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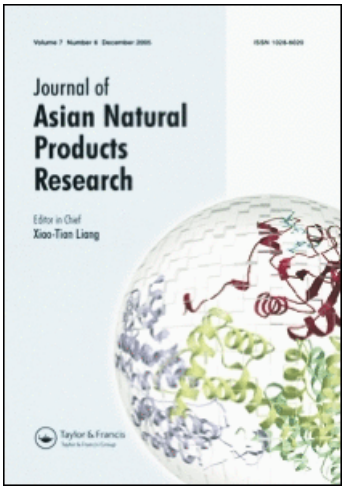

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A new triterpenoid saponin from *Albizia julibrissin* Durazz

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A new triterpenoid, saponin hehuanoside A, was isolated together with the known triterpenoid saponins **2**, **3**, and **4** from the stem bark of *Albizia julibrissin*. With the help of chemical and spectral analyzes (IR, MS, 1D-NMR, and 2D-NMR), the structure of the new triterpenoid saponin was elucidated as 21-*O*-[(6*S*)-2-*trans*-2,6-dimethyl-6-*O*-β-D-quinovopyranosyl-2,7-octadienoyl]-3-*O*-β-D-xylopyranosyl-(1 → 2)-β-D-fucopyranosyl-(1 → 6)-β-D-2-deoxy-2-acetamidoglucopyrasyl acacic acid 28-*O*-α-L-arabinofuranosyl-(1 → 4)-[-β-D-glucopyranosyl-(1 → 3)]-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl ester (**1**). Three known triterpenoid saponins **2**–**4** were identified on the basis of spectroscopic data.

Keywords: *Albizia julibrissin* Durazz; silktree siris; triterpenoid saponin; hehuanoside A

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1. Introduction

The stem bark of *Albizia julibrissin*, a Chinese traditional medicine named 'He Huan', has been recorded in Chinese Pharmacopoeia as a sedative agent and an anti-inflammatory drug for treating injuries due to falls, and removing carbuncles, skin ulcers, and wounds [1]. In the previous research, novel and complex triterpenoid saponins with cytotoxic activities were isolated and identified [2–4]. In this paper, we report the isolation and structure elucidation of a new triterpenoid saponin, hehuanoside A (**1**), together with three known triterpenoid saponins **2**, **3**, and **4** using 1D-NMR, 2D-NMR techniques, ESI-MS analysis as well as chemical methods.

2. Results and discussion

Hehuanoside A (**1**) was obtained as a white amorphous powder. The IR spectrum of **1** showed absorptions of carbonyl (1696 cm^{-1}) and α,β-unsaturated carbonyl groups (1640 cm^{-1}). In the ESI-MS, **1** showed a quasimolecular ion peak at *m/z* 1882.8847 $[M - H]^-$ corresponding the molecular formula of $C_{88}H_{140}NO_{42}$. Upon acid hydrolysis with HCl, **1** gave arabinose, fucose, glucose, quinovose, rhamnose, and xylose. However, signals of an *N*-acetamido group [IR 1640 and 1570 cm^{-1}; ^{1}H NMR δ 2.10 (3H, s, $NHCOCH_3$), 8.9 (1H d, $J = 8.8$ Hz, $NHCOCH_3$); ^{13}C NMR δ 23.8 ($COCH_3$) and 170.3 ($COCH_3$)], together with ^{1}H and ^{13}C NMR data of the C-2 of the glucose (H-2 δ 4.42 and C-2 δ 58.1), suggested the presence of the 2-deoxy-2-acetylaminoglucose unit. The ^{1}H NMR spectrum showed signals ascribable to nine tertiary methyl groups at δ 0.83, 0.88, 0.91, 0.94, 1.06, 1.36, 1.42, 1.85, 1.92, and one olefinic proton at δ 6.88 (1H, dt, $J = 1.5$, 7.6 Hz, MT H-3), and

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Table 1. ^{13}C NMR spectral data of compound **1** (δ (ppm), 400 MHz, C_5D_5N).

C	δ	C	δ	C	δ	C	δ	C	δ
1	39.0	20	35.5	8′	115.0	$COCH_3$	23.8	2	70.9
2	26.8	21	77.0	9′	12.9	Fuc 1	103.5	3	79.7
3	89.0	22	36.6	10′	23.9	2	82.3	4	84.6
4	39.5	23	28.3	C21-O-MT-6′		3	75.4	5	69.3
5	56.2	24	16.0	Qui 1	99.5	4	72.6	6	19.1
6	19.1	25	17.3	2	75.7	5	71.4	Glc 1″	105.9
7	33.8	26	17.4	3	78.6	6	17.5	2″	75.9
8	40.3	27	27.5	4	77.0	Xyl 1	107.1	3″	78.6
9	47.3	28	174.6	5	72.6	2	75.6	4″	71.5
10	37.3	29	29.0	6	19.1	3	78.3	5″	78.3
11	23.9	30	19.3	C3		4	70.8	6″	62.7
12	123.5	Cinnamoy l		glc-2-NHAc		5	67.7	Ara 1	111.2
13	143.5	1′	167.9	1	104.9	C 28 Glc 1′	95.8	2	82.2
14	41.2	2′	128.6	2	58.1	2′	79.2	3	78.6
15	35.6	3′	142.6	3	75.7	3′	77.0	4	85.7
16	74.0	4′	23.8	4	72.4	4′	71.5	5	62.9
17	51.8	5′	40.7	5	77.2	5′	78.3		
18	40.3	6′	79.7	6	70.1	6′	62.2		
19	48.0	7′	144.3	C═O	170.3	Rha 1	101.9		

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a set of 1-substituted olefinic proton signals at δ 6.15 (1H, dd, $J = 10.9$, 17.6 Hz, MT H-7), 5.28 (1H, d, $J = 11.0$ Hz, MT H-8a), 5.49 (1H, d, $J = 18.0$ Hz, MT H-8b). These observations suggested that **1** was a triterpenoid saponin. The ^{13}C NMR spectrum of **1** (Table 1) showed the presence of characteristic carbon signals including one ester carbonyl at δ 174.6, one α,β-unsaturated ester carbonyl at δ 167.9, one pair of the olefinic carbons of the aglycone part at δ 123.4, 143.5, one pair of trisubstituted olefinic carbons at δ 142.6, 128.6, one pair of monosubstituted olefinic carbons at δ 144.3, 115.0, one sugar-linked methine carbon at δ 89.0, eight anomeric carbon signals at δ 111.2, 107.0, 105.9, 104.9, 103.5, 101.9, 99.5, 95.8, a carbonyl signal at δ 170.3, and a typical amide carbon signal at δ 58.1. These data supported that **1** was an acacic acid glycoside acylated with one monoterpenic acid. On comparison of the ^{13}C NMR signals for aglycone of **1** with those of the known saponin prosapogenin-9 [5], all signals due to the aglycone of **1** were almost superimposable with those of prosapogenin-9, indicating that the aglycone of **1** was the same as that of prosapogenin-9, which was acacic acid (3β,16α,21β-trihydroxyolean-12-ene-28-oic acid) and its 3,21-hydroxy groups and the 28-carbonyl group carried a sugar moiety. Eight anomeric proton signals at δ 4.92 (1H, d, $J = 7.8$ Hz, glc-2-NHAc-H-1), 5.87 (1H, s, rha-H-1), 5.94 (1H, d, $J = 7.5$ Hz, glc′-H-1′), 5.21 (1H, d, $J = 7.5$ Hz, glc″-H-1″), 4.87 (1H, d, $J = 7.6$ Hz, fuc-H-1), 4.94 (1H, d, $J = 6.5$ Hz, xyl-H-1), 6.15 (1H, br s, araf-H-1), and 4.75 (1H, d, $J = 7.8$ Hz, qui-H-1), and three secondary methyl signals ascribable to 6-deoxyhexose [δ 1.77 (3H, d, $J = 6.0$ Hz, rha-H-6), 1.46 (3H, d, $J = 6.2$ Hz, fuc-H-6), 1.64 (3H, d, $J = 5.3$ Hz, qui-H6)], indicated that **1** had eight sugars including three 6-deoxyhexoses. Based on the ^1H and ^{13}C NMR data of **1**, the anomeric configuration of the sugar moieties were determined as β-configurations for glucose, 2-deoxy-2-acetamidoglucose, fucose, xylose, and quinovose, and α-configurations for rhamnose and arabinose. When the ^{13}C NMR signals of **1** were compared with those of prosapogenin-9, the ^{13}C NMR data of the monoterpene moiety of **1** (Table 1), as well as sugar signals were similar to those of prosapogenin-9, except for the appearance of 2-deoxy-2-acetamidoglucopyranosyl signals linked to C-3 instead of

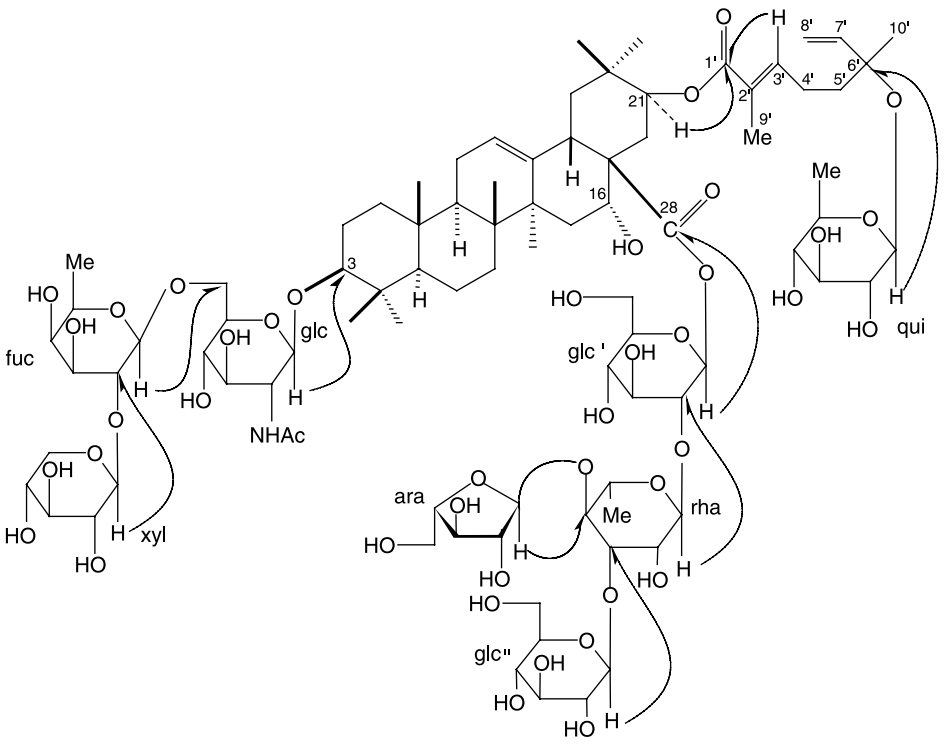

Figure 1. Structure and key HMBC correlations for **1**.

glucopyranosyl signals [5], indicating that the monoterpene moiety of **1** was the same as that of prosapogenin-9, including configurations of C-6′and C-2′. In the ^{13}C NMR data of **1**, the signals for C-20, C-21, and C-22 were shifted −1.3 ppm upfield, +2.6 ppm downfield, and −5.3 ppm upfield, respectively, when compared with those of acacic acid, as a consequence of acylation at C-21. The positions of the sugar residues in **1** were defined unambiguously by the HMBC experiment (Figure 1). The HMBC correlations between H-1 (δ 4.75) of the quinovose and C′-6 (δ 79.7) of the monoterpene indicated that quinovose was linked to C-6′ of monoterpene; the HMBC correlations between H-1 (δ 4.92) of 2-deoxy-2-acetamidoglucose and C-3 (δ 89.0) of the aglycone, H-1 (δ 4.87) of the fucose, and C-6 (δ 70.1) of 2-deoxy-2-acetamidoglucose, H-1 (δ 4.94) of the xylose and C-2 (δ 82.3) of fucose indicated that a trisaccharide moiety 3-*O*-β-D-xylopyranosyl-(1 → 2)-β-D-fucopyranosyl-(1 → 6)-β-D-2-deoxy-2-acetamidoglucopyranosyl was linked to C-3 of the aglycone. Additionally, the HMBC correlations between H′-1 (δ 5.94) of the inner glucose′ and C-28 (δ 174.6) of the acacic acid unit, H-1 (δ 5.87) of rhamnose and C-2′ (δ 79.2) of the inner glucose′, H-1″ (δ 5.21) of the glucose″ and C-3 (δ 79.7) of rhamnose, H-1 (δ 6.15) of the arabinose and C-4 (δ 84.6) of rhamnose showed that the tetrasaccharide residue *O*-α-L-arabinofuranosyl-(1 → 4)-[-β-D-glucopyranosyl-(1 → 3)]-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl was linked to the acacic acid unit at C-28. Therefore, the structure of **1** was determined as 21-*O*-[(6*S*)-2-*trans*-2,6-dimethyl-6-*O*-β-D-quinovopyranosyl 2,7-octadienoyl]-3-*O*-β-D-xylopyranosyl-(1 → 2)-β-D-fucopyranosyl-(1 → 6)-β-D-2-deoxy-2-acetamidoglucopyrasyl acacic acid 28-*O*-α-L-arabinofuranosyl-(1 → 4)-[-β-D-glucopyranosyl-(1 → 3)]-α-L-rhamnopyranosyl-(1 → 2)- β-D-glucopyranosyl ester.

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The three known compounds **2**–**4** were identified as prosapogenin-4 (2) [5], julibroside A_3 (**3**) [6], and julibroside A_2 (**4**) [6] by comparison of their physical and spectroscopic data with those reported in the literature.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a Kofler-microscope apparatus and are uncorrected. The optical rotations were obtained on a WZZ-15 autopolarimeter. The IR spectra were obtained using a Y-Zoom scroll Fourier transform infrared spectrometer with a KBr disk. The ESI-MS was recorded using LCQ-1700 ESI-MS instrument. The NMR spectra were obtained on a Bruker AM-500 instrument, using TMS as the internal standard. HPLC was performed using an ODS column (Shim-park PREF-ODS, 250 × 4.6 mm). Column chromatography was performed on silica gel (200–300 mesh, Qingdao Oceanic Chemical Industry, Qingdao, China) and reversed silica gel (25 × 2.5 cm, Nacalai Tesque, Kyoto, Japan). Macroporous resin D_{101} was obtained from Tianjin gel Co. Ltd, Tianjin, China. The spots were detected after spraying with 10% H_2SO_4.

3.2 Plant material

The stem bark of *A. julibrissin* Durazz was purchased from Chinese Medicinal Materials, Changchun, Jilin Province, China, in September 2004, and identified by Professor Minglu Deng, Changchun College of traditional Chinese medicine. A voucher specimen (040919) has been deposited in the Herbarium of Academy of Traditional Chinese Medicine and Material Medica of Jilin Province.

3.3 Extraction and isolation

The dried and powdered stem bark (7.5 kg) of the plant was extracted three times with water at the boiling temperature, and the extract was concentrated under reduced pressure, yielding a crude residue (125 g), which was chromatographed over a D_{101} macroporous resin column (10 × 80 cm) eluted successively with H_2O and 30% EtOH. The 30% EtOH eluate was concentrated to dryness (26 g crude saponin mixture) and chromatographed over a silica gel column (200–300 mesh, 500 g) eluted with $CHCl_3$–MeOH–H_2O (30:10:1 ~ 10:10:1) to give four fractions. Fraction 4 was subjected to HPLC (column: 10 × 250 mm, RP-18, 10 μm; flow rate: 3.0 ml/min) with MeOH–H_2O (8:2 ~ 7:4) as the mobile phase to afford compound **1** (63 mg).

*3.3.1 Hehuanoside A (**1**)*

White powder, mp 227–228°C, $[\alpha]_D^{18}$ − 39 (*c* 0.45, MeOH). IR (KBr; ν_{max}): 3424, 2929, 1696, 1640, 1570, 1450, 1265, 1073, 1030 cm^{-1}. ^1H NMR (500 MHz, pyridine-d_5) δ 0.83, 0.88, 0.91, 0.94, 1.06, 1.36, 1.42, (each 3H, s,CH_3), 5.21 (1H, m, H-16β), 6.10 (1H, m, H-21α), 1.46 (3H, d, J = 6.2 Hz, fuc-H-6), 1.64 (3H, d, J = 5.3 Hz, qui-H-6), 1.77 (3H, d, J = 6.0 Hz, rha-H-6), 6.88 (1H, dt, J = 1.5, 7.6 Hz, MT H-3), 6.15 (1H, dd, J = 10.9, 17.6 Hz, MT H-7), 5.28 (1H, d, J = 11.0 Hz, MT H-8a), 5.49 (1H, d, J = 18.0 Hz, MT H-8b), 4.92 (1H, d, J = 7.8 Hz, glc-2-NHAc-H-1), 5.87 (1H, s, rha-H-1), 5.94 (1H, d, J = 7.5 Hz, glc′-H-1′), 5.21 (1H, d, J = 7.5 Hz, glc″-H-1″), 4.87 (1H, d, J = 7.6 Hz, fuc-H-1), 4.94 (1H, d, J = 6.5 Hz, xyl-H-1), 6.15 (1H, br, s, araf-H-1), 4.75(1H, d, J = 7.8 Hz, qui-H-1), 2.10 (3H, s, NHCOCH_3), 8.91(1H d, J = 8.8 Hz, N*H*COCH_3), 4.42(1H, m, 2-NHAc-glc-H-2); the ^{13}C NMR (125 MHz, pyridine-d_5) spectral data are given in Table 1. ESI-MS *m/z* 1882.8847 $[M - H]^{-1}$ (calcd for $C_{88}H_{140}NO_{42}$, 1882.8850), 1750 $(M - H\text{-}132)^-$, 1720 $(M - H\text{-}162)^-$.

3.4 Acid hydrolysis

The saponin (**1**; 10 mg) was heated with 2 M HCl–MeOH (10 ml) under reflux for 3 h. The

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reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The water layer was neutralized with Na_2CO_3, concentrated, and subjected to TLC analysis with authentic samples of D-glucose, D-fucose, D-xylose, L-arabinose, L-rhamnose, and D-quinovose, and developed with CH_2Cl_2–MeOH–H_2O (15:6:1) and H_2O–MeOH–AcOH–EtOAc (15:15:20:65). Detection was carried out with aniline phthalate spray.

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