ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 324 (2000) 182–188

CARBOHYDRATE RESEARCH

Two diastereomeric saponins with cytotoxic activity from *Albizia julibrissin*

Kun Zou [a], Yuying Zhao [a,*], Guangzhong Tu [b], Jingrong Cui [a], Zhonghua Jia [c], Ruyi Zhang [a]

[a] *School of Pharmaceutical Sciences, Division of Natural Medicinal Chemistry, Beijing Medical University, Beijing 100083, PR China*

[b] *Beijing Institute of Microchemistry, Beijing 100091, PR China*

[c] *Department of Pharmacognosy, Toho University, Chiba, Japan*

Received 4 January 1999; accepted 28 October 1999

Abstract

Two diastereomeric saponins, julibrosides J_1 (**1**) and J_9 (**2**), both of which show cytotoxic activity, were obtained from the stem bark of *Albizia julibrissin* Durazz. On the basis of chemical and spectral evidence [L.B. Ma et al., *Carbohydr. Res.*, 281 (1996) 35–46], the structure of **1** was revised 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*-[4-*O*-((6*R*)-2-*trans*-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)-2,7-octadienoyl)-β-D-quinovopyranosyl]-2,7-octadienoyl}acacic acid-28-*O*-β-D-glucopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester. The diastereoisomer **2** of **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*-[4-*O*-((6*S*)-2-*trans*-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)-2,7-octadienoyl)-β-D-quinovopyranosyl]-2,7-octadienoyl}acacic acid-28-*O*-β-D-glucopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester. Saponin **2** is a new saponin named julibroside J_9. Both julibrosides J_1 and J_9 show good inhibitory action against the KB cancer cell line in vitro.

Keywords: *Albizia julibrissin*; Julibroside J_1; Julibroside J_9; Diastereomer; Cytotoxity

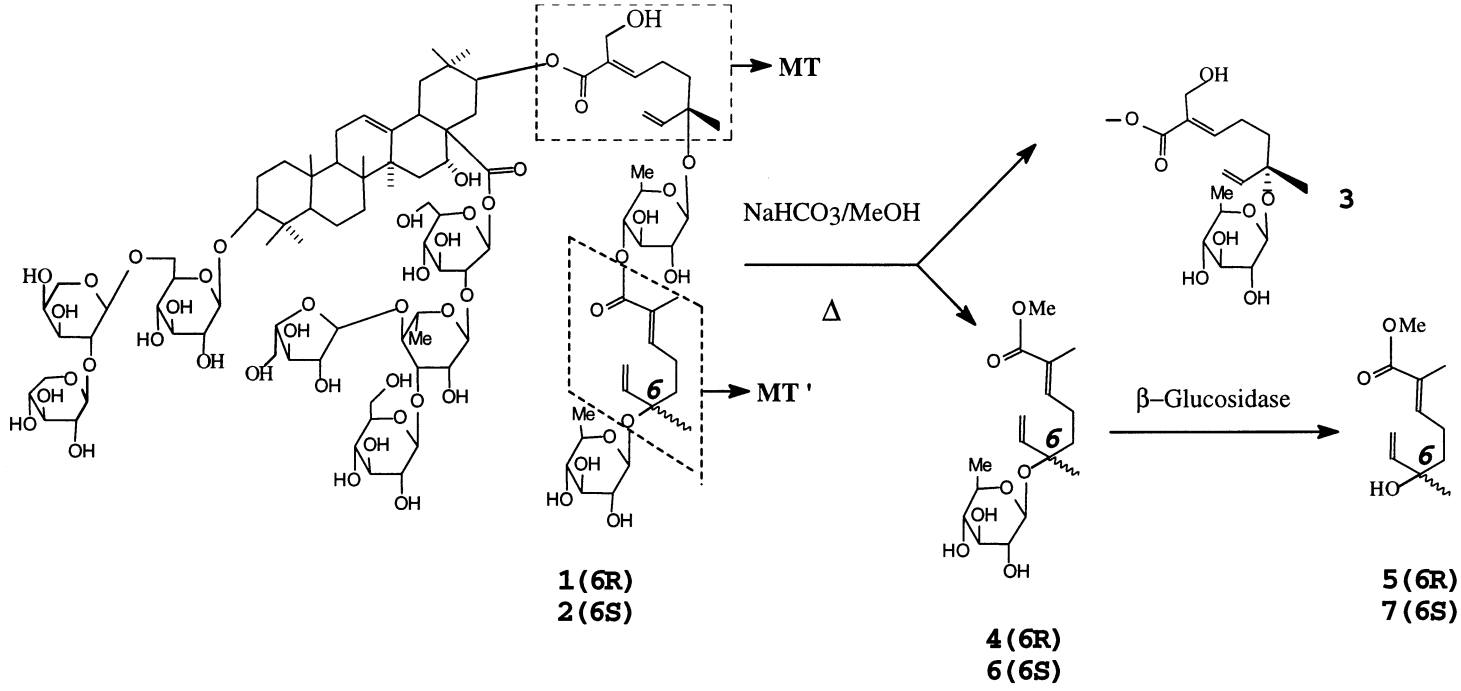
1. Introduction

Albizia julibrissin (Leguminosae) is a plant widely distributed in China. The stem bark of the plant has been used as a sedative drug and as an anti-inflammatory drug to treat swelling and pain in the lungs, skin ulcers, and in wounds [2].

Julibroside J_1 (**1**) has been reported in the literature [1,3]. During the course of our studies on the chemical constituents from the cortex of *Albizia*, two diastereomeric saponins **1** and **2** were isolated, and one of them was shown to be identical to julibroside J_1. However, its structure was subject to revision at the C-6 configuration in the MT′ region (see Scheme 1) based on our chemical and spectral studies. Compounds **1** and **2** showed marked cytotoxic activity against the KB cancer line (inhibition 94%) at 4 and 10 μM by the SRB method.

* Corresponding author.
E-mail address: nmechem@mail.bjmu.edu.cn (Y. Zhao)

0008-6215/00/$ - see front matter
PII: S0008-6215(99)00294-3



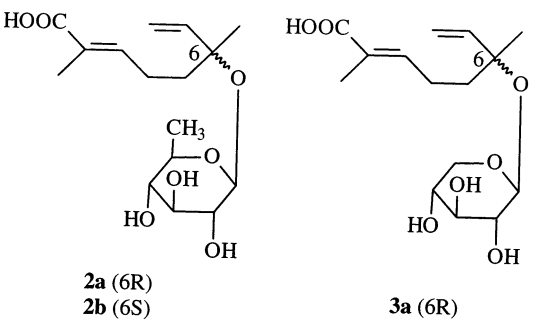
Scheme 1. Degradation of **1** and **2**.

2. Results and discussion

A 95% ethanolic extract of the stem bark of *A. julibrissin* was partitioned between water, $CHCl_3$, EtOAc and *n*-BuOH, respectively. The *n*-BuOH-soluble part was chromatographed over D_{101} macroporous resin, Sephadex LH-20, and silica gel columns to afford, after solvent removal, colorless powders (fractions 41–43). Two diastereomeric saponins **1** and **2** were obtained from fractions 41–43 by means of repeated reversed-phase C_{18} column chromatography and preparative high-performance liquid chromatography (HPLC).

Compound **1** was obtained as a white powder. It showed positive Molish and Liebermann–Buchard reactions, and its ^1H NMR spectrum had seven angular methyl signals and nine anomeric proton signals (see Section 3), which suggested that **1** was a triterpenoid saponin. Upon acidic hydrolysis with 2.0 M HCl, compound **1** gave a sapogenin that was identical to the authentic sample. Acacic acid lactone was identified by high-performance thin-layer chromatography (TLC), and D-glucose, L-arabinose, D-xylose, and L-rhamnose were identified by comparison with authentic samples (D-quinovose with data in the literature [4]).

The ESI mass spectrum (ESIMS, negative-ion) of **1** gave the quasi-molecular ion peak at m/z 1077.6 $[M-2]^{2-}$, and TOFMS showed m/z 2195 $[M+K]^+$, both of which were indicative of the formula $C_{101}H_{160}O_{49}$. The ^1H and ^{13}C NMR spectra of **1** were in good agreement with those of julibroside J_1, previously described [1]. Furthermore, saponin **1** and julibroside J_1 showed the same retention time by HPLC. Thus, the structure of **1** was determined to be the same as that of julibroside J_1. Upon hydrolyzing **1** with saturated $NaHCO_3$–CH_3OH, **3** and **4** were obtained. The ^1H and ^{13}C NMR data of **4** were quite similar to those of [(2*E*,6*R*)-2,6-dimethyl-6-hydroxy-2,7-octadienoic acid-6-*O*-β-D-xyloside (**3a**) (Scheme 2) [4]. Upon further enzymatic hydrolysis of **4**, compound **5** was obtained. The ^1H NMR data for **5** were quite similar to those of menthiafolic acid [4], and its rotation $\{[\alpha]_D^{14} -17.3°$ (*c* 0.035, $CHCl_3)\}$ was similar to that of (2*E*,6*R*)-2,6-dimethyl-6-hydroxy-2,7-octadienoic acid = (6*R*)-menthiafolic acid [4] $\{[\alpha]_D^{14} -18.0°$ (*c* 0.17, MeOH)$\}$. The above evidence indicated that the configuration of 6S in the MT′ region of julibroside J_1 should be corrected to 6R.



2a (6R)
2b (6S)

3a (6R)

Scheme 2. The structures of **2a**, **2b** and **3a**.

Compound **2** was obtained as a white amorphous powder with a longer retention time than that of compound **1** under several different HPLC conditions: t_R of **1** = 53.8 min, t_R of **2** = 59.5 min (29:21 CH_3CN–H_2O). Compound **2** showed quite similar MS, IR, ^1H, and ^{13}C NMR spectra to those of **1**, except for the ^1H and ^{13}C signals of the MT′ group. When **2** was hydrolyzed with HCl, the same sapogenin and monosaccharides as those found for **1** were detected in the hydrolysate. Hydrolysis of **2** with saturated $NaHCO_3$–CH_3OH yielded **3** and **6**. Enzymatic hydrolysis of **6** gave compound **7**. The optical rotation of **7** $[\alpha]_D^{14} +13.6°$ (*c* 0.024, $CHCl_3$) is similar to that of (6*S*)-methiafolic acid $\{[\alpha]_D^{14} +19.3°$ (*c* 0.15, $CHCl_3)\}$ [4], which showed the presence of the (6S) configuration in the MT′ group of **2**.

Saponins **1** and **2** possess markedly different ^{13}C NMR data due to differences in the MT′ group (see Table 3). A comparison of the ^{13}C NMR data of **2** with those of **1** showed that the signals of C-5 and C-10 of **2** undergo a downfield shift of 1.8 ppm and an upfield shift of 1.3 ppm, respectively. The results were quite similar to the ^{13}C NMR data of compound **2a** [(6*R*)-menthiafolic acid-6-*O*-β-D-quinoside] and **2b** [(6*S*)-menthiafolic acid-6-*O*-β-D-quinoside] (Scheme 2) measured in pyridine-d_5 (see Experimental [4]).

Thus, the structure of julibroside J_1 (**1**) is revised 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*-[4-*O*-((6*R*)-2-*trans*-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)-2,7-octadienoyl)-β-D-quinovopyranosyl]-2,7-octadienoyl}acacic acid-28-*O*-β-D-glucopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester. The structure of **2** was determined as 3-*O*-[β-D-xylopyranosyl-(1→2)-α-L-(1→6)-β-D-glucopyranosyl]-21-*O*-{(6*S*)-2-*trans*-2-hydroxymethyl-6-methyl-6-*O*-[4-*O*-((6*S*)-2-*trans*-2,6-dimethyl-6-*O*-(β-D-quinovopyranosyl)-2,7-octadienoyl)-β-D-quinovopyranosyl]-2,7-octadienoyl}acacic acid-28-*O*-β-D-glucopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester, named julibroside J_9. Compounds **1** and **2** are diastereomeric.

3. Experimental

General procedures.—Optical rotations were recorded at the indicated concentrations and temperatures with a Perkin–Elmer 241 spectropolarimeter using MeOH as solvent. IR spectra were measured on a Perkin–Elmer 983 FTIR instrument as samples in pressed KBr disks. 1D and 2D NMR spectra were recorded using Bruker AM 500 and Varian-300 instruments with Me_4Si as the intestinal standard. FAB mass spectra were recorded using a ZABspec mass spectrometer. HPLC was carried out using (1) a Gilson automatic system for preparative HPLC with an Alltima C_{18} column (5 μm, 60 Å pore size, 22 × 250 mm i.d. and 10 μm, 60 Å pore size, 22 × 250 mm i.d.), or (2) a Waters 600 semipreparative HPLC with a μBondpak C_{18} column (6 μm, 60 Å pore size, 7.8 × 300 mm i.d.). Macroporous resin D_{101} (Nandai), Silica Gel (10–40 μm, 200–300 mesh, Qingdao), Sephadex LH-20, RP C_{18} Silica Gel (100–200 mesh) (Ouya, Pharmacia) were 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 the Division of Natural Medicinal Chemistry of Beijing Medical University.

Extraction and isolation.—Air-dried powdered stem bark (13.5 kg) was extracted with 95% EtOH. The EtOH residues (1140 g) were suspended in water, then extracted with $CHCl_3$, EtOAc and *n*-BuOH, respectively. The *n*-BuOH-soluble extract was dissolved in MeOH, then poured dropwise into acetone. The resulting precipitate was chromatographed over a D_{101} resin column with gradient elution (100% water → 100% MeOH). The fraction from the MeOH elution (248 g) was subjected to Silica Gel column chromatography using a gradient solvent system of $CHCl_3$–CH_3OH–water, 100:0:0 → 6:4:1 to afford 68 fractions (500 mL/fraction). Fractions 41–43 were decolorized by activated 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 (63:37 MeOH–water, 6.0 mL/min, 216 nm detection) to afford **1** (202.0 mg) and **2** (164.7 mg).

Degradation of **1** *and* **2**.—A solution of **1** (50 mg) in satd $NaHCO_3$ in MeOH was refluxed for 45 min. The reaction mixture was concentrated in vacuo to dryness and was subjected to chromatography on a silica gel column and first eluted with $CHCl_3$–MeOH (100:0 → 15:5) to afford **4**, and then eluted with MeOH to give a MeOH eluate that was purified by HPLC to afford **3**. Compound **4** was hydrolyzed with emulsin in acetate buffer (pH 5, NaOAc–HOAc) for 72 h at 37 °C. The mixture was extracted with $CHCl_3$. The $CHCl_3$ solution was evaporated to give **5**. Compound **6** and **7** were obtained by the same method.

Identification.—Compound **1** was obtained as a white powder: $[\alpha]_D^{17}$ −30.1° (*c* 0.073, 70% CH_3OH). $C_{101}H_{160}O_{49}$, ESIMS (negative-ion) *m/z* 1077.6 $[M-2]^{2-}$; TOFMS *m/z* 2195 $[M+K]^+$. IR (KBr) ν_{max}: 3420, 2922, 1692, 1637, 1382, 1257, 1072 (cm^{-1}); ^1H NMR (500 MHz, pyr-d_5): δ 1.28, 1.00, 0.96, 1.15, 1.86, 1.06, 1.09 (3 H × 7, s, H-23, 24, 25, 26, 27, 29, 30), 5.61 (1 H, br s, H-12); 4.88 (1 H, d, *J* 7.6 Hz, H-Glc-1), 5.14 (1 H, br s, H-Ara*p*-1), 4.98 (1 H, d, *J* 7.6 Hz, H-Xyl-1), 6.03 (1 H, d, *J* 7.9

Table 1
^{13}C NMR data for the aglycone moieties of J_1, compounds **1** and **2** [a]

	J_1	**1**	**2**		J_1	**1**	**2**
1	38.9	38.98	38.98	16	74.8	73.8	73.8
2	26.9	26.8	26.8	17	51.7	51.7	51.6
3	88.9	88.8	88.7	18	40.9	40.8	40.9
4	39.7	39.6	39.6	19	47.9	47.9	47.9
5	56.1	56.1	56.1	20	35.6	35.4	35.4
6	18.7	18.8	18.8	21	77.1	77.2	76.8
7	33.7	33.6	33.6	22	36.4	36.4	36.4
8	40.2	40.2	40.1	23	28.3	28.3	28.2
9	47.2	47.1	47.1	24	17.1	17.1	17.1
10	37.1	37.1	37.1	25	15.9	15.8	15.8
11	23.9	23.7	23.9	26	17.3	17.4	17.4
12	124.1	123.0	123.1	27	27.3	27.3	27.2
13	143.3	143.3	143.3	28	174.4	174.4	174.4
14	43.3	42.1	42.0	29	29.3	29.2	89.2
15	35.9	35.9	35.9	30	19.1	19.1	19.1

[a] Determined in pyridine-d_5.

Hz, H-Glc′-1), 5.88 (1 H, s, H-Rha-1), 6.23 (1 H, s, H-Ara*f*-1), 5.30 (1 H, d, *J* 7.7 Hz, H-Glc″-1), 4.83 (1 H, d, *J* 7.8 Hz, H-Qui-1), 4.81 (1 H, d, *J* 7.8 Hz, H-Qui′-1), 1.74 (3 H, d, *J* 5.4 Hz, H-Rha-6), 1.57 (3 H, d, *J* 5.2 Hz, H-Qui′-6), 1.33 (3 H, d, *J* 6.0 Hz, H-Qui-6); 7.04 (1 H, t, *J* 7.4 Hz, H-MT-3), 6.19 (1 H, dd, *J* 11.1, 17.6 Hz, H-MT-7), 5.21 (1 H, d, *J* 11.1 Hz, H-MT-8a), 5.39 (1 H, d, *J* 17.6 Hz, H-MT-8b), 4.70 (2 H, s, H-MT-9), 1.49 (3 H, s, H-MT-10); 7.10 (1 H, t, *J* 7.4 Hz, H-MT′-3), 1.81 (2 H, t, *J* 8.5 Hz, H-MT′-5), 6.30 (1 H, *J* 11.1, 17.6 Hz, H-MT′-7), 5.18 (1 H, d, *J* 11.1 Hz, H-MT′-8a), 5.31 (1 H, d, *J* 17.6 Hz, H-MT′-8b), 1.92 (3 H, s, H-MT′-9), 1.44 (3 H, s, H-MT′-10). For ^{13}C NMR data see Tables 1–3.

Compound **3** was obtained as a white amorphous powder: $C_{85}H_{136}O_{43}$, FABMS (positive-ion) m/z 1846 $[M+2]^+$; IR ν_{max} (KBr) 3413 (OH), 2925 (CH), 1694 (C=O), 1639 (C=C). The IR data and t_R (HPLC) of **3** were identical to those of an authentic sample, julibroside J_{27} [5].

Compound **4** was obtained as a pale yellow wax: ^{1}H NMR (500 MHz, CD_3COCD_3): δ 6.73 (1 H, t, *J* 7.5 Hz, H-3), 6.02 (1 H, dd, *J* 11.0, 17.6 Hz, H-7), 5.21 (1 H, d, *J* 17.6 Hz, H-8b), 5.10 (1 H, d, *J* 11.0 Hz, H-8a), 4.33 (1 H, d, *J* 7.8 Hz, H-Qui-1), 3.62 (3 H, s, H–OMe), 2.31 (2 H, m, H-4), 1.78 (3 H, s, H-9), 1.68 (2 H, m, H-5), 1.29 (3 H, d, *J* 5.8 Hz, H-Qui-6). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 168.4 (C-1, 144.4 (C-7), 143.5 (C-3), 127.9 (C-2), 114.3 (C-8), 98.5 (C-Qui-1), 79.4 (C-6), 77.6 (C-Qui-3), 76.3 (C-Qui-4), 74.7 (C-Qui-2), 72.2 (C-Qui-5), 51.7 (C-OMe), 38.7 (C-5), 24.5 (C-10), 23.7 (C-4), 18.2 (C-Qui-6), 12.6 (C-9).

Compound **5**: $[\alpha]_D^{14}$ −17.3° (*c* 0.035, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.78 (1 H, t, *J* 7.5 Hz, H-3), 5.83 (1 H, dd, *J* 10.8, 17.4 Hz, H-7), 5.21 (1 H, d, *J* 17.4 Hz, H-8b), 5.01 (1 H, d, *J* 10.8 Hz, H-8a), 3.66 (3 H, s, H–OMe), 2.29 (2 H, m, H-4), 1.82 (3 H, s, H-9), 1.72 (2 H, m, H-5), 1.32 (3 H, s, H-10).

Table 2
^{13}C NMR data for the monoterpenes of J_1, compounds **1** and **2** [a]

MT	J_1	**1**	**2**	MT′	J_1	**1**	**2** (Δ = **2**−**1**)
1	167.5	167.8	167.7	1	167.8	167.5	167.5
2	134.9	133.8	133.8	2	127.9	127.9	127.9
3	145.2	145.2	145.4	3	143.5	143.5	143.9
4	23.7	23.7	23.6	4	23.7	23.7	23.7
5	40.9	40.98	41.0	5	38.6	38.6	40.4 (+1.8)
6	79.8	79.8	79.7	6	79.5	79.4	79.4
7	143.9	143.9	144.1	7	144.3	144.4	145.2
8	115.2	115.0	115.0	8	114.3	114.2	114.7
9	56.2	56.3	56.3	9	12.7	12.7	12.6
10	23.8	23.6	23.8	10	24.9	24.8	23.5 (−1.3)

[a] Determined in pyridine-d_5.

Table 3
^{13}C NMR data for the sugar moieties of J_1, compounds **1** and **2** [a]

		J_1	**1**	**2**			J_1	**1**	**2**
C-3					C-28				
Glc	1	106.76	106.7	106.7	Glc′	1	95.67	95.6	95.6
	2	75.60	75.6	76.1		2	76.82	76.8	76.8
	3	78.39	78.4	78.4		3	78.04	78.1	78.1
	4	72.22	72.2	72.2		4	71.22	71.3	71.3
	5	76.07	76.1	77.8		5	79.06	79.0	79.4
	6	69.52	69.5	69.5		6	61.95	62.0	62.0
Ara*p*	1	102.22	102.2	102.2	Rha	1	101.76	101.7	101.7
	2	80.36	80.3	80.2		2	70.53	70.8	70.6
	3	72.53	72.5	72.5		3	82.03	82.0	82.0
	4	67.39	67.4	67.4		4	78.93	78.4	78.9
	5	64.20	64.2	64.2		5	69.15	69.1	69.1
						6	18.81	18.7	18.4
Xyl	1	106.21	106.2	106.1	Ara*f*	1	111.02	111.0	111.0
	2	75.40	75.3	75.4		2	84.42	84.4	84.3
	3	77.87	77.9	77.2		3	78.39	78.4	78.4
	4	70.83	70.6	70.8		4	85.43	85.5	85.4
	5	67.16	67.3	67.2		5	62.55	62.6	62.6
C-21									
Qui	1	99.29	99.2	99.3	Glc′	1	105.73	105.7	105.7
	2	75.59	75.6	75.6		2	75.40	75.4	75.6
	3	75.59	75.6	75.6		3	78.39	78.4	78.4
	4	77.15	77.2	77.2		4	71.39	71.8	71.8
	5	70.17	70.2	70.2		5	78.14	78.2	78.4
	6	17.09	18.4	18.8		6	62.76	62.8	62.8
Qui′	1	99.19	99.3	99.3					
	2	75.40	75.4	75.5					
	3	78.39	78.4	78.4					
	4	76.82	76.8	76.8					
	5	72.64	72.6	72.5					
	6	18.81	18.8	18.8					

[a] Determined in pyridine-d_5.

Compound **2** was obtained as a white powder, $[\alpha]_D^{17}$ −31.6° (*c* 0.11, 70% CH_3OH); $C_{101}H_{160}O_{49}$, FABMS (positive-ion) *m/z*: 2181 $[M + Na + 2]^+$, 2049 $[M + Na + 2Xyl]^+$, 1753 $[M + Na + 2 - (Glc + Ara + Xyl)]^+$, 1578 $[M + Na + 2 - (2Glc + Rha + Ara)]^+$; IR (KBr) ν_{max}: 3402, 2927, 1692, 1639, 1383, 1275, 1072, 642 (cm^{-1}); ^1H NMR (500 MHz, pyr-d_5): δ 1.28, 1.00, 0.95, 1.14, 1.86, 1.04, 1.08 (3 H, s, H-23, 24, 25, 26, 27, 29, 30), 5.61 (1 H, br s, H-12), 4.91 (1 H, d, *J* 7.8 Hz, H-Glc-1), 5.15 (1 H, br s, H-Ara*p*-1), 4.98 (1 H, d, *J* 7.4 Hz, H-Xyl-1), 6.03 (1 H, d, *J* 7.2 Hz, H-Glc′-1), 5.88 (1 H, br s, H-Rha-1), 6.24 (1 H, br s, H-Ara*f*-1), 5.31 (1 H, d, *J* 7.5 Hz, H-Glc″-1), 4.83 (1 H, d, *J* 9.5 Hz, H-Qui-1), 4.85 (1 H, d, *J* 8.0 Hz, H-Qui′-1), 1.74 (3 H, d, *J* 5.5 Hz, H-Rha-6), 1.57 (3 H, d, *J* 5.0 Hz, H-Qui′-6), 1.32 (3 H, d, *J* 6.1 Hz, H-Qui-6); 7.02 (1 H, br s, H-MT-3), 6.19 (1 H, dd, *J* 11.1, 17.6 Hz, H-MT-7), 5.21 (1 H, d, *J* 11.1 Hz, H-MT-8a), 5.39 (1 H, d, *J* 17.6 Hz, H-MT-8b), 4.70 (2 H, s, H-MT-9), 1.49 (3 H, s, H-MT-10), 7.02 (1 H, br s, H-MT′-3), 1.71 (2 H, t, *J* 7.8 Hz, H-MT′-5), 6.19 (1 H, dd, *J* 11.1, 17.6 Hz, H-MT′-7), 5.21 (1 H, d, *J* 11.1 Hz, H-MT′-8a), 5.41 (1 H, d, *J* 17.6 Hz, H-MT′-8b), 1.86 (3 H, s, H-MT′-9), 1.52 (3 H, s, H-MT′-10). for ^{13}C NMR data see Tables 1–3.

Compound **6** was obtained as a pale-yellow wax, ^1H NMR (500 MHz, CD_3COCD_3): δ 6.71 (1 H, t, *J* 7.8 Hz, H-3), 5.92 (1 H, dd, *J* 10.8, 17.5 Hz, H-7), 5.24 (1 H, d, *J* 17.5 Hz, H-8b), 5.12 (1 H, d, *J* 10.8 Hz, H-8a), 4.32 (1 H, d, *J* 7.4 Hz, H-Qui-1), 3.65 (3 H, s, H-

OMe), 2.33 (2 H, m, H-4), 1.77 (3 H, s, H-9), 1.62 (2 H, m, H-5), 1.29 (3 H, d, J 5.8 Hz, H-Qui-6). ^{13}C NMR (125 MHz, CD_3COCD_3): δ 168.5 (C-1, 144.0 (C-7), 143.6 (C-3), 127.8 (C-2), 115.4 (C-8), 98.6 (C-Qui-1), 79.5 (C-6), 77.5 (C-Qui-3), 76.3 (C-Qui-4), 74.8 (C-Qui-2), 72.2 (C-Qui-5), 51.8 (C-OMe), 40.6 (C-5), 23.6 (C-10), 23.7 (C-4), 18.2 (C-Qui-6), 12.6 (C-9).

Compound **7**: $[\alpha]_D^{14}$ +13.6° (c 0.024, $CHCl_3$). ^{1}H NMR data of **7** were similar to those of compound **5**.

References

[1] L.B. Ma, G.Z. Tu, S.P. Chen, R.Y. Zhang, L.L. Lai, X.J. Xu, Y.Q. Tang, *Carbohydr. Res.*, 281 (1996) 35–46.
[2] The Pharmacopoeia Committee of People's Republic of China, *Pharmacopoeia (I)*, People Health Press, Beijing, 1995, pp. 119–120.
[3] S.P. Chen, R.Y. Zhang, L.B. Ma, G.Z. Tu, *Acta Pharm. Sin.*, 32 (1997) 110–115.
[4] F. Kiuchi, M.A. Gafur, T. Obata, A. Tachibana, Y. Tsuda, *Chem. Pharm. Bull.*, 45 (1997) 807–812.
[5] K. Zou, J.R. Cui, Y.Y. Zhao, R.Y. Zhang, J.H. Zheng, *Chin. Chem. Lett.*, 10 (1996), 11 (2000) 39.