·化学成分·

Grosmomoside Ⅰ, a new cucurbitane triterpenoid glycoside from fruits of *Momordica grosvenori*

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Abstract: Objective To carry out a systematic study on the chemical constituents in the fruits of *Momordica grosvenori*. **Methods** To isolate pure compounds by using repeated column chromatography, while the structure of a new compound was determined by detailed spectral analysis. **Results** Four cucurbitane triterpenoid glycosides, mogroside Ⅱ_E (Ⅰ), mogroside Ⅲ (Ⅱ), grosmomoside Ⅰ (Ⅲ), and mogroside Ⅴ (Ⅳ) were isolated from the 50% ethanolic extract of the fruits of *M. grosvenori*. **Conclusion** Grosmomoside Ⅰ is a new compound identified as mogrol-3-*O*-β-*D*-glucopyranoside-24-*O*-{[β-*D*-glucopyranosyl(2-1)]-[β-*D*-glucopyranosyl (6-1)]-β-*D*-galactopyranoside} and the other three compounds are known compounds.

Key words: *Momordica grosvenori* Swingle; triterpenoid saponin; grosmomoside Ⅰ

罗汉果中一新葫芦烷型三萜皂苷——光果木鳖皂苷Ⅰ

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摘 要:目的 研究罗汉果中的化学成分。**方法** 用各种色谱法分离和精制纯品化合物,通过各种谱学方法鉴定其结构。**结果** 从罗汉果乙醇提取物中得到 4 个葫芦烷型三萜皂苷,分别为:罗汉果皂苷 Ⅱ_E(mogroside Ⅱ_E, Ⅰ)、罗汉果皂苷Ⅲ(mogroside Ⅲ, Ⅱ)、光果木鳖皂苷Ⅰ(grosmomoside Ⅰ, Ⅲ)和罗汉果皂苷Ⅴ(mogroside Ⅴ, Ⅳ)。**结论** 光果木鳖皂苷Ⅰ为一新化合物,鉴定其结构为罗汉果醇-3-*O*-β-*D*-吡喃葡萄糖苷-24-*O*-{[β-*D*-吡喃葡萄糖基(2-1)]-[β-*D*-吡喃葡萄糖基(6-1)]-β-*D*-吡喃半乳糖苷{mogrol-3-*O*-β-*D*-glucopyranoside-24-*O*-[β-*D*-glucopyranosyl(2-1)]-[β-*D*-glucopyranosyl (6-1)]-β-*D*-galactopyranoside},其他 3 个化合物为已知化合物。

关键词:罗汉果;三萜皂苷;光果木鳖皂苷Ⅰ

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1 Introduction

Momordica grosvenori Swingle is a plant growing in Guangxi, Hunan, Guizhou, Guangdong, and Jiangxi Provinces of China. The fruits of the plant are used in traditional Chinese medicine as a pulmonary demulcent and emollient for the treatment of dry cough, sore throat, dire thirst, constipation[1]. A number of triterpenoid saponins were previously reported from this plant[2-5]. In this paper, the isolation and sturcture elucidation of a new cucurbitane type triterpenoid glycoside named as grosmomoside Ⅰ (Ⅲ), and known compounds mogroside Ⅱ_E (Ⅰ), mogroside Ⅲ (Ⅱ), and mogroside Ⅴ (Ⅳ). are reported

2 Materials and methods

2.1 Plant material. The frutis of *M. grosvenori*

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were obtained from the Anguo City in Hebei Province of China in April 2001 and identified by Professor Cai Shao-qing. A voucher specimen of the plant is deposited at the Herbarium of School of Pharmaceutical Sciences, Peking University.

2.2 General experimental procedures. Infrareds (IR) were taken on a Nexus 470 FT-IR spectrometer (nicolet). Optical rotations were determined on a Perkin-Elmer 243 Polarimeter. ^{1}H-NMR and ^{13}C-NMR spectra were performed on a Varian INOVA-500 spectrometer in pyridine-d_5 at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR. Chemical shifts are given in δ relative to TMS as an internal standard. ESI-TOF-MS and HR-SI-MS were performed on MDS SCIEX API QSTAR and APEX Ⅱ FT-ICR (Bruker Daltonics) mass spectrometer, respectively. Macroporous resin Diaion 101 was produced by Nankai University of China.

2.3 Extraction and isolation. Powdered fruits of *M. grosvenori* (8 kg) were refluxed with 50% EtOH to afford ethanolic extract. The extract was suspended in H_2O and partitioned successively with cyclohexane, EtOAc and BuOH to afford corresponding extracts, 16 g (yield 0.2%), 101 g (1.26%) and 569 g (7.11%), respectively. The BuOH extract was subjected to column chromatography over Diaion 101 eluting with H_2O (10 L), 20% EtOH (12 L) and 50% EtOH (2 L), respectively. The 50% EtOH fraction was subjected to column chromatography on silica gel (200 — 300 mesh) and eluted with $CHCl_3$-MeOH (9 ∶ 1→1 ∶ 1) to yield seven sub-fractions. They were purified repeatedly on silica gel and polyamide column chromatography to afford compound Ⅰ (60 mg) from the sub-fr. 2, compound Ⅱ (2 g) from the sub-fr. 3, compound Ⅲ (40 mg) from the sub-fr. 6, and compound Ⅳ (80 mg) from the sub-fr. 7, respectively.

3 Identification

Compound Ⅰ (mogroside Ⅱ_E): A white amorphous powder, $C_{42}H_{72}O_{14}$. $IR\nu_{max}^{KBr}$ cm^{-1}: 3 417 (OH), 1 644, 1 466, 1 381, 1 171, 1 076 (oligoglycosidic groups), 1 024, 630, 586. ESI-TOF-MS (positive) m/z: 801 $[M+1]^+$, 823 $[M+Na]^+$. ^{1}H-NMR (500 MHz, Py-d_5): aglycone moiety data, see Table 1. Sugar moieties, C_3-glc: δ 4.85 (1H, d, J=8.0 Hz, H-1), 4.00 (1H, t, J=8.5 Hz, H-2), 4.18 (1H, t, J=7.5 Hz, H-3), 4.17 (1H, t, J=7.5 Hz, H-4), 3.97 (1H, m, H-5), 4.33 (1H, dd, J=5.0, 12.0 Hz, H-6a), 4.51 (1H, dd, J=2.0, 12.0 Hz, H-6b); C_{24}-glc: δ 4.96 (1H, d, J=7.5 Hz, H-1), 3.92 (1H, t, J=8.3 Hz, H-2), 4.17 (1H, t, J=8.0 Hz, H-3), 4.13 (1H, t, J=8.0 Hz, H-4), 3.89 (1H, m, H-5), 4.29 (1H, dd, J=5.0, 12.0 Hz, H-6a), 4.47 (1H, dd, J=2.0, 12.0 Hz, H-6b), ^{13}C-NMR (125 MHz, Py-d_5): aglycone moiety data, see Table 1. Sugar moieties, C_3-Glc: δ 107.3 (C-1), 75.2 (C-2), 78.0 (C-3), 71.5 (C-4), 78.4 (C-5), 62.8 (C-6); C_{24}-glc: δ 105.8 (C-1), 75.3 (C-2), 78.3 (C-3), 71.6 (C-4), 78.5 (C-5), 62.5 (C-6).

Compound Ⅱ (mogroside Ⅲ): A white amorphous powder, $C_{48}H_{82}O_{19}$. $IR\nu_{max}^{KBr}$ cm^{-1}: 3 419 (OH), 1 640, 1 465, 1 382, 1 171, 1 076 (oligoglycosidic groups), 1 024, 630, 586. ESI-TOF-MS (positive) m/z: 963 $[M+1]^+$, 985 $[M+Na]^+$. ^{1}H-NMR (500 MHz, Py-d_5): 0.80 (3H, s, Me-30α), 0.88 (3H, s, Me-18β), 0.89 (1H, d, J=5.5 Hz, M-21β), 1.05 (1H, m, H-15β), 1.10 (1H, m, H-15α), 1.12 (3H, s, Me-26), 1.28 (3H, s, M-19β), 1.28 (3H, s, M-27β), 1.40 (3H, s, M-29β), 1.43 (1H, m, H-16β), 1.47 (1H, m, H-20α), 1.49 (1H, m, H-23α), 1.52 (3H, s, Me-28α), 1.61 (1H, d, J=7.0 Hz, H-8β), 1.63 (1H, d, J=6.0 Hz, H-7α), 1.64 (1H, m, H-17α), 1.67 (1H, m, H-23β), 1.70 (1H, m, H-22β), 1.73 (1H, m, H-22α), 1.82 (1H, m, H-16α), 1.93 (1H, t, J=10.5 Hz, H-1β), 1.98 (1H, m, H-12β), 2.03 (1H, m, H-12α), 2.04 (1H, t, J=10.5 Hz, H-2α), 2.26 (1H, dd, J=5.5, 17.5 Hz, H-7β), 2.40 (1H, d, J=10.5 Hz, H-2β), 2.74 (1H, d, J=10.5 Hz, H-10α), 2.88 (1H, d, J=10.5 Hz, H-1α), 3.64 (1H, m, H-3α), 3.72 (1H, d, J=10.0 Hz, H-24α), 4.16 (1H, d, J=8.5 Hz, H-11β), 5.43 (1H, d, J=6.0 Hz, H-6). Sugar moieties, C_3-glc (A): δ 4.80

Table 1 NMR data and ^{13}C-^{1}H correlation of aglycone of grosmomoside Ⅰ and mogroside Ⅱ$_E$ (in Py-d_5)

C	H	HSQC δ_H; J/Hz		HSQC δ_C		HMBC
		grosmomoside Ⅰ	mogroside Ⅱ$_E$	grosmomoside Ⅰ	mogroside Ⅱ$_E$	
1	1β	1.94 (t, 11.0)	1.93 (t, 11.0)	26.6 t	26.6	
	1α	2.94 (d, 11.0)	2.88 (d, 11.0)			
2	2α	2.11 (t, 11.0)	2.10 (t, 11.0)	29.2 t	29.4	H-1, H-29, H-10
	2β	2.43 (d, 11.0)	2.40 (t, 11.0)			
3	3α	3.64 (m)	3.64 (m)	87.2 d	87.8	H-A*1, H-28, H-29
4				42.1 s	42.2	H-28, H-29
5				144.1 s	144.1	H-3, H-7, H-8, H-28, H-29
6	6	5.41 (br s)	5.44 (d, 5.5)	118.2 d	118.3	H-7, H-8
	7α	1.61 (d, 6.5)	1.64 (d, 6.0)			
7	7β	2.22 (dd, 6.5, 18.5)	2.26 (dd, 6.5, 18.5)	24.3 t	24.4	H-8
8	8β	1.56 (d, 7.0)	1.61 (d, 7.5)	43.2 d	43.3	H-7, H-19, H-30
9				39.9 s	39.9	H-7, H-8, H-12, H-19
10	10α	2.74 (d, 11.0)	2.74 (d, 11.0)	36.5 d	36.3	H-8, H-19
11	11β	4.11 (d, 8.5)	4.14 (d, 9.0)	77.7 d	77.6	H-12, H-19
12	12β	2.04 (m)	1.99 (m)	40.7 t	40.9	H-18
	12α	2.09 (m)	2.05 (m)			
13				47.2 s	47.2	H-12, H-15, H-16, H-17, H-18, H-30
14				49.5 s	49.5	H-7, H-8, H-12, H-15, H-18, H-30
15	15β	0.95 (m)	1.04 (m)	34.3 t	34.4	H-8, H-30
	15α	1.10 (m)	1.10 (m)			
16	16β	1.38 (m)	1.43 (m)	28.3 t	28.2	H-17, H-18
	16α	2.06 (m)	1.87 (m)			
17	17α	1.66 (m)	1.63 (m)	50.6 d	50.8	H-18, H-20, H-21
18	18β	0.83 (s)	0.87 (s)	16.8 q	16.9	H-12, H-17
19	19β	1.27 (s)	1.28 (s)	26.0 q	26.2	H-8
20	20α	1.45 (m)	1.47 (m)	36.4 d	36.7	H-17, H-21, H-22, H-23
21	21β	1.02 (d, 5.5)	0.93 (d, 6.5)	18.9 q	18.7	H-17
22	22β	1.71 (m)	1.76 (m)	33.6 t	33.3	H-21
	22α	1.78 (m)	1.78 (m)			
23	23α	1.75 (m)	1.49 (m)	28.3 t	28.2	H-26, H-27
	23β	1.98 (m)	1.67 (m)			
24	24α	3.86 (d, 8.5)	3.82 (d, 8.0)	87.9 d	90.7	H-C*1, H-26, H-27
25				72.2 s	71.9	H-24, H-26, H-27
26	26	1.44 (s)	1.12 (s)	25.6 q	25.2	H-23, H-27
27	27	1.40 (s)	1.36 (s)	26.9 q	26.9	H-26
28	28α	1.04 (s)	1.52 (s)	27.4 q	27.6	H-29
29	29β	1.46 (s)	1.41 (s)	26.0 q	26.1	H-28
30	30α	0.82 (s)	0.80 (s)	19.1 q	19.1	H-7, H-8, H-15

*: A and C are presented for glucosyl group at C_3 of grosmomside Ⅰ and galactosyl group at C_{24} of grosmomoside Ⅰ, respectively in Fig. 1.

(1H, d, J=7.5 Hz, H-1), 3.83 (1H, m, H-5), 3.90 (1H, t, J=8.5 Hz, H-2), 4.11 (1H, t, J=7.5 Hz, H-4), 4.13 (1H, t, J=7.5 Hz, H-3), 4.32 (1H, dd, J=4.5, 9.0 Hz, H-6a), 4.47 (1H, dd, J=2.0, 9.0 Hz, H-6b); C_{24}-glc (B): δ 4.86 (1H, d, J=8.5 Hz, H-1), 4.19 (1H, m, H-5), 4.02 (1H, t, J=8.0 Hz, H-2), 4.03 (1H, t, J=8.5 Hz, H-4), 4.14 (1H, t, J=4.5 Hz, H-3), 3.93 (1H, dd, J=4.5, 9.0 Hz, H-6a), 4.92 (1H, d, J=8.5 Hz, H-6b), C_{24}-glc (C): δ 4.85 (1H, d, J=7.5 Hz, H-1), 3.89 (1H, m, H-5), 4.00 (1H, t, J=7.5 Hz, H-2), 4.22 (1H, t, J=7.5 Hz, H-4), 3.93 (1H, t, J=7.5 Hz, H-3), 4.34 (1H, t, J=3.0 Hz, H-6a), 4.46 (1H, d, J=10.0 Hz, H-6b). ^{13}C-NMR (125 MHz, Py-d_5): aglycone moiety, δ 26.6 (C-1), 29.4 (C-2), 87.8 (C-3), 42.2 (C-4), 144.1 (C-5), 118.3 (C-6), 24.4 (C-7), 43.3 (C-8), 39.9 (C-9), 36.7 (C-10), 77.6 (C-11), 40.9 (C-12), 47.2 (C-13), 49.5 (C-14), 34.4 (C-15), 28.1 (C-16), 50.9 (C-17), 16.9 (C-18), 26.2 (C-19), 36.1 (C-20), 18.6 (C-21), 32.9 (C-22), 29.4 (C-23), 92.6 (C-24), 72.5 (C-25), 24.1 (C-26), 26.8 (C-27), 27.6 (C-28), 26.1 (C-29), 19.1 (C-30); sugar

moieties, C_3-glc (A): δ 107.3 (C-1), 75.3 (C-2), 77.9 (C-3), 71.2 (C-4), 78.4 (C-5), 62.8 (C-6); C_{24}-glc (B): δ 106.2 (C-1), 74.9 (C-2), 78.5 (C-3), 71.9 (C-4), 76.2 (C-5), 70.3 (C-6); C_{24}-glc (C): δ 104.7 (C-1), 75.3 (C-2), 78.4 (C-3), 71.5 (C-4), 78.0 (C-5), 62.3 (C-6).

Compound Ⅲ (grosmomoside Ⅰ): A white amorphous powder, $C_{54}H_{92}O_{24}$. IRν_{max}^{KBr} cm^{-1}: 3 384 (OH), 1 643, 1 465, 1 381, 1 171, 1 075 (oligoglycosidic groups), 1 029, 629, 580. ESI-TOF-MS (negative) m/z: 1 223 $[M-1]^-$; ESI-TOF-MS (positive) m/z: 1 147 $[M+Na]^+$; HR-SI-MS m/z: calcd. for $C_{54}H_{92}NaO_{24}$: 1 147.587 0; found: 1 147.584 6 $[M+Na]^+$. ^{1}H-NMR and ^{13}C-NMR (500 MHz, Py-d_5) spectral analysis, see Tables 1 and 2.

Table 2 NMR data and ^{13}C-^{1}H correlation of sugar moieties of grosmomoside Ⅰ (in Py-d_5)

C	H	HSQC		HMBC
		δ_H; J/Hz	δ_C	
A glucose moiety				
1	1	4.74 (d, 7.5)	106.8 d	H-3, H-A2, H-A5
2	2	3.91 (dd, 4.5, 7.5)	75.1 d	H-A3, H-A4
3	3	4.40 (m)	77.5 d	H-A2, H-A4, H-A5
4	4	4.09 (m)	71.4 d	H-A2, H-A3, H-A5, H-A6
5	5	3.83 (m)	78.3 d	H-A1, H-A6
6	6a	4.30 (dd, 8.5, 11.5)	63.0 t	H-A4
	6b	4.47 (d, 11.5)		
B galactose moiety				
1	1	4.99 (d, 8.0)	101.7 d	H-24, H-B2
2	2	4.05 (dd, 4.5, 8.0)	83.5 d	H-D1, H-B3, H-B4
3	3	4.05 (t, 4.5)	78.2 d	H-B1, H-B2, H-B4, H-B5
4	4	4.03 (m)	71.9 d	H-B2, H-B3, H-B5, H-B6
5	5	3.97 (t-like)	77.1 d	H-B3, H-B4, H-B6
6	6a	4.37 (dd, 5.0, 11.0)	70.1 t	H-C1, H-B5
	6b	4.70 (d, 11.0)		
C glucose moiety				
1	1	5.08 (d, 8.0)	105.2 d	H-B6, H-C2
2	2	4.03 (t, 8.0)	75.0 d	H-C3
3	3	4.15 (m)	78.0 d	H-C1, H-C2, H-C4
4	4	3.92 (m)	71.1 d	H-C2, H-C3, H-C5
5	5	3.97 (dd, 4.5, 8.5)	78.1 d	H-C1, H-C3, H-C4, H-C6
6	6a	4.24 (dd, 8.5, 11.5)	62.2 t	H-C5
	6b	4.47 (d, 11.5)		
D glucose moiety				
1	1	5.27 (d, 8.0)	106.0 d	H-B2
2	2	4.04 (dd, 4.5, 8.0)	76.0 d	H-D1, H-D3, H-D4
3	3	4.09 (m)	78.0 d	H-D2, H-D4
4	4	3.89 (m)	71.4 d	H-D2, H-D3, H-D6
5	5	4.07 (dd, 4.5, 8.5)	78.0 d	H-D4, H-D6
6	6a	4.26 (dd, 8.5, 11.5)	62.5 t	H-D4, H-D5
	6b	4.44 (d, 11.5)		

Compound Ⅳ (mogroside Ⅴ): A white amorphous powder, $C_{60}H_{102}O_{29}$. IRν_{max}^{KBr} cm^{-1}: 3 419 (OH), 1 642, 1 465, 1 381, 1 169, 1 075 (oligoglycosidic groups), 1 033, 633, 588. ESI-TOF-MS (negative) m/z: 1 285 $[M-1]^-$; ESI-TOF-MS (positive) m/z: 1 309 $[M+Na]^+$; ^{1}H-NMR (500 MHz, Py-d_5), aglycone moiety δ: 0.90 (6H, s, Me-30α; Me-18β), 1.04 (1H, m, H-15β), 1.06 (3H, s, Me-28α), 1.06 (3H, d, J=6.5 Hz, Me-21β), 1.12 (1H, m, H-15α), 1.30 (3H, s, Me-27), 1.31 (3H, s, M-19β), 1.43 (3H, s, M-26), 1.45 (1H, m, H-16β), 1.49 (3H, s, Me-29β), 1.51 (1H, m, H-20α), 1.54 (1H, d, J=7.5 Hz, H-8β), 1.59 (1H, d, J=7.0 Hz, H-7α), 1.62 (1H, m, H-17α), 1.76 (1H, m, H-22β), 1.78 (1H, m, H-22α), 1.86 (1H, m, H-23α), 1.97 (1H, t, J=10.0 Hz, H-1β), 2.03 (1H, m, H-23α), 2.06 (1H, m, H-16α), 2.10 (1H, m, H-12β), 2.12 (1H, m, H-12α), 2.17 (1H, t, J=12.5 Hz, H-2α), 2.24 (1H, dd, J=7.0, 17.5

Hz, H-7β), 2.46 (1H, d, J=10.0 Hz, H-2β), 2.78 (1H, d, J=10.0 Hz, H-10α), 2.98 (1H, d, J=10.0 Hz, H-1α), 3.66 (1H, m, H-3α), 3.73 (1H, d, J=8.0 Hz, H-24α), 4.13 (1H, d, J=8.5 Hz, H-11β), 5.44 (1H, t-like, H-6). Sugar-moieties, C_3-glc (A): δ 4.78 (1H, d, J=8.0 Hz, H-1), 3.91 (1H, dd, J=5.0, 8.5 Hz, H-2), 4.23 (1H, m, H-3), 4.28 (1H, m, H-4), 4.00 (1H, t, J=5.0 Hz, H-5), 4.32 (1H, dd, J=5.0, 12.5 Hz, H-6a), 4.76 (1H, d, J=12.5 Hz, H-6b); C_3-glc (B): δ 5.14 (1H, d, J=7.5 Hz, H-1), 4.03 (1H, dd, J=5.0, 8.0 Hz, H-2), 4.26 (1H, m, H-3), 4.24 (1H, m, H-4), 3.88 (1H, m, H-5), 4.36 (1H, dd, J=5.0, 11.7 Hz, H-6a), 4.50 (1H, d, J=11.5 Hz, H-6b), C_{24}-glc (C): δ 4.90 (1H, d, J=7.0 Hz, H-1), 4.14 (1H, m, H-2), 4.20 (1H, m, H-3), 4.18 (1H, m, H-4), 4.02 (1H, m, H-5), 4.89 (1H, d, J=12.5 Hz, H-6b), 3.93 (1H, dd, J=5.0, 11.0 Hz, H-6a); C_{24}-glc (D): δ 4.84 (1H, d, J=7.5 Hz, H-1), 4.02 (1H, m, H-2), 4.22 (1H, m, H-3), 3.91 (1H, m, H-4), 4.02 (1H, m, H-5), 4.50 (1H, d, J=11.5 Hz, H-6b), 4.36 (1H, dd, J=5.0, 11.5 Hz, H-6a); C_{24}-glc (E): δ 5.43 (1H, d, J=7.5 Hz, H-1), 4.06 (1H, m, H-2), 4.17 (1H, m, H-3), 4.08 (1H, m, H-4), 3.93 (1H, m, H-5), 4.47 (1H, d, J=12.5 Hz, H-6b), 4.30 (1H, dd, J=5.0, 12.5 Hz, H-6a). ^{13}C-NMR (500 MHz, Py-d_5): aglycone moiety, δ 26.6 (C-1), 29.3 (C-2), 87.3 (C-3), 42.1 (C-4), 144.1 (C-5), 118.2 (C-6), 24.3 (C-7), 43.3 (C-8), 39.9 (C-9), 36.5 (C-10), 77.7 (C-11), 40.9 (C-12), 47.2 (C-13), 49.5 (C-14), 34.3 (C-15), 28.3 (C-16), 50.9 (C-17), 16.9 (C-18), 26.1 (C-19), 36.2 (C-20), 18.9 (C-21), 33.0 (C-22), 29.2 (C-23), 91.9 (C-24), 72.6 (C-25), 24.3 (C-26), 26.8 (C-27), 27.4 (C-28), 26.1 (C-29), 19.2 (C-30); sugar moieties, C_3-glc (A): δ 106.8 (C-1), 75.2 (C-2), 78.4 (C-3), 71.4 (C-4), 77.1 (C-5), 70.1 (C-6); C_3-glc (B): δ 105.4 (C-1), 75.1 (C-2), 78.3 (C-3), 71.4 (C-4), 78.1 (C-5), 62.5 (C-6); C_{24}-glc (C): δ 103.4 (C-1), 82.2 (C-2), 76.2 (C-3), 72.6 (C-4), 77.8 (C-5), 70.0 (C-6); C_{24}-glc (D): δ 104.6 (C-1), 75.0 (C-2), 78.2 (C-3), 71.2 (C-4), 78.0 (C-5), 62.3 (C-6); C_{24}-glc (E): δ 105.2 (C-1), 75.7 (C-2), 78.2 (C-3), 72.3 (C-4), 78.2 (C-5), 63.4 (C-6).

4 Results and discussion

The BuOH extract of a 50% ethanolic extract of the fruits of *M. grosvenori* was applied to chromatographed over the Diaion-101 eluted with H_2O, 20% EtOH, and 50% EtOH, respectively, to give corresponding fractons. The 50% EtOH fraction was further puritied over silica gel and polyamide column chromatography resulting in the isolation of the compounds Ⅰ — Ⅳ, respectively.

Compounds Ⅰ, Ⅱ, and Ⅳ were identified as mogroside Ⅱ_E, mogroside Ⅲ, and mogroside Ⅴ (Fig. 1), respectively by means of 1D and 2D NMR spectroscopic techniques including ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, NOESY, DEPT, HMQC, and HMBC.

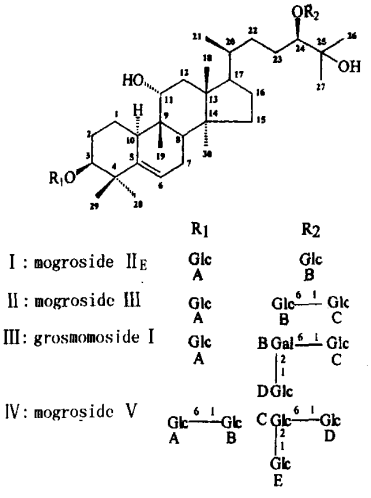

Fig. 1 Structures of compounds Ⅰ — Ⅳ

Compound Ⅲ was obtained as a white amorphous powder, showed a positive Lieberman-Burchard reaction, which suggested it was a triterpenoid. Its IR spectrum showed strong absorption bands (3 384 and 1 075 cm^{-1}) for hydroxyl groups and the oligoglycosidic structure[6]. The molecular formula $C_{54}H_{92}O_{24}$ was deduced from the molecular ion at m/z 1 147 $[M+Na]^+$ in its ESI-TOF-MS and confirmed by HR-SI-MS (1 147.584 6 $[M+Na]^+$, calcd. 1 147.587 0), and it was supported by ^{13}C-NMR and DEPT spectra. The ^{13}C-NMR

spectrum (Table 1) of compound Ⅲ suggested a triterpenoid with a basic structure similar to cucurbitane-glycosides[7], which revealed 24 carbon signals for the glycone portion and 30 carbon signals for the aglycone portion including a quaternary oxygenated carbon signal (δ 72.2), three methine oxygenated carbon signals (δ 87.2, 77.7, and 87.9), a tertiary olefinic carbon signal (δ 144.1) and a methine olefinic carbon signal (δ 118.2).

Comparing with the ^{13}C-NMR spectrum of compound Ⅰ (mogroside Ⅱ_E) which is mogrol -3-*O*-β-*D*-glucopyranoside-24-*O*-β-*D*-glucopyranoside, compound Ⅲ has mogrol-3-*O*-β-*D*-blucopyranoside moiety, while two sugar residues were added and the chemical shift of C_{24} was changed. This suggested that two additional sugar residues be correlated with glucopyranosyl group of C_{24}. After acid hydrolysis of compound Ⅲ, *D*-glucose and *D*-galactose were detected by PPC and compared with authentic samples. The ^{1}H-NMR spectrum of compound Ⅲ displayed signals of four anomeric protons at δ 4.74 (d, J=7.5 Hz), 4.99 (d, J=8.0 Hz), 5.08 (d, J=8.0 Hz), 5.27 (d, J=8.0 Hz), which correlated with the carbon signals at δ 106.8, 101.7, 105.2 and 106.0, respectively, in the HSQC spectrum. In the HMBC and ^{1}H-^{1}H COSY spectra of compound Ⅲ (Fig. 2), the signal of glucose (A) anomeric proton at δ 4.74 was correlated with that of mogrol C_3 at δ 87.2 and δ 4.74, 3.91, 4.10, 4.09, 3.83, 4.30, 4.47 belonged to the same spin system; the signal of galactose (B) anomeric proton at δ 4.99 was correlated with that of mogrol C_{24} at δ 101.7 and δ 4.99, 4.05, 4.05, 4.03, 3.97, 4.37, 4.70 belonged to the same spin system; the signal of glucose (C) anomeric proton at δ 5.08 was correlated with that of galactose C_6 at δ 70.1 and δ 5.08, 4.03, 4.15, 3.92, 3.97, 4.24, 4.47 belonged to the same spin system; the signal of glucose (D) anomeric proton at δ 5.27 was correlated with that of galactose C_2 at δ 83.5 and δ 5.27, 4.04, 4.09, 3.89, 4.07, 4.26, 4.44 belonged to the same spin system. Therefore, the glucose (A) was connected

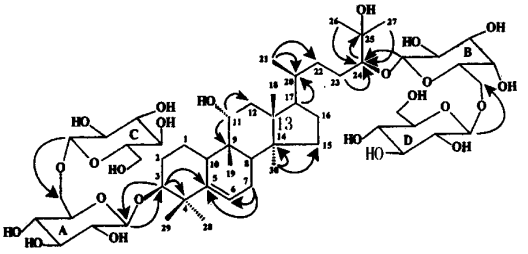

Fig. 2 Some key correlations observed in HMBC (H→C) for compound Ⅲ

with the C_3 of mogrol, galactose (B) was connected with the C_{24} of mogrol, the glucose (c) was connected with the C_6 of glucose, the glucose (d) was connected with the C_2 of galactose (Fig. 2). The large J values indicated β-glycosidic linkages in all cases. The orientation of the proton at C_{24} was established by the NOESY correlations of H-24 with H-23α and large J values (H-24, d, J= 8.5 Hz)[2-4, 8].

From these results, the structure of compound Ⅲ was established as mogrol-3-*O*-β-*D*-glucopyranoside-24-*O*-{[β-*D*-glucopyranosyl (2-1)]-[β-*D*-glucopyranosyl (6-1)]-β-*D*-galactopyranoside}, named as grosmomoside Ⅰ.

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