Four New Isoflavone Triglycosides from *Sophora japonica*

Yuping Tang,*,† Fengchang Lou,† Jinghua Wang,† and Shufei Zhuang‡

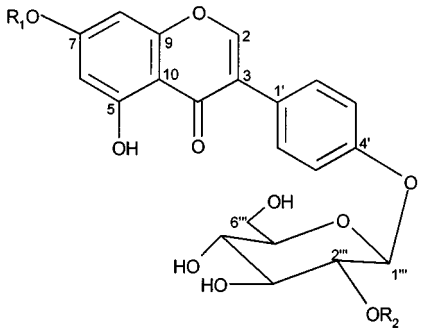
Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing 210038, People's Republic of China, and Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 200031, People's Republic of China

Received February 15, 2001

Four new isoflavone triglycosides, genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-*β*-D-glucopyranoside] (**1**), genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-[(*β*-D-glucopyranosyl)-(1→2)-*β*-D-glucopyranoside] (**2**), genistein 7-*O*-α-L-rhamnopyranoside-4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-*β*-D-glucopyranoside] (**3**), and genistein 7-*O*-α-L-rhamnopyranoside-4′-*O*-[(*β*-D-glucopyranosyl)-(1→2)-*β*-D-glucopyranoside] (**4**), together with nine known compounds, namely, genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-*β*-D-glucopyranoside, sophorabioside, prunetin 4′-*O*-*β*-D-glucopyranoside, sophororicoside, genistin, rutin, kaempferol 3-*O*-*β*-rutinoside, quercetin 3-*O*-*β*-D-glucopyranoside, and kaempferol 3-*O*-*β*-D-glucopyranoside, were isolated from the pericarps of *Sophora japonica*. The structures of **1**−**4** were determined by spectroscopic methods.

The fruits of *Sophora japonica* L. (Leguminosae) have been used as a hemostatic agent in traditional Chinese medicine, and flavonoids were discovered as hemostatic constituents from the buds of *S. japonica*.[1] To our knowledge, no phytochemical investigation on the pericarps of this species has been reported. In the present study, the 95% aqueous EtOH extract of the pericarps of *S. japonica* was separated by repeated column chromatography to give 13 flavonoid glycosides, namely, genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-*β*-D-glucopyranoside] (**1**), genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-[(*β*-D-glucopyranosyl)-(1→2)-*β*-D-glucopyranoside] (**2**), genistein 7-*O*-α-L-rhamnopyranoside-4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-*β*-D-glucopyranoside] (**3**), genistein 7-*O*-α-L-rhamnopyranoside-4′-*O*-[(*β*-D-glucopyranosyl)-(1→2)-*β*-D-glucopyranoside] (**4**), genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-*β*-D-glucopyranoside, sophorabioside, prunetin 4′-*O*-*β*-D-glucopyranoside, sophororicoside, genistin, rutin, kaempferol 3-*O*-*β*-rutinoside, quercetin 3-*O*-*β*-D-glucopyranoside, and kaempferol 3-*O*-*β*-D-glucopyranoside. Compounds **1**−**4** are new isoflavone glycosides. Genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-*β*-D-glucopyranoside, prunetin 4′-*O*-*β*-D-glucopyranoside, and genistin were isolated from this plant for the first time. Here, we report the isolation and structure elucidation of **1**−**4**.

Compounds **1**−**4** were obtained from the *n*-BuOH-soluble part of a 95% ethanolic extract of *S. japonica* pericarps. Compound **1** appeared as a white amorphous powder, whose molecular formula, $C_{33}H_{40}O_{19}$, was inferred from HRFABMS ($[M - H]^-$ *m*/*z* 739.2088), and it was supported by ^{13}C NMR and DEPT spectra, which showed 33 resonance lines consisting of one methyl, two methylenes, 20 methines, and eight quaternary carbons. The IR spectrum of compound **1** showed strong absorption bands at 3414 (OH), 1652 (α,*β*-unsaturated C=O), 1613, 1582, 1495 (C=C, aromatic), and a broad band at 1160−1000 cm^{-1}, indicating its glycosidic nature. The presence of a singlet at *δ* 8.49 in the ^1H NMR spectrum and UV absorption band at 261 nm suggested that it was an isoflavonoid.[2] Upon



	R_1	R_2
1	glc	rha
2	glc	glc
3	rha	rha
4	rha	glc

acid hydrolysis of **1**, genistein, glucose, and rhamnose were identified by TLC. Genistein was also identified by UV and ^1H NMR spectroscopy.[3] Its ^1H and ^{13}C NMR spectra showed the presence of a genistein moiety and three sugar residues.[2,4] A ^{13}C NMR signal at *δ* 163.1 was assigned to C-7, based on its long-range $^{13}C-^1H$ correlations to both H-6 (*δ* 6.49) and H-8 (*δ* 6.74), whereas C-7 showed a three-bond correlation with an anomeric proton at *δ* 5.07 in the HMBC spectrum. The 2D NMR spectra allowed the assignment of all ^1H and ^{13}C NMR signals of the 7-glycosyl residue (Table 1), which could be identified as a glucopyranoside unit.[5] The *β*-configuration of the anomeric carbon was evident from the coupling constant of H-1″ (J = 7.3 Hz) observed in the ^1H NMR spectrum.[6]

A methyl doublet, which appeared at *δ* 1.20 in the ^1H NMR spectrum of **1**, was assigned to the C-6 methyl protons of a rhamnose residue. All ^1H and ^{13}C NMR signals of the rhamnosyl moiety could be assigned on the basis of 2D NMR spectra data (Table 1). A TOCSY experiment showed a correlation between the C-6 methyl protons of rhamnose residue and the anomeric proton at *δ* 5.14, demonstrating that they belong to the same spin system. The anomeric proton of the rhamnosyl residue showed a long-range correlation with a ^{13}C NMR signal at *δ* 76.4, corresponding to a proton at *δ* 3.52 in the HMQC spectrum. The latter signal showed a $^1H-^1H$ correlation, observed in the DQF-COSY experiment, with the third anomeric proton

* Present address of corresponding author: State Key Laboratory of Bioorganic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China. Tel: +86-21-64163300-1599. Fax: +86-21-64166128. E-mail: yptang@pub.sioc.ac.cn.

† China Pharmaceutical University.

‡ Shanghai Institute of Materia Medica.

10.1021/np010081s CCC: $20.00
Published on Web 07/26/2001

Table 1. ^{13}C and ^{1}H NMR Spectral Data of Compounds **1**−**4** in DMSO-d_6

	1		**2**		**3**		**4**	
position	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
2	155.1	8.49 (s)	155.1	8.48 (s)	155.1	8.50 (s)	155.1	8.50 (s)
3	124.1		124.1		124.0		124.0	
4	180.4		180.4		180.4		180.4	
5	161.6		161.6		161.6		161.6	
6	99.7	6.49 (d, 1.9)	99.7	6.48 (d, 1.8)	99.7	6.44 (d, 1.8)	99.7	6.45 (d, 1.8)
7	163.1		163.1		161.3		161.3	
8	94.7	6.74 (d, 1.9)	94.7	6.74 (d, 1.8)	94.7	6.71 (d, 1.8)	94.7	6.70 (d, 1.8)
9	157.3		157.2		157.2		157.2	
10	106.1		106.1		106.1		106.1	
1′	122.2		122.2		122.3		122.2	
2′,6′	130.2	7.52 (d, 8.8)	130.2	7.51 (d, 8.6)	130.2	7.51 (d, 8.7)	130.2	7.50 (d, 8.6)
3′,5′	115.7	7.06 (d, 8.8)	115.6	7.04 (d, 8.6)	115.7	7.06 (d, 8.7)	115.6	7.04 (d, 8.6)
4′	157.1		157.1		157.1		157.1	
5-OH		12.88 (s)		12.92 (s)		12.90 (s)		12.91 (s)
1″	99.9	5.07 (d, 7.3)	99.9	5.07 (d, 7.2)	98.4	5.60 (brs)	98.5	5.60 (brs)
2″	73.1	3.73 (m)	73.1	3.72 (m)	70.3	3.70 (m)	70.3	3.71 (m)
3″	76.4	3.30 (m)	76.4	3.32 (m)	69.8	3.91 (m)	69.8	3.90 (m)
4″	69.6	3.18 (m)	69.6	3.20 (m)	71.6	3.37 (m)	71.7	3.39 (m)
5″	77.2	3.45 (m)	77.2	3.45 (m)	70.1	3.51 (m)	70.1	3.52 (m)
6″	60.7	3.70 (m)	60.7	3.69 (m)	18.0	1.19 (d, 6.1)	18.0	1.19 (d, 6.2)
1‴	98.2	5.06 (d, 7.4)	98.3	5.36 (d, 7.2)	98.2	5.06 (d, 7.3)	98.3	5.36 (d, 7.1)
2‴	76.4	3.52 (m)	82.4	3.54 (m)	76.4	3.51 (m)	82.4	3.55 (m)
3‴	77.4	3.49 (m)	76.6	3.55 (m)	77.4	3.49 (m)	76.6	3.55 (m)
4‴	69.8	3.20 (m)	69.7	3.17 (m)	69.8	3.21 (m)	69.7	3.18 (m)
5‴	76.9	3.40 (m)	76.9	3.20 (m)	76.9	3.40 (m)	76.9	3.21 (m)
6‴	60.6	3.46 (m)	60.6	3.33 (m)	60.6	3.45 (m)	60.6	3.34 (m)
				3.57 (m)				3.56 (m)
1⁗	100.5	5.14 (brs)	104.1	4.68 (d, 7.6)	100.4	5.14 (brs)	104.1	4.68 (d, 7.5)
2⁗	70.5	3.36 (m)	74.4	3.13 (m)	70.6	3.36 (m)	74.4	3.12 (m)
3⁗	70.5	3.70 (m)	76.7	3.24 (m)	70.5	3.71 (m)	76.7	3.25 (m)
4⁗	71.9	3.22 (m)	69.9	3.20 (m)	71.9	3.20 (m)	69.9	3.20 (m)
5⁗	68.3	3.87 (m)	77.0	3.17 (m)	68.3	3.85 (m)	77.0	3.18 (m)
6⁗	18.1	1.20 (d, 6.2)	60.8	3.55 (m)	18.0	1.20 (d, 6.2)	60.8	3.56 (m)
				3.64 (m)				3.64 (m)

at δ 5.06, assigned to H-1‴ of the second glucosyl moiety. Therefore, glycosylation of the second glucose at the C-2‴ position became evident. The β-configuration of the anomeric carbon was evident from the coupling constant of H-1‴ (J = 7.4 Hz) observed in the ^{1}H NMR spectrum.[5] In the HMBC spectrum, C-4′ (δ 157.1) showed a three-bond correlation with the anomeric proton of the second glucose unit. These showed the presence of a 4′-neohesperidosyl residue in **1**. The ^{1}H and ^{13}C NMR signals of the 4′-neohesperidosyl residue were closely comparable to those of a genistein 4′-neohesperidoside derivative from the literature.[7] Therefore, compound **1** was identified as genistein 7-*O*-β-D-glucopyranoside-4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-β-D-glucopyranoside].

Compound **2** was obtained as a white amorphous powder. Upon acid hydrolysis of **2**, genistein and glucose were identified by TLC. Genistein was also identified by UV and ^{1}H NMR spectroscopy.[3] The UV and IR spectra of **2** were similar to those of compound **1**. The molecular formula, $C_{33}H_{40}O_{20}$, was inferred from the HRFABMS ([M − H]$^-$ m/z 755.2027), and it was supported by ^{13}C NMR and DEPT spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra of **2** showed the presence of a genistein moiety and three sugar residues.[2,4] Its ^{1}H NMR, ^{13}C NMR, and 2D NMR spectra showed the presence of a genistein 7-*O*-β-D-glucopyranoside unit, as found for **1** (Table 1). A ^{13}C NMR signal at δ 157.1 was assigned to C-4′, on the basis of its long-range $^{13}C-^{1}H$ correlation observed in a HMBC experiment with the two ^{1}H NMR signals at δ 7.04 (H-3′,5′) and 7.51 (H-2′,6′). The C-4′ signal showed a three-bond correlation with the anomeric proton of a second glucosyl unit at δ 5.36. The anomeric proton of the third glucosyl residue at δ 4.68 showed a long-range correlation with a ^{13}C NMR signal at δ 82.4, corresponding to a proton at δ 3.54 in the HMQC spectrum. The latter signal showed a $^{1}H-^{1}H$ correlation, observed in the DQF-COSY experiment, with the anomeric proton at δ 5.36, assigned to H-1‴ of the second glucosyl moiety. Therefore, glycosylation of the second glucose at the C-2‴ position became evident. 2D NMR allowed the assignment of all ^{1}H and ^{13}C NMR signals of the second and third glucosyl moieties (Table 1). The β-configuration of two anomeric carbons was evident from the coupling constants of H-1‴ (J = 7.2 Hz) and H-1⁗ (J = 7.6 Hz) observed in the ^{1}H NMR spectrum.[6] These showed the presence of 4′-sophorosyl residue. The ^{13}C NMR signals of the 4′-sophorosyl residue were the same as those of a flavonoid sophoroside described in the literature.[4] Therefore, compound **2** was identified as genistein 7-*O*-β-D-glucopyranoside-4′-*O*-[(β-D-glucopyranosyl)-(1→2)-β-D-glucopyranoside].

Compound **3** appeared as a white amorphous powder. Upon acid hydrolysis of **3**, genistein, glucose, and rhamnose were identified by TLC. Genistein was also identified by UV and ^{1}H NMR spectroscopy.[3] The UV and IR spectra of **3** were similar to those of compounds **1** and **2**. The molecular formula, $C_{33}H_{40}O_{18}$, was inferred from the HRFABMS ([M − H]$^-$ m/z 723.2131), and it was supported by ^{13}C NMR and DEPT spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra of **3** showed the presence of a genistein moiety and three sugar residues.[2,4] Its ^{1}H NMR, ^{13}C NMR, and 2D NMR spectra were indicative of a genistein 4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-β-D-glucopyranoside] unit, as found for **1** (Table 1). A ^{13}C NMR signal at δ 161.3 was assigned to C-7, on the basis of its long-range $^{13}C-^{1}H$ correlations observed in a HMBC experiment with the ^{1}H NMR signals at δ 6.44 (H-6) and 6.71 (H-8). The C-7 signal

showed a three-bond correlation with an anomeric proton at δ 5.60. A methyl doublet, observed at δ 1.19 in the ^{1}H NMR spectrum of **3**, was assigned to the C-6 methyl group of a rhamnose residue. All ^{1}H and ^{13}C NMR signals of the rhamnosyl moiety could be assigned on the basis of the 2D NMR spectra data (Table 1). A TOCSY experiment showed a correlation between the rhamnose methyl protons at C-6 and the anomeric proton at δ 5.60, demonstrating that they belong to the same spin system, consistent with a 7-rhamnosyl residue. The ^{13}C NMR signals of the 7-rhamnosyl residue were comparable with literature values for a flavonoid 7-rhamnoside.[4] Therefore, compound **3** was identified as genistein 7-*O*-α-L-rhamnopyranoside-4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-*β*-D-glucopyranoside].

Compound **4** was a white amorphous powder. Upon acid hydrolysis of **4**, genistein, glucose, and rhamnose were identified by TLC. Genistein was also identified by UV and ^{1}H NMR spectroscopy.[3] The UV and IR spectra of **4** were similar to those of compounds **1**−**3**. The molecular formula, $C_{33}H_{40}O_{19}$, was inferred from the HRFABMS ([M − H]$^-$ *m*/*z* 739.2083), and it was supported by ^{13}C NMR and DEPT spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra of **4** showed the presence of a genistein moiety and three sugar residues.[2,4] Its ^{1}H NMR, ^{13}C NMR, and 2D NMR spectra showed the presence of a genistein 4′-*O*-[(*β*-D-glucopyranosyl)-(1→2)-*β*-D-glucopyranoside] unit, the same as **2**, and a genistein 7-*O*-α-L-rhamnopyranoside unit, as in **3** (Table 1). Therefore, compound **4** was identified as genistein 7-*O*-α-L-rhamnopyranoside-4′-*O*-[(*β*-D-glucopyranosyl)-(1→2)-*β*-D-glucopyranoside].

Five of the known compounds were identified by comparing their physical and spectral data with literature values, namely, genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-*β*-D-glucopyranoside,[2] sophorabioside,[7] prunetin 4′-*O*-*β*-D-glucopyranoside,[7] sophororicoside,[2] and genistin.[2] In addition, four known substances were identified by comparison of spectral data with those of authentic samples: rutin, kaempferol 3-*O*-*β*-rutinoside, quercetin 3-*O*-*β*-D-glucopyranoside, and kaempferol 3-*O*-*β*-D-glucopyranoside.

Experimental Section

General Experimental Procedures. Melting points were determined on an Electrothermal 9200 micro melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer model 241 polarimeter. UV and IR spectra were measured on a Shimadzu UV-1601 instrument and on a Perkin-Elmer 983 spectrometer, respectively. All NMR spectra were run on a Bruker DRX-400 instrument operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C, using standard pulse sequences. Chemical shifts are reported on the δ scale in parts per million, downfield from TMS. Carbon multiplicities were determined from DEPT-135 and DEPT-90 experiments. All 2D NMR spectra were recorded using pulsed field gradients. ^{1}H−^{1}H correlations were observed in double quantum filtered (DQF) COSY and TOCSY experiments. One-bond ^{13}C−^{1}H correlations were observed in a HMQC experiment. Long-range ^{13}C−^{1}H correlations were observed in HMBC experiments. FABMS were obtained on a JEOL JMS DX-303HF mass spectrometer. Column chromatography was performed on Si gel (Marine Chemical Factory, Qingdao, People's Republic of China), Sephadex LH-20 (Pharmacia), and RP-18 (Shimadzu). TLC was carried out on precoated Si gel 60 F_{254} plates (Merck), developed with EtOAc−HOAc−HCOOH−H_2O (30:0.9:1.1:8, upper phase, and 10:1:1:2), *n*-BuOH−HOAc−H_2O (4:1:5, upper phase), and for sugars EtOAc−HOAc−MeOH−H_2O (13:4:3:3). For visualization, 1% methanolic $AlCl_3$ was used for the isoflavonoids, and thymol in H_2SO_4 (0.5 g thymol in 95 mL of EtOH and 5 mL of H_2SO_4) was used for the sugars (plates were heated to 120 °C for 15−20 min).

Plant Material. Fruits of *S. japonica* L. were collected from mature trees, growing in Nanjing, People's Republic of China, in November 1998, and were identified by Prof. Luoshan Xu, China Pharmaceutical University. A voucher specimen (No. CPUT-981120) was deposited in the herbarium of China Pharmaceutical University.

Extraction and Isolation. Dried and powdered pericarps of *S. japonica* (8.0 kg) were extracted three times with 95% EtOH using an ultrasonic apparatus for 3 h each time, with the solvent removed under reduced pressure, and the residue dissolved in hot water. This residue was left in the refrigerator overnight and filtered. The filtrate was partitioned with $CHCl_3$, EtOAc, and *n*-BuOH, successively. The *n*-BuOH-soluble fraction was concentrated and subjected to Si gel column chromatography eluting with $CHCl_3$−MeOH (25:1) followed by stepwise addition of MeOH to yield 15 fractions. Fraction 8 (23.2 g) was subjected to Si gel ($CHCl_3$−MeOH, 10:3) and Sephadex LH-20 (MeOH) chromatography and purified by HPLC (RP_{18}, 4 μm, 260 nm, MeOH−1% acetic acid, 18:82; **1**, t_R = 10.95 min; **2**, t_R = 8.72 min; **3**, t_R = 12.65 min; **4**, t_R = 10.02 min) to give compounds **1** (25 mg), **2** (28 mg), **3** (30 mg), and **4** (30 mg), respectively. Fraction 9 (28.6 g) was subjected to Si gel ($CHCl_3$−MeOH, 10:4) and Sephadex LH-20 (MeOH) chromatography to give genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-*β*-D-glucopyranoside (40 mg). Fraction 7 (56.7 g) was subjected to Si gel ($CHCl_3$−MeOH, 10:2) and Sephadex LH-20 (MeOH) chromatography to give sophorabioside (5300 mg), rutin (50 mg), and kaempferol 3-*O*-*β*-rutinoside (25 mg). Fraction 7 (46.9 g) was subjected to silica gel ($CHCl_3$−MeOH, 9:1) and Sephadex LH-20 (MeOH) chromatography to give prunetin 4′-*O*-*β*-D-glucopyranoside (50 mg), sophororicoside (3050 mg), genistin (42 mg), quercetin 3-*O*-*β*-D-glucopyranoside (28 mg), and kaempferol 3-*O*-*β*-D-glucopyranoside (75 mg).

For acid hydrolysis, a solution of each of compound (**1**−**4**) in 5 mL of 6% HCl was heated for 3 h. Each reaction mixture was extracted with EtOAc. The EtOAc fraction (aglycon) and the aqueous fraction (sugars) were concentrated to dryness for identification.

Genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-*β*-D-glucopyranoside] (1): white amorphous powder; mp 229−231 °C; $[\alpha]^{25}_D$ −73° (*c* 0.001, DMSO); UV (MeOH) λ_{max} 261 nm (log ϵ 4.25); IR ν^{KBr}_{max} 3414, 2970, 2930, 1652, 1613, 1582, 1512, 1495, 1442, 1384, 1367, 1305, 1240, 1182, 1160−1000 cm^{-1}; ^{1}H and ^{13}C NMR (DMSO-d_6), see Table 1; HRFABMS *m*/*z* 739.2088 [M − H]$^-$ (calcd for $C_{33}H_{39}O_{19}$ 739.2085).

Genistein 7-*O*-*β*-D-glucopyranoside-4′-*O*-[(*β*-D-glucopyranosyl)-(1→2)-*β*-D-glucopyranoside] (2): white amorphous powder; mp 241−243 °C; $[\alpha]^{25}_D$ −65° (*c* 0.001, DMSO); UV (MeOH) λ_{max} 260 nm (log ϵ 4.18); IR ν^{KBr}_{max} 3418, 2974, 2930, 1652, 1612, 1580, 1512, 1496, 1443, 1383, 1367, 1302, 1240, 1184, 1160−1000 cm^{-1}; ^{1}H and ^{13}C NMR (DMSO-d_6), see Table 1; HRFABMS *m*/*z* 755.2027 [M − H]$^-$ (calcd for $C_{33}H_{39}O_{20}$ 755.2030).

Genistein 7-*O*-α-L-rhamnopyranoside-4′-*O*-[(α-L-rhamnopyranosyl)-(1→2)-*β*-D-glucopyranoside] (3): white amorphous powder; mp 212−214 °C; $[\alpha]^{25}_D$ −95° (*c* 0.001, DMSO); UV (MeOH) λ_{max} 260 nm (log ϵ 4.22); IR ν^{KBr}_{max} 3410, 2976, 2930, 1652, 1613, 1581, 1512, 1497, 1441, 1385, 1366, 1304, 1245, 1188, 1160−1000 cm^{-1}; ^{1}H and ^{13}C NMR (DMSO-d_6), see Table 1; HRFABMS *m*/*z* 723.2131 [M − H]$^-$ (calcd for $C_{33}H_{39}O_{18}$ 723.2136). $C_{33}H_{40}O_{18}$, was inferred from the HRFABMS ([M − H]$^-$ *m*/*z* 723.2131).

Genistein 7-*O*-α-L-rhamnopyranoside-4′-*O*-[(*β*-D-glucopyranosyl)-(1→2)-*β*-D-glucopyranoside] (4): white amorphous powder; mp 211−213 °C; $[\alpha]^{25}_D$ −85° (*c* 0.001, DMSO); UV spectra λ_{max} 260 nm (log ϵ 4.29); IR ν^{KBr}_{max} 3410, 2975, 2928, 1651, 1613, 1584, 1510, 1497, 1440, 1383, 1366, 1306, 1242, 1181, 1160−1000 cm^{-1}; ^{1}H and ^{13}C NMR (DMSO-d_6), see Table 1; HRFABMS *m*/*z* 739.2083 [M − H]$^-$ (calcd for $C_{33}H_{39}O_{19}$ 739.2085).

Acknowledgment. This work was supported in part by the Chinese National New Drug Foundation (No. 93-67-N-45). The authors are grateful to Mr. Yihua Yu (Department of Analysis, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai, People's Republic of China) for the NMR experiments. The authors also wish to thank Prof. Luoshan Xu (Division of Pharmacognosy, China Pharmaceutical University, Nanjing, People's Republic of China) for the plant identification.

References and Notes

(1) Ishida, H.; Umino, T.; Tsuji, K.; Kosuge, T. *Chem. Pharm. Bull.* **1989**, *37*, 1616−1618.
(2) Watanabe, K.; Kinjo, J.; Nohara, T. *Chem. Pharm. Bull.* **1993**, *41*, 394−396.
(3) Huang, W.-Z.; Duan, J.-A.; Li, Z.-L. *Zhongguo Yaoke Daxue Xuebao* **2000**, *31*, 8−10.
(4) Markham, K. R.; Terlai, B.; Stanley, R.; Geiger, H.; Mabry, T. L. *Tetrahedron* **1978**, *34*, 1389−1397.
(5) Markham, K. R.; Chari, V. M.; Mabry, T. J. In *The Flavonoids: Advances in Research*; Harborne, J. B., Mabry, T. J., Eds.; Chapman & Hall: London, 1982; pp 19−134.
(6) Markham, K. R.; Geiger, H. In *The Flavonoids: Advances in Research since 1986*; Harborne, J. B., Ed.; Chapman & Hall: London, 1994; pp 441−497.
(7) Tang, Y.-P.; Lou, F.-C.; Ma, W.; Wang, J.-H.; Li, Y.-F. *Zhongguo Yaoke Daxue Xuebao* **2001**, *32*, 187−189.

NP010081S