Triterpenoid Saponins from Yellowflower Milkwort Root (*Polygala arillata*)

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Abstract Six new oleanane-type saponins, arilloside A-F (Ⅰ～Ⅵ), along with a known saponin, polygalasaponin XXXV (Ⅶ), were isolated from the root of *Polygala arillata* Buch.-Ham.. The structures of these new compounds were elucidated as 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-(3, 4-di-*O*-acetyl)-β-*D*-fucopyranoside(Ⅰ); 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-β-*D*-fucopyranoside(Ⅱ); 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-(3,4-di-*O*-acetyl)-β-*D*-fucopyranoside(Ⅲ); 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-[β-*D*-galactopyranosyl (1→4)]-β-*D*-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-β-*D*-fucopyranoside(Ⅳ); 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-[β-*D*-galactopyranosyl (1→4)]-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-(3-*O*-acetyl)-β-*D*-fucopyranoside(Ⅴ) and 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-[β-*D*-galactopyranosyl (1→4)]-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-(3,4-di-*O*-acetyl)-β-*D*-fucopyranoside(Ⅵ) on the basis of spectroscopic and chemical methods.

Key words *Polygala arillata* Buch.-Ham. *Polygalaceae* triterpenoid presenegenin oleananetype saponin

摘 要 中药黄花远志 *Polygala arillata* Buch.-Ham. 远志科远志属植物，为落叶灌木或小乔木，分布于西南、华东、陕西、湖北等地。其根具有祛风除湿，补虚消肿，调经活血等功效。我们对采自云南省文山县黄花远志的皂苷成分进行了研究，从甲醇提取物中分得7个单体三萜皂苷，经波谱和文献分析确定了它们的结构，其中有6个新三萜皂苷并命名为arilloside A～F。

关键词 黄花远志 三萜皂苷 arilloside A～F

Introduction

Polygala arillata Buch.-Ham. is a Chinese medicinal plant, the root of which was used as a tonic, anticoagulant or for the treatment of hepatitis[1,2]. Six new triterpenoid saponins christened as arilloside A～F (Ⅰ～Ⅵ) and one known saponin, polygalasaponin XXXV (Ⅶ) were isolated from its root. The last of which, Ⅶ has been previously isolated from *P. fallax* Hemsl.[3]. In this paper, we wish to present the structure elucidation of arilloside A～F(Ⅰ～Ⅵ).

Results and Discussion

A crude saponin fraction of the methanol extract of the root of *P. arillata* Buch.-Ham. was subjected to pass through a porous polymer gel (D_{101}) column and the adsorbed materials were eluted successively with 30% aq. MeOH and MeOH. The methanol eluate was repeatedly chromatographed on silica gel RP-8 to give saponins (Ⅰ～Ⅶ). On alkaline hydrolysis, saponins Ⅰ～Ⅶ afforded tenuifolin ($Ⅰ_a$)[4], the 3-*O*-β-*D*-glucopyranoside of

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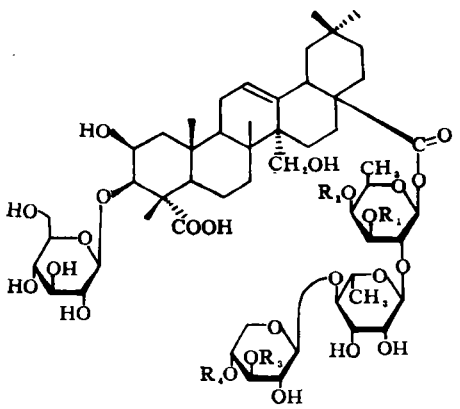
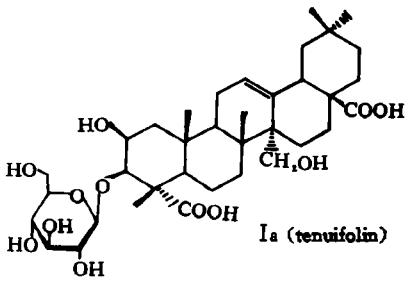
presenegenin. Therefore, it was justifiable to claim that these saponins Ⅰ～Ⅶ (Fig. 1) were analogs of presenegenin glycosides.

Arilloside A (Ⅰ) showed a $[M-H]^-$



	R_1	R_2	R_3	R_4	
Ⅰ	Ac	Ac	H	H	
Ⅱ	H	H	Xyl	H	
Ⅲ	Ac	Ac	Xyl	H	
Ⅳ	H	H	Xyl	Gal	
Ⅴ	H	Ac	Xyl	Gal	
Ⅵ	Ac	Ac	Xyl	Gal	
Ⅶ	Ac	Ac	H	Gal	(polgalasaponin xxxv)



Ia (tenuifolin)

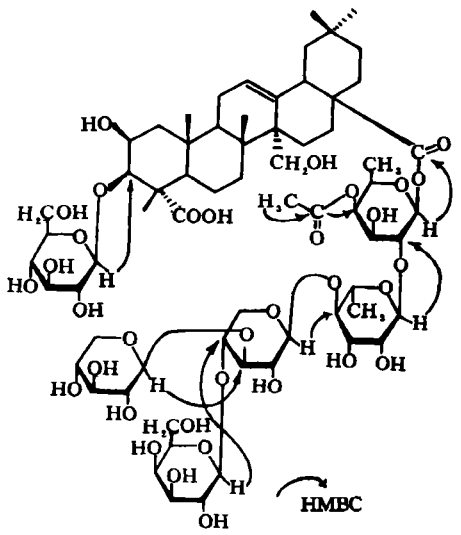


Fig 1 Chemical structure of Ⅰ～Ⅶ, Ia and HMBC Correlation of Arilloside E (Ⅴ)

ion peak at m/z 1 187 in the negative FAB-MS and combined with DEPT spectrum to give the molecular formula $C_{57}H_{72}O_{27}$. On acid hydrolysis, Ⅰ afforded glucose, fucose, rhamnose and xylose as its sugar moieties. On alkaline hydrolysis, Ⅰ gave a presenegenin 3-*O*-β-*D*-glucopyranoside, tenuifolin. The ^{1}HNMR spectrum exhibited the presence of five single methyl signals (δ 0.76, 0.88, 1.05, 1.51 and 1.89), a trisubstituted olefinic proton [δ 5.71 (t-like)] in the aglycone moiety and four anomeric protons [δ 5.00 (d, J=6.8 Hz), 5.05 (d, J=7.1 Hz), 5.68 (br s) and 6.13 (d, J=8.0 Hz)]. The ^{13}CNMR spectrum suggested the presence of a carboxyl signal (δ 182.7), three ester carbonyl signals (δ 170.2, 170.9 and 176.4) and four anomeric carbon signals (δ 94.3, 102.0, 105.2 and 107.2). By comparison of the carbon NMR data of compound Ⅰ with that of polygalasaponin XXⅧ[5], compound Ⅰ was found to contain two acetyl groups than polygalasaponin XXⅧ. The ester carbonyl signals at δ 170.2 and 170.9 attaching to the positions C-3 and C-4 of fucose unit showed the HMBC correlation between the ester carbonyl signal (δ 170.2) and H-3 (δ 5.55) of fucose, and the ester carbonyl signal (δ 170.9) and H-4 (δ 5.55) of fucose. The proton signals of H-3, H-4 were overlapped and assigned by its TOCSY and HMQC

spectra. Thus, the structure of arilloside A was elucidated as 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-(3,4-di-*O*-acetyl)-β-*D*-fucopyranoside.

Arilloside B (Ⅱ) showed a $[M-H]^-$ ion peak at m/z 1235 in the negative FAB-MS, suggesting the molecular formula $C_{58}H_{76}O_{29}$, combined with the DEPT spectrum. Compound Ⅱ afforded glucose, fucose, rhamnose, xylose as the sugar components on acid hydrolysis. In the NMR spectra, Ⅱ showed five anomeric proton and carbon signals [δc 94.9/δ_H 6.00(d, J=7.9 Hz); δ_c 101.1/δ_H 6.45 (br s); δ_c 105.3/δ_H 5.01 (d, J=7.0 Hz); δ_c 105.9/δ_H 5.12 (d, J=6.5 Hz) and δ_c 106.8/δ_H 5.02 (d, J=7.2 Hz)]. The sugar proton and carbon signals in the NMR spectrum were assigned by HMQC, TOCSY, ^{1}H-^{1}H COSY and HMBC spectra (see Table 1). In the HMBC spectrum, long range coupling were observed between the anomeric proton signal at δ 5.01 (H-1 of Glc) and the carbon signal at δ 86.4 due to C-3 of the aglycone; between the anomeric proton signal at δ 6.00 (H-1 of Fuc) and the carbon signal at δ 176.7 due to C-28 of the aglycone; between the anomeric proton signal at δ 6.45 (H-1 of Rha) and the carbon signal at δ 73.5 due to C-2 of the fucose; between the anomeric proton signal at δ 5.02 [H-1 of Xyl (inn.)]and the carbon signal at δ 85.4 due to C-4 of the rhamnose; between the anomeric proton signal at δ 5.12 [H-1 of Xyl (ter.)] and the carbon signal at δ 87.8 due to C-3 of the xylose (inn.). From these evidences, the structure of arilloside B was elucidated as 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-β-*D*-fucopyranoside.

Arilloside C (Ⅲ) showed a $[M-H]^-$ ion peak at m/z 1319 in the negative FAB-MS, combined with the DEPT spectrum, its molecular formula was deduced to be $C_{62}H_{80}O_{31}$. The ^{1}HNMR spectrum suggesting the presence of two acetyl methyl proton signals (δ 2.00 and 2.02) and five anomeric proton signal [δ 5.05 (d, J=7.0 Hz); 5.10 (d, J=7.1 Hz); 5.18 (d, J=6.7 Hz); 5.69 (br s) and δ 6.17 (d, J=7.9 Hz)]. On acid hydrolysis, compound Ⅲ afforded glucose, fucose, rhamnose and xylose. The positions of the acetyl groups were that of C-3, C-4 of the fucose moiety by comparing its NMR data with those of compounds Ⅰ and Ⅱ. The data of the HMBC spectrum enable us to identify the structure of Ⅲ as 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopranosyl (1→3)-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-(3, 4-di-*O*-acetyl)-β-*D*-fucopyranoside.

Arilloside D (Ⅳ) showed six anomeric proton signals in the ^{1}HNMR spectrum at δ 4.85, (d, J=7.0 Hz), 4.91 (d, J=7.0 Hz), 4.95 (d, J=6.7 Hz), 5.16 (d, J=7.9 Hz) and 6.39 (br s). By ^{13}CNMR spectrum combined with HMQC spectrum, the carbon signal positions and chemical shifts of the six anomeric carbon signals were assigned at δ 103.0, 106.2, 105.0, 105.4, 94.7 and 100.9, respectively. On acid hydrolysis, compound Ⅳ afforded glucose, fucose, rhamnose, xylose and galactose as sugar moieties. Its molecular ior was revealed m/z 1 397 $[M-H]^-$ in the negative FAB-MS and main fragment ions 1 265, 1 355, 941 and 679. Sugar linkages were decided by the HMBC spectrum. The HM-

BC correlation were observed between the following carbons and protons in the sugar moiety of Ⅳ: C-3 and H-1 of Glc; C-28 and H-1 of Fuc; C-2 of Fuc and H-1 of Rha; C-4 of Rha and H-1 of Xyl (inn.); C-3 of xyl (inn.) and H-1 of Xyl (ter.); C-4 of Xyl (inn.) and H-1 of Gal. Based on these evidences, the structure of arilloside D was elucidated as 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-[β-*D*-galactopyranosyl (1→4)]-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-β-*D*-fucopyranoside.

Arilloside E (Ⅴ) afforded glucose, fucose, rhamnose, xylose and galactose on acid hydrolysis. Its molecular formula is $C_{66}H_{88}O_{35}$ from the negative FAB-MS and DEPT spectrum. The ^1H, ^{13}CNMR spectra of Ⅴ exhibited an acetyl signal at δ_H 1.92, δc 171.0 and six anomeric proton and carbon signals at δ 4.85 (d, J=6.1 Hz), 4.93 (d, J=6.3 Hz), 4.98 (d, J=6.7 Hz), 5.14 (d, J=6.4 Hz), 6.01 (d, J=7.9 Hz) and 6.32 (br s); 103.0, 106.2, 105.1, 105.2, 94.5 and 101.5, respectively. The proton and carbon chemical shifts of Ⅴ were similar to those of Ⅳ except for the signals due to fucose moiety. The signal δ 3.93 (H-4 of Fuc) in Ⅳ was changed to δ 5.48 in Ⅴ, and HMBC correlation was observed between the carbonyl carbon δ 171.0 and H-4 (δ 5.48) of fucose moiety. Therefore, arilloside E was elucidated as 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-[β-*D*-galactopyranosyl (1→4)]-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-(3-*O*-acetyl)-β-*D*-fucopyranoside.

Arilloside F (Ⅵ) showed its $[M-H]^-$ ion peak at m/z 1481 in the negative FAB-MS. The ^1H, ^{13}CNMR spectra exhibited two acetyl signals δ_H 2.01, 202/δc 170.2, 170.9 and six anomeric proton and carbon signals at δ 4.90 (d, J=7.0 Hz); 4.97 (d, J=6.4 Hz); 5.00 (d, J=7.07 Hz), 5.27 (d, J=7.1 Hz), 5.69 (br s) and 6.14 (d, J=7.8 Hz); 103.3, 106.1, 105.3, 105.5, 102.1 and 94.3, respectively. On acid hydrolysis, compound Ⅵ afforded glucose, fucose, rhamnose, xylose and galactose as sugar moieties. The positions of the acetyl groups were at C-3, C-4 of fucose moiety by comparison of the NMR data with those of compounds Ⅰ, Ⅲ, Ⅴ (see Table 1.). The HMBC correlation of Ⅵ enable us to identify the structure of Ⅵ as 3-*O*-β-*D*-glucopyranosyl presenegenin 28-*O*-β-*D*-xylopyranosyl (1→3)-[β-*D*-galactopyranosyl (1→4)]-β-*D*-xylopyranosyl (1→4)-α-*L*-rhamnopyranosyl (1→2)-(3, 4-di-*O*-acetyl)-β-*D*-fucopyranoside.

Experimental

General procedure: ^1H, ^{13}CNMR spectra were obtained with Bruker AM-400, DRX-500 spectrometer; FAB mass spectrum were taken on VG Autospec 3000 system spectrometer; chromatographic materials used was RP-8 (40～60 μm, Merck), silica gel (160～200 mesh and 10～40 μm); spots were detected by spraying with 5% H_2SO_4 followed by heating.

Extraction and isolation: *Polygala arillata* Buch.-Ham. was collected in Wenshan, Yunnan province, China in July 1996 and voucher specimen was deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences. The dried root (2 kg) was extracted with 70% MeOH. The extract (150 g) was passed through a porous polymer gel (D_{101}) col-

umn. After the contents of the adsorbed materials were eluted with MeOH. The MeOH eluate (45 g) was chromatographed on silica gel with $CHCl_3$-MeOH-H_2O (7 : 3 : 0.5) to give ten fractions. Fr. V～Fr. X were repeatedly by chromatographed RP-8 gel column (eluting with MeOH-H_2O/5 : 5～7 : 3), and finally purified on silica gel (10～40 m) with $CHCl_3$-MeOH-H_2O (8 : 2 : 0.5～7 : 3 : 0.5) to give: Ⅰ (70 mg), Ⅱ (60 mg), Ⅲ (43 mg), Ⅳ (205 mg), Ⅴ (170 mg), Ⅵ (200 mg) and Ⅶ (87 mg).

Arilloside A, $C_{57}H_{72}O_{27}$, ^{1}HNMR: δ 0.76 (3 H, s, H-29), 0.88 (3 H, s, H-30), 1.05 (3 H, s, H-26), 1.51 (3 H, s, H-25), 1.89 (3 H, s, H-24), 3.79 (1 H, H-27), 4.05 (1 H, H-27), 4.70 (H-2), 4.59 (H-3), 5.71 (H-12), 2.01 (3 H, Ac), 2.02 (3 H, Ac), 5.00 (1 H, d, J=6.8 Hz, H-1 of Glc), 5.05 (1 H, d, J=7.1 Hz, H-1 of Xyl), 5.68 (1 H, br s, H-1 of Rha), 1.70 (3 H, d, J=4.5 Hz, H-6 of Rha), 6.13 (1 H, d, J=8.0 Hz, H-1 of Fuc), 1.16 (3 H, d, J=4.7 Hz, H-6 of Fuc); FAB-MS m/z: 1 187 $[M-H]^-$, 1 025 $[M-H-162]^-$, 893 $[M-H-162-132]^-$, 747 $[M-H-162-132-146]^-$, 679 $[M-H-132-146\times2]^-$, ^{13}CNMR data see Table 1.

Arilloside B, $C_{58}H_{76}O_{29}$, ^{1}HNMR: δ 0.76 (3 H, s, H-29), 0.85 (3 H, s, H-30), 1.10 (3 H, s, H-26), 1.52 (3 H, s, H-25), 1.90 (3 H, s, H-24), 3.80 (1 H, H-27), 4.10 (1 H, H-27), 4.63 (H-2), 4.51 (H-3), 5.79 (H-12), 5.01 (1 H, d, J=7.2 Hz, H-1 of Glc), 5.02 (1 H, d, J=7.1 Hz, H-1 of Xyl (inn.)], 5.12 [1 H, d, J=6.2 Hz, H-1 of Xyl (ter.)], 6.00 (1 H, d, J=7.9 Hz, H-1 of Fuc), 1.47 (3 H, d, J=4.6 Hz, H-6 of Fuc), 6.45 (1 H, br s, H-1 of Rha), 1.63 (3 H, d, J=4.4 Hz, H-6 of Rha); FAB-MS m/z: 1 235 $[M-H]^-$, 1 103 $[M-H-132]^-$, 1 073 $[M-H-162]^-$, 971 $[M-H-132\times2]^-$, 679 $[M-H-132\times2-146\times2]^-$, ^{13}CNMR data see Table 1.

Arilloside C, $C_{62}H_{80}O_{31}$, ^{1}HNMR: δ 0.77(3 H, s, H-29), 0.90 (3 H, s, H-30), 1.09 (3 H, s, H-26), 1.61 (3 H, s, H-25), 1.95 (3 H, s, H-24), 3.76 (1 H, H-27), 4.00 (1 H, H-27), 4.70 (H-2), 3.59 (H-3), 5.78 (H-12), 2.01 (3 H, Ac), 2.02 (3 H, Ac), 5.05 [1 H, d, J=7.0 Hz, H-1 of Glc], 5.10 [1 H, d, J=7.1 Hz, H-1 of Xyl (inn.)], 5.18 [1 H, d, J=6.7 Hz, H-1 of Xyl (ter.)], 5.69 (1 H, br s, H-1 of Rha), 1.70 (3 H, d, J=4.6 Hz, H-6 of Rha), 6.17 (1 H, d, J=7.9 Hz, H-1 of Fuc), 1.19 (3 H, d, J=4.5 Hz, H-6 of Fuc); FAB-MS m/z: 1 319 $[M-H]^-$, 1 187 $[M-H-132]^-$, 1 025 $[M-H-132-162]^-$, 893$[M-H-162-132\times2]^-$.

Arilloside D, $C_{64}H_{86}O_{34}$, ^{1}HNMR: δ 0.76(3 H, s, H-29), 0.83 (3 H, s, H-30), 1.07 (3 H, s, H-26), 1.48 (3 H, s, H-25), 1.86 (3 H, s, H-24), 3.77 (1 H, H-27), 4.08 (1 H, H-27), 4.62 (H-2), 4.47. (H-3), 5.48 (H-12), 4.85 (1 H, d, J=7.0 Hz, H-1 of Gal), 4.91 [1 H, d, J=7.0 Hz, H-1 of Xyl(inn.)], 4.95 (1 H, d, J=6.7 Hz, H-1 of Glc), 5.16 [1 H, d, J=6.5 Hz, H-1 of Xyl (ter.)], 5.97 [1 H, d, J=7.9 Hz, H-1 of Fuc], 1.44 (3 H, d, J=4.5 Hz, H-6 of Fuc), 6.39 (1 H, br s, H-1 of Rha), 1.56 (3 H, d, J=4.3 Hz, H-6 of Rha), FAB-MS m/z: 1 397 $[M-H]^-$, 1 266 $[M-H-132]^-$, 1 235 $[M-H-162]^-$, 941 $[M-H-162\times2-132]^-$, 679 $[M-H-162-132\times2-146\times2]^-$, ^{13}CNMR data see Table 1.

Arilloside E, $C_{66}H_{88}O_{35}$, ^{1}HNMR: δ 0.75(3 H, s, H-29), 0.82 (3 H, s, H-30), 1.06 (3 H, s, H-26), 1.47 (3 H, s, H-25), 1.85 (3 H, s, H-24), 3.76 (1 H, H-27), 4.06 (1 H, H-27), 4.60 (H-2), 4.48 (H-3), 5.61 (H-12), 1.92 (3 H, s, Ac), 4.85 (1 H, d, J = 6.1 Hz, H-1 of Gal), 4.93 [1 H, d, J = 6.3 Hz, H-1 of Xyl (inn.)], 4.98 (1 H, d, J = 6.7 Hz, H-1 of Glc), 5.14 [1 H, d, J = 6.4 Hz, H-1 of Xyl (ter.)], 6.01 [1 H, d, J = 7.9 Hz, H-1 of Fuc], 1.20 (3 H, d, J = 5.7 Hz, H-6 of Fuc), 6.32 (1 H, br s, H-1 of Rha), 1.68 (3 H, d, J = 5.0 Hz, H-6 of Rha), FAB-MS m/z: 1 439 $[M-H]^-$, 1 307 $[M-H-132]^-$, 1 277 $[M-H-162]^-$, 1 145 $[M-H-162-132]^-$, 679 $[M-H-162-132\times2-146\times2-42]^-$, ^{13}CNMR data see Table 1.

Arilloside F, $C_{68}H_{89}O_{36}$, ^{1}HNMR: δ 0.78(3 H, s, H-29), 0.89 (3 H, s, H-30), 1.08 (3 H, s, H-26), 1.54 (3 H, s, H-25), 1.92 (3 H, s, H-24), 3.80 (1 H, H-27), 4.06 (1 H, H-27), 4.50 (H-2), 4.55 (H-3), 5.79 (H-12), 2.01 (3 H, s, Ac), 2.02 (3 H, s, Ac), 4.90 (1 H, d, J = 7.0 Hz, H-1 of Gal), 4.97 [1 H, d, J = 6.4 Hz, H-1 of Xyl (inn.)], 5.00 [1 H, d, J = 7.0 Hz, H-1 of Glc], 5.27 [1 H, d, J = 7.1 Hz, H-1 of Xyl (ter.)], 6.14 [1 H, d, J = 7.8 Hz, H-1 of Fuc], 1.18 (3 H, d, J = 5.5 Hz, H-6 of Fuc), 5.69 (1 H, br s, H-1 of Rha), 1.64 (3 H, d, J = 4.5 Hz, H-6 of Rha); FAB-MS m/z: 1 481 $[M-H]^-$, 1 349 $[M-H-132]^-$, 1 319 $[M-H-162]^-$, 1 187 $[M-H-162-132]^-$, 1 025 $[M-H-162\times2-132]^-$, 679 $[M-H-162-132\times2-146\times2-42\times2]^-$, ^{13}CNMR data see Table 1.

Alkaline hydrolysis of Ⅰ ~ Ⅵ. Each compound (3 mg) except for compound Ⅳ. As an example, Ⅳ (50 mg) was treated with 5% NaOH (10 mL) for 6 h at 50 ℃ and the reaction mixture was added to 0.5 mol/L HCl to pH = 7.0. The hydrolysate was passed through porous MCI gel column and washed with water, the adsorbed materials was eluted with aq. MeOH. The methanol eluate (20 mg) obtained, proved to be tenuifolin, with NMR data as follows: δc: 180.6 (C-23), 180.2 (C-28), 139.6 (C-13), 127.7 (C-12), 86.0 (C-3), 70.2 (C-2), 64.6 (C-27), 52.9 (C-4), 52.5 (C-5), 49.2 (C-9), 48.1 (C-17), 46.5 (C-14), 45.6 (C-19), 44.2 (C-1), 41.6 (C-18), 40.9 (C-8), 37.1 (C-10), 34.2 (C-21), 33.5 (C-7), 33.2 (C-29), 33.1 (C-22), 31.0 (C-30), 24.6 (C-15), 24.1 (C-16), 24.0 (C-30), 23.8 (C-11),

Table 1 ^{13}CNMR chemical shifts of compounds Ⅰ ~ Ⅶ (pyridine-d_5)

Algycone	Ⅰ	Ⅱ	Ⅲ	Ⅳ	Ⅴ	Ⅵ	Ⅶ
1	44.4	44.1	44.3	44.2	44.1	44.2	44.3
2	70.5	70.4	70.3	70.3	70.4	70.2	70.3
3	86.5	86.4	86.1	86.6	86.9	86.7	87.2
4	53.2	52.8	52.9	53.0	53.1	53.1	53.4
5	52.5	52.2	52.5	52.3	52.2	52.2	52.5
6	21.5	21.4	21.4	21.4	21.4	21.5	21.2
7	33.9	33.6	33.6	32.2	32.3	32.3	33.6
8	41.2	41.3	41.2	41.0	41.0	41.2	41.1
9	49.4	49.2	49.4	49.2	49.2	49.2	49.3
10	37.1	37.1	37.1	36.8	36.9	37.1	37.1
11	23.7	23.6	23.0	23.3	23.3	23.4	23.4
12	128.0	127.9	127.9	127.8	127.9	128.0	128.2
13	139.1	139.1	139.0	138.9	138.8	139.0	138.8
14	47.2	47.1	47.1	46.9	47.0	47.2	47.2
15	24.8	24.3	24.6	24.5	24.4	24.4	24.6
16	24.6	24.2	24.0	24.3	24.2	24.2	24.2
17	48.2	48.2	48.1	48.1	48.1	48.1	48.2
18	41.7	42.1	42.0	41.9	42.0	41.9	41.8
19	45.5	45.2	45.5	45.2	45.2	45.1	45.9
20	30.6	30.9	30.8	30.6	30.6	30.6	30.7
21	34.0	33.8	33.9	33.8	33.8	33.7	34.0
22	32.5	32.2	32.3	32.2	32.1	32.2	32.5
23	182.7	182.1	182.0	183.0	182.9	182.4	182.5
24	14.6	14.4	14.3	14.2	14.4	14.4	14.9
25	17.6	17.6	17.5	17.4	17.4	17.6	17.6
26	18.9	18.9	18.9	19.0	18.7	18.9	18.9
27	64.5	64.2	64.5	64.2	64.1	64.2	64.3
28	176.4	176.7	176.4	176.5	176.5	176.5	176.5

Table 1-continue

Sugar	Ⅰ	Ⅱ	Ⅲ	Ⅳ	Ⅴ	Ⅵ	Ⅶ
29	33.2	33.2	33.1	32.9	32.9	33.2	33.1
30	24.0	24.0	24.0	23.7	23.7	24.0	23.8
C-3-Glc							
1	105.2	105.3	105.2	105.0	105.1	105.3	105.2
2	75.3	75.4	75.3	75.1	75.1	75.2	75.3
3	78.0	78.2	78.3	77.8	77.9	78.2	77.6
4	71.6	71.6	71.7	71.3	71.3	71.4	71.6
5	78.2	78.3	78.3	77.9	78.4	78.2	77.8
6	62.7	62.7	62.8	62.4	62.4	62.7	62.5
C-28-Fuc							
1	94.3	94.9	94.3	94.7	94.5	94.3	94.1
2	72.7	73.5	73.0	73.2	72.4	72.4	72.5
3	74.9	76.9	74.5	76.7	74.3	74.8	74.9
4	70.8	73.3	71.4	73.1	74.7	71.1	71.3
5	70.1	72.5	70.1	72.3	70.5	70.4	70.1
6	16.2	17.6	16.1	16.8	16.4	16.2	16.3
Ac at C-3	20.5		20.4			20.5	20.3
	170.2		170.1			170.2	170.2
Ac at C-4	20.8		20.6		20.6	20.7	20.7
	170.9		170.8		171.0	170.9	170.8
Rha							
1	102.0	101.1	102.0	100.9	101.5	102.1	102.2
2	71.5	71.8	72.4	71.6	71.6	71.6	71.5
3	71.6	72.5	72.9	72.4	71.3	71.2	71.8
4	84.5	85.4	84.4	85.2	85.1	84.3	84.6
5	69.0	68.0	69.0	67.7	68.0	68.9	68.9
6	18.6	18.5	18.6	18.2	18.4	18.7	18.7
Xyl		inn.	inn.	inn.	inn.	inn.	
1	107.2	106.8	106.6	106.2	106.2	106.1	106.7
2	76.0	75.4	76.2	75.8	75.8	75.8	75.3
3	78.6	87.8	87.3	84.1	84.6	85.3	76.7
4	77.1	70.7	71.3	71.1	70.9	71.4	77.5
5	67.4	67.3	67.6	65.4	66.1	66.2	64.9
Gal							
1				103.0	103.0	103.0	103.8
2				70.0	70.0	71.4	71.9
3				74.4	74.4	74.8	75.0
4				69.9	69.7	69.9	70.2
5				77.3	77.6	77.5	77.1
6				62.1	62.1	62.3	62.1
Xyl		ter.	ter.	ter.	ter.	ter.	
1		105.9	105.8	105.4	105.2	105.5	
2		75.3	74.9	74.8	74.8	74.8	
3		78.0	78.1	77.1	77.2	77.6	
4		68.9	70.3	69.9	70.0	70.1	
5		67.0	67.0	66.7	66.7	67.0	

21.3 (C-6), 18.8 (C-26), 17.3 (C-25), 14.2 (C-24), Glu δc: 105.4 (C-1), 75.3 (C-2), 78.4 (C-3), 71.7 (C-4), 78.4 (C-5), 62.5 (C-6); ^{1}HNMR: δ 0.85 (3 H, s, H-29), 0.99 (3 H, s, H-30), 1.04 (3 H, s, H-26), 1.51 (3 H, s, H-25), 1.97 (3 H, s, H-24), 3.36 (1 H, dd, J=4, 14 Hz, H-18), 4.61 (1 H, d, J=2.9 Hz, H-3), 4.71 (1 H, m, H-2), 4.48 [H-3), 5.85 (1 H, t-like, H-12), 5.08 (1 H d, J=7.8 Hz, H-1 of Glu); FAB-MS m/z: 679 $[M-H]^-$, 517 $[M-H]^-$. Compounds Ⅰ ~ Ⅲ and Ⅴ ~ Ⅵ gave the same product, tenuifolin on alkaline hydrolysis as proved by comparing with TLC.

Acid hydrolysis of Ⅰ ~ Ⅵ. Each saponin (3 mg) in 1 mL MeOH was refluxed in 10 mL 4 mol/L HCl for 10 h. The hydrolysate was extracted with AcOEt. The aqueous layer was then adjusted to pH 7 with $NaHCO_3$. After evaporating to dryness, the mixture sugars were extracted with pyridine from the residue and analyzed by TLC using the authentic sugar (*D*-glucose, *D*-fucose, *D*-xylose and *D*-galactose) on silica gel with $CHCl_3$-MeOH-H_2O (7∶3∶0.5); sugar detected with 4% α-naphthol-EtOH-5% H_2SO_4.

The anomeric configurations of glucose, fucose, xylose and galactose in these saponins were all determined to be β and that of rhamnose was determined to be α (J_{H1-H2} < 2 Hz) from the J_{H1-H2} value of the anomeric proton signals.

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