Two New Megastigmane Glycosides and a New Iridoid Glycoside from *Gelsemium elegans*

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Two new megastigmane glycosides, eleganosides A and B (**1** and **3**, resp.), and one new iridoid glycoside, gouwenoside A (**4**), together with two known compounds, foliasalacioside B_1 (**2**) and loganin (**5**), were isolated from the aerial parts of *Gelsemium elegans* (GARDN. et CHAMP.) BENTH. (Loganiaceae). Their structures were elucidated by spectroscopic methods including 1D- and 2D-NMR techniques. The absolute configuration of **1** was determined by CD spectroscopy.

Introduction. – *Gelsemium elegans* (GARDN. et CHAMP.) BENTH. (Loganiaceae; *Gouwen* in Chinese), mainly distributed in south and southwest China, has long been used as a folk medicine for relief of rheumatoid and nervous pain, treatment of skin ulcers, and cancers [1][2]. Previous chemical investigations of this plant resulted in the isolation of indole alkaloids [3–19], iridoids [20][21], lignans [22], and flavones [23]. In our continuing studies of this plant [18][23], two new megastigmane glycosides, eleganosides A and B (**1** and **3**, resp.), and one new iridoid glycoside, gouwenoside A (**4**), together with two known compounds, foliasalacioside B_1 (**2**) [24] and loganin (**5**) [25], were isolated (*Fig. 1*). Of these components, megastigmane glycosides **1**–**3** were isolated from the genus *Gelsemium* for the first time. Here, we report the isolation and structure elucidation of these new compounds.

Results and Discussion. – Compound **1** was obtained as an amorphous powder. The molecular formula $C_{24}H_{40}O_{11}$ was determined by HR-ESI-MS ($[M + Na]^+$ peak at *m/z* 527.2471), indicating five degrees of unsaturation. The ^{1}H- and ^{13}C-NMR data of **1** (*Table 1*) indicated a glycosylated megastigmane skeleton. The aglycone part contained four Me (δ(H) 1.01 (*s*), 1.08 (*s*), 1.17 (*d*, $J = 6.5$), and 2.04 (*d*, $J = 1.0$)), three CH_2 (δ(H) 1.58–1.69 (*m*, 2 H); 1.58–1.69 (*m*, 1 H) and 1.77–1.83 (*m*, 1 H); 1.98 (*d*, $J = 17.0$, 1 H); and 2.46 (*d*, $J = 17.0$, 1 H)), two sp^3 CH groups (δ(H) 1.96–2.00 (*m*) and 3.84–3.88 (*m*)), one sp^3 quaternary C-atom (δ(C) 37.6), one C=O (δ(C) 202.8), and one CH=C moiety (δ(H) 5.80 (*s*); δ(C) 125.7 and 170.5). The saccharide part was composed of two sugar moieties (glucopyranosyl (Glc): δ(H) 4.31 (*d*, $J = 8.0$); δ(C) 102.5, 78.3, 77.1, 75.4, 72.1, and 70.1; arabinopyranosyl (Ara*p*): δ(H) 4.28 (*d*, $J = 6.5$);

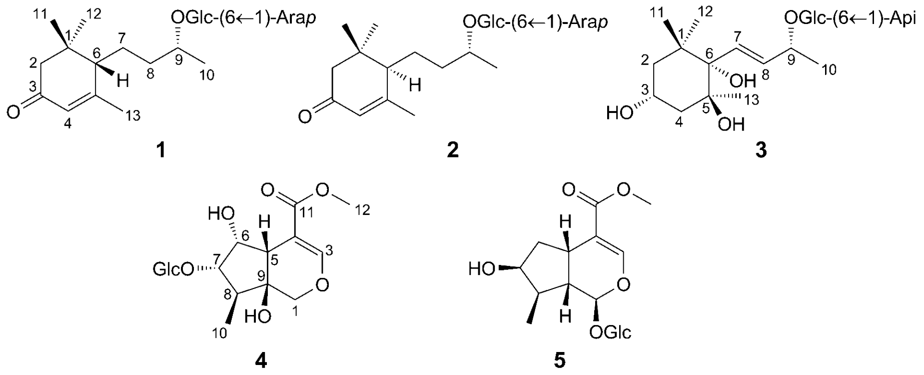


Fig. 1. *Structures of compounds* **1**–**5**

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1** *and* **2**. δ in ppm, J in Hz. C-Atom numbering as indicated in *Fig. 1*.

	1		**2**	
	δ(H)[a])	δ(C)[b])	δ(H)[a])	δ(C)[b])
C(1)		37.6		37.6
CH$_2$(2)	2.46 (*d*, J = 17.0), 1.98 (*d*, J = 17.0)	48.5	2.46 (*d*, J = 17.0), 1.97 (*d*, J = 17.0)	48.4
C(3)		202.8		202.8
H–C(4)	5.80 (*s*)	125.7	5.79 (*s*)	125.6
C(5)		170.5		170.6
H–C(6)	1.96–2.00 (*m*)	52.8	1.95–1.99[c])	52.7
CH$_2$(7)	1.77–1.83 (*m*), 1.58–1.69 (*m*)	27.4	1.95–1.99[c]), 1.47–1.51 (*m*)	27.3
CH$_2$(8)	1.58–1.69 (*m*)	38.3	1.59–1.64 (*m*)	38.2
H–C(9)	3.84–3.88 (*m*)	76.1	3.82–3.87[c])	76.0
Me(10)	1.17 (*d*, J = 6.5)	20.2	1.17 (*d*, J = 6.0)	20.4
Me(11)	1.08 (*s*)	27.8	1.09 (*s*)	27.9
Me(12)	1.01 (*s*)	29.4	1.00 (*s*)	29.3
Me(13)	2.04 (*d*, J = 1.0)	25.3	2.05 (*s*)	25.3
Glc				
H–C(1′)	4.31 (*d*, J = 8.0)	102.5	4.31 (*d*, J = 8.0)	102.5
H–C(2′)	3.13 (*t*, J = 8.5)	75.4	3.13 (*t*, J = 8.3)	75.4
H–C(3′)	3.29–3.34[c])	78.3	3.30–3.34[c])	78.3
H–C(4′)	3.29–3.34[c])	72.1	3.30–3.34[c])	72.1
H–C(5′)	3.39–3.41 (*m*)	77.1	3.39–3.42 (*m*)	77.1
CH$_2$(6′)	4.06 (*dd*, J = 11.5, 2.0), 3.68 (*dd*, J = 11.5, 6.0)	70.1	4.06 (*dd*, J = 11.5, 1.5), 3.68 (*dd*, J = 11.3, 5.8)	70.1
Ara				
H–C(1″)	4.28 (*d*, J = 6.5)	105.6	4.28 (*d*, J = 6.5)	105.6
H–C(2″)	3.57 (*dd*, J = 8.8, 6.5)	72.6	3.57 (*dd*, J = 8.3, 6.5)	72.7
H–C(3″)	3.48–3.50[c])	74.5	3.47–3.50[c])	74.5
H–C(4″)	3.78–3.79 (*m*)	69.7	3.79 (*d*, J = 1.5)	69.7
CH$_2$(5″)	3.84 (*dd*, J = 12.5, 3.5), 3.49 (*dd*, J = 12.0, 1.5)	66.9	3.82–3.87[c]), 3.47–3.50[c])	66.9

[a]) Recorded at 500 MHz in CD$_3$OD. [b]) Recorded at 125 MHz in CD$_3$OD. [c]) Overlapped signals.

δ(C) 105.6, 74.5, 72.6, 69.7, and 66.9). The NMR data of **1** were very similar to those of a known compound, foliasalacioside B$_1$ (**2**) [24] (*Table 1*). The only difference was that the H-atom signals at δ(H) 1.47–1.51 and 1.95–1.99 (2*m*, 1 H each, CH$_2$(7)) in **2** shifted to 1.58–1.69 and 1.77–1.83 (2*m*, 1 H each, CH$_2$(7)) in **1**, suggesting the configuration at C(6) in **1** different from that in **2**. The configuration at C(6) in **1** was further confirmed as (*S*) by CD spectrum, which showed negative *Cotton* effects at 239.8 nm ($\Delta\varepsilon$ −4.72) and 325.8 nm ($\Delta\varepsilon$ −1.66), while compound **2** with (*R*)-configuration at C(6) showed positive *Cotton* effects at 236.1 nm ($\Delta\varepsilon$ +7.61) and 336.5 nm ($\Delta\varepsilon$ +1.27) (*Fig. 2*). The configuration at C(9) in **1** was deduced to be (*R*) by comparing its C-atom signal (δ(C) 76.1) with that of **2** (δ(C) 76.0). In case of C(9) with (*S*)-configuration, the C-atom signal would be shifted upfield to δ(C) 74.6 as reported for salvionoside C [26]. The connection of glucosyl to C(9) and a 1 → 6 linkage of arabinosyl to glucosyl were deduced from the HMBCs H–C(1′)/C(9) and H–C(9)/C(1′), and H–C(1″)/C(6′) and CH$_2$(6′)/C(1″) (*Fig. 3*). The configurations of the sugars in **1** were determined as β-D-glucopyranose and α-L-arabinopyranose by comparing their NMR data with those of **2**, and by further GC/MS analysis. 2D-NMR Correlations, which confirmed the skeleton of **1**, are shown in *Figs. 3* and *4*. Therefore, the structure of **1** was determined as (6*S*,9*R*)-hydroxymegastigm-4-en-3-one 9-*O*-α-L-arabinopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside, an epimer of **2**, and named as eleganoside A.

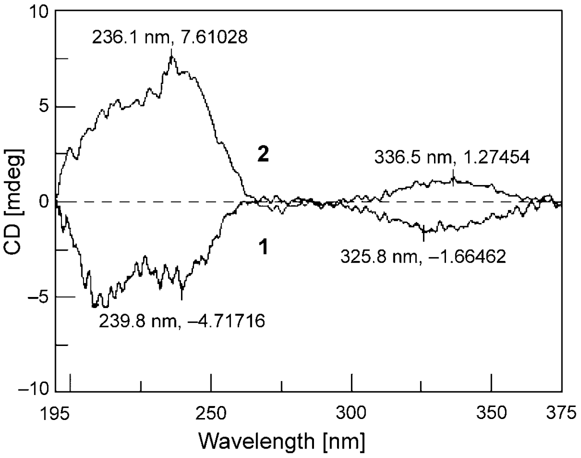
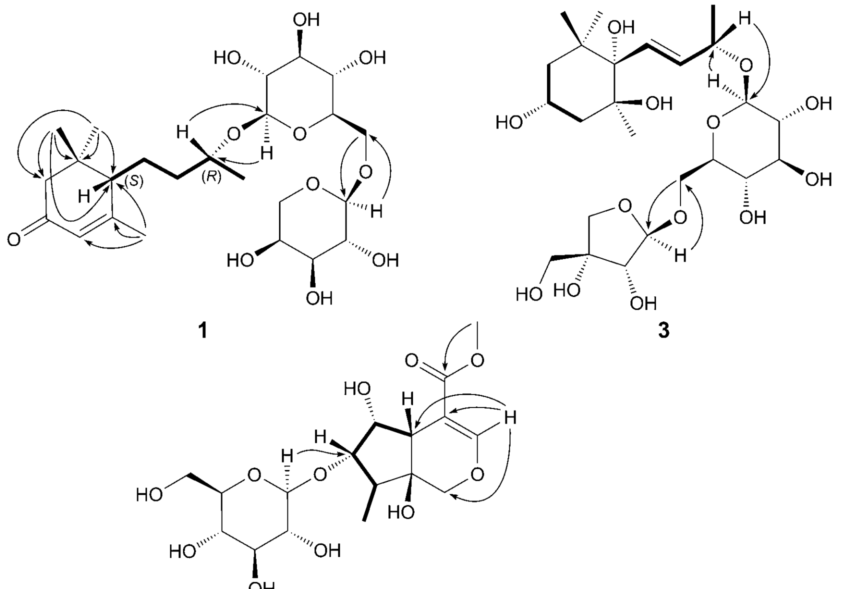


Fig. 2. *CD Spectra* (MeOH) *of* **1** *and* **2**

Compound **3** was obtained as an amorphous powder. The molecular formula $C_{24}H_{42}O_{13}$ was determined by HR-ESI-MS ($[M + Na]^+$ peak at *m/z* 561.2531), indicating four degrees of unsaturation. The ^{1}H- and ^{13}C-NMR data of **3** (*Table 2*) indicated also a megastigmane glycoside with a β-D-glucopyranosyl and an apiofuranosyl unit. The megastigmane skeleton possessed a (*E*)-C=C bond (δ(H) 6.02 (*d*, *J* = 16.0) and 5.75 (*dd*, *J* = 16.0, 7.0); δ(C) 133.4 and 134.7) and four O-bearing C-atoms (δ(C) 65.6, 78.0, 78.7, and 79.4). Compound **3** was identified as an apiofuranosyl



1 3 4

Fig. 3. *Selected HMBC* (H → C) *and* $^1H,^1H$*-COSY* (—) *correlations of* **1**, **3**, *and* **4**

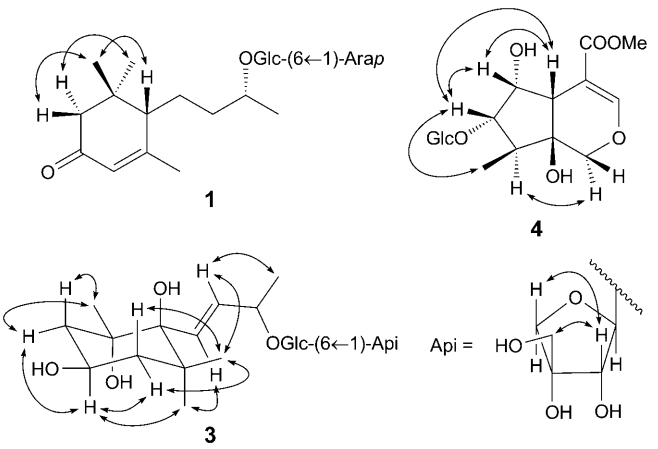


Fig. 4. *Key NOESY correlations of* **1**, **3**, *and* **4**

derivative of a known compound, bridelionoside B, by comparing the NMR data of **3** with those of the literature [27] (*Table 2*). The linkage of apiofuranosyl to C(6′) of the glucopyranosyl moiety was deduced from a large downfield chemical shift for C(6′) (+6.7 ppm), and further confirmed by the HMBCs H–C(1″)/C(6′) and CH_2(6′)/C(1″) (*Fig. 3*). The β-D configuration of the apiofuranose was deduced from its NMR data [28][29] and NOE correlations H–C(2″)/CH_2(5″) and H–C(2″)/H_b–C(4″) (*Fig. 4*),

Table 2. *^{1}H- and ^{13}C-NMR Data of* **3** *and Bridelionoside B.* δ in ppm, J in Hz. C-Atom numbering as indicated in *Fig. 1.*

	3		Bridelionoside B[a])	
	δ(H)[b])	δ(C)[c])	δ(H)[d])	δ(C)[e])
C(1)		41.0		40.8
H$_{ax}$–C(2)	1.54 (*dd*, $J = 12.0, 12.0$)	46.7	1.60 (*t*, $J = 12$)	46.4
H$_{eq}$–C(2)	1.35 (*dd*, $J = 12.0, 2.5$)		1.41 (*ddd*, $J = 12, 4, 2$)	
H–C(3)	3.93–3.98 (*m*)	65.6	4.01 (*tt*, $J = 12, 6$)	65.3
H$_{eq}$–C(4)	1.69 (*dd*, $J = 12.0, 3.0$)	46.0	1.73 (*ddd*, $J = 12, 6, 2$)	45.7
H$_{ax}$–C(4)	1.64 (*dd*, $J = 12.0, 12.0$)		1.69 (*t*, $J = 12$)	
C(5)		78.0		77.8
C(6)		79.4		78.3
H–C(7)	6.02 (*d*, $J = 16.0$)	133.4	6.08 (*dd*, $J = 16, 1$)	132.9
H–C(8)	5.75 (*dd*, $J = 16.0, 7.0$)	134.7	5.81 (*dd*, $J = 16, 7$)	134.3
H–C(9)	4.31–4.34 (*m*)	78.7	4.39 (*quint*, $J = 6$)	79.1
Me(10)	1.23 (*d*, $J = 6.5$)	21.9	1.28 (*d*, $J = 6$)	21.5
Me(11)	1.08 (*s*)	26.5	1.06 (*s*)	27.9
Me(12)	0.75 (*s*)	27.8	0.83 (*s*)	26.3
Me(13)	1.06 (*s*)	27.9	1.18 (*s*)	27.1
Glc				
H–C(1′)	4.25 (*d*, $J = 8.0$)	102.6	4.31 (*d*, $J = 8$)	102.6
H–C(2′)	3.08 (*dd*, $J = 9.0, 8.0$)	75.6	[f])	75.4
H–C(3′)	3.21–3.26 (*m*)	78.4	[f])	77.9
H–C(4′)	3.15 (*t*, $J = 9.0$)	72.1	[f])	71.5
H–C(5′)	3.21–3.26 (*m*)	77.1	[f])	78.3
CH$_2$(6′)	3.85–3.88[g]), 3.46 (*dd*, $J = 11.0, 6.5$)	69.3	3.77 (*dd*, $J = 12, 2$), 3.61 (*dd*, $J = 12, 5$)	62.6
Api				
H–C(1″)	4.89 (*d*, $J = 3.0$)	111.4	[f])	
H–C(2″)	3.85 (*d*, $J = 3.0$)	78.3	[f])	
C(3″)		80.9	[f])	
CH$_2$(4″)	3.89 (*d*, $J = 9.5$), 3.67 (*d*, $J = 9.5$)	75.4	[f])	
CH$_2$(5″)	3.48 (br. *s*)	65.9	[f])	

[a]) From [27]. [b]) Recorded at 500 MHz in CD$_3$OD. [c]) Recorded at 125 MHz in CD$_3$OD. [d]) Recorded at 400 MHz in CD$_3$OD. [e]) Recorded at 100 MHz in CD$_3$OD. [f]) Signals not reported in [27]. [g]) Overlapped signals.

which indicated that H–C(2″), CH$_2$(5″), and H$_b$–C(4″) were on the same side of the ring for this sugar. The absolute configuration of the apiofuranose was further confirmed by GC/MS analysis after derivatization with (*S*)-1-aminopropan-2-ol and acetylation.

The OH group at C(3) could be determined as equatorially oriented on the basis of the ^{1}H-NMR data, as the coupling-constant values of $J(2_{ax},3)$ and $J(3,4_{ax})$ were both 12 Hz, which could be calculated from the well-resolved H-atom signals (H$_{ax}$–C(2) and H$_{ax}$–C(4); *Table 2*). Me(13) and the side chain at C(6) were also equatorially oriented, as suggested by NOE correlations Me(13)/H$_{eq}$–C(4), Me(13)/H$_{ax}$–C(4), H–C(7)/Me$_{ax}$(11), and H–C(8)/Me$_{eq}$(12) (*Fig. 4*). Thus, the OH groups at C(3), C(5), and C(6) were α-, β-, and α-oriented, respectively, which indicated that the relative configuration of the megastigmane ring portion of **3** was the same as that of bridelionoside B. The absolute configuration at C(9) as (*R*) was determined based on its C-atom signal (δ(C) 78.7), as reported for bridelionoside B and bridelionoside C; both of them had (*R*)-configurations at C(9) and showed a similar chemical shift (δ(C) 79.1) [27], whereas the chemical shifts of C(9) in euodionoside C and euodionoside D, both with (*S*)-configurations, were observed at δ(C) 74.8 and 75.7, respectively [30]. On the basis of above analysis, compound **3** was identified as (3α,5β,6α,7*E*,9*R*)-megastigm-7-ene-3,5,6,9-tetrol 9-*O*-β-D-apiofuranosyl-($1 \rightarrow 6$)-*O*-β-D-glucopyranoside, and named as eleganoside B.

Compound **4** was obtained as an amorphous powder. The molecular formula $C_{17}H_{26}O_{11}$ was determined by HR-ESI-MS ($[M + Na]^+$ peak at *m/z* 429.1359), indicating five degrees of unsaturation. The ^{1}H- and ^{13}C-NMR data of **4** (*Table 3*) exhibited signals for an iridoid skeleton and a glucopyranosyl moiety. The NMR data of the aglycone of **4** were similar to those of a known compound, GEIR-3 [21] (*Table 3*), with the exception of signals for a methoxycarbonyl group in **4** (δ(H): 3.71 (*s*); δ(C): 52.0), which was confirmed by the HMBC of Me(12) and C(11) (C=O; *Fig. 3*). The linkage of glucosyl to C(7) was deduced from the chemical shifts of C(6) (− 9.8 ppm), C(7) (+ 13.9 ppm), and C(8) (− 1.3 ppm), and further confirmed by the HMBC correlation H–C(1′)/C(7) (*Fig. 3*). The anomeric H-atom signal at δ(H) 4.40 (*d*,

Table 3. *^{1}H- and ^{13}C-NMR Data of* **4** *and GEIR-3*. δ in ppm, *J* in Hz. Arbitrary atom numbering.

	4		GEIR-3a)	
	δ(H)b)	δ(C)c)	δ(H)d)	δ(C)c)
H_β–C(1)	3.99–4.01e)	74.7	3.94 (*dd*, *J* = 11.0, 2.0)	74.1
H_α–C(1)	3.77 (*d*, *J* = 11.0)		3.75 (*d*, *J* = 11.0)	
H–C(3)	7.76 (*s*)	158.5	7.73 (*s*)	157.0
C(4)		105.0		107.1
H–C(5)	2.50 (br. *s*)	46.3	2.49 (br. *s*)	46.9
H–C(6)	4.42 (*d*, *J* = 3.5)	70.5	4.24 (*dd*, *J* = 4.0, 4.0)	80.3
H–C(7)	3.99–4.01e)	87.0	3.70 (*dd*, *J* = 9.3, 4.0)	73.1
H–C(8)	1.78–1.83 (*m*)	43.1	1.62 (*m*)	44.4
C(9)		74.2		74.4
Me(10)	1.11 (*d*, *J* = 7.0)	13.0	1.08 (*d*, *J* = 7.1)	12.9
C(11)		170.2		174.0
Me(12)	3.71 (*s*)	52.0		
Glc				
H–C(1′)	4.40 (*d*, *J* = 7.5)	103.1		
H–C(2′)	3.19–3.22 (*m*)	75.6		
H–C(3′)	3.31–3.39e)	78.5		
H–C(4′)	3.31–3.39e)	71.9		
H–C(5′)	3.31–3.39e)	78.3		
CH_2(6′)	3.88 (*d*, *J* = 12.0), 3.68 (*dd*, *J* = 11.5, 4.0)	63.1		

a) From [21]. b) Recorded at 500 MHz in CD_3OD. c) Recorded at 125 MHz in CD_3OD. d) Recorded at 400 MHz in CD_3OD. e) Overlapped signals.

$J = 7.5$) indicated β-configuration of the glucose. The relative configuration of the aglycone was derived from the NOESY experiment. The NOE correlations H_{α}–C(1)/H–C(8), H–C(6)/H–C(5), H–C(7)/H–C(5), H–C(6)/H–C(7), and H–C(7)/Me(10) implied that H–C(5), H–C(6), H–C(7), and Me(10) were in β-position (*Fig. 4*). HO–C(9) in **4** was also determined to be β-oriented on the basis of the biogenetic pathway of iridiods from the genus *Gelsemium* [20][21][31]. Therefore, the structure of **4** was determined as methyl *rel*-(4a*S*,5*R*,6*S*,7*S*,7a*S*)-1,4a,5,6,7,7a-hexahydro-6-(β-D-glucopyranosyloxy)-5,7a-dihydroxy-7-methylcyclopenta[*c*]pyran-4-carboxylate, and named gouwenoside A.

Megastigmane derivatives are commonly encountered as natural products. However, no reports have been published on megastigmane constituents from the genus *Gelsemium*.

Iridoids like gouwenoside A (**4**), without OH substitution (or glycosylation) at C(1), are not very common among naturally occurring iridoids [32–34]. However, several iridoids of this type have been isolated from *Gelsemium* plants, such as gelsemide, gelsemide 7-glucoside, semperoside, 9-hydroxysemperoside [31], 7-deoxygelsemide, 9-deoxygelsemide [20], GEIR-1, GEIR-2, GEIR-3, and GRIR-1 [21].

Experimental Part

General. TLC: silica-gel GF_{254} plates (0.15 or 0.40 mm; *Yantai Jiangyou Chemical Inc.*, P. R. China). Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Marine Chemical Inc.*, P. R. China), *D101* resin (*Cangzhou Baoen Chemical Inc.*, P. R. China), *Sephadex LH-20* (*GE-Healthcare Bio-Sciences AB*, Sweden), and *RP-18* gel (40–60 μm, *Sepax Technologies Inc.*). Semiprep. HPLC: *Waters 600* instrument; *YMC-Pack ODS-A* column (250 × 10 mm i.d., 5 μm), flow rate 3.0 ml/min. GC/MS: *Thermo DSQ* gas chromatograph; *Thermo TR-5MS* column (60 m × 0.25 mm i.d., 2.5 μm); N_2 as carrier gas, flow rate 1.0 ml/min. Optical rotation: *KRÜSS P800-T* polarimeter. IR Spectra: *Nicolet*™ *380* spectrometer (*Thermo Electron*). CD Spectra: *JASCO J-180* spectrometer (Japan). 1D- and 2D-NMR spectra: *Bruker AV-500* spectrometer. ESI-MS: $\mathit{LCQ\ DECAXP}^{plus}$ mass spectrometer. HR-ESI-MS: *APEXIII 7.0 TESLA FTMS* mass spectrometer.

Plant Material. The aerial parts of *G. elegans* were collected in Fujian Province, P. R. China in 2006 and authenticated by Dr. *Li-Hong Wu* (Institute of Chinese Materia Medica, Shanghai University of Traditional Chinese Medicine). A voucher specimen (No. GW-090630) was deposited with the laboratory of Shanghai R&D Center for Standardization of Chinese Medicines.

Extraction and Isolation. The dried aerial parts of *G. elegans* (3.4 kg) were extracted under reflux with MeOH (3 × 15 l) for 2 h each time. The MeOH extract was evaporated to yield a residue (593 g), which was suspended in H_2O (500 ml), and then extracted with petroleum ether (5 × 1 l), AcOEt (5 × 1 l), and BuOH (5 × 1 l), successively. The BuOH extract (92 g) was subjected to CC (*D101* resin) and eluted with 30, 50, and 90% aq. EtOH successively, after washing with H_2O. The 30% aq. EtOH eluate (29.5 g) was then subjected to CC (*Sephadex LH-20*; MeOH) to give *Fractions 1–5*. *Fr. 2* (10.3 g) was again subjected to CC (SiO_2; AcOEt/MeOH 20:1) to yield *Frs. 2A–2C*. *Fr. 2A* (2.4 g) was purified by CC (*RP-18*; 10% → 80% aq. MeOH) and semiprep. HPLC (20% aq. MeCN) to afford **4** (4.5 mg; t_R 9.0 min) and **5** (6 mg; t_R 14.2 min). *Fr. 2B* (1.0 g) was separated by repeated CC (*RP-18*, 10% → 80% aq. MeOH; *Sephadex LH-20*, MeOH) to yield *Frs. 2B.1–2B.4*. Compounds **1** (4 mg; t_R 15.8 min) and **2** (4 mg; t_R 17.6 min) were isolated from *Fr. 2B.2* (30.0 mg) by semiprep. HPLC (18% aq. MeCN), and **3** (5 mg) was obtained from *Fr. 2B.4* (21.5 mg) by prep. TLC (AcOEt/MeOH/H_2O 5:1:0.5; R_f 0.45).

Eleganoside A (=*(2*R*)-4-[(1*S*)-2,6,6-Trimethyl-4-oxocyclohex-2-en-1-yl]butan-2-yl 6*-O-α-L-*Arabinopyranosyl-*β-D-*glucopyranoside*; **1**). Amorphous powder. $[\alpha]_D^{20} = -30.2$ ($c = 0.05$, MeOH). UV (MeOH): 241 (3.53). IR (KBr): 3409, 2935, 1649, 1376, 1073, 1010, 826. CD (MeOH): 239.8 (−4.72), 325.8 (−1.66). ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS: 527.2471 ([M + Na]$^+$, $C_{24}H_{40}NaO_{11}^+$; calc. 527.2468).

Eleganoside B (*=(2*R*,3*E*)-4-[(1*S*,2*S*,4*R*)-1,2,4-Trihydroxy-2,6,6-trimethylcyclohexyl]but-3-en-2-yl 6-*O*-β-*D*-Apiofuranosyl-β-*D*-glucopyranoside*; **3**). Amorphous powder. $[\alpha]_D^{20} = -76.5$ ($c = 0.05$, MeOH). IR (KBr): 3409, 2929, 1655, 1637, 1375, 1458, 1072, 1039, 573. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS: 561.2531 ([M + Na]$^+$, $C_{24}H_{42}NaO_{13}^+$; calc. 561.2523).

Gouwenoside A (*= Methyl* rel-*(4a*S*,5*R*,6*S*,7*S*,7a*S*)-6-(β-*D*-Glucopyranosyloxy)-1,4a,5,6,7,7a-hexahydro-5,7a-dihydroxy-7-methylcyclopenta[*c*]pyran-4-carboxylate*; **4**). Amorphous powder. $[\alpha]_D^{20} = -90.6$ ($c = 0.05$, MeOH). UV (MeOH): 239 (3.12). IR (KBr): 3491, 3405, 3335, 2980, 2935, 2875, 1680, 1627, 1015, 966, 930. ^{1}H- and ^{13}C-NMR: see *Table 3*. HR-ESI-MS: 429.1359 ([M + Na]$^+$, $C_{17}H_{26}NaO_{11}^+$; calc. 429.1373).

Acid Hydrolysis and Sugars Analysis. Compounds **1**, **3**, and **4** (1 mg each) were hydrolyzed with 3M CF_3COOH (2 ml) at 120° for 2 h in a sealed tube, resp. The mixture was transferred into a vial and evaporated to dryness. To the residue, dried overnight, the following solns. were added: *a*) (*S*)-1-amino-2-propanol/MeOH 1:8 (20 μl); *b*) glacial AcOH/MeOH 1:4 (17 μl); *c*) $NaBH_3CN$ in MeOH (3%; 17 μl), and the mixture was left at 65° for 1.5 h in a capped vial. After cooling, 3M CF_3COOH was added to adjust the pH to 1–2, and the mixture was evaporated to dryness. The residue was then treated with pyridine/Ac_2O 1:1 (0.4 ml) for 45 min at 100°. After cooling, the derivative was extracted with $CHCl_3$ (1 ml), and washed with 0.5M aq. Na_2CO_3 (3 × 1 ml) and H_2O (3 × 1 ml). The $CHCl_3$ phase was then dried (Na_2SO_4) and subjected to GC/MS for sugar identification: D-glucopyranose, t_R 36.77 min; L-arabinopyranose, t_R 29.42 min; D-apiofuranose, t_R 29.78 min; **1**, t_R 29.43 and 36.77 min; **3**, t_R 29.77 and 36.76 min; and **4** t_R 36.77 min.

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