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ARALIASAPONINS XII–XVIII, TRITERPENE SAPONINS FROM THE ROOTS OF *ARALIA CHINENSIS*

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Key Word Index—*Aralia chinensis*; Araliaceae; araliasaponin; oleanane-type saponin; glucuronide saponin.

Abstract—Seven new oleanane-type saponins, named araliasaponins XII–XVIII, were isolated from the roots of *Aralia chinensis*, together with 14 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-glucopyranosyl(1 → 3)-[β-D-glucopyranosyl(1 → 2)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester, 3-*O*-β-D-glucopyranosyl(1 → 3)-[β-D-xylopyranosyl(1 → 2)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl ester, 3-*O*-β-D-glucopyranosyl(1 → 3)-[β-D-galactopyranosyl(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-glucopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl ester, 3-*O*-β-D-glucopyranosyl(1 → 3)-[β-D-galactopyranosyl(1 → 2)]-β-D-galactopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester, 3-*O*-α-L-arabinofuranosyl(1 → 4)-[β-D-glucopyranosyl(1 → 2)]-β-D-glucuronopyranosyl oleanolic acid dimethyl ester and 3-*O*-α-L-arabinofuranosyl(1 → 4)-[β-D-glucopyranosyl(1 → 2)]-β-D-glucuronopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl methyl ester, respectively.

INTRODUCTION

In a previous paper [1], we reported the isolation and the structural characterization of nine oleanane-type and six ursane-type triterpene saponins from the roots of *Aralia decaisneana*. In this paper we report the isolation and structural elucidation of seven new oleanane-type triterpene saponins, named araliasaponins (XII–XVIII), and 14 known oleanane-type triterpene saponins from *A. chinensis* L. Sun *et al.* [2] reported the isolation of three oleanane-type triterpene saponins, aralosides A and D and narcissiflorine, from the root barks of this plant.

RESULTS AND DISCUSSION

The roots of *A. chinensis* L. were extracted with ethanol–water (7:3) under reflux. The concentrated extract was diluted with water and passed through a porous polymer gel (Diaion HP-20) column. The methanolic eluate was chroamtographed on a silica gel column and separated into 11 fractions. Each fraction was treated with diazomethane and further purified by preparative HPLC, which resulted in the isolation of 21 triterpene saponins. By comparison of the NMR data, 14 known compounds were identified as elatoside F (**2**) [3], araliasaponins II (**3**), III (**4**), VI (**9**) and VII (**10**) [1], chikusetsusaponin IVa methyl ester (**11**) [4], zingibroside-R_1 dimethyl ester (**12**) [5], chikusetsusaponin V methyl ester (**13**) [6], hemsloside G_2 methyl ester (**14**) [7], tarasaponin IV methyl ester (**16**) [8], 3-*O*-β-D-arabinofuranosyl(1→4)-[β-D-glucopyranosyl(1→2)]-β-D-glucuronopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl methyl ester (**18**) [9], tarasaponin II methyl ester (**19**) [10], tarasaponin VI methyl ester (**20**) [8] and araloside A methyl ester (**21**) [11].

Araliasaponin XII (**1**) revealed a quasi-molecular ion peak $[M + Na]^+$ at *m/z* 1098 in the FAB mass spectrum and elemental analysis data was consistent with the molecular formula $C_{53}H_{86}O_{22}$. The ^1H NMR spectrum contained the signals of seven singlet groups at δ 0.85, 0.90, 0.92, 1.09, 1.09, 1.25 and 1.25, one trisubstituted olefinic proton at δ 5.42 and four anomeric protons at δ 4.78 (*d*, *J* = 7 Hz), 5.28 (*d*, *J* = 8 Hz), 5.50 (*d*, *J* = 8 Hz) and 6.32 (*d*, *J* = 8 Hz). The ^{13}C NMR data revealed the presence of six C-saturated quaternary carbons at δ 30.8, 37.1, 39.7, 40.0, 42.2 and 47.1, a pair of olefinic carbons at δ 122.9 and 144.1, one ester carbonyl carbon at δ 176.4 and four anomeric carbons at δ 95.8, 104.4, 105.0 and 105.4. The numbers and chemical shift of the tertiary methyl functions and quaternary carbons suggested that **1** was an oleanane-type triterpene saponin with one ester-type and three acetal-type glycosidic linkages. Upon acid hydrolysis, compound **1** gave oleanolic acid as an

aglycone moiety, and L-arabinose and D-glucose as a sugar moiety. The anomeric centres of the three D-glucosyl moieties were each determined to have the β-configuration based on the large $^3J_{H1-H2}$ values (8 Hz) and that of the L-arabinosyl moiety was in the α-configuration based on 7 Hz. The NOE difference spectrum was used to decide the sugar sequence after assignment of the protons and the carbons by the Hartmann–Hahn (HOHAHA) and heteronuclear single quantum coherence (HSQC) spectrum. When the signal at δ 5.28 (H-1 of Glc) was irradiated, a NOE was observed at δ 4.32 due to H-3 of arabinose. On irradiation of the signal at δ 5.50 (H-1 of Glc), a NOE was observed at the signal at δ 4.71 due to H-2 of arabinose. When the signal at δ 4.78 (H-1 of Ara) was irradiated, a NOE was observed at δ 3.24 due to H-3 of the aglycone moiety. In the heteronuclear multiple bond connectivity (HMBC) spectrum, the $^1H-^{13}C$ long-range couplings were observed between H-1 of glucose (δ 5.28) and C-3 of arabinose (δ 83.3), H-1 of glucose (δ 5.50) and C-2 of arabinose (δ 77.4), H-1 of arabinose (δ 4.78) and C-3 of the aglycone moiety (δ 89.0), and H-1 of glucose (δ 6.32) and C-28 of the aglycone moiety (δ 176.4). Thus, the structure of araliasaponin XII was concluded to be 3-*O*-β-D-glucopyranosyl(1 $\rightarrow$ 3)-[β-D-glucopyranosyl(1 $\rightarrow$ 2)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester.

Araliasaponin XIII (**5**) exhibited a quasi-molecular ion peak $[M + Na]^+$ at *m/z* 1376 in the FAB-mass spectrum. On acid hydrolysis, compound **5** afforded oleanolic acid and L-arabinose, D-glucose, D-xylose and L-rhamnose. The ^1H and ^{13}C NMR spectra showed the presence of six anomeric signals at δ 4.74 (*d*, *J* = 7.5 Hz), 4.97 (*d*, *J* = 8 Hz), 5.27 (*d*, *J* = 8 Hz), 5.38 (*d*, *J* = 8 Hz), 5.82 (*br s*) and 6.22 (*d*, *J* = 8 Hz) and 95.7, 102.8, 104.9, 105.1 (2C) and 105.6, respectively. To decide the sugar sequences we employed the NOE difference and HMBC spectrum after assignment of the sugar proton and carbon signals. When the signal at δ 5.27 (H-1 of Glc) was irradiated, a NOE was observed at δ 4.26 (*dd*, *J* = 9 and 3 Hz) due to H-3 of arabinose. On irradiation of the signal at δ 5.38 (H-1 of Xyl), a NOE was observed at δ 4.65 (overlapped) due to H-2 of arabinose. On irradiation of the signal at δ 4.74 (H-1 of Ara), a NOE was observed at δ 3.26 (*dd*, *J* = 12 and 4 Hz) due to H-3 of aglycone. In the HMBC spectrum, $^3J_{COCH}$ was observed between H-1 of glucose (δ 5.27) and C-3 of arabinose (δ 83.7), H-1 of xylose (δ 5.38) and C-2 of arabinose (δ 77.5), and H-1 of arabinose (δ 4.74) and C-3 of aglycone (δ 89.2). The carbon signal of C-28 was shifted upfield at δ 176.5, suggesting the presence of an ester-type glycosidic linkage. In the NOE difference spectrum, NOEs were observed at H-4 of glucose [δ 4.38 (*t*, *J* = 9.5 Hz)] and H_2-6 of glucose [δ 4.49 and 4.64 (overlapped)] on irradiation at H-1 of rhamnose [δ 5.82 (*br s*)] and H-1 of glucose [δ 4.97 (*d*, *J* = 8 Hz], respectively. In the HMBC spectrum, long-range couplings were observed between H-1 of rhamnose (δ 5.82) and C-4 of glucose (δ 78.4), H-1 of glucose (δ 4.97) and C-6 of glucose (δ 69.3), and H-1 of glucose (δ 6.22) and C-28 of aglycone (δ 176.5). These results led us to conclude that the structure of araliasaponin XIII was 3-*O*-β-D-glucopyranosyl(1 $\rightarrow$ 3)-β-D-xylopyranosyl(1 $\rightarrow$ 2)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-α-L-rhamnopyranosyl(1 $\rightarrow$ 4)-β-D-glucopyranosyl(1 $\rightarrow$ 6)-β-D-glucopyranosyl ester.

Araliasaponin XIV (**6**) showed a quasi-molecular ion peak at *m/z* 1128 $[M + Na]^+$ in the FAB-mass spectrum, corresponding to the molecular formula $C_{54}H_{88}O_{23}$. On acid hydrolysis, compound **6** gave oleanolic acid, D-glucose and D-galactose. The ^1H and ^{13}C NMR spectral data showed four anomeric signals (δ 4.83, 5.31, 5.55 and 6.31, and 95.8, 104.6, 104.7 and 105.0). Because the C-3 chemical shift in the aglycone was shifted downfield at δ 89.4 and the C-28 shifted upfield at δ 176.4, compound **6** was a bis-desmoside. NOEs were observed at H-3 of glucose (δ 4.21), H-2 of glucose (δ 4.36) and H-3 of aglycone [δ 3.30 (*dd*, *J* = 12 and 4 Hz)] on irradiation at H-1 of glucose [δ 5.31 (*d*, *J* = 8 Hz)], H-1 of galactose [δ 5.55 (*d*, *J* = 8 Hz)] and H-1 of glucose [δ 4.83 (*d*, *J* = 8 Hz)], respectively. In the HMBC spectrum, heteronuclear long-range couplings were observed between H-1 of glucose (δ 5.31) and C-3 of glucose (δ 88.7), H-1 of galactose (δ 5.55) and C-2 of glucose (δ 79.7), H-1 of glucose and C-3 of aglycone (δ 89.4), and H-1 of glucose (δ 6.31) and C-28 of aglycone. Thus, the structure of araliasaponin XIV was concluded to be 3-*O*-β-D-glucopyranosyl(1 $\rightarrow$ 3)-[β-D-galactopyranosyl-(1 $\rightarrow$ 2)]-β-D-glucopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester.

Araliasaponin XV (**7**) showed spectroscopic propaties similar to those of araliasaponin IV [1]. The molecular formula, $C_{59}H_{96}O_{27}$, was established by FAB-mass spectrum, which showed a quasi-molecular ion peak at *m/z* 1260 $[M + Na]^+$, and elemental analysis data. This was 162 mass units more than that of araliasaponin IV and indicated the presence of one more hexose in **7**. In the ^{13}C NMR spectrum of **7**, six more carbon signals due to glucose were observed and C-6 of glucose was shifted downfield by 7.2 ppm and C-5 of glucose shifted upfield by 1.3 ppm in the glucosyl moiety at C-28 by comparing with those of araliasaponin IV. Consequently, the structure of araliasaponin XV was established as 3-*O*-β-D-glucopyranosyl(1 $\rightarrow$ 3)-[β-D-xylopyranosyl(1 $\rightarrow$ 2)]-β-D-glucopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl(1 $\rightarrow$ 6)-β-D-glucopyranosyl ester. NOE difference and HMBC spectra also supported this structure.

The NMR spectra of araliasaponin XVI (**8**) were similar to those of araliasaponin VI [1]. The FAB-mass spectrum showed a quasi-molecular ion peak at *m/z* 1128 $[M + Na]^+$, suggesting that araliasaponin XVI had hexose instead of xylose in araliasaponin VI. From the data of NOE difference and HMBC spectra, the structure of araliasaponin XVI was elucidated as 3-*O*-β-D-glucopyranosyl(1 $\rightarrow$ 3)-[β-D-galactopyran-

osyl(1→2)]-β-D-galactopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester.

Araliasaponin XVII dimethyl ester (**15**) showed a quasi-molecular ion peak at *m/z* 978 $[M+Na]^+$ in the FAB-mass spectrum, indicating its molecular formula to be $C_{49}H_{78}O_{18}$. The ^1H and ^{13}C NMR spectra were similar to those of **16** [8] except for the lack of ester-linked glucose. A NOE difference spectrum irradiating each anomeric proton signal and the HMBC spectrum established the structure of araliasaponin XVII as 3-*O*-α-L-arabinofuranosyl(1→4)-[β-D-glucopyranosyl(1→2)]-β-D-glucuronopyranosyl oleanolic acid dimethyl ester.

The ^{13}C NMR spectrum of araliasaponin XVIII methyl ester (**17**) showed the presence of one more glucose by comparison with that of tarasaponin IV methyl ester (**16**) [8]. The ^{13}C NMR data due to the sugar chain at C-3 were superimposable to those of **16**. When the anomeric proton signal at δ 5.02 was irradiated, a NOE was observed at the signal due to H-6 of ester-linked glucose [δ 4.70 (*br d*, *J* = 11 Hz)]. In the HMBC spectrum, the cross peak was observed between H-1 of glucose (δ 5.02) and C-6 of ester-linked glucose (δ 69.5). These results led us to conclude that the structure of araliasaponin XVIII methyl ester was 3-*O*-α-L-arabinofuranosyl(1→4)-[β-D-glucopyranosyl(1→2)]-β-D-glucuronopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl ester.

The anomeric configurations of D-glucose, D-galactose and D-xylose were determined to be all β and that of L-arabinose to be α from each $^3J_{H1-H2}$ value and that of L-rhamnose was determined to be α by comparison of the ^{13}C NMR data for C-3 and C-5 [12].

EXPERIMENTAL

The instruments used were the same as described in ref. [1].

Plant material. Aralia chinensis L. was collected in An Hui, China, in July 1993 and was identified by Dr Gui Xin Chou, An Hui Traditional Chinese Medical College, An Hui, China, and a voucher specimen is deposited in the Herbarium of this institute.

Extraction and isolation. Dried roots (5 kg) of *A. chinensis* were extracted 2× with EtOH–H_2O (7:3) under reflux. The extract was concd under red. pres. and the concd extract was diluted with water H_2O (8 l) and the soln was passed through Diaion HP-20 (Mitsubishikasei Co.) (9 × 42 cm). The column was washed with H_2O and the adsorbed materials were eluted with MeOH. The MeOH eluate (90 g) was subjected to CC on silica gel (900 g) with $CHCl_3$–MeOH–H_2O (65:33:2) increasing the proportions of MeOH to give 11 frs (Frs A–K). After passing through a cation exchanger (Amberlyst 15), each fr. was treated with CH_2N_2. From these methylated frs, 21 saponins were isolated by prep. HPLC [Develosil Lop-ODS, 5 × 50 cm × 2; H_2O–MeOH (1:1 → 1:4) linear gradient: **1** (104 mg), **2** (160 mg), **3** (50 mg), **4** (416 mg), **5** (60 mg), **6** (54 mg), **7** (15 mg), **8** (30 mg), **9** (156 mg), **10** (20 mg), **11** (84 mg), **12** (26 mg), **13** (20 mg), **14** (40 mg), **15** (50 mg), **16** (340 mg), **17** (30 mg), **18** (34 mg), **19** (70 mg), **20** (24 mg), **21** (320 mg).

Araliasaponin XII (**1**). Amorphous powder, $[\alpha]_D^{27}$ +15.3° (MeOH; *c* 1.37). (Found: C, 53.30; H, 8.23. $C_{53}H_{86}O_{22}.13/2H_2O$ requires C, 53.39; H, 8.37%). FAB-MS *m/z*: 1098 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin XIII (**5**). Amorphous powder, $[\alpha]_D^{26}$ −7.1° (MeOH; *c* 1.89). (Found: C, 52.00; H, 8.21. $C_{64}H_{104}O_{30}.7H_2O$ requires C, 51.98; H, 8.04%). FAB-MS *m/z*: 1376 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin XIV (**6**). Amorphous powder, $[\alpha]_D^{26}$ +16.8° (MeOH; *c* 1.37). (Found: C, 55.21; H, 8.17. $C_{54}H_{88}O_{23}.4H_2O$ requires C, 55.09; H, 8.22%). FAB-MS *m/z*: 1128 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin XV (**7**). Amorphous powder, $[\alpha]_D^{26}$ +2.8° (MeOH; *c* 1.01). (Found: C, 51.77; H, 8.28. $C_{59}H_{96}O_{27}.7H_2O$ requires C, 51.97; H, 8.13%). FAB-MS *m/z*: 1260 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin XVI (**8**). Amorphous powder, $[\alpha]_D^{25}$ +15.9° (MeOH; *c* 0.76). (Found: C, 56.56; H, 8.34. $C_{54}H_{88}O_{23}.5/2H_2O$ requires C, 56.38; H, 8.15%). FAB-MS *m/z*: 1128 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin XVII dimethyl ester (**15**). Amorphous powder, $[\alpha]_D^{27}$ −19.8° (MeOH; *c* 1.29). (Found: C, 58.89; H, 8.35. $C_{49}H_{78}O_{18}.5/2H_2O$ requires C, 58.84; H, 8.36%). FAB-MS *m/z*: 978 $[M+Na]^-$. ^1H and ^{13}C NMR: Tables 1 and 2.

Araliasaponin XVIII methyl ester (**17**). Amorphous powder, $[\alpha]_D^{25}$ −33.3° (MeOH; *c* 3.74). (Found: C, 55.53; H, 8.02. $C_{60}H_{96}O_{28}.2H_2O$ requires C, 55.37; H, 7.75%). FAB-MS *m/z*: 1228 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Acid hydrolysis of **1**, **5–8**, **15** *and* **17**. Each compound (1 mg) was heated with 5% H_2SO_4 (0.05 ml) and dioxane (0.1 ml) at 100° for 1 hr. After dilution with H_2O, the reaction mixt. was extracted 2× with EtOAc and the H_2O layer was passed through an Amberlite IRA-60E column. The H_2O eluate was concd and derivatized to thiazolidine as described previously [13]. Monosaccharides were detected by GC: D-glucose, L-arabinose from **1**, **15**, **17**; D-glucose, D-xylose, L-arabinose, L-rhamnose from **5**; D-glucose, D-galactose from **6**, **8**; D-glucose, D-xylose from **7**. From the EtOAc layer, oleanolic acid was detected by HPLC [Develosil ODS-5, 4.6 mm × 15 cm, MeOH–H_2O (9:1) + 0.05% TFA; flow rate, 1.0 ml min^{-1}, UV 205 nm, R_t 11.0 min].

Acknowledgement—We thank the staff of the Central Analytical Laboratory of the University of Shizuoka for measurement of FAB-mass spectra and elemental analyses.

Table 1. ^{1}H NMR data for compounds **1**, **5–8**, **15** and **17** in pyridine-d_5 at 35°

	1	**5**	**6**	**7**	**8**	**15**	**17**
Aglycone moiety							
3	3.24 *dd* (12, 4)	3.26 *dd* (12, 4)	3.30 *dd* (12, 4)	3.27 *dd* (12, 4)	3.26 *dd* (12, 4)	3.21 *dd* (12, 4)	3.19 *
12	5.42 *t*-like	5.41 *t*-like	5.43 *t*-like	5.54 *t*-like	5.42 *t*-like	5.37 *t*-like	5.40 *
23	1.25 *s*	1.27 *s*	1.33 *s*	1.27 *s*	1.34 *s*	1.24 *s*	1.22 *s*
24	1.09 *s*	1.10 *s*	1.12 *s*	1.08 *s*	1.13 *s*	1.06 *s*	1.05 *s*
25	0.85 *s*	0.90 *s*	0.84 *s*	0.88 *s*	0.84 *s*	0.84 *s*	0.85 *s*
26	1.09 *s*	1.09 *s*	1.09 *s*	1.09 *s*	1.08 *s*	0.81 *s*	1.08 *s*
27	1.25 *s*	1.24 *s*	1.25 *s*	1.26 *s*	1.26 *s*	1.22 *s*	1.23 *s*
29	0.92 *s*	0.90 *s*	0.91 *s*	0.89 *s*	0.91 *s*	0.92 *s*	0.89 *s*
30	0.90 *s*	0.90 *s*	0.89 *s*	0.89 *s*	0.89 *s*	0.94 *s*	0.89 *s*
COOMe						3.71 *s*	
Sugar moiety							
at C-3	(Ara)	(Ara)	(Glc)	(Glc)	(Gal)	(GlcA)	(GlcA)
1	4.78 *d* (7)	4.74 *d* (7.5)	4.83 *d* (8)	4.81 *d* (8)	4.80 *d* (8)	4.89 *d* (7)	4.89 *d* (8)
2	4.71 *dd* (9, 7)	4.65 *	4.36 *	4.28 *	4.76 *	4.28 *	4.28 *
3	4.32 *	4.26 *dd* (9, 3)	4.21 *	4.20 *	4.28 *	4.48 *	—
4	4.48 *	4.48 *	—	4.03 *	4.55 *br d* (3.5)	4.77 *	4.48 *
5	3.66 *br d* (12)	3.64 *	3.79 *m*	3.80 *m*	3.97 *	4.48 *	4.48 *
5	—	—					
6				—	—		
6			—	—	—		
Me						3.74 *s*	3.74 *s*
Sugar at C-2 of inner sugar							
	(Glc)	(Xyl)	(Gal)	(Xyl)	(Gal)	(Glc)	(Glc)
1	5.50 *d* (8)	5.38 *d* (8)	5.55 *d* (8)	5.57 *d* (8)	5.54 *d* (8)	5.38 *d* (8)	5.39 *d* (8)
2	4.03 *	4.01 *t* (8)	4.49 *	4.03 *	4.46 *	4.06 *t* (8)	4.06 *t* (8)
3	4.19 *	4.09 *	4.17 *	4.16 *	4.09 *dd* (9.5, 3.5)	4.22 *	4.22 *
4	—	4.19 *	4.59 *br d* (3)	4.21 *	4.76 *	4.24 *	4.26 *
5	3.70 *m*	3.45 *br t* (10)	3.95 *br t* (6.5)	3.59 *t* (10)	3.79 *br t* (7)	3.91 *m*	3.91 *m*
5		—		4.30 *			
6	—		—		—	4.13 *dd* (12, 4)	4.41 *dd* (11, 4.5)
6	—		—			4.26 *	4.46 *

Sugar at C-3 or C-4 of inner sugar							
	(Glc)	(Glc)	(Glc)	(Glc)	(Glc)	(Ara)	(Ara)
1	5.28 *d* (8)	5.27 *d* (8)	5.31 *d* (8)	5.33 *d* (8)	5.28 *d* (8)	5.69 *br s*	5.70 *br s*
2	3.99 *	3.99 *t* (8)	4.03 *	4.03 *	3.98 *	4.76 *	4.77 *
3	4.17 *	4.19 *	4.15 *	4.20 *	4.18 *	4.28 *	—
4	—	—	—	4.14 *	—	4.84 *dd* (9, 4.5)	4.85 *m*
5	3.92 *m*	3.92 *	4.01 *	4.00 *	3.86 *m*	4.42 *dd* (11.5, 4.5)	—
5						4.49 *dd* (11.5, 3)	
6	—		—	4.52 *br d* (11)	—		
6	—	—	—		—		
Sugar moiety at C-28							
	(Glc)	(Glc)	(Glc)	(Glc)	(Glc)		
1	6.32 d (8)	6.22 d (8)	6.31 d (8)	6.23 d (8)	6.30 d (8)		
2	4.17 *	—	4.19 *	4.12 *	4.18 *		
3	4.27 *	4.19 *	4.26 *	4.21 *	4.26 *		
4	—	4.28 t (9)	4.33 *	4.30 *	—		
5	4.02 *	4.09 *	4.01 *	4.10 *	4.02 *		
6	—	4.49 *	—	4.35 *	—		
6	—	4.64 *	—	4.69 br d (11)	—		
Sugar at C-6 of inner sugar							
		(Glc)		(Glc)			
1		4.97 *d* (8)		5.02 *d* (8)			
2		3.92 *		4.00 *			
3		4.13 *		4.16 *			
4		4.38 *t* (9.5)		4.20 *			
5		3.64 *		3.87 *m*			
6		—		4.34 *			
6		—		4.46 *			
		(Rha)					
1		5.82 br s					
2		4.65 *					
3		4.53 dd (9.5, 3.5)					
4		—					
5		4.92 dd (9.5, 6)					
6		1.69 d (6)					

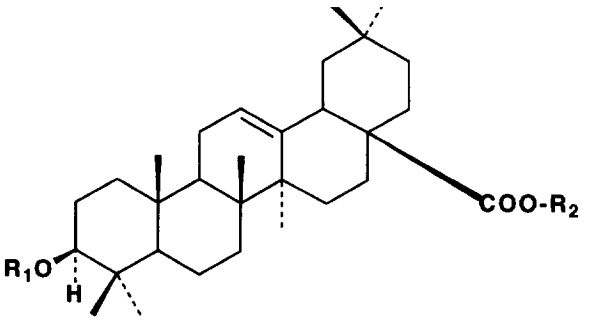
*Obscured by other signals; couplings could not be accurately determined.

—Obscured by other signals; chemical shifts could not be accurately determined.

Table 2. ^{13}C NMR data for the sugar moieties of compounds **1**, **5–8**, **15** and **17** in pyridine-d_5 at 35°

	1	**5**	**6**	**7**	**8**	**15**	**17**
At C-3	(Ara)	(Ara)	(Glc)	(Glc)	(Gal)	(GlcA)	(GlcA)
1	105.4	105.6	105.0	104.7	105.4	105.0	105.0
2	77.4	77.5	79.7	79.0	77.6	81.7	81.5
3	83.3	83.7	88.7	89.0	84.6	74.8	74.8
4	68.7	68.9	70.2	70.2	69.7	78.4	78.3‡
5	65.9	66.1	77.7	77.8	76.1	76.8	76.8
6			62.3*	62.4	62.4	170.0	170.0
Me						52.4	52.4
Sugar at C-2 of inner sugar							
	(Glc)	(Xyl)	(Gal)	(Xyl)	(Gal)	(Glc)	(Glc)
1	104.4	105.1	104.6	105.0	104.9	105.5	105.4
2	76.2	76.0	73.9	76.3	73.7	76.8	76.8
3	78.5	79.0	75.4	79.4	75.5	78.1	78.3†
4	72.5	71.4	69.8	71.4	69.8	71.9	71.9
5	77.5	67.1	76.5	67.3	76.3	78.3	78.1
6	63.3		61.6*		61.6	62.5	62.5
Sugar at C-3 or 4 of inner sugar							
	(Glc)	(Glc)	(Glc)	(Glc)	(Glc)	(Ara)	(Ara)
1	105.0	105.1	104.7	104.8	105.1	108.9	108.9
2	75.3	75.3	75.4	75.4	75.4	82.7	82.7
3	78.7	78.5	78.6	78.7	78.3	75.8	75.8
4	71.6	71.6	71.6	71.6	71.6	87.3	87.3
5	78.3	78.4	78.6	78.6	78.4	62.9	62.9
6	62.6	62.6	62.7	62.8	62.5		
At C-28							
	(Glc)	(Glc)	(Glc)	(Glc)	(Glc)		(Glc)
1	95.8	95.7	95.8	95.7	95.8		95.7
2	74.2	73.9	74.2	74.0	74.2		74.0
3	78.9	78.8	78.9	78.8	78.9		78.8
4	71.3	71.0	71.3	71.1	71.3		71.1
5	79.3	78.1	79.3	78.0	79.3		78.0
6	62.3	69.3	62.3*	69.6	62.4		69.5
Sugar at C-6 of inner sugar							
		(Glc)		(Glc)			(Glc)
1		104.9		105.3			105.3
2		75.3		75.2			75.2
3		77.2		78.4			78.4†
4		78.4		71.6			71.6
5		76.6		78.4			78.4†
6		61.4		62.8			62.7
		(Rha)					
1		102.8					
2		72.6					
3		72.8					
4		74.0					
5		70.3					
6		18.5					

*†Assignments may be interchanged in each column.



	R_1	R_2
1:	-Ara•(*p*)^{2}—Glc (|3 Glc)	-Glc
2:	-Ara•(*p*)^{2}—Xyl (|3 Glc)	-Glc
3:	-Ara•(*p*)^{3}—Glc	-Glc^{6}—Glc
4:	-Ara•(*p*)^{2}—Xyl (|3 Glc)	-Glc^{6}—Glc
5:	-Ara•(*p*)^{2}—Xyl (|3 Glc)	-Glc^{6}—Glc (|4 Rha)
6:	-Glc^{2}—Gal (|3 Glc)	-Glc
7:	-Glc^{2}—Xyl (|3 Glc)	-Glc^{6}—Glc
8:	-Gal^{2}—Gal (|3 Glc)	-Glc
9:	-Gal^{2}—Xyl (|3 Glc)	-Glc
10:	-Gal^{2}—Xyl (|3 Glc)	-Glc^{6}—Glc
11:	-GlcA•Me	-Glc
12:	-GlcA•Me^{2}—Glc	-Me
13:	-GlcA•Me^{2}—Glc	-Glc
14:	-GlcA•Me^{2}—Glc	-Glc^{6}—Glc
15:	-GlcA•Me^{2}—Glc (|4 Ara•(*f*))	-Me
16:	-GlcA•Me^{2}—Glc (|4 Ara•(*f*))	-Glc
17:	-GlcA•Me^{2}—Glc (|4 Ara•(*f*))	-Glc^{6}—Glc
18:	-GlcA•Me^{2}—Glc (|3 Gal)	-Glc
19:	-GlcA•Me^{2}—Xyl (|3 Gal)	-Me
20:	-GlcA•Me^{2}—Xyl (|3 Gal)	-Glc
21:	-GlcA•Me^{4}—Ara•(*f*)	-Glc

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