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TRITERPENOID GLUCURONIDE SAPONINS FROM ROOT BARK OF *ARALIA ARMATA**

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Key Word Index—*Aralia armata*; Araliaceae; root bark; triterpenoid saponin; oleanolic acid glucuronide.

Abstract—Seventeen oleanane-type saponins were isolated from the root bark of *Aralia armata*. Their structures were elucidated by chemical and spectral evidence. Except for oleanolic acid 28-*O*-β-D-glucopyranoside, all the saponins have a glucuronopyranosyl residue at the C-3 position of the aglycones and other sugar substitutes bind to glucuronic acid at positions C-3 and/or C-4. A comparison of saponin constituents of this plant with other araliaceous plants is provided.

INTRODUCTION

It is known that the roots of several members of *Aralia* species have been used as folk medicines for rheumatism, tonic and diabetes in China, Japan and Russia. In the early part of the sixties, Kochetkov *et al.* [1] isolated physiologically active saponins, aralosides A, B and C, first from this genus. Many triterpenoid saponins have recently been isolated from several *Aralia* species [2–9]. *A. armata* (Wall.) Seem. is one of common herbal medicines of the genus *Aralia* in China. No chemical work, however, has been done on this plant. The present paper deals with the isolation and structure determination of 16 oleanolic acid-based saponins along with a minor saponin of hederagenin from the root bark of this plant.

RESULTS AND DISCUSSION

The air-dried sample was percolated with cold methanol. A suspension of the methanol extract was washed with ether, and was then extracted with butanol saturated with water. The butanol phase on repeated chromatographic purification led to the isolation of 17 oleanane-type saponins, **1**–**17** (Chart 1).

The 11 known saponins were identified as calenduloside E (**1**) [10] and its methyl ester (**2**) [11], narcissiflorine (**4**) [12], momordin Ia (**6**) [13], calenduloside G (**7**) [14], stipuleanoside R_1 (**10**) [15], chikusetsusaponin IVa (**11**) [16] and its methyl ester (**12**) [17], araloside A methyl ester (**14**) [3], oleanolic acid 28-*O*-β-D-glucopyranoside (**16**) [18], and hederagenin 3-*O*-β-D-glucuronopyranoside-6′-*O*-methyl ester (**17**) [19] mainly by the comparison of the ^{1}H NMR and ^{13}C NMR spectral data with the published values.

Compound **5** was obtained as a powder and gave a quasi molecular ion at *m/z* 801 $[M + Na]^+$ in the secondary ion (SI) mass spectrum. When compared with narcissiflorine (**4**), the presence of an additional methyl group in **5** was indicated by a signal at δ3.73 in the ^{1}H NMR spectrum as well as a signal at δ52.3 in the ^{13}C NMR spectrum. Comparison of the ^{13}C NMR data of **5** with those of **4** [12] showed that the C-5 signal of glucuronyl unit was displaced upfield by 0.6 ppm, whereas C-6 was deshielded by 1.7 ppm. The other signals remained almost unaffected. This indicated that the methyl group in **5** is located at the 6-carboxyl group of glucuronic acid. Hence the structure of saponin **5** was established as oleanolic acid 3-*O*-[α-L-arabinofuranosyl-(1–4)-β-D-glucuronopyranoside-6-*O*-methyl ester], namely, narcissiflorine methyl ester.

Compound **8**, obtained as a powder, showed the $[M + Na]^+$ peak at *m/z* 831 in the SI mass spectrum. The ^{13}C NMR spectrum indicated the presence of two anomeric carbons (δ106.7 and 106.4). Acid hydrolysis of **8** yielded oleanolic acid and D-glucuronic acid together with D-galactose. The ^{13}C NMR signals assignable to the terminal sugar was coincident with methyl β-D-galactopyranoside. Since **8** was not hydrolysed with 0.5 N potassium hydroxide and the ^{13}C NMR signal of C-28 carboxyl of oleanolic acid moiety appeared at δ180.2, the 28-carboxyl function was not esterified. The ^{13}C NMR

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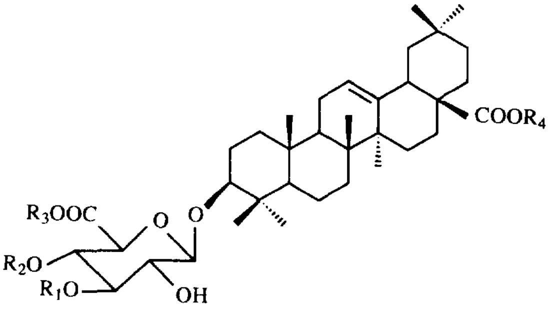
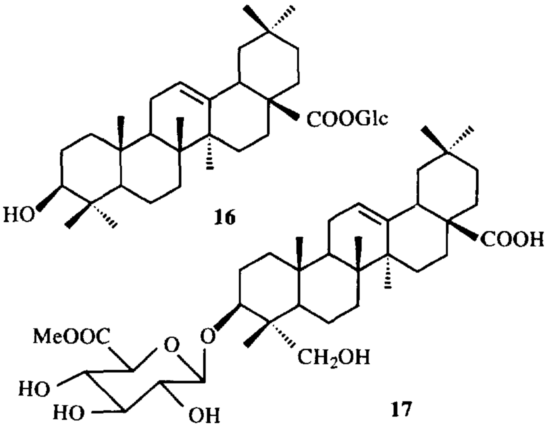


Saponin	R$_1$	R$_2$	R$_3$	R$_4$
1	H	H	H	H
2	H	H	Me	H
3	H	H	Bu	H
4	H	Ara*f*	H	H
5	H	Ara*f*	Me	H
6	Ara*p*	H	H	H
7	Gal	H	H	H
8	Gal	H	Me	H
9	Gal	H	Bu	H
10	Glc	Ara*f*	H	H
11	H	H	H	Glc
12	H	H	Me	Glc
13	H	H	Bu	Glc
14	H	Ara*f*	Me	Glc
15	Gal	H	Me	Glc



16

17

Chart 1.

signals of the C-3 of oleanolic acid moiety (δ89.3) in **8**, combined with above fact, indicated that **8** was oleanolic acid 3-*O*-glycoside. The β-linkage of glucuronic acid moiety was suggested by the *J* value of the anomeric proton ($J = 7.8$ Hz). The C-3 signal of the glucuronyl unit of **8** was shifted downfield by 9.2 ppm compared with the co-occurring saponin **1**. Thus, it was apparent that the terminal sugar in **8** was linked to the 3-hydroxyl of the glucuronyl unit. From these results **8** was determined to be oleanolic acid 3-*O*-[β-D-galactopyranosyl-(1–3)-β-D-glucuronopyranoside-6-*O*-methyl ester].

Three compounds, **3**, **9** and **13** showed a close resemblance with **2**, **8**, and **12**, respectively, in the ^{13}C NMR spectra except for the signals at δ65, 31, 19 and 14, suggesting the presence of an ester-linked butyl group. Acid hydrolysis of **9** afforded, besides oleanolic acid, D-glucuronic acid and D-galactose, while alkaline hydrolysis of **13** with 0.5 N potassium hydroxide only yielded D-glucose as sugar together with saponin **1**. These results were the same with the products of hydrolysis of **8** and **12**, respectively. The quasi molecular ions in the SI mass spectra also confirmed that the carboxylic group of glucuronic acid in **3**, **9** and **13** was esterified with a butyl group instead of a methyl group. Therefore, **3**, **9** and **13** can be formulated as illustrated in Chart 1.

The SI-mass spectrum of **15** showed the $[M + Na]^+$ peak at *m*/*z* 993. Alkaline hydrolysis of **15** with 0.5 N potassium hydroxide gave the corresponding prosapogenin **7** and D-glucose. Thus, **15** was a bisglycosidic saponin with glucose attached to the 28-carboxyl group of oleanolic acid. The anomeric proton signal of the glucose appeared at δ6.30 ($J = 8.0$ Hz) in its ^{1}H NMR spectrum and the anomeric carbon signal of that at δ95.8 in the ^{13}C NMR spectrum, indicating that the glucose moiety gave a β-configuration. Thus, **15** was concluded to be oleanolic acid 3-*O*-[β-D-galactopyranosyl-(1–3)-β-D-glucuronopyranoside-6-*O*-methyl ester]-28-*O*-β-D-glucopyranoside.

The methanol extract of *A. armata* contains many kinds of triterpenoid saponins, as the TLC analysis revealed. It is formed of numerous glycosides of oleanolic acid, but only traces of saponins of hederagenin could be isolated. All the saponins obtained from *A. armata* have a glucuronopyranosyl residue at the 3-hydroxyl of the aglycone except for **16**, which is an ester glycoside of oleanolic acid possessing no sugar moiety at the C-3 hydroxyl group. Of these saponins, **3**, **5**, **8**, **9** and **13** are new compounds; **15** is reported for the first time as a natural constituent although it has been reported as a methyl ester derivative after treating the crude saponin-containing fraction of the root bark of *A. elata* with diazomethane [4]. Saponins **2**, **6**, **7** and **10** were found previously only from a single natural source respectively, and therefore, this is the second report of their existence. In addition, we also found that the saponins of this plant showed some interesting relationships with those of some other araliaceous plants:

(1) Saponins **1**, **11** and **12** have been reported to be the main constituents of the rhizome of many *Panax* species which have horizontally elongated rhizomes.

(2) Saponins **2**, **3**, **5**, **8**, **9**, **12** and **13** were identified as the methyl or butyl esters of **1**, **4**, **7** and **11**. A thorough survey of the literature showed that many plants contain a fairly large amount of **1**, **4** or **11**, but corresponding esterified derivatives were only found from some species of Araliaceae [3, 11, 19–22] and a few other plants, in which the structures of saponins are related significantly to the major oleanane-saponins of araliaceous plants [13, 17, 23].

Table 1. ^{13}C NMR chemical shifts of **1**–**17** (δ: ppm, 100 MHz, pyridine-d_5)

Carbon	1	2	3	4	5	6	7	8	9
Oleanolic acid									
3	89.2	89.2	89.2	89.2	89.3	89.4	89.2	89.3	89.3
4	39.5	39.5	39.6	39.5	39.5	39.5	39.5	39.5	39.5
5	55.9	55.8	55.8	55.8	55.8	55.6	55.8	55.7	55.8
23	28.3	28.2	28.4	28.2	28.2	28.1	28.2	28.1	28.1
24	17.0	16.9	16.9	17.0	16.9	16.9	17.0	16.9	16.9
28	180.2	180.2	nd	180.2	180.2	180.1	180.2	180.2	180.2
Glucuronic acid									
1	106.8	107.3	107.4	107.0	106.9	106.8	106.6	106.7	106.8
2	75.4	75.4	75.5	75.4	75.1	74.6	74.3	74.1	74.2
3	78.2	77.9	78.1	76.3	76.0	85.7	87.7	87.4	87.6
4	73.6	73.2	73.1	78.8	78.5	71.2	71.7	71.4	71.3
5	77.1	77.2	77.4	nd	75.1	76.8	nd	76.6	76.8
6	nd	170.8	170.7	nd	170.3	170.3	nd	170.2	169.7
Ester moiety									
COOMe		52.0			52.3	52.2		52.1	
COOBu			65.0						65.1
			30.9						30.9
			19.3						19.2
			13.8						13.7
Arabinose									
1				108.6	108.7	106.0			
2				82.5	82.6	72.9			
3				76.8	77.0	74.5			
4				87.8	87.5	69.3			
5				62.7	62.6	67.2			
Galactose									
1							106.4	106.4	106.5
2							73.0	73.1	73.1
3							75.1	75.1	75.2
4							70.2	70.1	70.2
5							77.3	77.3	77.3
6							62.2	62.1	62.1

(3) A pair of saponins, **5** and **6** were simultaneously isolated in the present study, which suggested that *A. armata* contains arabinopyranoside as well as arabinofuranoside of the same aglycone. It is interesting that this rare coexisting phenomenon also occurred in *A. chinensis* [6], *Panax* spp. [24] and some related plants [25, 26]. The structural similarity of saponins in *A. armata* and in some other species of Araliaceae is of chemotaxonomic and pharmacological importances.

The saponins obtained in the present study cause potent membrane perturbations in liposomes produced from egg phospholipid or cholesterol-containing liposomes [27].

EXPERIMENTAL

General. The NMR spectra were measured in pyridine-d_5 and were recorded at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR on a Bruker AM-400 apparatus. Chemical shifts are given in δ values relative to TMS.

Plant material. The root barks of *Aralia armata* were collected at Guangxi, China. A voucher specimen is deposited in the Institute of Medicinal Plant Development, Beijing.

Isolation and purification of saponins. Air-dried and powdered root barks (5.5 kg) were percolated at room temp. with MeOH. After concn under red. pres., the percolate was suspended in hot water and successively partitioned with Et_2O and n-BuOH satd with H_2O. The BuOH layer was evapd to dryness yielding a brown mass (*ca* 300 g). The MeOH-soluble part (dry wt 80 g) was first chromatographed on a dry column of silica gel eluting with $CHCl_3$ containing increasing proportions of MeOH. The eluates were further repeatedly sepd by following chromatographic methods: Diaion HP-20 column using MeOH–H_2O as the solvent; medium-pressure column of silica gel (CIG column system, Kusano) by elution with $CHCl_3$–MeOH–H_2O mixts of increasing polarity; Sephadex LH-20 column eluted with a gradient of MeOH–H_2O; prep. TLC developed with $CHCl_3$–MeOH–H_2O–HOAc (6:2.2:0.3:1). The purification was finally performed over HPLC (ODS, 10/20 i.d. × 250 mm, Tokyo Kasei, Japan; refractive index detector; solvent, MeOH–H_2O system). The above purification gave saponins **1** (37 mg), **2** (200 mg) **3** (1 mg),

Table 1. *Continued*

Carbon	10	11	12	13	14	15	16	17
Oleanolic acid								
3	89.4	89.3	89.3	89.1	89.3	89.3	78.2	82.4
4	39.6	39.6	39.6	39.5	39.5	39.5	39.4	43.5
5	55.7	55.9	55.9	55.8	55.8	55.8	55.9	47.6
23	28.1	28.2	28.3	28.2	28.2	28.1	28.2	64.5
24	17.0	16.9	16.9	16.9	16.9	16.9	16.5	13.6
28	180.2	176.4	176.4	176.4	176.4	176.4	nd	180.2
Glucuronic acid								
1	106.4	107.2	107.2	107.3	107.0	106.5		106.5
2	75.7	75.5	75.4	75.4	75.2	74.1		74.1
3	82.0	78.1	78.0	78.0	76.0	85.5		87.5
4	78.4	73.4	73.1	73.1	78.6	71.4		71.4
5	76.0	77.2	77.2	77.4	75.2	76.6		77.4
6	172.6	172.8	170.7	170.3	170.4	170.2		170.2
Ester moiety								
COOMe			52.0		52.3	52.1		52.1
COOBu				65.0				
				30.9				
				19.3				
				13.7				
Arabinose								
1	108.1				108.7			
2	82.5				82.7			
3	76.4				77.0			
4	87.7				87.6			
5	62.4				62.3			
Galactose								
1						106.7		
2						73.1		
3						75.1		
4						70.2		
5						77.4		
6						62.1		
Glucose								
1	105.6	95.7	95.8	95.8	95.8	95.8	95.8	
2	73.9	74.1	74.2	74.2	74.2	74.2	74.2	
3	78.7	78.8	78.9	78.9	79.0	79.0	79.0	
4	70.8	71.1	71.4	71.2	71.2	71.2	71.2	
5	79.5	79.2	79.2	79.3	79.3	79.3	79.3	
6	62.2	62.2	62.4	62.3	62.6	62.3	62.3	

nd: Not detected.

4 (14 mg), **5** (75 mg), **6** (26 mg), **7** (15 mg), **8** (15 mg), **9** (10 mg), **10** (9 mg), **11** (280 mg), **12** (60 mg), **13** (20 mg), **14** (18 mg), **15** (14 mg), **16** (0.6 mg) and **17** (4 mg). The major composition of the remaining impurities was considered to be **12** based on TLC.

Saponin **3**, *oleanolic acid* 3-O-β-D-*glucuronopyranoside*-6-O-*butyl ester*. Powder. SI-MS *m/z*: 729 $[M + Na]^+$. ^{1}H NMR: 5.48 (1H, *br*, H-12), 5.00 (1H, *d*, $J = 7.9$ Hz, ClcUA-butyl ester, H-1), 4.62–4.10 (4H, ClcUA-butyl ester, H-2, 3, 4 and 5), 3.7 (2H, *br*, ClcUA-butyl ester, $COOCH_2$-), 3.37 (1H, *dd*, $J = 4.3$, 11.8 Hz, H-3), 3.31 (1H, *dd*, $J = 3.9$, 13.6 Hz, H-18), 1.32, 1.30, 1.01, 0.98, 0.97, 0.96, 0.83 (each *s*, Me), 0.78 (3H, *t*, $J = 7.4$ Hz, ClcUA-butyl ester, Me).

Saponin **5**, *oleanolic acid* 3-O-[α-L-*arabinofuranosyl*-(1–4)-β-D-*glucuronopyranoside*-6-O-*methyl ester*. Powder. $[\alpha]^{30}$ −17.9° (MeOH; *c* 0.48). SI-MS *m/z*: 801 $[M + Na]^+$. Found: C, 63.7; H, 8.4. $C_{42}H_{66}O_{13} \cdot H_2O$ requires: C, 63.3; H, 8.6%. IR ν_{max} cm^{-1}: 3419 (OH), 1748 (COOR), 1696 (COOH). ^{1}H NMR: 5.75 (1H, *d*, $J = 0.95$, Ara, H-1), 5.46 (1H, *br*, H-12), 4.92 (1H, *m*, $W_{1/2} = 7.5$ Hz, ClcUA-methyl ester, H-1), 4.91–4.01 (9H, *m*, sugars), 3.73 (3H, *s*, ClcUA-methyl ester, COOMe), 3.33 (1H, *dd*, $J = 4.4$, 11.8 Hz, H-3), 3.29 (1H, *dd*, $J = 4.2$, 14.3 Hz, H-18), 1.31, 1.29, 1.02, 0.98, 0.96, 0.95, 0.81 (each *s*, Me).

Acid hydrolysis of saponin **5**. Compound **5** (5 mg) with 2.5 ml of 2 N HCl-dioxane (1 : 1) was held at 100° for 4 hr under N_2 gas. After being cooled, the reaction mixt. was neutralized with 1 N NaOH, and then passed through a Sep-Pac C-18 cartridge eluted successively with H_2O and MeOH. The MeOH eluate yielded oleanolic acid and the H_2O eluate gave D-glucuronic acid and L-arabinose.

Saponin **8** and **9** were also hydrolysed by the same method.

Saponin **8**, *oleanolic acid* 3-O-[β-D-*galactopyranosyl*-(1–3)-(β-D-*glucuronopyranoside*-6-O-*methyl ester*]. Powder. $[\alpha]^{28.4}$ + 22.2° (MeOH; *c* 0.47). SI-MS *m/z*: 831 $[M + Na]^+$. Found: C, 61.5; H, 8.4. $C_{43}H_{68}O_{14} \cdot 3/2\ H_2O$ requires: C, 61.8; H, 8.6%. IR ν_{max} cm^{-1}: 3420 (OH), 1748 (COOR), 1700 (COOH). ^{1}H NMR: 5.47 (1H, *br*, H-12), 5.23 (1H, *d*, *J* = 7.8, Gal, H-1), 4.93 (1H, *d*, *J* = 7.8 Hz, ClcUA-methyl ester, H-1), 4.53–4.04 (10H, *m*, sugar), 3.73 (3H, *s*, ClcUA-methyl ester, COOMe), 3.34 (1H, *dd*, *J* = 4.6, 11.9 Hz, H-3), 3.29 (1H, *dd*, *J* = 3.9, 13.6 Hz, H-18), 1.32, 1.29, 1.02, 0.99, 0.97, 0.95, 0.80 (each *s*, Me).

Saponin **9**, *oleanolic acid* 3-O-[β-D-*galactopyranosyl*-(1–3)-β-D-*glucuronopyranoside*-6-O-*butyl ester*. Powder. $[\alpha]^{28.8}$ + 26.4° (MeOH; *c* 0.25). SI-MS *m/z*: 873 $[M + Na]^+$. ^{1}H NMR: 5.47 (1H, *br*, H-12), 5.25 (1H, *d*, *J* = 7.8 Hz, Gal H-1), 4.94 (1H, *d*, *J* = 7.7 Hz, ClcUA-butyl ester, H-1), 4.53–4.05 (12H, *m*, sugars and ClcUA-butyl ester, $COOCH_2$-), 3.35 (1H, *dd*, *J* = 4.2, 12 Hz, H-3), 3.30 (1H, *dd*, *J* = 4.2, 14 Hz, H-18), 1.33, 1.29, 1.02, 1.00, 0.97, 0.96, 0.82 (each, *s*, Me), 0.79 (3H, *t*, *J* = 7.4 Hz, ClcUA-butyl ester, Me).

Saponin **13**, *oleanolic acid* 3-O-[β-D-*glucuronopyranoside*-6-O-*butyl ester*]-28-O-β-D-*glucopyranoside*. Powder. $[\alpha]^{28.8}$ + 6.0° (MeOH; *c* 0.83). SI-MS *m/z*: 891 $[M + Na]^+$. ^{1}H NMR: 6.33 (1H, *d*, *J* = 8.0 Hz, Glc H-1), 5.43 (1H, *br*, H-12), 4.99 (1H, *d*, *J* = 7.3 Hz, ClcUA-butyl ester, H-1), 4.58–4.03 (12H, *m*, sugars and ClcUA-butyl ester, $COOCH_2$-), 3.36 (1H, *dd*, *J* = 4.2, 11.4 Hz, H-3), 3.20 (1H, *dd*, *J* = 4, 13 Hz, H-18), 1.29, 1.28, 1.10, 0.98, 0.92, 0.90, 0.86 (each *s*, Me), 0.78 (3H, *t*, *J* = 7.4 Hz, ClcUA-butyl ester, Me).

Saponin **15**, *oleanolic acid* 3-O-[β-D-*galactopyranosyl*-(1–3)-β-D-*glucuronopyranoside*-6-O-*methyl ester*]-28-O-β-D-*glucopyranoside*. Powder. $[\alpha]^{30}$ + 12.4° (MeOH; *c* 0.50). SI-MS *m/z*: 993 $[M + Na]^+$. Found: C, 58.4; H, 8.0. $C_{49}H_{78}O_{19} \cdot 2H_2O$ requires: C, 58.4; H, 8.2%. IR ν_{max} cm^{-1}: 3420 (OH), 1745 (COOR), ^{1}H NMR: 6.32 (1H, *d*, *J* = 8.0 Hz, Glc, H-1), 5.42 (1H, *br s*, H-12), 5.22 (1H, *d*, *J* = 7.9 Hz, Gal, H-1), 4.93 (1H, *d*, *J* = 7.8 Hz, ClcUA-methyl ester, H-1), 4.52–4.01 (15H, *m*, sugars), 3.73 (3H, *s*, ClcUA-methyl ester, COOMe), 3.33 (1H, *dd*, *J* = 4.3, 11.9 Hz, H-3), 3.20 (1H, *dd*, *J* = 4.1, 13.7 Hz, H-5), 1.28, 1.28, 1.09, 0.96, 0.92, 0.90, 0.83 (each *s*, Me).

Alkaline hydrolysis of **15**. Treatment of **15** (10 mg) with 1 ml of 0.5 N KOH at 70° for 1 hr. The reaction mixt. was deionized with Amberlite MB-3 resin and concd to a small vol., followed by passing through a Sep-Pac C-18 cartridge like the acid hydrolysis. The MeOH eluate gave prosapogenin, being identical with **8** (TLC, ^{1}H NMR, IR), and the H_2O eluate gave D-glucose.

Saponins **8**, **11**, **12** and **13** were also treated by the same method.

^{13}C NMR data of saponins **1**–**17** are summarized in Table 1.

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