Sucrose Esters and Xanthone *C*-Glycosides from the Roots of *Polygala sibirica*

Toshio Miyase,*,† Hiroshi Noguchi,† and Xin-Min Chen‡

School of Pharmaceutical Sciences, University of Shizuoka, 52-1, Yada, Shizuoka 422-8526 Japan, and Division of Phytochemistry, Chengdu Institute of Biology, Academia Sinica, 4-9, Ren Ming Nan Lu, Chengdu, Sichuan, People's Republic of China

Received March 3, 1999

Six new sucrose esters, sibiricoses A_1−A_6 (**1**−**6**), two new xanthone *C*-glycosides, sibiricaxanthones A (**7**) and B (**8**), and a new acetophenone glycoside, sibiricaphenone (**9**), were isolated from the roots of *Polygala sibirica* together with six known glycosides. The structures of new compounds were elucidated on the basis of chemical and spectroscopic evidence. The structure of the known xanthone glycoside, polygalaxanthone III (**10**), was revised.

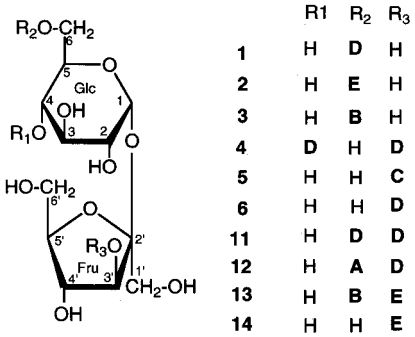
In the course of a research program on the oligosaccharide esters from *Polygala* species,[1] we investigated *P. sibirica* L. (Polygalaceae). *P. sibirica* is widely distributed in China, and its root is used as a traditional medicine like Yuan zhi (root of *P. tenuifolia* Willd.) to tranquilize, act as a tonic, and prevent a failure of memory.[2] No previous investigation has been reported on this plant. We now report the isolation and structural elucidation of six new sucrose esters, sibiricoses A_1−A_6 (**1**−**6**), two new xanthone *C*-glycosides, sibiricaxanthones A (**7**) and B (**8**), a new acetophenone glycoside, sibiricaphenone (**9**). We also report the structure revision of polygalaxanthone III (**10**).[3] Six known compounds isolated from this plant were identified by comparison of the spectral data with reported data as 3′,6-disinapoyl sucrose (**11**),[4] 3′-sinapoyl-6-benzoyl sucrose (**12**),[4] tenuifoliside A (**13**),[4] glomeratose A (**14**),[1] and polygalaxanthone III (**10**)[3] and lancerin (**15**).[5]

Results and Discussion

The air-dried roots of *P. sibirica* were extracted with MeOH under reflux. The MeOH extract was suspended in H_2O and adsorbed on a porous polymer gel (Diaion HP-20) column. The material was eluted with 50% aq. MeOH, 70% aq. MeOH, and MeOH, successively. The 50% MeOH eluate was chromatographed on a silica gel column using $CHCl_3$−MeOH−H_2O and selected fractions were then subjected to preparative HPLC, using a reversed-phase (ODS), which led to the isolation of 10 sucrose esters (**1**−**6**, **11**−**14**), four xanthone *C*-glycosides (**7**, **8**, **10**, **15**) and an acetophenone glycoside (**9**) (Chart 1).

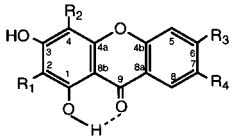
Sibiricose A_1 (**1**) was isolated as an amorphous powder. The UV spectrum showed absorption maxima suggesting the presence of an oxycinnamate residue.[1] The positive mode FABMS revealed quasi-molecular ion peaks at *m/z* 571 $[M + Na]^+$ and *m/z* 549 $[M + H]^+$, consistent with a molecular formula of $C_{23}H_{32}O_{15}$. The ^{1}H NMR spectrum displayed signals for a methoxyl group, an α-D-glucosidic anomeric proton, two *trans* olefinic protons, and two equivalent aromatic protons. Alkaline hydrolysis afforded sinapic acid and sucrose. When the ^{1}H NMR spectrum was compared with that of glomeratose A (**14**), the methylene proton signals of the glucosyl moiety were shifted downfield to δ 4.27 and 4.52. In the ^{13}C NMR spectrum, C-6 of the glucosyl residue was also shifted downfield by 1.8 ppm in

Chart 1

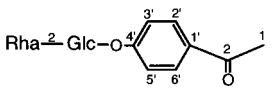


	R1	R2	R3
1	H	D	H
2	H	E	H
3	H	B	H
4	D	H	D
5	H	H	C
6	H	H	D
11	H	D	D
12	H	A	D
13	H	B	E
14	H	H	E

A: benzoyl
B: *p*-hydroxybenzoyl
C: feruloyl
D: sinapoyl
E: 3,4,5-trimethoxycinnamoyl



	R_1	R_2	R_3	R_4
7	-Glc-(6)-Api	H	H	OH
8	-Glc-(2)-Api	H	H	OH
10	-Glc-(6)-Api	H	OH	OMe
15	H	-Glc	H	OH



9

1. These data led us to conclude that sibiricose A_1 (**1**) was 6-*O*-sinapoyl sucrose.

The FABMS of sibiricose A_2 (**2**) gave a quasi-molecular ion peak at *m/z* 585 $[M + Na]^+$, 14 mass units higher than that of **1**, and ^{13}C NMR data were consistent with a molecular formula of $C_{24}H_{34}O_{15}$. The ^{1}H NMR spectrum was very similar to that of **1** except for the presence of a methoxyl signal at δ 3.79 (3H, s). Alkaline hydrolysis afforded 3,4,5-trimethoxycinnamic acid and sucrose. The

* To whom correspondence should be addressed: Tel.: +81 054-264-5661. E-mail: miyase@ys7.u-shizuoka-ken.ac.jp.
† University of Shizuoka.
‡ Academia Sinica.

10.1021/np990084t CCC: $18.00
Published on Web 07/02/1999

methylene proton signals of the glucosyl moiety were again shifted downfield. Therefore, **2** was defined to be 6-*O*-3,4,5-trimethoxycinnamoyl sucrose.

The UV spectrum of sibiricose A_3 (**3**) showed an absorption maximum at 258 (4.03) nm (log ϵ). The ^{1}H NMR spectrum showed signals for A_2B_2-type aromatic protons and the downfield shifted methylene protons of the glucosyl moiety. Alkaline hydrolysis gave *p*-hydroxybenzoic acid and sucrose. Thus, **3** was determined to be 6-*O*-*p*-hydroxybenzoyl sucrose.

Sibiricose A_4 (**4**) was obtained as an amorphous power. The FABMS of **4** showed quasi-molecular ion peaks at *m*/*z* 777 $[M + Na]^+$ and 755 $[M + H]^+$. Alkaline hydrolysis afforded sinapic acid and sucrose. Full assignments of the proton and carbon signals were secured by a HOHAHA difference spectrum on irradiating at the glucosyl anomeric proton signal, ^{1}H−^{1}H COSY, HMQC, and HMBC experiments. In the HMBC spectrum, H-4 of the glucosyl residue and H-3 of the fructosyl residue were correlated to an ester carbonyl carbon at δ 168.5 and 167.9, respectively. Thus **4** was deduced to be 3′,4-*O*-disinapoyl sucrose.

The ^{1}H NMR spectra of sibiricoses A_5 (**5**) and A_6 (**6**) showed downfield-shifted oxymethine protons due to H-3 of the fructosyl moiety at δ 5.45 and 5.46, respectively. Alkaline hydrolysis afforded ferulic acid and sinapic acid, respectively. Therefore **5** was deduced to be 3′-feruloyl sucrose and **6** to be 3′-sinapoyl sucrose.

Sibiricaxanthone A (**7**) showed absorption maxima in the UV spectrum suggesting that **7** had a hydroxyxanthone skeleton.[3] The FABMS of **7** exhibited a quasi-molecular ion peak at *m*/*z* 539 $[M + H]^+$ and in conjunction with the analysis of the ^{13}C NMR spectrum, its molecular formula was deduced to be $C_{24}H_{26}O_{14}$. On mild acid hydrolysis, **7** afforded D-apiose as a sugar residue. The ^{1}H NMR spectrum of **7** displayed two anomeric proton signals, an isolated aromatic proton signal, ABC-type aromatic proton signals and a hydrogen bonded hydroxyl proton signal in DMSO. All proton and carbon signals were assigned by ^{1}H−^{1}H COSY, HMQC, and HMBC spectra. The anomeric proton signal of the apiosyl residue was correlated to C-6 of the glucosyl residue, and the anomeric proton signal of the glucosyl residue was correlated to the carbon signals at δ 107.6, 161.9, and 164.7 in the HMBC spectrum. The signals at δ 107.6 and 161.9 were also correlated to the hydrogen bonded hydroxyl proton at δ 13.50 corresponding to C-2 and C-1 in the aglycone moiety, respectively. The anomeric configuration of the D-apiosyl residue was deduced to be β by comparison of the ^{13}C NMR data of the apiosyl residue,[6] and that of the D-glucosyl residue to be β from the $^3J_{H1-H2}$ of the anomeric proton signal. Thus, **7** was shown to be 2-*C*-[β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl]-1,3,7-trihydroxyxanthone.

The FABMS of sibiricaxanthone B (**8**) showed a quasi-molecular ion peak at *m*/*z* 539 $[M + H]^+$ and the UV and ^{1}H NMR spectra were also similar to those of **7**. The anomeric proton signal of the apiosyl residue was shifted downfield by 0.40 ppm compared to that of **7**. Mild acid hydrolysis afforded D-apiose. In the HMBC spectrum, the apiosyl anomeric proton signal correlated to the carbon signal at δ 79.3 which was assigned to C-2 of the glucosyl moiety. ^{1}H−^{13}C long-range correlations were observed as shown in the Experimental Section, and **8** was identified as 2-*C*-[β-D-apiofuranosyl-(1→2)-β-D-glucopyranosyl]-1,3,7-trihydroxyxanthone.

^{1}H and ^{13}C NMR spectra of compound **10**, in pyridine-d_5, were identical to those of polygalaxanthone III which was isolated from *P. tenuifolia* by Ikeya et al.[3] Polygalaxanthone III was reported to be 4-*C*-[β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl]-1,3,6-trihydroxy-7-methoxyxanthone by chemical and spectroscopic evidence. Our NMR studies in DMSO allowed us to revise the glycosidic position to be C-2 of the aglycone from the following evidences. The anomeric proton signal of the glucosyl residue correlated to C-1 (δ 161.7), C-2 (δ 107.6), and C-3 (δ 163.8), and the hydrogen-bonded hydroxyl proton signal at δ 13.75 (s) correlated to C-8b (δ 101.3), C-1 (δ 161.7), and C-2 (δ 107.6) in the HMBC spectrum.

The FABMS of sibiricaphenone (**9**) showed quasi-molecular ion peaks at *m*/*z* 467 $[M + Na]^+$ and 445 $[M + H]^+$, consistent with molecular formula $C_{20}H_{28}O_{11}$. The ^{1}H NMR spectrum revealed an acetyl methyl, two anomeric protons, and A_2B_2-type aromatic protons. Acid hydrolysis afforded L-rhamnose and D-glucose and acetophenone as an aglycone. All proton signals were assigned with the aid of ^{1}H−^{1}H COSY, HMQC, and HMBC spectra. The rhamnosyl anomeric proton at δ 5.28 was correlated to C-2 of the glucosyl moiety (δ 79.1) and the glucosyl anomeric proton at δ 5.14 to C-4′ (δ 162.7). Thus, sibiricaphenone (**9**) was established to be 4′-*O*-[α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl] acetophenone. The anomeric configuration of the rhamnosyl residue was determined to be α from the ^{13}C NMR chemical shifts of C-3 and C-5.[7]

Sucrose esters (**4**, **6**, **7**) and xanthone *C*-glycosides (**10**) isolated from the roots of *P. sibirica* were also isolated from the roots of *P. tenuifolia*.[3,4]

Experimental Section

General Experimental Procedures. The following instruments were used in this work: JASCO DIP-1000 digital polarimeter for optical rotation; JEOL α-400 FT-NMR spectrometer for NMR spectra (^{1}H, 400 MHz, ^{13}C, 100 MHz), inverse-detected heteronuclear correlations were measured using HMQC (optimized for $^1J_{C-H}$ = 145 Hz) and HMBC (optimized for $^nJ_{C-H}$ = 8 Hz) pulse sequences with a pulse-field gradient; JEOL JMS−SX102 spectrometer for positive mode FABMS (matrix *m*-nitrobenzyl alcohol); Hitachi G-3000 gas chromatograph for GC; Hitachi U-3410 spectrometer for UV; JASCO System 800 for HPLC.

Plant Material. *P. sibirica* L. was collected in May 1996, Sichuan, China. The plant was identified by Prof. Zhaoguang Liu, Chengdu Institute of Biology, Academia Sinica, China, and the voucher specimen (No. 960530) was deposited in the Herbarium, School of Pharmaceutical Sciences, University of Shizuoka.

Extraction and Isolation. The dried and powdered roots of *P. sibirica* (660 g) were extracted thrice with MeOH under reflux. After evaporation of the solvent under reduced pressure, the MeOH extract was suspended in H_2O and subjected to porous polymer gel Mitsubishi Diaion HP-20 column (9 × 41 cm). The adsorbed material was eluted with 50% aq. MeOH, 70% aq. MeOH, and MeOH successively, after washing with H_2O. The 50% MeOH aq. eluate (13.1 g) was chromatographed on a silica gel (200 g) column using $CHCl_3$−MeOH−H_2O (74:23:3) as an eluent to afford fractions A−M. Fraction E (152 mg) was chromatographed on an ODS column (2 × 25 cm) and eluted with CH_3CN−H_2O (15:85) to afford **4** (3 mg), **11** (24 mg), **12** (1 mg), and **13** (1 mg). In the same manner, fraction F (382 mg) afforded **11** (42 mg) and **14** (60 mg). Fraction I (1.87 g) was subjected to preparative HPLC [ODS 5 × 100 cm; CH_3CN−H_2O (10:90) → (18:82)] to afford **1** (46 mg), **2** (1 mg), **5** (23 mg), **6** (68 mg), **7** (79 mg), **9** (8 mg), **10** (378 mg), and **15** (19 mg). Fraction J (1.05 g) was subjected to preparative HPLC [ODS 5 × 100 cm; CH_3CN−H_2O (10:90)] to afford **3** (10 mg), **5** (6 mg), **6** (6 mg), **7** (76 mg), **8** (112 mg), and **10** (524 mg).

Sibiricose A_1 (1): amorphous powder, $[\alpha]^{23}_D$ +18° (*c* 4.36, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 224.5 (sh) (4.10), 239.5 (4.13), 328 (4.18); FABMS *m*/*z*: 571 $[M + Na]^+$, 549 $[M + H]^+$; ^{1}H and ^{13}C NMR: Tables 1 and 2.

Table 1. ^{1}H NMR Data of Sibiricoses A_1−A_6 (**1**−**6**) in CD_3OD at 35 °C

	1	**2**	**3**	**4**[b]	**5**	**6**
sugar moiety						
Glc-1	5.43 d (4)	5.42 d (4)	5.42 d (3.5)	5.54 d (4)	5.43 d (4)	5.44 d (4)
2	3.48 dd (10, 4)	3.46 dd (10, 4)	3.46 dd (9.5, 3.5)	3.57 dd (10, 4)	3.43 dd (10, 4)	3.43 dd (10, 4)
3	3.75 dd (10, 9.5)	3.73 dd (10, 9)	3.76[a]	3.95 dd (10, 9.5)	3.67 dd (10, 9)	3.67 dd (10, 9.5)
4	3.34 dd (9.5, 9)	3.32[a]	3.45 dd (9.5, 9.5)	4.91 dd (10, 9.5)	3.40 dd (9, 9)	3.40 dd (9.5, 9)
5	4.13 m	4.13 m	4.14 m	4.20 m	3.93 m	3.93 m
6	4.27 dd (12.5, 6)	4.27 dd (12, 6)	4.44 dd (12, 4.5)	3.61[a]	3.77 dd (12, 4.5)	3.77 dd (12, 4.5)
	4.52 dd (12.5, 2.5)	4.52 dd (12, 2)	4.55 dd (12, 3)	3.71 dd (12, 3)	3.82[a]	3.86[a]
Fru-1	3.62 d (12.5)	3.60 d (12)	3.61 d (12)	3.64 d (12)	3.60 d (12)	3.59 d (12)
	3.64 d (12.5)	3.63 d (12)	3.64 d (12)	3.70 d (12)	3.67 d (12)	3.66 d (12)
3	4.08 d (8)	4.09 d (8)	4.10 d (8)	5.46 d (7.5)	5.45 d (8)	5.46 d (8)
4	4.07 dd (8, 8)	4.06 dd (8, 8)	4.01 dd (8, 8)	4.39 dd (8, 7.5)	4.38 dd (8, 7.5)	4.38 dd (8, 8)
5	3.84[a]	3.84[a]	3.67 m	3.93 m	3.94 m	3.94 m
6	3.78[a]	3.77[a]	3.74[a]	3.85[a]	3.83[a]	3.81[a]
	3.81[a]	3.84[a]	3.76[a]	3.85[a]	3.83[a]	3.83[a]
acid moiety				(at C-4 of Glc)		
β	6.45 d (16)	6.54 d (16)		6.21 d (16)	6.42 d (16)	6.44 d (16)
γ	7.62 d (16)	7.65 d (16)		7.54 d (16)	7.71 d (16)	7.71 d (16)
2	6.93 s	6.96 s	7.90 d (9)	6.72 s	7.22 d (2)	6.96 s
3			6.83 d (9)			
5			6.83 d (9)		6.82 d (8)	
6	6.93 s	6.96 s	7.90 d (9)	6.72 s	7.13 dd (8, 2)	6.96 s
OMe	3.87 s	3.79 s		3.82 s	3.90 s	3.89 s
		3.87 s				
β				(at C-3 of Fru)		
γ				6.56 d (16)		
2, 6				7.78 d (16)		
OMe				6.92 s		
				3.79 s		

[a] Overlapped. [b] Assigned with the aid of HMQC and HMBC spectra.

Sibiricose A_2 (2): amorphous powder, $[\alpha]^{23}_D$ +19° (*c* 0.56, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 230 (4.22), 308.5 (4.14); FABMS *m/z*: 585 $[M + Na]^+$; ^{1}H and ^{13}C NMR: Tables 1 and 2.

Sibiricose A_3 (3): amorphous powder, $[\alpha]^{23}_D$ +29° (*c* 1.30, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 258 (4.03); FABMS *m/z*: 485 $[M + Na]^+$; ^{1}H and ^{13}C NMR: Tables 1 and 2.

Sibiricose A_4 (4): amorphous powder, $[\alpha]^{23}_D$ −23° (*c* 1.13, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 234 (4.48), 316 (4.47); FABMS *m/z*: 777 $[M + Na]^+$, 755 $[M + H]^+$; ^{1}H and ^{13}C NMR: Tables 1 and 2.

Sibiricose A_5 (5): amorphous powder, $[\alpha]^{23}_D$ −6° (*c* 2.27, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 217.5 (sh) (3.89), 232.5 (sh) (3.79), 297 (sh) (3.75), 326.5 (3.91); FABMS *m/z*: 541 $[M + Na]^+$; ^{1}H and ^{13}C NMR: Tables 1 and 2.

Sibiricose A_6 (6): amorphous powder, $[\alpha]^{23}_D$ −2° (*c* 0.72, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 239 (4.03), 330 (4.04); FABMS *m/z*: 571 $[M + Na]^+$, 549 $[M + H]^+$, 548 $[M]^+$; ^{1}H and ^{13}C NMR: Tables 1 and 2.

Sibiricaxanthone A (7): yellow amorphous powder, $[\alpha]^{23}_D$ +13° (*c* 0.85, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 239 (4.38), 262 (4.48), 311.5 (4.03), 374 (3.67); FABMS *m/z*: 539 $[M + H]^+$; ^{1}H NMR (DMSO-d_6, 35 °C) δ 3.13 (1H, m, H-5 of Glc), 3.24 (1H, dd, J = 9, 9 Hz, H-4 of Glc), 3.31 (1H, d, J = 11 Hz, H-5 of Api), 3.34 (1H, d, J = 11 Hz, H-5 of Api), 3.35 (overlapped, H_2-6 of Glc), 3.37 (overlapped, H-3 of Glc), 3.58 (1H, d, J = 9.5 Hz, H-4 of Api), 3.76 (1H, br s, H-2 of Api), 3.86 (1H, d, J = 9.5 Hz, H-4 of Api), 4.06 (1H, dd, J = 9.5, 9 Hz, H-2 of Glc), 4.61 (1H, d, J = 9.5 Hz, H-1 of Glc) (HMBC to C-1, 2, 3), 4.80 (1H, d, J = 3 Hz, H-1 of Api) (HMBC to C-6 of Glc), 6.43 (1H, s, H-4) (HMBC to C-2, 3, 4a, 8b, 9), 7.29 (1H, dd, J = 9, 3 Hz, H-6) (HMBC to C-4b, 7, 8), 7.43 (1H, d, J = 3 Hz, H-8) (HMBC to C-4b, 6, 7, 8a, 9), 7.47 (1H, d, J = 9 Hz, H-5) (HMBC to C-7, 8a), 13.50 (1H, s, OH at C-1) (HMBC to C-1, 2, 8b).^{13}C NMR (DMSO-d_6, 35 °C) δ 63.0 (C-5 of Api), 68.4 (C-6 of Glc), 70.1 (C-2 of Glc), 70.6 (C-4 of Glc), 73.0 (C-1 of Glc), 73.2 (C-4 of Api), 75.7 (C-2 of Api), 78.7 (C-3 of Api), 78.8 (C-3 of Glc), 79.8 (C-5 of Glc), 93.5 (C-4), 101.7 (C-8b), 107.6 (C-2), 108.0 (C-8), 109.0 (C-1 of Api), 118.8 (C-5), 120.3 (C-8a), 124.4 (C-6), 148.8 (C-4b), 153.9 (C-7), 156.4 (C-4a), 161.9 (C-1), 164.7 (C-3), 179.9 (C-9).

Table 2. ^{13}C NMR Data of Sibiricoses A_1−A_6 (**1**−**6**) in CD_3OD at 35 °C

	1	**2**	**3**	**4**[a]	**5**	**6**
sugar moiety						
Glc-1	93.2	93.3	93.6	93.1	93.3	93.3
2	73.2	73.2	73.2	72.9	73.1	73.2
3	74.6	74.8	74.6	72.9	75.0	75.0
4	71.9	72.0	71.7	72.9	71.3	71.3
5	72.0	72.1	72.2	72.8	73.9	74.0
6	64.2	64.2	64.2	62.5	62.4	62.5
Fru-1	65.2	65.3	64.7	65.6	65.4	65.5
2	105.2	105.3	105.3	105.3	104.9	104.9
3	79.3	79.5	79.5	79.9	79.8	79.8
4	76.1	76.2	76.0	74.3	74.6	74.6
5	83.8	83.9	83.8	84.7	84.2	84.2
6	64.3	64.4	63.9	63.0	62.9	62.9
acid moiety				(at C-4 of Glc)		
α	169.1	168.7	168.2	168.5	168.3	168.2
β	115.8	118.2		115.4	115.1	115.6
γ	147.2	146.5		147.9	147.7	147.9
1	126.6	131.6	122.0	126.5	127.7	126.7
2	107.0	107.0	133.0	107.1	112.3	107.3
3	149.4	154.9	109.8	147.9	149.4	149.5
4	139.6	141.5	163.6	140.0	150.7	139.8
5	149.4	154.9	109.8	147.9	116.3	149.5
6	107.0	107.0	133.0	107.1	124.2	107.3
OMe	56.8	56.8		56.9	56.6	57.0
				(at C-3 of Fru)		
α				167.9		
β				115.6		
γ				147.9		
1				126.5		
2				107.2		
3				147.9		
4				140.0		
5				147.9		
6				1072		
OMe				56.9		

[a] Assigned with the aid of an HMBC spectrum.

Sibiricaxanthone B (8): yellow amorphous powder, $[\alpha]^{23}_D$ −11° (*c* 1.44, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 240 (4.40), 262 (4.49), 310 (4.05), 371 (3.70); FABMS *m/z*: 539 $[M+H]^+$; ^{1}H

NMR (DMSO-d_6, 80 °C) δ 2.70 (1H, d, J = 9.5 Hz, H-4 of Api), 3.01 (1H, d, J = 11 Hz, H-5 of Api), 3.10 (1H, d, J = 9.5 Hz, H-4 of Api), 3.16 (1H, d, J = 11 Hz, H-5 of Api), 3.27 (overlapped, H-2 of Glc, H-4 of Glc, H-5 of Glc), 3.49 (1H, dd, J = 12, 5 Hz, H-6 of Glc), 3.60 (1H, br s, H-2 of Api), 3.71 (1H, dd, J = 12, 2 Hz, H-6 of Glc), 4.23 (1H, m, H-3 of Glc), 4.71 (1H, d, J = 10 Hz, H-1 of Glc) (HMBC to C-1, 2, 3), 5.20 (1H, br s, H-1 of Api) (HMBC to C-2 of Glc), 6.40 (1H, s, H-4) (HMBC to C-2, 4a, 8b, 9), 7.27 (1H, dd, J = 9, 2.5 Hz, H-6) (HMBC to C-4b, 5, 7, 8), 7.42 (1H, d, J = 9 Hz, H-5) (HMBC to C-8a), 7.45 (1H, d, J = 2.5 Hz, H-8) (HMBC to C-4b, 6, 7, 9), 13.41 (1H, s, OH at C-1) (HMBC to C-2, 8b). ^{13}C NMR (DMSO-d_6, 80 °C) δ 61.3 (C-6 of Glc), 64.4 (C-5 of Api), 70.6 (C-4 of Glc), 71.2 (C-1 of Glc), 73.5 (C-4 of Api), 74.1 (C-3 of Glc), 75.8 (C-2 of Api), 78.9 (C-3 of Api), 79.3 (C-2 of Glc), 81.4 (C-5 of Glc), 93.8 (C-4), 101.4 (C-8b), 107.5 (C-2), 108.1 (C-8), 108.9 (C-1 of Api), 118.9 (C-5), 120.3 (C-8a), 124.3 (C-6), 148.8 (C-4b), 153.9 (C-7), 156.5 (C-4a), 161.0 (C-1), 165.2 (C-3), 179.7 (C-9).

Polygalaxanthone III (10): amorphous powder, ^{1}H NMR (DMSO-d_6, 35 °C) δ 3.11 (1H, m, H-5 of Glc), 3.22 (1H, dd, J = 9, 9 Hz, H-4 of Glc), 3.31 (1H, d, J = 11 Hz, H-4 of Api), 3.32 (1H, dd, J = 9, 9 Hz, H-3 of Glc), 3.34 (1H, d, J = 11 Hz, H-4 of Api), 3.35 (overlapped, H_2-6 of Glc), 3.58 (1H, d, J = 9.5 Hz, H-5 of Api), 3.75 (1H, d, J = 3 Hz, H-2 of Api), 3.86 (1H, d, J = 9.5 Hz, H-5 of Api), 3.89 (3H, s, OMe), 4.06 (1H, dd, J = 10, 9 Hz, H-2 of Glc), 4.60 (1H, d, J = 10 Hz, H-1 of Glc) (HMBC to C-1, 2, 3, 8b), 4.78 (1H, d, J = 3 Hz, H-1 of Api) (HMBC to C-6 of Glc), 6.40 (1H, s, H-4) (HMBC to C-2, 3, 4, 4a, 8b, 9), 6.91 (1H, s, H-5) (HMBC to C-4b, 6, 7, 8a, 9), 7.46 (1H, s, H-8) (HMBC to C-4b, 6, 7, 8a, 9), 13.75 (1H, s, OH at C-1) (HMBC to C-1, 2, 8b). ^{13}C NMR (DMSO-d_6, 35 °C) δ 55.9 (OMe), 63.0 (C-5 of Api), 68.3 (C-6 of Glc), 70.1 (C-2 of Glc), 70.6 (C-4 of Glc), 73.0 (C-1 of Glc, C-4 of Api), 75.6 (C-2 of Api), 78.7 (C-3 of Api), 78.9 (C-3 of Glc), 79.8 (C-5 of Glc), 93.4 (C-4), 101.3 (C-8b), 102.7 (C-5), 104.8 (C-8), 107.6 (C-2), 109.0 (C-1 of Api), 111.4 (C-8a), 146.0 (C-7), 151.7 (C-4b), 154.6 (C-6), 156.1 (C-4a), 161.7 (C-1), 163.8 (C-3), 178.9 (C-9).

Lancerin (15): amorphous powder, ^{1}H NMR (DMSO-d_6, 60 °C) δ 3.29 (overlapped, H-2 of Glc, H-3 of Glc, H-5 of Glc), 3.48 (1H, dd, J = 11.5, 5 Hz, H-6 of Glc), 3.72 (1H, br d, J = 11.5 Hz, H-6 of Glc), 4.00 (1H, m, H-4 of Glc), 4.78 (1H, d, J = 10 Hz, H-1 of Glc), 6.28 (1H, s, H-2) (HMBC to C-1, 3, 4, 8b, 9, 1 of Glc), 7.30 (1H, dd, J = 9, 3 Hz, H-6), 7.42 (1H, d, J = 3 Hz, H-8), 7.42 (1H, d, J = 9 Hz, H-5), 13.03 (1H, s, OH at C-1) (HMBC to C-1, 2, 8b). ^{13}C NMR (DMSO-d_6, 60 °C) δ 61.4 (C-6 of Glc), 70.5 (C-2 of Glc), 70.9 (C-4 of Glc), 73.2 (C-1 of Glc), 78.5 (C-3 of Glc), 81.1 (C-5 of Glc), 97.5 (C-2), 101.9 (C-8b), 104.0 (C-4), 107.7 (C-8), 118.8 (C-5), 119.8 (C-8a), 124.3 (C-6), 148.7 (C-4b), 153.7 (C-7), 155.8 (C-4a), 161.5 (C-1), 164.2 (C-3), 179.9 (C-9).

Sibiricaphenone (9): amorphous powder, $[\alpha]^{23}_D$ −62° (c 0.97, MeOH); UV λ_{max}^{MeOH} nm (log ϵ): 213 (sh) (4.00), 263 (3.91); FABMS m/z: 467 $[M + Na]^+$, 445 $[M + H]^+$; ^{1}H NMR (CD_3-OD, 35 °C) δ 1.29 (3H, d, J = 6 Hz, H_3-6 of Rha), 2.55 (3H, s, CH_3), 3.39 (1H, dd, J = 10, 10 Hz, H-4 of Glc), 3.40 (1H, dd, J = 10, 9 Hz, H-4 of Rha), 3.47 (overlapped, H-3 of Glc), 3.58 (1H, m, H-5 of Glc), 3.60 (overlapped, H-6 of Glc, H-3 of Rha), 3.70 (1H, dd, J = 9, 7.5 Hz, H-2 of Glc), 3.90 (overlapped, H-6 of Glc), 3.94 (overlapped, H-2 of Rha), 3.95 (overlapped, H-5 of Rha), 5.14 (1H, d, J = 7.5 Hz, H-1 of Glc), 5.28 (1H, d, J = 1 Hz, H-1 of Rha), 7.13 (2H, d, J = 9 Hz, H-3′, H-5′), 7.97 (2H, d, J = 9 Hz, H-2′, H-6′). ^{13}C NMR (CD_3OD, 35 °C) δ 18.1 (C-6 of Rha), 26.4 (C-1), 62.5 (C-6 of Glc), 70.0 (C-5 of Rha), 71.4 (C-4 of Glc), 72.2 (C-2 of Rha), 72.3 (C-3 of Rha), 74.0 (C-4 of Rha), 78.2 (C-3 of Glc), 79.1 (C-2 of Glc, C-5 of Glc), 99.9 (C-1 of Glc), 102.5 (C-1 of Rha), 117.1 (C-3′, C-5′), 131.7 (C-2′, C-6′), 132.7 (C-1′), 162.7 (C-4′), 199.4 (C-2).

Alkaline Hydrolysis of 1−6. Each compound (1 mg) was treated with 2% aq. NaOH (50 μL) for 2 h at room temperature in a N_2 atmosphere, and the reaction mixture was passed through a column equipped with Amberlite IR-120B on a Mitsubishi Diaion HP-20 instrument. From the H_2O eluate, sucrose was detected by HPLC [Asahipak NH_2P-50, 4.6 mm × 25 cm, CH_3CN-H_2O (65:35), 1.0 mL/min, UV 195 nm,[8] t_R 5.2 min]. From the MeOH eluate, ferulic acid (9.1 min) was detected from **5**; sinapic acid (8.6 min) was detected from **1**, **4**, **6**; 3,4,5-trimethoxycinnamic acid (24.8 min) was detected from **2**; *p*-hydroxybenzoic acid (5.7 min) was detected from **3** by HPLC [YMC R-ODS-5, 4.6 mm × 25 cm, CH_3CN-H_2O (22.5:77.5) + 0.05% CF_3COOH, 1.0 mL/min, UV 280 mn].

Acid Hydrolysis of 7 and 8. Each compound (1 mg) was heated on a boiling water bath with 2 N HCl (50 μL) for 10 min. The reaction mixture was passed through an Amberlite IRA-60E column, and the eluate was concentrated. The residue was warmed at 60 °C with a solution of D-cysteine methyl ester in pyridine (3 mg/25 μL) for 90 min and to the reaction mixture hexamethyldisilazane (10 μL) and trimethylsilyl chloride (10 μL) were added and the reaction mixture was stirred at 60 °C for 30 min. The reaction mixture was subjected to GC. Conditions: column Supelco SPB-1, 0.25 mm × 27 m; temp. 230 °C; carrier gas, N_2. D-Apiose (8.0 min) was detected from **7** and **8**.[9]

Acid Hydrolysis of 9. Compound **9** (1 mg) was heated with 5% H_2SO_4 (50 μL) and dioxane (50 μL) on a boiling water bath for 1 h. The reaction mixture was passed through a column equippsed with Amberlite IRA-60E on a Mitsubishi Diaion HP-20 instrument. From the H_2O eluate, D-glucose (14.0 min) and L-rhamnose (9.6 min) were detected by GC in the same manner as **7**.[9] *p*-Hydroxyacetophenone was detected in the MeOH eluate by HPLC [YMC R-ODS-5, 4.6 mm × 25 cm; CH_3CN-H_2O (22.5:77.5); 1.0 mL/min; UV 260 nm; t_R 8.7 min].

Acknowledgment. We thank the staff of the Analytical Center, University of Shizuoka, for measurement of FABMS.

References and Notes

(1) Zhang, D.-M.; Miyase, T.; Kuroyanagi, M.; Umehara, K.; Noguchi, H.; *Phytochemistry* **1998**, *47*, 45−52 and references therein.
(2) Jian, S. *New Medicinal College Dictionary of Chinese Drugs*; Shanghai Scientific Technologic Publisher: Shanghai, 1997; p 2174.
(3) Ikeya, Y.; Sugama, K.; Maruno, M.; *Chem. Pharm. Bull.* **1994**, *42*, 2305−2308.
(4) Miyase, T.; Ueno, A. *Shoyakugaku Zasshi* **1993**, *47*, 267−278.
(5) Lin, C.-H.; Chang, C.-H.; Arisawa, M.; Shimizu, M.; Morita, N. *Phytochemistry* **1982**, *21*, 205−208.
(6) Kitagawa, I.; Sakagami, M.; Hashiuchi, M.; Zhou, J. L.; Yoshikawa, M.; Ren, J. *Chem. Pharm. Bull.* **1989**, *37*, 551−553.
(7) Kasai, R.; Okihara, M.; Asakawa, J.; Mizutani, K.; Tanaka, O. *Tetrahedron* **1979**, *35*, 1427−1432.
(8) Binder, H. *J. Chromatgr.* **1980**, *189*, 414−420.
(9) t_R values for L-glucose (13.5 min), L-apiose (7.5 min), and D-rhamnose (9.4 min) were obtained from each enantiomer (D-apiose + L-cysteine methyl ester, L-rhamnose + L-cysteine methyl ester).

NP990084T