Cucurbitane-Type Triterpenoids from *Momordica charantia*

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The six new cucurbitane-type triterpenoids **1**–**6**, along with the ten known triterpenoids **7**–**16**, were isolated from the vines and leaves of *Momordica charantia*. The structures of the new compounds were elucidated as (3*β*,7*β*,15*β*,23*E*)-3,7,15,25-tetrahydroxycucurbita-5,23-dien-19-al (**1**), (3*β*,7*β*)-3,7,22,23-tetrahydroxycucurbita-5,24-dien-19-al (**2**), (3*β*,7*β*)-3,7,23,24-tetrahydroxycucurbita-5,25-dien-19-al (**3**), (3*β*,7*β*,23*S*)-3,7,23-trihydroxycucurbita-5,24-dien-19-al 7-*β*-D-glucopyranoside (**4**), (3*β*,7*β*,23*E*)-cucurbita-5,23-diene-3,7,19,25-tetrol 7-*β*-D-glucopyranoside (**5**), and (3*β*,7*β*,23*E*)-3,7-dihydroxy-25-methoxycucurbita-5,23-dien-19-al 3-*β*-D-allopyranoside (**6**), by extensive analyses of their spectral data, as well as by chemical methods.

Introduction. – The Cucurbitaceae plant *Momordica charantia* L. is an annual liane, which is widely distributed in many tropical and subtropical countries, including China, India, Thailand, and Japan. Its fruit, called bitter melon or bitter gourd, has been used for centuries to treat diabetes, dysentery, ophthalmalgia, toothache, and inflammation in China [1]. Moreover, bitter melon is now widely used as dietary supplement in diabetics to regulate the blood glucose levels. *M. charantia* had been paid much attention recently owing to cucurbitane-type triterpenoids and their biological activities, such as antidiabetic, antitumor, antiulcerogenic, and antioxidant activity [2–5] (cucurbitane = (5*ξ*,9*β*,10*α*)-9-methyl-19-norlanostane). The antidiabetic study revealed that cucurbitane glycosides from the fruit of *M. charantia* activate the AMPK signaling pathway, and further adjust glucose uptake and fatty acid oxidation [6–7].

Previously, we have obtained from *M. charantia* a series of cucurbitane-type triterpernoids, possessing several structure types [8–11]. In continuation of our study, the components of the butanol extract of the leaves and vines of this species was now studied, which resulted in the isolation of sixteen cucurbitane triterpenes, including the six new compounds **1**–**6** (see *Fig. 1*). Herein, the details of the purification and elucidation of those new compounds are discussed.

Results and Discussion. – Compound **1** was obtained as colorless needles, and the molecular formula $C_{30}H_{48}O_5$ was established by HR-FAB-MS (*m/z* 523.3168 ([*M* + Cl]$^-$)). Its IR spectrum showed absorptions for OH (2406 cm^{-1}), CHO (1709 cm^{-1}), and C=C moieties (1630 cm^{-1}). The typical ^{13}C-NMR signals (*Table 1*) of CHO (*δ*(C) 208.0) and two isolated C=C bonds (*δ*(C) 124.3 (*d*) and 146.0 (*s*); *δ*(C) 124.4 (*d*) and 141.7 (*d*)), in addition to the resonances of seven Me groups (*δ*(C) 17.2, 18.1, 19.1, 26.3, 27.4, 30.9, and 30.9), six CH_2 groups (*δ*(C) 21.8, 22.8, 30.1, 31.1, 39.6, and 40.9), seven

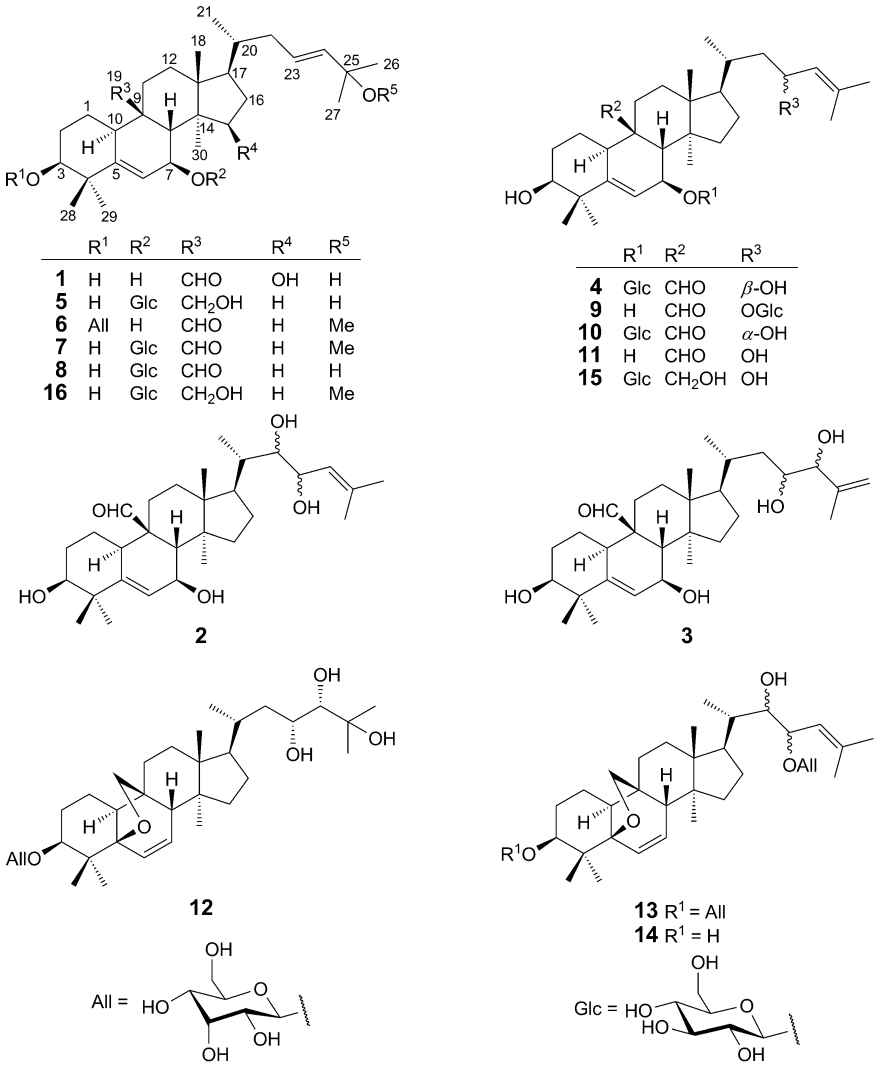

Fig. 1. *Compounds* **1**–**16**, *isolated from* Momordica charantia

CH groups (δ(C) 36.6, 37.6, 45.3, 50.9, 65.5, 75.8, and 76.1), and five quaternary C-atoms (δ(C) 41.9, 45.2, 50.5, 51.9, and 69.8) revealed that **1** was a cucurbita-5,23-diene-type triterpene. Detailed comparison of the ^{1}H- and ^{13}C-NMR and DEPT data of **1** (*Tables 2* and *1*) with those of (3*β*,7*β*,23*E*)-3,7,25-trihydroxycucurbita-5,23-dien-19-al [9] showed similarities, except for the presence of an OH group at C(15) and the absence of a CH_2 group in **1**. This suggestion was supported by the HMBCs δ(H) 4.10 (*d*, $J = 8.5$ Hz, H–C(15))/δ(C) 51.9 (C(14)), 40.9 (C(16)), 50.9 (C(17)), and 18.1 (C(30)), and by the ^{1}H,^{1}H-COSYs δ(H) 4.10 (H–C(15))/δ(H) 2.62–2.66 (*m*, H–C(16)), and δ(H) 1.56–1.61 (*m*, H–C(17))/δ(H) 2.62–2.66 (*m*, H–C(16))

(*Fig. 2*). The α-orientation of H–C(15) was determined by the ROESY correlations δ(H) 4.10 (H–C(15))/δ(H) 0.82 (*s*, Me(30)) (*Fig. 2*). Therefore, **1** was elucidated to be (3β,7β,15β,23*E*)-3,7,15,25-tetrahydroxycucurbita-5,23-dien-19-al.

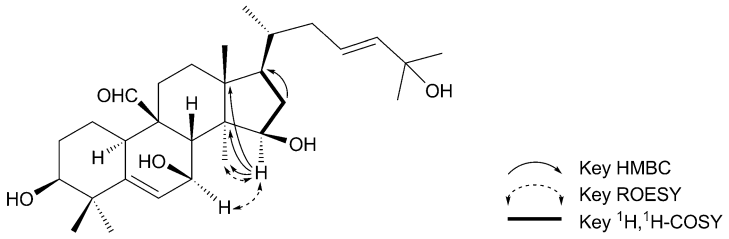

Fig. 2. *Key HMBC, ROESY, and ^{1}H,^{1}H-COSY features of compound* **1**

Compound **2** was isolated as colorless needles. The FAB-MS showed a quasimolecular-ion peak at *m*/*z* 487 ($[M-H]^-$), and the molecular formula $C_{30}H_{48}O_5$ was determined by the HR-FAB-MS (*m*/*z* 523.3914 ($[M+Cl]^-$)). The ^{13}C-NMR spectrum combined with DEPT data (*Table 1*) and the ^{1}H-NMR spectrum (*Table 2*) revealed that **2** had similar spectroscopic data to those of (3β,7β,23*E*)-3,7,25-trihydroxycucurbita-5,23-dien-19-al [9], except for the signals of the side chain. The ^{1}H,^{1}H-COSY cross-peaks δ(H) 3.89 (*dd*, *J* = 3.0, 7.5 Hz, H–C(22))/δ(H) 4.67 (*dd*, *J* = 7.5, 9.5 Hz, H–C(23)), and δ(H) 4.67 (H–C(23))/δ(H) 5.64 (*d*, *J* = 9.5 Hz, H–C(24)) suggested that **2** had a 24,25-unsaturated 22,23-dihydroxy-substituted side chain. The HMBCs δ(H) 3.89 (H–C(22))/δ(C) 76.3 (C(23)) and 128.2 (C(24)), and δ(H) 5.64 (H–C(24))/δ(C) 76.3 (C(23)), 133.2 (C(25)), 26.1 (C(26)), and 18.5 (C(27)) confirmed this deduction. So the structure of **2** was assigned as (3β,7β)-3,7,22,23-tetrahydroxycucurbita-5,24-dien-19-al.

Compound **3** had the molecular formula $C_{30}H_{48}O_5$, determined from the HR-FAB-MS (*m*/*z* 523.3220 ($C_{30}H_{48}ClO_5^-$, $[M+Cl]^-$)). Comparison of the ^{1}H- and ^{13}C-NMR data of **3** (*Tables 2* and *1*) with those of **2** revealed similarities in rings *A* – *D* but differences in the side chain. Two H-atoms at δ(H) 4.16 (*dd*, *J* = 9.0, 12.0 Hz, H–C(23)) and 4.30 (*d*, *J* = 9.0 Hz, H–C(24)) shared the same coupling constant *J* = 9.0 Hz, which suggested that two OH groups were positioned at two adjacent C-atoms. The diagnostic signals in the ^{13}C-NMR and DEPT spectra at δ(C) 147.5 (*s*, C(25)) and 113.0 (*t*, C(26)) were typical for the presence of a terminal C=C bond at C(25). The HMBCs from δ(H) 5.02 and 5.25 (2*s*, 1 H each, CH_2(26)) to δ(C) 80.9 (*d*, C(24)) combined with the above described evidences revealed that the side chain of **3** was a 25,26-unsaturated 23,24-dihydroxy-substituted moiety. The ^{1}H,^{1}H-COSY δ(H) 4.16 (H–C(23))/δ(H) 1.88 – 1.94 (*m*, H–C(22)) and 4.30 (H–C(24)) also supported this deduction. All the ^{1}H- and ^{13}C-NMR data were assigned by 2D-NMR experiments. Finally, the structure of **3** was determined to be (3β,7β)-3,7,23,24-tetrahydroxycucurbita-5,25-dien-19-al.

Compound **4**, a white powder, was assigned the formula $C_{36}H_{58}O_9$ from its $[M+Cl]^-$ ion at *m*/*z* 669.3780 in the HR-FAB-MS. Compound **4** had ^{1}H- and ^{13}C-NMR spectra closely similar (*Tables 2* and *1*) to those of **10** except for the signals due to the side chain. Compound **4** exhibited ^{1}H-NMR signals for the side chain H-atoms at δ(H)

Table 1. *^{13}C-NMR Data* (125 MHz, C_5D_5N) *of Compounds* **1**–**6**. δ in ppm.

C-Atom	**1**	**2**	**3**	**4**	**5**	**6**
C(1)	21.8 (*t*)	21.8 (*t*)	21.7 (*t*)	22.0 (*t*)	20.1 (*t*)	22.6 (*t*)
C(2)	30.1 (*t*)	29.9 (*t*)	29.9 (*t*)	30.1 (*t*)	30.5 (*t*)	28.6 (*t*)
C(3)	75.8 (*d*)	75.7 (*d*)	75.7 (*d*)	75.7 (*d*)	76.1 (*d*)	87.2 (*d*)
C(4)	41.9 (*s*)	41.7 (*s*)	41.8 (*s*)	42.1 (*s*)	42.1 (*s*)	41.9 (*s*)
C(5)	146.0 (*s*)	145.8 (*s*)	145.8 (*s*)	147.8 (*s*)	148.9 (*s*)	145.7 (*s*)
C(6)	124.3 (*d*)	124.3 (*d*)	124.3 (*d*)	122.3 (*d*)	121.0 (*d*)	123.8 (*d*)
C(7)	65.5 (*d*)	65.8 (*d*)	65.7 (*d*)	71.9 (*d*)	72.9 (*d*)	65.7 (*d*)
C(8)	45.3 (*d*)	50.7 (*d*)	50.7 (*d*)	45.7 (*d*)	39.3 (*d*)	50.7 (*d*)
C(9)	50.5 (*s*)	50.7 (*s*)	50.6 (*s*)	50.5 (*s*)	39.1 (*s*)	50.5 (*s*)
C(10)	37.6 (*d*)	36.8 (*d*)	36.9 (*d*)	36.8 (*d*)	39.1 (*d*)	36.9 (*d*)
C(11)	22.8 (*t*)	22.6 (*t*)	22.7 (*t*)	22.7 (*t*)	26.9 (*t*)	22.7 (*t*)
C(12)	31.1 (*t*)	29.7 (*t*)	29.6 (*t*)	30.1 (*t*)	28.1 (*t*)	29.4 (*t*)
C(13)	45.2 (*s*)	46.6 (*s*)	46.0 (*s*)	45.2 (*s*)	46.2 (*s*)	45.8 (*s*)
C(14)	51.9 (*s*)	48.0 (*s*)	48.4 (*s*)	48.3 (*s*)	47.7 (*s*)	48.3 (*s*)
C(15)	76.1 (*d*)	35.2 (*t*)	34.9 (*t*)	34.9 (*t*)	35.4 (*t*)	34.9 (*t*)
C(16)	40.9 (*t*)	27.7 (*t*)	28.0 (*t*)	28.3 (*t*)	30.2 (*t*)	27.9 (*t*)
C(17)	50.9 (*d*)	46.9 (*d*)	51.4 (*d*)	51.5 (*d*)	50.4 (*d*)	50.2 (*d*)
C(18)	17.2 (*q*)	14.8 (*q*)	15.0 (*q*)	14.9 (*q*)	15.1 (*q*)	15.0 (*q*)
C(19)	208.0 (*d*)	207.9 (*d*)	208.0 (*d*)	207.8 (*d*)	65.6 (*t*)	207.9 (*d*)
C(20)	36.6 (*d*)	41.8 (*d*)	32.9 (*d*)	34.1 (*d*)	36.7 (*d*)	36.4 (*d*)
C(21)	19.1 (*q*)	14.6 (*q*)	18.9 (*q*)	20.2 (*q*)	19.1 (*q*)	19.0 (*q*)
C(22)	39.6 (*t*)	68.1 (*d*)	40.7 (*t*)	45.8 (*t*)	39.7 (*t*)	39.7 (*t*)
C(23)	124.4 (*d*)	76.3 (*d*)	70.0 (*d*)	66.8 (*d*)	124.4 (*d*)	128.5 (*d*)
C(24)	141.7 (*d*)	128.2 (*d*)	80.9 (*d*)	131.2 (*d*)	141.7 (*d*)	137.7 (*d*)
C(25)	69.8 (*s*)	133.2 (*s*)	147.5 (*s*)	133.1 (*s*)	69.8 (*s*)	74.9 (*s*)
C(26)	30.9 (*q*)	26.1 (*q*)	113.0 (*t*)	26.1 (*q*)	30.9 (*q*)	26.5 (*q*)
C(27)	30.9 (*q*)	18.5 (*q*)	18.4 (*q*)	18.5 (*q*)	30.9 (*q*)	25.8 (*q*)
C(28)	26.3 (*q*)	26.3 (*q*)	26.3 (*q*)	26.4 (*q*)	26.3 (*q*)	26.1 (*q*)
C(29)	27.4 (*q*)	27.3 (*q*)	27.3 (*q*)	27.5 (*q*)	28.3 (*q*)	27.9 (*q*)
C(30)	18.1 (*q*)	18.2 (*q*)	18.3 (*q*)	18.3 (*q*)	18.4 (*q*)	18.2 (*q*)
C(1′)				101.9 (*d*)	101.3 (*d*)	104.9 (*d*)
C(2′)				75.1 (*d*)	75.0 (*d*)	73.5 (*d*)
C(3′)				79.0 (*d*)	79.2 (*d*)	72.2 (*d*)
C(4′)				71.9 (*d*)	71.9 (*d*)	69.2 (*d*)
C(5′)				78.8 (*d*)	79.0 (*d*)	75.8 (*d*)
C(6′)				63.0 (*t*)	62.9 (*t*)	63.3 (*t*)
*Me*O–C(25)						50.2 (*q*)

1.10 (*d*, $J = 6.3$ Hz, Me(21)), 1.47 (*s*, Me(26)), 1.45–1.50 (*m*, H–C(20)), 1.75 (*s*, Me(27)), 1.70–1.75 and 1.85–1.90 (2*m*, CH_2(22)), 4.80–4.90 (*m*, H–C(23)), and 5.50 (br. *s*, H–C(24)), which were assigned by 2D-NMR data and established a 24,25-unsaturated (23ζ)-23-hydroxy-substituted side chain. The configuration at C(23) of **4** and **10** was deduced to be (*S*) and (*R*), respectively, by comparison of their side-chain ^{13}C-NMR signals with those of charantoside II ((23*R*)) and charantoside VI ((23*S*)) [12]. Thus, the $\Delta\delta$(C) values (δ(C(**10**)) – δ(C(**4**))) for the side-chain signals were calculated as –1.1 (C(20)), –1.0 (C(21)), +0.1 (C(22)), –1.6 (C(23)), +0.7 (C(24)), –2.2 (C(25)), –0.2 (C(26)), and –0.3 (C(27)) ppm (*Table 3*), which were

Table 2. *^{1}H-NMR Data* (500 MHz, C_5D_5N) *of Compounds* **1**–**6**. δ in ppm, J in Hz.

H-Atom	**1**	**2**	**3**	**4**	**5**	**6**
CH_2(1)	1.74–1.80, 2.06–2.12 (2*m*)	1.70–1.75, 2.00–2.06 (2*m*)	1.75–1.79, 2.05–2.10 (2*m*)	1.50–1.60, 1.90–2.00 (2*m*)	1.60–1.70, 1.95–2.05 (2*m*)	1.50–1.60, 1.90–2.00 (2*m*)
CH_2(2)	1.93–1.96, 2.06–2.12 (2*m*)	1.65–1.70, 2.00–2.06 (2*m*)	1.65–1.71, 1.91–2.97 (2*m*)	1.65–1.75, 1.90–2.00 (2*m*)	1.95–2.05 (*m*)	1.60–1.70, 1.90–2.00 (2*m*)
H–C(3)	3.83 (br. *s*)	3.79 (br. *s*)	3.82 (*s*)	3.78 (br. *s*)	3.78 (br. *s*)	3.68 (br. *s*)
H–C(6)	6.31 (*d*, *J* = 6.0)	6.28 (*d*, *J* = 5.0)	6.28 (*d*, *J* = 6.5)	6.15 (*d*, *J* = 5.3)	6.01 (*d*, *J* = 7.0)	6.21 (*d*, *J* = 6.0)
H–C(7)	4.70 (*d*, *J* = 6.0)	4.37 (*d*, *J* = 5.0)	4.36 (*d*, *J* = 6.5)	4.56 (*d*, *J* = 6.5)	4.53 (*d*, *J* = 7.0)	4.32 (*d*, *J* = 6.0)
H–C(8)	3.13 (br. *s*)	2.39 (br. *s*)	2.38 (*s*)	2.52 (*s*)	3.10 (br. *s*)	2.35 (*s*)
H–C(10)	2.69–2.72 (*m*)	2.70–2.75 (*m*)	2.69–2.74 (*m*)	2.66–2.74 (*m*)	2.50–2.60 (*m*)	2.55–2.65 (*m*)
CH_2(11)	1.60–1.66, 2.69–2.72 (2*m*)	1.60–1.66, 2.70–2.76 (2*m*)	1.63–1.69, 2.73–2.78 (2*m*)	1.55–1.65, 2.55–2.65 (2*m*)	1.50–1.60, 2.20–2.30 (2*m*)	2.72 (*m*)
CH_2(12)	1.63–1.67 (*m*)	1.45–1.50, 1.90–2.00 (2*m*)	1.68–1.75, 1.90–1.96 (2*m*)	1.49–1.56, 1.90–2.00 (2*m*)	1.40–1.50, 1.95–2.05 (2*m*)	1.50–1.60 (*m*)
H–C(15) or CH_2(15)	4.10 (*d*, *J* = 8.5)	1.36–1.48 (*m*)	1.30–1.40 (*m*)	1.45–1.55 (*m*)	1.50–1.60 (*m*)	1.30–1.40 (*m*)
CH_2(16)	1.69–1.74, 2.62–2.66 (2*m*)	1.40–1.45, 1.85–1.95 (2*m*)	1.38–1.45, 1.80–1.90 (2*m*)	1.20–1.30, 1.90–2.00 (2*m*)	1.20–1.30, 1.95–2.05 (2*m*)	1.20–1.30, 1.85–1.95 (2*m*)
H–C(17)	1.56–1.61 (*m*)	1.85–1.95 (*m*)	1.52–1.60 (*m*)	1.50–1.60 (*m*)	1.50–1.60 (*m*)	1.45–1.55 (*m*)
Me(18)	1.43 (*s*)	0.89 (*s*)	0.92 (*s*)	0.83 (*s*)	1.16 (*s*)	0.84 (*s*)
H–C(19) or CH_2(19)	10.73 (*s*)	10.67 (*s*)	10.67 (*s*)	10.48 (*s*)	3.56, 4.35 (2*d*, *J* = 13.0)	10.58 (*s*)
H–C(20)	1.69–1.74 (*m*)	2.05–2.15 (*m*)	2.10–2.18 (*m*)	1.45–1.50 (*m*)	1.50–1.60 (*m*)	1.45–1.55 (*m*)
Me(21)	1.02 (*d*, *J* = 7.5)	1.26 (*d*, *J* = 7.0)	1.11 (*d*, *J* = 7.5)	1.10 (*d*, *J* = 6.3)	0.97 (*d*, *J* = 6.5)	0.95 (*d*, *J* = 6.5)
CH_2(22) or H–C(22)	1.87–1.92, 2.26–2.32 (2*m*)	3.89 (*dd*, *J* = 3.0, 7.5)	1.25–1.30, 1.88–1.94 (2*m*)	1.70–1.75, 1.85–1.90 (2*m*)	1.85–1.95, 2.60–2.70 (2*m*)	1.75–1.85, 2.10–2.20 (2*m*)
H–C(23)	5.88–5.95 (*m*)	4.67 (*dd*, *J* = 7.5, 9.5)	4.16 (*dd*, *J* = 9.0, 12.0)	4.80–4.90 (*m*)	5.94 (br. *m*)	5.55–5.65 (*m*)
H–C(24)	5.88–5.95 (*m*)	5.64 (*d*, *J* = 9.5)	4.30 (*d*, *J* = 9.0)	5.50 (br. *s*)[a])	5.93 (br. *m*)	5.45–5.55 (*m*)
Me(26) or CH_2(26)	1.54 (*s*)	1.73 (*s*)	5.25, 5.02 (2*s*)	1.47 (*s*)	1.54 (*s*)	1.56 (*s*)
Me(27)	1.54 (*s*)	1.73 (*s*)	2.00 (*s*)	1.75 (*s*)	1.54 (*s*)	1.56 (*s*)
Me(28)	1.48 (*s*)	1.47 (*s*)	1.48 (*s*)	1.76 (*s*)	1.37 (*s*)	1.30 (*s*)
Me(29)	1.19 (*s*)	1.15 (*s*)	1.12 (*s*)	1.20 (*s*)	1.11 (*s*)	1.09 (*s*)

Table 2 (cont.)

H-Atom	**1**	**2**	**3**	**4**	**5**	**6**
Me(30)	0.82 (*s*)	0.85 (*s*)	0.85 (*s*)	0.72 (*s*)	0.75 (*s*)	0.80 (*s*)
H–C(1′)				4.94 (*d*, *J* = 9.7)	5.16 (*d*, *J* = 9.5)	5.30 (*d*, *J* = 9.5)
H–C(2′)				4.00–4.05 (*m*)	4.10–4.15 (*m*)	3.85 (*dd*, *J* = 2.5, 9.5)
H–C(3′)				4.25–4.35 (*m*)	4.25–4.35 (*m*)	4.65 (br. *s*)
H–C(4′)				4.20–4.30 (*m*)	4.25–4.35 (*m*)	4.14 (*dd*, *J* = 2.5, 12.0)
H–C(5′)				3.95–4.00 (*m*)	4.00–4.10 (*m*)	4.40–4.50 (*m*)
CH_2(6′)				4.41 (*dd*, *J* = 7.1, 15.0), 4.63 (*dd*, *J* = 2.4, 14.8)	4.45 (*dd*, *J* = 7.0, 15.0), 4.65 (*dd*, *J* = 2.0, 15.0)	4.34 (*d*, *J* = 14), 4.49 (*d*, *J* = 14)
MeO						3.19 (*s*)

[a]) Overlapped with H_2O.

almost consistent with the $\Delta\delta$(C) values (δ(C)(charantoside II-23(R)) – δ(C)(charantoside VI-23(S))) of −0.5 (C(20)), −1.0 (C(21)), 0 (C(22)), −1.0 (C(23)), +0.7 (C(24)), −1.8 (C(25)), 0 (C(26)), 0 (C(27)) ppm. These data established that **4** and **10** possessed the structure (3β,7β,23S)-3,7,23-trihydroxycucurbita-5,24-dien-19-al 7-β-D-glucopyranoside and (3β,7β,23R)-3,7,23-trihydroxycucurbita-5,24-dien-19-al 7-β-D-glucopyranoside, respectively.

Table 3. *Key Differences of Chemical Shifts between* **4** *and* **10** *in the* ^{13}*C-NMR Spectra* (125 MHz, (D_5)pyridine). δ in ppm.

C-Atom	**4**	**10**	δ(C)(**10**) – δ(C)(**4**)
C(20)	34.1 (*d*)	33.0 (*d*)	−1.1
C(21)	20.2 (*q*)	19.2 (*q*)	−1.0
C(22)	45.8 (*t*)	45.9 (*t*)	0.1
C(23)	66.8 (*d*)	65.2 (*d*)	−1.6
C(24)	131.2 (*d*)	131.9 (*d*)	0.7
C(25)	133.1 (*s*)	130.9 (*s*)	−2.2
C(26)	26.1 (*q*)	25.9 (*q*)	−0.2
C(27)	18.5 (*q*)	18.2 (*q*)	−0.3

Compound **5**, a white powder, exhibited a quasimolecular-ion peak at m/z 671.3914 ($[M+Cl]^-$) in the HR-FAB-MS, in accordance with an empirical molecular formula $C_{36}H_{60}O_9$. Its IR spectrum disclosed strong absorptions at 3421, 1079, and 1037 cm^{-1} for OH groups, suggesting the presence of a glycosidic function. Acid hydrolysis of **5** with 5% dry HCl/MeOH furnished D-glucose, which was identified by HPLC analysis of the 1-phenyl-3-methylpyrazol-5-one (=2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one; PMP) derivative. Comparison of the ^{1}H- and ^{13}C-NMR data of **5** (*Tables 2* and *1*) with those of momordicoside L [13] showed similarities, except for the signal of a CH_2OH group at C(9) in **5** instead of a CHO group at C(9) in momordicoside L. The correlations in the HMBC spectrum from δ(H) 3.56 and 4.35 (2*d*, J = 13.0 Hz, 1 H each, CH_2(19)) to δ(C) 39.3 (C(8)), 39.1 (C(9)), 39.1 (C(10)), and 26.9 (C(11)) determined the structure of **5** as (3β,7β,23E)-cucurbita-5,23-diene-3,7,19,25-tetrol 7-β-D-glucopyranoside.

The HR-FAB-MS (m/z 683.3912 ($[M+Cl]^-$)) afforded the molecular formula $C_{37}H_{60}O_9$ for **6**, which indicated an additional MeO group in **6** compared to (3β,7β,23E)-3,7,25-trihydroxycucurbita-5,23-dien-19-al 3-β-D-allopyranoside [14]. Comparison of the ^{13}C-NMR data of **6** with those of (3β,7β,23E)-3,7,25-trihydroxycucurbita-5,23-dien-19-al 3-β-D-allopyranoside showed similarities, except for the δ(C) 69.6 (*s*, C(25)) of the latter which was shifted downfield to δ(C) 74.9 (*s*, C(25)) in **6**. The HMBC δ(H) 3.19 (*s*, MeO)/δ(C) 74.9 (C(25)) also validated the presence of a MeO group at C(25) of **6**. These findings combined with ^{1}H,^{1}H-COSY and HSQC data established the structure of **6** as (3β,7β,23E)-3,7-dihydroxy-25-methoxycucurbita-5,23-dien-19-al 3-β-D-allopyranoside.

The known compounds were identified as momordicoside K (**7**) [13], momordicoside L (**8**) [13], momordicine II (**9**) [15], momordicine IV (**10**) [16], momordicine I (**11**) [15], karaviloside XI (**12**) [17], karaviloside X (**13**) [17], karaviloside VIII (**14**) [17], kuguaglycoside D (**15**) [11], and (3β,7β,23E)-25-methoxycucurbita-5,23-diene-3,7,19-

triol 7-β-D-glucopyranoside (**16**) [18] by comparing their spectral data with those reported. Compound **16** was a synthetic reduction derivative of momordicoside K (**7**) [18]; thus, this is the first report on the isolation of **16** from a natural source.

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Experimental Part

General. The hydrolyzed monosaccharides D-glucose and D-allose (*Sigma*) were treated with 1-phenyl-3-methylpyrazol-5-one (=2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one; PMP; *Aldrich*) and analyzed by HPLC. (*Agilent-1100* system), see below. Column chromatography (CC): silica gel (SiO_2, 200–300 mesh; *Qingdao Marine Chemical Inc.*, Qingdao, P. R. China), or *Lichroprep RP-18* gel (40–63 μm; *Merck*, Darmstadt, Germany). TLC: SiO_2; detection by spraying with 10% H_2SO_4/H_2O followed by heating. Optical rotations: *Perkin-Elmer-241* polarimeter. IR Spectra: *Bio-Rad-FTS-135* spectrometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^1H-, ^{13}C-, and 2D-NMR Spectra: *Bruker-DRX-500* instrument; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. MS: *VG-AutoSpec-3000* spectrometer; in *m*/*z*.

Plant Material. The vines and leaves were cultivated at Dahanying Village, Anning County, Yunnan Province, P. R. China, in August 2005. The sample was identified by Prof. *Shu-Kun Chen*, and a voucher specimen (No. KIB 2005-8-10) has been deposited with the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. Air-dried vines and leaves of *M. charantia* L. (30 kg) were mechanically powdered and extracted with MeOH (3 × 10 l, 4 h each) at 70°. The residue obtained after evaporation was suspended in H_2O and subsequently partitioned with AcOEt (4 × 4 l) and BuOH (4 × 4 l). The BuOH extract (250 g) was subjected to CC (macroporous resin, H_2O, MeOH, and acetone (each 5 l)) to give an MeOH fraction (70 g) after concentration. The MeOH fraction was subjected to CC (SiO_2, $CHCl_3$/MeOH 100:1 → 5:1 (10 l) and MeOH (2 l): *Fractions 1–6* (TLC monitoring). *Fr. 3* (16 g) was subjected to CC (octadecylsilane (ODS) *C-18*, MeOH/H_2O 50:50 → 100:0 (10 l): *Frs. 3.1–3.12*. *Fr. 3.6* (3 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH 100:0 → 20:1 (10 l)): *Frs. 3.6.1–3.6.10*). *Fr. 3.6.3* (800 mg) was subjected to CC (ODS *C-18*): **4** (6 mg), **8** (24 mg), **9** (44 mg), and **10** (192 mg). After repeated CC (ODS *C-18*, MeOH/H_2O 50:50 → 80:20 (10 l) and 100:0 (2 l); SiO_2 $CHCl_3$/MeOH 100:0 → 10:1 (10 l)), **7** (26 mg) and **16** (51 mg) were isolated from *Fr. 3.7* (2 g), and **1** (10 mg) and **11** (15 mg) were isolated from *Fr. 3.9* (1 g). *Fr. 4* (8 g) was further subjected to CC (ODS *C-18*, MeOH/H_2O 50:50 → 100:0 (10 l): *Frs. 4.1–4.14*. *Fr. 4.7* (3 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH 100:1 → 10:1 (10 l): *Frs. 4.7.1–4.7.12*. Compounds **5** (15 mg), **6** (17 mg), **14** (6 mg), and **15** (80 mg) were obtained from *Fr. 4.7.2* (200 mg), *Fr. 4.7.5* (400 mg), *Fr. 4.7.8* (100 mg), and *Fr. 4.7.10* (400 mg), resp., by CC (ODS *C-18*, MeOH/H_2O 50:50 → 80:20 (10 l) and 100:0 (1 l); *Sephadex LH-20*, MeOH (2 l)). CC (SiO_2, $CHCl_3$/MeOH 100:1 → 10:1) of *Fr. 4.10* (2 g) gave *Frs. 4.10.1–4.10.8*. *Fr. 4.10.4* (300 mg) and *Fr. 4.10.7* (400 mg) were purified by CC (ODS *C-18*, MeOH/H_2O 50:50 → 80:20 (10 l) and 100:0 (1 l)): **2** (6 mg) and **3** (12 mg), resp. *Fr. 4.6* (1 g), *Fr. 4.8* (500 mg), and *Fr. 4.9* (500 mg), were subjected to repeated CC (SiO_2, $CHCl_3$/MeOH 100:1 → 10:1 (10 l); ODS *C18*, MeOH/H_2O 1:1): **12** (4 mg) and **13** (146 mg).

*(3β,7β,15β,23*E*)-3,7,15,25-Tetrahydroxycucurbita-5,23-dien-19-al* (=*(3β,7β,9β,10α,15β,23*E*)-3,7,15,25-Tetrahydroxy-19-norlanosta-5,23-diene-9-carboxaldehyde*; **1**): Colorless needles. $[\alpha]_D^{21} = +70.8$ ($c = 0.1$, pyridine). IR: 3406, 2946, 2877, 1710, 1471, 1380. ^1H- and ^{13}C-NMR: *Tables 2* and *1*. HR-FAB-MS: 523.3168 ($[M+Cl]^-$, $C_{30}H_{48}ClO_5^-$; calc. 523.3190).

(3β,7β)-3,7,22,23-Tetrahydroxycucurbita-5,24-dien-19-al (=*(3β,7β,9β,10α)-3,7,22,23-Tetrahydroxy-19-norlanosta-5,24-diene-9-carboxaldehyde*; **2**): Colorless needles. $[\alpha]_D^{21} = +88.5$ ($c = 0.1$, pyridine). IR: 3408, 2946, 2879, 1707, 1470, 1382, 1032. ^1H- and ^{13}C-NMR: *Tables 2* and *1*. HR-FAB-MS (neg.): 523.3914 ($[M+Cl]^-$, $C_{30}H_{48}ClO_5^-$; calc. 523.3190).

(3β,7β)-3,7,23,24-Tetrahydroxycucurbita-5,25-dien-19-al (=*(3β,7β,9β,10α)-3,7,23,24-Tetrahydroxy-19-norlanosta-5,25-diene-9-carboxaldehyde*; **3**): Colorless needles. $[\alpha]_D^{21} = +82.5$ ($c = 0.1$, pyridine). IR: 3401, 2947, 2876, 1707, 1653, 1460, 1375, 1035. ^{1}H- and ^{13}C-NMR: *Tables 2* and *1*. HR-FAB-MS (neg.): 523.3220 ($[M+Cl]^-$, $C_{30}H_{48}ClO_5^-$; calc. 523.3190).

*(3β,7β,23*S*)-3,7,23-Trihydroxycucurbita-5,24-dien-19-al 7-β-*D*-Glucopyranoside* (=*(3β,7β,9β,10α, 23*S*)-7-(β-*D*-Glucopyranosyloxy)-3,23-dihydroxy-19-norlanosta-5,24-diene-9-carboxaldehyde*; **4**): White powder. $[\alpha]_D^{21} = +43.3$ ($c = 0.1$, pyridine). IR: 3406, 2925, 2876, 1703, 1634, 1391, 1078, 1017. ^{1}H- and ^{13}C-NMR: *Tables 2* and *1*. HR-FAB-MS (neg.): 669.3780 ($[M+Cl]^-$, $C_{36}H_{58}ClO_9^-$; calc. 669.3679).

*(3β,7β,23*E*)-Cucurbita-5,23-diene-3,7,19,25-tetrol 7-β-*D*-Glucopyranoside* (=*(3β,7β,9β,10α,23*E*)-3,25-Dihydroxy-9-(hydroxymethyl)-19-norlanosta-5,25-dien-7-yl β-*D*-Glucopyranoside*; **5**): White powder. $[\alpha]_D^{21} = +29.4$ ($c = 0.1$, pyridine). IR: 3421, 2922, 2887, 1713. ^{1}H- and ^{13}C-NMR: *Tables 2* and *1*. HR-FAB-MS (neg.): 671.3914 ($[M+Cl]^-$, $C_{36}H_{60}ClO_9^-$; calc. 671.3925).

*(3β,7β,23*E*)-3,7-Dihydroxy-25-methoxycucurbita-5,23-dien-19-al 3-β-*D*-Allopyranoside* (=*(3β,7β,9β, 10α,23*E*)-3-(β-*D*-Allopyranosyloxy)-7-hydroxy-25-methoxy-9-norlanosta-5,23-diene-9-carboxaldehyde*; **6**): White powder. $[\alpha]_D^{21} = +21.3$ ($c = 0.1$, pyridine). IR: 3452, 2940, 2876, 1712, 1645, 1383, 1079, 1037. ^{1}H- and ^{13}C-NMR: *Tables 2* and *1*. HR-FAB-MS (neg.): 683.3912 ($[M+Cl]^-$, $C_{37}H_{60}ClO_9^-$; calc. 683.3925).

Monosaccharides Identification. To **4**, **5**, or **6** (2 mg) was added 5% dry HCl/MeOH (5 ml), and the mixture was heated at 80° for 4 h. After extraction with $CHCl_3/H_2O$ (1:1), the H_2O-soluble part was neutralized with Na_2CO_3 and treated with 1-phenyl-3-methylpyrazol-5-one (PMP) as described previously [19]. Briefly, the sample was treated with 0.75 M PMP in MeOH (4 ml), after the addition of dist. H_2O (2 ml) and 6 M NaOH in H_2O (320 µl). The mixture was allowed to react at 70° for 1 h to complete the derivatization. Thereafter, the soln. was cooled to r.t. and neutralized by addition of 6M HCl in H_2O (320 µl). The resulting soln. was extracted with $CHCl_3$ (3 × 3 ml); then the aq. layer was diluted 100-fold and filtered through a 0.45 µm membrane for HPLC analysis. HPLC (*Agilent-Extend-C18* column (4.6 × 250 mm i.d.; 5 µm), r.t., isocratic 42% *B*/*A* for 10 min (*A* = 70% MeCN in H_2O, *B* = 30 mM ammonium phosphate buffer at pH 4.8); flow rate 1.5 ml/min; injection volume 10 µl; detection at 245 nm): PMP-labeled D-glucose at t_R 6.16 min and PMP-labeled D-allose at t_R 4.11 min as established by comparison with the corresponding standard D-allose and D-glucose derivatives.

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