Steroidal Glycosides and Aromatic Compounds from *Smilax riparia*

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Two new steroidal glycosides named riparosides A (1) and B (2), and two aromatic compounds (3, 4), together with four known flavonoid derivatives have been isolated from the EtOH extract of the rhizomes and roots of *Smilax riparia* A. DC. The structure of riparoside A (1) was determined to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl 3β,20α-dihydroxy-5α-furost-22(23)-ene 26-*O*-β-D-glucopyranoside. Riparoside B (2) was characterized as 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl 3β,16β-dihydroxy-5α-pregnan-20-one 16-*O*-[5-*O*-β-D-glucopyranosyl 5-hydroxy-4-methyl-pentanoic acid]-ester 26-*O*-β-D-glucopyranoside. Compounds 3 and 4 were elucidated as a sucrosyl ferulic acid ester and 7-*O*-methyl-10-oxythymol gentiobioside, respectively.

Key words *Smilax riparia*; steroidal glycoside; furostanol; 16-acylpregnane; flavonoid

Smilax riparia A. DC. is distributed in the south and midland of China, and the rhizomes and roots are a source of Chinese crude drug "Niu-Wei-Cai", which has been used for treatment of bronchitis, lumbago of renal asthenia, traumatic injury, asthenia edema, and bronchial dilation agents.[1)] It is a commonly used as traditional Chinese medicine and it has been recorded in an endemic Pharmacopoeia in China. Until now, only one literature of chemical investigation was reported on the rhizomes and roots of this plant, and two neotigogenin glycosides were isolated from the rhizomes and roots of *S. riparia*.[2)] As a part of our ongoing analyses of Chinese medicinal plants, we have surveyed the constituents of the rhizomes and roots of *S. riparia*. Here we report the isolation and characterization of four new constituents, 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl 3β,20α-dihydroxy-5α-furost-22(23)-ene 26-*O*-β-D-glucopyranoside, named riparoside A (**1**), 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl 3β,16β-dihydroxy-5α-pregnan-20-one 16-*O*-[5-*O*-β-D-glucopyranosyl 5-hydroxy-4-methyl-pentanoic acid]-ester 26-*O*-β-D-glucopyranoside, named riparoside B (**2**), sucrosyl ferulic acid ester (**3**), and 3-methoxy-4-isopropylbenzyl alcohol gentiobioside (**4**) together with 4 known flavonoid derivatives, rhamnetin,[3)] luteolin,[4)] quercetin[5)] and luteoloside[6)] by analysis of their ^{1}H- and ^{13}C-NMR spectra and comparison with published data.

The powdered rhizomes and roots of *S. riparia* were extracted with EtOH. After evaporation of EtOH *in vacuo*, the ethanolic extract suspended in water was subjected to Diaion HP-20. The first aqueous eluate was discarded and the next methanolic eluate was recovered. After removed of solvent, the resultant was repeatedly column-chromatographed on silica gel and ODS to obtain eight compounds. Four flavonoid compounds were identified as known compounds; rhamnetin,[3)] luteolin,[4)] quercetin[5)] and luteoloside[6)] by comparison of their physical and spectral data with the reported values and on the basis of the spectroscopic evidence. Other two new steroidal compounds were named as riparoside A (**1**) and riparoside B (**2**), while the remaining two compounds (**3**, **4**) were also new.

Riparoside A (**1**), an amorphous power, $[\alpha]_D$ −52.5° (MeOH), had a molecular formula of $C_{51}H_{84}O_{22}$ determined by high resolution HR-FAB-MS (*m/z* 1071.3802 $[M+Na]^+$) as well as its ^{13}C and distortionless enhancement by polarization transfer (DEPT) NMR data. The ^{1}H-NMR spectrum (in CD_3OD) showed three tertiary methyl signals at δ 0.81 (3H, s), 0.84 (3H, s), and 1.48 (3H, s), one secondary methyl signal at δ 0.94 (3H, d, *J*=6.7 Hz), one olefinic proton signal at δ 4.35 (1H, dd, *J*=7.3, 14.6 Hz), a proton signal at δ 4.84 (1H, m) attached to an ester group, together with four anomeric proton signals at δ 4.23 (1H, d, *J*=7.9 Hz), 4.38 (1H, d, *J*=7.9 Hz), 4.70 (1H, s) and 4.83 (1H, s). The ^{13}C-NMR spectrum (in CD_3OD) displayed total 51 carbon signals, which were composed of 27 signals due to steroidal sapogenol moiety and 24 carbon signals due to a sugar moiety. Sugar signals were assigned to be two terminal α-L-rhamnopyranosyl (rha I, II, C-1-6: δ 101.7, 102.8; 72.4, 70.7; 72.3, 72.5; 73.8, 74.0; 69.8, 70.7; 18.1, 17.8, respectively), 26-*O*-terminal β-D-glucopyranosyl (C-1-6: δ 104.7, 75.3, 75.2, 72.3, 79.8, 62.8), and 2,6-di-*O*-sugar-substituted-β-D-glucopyranosyl (C-1-6 δ 102.6, 79.6, 75.4, 71.7, 76.8, 67.1) moieties. The heteronuclear multiple bonds correlation (HMBC) indicated the bounding sites of two terminal rhamnopyranosyl moieties, one terminal glucopyranosyl moiety and one substituted-glucopyranosyl moiety. That is, the HMBC between rhamnopyranosyl (I) H-1 at δ_H 4.70 and glucopyranosyl (I) C-2 at δ_C 79.6; rhamnopyranosyl (II) H-1 at δ_H 4.83 and glucopyranosyl (I) C-6 at δ_C 67.1; glucopyranosyl (I) H-1 at δ_H 4.38 and sapogenol C-3 at δ_C 77.9; and glucopyranosyl (II) H-1 at δ_H 4.23 and sapogenol C-26 at δ_C 76.1 were observed. Therefore, **1** showed the presence of 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl and 26-*O*-β-D-glucopyranosyl moieties. Moreover, the remaining carbon signals deducted the sugar-originating signals were 27, which were composed of three methyl carbons at δ 12.7, 14.2, 21.5, nine methylene carbon at δ 21.6, 2×29.9, 30.7, 33.2, 34.1, 35.6, 38.2, 40.5, one hydroxymethyl carbon at δ 76.1, two oxygen-bearing

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methine carbons at δ 77.9, 84.9, one oxygen-bearing quaternary carbon at δ 78.2, and two sp^2 carbons at δ 93.2 and 163.0 to form one double bond. The methyl group appeared as singlet at δ 0.84 showed the HMBC to the quaternary carbon at δ 163.0, and the nuclear Overhouse effect spectroscopy (NOESY) between H_3-18 at δ 0.84 and H_3-21 at δ 1.48; H_3-21 at 1.48 and an olefinic proton at δ 4.35 as shown in Fig. 1. Hence, two quaternary carbons at δ 78.2 and 163.0 were decided to be located at C-20 and C-22. Furthermore, the above NOESY exhibited the stereo-configurations of C-20 *S* (β-Me) and (*Z*)-C-22-23 double bond. The signals due to C-1—16, C-18, C-19 were coincident with those of tomatidine. The configuration at C-25 was not stipulated. This aglycone moiety is regarded as the same with that of tuberoside I obtained from the *Allium tuberosum*.[7] Consequently, the structure of riparoside A (**1**) was characterized as 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl 3β,20α-dihydroxy-5α-furost-22(23)-ene 26-*O*-β-D-glucopyranoside.

Table 1. ^{13}C-NMR Spectral Data for the Aglycone Parts of **1** (in CD_3OD) and **2** (in C_5D_5N)

C	**1**	**2**
1	38.2	37.1
2	33.2	30.0
3	77.9	77.8
4	40.5	34.9
5	46.1	44.6
6	29.9	29.0
7	30.7	31.9
8	35.3	34.4
9	55.6	54.4
10	36.8	35.8
11	21.6	20.8
12	35.6	38.3
13	41.7	42.6
14	58.0	53.7
15	34.1	38.3
16	84.9	75.1
17	68.3	66.7
18	12.7	12.2
19	14.2	13.9
20	78.2	205.9
21	21.5	30.5
22	163.0	173.3
23	93.2	32.2
24	29.9	28.8
25	35.9	33.4
26	76.1	74.7
27	17.5	16.8

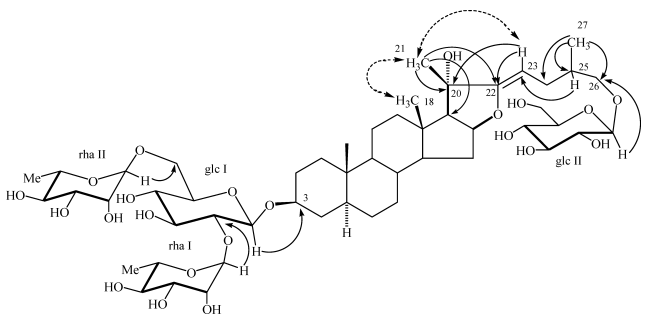

Fig. 1. Significant HMBC (⟶) and NOESY (⇢) Correlations of **1**

Riparoside B (**2**), an amorphous powder $[\alpha]_D$ −42.6° (MeOH), had a molecular formula of $C_{51}H_{84}O_{23}$ determined by HR-FAB-MS (*m/z* 1087.3909 $[M+Na]^+$). Its IR spectrum revealed the presence of hydroxyl groups (3409 cm^{-1}) and carbonyl groups (1710, 1660, 1652 cm^{-1}). The ^{1}H-NMR spectrum (in C_5D_5N) showed three tertiary methyl signals at δ 0.68 (3H, s), 1.17 (3H, s) and 2.02 (3H, s), and one secondary methyl signal at δ 0.92 (3H, d, *J*=6.6 Hz), together with four anomatic proton signals at δ 4.76 (1H, d, *J*=7.9 Hz), δ 4.89 (1H, d, *J*=7.9 Hz), 5.36 (1H, s) and 5.60 (1H, s). In the ^{13}C-NMR spectrum (in C_5D_5N), signals due to sugar moiety were shown to be superimposable on there of riparoside A (**1**) and the rest signals were composed of four methyls at δ 12.2, 13.9, 16.8 and 30.5, nine methylene carbons at δ 20.8, 28.8, 29.0, 30.0, 31.9, 34.9, 37.1, 2×38.3, six methine carbons at δ 33.4, 34.4, 44.6, 53.7, 54.4, 66.7, two quaternary carbons at δ 35.8 and 42.6, one hydroxymethyl cabon at δ 74.7, two oxygen-bearing carbons at δ 75.1, 77.8, and two carbonyl carbons at δ 173.3, 205.9. The HMBC from H_3-18 (δ_H 0.68) enabled the assignment of C-17 (δ_C 66.7), which simultaneously revealed the signal due to H-17 (δ_H 2.49, 1H, d, *J*=7.9 Hz) in the heteronuclear multiple quantum coherence (HMQC). Moreover, the assignment by the HMQC and HMBC disclosed the presence of the signals of H-16 (δ 5.70), C-16 (δ 75.1), H_3-21 (δ 2.02), C-21 (δ 30.5), C-16 ester carbonyl (δ 205.9) as showed in Fig. 2. This aglycone part is regarded to be a new structure of 5α-3β,26-dihydroxy-16,22-dioxo-cholestane. Therefore, the stracture of riparoside B (**2**) was represented as 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl 3β,16β-dihydroxy-5α-pregnan-20-one 16-*O*-[5-*O*-β-D-glucopyranosyl 5-hydroxy-4-methyl-pentanoic acid]-ester 26-*O*-β-D-glucopyranoside.

Compound **3**, an amorphous powder, had a molecular formula $C_{42}H_{46}O_{20}$ determined by HR-FAB-MS (*m/z* 893.1412 $[M+Na]^+$). The ^{1}H-NMR spectrum (in CD_3OD) showed signals due to three methoxyl groups at δ 3.81 (3H, s), 3.84 (3H, s), 3.84 (3H, s), sugar-originating protons at δ 3.3—5.6, and complicated olefic and aromatic protons at δ 6.3—7.8. The occurrence of total twelve signals at δ 103.6 (s), 93.6 (d), 81.1 (d), 79.3 (d), 75.0 (d), 74.4 (d), 74.2 (d), 73.1 (d), 71.7 (d), 66.2 (t), 65.9 (t), 62.8 (t) due to sugar moiety indicated **3** to be a sucrose derivative. Moreover, three signals at δ 168.3, 168.5, 169.1 were assigned to ester carbonyl group. 2D-NMR spectrum of chemical shift correlation spectrum (COSY), HMQC and HMBC revealed the presence of three ferulic acid ester moieties, that is, three ABX systems on the aromatic rings at δ 6.75 (1H, d, *J*=8.5 Hz), 6.80 (1H, d, *J*=7.9 Hz), 6.81 (1H, d, *J*=8.0 Hz), 7.01 (1H, br d, *J*=7.9 Hz), 7.08 (1H, br d, *J*=8.0 Hz), 7.10 (1H, br d, *J*=8.5 Hz), 7.10 (1H, br s), 7.16 (2H, br s), six olefinic protons at δ 6.36 (1H, d, *J*=15.9 Hz), 6.40 (1H, d, *J*=15.9 Hz), 6.44 (1H, d, *J*=15.9 Hz), 7.64 (2H, d, *J*=15.9 Hz) and 7.70 (1H, d, *J*=15.9 Hz) attached to the *E*-double bond moiety. Signals due to the sugar part were also assigned as follows: δ 5.61 (1H, d, *J*=7.9 Hz, fructose H-3), 5.52 (1H, d, *J*=3.6 Hz, glc H-1), 4.56 (1H, m, fructose H-4), 4.37, 4.54 (each 1H, m, fructose H-6), the latter three fructosyl proton signals were lower-shifted, so that it was estimated that the ester group was attached to the hydroxyl groups at the C-3, C-4 and C-6 of the fructosyl moiety. Furthermore, HMBC between three

Table 2. ^{1}H- and ^{13}C-NMR Spectral Data for the Sugar Moieties of **1** (in CD_3OD) and **2** (in C_5D_5N)

		1		**2**	
		δ_C	δ_H	δ_C	δ_H
26-*O*-Glucose					
	1	104.7	4.23 (d, *J*=7.9 Hz)	104.9	4.76 (d, *J*=7.9 Hz)
	2	75.3	3.18 m	75.2	3.87 m
	3	75.2	3.17 m	76.6	4.18 m
	4	72.3	3.63 m	75.1	4.17 m
	5	79.8	3.50 m	78.3	3.84 m
	6	62.8	3.65 m 3.84 m	62.8	4.31 m 4.50 m
3-*O*-Glucose					
	1	102.6	4.38 (d, *J*=7.9 Hz)	102.2	4.89 (d, *J*=7.9 Hz)
	2	79.6	3.65 m	79.5	4.08 m
	3	75.4	3.19 m	75.1	4.09 m
	4	71.7	3.82 m	75.3	3.86 m
	5	76.8	3.42 m	78.4	4.18 m
	6	67.1	3.61 m 3.86 m	67.2	3.94 m 4.31 m
Rhamnose I					
	1	101.7	4.70 s	102.0	5.36 s
	2	72.4	3.62 m	71.7	4.19 m
	3	72.3	3.63 m	72.6	4.55 m
	4	73.8	4.31 m	73.9	4.29 m
	5	69.8	3.71 m	69.7	4.27 m
	6	18.1	1.25 (d, *J*=6.1 Hz)	18.6	1.67 (d, *J*=6.1 Hz)
Rhamnose II					
	1	102.8	4.83 s	102.7	5.60 s
	2	70.7	3.69 m	70.5	4.51 m
	3	72.5	3.62 m	72.2	4.55 m
	4	74.0	3.19 m	73.7	4.23 m
	5	70.7	3.80 m	66.6	4.83 m
	6	17.8	1.26 (d, *J*=6.1 Hz)	18.4	1.63 (d, *J*=6.1 Hz)

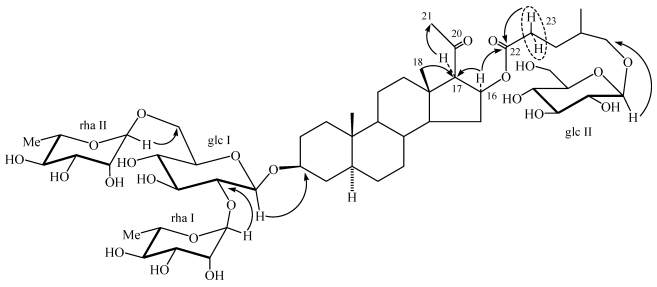

Fig. 2. Significant HMBC (⟶) Correlations of **2**

ester carbonyl groups and the H-3, H-4, H-6 of fructosyl moiety. Consequently, the structure of **3** was determined as 3′,4′,6′-*O*-tri-ferulic acid ester of sucrose.

Compound **4**, an amorphous powder, $[\alpha]_D$ −37.4° (MeOH), was a molecular formula as $C_{23}H_{36}O_{12}$ on the bases of HR FAB-MS (*m*/*z* 526.9759 $[M+Na]^+$) The ^{1}H-NMR spectrum (in CD_3OD) showed signals due to two secondary methyls at δ 1.17 (6H, d, *J*=6.7 Hz), one methoxyl at δ 3.83, three hydroxymethyls at δ 3.67 (1H, dd, *J*=5.1, 11.9 Hz), 3.86 (1H, dd, *J*=1.8, 11.9 Hz), 3.82 (1H, dd, *J*=5.5, 11.6 Hz), 4.17 (1H, dd, *J*=1.8, 11.6 Hz) and 4.62 (1H, d, *J*=11.9 Hz), 4.65 (1H, d, *J*=11.9 Hz), two hexosyl anomeric protons at δ 4.35 (1H, d, *J*=7.9 Hz), 4.42 (1H, d, *J*=7.9 Hz), and a ABX system aromatic protons at δ 6.92 (1H, br d, *J*=7.9 Hz), 7.12 (1H, d, *J*=7.9 Hz), and 7.04 (1H, br s). The ^{13}C-NMR (in CD_3OD) spectrum indicated the presence of β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl moiety, gentiobioside, that is terminal glucosyl C-1—6: δ 104.9, 75.1, 78.1, 71.7, 78.0. 62.8, inner glucosyl C-1—6: δ 103.2, 75.1, 78.1, 71.6, 77.2, 69.9. The remaining signals comprised of

Table 3. ^{1}H- and ^{13}C-NMR Spectral Data for **3** (in CD_3OD)

		δ_C	δ_H
Sugar moiety			
Glucose	1	93.6	5.52 (1H, d, *J*=3.6 Hz)
	2	74.4	4.02 (1H, m)
	3	73.1	3.45 (1H, dd, *J*=9.8, 8.0 Hz)
	4	75.0	3.68 (1H, dd, *J*=9.8, 8.2 Hz)
	5	71.7	3.41 (1H, m)
	6	62.8	3.84 (1H, m), 3.89 (1H, m)
Fructose	1	66.2	4.54 (1H, m)
	2	103.6	
	3	79.3	5.61 (1H, d, *J*=7.9 Hz)
	4	74.2	4.56 (1H, m)
	5	81.1	4.21 (1H, m)
	6	65.9	4.54 (1H, m), 4.37 (1H, m)
Ferulic acid moiety			
	α	168.5	
	β	114.7	6.44 (1H, d, *J*=15.9 Hz)
	γ	148.1	7.70 (1H, d, *J*=15.9 Hz)
	1	126.8	
	2	111.8	7.10 (1H, br s)
	3	149.3	
	4	150.6	
	5	116.5	6.80 (1H, d, *J*=7.9 Hz)
	6	124.3	7.01 (1H, br d, *J*=7.9 Hz)
	OMe	56.6	3.81 (3H, s)
	α'	169.1	
	β'	115.2	6.40 (1H, d, *J*=15.9 Hz)
	γ'	147.2	7.64 (1H, d, *J*=15.9 Hz)
	1′	127.6	
	2′	111.8	7.16 (1H, br s)
	3′	149.3	
	4′	150.6	
	5′	116.5	6.75 (1H, d, *J*=8.5 Hz)
	6′	124.3	7.10 (1H, br d, *J*=8.5 Hz)
	OMe′	56.4	3.84 (3H, s)
	α''	168.3	
	β''	115.0	6.36 (1H, d, *J*=15.9 Hz)
	γ''	147.4	7.64 (1H, d, *J*=15.9 Hz)
	1″	127.7	
	2″	112.2	7.16 (1H, br s)
	3″	149.3	
	4″	150.7	
	5″	116.5	6.81 (1H, d, *J*=8.0 Hz)
	6″	124.3	7.08 (1H, br d, *J*=8.0 Hz)
	OMe″	56.6	3.84 (3H, s)

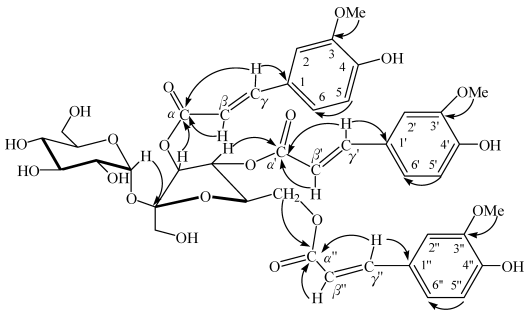

Fig. 3. Significant HMBC (⟶) Correlations of **3**

Table 4. ^{1}H- and ^{13}C-NMR Spectral Data for **4** (in CD_3OD)

	δ_C	δ_H
1	23.1	1.17 (3H, d, J=6.7 Hz)
2	23.1	1.17 (3H, d, J=6.7 Hz)
3	27.9	3.28 (1H, m)
4	137.5	
5	126.7	7.12 (1H, d, J=7.9 Hz)
6	121.4	6.92 (1H, br d, J=7.9 Hz)
7	71.9	4.62 (1H, d, J=11.9 Hz)
		4.65 (1H, d, J=11.9 Hz)
8	137.5	
9	111.7	7.04 (1H, br s)
10	158.3	
–OMe	56.0	3.83 (3H, s)
Glucose I		
1	103.2	4.35 (1H, d, J=7.9 Hz)
2	75.1	3.62 (1H, m)
3	78.1	3.34 (1H, m)
4	71.6	4.64 (1H, m)
5	77.2	3.45 (1H, m)
6	69.9	3.82 (1H, dd, J=5.5, 11.6 Hz)
		4.17 (1H, dd, J=1.8, 11.6 Hz)
Glucose II		
1	104.9	4.42 (1H, d, J=7.9 Hz)
2	75.1	3.28 (1H, m)
3	78.1	3.27 (1H, m)
4	71.7	4.87 (1H, m)
5	78.0	3.38 (1H, m)
6	62.8	3.67 (1H, dd, J=5.1, 11.9 Hz)
		3.86 (1H, dd, J=1.8, 11.9 Hz)

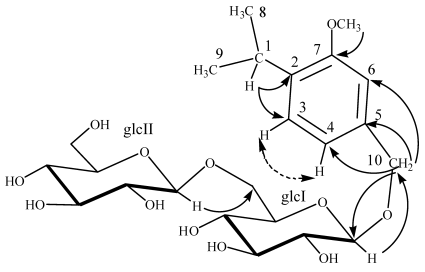

Fig. 4. Significant HMBC (⟶) and COSY (⇢) Correlations of **4**

six aromatic carbons at δ 111.7, 121.4, 126.7, 2×137.5, 158.3, one hydroxyl methyl carbon (δ 71.9), two methyl carbons (2×δ 23.1), and one methine carbon (δ 27.9). The HMBC (Fig. 4) between the hydroxylmethyl protons at δ 4.62, 4.65 and aromatic carbons at δ 111.7, 121.4, 137.5; the anomeric carbon (δ 103.2) of the inner glucosyl moiety. Methoxyl group correlated to the aromatic carbon at δ 158.3 and the methine proton at δ 3.28 correlated to the aromatic carbons at δ 126.7 and 137.5. Therefore, the structure of **4** was determined as 7-*O*-methyl-10-oxy-thymol gentiobioside.

Experimental

General Procedures Optical rotations were determined on a JASCO DIP-1000 polarimeter. FAB-MS and HR-FAB-MS were obtained using a JEOL JMS-DX300 and JMS-DX303HF spectrometer, respectively. NMR spectra were measured in CD_3OD and C_5D_5N on a JEOL α-500 spectrometer (500 MHz) and chemical shifts were referenced to TMS. Column chromatography was carried out on silica gel 60 (230—400 mesh, Merck) and Chromatorex ODS (30—50 μm, Fuji Silysia Chemical Ltd.). TLC was performed on precoated silica gel 60 F_{254} (0.2 mm, Merck).

Plant Material The rhizomes and roots of *S. riparia* A. DC. were collected at Chibi, midland of Hubei province, China, in June 2004. The plants were identified by botanist Ya-Hua Zhan and Prof. Ke-Li Chen (Department of Pharmaceutical Sciences, Hubei College of Traditional Chinese Medicine). A voucher specimen (SR 62004) was deposited in the Herbarium of the Department of Medical and Pharmaceutical Sciences, Kumamoto University, Kumamoto, Japan.

Extraction and Isolation The dry rhizomes and roots of *S. riparia* (4 kg) were extracted with 95% EtOH three times under reflux. After evaporation of MeOH *in vacuo*, the residue (250 g) was suspended in water to be subjected to Diaion HP-20 using a MeOH/H_2O in a gradient system (0—100%). The fraction eluted (36 g) with 60% MeOH was subjected to Sephadex LH-20 column chromatography with MeOH. The fraction eluted with MeOH was subjected to silica gel column chromatography with a $CHCl_3$/MeOH/H_2O solvent system (9 : 1 : 0.5—7 : 3 : 0.5). Finally, the fractions eluted by $CHCl_3$/MeOH/H_2O (9 : 1 : 0.5—7 : 3 : 0.5) were subjected to RP-18 column chromatography to give compounds **1** (12 mg), **2** (35 mg), **3** (8 mg), **4** (10 mg), **5** rhamnetin (7 mg), **6** luteolin (5 mg), **7** quercetin (13 mg), and **8** luteoloside (9 mg).

Compound **1**: An amorphous solid, $[\alpha]_D^{25}$ −52.5° (c=0.5, MeOH), HR-FAB-MS (m/z 1071.3802 $[M+Na]^+$, Calcd 1071.3800 for $C_{51}H_{84}O_{22}Na$), ^{1}H-NMR (CD_3OD) δ: 0.81 (3H, s), 0.84 (3H, s), 0.94 (3H, d, J=6.7 Hz), 1.48 (3H, s), 1.90 (1H, d, J=6.8 Hz, H-17), 3.25 (1H, m, H-3), 3.26 (1H, dd, J=7.3, 9.2 Hz, H_a-26), 3.80 (1H, m, H_b-26), 4.23 (1H, d, J=7.9 Hz), 4.35 (1H, dd, J=7.3, 14.6 Hz), 4.38 (1H, d, J=7.9 Hz), 4.70 (1H, s), 4.83 (1H, s) and 4.84 (1H, m, H-16). ^{13}C-NMR (CD_3OD): see Tables 1 and 2.

Compound **2**: An amorphous solid, $[\alpha]_D^{25}$ −42.6° (c=0.3, MeOH), HR-FAB-MS (m/z 1087.3909 $[M+Na]^+$, Calcd 1087.3900 for $C_{51}H_{84}O_{23}Na$), IR (KBr): 3409 (OH), 2933 (CH), 1710 (C=O), 1660, 1652 (C=O), 1452, 1386, 1257, 1232, 1066, 1039, 981, 914, 836, 809, 622 cm^{-1}. ^{1}H-NMR (C_5D_5N) δ: 0.68 (3H, s), 0.92 (3H, d, J=6.6 Hz), 1.17 (3H, s), 2.02 (3H, s), 2.49 (1H, d, J=7.9 Hz, H-17), 3.43 (1H, dd, J=6.7, 9.8 Hz, H_a-26), 3.92 (1H, m, H_b-26), 4.08 (1H, m, H-16), 4.16 (1H, m, H-3), 4.76 (1H, d, J=7.9 Hz), 4.90 (1H, d, J=7.9 Hz), 5.36 (1H, s), 5.60 (1H, s). ^{13}C-NMR (C_5D_5N): see Tables 1 and 2.

Compound **3**: An amorphous solid $[\alpha]_D^{25}$ +57.0° (c=0.5, MeOH), HR-FAB-MS (m/z 892.8107 $[M+Na]^+$, Calcd 892.8100 for $C_{42}H_{46}O_{20}Na$), ^{1}H-NMR (CD_3OD) and ^{13}C-NMR (CD_3OD): see Table 3.

Compound **4**: An amorphous solid, $[\alpha]_D^{25}$ −37.4° (c=0.4 MeOH), HR-FAB-MS (m/z 526.9759 $[M+Na]^+$, Calcd 526.9759 for $C_{23}H_{36}O_{12}Na$), ^{1}H-NMR (CD_3OD) and ^{13}C-NMR (CD_3OD): see Table 4.

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