ent-Kaurane Diterpenoids from *Isodon angustifolius* var. *glabresecens*

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Sixteen new *ent*-kaurane diterpenoids, glabcensins **A**−**P** (**1**−**16**), were isolated from the leaves of *Isodon angustifolius* var. *glabrescens*, and their structures were determined by detailed spectroscopic analyses.

Plants of genus *Isodon* (family Labiatae) have proved to be a rich source of diterpenoids, especially the highly oxidized *ent*-kaurane diterpenoids with various biological activity.[1−4] Our previous studies on the plants of this genus led to the isolation of more than 100 new diterpenoids.[5−8] As a continuation of our studies on the bioactive diterpenoids from this genus, we have investigated chemical constituents of *Isodon angustifolius* (Dunn) var. *glabrescens* X. W. Li, a perennial herb growing in the northwestern area of Yunnan province,[9] which has not been previously investigated chemically. From the dried leaves of this herb, sixteen new diterpenoids were isolated. This paper deals with the isolation and structure elucidation of these compounds.

Results and Discussion

Glabcensin A (**1**), $C_{28}H_{38}O_{10}$ ([M]$^+$ *m*/*z* 534), showed the presence of a hydroxyl group absorption (3420 cm^{-1}) in its IR spectrum. The major fragment ion peaks of EIMS (*m*/*z* 474, 414, 354, 294) resulting from [M−n × AcOH]$^+$ (n = 1, 2, 3, 4) clearly indicated that **1** contained four acetoxyl groups. This was consistent with its NMR data [δ 2.25 (s), 2.14 (s), 2.11 (s), and 1.96 (s) for acetyl methyls in the ^{1}H-NMR and at δ 170.84 (s), 169.64 (s), 169.48 (s), and 169.06 (s) for ester carbonyls in ^{13}C-NMR]. The ^{1}H- and ^{13}C-NMR spectral data of **1** showed the presence of three methyl groups, four methylene groups (including an *exo*-methylene group), eight methine groups (including five oxygenated methines), and a ketonic carbon. It was also suggested that it contained a ketone conjugated with an *exo*cyclic methylene group by the following spectral data: UV(MeOH) λ_{max} nm (log ϵ): 239 (5.88); IR (KBr)ν_{max}: 1725 and 1660 cm^{-1}; ^{1}H-NMR δ: 5.95, 5.23 (each 1H, br s), and ^{13}C-NMR δ: 204.62 (s), 149.62 (s), and 113.17 (t).

These data, together with a consideration of the structure of diterpenoids from the genus *Isodon*[10] suggested that **1** possessed a structure in which four acetoxyls and a hydroxyl were introduced to a basic skeleton, *ent*-kaur-16-en-15-one. The placement of the five oxygenated functional groups (four acetoxyl groups and one hydroxyl group) was aided 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 **1**, the following correlations were observed. The signal at δ 5.34 (1H, d, *J* = 2.6 Hz, H-3α) showed correlation with the signal at δ 4.51 (1H, ddd, *J* = 11.8, 4.0, 2.6 Hz, H-2α), the latter showed correlations with both the signal at δ 2.42 (1H, overlapped, H-1α) and the signal at δ 2.04 (1H, overlapped, H-1β). Thus, an acetoxyl group and a hydroxyl group should be located at the C-3 and C-2 positions, respectively, similar to the case of leukamenin A.[11] The stereochemistry was established as 2β-OH and 3β-OAc by considering the coupling constants of H-2 and H-3. The signal at δ 5.50 (1H, d, *J* = 3.4 Hz, H-7α) showed a correlation with the signal at δ 5.39 (1H, dd, *J* = 3.4, 1.8 Hz), and the latter showed a correlation with the signal at δ 2.40 (1H, br s, H-5β). These results suggested that two acetyl groups should be located at the C-6 and C-7 positions. The chemical shift of C-5 (δ 43.44 in the ^{13}C-NMR) showed an upfield shift owing to the strong γ-gauche effect of the C-3 and C-7 substituents,[12] which indicated that the acetoxy group at C-7 must be in the β-orientation. According to the coupling patterns of H-6 and H-5, the acetoxyl group at C-6 should be α-oriented. The downfield shift of C-19 (δ 23.57) and C-20 (δ 20.66) was attributed to a δ-syn−axial effect caused by the 6α-acetoxyl group,[13] which further supported the configuration of the C-6−OAc as α-oriented. The signal at δ 5.45 (1H, d, *J* = 4.2 Hz, H-11α) showed a correlation with the methylene protons H-12α [δ 2.00 (1H, ddd, *J* = 13.6, 4.2, 3.0 Hz)] and H-12β [δ 2.15 (1H, m)], and the latter showed cross peaks with the signal at δ 2.93 (1H, dd, *J* = 4.0, 3.0 Hz, H-13α). Thus, a acetoxyl group must be located at C-11 in a β-orientation.[14]

The unambiguous assignments of the oxygenated methenyl positions in **1** were achieved by an NOESY experiment; most of the NOESY correlations are shown by the arrows in Figure 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-6α and Me-18, H-7α and H-14β, and H-11α with the H-1α protons confirmed that the C-2 hydroxyl group, and the C-3, C-6, C-7, and C-11 acetoxyl groups have the 2β, 3β, 6α, 7β, and 11β orientations, respectively. Therefore, glabcensin A (**1**) was elucidated as *ent*-2α-hydroxy-3α,6β,7α,11α-tetraacetoxykaur-16-en-15-one.

Glabcensin B **(2)**, $C_{28}H_{38}O_{10}$ ([M]$^+$ *m*/*z* 534), an amorphous powder, possessed the same formula as **1** and showed very similar spectral data to those of **1**. It was presumed to be an isomer concerning the position of one acetoxy group. The signal at δ 4.51 (1H, ddd, *J* = 11.8, 4.0, 2.6 Hz) due to H-2α in **1** was shifted downfield to δ 5.58 (1H, ddd, *J* = 10.6, 4.4, 2.3 Hz), suggesting that the replacement of an acetoxyl group at the C-2β position in **2**. The signal at δ 5.34 (1H, d, *J* = 2.6 Hz) due to H-3α in **1** was shifted upfield to δ 3.86 (1H, d, *J* = 2.3 Hz), indicating the presence of a

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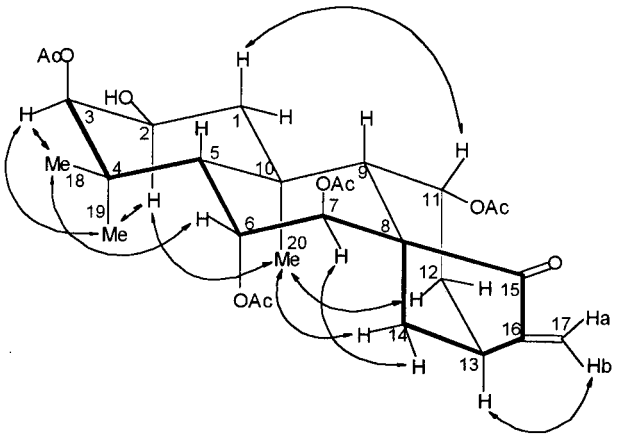


Figure 1. NOE effects observed in glabcensin A (**1**).

β-oriented hydroxyl group at the C-3 position in **2**. Therefore, glabcensin B (**2**) was elucidated as *ent*-3α-hydroxy-2α,6β,7α,11α-tetraacetoxykaur-16-en-15-one.

Glabcensin C **(3)**, $C_{26}H_{36}O_9$ ($[M]^+$ *m/z* 492), an amorphous powder, differed from **1** only in the lack of one acetyl group. The upfield shift of the H-6β from δ 5.39 (1H, dd, J = 3.4 1.8 Hz) in **1** to δ 4.34 (1H, dd, J = 3.5, 1.8 Hz) in **3** indicated that the hydroxyl group at the C-6α position in **3** had replaced the acetoxyl group in **1**. This conclusion was confirmed by the downfield shift of C-7 (δ 76.07) in **3** due to a β-downfield effect of the 6α-hydroxyl group.[15] Therefore, glabcesin C (**3**) was established as *ent*-2α,6β-dihydroxy-3α,7α,11α-triacetoxykaur-16-en-15-one.

Glabcensin D **(4)**, $C_{26}H_{36}O_9$ ($[M]^+$ *m/z* 492), was obtained as an amorphous powder. The ^{1}H- and ^{13}C-NMR spectra resembled to those of **2,** except for the presence of a hydroxyl group instead of an acetoxyl group at the C-7 position in **4**. The orientation of the hydroxyl group at C-7 was established as follows. The signal at δ 5.52 (1H, d, J = 3.5 Hz, H-7α) in **2** was shifted upfield to δ 4.03 (1H, d, J = 3.4 Hz) in **4**, which indicated that a β-oriented hydroxyl group was located at C-7 in **4**. As further proof of the presence of a 7β-hydroxyl group in **4**, C-15 (δ 212.98) showed a downfield shift owing to the presence of intramolecular hydrogen bonding between the β-oriented hydroxyl group at C-7 with the carbonyl group at C-15. On the basis of above evidences, glabcensin D (**4**) was represented as *ent*-3α,7α-dihydroxy-2α,6β,11α-triacetoxykaur-16-en-15-one.

Glabcensin E **(5)**, $C_{26}H_{36}O_9$ ($[M]^+$ *m/z* 492), an amorphous powder, differed from **1** only in the lack of one acetyl group. Comparison of the ^{1}H- and ^{13}C-NMR spectra revealed that the signals at δ 5.45 (1H, d, J = 4.2 Hz, H-11α) and δ 68.35 (d, C-11) in **1** were shifted upfield to δ 4.48 (1H, d, J = 4.3 Hz, H-11α) and δ 65.02 (d, C-11) in **5,** respectively, which indicated that a β-oriented hydroxyl group was attached to the C-11 position in **5**. Other noticeable differences between **1** and **5** were that the two signals at δ 55.78 (d, C-9) and δ 38.13 (t, C-12) in **1** were shifted downfield to δ 59.45 (d, C-9) and δ 40.97 (t, C-12) in **5** due to the replacement of a β-oriented hydroxyl group at C-11. Thus, glabcensin E (**5**) was characterized as *ent*-2α,11α-dihydroxy-3α,6β,7α-triacetoxykaur-16-en-15-one.

Glabcensin F (**6**), $C_{26}H_{36}O_9$ ($[M]^+$ *m/z* 492), was obtained as an amorphous powder. Its ^{1}H- and ^{13}C-NMR spectra showed very similar spectral data to those of **5,** except for the signals of ring A. Comparison of the ^{1}H- and ^{13}C-NMR spectra of **5** and **6** showed that the signals at δ 4.52 (1H, ddd, J = 11.8, 3.9, 2.8 Hz, H-2α) and δ 63.94 (d, C-2) in **5** were shifted downfield to δ 5.56 (1H, ddd, J = 12.2, 3.9, 2.7 Hz, H-2α) and δ 70.89 (d, C-2) in **6**, respectively. The two signals at δ 5.35 (1H, d, J = 2.8 Hz, H-3α) and δ 81.50 (d, C-3) in **5** were shifted upfield to δ 3.82 (1H, d, J = 2.7 Hz, H-3α) and δ 76.69 (d, C-3) in **6**, respectively. This suggested that a hydroxyl group and an acetoxyl group should be located at the C-2β and C-3β positions, respectively. Thus, glabcensin F (**6**) was determined as *ent*-3α,11α-dihydroxy-2α,6β,7α-triacetoxykaur-16-en-15-one.

Glabcensin G (**7**), $C_{26}H_{36}O_9$ ($[M]^+$*m/z* 492), was obtained as an amorphous powder. It showed similar spectral data to those of **6** and was presumed to be an isomer concerning the position of one of the acetoxy group. Examination of the ^{1}H-NMR spectra of **7** and **6** revealed that the signal at δ 3.82 (1H, d, J = 2.7 Hz, H-3α) in **6** was shifted downfield to δ 5.30 (1H, d, J = 3.0 Hz, H-3α) in **7**. The signal at δ 5.51 (1H, dd, J = 3.6, 1.8 Hz H-6) in **6** was shifted upfield to δ 4.41 (1H, dd, J = 3.5, 1.8 Hz, H-6) in **7**. From these data, an acetoxy group and a hydroxyl group should be located at the C-3β position and at the C-6α position, respectively. Therefore, glabcensin G (**7**) was elucidated as *ent*-6β,11α-dihydroxy-2α,3α,7α-triacetoxykaur-16-en-15-one.

Glabcensin H (**8**), $C_{24}H_{34}O_8$ ($[M]^+$*m/z* 450), was an amorphous powder, differing from **7** only in the absence of one acetyl group. The upfield shift of H-3α from δ 5.30 (1H, d, J = 3.0 Hz) in **7** to δ 3.87 (1H, d, J = 2.5 Hz) in **8** indicated that a hydroxyl group at the C-3β position in **8** had replaced the acetoxyl group in **7**. Therefore, glabcensin H (**8**) was established as *ent*-2α,7α-diacetoxy-3α,6β,11α-trihydroxykaur-16-en-15-one.

Glabcensin I (**9**), $C_{24}H_{34}O_8$ ($[M]^+$*m/z* 450), an amorphous powder, differed from **7** only in the absence of one acetyl group. The upfield shift of H-2α from δ 5.63 (1H, ddd, J = 12.0, 3.5, 3.0 Hz) in **7** to δ 4.65 (1H, ddd, J = 11.8, 3.7, 3.2 Hz) in **9** indicated that the hydroxyl group at C-2β position in **9** replaced the acetoxy group at C-2 in **7**. This conclusion was confirmed by the downfield shift of C-1 (δ 45.24) in **9** due to the presence of a C-2β hydroxyl group. Therefore, glabcensin H (**9**) was elucidated as *ent*-3α,7α-diacetoxy-2α,6β,11α-trihydroxykaur-16-en-15-one.

Glabcensin J **(10)**, $C_{22}H_{32}O_6$, was an amorphous powder. The ^{1}H- and ^{13}C-NMR spectra resembled those of **5 ,** except for the presence of a hydroxyl group (instead of an acetoxy group at C-3) and the lack of an oxygenated substituent at C-7. In the ^{13}C-NMR spectrum of **10**, the downfield shift of C-5 (δ 50.19) verified that there was no oxygenated substituent at C-7β. Examination of the ^{1}H-NMR spectrum of **10** showed that the signal at δ 5.35 (1H, d, J = 2.8 Hz, H-3α) in **5** was shifted to δ 4.64 (1H, d, J = 2.3 Hz, H-3α) in **10**. This revealed that the hydroxyl group at C-3 in **10** had replaced the acetoxyl group at C-3 in **5**. Therefore, glabcensin J (**10**) was represented by *ent*-6β-acetoxy-2α,3α,11α-trihydroxykaur-16-en-15-one.

Glabcensin K (**11**), $C_{24}H_{36}O_8$ ($[M]^+$ *m/z* 452), an amorphous powder, showed similar spectral data to those of glabcensin I (**9**). This compound showed no

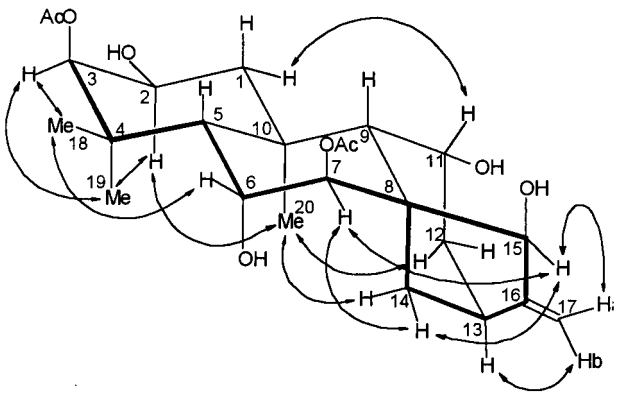


Figure 2. NOE effects observed in glabcensin K (**11**).

characteristic absorption bands above 220 nm in its UV spectrum, but showed the presence of an exocyclic methylene moiety [δ 5.33, 5.14 (each 1H, br s, H-17) in its ^{1}H-NMR spectrum; δ 158.9 (s), 105.83 (t) in its ^{13}C-NMR spectrum]. Its mass spectrum showed a molecular ion at *m/z* 452, two mass units more than that of **9**. This suggested that glabcensin K (**11**) should have a structure corresponding to dihydroglabcensin I in which the ketone group at C-15 was reduced to an allylic alcohol. The upfield shift of C-9 (δ 53.21) due to the γ-steric compression effect between 15β-OH and C-9, suggested that the configuration of the hydroxyl group at C-15 was determined as β-oriented.[16]

The unambiguous assignment of the oxygenated methylene positions in **11** were achieved by a NOESY experiment, most of the NOESY correlations are shown by the arrows in Figure 2. Observation of the NOESY correlation between the H-15α with H-7α and H-14β, and the H-17α protons conformed that the C-15 hydroxyl group has the 15β orientation. Therefore, glabcensin K (**11**) was elucidated as *ent*-3α,7α-diacetoxy-2α,6β,11α,15α-tetrahydroxykaur-16-ene.

Glabcensin L **(12)**, $C_{26}H_{38}O_9$ ([M]$^+$ *m/z* 494), was obtained as amorphous powder from this plant. Its mass spectrum showed a molecular ion (*m/z* 494) two amu more than that of **3**. The ^{1}H- and ^{13}C-NMR spectra of **12** were very similar to those of **3**, and the only observed differences were that **12** has one more hydroxyl group and the absence of one ketone carbonyl group. Inspection of the ^{1}H- and ^{13}C-NMR data of **12**, suggested that the additional hydroxyl group was assigned to the 15β-position. The upfield shift of C-9 (δ 50.34) of **12** is attributed to the γ-steric compression effect between the C-15β-OH and C-9, similar to the case of **11**. Comparison of the ^{13}C-NMR spectrum of **12** with that of **3**, indicated the downfield shift of C-7 (δ 82.03) was ascribed to the absence of the C-15 ketone group. Thus, glabcensin L (**12**) was established as *ent*-3α,7α,11α-triacetoxy-2α,6β,15α-trihydroxykaur-16-ene.

Glabcensin M (**13**), $C_{26}H_{38}O_9$ ([M]$^+$ *m/z* 494), was an amorphous powder, whose ^{1}H- and ^{13}C-NMR spectra were very similar to those of **11**, except that **13** had one more acetyl group than **11**. The downfield shift of the H-6β signal from δ 4.45 (1H, dd, J = 3.2, 1.8 Hz) in **11** to δ 5.49 (1H, dd, J = 3.1, 1.6 Hz) in **13** indicated that the acetoxyl group at C-6 in **13** had replaced the hydroxyl group at C-6 in **11**. This was supported by the upfield shift of C-7 (δ 76.82) due to the presence of an acetoxyl group at C-6α. Thus, glabcensin M (**13**) was determined as *ent*-3α,6β,7α-triacetoxy-2α,11α,15α-trihydroxykaur-16-ene.

Glabcensin N **(14)**, $C_{30}H_{42}O_{11}$, an amorphous powder, showed similar spectral data to those of **13**. This compound showed no characteristic UV absorption above 220 nm and no ketone carbonyl signals in its ^{13}C-NMR spectrum, but showed the presence of an exocyclic methylene moiety [δ 5.26, 5.04 (each 1H, br s, H$_2$-17) in its ^{1}H-NMR spectrum; δ 158.16 (s), 105.90 (t) in its ^{13}C-NMR spectrum]. The difference between **14** and **13** was that **14** had two more acetyl groups than **13**. This conclusion was reached by comparison of the ^{1}H and ^{13}C NMR of **14** with those of **13.** The signals at δ 4.95 (1H, d, J = 4.8 Hz, H-11α) and δ 65.05 (d, C-11) in **13** were shifted downfield to δ 5.38 (1H, d, J = 4.2 Hz, H-11α) and δ 68.76 (d, C-11) in **14** due to acetylation. Other differences between **14** and **13** were that signals at δ 4.56 (1H, ddd, J = 12.0, 4.0, 2.9 Hz, H-2α) and δ 64.19 (d, C-2) in **13** were shifted downfield to δ 5.53 (1H, ddd, J = 11.8, 4.0, 2.8 Hz, H-2α) and δ 67.24 (d, C-2), respectively, in **14**, which suggested that an acetoxyl group at C-2α in **14** replaced the hydroxyl group in **13**. According to the upfield shift of C-9 (δ 49.45) due to the γ-steric compression effect between 15β-OH and C-9, the configuration of the hydroxyl group at C-15 was determined as β. Thus, glabcensin N (**14**) was elucidated as *ent*-15α-hydroxy-2α,3α,6β,7α,11α-pentaacetoxykaur-16-ene.

Glabcensin O **(15)**, $C_{29}H_{42}O_{11}$, an amorphous powder, showed no characteristic UV or IR absorption bands for an α,β-unsaturated ketone group. The ^{1}H- and ^{13}C-NMR spectral data of **15** were similar to those of **4**. Comparison of the ^{1}H- and ^{13}C-NMR spectral data with those of **4** revealed that the exocyclic methylene group at C-17 in **4** were replaced by a methoxymethyl group in **15**, as judged from the following spectral data of **15**: the signals at δ 3.36 (3H, s, OMe), 3.99 (1H, dd, J = 10.4, 4.3 Hz, H-17a), and 3.85 (1H, dd, J = 10.4, 8.2 Hz, H-17b) in the ^{1}H-NMR spectrum and the signals at δ 56.45 (d, C-16), 70.17 (t, C-17), and 58.56 (q, OMe). The methoxymethyl group should have a β-orientation based on the abnormal upfield shift of C-13 (δ 32.92) due to the γ-steric compression effect[16] between the 16β-methoxymethyl group and C-13. Another difference between **4** and **15** was that the signal at δ 3.85 (1H, d, J = 2.4 Hz, H-3α) in **4** was shifted downfield to δ 5.30 (1H, d, J = 2.6 Hz, H-3α), which indicated that the acetoxyl group at C-3 in **15** had replaced the hydroxyl group at C-3 in **4**.

The unambiguous assignment of the oxygenated methylene positions in **15** were achieved by an NOESY experiment, most of the NOESY correlations are shown by the arrows in Figure 3. Observation of the NOESY correlation between the H-16α with H-13α and H-14β, and the H$_2$-17 protons confirmed that the C-16 methoxymethyl group has the 16β orientation. Therefore, glabcensin O (**15**) was represented as *ent*-7α-hydroxyl-16α-methoxymethyl-2α,3α,6β,11α-tetraacetoxykaur-15-one.

Glabcensin P **(16)**, $C_{27}H_{40}O_{10}$, an amorphous powder, differed from **15** only in the absence of an acetyl group. The H-2α signal at δ 5.57 (1H, ddd, J = 12.4, 4.0, 2.6 Hz, H-2α) in **15** was shifted upfield to δ 4.55 (1H, ddd, J = 11.8, 4.1, 2.8 Hz, H-2α) in **16**, which indicated that a hydroxyl group at C-2 in **16** had replaced the acetoxyl group at C-2 in **15**. Glabcensin P (**16**) was thus

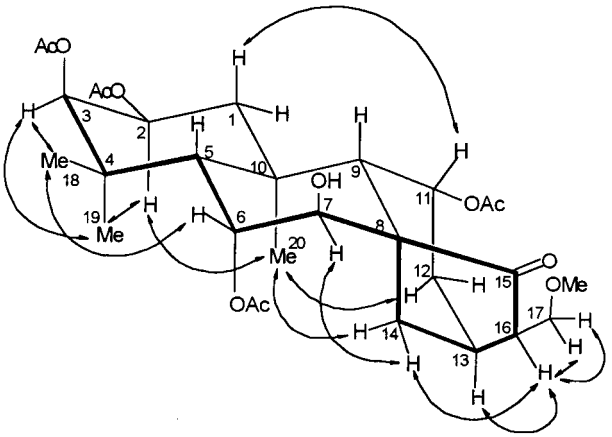


Figure 3. NOE effects observed in glabcensin O (**15**).

established as *ent*-2α,7α-dihydroxy-16α-methoxymethyl-3α,6*β*,11α-triacetoxykaur-15-one.

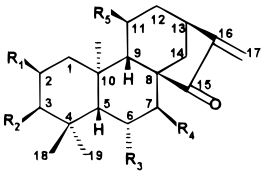
Experimental Section

General Experimental Procedures. All the mps 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}H-NMR, ^{1}H−^{1}H COSY, NOESY spectra were recorded at 400.13 MHz; ^{13}C-NMR and DEPT spectra were recorded at 100.6 MHz. ^{13}C-NMR 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-300 Spectrometer.

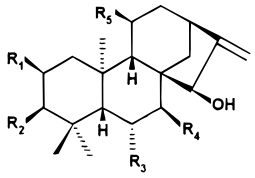
Plant Material. Plant material was collected in Dali County of Yunnan Province in September 1993, and identified as *I. angustifolius* (Dunn) var. *glabrescens* by Prof. Li Xi-Wen. A voucher specimen is deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany.

Extraction and Isolation. Dried leaves (3 kg) of *I. angustifoliu* 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 Si gel (200−300 mesh, 1.5 kg). The column was eluted with $CHCl_3$−Me_2CO (9.5: 0.5, 9:1, 8:2, 7:3, 6:4) and Me_2CO. The eluates 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 employing HPLC) and recystallized to give compounds **1**−**16**.

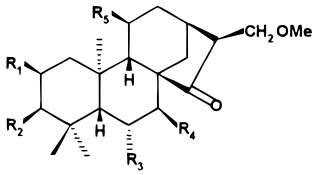
Glabcensin A (1): obtained as colorless crystals, mp 198−199 °C (MeOH); $[\alpha]^{22}_D$ −74.9° (*c* 0.57, MeOH); UV-(MeOH) λ_{max} (log ϵ) 239 (5.88) nm; IR (KBr) ν_{max} 3420, 2910, 1725, 1660, 1450, 1400, 1280, 1060 cm^{-1}; ^{1}H NMR (pyridine-d_5, 400 MHz) δ 2.42 (1H, overlapped, H-1α), 2.04 (1H, overlapped, H-1*β*), 4.51 (1H, ddd, J = 11.8, 4.0, 2.6 Hz, H-2α), 5.34 (1H, d, J = 2.6 Hz, H-3α), 2.40 (1H, br s, H-5*β*), 5.39 (1H, dd, J = 3.4, 1.8 Hz, H-6*β*), 5.50 (1H, d, J = 3.4 Hz, H-7α), 2.37 (1H, br s, H-9*β*), 5.45 (1H, d, J = 4.2 Hz, H-11α), 2.15 (1H, m, H-12*β*), 2.00 (1H, ddd, J = 13.6, 4.2, 3.0 Hz, H-12α), 2.93 (1H, dd, J = 4.0, 3.0 Hz, H-13α), 2.64 (1H, d, J = 12.4 Hz, H-14α), 1.45 (1H, dd, J = 12.4, 4.0 Hz, H-14*β*), 5.95 (1H, br s, H-17a), 5.23 (1H, br s, H-17b), 1.05 (3H, s, Me-18), 1.10 (3H, s, Me-19), 1.48 (3H, s, Me-20), 2.25, 2.14, 2.07, 1.96 (each 3H, s, 4 × Ac); EIMS (70eV) m/z 535 [M + 1]$^+$(2), 534 [M]$^+$(2), 474 [M − AcOH]$^+$ (15), 459 [M − AcOH − Me]$^+$ (10), 432 [M − AcOH − $COCH_2$]$^+$(35), 414 [M − 2 × AcOH]$^+$(40), 354 [M − 3 × AcOH]$^+$(50), 297 (93), 279 (100), 255 (87), 228 (80); ^{13}C NMR, see Table 1.



1: R_1=OH, R_2=OAc, R_3=OAc, R_4=OAc, R_5=OAc
2: R_1=OAc, R_2=OH, R_3=OAc, R_4=OAc, R_5=OAc
3: R_1=OH, R_2=OAc, R_3=OH, R_4=OAc, R_5=OAc
4: R_1=OAc, R_2=OH, R_3=OAc, R_4=OH, R_5=OAc
5: R_1=OH, R_2=OAc, R_3=OAc, R_4=OAc, R_5=OH
6: R_1=OAc, R_2=OH, R_3=OAc, R_4=OAc, R_5=OH
7: R_1=OAc, R_2=OAc, R_3=OH, R_4=OAc, R_5=OH
8: R_1=OAc, R_2=OH, R_3=OH, R_4=OAc, R_5=OH
9: R_1=OH, R_2=OAc, R_3=OH, R_4=OAc, R_5=OH
10: R_1=OH, R_2=OH, R_3=OAc, R_4=H, R_5=OH



11: R_1=OH, R_2=OAc, R_3=OH, R_4=OAc, R_5=OH
12: R_1=OH, R_2=OAc, R_3=OH, R_4=OAc, R_5=OAc
13: R_1=OH, R_2=OAc, R_3=OAc, R_4=OAc, R_5=OH
14: R_1=OAc, R_2=OAc, R_3=OAc, R_4=OAc, R_5=OAc



15: R_1=OAc, R_2=OAc, R_3=OAc, R_4=OH, R_5=OAc
16: R_1=OH, R_2=OAc, R_3=OAc, R_4=OH, R_5=OAc

Glabcensin B (2): obtained as an amorphous powder; $[\alpha]^{22}_D$ −54.7° (*c* 0.51, MeOH); UV(MeOH) λ_{max} (log ϵ) 237.5 (5.86) nm; IR (KBr) ν_{max} 3500, 2920, 1730, 1640, 1370, 1245, 1045 cm^{-1}; ^{1}H NMR (pyridine-d_5, 400 MHz) δ 6.86 (1H, br s, OH, D_2O exchangeable), 5.58 (1H, ddd, J = 10.6, 4.2, 2.3 Hz, H-2α), 3.86 (1H, d, J = 2.3 Hz, H-3α), 2.73 (1H, br s, H-5*β*), 5.49 (1H, dd, J = 3.5, 1.2 Hz, H-6*β*), 5.52 (1H, d, J = 3.5 Hz, H-7α), 2.41 (1H, br s, H-9*β*), 5.39 (1H, d, J = 4.4 Hz, H-11α), 2.91 (1H, br s, H-13α), 2.65 (1H, d, J = 12.4 Hz, H-14α), 5.95 (1H, br s, H-17a), 5.33 (1H, br s, H-17b), 1.17 (3H, s, Me-18), 1.32 (3H, br s, Me-19), 1.50 (3H, br s, Me-20), 2.12, 2.06, 1.78, 1.73 (each 3H, s, 4 × Ac); EIMS (70eV) m/z 535 [M + 1]$^+$(2), 474 [M − AcOH]$^+$(8), 432 [M − AcOH −

Table 1. ^{13}C-NMR Data of Compounds **1**−**5** (Pyridine-d_5)

C	1	2	3	4	5
1	45.14 t	39.47 t	45.45 t	40.20 t	44.95 t
2	63.61 d	68.24 d	64.17 d	68.42 d	63.94 d
3	81.25 d	76.58 d	81.81 d	76.72 d	81.50 d
4	38.44 s	39.47 s	38.80 s	39.51 s	38.42 s
5	43.44 d	42.10 d	44.24 d	40.55 d	43.42 d
6	69.98 d	70.63 d	68.60 d	72.06 d	70.37 d
7	71.41 d	71.60 d	76.07 d	73.14 d	71.75 d
8	49.70 s	48.62 s	49.14 s	50.18 s	48.63 s
9	55.78 d	55.80 d	56.27 d	55.36 d	59.45 d
10	39.70 s	40.26 s	39.13 s	39.96 s	39.48s
11	68.35 d	68.24 d	68.73 d	68.42 d	65.02d
12	38.13 t	38.15 t	38.50 t	37.46 t	40.97 t
13	36.75 d	36.78 d	37.00d	37.00 d	37.52 d
14	35.12 t	35.15 t	35.39 t	34.58 t	35.67 t
15	204.62 s	204.54 s	204.34 s	212.98 s	204.94 s
16	149.62 s	150.40 s	150.91 s	150.17 s	151.24 s
17	113.17 t	112.95 t	112.44 t	114.30 t	111.29 t
18	28.28 q	29.43 q	28.71 q	29.42 q	28.31q
19	23.57 q	23.43 q	24.09 q	23.65 q	23.54 q
20	20.66 q	20.60 q	20.48 q	21.23 q	20.79 q
Ac	170.84 s	170.55 s	170.96 s	170.57 s	170.80 s
	169.64 s	169.63 s	170.16 s	169.82 s	169.70 s
	169.48 s	169.62 s	169.02 s	168.89 s	169.52 s
	169.06 s	169.00 s	21.48 q	21.30 q	21.38 q
	21.21 q	21.21 q	21.20 q	21.13 q	21.25 q
	21.21 q	21.21 q	20.90 q	21.13 q	20.96 q
	21.01 q	20.84 q			
	21.01 q	20.84 q			

Table 2. ^{13}C-NMR Data of Compounds **6**−**10** (Pyridine-d_5)

C	6	7	8	9	10
1	41.15 t	41.12 t	41.37 t	45.24 t	43.44 t
2	70.89 d	68.29 d	69.59 d	64.30 d	65.34 d
3	76.69 d	78.25 d	77.15 d	82.04 d	78.32 d
4	39.46 s	38.68 s	39.80 s	38.79 s	39.11 s
5	42.14 d	44.15 d	42.96 d	44.20 d	50.09 d
6	71.01 d	68.95 d	71.48 d	69.09 d	68.83 d
7	71.93 d	76.16 d	76.56 d	76.38 d	41.60 t
8	48.61 s	48.98 s	49.15 s	49.13 s	49.30 s
9	59.40 d	59.64 d	59.95 d	59.97 d	64.28 d
10	39.67 s	39.66 s	39.93 s	39.67 s	40.00 s
11	65.01 d	63.24 d	65.34 d	65.31 d	65.65 d
12	40.30 t	41.42 t	40.59 t	41.17 t	41.60 t
13	37.47 d	37.69 d	37.74d	37.77 d	38.24 d
14	35.68 t	36.68 t	36.71 t	36.66 t	38.85 t
15	204.80 s	206.01 s	205.96 s	206.04 s	203.00 s
16	151.27 s	151.66 s	151.84 s	151.81 s	151.42 s
17	111.27 t	110.92 t	110.69 t	110.63 t	111.14 t
18	29.46 q	28.47 q	29.90 q	28.71 q	28.10 q
19	23.55 q	23.82 q	24.51 q	24.07 q	23.43 q
20	20.83 q	20.72 q	21.07 q	20.59 q	20.20 q
Ac	170.55 s	170.58 s	170.60 s	170.92 s	170.59 s
	169.74 s	170.42 s	170.60 s	170.20 s	21.00 q
	169.74 s	170.25 s	21.61 q	21.57 q	
	21.32 q	21.60 q	21.30 q	21.01 q	
	21.32 q	21.11 q			
	21.32 q	20.72 q			

$COCH_2]^+$(41), 414 [M − 2 × AcOH]$^+$(28), 390 (65), 312 (70), 297 (82), 179 (74), 255 (100); ^{13}C-NMR, see Table 1.

Glabcensin C (3): obtained as an amorphous compound; $[\alpha]^{22}_D$ −28.5° (*c* 0.57, $CHCl_3$); UV(MeOH) λ_{max} (log ϵ) 230 (6.25) nm; IR (KBr) ν_{max} 3400, 2905, 1720, 1630, 1370, 1240, 1020 cm^{-1}; ^{1}H NMR (pyridine-d_5, 400 MHz) δ 7.05 (1H, br s, OH, D_2O exchangable), 6.95 (1H, OH, D_2O exchangeable), 4.64 (1H, ddd, J = 11.6, 3.9, 2.4 Hz, H-2α), 5.45 (1H, d, J = 2.4 Hz, H-3α), 2.43 (1H, br s, H-5β), 4.34 (1H, dd, J = 3.5, 1.8 Hz, H-6β), 5.59 (1H, d, J = 3.5 Hz, H-7α), 2.26 (1H, br s, H-9β), 5.52 (1H, d, J = 4.6 Hz, H-11α), 2.92 (1H, br s, H-13α), 3.08 (1H, d, J = 12.8 Hz, H-14α), 5.95 (1H, br s, H-17a), 5.24 (1H, br s, H-17b), 1.10 (3H, s, Me-18), 1.10 (3H, s, Me-19), 1.53 (3H, s, Me-20), 2.26, 2.12, 1.96 (each 3H, 3 × Ac); EIMS (70eV) *m*/*z* [M]$^+$ 492 (10), 474 [M − H_2O]$^+$-(15), 432 [M − AcOH]$^+$(80), 414 [M − AcOH − H_2O]$^+$-(100); ^{13}C NMR, see Table 1.

Glabcensin D (4): obtained as amorphous compound; $[\alpha]^{22}_D$ −37.9° (*c* 0.44, $CHCl_3$); UV(MeOH) λ_{max} (log ϵ) 238.5 (5.83) nm; IR (KBr) ν_{max} 3420, 2920, 1725, 1635, 1372, 1230, 1035 cm^{-1}; ^{1}H NMR δ 6.75 (1H, br s, OH, D_2O exchangeable), 5.57 (1H, ddd, J = 12.1, 3.9, 2.4 Hz, H-2α), 3.85 (1H,d, J = 2.4 Hz, H-3α), 2.99 (1H, br s, H-5β), 5.67 (1H, dd, J = 3.4, 1.6 Hz, H-6β), 4.03 (1H, d, J = 3.4 Hz, H-7α), 2.32 (1H, br s, H-9β), 5.51 (1H, d, J = 4.4 Hz, H-11α), 2.96 (1H, br s, H-13α), 2.56 (1H, d, J = 12.5 Hz, H-14α), 5.96 (1H, br s, H-17a), 5.55 (1H, br s, H-17b), 1.18 (3H, s, Me-18), 1.33 (3H, s, Me-19), 1.77 (3H, s, Me-20), 2.12, 1.88, 1.80 (each 3H, s, 3 × Ac); EIMS (70eV) *m*/*z* 492 [M]$^+$(5), 432 [M − AcOH]$^+$(30), 372 [M − 2 × AcOH]$^+$(40), 312 [M − 3 × AcOH]$^+$(100), 294 [M − 3 × AcOH − H_2O]$^+$(65), 255 (95); ^{13}C NMR, see Table 1.

Glabcensin E (5): obtained as an amorphous powder; $[\alpha]^{22}_D$ −46.9° (*c* 0.46, MeOH); UV(MeOH) λ_{max} (log ϵ) 237 (5.90) nm; IR (KBr) ν_{max} 3400, 2910, 1725, 1650, 1450, 1250, 1040, 1037 cm^{-1}; ^{1}H NMR δ 4.52 (1H,ddd, J = 11.8, 3.9, 2.8 Hz, H-2α), 5.35 (1H, d, J = 2.8 Hz, H-3α), 2.65 (1H, br s, H-5β), 5.46 (1H, dd, J = 3.4, 2.0 Hz, H-6β), 5.52 (1H, d, J = 3.4 Hz, H-7α), 2.37 (1H, br s, H-9β), 4.48 (1H, d, J = 4.3 Hz, H-11α), 2.97 (1H, br s, H-13α), 2.67 (1H, d, J = 12.8 Hz, H-14α), 5.93 (1H, s, H-17a), 5.22 (1H, s, H-17b), 1.04 (3H, s, Me-18), 1.13 (3H, s, Me-19), 1.51 (3H, s, Me-20), 2.22, 2.02, 1.97 (each 3H, s, 3 × Ac); EIMS (70eV) *m*/*z* 492 [M]$^+$(2), 432 [M − AcOH]$^+$(5), 372 [M − 2 × AcOH]$^+$(15), 312 [M − 3 × AcOH]$^+$(20), 297 [M − 3 × AcOH − Me]$^+$(95), 294 [M − 3 × AcOH − H_2O]$^+$(65), 255 (95); ^{13}C NMR, see Table 1.

Glabcensin F (6): obtained as an amorphous powder; $[\alpha]^{22}_D$ −39.2° (*c* 0.49, $CHCl_3$); UV(MeOH) λ_{max} (log ϵ) 238 (5.85) nm; IR (KBr) ν_{max} 3450, 2905, 1720, 1645, 1360, 1240, 1035 nm; ^{1}H-NMR (pyridine-d_5, 400 MHz) δ 6.62, 6.19, (each 1H, br s, 2 × OH, D_2O exchangeable), 5.56 (1H, ddd, J = 12.2, 3.9, 2.7 Hz, H-2α), 3.82 (1H, d, J = 2.7 Hz, H-3α), 2.72 (1H, br s, H-5β), 5.51 (1H, dd, J = 3.6, 1.8 Hz, H-6β), 5.58 (1H, d, J = 3.6 Hz, H-7α), 2.68 (1H, br s, H-9β), 4.43 (1H, d, J = 4.2 Hz, H-11α), 2.98 (1H, br s, H-13α), 2.70 (1H, d, J = 12.4 Hz, H-14α), 5.89 (1H, s, H-17a), 5.23 (1H, s, H-17b), 1.19 (3H, s, Me-18), 1.23 (3H, s, Me-19), 1.60 (3H, s, Me-20), 2.15, 2.16, 1.96 (each 3H, s, 3 × Ac); EIMS (70eV) *m*/*z* 492 [M]$^+$(1), 432 [M − AcOH]$^+$(5), 390 [Me-AcOH − $COCH_2$]$^+$(100), 372 [M − 2 × AcOH]$^+$(15), 312 [M − 3 × AcOH]$^+$(30), 297 [M − 3 × AcOH − Me]$^+$(70), 294 [M − 3 × AcOH − H_2O]$^+$ (65), 279 (50), 255 (95); ^{13}C NMR, see Table 2.

Glabcensin G (7): obtained amorphous powder; $[\alpha]^{22}_D$ −11.1° (*c* 0.45, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 239 (5.81) nm; IR (KBr) ν_{max} 3410, 2920, 1710, 1645, 1370, 1250, 1030 cm^{-1}; ^{1}H NMR (pyridine-d_5, 400 MHz) δ 6.94, 6.85 (each 1H, br s, 2 × OH, D_2O exchangeable), 5.63 (1H, ddd, J = 12.0, 3.5, 3.0 Hz, H-2α), 5.30 (1H, d, J = 3.0 Hz, H-3α), 2.61 (1H, br s, H-5β), 4.41 (1H, br s, J = 3.5 Hz, H-6β), 2.34 (1H, br s, H-9β), 4.30 (1H, d, J = 4.4 Hz, H-11α), 3.00 (1H, br s, H-13α), 3.10 (1H, d, J = 12.4 Hz, H-14α), 5.93 (1H, br s, H-17a), 5.21 (1H, br s, H-17b), 1.00 (3H, s, Me-18), 1.60 (3H, s, Me-19), 1.80 (3H, s, Me-20), 2.29, 2.14, 2.00 (each 3H, s, 3 × Ac);

EIMS (70eV) *m/z* 492 $[M]^+$(2), 432 $[M - AcOH]^+$(43), 372 $[M - 2 \times AcOH]^+$(18), 312 $[M - 3 \times AcOH]^+$(100), 297 $[M - 3 \times AcOH - Me]^+$(80), 279 $[M - 3 \times AcOH - H_2O - Me]^+$(50); ^{13}C NMR, see Table 2.

Glabcensin H (8): obtained as an amorphous powder; $[\alpha]^{22}_D$ −16.1° (*c* 0.53, $CHCl_3$); UV(MeOH) λ_{max} (log ϵ) 239 (5.46) nm; IR (KBr) ν_{max} 3400, 2920, 1725, 1645, 1370, 1245, 1032 cm^{-1}; ^1H-NMR δ 6.90, 6.36, 6.00 (each 1H, br s, 3 × OH, D_2O exchangeable), 5.72 (1H, ddd, *J* = 11.6, 4.0, 2.5 Hz, H-2α), 3.87 (1H, d, *J* = 2.5 Hz, H-3α), 2.76 (1H, br s, H-5*β*), 4.45 (1H, dd, *J* = 3.3, 1.8 Hz, H-6*β*), 5.64 (1H, d, *J* = 3.3 Hz, H-7α), 2.60 (1H, s, H-9*β*), 4.44 (1H, d, *J* = 4.3 Hz, H-11α), 3.00 (1H, br s, H-13α), 3.16 (1H, d, *J* = 12.5 Hz, H-14α), 5.89 (1H, br s, H-17a), 5.20 (1H, br s, H-17b), 1.35 (3H, s, Me-18), 1.67 (3H, s, Me-19), 1.83 (3H, s, Me-20), 2.20, 1.94 (each 3H, s, 2 × Ac); EIMS (70eV) *m/z* 450 $[M]^+$(2), 390 $[M - AcOH]^+$-(42), 315 $[M - 2 \times AcOH - Me]^+$(80), 297 $[M - 2 \times AcOH - H_2O - Me]^+$ (100); ^{13}C NMR, see Table 2.

Glabcensin I (9): obtained as an amorphous powder; $[\alpha]^{22}_D$ −39.6° (*c* 0.52, MeOH); UV(MeOH) λ_{max} (log ϵ) 240 (5.49) nm; IR (KBr) ν_{max} 3490, 2910, 1715, 1640, 1370, 1250, 1050, 1030 cm^{-1}; ^1H NMR δ 6.95, 6.32, 6.10 (each 1H, br s, 3 × OH, D_2O exchangeable), 4.65 (1H, ddd, *J* = 11.8, 3.7, 3.2 Hz, H-2α), 5.40 (1H, d, *J* = 3.2 Hz, H-3α), 2.73 (1H, br s, H-5*β*), 4.54 (1H, d, *J* = 3.3, 1.7 Hz, H-6*β*), 5.41 (1H, d, *J* = 3.3 Hz, H-7α), 2.36 (1H, br s, H-9*β*), 4.40 (1H, d, *J* = 4.3 Hz, H-11α), 2.74 (1H, br s, H-13α), 3.16 (1H, d, *J* = 12.5 Hz, H-14α), 5.90 (1H,-br s, H-17a), 5.07 (1H, br s, H-17b), 1.06 (3H, s, Me-18), 1.52 (1H, s, Me-19), 1.71 (1H, s, Me-20), 2.26, 2.20 (each 3H, s, 2 × Ac); EIMS (70eV) *m/z* 450 $[M]^+$(1), 390 $[M - AcOH]^+$(18), 330 $[M - 2 \times AcOH]^+$(25), 315 $[M - 2 \times AcOH - Me]^+$(40), 297 $[M - 2 \times AcOH - H_2O\text{-}Me]^+$ (55); ^{13}C NMR, see Table 2.

Glabcensin J (10): obtained as an amorphous powder; $[\alpha]^{22}_D$ −32.4° (*c* 0.48, $CHCl_3$); UV(MeOH) λ_{max} (log ϵ) 239 (5.27) nm; IR (KBr) ν_{max} 3400, 2920, 1725, 1635, 1365, 1225, 1032 cm^{-1}; ^1H NMR δ 4.33 (1H, ddd, *J* = 11.5, 3.9, 2.3 Hz, H-2α), 4.64 (1H, d, *J* = 2.3 Hz, H-3α), 5.63 (1H, dd, *J* = 3.8, 1.7 Hz, H-6*β*), 4.40 (1H, d, *J* = 3.8 Hz, H-11α), 3.06 (1H, d, *J* = 12.1 Hz, H-14α), 6.02 (1H, br s, H-17a), 5.26 (1H, br s, H-17b), 1.04 (3H, s, Me-18), 1.61 (3H, s, Me-19), 1.75 (3H, s, Me-20), 2.00 (3H, s, Ac); EIMS (70eV) *m/z* 392 $[M]^+$(3), 374 $[M - H_2O]^+$(28), 356 $[M - 2 \times H_2O]^+$(20), 341 $[M - 2 \times H_2O\text{-}Me]^+$(15), 314 $[M - AcOH - H_2O]^+$(65), 296 $[M - AcOH - 2 \times H_2O]^+$(55); ^{13}C NMR, see Table 2.

Glabcensin K (11): obtained as an amorphous powder; $[\alpha]^{22}_D$ −34.5° (*c* 0.52, MeOH); IR (KBr) ν_{max} 3400, 2910, 1705, 1372, 1250, 1030 cm^{-1}; ^1H NMR δ 6.85, 6.80, 6.45 (each 1H, br s, 3 × OH, D_2O exchangeable), 4.67 (1H, ddd, *J* = 11.8, 3.8, 3.0 Hz , H-2α), 5.33 (1H, d, *J* = 3.0 Hz, H-3α), 2.66 (1H, br s, H-5*β*), 4.45 (1H, dd, *J* = 3.2, 1.8 Hz, H-6*β*), 5.45 (1H, d, *J* = 3.2 Hz, H-7α), 2.23 (1H, br s, H-9*β*), 4.47 (1H, d, *J* = 4.4 Hz, H-11α), 2.65 (1H, br s, H-13α), 2.75 (1H, d, *J* = 12.5 Hz, H-14α), 4.56 (1H, br s, H-15α), 5.33 (1H, br s, H-17a), 5.14 (1H, br s, H-17b), 1.12 (3H, s, Me-18), 1.62 (3H, s, Me-19), 1.72 (3H, s, Me-20), 2.22, 2.03 (each 3H, 2 × Ac); EIMS (70eV) *m/z* 452 $[M]^+$(2), 392 $[M - AcOH]^+$(9), 374 $[M - AcOH - H_2O]^+$(40), 299 (50), 281 (63), 257 (45); ^{13}C NMR, see Table 3.

Glabcensin L (12): obtained as an amorphous powder; $[\alpha]^{22}_D$ −33.5° (*c* 0.48, $CHCl_3$); IR (KBr) ν_{max} 3450, 2905, 1715, 1371, 1240, 1025 cm^{-1}; ^1H NMR δ 6.92, 6.85, 6.78 (each 1H, br s, 3 × OH, D_2O exchangeable), 4.64 (1H, ddd, *J* = 11.9, 4.0, 3.0 Hz, H-2α), 5.45 (1H, d, *J* = 3.0 Hz, H-3α), 2.57 (1H, br s, H-5*β*), 4.42 (1H, d, *J* = 3.4, 1.8 Hz, H-6*β*), 5.37 (1H, d, *J* = 3.4 Hz, H-7α), 2.25 (1H, br s, H-9*β*), 5.53 (1H, d, *J* = 5.0 Hz, H-11α), 2.57 (1H, br s, H-13α), 2.62 (1H, d, *J* = 12.7 Hz, H-14α), 4.52 (1H, br s, H-15α), 5.26 (1H, br s, H-17a), 5.03 (1H, br s, H-17b), 1.11 (3H, s, Me-18), 1.54 (3H, s, Me-19), 1.63 (3H, s, Me-20), 2.25, 2.08, 1.93 (each 3H, s, 3 × Ac); EIMS (70eV) *m/z* 494 $[M]^+$(7), 434 $[M - AcOH]^+$(5), 416 $[M - AcOH - H_2O]^+$(3), 374 $[M - 2 \times AcOH]^+$, 314 $[M - 3 \times AcOH]^+$ (35), 299 $[M - 3 \times AcOH - Me]^+$ (80), 281 $[M - 3 \times AcOH - Me\text{-}H_2O]^+$(65); ^{13}C NMR, see Table 3.

Glabcensin M(13): obtained as a white powder; $[\alpha]^{22}_D$ −45.4° (*c* 0.54, MeOH); IR (KBr) ν_{max} 3400, 2920, 1726, 1450, 1370, 1030 cm^{-1}; ^1H NMR δ 4.56 (1H, ddd, *J* = 12.0, 4.0, 2.9 Hz, H-2α), 5.38 (1H, d, *J* = 2.9 Hz, H-3α), 2.68 (1H, br s, H-5*β*), 5.49 (1H, dd, *J* = 3.1, 1.6 Hz, H-6*β*), 5.35 (1H, d, *J* = 3.1 Hz, H-7α), 2.25 (1H, br s, H-9*β*), 4.95 (1H, d, *J* = 4.8 Hz, H-11α), 2.62 (1H, br s, H-13α), 5.26 (1H, br s, H-17a), 5.02 (1H, br s, H-17b), 1.12 (3H, s, Me-18), 1.10 (3H, s, Me-19), 1.52 (3H, s, Me-20), 2.25, 2.07, 2.01 (each 3H, s, 3 × Ac); EIMS (70eV) *m/z* 494 $[M]^+$(3), 434 $[M - AcOH]^+$(3), 416 $[M - AcOH - H_2O]^+$(5), 374 $[M - 2 \times AcOH]^+$(20), 356 $[M - 2 \times AcOH - H_2O]^+$(35), 314 $[M - 3 \times AcOH]^+$(30), 296 $[M - 3 \times AcOH - H_2O]^+$(50), 281 $[M - 3 \times AcOH - Me\text{-}H_2O]^+$(35); ^{13}C NMR, see Table 3.

Glabcensin N(14): obtained as an amorphous powder; $[\alpha]^{22}_D$ −22.18° (*c* 0.50, $CHCl_3$); IR (KBr) ν_{max} 3420, 2910, 1735, 1365, 1240, 1030 cm^{-1}; ^1H NMR δ 7.19, 7.10, 6.94 (each 1H, br s, 3 × OH, D_2O exchangeable), 5.53 (1H, ddd, *J* = 11.8, 4.0, 2.8 Hz, H-2α), 5.39 (1H, d, *J* = 2.8 Hz, H-3α), 2.55 (1H, br s, H-5*β*), 5.41 (1H, br s, H-6*β*), 5.31 (1H, d, *J* = 3.2 Hz, H-7α), 2.31 (1H, br s, H-9*β*), 5.38 (1H, d, *J* = 4.2 Hz, H-11α), 2.56 (1H, br s,

Table 3. ^{13}C-NMR Data of Compounds **11**−**14** (Pyridine-d_5)

C	11	12	13	14
1	45.77 t	45.62 t	45.54 t	41.19 t
2	64.54 d	64.24 d	64.19 d	67.24 d
3	81.69 d	81.68 d	81.58 d	77.63 d
4	38.85 s	38.73 s	38.46 s	38.85 s
5	44.54 d	44.34 d	43.61 d	43.39 d
6	68.97 d	69.31d	70.68 d	70.13 d
7	82.13 d	82.03 d	76.82 d	76.24 d
8	46.58 s	46.03 s	46.62 s	46.05 s
9	53.21 d	50.34 d	52.51 d	49.45 d
10	38.93 s	39.11 s	38.83 s	39.13 s
11	65.35 d	68.69 d	65.05 d	68.76 d
12	42.92 t	39.94 t	42.64 t	39.58 t
13	40.28 d	39.11 d	39.47 d	38.27 d
14	36.00 t	35.37 t	34.77 t	34.13 t
15	82.13 d	81.83 d	81.04 d	81.21 d
16	158.9 s	157.83 s	158.16 s	156.90 s
17	105.83t	105.90 t	105.90 t	106.08 t
18	28.74 q	28.71 q	28.32 q	28.02 q
19	24.27 q	24.22 q	23.37 q	23.07 q
20	20.60 q	20.49 q	20.34 q	20.45 q
Ac	170.08 s	170.20s	170.90 s	170.44 s
	171.08 s	170.03 s	170.06 s	170.32 s
	21.53 q	169.85 s	169.68 s	169.88 s
	21.08 q	21.08 q	21.26 q	169.65 s
		21.42 q	21.26 q	168.79 s
		21.42 q	20.95 q	21.36 q
				21.36 q
				21.18 q
				20.93 q
				20.52 q

Table 4. ^{13}C-NMR Data of Compounds **15** and **16** (pyridine-d_5)

C	**15**	**16**	C	**15**	**16**
1	40.76 t	44.97 t	16	56.45 s	56.57 s
2	67.43 d	63.79 d	17	70.17 t	70.19 t
3	77.70 d	81.44 d	18	27.85 q	28.14 q
4	38.32 s	38.47 s	19	23.00 q	23.53q
5	41.94 d	42.02 d	20	20.57 q	20.95 q
6	71.25 d	71.49 d	Ac	170.35 s	170.89 s
7	72.79 d	73.00 d		170.30 s	169.79 s
8	50.47 s	50.58 s		170.29 s	169.00 s
9	54.46 d	55.47 d		169.00 s	21.17 q
10	39.47 s	39.45 s		20.56 q	21.10 q
11	67.69 d	67.48 d		20.48 q	21.00 q
12	35.29 t	35.36 t		20.42 q	
13	32.92 d	32.98 d		20.35 q	
14	32.00 t	32.00 t			
15	222.86 s	223.12 s	OMe	58.56 q	58.45 q

H-13α), 4.54 (1H, br s, H-15α), 5.26 (1H, br s, H-17a), 5.04 (1H, br s, H-17b), 1.00 (3H, s, Me-18), 1.11 (3H, s, Me-19), 1.44 (3H, s, Me-20), 2.30, 2.14, 2.00 (each 3H, s, 3 × Ac); EIMS (70eV) *m/z* 578 $[M]^+$(15), 518 $[M - AcOH]^+$(5), 476 $[M - AcOH - COCH_2]^+$(14), 458 $[M - 2 \times AcOH]^+$(20), 416 $[M - 2 \times AcOH - COCH_2]^+$(85), 398 $[M - 3 \times AcOH]^+$ (87), 356 $[M - 3 \times AcOH - COCH_2]^+$(25), 338 (67), 296 (78), 278 (100), 263 (95), 239 (90); ^{13}C NMR, see Table 3.

Glabcensin O (15): obtained as an amorphous powder; $[\alpha]^{22}_D$ −26.5° (*c* 0.49, $CHCl_3$); IR (KBr) ν_{max} 3400, 2910, 1730, 1460, 1371, 1225, 1030 cm^{-1}; ^{1}H NMR δ 6.92 (1H, br s, OH, D_2O exchangeable), 5.57 (1H, ddd J = 12.4, 4.0, 2.6 Hz, H-2α), 5.30 (1H, d, J = 2.6 Hz, H-3α), 5.56 (1H, d, J = 3.5, 1.7 Hz, H-6β), 4.01 (1H, d, J = 3.5 Hz, H-7α), 5.34 (1H, d, J = 5.2 Hz, H-11α), 2.70 (1H, m, H-13α), 2.69 (1H, d, J = 12.5 Hz, H-14α), 2.97-(1H, m, H-16α), 3.99 (1H, dd, J = 10.4, 4.3 Hz, H-17a), 3.85 (1H, dd, J = 10.4, 8.2 Hz, H-17b), 1.08 (3H, s, Me-18), 1.12 (3H, s, Me-19), 1.49 (3H, s, Me-20), 2.15, 1.96, 1.94, 1.90 (each 3H, s, 4 × Ac), 3.36 (3H, s, OMe); EIMS (70eV) *m/z* 566 $[M]^+$(1), 535 $[M - OMe]^+$(2), 464 $[M - AcOH - COCH_2]^+$(20), 446 $[M - AcOH - COCH_2-H_2O]^+$(37), 386 $[M - 3 \times AcOH]^+$ (100), 355 $[M - 3 \times AcOH - OMe]^+$(25), 326 $[M - 4 \times AcOH]^+$(80); ^{13}C NMR, see Table 4.

Glabcensin P (16): obtained as an amorpous powder; $[\alpha]^{22}_D$ −31.8° (*c* 0.42, $CHCl_3$); IR (KBr) ν_{max} 3400, 2910, 1730, 1450, 1370, 1230, 1032 cm^{-1}; ^{1}H NMR δ 6.72, 6.65 (each 1H, br s, 2 × OH, D_2O exchangeable), 4.55 (1H, ddd, J = 11.8, 4.1, 2.8 Hz, H-2α), 5.32 (1H, d, J = 2.8 Hz, H-3α), 5.54 (1H, dd, J = 3.7, 1.6 Hz , H-6β), 4.02 (1H, d, J = 3.7 Hz, H-7α), 5.44 (1H, d, J = 4.8 Hz, H-11α), 2.72 (1H, m, H-13α), 2.98 (1H, m, H-16α), 3.99 (1H, dd, J = 10.2, 4.2 Hz, H-17a), 3.84 (1H, dd, J = 10.2, 7.9 Hz, H-17b), 1.08 (3H, s, Me-18), 1.11 (3H, s, Me-19), 1.52 (3H, s, Me-20), 2.15, 1.95, 1.94 (each 3H, s, 3 × Ac), 3.36 (3H, s, OMe); EIMS (70eV) *m/z* 524 $[M]^+$-(2), 492 $[M - MeOH]^+$(2), 464 $[M - AcOH]^+$(5), 432 $[M - AcOH - MeOH]^+$(13), 404 $[M - 2 \times AcOH]^+$(100); ^{13}C NMR, see Table 4.

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