Abietane Lactones and Iridoids from *Goldfussia yunnanensis*

Hong-Wei YU,[a,b] Bo-Gang LI,[a] Guo-You LI,[a] Chang-Song LI,[a,b] Dong-Mei FANG,[a] and Guo-Lin ZHANG*,[a]

[a] *Chengdu Institute of Biology, Chinese Academy of Sciences; Chengdu 610041, P. R. China: and* [b] *Graduate School of the Chinese Academy of Sciences; Beijing 100039, P. R. China.* Received June 10, 2007; accepted September 3, 2007

Two new abietane diterpene lactones (1—2), three new abietane diterpene lactone glycosides (3—5) and a new iridoid glycoside (6), together with five known compounds, were isolated from the aerial parts of *Goldfussia yunnanensis*. The new compounds were determined to be 18-hydroxyhelioscopinolide A (1), 18-oxohelioscopinolide A (2), 18-hydroxy-3-*O*-*β*-D-glucopyranosylhelioscopinolide A (3), 3-*O*-*β*-D-glucopyranosylhelioscopinolide A (4), 3-*O*-*β*-D-galactopyranosylhelioscopinolide A (5), and 6-*O*-*trans*-cinnamoyl E-harpagoside (6) on the basis of spectral data and chemical evidence.

Key words *Goldfussia yunnanensis*; helioscopinolide A; E-harpagoside

The genus *Goldfussia* NEES (Acanthaceae) with more than 30 species is distributed in India, Malaysia and China.[1] About nine species are distributed in southwestern part of China.[1] The ethanolic extract of *G. psilostachys* showed antiproliferative activity against K562 leukemia cells.[2] Some sesquiterpenes were isolated from this plant.[3] *Goldfussia yunnanensis* (DIELS) TSUI is a shrub distributed in Yunnan Province of China. There is no report on investigation of its chemical composition.

In this study, two new abietane diterpene lactones (**1**, **2**), three new abietane diterpene lactone glycosides (**3**—**5**) and a new iridoid glycoside (**6**) were isolated from the aerial parts of *G. yunnanensis*, along with *β*-sitosterol, *β*-daucosterol, cinnamic acid, helioscopinolide A,[4] and E-harpagoside[5] from the *G. yunnanensis*. The new compounds were determined to be 18-hydroxyhelioscopinolide A (**1**), 18-oxohelioscopinolide A (**2**), 18-hydroxy-3-*O*-*β*-D-glucopyranosylhelioscopinolide A (**3**), 3-*O*-*β*-D-glucopyranosylhelioscopinolide A (**4**), 3-*O*-*β*-D-galactopyranosylhelioscopinolide A (**5**), and 6-*O*-*trans*-cinnamoyl E-harpagoside (**6**), predominantly by spectral data.

Results and Discussion

Compound **1** was obtained as colorless needles. The molecular formula $C_{20}H_{28}O_4$ was determined from the quasi-molecular ion peak at *m*/*z* 355.1886 $[M+Na]^+$ in the HR-ESI-MS. The IR spectrum suggested the presence of hydroxyl groups (3494 cm^{-1}). The IR absorptions at 1728 and 1660 cm^{-1} and the ^{13}C-NMR signals (Table 1) at δ 175.2, 155.8, and 116.7 revealed the presence of an α,β-unsaturated γ-lactone. The ^{13}C-NMR spectrum showed 20 signals. Three methyls (δ_C 8.2, 11.6, 17.2; δ_H 1.83, 0.89, 0.98, each s, 3H) and one hydroxymethyl group (δ_C 70.6; δ_H 3.72, m, 1H and 3.42, d, J=10.5 Hz, 1H) were recognized from the NMR data. The evidence mentioned above suggested that compound **1** was an abietane diterpene with an α,β-unsaturated γ-lactone. The ^{1}H- and ^{13}C-NMR data were very similar to those of helioscopinolide A, but compound **1** possesses one more hydroxymethyl group (δ_C 70.6) and one less methyl group (δ_C 28.6) than helioscopinolide A.[6] The hydroxymethyl group was assigned to C-18 on the basis of the HMBC correlations of H-19 (δ 0.89) with C-4 (δ 42.3) and C-18 (δ 70.6) as well as the NOESY correlations of H-18 with H-3 and H-5, and H-20 with H-12 and H-19. Compound **1** was oxidized by TEMPO[7] and then reduced by $NaBH_3CN$[8] to afford helioscopinolide A with known absolute configuration[9] (see Fig. 3). Thus, compound **1** was determined to be 18-hydroxyhelioscopinolide A.

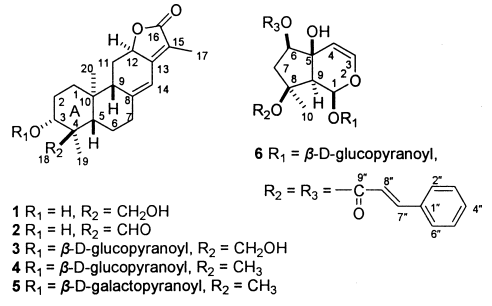

Fig. 1. Structures of Compounds **1**—**6**

The ^{1}H- and ^{13}C-NMR spectra of compounds **2**—**5** showed the same general structure as that of compound **1** with modifications only on ring A.

Compound **2** was isolated as colorless needles. The molecular formula was assigned as $C_{20}H_{26}O_4$ on the basis of the quasi-molecular ion peak at *m*/*z* 353.1735 $[M+Na]^+$ in the HR-ESI-MS. A formyl group (δ_H 9.43 and δ_C 206.0) is present instead a hydroxymethyl group (δ_C 70.6) as that in compound **1**. This formyl group was assigned to C-18 in view of the HMBC correlations H-18/C-4 (55.0) and C-19 (9.2) and the NOESY correlations of H-18 with H-3 and H-5, and H-20 with H-12 and H-19. Compound **2** was reduced by $NaBH_3CN$[8] to afford helioscopinolide A (see Fig. 3). So, compound **2** was characterized as 18-oxohelioscopinolide A.

Compound **3** was isolated as white amorphous powder. Its molecular formula was determined to be $C_{26}H_{38}O_9$ from the quasi-molecular ion peak at *m*/*z* 517.2420 $[M+Na]^+$ in the HR-ESI-MS. The acid hydrolysis of compound **3** afforded D-glucose and compound **1**. The presence of 3-*O*-*β*-D-glucopyranosyl moiety was concluded from the ^{1}H-NMR signal at δ 4.30 (1H, d, J=7.8 Hz, H-1′) and the ^{13}C-NMR signal at 101.4, as well as the HMBC correlation of H-1′ with C-3 (δ 78.3). Besides the signals for the *β*-D-glucopyranosyl moiety, the rest of the NMR data closely resemble those of compound **1**, which suggested that compound **3** was 18-hydroxy-

* To whom correspondence should be addressed. e-mail: zhanggl@cib.ac.cn

Table 1. NMR Data of Compounds **1**—**5** (^{1}H: 600 MHz; ^{13}C: 150 MHz)[a,b]

No.	**1**		**2**		**3**		**4**		**5**	
	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C
1α	1.25 (m)	37.1	1.33 (m)	36.9	1.23 (m)	36.8	1.28 (m)	36.8	1.28 (m)	36.9
1β	1.99 (m)		2.03 (m)		2.02 (m)		2.00 (m)		2.02 (m)	
2α	1.66 (m)	27.5	1.73 (m)	26.7	1.76 (m)	22.7	1.67 (m)	23.1	1.67 (m)	23.2
2β	1.76 (m)		1.88 (m)		1.87 (m)		1.87 (m)		1.88 (m)	
3	3.71 (m)	75.8	3.83 (dd, 11.8, 4.5)	72.1	3.72 (dd, 12.0, 4.6)	78.3	3.42 (dd, 11.8, 4.0)	84.0	3.40 (dd, 11.9, 4.2)	84.1
4		42.3		55.0		42.4		38.1		38.1
5	1.38 (dd, 12.4, 2.3)	48.3	1.69 (m)	47.1	1.71 (dd, 14.6, 2.0)	45.5	1.26 (m)	54.6	1.26 (m)	54.6
6α	1.47 (m)	23.4	1.31 (m)	25.1	1.48 (m)	23.2	1.50 (m)	23.1	1.48 (m)	23.3
6β	1.68 (m)		1.58 (m)		1.77 (m)		1.89 (m)		1.89 (m)	
7α	2.21 (m)	36.6	2.25 (m)	36.3	2.30 (m)	36.1	2.28 (m)	36.4	2.27 (m)	36.5
7β	2.50 (m)		2.47 (m)		2.53 (m)		2.57 (m)		2.55 (m)	
8		151.0		149.8		152.8		152.8		152.8
9	2.24 (m)	51.5	2.21 (m)	51.3	2.31 (m)	51.5	2.25 (m)	51.4	2.23 (m)	51.4
10		41.1		40.1		40.7		40.9		40.9
11α	1.52 (m)	27.2	1.55 (m)		1.52 (m)	27.3	1.50 (m)	27.2	1.51 (m)	27.2
11β	2.55 (dd, 13.4, 6.2)		2.55 (dd, 13.5, 6.2)	27.5	2.60 (dd, 13.3, 6.2)		2.61 (dd, 13.3, 6.1)		2.57 (m)	
12	4.86 (dd, 13.8, 4.8)	75.4	4.86 (dd, 13.3, 6.4)	75.6	4.97 (dd, 13.8, 6.1)	76.4	4.98 (dd, 13.2, 5.6)	76.3	4.96 (dd, 12.9, 5.1)	76.4
13		155.8		155.4		157.5		157.5		157.5
14	6.28 (s)	114.3	6.30 (s)	115.0	6.38 (s)	113.4	6.40 (s)	113.4	6.38 (s)	113.4
15		116.7		117.2		115.4		115.4		115.4
16		175.2		175.0		176.2		176.2		176.2
17	1.83 (s)	8.2	1.83 (s)	8.3	1.79 (s)	6.6	1.80 (s)	6.6	1.80 (s)	6.6
18	3.72 (m)	70.6	9.43 (s)	206.0	3.21 (d, 11.5)	63.0	1.08 (s)	27.9	1.08 (s)	27.9
	3.42 (d, 10.5)				3.63 (d, 11.5)					
19	0.89 (s)	11.6	1.12 (s)	9.2	0.69 (s)	12.0	0.86 (s)	15.7	0.85 (s)	15.7
20	0.98 (s)	17.2	0.98 (s)	17.0	1.01 (s)	16.3	0.99 (s)	15.7	0.98 (s)	15.7
1′					4.30 (d, 7.8)	101.4	4.32 (d, 7.8)	100.5	4.70 (d, 8.0)	98.0
2′					3.14 (m)	73.5	3.16 (m)	73.7	3.28 (m)	70.9
3′					3.35 (t, 9.0)	76.8	3.36 (m)	76.8	4.07 (m)	71.7
4′					3.16 (m)	71.3	3.28 (m)	70.4	3.49 (m)	67.8
5′					3.33 (m)	76.0	3.23 (m)	76.4	3.65 (m)	73.8
6′					3.52 (dd, 11.4, 8.4)	62.1	3.66 (dd, 11.8, 5.9)	61.5	3.66 (dd, 14.1, 5.1)	62.0
					3.92 (dd, 11.2, 2.4)		3.86 (dd, 11.8, 8.1)		3.83 (dd, 14.1, 5.3)	

a) Assignments based on HSQC and HMBC. *b*) **1**, **2** in $CDCl_3$; **3**—**5** in CD_3OD.

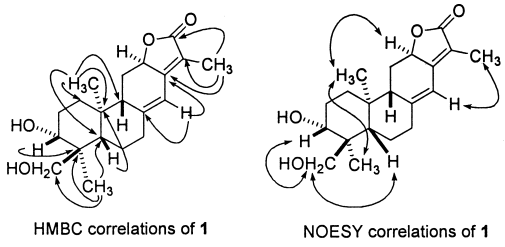

Fig. 2. Key HMBC and NOESY Correlations of Compound **1**

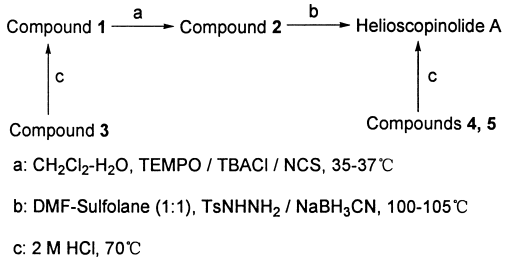

Fig. 3. Conversion of Compounds **1**—**5**

3-*O*-β-D-glucopyranosyl helioscopinolide A.

Compounds **4** and **5** were both isolated as white amorphous powder. The same molecular formula, $C_{26}H_{38}O_8$, was provided by the quasi-molecular ion peak at *m/z* 501.2445 $[M_4+Na]^+$ and 501.2470 $[M_5+Na]^+$ in their HR-ESI-MS. Acid hydrolysis of compounds **4** and **5** afforded, respectively, D-glucose and D-galactose, which were determined by optical rotations and by comparing them with authentic samples on TLC. The 3-*O*-β-D-glucopyranosyl in compound **4** was concluded from the ^{1}H-NMR signal at δ 4.32 (1H, d, J=7.8 Hz, H-1′) and the ^{13}C-NMR signal at 100.5, and the 3-*O*-β-D-galactopyranosyl in compound **5** from the ^{1}H-NMR signal at 4.70 (1H, d, J=8.0 Hz, H-1′) and the ^{13}C-NMR signal at 98.0, as well as the HMBC correlation of H-1′ with C-3. The aglycon of compounds **4** and **5** was characterized to be helioscopinolide A by NMR data and optical rotation.[4] Therefore, compounds **4** and **5** were assigned as 3-*O*-β-D-glucopyranosyl helioscopinolide A and 3-*O*-β-D-galactopyranosyl helioscopinolide A, respectively.

Compound **6** was obtained as white amorphous powder. Its molecular formula $C_{33}H_{36}O_{12}$ was suggested by the quasi-molecular ion peak at *m/z* 647.2123 $[M+Na]^+$ in the HR-ESI-MS. It gave a deep blue coloration when reacted with anisaldehyde-sulfuric reagent on TLC. Its NMR spectra showed typical signals of H-1 (6.19) and C-1 (93.0) in iridoid glycoside.[10] The ^{1}H-NMR spectrum displayed ten aromatic protons (δ_H 7.14—7.39), two pair of *trans* olefinic protons (δ 6.50, 7.74, 6.41 and 7.63, each d, J=16.0 Hz) from two *trans*-cinnamoyl moieties. Acid hydrolysis of **6** afforded D-glucose. The ^{1}H-NMR signal at δ 4.65 (1H, d, J=7.8 Hz) and

the ^{13}C-NMR signal at 98.9 demonstrated a β-D-glucopyranosyl unit. The above evidence is in accordance with the observation of 33 ^{13}C-NMR signals, 18 for two *trans*-cinnamoyl residues, 6 for the hexose moiety, and 9 for the iridoid skeleton. Except for the signals for *trans*-cinnamoyl residue in compound **6**, the ^{1}H- and ^{13}C-NMR data of **6** were similar to those of E-harpagoside.[5] In the NMR spectra, the downfield shift of H-6 at δ 4.96 ($\Delta\delta$=1.3 ppm), and the upfield shifts of C-5 at δ 71.7 ($\Delta\delta$=2.1 ppm) and C-7 at δ 42.6 ($\Delta\delta$=4.0 ppm) compared with E-harpagoside suggested the presence of 6-*O*-*trans*-cinnamoyl. Therefore, compound **6** could be determined as 6-*O*-*trans*-cinnamoyl E-harpagoside.

Experimental

General Melting points were determined on an X-6 precise melting point apparatus (Beijing Fukai Science and Technology Development Company Limited) and are uncorrected. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. UV spectra and IR spectra were carried out on a Perkin-Elmer Lambda 35 UV/VIS spectrometer and a Perkin-Elmer Spectrum One FT-IR spectrometer, respectively. NMR spectra were performed on a Bruker Avance 600 spectrometer. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were obtained on a BioTOF-Q mass spectrometer. Silica gel (160—200, 200—300 mesh) for column chromatography and silica gel GF254 (10—40 μm) for TLC were obtained from Qingdao Haiyang Chemical Company, China. All solvents including petroleum ether (60—90 °C) were distilled prior to use. All other reagents used for oxidation and reduction were commercial samples and used directly.

Plant Material Aerial parts of *Goldfussia yunnanensis* were collected from Xishuangbanna, Yunnan Province, China, in September 1999. The plant sample was identified by Professor Jinyun Cui at Xishuangbanna Tropical Botanical Garden, the Chinese Academy of Sciences. A voucher specimen (A-185) was deposited at the Herbarium of Chengdu Institute of Biology, the Chinese Academy of Sciences.

Extraction and Isolation Air-dried and powdered aerial parts of *G. yunnanensis* (8 kg) were percolated with 95% EtOH (20 l×3, each 7 d) at room temperature. After the ethanol was removed under reduced pressure, *ca.* 450 g residue was obtained. This residue was dissolved in H_2O (1 l) and extracted successively with petroleum ether (1.0 l×3), EtOAc (1.0 l×5) and *n*-BuOH (0.5 l×3) to afford corresponding fractions P (125 g), E (80 g), and B (114 g). Fraction E (40 g) was separated over a silica gel column (700 g, 160—200 mesh, Φ 150 mm×330 mm) eluted gradiently with $CHCl_3$–MeOH (60 : 1 to 3 : 1) to give fractions EA-EG. The separation of EA (4.2 g) over a silica gel column (100 g, 200—300 mesh, Φ 40 mm×250 mm) with petroleum ether (60—90 °C)–acetone (10 : 1) as solvents afforded β-sitosterol (2.5 g) and cinnamic acid (0.4 g). Helioscopinolide A (0.6 g) was obtained by recrystallization of EB (7.4 g) from acetone. The remnant of EB (6.1 g) was applied on a silica gel column (180 g, 200—300 mesh, Φ 60 mm×250 mm) eluted with $CHCl_3$–acetone (5 : 1) to afford **1** (250 mg), **2** (8 mg) and β-daucosterol (2.5 g). ED (18.7 g) was separated over a silica gel column (400 g, 200—300 mesh, Φ 80 mm×230 mm) eluted with $CHCl_3$–MeOH (10 : 1 to 3 : 1) to afford **3** (12 mg), **4** (3.2 g) and **5** (280 mg). Fraction B (60 g) was subjected to a macroporous resin column (D_{101}, 26—60 mesh, Φ 90 mm×500 mm) by using CH_3OH–H_2O (0 : 1, 1 : 4, 1 : 2, 1 : 1, 2 : 1, 1 : 0) as solvents to give fractions BA-BE. The separation of fraction BC (1.2 g) over a silica gel column (50 g, 200—300 mesh, Φ 30 mm×160 mm) eluted with $CHCl_3$–MeOH–H_2O (4 : 1 : 0.05) yielded E-harpagoside (25 mg) and **6** (10 mg).

Acid Hydrolysis of 3—6 Compound **3** (10 mg) was dissolved in MeOH (0.5 ml) and then heated with 2 M HCl (2 ml, aq.) at 70 °C for 3 h. After 5 ml of H_2O was added and the mixture was extracted with EtOAc (3×5 ml), the aqueous phase was evaporated under reduced pressure repeatedly by adding CH_3OH–H_2O (1 : 1) until pH 7 to afford D-glucose (2.0 mg), which was identified by comparison with an authentic sample on TLC and its optical rotation $[\alpha]_D^{25}$ +50.8° (c=0.10, H_2O). The separation of fraction EtOAc over a silica gel column eluted with petroleum ether–ethyl acetate (5 : 1) yielded compound **2** (4.0 mg) determined by NMR data and optical rotation. Following the same procedure, compounds **4** and **6** both gave D-glucose with optical rotation $[\alpha]_D^{25}$ +52.4° (c=0.30, H_2O) and $[\alpha]_D^{25}$ +50.2° (c=0.10, H_2O), compound **5** yielded D-galactose with optical rotation $[\alpha]_D^{25}$ +54.7° (c=0.25, H_2O).

Conversion of Compounds 1 and 2 to Helioscopinolide A The oxidation of compound **1** was performed according to the method described by Einhorn *et al.*[7] To a solution of compound **1** (0.1 mmol, 33.2 mg), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (0.01 mmol, 1.6 mg), and tetrabutylammonium chloride (TBACl) (0.01 mmol, 2.8 mg) in 2.5 ml of dichloromethane, and 2.5 ml of an aqueous solution of $NaHCO_3$ (0.5 M) and K_2CO_3 (0.05 M) was added *N*-chlorosuccinimide (NCS, 0.15 mmol, 20.0 mg) under stirring at 35—37 °C. The reaction was monitored by TLC. Three hours later, the separation of organic layer over a silica gel column with petroleum ether–acetone (5 : 1) as solvents afforded 23 mg compound **2**. The reduction of compound **2** was performed following the procedure described by Hutchins *et al.*[8] Compound **2** (0.05 mmol, 16.5 mg) and *p*-toluenesulfonylhydrazide (0.07 mmol, 13.0 mg) were dissolved in 5 ml of DMF–sulfolane (1 : 1) containing 0.01 mmol *p*-toluenesulfonic acid at 100 °C. To this mixture was added $NaBH_3CN$ (0.2 mmol, 12.6 mg). The reaction mixture was kept at 100—105 °C for 2 h and then diluted with 10 ml of water and extracted three times with EtOAc. The EtOAc layer was washed twice with water, concentrated and purified over a silica gel column eluted with petroleum ether–ethyl acetate (10 : 1) to give 11 mg helioscopinolide A with optical rotation $[\alpha]_D^{25}$ +178.0° (c=0.10, $CHCl_3$).

18-Oxohelioscopinolide A (**1**): Colorless needles (acetone), mp 165—166 °C; $[\alpha]_D^{25}$ +315.0° (c=0.10, MeOH); UV (MeOH) λ_{max} nm (log ε) 276 (4.46), 200 (3.98); IR (KBr) ν_{max} 3494, 2869, 1728, 1660, 1456, 1392, 1052 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Table 1; HR-ESI-MS *m*/*z* 355.1886 $[M+Na]^+$ (Calcd for $C_{20}H_{28}NaO_4$, 355.1880).

18-Oxohelioscopinolide A (**2**): Colorless needles (acetone), mp 231—232 °C; $[\alpha]_D^{25}$ +213.0° (c=0.10, MeOH); UV (MeOH) λ_{max} nm (log ε) 274 (4.36), 202 (3.88); IR (KBr) ν_{max} 3479, 2927, 2866, 1725, 1659, 1449, 1394, 1097, 1024 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Table 1; HR-ESI-MS *m*/*z* 353.1735 $[M+Na]^+$ (Calcd for $C_{20}H_{26}NaO_4$, 353.1723).

18-Hydroxy-3-*O*-β-D-glucopyranosylhelioscopinolide A (**3**): White amorphous powder (MeOH); $[\alpha]_D^{25}$ +112.0° (c=0.10, MeOH); UV (MeOH) λ_{max} nm (log ε) 276 (4.36), 201 (4.11); IR (KBr) ν_{max} 3430, 2929, 1732, 1661, 1385, 1077, 1040 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Table 1; HR-ESI-MS *m*/*z* 517.2420 $[M+Na]^+$ (Calcd for $C_{26}H_{38}NaO_9$, 517.2408).

3-*O*-β-D-Glucopyranosylhelioscopinolide A (**4**): White amorphous powder (MeOH); $[\alpha]_D^{25}$ +204.0° (c=0.10, MeOH), UV (MeOH) λ_{max} nm (log ε) 276 (4.33), 202 (4.07); IR (KBr) ν_{max} 3428, 2936, 1758, 1672, 1456, 1157, 1071, 1028 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Table 1; HR-ESI-MS *m*/*z* 501.2445 $[M+Na]^+$ (Calcd for $C_{26}H_{38}NaO_8$, 501.2459).

3-*O*-β-D-Galactopyranosylhelioscopinolide A (**5**): White amorphous powder (MeOH); $[\alpha]_D^{25}$ +131.0° (c=0.10, MeOH), UV (MeOH) λ_{max} nm (log ε) 276 (4.38), 201 (4.09); IR (KBr) ν_{max} 3429, 2927, 2876, 1738, 1664, 1455, 1393, 1086, 1036 cm^{-1}; ^{1}H- and ^{13}C-NMR data, see Table 1; HR-ESI-MS *m*/*z* 501.2470 $[M+Na]^+$ (Calcd for $C_{26}H_{38}NaO_8$, 501.2459).

6-*O*-*trans*-Cinnamoyl E-harpagoside (**6**): White amorphous powder (MeOH); $[\alpha]_D^{25}$ +40.0° (c=0.10, MeOH); UV (MeOH) λ_{max} nm (log ε) 273 (4.66), 216 (4.50), 203 (4.56); IR (KBr) ν_{max} 3418, 2960, 2929, 1704, 1636, 1450, 1282, 1204, 1076, 1028 cm^{-1}; HR-ESI-MS *m*/*z* 647.2123 $[M+Na]^+$ (Calcd for $C_{33}H_{36}NaO_{12}$, 647.2099). ^{1}H-NMR (CD_3OD, 600 MHz) aglycon: δ 6.51 (1H, m, H-3), 6.19 (1H, s, H-1), 5.06 (1H, m, H-4), 4.96 (1 H, d, J=3.7 Hz, H-6), 3.09 (1H, s, H-9), 2.45 (1 H, d, J=16.0 Hz, H-7a), 2.12 (1H, dd, J=16.0, 4.0 Hz, H-7b), 1.60 (3H, s, H-10); β-D-glucopyranosyl: δ 4.65 (1H, d, J=7.8 Hz, H-1′), 3.95 (1H, dd, J=12.6, 2.4 Hz, H-6a′), 3.74 (1H, dd, J=12.6, 6.2 Hz, H-6b′), 3.41 (1H, m, H-3′), 3.38 (1H, m, H-5′), 3.32 (1H, m, H-4′), 3.23 (1H, dd, J=9.0, 7.8 Hz, H-2′); 6-*O*-*trans*-cinnamoyl: δ 7.63 (1H, d, J=16.0 Hz, H-7″), 7.38 (2H, d, J=7.3 Hz, H-2″, H-6″), 7.25 (1H, t, J=7.3 Hz, H-4″), 7.14 (2H, t, J=7.6 Hz, H-3″, H-5″), 6.41 (1H, d, J=16.0 Hz, H-8″); 8-*O*-*trans*-cinnamoyl: δ 7.74 (1H, d, J=16.0 Hz, H-7‴), 7.39 (2H, d, J=7.2 Hz, H-2‴, H-6‴), 7.30 (1H, t, J=7.3 Hz, H-4‴), 7.20 (2H, t, J=7.6 Hz, H-3‴, H-5‴), 6.50 (1H, d, J=16.0 Hz, H-8‴); ^{13}C-NMR (CD_3OD, 150 MHz) aglycon: δ 143.4 (C-3), 104.5 (C-4), 93.0 (C-1), 87.4 (C-8), 78.9 (C-6), 71.7 (C-5), 54.7 (C-9), 42.6 (C-7), 20.9 (C-10); β-D-glucopyranosyl: δ 98.9 (C-1′), 76.8 (C-3′), 76.2 (C-5′), 73.2 (C-2′), 70.4 (C-4′), 61.6 (C-6′); 6-*O*-*trans*-cinnamoyl: δ 166.5 (C-9″), 145.1 (C-7″), 133.9 (C-1″), 129.9 (C-4″), 128.5 (C-5″), 128.4 (C-3″), 127.8 (C-2″, C-6″), 117.6 (C-8″); 8-*O*-*trans*-cinnamoyl: δ 166.9 (C-9‴), 145.3 (C-7‴), 134.1 (C-1‴), 130.0 (C-4‴), 128.5 (C-5‴), 128.4 (C-3‴), 127.8 (C-2‴, C-6‴), 118.4 (C-8‴).

Acknowledgements The work was financially supported by Di-Ao Group in Chengdu. The authors are grateful to Mr. Jian Gu at Chengdou Institute of Biology of the Chinese Academy of Sciences for collecting plant material.

References

1) How F. C., Wu T. L., Ko W. C., Chen T. C., "A Dictionary of the Families and Genera of Chinese Seed Plants," 2nd ed., South China Institute of Botany, Academic Sinica, Science Press, Beijing, 1998, pp. 211—212.
2) Gao X. P., Zhang G. L., Zhou M., Luo D. X., Li B. G., *Fitoterapia*, **75**, 639—644 (2004).
3) Luo Y. G., Zhou M., Qi H. Y., Li B. G., Zhang G. L., *Planta Med.*, **71**, 1081—1084 (2005).
4) Shizuri Y., Kosemura S., Yamamura S., Ohba S., Ito M., Saito Y., *Chem. Lett.*, **1983**, 65—68 (1983).
5) Li Y. M., Jiang S. H., Gao W. Y., Zhu D. Y., *Phytochemistry*, **50**, 101—104 (1999).
6) Borghi D., Baumer L., Ballabio M., Arlandini E., *J. Nat. Prod.*, **54**, 1503—1508 (1991).
7) Einhorn J., Einhorn C., Ratajczak F., Pierre J. L., *J. Org. Chem.*, **61**, 1696—1699 (2002).
8) Hutchins R. O., Milewski C. A., Maryanoff B. E., *J. Amer. Soc.*, **95**, 3662—3668 (1973).
9) Ohba S., Ito M., Satto Y., Shizuri Y., Kosemura S., Yamamura S., *Acta Cryst. C*, **39**, 1139—1141 (1983).
10) Kim S. R., Lee K. Y., Koo K. K., Sung S. H., Lee N. G., Kim J. W., Kim Y. C., *J. Nat. Prod.*, **65**, 1696—1699 (2002).