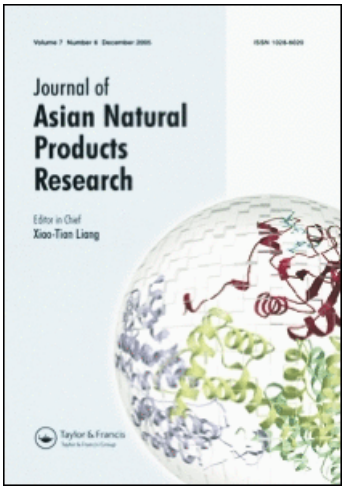

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GLABCENSIN Q–U, FIVE NEW *ent*-KAURANE DITERPENOIDS FROM *ISODON ANGUSTIFOLIUS* VAR. *GLABRESCENS*

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Examination of the diterpenoid constituents of the dried leaves of *Isodon angustifolius* var. *glabrescens* led to the isolation of five new *ent*-kaurane diterpenoids, named as glabcensin Q–U (**2–6**). The structures were elucidated on the basis of spectroscopic evidences.

Keywords: *Isodon angustifolius* var. *glabrescens*; Labiatae; *ent*-Kaurane diterpenoids; Glabcensin Q–U (**2–6**)

INTRODUCTION

In a preceding paper [1], we isolated sixteen new diterpenoids, glabcensin A–P from the dried leaves of *Isodon angustifolius* var. *glabrescens* [2], and determined their structures. During the course of a systematic investigation of the biologically active diterpenoids from *Isodon* plants, we further examined the constituents of the same plant and isolated five new diterpenoids, named as glabcensin Q–U (**2–6**). This paper deals with the structural elucidation of these new compounds.

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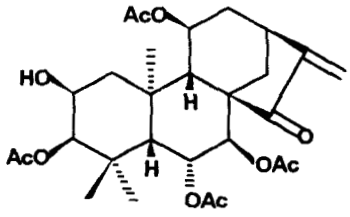

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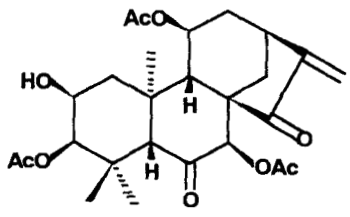

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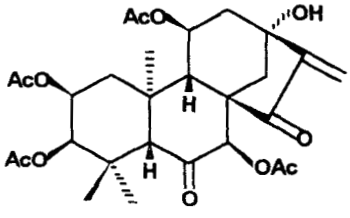

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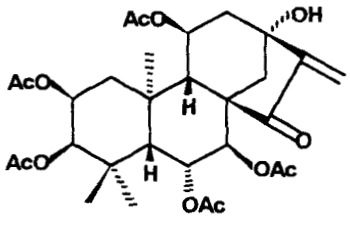

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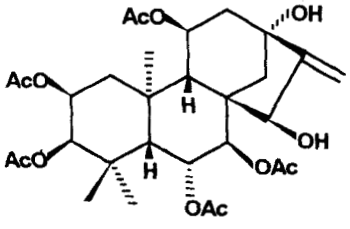

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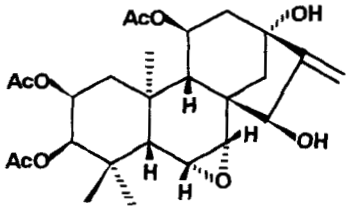

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RESULTS AND DISCUSSION

Glabcensin Q (**2**), $C_{26}H_{34}O_9$ ($[M]^+ m/z$ 490), an amorphous powder, exhibited a typical α,β-unsaturated ketone absorption in its UV spectrum [λ_{max} 236.5 (3.78)] and a hydroxyl group absorption in its IR spectrum (3420 cm^{-1}). The ^1H- and ^{13}CNMR spectral data showed the presence of three acetoxyl groups, one hydroxyl group, three methyl groups, four methylene groups (including an *exo*-methylene group), seven methine groups (including four oxygenated methine groups), and two ketonic carbons (including an isolated ketone). All above observations, together with the consideration of the structure of diterpenoids isolated so far from the

Isodon genus, suggested that **2** had a structure in which three acetoxyl groups, one hydroxyl group and an isolated ketone, were introduced into *ent*-kaur-16-ene-15-one as a basic skeleton. Comparison of the ^{1}H and ^{13}CNMR spectral data with those of glabcensin A (**1**) showed that both compounds were quite similar except for the signals of ring **B**. This compound did not display any signal due to H-6 in its ^{1}HNMR spectrum, but showed the signal (δ 203.5) for an isolated ketone in its ^{13}CNMR spectrum. All above findings led to an assumption that **2** had a structure in which an isolated ketonic carbon and acetoxyl group were located at C-6 and C-7, respectively. This assumption was confirmed by the following facts: two singlet signals at δ 3.74 (1H, s, H-5β) and δ 5.52 (1H, s, H-7α) showed a special downfield shift owing to the presence of the carbonyl group at C-6 and an acetoxyl group at C-7, similar to the case of adenanthin [3,4]. Therefore, glabcensin Q (**2**) was elucidated as 2β-hydroxyl-3β,7β,11β-triacetoxy-*ent*-kaur-16-ene-6,15-dione.

Glabcensin R (**3**), $C_{28}H_{36}O_{11}$ ($[M]^{+}m/z$ 548), was obtained as an amorphous powder. Its IR spectrum exhibited a hydroxyl group absorption (3430 cm^{-1}). In the EIMS spectrum of **3**, the major fragments at m/z 506, 488, 428, 368 and 308 resulting from [M$-n\times$AcOH] ($n=1,2,3,4$) suggested that **3** contained four acetoxyl groups. This was identical with its NMR data (δ 2.23, 2.11, 1.98 and 1.77 for acetyl methyls in its ^{1}HNMR spectrum; δ 170.30, 170.30, 169.67 and 169.13 for ester carbonyls in its ^{13}CNMR spectrum). The ^{1}H- and ^{13}CNMR spectral data showed the presence of three methyl groups, four methylene groups (including an *exo*-methylene group), six methine groups (including five oxygenated methine groups), two ketonic carbons (including an isolated ketone). The presence of a ketone conjugated with an *exo*-methylene group was suggested by the following spectral data: UV (MeOH) λ_{max} (log ϵ): 235 (3.77) nm; IR (KBr) ν_{max}: 1725 and 1650 cm^{-1}; ^{1}HNMR δ: 6.22, 5.76 (each 1H, br s); ^{13}CNMR δ: 205.57(s), 153.62 (s), 114.66(t). All above evidence suggested that **3** possessed an *ent*-kaur-16-ene-15-one basic skeleton. The locations of the four acetoxyl groups, one hydroxyl group and an isolated ketone were defined by the $^{1}H-^{1}H$ COSY spectrum, which was further confirmed by a $^{13}C-^{1}H$ COSY experiment. In the $^{1}H-^{1}H$ COSY spectrum of **3**, the following correlations were observed. The signal at δ 5.26 (1H, d, $J=2.7$ Hz, H-3α) showed correlation with the signal at δ 5.56 (1H, ddd, $J=11.6$, 4.2, 2.7, H-2α), the latter showed correlation with both the signal at δ 2.35 (1H, overlapped, H-1α) and the signal at δ 2.27 (1H, overlapped, H-1β). Thus, two acetoxyl groups should be located at C-2 and C-3, respectively, similar to the case of glabcensin A [1]. The stereochemistry was established as

2β-OAc and 3β-OAc by considering the coupling constants of H-2 and H-3. The signals at δ 3.79 (1H, s, H-5β) and 5.45 (1H, s, H-7α) showed no correlation with any proton, thus an isolated ketone and an acetoxyl group were located at C-6 and C-7, respectively, similar to the case of glabcensin Q (**2**). The signal at δ 5.58 (1H, d, $J=5.1$ Hz, H-11α) showed correlation with the signal at δ 2.62 (1H, dd, $J=14.6, 5.1$ Hz, H-12β), whereas the signal at δ 2.40 (1H, d, $J=14.6$ Hz, H-12α) only showed correlation with δ 2.62 (1H, dd, $J=14.6, 5.1$ Hz, H-12β). The presence of a hydroxyl group at C-13α was deduced from the signal at δ 74.20 (s, C-13) and the absence of H-13 in rosthornin [5]. Moreover, this compound showed no signal for H-6 in ^{1}HNMR spectrum, but showed the signal at δ 200.77 (s, C-6) for an isolated ketone in its ^{13}CNMR spectrum. These results further confirmed the presence of an isolated ketone at C-6 and a hydroxyl group at C-13.

The unambiguous assignments of the oxygenated methine positions in **3** were achieved by a NOESY experiment; most of the NOESY correlations are shown by the arrows in Fig. 1. Observation of the NOESY correlation between the H-2α with Me-19 and Me-20, H-3α with Me-18 and Me-19, H-7α with H-14β, H-11α with H-1α, H-14α with H-12α and Me-20, and H-12α with Me-20 protons confirmed that the C-2, C-3, C-7, C-11 acetoxyl groups and the C-13 hydroxyl group possessed the 2β, 3β, 7β, 11β and 13α orientations, respectively. Therefore, glabcensin R (**3**) was elucidated as 13α-hydroxyl-2β,3β,7β,11β-tetraacetoxy-*ent*-kaur-16-ene-6,15-dione.

Glabcensin S (**4**), $C_{30}H_{40}O_{12}$ ([M]$^+$ *m/z* 592), an amorphous powder, showed spectral data very similar to those of **3** except for the signals of

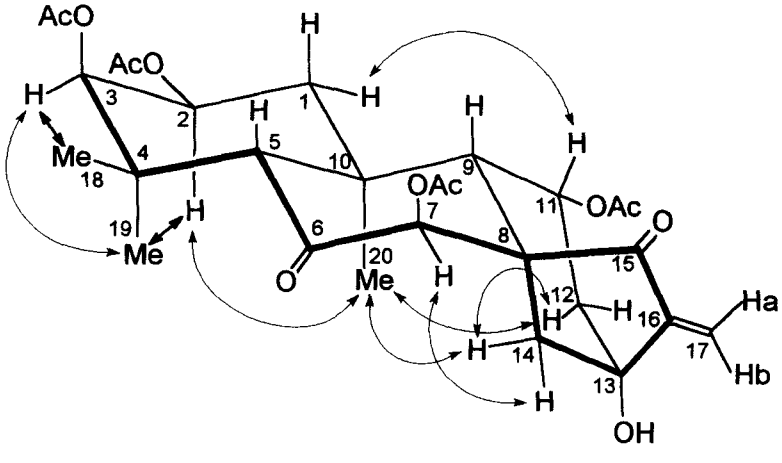

FIGURE 1 NOE correlations observed in glabcensin R (**3**).

ring B. The only difference between **4** and **3** was that **4** had one acetoxyl group more and one isolated ketone group less than **3**. In the ^{1}HNMR spectrum of **4**, the signal at δ 5.70 (1H, d, $J=3.5$ Hz, H-7α) and the signal at δ 5.44 (1H, dd, $J=3.5, 1.8$ Hz, H-6β) indicated that two acetoxyl groups were located at C-6 and C-7, respectively. The stereochemistry was established as 6α-OAc and 7β-OAc according to the coupling pattern of H-6 and H-7. Finally, the locations of the functional groups were further confirmed by the following observations in the ^{1}H–^{1}H COSY spectrum of **4**. The connections for H-11α (δ 5.62, d, $J=5.0$ Hz) → H-12β (δ 2.72, dd, $J=14.2, 5.0$ Hz) → 12α (δ 2.46, d, $J=14.2$ Hz), those for H-7α (δ 5.70, d, $J=3.5$ Hz) → H-6β (δ 5.44, dd, $J=3.5, 1.8$ Hz) → H-5β (δ 2.44, br s), those for H-3α (δ 5.56, d, $J=2.7$ Hz) → H-2α (δ 5.33, ddd, $J=11.5, 4.2, 2.7$ Hz) → H-1α (2.32, overlapped) → H-1β (δ 2.10, overlapped), and those for H-14β (δ 3.03, d, $J=11.8$ Hz) → H-14α (δ 2.02, d, $J=11.8$ Hz) were observed. On the basis of the above findings, glabcensin S (**4**) was established as 13α-hydroxy-2β,3β,6α,7β,11β-pentaacetoxy-*ent*-kaur-16-ene-15-one.

Glabcensin T (**5**), $C_{30}H_{42}O_{12}$ ([M]$^+$ *m/z* 594), an amorphous powder, showed hydroxyl group absorption in its IR spectrum. However, no absorption for an α,β-unsaturated ketone was found in its IR and UV spectrum. Its mass spectrum showed a molecular ion at *m/z* 594 two amu more than **4**. The ^{1}H and ^{13}CNMR spectra resembled those of **4** except for the presence of a hydroxyl group instead of the ketone at C-15. The position of the hydroxyl group at C-15 was confirmed as follows. In the ^{1}H–^{1}H COSY spectrum of **5**, the signal at δ 4.78 (1H, br s, H-15) showed correlation with the signals at δ 5.56, 5.49 (each 1H, br s, H_2-17) caused by the weak long-range coupling between H-15 and H_2-17. The configuration of the hydroxyl group at C-15 was determined as β-orientation according to the downfield shift of C-9 (δ 48.77) due to the γ-gauche steric compression between HO-15β and C-9 [1]. Thus, glabcensin T (**5**) was elucidated as 13α,15β-dihydroxy-2β,3β,6α,7β,11β-pentaacetoxy-*ent*-kaur-16-ene.

Glabcensin U (**6**), $C_{26}H_{36}O_9$ ([M]$^+$ *m/z* 492), an amorphous powder, showed the presence of a hydroxyl group (3400 cm^{-1}) in its IR spectrum. The major fragment ion peaks of EIMS spectrum (*m/z* 432, 372, 312) resulting from [M$-n\times$AcOH] ($n=1,2,3$) indicated that **6** contained three acetoxyl groups, which was identical with its NMR data (δ 2.06, 1.91, 1.89 for acetyl methyls in ^{1}HNMR and δ 170.70, 170.30, 169.38 for ester carbonyls in ^{13}CNMR). Its IR and UV showed no characteristic absorption for an α,β-unsaturated ketone. The ^{1}H- and ^{13}CNMR (DEPT) data showed the presence of three methyl groups, four methylene groups

(including an *exo*-methylene group), eight methine groups (including five oxygenated methines), three acetoxyl groups and two hydroxyl groups. These data led to an assumption that **6** had an *ent*-kaur-16-ene skeleton. Direct comparison of the ^{1}H- and ^{13}CNMR (DEPT) data of **6** with those of **5** showed that they were quite similar except for ring B. The signals at δ 53.33 (d, C-6), δ 57.88 (d, C-7), δ 3.33 (1H, d, $J=4.4$ Hz, H-6) and δ 3.00 (1H, d, $J=4.4$ Hz, H-7) suggested the presence of a 6,7-epoxide ring, similar to the case of wikestroemioidin A [6]. This conclusion was further confirmed by the following facts: In the ^{1}H–^{1}H COSY spectrum of **6**, the signal at δ 3.00 (1H, d, $J=4.4$ Hz, H-7) showed correlation with the signal at δ 3.33 (1H, d, $J=4.4$ Hz, H-6), the latter showed correlation with the signal at δ 1.85 (1H, br s, H-5β). The configuration of the 6,7-epoxide ring was determined as α-orientation according to the coupling constant of H-6β with H-7β, whereas the signal showed only small coupling with H-5β since the dihedral angle of H-6β and -5β was nearly 90°. The locations of the other functional groups were further examined by the ^{1}H–^{1}H COSY experiment. The connectivities for H-3α (δ 5.00, d, $J=3.1$ Hz) → H-2α (δ 5.30, ddd, $J=12.4$, 4.4, 3.1 Hz) → H-1α (δ 2.35, overlapped) → H-1β (δ 2.14, overlapped) revealed that two β-oriented acetoxyl groups should be located at C-2 and C-3, respectively. The connections for H-11α (δ 5.14, br d, $J=4.0$ Hz) → H-12β (δ 2.70, dd, $J=14.2$, 5.0 Hz) → H-12α (δ 2.34, d, $J=14.2$ Hz) showed the presence of an acetoxyl group and a hydroxyl group at C-11β and C-13α, respectively. The signal at δ 4.44 (1H, br s, H-15) showed correlation with the signals at δ 5.19, 5.18 (each 1H, br s, H_2-17) due to long-range coupling between H-15α and H_2-17, which indicated that a hydroxyl group was located at C-15. The downfield shift of C-9 (δ 49.51) demonstrated a β configuration of HO-15 owing to the steric compression between HO-15β and C-9 [1]. All above assignments were confirmed by ^{1}H–^{13}C COSY and COLOC spectra of **6**. Therefore, glabcensin U (**6**) was established as 13α,15β-dihydroxy-2β,3β,11β-triacetoxy-6α,7α-epoxy-*ent*-kaur-16-ene.

EXPERIMENTAL SECTION

General Experimental Procedures All mp's were obtained on a Kofler apparatus and are uncorrected. IR spectral data were measured on a Perkin-Elmer 577 spectrometer with KBr pellets. NMR spectra were recorded on a Bruker AM-400 instrument with TMS as internal standard and pyridine-d_5 as solvent. ^{1}HNMR, ^{1}H–^{1}H COSY, NOESY spectra were

recorded at 400.13 MHz; ^{13}CNMR and DEPT spectra were recorded at 100.6 MHz. ^{13}CNMR assignments were determined by ^{13}C–^{1}H COSY and COLOC spectra. NOESY: SW 2000 Hz, D 1 s, 2 048 512 increments, 900 shifted sine-bell-squared apodization, zero-filled to 1024 in one dimension during processing, mixing time 1 s. The EIMS data were carried out on a VG Autospec-3000 spectrometer.

Plant Material Plant material was collected in Dali county, Yunnan province, China, in Sept. 1993, and identified as *I. angustifolius* (Dunn) var. *glabrescens* by Prof. Li Xi-Wen. A voucher specimen is deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany.

Extraction and Isolation Dried leaves (3 kg) of *I. angustifolius* var. *glabrescens* were extracted with 3 L EtOH five times under reflux. The extract was concentrated *in vacuo* to give a residue (300 g) that was chromatographed over silica gel (200–300 mesh, 1.5 kg). The column was eluted with $CHCl_3$–Me_2CO (9.5:0.95, 9:1, 8:2, 7:3, 6:4) and Me_2CO. The elutes were collected as 500 ml fractions, and all components were purified by column chromatography (including CC on MCI gel CHP-20, RP-18 and RP-8 gel and employing the HPLC) and recrystallized to give compounds **2** (80 mg), **3** (30 mg), **4** (80 mg), **5** (180 mg) and **6** (10 mg). The physical properties of the diterpenoids are listed below.

Glabcensin Q (*2*) $C_{26}H_{34}O_9$, an amorphous powder, $[\alpha]_D^{22}$: −32.8 ($CHCl_3$, $c=0.46$), UV (MeOH) λ_{max} (log ϵ): 236.5 (3.78) nm; IR (KBr) ν_{max}: 3420, 2910, 1725, 1645, 1370, 1225, 1030 cm^{-1}; EIMS *m/z* (rel. int.): 490[M]$^+$(18), 472[M−H_2O]$^+$(5), 430[M−AcOH]$^+$(20), 388[M−AcOH−$COCH_2$]$^+$(20), 370[M−2 × AcOH]$^+$(30), 328[M−2 × AcOH−$COCH_2$]$^+$(65), 310[M−3 × AcOH]$^+$(48), 295[M−3 × AcOH−Me]$^+$(70); ^{1}HNMR δ: 2.50 (1H, m, H-1α), 2.10 (1H, m, H-1β), 4.50 (1H, ddd, $J=11.5$, 4.2, 2.8 Hz, H-2α), 5.31 (1H, d, $J=2.8$ Hz, H-3α), 3.74 (1H, s, H-5β), 5.52 (1H, s, H-7α), 2.77 (1H, br s, H-9β), 5.45 (1H, d, $J=5.2$ Hz, H-11α), 2.20 (1H, m, H-12β), 2.00 (1H, m, H-12α), 5.94 (1H, br s, H-17a), 5.25 (1H, br s, H-17b), 1.06 (3H, s, Me-18), 1.19 (3H, s, Me-19), 1.44 (1H, s, Me-20), 2.24, 2.06, 1.74 (each 3H, s, 3 × Ac), ^{13}CNMR see Table I.

Glabcensin R (*3*) $C_{28}H_{36}O_{11}$, an amorphous powder, $[\alpha]_D^{22}$: −28.2 ($CHCl_3$, $c=0.48$), UV (MeOH) λ_{max} (log ϵ): 235 (3.77) nm; IR (KBr) ν_{max}: 3430, 2930, 1725, 1650, 1365, 1230, 1030 cm^{-1}; EIMS *m/z* (rel. int.): 548[M]$^+$(39), 530[M-H_2O]$^+$(2), 506[M−$COCH_2$]$^+$(17), 488[M−AcOH]$^+$(12), 446[M−AcOH−$COCH_2$]$^+$(56), 428[M−2 × AcOH]$^+$(32), 386[M−2 × AcOH−$COCH_2$]$^+$(52), 368[M−3 × AcOH]$^+$(30), 344[M−2 × AcOH−2 × $COCH_2$]$^+$(40), 308[M−4 × AcOH]$^+$(53); ^{1}HNMR δ: 2.35 (1H, overlapped, H-1α), 2.27 (1H, overlapped, H-1β), 5.56 (1H, ddd, $J=11.6$, 4.2, 2.7 Hz,

TABLE I ^{13}CNMR data of compounds **1**–**6** (pyridine-d_5)

C	**1**	**2**	**3**	**4**	**5**	**6**
1	45.14t	43.57t	39.30t	40.90t	41.14t	39.48t
2	63.61d	63.82d	67.50d	67.54d	67.74d	68.30d
3	81.25d	80.37d	76.65d	77.58d	77.60d	76.81d
4	38.44s	37.48s	37.25s	38.35s	38.28s	38.94s
5	43.44d	54.44d	53.89d	43.46d	43.46d	47.72d
6	69.98d	203.5s	200.77s	69.74d	70.05d	53.33d
7	71.41d	80.37d	80.35d	71.11d	76.28d	57.88d
8	49.70s	53.35s	56.16s	51.61s	46.67s	45.97s
9	55.78d	55.73d	54.74d	54.82d	48.77d	49.51d
10	39.70s	46.39s	46.43s	39.79s	39.15s	39.48s
11	68.35d	67.67d	68.88d	69.39d	70.12d	69.68d
12	38.13t	37.95t	45.89t	46.33t	47.35t	48.33t
13	36.75d	36.19d	74.20s	74.51s	75.43s	75.18s
14	35.12t	33.28t	41.76t	43.46t	42.67t	42.58t
15	204.62s	206.21s	205.57s	203.42s	79.88d	81.36d
16	149.62s	150.17s	153.62s	153.60s	159.39s	159.59s
17	113.17t	114.43t	114.66t	113.54t	105.97t	106.87t
18	28.28q	27.28q	26.87q	28.01q	28.04q	28.22q
19	23.57q	22.09q	21.82q	22.95q	23.02q	23.09q
20	20.66q	19.90q	19.61q	20.40q	20.00q	20.64q
Ac	170.84s	170.19s	170.30s	170.48s	170.35s	170.70s
	169.64s	169.69s	170.30s	170.36s	170.35s	170.30s
	169.48s	168.99s	169.67s	169.45s	169.98s	169.38s
	169.06s	20.89q	169.13s	169.45s	169.59s	21.49q
	21.21q	20.89q	21.82q	169.19s	168.88s	20.80q
	21.21q	20.51q	20.92q	21.31q	21.36q	20.74q
	21.01q		20.92q	21.13q	21.36q	
	21.01q		20.50q	21.01q	21.06q	
				21.01q	21.06q	
				20.58q	20.56q	

H-2α), 5.26 (1H, d, $J=2.7$ Hz, H-3α), 3.79 (1H, s, H-5β), 5.45 (1H, s, H-7α), 2.85 (1H, br s, H-9β), 5.58 (1H, d, $J=5.1$ Hz, H-11α), 2.62 (1H, dd, $J=$ 14.6, 5.1 Hz, H-12β), 2.41 (1H, d, $J=14.6$ Hz, H-12α), 2.59 (1H, $J=11.7$ Hz, H-14β), 2.15 (1H, $J=11.7$ Hz, H-14α), 6.22 (1H, s, H-17a), 5.76 (1H, s, H-17b), 0.97 (3H, s, Me-18), 1.28 (3H, s, Me-19), 1.46 (3H, s, Me-20), 2.23, 2.11, 1.98, 1.77 (each 3H, s, 4 × Ac), ^{13}CNMR see Table I.

Glabcensin S (*4*) $C_{30}H_{40}O_{12}$, an amorphous powder, $[\alpha]_D^{22}$: −36.5 ($CHCl_3$, $c=0.45$), UV (MeOH) λ_{max} (log ϵ): 229.5 (3.56) nm; IR (KBr) ν_{max}: 3490, 2910, 1720, 1640, 1360, 1240, 1035 cm^{-1}; EIMS *m/z* (rel. int.): 592[M]$^+$(2), 532[M−AcOH]$^+$(7), 490[M−AcOH−$COCH_2$]$^+$(27), 472[M− 2 × AcOH]$^+$(18), 430[M−2 × AcOH−$COCH_2$]$^+$(68), 412[M−3 × AcOH]$^+$(34), 370 [M−3 × AcOH−$COCH_2$]$^+$(49), 352[M−4 × AcOH]$^+$(28), 310[M−4 × AcOH−$COCH_2$]$^+$(93), 292[M−5 × AcOH]$^+$(87), 277[M−5 × AcOH−CH_3]$^+$(90); ^{1}HNMR δ: 2.32 (1H, overlapped, H-1α), 2.10 (1H, overlapped, H-1β), 5.33 (1H, ddd, $J=11.5, 4.2, 2.7$ Hz, H-2α), 5.56

(1H, d, $J=2.7$ Hz, H-3α), 2.44 (1H, br s, H-5β), 5.44 (1H, dd, $J=$ 3.5, 1.8 Hz, H-6β), 5.70 (1H, d, $J=3.5$ Hz, H-7α), 2.27 (1H, br s, H-9β), 5.62 (1H, d, $J=5.0$ Hz, H-11α), 2.72 (1H, dd, $J=14.2$, 5.0 Hz, H-12β), 2.46 (1H, d, $J=14.2$ Hz, H-12α), 3.03 (1H, d, $J=11.8$ Hz, H-14β), 2.02 (1H, d, $J=11.8$ Hz, H-14α), 5.44 (1H, br s, H-17a), 5.27 (1H, br s, H-17b), 1.00 (1H, s, Me-18), 1.14 (1H, s, Me-19), 1.57 (3H, s, Me-20), 2.23, 2.11, 1.98, 1.97, 1.78 (each, 3H, 5 × Ac), ^{13}CNMR see Table I.

Glabcensin T (*5*) $C_{30}H_{42}O_{12}$, an amorphous powder, $[\alpha]_D^{22}$: −37.5 ($CHCl_3$, $c=0.52$), UV (MeOH) λ_{max}: end absorption; IR (KBr) ν_{max}: 3480, 2940, 1730, 1365, 1225, 1030 cm^{-1}; EIMS *m/z* (rel. int.): 594[M]$^+$(3), 534[M−AcOH]$^+$(5), 474[M−2 × AcOH]$^+$(16), 414[M−3 × AcOH]$^+$(42), 354[M−4 × AcOH]$^+$(50), 294[M−5 × AcOH]$^+$(100), 279[M−5 × AcOH-Me]$^+$(84); ^{1}HNMR δ: 2.30 (1H, overlapped, H-1α), 2.00 (1H, overlapped, H-1β), 5.58 (1H, ddd, $J=11.2$, 4.5, 3.4 Hz, H-2α), 5.35 (1H, d, $J=3.4$ Hz, H-3α), 2.48 (1H, br s, H-5β), 5.44 (1H, dd, $J=3.4$, 1,8 Hz, H-6β), 5.64 (1H, d, $J=3.4$ Hz, H-7α), 2.31 (1H, br s, H-9β), 5.62 (1H, d, $J=4.7$ Hz, H-11α), 2.65 (1H, dd, $J=14.2$, 5.0 Hz, H-12β), 2.20 (1H, d, $J=14.2$ Hz, H-12α), 3.06 (1H, d, $J=11.4$ Hz, H-14β), 2.02 (1H, d, $J=11.4$ Hz, H-14α), 4.78 (1H, br s, H-15α), 5.56 (1H, br s, H-17a), 5.49 (1H, br s, H-17b), 1.00 (3H, s, 18-Me), 1.10 (3H, s, 19-Me), 1.52 (3H, s, Me-20), 2.18, 2.05, 2.00, 1.97, 1.94 (each 3H, s, 5 × Ac), ^{13}CNMR see Table I.

Glabcensin U (*6*) $C_{26}H_{36}O_9$, an amorphous powder, $[\alpha]_D^{22}$: −21.5 ($CHCl_3$, $c=0.45$), UV (MeOH) λ_{max}: end absorption; IR (KBr) ν_{max}: 3400, 2910, 1725, 1370, 1270, 1032 cm^{-1}; EIMS *m/z* (rel. int.): 492[M]$^+$(2), 432[M−AcOH]$^+$(21), 414[M−AcOH-H_2O]$^+$(11), 372[M-2 × AcOH]$^+$(17), 312[M-3 × AcOH]$^+$(45), 294[M−3 × AcOH-H_2O]$^+$(47); ^{1}HNMR δ: 2.35 (1H, overlapped, H-1α), 2.14 (1H, overlapped, H-1β), 5.30 (1H, ddd, $J=12.4$, 4.4, 3.1 Hz, H-2α), 5.00 (1H, d, $J=3.1$ Hz, H-3α), 1.85 (1H, br s, H-5β), 3.33 (1H, d, $J=4.4$ Hz, H-6β), 3.00 (1H, d, $J=4.4$ Hz, H-7β), 1.91 (1H, br s, H-9β), 5.14 (1H, br d, $J=4.0$ Hz, H-11α), 2.70 (1H, dd, $J=14.2$, 5.0 Hz, H-12β), 2.34 (1H, d, $J=14.2$ Hz, H-12α), 3.00 (1H, d, $J=12.1$ Hz, H-14β), 2.15 (1H, d, $J=12.1$ Hz, H-14α), 4.44 (1H, br s, H-15α), 5.19 (1H, br s, H-17a), 5.18 (1H, br s, H-17b), 1.06 (3H, s, Me-18), 1.23 (3H, s, Me-19), 1.34 (3H, s, Me-20), 2.06, 1.91, 1.89 (each 3H, 3 × Ac), ^{13}CNMR see Table I.

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