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ARALIASAPONINS I–XI, TRITERPENE SAPONINS FROM THE ROOTS OF *ARALIA DECAISNEANA*

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Key Word Index—*Aralia decaisneana*; Araliaceae; araliasaponin; oleanane-type saponin; ursane-type saponin.

Abstract—Seven new oleanane-type and four new ursane-type triterpene saponins, named araliasaponins I–XI were isolated from the roots of *Aralia decaisneana*, together with four known triterpene saponins. On the basis of the chemical and spectroscopic evidence, the structures of these new saponins were elucidated as follows: 3-*O*-*β*-D-xylopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranosyl ester, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-α-L-arabinopyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranosyl ester, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranosyl ester, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*β*-D-glucopyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranosyl ester, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*β*-D-galactopyranosyl oleanolic acid, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*β*-D-galactopyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranosyl ester, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*β*-D-galactopyranosyl oleanolic acid 28-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranosyl ester, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-α-L-arabinopyranosyl ursolic acid 28-*O*-*β*-D-glucopyranosyl ester, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-α-L-arabinopyranosyl ursolic acid, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-α-L-arabinopyranosyl ursolic acid 28- *O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranosyl ester and 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*β*-D-glucopyranosyl ursolic acid 28-*O*-*β*-D-glucopyranosyl ester.

INTRODUCTION

Aralia species are known to contain many oleanane-type triterpene saponins [1–9], and in particular *A. elata* Seem. has been studied for its saponin content in connection with diabetic activity [1–5]. *A. decaisneana* Hance is distributed in south China and North Vietnam and its root is used as a folk medicine for rheumathism, lumbago, hepatitis, bruise, nephritis and oedema [10]. Fang *et al.* [7] reported the structures of three oleanane-type glucuronide saponins isolated from the root bark of *A. decaisneana*.

RESULTS AND DISCUSSION

We investigated the saponins of the root of *A. decaisneana* and isolated nine oleanane-type and six ursane-type triterpene saponins. Four were identified as elatosides E (**1**) [1], F (tarasaponin VII) (**2**) [1, 4], ursolic acid 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-α-L-arabinopyranoside (**10**) [11, 12] and matesaponin 1 (**11**) [12] by comparison of the spectral data with reported data. The structures of 11 new compounds were elucidated as follows. The 70% ethanolic water extract of the roots of *A. decaisneana* was chromatographed on a silica gel column using a chloroform–methanol–water system to give 13 fractions. These fractions were subjected to preparative HPLC using acetonitrile–water or methanol–water systems to give 15 pure saponins.

Araliasaponin I (**3**) showed a $[M + Na]^+$ ion peak at *m/z* 1200 in the FAB-mass spectrum and the molecular formula $C_{57}H_{92}O_{25}$ was obtained by elemental analysis. The ^1H NMR spectrum (Table 1) showed the presence of seven singlet methyl proton (*δ*0.88, 0.90, 0.92 (each 3H, *s*), 1.09, 1.26 (each 6H, *s*), a trisubstituted olefinic proton (*δ*5.43 (*t*-like)) and a methine proton signal (*δ*3.24 (*br dd*, *J* = 14, 4 Hz)) in the aglycone moiety which are characteristic of an oleanane-type triterpene [13] and five anomeric proton signals [*δ*4.73 (*d*, *J* = 8 Hz), 5.15 (*d*, *J* = 8 Hz), 5.27 (*d*, *J* = 8 Hz), 5.32 (*d*, *J* = 7.5 Hz), 6.31 (*d*, *J* = 8 Hz)]. The ^{13}C NMR spectrum (Table 2) showed the presence of an ester carbonyl (*δ*176.4) and five anomeric carbon signals (*δ*95.8, 104.7, 105.0, 105.6, 106.1). Compound **3** gave D-glucose, D-xylose, L-arabinose in the ratio 2:2:1 and oleanolic acid (**3a**) on acid hydrolysis. The ^1H NMR signal of **3** at *δ*6.31 and the ^{13}C NMR signal at *δ*95.8 suggested the presence of the ester-linked sugar. The ^1H NMR signals (H-1, H-2, H-3 and H-5α) of

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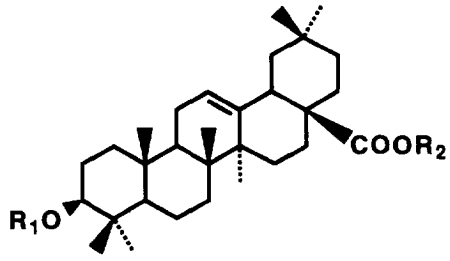

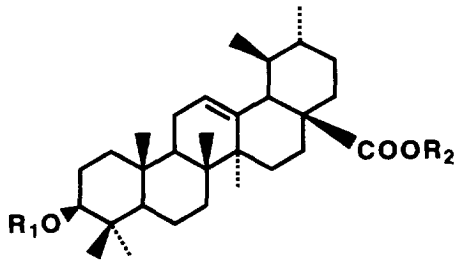

	R_1	R_2
1:	-Ara(3→) Glc (2→) Xyl	-H
2:	-Ara(3→) Glc (2→) Xyl	-Glc
3:	-Ara(3→) Glc (2→) Xyl (3→) Xyl	-Glc
3a:	-H	-H
4:	-Ara(3→) Glc	-Glc(6→) Glc
5:	-Ara(3→) Glc (2→) Xyl	-Glc(6→) Glc
6:	-Glc(3→) Glc (2→) Xyl	-Glc
7:	-Gal(3→) Glc (2→) Xyl	-H
8:	-Gal(3→) Glc (2→) Xyl	-Glc
9:	-Gal(3→) Glc (2→) Xyl	-Glc(6→) Glc

	R_1	R_2
10:	-Ara(3→) Glc	-H
11:	-Ara(3→) Glc	-Glc
12:	-Ara(3→) Glc (2→) Xyl	-Glc
12a:	-H	-H
13:	-Ara(3→) Glc (2→) Xyl	-H
14:	-Ara(3→) Glc	-Glc(6→) Glc
15:	-Glc(3→) Glc (2→) Xyl	-Glc

the sugar moiety were assigned from the homonuclear Hartmann–Hahn (HOHAHA) difference and nuclear Overhauser effect (NOE) difference spectra irradiating at each anomeric proton signal (Tables 1 and 3). When the signal at δ5.15 (H-1 of Xyl) was irradiated, a NOE was obtained at δ4.20 and this proton signal was assigned to H-3 of ether-linked glucose. On irradiation the signal at δ5.27 (H-1 of ether-linked Glc), a NOE was obtained at the signal at δ4.26 (H-3 of Ara). When the signals at δ5.32 (H-1 of Xyl) and δ4.73 (H-1 of Ara) were irradiated, NOEs were observed at the signal at δ4.63 (H-2 of Ara) and δ3.24 (H-3), respectively (Table 2). In the heteronuclear multiple bond connectivity (HMBC) spectrum, long-range ^{13}C–^{1}H correlations were observed between each anomeric proton signal and sugar-linked carbon as shown in Table 3; the structure of **3** was concluded to be 28-*O*-β-D-glucopyranosyl oleanolic acid 3-*O*-β-D-xylopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)-[β-D-xylopyranosyl-(1 → 2)]-α-L-arabinopyranoside.

Araliasaponin II (**4**) showed its $[M + Na]^+$ ion peak at *m/z* 1098 in the FAB-mass spectrum and the elemental analysis data was consistent with $C_{53}H_{86}O_{22}$. The ^{1}H and ^{13}C NMR spectra suggested the presence of four anomeric signals (δ4.74 (*d*, *J* = 8 Hz); 107.3, 5.02 (*d*, *J* = 8 Hz); 105.3, 5.36 (*d*, *J* = 8 Hz); 106.4, 6.24 (*d*, *J* = 8 Hz); 95.7) which were assigned by a heteronuclear single-quantum coherence (HSQC) spectrum. On acid hydrolysis, **4** yielded oleanolic acid (**3a**) as an aglycone, and D-glucose and L-arabinose in the ratio 3:1. In the NOE difference spectra, NOEs were observed between H-1 of Ara (δ4.74 (*d*, *J* = 8 Hz)] and H-3 of aglycone (δ3.35 (*dd*, *J* = 12, 4 Hz)), H-1 of Glc (δ5.36 (*d*, *J* = 8 Hz)) and H-3 of Ara (δ4.22 (overlapped)), H-1 of Glc (δ5.02 (*d*, *J* = 8 Hz)] and H_2-6 (δ4.32 (overlapped); 4.70 (*dd*, *J* = 11, 2 Hz)] of ester-linked Glc. These data led us to conclude that the structure of araliasaponin II is 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl oleanolic acid 3-*O*-β-D-glucopyranosyl-(1 → 3)-α-L-arabinopyranoside.

Araliasaponin III (**5**) showed its $[M + Na]^+$ ion peak at *m/z* 1230 in the FAB-mass spectrum and elemental analysis data was consistent with $C_{58}H_{94}O_{26}$. The ^{1}H and ^{13}C NMR spectra suggested the presence of five anomeric signals (δ4.74 (*d*, *J* = 7 Hz); 105.6, 5.02 (*d*, *J* = 8 Hz); 105.3, 5.27 (*d*, *J* = 8 Hz); 105.1, 5.38 (*d*, *J* = 7.5 Hz); 105.1, 6.24 (*d*, *J* = 8 Hz); 95.7). On acid hydrolysis compound **5** yielded oleanolic acid (**3a**), as an aglycone, and D-glucose, D-xylose and L-arabinose in the ratio 3:1:1. We undertook a NOE difference and HMBC spectrum to decide the binding sites of each sugar after assignment of the proton signals due to a sugar moiety by HOHAHA difference spectrum and the results are summarized in Table 3: the sugar chain at C-3 was β-D-glucopyranosyl-(1 → 3)-[β-D-xylopyranosyl(1 → 2)]-α-L-arabinopyranosyl and that at C-28 was β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl group.

Araliasaponin IV (**6**) showed its $[M + Na]^+$ ion peaks at *m/z* 1098 in the FAB-mass spectrum and elemental analysis data was consistent with $C_{53}H_{86}O_{22}$. The ^{1}H and ^{13}C NMR spectra suggested that compound **6** had four monosaccharide at C-3 and C-28 showing four anomeric signals [δ4.81 (*d*, *J* = 8 Hz); 105.0, 5.34 (*d*, *J* = 8 Hz); 104.8, 5.57 (*d*, *J* = 8 Hz); 104.7, 6.31 (*d*, *J* = 8 Hz); 95.8]. Compound **6** yielded oleanolic acid (**3a**) as an aglycone and D-glucose, D-xylose (3:1). The NOE difference and HMBC spectrum (Table 3) led us to conclude the structure of **6** to be 28-*O*-β-D-glucopyranosyl

oleanolic acid 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*β*-D-glucopyranoside.

Araliasaponins V (**7**), $C_{47}H_{76}O_{17}$, VI (**8**), $C_{53}H_{86}O_{22}$, VII (**9**), $C_{59}H_{96}O_{27}$ showed $[M + Na]^+$ peaks at *m/z* 936, 1098, 1260, respectively, in the FAB-mass spectra. On acid hydrolysis, these compounds yielded oleanolic acid (**3a**), as an aglycone, and D-galactose, D-glucose and D-xylose in the ratio 1:1:1, 1:2:1, 1:3:1, respectively, as a sugar moiety. NOE difference and HMBC spectrum (Table 3) suggested that the sugar chain at C-3 was *β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*β*-D-galactopyranosyl in compounds **7**– **9** and that C-28 was *β*-D-glucopyranosyl and *β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranosyl in compounds **8** and **9**, respectively.

Araliasaponins VIII (**12**), $C_{52}H_{84}O_{21}$ and IX (**13**), $C_{46}H_{74}O_{16}$ showed a $[M + Na]^+$ peak at *m/z* 1068 and 905 in the FAB-mass spectra, respectively. The ^1H NMR spectrum of compound **12** suggested the presence of five singlet methyl protons (*δ*0.90, 1.10, 1.14, 1.21, 1.29), two doublet methyl protons (*δ*0.91 (*d*, *J* = 6 Hz), 0.95 (*d*, *J* = 7 Hz)), a methine proton (*δ*2.53 (*d*, *J* = 11 Hz)) and a trisubstituted olefinic proton signal (*δ*5.45 (*t*-like)) in the aglycone moiety which are characteristic of an ursane-type triterpene [13] and four anomeric proton signals (*δ*4.76 (*d*, *J* = 7 Hz), 5.27 (*d*, *J* = 8 Hz), 5.37 (*d*, *J* = 8 Hz), 6.25 (*d*, *J* = 8 Hz)). The ^1H NMR spectrum of compound **13** was similar to that of **12**, except for the absence of an ester-linked glucosyl signal. Acid hydrolysis of compound **12** gave ursolic acid (**12a**), as an aglycone, and D-glucose, D-xylose and L-arabinose in the ratio 2:1:1, while that of compound **13** gave the same aglycone and monosacchride in the ratio 1:1:1. The NOE difference and HMBC spectral data led us to conclude the structure of compounds **12** and **13** to be 28-*O*-*β*-D-glucopyranosyl ursolic acid 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*α*-L-arabinopyranoside and ursolic acid 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*α*-L-arabinopyranoside, respectively.

Araliasaponin X (**14**), $C_{53}H_{86}O_{22}$ showed its $[M + Na]^+$ peak at *m/z* 1098 in the FAB-mass spectrum. Acid hydrolysis gave ursolic acid (**12a**), and D-glucose and L-arabinose in the ratio 3:1. The ^{13}C NMR data of the sugar moiety were similar to those of compound **4**. The NOE and HMBC data (Table 3) also supported the notion that the sugar linkage was the same as that of compound **4**. The structure of **14** was therefore determined to be 28-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranosyl ursolic acid 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-*α*-L-arabinopyranoside.

Araliasaponin XI (**15**), $C_{53}H_{86}O_{22}$ showed its $[M + Na]^+$ peak at *m/z* 1098 in the FAB-mass spectrum. This compound was composed of ursolic acid (**12a**), one D-xylose and three D-glucose. The ^{13}C NMR, NOE and HMBC data (Tables 2 and 3) confirmed that the sugar linkage was the same as that of compound **6**. The structure of **15** was therefore determined to be 28-*O*-*β*-D-glucopyranosyl ursolic acid 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-[*β*-D-xylopyranosyl-(1 → 2)]-*β*-D-glucopyranoside.

This is the first report of the isolation of oleanane-type saponins and ursane-type saponins together from *Aralia* species. In our study, we could not isolate the glucuronide saponins reported by Fang *et al.* [7] from the root bark of the same plant.

EXPERIMENTAL

General procedures. ^1H and ^{13}C NMR spectra were obtained with a JEOL *α*-400 FT NMR spectrometer and chemical shifts were given in *δ* with tetramethylsilane as an internal standard at 35°. FAB-MS were recorded on a JEOL JMS SX102 spectrometer and the mass number was counted in frs of 0.5 and over as a unit and cut away the rest. Optical rotations were measured with a JASCO DIP-360 digital polarimeter. GC was performed on a HITACHI G-3000 gas chromatograph. Preparative and analytical HPLC were performed on a JASCO model 800 instrument.

Extraction and isolation. A. decaisneana was collected in Quangxi, China, in September 1993 and was identified by Prof. Ian Mao Xiang, Guangxi Zhuangzu Zizhiqu Institute of Traditional Chinese Medical and Materia Medica, Nan Ning, China. A voucher specimen is deposited in the Herbarium of this Institute. The dried roots (5 kg) were extracted 3 × with EtOH–H_2O (7:3) under reflux. The extract was concd under red. pres. to give a reddish brown gum (360 g). The gum (150 g) was chromatographed on a silica gel (900 g) column and eluted with $CHCl_3$–MeOH–H_2O (13:7:0.16) increasing the proportion of MeOH and H_2O to give 13 frs (A–M); 5.0 g of the fr. D (15.2 g) was separated into 17 frs (a–q) by prep. HPLC (Develosil Lop-ODS, 5 × 50 cm × 2; MeOH–H_2O (7:3 → 4:1) linear gradient). Compounds obtained: fr. d, **8** (375 mg); from fr. j, **7** (20 mg); fr. o, **10** (32 mg). Fr. g (1.9 g) was chromatographed on HPLC (Develosil ODS 10/20, 5 × 50 cm × 2; CH_3CN–H_2O (13:7) recycle) to give **2** (300 mg), **3** (132 mg), **11** (135 mg), **12** (422 mg). Fr. e (184 mg) was chromatographed on HPLC (Develosil PhA-7, 2 × 25 cm; CH_3CN–H_2O (3:7) to give fr. 1 (70 mg) and fr. 2 (75 mg). Fr. 1 was chromatographed on HPLC (YMC Pack SH-843-5 C_4, 2 × 25 cm; CH_3CN–H_2O (13:27) recycle) to give **4** (30 mg), **14** (32 mg). Fr. 2 was chromatographed on HPLC (YMC Pack SH-843-5 C_4, 2 × 25 cm; CH_3CN–H_2O (3:7) recycle] to give **6** (40 mg), **15** (18 mg). Fr. m (250 mg) was chromatographed on HPLC (YMC Pack SH-843-5 C_4, 2 × 25 cm; CH_3CN–H_2O (2:3) + 0.05% TFA recycle) to give **1** (112 mg), **13** (90 mg). Fr. I (2.0 g) was chromatographed on HPLC (Develosil Lop-ODS, 5 × 50 cm × 2; MeOH–H_2O (13:7 → 7:3) linear gradient) to give **5** (160 mg), **9** (435 mg).

Araliasaponin I (**3**). Amorphous powder, $[\alpha]_D^{20}$ + 17.6° (MeOH; *c* 1.36). Found: C, 56.42, H, 7.98. $C_{57}H_{92}O_{25} \cdot 2H_2O$ requires C, 56.36; H, 8.05%. FAB-MS *m/z*: 1200 $[M + Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin II (**4**). Amorphous powder, $[\alpha]_D^{20}$ + 5.5° (MeOH; *c* 1.28). Found: C, 55.89; H, 8.10.

Table 1. The ^{1}H NMR spectral data

Proton no.	3	4	5	6	7
Aglycone moiety					
3	3.24 *dd* (12, 4)	3.35 *dd* (12, 4)	3.25 *dd* (11, 4.5)	3.27 dd (12, 4)	3.27 *dd* (12, 4)
12	5.43 *t*-like	5.42 *t*-like	5.41 *t*-like	5.43 *t*-like	5.46 *t*-like
18	3.20 *br dd* (14, 4)	3.20 *br dd* (14, 4)	3.19 *br dd* (14, 4)	3.20 *br dd* (14, 4)	3.30 *br dd* (14, 4)
23	1.26 *s*	1.29 *s*	1.27 *s*	1.27 *s*	1.30 *s*
24	1.09 *s*	0.99 *s*	1.10 *s*	1.08 *s*	1.09 *s*
25	0.88 *s*	0.90 *s*	0.90 *s*	0.86 *s*	0.83 *s*
26	1.09 *s*	1.10 *s*	1.10 *s*	1.09 *s*	0.98 *s*
27	1.26 *s*	1.26 *s*	1.25 *s*	1.27 *s*	1.32 *s*
29	0.92 *s*	0.90 *s*	0.90 *s*	0.91 *s*	0.96 *s*
30	0.90 *s*	0.90 *s*	0.90 *s*	0.89 *s*	1.02 *s*
Sugar moiety at C-3					
	(Ara)	(Ara)	(Ara)	(Glc)	(Gal)
1	4.73 *d* (8)	4.74 *d* (8)	4.74 *d* (7)	4.81 *d* (8)	4.81 *d* (8)
2	4.63 *dd* (9, 8)	4.57 *dd* (9, 8)	4.66 *dd* (9, 7)	4.28*	4.71 *dd* (9.5, 8)
3	4.26*	4.22*	4.26*	4.23*	4.30*
5α	3.64 *br d* (11)	3.74 *br d* (12)	3.66 *br d* (11)	3.81 *m*	4.00*
Xyl					
1	5.32 *d* (7.5)		5.38 *d* (7.5)	5.57 *d* (8)	5.45 *d* (8)
2	4.00*		4.01*	4.03*	4.03 *dd* (8.5, 8)
3	4.06*		4.12*	4.21*	
5α	3.43 *t* (10)		3.45 *t* (10)	3.60*	3.43 *t* (11)
Glc					
1	5.27 *d* (8)	5.36 *d* (8)	5.27 *d* (8)	5.34 *d* (8)	5.33 *d* (8)
2	4.00*	4.02 *t* (8)	4.00*	4.03*	3.98*
3	4.20*	4.22*	4.20*	4.17*	4.21*
5	3.88 *m*	3.98*	3.92 *m*	4.02*	3.98 *m*
Xyl (at C-3 of Glc)					
1	5.15 *d* (8)				
2	3.97 *t* (8)				
3	4.06*				
5α	3.99 *t* (10)				
Sugar moiety at C-28					
Glc (inner)					
1	6.31 *d* (8)	6.24 *d* (8)	6.24 *d* (8)	6.31 *d* (8)	
2	4.20*	4.12 *dd* (8.5, 8)	4.12*	4.20*	
3	4.01*	4.20*	4.20*		
5	4.01*	4.10 *m*	4.15*	4.02*	
6		4.32*	4.35 *dd* (11, 5)		
		4.70 *dd* (11, 2)	4.70 *dd* (11, 2)		
Glc (terminal)					
1		5.02 *d* (8)	5.02 *d* (8)		
2		3.98*	4.01*		
3		4.17*	4.18*		
5		3.87 *m*	3.88 *m*		

Assignements are based on HOHAHA difference and NOE difference spectra, and coupling constants (Hz) are in parentheses. *Overlapped.

$C_{53}H_{86}O_{22} \cdot 7/2H_2O$ requires C, 55.92; H, 8.24%. FAB-MS *m/z*: 1098 $[M + Na]^+$. ^{1}H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin III (**5**). Amorphous powder, $[\alpha]_D^{20}$ + 6.4° (MeOH; *c* 2.59). Found: C, 53.29; H, 8.05. $C_{58}H_{94}O_{26} \cdot 11/2H_2O$ requires C, 53.32; H, 8.10%. FAB-MS *m/z*: 1230 $[M + Na]^+$. ^{1}H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin IV (**6**). Amorphous powder, $[\alpha]_D^{20}$ + 11.9° (MeOH; *c* 1.26). Found: C, 55.60, H, 8.11. $C_{53}H_{86}O_{22} \cdot 4H_2O$ requires C, 55.48; H, 8.26%. FAB-MS *m/z*: 1098 $[M + Na]^+$. ^{1}H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin V (**7**). Amorphous powder, $[\alpha]_D^{20}$ + 32.5° (MeOH; *c* 2.26). Found: C, 59.52; H, 8.47. $C_{47}H_{76}O_{17} \cdot 2H_2O$ requires C, 59.48; H, 8.50%. FAB-

of compounds **3**–**9**, and **12**–**15**

8	9	12	13	14	15
3.24 *dd* (12, 4)	3.26 *dd* (12, 4)	3.27 *dd* (12, 4)	3.28 *dd* (12, 4)	3.36 *dd* (12, 4.5)	3.29 *dd* (12, 4)
5.41 *t*-like	5.41 *t*-like	5.45 *t*-like	5.47 *t*-like	5.44 *t*-like	5.45 *t*-like
3.17 *br dd* (14, 4)	3.19 *br dd* (14, 4)	2.53 *d* (11)	2.63 *d* (11)	2.51 *d* (11)	2.52 *d* (11)
1.27 *s*	1.29 *s*	1.29 *s*	1.29 *s*	1.29 *s*	1.28 *s*
1.07 *s*	1.09 *s*	1.10 *s*	1.08 *s*	0.98 *s*	1.08 *s*
0.84 *s*	0.88 *s*	0.90 *s*	0.86 *s*	0.92 *s*	0.87 *s*
1.07 *s*	1.09 *s*	1.14 *s*	1.02 *s*	1.14 *s*	1.13 *s*
1.26 *s*	1.26 *s*	1.21 *s*	1.25 *s*	1.21 *s*	1.21 *s*
0.90 *s*	0.89 *s*	0.95 *d* (7)	1.00 *d* (6)	0.93 *d* (6)	0.97 *d* (6.5)
0.88 *s*	0.89 *s*	0.91 *d* (6)	0.97 *d* (6)	0.89 *d* (6)	0.91 *d* (6)
(Gal)	(Gal)	(Ara)	(Ara)	(Ara)	
4.79 *d* (8)	4.80 *d* (8)	4.76 *d* (7)	4.76 *d* (7)	4.74 *d* (7.5)	4.82 *d* (8)
4.68 *dd* (9, 8)	4.71 *dd* (9, 8)	4.65 *dd* (9, 7)	4.64 *dd* (8, 7)	4.56 *dd* (8.5, 7.5)	4.28*
4.29*	4.30*	4.28*	4.25*	4.20*	4.20*
3.98*	4.00*	3.66 *br d* (11)	3.66 *br d* (12)	3.72 *br d* (12)	3.81 *m*
5.43 *d* (8)	5.45 *d* (8)	5.37 *d* (8)	5.34 *d* (8)		5.56 *d* (7.5)
4.00*	—	4.01*	4.00*		4.03*
4.08 *t* (9)	4.10*	4.09 *t* (8)	4.07*		4.16*
3.40 *t* (11)	3.42 *t* (11)	3.44 *t* (10)	3.43 *t* (11)		3.59 *t* (10.5)
5.30 *d* (8)	5.32 *d* (8)	5.27 *d* (8)	5.24 *d* (8)	5.35 *d* (8)	5.33 *d* (8)
3.96*	4.00*	4.01*	3.98*	4.01 *dd* (9, 8)	4.03*
4.19*	4.20*	4.20*	4.19*	4.19*	4.20*
3.87 *m*	3.88 *m*	3.92 *m*	3.91 *m*	3.97 *m*	4.00*
6.28 *d* (8)	6.23 *d* (8)	6.25 *d* (8)		6.18 *d* (8)	6.25 *d* (8)
4.17*	—	4.19*		4.12 *dd* (9, 8)	4.18*
4.25*	4.20*	4.27*		4.19*	4.26*
3.99*	4.10*	4.01*		4.09 *m*	4.00*
	4.34*			4.33*	
	4.71 *br d* (11)			4.69 *br d* (11)	
	5.01 *d* (8)			5.02 *d* (8)	
	3.98*			3.99*	
	4.17*			4.17*	
	3.88 *m*			3.88 *m*	

MS *m/z*: 936 $[M + Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin VI (**8**). Amorphous powder, $[\alpha]_D^{20}$ + 21.5° (MeOH; *c* 1.68). Found: C, 57.02; H, 8.16. $C_{53}H_{86}O_{22} \cdot 2H_2O$ requires C, 57.28; H, 8.16%. FAB-MS *m/z*: 1098 $[M + Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin VII (**9**). Amorphous powder, $[\alpha]_D^{20}$ + 5.5° (MeOH; *c* 2.75). Found: C, 55.01, H, 7.98. $C_{59}H_{96}O_{27} \cdot 3H_2O$ requires C, 54.87; H, 7.96%. FAB-MS *m/z*: 1260 $[M + Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin VIII (**12**). Amorphous powder, $[\alpha]_D^{20}$ + 22.6° (MeOH; *c* 1.15). Found: C, 58.40; H, 8.21. $C_{52}H_{84}O_{21} \cdot 3/2H_2O$ requires C, 58.25; H, 8.18%. FAB-MS *m/z*: 1068 $[M + Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Table 2. The ^{13}C NMR spectral data of compounds **3**–**9** and **12**–**15**

Carbon no.	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**12**	**13**	**14**	**15**
Aglycone moiety											
1	38.9	38.9	38.9	38.8	38.8	38.9	38.9	39.1	39.0	39.1	39.1
2	26.7	26.7	26.8	26.6	26.7	26.7	26.8	26.8	26.8	26.8	26.7
3	89.3	88.7	89.2	89.6	89.5	89.5	89.5	89.3	89.3	88.8	89.7
4	39.8	39.7	39.8	39.7	39.8	39.8	39.8	39.8	39.9	40.2	39.7
5	56.1	56.0	56.1	56.0	56.0	56.0	56.0	56.1	56.1	56.0	56.0
6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6
7	33.2	33.2	33.1	33.2	33.3	33.2	33.2	33.6	33.6	33.6	33.6
8	40.0	40.0	40.0	40.0	39.8	40.0	40.0	39.2	39.5	39.6	40.2
9	48.2	48.2	48.2	48.1	48.1	48.1	48.1	48.1	48.1	48.1	48.1
10	37.1	37.1	37.1	37.0	37.1	37.1	37.0	37.0	37.0	37.0	36.9
11	23.5	23.5	23.5	23.5	23.8	23.5	23.5	23.7	23.7	23.7	23.7
12	123.3	123.0	123.0	123.0	123.3	123.0	122.9	126.2	125.7	126.1	126.2
13	144.2	144.2	144.2	144.2	145.0	144.2	144.2	138.5	139.3	138.5	138.5
14	42.2	42.2	42.2	42.2	42.2	42.2	42.2	42.6	42.6	42.6	42.6
15	28.3	28.4	28.3	28.3	28.4	28.4	28.3	28.7	28.8	28.8	28.7
16	23.9	23.9	23.9	23.8	23.8	23.9	23.8	24.7	25.0	24.7	24.7
17	47.0	47.1	47.1	47.1	46.7	47.1	47.1	48.4	48.1	48.5	48.4
18	41.8	41.8	41.7	41.8	42.1	41.8	41.8	53.4	53.6	53.3	53.4
19	46.3	46.3	46.3	46.3	46.6	46.3	46.4	39.4	39.6	39.4	39.4
20	30.8	30.8	30.8	30.8	31.0	30.8	30.8	40.2	40.1	39.1	39.1
21	34.1	34.1	34.1	34.1	34.3	34.1	34.1	30.9	31.2	31.9	30.9
22	32.6	32.6	32.8	32.6	33.3	32.6	32.6	36.8	37.5	36.9	36.8
23	27.9	28.2	27.9	27.9	27.9	27.9	27.9	28.0	28.0	28.3	27.9
24	16.5	17.0	16.5	16.5	16.5	16.6	16.5	16.6	16.6	17.0	16.6
25	15.6	15.7	15.7	15.6	15.5	15.6	15.6	15.8	15.7	15.9	15.8
26	17.5	17.6	17.6	17.5	17.4	17.5	17.6	17.7	17.6	17.8	17.4
27	26.1	26.1	26.1	26.2	26.2	26.2	26.2	23.8	24.0	23.8	23.8
28	176.4	176.6	176.5	176.5	180.4	176.5	176.5	176.2	179.9	176.3	176.2
29	33.2	33.2	33.1	33.2	33.3	33.2	33.2	17.4	17.5	17.4	17.7
30	23.7	23.7	23.7	23.9	23.8	23.7	23.7	21.3	21.5	21.3	21.3
Sugar moiety											
at C-3	(Ara)	(Ara)	(Ara)	(Glc)	(Gal)	(Gal)	(Gal)	(Ara)	(Ara)	(Ara)	(Glc)
1	105.6	107.3	105.6	105.0	105.5	105.5	105.5	105.6	105.6	107.3	105.1
2	77.3	71.9	77.5	79.0	77.4	77.4	77.4	77.4	77.4	71.9	78.9
3	83.6	84.2	83.7	88.9	84.9	84.9	84.9	83.7	83.7	84.2	88.9
4	68.8	69.3	68.9	70.2	69.8	69.8	69.8	68.9	68.8	69.3	70.3
5	66.0	67.0	66.2	77.8	76.2	76.3	76.2	66.1	66.1	66.9	77.8
6				62.4	62.4	62.4	62.4				62.5
Xyl											
1	105.0		105.1	104.7	104.9	105.0	104.9	105.1	105.1		104.7
2	76.1		76.0	76.3	76.2	76.1	76.1	76.0	76.0		76.3
3	78.9		79.0	79.4	79.1	79.1	79.1	79.0	79.0		79.5
4	71.3		71.4	71.4	71.4	71.4	71.4	71.3	71.4		71.5
5	67.0		67.2	67.3	67.1	67.1	67.1	67.1	67.2		67.3
Glc											
1	104.7	106.4	105.1	104.8	105.2	105.2	105.2	105.1	105.1	106.3	104.8
2	74.4	75.8	75.3	75.4	75.4	75.4	75.4	75.3	75.3	75.8	75.4
3	87.3	78.4	78.4	78.6	78.3	78.3	78.3	78.4	78.3	78.4	78.6
4	69.5	71.7	71.7	71.7	71.7	71.7	71.6	71.6	71.6	71.2	71.7
5	79.9	78.7	78.5	78.7	78.5	78.4	78.4	78.5	78.4	78.7	78.6
6	62.2	62.8	62.6	62.7	62.6	62.6	62.6	62.6	62.5	62.8	62.7
Xyl (at C-3 of Glc)											
1	106.1										
2	75.4										
3	78.1										
4	70.9										
5	67.2										

Table 2. *Continued*

Carbon no.	3	4	5	6	7	8	9	12	13	14	15
Glc (inner)											
1	95.8	95.7	95.7	95.8		95.8	95.7	95.8		95.7	95.8
2	74.2	74.0	74.0	74.2		74.2	74.0	74.1		73.9	74.1
3	78.9	78.8	78.8	79.0		78.9	78.8	78.9		78.8	78.9
4	71.3	71.1	71.1	71.3		71.3	71.1	71.3		71.2	71.4
5	79.3	78.0	78.0	79.3		79.3	78.0	79.2		78.0	79.2
6	62.3	69.5	69.5	62.4		62.3	69.5	62.4		69.7	62.4
Glc (terminal)											
1		105.3	105.3				105.3			105.3	
2		75.2	75.2				75.2			75.3	
3		78.4	78.3				78.4			78.4	
4		71.7	71.7				71.6			71.7	
5		78.4	78.4				78.4			78.4	
6		62.8	62.7				62.7			62.8	

Assigned by HSQC and HMBC spectra.

Table 3. The NOE and HMBC correlation of compounds **3**–**9**, **12**–**15**

		Sugar moiety at C-3			Sugar moiety at C-28	
Compound	Proton	NOE* (proton)	HMBC† (carbon)	Proton	NOE* (proton)	HMBC† (carbon)
3	Ara-1	Agl-3	Agl-3	Glc_{inn}-1		Agl-28
	Glc-1	Ara-3	Ara-3			
	Xyl-1	Ara-2	Ara-2			
	Xyl-1	Glc-3	Glc-3			
4	Ara-1	Agl-3	Agl-3	Glc_{inn}-1		Agl-28
	Glc-1	Ara-3	Ara-3	Glc_{ter}-1	Glc_{inn}-6,6′	Glc_{inn}-6
5	Ara-1	Agl-3	Agl-3	Glc_{inn}-1		Agl-28
	Glc-1	Ara-3	Ara-3	Glc_{ter}-1	Glc_{inn}-6,6′	Glc_{inn}-6
	Xyl-1	Ara-2	Ara-2			
6	Glc_{inn}-1	Agl-3	Agl-3	Glc-1		Agl-28
	Glc_{ter}-1	Glc_{inn}-3	Glc_{inn}-3			
	Xyl-1	Glc_{inn}-2	Glc_{inn}-2			
7	Gal-1	Agl-3	Agl-3			
	Glc-1	Gal-3	Gal-3			
	Xyl-1	Gal-2	Gal-2			
8	Gal-1	Agl-3	Agl-3	Glc-1		Agl-28
	Glc-1	Gal-3	Gal-3			
	Xyl-1	Gal-2	Gal-2			
9	Gal-1	Agl-3	Agl-3	Glc_{inn}-1		Agl-28
	Glc-1	Gal-3	Gal-3	Glc_{ter}-1	Glc_{inn}-6,6′	Glc_{inn}-6
	Xyl-1	Gal-2	Gal-2			
12	Ara-1	Agl-3	Agl-3	Glc-1		Agl-28
	Glc-1	Ara-3	Ara-3			
	Xyl-1	Ara-2	Ara-2			
13	Ara-1	Agl-3	Agl-3			
	Glc-1	Ara-3	Ara-3			
	Xyl-1	Ara-2	Ara-2			
14	Ara-1	Agl-3	Agl-3	Glc_{inn}-1		Agl-28
	Glc-1	Ara-3	Ara-3	Glc_{ter}-1	Glc_{inn}-6,6′	Glc_{inn}-6
15	Glc_{inn}-1	Agl-3	Agl-3	Glc-1		Agl-28
	Glc_{ter}-1	Glc_{inn}-3	Glc_{inn}-3			
	Xyl-1	Glc_{inn}-2	Glc_{inn}-2			

inn: inner; ter: terminal.
*The NOEs were observed also at H-3 and H-5α of the sugar which anomeric proton was irradiated.
†The $^{n}J_{C-H} = 8$ Hz was used for HMBC spectrum.

Araliasaponin IX (**13**). Amorphous powder, $[\alpha]_D^{20}$ +16.7° (MeOH; *c* 0.33). Found: C, 58.12; H, 8.56. $C_{46}H_{74}O_{16} \cdot 7/2H_2O$ requires C, 58.39; H, 8.63%. FAB-MS *m/z*: 905 $[M + Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin X (**14**). Amorphous powder, $[\alpha]_D^{20}$ + 5.6° (MeOH; *c* 1.53). Found: C, 55.20; H, 8.30. $C_{53}H_{86}O_{22} \cdot 9/2H_2O$ requires C, 55.05; H, 8.28%. FAB-MS *m/z*: 1098 $[M + Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin XI (**15**). Amorphous powder, $[\alpha]_D^{20}$ + 8.2° (MeOH; *c* 0.79). Found: C, 55.68, H, 8.47. $C_{53}H_{86}O_{22} \cdot 4H_2O$ requires C, 55.48; H, 8.26%. FAB-MS *m/z*: 1098 $[M + Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Acid hydrolysis of **3–9** *and* **12–15**. Compound **3** (44 mg) was refluxed with 5% H_2SO_4 (1.5 ml) and dioxane (3 ml) for 4 hr. The reaction mixture was diluted with H_2O and extracted 3 × with EtOAc. The EtOAc layer was washed with H_2O and concd. The residue was subjected to HPLC (YMC Pack D-ODS-7, 2 × 25 cm; CH_3CN–H_2O (4:1) + 0.05% TFA) to give oleanolic acid (**3a**) (8.4 mg); the H_2O layer was passed through an Amberlite IRA-60E column. Compound **12** (60 mg) was treated in the same manner to give ursolic acid (**12a**) (23 mg). Compounds **4–9** and **13–15** (each 1 mg) were heated with 5% H_2SO_4 (0.05 ml) and dioxane (0.1 ml) at 100° for 2 hr. After dilution with H_2O, the reaction mixture was extracted 2 × with EtOAc and the H_2O layer was passed through an Amberlite IRA-60E coloum. From the EtOAc layer of compounds **4–9**, oleanolic acid (**3a**) was detected by HPLC (YMC Pack R-ODS-7, 4.6 mm × 25 cm, MeOH–H_2O (90:10) + 0.05% TFA; flow rate, 1.0 ml min^{-1}, UV 205 nm, R_t 12.4 min) and from that of compounds **13–15**, ursolic acid (**12a**) was detected under the same conditions, R_t, 12.8 min. From the H_2O layer, each monosacchride was detected as the alditol acetate [14] and as the thiazolidine derivative [15] by GC.

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