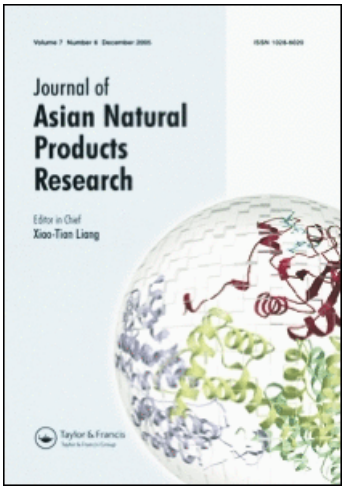

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Two new saponins from the bud of *Aralia elata* (Miq.) Seem

Z.-Q. MA, S.-J. SONG*, W. LI and S.-X. XU*

School of Traditional Chinese Material Medica, Shenyang Pharmaceutical University, 103 Wenhua Road, Shenhe District, Shenyang 110016, China

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Two new saponins, named congmuyanoside A and congmuyanoside B, have been isolated from the buds of *Aralia elata* (Miq.) Seem. Their structures have been determined on the basis of chemical and spectroscopic evidence.

Keywords: Araliaceae; *Aralia elata*; Congmuyanoside A; Congmuyanoside B; Triterpenoidal saponin

1. Introduction

Aralia elata (Miq.) Seem. (Araliaceae) is widely distributed in the northeast of China and Korea. Its root bark has been used as a folk medicine for rheumatism, diabetes and as a tonic in China, Japan and Russia [1]. Triterpenoidal saponins are reported to be the main active principles [2]. The pharmacological action and the chemical components of its bud, which is called "cilaoya", have rarely been reported. In this paper, we describe the isolation and the structure elucidation of two new saponins obtained from the buds of *Aralia elata*.

2. Results and discussion

Compound **1** was obtained as a white amorphous powder. The molecular formula of **1** was determined as $C_{41}H_{66}O_{14}$ by HR-ESIMS, which shows a quasi-molecular ion peak at *m/z* 783.4525 $[M+H]^+$. The IR spectrum indicates the presence of a carbonyl group (1693 cm^{-1}). The ^1H NMR spectrum of **1** exhibits signals characteristic for six methyl singlets at δ 0.93, 0.97, 1.04, 1.06, 1.17, 1.79, one trisubstituted olefinic proton at δ 5.64 and two anomeric protons at δ 4.94 and 5.28. The ^{13}C NMR spectrum of **1** shows signals of a pair of olefinic carbons at δ 122.5 and 145.1, two anomeric carbons of sugars at δ 106.4, 106.5 and a free carboxyl carbon at δ 180.0. The ^1H and ^{13}C NMR spectral data suggests that the aglycone consists of oleanolic acid with a free carboxyl group. Some characteristic chemical

*Corresponding author. Tel.: +86-24-23896143. E-mail: suixuxu@yahoo.com.cn

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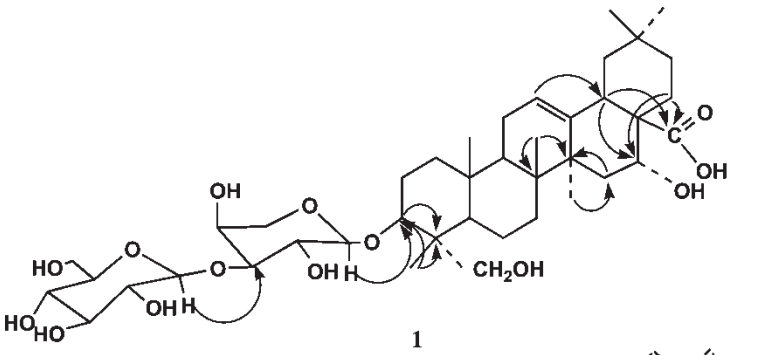
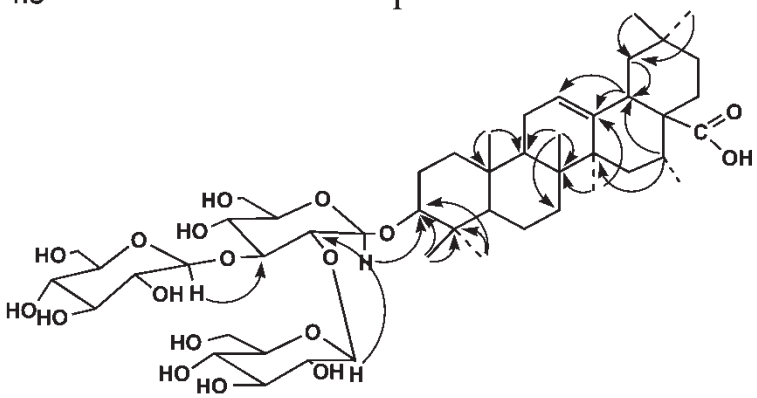
shifts such as δ 64.4 (C-23), 13.7 (C-24), 47.8 (C-5), 81.9 (C-3), 74.8 (C-16), 36.3 (C-15) and 180.0 (C-28) further revealed that compound **1** was a caulophyllogenin glycoside with two sugars attached at C-3. The sugar moieties were identified as arabinose and glucose by co-TLC with authentic samples after acid hydrolysis. The chemical shifts of the sugar moiety in ^{13}C NMR also confirmed the presence of one arabinose and one glucose. The sugar linkages were determined on the basis of the HMBC spectrum. HMBC correlation occurs between a proton signal at δ 4.94 (ara-H-1′) and a carbon signal at δ 81.9 due to C-3 of the aglycone moiety, while an anomeric proton signal at δ 5.28 (glc-H-1″) shows a correlation with a carbon signal at δ 84.3 due to C-3′ of the inner sugar, suggesting glycosylation at C-3 of the aglycone with a glc(1 → 3)-ara moiety. The anomeric configurations of the sugar moieties were determined to be β for glucose and α for arabinose on the basis of the J_{H-H} values (7.5 and 7.2 Hz, respectively). The ^{13}C NMR spectral data of compound **1** is almost the same as that of the known compound congmunoside II [3] (3-*O*-[β-D-glucopyranosyl(1 → 3)-α-L-arabinopyranosyl] caulophyllogenin 28-*O*-β-D-glucopyranosyl ester) except for an additional set of signals due to a glucose, and a highfield shift of C-28 to 175.9 in congmunoside II. All these data confirm that the aglycone of compound **1** is caulophyllogenin, with a glc (1 → 3) sugar moiety at C-3. From the above evidences, the structure of **1** was concluded to be 3-*O*-[β-D-glucopyranosyl (1 → 3)-α-L-arabinopyranosyl] caulophyllogenin. This is a new compound, named here as congmuyanoside A (figure 1).

Compound **2**, a white amorphous powder, shows an absorption band at 1693 cm^{-1} for a carbonyl group in the IR spectrum. Its HR-ESIMS spectrum exhibits a quasi-molecular ion



1



2

Figure 1. Structures and key HMBC correlations of **1** and **2**.

peak at *m/z* 959.5242 $[M + H]^+$, corresponding to the molecular formula $C_{48}H_{78}O_{19}$. The ^1H NMR spectrum of **2** displays signals characteristic for seven methyl singlets at δ 0.81, 1.00, 1.05, 1.06, 1.17, 1.24 and 1.84, one trisubstituted olefinic proton at δ 5.63, and three anomeric protons at δ 4.83, 5.36, and 5.71. The ^{13}C NMR spectrum of **1** shows signals of a pair of olefinic carbons at δ 122.4 and 145.2, three anomeric carbons of sugars at δ 103.9, 104.8, 105.0 and a free carboxyl carbon at δ 180.0. The ^1H and ^{13}C NMR spectral data suggest that the aglycone is oleanolic acid with a free carboxyl group. By comparing the ^{13}C NMR spectral data of **2** with that of oleanolic acid, the signal due to C-16 was shifted downfield by 51 ppm, signals due to C-15 and C-17 were shifted lower field by 8 and 2 ppm, respectively, while the others were almost the same. This indicates that the aglycone of **2** is echinocystic acid with a sugar moiety composed of three sugars at C-3 [4]. The sugar moieties were identified as glucose only by co-TLC with authentic samples after acid hydrolysis. The sugar linkages were determined on the basis of the HMBC spectrum which shows correlation between a proton signal at δ 4.83 (glc-H-1′) and a carbon signal at δ 89.4 due to C-3 of the aglycone moiety, while anomeric proton signals at δ 5.36 (glc-H-1″) and 5.71 (glc-H-1‴) show correlations with carbon signals at δ 88.8 and 79.4 due to C-3′ and C-2′ of the inner sugar, respectively, suggesting glycosylation at C-3 of aglycone with a [glc (1 → 2)]-[glc (1 → 3)] glc moiety. The anomeric configurations of the glucoses were determined to be β on the basis of the J_{H-H} values (7.6, 7.7, 7.7 Hz respectively). From the above evidences, the structure of **2** is concluded to be 3-*O*-[β-D-glucopyranosyl (1 → 2)]-[β-D-glucopyranosyl(1 → 3)] β-D-glucopyranosyl echinocystic acid. This compound has not been reported previously, and is named congmuyanoside B.

3. Experimental

3.1. General experimental procedures

Optical rotations were performed with a Perkin–Elmer 241MC polarimeter. Positive HRESI-MS was taken on a Bruker Daltonics Inc. APEX II FT-ICRMS. IR spectra were measured with a Bruker IFS-55 infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker ARX-300 NMR spectrometer. ESI-MS was taken on a Finnigan LCQ LC-MS analyzer. Column chromatography was carried out on silica gel (Qingdao Haiyang chemical co., Ltd. 200–300 mesh). Preparative HPLC was carried out on a Hitachi LC system with a RI detector and an Alltech ODS column (21.5 × 300 mm, 10 μm). Spots were visualized by spraying with ethanol–10% H_2SO_4 and heating (110°C, 5 min).

3.2. Plant material

Buds of *Aralia elata* collected from Liaoning Province of China in August 2000 were taxonomically identified by Professor Sun Qishi of Shenyang Pharmaceutical University. A voucher specimen has been deposited at the School of Traditional Chinese Material Medica, Shenyang Pharmaceutical University.

3.3. Extraction and isolation

The air-dried buds (10 kg) were first extracted with 75% ethanol (3 ×) under reflux. The combined solutions were then concentrated *in vacuo*, and subsequently subjected to

Table 1. ^{13}C NMR data of **1** and **2** (ppm, in C_5D_5N).

	1		***2***	
Carbon	δ_C *(ppm)*	δ_H *(ppm) (J in Hz)*	δ_C *(ppm)*	δ_H *(ppm) (J in Hz)*
1	38.9		38.8	
2	26.3		26.6	
3	81.9	4.28	89.4	3.29d (7.9)
4	43.6		39.6	
5	47.8	1.71	56.0	
6	18.2		18.6	
7	32.9		32.9	
8	40.0		40.0	
9	47.4		47.2	
10	37.1		37.0	
11	23.9		23.9	
12	122.5	5.64 (br.s)	122.4	5.63 (br.s)
13	145.1		145.2	
14	42.2		42.2	
15	36.3	2.34	36.3	
16	74.8	5.21 (br.s)	74.8	4.85 (br.s)
17	48.9		49.0	
18	41.5	3.62d (12)	41.5	3.61d (11.4)
19	47.3		47.4	
20	31.1		31.1	
21	36.3		33.4	
22	33.4		33.4	
23	64.4		28.1	1.24s
24	13.7	0.93s	16.8	1.06s
25	16.3	0.97s	15.6	0.81s
26	17.6	1.06s	17.5	1.00s
27	27.2	1.79s	27.3	1.84s
28	180.0		180.0	
29	33.4	1.04s	33.4	1.05s
30	24.8	1.17s	24.8	1.17s
3-O-sugar	Arabinose		Glucose	
$1'$	106.5	4.94d (7.2)	105.0	4.83d (7.6)
$2'$	72.1	4.56	79.4	4.38
$3'$	84.3	4.07	88.8	4.24
$4'$	69.3	4.34	70.1	4.02
$5'$	67.1	3.52, 4.13	77.8	3.85
$6'$			63.5[a]	4.52[a]
	glucose			
$1''$	106.4	5.28d (7.5)	103.9	5.71d (7.7)
$2''$	75.8	4.0	76.5	4.08
$3''$	78.4	4.24	78.7	4.24
$4''$	71.7	4.18	71.7	4.18
$5''$	78.7	3.98	77.7	3.89
$6''$	62.8	4.51	62.4[a]	4.44[a]
$1'''$			104.8	5.36d (7.7)
$2'''$			75.5	4.05
$3'''$			78.7	4.21
$4'''$			72.6	4.15
$5'''$			78.7	4.21
$6'''$			62.6[a]	4.28[a]

[a] Signals in each column may be interchangeable. All signals were assigned by ^1H and ^{13}C NMR, HMQC and HMBC.

macroporous resin D101 column chromatography, eluting with 60% EtOH. The solution was then evaporated to dryness under vacuum to afford a residue (150 g) that was chromatographed on silica gel with $CHCl_3$–MeOH (in gradient) to give 12 fractions (fr. 1–12). Fraction 7 (23 g) was further separated by silica-gel column chromatography with a solvent system of EtOAc–EtOH–H_2O (9:1:0.1) to give **1** (80 mg). Fractions 11 and 12

(22 g together) were repeatedly chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (85:15:10) to obtain 5 fractions, of which fraction 1 (1.44 g) was separated with preparative RP-18 HPLC (MeOH–H_2O 1:1) to yield **2** (62 mg).

Compound 1. White amorphous powder; $[\alpha]_D^{25}$ +21.8 (MeOH, *c* 0.11); IR (KBr) (ν cm^{-1}): 3426, 2944, 1693, 1448, 1386, 1258, 1077, 1035, 786; ^{1}H, ^{13}C NMR data see table 1. Positive ESI-MS: *m*/*z* 805, 783, 621, 347, 282, 279; HR-ESIMS *m*/*z* 783.4525 (calcd for $C_{41}H_{67}O_{14}$, 783.4425).

Compound 2. White amorphous powder; $[\alpha]_D^{25}$ +13.3 (MeOH, *c* 0.06); IR (KBr) (ν cm^{-1}): 3408, 2944, 1693, 1387, 1159, 1078, 637. Positive ESI-MS: *m*/*z* 958, 796, 778, 634, 616, 486, 455, 324; ^{1}H, ^{13}C NMR data see table 1. HRESIMS: *m*/*z* 959.5242 (calcd for $C_{48}H_{79}O_{19}$, 959.5210).

Acid hydrolysis of 1 and 2. Each saponin was added on a silica gel TLC plate that was then kept in HCl moisture at 80°C for 2 h, and was then taken out and dried. The plate was developed in a solution of $CHCl_3$–MeOH–H_2O (65:35:10 lower layer) together with authentic samples of sugar, R_f: L-arabinose, 0.69; D-glucose, 0.61.

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