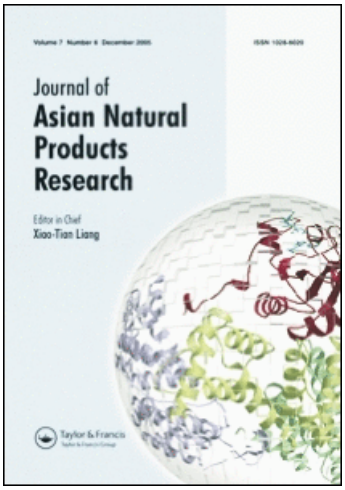

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A TRITERPENOID SAPONIN FROM *ALBIZIA JULIBRISSIN*

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A triterpenoid saponin (**1**) was obtained from the stem barks of *Albizia julibrissin* Durazz. Its structure was elucidated as 3-*O*-[β-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranosyl]-21-*O*-[(6*S*)-2-trans-2-hydroxymethyl-6-methyl-6-*O*-β-D-quinovopyranosyl-2, 7-octadienoyl]-16-deoxy-acacic acid 28-*O*-β-D-glucopyranosyl-(1 → 3)-[α-L-arabinofuranosyl-(1 → 4)]-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl ester (**1**), named as Julibroside J_{26}, based on the chemical and spectral methods.

Keywords: *Albizia julibrissin*; Triterpenoid saponin; Julibroside J_{26}

INTRODUCTION

Albizia julibrissin Durazz (leguminosae) is usually cultivated as an ornamental plant throughout China. The stem barks of the plant are specified in Chinese Pharmacopoeia as a sedative, and as an anti-inflammatory agent to treat swelling and pain of lungs, skin ulcer and wounds [1].

In previous research [2–4], we isolated several novel and complicated triterpenoid saponins. In the present paper, we report the isolation and structural elucidation of a new triterpenoid saponin, Julibroside J_{26} (**1**).

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RESULT AND DISCUSSION

Ninety-five percent ethanol extracts of stem barks of *A. julibrissin* were partitioned between H_2O and $CHCl_3$, EtOAc, *n*-BuOH, respectively. The *n*-BuOH-soluble part was chromatographed over D_{101} macroporous resin, Sephadex LH-20 and silica gel columns to afford colorless powders (Frs. 41–43). A triterpenoid saponin (**1**) was obtained by means of repeated Rp C18 column chromatography and preparative HPLC.

Saponin **1** was obtained as a white powder. It showed positive Molish and Liebermann–Burchard reactions, the ^1H NMR of **1** exhibited seven angular methyl and eight anomeric proton signals, which suggested **1** was a triterpenoid saponin. When **1** was hydrolyzed with 2.0 mol/l HCl a sapogenin was obtained which was identical with the authentic sample of 16-deoxy acacic acid lactone on HPTLC. D-glucose, L-arabinose, D-xylose, L-rhamnose and D-quinovose were detected to be present in the hydrolysate also, compared with authentic samples (with the literature [5] for D-quinovose).

In the ^1H NMR spectrum of **1**, seven three-proton singlets at δ 0.94, 0.95, 0.95, 1.03, 1.14, 1.30, 1.35 were attributed to the presence of seven tertiary methyls. A comparison of the ^1H NMR data of **1** with those of Julibroside J_1[3] showed an upfield shift of H-16 signal from δ 5.20 to δ 2.6, suggesting the absence of 16-hydroxyl group in **1**, which were further confirmed by 0.50 and 0.3 ppm of upfield for H-27 and H-β-18 and the absence of an oxygenate 16-C signal in ^{13}C NMR spectrum. The ^{13}C NMR spectrum of **1** showed 30 distinct signals due to aglycone (see Table I). The spectral

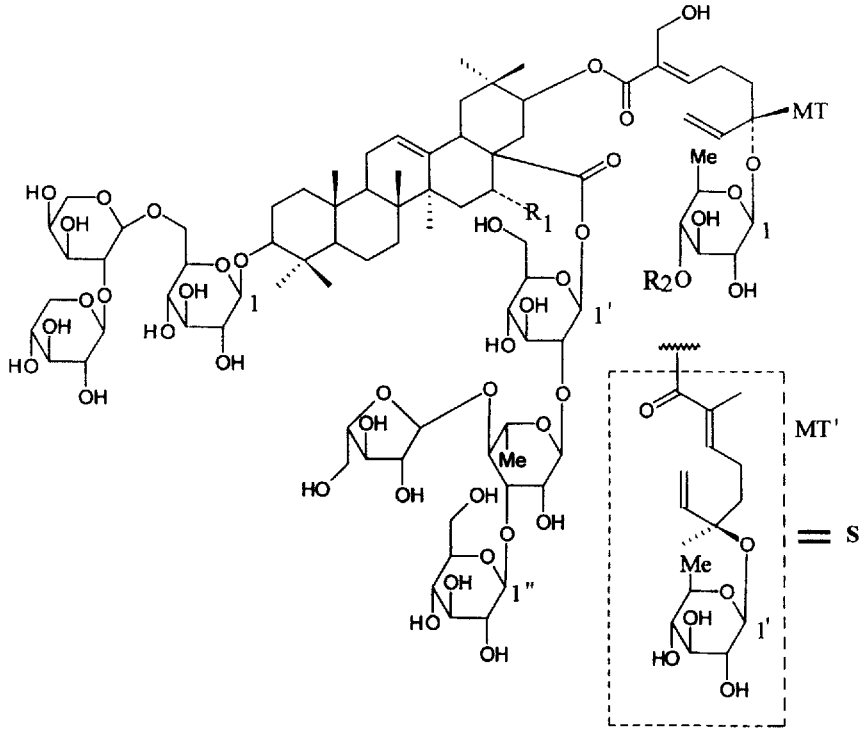
TABLE I ^{13}C NMR data of aglycone and MT moieties of **1** and **2** (py-d_5)

Aglycone						*Monoterpenoid*		
C	**1**	**2**	C	**1**	**2**	C	**1**	**2**
1	39.1	38.9	16	24.8	74.8	1	167.4	167.5
2	26.7	26.9	17	48.7	51.7	2	133.7	134.9
3	88.6	88.9	18	41.4	40.9	3	146.3	145.2
4	39.7	39.7	19	46.6	47.9	4	23.8	23.7
5	56.1	56.1	20	35.7	35.6	5	40.2	40.9
6	18.6	18.7	21	76.9	77.1	6	79.6	79.8
7	33.6	33.7	22	36.5	36.4	7	144.1	143.9
8	40.0	40.2	23	28.2	28.3	8	114.8	115.2
9	47.2	47.2	24	17.1	17.1	9	56.4	56.2
10	37.2	37.1	25	15.8	15.9	10	23.7	23.8
11	23.8	23.9	26	17.4	17.3			
12	123.1	124.1	27	25.9	27.3			
13	143.3	143.3	28	174.9	174.4			
14	42.4	43.0	29	29.2	29.3			
15	28.9	35.9	30	19.2	19.1			

data for aglycone moiety of **1** were in good agreement with those [6] of compound II (machaerime acid lactone), which further confirmed the aglycone of **1** to be 16-deoxy acacic acid.

In the ^{1}H NMR spectrum of **1**, eight signals for the anomeric protons of the sugar moieties were observed at δ 4.87(1H, d, $J=7.5$ Hz, H-glc-1), 5.16(1H, br s, H-arap-1), 4.98(1H, d, $J=6.8$ Hz, H-xyl-1), 6.06(1H, d, $J=7.8$ Hz, H-glc′-1), 5.84(1H, s, H-rha-1), 6.19(1H, s, H-araf-1), 5.32(1H, d, $J=7.5$ Hz, H-glc″-1), δ 4.84(1H, d, $J=7.6$ Hz, H-qui-1). Two three-proton doublets at δ 1.58(3H, d, $J=5.2$ Hz), δ 1.79(3H, d, $J=5.7$ Hz) due to methyls of deoxy-sugar moieties: quinovose and rhamnose, were observed also. The ^{13}C NMR spectrum of **1** contained eight carbon-13 signals due to the anomeric carbons of sugar moieties at δ 95.6, 99.3, 101.7, 102.4, 105.8, 106.7, 106.3 and 111.0, and two methyl carbon-13 signals due to sugar moieties at δ 18.8, 18.9. Combined with the results of the HCl-hydrolysis of **1**, it can be deduced that **1** contained three units of β-D-glucose, two units of α-L-arabinoses, and one unit each of β-D-xylose, α-L-rhamnose and β-D-quinovose. Another group of proton and carbon-13 signals were observed in the ^{1}H and ^{13}C NMR spectra of **1**: proton signals at δ 7.06(1H, t, $J=7.7$ Hz, H-MT-3), 6.18(1H, dd, $J=11.1, 17.7$ Hz, H-MT-7), 5.17(1H, d, $J=11.1$ Hz, H-MT-8a), 5.38(1H, d, $J=17.7$ Hz, H-MT-8b), 4.71(2H, s, H-MT-9) and 1.51(3H, s, H-MT-10); the carbon-13 signals see Table II. These data were quite similar to those of inner monoterpenoid moiety in Julibroside J_1, which indicated the presence of one unit of (6*S*)-2-hydroxymethyl-6-methyl-6-hydroxy-2-trans-2,7-octadienoic acid moiety in saponin **1**. In the carbon-13 NMR spectrum of **1** the signals for eight sugars and a monoterpene acid (MT) were almost superimposable to those of Julibroside J_1, except for the absence of the signals of outer MT and quinovose. One and two-dimensional NMR techniques and a comparison of ^{13}C NMR data of **1** with those of Julibroside J_1 permitted assignment of all ^{1}H and ^{13}C NMR signals of **1**. And this conclusion was further supported by the result of the FAB-MS data. The FAB-MS of **1** in positive ion mode exhibited a quasi-molecular ion peak at *m/z*: 1852$[M+Na+H]^+$, which was consistent with its molecular weight as calculated for $C_{85}H_{136}O_{42}$ (composed of 16-deoxy acacic acid, eight monosaccharides and one monoterpenoid).

Therefore, saponin **1** was identified as 3-*O*-[β-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranosyl]-21-*O*-[(6*S*)-2-trans-2-hydroxymethyl-6-methyl-6-*O*-β-D-quinovopyranosyl-2,7-octadienoyl]-16-deoxy-acacic acid-28-*O*-β-D-glucopyranosyl-(1 → 3)-[α-L-arabinofuranosyl-(1 → 4)]-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl ester, being a new compound named Julibroside J_{26} (Scheme 1).



1 (**Julibroside J$_{26}$**): R_1=R_2=H

2 (**Julibroside J$_1$**): R_1=OH R_2=S

SCHEME 1

EXPERIMENTAL SECTION

General Experimental Procedures

IR spectra were measured on a Perkin-Elmer 983 FT-IR as pressed KBr disks. 1D and 2D NMR spectra were recorded using Bruker AM-500 and Varian-300 instruments with TMS as the internal standard. FABMS were recorded using a ZABspec mass spectrometer. High performance liquid chromatography was carried out using Gilson automatic system for preparative HPLC with chromatography column: Alltima C_{18} (5 μ, 60A, 22 × 250 mm ID and 10 μ, 60A, 22 × 250 mm ID), using Waters 600 HPLC meter for semi-preparative HPLC with chromatography column: μBondpak

TABLE II ^{13}C NMR data of sugars in **1** and **2** (py-d_5)

		1	2			1	2
glc	1	106.7	106.76	araf	1	111.0	111.02
	2	76.8	75.60		2	84.4	84.42
	3	78.4	78.39		3	78.4	78.39
	4	72.3	72.22		4	84.8	85.43
	5	77.8	76.07		5	62.6	62.55
	6	69.6	69.52	glc″	1	105.8	105.73
araf	1	102.4	102.22		2	75.7	75.40
	2	80.5	80.36		3	78.2	78.39
	3	72.6	72.53		4	71.9	71.39
	4	67.4	67.39		5	78.4	78.14
	5	64.4	64.20		6	62.9	62.76
xyl	1	106.3	106.21	qui	1	99.3	99.29
	2	75.5	75.40		2	75.2	75.59
	3	77.1	77.87		3	78.3	75.59
	4	70.8	70.83		4	77.0	77.15
	5	67.3	67.16		5	72.7	70.17
glc′	1	95.6	95.67		6	18.8	17.09
	2	76.8	76.82	qui′	1		99.19
	3	78.1	78.04		2		75.40
	4	71.4	71.22		3		78.39
	5	79.0	79.06		4		76.82
	6	62.1	61.95		5		72.64
rha	1	101.7	101.76		6		18.81
	2	70.8	70.53				
	3	82.1	82.03				
	4	79.0	78.93				
	5	69.2	69.15				
	6	18.9	18.81				

C18 (6 μ, 60A, 7.8 × 300 mm ID). Macroporous resin D_{101} (Nankai), silica gel (10–40 μ, 200–300 mesh, Qingdao), Sephadex LH-20 (Pharmacia), Rp C_{18} silica gel (100–200 mesh, Ouya) was used as normal- and reversed-phases for chromatographic separations, respectively.

Plant Material

Dried stem bark of *A. julibrissin* was purchased from Mianyang Medicinal Company of Sichuan Province in October 1995. A sample has been deposited in Department of Natural Medicines, Beijing Medical University.

Extraction and Isolation

Air-dried powdered stem bark (13.5 kg) was extracted with 95% ethanol. The ethanol residue (1140 g) was suspended in H_2O, then extracted with

$CHCl_3$, EtOAc and *n*-BuOH, respectively. The *n*-BuOH soluble part was dissolved in MeOH, then poured into acetone dropwise. Precipitates were chromatographed over D_{101} resin column by elution with gradient solvent system (100% $H_2O \rightarrow$ 100% MeOH), MeOH part (248 g) was subjected to silica gel column chromatography eluted with gradient solvent system ($CHCl_3$–CH_3OH–H_2O, 100 : 0 : 0 → 6 : 4 : 1) to afford 68 fractions (500 ml/Fr.). Fractions 41–43 was decolorized by active charcoal in MeOH to give a white powder (22.5 g). The white powder (10.5 g) was subjected to repeated Sephadex LH-20 and Rp C_{18} silica gel column chromatography, and finally preparative HPLC (62% MeOH/H_2O, 6.0 ml/min, 216 nm) to afford **1** (t_R: 61.5 min, weight: 15.8 mg).

Julibroside J_{26} (1) was obtained as a white powder; $C_{85}H_{136}O_{42}$, positive FAB-MS *m/z*: 1852$[M+Na+H]^+$, 1830$[M+2H]^+$, 1266$[M+K+H-(2glc+rha+ara)]^+$; IR (KBr) ν_{max}: 3404, 2928, 1692, 1636, 1383, 1256, 1073 (cm^{-1}).

Acknowledgment

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