Three New Triterpene Saponins from *Hemsleya chinensis*

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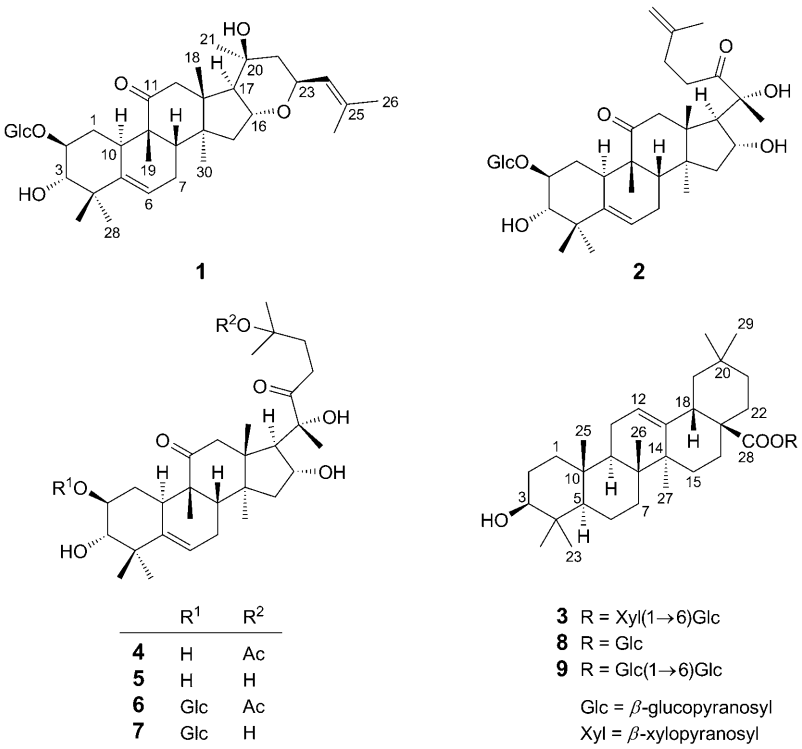
Three new triterpenoid saponins, xuedanglycosides A – C (**1** – **3**, resp.), along with six known ones, were isolated from the rhizomes of *Hemsleya chinensis*. By detailed analysis of the NMR spectra, by chemical methods, and by comparison with spectral data of known compounds, the structures of new compounds were determined to be 16α,23α-epoxy-2β,3α,20β-trihydroxy-10α,23α-cucurbita-5,24-dien-11-on-2-yl β-D-glucopyranoside (**1**), 2β,3α,16α,20β-tetrahydroxycucurbita-5,25-diene-11,22-dion-2-yl β-D-glucopyranoside (**2**), and oleanolic acid 28-*O*-β-xylopyranosyl-(1 → 6)-*O*-β-glucopyranoside (**3**). In addition, hemslecin A 2-*O*-β-D-glucopyranoside (**6**), hemsamabilinin B (**7**), and hemslonin A (**9**) were obtained for the first time from this plant.

Introduction. – The genus *Hemsleya* (Cucurbitaceae), containing 31 species, has its centre of distribution in Yunnan and Sichuan Provinces. The tubers of some *Hemsleya* species are used as folk medicine to treat bronchitis, bacillary dysentery, and tuberculosis [1]. Up to now, more than 80 new triterpenoids and their glycosides have been isolated from this genus [2 – 16], and some even showed interesting activities. For example, a mixture of hemslecins A (25-acetoxy-23,24-dihydrocucurbitacin F) and B (23,24-dihydrocucurbitacin F) occurring in many *Hemsleya* species is being manufactured in pharmaceutical factories as a treatment for bacterial diseases [17]. Hemslosides Ma2 and Ma3, obtained from *Hemsleya chinensis* COGN, could increase the water solubility of saikosaponin-a, a pharmacologically active saponin of *Bupleuri radix* [7]. Cucurbitane compounds are known as bitter principles of many cucurbitaceous plants. However, like several cucurbitane glycosides from the genera *Bryonia siraitia*, some analogues from the genus *Hemsleya* are sweet tasting [8]. In a previous study, several new compounds were discovered from the tubers of *H. chinensis* [4]. Aimed at finding potentially bioactive and novel compounds, we further investigated this species. As a result, three new triterpene saponins, named xuedanglycosides A – C (**1** – **3**), along with six known triterpenoids, hemslecin A (**4**) [2], hemslecin B (**5**) [2], hemslecin A 2-*O*-β-D-glucopyranoside (**6**) [3], hemsamabilinin B (**7**) [6], oleanolic acid 28-*O*-β-D-glucopyranoside (**8**) [4], and hemslonin A (**9**) [13] (*Fig. 1*), were isolated. This report refers to the structural elucidation of the new triterpenoid saponins based on spectroscopic analysis and chemical methods.



	R^1	R^2
4	H	Ac
5	H	H
6	Glc	Ac
7	Glc	H

Fig. 1. *Structures of compounds* **1**–**9**[1])

Results and Discussion. – Compound **1** was obtained as a white powder with an optical rotation $[\alpha]_D^{24} = +108.4$ ($c = 1.6$, MeOH). The molecular formula was determined as $C_{36}H_{56}O_{10}$ by HR-FAB-MS (m/z 647.3798 ($[M-H]^-$; calc. 647.3795), ^{13}C-NMR, and DEPT experiments. The IR spectrum (KBr) showed the presence of OH (3532, 3467, 3371, 3276 cm^{-1}) and C=O (1687 cm^{-1}) groups. After acid hydrolysis of **1** with 3% dry HCl/MeOH, glucose was detected by GC analysis. In the ^{1}H-NMR spectrum, the aglycone showed resonances for eight Me *singlet*s at δ(H) 1.14, 1.22, 1.29, 1.36, 1.64, 1.65 (6*s*, 3 H each) and 1.42 (*s*, 2 × 3 H). The anomeric H-atom signal at δ(H) 5.25 (*d*, $J = 7.8$) (*Table 1*) suggested the presence of a β-glucopyranosyl moiety. Comparison of the NMR data of **1** with those of scandenogenin D [10], indicated that the two compounds were very similar except for two Me groups and one additional sugar unit in **1**. Two HO–CH_2 groups at δ(C) 65.1 (*t*) and 58.1 (*t*) due to C(26) and C(27) in scandenogenin D were replaced by two Me groups at δ(C) 18.0 (*q*, C(26)) and δ(C) 26.1 (*q*, C(27)). In addition, C(24) and C(25) were shifted downfield by 0.8 ppm and 8.9 ppm in **1**, respectively. The chemical shift value of C(2) was shifted downfield from δ(C) 71.0 (*d*) in scandenogenin D to δ(C) 83.5 (*d*) in **1**, which indicated that the sugar unit was linked to C(2) in **1**. The HMBC correlations from the anomeric H-atom

[1]) Arbitrary numbering. For systematic names, see *Exper. Part.*

Table 1. *^{1}H- and ^{13}C-NMR Data of Compounds* **1** *and* **2** *in C_5D_5N*[a])[1]). δ in ppm, J in Hz.

	1		**2**	
	δ(H)[b])	δ(C)[c])	δ(H)[b])	δ(C)[d])
CH_2(1)	1.50–1.55 (*m*, H_α), 2.56–2.58 (*m*, H_β)	33.4 (*t*)	1.52–1.57 (overlapped, H_α), 2.74–2.81 (overlapped, H_β)	33.3 (*t*)
H–C(2)	4.25 (*t*, *J* = 9.2)	83.5 (*d*)	4.27–4.32 (overlapped)	83.4 (*d*)
H–C(3)	3.50 (*d*, *J* = 9.1)	80.8 (*d*)	3.53 (*d*, *J* = 11.0)	80.8 (*d*)
C(4)		42.6 (*s*)		42.6 (*s*)
C(5)		141.8 (*s*)		141.7 (*s*)
H–C(6)	5.67 (*d*, *J* = 5.0)	119.1 (*d*)	5.69 (*d*, *J* = 3.9)	119.1 (*d*)
CH_2(7)	1.86 (*t*, *J* = 12.5, H_α), 2.20–2.27 (*m*, H_β)	24.3 (*t*)	1.86–1.91 (overlapped, H_α), 2.24–2.33 (*m*, H_β)	24.1 (*t*)
H–C(8)	1.89–1.92 (overlapped)	42.7 (*d*)	1.86–1.91 (overlapped)	43.0 (*d*)
C(9)		48.9 (*s*)		48.2 (*s*)
H–C(10)	2.70 (*d*, *J* = 12.5)	34.0 (*d*)	2.74–2.81 (overlapped)	34.2 (*d*)
C(11)		213.1 (*s*)		213.2 (*s*)
CH_2(12)	2.52 (*d*, *J* = 14.8, H_β), 3.00 (*d*, *J* = 14.7, H_α)	48.8 (*t*)	2.62–2.70 (*m*, H_β), 3.29–3.35 (*m*, H_α)	49.3 (*t*)
C(13)		48.7 (*s*)		48.8 (*s*)
C(14)		49.3 (*s*)		51.1 (*s*)
CH_2(15)	1.60–1.66 (*m*, H_α), 1.89–1.92 (overlapped, H_β)	41.8 (*t*)	1.67–1.71 (overlapped), 1.86–1.91 (overlapped)	46.4 (*t*)
H–C(16)	5.03–5.07 (*m*)	70.6 (*d*)	4.87–4.92 (*m*)	70.4 (*d*)
H–C(17)	2.13 (*d*, *J* = 9.4)	56.3 (*d*)	2.85–2.92 (*m*)	58.9 (*d*)
Me(18)	1.22 (*s*)	20.2 (*q*)	1.17 (*s*)	20.4 (*q*)
Me(19)	1.14 (*s*)	20.5 (*q*)	1.16 (*s*)	20.3 (*q*)
C(20)		72.6 (*s*)		80.0 (*s*)
Me(21)	1.42 (*s*)	30.4 (*q*)	1.54 (*s*)	25.3 (*q*)
CH_2(22)	1.73 (*d*, *J* = 13.6, H_α), 1.95–1.99 (*m*, H_β)	46.4 (*t*)		214.9 (*s*)
H–C(23) or CH_2(23)	4.90 (*t*, *J* = 7.5)	71.7 (*d*)	3.03–3.13 (overlapped, H_α), 3.27–3.35 (*m*, H_β)	35.8 (*t*)
H–C(24) or CH_2(24)	6.54 (*d*, *J* = 8.4)	127.7 (*d*)	1.51–1.54 (*m*, H_α), 2.53–2.58 (*m*, H_β)	32.3 (*t*)
C(25)		133.6 (*s*)		145.6 (*s*)
Me(26) or CH_2(26)	1.65 (*s*)	18.0 (*q*)	4.76 (*s*), 4.83 (*s*)	110.4 (*t*)
Me(27)	1.64 (*s*)	26.1 (*q*)	1.68 (*s*)	22.9 (*q*)
Me(28)	1.42 (*s*)	29.3 (*q*)	1.44 (*s*)	25.4 (*q*)
Me(29)	1.29 (*s*)	22.3 (*q*)	1.33 (*s*)	22.4 (*q*)
Me(30)	1.36 (*s*)	21.1 (*q*)	1.51 (*s*)	19.1 (*q*)
Glc:				
H–C(1′)	5.25 (*d*, *J* = 7.8)	106.6 (*d*)	5.31 (*d*, *J* = 7.6)	106.6 (*d*)
H–C(2′)	4.05 (*t*, *J* = 8.5)	76.0 (*d*)	4.04–4.10 (*m*)	76.0 (*d*)
H–C(3′)	4.16 (*t*, *J* = 8.9)	78.5 (*d*)	4.18 (*t*, *J* = 11.0)	78.6 (*d*)
H–C(4′)	4.25 (*t*, *J* = 9.2) (overlapped)	71.2 (*d*)	4.27–4.32 (overlapped)	71.2 (*d*)
H–C(5′)	3.81–3.84 (*m*)	78.6 (*d*)	3.81–3.88 (*m*)	78.6 (*d*)
CH_2(6′)	4.23–4.26 (*m*), 4.33 (*dd*, *J* = 11.9, 4.6)	62.4 (*t*)	4.36 (*dd*, *J* = 12.0, 4.4), 4.47 (*d*, *J* = 11.6)	62.5 (*t*)

[a]) Assignments were established with HSQC, HMBC, and ROESY spectra. [b]) Recorded at 400 MHz. [c]) Recorded at 125 MHz. [d]) Recorded at 100 MHz.

at δ(H) 5.25 (*d*, H–C(1′)) to C(2) (δ(C) 83.5), as well as from the H-atom signals at δ(H) 1.65 (*s*, Me(26)) and δ(H) 1.64 (*s*, Me(27)) to C(24) (δ(C) 127.7) and C(25) (δ(C) 133.6) in **1** further confirmed above deduction (*Fig. 2*). The ROESY correlations of H–C(2) to H–C(10)[1]) and Me(28), of H–C(3) to Me(29), of H–C(16) to Me(18) and of H–C(23) to Me(21) established the orientations of H–C(2), H–C(3), H–C(16), and H–C(23) as α, β, β, and α, respectively (*Fig. 3*). Hence, the structure of **1** was formulated as 16α,23α-epoxy-2β,3α,20β-trihydroxy-10α,23α-cucurbita-5,24-dien-11-on-2-yl β-D-glucopyranoside.

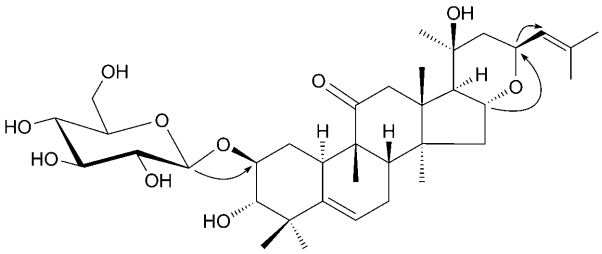


Fig. 2. *Key HMBCs* (H → C) *of compound* **1**

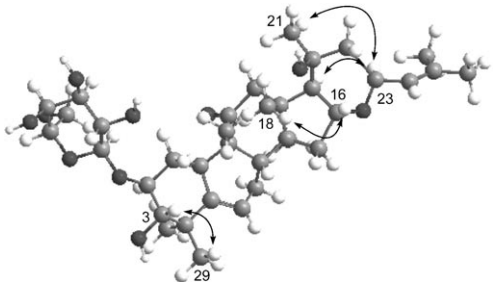


Fig. 3. *Key ROESY* (↔) *correlations of compound* **1**

Compound **2** was obtained as a white powder with an optical rotation $[\alpha]_D^{24} = +98.0$ ($c = 1.7$, MeOH). The molecular formula was determined as $C_{36}H_{56}O_{11}$ from the HR-FAB-MS (negative-ion mode; m/z 663.3726, $[M-H]^-$; calc. 663.3744) and NMR data. The IR spectrum (KBr) indicated OH (3450, 3372 cm^{-1}) and C=O (1689 cm^{-1}) groups. After acid hydrolysis of **2** with 3% dry HCl/MeOH, glucose was detected by GC analysis. The ^{1}H-NMR spectrum of **2** showed the presence of seven Me *singlet*s at δ(H) 1.16, 1.17, 1.33, 1.44, 1.51, 1.54, 1.68 (7*s*, 3 H each) and a terminal CH_2 group at δ(H) 4.76 (*s*, 1 H) and 4.83 (*s*, 1 H). The anomeric H-atom signal at δ(H) 5.31 (*d*, $J = 7.6$) (*Table 1*) suggested the presence of a β-glucopyranosyl moiety. Careful comparison of the ^{13}C-NMR and DEPT data of **2** and hemsamabilinin B (**7**) [6] indicated that the two compounds were very similar, except for the appearance of a C=C bond at δ(C) 145.6 (*s*, C(25)) and δ(C) 110.4 (*t*, C(26)) in **2** instead of a quarternary C-atom group at δ(C) 69.3 (*s*, C(25)) and a Me group at δ(C) 30.1 (*q*, C(26)) in hemsamabilinin B (**7**). In the HMBC spectrum of **2**, long-range correlations observed from the anomeric H-atom at

δ(H) 5.31 (H–C(1′)) to C(2) (δ(C) 83.4), as well as from δ(H) 4.76 and 4.83 (*s*, CH_2(26)) to C(25) (δ(C) 145.6) also supported the above suggestion. Therefore, the structure of **2** was elucidated as 2β,3α,16α,20β-tetrahydroxycucurbita-5,25-diene-11,22-dion-2-yl β-D-glucopyranoside.

Compound **3** was obtained as a white powder with an optical rotation $[\alpha]_D^{24} = +34.8$ ($c = 0.9$, MeOH). The molecular formula $C_{41}H_{66}O_{12}$ was deduced from the HR-FAB-MS (*m*/*z* 749.4486 ($[M-H]^-$); calc. 749.4476), as well as from the ^{13}C-NMR and DEPT data. The IR spectrum (KBr) showed absorptions for OH (3533, 3460, 3296 cm^{-1}), C=C (1635 cm^{-1}), C=O (1739 cm^{-1}), and C–O–C groups (1174 cm^{-1}). After acid hydrolysis of **3** with 3% dry HCl/MeOH, glucose and xylose were detected by GC analysis. The ^{13}C-NMR signals of two anomeric C-atoms (δ(C) 95.7 (*d*) and 105.7 (*d*)), two CH_2 (δ(C) 67.2 (*t*) and 69.2 (*t*)), and seven CH groups (δ(C) 70.9–78.8) (*Table 2*) were consistent with glucose and xylose units. Two anomeric H-atom signals at δ(H) 6.27 (*d*, $J = 8.2$) and 4.92 (*d*, $J = 7.5$) suggested the presence of a β-glucopyranosyl and β-xylopyranosyl moiety, respectively. The C-atom signal δ(C) 62.2 (*t*) attributable to the C(6′) of the sugar in oleanolic acid 28-*O*-β-D-glucopyranoside (**8**) [4] was shifted downfield to δ(C) 69.2 (*t*, C(6′)) in **3**, which indicated that the additional sugar was attached to C(6′) of this sugar moiety in **3**. This was confirmed by the HMBC correlation from the anomeric H-atom at δ(H) 4.92 (*d*, H–C(1″)) to C(6′) (δ(C) 69.2). Consequently, the structure of **3** was deduced as oleanolic acid 28-*O*-β-xylopyranosyl-(1 → 6)-*O*-β-glucopyranoside.

The compounds **4**–**9** were identified by comparison of their spectroscopic data with literature values. Compounds **6**, **7**, and **9** were obtained for the first time from this plant.

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Experimental Part

General. Glucose and xylose were purchased from *Sigma* (USA) and *New Jersey* (USA), resp. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh, *Qingdao Marine Chemical*, P. R. China); *Lichroprep RP-18* (40–63 μm, *Merck*, Darmstadt, Germany); and *Sephadex LH-20* (*Pharmacia Fine Chemical Co.*, *Ltd.*). Fractions were monitored by TLC, and spots were visualized by heating TLC sprayed with 10% H_2SO_4. GC: *Shimadzu GC-17A* gas chromatograph equipped with an H_2 flame ionization detector; column: *TC-1* capillary column (30 m × 0.25 mm); detector, FID. Optical rotations: *JASCO DIP-370* digital polarimeter. IR Spectra: *Shimadzu IR-450* instrument; in cm^{-1}; KBr pellets. NMR Spectra: *Bruker AV-400*, or *DRX-500* instruments; chemical shifts (δ) in ppm; TMS as the internal standard; *J* in Hz. FAB-MS and HR-FAB-MS: *VG-AUTOSPEC-3000* spectrometer; in *m*/*z* (rel. int. in % of the base peak).

Plant Material. The tubers of *H. chinensis* were collected at Dongchuan County, Kunming City, Yunnan Province of China, in October 2004. It was identified by Prof. *S. K. Chen*, and a specimen (No. KIB20050623) was deposited with the Laboratory of Phytochemistry, Kunming Institute of Botany.

Extraction and Isolation. The dried and powdered tubers of *H. chinensis* (3.84 kg) were extracted with MeOH (7 l × 6, each 8 h) at 60°. After removal of the solvent under reduced pressure, a residue (1.21 kg) was obtained. This residue was dissolved in H_2O (3 l), and then extracted successively with AcOEt (2 l × 3) and BuOH (2 l × 3). The AcOEt and BuOH layers were concentrated to dryness, resp., to give an AcOEt (220.10 g) and a BuOH extract (309.40 g). The AcOEt extract was subjected to CC

Table 2. *^{1}H-and ^{13}C-NMR Data of Compound* **3** *in C_5D_5N*[a]). δ in ppm, J in Hz.

	δ(H)[b]	δ(C)[c]		δ(H)[b]	δ(C)[c]
CH_2(1)	0.97 (*d*, *J* = 4.1), 1.52 (*dd*, *J* = 13.2, 3.3) (overlapped)	39.0 (*t*)	CH_2(16)	4.95–5.09 (*m*), 5.10–5.14 (*m*)	23.4 (*t*)
CH_2(2)	1.78–1.82 (overlapped), 2.30–2.36 (*m*)	28.1 (*t*)	C(17)		47.1 (*s*)
H–C(3)	3.42 (*dd*, *J* = 10.6, 5.1)	78.1 (*d*)	H–C(18)	3.19 (*dd*, *J* = 13.7, 4.1)	41.8 (*d*)
C(4)		39.4 (*s*)	CH_2(19)	1.24 (*d*, *J* = 4.2), 1.70–1.75 (*m*)	46.3 (*t*)
H–C(5)	0.82–0.87 (*m*)	55.9 (*d*)	C(20)		30.8 (*s*)
CH_2(6)	1.31–1.37 (overlapped), 1.45–1.53 (*m*)	18.8 (*t*)	CH_2(21)	1.10–1.14 (*m*), 1.31–1.37 (overlapped)	34.0 (*t*)
CH_2(7)	1.31–1.37 (overlapped), 1.82–1.87 (*m*)	33.2 (*t*)	CH_2(22)	1.31–1.37 (overlapped), 1.45–1.48 (*m*)	32.6 (*t*)
C(8)		39.9 (*s*)	Me(23)	1.21 (*s*)	28.8 (*q*)
H–C(9)	1.64 (*dd*, *J* = 10.7, 7.1)	48.2 (*d*)	Me(24)	1.02 (*s*)	16.6 (*q*)
C(10)		37.4 (*s*)	Me(25)	0.93 (*s*)	15.7 (*q*)
CH_2(11)	0.83–0.87 (overlapped), 1.86–1.95 (*m*)	23.9 (*t*)	Me(26)	1.16 (*s*)	17.6 (*q*)
H–C(12)	5.42 (*t*, *J* = 3.3)	122.9 (*d*)	Me(27)	1.21 (*s*)	26.2 (*q*)
C(13)		144.2 (*s*)	C(28)		176.6 (*s*)
C(14)		42.2 (*s*)	Me(29)	0.87 (*s*)	33.2 (*q*)
CH_2(15)	1.17 (*d*, *J* = 3.4), 1.78–1.82 (overlapped)	28.3 (*t*)	Me(30)	0.87 (*s*)	23.7 (*q*)
Glc:			Xyl:		
H–C(1′)	6.27 (*d*, *J* = 8.2)	95.7 (*d*)	H–C(1″)	4.92 (*d*, *J* = 7.5)	105.7 (*d*)
H–C(2′)	4.08–4.13 (*m*)	73.9 (*d*)	H–C(2″)	3.98 (*t*, *J* = 6.0)	74.9 (*d*)
H–C(3′)	4.23 (*t*, *J* = 8.9)	78.8 (*d*)	H–C(3″)	4.08–4.13 (*m*)	77.9 (*d*)
H–C(4′)	4.34–4.38 (*m*)	71.1 (*d*)	H–C(4″)	4.15–4.19 (*m*)	70.9 (*d*)
H–C(5′)	4.34–4.38 (*m*)	78.2 (*d*)	CH_2(5″)	3.59–3.65 (*m*), 4.30 (*dd*, *J* = 11.3, 5.2)	67.2 (*t*)
CH_2(6′)	4.36 (*d*, *J* = 7.2), 4.71 (*d*, *J* = 9.5)	69.2 (*t*)			

[a]) Assignments were established with HSQC and HMBC. [b]) Recorded at 400 MHz. [c]) Recorded at 100 MHz.

(SiO_2; $CHCl_3$/MeOH 1:0, 50:1, 20:1, 10:1, 0:1) to yield five fractions (*Fr. 1–5*). *Fr. 2* (31.15 g) was separated by CC (*RP-18*; MeOH/H_2O 55:45) to afford **4** (20.06 g). *Fr. 3* (19.76 g) was chromatographed (SiO_2; petroleum ether/AcOEt 3:1) to give **5** (10.10 g).

The BuOH extract (309.60 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 20:1, 10:1, 5:1, 2:1, 0:1) to afford five fractions (*Fr. I–V*). *Fr. II* (18.25 g) was chromatographed (SiO_2; $CHCl_3$/Me_2CO 9:1 and *RP-18*; MeOH/H_2O 60:40) to yield **1** (15 mg), **2** (12 mg), **6** (500 mg), and **8** (70 mg). Compounds **3** (2.75 g) and **7** (40 mg) were isolated from *Fr. III* (30.46 g) by repeated CC (*RP-18*; MeOH/H_2O 55:45 to 75:25). Similarly, *Fr. IV* (40.65 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH/H_2O 8:2:0.2 and *Sephadex LH-20*; MeOH/H_2O 90:10) to yield **9** (19 mg).

Acid Hydrolysis of **1**–**3**. Compounds **1**–**3** (each 2 mg) were treated with 3% HCl in MeOH (5 ml) at 92° for 3 h, resp. 5 ml $CHCl_3$/H_2O (1:1) were used for extraction. The aq. phase was neutralized with Ag_2CO_3. The filtrate was concentrated to dryness under reduced pressure.

Sugar Determination in **1**–**3**. Each neutralized hydrolysate of **1**–**3** was dissolved in 0.6 ml of pyridine, then 0.4 ml hexamethyl disilazane and 0.2 ml trimethylchlorosilane were added successively. The mixture was kept at 60° for 10 min in a water bath. Next, the mixture was centrifuged for 20 min at

1.0×10^4 rpm. The supernatant was subjected to GC analysis under the following conditions: *Shimadzu GC-17A* gas chromatograph equipped with an H_2 flame ionization detector. Column: *TC-1* capillary column (30 m × 0.25 mm). Column temperature: 200°/260°, programmed increase: 3°/min, carrier gas: N_2 (1 ml/min). Injector and detector temperature: 260°; injection volume: 1 µl; split ratio: 1/50. GC Analysis showed the presence of glucose (t_R 12.04) in **1**–**3** and xylose (t_R 11.39) in **3**.

Xuedanglycoside A (=*16α,23α-Epoxy-2β,3α,20β-trihydroxy-10α,23α-cucurbita-5,24-dien-11-on-2-yl β-*D*-Glucopyranoside*[1]) = *(1S,2S,4R,9β,16α,23S)-1,20-Dihydroxy-9,10,14-trimethyl-11-oxo-16,23-epoxy-4,9-cyclo-9,10-secocholesta-5,24-dien-2-yl β-*D*-Glucopyranoside*; **1**). White amorphous powder. $[\alpha]_D^{24} = +108.4$ ($c = 1.6$, MeOH). IR (KBr): 3532, 3467, 3371, 3276, 2969, 2930, 2881, 2729, 1687, 1454, 1377, 1269, 1209, 1160, 1077, 1031, 636, 465. ^{1}H-NMR (C_5D_5N, 500 MHz): *Table 1*. ^{13}C-NMR (C_5D_5N, 125 Hz): *Table 1*. FAB-MS (neg.): 647 ($[M-H]^-$). HR-FAB-MS (neg.): 647.3798 ($[M-H]^-$, $C_{36}H_{55}O_{10}^-$; calc. 647.3795).

Xuedanglycoside B (=*2β,3α,16α,20β-Tetrahydroxycucurbita-5,25-dien-11,22-dion-2-yl β-*D*-Glucopyranoside* = *(1S,2S,4R,9β,16α)-1,16,20-Trihydroxy-9,10,14-trimethyl-11,22-dioxo-4,9-cyclo-9,10-secocholesta-5,25-dien-2-yl β-*D*-Glucopyranoside*; **2**). White amorphous powder. $[\alpha]_D^{24} = +98.0$ ($c = 1.7$, MeOH). IR (KBr): 3450, 3372, 2971, 2880, 1689, 1651, 1428, 1387, 1079, 1028. ^{1}H-NMR (C_5D_5N, 500 MHz): *Table 1*. ^{13}C-NMR (C_5D_5N, 100 Hz): *Table 1*. FAB-MS (neg.): 647 ($[M-OH]^-$). HR-FAB-MS (neg.): 663.3726 ($[M-H]^-$, $C_{36}H_{55}O_{11}^-$; calc. 663.3744).

Xuedanglycoside C (=*Oleanolic Acid 28-*O*-β-*D*-Xylopyranosyl-(1→6)-*O*-β-*D*-glucopyranoside* = *1-*O*-[(3β)-3-Hydroxy-28-oxoolean-12-en-28-yl]-6-*O*-β-*D*-xylopyranosyl-β-*D*-glucopyranose*; **3**). White amorphous powder. $[\alpha]_D^{24} = +34.8$ ($c = 0.9$, MeOH). IR (KBr): 3972, 3533, 3460, 3296, 2944, 2929, 2863, 1739, 1635, 1463, 1388, 1174, 1074, 1043, 995. ^{1}H-NMR (C_5D_5N, 400 MHz): *Table 2*. ^{13}C-NMR (C_5D_5N, 100 Hz): *Table 2*. FAB-MS (neg.): 750 (M^-). HR-FAB-MS (neg.): 749.4486 ($[M-H]^-$, $C_{41}H_{65}O_{12}^-$; calc. 749.4476).

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