ent-Abietanoids and *ent*-Isopimaranoid Glycosides from *Isodon nervosus*

by **Li-Mei Li**[a])[b]), **Guo-You Li**[c]), **Li-Sheng Ding**[c]), **Jian-Xin Pu**[a]), **Wei-Lie Xiao**[a]), **Quan-Bin Han**[a]), and **Han-Dong Sun***[a])

[a]) State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, P. R. China (phone: +86-871-5223251; fax: +86-871-5216343; e-mail: hdsun@mail.kib.ac.cn)

[b]) Scientific Research Center, Chengdu Medical College, Chengdu 610083, P. R. China

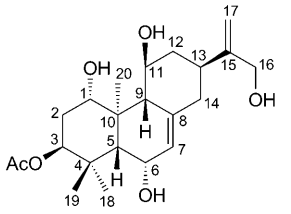
[c]) Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, P. R. China

Three new and one known *ent*-abietanoids, *i.e.*, *ent*-abienervonins A – C (**1** – **3**, resp.) and hebeiabinin B (**4**), and two new *ent*-isopimaranoid glycosides, *i.e.*, *ent*-isopimanervosides A and B (**5** and **6**, resp.), along with seven known phenolic glycosides were isolated from the aerial parts of *Isodon nervosus*. The structures of the new compounds were elucidated on the basis of spectroscopic and chemical evidence.

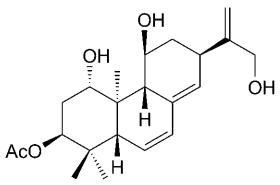
Introduction. – *Isodon nervosus* (HEMSL.) KUDO (Lamiaceae), a perennial herb, is distributed mainly in the south of China. Its stems and leaves have been used to treat hepatitis, fester, and eczema in traditional Chinese medicine [1]. Previous phytochemical investigations on the areial parts of *I. nervosus* led to the discovery of a series of *ent*-kauranoids [2]. In this article, we report the isolation and structural elucidation of three new and one known *ent*-abietanoids, *i.e.*, *ent*-abienervonins A – C (**1** – **3**) and hebeiabinin B (**4**) [3], and two new *ent*-isopimaranoid glycosides, *i.e.*, *ent*-isopimanervosides A and B (**5** and **6**). In addition, seven known phenolic glycosides were isolated and identified as urolignoside [4], glochidioboside [5], (−)-secoisorariciresinol-9′-*O*-*β*-D-glucoside [6], (+)-pinoresinol-4-*O*-*β*-D-glucoside [7], 8-hydroxypinoresiol-4′-*O*-*β*-D-glucoside [8], 8-hydroxypinoresiol-4-*O*-*β*-D-glucoside [8], and daidzein-4′-*O*-*β*-D-glucoside [9] by comparing their NMR data with those reported.

Results and Discussion. – Compound **1** was isolated as colorless needles. A molecular formula of $C_{22}H_{34}O_6$ was determined for **1** from its HR-ESI-MS (*m*/*z* 417.2263, $[M+Na]^+$) and NMR data (*Table 1*). The ^{13}C-NMR and DEPT data displayed signals for 22 C-atoms, which were classified as two quaternary sp^2 C-atoms (δ(C) 154.4 and 137.4), one sp^2 CH group (δ(C) 128.2), one sp^2 CH_2 group (δ(C) 107.3), four sp^3 O−CH groups (δ(C) 80.5, 74.5, 70.2, and 64.9), one sp^3 O−CH_2 group (δ(C) 64.5), three sp^3 CH groups (δ(C) 60.4, 47.8, and 38.0), three sp^3 CH_2 groups (δ(C) 43.1, 42.9, and 33.0), two quaternary sp^3 C-atoms (δ(C) 43.6 and 38.2), three Me groups (δ(C) 28.3, 25.1, and 11.7), and one AcO group (δ(C) 170.5 and 21.1). Compared with the classical *ent*-kaurane diterpenoids, one characteristic quaternary C-atom disappeared in the high field of the ^{13}C-NMR spectrum of **1**. These information and the tricyclic diterpenoids isolated from the genus *Isodon*, suggested that compound **1** was

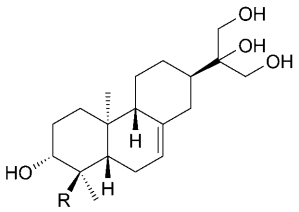
© 2009 Verlag Helvetica Chimica Acta AG, Zürich



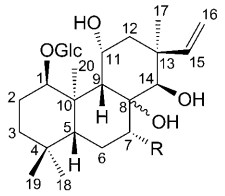
1



2



3 R = CHO
4 R = CH_2OH



5 R = H
6 R = OH

an *ent*-abietanoid, similar to parvifoline L [10]. The positions of the OH groups at C(1), C(6), C(11), and C(16), of the AcO group at C(3), as well as the C=C bonds between C(7) and C(8), and C(15) and C(17) in **1** were determined on the basis of the HMBC correlations from H–C(1) to C(2), C(9), and C(20), from H–C(3) to C(1), C(5), and C=O(Ac), from H–C(7) to C(5), C(6), C(9), and C(14), from H–C(11) to C(9) and C(13), and from H–C(16) to C(13), C(15), and C(17) (*Fig. 1*). In the ROESY spectrum, H–C(1) correlated with H_β–C(5) and H_β–C(9), H–C(6) correlated with H_β–C(5), H–C(7), and Me(19), H–C(3) correlated with Me(18), and H–C(11) correlated with H_α–C(12), H_α–C(13), and Me(20) (*Fig. 1*). These observations indicated that both H–C(1) and H–C(6) adopt β-orientations, while H–C(3) and H–C(11) are α-oriented. Thus, the structure of compound **1** was assigned as (1α,3β,5β,6α,9β,10α,11β,13β)-1,6,11,16-tetrahydroxyabieta-7,15(17)-dien-3-yl acetate, and named as *ent*-abienervonin A.

The molecular formula of compound **2** was determined to be $C_{22}H_{32}O_5$ by HR-ESI-MS (*m*/*z* 399.2152, $[M+Na]^+$) and NMR data (*Table 1*). The NMR data of compound

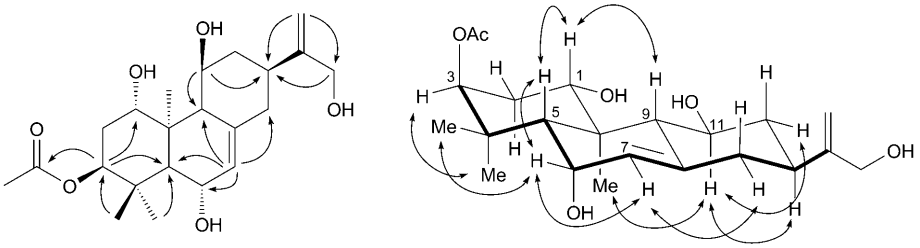


Fig. 1. *Key HMBC and ROESY data of* **1**

Table 1. *^{1}H- and ^{13}C-NMR Data of Compounds* **1**–**3** (400 and 100 MHz, resp.; δ in ppm; J in Hz)

	1[a])		**2**[b])		**3**[a])	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
H_α–C(1)		74.5		71.2	1.75–1.81 (overlap)	37.8
H_β–C(1)	4.22–2.27 (*m*)		4.06 (*dd*, *J* = 11.7, 4.6)		1.10–1.14 (overlap)	
H_α–C(2)	2.37–2.41 (overlap, 2 H)	33.0	2.00–2.05 (*m*)	32.0	1.85–1.90 (*m*, 2 H)	27.4
H_β–C(2)			1.90–1.95 (*m*)			
H–C(3)	5.02 (br. *s*)	80.5	4.83 (*t*, *J* = 2.8)	78.0	4.05–4.11 (*m*)	72.4
C(4)		38.2		36.2		55.8
H_β–C(5)	1.87 (br. *s*)	47.8	2.48 (br. *s*)	48.4	1.68 (*dd*, *J* = 12.4, 4.0)	42.2
H_α–C(6)		64.9	5.53 (*d*, *J* = 9.9)	126.1	1.95–2.00 (*m*)	24.8
H_β–C(6)	4.65 (br. *s*)				1.42–1.47 (overlap)	
H–C(7)	6.01 (*d*, *J* = 4.8)	128.2	6.12 (*d*, *J* = 9.9)	130.9	5.29 (*d*, *J* = 4.4)	119.3
C(8)		137.4		135.2		138.5
H_β–C(9)	2.37–2.41 (overlap)	60.4	2.32 (*d*, *J* = 9.1)	57.2	1.75–1.80 (overlap)	52.7
C(10)		43.6		44.2		34.3
H_α–C(11)	3.99–4.04 (*m*)	70.2	3.92–3.97 (*m*)	67.5	1.10–1.15 (overlap)	26.0
H_β–C(11)					1.75–1.80 (overlap)	
H_α–C(12)	2.60 (br. *d*, *J* = 13.2)	42.9	2.14–2.18 (*m*)	38.4	2.27 (*d*, *J* = 12.4)	26.7
H_β–C(12)	1.88–1.92 (overlap)		1.52–1.57 (*m*)		1.59 (*dt*, *J* = 12.8, 12.5)	
H_α–C(13)	2.37–2.41 (overlap)	38.0	3.10 (br. *d*, *J* = 11.2)	39.0	2.09 (*t*, *J* = 12.4)	42.2
H_α–C(14)	2.53 (br. *d*, *J* = 13.5)	43.1	5.52 (br. *s*)	129.3	2.46 (*t*, *J* = 13.2)	35.8
H_β–C(14)	2.13 (*d*, *J* = 13.5)				2.80 (*d*, *J* = 14.0)	
C(15)		154.4		151.5		75.5
CH_2(16)	4.44 (*s*, 2 H)	64.5	4.15 (*s*, 2 H)	64.8	4.25 (*s*, 2 H)	65.0
CH_2(17)	5.45 (br. *s*),	107.3	5.10 (br. *s*),	110.3	4.25 (*s*, 2 H)	65.0
	3.11 (br. *s*)		4.96 (br. *s*)			
Me(18) or H–C(18)	1.72 (*s*, 3 H)	25.1	0.94 (*s*, 3 H)	21.7	1.42 (*s*, 3 H)	9.8
Me(19)	1.19 (*s*, 3 H)	28.3	0.92 (*s*, 3 H)	26.6	9.57 (*s*)	206.8
Me(20)	1.84 (*s*, 3 H)	11.7	0.83 (*s*, 3 H)	9.2	0.80 (*s*, 3 H)	15.6
Me*C*O		170.5		170.5		
*Me*CO	2.09 (*s*, 3 H)	21.1	2.07 (*s*, 3 H)	21.2		

[a]) In C_5D_5N. [b]) In $CDCl_3$.

2 suggested it also to be an *ent*-abietanoid, similar to compound **1**. The main difference between **1** and **2** was that compound **2** has one more 1,2-disubstituted C=C bond and one O–CH less than compound **1**. In the HMBC spectrum, H–C(6) correlated with C(4), C(5), C(7), and C(10), H–C(7) correlated to C(5), C(9), C(8), and C(14), and H–C(14) correlated to C(7), C(8), C(9), and C(13) (*Fig. 2*), which established that the OH group at C(6) in **1** was absent in **2**, and the 1,2-disubstituted and trisubstituted C=C bonds were formed between C(6) and C(7), and C(8) and C(14). The location and orientation of the other substituents in **2** were the same as those in **1** on the basis of HMBC and ROESY data. Therefore, compound **2** was elucidated as (1α,3β,5β,9β,10α,11β,13β)-1,11,16-trihydroxyabieta-6,8(14),15(17)-trien-3-yl acetate, and named as ent-abienervonin B.

The ^{1}H- and ^{13}C-NMR (*Table 1*) data of compound **3** showed close resemblance to those of compound **4** [3]. The notable difference was that the sp^3 O–CH_2 group (δ(C)

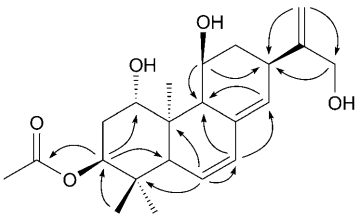


Fig. 2. *Key HMBC data of* **2**

67.9) at C(18) of **4** was oxidized to a CHO group (δ(C) 206.8) in **3**, which caused a considerable downfield shift of C(4) to δ(C) 55.8 and an upfield shift of C(19) to δ(C) 9.8. The above deduction was confirmed by HMBC and ROESY experiments. Accordingly, compound **3** was identified as (3α,5β,9β,10α,13β)-3,15,16,17-tetrahydroxy-abiet-7-en-19-al, and named as ent-abienervonin C.

The HR-ESI-MS (negative-ion mode) of compound **5** showed a *quasi*-molecular ion peak at *m*/*z* 499.2896 ($[M-H]^-$), corresponding to a molecular formula $C_{26}H_{44}O_9$. The ^{1}H- and ^{13}C-NMR spectra displayed signals of a hexose group and a diterpenoid aglycone. The hexose group appeared at δ(C) 106.6 (*d*), 79.2 (*d*), 78.3 (*d*), 75.4 (*d*), 71.9 (*d*), and 63.2 (*t*). Acid hydrolysis of **5** with 5% HCl yielded D-glucose, which was identified by TLC and the optical rotation ($[\alpha]_D^{18} = +52$, $c = 0.25$). The anomeric H-atom signal at δ(H) 4.84 (*d*, $J = 8.0$) indicated that the glucose is β-configured. The aglycone contained four terminal Me groups (δ(C) 34.1, 27.9, 23.1, and 18.4; δ(H) 1.91 (*s*), 1.86 (*s*), 0.95 (*s*), and 0.80 (*s*)), five CH_2 groups (δ(C) 39.7, 38.1, 35.6, 24.1, and 18.8), two CH groups (δ(C) 49.5 and 41.4), four quaternary sp^3 C-atoms (δ(C) 79.5, 43.7, 41.7, and 33.2), three O–CH groups (δ(C) 83.5, 80.6, and 69.6), and one monosubstituted C=C bond (δ(C) 151.4 and 109.9; δ(H) 6.32 (*dd*, $J = 17.8$, 10.8), 5.05 (*d*, $J = 17.8$), 4.94 (*d*, $J = 10.8$)) (*Table 2*). On the basis of this evidence and the following HMBC data, the aglycone of compound **5** was presumed to be a pimarane-type diterpene, which was substituted by four OH groups. The positions of the four OH groups were determined by the HMBC from H–C(1) to C(3), C(5), C(10), and C(20), from H–C(11) to C(8), C(9), and C(13), and from H–C(14) to C(7), C(8), C(9), C(12), C(15), and C(17). The glycosyl moiety was attached at C(1), which was confirmed by the HMBC between H–C(1′) and C(1) (*Fig. 3*). The ROESY correlations of H–C(1)/Me(20), H–C(11)/H$_\beta$–C(9), H$_\beta$–C(5)/H$_\beta$–C(9), and H–C(14)/H–C(15), further suggested the α-orientation of H–C(1) and H–C(14), the β-orientation of H–C(11), and an isopimarane-type diterpene for this aglycone. The orientation of the OH group at C(8) was not established. Considering *ent*-kauranoids isolated from *I. nervosus* [2], the aglycone of compound **5** was postulated to possess an *ent*-configuration. Therefore, compound **5** was determined to be 1β,5β,8ξ,9β,10α,11α,14β)-8,11,14-trihydroxypimar-15-en-1-yl β-D-glucopyranoside, and named as *ent*-isopimanervoside A.

The ^{1}H- and ^{13}C-NMR spectra of **6** closely resembled those of **5**, except for one more OH group in **6** than in **5**. In the HMBC spectrum (*Fig. 4*), the H-atom at δ(H) 4.73 (*dd*, $J = 11.5$, 5.0), assigned to δ(C) 71.5 in the HSQC spectrum, showed correlations with C(5), C(6), and C(14). In addition, this H-atom correlated to H$_\beta$–C(5) and H$_\beta$–C(9) in the ROESY spectrum. These observations suggested that an

Table 2. *^{1}H- and ^{13}C-NMR Data of Compounds* **5** *and* **6** (500 and 125 MHz, resp.; δ in ppm; J in Hz; in C_5D_5N)

	5		**6**	
	δ(H)	δ(C)	δ(H)	δ(C)
H_α–C(1)	4.12–4.19 (overlap)	83.5	4.13–4.19 (overlap)	83.2
H_α–C(2)	2.00–2.05 (*m*)	24.1	2.00–2.05 (overlap)	24.1
H_β–C(2)	2.40 (*dd*, J = 13.5, 3.0)		2.38 (*dd*, J = 13.5, 3.0)	
H_α–C(3)	1.12 (*d*, J = 13.0)	35.6	1.11 (*d*, J = 13.0)	35.4
H_β–C(3)	2.10–2.15 (overlap)		2.10–2.15 (overlap)	
C(4)		33.2		32.9
H_β–C(5)	1.75 (*d*, J = 12.0)	49.5	1.75 (*d*, J = 12.5)	46.0
H_α–C(6)	2.10–2.15 (overlap)	18.8	2.10–2.15 (overlap)	28.2
H_β–C(6)	1.58 (br. *d*, J = 13.0)		2.00–2.05 (overlap)	
H_α–C(7)	1.85–1.90 (*m*)	38.1		71.5
H_β–C(7)	2.65–2.70 (*m*)		4.73 (*dd*, J = 11.5, 5.0)	
C(8)		79.5		81.0
H_β–C(9)	3.04 (br. *s*)	41.4	3.05 (br. *s*)	40.9
C(10)		43.7		43.3
H_β–C(11)	5.22 (br. *s*)	69.6	5.16 (br. *s*)	69.6
H_α–C(12)	2.10–2.15 (overlap)	39.7	2.10–2.15 (overlap)	39.5
H_β–C(12)	2.94 (*d*, J = 13.5)		2.93 (*d*, J = 14.0)	
C(13)		41.7		41.3
H_α–C(14)	3.62 (br. *s*)	80.6	4.26 (br. *s*)	75.1
H–C(15)	6.32 (*dd*, J = 17.8, 10.8)	151.4	6.30 (*dd*, J = 17.8, 10.8)	151.3
CH_2(16)	5.05 (*d*, J = 17.8),	109.9	5.04 (*d*, J = 17.8),	110.0
	4.94 (*d*, J = 10.8)		4.93 (*d*, J = 10.8)	
Me(17)	1.86 (*s*, 3 H)	27.9	1.81 (*s*, 3 H)	27.7
Me(18)	0.95 (*s*, 3 H)	23.1	0.92 (*s*, 3 H)	23.1
Me(19)	0.80 (*s*, 3 H)	34.1	0.77 (*s*, 3 H)	33.9
Me(20)	1.91 (*s*, 3 H)	18.4	1.86 (*s*, 3 H)	18.3
H–C(1′)	4.84 (*d*, J = 8.0)	106.6	4.84 (*d*, J = 7.5)	106.4
H–C(2′)	4.02 (*t*, J = 8.0)	75.4	3.98–4.03 (*m*)	75.3
H–C(3′)	4.12–4.19 (overlap)	79.2	4.13–4.19 (overlap)	79.1
H–C(4′)	4.12–4.19 (overlap)	71.9	4.13–4.19 (overlap)	71.9
H–C(5′)	3.89 (br. *s*)	78.3	3.89 (br. *s*)	78.2
CH_2(6′)	4.51 (*dd*, J = 11.5, 2.0),	63.2	4.50 (*dd*, J = 11.5, 2.0),	63.2
	4.34 (*dd*, J = 11.5, 5.5)		4.35 (*dd*, J = 11.5, 5.5)	

α-oriented OH group was placed at C(7) in **6**. Thus, compound **6** was characterized as 1β,5β,7α,8ξ,9β,10α,11α,14β)-7,8,11,14-tetrahydroxypimar-15-en-1-yl β-D-glucopyranoside, and named as ent-isopimanervoside B.

ent-Isopimarane diterpenes were found in the genus *Isodon* for the first time. Although *ent*-abietane diterpenes [3][10] and various phenolic compounds [11][12], including lignans and flavonoids, have been isolated from this genus, it is the first time to isolate them from this plant species [13].

Financial support of this research project was provided by the *Natural Science Foundation of Yunnan Province* (No. 2004C0008Z), the *National Natural Science Foundation of China* (No. 20502026 and 30772637), and the *Major Direction Project Foundation of ACS* (No. KSCX2-YW-R-25).

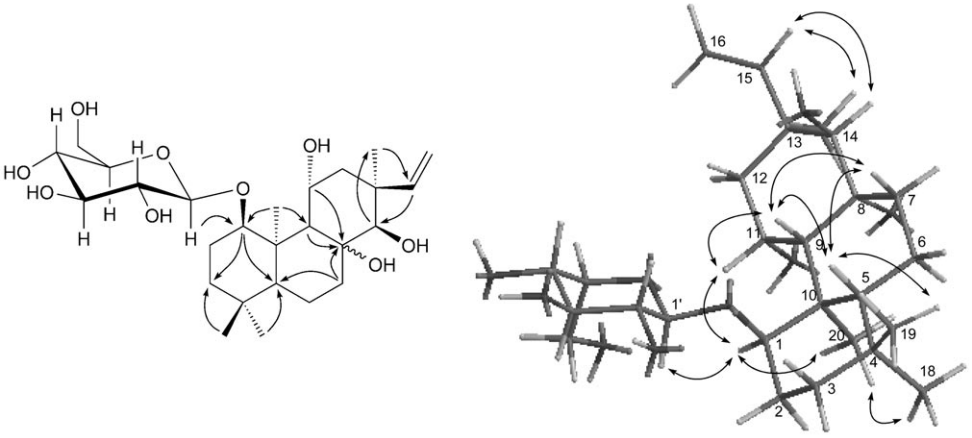


Fig. 3. *Key HMBC and ROESY data of* **5**

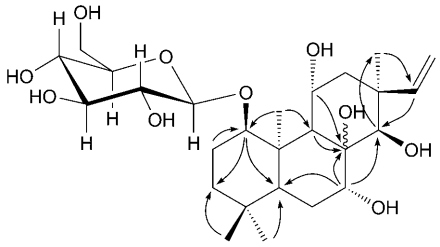


Fig. 4. *Key HMBC data of* **6**

Experimental Part

General. All solvents were distilled before use. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh, *Qingdao Marine Chemical Factory*, Qingdao, P. R. China); *Lichroprep C_{18}* reversed-phase (*RP-18*) SiO_2 (40–63 μm, *Merck*, Darmstadt, Germany); *Sephadex LH-20* (*General Electric Company*, Fairfield, USA); *MCI* gel *CHP20P* (75–150 μm, *Mitsubishi Chemical Corporation*, Tokyo, Japan). TLC: SiO_2 *GF_{254}* (10–40 μm; *Qingdao Marine Chemical Factory*, Qingdao, P. R. China). Semi-prep. HPLC: *Agilent 1100* apparatus equipped with a diode-array detector and a *Zorbax SB-C_{18}* column (*Agilent*, 9.4 mm × 25 cm, 10 μm, flow rate, 3 ml/min). Melting points: *XRC-1* micro-melting-point apparatus; uncorrected. Optical rotations: *Jasco 20C* digital polarimeter. UV Spectra: *Shimadzu UV-2401PC* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Bruker Tensor-27-FT-IR* spectrophotometer; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker AM-400* and *DRX-500* spectrometers. ESI-MS: VG *Auto-Spec-3000* spectrometer. HR-ESI-MS: *API QSTAR-Pulsar-1* spectrometer.

Plant Material. The aerial parts of *Isodon nervosus* were collected in Xichang City of Sichuan Province, P. R. China, in August 2005. The sample was identified by Prof. *Xi-Wen Li*, and a voucher specimen (KIB 050810304) 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. The air-dried, milled plant material (1.5 kg) was soaked with acetone (3 × 4 l, each 3 d) at r.t. and filtered. The filtrate was evaporated *in vacuo* at 55° to afford a residue, which was suspended in H_2O (2 l), and then defatted with petroleum ether (PE) (2 × 2 l). The aq. layer was further extracted with AcOEt (4 × 2 l). The AcOEt extract (38.0 g) was decolorized using *MCI* gel *CHP20P*

eluted with MeOH/H_2O (9:1) to yield a yellow gum (27.5 g). The gum was separated through a SiO_2 column eluted with $CHCl_3$/Me_2CO (1:0 → 0:1) to yield seven fractions (*Fr. A–G*). *Fr. E* (0.9 g) was chromatographed over SiO_2 (PE/Me_2CO, 5:1 → 2:1) to afford three subfractions (*Fr. E1–E3*). *Fr. E1* (45 mg) was subjected to semi-prep. HPLC by elution with MeOH/H_2O (4:6) to give **1** (20 mg, t_R 10.8 min) and **2** (2 mg, t_R 14.1 min). *Fr. E2* (0.2 g) was first chromatographed over *Sephadex LH-20* (MeOH) and then purified by semi-prep. HPLC (MeOH/H_2O, 5:5) to afford **3** (7 mg, t_R 8.5 min) and **4** (16 mg, t_R 15.2 min). *Fr. F* (1.4 g) was chromatographed through a column of *RP-18* SiO_2 eluted with MeOH/H_2O (3:7 → 7:3) to give three subfractions (*Fr. F1–F3*). Compound **5** (19 mg) was obtained from *Fr. F1* (56 mg) by a SiO_2 column eluted with $CHCl_3$/MeOH (10:1). *Fr. F2* (0.5 g) was subjected to CC of *Sephadex LH-20* (MeOH) and SiO_2 ($CHCl_3$/MeOH, 15:1 → 10:1) to afford three sub-subfractions (*Fr. F2a–Fr. F2c*). *Fr. F2a* (45 mg) was purified by semi-prep. HPLC (MeOH/H_2O, 3:7) to give **6** (15 mg, t_R 24.5 min), urolignoside (2 mg, t_R 18.0 min), and glochidioboside (3 mg, t_R 13.7 min). *Fr. F2b* (52 mg) was separated by semi-prep. HPLC (MeCN/H_2O, 2:8) to afford (−)-secoisoraricir-esinol-9′-*O*-*β*-D-glucoside (2 mg, t_R 7.8 min), (+)-pinoresinol-4-*O*-*β*-D-glucoside (17 mg, t_R 13.0 min), 8-hydroxypinoresiol-4′-*O*-*β*-D-glucoside (4 mg, t_R 18.4 min), 8-hydroxypinoresiol-4-*O*-*β*-D-glucoside (7 mg, t_R 21.3 min), and daidzein-4′-*O*-*β*-D-glucoside (8 mg, t_R 26.4 min).

ent-*Abienervonin A* (= *(1α,3β,5β,6α,9β,10α,11β,13β)-1,6,11,16-Tetrahydroxyabieta-7,15(17)-dien-3-yl Acetate*; **1**). Colorless needles. M.p. 194–195°. $[\alpha]_D^{16} = +73.3$ ($c = 0.15$, MeOH). UV (MeOH): 205 (3.85). IR (KBr): 3449, 3331, 2980, 2947, 2935, 2908, 2854, 2826, 1711, 1646, 1481, 1447, 1428, 1377, 1270, 1197, 1185, 1081, 1069, 1031, 1003. ^{1}H- and ^{13}C-NMR: see *Table 1*. ESI-MS (pos.): 417 ($[M+Na]^+$), 811 ($[2\,M+Na]^+$). HR-ESI-MS (pos.): 417.2263 ($[M+Na]^+$, $C_{22}H_{34}NaO_6^+$; calc. 417.2253).

ent-*Abienervonin B* (= *(1α,3β,5β,9β,10α,11β,13β)-1,11,16-Trihydroxyabieta-6,8(14),15(17)-trien-3-yl Acetate*; **2**). White powder. $[\alpha]_D^{17} = +65.3$ ($c = 0.07$, MeOH). UV (MeOH): 242 (3.99), 234 (3.97). IR (KBr): 3430, 2951, 2876, 1729, 1715, 1643, 1458, 1375, 1247, 1184, 1068, 1041, 1011. ^{1}H- and ^{13}C-NMR: see *Table 1*. ESI-MS (pos.): 399 ($[M+Na]^+$), 775 ($[2\,M+Na]^+$). HR-ESI-MS (pos.): 399.2152 ($[M+Na]^+$, $C_{22}H_{32}NaO_5^+$; calc. 399.2147).

ent-*Abienervonin C* (= *(3α,5β,9β,10α,13β)-3,15,16,17-Tetrahydroxyabiet-7-en-19-al*; **3**). Colorless needles. M.p. 197–198°. $[\alpha]_D^{13} = -7.7$ ($c = 0.14$, MeOH). UV (MeOH): 205 (3.71). IR (KBr): 3561, 3407, 2936, 2891, 2854, 2711, 1724, 1635, 1446, 1384, 1222, 1089, 1049, 1026. ^{1}H- and ^{13}C-NMR: see *Table 1*. ESI-MS (pos.): 375 ($[M+Na]^+$), 727 ($[2\,M+Na]^+$). HR-ESI-MS (pos.): 375.2142 ($[M+Na]^+$, $C_{20}H_{32}NaO_5^+$; calc. 375.2147).

ent-*Isopimanervoside A* (= *(1β,5β,8ξ,9β,10α,11α,14β)-8,11,14-Trihydroxypimar-15-en-1-yl β-*D*-Glucopyranoside*; **5**). White powder. $[\alpha]_D^{17} = +22.9$ ($c = 0.22$, MeOH). UV (MeOH): no absorption. IR (KBr): 3407, 2936, 2874, 1706, 1637, 1462, 1449, 1416, 1389, 1363, 1265, 1235, 1166, 1075, 1051, 1015. ^{1}H- and ^{13}C-NMR: see *Table 2*. ESI-MS (neg.): 499 ($[M-H]^-$), 535 ($[M+Cl]^-$), 999 ($[2\,M-H]^-$), 1035 ($[2\,M+Cl]^-$). HR-ESI-MS (neg.): 499.2896 ($[M-H]^-$, $C_{26}H_{43}O_9^-$; calc. 499.2907).

ent-*Isopimanervoside B* (= *(1β,5β,7α,8ξ,9β,10α,11α,14β)-7,8,11,14-Tetrahydroxypimar-15-en-1-yl β-*D*-Glucopyranoside*; **6**). Colorless needles. M.p. 243–244°. $[\alpha]_D^{17} = +12.7$ ($c = 0.24$, MeOH). UV (MeOH): 205 (3.52). IR (KBr): 3423, 2953, 2877, 1636, 1462, 1420, 1393, 1369, 1257, 1159, 1130, 1077, 1062, 1022. ^{1}H- and ^{13}C-NMR: see *Table 2*. ESI-MS (neg.): 515 ($[M-H]^-$), 551 ($[M+Cl]^-$), 1031 ($[2\,M-H]^-$), 1067 ($[2\,M+Cl]^-$). HR-ESI-MS (neg.): 515.2871 ($[M-H]^-$, $C_{26}H_{43}O_{10}^-$; calc. 515.2856).

Acid Hydrolysis. Compounds **5** and **6** (8 mg each) were hydrolyzed with HCl (5%, 4 ml) at 80° for 2 h, resp. After 2 ml of H_2O was added, the mixture was extracted with AcOEt (3 × 3 ml). The glucose was identified from the aq. phase by comparing with an authentic sample ($CHCl_3$/MeOH/H_2O/AcOH = 7:3:0.5:1, $R_f = 0.45$). Then, the aq. phase was left to stand for 1 d. After filtrating the precipitate, the soln. was evaporated *in vacuo* to afford D-glucose with the optical rotation of $[\alpha]_D^{18} = +52$ ($c = 0.25$, H_2O) from **5** and $[\alpha]_D^{18} = +67$ ($c = 0.35$, H_2O) from **6**.

REFERENCES

[1] Jiangsu New Medical College, 'A Dictionary of Chinese Herb', Shanghai Science and Technology Press, Shanghai, 1986, p. 159.

[2] X.-R. Wang, H.-P. Hu, H.-P. Wang, S.-Q. Wang, S. Ueda, T. Fujita, *Chin. Tradit. Herb. Drugs* **1994**, *25*, 115; X.-R. Wang, H.-P. Hu, H.-P. Wang, S.-Q. Wang, S. Ueda, T. Fujita, *Phytochemistry* **1994**, *37*, 1367; S. Hua, Q. Wang, G. Bai, Y. Chen, *Acta Crystallogr., Sect. C* **1989**, *45*, 748; Q.-G. Wang, S.-M. Hua, G. Bai, Y.-Z. Chen, *J. Nat. Prod.* **1988**, *51*, 775; Y.-H. Gao, Z.-G. Wan, X.-W. Lai, Y. Zhu, G.-Y. Li, S.-H. Wu, *China J. Chin. Mat. Med.* **1994**, *19*, 295; Y.-H. Gao, S.-H. Wu, R.-J. Zhong, G.-Y. Li, *Chin. Tradit. Herb. Drugs* **1996**, *27*, 579; Y.-H. Gao, Y. Cheng, S.-H. Wu, *Chin. Tradit. Herb. Drugs* **1999**, *30*, 407; J.-H. Chao, Q.-Z. Zhao, H.-Q. Wang, H.-D. Sun, *Acta Bot. Yunnan.* **1983**, *5*, 311; H.-D. Sun, Q.-Z. Zhao, J.-H. Chao, H.-Q. Wang, Z.-W. Lin, Y.-H. Gong, *Acta Bot. Yunnan.* **1984**, *6*, 235; H.-D. Sun, Z.-W. Lin, Z.-D. Wang, Y.-H. Gong, Q.-Z. Zhao, J.-H. Chao, H.-Q. Wang, *Acta Chim. Sin.* **1985**, *43*, 481; H. Sun, F. Niu, Y. Chen, Z. Lin, *Phytochemistry* **1992**, *31*, 695; M.-J. Xu, M. Tang, P.-Y. Cheng, *Chin. Tradit. Herb. Drugs* **1985**, *16*, 3; M.-J. Xu, P.-Y. Cheng, M. Tang, Z.-M. Wang, Y.-J. Xia, J. Ji, *Acta Bot. Sin.* **1993**, *35*, 161; L.-M. Li, G.-Y. Li, L.-S. Ding, L.-B. Yang, Y. Zhao, J.-X. Pu, W.-L. Xiao, Q.-B. Han, H.-D. Sun, *J. Nat. Prod.* **2008**, *71*, 684.

[3] S.-X. Huang, J.-X. Pu, W.-L. Xiao, L.-M. Li, Z.-Y. Weng, Y. Zhou, Q.-B. Han, S.-L. Peng, L.-S. Ding, L.-G. Lou, H.-D. Sun, *Phytochemistry* **2007**, *68*, 616.

[4] Y.-C. Shen, P.-W. Hsieh, Y.-H. Kuo, *Phytochemistry* **1998**, *48*, 719.

[5] Y. Takeda, C. Mima, T. Masuda, E. Hirata, A. Takushi, H. Otsuka, *Phytochemistry* **1998**, *49*, 2137.

[6] S. Inoshiri, M. Sasaki, H. Kohda, H. Otsuka, K. Yamasaki, *Phytochemistry* **1987**, *26*, 2811.

[7] M. Chiba, S. Hisada, S. Nishibe, H. Thieme, *Phytochemistry* **1980**, *19*, 335.

[8] B. Schumacher, S. Scholle, J. Hölzl, N. Khudeir, S. Hess, C. E. Müller, *J. Nat. Prod.* **2002**, *65*, 1479.

[9] Y.-S. Sang, H.-M. Shi, Z.-D. Min, *Chin. Tradit. Herb. Drugs* **2002**, *33*, 776.

[10] L.-M. Li, S.-X. Huang, L.-Y. Peng, G.-Y. Li, W.-L. Xiao, Y. Zhou, Q.-B. Han, L.-S. Ding, H.-D. Sun, *Chem. Pharm. Bull.* **2006**, *54*, 1050.

[11] H. Huang, H.-D. Sun, M.-S. Wang, S.-X. Zhao, *J. Nat. Prod.* **1996**, *59*, 1079.

[12] H. Huang, H.-D. Sun, S.-X. Zhao, *Phytochemistry* **1996**, *42*, 1247.

[13] B. Jiang, X.-R. Chen, Z.-Q. Lu, H.-D. Sun, *Zhiwu Xuebao* **2000**, *42*, 95.

Received July 16, 2008