ($\delta_{\text{C}} 129.4$), C-25 ($\delta_{\text{C}} 142.2$), and C-26 ($\delta_{\text{C}} 18.7$) were observed. The relative configurations of methyl groups and other protons in the tetracyclic rings were determined by significant NOE correlations between H-3 ($\delta_{\text{H}} 3.52$) and H-28 ($\delta_{\text{H}} 4.83$), H-7 ($\delta_{\text{H}} 3.92$) and H-30 ($\delta_{\text{H}} 0.69$), and H-30 ($\delta_{\text{H}} 0.69$) and H-17 ($\delta_{\text{H}} 1.46$) in the NOESY spectrum. Thus, compound **2** was elucidated as (23*E*)-cucurbita-5,23,25-triene-3 β ,7 β -diol.

By HREIMS, compound **3** revealed a molecular formula of $\text{C}_{30}\text{H}_{46}\text{O}_3$ from the molecular ion at $m/z [M]^+$ 454.3423, indicating the presence of eight degrees of unsaturation. The IR spectrum showed absorption bands at 3400 cm^{-1} (hydroxyl), 1710 cm^{-1} (isolated ketone), and 1655 cm^{-1} (conjugated ketone). The UV spectrum displayed an absorption maximum at 256 nm. The ^1H and ^{13}C NMR spectra of **3** (Tables 1 and 2) exhibited seven tertiary methyls [$\delta_{\text{H}} 0.86, 0.87, 0.93, 1.31, 1.33 (3\text{H each, s})$ and $1.28 (3\text{H} \times 2, \text{s})]$ and a secondary methyl [$\delta_{\text{H}} 0.88 (3\text{H}, d, J = 6.6 \text{ Hz})]$ and an α,β -unsaturated carbonyl system [$\delta_{\text{H}} 6.14 (1\text{H}, d, J = 2.4 \text{ Hz}); \delta_{\text{C}} 125.4 (d), 167.6 (s), 202.4 (s)$]. Unambiguous comparison of ^1H and ^{13}C NMR data between **1** and **3** revealed that two oxymethines at C-3 and C-7 in **1** were absent. Instead, an isolated ketone and α,β -unsaturated carbonyl carbons at $\delta_{\text{C}} 211.6 (C-3)$ and $202.4 (C-7)$ and a low-field-shifted carbon at $\delta_{\text{C}} 38.1 (C-2)$ were observed, indicating that **3** is an oxidized derivative of **1**. The isolated ketone and α,β -unsaturated carbonyl carbons were respectively assigned at C-3 and C-7, which were supported by the HMBC correlations between H-2 ($\delta_{\text{H}} 2.50, 2.58$) and C-1 (δ_{C}

Table 2. ^{13}C NMR Data for **1–5** (75 MHz in CDCl_3)

position	1	2	3	4	5
1	20.9	21.0	23.6	23.6	17.6
2	28.6	28.7	38.1	38.1	27.3
3	76.7	76.7	211.6	211.6	76.1
4	41.5	41.5	51.4	51.4	37.2
5	146.8	146.7	167.6	167.6	87.5
6	122.6	122.5	125.4	125.4	131.9
7	68.2	68.2	202.4	202.3	131.5
8	53.2	53.1	59.2	59.2	52.0
9	33.9	33.9	36.8	36.8	45.4
10	38.5	38.6	41.2	41.2	38.8
11	32.4	32.5	31.3	31.3	23.5
12	30.0	30.0	29.7	29.7	30.8
13	45.9	45.9	48.5	48.5	45.4
14	48.2	48.2	45.7	45.8	48.8
15	34.6	34.6	34.5	34.5	33.1
16	27.7	27.8	27.7	27.8	28.0
17	49.9	50.1	49.4	49.6	50.0
18	15.4	15.4	15.4	15.4	14.9
19	29.5	29.6	27.2	27.2	79.8
20	36.1	36.6	36.2	36.6	36.1
21	18.7	18.8	18.7	18.9	18.6
22	39.4	39.7	39.0	39.6	39.1
23	128.5	129.4	125.0	129.0	125.1
24	136.7	134.1	139.6	134.3	139.6
25	74.8	142.2	70.7	142.1	71.0
26	25.8	18.7	30.0	18.7	29.8
27	26.1	114.0	29.9	114.2	29.9
28	25.4	25.4	23.0	23.0	20.5
29	27.7	27.7	28.4	28.4	24.5
30	17.7	17.8	17.9	18.0	20.0
OCH ₃	50.2				

23.6), C-3 ($\delta_{\text{C}} 211.6$), and C-10 ($\delta_{\text{C}} 41.2$) and between H-6 ($\delta_{\text{H}} 6.14$) and C-4 ($\delta_{\text{C}} 51.4$), C-7 ($\delta_{\text{C}} 202.4$), C-8 ($\delta_{\text{C}} 59.2$), and C-10 ($\delta_{\text{C}} 41.2$). ^1H – ^1H COSY, HMQC, and HMBC analysis, together with the fragment ion at $m/z 355 [\text{M} - \text{CH}_2\text{CHCHC}(\text{CH}_3)_2\text{OH}]^+$, confirmed the side chain to be $\text{CH}_2\text{CHCHC}(\text{CH}_3)_2\text{OH}$. Compound **3** was accordingly determined as (23*E*)-25-hydroxycucurbita-5,23-diene-3,7-dione.

The molecular formula of compound **4** was assigned as $\text{C}_{30}\text{H}_{44}\text{O}_2$, on the basis of the HREIMS ($[M]^+$ m/z 436.3342), ^{13}C NMR, and DEPT spectra. Analysis of the IR spectrum of **4** suggested that it contains an isolated ketone (1715 cm^{-1}), a conjugated ketone (1665 cm^{-1}), and a conjugated terminal double bond ($3085, 1655,$

880 cm^{-1}). The UV spectrum exhibited an absorption maximum at 258 nm. ^1H and ^{13}C NMR data (Tables 1 and 2) of the tetracyclic part of the triterpene skeleton were almost the same as compound **3**, but the data in the side chain were very similar to that of **2**. The proposed structure was also supported by the fragment ion peaks in the EIMS at m/z 81 [$\text{CH}_2\text{CHCHC}(\text{CH}_3)\text{CH}_2^+$], m/z 109 [side chain] $^+$, m/z 327 [$\text{M} - \text{side chain}$] $^+$, and m/z 355 [$\text{M} - \text{CH}_2\text{CHCHC}(\text{CH}_3)\text{CH}_2^+$]. Thus, compound **4** was elucidated as (23*E*)-cucurbita-5,23,25-triene-3,7-dione.

Compound **5** was deduced to be a triterpenoid due to a positive Liebermann-Burchard test and was assigned the molecular formula $\text{C}_{30}\text{H}_{48}\text{O}_3$, on the basis of molecular ion peak at m/z 456.3588 in the HREIMS. The IR spectrum of **5** showed bands attributable to hydroxyl group (3360 cm^{-1}) and double-bond (1623 and 700 cm^{-1}) functionalities. The ^1H and ^{13}C NMR data (Tables 1 and 2) indicated the presence of six tertiary methyls [δ_{H} 0.87, 1.18 (3H each, s), 0.84, 1.29 (3H \times 2, s)], a secondary methyl [δ_{H} 0.87 (3H, d, $J = 6.6$ Hz)], an oxomethylene [δ_{H} 3.50 (1H, d, $J = 8.4$ Hz), 3.65 (1H, d, $J = 8.4$ Hz); δ_{C} 79.8 (t)], and a multiplet oxymethine [δ_{H} 3.36 (1H, $W_{1/2} = 6.6$ Hz, H-3)] coupling to a hydroxyl group [δ_{H} 3.98 (1H, d, $J = 9.6$ Hz); disappeared on D_2O exchange]. In addition, the NMR signals for an allylic ABX system of *cis*-oriented cyclohexene [δ_{H} 6.02 (1H, dd, $J = 9.6, 1.6$ Hz, H-6), 5.61 (1H, dd, $J = 9.6, 3.6$ Hz, H-7), 2.32 (1H, br s); δ_{C} 131.9 (d), 131.5 (d), 52.0 (d)] were also found. The above NMR data of **5** were very similar to those of the known compound (23*E*)-5 β ,19-epoxy-25-methoxycucurbita-6,23-diene-3 β -diol (**6**),¹⁴ except that the methoxy group was replaced by a hydroxyl group at C-25. The structure of the side chain of **5** was also supported by the base peak of EIMS at m/z 109 ([side chain - H_2O] $^+$). Thus, compound **5** was determined as (23*E*)-5 β ,19-epoxycucurbita-6,23-diene-3 β ,25-diol. Although compound **5** has been obtained by the hydrolysis of momordicoside I,³ it was isolated for the first time as a natural product in the present investigation.

Experimental Section

General Experimental Procedures. Optical rotations were measured using a JASCO DIP-180 digital spectropolarimeter. UV spectra were measured in MeOH on a Shimadzu UV-1601PC spectrophotometer. IR spectra were recorded on a Nicolet 510P FT-IR spectrometer. NMR spectra were recorded in CDCl_3 at room temperature on a Varian Mercury plus 400 NMR spectrometer, and the solvent resonance was used as internal shift reference (TMS as standard). The 2D NMR spectra were recorded using standard pulse sequences. EIMS and HREIMS were recorded on a Finnigan TSQ-700 and a JEOL SX-102A spectrometer, respectively. TLC was performed by using silica gel 60 F_{254} plates (200 μm , Merck). CC was performed on silica gel (230–400 mesh ASTM, Merck). HPLC was performed by using a Lichrosorb silica gel 60 (5 μm) column (250 \times 10 mm).

Plant Material. The stems of *Momordica charantia* were collected in Ping-Tung, Taiwan, in July 2003. The plant material was identified by Prof. Sheng-Zehn Yang, Department of Forestry, National Pingtung University of Science and Technology. A voucher specimen (no. 2013) has been deposited at the Herbarium of this same institution.

Extraction and Isolation. Air-dried pieces of the stems of *M. charantia* (18 kg) were extracted three times with methanol (30 L) at room temperature (7 days each). The MeOH extract was evaporated in vacuo to afford a black residue, which was suspended in H_2O (3 L) and then partitioned sequentially using EtOAc and *n*-BuOH (2 L \times 3). The EtOAc fraction (386 g) was chromatographed over silica gel, using mixtures of *n*-hexane and EtOAc of increasing polarity as eluents. Eleven fractions were collected as follows: 1 [5000 mL, *n*-hexane], 2 [4000 mL, *n*-hexane–EtOAc (49:1)], 3 [4000 mL, *n*-hexane–EtOAc (19:1)], 4 [4000 mL, *n*-hexane–EtOAc (9:1)], 5 [4000 mL, *n*-hexane–EtOAc (17:3)], 6 [4000 mL, *n*-hexane–EtOAc (8:2)], 7 [4000 mL, *n*-hexane–EtOAc (7:3)], 8 [3000 mL, *n*-hexane–EtOAc (5:5)], 9 [3000 mL, *n*-hexane–EtOAc (4:6)], 10 [3000 mL, *n*-hexane–EtOAc (2:8)], 11 (6000 mL, EtOAc). Fraction 5 was further chromatographed on a silica gel column (7 \times 45 cm), eluted with *n*-hexane– CH_2Cl_2 –EtOAc (8:6:1) to yield eight fractions (each 700 mL), 5A–5H. HPLC of

fraction 5D with *n*-hexane–EtOAc (8:2) as eluent, 2 mL/min, afforded **6**¹⁴ (16 mg, $t_{\text{R}} = 12.2$ min) and **5** (12 mg, $t_{\text{R}} = 21.3$ min), respectively. Fraction 6 was further purified on a silica gel column (5 \times 45 cm) eluted with CH_2Cl_2 –EtOAc (8:1). Seven fractions (6A–6G) (each 700 mL) were obtained as follows: HPLC of fraction 6E with *n*-hexane– CH_2Cl_2 –EtOAc (8:6:1) as eluent, 2 mL/min, afforded **2** (10 mg, $t_{\text{R}} = 15.6$ min) and **1** (8 mg, $t_{\text{R}} = 18.2$ min), respectively. Fraction 7 was further chromatographed on a silica gel column (5 \times 45 cm), eluted with CH_2Cl_2 –EtOAc (8:1), to generate seven fractions (each 600 mL), 7A–7G. HPLC of fraction 6F with *n*-hexane–EtOAc (17:3) as eluent, 2 mL/min, afforded **4** (9 mg, $t_{\text{R}} = 13.5$ min) and **3** (12 mg, $t_{\text{R}} = 20.2$ min), respectively.

(23*E*)-Methoxycucurbit-23-ene-3 β ,7 β -diol (1): amorphous, white powder; [α]_D²⁵ +86.6 (c 0.4, CHCl_3); IR (KBr) ν_{max} 3360, 1625, 1463, 1379, 1242, 1191, 1131, 1021, 957, 825, 700 cm^{-1} ; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS m/z 472 [M] $^+$ (3), 454 (14), 422 (27), 389 (100), 185 (12), 171 (13), 109 (15); HREIMS m/z 472.3916 (calcd for $\text{C}_{31}\text{H}_{52}\text{O}_3$ 472.3819).

(23*E*)-Cucurbita-5,23,23-triene-3 β ,7 β -diol (2): amorphous, white powder; [α]_D²⁵ +81.5 (c 0.3, CHCl_3); IR (KBr) ν_{max} 3350, 3080, 1650, 1463, 1379, 1264, 1241, 1151, 1081, 1062, 953, 875 cm^{-1} ; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS m/z 440 [M] $^+$ (1), 422 (18), 407 (14), 389 (18), 325 (5), 135 (19), 109 (30), 81 (100); HREIMS m/z 440.3625 (calcd for $\text{C}_{30}\text{H}_{48}\text{O}_2$ 440.3642).

(23*E*)-25-Hydroxycucurbita-5,23-diene-3,7-dione (3): amorphous, white powder; [α]_D²⁵ +88.3 (c 0.3, CHCl_3); IR (KBr) ν_{max} 3400, 1710, 1655, 1467, 1338, 1224, 1152, 1076, 958, 735 cm^{-1} ; UV (MeOH) λ_{max} (log ϵ) 202 (4.30), 256 (3.76) nm; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS m/z 454 [M] $^+$ (1), 355 (22), 205 (13), 121 (100), 95 (82); HREIMS m/z 454.3423 (calcd for $\text{C}_{30}\text{H}_{46}\text{O}_3$ 454.3435).

(23*E*)-Cucurbita-5,23,25-triene-3,7-dione (4): amorphous, white powder; [α]_D²⁵ +97.6 (c 0.4, CHCl_3); IR (KBr) ν_{max} 3085, 1715, 1665, 1655, 1554, 1458, 1363, 1128, 1068, 998, 880, 737 cm^{-1} ; UV (MeOH) λ_{max} (log ϵ) 202 (4.35), 258 (3.76) nm; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS m/z 436 [M] $^+$ (5), 393 (5), 355 (25), 327 (8), 149 (37), 121 (100), 79 (75); HREIMS m/z 436.3342 (calcd for $\text{C}_{30}\text{H}_{44}\text{O}_2$ 436.333).

(23*E*)-5 β ,19-Epoxycucurbita-6,23-diene-3 β ,25-diol (5): amorphous, white powder; [α]_D²⁵ –82.2 (c 0.3, CHCl_3); ^1H and ^{13}C NMR data, see Tables 1 and 2; IR (KBr) ν_{max} 3360, 1623, 1457, 1375, 1236, 1160, 1035, 983, 851, 778, 700 cm^{-1} ; EIMS m/z 456 [M] $^+$ (8), 438 (45), 390 (80), 309 (100), 281 (65); HREIMS m/z 456.3588 [M] $^+$ (calcd for $\text{C}_{30}\text{H}_{48}\text{O}_3$ 456.3605).

Acknowledgment. This research was supported by grants from the National Science Council of the Republic of China (NSC 93-2317-B-020-002 and NSC 94-2317-B-020-001). We thank Ms. S.-L. Huang and Ms. S.-Y. Sun for the NMR data acquisition and HREIMS measurement in the Instrumentation Center of the College of Science, National Taiwan University.

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NP068008V