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FLAVONOIDS FROM THE ROOT AND STEM OF *SOPHORA TOMENTOSA*

TOSHIYUKI TANAKA, MUNEKAZU IINUMA,* FUJIO ASAI, MASAYOSI OHYAMA and CHARLES L. BURANDT†

Department of Pharmacognosy, Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5 chrome, Gifu 502, Japan; † Research Institute of Pharmaceutical Sciences, School of Pharmacy, The University of Mississippi, University, MS 38677, U.S.A.

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Key Word Index—*Sophora tomentosa*; Leguminosae; isoflavanone; 3-hydroxyisoflavanone; isoflavanone; tomentosanol A; tomentosanol E.

Abstract—From the root and the stem of *Sophora tomentosa*, five new flavonoids, tomentosanols A–E, were isolated in addition to 15 known flavonoids. The structures were determined by spectral analysis including 2D-NMR techniques. © 1997 Elsevier Science Ltd

INTRODUCTION

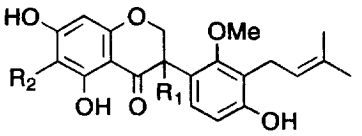
In previous chemosystematic studies in the genus *sophora* (Leguminosae), we have characterized the structures of flavonoids and stilbenoids of eight species of *Sophora* plants; *S. leachiana* Peck [1–9] and *S. secundiflora* Lag. et DC. [10] from the U.S.A., *S. exigua* Criab [11–13] from Thailand, *S. fraseri* Benth. [14] from Australia, *S. koreensis* Nakai [15–18] from Korea, *S. prostrata* Buchanan [19, 20] and *S. tetraptera* J. S. Mill [21, 22] from New Zealand, and *S. alopecuroides* L. [23] from China. Some flavonoids have been found to have potent antimicrobial activity against methicillin resistant *Staphylococcus aureus* [24]. In the present paper we describe the isolation and structural determination of 20 flavonoids including five new compounds from the root and the stem of *S. tomentosa* L. (subgenus *Sophora* [25, 26]), collected in the U.S.A.

RESULTS AND DISCUSSION

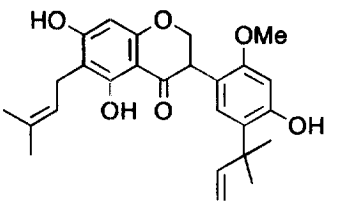
Acetone extracts of roots and stems of *Sophora tomentosa* were subjected to column chromatography on silica gel eluted with a chloroform–methanol mixture. By repeated chromatography, preparative TLC and recrystallization, 17 flavonoids (**1**–**7**, **9**, **11**, **12** and **14**–**20**) were isolated from the root extract, and three (**8**, **10**, and **13**) were found in both root and stem extracts. Among these flavonoids, sophoraisoflavanone A (**1**) [27], isosophoranone (**2**) [28], sophoronol (**7**) [28, 29], sophoraflavanone B (**14**), sophoraflavanone A (**17**) [30–32], sophoraflavanone C (**18**) [33], sophoraflavanone D (**19**), and sophoraflavanone E (**20**) [16] have already been characterized in this plant. However, the structure of sophoronol was elucidated firstly as a flavanonol [28], but when the same compound was subsequently isolated from *S. koreensis* the structure was revised to 3-hydroxylisoflavanone [29]. Sophora-flavanones A (**17**) and B (**14**) were isolated from roots of *S. tomentosa* and were characterized as 6-isoprenylnaringenin derivatives, but the structures were later revised to the 8-isoprenylnaringenin isomers by LSPD technique in NMR spectrum [32]. Sophoraflavanones D (**19**) and E (**20**) were also isolated from both *S. tomentosa* and *S. koreensis* [16].

Compound **3** was obtained as a colourless oil and gave $[M]^+$ at *m/z* 438 in EI mass spectrum. A set of three protons [δ 4.24 (*dd*, $J = 11$, 5 Hz), 4.36 (*dd*, $J = 11$, 5 Hz) and 4.51 (*t*, $J = 11$ Hz)] observed in the ^{1}H NMR spectrum was assigned to H-3 and H-2 in an isoflavanone skeleton. The spectrum further exhibited the presence of an isoprenyl [δ 1.64, 1.75 (3H each, *br s*, Me), 3.25 (2H, *br d*, $J = 7$ Hz, CH_2), 5.25 (1H, *t* like *m*, CH=)], an α,α-dimethylallyl [δ 1.42 (6H, *s*, Me × 2), 4.92 (1H, *dd*, $J = 11$, 1 Hz, CH=CH_2), 4.98 (1H, *dd*, $J = 17$, 1 Hz, CH=CH_2), 6.24 (1H, *dd*, $J = 17$, 11 Hz, CH=CH_2), a methoxyl (δ 3.71), and three phenolic hydroxyl groups [δ 8.07, 9.48 and 12.66 (chelated)] in addition to three singlets due to aromatic protons (δ 6.01, 6.52 and 7.03). Significant fragments appearing at *m/z* 221 (**3a**), 218 (**3b**), 165 (**3c**), and 203 (**3d**) in the EI mass spectrum can be explained by the respective ions shown in Fig. 1, indicating that two hydroxyl groups and one of C_5-alkyl chains were located on the A ring and a hydroxyl, a methoxyl

* Author to whom correspondence should be addressed.



1: $R_1 = R_2 = H$
2: $R_1 = H$, R_2 = isoprenyl
5: $R_1 = OH$, $R_2 = H$
6: $R_1 = OH$, R_2 = isoprenyl



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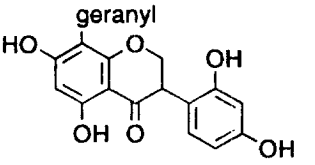

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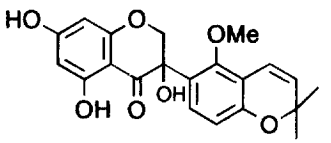

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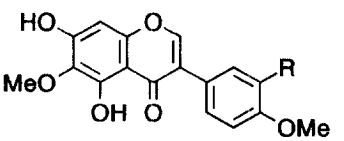
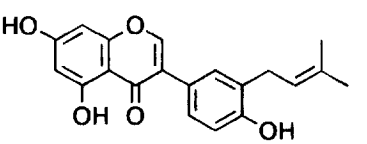


8: R = H
9: R = OH



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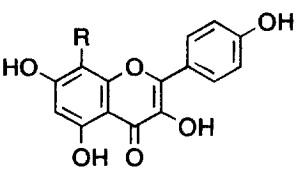
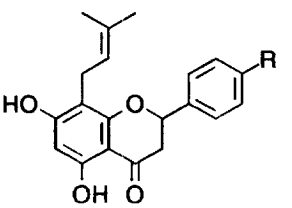
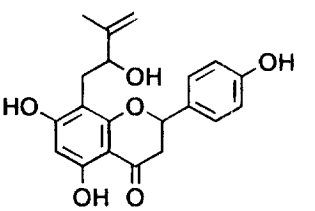


11: R = isoprenyl
12: R = geranyl



13: R = H
14: R = OH



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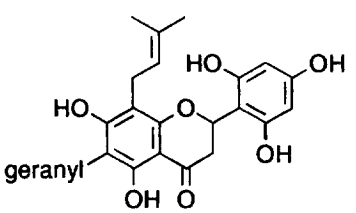

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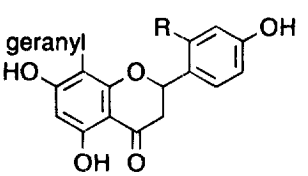
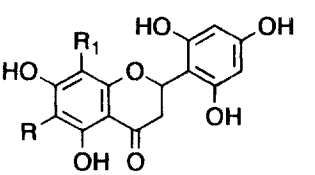


17: R = H
18: R = OH



19: R = geranyl, R_1 = H
20: R = H, R_1 = geranyl

group and another C_5-alkyl chain were on the B ring. NOEs in the ^1H NMR spectrum were observed at H-3 and H-3′ (δ 6.52) when the methoxyl group was irradiated, H-6′ (δ 7.03) when the methyl on the α,α-dimethylallyl group was irradiated, and at H-3 when H-6′ was irradiated (Fig. 2). Therefore the B ring has a 5′-α,α-dimethylallyl-4′-hydroxy-2′-methoxyl substitution. The chemical shifts due to protons of the B ring moiety, and H-2 and H-3 of the isoflavanone skeleton are superimposable on those of fraserinone A which has an identical partial structure and was isolated previously from roots of *S. fraseri* [14]. The position of the isoprenyl group could be at C-6 or C-8 on the A ring. The chelated hydroxyl group at C-5 was observed at δ 12.66 and shifted down field by 0.28 ppm more than that of fraserinone A (δ 12.38) indicative of the position of the isoprenyl group at C-6 [33]. Consequently **3** is 5″-α,α-dimethylallyl-5,7,4′-

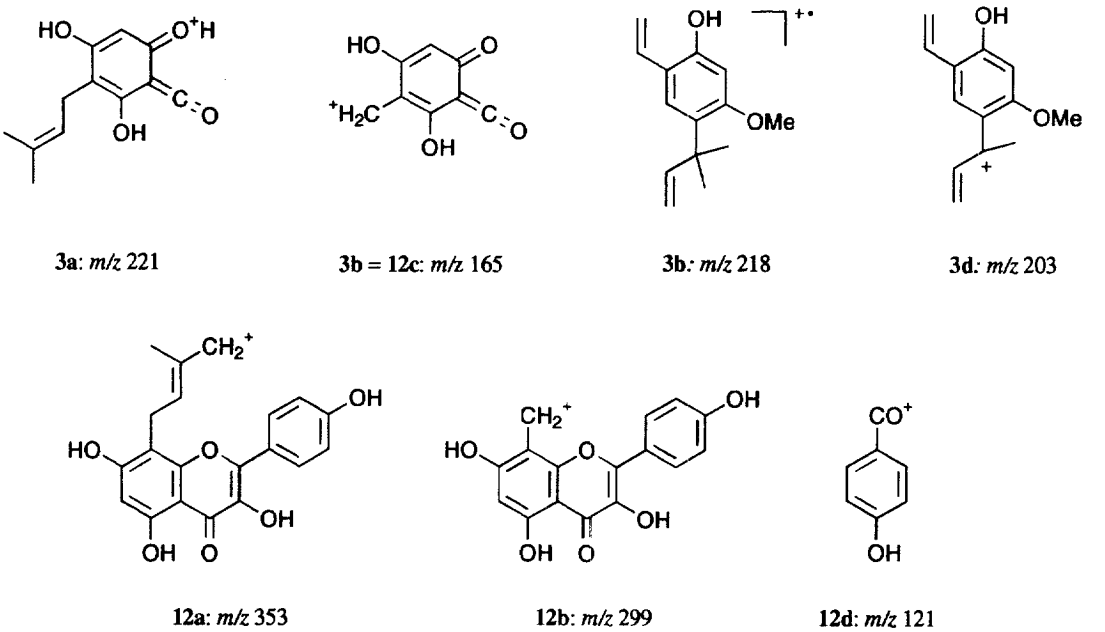


Fig. 1. Prominant fragment ions for structural elucidation.

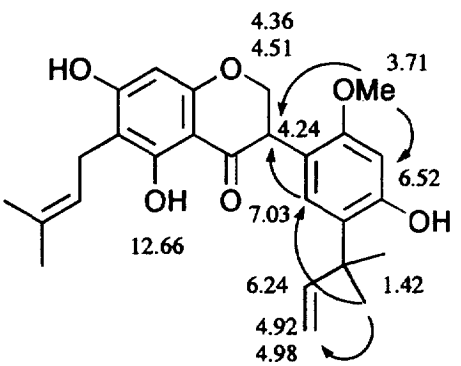


Fig. 2. NOEs in DIFNOE spectrum of **3**.

trihydroxy-6-isopropyl-2′-methoxyisoflavanone, and is named tomentosanol A.

Compounds **4** and **5** were isolated as a pale yellow oil and gave $[M]^+$ at *m/z* 424 and 386 in the EI mass spectrum respectively. The ^1H NMR spectrum showed that **4** was an isoflavanone derivative with a geranyl and four hydroxyl groups including a chelated one. By direct comparison with authentic samples. **4** was identified as kenusanone H (8-geranyl-5,7,2′,4′-tetrahydroxylisoflavanone) and **5** as 3,5,7,4′-tetrahydroxy-3′-isoprenyl-2′-methoxyisoflavanone, kenusanon F, previously isolated from *S. koreensis* [16].

Compound **6**, a pale yellow oil, reacted positively to $FeCl_3$ test and gave $[M]^+$ at *m/z* 454 in the EI mass spectrum. The ^1H NMR spectrum exhibited the presence of two isoprenyls [δ 1.65, 1.66, 1.73, 1.75 (3H each, *br s*, Me), 3.26 (2H, *br d*, J = 7 Hz, CH_2), 3.33 (2H, *t* like *m*, CH_2), 3.28 (2H, *m*, CH × 2)], a methoxyl [δ 3.61 (*s*)], an alcoholic hydroxyl [δ 5.43 (*s*)], and a chelated hydroxyl group [δ 12.43 (*s*)]. The spectrum further showed two one-proton doublets at δ 4.07 and 4.75 (each J = 12 Hz), which were located near an oxygen function, a singlet at δ 6.00, and two one-proton *ortho*-coupled doublets [δ 6.67 and 7.29 (J = 9 Hz)]. The doublets in J = 12 Hz were assigned to H-2 and the alcoholic hydroxyl group to a hydroxyl group at C-3 in a 3-hydroxylisoflavanone such as **5** (H-2: δ 4.10 and 4.76, OH at C-3: 5.47), **7** (H-2: δ 4.14 and 4.71, OH at C-3: 5.56), and echinoisosophoranone (H-2: δ 4.10 and 4.77, OH at C-3: 5.58) [15]. In the EI mass spectrum, prominent fragments at *m/z* 221 (**3a**) and 165 indicated that two hydroxyls and the isoprenyl group were substituted on the ring A. Consequently the B ring moiety had a hydroxyl, a methoxyl group, and an isoprenyl group. Methoxyl groups at C-2′ in three 3-hydroxylisoflavanones described above were observed at slightly higher field (*ca* δ 3.6) in ^1H NMR spectra than a normal methoxyl group, which indicated that they were influenced by a 3-hydroxyl group. Furthermore, the chemical shifts of the *ortho*-coupled protons (δ 6.67 and 7.29), the hydroxyl group at C-3, and two protons at C-2 corresponded to those of **5** with a 4′-hydroxy-3′-isoprenyl-2′-methoxyl ring, indicating that **6** had the same substitution on the B ring as **5**. The substitution of the A ring was determined as follows. From the biogenetic standpoint and from the ^1H NMR spectral data, two hydroxyl groups were located at C-5 and C-7. Additional isoprenylation at C-6 in **2** caused a down field shift of a chelated hydroxyl group by 0.3 ppm when compared with the data for **1**. A similar comparison between **5** to **6** indicated that **6** has an isoprenyl substituents at C-6 on the A ring. Therefore **6** is 3,5,7,4′-tetrahydroxy-6,3′-

diisoprenyl-2′-methoxy-isoflavanone and is named tomentosanol B.

Compounds **8**–**11** and **13** were characterized as irisolidone (**8**) [34], iristectorigenin A (**9**) [35], 3′-isoprenylgenistein (**10**) [36], des-*O*-methylanhydroicaritin (**11**) and glabranin (**13**), respectively. Compound **12**, a yellow powder, reacted positively with $FeCl_3$ and $[M]^+$ observed at *m/z* 422.1710 in HR-EI mass spectrum corresponded to the formula $C_{25}H_{26}O_6$. The IR spectrum exhibited the presence of hydroxyl groups (3300 cm^{-1}) and a conjugated carbonyl group (1650 cm^{-1}). The UV spectrum suggested that **12** was a kaempferol derivative. The presence of three vinyl methyls [δ 1.50, 1.55 and 1.83 (each *s*)], CH_2CH_2 [δ 2.07 (4H, *m*)], $ArCH_2$ [δ 3.58 (*br d*, J = 6 Hz)], two olefinic protons [δ 5.03 and 5.31 (each *t* like *m*)] was revealed by the ^1H NMR spectrum, and the protons were attributable to a geranyl group after analysis of ^1H and ^{13}C NMR including 2D NMR [HH and CH COSY]. The ^1H NMR spectrum further showed the presence of an aromatic singlet at δ 6.36 and an A_2B_2 system (J = 9 Hz) with four protons and four hydroxyl groups [δ 8.18, 8.20 and 12.11 (chelated)]. The significant fragments in the EI mass spectrum observed at *m/z* 353 (**12a**), 299 (**12b**), 165 (**12c**), and 121 (**12d**), indicated that two hydroxyls and the geranyl group were on the A ring and one hydroxyl group on the B ring. Compound **12** could be either 6- or 8-geranylkaempferol. In the ^1H NMR spectrum of kaempferol, H-6 and H-8 were observed at δ 6.28 and 6.54. The aromatic singlet (δ 6.36) of **12** was preferably assigned to H-6 and the geranyl group at C-8, which was finally substantiated by the 2D NMR spectrum. The singlet (δ 6.36) was correlated with a carbon (δ 98.9) in the CH COSY spectrum, and the carbon was further correlated with the hydroxyl group (δ 12.11) at C-5 through ^3J coupling in the COLOC spectrum (Fig. 3). Thus **12** is 8-geranylkaempferol and is named tomentosanol C.

Compound **15**, a colourless amorphous powder, showed $[M]^+$ at *m/z* 356 in the EI mass spectrum which corresponds to $C_{20}H_{20}O_6$. A one-proton double doublet at δ 5.43 (J = 13, 2 Hz) and two-proton multiplets at δ 2.80–3.10 assignable to H-2 and H-3 in a flavanone skeleton were observed in the ^1H NMR spectrum in addition to a set of two-proton doublets in an A_2X_2 system [δ 6.90 and 7.42 (J = 8 Hz)] assignable to a *p*-substituted benzene ring, a singlet of an aromatic proton (δ 5.98), and three hydroxyl groups [δ 8.50, 9.98 and 12.16 (chelated one)]. The presence of a vinyl methyl [δ 1.69 (*br s*)], a benzyl methylene [δ 2.80–3.10 (*m*, overlapped with H-3)], a methine attaching to an oxygen function (δ 4.34 (*m*)], and a methylene group [δ 4.74 and 4.88 (1H each, *br s*)] assigned to a 2-hydroxy-3-methyl-3-butenyl group was also confirmed by the ^1H NMR spectrum. Significant fragments in the EI mass spectrum appeared at *m/z* 236, 165 and 120. These results suggested that two hydroxyls and the 2-hydroxy-3-methyl-3-butenyl group were located on the A ring, and one hydroxyl group on the B ring. The chemical shift of the chelated hydroxyl group was similar to that of **14**, indicating that the alkyl group was attached to C-8 [30–32]. Hence **15** is 8-(2-hydroxy-3-methyl-3-butenyl) naringenin and is named tomentasanol D.

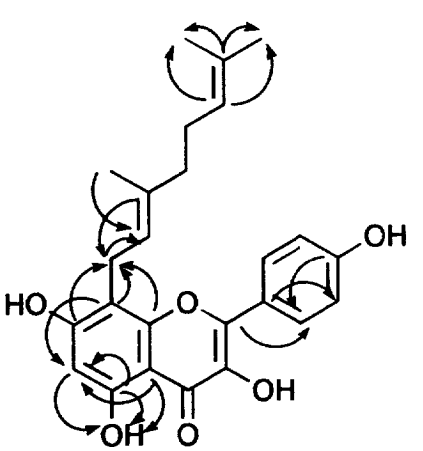


Fig. 3. CH long-range correlations in COLOC spectrum (J = 10 Hz) of **12**.

Compound **16**, a pale yellow amorphous powder, showed $[M]^+$ at *m/z* 508.2478 in the HR-EI mass spectrum which is equal to the formula $C_{30}H_{36}O_7$. The UV spectrum suggested that **16** had a flavanone skeleton and had partially a 2′,6′-dioxygenated ring because a set of three one-proton double doublets [δ 2.50 (J = 17, 3 Hz), 3.82 (J = 17, 12 Hz), and 5.88 (J = 12, 3 Hz)] in the ^1H NMR spectrum was characteristically assigned to H-2 and H-3, and H-3′ (H-5′) [17]. A two-proton singlet at δ 6.03 assignable to H-3′ and H-5′ in the ^1H NMR spectrum and a significant fragment ion (*m/z* 126) caused by the B ring moiety [16, 17] indicated that the B ring had a 2′,4′,6′-trihydroxyl substitution. The ^1H NMR spectrum also exhibited the presence of four hydroxyl groups [δ 8.20, 8.36 (×2), 9.60 and 12.60 (chelated) as well as five vinyl methyl groups [δ 1.57 (3H, *br s*), 1.60 (6H, *br s*), 1.63 1.77 (3H each, *br s*)], one CH_2CH_2 moiety [δ 1.97 (*m*) and 2.06 (*m*)], two benzyl methylenes [δ 3.26 (*t*, J = 7 Hz), 3.34 (*br d*, J = 7 Hz)], three CH = [(δ 5.08, 5.14 and 5.21 (each *t* like *m*) which were attributable to a geranyl and an isoprenyl group after analysis of the HH COSY, HH long range and CH COSY spectrum. In the COLOC spectrum (Fig. 4) a carbon (δ 107.5) was correlated with H-1 of the geranyl group (δ 3.34) and the chelated hydroxyl group (δ 12.60). The carbon then assigned to C-6, and the geranyl was substituted at C-6 and the isoprenyl group at C-8, respectively. The structure of **16** is shown to be 6-geranyl-5,7,2′,4′,6′-pentahydroxy-8-isoprenylflavanone and is named tomentasanol E. A flavanone that has a geranyl and an isoprenyl group on the A ring has only been isolated before from *S. koreensis* (= *Echinosophora koreensis*) as kenusanone C [17].

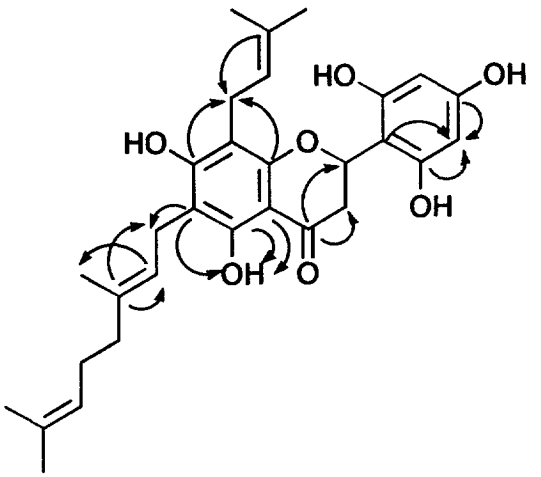


Fig. 4. CH long-range correlations in COLOC spectrum (J = 10 Hz) of **16**.

EXPERIMENTAL

Plant material. Roots and stems of *Sophora tomentosa* L. were collected at Texas, in August 1993. Voucher specimens have been deposited in the herbarium of Gifu Pharmaceutical University.

Extraction and isolation. The dried and ground roots (900 g) and the stems (900 g) of *S. tomentosa* were respectively extracted with Me_2CO at room temp, and each concd *in vacuo* to give a brownish syrup (61 g and 22 g). A part of the root extract (54 g) was chromatographed on silica gel (2 kg) eluted with varying proportions of $CHCl_3$–MeOH. The $CHCl_3$–MeOH (15:1) fr. was repeatedly rechromatographed on silica gel (solvent system: $CHCl_3$–MeOH = 2:1, 10:1, *n*-hexane–Me_2CO = 3:1, C_6H_6-EtOAc–MeOH = 10:1:1), prep. TLC (same solvent systems as silica gel CC), Sephadex LH 20 CC with MeOH or Me_2CO) and recryst. to give **1** (12 mg), **2** (8 mg), **3** (4 mg), **4** (7 mg), **5** (4 mg), **6** (5 mg), **7** (1.2 g), **9** (7 mg), **11** (3 mg), **12** (250 mg), **14** (12 mg), **15** (3 mg), **16** (10 mg), **17** (6 mg), **18** (6 mg), **19** (120 mg), **20** (100 mg), respectively. The stem extract was purified in the same manner to give **8** (12 mg), **10** (8 mg) and **13** (11 mg) in addition to the root constituents.

Compound **3** (*tomentosanol A*). A colourless oil, HREIMS m/z 438.2043 for $C_{26}H_{30}O_6$ (calcd 438.2041), EIMS m/z (rel. int.): 438 (77), 383 (12), 221 (100), 218 (51), 217 (23), 205 (36), 203 (54), 178 (74), 165 (60), UV (nm, MeOH): 228, 291, ^{1}H NMR (400 MHz, Me_2CO-d_6): δ 1.42 (6H, *s*, Me × 2, H-2‴,3‴), 1.64, 1.75 (3H each, *br s*, Me, H-4‴,5‴), 3.25 (2H, *br d*, J = 7 Hz, CH_2, H-1″), 3.71 (3H, *s*, OMe), 4.24 (1H, *dd*, J = 11, 5 Hz, H-3), 4.36 (1H, *dd*, J = 11, 5 Hz, H-2*cis*), 4.51 (1H, *t*, J = 11 Hz, H-2*trans*), 4.92 (1H, *dd*, J = 11, 1 Hz, H-5‴*Z*), 4.98 (1H, *dd*, J = 17, 1 Hz, H-5‴*Z*), 5.25 (1H, *t* like *m*, CH=, H-2″), 6.01 (1H, *s*, H-8), 6.24 (1H, *dd*, J = 17, 11 Hz, H-4‴), 6.52 (1H, *s*, H-3′), 7.03 (1H, *s*, H-6′), 8.07 (1H, *br s*, C-4′-OH), 9.48 (1H, *br s*, C-7-OH), 12.66 (1H, *s*, C-5-OH).

Compound **6** (*tomentosanol B*). A pale yellow oil, HREIMS m/z 454.1994 for $C_{26}H_{30}O_7$ (calcd 454.1988), EIMS m/z (rel. int.): 454 (13), 436 (5), 268 (85), 221 (100), 219 (20), 217 (54), 165 (77), 132 (28), UV (nm, MeOH): 227, 291, 335sh, ^{1}H NMR (400 MHz, Me_2CO-d_6): δ 1.65, 1.66, 1.73 1.75 (3H each, *br s*, Me, H-4″,4‴,5″,5‴), 3.26 (2H, *br d*, J = 7 Hz, CH_2), 3.33 (2H, *t* like *m*, CH_2), 3.61 (3H, *s*, OMe), 4.07, 4.75 (1H each, *d*, J = 12 Hz, H-2), 5.28 (2H, *m*, CH=× 2, H-2″,2‴), 5.43 (1H, *s*, C-3-OH), 6.00 (1H, *s*, H-8), 6.67 (1H, *d*, J = 9 Hz, H-5′), 7.29 (1H, *d*, J = 9 Hz, H-6′), 12.43 (1H, *s*, C-5-OH).

Compound **8** (*irisolidone*). A pale yellow amorphous powder, EIMS m/z (rel. int.): 314 (100), 299 (52), 296 (38), 271 (50), 268 (25), 132 (6), ^{1}H NMR (400 MHz, Me_2CO-d_6): δ 3.84, 3.88 (3H each, *s*, OMe), 6.51 (1H, *s*, H-8), 7.00 (2H, *d*, J = 9 Hz, H-3′,5′), 7.55 (1H, *d*, J = 9 Hz, H-2′,6′), 8.22 (1H, *s*, H-3), 9.20 (1H, *br s*, C-7-OH), 13.22 (1H, *s*, C-5-OH).

Compound **9** (*iristectorigenin A*). A pale yellow amorphous powder, EIMS m/z (rel. int.): 330 (100), 315 (55), 312 (38), 287 (52), 149 (22), ^{1}H NMR (400 MHz, Me_2CO-d_6): δ 3.88, 3.89 (3H each, **s**, OMe), 6.51 (1H, *s*, H-8), 7.00 (1H, *d*, J = 8 Hz, H-5′), 7.06 (1H, *dd*, J = 8, 2 Hz, H-6′), 7.14 (1H, *d*, J = 2 Hz, H-2′), 7.65 (1H, *br s*, C-3′-OH), 8.20 (1H, *s*, H-2), 9.21 (1H, *br s*, C-7-OH), 14.25 (1H, *s*, C-5-OH).

Compound **10** (*3′-isoprenylgenstein*). A pale yellow amorphous powder, UV (nm, MeOH): 262, 295sh, 330sh; +$AlCl_3$: 272, 310sh, 370; +AcONa: 262, 295sh, 335sh, EIMS m/z (rel. int.): 338 (100), 323 (15), 309 (12), 295 (15), 283 (70), 253 (20), 217 (10), 153 (25), ^{1}H NMR (400 MHz, Me_2CO-d_6): δ 1.72, 1.73 (3H each, *br s*, Me, H-4″,5″), 3.36 (2H, *d*, J = 7 Hz, CH_2, H-1″), 5.38 (1H, *t* like *m*, CH=, H-2″), 6.28 (1H, *d*, J = 2 Hz, H-6), 6.41 (1H, *d*, J = 2 Hz, H-8), 6.89 (1H, *d*, J = 8 Hz, H-5′), 7.27 (1H, *dd*, J = 8, 2 Hz, H-6′), 7.36 (1H, *d*, J = 2 Hz, H-2′), 8.12 (1H, *s*, H-2), 13.05 (1H, *s*, C-5-OH).

Compound **13** (*glabranin*). A colourless amorphous powder, EIMS m/z (rel. int.): 324 (100), 309 (36), 281 (21), 269 (20), 205 (50), 221 (8), 220 (10), 192 (25), 177 (37), 165 (23), 104 (12), ^{1}H NMR (400 MHz, Me_2CO-d_6): δ 1.61 (6H, *br s*, Me × 2, H-4″,5″), 2.80 (1H, *dd*, J = 16, 3 Hz, H-3*cis*), 3.13 (1H, *dd*, J = 16, 13 Hz, H-3*trans*), 3.25 (2H, *d*, J = 7 Hz, CH_2, H-1″), 5.21 (1H, *t* like *m*, CH=, H-2″), 5.58 (1H, *dd*, J = 13, 3 Hz, H-2), 6.04 (1H, *s*, H-6), 7.41–7.47 (3H, *m*, H-3′-5′), 7.59 (2H, *br d*, J = 7 Hz, H-2′,6′), 9.57 (1H, *br s*, C-7-OH), 12.12 (1H, *s*, C-5-OH).

Compound **12** (*tomentosanol C*). A yellow powder, HREIMS m/z: 422.1710, calcd for $C_{25}H_{26}O_7$: 422.1722, IR (KBr, cm^{-1}): 3300, 1650, 1630, 1603, UV (nm, MeOH): 271, 325, 374; +NaOMe: 281, 327, 423; +$AlCl_3$: 272, 310sh, 359, 432; +$AlCl_3$–HCl: 272, 322sh, 375; +AcONa: 280, 317sh, 405; +AcONa–H_3BO_3: 272, 322sh, 375, EIMS m/z (rel. int.): 422 (68), 353 (77), 337 (62), 299 (100), 286 (20), 203 (8), 165 (12), 149 (7), 121 (23), ^{1}H NMR (400 MHz, Me_2CO-d_6): δ 1.50, 1.55, 1.83 (3H each, *br s*, Me, H-5″,9″,10″), 2.07 (4H, *m*, CH_2CH_2, H-4″, 8″), 3.58

Table 1. ^{13}C NMR Spectral Data of **12** and **16**

Carbon no.	**12**	**16**
2	147.0 *s*	73.5 *d*
3	136.5 *s*	41.0 *t*
4	176.8 *s*	199.0 *s*
5	159.9 *s*	160.0 *s*
6	98.9 *d*	107.5 *s*
7	162.0 *s*	161.3 *s*
8	107.3 *s*	108.1 *s*
9	155.1 *s*	159.5 *s*
10	104.2 *s*	103.6 *s*
1′	123.7 *s*	103.9 *s*
2′,6′	130.5 *d*	158.2 *s*
3′,5′	116.3 *d*	95.8 *d*
4′	160.0 *s*	159.5 *s*
1″	22.1 *t*	21.4 *t*
2″	123.5 *d*	123.0 *d*
3″	135.8 *s*	135.7 *s*
4″	40.4 *t*	40.1 *t*
5″	16.4 *q*	16.0 *q*
6″	27.3 *t*	27.0 *t*
7″	125.0 *d*	124.7 *d*
8″	131.6 *s*	131.3 *s*
9″	25.7 *q*	25.6 *q*
10″	17.6 *q*	17.3 *q*
1‴		22.1 *t*
2‴		123.0 *d*
3‴		131.3 *s*
4‴		25.6 *q*
5‴		17.3 *q*

Measured in acetone-d_6. All carbons were assigned by aid of CH COSY and COLOC spectrum.

(2H, *br d*, J = 6 Hz, CH_2, H-1″), 2.07 (4H, *m*, $C\underline{H}_2C\underline{H}_2$, H-4″,6″), 5.03 (1H, *t* like *m*, CH═, H-7″), 5.31 (1H, *t* like *m*, CH═, H-2″), 6.36 (1H, *s*, H-6), 7.03 (2H, *d*, J = 9 Hz, H-3′,5′), 8.19 (2H, *d*, J = 9 Hz, H-2′,6′), 8.18, 8.20 (1H each, *br s*, OH), 12.11 (1H, *s*, C-5-OH). ^{13}C NMR spectral data are shown in Table 1.

Compound **15** (*tomentosanol D*). A colourless amorphous powder, HREIMS *m/z* 356.1254 for $C_{20}H_{20}O_6$ (calcd 356.1259), EIMS *m/z* (rel. int.): 356 (7), 338 (5), 285 (100), 236 (3), 218 (3), 165 (95), 120 (13), ^1H NMR (400 MHz, Me_2CO-d_6): δ 1.69 (3H, *br s*, Me, H-5″), 2.80–3.10 (4H, *m*, H-2, H-1″), 4.34 (1H, *m*, CH, H-2″), 4.74, 4.88 (1H each, *br s*, CH_2═, H-4″), 5.43 (1H, *dd*, J = 13, 2 Hz, H-2), 5.98 (1H, *s*, H-6), 6.90 (2H, *d*, J = 8 Hz, H-3′,5′), 7.42 (2H, *br d*, J = 8 Hz, H-2′,6′), 8.50, 9.98 (1H each, *br s*, OH), 12.16 (1H, *s*, C-5-OH).

Compound **16** (*tomentosanol E*). A colourless amorphous powder, HREIMS *m/z*: 508.2478, calcd for $C_{30}H_{36}O_7$: 508.2445, UV (nm, MeOH): 256sh, 290, 350sh; +$AlCl_3$: 289, 350sh, EIMS *m/z* (rel. int.): 508 (38), 490 (7), 454 (26), 382 (50), 368 (30), 367 (29), 325 (25), 313 (44), 301 (52), 300 (35), 257 (75), 219 (100), 203 (60), 165 (76), 153 (26), 126 (56), ^1H NMR (400 MHz, Me_2CO-d_6): δ 1.57 (3H, *br s*, Me), 1.60 (6H, *br s*, Me × 2), 1.63, 1.77 (3H each, *br s*, Me), 1.97 (2H, *m*, CH_2, H-4″), 2.06 (2H, *m*, CH_2, H-6″), 2.50 (1H, *dd*, J = 17, 3 Hz, H-3*eq*), 3.26 (2H, *t*, J = 7 Hz, CH_2, H-1‴), 3.34 (2H, *br d*, J = 7 Hz, CH_2, H-1″), 3.82 (1H, *dd*, J = 17, 12 Hz, H-3*ax*), 5.08 (1H, *t* like *m*, CH═, H-7″), 5.14 (1H, *t* like *m*, CH═, H-1‴), 5.21 (1H, *t* like *m*, CH═, H-2‴), 5.88 (1H, *dd*, J = 12, 3 Hz, H-2), 6.03 (2H, *s*, H-3′,5′), 8.20 (1H, *br s*, OH), 8.36 (2H, *br s*, OH × 2), 9.60 (1H, *br s*, OH), 12.60 (1H, *s*, C-5-OH). ^{13}C NMR spectral data are listed in Table 1.

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