Five New Xanthenone *O*-Glycosides from the Roots of *Polygala sibirica* L.

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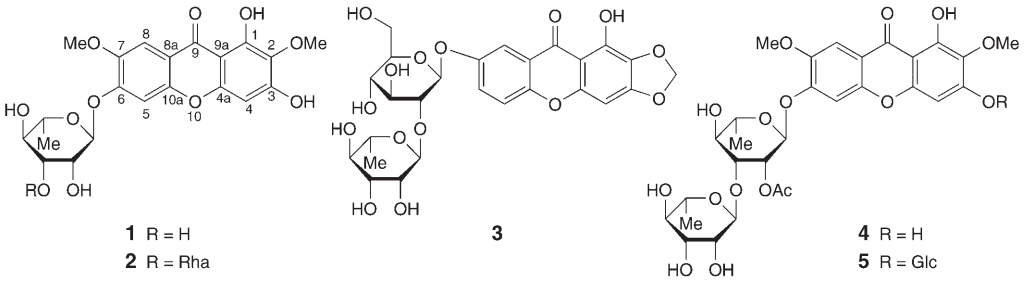
Five new xanthenone *O*-glycosides, sibiricaxanthone C (**1**), sibiricaxanthone D (**2**), sibiricaxanthone E (**3**), sibiricaxanthone F (**4**), and sibiricaxanthone G (**5**) were isolated from the roots of *Polygala sibirica* L., together with the six known xanthenone glycosides **6**–**11**. The structures of new compounds were elucidated on the basis of spectral data and acid hydrolysis.

Introduction. – In continuation of our search for new bioactive compounds in *Polygalaceae* species [1–7], we have now investigated the chemical constituents of the roots of *Polygala sibirica* L., one of the authorized sources of 'Yuan Zhi' in the Chinese Pharmacopoeia. 'Yuan Zhi' is a commonly used traditional Chinese medicine (TCM), which acts as a tonic, sedative, and expectorant agent. Up to now, there is only one paper reporting the isolation of several sucrose esters and xanthenone *C*-glycosides from *P. sibirica* [8]. In this paper, we describe the isolation and structure elucidation of the five new xanthenone *O*-glycosides sibiricaxanthones C–G (**1**–**5**) from *Polygala sibirica* L., which were accompanied by six known xanthone glycosides. The known compounds were identified by extensive NMR analyses as polygalaxanthone VI (=6-(*β*-D-glucopyranosyloxy)-1,2,3,7-tetramethoxy-9*H*-xanthen-9-one) [1], 7-*O*-methylmangiferin (=2-*β*-D-glucopyranosyl-1,3,6-tetrahydroxy-7-methoxy-9*H*-xanthen-9-one) [7], polygalaxanthone III (=2-(6-*O*-D-apio-*β*-D-furanosyl-*β*-D-glucopyranosyl)-1,3,6-trihydroxy-7-methoxy-9*H*-xanthen-9-one) [8], sibiricaxanthone B (=2-(2-*O*-D-apio-*β*-D-furanosyl-*β*-D-glucopyranosyl)-1,3,7-trihydroxy-9*H*-xanthen-9-one) [8], mangiferin (=2-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxy-9*H*-xanthen-9-one) [9], and 4-*β*-D-glucopyranosyl-1,3,6-trihydroxy-7-methoxy-9*H*-xanthen-9-one [10].

Results and Discussion. – Compound **1** was obtained as a pale yellow powder, and its molecular formula was deduced to be $C_{21}H_{22}O_{11}$ from the HR-ESI-MS (*m*/*z* 451.1239 ($[M+H]^+$)). Its UV spectrum in MeOH (λ_{max} 235, 243, 260, 320, and 362 nm) showed the characteristic absorption of a 9*H*-xanthen-9-one. The IR spectrum of **1** showed the presence of OH groups (3419 cm^{-1}), a H-bonded C=O group (1651 cm^{-1}), and aromatic rings (1614, 1589, and 1485 cm^{-1}). Acid hydrolysis of **1** yielded L-rhamnose, which was identifiedd by TLC and GC analysis. The ^1H- and ^{13}C-NMR (*Table 1*) and HMBC data established the structure of **1** as 1,3-dihydroxy-2,7-



1 R = H
2 R = Rha

3

4 R = H
5 R = Glc

Table 1. *^{1}H- and ^{13}C-NMR Data* (500 and 125 MHz, resp., (D_6)DMSO) *of Compounds* **1**, **2**, *and* **3**. δ in ppm, J in Hz.

	1		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(1)		153.8		153.8		153.0
C(2)		130.6		130.6		128.9
C(3)		158.3		158.3		155.2
H–C(4)	6.49 (*s*)	93.9	6.50 (*s*)	93.9	6.85 (*s*)	89.6
C(4a)		152.5		152.5		153.2
H–C(5)	7.27 (*s*)	103.5	7.29 (*s*)	103.9	7.63 (*d*, J = 9.5)	119.3
C(6) or H–C(6)		151.7		151.8	7.49 (*dd*, J = 3, 9.5)	124.9
C(7)		146.9		147.0		153.4
H–C(8)	7.48 (*s*)	104.6	7.50 (*s*)	105.0	7.65 (*d*, J = 3.0)	109.2
C(8a)		112.9		113.1		119.8
C(9)		179.2		179.2		180.3
C(9a)		101.9		102.2		104.4
C(10a)		151.1		151.1		150.7
MeO–C(2)	3.76 (*s*)	60.0	3.79 (*s*)	60.0		
MeO–C(7)	3.90 (*s*)	56.0	3.97 (*s*)	56.2		
OH–C(1)	13.05 (*s*)		13.04 (*s*)		12.63 (*s*)	
OH–C(3)	10.88 (br. *s*)		10.87 (br. *s*)			
OCH_2O					6.18 (*s*)	103.0
Rha or Glc:	Rha		Rha-1		Glc	
H–C(1)	5.62 (br. *s*)	99.0	5.58 (*d*, J = 1.5)	99.3	5.16 (*d*, J = 7.0)	98.5
H–C(2)	3.46–3.48 (*m*)	70.1	3.45–3.46 (*m*)	70.4	3.31 (overlapped)	76.6
H–C(3)	3.71–3.72 (*m*)	70.2	3.81–3.82 (*m*)	76.5	3.51–3.52 (*m*)	76.9
H–C(4)	3.33–3.36 (*m*)	71.4	3.78–3.79 (*m*)	70.7	3.22–3.24 (*m*)	69.6
H–C(5)	3.89 (overlapped)	69.9	3.97 (overlapped)	69.4	3.41–3.43 (*m*)	77.1
Me(6) or CH_2(6)	1.14 (*d*, J = 6.0)	17.8	1.14 (*d*, J = 6.0)	17.7	3.68–3.70 (*m*), 3.30–3.31 (*m*)	60.4
Rha:			Rha-2		Rha	
H–C(1)			4.91 (*d*, J = 1.5)	102.0	5.12 (br. *s*)	100.6
H–C(2)			3.47–3.48 (*m*)	70.4	3.29–3.30 (*m*)	70.4
H–C(3)			3.56–3.57 (*m*)	70.4	3.70–3.72 (*m*)	70.5
H–C(4)			3.23–3.25 (*m*)	72.0	3.18–3.19 (*m*)	71.8
H–C(5)			3.70–3.71 (*m*)	68.5	3.80–3.81 (*m*)	68.3
Me(6)			1.13 (*d*, J = 6.0)	18.0	1.19 (*d*, J = 6.0)	18.0

dimethoxy-6-(α-L-rhamnopyranosyloxy)-9*H*-xanthen-9-one which was named sibiricaxanthone C.

The ^{1}H-NMR spectrum of **1** displayed three uncoupled aromatic H-atoms at δ 6.49, 7.27, and 7.48, a H-bonded OH group at δ 13.05 (*s*), a free phenolic OH group at δ 10.88 (br. *s*), two MeO groups at δ 3.90 (*s*) and 3.76 (*s*), and an anomeric H-atom at δ 5.62 (br. *s*). From the characteristic UV, IR, and NMR data, **1** was deduced as a 9*H*-xanthen-9-one glycoside with a disubstituted and a trisubstituted benzo moiety. The anomeric configuration of the L-rhamnosyl residue was determined to be α from the ^{13}C-NMR chemical shifts of its C(3) (δ 70.2) and C(5) (δ 69.9) [11][12]. In the HMBC plot (*Figure*), the rhamnose anomeric H-atom at δ 5.62 was correlated with C(6) at δ 151.7, the MeO group at δ 3.90 with C(7) at δ 146.9, and another MeO group at δ 3.76 with C(2) at δ 130.6.

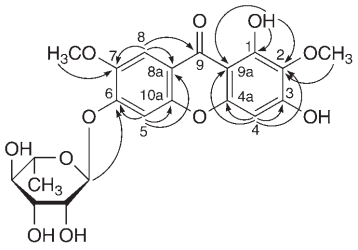


Figure. *Key HMBC correlations* (H → C) *of compound* **1**

Compound **2** was isolated as a yellow powder with a molecular formula $C_{27}H_{32}O_{15}$, as deduced from the HR-ESI-MS (*m*/*z* 597.1801 ([*M* + H]$^+$)). Acid hydrolysis of **2** yielded L-rhamnose. The ^{1}H- and ^{13}C-NMR data of **2** (*Table 1*) were similar to those of **1**, except for the signals of an additional L-rhamnose in **2**. On the basis of further data, **2** was characterized as 1,3-dihydroxy-2,7-dimethoxy-6-{[α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl]oxy}-9*H*-xanthen-9-one which was named sibiricaxanthone D.

The ^{1}H-NMR spectrum of **2** showed three uncoupled aromatic H-atoms at δ 6.50, 7.29, and 7.50, two phenolic OH groups at δ 13.04 (*s*) and 10.87 (br. *s*), two MeO groups at δ 3.79 (*s*) and 3.97 (*s*), and two anomeric H-atoms at δ 5.58 (*d*, *J* = 1.5 Hz) and 4.91 (*d*, *J* = 1.5 Hz). The cross-peak observed in the HMBC plot between the anomeric H-atom signal at δ 4.91 (H–C(1) of Rha-2) and the C-atom signal at δ 76.5 (C(3) of Rha-1) indicated a (1 → 3) linkage between the two rhamnose units.

Compound **3** was isolated as a yellow powder with a molecular formula $C_{26}H_{28}O_{15}$, as deduced from the HR-ESI-MS (*m*/*z* 581.1490 ([*M* + H]$^+$)). Comparison of the ^{1}H- and ^{13}C-NMR data of **3** (*Table 1*) with those of 1,7-dihydroxy-2,3-(methylenedioxy)-9*H*-xanthen-9-one [13] suggested that **3** contained as aglycone 1,7-dihydroxy-2,3-(methylenedioxy)-9*H*-xanthen-9-one. By comparison with NMR chemical-shift values and coupling constants, as well as by acid hydrolysis, followed by TLC and GC analyses, one β-D-glucopyranosyl and one α-L-rhamnopyranosyl moiety were identified. Finally **3** was identified as 1-hydroxy-2,3-(methylenedioxy)-7-{[α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl]oxy}-9*H*-xanthen-9-one which was named sibiricaxanthone E.

The ^{1}H-NMR spectrum of **3** exhibited an *ABX* aromatic system at δ 7.65 (*d*, *J* = 3.0 Hz), 7.63 (*d*, *J* = 9.5 Hz), and 7.49 (*dd*, *J* = 3.0, 9.5 Hz), a single H-atom at δ 6.85, a phenolic OH group at δ 12.63, an OCH_2O group at δ 6.18 (*s*, 2 H)), and two anomeric H-atoms at δ 5.16 (*d*, *J* = 7.0 Hz) and 5.12 (br. *s*). In the HMBC plot, the rhamnose anomeric H-atom (δ 5.12) was correlated with C(2) (δ 76.6) of the

glucosyl residue, and the glucosyl anomeric H-atom (δ 5.16) was correlated with the C(7) (δ 153.4) of the aglycone.

Compound **4** was obtained as a yellow amorphous powder with a molecular formula $C_{29}H_{34}O_{16}$, as deduced from HR-ESI-MS (*m/z* 639.1910 ($[M+H]^+$)). Comparison of the ^{1}H- and ^{13}C-NMR data of **4** (*Table 2*) with those of **2** suggested that the structure of

Table 2. *^{1}H- and ^{13}C-NMR Data* (500 and 125 MHz, resp., (D_6)DMSO) *of Compounds* **4** *and* **5**. δ in ppm, *J* in Hz.

	4		**5**	
	δ(H)	δ(C)	δ(H)	δ(C)
C(1)		153.8		153.4
C(2)		130.7		131.7
C(3)		158.5		157.4
H–C(4)	6.44 (*s*)	94.0	6.87 (*s*)	93.9
C(4a)		152.6		152.3
H–C(5)	7.31 (*s*)	104.2	7.37 (*s*)	104.1
C(6)		151.1		151.5
C(7)		146.9		147.1
H–C(8)	7.49 (*s*)	105.1	7.54 (*s*)	105.1
C(8a)		113.6		113.6
C(9)		179.2		179.6
C(9a)		102.0		103.6
C(10a)		151.0		151.3
MeO–C(2)	3.74 (*s*)	60.0	3.78 (*s*)	60.3
MeO–C(7)	3.89 (*s*)	56.3	3.94 (*s*)	56.3
OH–C(1)	12.97 (*s*)		12.88 (*s*)	
Glc:				
H–C(1)			5.13 (*d*, *J* = 7.5)	100.1
H–C(2)			3.37 (overlapped)	73.1
H–C(3)			3.32–3.33 (*m*)	76.6
H–C(4)			3.45–3.47 (*m*)	69.5
H–C(5)			3.41–3.42 (*m*)	77.2
CH_2(6)			3.75–3.77 (*m*), 3.50–3.52 (*m*)	60.6
Rha-1:				
H–C(1)	5.73 (*d*, *J* = 1.5)	96.0	5.81 (br. *s*)	96.0
H–C(2)	5.19 (*dd*, *J* = 1.5, 3.5)	70.9	5.22 (*dd*, *J* = 1.5, 3.5)	70.8
H–C(3)	3.96 (*dd*, *J* = 3.5, 9.5)	74.6	4.00 (*dd*, *J* = 3.5, 9.5)	74.5
H–C(4)	3.38–3.39 (*m*)	71.2	3.40–3.41 (*m*)	71.2
H–C(5)	3.61–3.63 (*m*)	70.3	3.62–3.64 (*m*)	70.2
Me(6)	1.17 (*d*, *J* = 6.0)	17.6	1.19 (*d*, *J* = 6.0)	17.6
AcO–C(2)	2.15 (*s*)	169.7, 20.7	2.12 (*s*)	169.7, 20.7
Rha-2:				
H–C(1′)	4.88 (*d*, *J* = 1.5)	102.5	4.91 (br. *s*)	102.5
H–C(2′)	3.74–3.75 (*m*)	70.3	3.74–3.75 (*m*)	70.3
H–C(3′)	3.38–3.39 (*m*)	70.5	3.39–3.40 (*m*)	70.4
H–C(4′)	3.18–3.19 (*m*)	71.7	3.17–3.18 (*m*)	71.7
H–C(5′)	3.36–3.37 (*m*)	69.1	3.39–3.40 (*m*)	69.1
Me(6′)	1.09 (*d*, *J* = 6.0)	17.6	1.12 (*d*, *J* = 6.0)	17.7

4 is closely related to that of **2**, except for the presence of an Ac group in **4**. All the H- and C-atoms of **4** were unambiguously assigned by ^{1}H,^{1}H-COSY, HSQC, and HMBC experiments. These data led us to conclude that **4** was 1,3-dihydroxy-2,7-dimethoxy-6-{[α-L-rhamnopyranosyl-(1 → 3)-2-*O*-acetyl-α-L-rhamnopyranosyl]oxy}-9*H*-xanthen-9-one which was named sibiricaxanthone F.

The ^{1}H-NMR spectrum of **4** showed three uncoupled aromatic H-atoms at δ 7.49, 7.31, and 6.44, a H-bonded OH group at δ 12.97 (OH–C(1)), two anomeric H-atoms at δ 5.73 (*d*, J = 1.5 Hz) and 4.88 (*d*, J = 1.5 Hz), and two MeO groups at δ 3.89 (*s*) and 3.74 (*s*). In the HMBC plot, the H-atom at δ 5.19 (H–C(2) of Rha-1) was correlated with the C=O group of Ac at δ 169.7. The ^{1}H,^{1}H-COSY correlation between δ 5.19 (H–C(2) of Rha-1) and δ 5.73 (H–C(1) of Rha-1) confirmed the position of the AcO group at C(2) of Rha-1. Moreover, in the HMBC plot, the anomeric H-atom at δ 4.88 (H–C(1) of Rha-2) was correlated with the C-atom at δ 74.6 (C(3) of Rha-1), and the anomeric H-atom at δ 5.73 (H–C(1) of Rha-1) with C(6) of the aglycone at δ 151.1.

Compound **5** was isolated as a yellow powder with the molecular formula $C_{35}H_{44}O_{21}$, as deduced from the HR-ESI-MS (*m*/*z* 801.2434 ([M + H]$^+$)). The ^{1}H- and ^{13}C-NMR data of **5** (*Table 2*) were similar to those of **4**, except for the presence of an additional set of signals assigned to a glucosyl residue. The cross-peak observed in the HMBC plot of **5** between the glucosyl anomeric H-atom (δ 5.13) and C(3) of the aglycone (δ 157.4) indicated that the additional glycosyl unit was connected to C(3). From the spectral data, the structure of **5** was established as 3-(β-D-glucopyranosyloxy)-1-hydroxy-2,7-dimethoxy-6-[α-L-rhamnopyranosyl-(1 → 3)-2-*O*-acetyl-α-L-rhamnopyranosyl]oxy}-9*H*-xanthen-9-one which was named sibiricaxanthone G.

Xanthenone glycosides are familiar constituents in *Polygalaceae* plants [1–7]. However, compounds such as **4** and **5** which have a sugar sequence α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl with an AcO group located at C(2) of the inner rhamnose residue are reported from the *Polygalaceae* family for the first time. Among the known compounds, polygalaxanthone III and sibiricaxanthone B have been found in *Polygala sibirica* before [8], and the others have been previously reported in the genus *Polygala* [1][7][9][10] but are described here firstly in *Polygala sibirica.*

This work was supported by the *Program for Changjiang Scholar and Innovative Team in University* (No. 985-2-063-112), and by the *Program for New Century Excellent Talents in University* (No. 985-2-102-113).

Experimental Part

General. Column chromatography (CC): SiO_2 (100–200 or 200–300 mesh; *Qingdao Marine Chem. Co. Ltd.*), *D101* porous polymer resin (*Tianjin Chem. Ind. Co. Ltd.*), *Sephadex LH-20* (*Pharmacia*), and octadecyl silica gel (*ODS*; 25–40 μm; *Merck*). TLC: *HSGF254*-precoated SiO_2 plates (*Merck*). Semiprep. HPLC: *Waters-600* instrument; *Waters* column prep. *NovaPak HR* C_{18} (300 × 10 mm i.d., 6 μm), flow rate 2.0 ml/min; *Waters 2487* dual λ absorbance detector (detection wavelength at 228 and 310 nm). GC: *Agilent 6890N* gas chromatograph; *HP-5* capillary column (28 m × 0.32 mm i.d.); FID detection, detector temp. 260°; column temp. 180°; carrier gas N_2, flow rate 40 ml/min. Optical rotations: *Perkin-Elmer 243B* digital polarimeter. UV Spectra: *Shimadzu* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra (KBr): *Nicolet Avatar-360* spectrometer; in cm^{-1}. NMR Spectra: *Varian INOVA-500* or *Jeol JNM-A300* spectrometers with Me_4Si as internal standard. ESI-TOF-MS: *Applied-Biosystems QSTAR* mass spectrometer in the positive mode; in *m*/*z*. HR-ESI-MS: *Apex-II-FT-ICRMS* (*Bruker Daltonics*) spectrometer.

Plant Material. The roots of *Polygala sibirica* were collected from Shanxi Province, P. R. China, in July 2006, and identified by one of the authors, Professor *Peng-Fei Tu*. A voucher specimen (A20060715) is deposited in the herbarium of the Modern Research Center for Traditional Chinese Medicine, Peking University Health Science Center, Beijing, China.

Extraction and Isolation. The air-dried roots of *Polygala sibirica* (9.0 kg) were extracted under reflux three times with 95% EtOH (2 × 70 l) for 3 h each time. The extract was combined and concentrated to yield 2.2 kg of residue, a portion (2.0 kg) of which was suspended in H_2O (4 l) and defatted with petroleum ether (8 l). The aq. layer was further extracted successively with $CHCl_3$ (12 l) and BuOH (12 l) to obtain the $CHCl_3$ extract (135 g) and BuOH extract (545 g). A portion of the BuOH extract (500 g) was subjected to CC (*HPD-100* resin, washed successively with H_2O and 25, 50, and 70% aq. EtOH). The 25% aq. EtOH eluate (87 g) was subjected to CC (SiO_2 (100–200 mesh; 1.8 kg), $CHCl_3$/MeOH 10:1 → 1:1) *Fr. A–H*. *Fr. D* (2.8 g) was subjected to CC (SiO_2 (200–300 mesh; 45 g), $CHCl_3$/MeOH/H_2O 7:1:0.1), then purified by semiprep. HPLC (MeCN/H_2O 20:80): polygalaxanthone VI (11 mg; t_R 15 min). *Fr. G* (9.8 g) was subjected to CC (SiO_2 (200–300 mesh; 100 g), $CHCl_3$/MeOH/H_2O 7:1:0.1 → 7:3:0.3): *Fr. G.1–G.5*. *Fr. G.4* was purified by CC (*Sephadex LH-20*, MeOH): 4-*β*-D-glucopyranosyl-1,3,6-trihydroxy-7-methoxy-9*H*-xanthen-9-one (14 mg). *Fr. H* (12 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH/H_2O 8:2:0.2 → 7:3:0.3): *Fr. H.1–H.8*. *Fr. H.8* was concentrated and kept standing overnight at r.t. After filtration, the resulting precipitate was washed with MeOH: polygalaxanthone III (23 mg). *Fr. H.7* was applied to CC (*Sephadex LH-20*, MeOH) and then purified by semiprep. HPLC (MeOH/H_2O 30:70): magniferin (8 mg; t_R 34.1 min), sibiricaxanthone B (10 mg; t_R 38.6 min), and 7-*O*-methylmagniferin (5 mg; t_R 48.4 min).

The 50% aq. EtOH eluate (300 g) was subjected to CC (SiO_2 (100–200 mesh; 3.6 kg), $CHCl_3$/MeOH/H_2O 10:1:0 → 60:40:5): *Fr. A–M*. *Fr. D* (5 g) was subjected to CC (*Sephadex LH-20*, MeOH) and then purified by semiprep. HPLC (MeOH/H_2O 48:52 containing 0.05% CF_3COOH; flow rate of 2 ml/min); **1** (46 mg; t_R 30.1 min). *Fr. F* (16 g) was subjected to reversed-phase CC (*ODS*, H_2O/MeOH 20:80 → 0:100). Then *Fr. F.16* was concentrated and kept standing overnight at r.t. After filtration, the resulting precipitate was washed with MeOH: **4** (26 mg). *Fr. G* (10 g) was subjected to reversed-phase CC (*ODS*, H_2O/MeOH 10:90 → 0:100). Then *Fr. G.11* was purified by CC (*Sephadex LH-20*, MeOH): **2** (15 mg). *Fr. I* (8 g) was subjected to reversed-phase CC (*ODS*, H_2O/MeOH 10:90 → 0:100) and then purified by CC (*Sephadex LH-20*, MeOH): **5** (10 mg) and **3** (17 mg), resp.

Sibiricaxanthone C (=*6-[(6-Deoxy-α-*L*-mannopyranosyl)oxy]-1,3-dihydroxy-2,7-dimethoxy-9*H*-xanthen-9-one*; **1**): Pale yellow powder. $[\alpha]_D^{20} = -84.0$ ($c = 0.175$, MeOH). UV (MeOH): 235 (2.77), 243 (2.78), 260 (2.80), 320 (2.61), 362 (2.31). IR (KBr): 3419 (OH), 1651 (C=O), 1614, 1589, 1485. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-TOF-MS (pos.): 473.30 ($[M+Na]^+$), 451.30 ($[M+H]^+$). HR-ESI-MS (pos.): 451.1239 ($[M+H]^+$, $C_{21}H_{23}O_{11}^+$; calc. 451.1235).

Sibiricaxanthone D (=*6-{[6-Deoxy-3-*O*-(6-deoxy-α-*L*-mannopyranosyl)-α-*L*-mannopyranosyl]oxy}-1,3-dihydroxy-2,7-dimethoxy-9*H*-xanthen-9-one*; **2**): Yellow powder. $[\alpha]_D^{20} = -70.9$ ($c = 0.185$, MeOH). UV (MeOH): 243 (2.71), 260 (2.74), 320 (2.56), 364 (2.24). IR (KBr): 3419 (OH), 1653 (C=O), 1613, 1587, 1485. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-TOF-MS (pos.): 619.35 ($[M+Na]^+$), 597.36 ($[M+H]^+$). HR-ESI-MS (pos.): 597.1801 ($[M+H]^+$, $C_{27}H_{33}O_{15}^+$; calc. 597.1814).

Sibiricaxanthone E (=*7-{[2-*O*-(6-Deoxy-α-*L*-mannopyranosyl)-β-*D*-glucopyranosyl]oxy}-1-hydroxy-2,3-(methylenedioxy)-9*H*-xanthen-9-one = 8-{[2-*O*-(6-Deoxy-α-*L*-mannopyranosyl)-β-*D*-glucopyranosyl]oxy}-11-hydroxy-10*H*-1,3-dioxolo[4,5-*b*]xanthen-10-one*; **3**): Yellow powder. $[\alpha]_D^{20} = +63.5$ ($c =$ 0.160, MeOH). UV (MeOH): 225 (2.63), 250 (2.63), 288 (2.30), 316 (2.31). IR (KBr): 3418 (OH), 1680 (C=O), 1618, 1581, 1484. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-TOF-MS (pos.): 603.12 ($[M+Na]^+$), 581.13 ($[M+H]^+$). HR-ESI-MS (pos.): 581.1490 ($[M+H]^+$, $C_{26}H_{29}O_{15}^+$; calc. 581.1501).

Sibiricaxanthone F (=*6-{[2-*O*-Acetyl-6-deoxy-3-*O*-(6-deoxy-α-*L*-mannopyranosyl)-α-*L*-mannopyranosyl]oxy}-1,3-dihydroxy-2,7-dimethoxy-9*H*-xanthen-9-one*; **4**): Yellow powder. $[\alpha]_D^{20} = -104.8$ ($c = 0.185$, MeOH). UV (MeOH): 234 (2.76), 243 (2.76), 260 (2.78), 320 (2.59), 364 (2.25). IR (KBr): 3422 (OH), 1651 (C=O), 1614, 1578, 1477. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-TOF-MS (pos.): 661.36 ($[M+Na]^+$), 639.37 ($[M+H]^+$). HR-ESI-MS (pos.): 639.1910 ($[M+H]^+$, $C_{29}H_{35}O_{16}^+$; calc. 639.1920).

Sibiricaxanthone G (=*6-{[2-*O*-Acetyl-6-deoxy-3-*O*-(6-deoxy-α-*L*-mannopyranosyl)-α-*L*-mannopyranosyl]oxy}-3-(β-*D*-glucopyranosyloxy)-1-hydroxy-2,7-dimethoxy-9*H*-xanthen-9-one*; **5**): Yellow pow-

der. $[\alpha]_D^{20} = -70.9$ ($c = 0.175$, MeOH). UV (MeOH): 243 (2.73), 260 (2.74), 297 (2.34), 316 (2.37). IR (KBr): 3445 (OH), 1653 (C=O), 1613, 1477. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-TOF-MS (pos.): 823.51 ($[M+Na]^+$), 801.52 ($[M+H]^+$). HR-ESI-MS (pos.): 801.2434 ($[M+H]^+$, $C_{35}H_{45}O_{21}^+$; calc. 801.2448).

Acid Hydrolysis and Analysis of Sugars. Each of the compounds **1**–**5** (3 mg) was heated in 2N aq. CF_3COOH (5 ml) at 110° for 6 h in a sealed tube. Then, the mixture was diluted in H_2O (15 ml) and extracted with CH_2Cl_2 (3×5 ml). The aq. layer was repeatedly concentrated with MeOH until neutral. The sugars were identified by co-TLC (BuOH/AcOH/H_2O 4:2:1, detection by spraying with 95% EtOH/H_2SO_4 9:1 (*v*/*v*) with authentic samples: R_f of glucose 0.53 and R_f of rhamnose 0.66).

The sugar components present in the aq. layer after hydrolysis of each of **1**–**5** were analyzed by GC. The aq. layer was evaporated and the residue dissolved in anh. pyridine (100 µl). Then 0.1M L-cysteine methyl ester hydrochloride (200 µl; *Sigma*) was added, and the mixture was warmed at 60° for 1 h. The trimethysilylation reagent HMDS-TMCS (hexamethyldisilazane/trimethylchlorosilane/pyridine 2:1:10; *Acros Organics*, Belgium) was added, and the mixture was warmed at 60° for 30 min. The supernatant was subjected to GC for sugar identification: D-glucose (t_R 12.73 min) and L-rhamnose (t_R 5.62 min).

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Received December 12, 2007