Novel Acylated Saponins from Montbretia (*Crocosmia crocosmiiflora*). II.[1] The Structures of Crocosmiosides C, D, E, F, G and I

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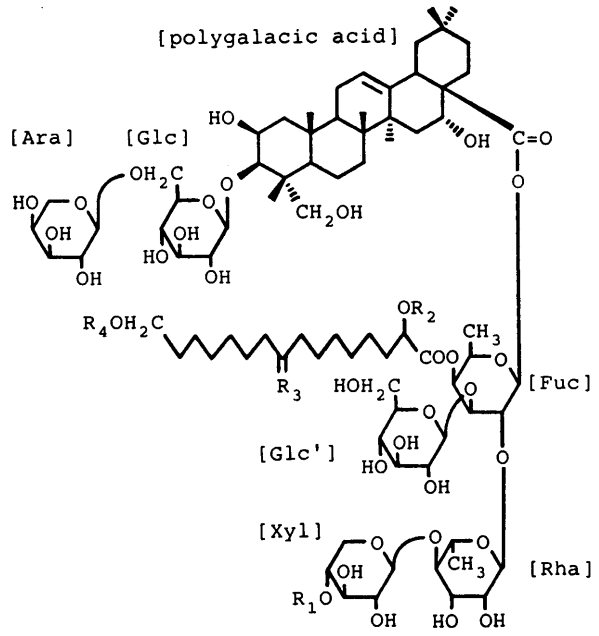
Six novel triterpenoid saponins, named crocosmiosides C, D, E, F, G, and I, were isolated from the corms of montbretia (*Crocosmia crocosmiiflora* N.E.Br., Iridaceae). The structures of these saponins were determined on the basis of spectral and chemical evidence. They are 3,28-di-*O*-glycosides of polygalacic acid, carrying hydroxylated palmitic acid derivatives at the C-4 position of the β-D-fucopyranosyl moiety. Namely, crocosmiosides C (1), D (2), E (3), F (4), and G (5) bear 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-28-*O*-{2-*O*-[β-D-apio-D-furanosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-3-*O*-(β-D-glucopyranosyl)-β-D-fucopyranosyl}-polygalacic acid as a common structural unit of the desacylsaponin moiety, while the structures of the acyl moiety of crocosmiosides C (1), D (2), E (3), F (4), and G (5) are 9-oxo-16-hydroxy-2-β-D-xylopyranosyloxyhexadecanoic acid, 9,16-dihydroxy-2-β-D-xylopyranosyloxyhexadecanoic acid, 2,9,16-trihydroxyhexadecanoic acid, 2,9-dihydroxy-16-α-L-rhamnopyranosyloxyhexadecanoic acid, and 9-oxo-16-α-L-rhamnopyranosyloxy-2-β-D-xylopyranosyloxyhexadecanoic acid, respectively. In addition, the structure of crocosmioside I (6) which has a different desacylsaponin moiety was elucidated as 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-28-*O*-{2-*O*-[β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-3-*O*-(β-D-glucopyranosyl)-4-*O*-(2,9-dihydroxy-16-α-L-rhamnopyranosyloxyhexadecanoyl)-β-D-fucopyranosyl}-polygalacic acid.

Keywords *Crocosmia crocosmiiflora*; montbretia; Iridaceae; triterpenoid saponin; crocosmioside C; crocosmioside D; crocosmioside F; 2,9,16-trihydroxypalmitic acid; 2,16-dihydroxy-9-oxopalmitic acid; polygalacic acid

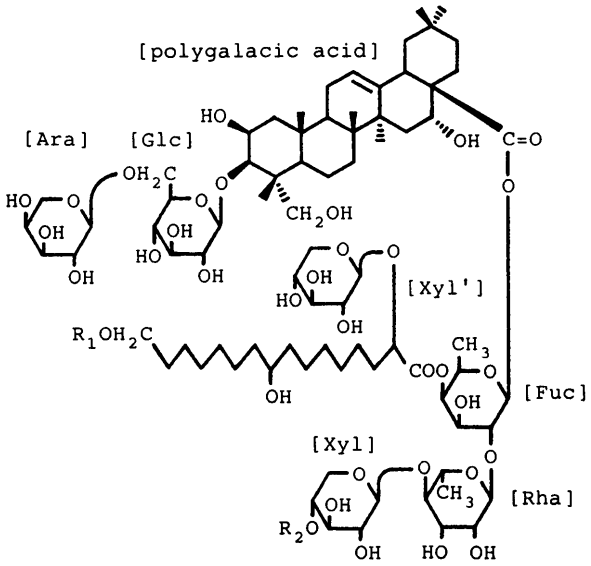
As we reported in previous papers,[1] nine novel triterpenoid saponins, named crocosmiosides A, B, C, D, E, F, G, H and I were isolated from the corms of montbretia (*Crocosmia crocosmiiflora* N.E.Br., Iridaceae), and the structures of crocosmiosides A (**7**), B (**8**) and H (**9**) have been established. This paper describes the structure elucidation of crocosmiosides C, D, E, F, G and I, which led to the assignment of the structures **1**, **2**, **3**, **4**, **5** and **6**, respectively.



crocosmioside C (**1**): R_1=Api, R_2=Xyl′, R_3=O, R_4=H
crocosmioside D (**2**): R_1=Api, R_2=Xyl′, R_3=H, OH, R_4=H
crocosmioside E (**3**): R_1=Api, R_2=H, R_3=H, OH, R_4=H
crocosmioside F (**4**): R_1=Api, R_2=H, R_3=H, OH, R_4=Rha′
crocosmioside G (**5**): R_1=Api, R_2=Xyl′, R_3=O, R_4=Rha′
crocosmioside I (**6**): R_1=H, R_2=H, R_3=H, OH, R_4=Rha′

Chart 1

On acidic hydrolysis, crocosmioside C (**1**) yielded D-apiose, D-fucose, D-glucose, D-xylose, L-arabinose, L-rhamnose[2] and polygalacic acid.[3] The aglycone was isolated as the methyl ester (**10**) by treatment with diazomethane, and identified by comparison of the infrared (IR), and proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra with those of an authentic sample. In the positive ion fast atom bombardment mass spectrum (FAB-MS), **1** revealed the $(M+Na)^+$ ion peak at *m/z* 1955 and the same fragment ion peak at *m/z* 821 $(aglycone-Glc-Ara+Na)^+$ as that of crocosmioside A (**7**). The IR spectrum showed absorptions at 3400 cm^{-1} (OH), 1740 cm^{-1} (ester) and 1710 cm^{-1} (carbonyl). The ^{1}H-



crocosmioside A (**7**): R_1=Rha′, R_2=Api
crocosmioside B (**8**): R_1=H, R_2=Api
crocosmioside H (**9**): R_1=Rha′, R_2=H

Chart 2

TABLE I. ^{13}C-NMR Chemical Shifts of Aglycone Moieties of Crocosmiosides C (**1**), D (**2**), E (**3**), F (**4**), G (**5**) and I (**6**) and Related Compounds[a)]

Carbon No.	1	2	3	4	5	6	10	12	14
1	44.7 (44.4)	44.7	44.7	44.7	44.7	44.7	45.1	44.4	44.3
2	70.8 (70.1)	70.9	70.9	70.9	70.9	70.9	70.2	70.0	70.0
3	84.3 (84.5)	84.3	84.3	84.4	84.4	84.4	73.2	84.5	84.5
4	43.4 (43.0)	43.4	43.4	43.4	43.4	43.4	42.6	43.0	43.0
5	48.4 (48.0)	48.4	48.4	48.4	48.4	48.4	48.4	47.9	47.9
6	19.2 (18.6)	19.2	19.2	19.2	19.2	19.1	18.4	18.5	18.6
7	34.1 (33.5)	34.1	34.1	34.1	34.1	34.1	33.3	33.5	33.4
8	41.2 (40.4)	41.3	41.2	41.2	41.2	41.2	40.1	40.4	40.4
9	48.7 (47.6)	48.7	48.7	48.7	48.7	48.7	47.7	47.7	47.7
10	37.8 (37.2)	37.9	37.8	37.8	37.9	37.9	37.4	37.2	37.2
11	25.1 (24.2)	25.2	25.0	25.0	25.1	25.1	24.1	24.2	24.2
12	123.9 (123.0)	123.9	123.9	123.9	124.0	124.0	123.0	122.8	122.8
13	144.9 (144.3)	144.9	144.9	144.9	144.9	144.9	144.6	144.6	144.6
14	43.3 (42.5)	43.3	43.3	43.3	43.3	43.3	42.2	42.5	42.5
15	36.7 (36.4)	36.7	36.7	36.7	36.7	36.7	36.1	36.4	36.4
16	74.9 (74.0)	74.9	74.9	74.9	75.0	75.0	74.5	74.0	74.3
17	50.5 (49.5)	50.6	50.5	50.5	50.5	50.5	49.2	49.5	49.4
18	42.8 (42.0)	42.9	42.8	42.8	42.8	42.9	41.4	41.9	41.9
19	48.4 (47.6)	48.4	48.4	48.4	48.3	48.4	47.1	47.7	47.7
20	31.7 (30.9)	31.8	31.7	31.7	31.7	31.7	31.0	30.9	30.9
21	36.9 (36.1)	36.9	36.9	36.9	36.8	36.9	36.0	36.2	36.2
22	32.2 (31.9)	32.2	32.1	32.1	32.1	32.1	32.7	32.0	32.1
23	65.8 (66.3)	65.9	65.9	65.9	65.9	65.9	67.8	66.3	66.3
24	15.3 (15.4)	15.3	15.2	15.2	15.2	15.2	14.7	15.4	15.4
25	18.4 (17.7)	18.4	18.3	18.3	18.3	18.3	17.5	17.7	17.7
26	18.1 (17.7)	18.2	18.1	18.1	18.1	18.1	17.5	17.7	17.7
27	27.6 (27.2)	27.6	27.6	27.6	27.6	27.6	27.3	27.2	27.3
28	177.5 (176.3)	177.6	177.5	177.6	177.6	177.6	177.9	176.3	176.2
29	33.8 (33.3)	33.8	33.7	33.8	33.7	33.8	33.3	33.3	33.4
30	25.4 (24.7)	25.5	25.4	25.4	25.4	25.4	24.7	24.6	24.6
MeO							51.9		

a) The spectra of **1**—**6** were measured in CD_3OD, and those of **1** (in parenthesis), **10**, **12** and **14** in C_5D_5N. Assignments of carbon signals were achieved by analyses of HH- and CH-COSY spectra and a comparison of the ^{13}C-NMR spectrum with reference data.[9)]

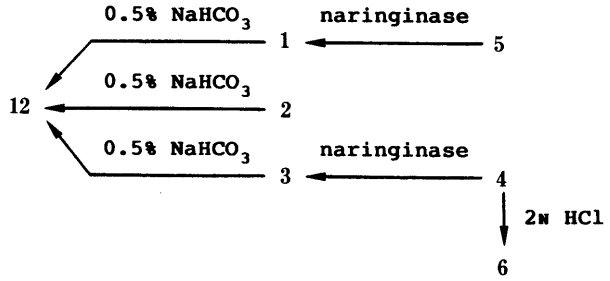
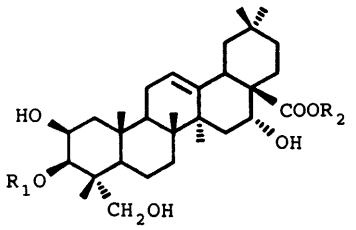


Chart 3

NMR spectrum showed signals of six tertiary methyl groups at δ 0.79, 0.88, 0.93, 0.97, 1.28, 1.39 and two secondary methyl groups at δ 1.08, 1.33. It also showed eight anomeric proton signals at δ 4.24 (1H, d, J=6.8 Hz), 4.29 (1H, d, J=7.0 Hz), 4.43 (1H, d, J=8.0 Hz), 4.48 (1H, d, J=7.8 Hz), 4.49 (1H, d, J=7.8 Hz), 5.05 (1H, d, J=3.0 Hz), 5.39 (1H, d, J=1.5 Hz) and 5.44 (1H, d, J=8.0 Hz). The ^{13}C-NMR spectrum showed eight anomeric carbon signals at δ 95.1, 101.7, 105.0, 105.2, 105.5, 105.9, 107.2, 109.5 and two ester carbon signals at δ 174.7 and 177.5. Also, methylene carbon signals due to hydroxylated fatty acid were observed at δ 20—40 as in the case of crocosmioside A (**7**) and then a carbonyl carbon signal was observed at δ 214.6 (Tables I, II and III).

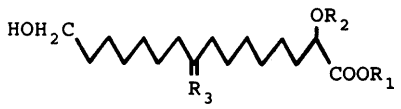
As the IR absorption at 1740 cm^{-1} and the signals at δ 174.7 and 177.5 in the ^{13}C-NMR spectrum suggested the presence of two kinds of ester groups in **1**, weak alkaline



10: R_1=H, R_2=Me

12: R_1=-Glc^6-Ara, R_2=-Fuc^2-Rha^4-Xyl^4-Api
Glc^3

14: R_1=-Glc^6-Ara, R_2=-Fuc^2-Rha^4-Xyl^4-Api



11: R_1=H, R_2=Xyl, R_3=O

15: R_1=H, R_2=Xyl, R_3=H, OH

16: R_1=Me, R_2=H, R_3=H, OH

13:

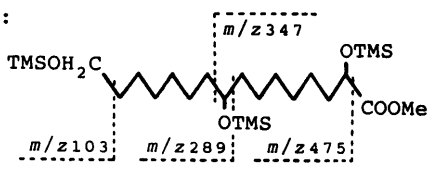


Chart 4

TABLE II ^{13}C-NMR Chemical Shifts of Sugar Moieties of Crocosmiosides C (**1**), D (**2**), E (**3**), F (**4**), G (**5**) and I (**6**) and Related Compounds[a]

		1	2	3	4	5	6	12	14
C-3 Sugars									
Glc	1	105.0 (105.6)	105.0	105.0	105.0	105.0	105.0	105.6	105.6
	2	75.5 (75.4)	75.5	75.5	75.5	75.5	75.6	75.5	75.5
	3	78.5 (78.7)	78.5	78.5	78.5	78.6	78.6	78.7	78.7
	4	72.2 (72.2)	72.2	72.2	72.2	72.2	72.2	72.2	72.2
	5	76.7 (76.7)	76.8	76.8	76.8	76.8	76.8	76.7	76.6
	6	70.0 (69.8)	70.1	70.1	70.0	70.1	70.1	69.8	69.8
Ara	1	105.2 (105.1)	105.2	105.2	105.2	105.2	105.2	105.1	105.1
	2	72.7 (72.6)	72.8	72.8	72.8	72.8	72.8	72.6	72.6
	3	74.3 (74.3)	74.3	74.3	74.3	74.4	74.4	74.3	74.3
	4	69.7 (69.2)	69.8	69.8	69.8	69.8	69.8	69.2	69.2
	5	67.0 (66.6)	67.0	67.0	67.0	67.1	67.0	66.5	66.6
C-28 Sugars									
Fuc	1	95.1 (94.5)	95.2	95.1	95.1	95.2	95.2	94.9	95.1
	2	74.1 (72.4)	74.1	74.1	74.2	74.1	74.1	72.4	73.6
	3	83.9 (83.6)	83.9	83.8	83.8	84.0	83.7	85.5	76.9
	4	75.5 (74.8)	75.5	75.5	75.5	75.5	75.6	72.4	73.4
	5	71.2 (70.8)	71.2	71.2	71.2	71.3	71.3	72.2	73.6
	6	17.0 (16.6)	17.1	17.2	17.2	17.0	17.2	17.0	17.1
Rha	1	101.7 (101.5)	101.7	101.7	101.7	101.7	101.7	101.3	101.2
	2	72.1 (72.1)	72.1	72.1	72.2	72.2	72.2	72.1	72.1
	3	72.4 (73.0)	72.4	72.4	72.4	72.4	72.5	72.6	72.6
	4	84.5 (83.9)	84.5	84.5	84.5	84.6	84.4	83.7	83.5
	5	69.2 (68.6)	69.3	69.3	69.3	69.3	69.3	68.5	68.3
	6	18.9 (18.8)	19.0	18.8	18.8	18.9	18.8	18.7	18.6
Xyl	1	107.2 (106.7)	107.2	107.2	107.2	107.2	107.4	106.6	106.5
	2	76.1 (76.0)	76.2	76.2	76.2	76.2	76.4	76.1	76.1
	3	76.7 (76.4)	76.8	76.8	76.8	76.8	78.4	76.4	76.4
	4	77.5 (76.4)	77.5	77.5	77.6	77.6	71.4	76.4	76.7
	5	65.0 (64.5)	65.0	65.0	65.0	65.0	67.6	64.5	64.5
Api	1	109.5 (109.1)	109.6	109.6	109.6	109.6		109.1	109.1
	2	78.2 (77.7)	78.2	78.2	78.3	78.3		77.7	77.7
	3	80.6 (80.4)	80.7	80.7	80.7	80.7		80.4	80.4
	4	65.3 (65.3)	65.3	65.3	65.4	65.4		65.3	65.3
	5	75.3 (75.4)	75.4	75.4	75.4	75.4		75.4	75.4
Glc′	1	105.9 (105.9)	105.9	105.7	105.7	105.9	105.7	105.8	
	2	75.8 (75.1)	75.8	75.6	75.6	75.9	75.7	75.1	
	3	78.2[b](78.6[b])	78.2[b]	78.4[b]	78.3[b]	78.3[b]	78.5[b]	78.7	
	4	71.3 (71.0)	71.4	71.4	71.4	71.4	71.4	71.7	
	5	78.4[b](78.4[b])	78.4[b]	78.5[b]	78.5[b]	78.5[b]	78.6[b]	78.7	
	6	62.9 (62.6)	62.9	62.8	62.8	62.9	62.8	62.7	

a) The spectra of **1**, **2**, **3**, **4**, **5** and **6** were measured in CD_3OD, and those of **1** (in parenthesis), **12** and **14** in C_5D_5N. *b*) Assignments may be interchangeable within the same column. Glc, β-D-glucopyranosyl; Ara, α-L-arabinopyranosyl; Fuc, β-D-fucopyranosyl; Rha, α-L-rhamnopyranosyl; Xyl, β-D-xylopyranosyl; Api, β-D-apio-D-furanosyl.

treatment was examined to hydrolyze one of them. On hydrolysis with 0.5% $NaHCO_3$, **1** afforded a carboxylic acid glycoside (**11**) and desacylsaponin (**12**) (Chart 3). The positions of the OH groups in **11** were determined to be C-2 and C-16 on the basis of the analyses of the ^{1}H- and ^{13}C-NMR spectra. Namely, the ^{13}C-NMR spectrum of **11**, MS *m/z* 457 $(M+Na)^+$, showed signals due to the xylopyranoside moiety and signals due to a primary hydroxy group, a secondary hydroxy group and a carbonyl group in the palmitic acid derivative at δ 62.2 (t), 79.1 (d), 210.5 (s). Moreover, in the ^{1}H-NMR spectrum of **11**, the signals attributable to H-2 and H-16 were observed at δ 4.60 (1H, dd, $J=6.3$, 6.3 Hz) and 3.73 (2H, t, $J=6.0$ Hz), respectively. The position of the carbonyl group was established to be C-9 by the MS fragmentation of the methyl ester trimethylsilyl (TMS) ether (**13**) derived from **11** (Chart 4). As the glycosylation-shifted methine carbon signal at δ 79.1 was assigned to C-2 on the basis of the ^{13}C–^{1}H heteronuclear shift correlation 2D spectrum (CH-COSY), the location of the xylopyranoside moiety in **11** was determined to be C-2. The anomeric configuration of the xyloside linkage was determined to be β from the *J* value of its anomeric proton signal; δ 4.88 (1H, d, $J=7.0$ Hz). These findings led us to formulate the carboxylic acid glycoside as **11**, except for the C-2 configuration. On the other hand, the ^{13}C-NMR spectrum of **12** showed seven anomeric carbon signals at δ 94.9, 101.3, 105.1, 105.6, 105.8, 106.6, 109.1 and an ester carbon signal at δ 176.3. In comparing the ^{13}C-NMR spectra of **12** and desacylcrocosmioside A (**14**),[1] signals due to the additional glucopyranosyl moiety and a glycosylation shift[4] for the C-3 carbon of the fucopyranosyl moiety were observed in **12** (δ 85.5, downfield shift by 8.6 ppm compared with that of **14**). The result of methylation analysis[5] of **12** by gas chromatography-mass spectrometry (GC-MS) supported the above spectral evidence. Namely, the analytical result for **12** suggested the presence of 6-linked glucopyranoside, terminal arabinopyranoside or xylopyranoside, 2,3-linked fucopyranoside, 4-linked rhamnopyranoside, 4-linked xylopyranoside, terminal apiofuranoside and terminal glucopyranoside (Table IV). The physicochemical properties and ^{1}H- and ^{13}C-NMR spectral data of **12** were found to be identical with those of

TABLE III. ^{13}C-NMR Chemical Shifts of Carboxylic Acid Moieties of Crocosmiosides C (**1**), D (**2**), E (**3**), F (**4**), G (**5**) and I (**6**) and Related Compounds[a]

	Carbon No.	1	2	3	4	5	6	11	15	16
	1	174.7 (173.4)	174.8	176.5	176.5	174.8	176.5	175.8	175.8	176.1
	2	79.6 (79.3)	79.6	72.2	72.2	79.6	72.2	79.1	79.1	71.0
	3	34.4 (33.8)	34.5	35.9	35.9	34.4	35.9	33.7	33.8	35.3
	4	26.1 (25.4)	26.3	26.6	26.5	26.1	26.6	25.6	25.7	25.9
	5	30.5[b](29.6[b])	30.9[b]	30.9[b]	30.8[b]	30.5[b]	30.8[b]	29.8[b]	30.2[b]	30.3[b]
	6	30.7[b](29.5[b])	31.1[b]	31.1[b]	31.1[b]	30.6[b]	31.1[b]	29.7[b]	30.2[b]	30.2[b]
	7	25.2 (24.2)	27.2	27.8[c]	27.2[c]	25.2	27.2[c]	24.2	26.5	26.5
	8	43.8 (42.9)	38.7[d]	38.7[d]	38.7	43.8	38.8	42.8	38.6[d]	38.6[d]
	9	214.6 (210.7)	72.8	72.8	72.8	214.7	72.8	210.5	71.0	71.3
	10	43.8 (42.8)	38.8[d]	38.8[d]	38.7	43.8	38.8	42.8	38.7[d]	38.7[d]
	11	25.2 (24.2)	27.2	27.1[c]	27.1[c]	25.2	27.1[c]	24.2	26.5	26.5
	12	30.7[b](29.7[b])	31.3[b]	31.2[b]	31.1[b]	30.9[b]	31.1[b]	29.5[b]	30.1[b]	30.0[b]
	13	30.7[b](29.9[b])	31.0[b]	30.9[b]	30.9[b]	30.6[b]	31.0[b]	29.8[b]	30.4[b]	30.4[b]
	14	27.1 (26.5)	27.3	27.2	27.6	27.5	27.7	26.5	26.7	26.7
	15	33.9 (33.8)	34.0	34.0	30.8	30.6	30.8	33.9	34.0	33.9
	16	63.2 (62.2)	63.3	63.3	68.9	68.8	68.9	62.2	62.3	62.3
Sugar moieties										
Xyl′	1	105.5 (106.0)	105.6			105.6		105.6	105.6	
	2	74.9 (74.6)	74.9			75.0		74.8	74.8	
	3	77.8 (78.2)	77.8			77.9		78.3	78.2	
	4	71.3 (71.0)	71.4			71.4		71.2	71.2	
	5	67.2 (67.3)	67.3			67.3		67.5	67.4	
Rha′	1				101.9	101.9	101.9			
	2				72.7	72.7	72.7			
	3				72.8	72.8	72.8			
	4				74.3	74.3	74.3			
	5				70.0	70.0	70.1			
	6				18.4	18.4	18.4			
OCH_3										51.7

a) The spectra of **1**, **2**, **3**, **4**, **5** and **6** were measured in CD_3OD, and those of **1** (in parenthesis), **11**, **15** and **16** in C_5D_5N. *b*—*d*) Assignments may be interchangeable within the same column.

TABLE IV. Relative Retention Time (Rt_R-Value) of Partially Methylated Alditol Acetate on OV-225[a]

	a	b	c	d	e	f	g	h	i
Crocosmioside C (**1**)		0.49	0.55	0.55	0.91	1.00	1.16	1.75	2.21
Crocosmioside D (**2**)		0.49	0.55	0.55	0.91	1.00	1.16	1.73	2.21
Crocosmioside E (**3**)		0.48	0.54		0.90	1.00	1.16	1.75	2.24
Crocosmioside F (**4**)	0.45	0.48	0.55		0.91	1.00	1.17	1.75	2.23
Crocosmioside G (**5**)	0.45	0.49	0.55	0.55	0.91	1.00	1.17	1.74	2.23
Crocosmioside I (**6**)	0.45		0.55		0.90	1.00		1.74	2.23
Desacylmasonoside 1 (**12**)		0.49	0.55		0.91	1.00	1.17	1.75	2.24

a, 1,5-Di-*O*-acetyl-2,3,4-tri-*O*-methylrhamnitol: *m/z* 175, 161, 131, 117. b, 1,5-Di-*O*-acetyl-2,3,4-tri-*O*-methylapitol: *m/z* 233, 205, 161, 117. c, 1,5-Di-*O*-acetyl-2,3,4-tri-*O*-methylarabinitol: *m/z* 161, 117. d, 1,5-Di-*O*-acetyl-2,3,4-tri-*O*-methylxylitol: *m/z* 161, 117. e, 1,4,5-Tri-*O*-acetyl-2,3-di-*O*-methylrhamnitol: *m/z* 203, 161, 117. f, 1,5-Di-*O*-acetyl-2,3,4,6-tetra-*O*-methylglucitol: *m/z* 205, 145, 161, 117. g, 1,4,5-Tri-*O*-acetyl-2,3-di-*O*-methylxylitol: *m/z* 189, 117. h, 1,2,3,5-Tetra-*O*-acetyl-4-*O*-methylfucitol: *m/z* 261, 131. i, 1,5,6-Tri-*O*-acetyl-2,3,4-tri-*O*-methylglucitol: *m/z* 223, 189, 161, 117. *a*) Column, 1% OV-225 (3 mm × 2 m); carrier gas, N_2 (20 ml/min); column temperature, 170 °C.

desacylmasonoside 1, which was previously obtained from *Crocosmia masonorum* (Iridaceae).[6]

In the ^{1}H-NMR spectrum (CD_3OD) of **1**, a characteristic doublet signal[7] which was observed at δ 5.43 (1H, d, J = 3.5 Hz) in analogy with that of crocosmioside A (**7**), was assigned to the C-4 proton of the fucopyranoside moiety from the ^{1}H–^{1}H homonuclear shift correlation 2D spectrum (HH-COSY) of **1**. In comparing the ^{1}H-NMR spectra (C_5D_5N) of **1** and **12**, the C-4 proton signal of fucopyranose was observed at δ 5.87 (1H, d, J = 3.5 Hz) in **1**, while that of **12** was observed at δ 4.30 (1H, d, J = 3.5 Hz). Furthermore, in comparing the ^{13}C-NMR spectra of **1** and **12**, acylation shifts[8] were observed for the signals due to C-3 (−1.9 ppm), C-4 (+2.4 ppm) and C-5 (−1.4 ppm) of fucopyranose. Consequently, the linkage site of the carboxylic acid glycoside (**11**) in **1** was determined to be the C-4 position of the fucopyranoside moiety.

Based on the above evidence, the structure of crocosmioside C, except for the absolute configuration of the 2-OH group in the carboxylic acid moiety, was concluded to be 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-28-*O*-{2-*O*-[β-D-apio-D-furanosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-3-*O*-(β-D-glucopyranosyl)-4-*O*-(9-oxo-16-hydroxy-2-β-D-xylopyranosyloxyhexadecanoyl)-β-D-fucopyranosyl}-polygalacic acid (**1**).

Crocosmioside D (**2**) revealed the $(M+Na)^+$ ion peak at *m/z* 1957, which is larger by 2 mass units than that of **1** and a fragment ion peak at *m/z* 821 in the positive ion FAB-MS. The IR spectrum showed hydroxyl and ester absorption bands, while it lacked the carbonyl absorption band which

was observed in **1**. The ^{1}H-NMR spectrum of **2** showed signals of six tertiary methyl groups, two secondary methyl groups and eight anomeric protons in analogy with that of **1**. In comparing the ^{13}C-NMR spectra of **1** and **2**, all of the aglycone and sugar carbon signals of **2** were almost superimposable on those of **1**, while some differences were observed for the signals due to the hydroxylated fatty acid moiety, indicating that **2** has the same aglycone and sugar linkage and the same linkage position of the hydroxylated fatty acid derivative as **1**.

Alkaline hydrolysis of **2** with 0.5% $NaHCO_3$ gave a carboxylic acid glycoside (**15**) and desacylmasonoside 1 (**12**). In the positive ion FAB-MS, **15** revealed the $(M+Na)^+$ ion peak at *m/z* 459, which is 2 mass units more than that of **11**. The ^{13}C-NMR spectrum of **15** showed signals due to the xylopyranoside moiety and signals at δ 62.3 (t), 71.0 (d), 79.1 (d), which suggested the presence of a primary hydroxy and two secondary hydroxy groups in palmitic acid. The positions of the OH groups were determined to be C-2, C-9, and C-16 from the ^{1}H- and ^{13}C-NMR spectra of **15** and the MS fragmentation of the methyl ester TMS ether (**13**) derived from **15** (Chart 4). The location of the β-D-xylopyranose in **15**, in which the anomeric proton was observed at δ 4.88 (1H, d, $J=7.0$ Hz) in the ^{1}H-NMR spectrum, was determined to be C-2 on the basis of the CH-COSY spectrum as in the case of **11**. These results led us to formulate the carboxylic acid glycoside as **15**, except for the C-2 and C-9 configurations.

As a characteristic doublet signal at δ 5.43 (1H, d, $J=$ 3.5 Hz) in the ^{1}H-NMR spectrum of **2** was assigned to the C-4 proton of fucopyranose from the HH-COSY spectrum, as in the case of **1**, the linkage site of the carboxylic acid glycoside (**15**) in **2** was determined to be the C-4 position of the fucopyranosyl moiety.

Based on the above evidence, the structure of crocosmioside D, except for the absolute configurations of the 2- and 9-OH groups in the carboxylic acid moiety, was elucidated as 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-28-*O*-{2-*O*-[β-D-apio-D-furanosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-3-*O*-(β-D-glucopyranosyl)-4-*O*-(9,16-dihydroxy-2-β-D-xylopyranosyloxyhexadecanoyl)-β-D-fucopyranosyl}-polygalacic acid (**2**).

In the positive ion FAB-MS, crocosmioside E (**3**) revealed the $(M+Na)^+$ ion peak at *m/z* 1825, which is 132 mass units (pentose) less than that of **2**, and a fragment ion peak at *m/z* 821. The ^{1}H-NMR spectrum of **3** showed signals of six tertiary methyl and two secondary methyl groups in analogy with that of **2**. But it lacked the anomeric proton signal at δ 4.29 (1H, d, $J=7.0$ Hz) which was observed in that of **2**. In the ^{13}C-NMR spectrum, all of the aglycone carbon signals of **3** were almost superimposable on those of **2**, indicating that **3** has the same aglycone as **2**. The ^{13}C-NMR spectrum further showed seven anomeric carbon signals and two ester carbon signals. Detailed comparisons of the ^{1}H- and ^{13}C-NMR spectra of **3** with those of **2** have suggested that those of **3** lack the signals due to a terminal xylopyranosyl moiety.

On alkaline hydrolysis with 0.5% $NaHCO_3$, **3** afforded a carboxylic acid and desacylmasonoside 1 (**12**). The carboxylic acid was isolated as the methyl ester by diazomethane methylation. The ^{13}C-NMR spectrum of the carboxylic ester (**16**), MS *m/z* 341 $(M+Na)^+$, showed signals at δ 62.3 (t), 71.0 (d), 71.3 (d) which indicated the presence of a primary hydroxy and two secondary hydroxy groups in methyl ester of palmitic acid. The positions of the OH groups were determined to be C-2, C-9, and C-16 from the ^{1}H- and ^{13}C-NMR spectra of **16** and the MS fragmentation of the methyl ester TMS ether (**13**) derived from **16** (Chart 4). These findings led us to formulate the carboxylic ester as **16**, except for the C-2 and C-9 configurations. The linkage site of the 2,9,16-trihydroxypalmitic acid in **3** was determined to be the C-4 position of fucopyranose on the basis of analysis of the HH-COSY spectrum, which suggested that a characteristic doublet signal at δ 5.40 (1H, d, $J=3.5$ Hz) is due to the C-4 proton of fucopyranose.

Based on the above evidence, the structure of crocosmioside E (**3**), except for the absolute configurations of the 2- and 9-OH groups in the carboxylic acid moiety, was concluded as 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-28-*O*-{2-*O*-[β-D-apio-D-furanosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-3-*O*-(β-D-glucopyranosyl)-4-*O*-(2,9,16-trihydroxyhexadecanoyl)-β-D-fucopyranosyl}-polygalacic acid (**3**).

The positive ion FAB-MS of crocosmioside F (**4**) revealed the $(M+Na)^+$ ion peak at *m/z* 1971, which is 146 mass units (deoxyhexose) more than that of **3**, and a fragment ion peak at *m/z* 821. The ^{1}H-NMR spectrum showed three secondary methyl signals ascribable to deoxyhexose and eight anomeric proton signals. In comparing the ^{13}C-NMR spectra of **4** and **3**, the carbon signals due to an additional rhamnopyranoside moiety were observed in **4**. By detailed comparisons of the ^{1}H- and ^{13}C-NMR spectra of **4** with those of **3**, the structure of **4** was presumed to have a terminal rhamnopyranosyl moiety in addition to that of **3**.

In order to verify this presumption, **4** was hydrolyzed with naringinase to yield **3** and L-rhamnose. The hydrolyzate (**3**) was identified by comparison of physical constants and ^{1}H- and ^{13}C-NMR spectra with those of crocosmioside E. Analyses of ^{13}C-NMR spectral data of **3** and **4** suggested that the rhamnoside moiety is attached to the 16-OH group in the carboxylic acid. Namely, comparing the signals at C-16 and C-15 of the carboxylic acid in **4** with those in **3**, glycosylation shifts of +5.6 ppm (C-16) and −3.2 ppm (C-15) were observed.

The anomeric configuration of the terminal L-rhamnoside linkage was considered to be α on the basis of the comparison of ^{13}C-NMR spectral data of **4** with those of crocosmioside A (**7**).

Based on the above evidence, the structure of crocosmioside F, except for the absolute configurations of the 2- and 9-OH groups in the carboxylic acid moiety, was determined as 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-28-*O*-{2-*O*-[β-D-apio-D-furanosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-3-*O*-(β-D-glucopyranosyl)-4-*O*-(2,9-dihydroxy-16-α-L-rhamnopyranosyloxyhexadecanoyl)-β-D-fucopyranosyl}-polygalacic acid (**4**).

Crocosmioside G (**5**) revealed the $(M+Na)^+$ ion peak at *m/z* 2101, which is 146 mass units (deoxyhexose) more than that of **1**, and a fragment ion peak at *m/z* 821 in the positive ion FAB-MS. The IR spectrum showed absorption bands ascribable to hydroxyl, ester and carbonyl functions. The ^{1}H-NMR spectrum showed three secondary methyl signals ascribable to deoxyhexose and nine anomeric proton sig-

nals. The ^{13}C-NMR spectrum also showed nine anomeric carbon signals, two ester carbon signals and a carbonyl carbon signal at δ 214.7. By detailed comparisons of the ^{1}H- and ^{13}C-NMR spectra of **5** with those of **1**, the structure of **5** was presumed to have a terminal rhamnopyranosyl moiety in addition to that of **1**.

The positions of hydroxy and carbonyl groups in the carboxylic acid moiety were confirmed from the ^{1}H- and ^{13}C-NMR spectra of **5** and the MS fragmentation of the methyl ester TMS ether (**13**) derived from **5** (Chart 4).

On enzymatic hydrolysis with naringinase, **5** yielded **1** and L-rhamnose. The hydrolyzate (**1**) was identified by comparison of the physical constants and ^{1}H- and ^{13}C-NMR spectra with those of crocosmioside C. The linkage site of the rhamnoside moiety in **5** was determined to be the 16-OH group on the basis of the comparison of the ^{13}C-NMR data of **1** and **5**. Namely, comparing the signals at C-16 and C-15 of carboxylic acid in **5** with those in **1**, glycosylation shifts of +5.6 ppm (C-16) and −3.3 ppm (C-15) were observed. The anomeric configuration of the L-rhamnoside linkage was defined as α on the basis of the comparison of the ^{13}C-NMR data of **5** and crocosmioside A (**7**).

Based on the above evidence, the structure of crocosmioside G (**5**), except for the absolute configuration of the 2-OH group in the carboxylic acid moiety, was elucidated as 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-28-*O*-{2-*O*-[β-D-apio-D-furanosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-3-*O*-(β-D-glucopyranosyl)-4-*O*-(9-oxo-16-α-L-rhamnopyranosyloxy-2-β-D-xylopyranosyloxyhexadecanoyl)-β-D-fucopyranosyl}-polygalacic acid (**5**).

The positive ion FAB-MS of crocosmioside I (**6**) revealed the $(M+Na)^+$ ion peak at *m/z* 1839, which is 132 mass units (pentose) less than that of **4**, and a fragment ion peak at *m/z* 821. The ^{1}H-NMR spectrum of **6** showed signals of six tertiary methyl and three secondary methyl groups in analogy with those of **4**. But it lacked the anomeric proton signal at δ 5.05 (1H, d, J=3.0 Hz) which was observed in **4**. Detailed comparisons of the ^{1}H- and ^{13}C-NMR spectra of **6** with those of **4** suggested that those of **6** lack the signals due to an apiofuranosyl moiety.

In order to ascertain the structure of **6**, **4** was hydrolyzed with 2 N HCl at room temperature. The hydrolyzate (**6**) was identified by comparison of physical constants and ^{1}H- and ^{13}C-NMR spectra with those of crocosmioside I.

Based on the above evidence, the structure of crocosmioside I, except for the absolute configurations of the 2- and 9-OH groups in the carboxylic acid moiety, was concluded to be 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]-28-*O*-{2-*O*-[β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-3-*O*-(β-D-glucopyranosyl)-4-*O*-(2,9-dihydroxy-16-α-L-rhamnopyranosyloxyhexadecanoyl)-β-D-fucopyranosyl}-polygalacic acid (**6**).

The biological activities of crocosmiosides A, B, C, D, E, F, G, H and I will be reported elsewhere.

Experimental

Optical rotations were measured with a JASCO DIP-181 polarimeter in a 0.5 dm tube. IR spectra were taken on a JASCO IRA-I spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian XL-400 spectrometer. Chemical shifts are given on the δ scale (ppm). The following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet and br=broad. Coupling constants (J values) are given in hertz (Hz). HH-COSY, CH-COSY and DEPT measurements were carried out to verify the assignments in **1**—**6**, **10** and **12**. Positive ion FAB-MS were taken on a JEOL JMS DX-300. For gas liquid chromatography (GLC), a Shimadzu GC-9A gas chromatograph was used. For column chromatography, Sephadex LH-20 (Pharmacia Fine Chemicals) were used. Thin layer chromatography was performed on precoated Silica gel 60 F_{254} plates (Merck) [solvent: $CHCl_3$: MeOH : H_2O = 6 : 4 : 1] and RP-18 F_{254s} plates (Merck) [solvent: MeOH : H_2O : dioxane = 70 : 30 : 5].

Crocosmioside C (1) White powder, $[\alpha]_D^{30}$ −16.8° (c=0.88, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740, 1710. *Anal.* Calcd for $C_{90}H_{148}O_{44}\cdot 5H_2O$: C, 53.40; H, 7.37. Found: C, 53.47; H, 7.51. Positive ion FAB-MS *m/z*: 1955 $(M+Na)^+$, 1157, 821 (aglycone−Glc−Ara+Na)$^+$. ^{1}H-NMR (CD_3OD) δ: 0.79, 0.88, 0.93, 0.97, 1.28, 1.39 (each 3H, s), 1.08 (3H, d, J=6.5 Hz, Fuc-6), 1.33 (3H, d, J=6.0 Hz, Rha-6), 2.31 (1H, dd, J=13.5, 13.5 Hz, 19-H_{ax}), 2.95 (1H, dd, J=13.5, 4.0 Hz, 18-H), 3.16 (1H, dd, J=9.0, 8.0 Hz, Glc′-2), 3.58 (2H, t, J=6.5 Hz, CA-16), 3.79 (1H, d, J=10.0 Hz, Api-5H_a), 3.89 (1H, d, J=3.0 Hz, Api-2), 3.91 (1H, dd, J=9.0, 8.0 Hz, Fuc-2), 3.96 (1H, dd, J=3.5, 1.5 Hz, Rha-2), 4.03 (1H, dd, J=9.0, 3.5 Hz, Fuc-3), 4.10 (1H, d, J=10.0 Hz, Api-5H_b), 4.22 (1H, dd, J=6.5, 6.0 Hz, CA-2), 4.24 (1H, d, J=6.8 Hz, Ara-1), 4.29 (1H, d, J=7.0 Hz, Xyl′-1), 4.43 (1H, d, J=8.0 Hz, Glc-1), 4.46 (1H, br s, 16-H), 4.48 (1H, d, J=7.8 Hz, Glc′-1), 4.49 (1H, d, J=7.8 Hz, Xyl-1), 5.05 (1H, d, J=3.0 Hz, Api-1), 5.34 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.39 (1H, d, J=1.5 Hz, Rha-1), 5.43 (1H, d, J=3.5 Hz, Fuc-4), 5.44 (1H, d, J=8.0 Hz, Fuc-1); δ (C_5D_5N): 0.79, 0.83, 1.06, 1.20, 1.43, 1.59 (each 3H, s), 1.19 (3H, d, J=6.5 Hz, Fuc-6), 1.54 (3H, d, J=6.0 Hz, Rha-6), 2.60 (1H, dd, J=14.0, 13.0 Hz, 19-H_{ax}), 3.25 (1H, dd, J=14.0, 4.0 Hz, 18-H), 3.62 (1H, d, J=10.5 Hz, 23-H_a), 3.73 (2H, t, J=6.5 Hz, CA-16), 4.00 (2H, s, Api-4), 4.20 (1H, d, J=9.5 Hz, Api-5H_a), 4.26 (1H, dd, J=9.0, 3.5 Hz, Fuc-3), 4.43 (1H, dd, J=7.0, 5.0 Hz, CA-2), 4.52 (1H, d, J=9.0, 8.0 Hz, Fuc-2), 4.56 (1H, d, J=3.0 Hz, Api-2), 4.56 (1H, d, J=9.5 Hz, Api-5H_b), 4.65 (1H, d, J=7.0 Hz, Xyl′-1), 4.68 (1H, d, J=6.5 Hz, Ara-1), 4.88 (1H, d, J=7.8 Hz, Glc-1), 4.92 (1H, d, J=7.8 Hz, Glc′-1), 4.95 (1H, d, J=7.0 Hz, Xyl-1), 5.04 (1H, br s, 16-H), 5.50 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.59 (1H, d, J=3.0 Hz, Api-1), 5.87 (1H, d, J=3.5 Hz, Fuc-4), 5.91 (1H, d, J=8.0 Hz, Fuc-1), 6.31 (1H, br s, Rha-1).

Crocosmioside D (2) White powder, $[\alpha]_D^{30}$ −16.9° (c=2.03, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740. *Anal.* Calcd for $C_{90}H_{150}O_{44}\cdot 6H_2O$: C, 53.27; H, 7.40. Found: C, 52.78; H, 7.81. Positive ion FAB-MS *m/z*: 1957 $(M+Na)^+$, 1159, 821 (aglycone−Glc−Ara+Na)$^+$. ^{1}H-NMR (CD_3OD) δ: 0.79, 0.88, 0.93, 0.97, 1.28, 1.39 (each 3H, s), 1.08 (3H, d, J=6.5 Hz, Fuc-6), 1.33 (3H, d, J=6.0 Hz, Rha-6), 2.30 (1H, dd, J=13.5, 13.5 Hz, 19-H_{ax}), 2.95 (1H, dd, J=13.5, 4.0 Hz, 18-H), 3.16 (1H, dd, J=9.0, 8.0 Hz, Glc′-2), 3.54 (2H, t, J=6.5 Hz, CA-16), 3.79 (1H, d, J=10.0 Hz, Api-5H_a), 3.89 (1H, d, J=3.0 Hz, Api-2), 3.91 (1H, dd, J=9.0, 8.0 Hz, Fuc-2), 3.96 (1H, dd, J=3.5, 1.5 Hz, Rha-2), 4.03 (1H, dd, J=9.0, 3.5 Hz, Fuc-3), 4.10 (1H, d, J=10.0 Hz, Api-5H_b), 4.22 (1H, dd, J=7.0, 6.0 Hz, CA-2), 4.24 (1H, d, J=6.5 Hz, Ara-1), 4.29 (1H, d, J=7.0 Hz, Xyl′-1), 4.43 (1H, d, J=8.0 Hz, Glc-1), 4.45 (1H, br s, 16-H), 4.48 (1H, d, J=7.8 Hz, Glc′-1), 4.49 (1H, d, J=7.8 Hz, Xyl-1), 5.05 (1H, d, J=3.0 Hz, Api-1), 5.34 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.39 (1H, d, J=1.5 Hz, Rha-1), 5.43 (1H, d, J=3.5 Hz, Fuc-4), 5.43 (1H, d, J=8.0 Hz, Fuc-1).

Crocosmioside E (3) White powder, $[\alpha]_D^{21}$ −15.4° (c=0.80, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3410, 1740. *Anal.* Calcd for $C_{85}H_{142}O_{40}\cdot 3H_2O$: C, 54.94; H, 8.03. Found: C, 55.15; H, 7.90. Positive ion FAB-MS *m/z*: 1825 $(M+Na)^+$, 1027, 821 (aglycone−Glc−Ara+Na)$^+$. ^{1}H-NMR (CD_3OD) δ: 0.78, 0.88, 0.93, 0.96, 1.27, 1.39 (each 3H, s), 1.07 (3H, d, J=6.5 Hz, Fuc-6), 1.32 (3H, d, J=6.0 Hz, Rha-6), 2.30 (1H, dd, J=13.5, 13.5 Hz, 19-H_{ax}), 2.94 (1H, dd, J=13.5, 3.5 Hz, 18-H), 3.15 (1H, dd, J=9.0, 7.8 Hz, Glc′-2), 3.54 (2H, t, J=6.5 Hz, CA-16), 3.79 (1H, d, J=9.5 Hz, Api-5H_a), 3.89 (1H, d, J=3.0 Hz, Api-2), 3.92 (1H, dd, J=9.5, 8.0 Hz, Fuc-2), 3.96 (1H, dd, J=3.5, 1.5 Hz, Rha-2), 4.05 (1H, dd, J=9.5, 3.5 Hz, Fuc-3), 4.10 (1H, d, J=9.5 Hz, Api-5H_b), 4.23 (1H, dd, J=7.5, 5.0 Hz, CA-2), 4.24 (1H, d, J=6.5 Hz, Ara-1), 4.43 (1H, d, J=7.8 Hz, Glc-1), 4.45 (1H, br s, 16-H), 4.48 (1H, d, J=7.8 Hz, Glc′-1), 4.49 (1H, d, J=7.8 Hz, Xyl-1), 5.05 (1H, d, J=3.0 Hz, Api-1), 5.33 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.40 (1H, d, J=3.5 Hz, Fuc-4), 5.40 (1H, d, J=1.5 Hz, Rha-1), 5.44 (1H, d, J=8.0 Hz, Fuc-1).

Crocosmioside F (4) White powder, $[\alpha]_D^{21}$ −20.4° (c=0.83, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3410, 1740. *Anal.* Calcd for $C_{91}H_{152}O_{44}\cdot 4H_2O$: C, 54.05; H, 7.98. Found: C, 53.91; H, 7.91. Positive ion FAB-MS *m/z*: 1971 $(M+Na)^+$, 1173, 821 (aglycone−Glc−Ara+Na)$^+$. ^{1}H-NMR (CD_3OD) δ: 0.79, 0.88, 0.93, 0.96, 1.27, 1.39 (each 3H, s), 1.07 (3H, d, J=6.5 Hz, Fuc-6), 1.26 (1H, d, J=6.0 Hz, Rha′-6), 1.32 (3H, d, J=6.0 Hz, Rha-6), 2.30 (1H, dd, J=13.5, 13.5 Hz, 19-H_{ax}), 2.94 (1H, dd, J=13.5, 4.0 Hz, 18-

H), 3.15 (1H, dd, J=9.0, 7.8 Hz, Glc′-2), 3.79 (1H, d, J=9.5 Hz, Api-5H$_a$), 3.89 (1H, d, J=3.0 Hz, Api-2), 3.92 (1H, dd, J=9.5, 8.0 Hz, Fuc-2), 3.96 (1H, dd, J=3.0, 1.5 Hz, Rha-2), 4.05 (1H, dd, J=9.5, 3.5 Hz, Fuc-3), 4.10 (1H, d, J=9.5 Hz, Api-5H$_b$), 4.23 (1H, dd, J=7.5, 5.0 Hz, CA-2), 4.25 (1H, d, J=6.5 Hz, Ara-1), 4.43 (1H, d, J=7.8 Hz, Glc-1), 4.46 (1H, br s, 16-H), 4.48 (1H, d, J=7.8 Hz, Glc′-1), 4.50 (1H, d, J=7.8 Hz, Xyl-1), 4.65 (1H, d, J=1.5 Hz, Rha′-1), 5.05 (1H, d, J=3.0 Hz, Api-1), 5.33 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.39 (1H, d, J=3.5 Hz, Fuc-4), 5.40 (1H, d, J=1.5 Hz, Rha-1), 5.44 (1H, d, J=8.0 Hz, Fuc-1).

Crocosmioside G (5) White powder, $[\alpha]_D^{20}$ −20.8° (c=0.48, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740, 1710. *Anal.* Calcd for $C_{96}H_{158}O_{48}\cdot 2H_2O$: C, 54.48; H, 7.71. Found: C, 54.40; H, 7.80. Positive ion FAB-MS m/z: 2101 (M+Na)$^+$, 1303, 821 (aglycone−Glc−Ara+Na)$^+$. ^{1}H-NMR (CD_3OD) δ: 0.79, 0.88, 0.93, 0.97, 1.27, 1.39 (each 3H, s), 1.08 (3H, d, J=6.5 Hz, Fuc-6), 1.25 (3H, d, J=6.0 Hz, Rha′-6), 1.32 (3H, d, J=6.0 Hz, Rha-6), 2.30 (1H, dd, J=13.5, 13.5 Hz, 19-H$_{ax}$), 2.95 (1H, dd, J=13.5, 3.5 Hz, 18-H), 3.16 (1H, dd, J=9.5, 7.8 Hz, Glc′-2), 3.79 (1H, d, J=10.0 Hz, Api-5H$_a$), 3.89 (1H, d, J=3.0 Hz, Api-2), 3.91 (1H, dd, J=9.0, 8.0 Hz, Fuc-2), 3.96 (1H, dd, J=3.0, 1.5 Hz, Rha-2), 4.02 (1H, dd, J=9.0, 3.5 Hz, Fuc-3), 4.10 (1H, d, J=10.0 Hz, Api-5H$_b$), 4.22 (1H, dd, J=7.0 Hz, 5.5 Hz, CA-2), 4.25 (1H, d, J=6.5 Hz, Ara-1), 4.30 (1H, d, J=7.0 Hz, Xyl′-1), 4.43 (1H, d, J=7.8 Hz, Glc-1), 4.46 (1H, br s, 16-H), 4.49 (1H, d, J=7.8 Hz, Glc′-1), 4.49 (1H, d, J=7.8 Hz, Xyl-1), 4.65 (1H, d, J=1.5 Hz, Rha′-1), 5.05 (1H, d, J=3.0 Hz, Api-1), 5.34 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.40 (1H, d, J=1.5 Hz, Rha-1), 5.44 (1H, d, J=3.5 Hz, Fuc-4), 5.44 (1H, d, J=8.0 Hz, Fuc-1).

Crocosmioside I (6) White powder, $[\alpha]_D^{20}$ −10.5° (c=0.42, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3420, 1735. *Anal.* Calcd for $C_{86}H_{144}O_{40}\cdot 3H_2O$: C, 55.17; H, 8.08. Found: C, 55.31; H, 8.09. Positive ion FAB-MS m/z: 1839 (M+Na)$^+$, 1041, 821 (aglycone−Glc−Ara+Na)$^+$. ^{1}H-NMR (CD_3OD) δ: 0.78, 0.88, 0.92, 0.97, 1.27, 1.39 (each 3H, s), 1.07 (3H, d, J=6.5 Hz, Fuc-6), 1.25 (1H, d, J=6.0 Hz, Rha′-6), 1.32 (3H, d, J=6.0 Hz, Rha-6), 2.30 (1H, dd, J=13.5, 13.5 Hz, 19-H$_{ax}$), 2.95 (1H, dd, J=13.5, 3.5 Hz, 18-H), 3.15 (1H, dd, J=9.0, 7.8 Hz, Glc′-2), 3.78 (1H, dd, J=3.5, 1.5 Hz, Rha′-2), 3.93 (1H, dd, J=9.0, 8.0 Hz, Fuc-2), 3.95 (1H, dd, J=3.5, 1.5 Hz, Rha-2), 4.05 (1H, dd, J=9.0, 3.5 Hz, Fuc-3), 4.23 (1H, dd, J=7.5, 5.0 Hz, CA-2), 4.25 (1H, d, J=6.5 Hz, Ara-1), 4.43 (1H, d, J=8.0 Hz, Glc-1), 4.45 (1H, br s, 16-H), 4.48 (1H, d, J=7.8 Hz, Glc′-1), 4.48 (1H, d, J=7.8 Hz, Xyl-1), 4.65 (1H, d, J=1.5 Hz, Rha′-1), 5.33 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.40 (1H, d, J=3.5 Hz, Fuc-4), 5.41 (1H, d, J=1.5 Hz, Rha-1), 5.43 (1H, d, J=8.0 Hz, Fuc-1).

Acidic Hydrolysis of 1 and Identification of Component Sugars and D-L Series A solution of **1** (15 mg) in 2 N HCl–dioxane (1 : 1, 2 ml) was heated under N_2 gas at 100 °C for 1 h. The reaction mixture was diluted with H_2O and evaporated to remove dioxane. The solution was extracted with EtOAc and the extract was treated with excess diazomethane in ether–MeOH. The methylated extract was purified by high performance liquid chromatography (HPLC) to give **10** (1.1 mg). Conditions of HPLC: column, Senshu Pak NP-118 (10×300 mm); solvent, 85% MeOH; flow rate, 3 ml/min; detection, RI (32×). Identification of **10** as methyl polygalacate was established by comparison of the IR, ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample. **10**: IR ν_{max}^{KBr} cm^{-1}: 3430, 1710. ^{1}H-NMR (C_5D_5N) δ: 0.86, 0.87, 0.96, 1.27, 1.55, 1.63 (each 3H, s), 2.63 (1H, dd, J=14.0, 13.0 Hz, 19-H), 3.29 (1H, dd, J=14.0, 14.0 Hz, 18-H), 3.58 (3H, s, OC$\underline{H}_3$), 3.59 (1H, d, J=4.0, 3.5, 3.5 Hz, 3-H), 5.46 (1H, dd, J=3.5, 3.5 Hz, 12-H), 6.34 (1H, d, J=5.0 Hz, 16-O$\underline{H}$).

The aqueous layer was neutralized with Amberlite IRA-93 (OH^- form) to give a sugar fraction. Half of the sugar fraction in 2 ml of H_2O was reduced with $NaBH_4$ (25 mg) at room temperature for 2 h. The reaction mixture was acidified by the use of Dowex 50W-X8 (H^+ form) and concentrated to dryness. Boric acid in the residue was removed by repeated co-distillation with MeOH. The resulting alditol mixture was acetylated with Ac_2O–C_5H_5N (1 : 1, 2 ml) and *p*-dimethylaminopyridine (20 mg) at room temperature overnight. The reagent was removed by co-distillation with toluene. The alditol acetate mixture worked up in the usual manner was subjected to GLC: glass column (2.3 mm×2 m) packed with 3% ECNSS-M on Gaschrom Q; detector, FID; injection temperature, 220 °C; column temperature, 195 °C; carrier gas, N_2 (50 ml/min). Retention times (min) of alditol acetates: rhamnitol acetate 9.2, fucitol acetate 10.1, arabinitol acetate 15.4, apitol acetate 20.0, xylitol acetate 21.2 and glucitol acetate 52.9.

A solution of the remaining sugar fraction in 1 ml of H_2O was treated with a solution of L(−)-α-methylbenzylamine (150 μl) and $NaBH_3CN$ (8 mg) in 1 ml of EtOH, and the mixture was kept at 40 °C for 3 h. Then several drops of acetic acid were added, and the mixture was concentrated to dryness. The residue was acetylated under the same conditions as used for alditols to give the acetate mixture. It was loaded into a SEP-PAK C_{18} cartridge (Waters) and eluted with 20% CH_3CN (total 7 ml) and 100% CH_3CN. The latter eluate was analyzed by normal- and reversed-phase HPLC. Conditions of normal-phase HPLC: column, Senshu Pak Silica-4301-N 5 μm (10×300 mm); solvent, hexane–EtOH (95 : 5); flow rate, 4 ml/min; detection, UV (230 nm). Retention times (min) of 1-(L(−)-*N*-acetyl-α-methylbenzylamino)-1-deoxyalditol acetates: L-rhamnose 25.9, D-fucose 28.7, L-arabinose 36.1, D-xylose and D-apiose 41.2, D-glucose 41.2, (reference: D-rhamnose 23.3, L-fucose 24.5, D-arabinose 32.1, L-apiose 37.1, L-xylose 38.0, L-glucose 39.6). Conditions of reversed-phase HPLC: column: Senshu Pak NP-118; solvent, 40% CH_3CN; flow rate, 3 ml/min; detection, UV (230 nm). Retention times (min) of 1-(L(−)-*N*-acetyl-α-methylbenzylamino)-1-deoxyalditol acetates: L-arabinose 22.0, D-xylose and D-apiose 23.1, D-fucose 26.0, D-glucose 29.4, L-rhamnose 33.4, (reference: D-arabinose 23.0, L-xylose 22.4, L-apiose 23.1, L-fucose 28.0, L-glucose 28.0, D-rhamnose 33.4). 1-(L(−)-*N*-acetyl-α-methylbenzylamino)-1-deoxyalditol acetates were identified by direct comparison with authentic specimens.

Hydrolysis of 1 with 0.5% $NaHCO_3$ A solution of **1** (31.2 mg) in 1% $NaHCO_3$–EtOH (1 : 1, 6 ml) was refluxed for 45 min. The reaction mixture was neutralized with Dowex 50W-X8 (H^+ form), and evaporated to remove EtOH. The solution was passed through a Diaion HP-20 column and eluted with H_2O and MeOH. The MeOH eluate was subjected to HPLC to give **12** (17.8 mg) and a carboxylic acid glycoside fraction. Conditions of HPLC: column, Senshu Pak NP-118; solvent, 35% dioxane; flow rate, 3 ml/min. The carboxylic acid glycoside fraction was further purified by a Sephadex LH-20 column (10×480 mm) [solvent: 100% MeOH] to give **11** (4.4 mg). **11**: White powder, $[\alpha]_D^{27}$ −21.7° (c=0.24, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3340, 1735, 1705. Positive ion FAB-MS m/z: 457 (M+Na)$^+$. ^{1}H-NMR (C_5D_5N) δ: 3.61 (1H, dd, J=11.5, 9.5 Hz, Xyl-5H$_{ax}$), 3.73 (2H, t, J=6.0 Hz, 16-H), 4.01 (1H, dd, J=8.5, 7.0 Hz, Xyl-2), 4.24 (1H, dd, J=11.5, 5.0 Hz, Xyl-5H$_{eq}$), 4.60 (1H, dd, J=6.3, 6.3 Hz, 2-H), 4.88 (1H, d, J=7.0 Hz, Xyl-1). **12**: White powder, $[\alpha]_D^{27}$ −19.0° (c=1.78, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740. Positive ion FAB-MS m/z: 1539 (M+Na)$^+$, 821 (aglycone−Glc−Ara+Na)$^+$, 741. ^{1}H-NMR (C_5D_5N) δ: 0.81, 0.84, 1.09, 1.20, 1.43, 1.60 (each 3H, s), 1.23 (3H, d, J=6.5 Hz, Fuc-6), 1.47 (3H, d, J=6.0 Hz, Rha-6), 2.61 (1H, dd, J=14.0, 13.0 Hz, 19-H$_{ax}$), 3.26 (1H, dd, J=14.0, 4.0 Hz, 18-H), 3.61 (1H, d, J=10.5 Hz, 23-H$_a$), 4.00 (2H, s, Api-4), 4.11 (1H, dd, J=9.0, 3.5 Hz, Fuc-3), 4.19 (1H, d, J=9.0 Hz, Api-5H$_a$), 4.30 (1H, d, J=3.5 Hz, Fuc-4), 4.32 (1H, dd, J=8.0, 6.5 Hz, Ara-2), 4.55 (1H, d, J=3.0 Hz, Api-2), 4.56 (1H, d, J=9.0 Hz, Api-5H$_b$), 4.63 (1H, dd, J=9.0, 8.0 Hz, Fuc-2), 4.69 (1H, d, J=6.5 Hz, Ara-1), 4.89 (1H, d, J=7.8 Hz, Glc-1), 4.96 (1H, d, J=7.0 Hz, Xyl-1, 5.00 (1H, d, J=7.8 Hz, Glc′-1), 5.07 (1H, br s, 16-H), 5.47 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.58 (1H, d, J=3.0 Hz, Api-1), 5.86 (1H, d, J=8.0 Hz, Fuc-1), 6.30 (1H, br s, Rha-1). The hydrolyzate (**12**) was identical with desacylmasonoside I obtained from *Crocosmia masonorum* on the basis of $[\alpha]_D$, FAB-MS, ^{1}H- and ^{13}C-NMR spectral data.

Preparation of Trimethylsilyl Ether (13) from 11 Hesperidinase (4.0 mg) was added to a solution of **11** (0.3 mg) in H_2O (0.2 ml). The reaction mixture was incubated at 37 °C for 2 d, applied to a SEP-PAK C_{18} cartridge and eluted with H_2O and MeOH. The MeOH eluate was reduced with $NaBH_3CN$ (10 mg) in MeOH–AcOH (9 : 1, 2 ml) at room temperature for 3 h. The solution was evaporated to dryness and the residue was esterified by treatment with excess diazomethane in ether–MeOH. The methyl ester in pyridine (0.2 ml) was treated with *N,O*-bis(trimethylsilyl)-acetamide (BSA) (50 μl) to give TMS ether (**13**). Compound **13** was subjected to GC-MS, on a JEOL JMS DX-300 spectrometer equipped with a glass column (2.3 mm×2 m) packed with 1% SE-30 on Gas chrom Q at 200 °C, and operated at an ionization voltage of 70 eV. Retention time of **13** (min): 22.5. **13**: EI-MS m/z (%): 519 (M−15, 5), 475 (4), 347 (100), 289 (68), 103 (23).

Methylation Analysis by GC-MS According to Hakomori's method, NaH (1.5 g) was stirred with dimethyl sulfoxide (DMSO, 15 ml) at 65 °C for 1 h under N_2 gas flow. This reagent (methylsulfinyl carbanion, 0.5 ml) was added to a solution of saponin (2 mg) in DMSO (1 ml) and the mixture was sonicated at room temperature for 1 h. To this solution, CH_3I (1 ml) was added under cooling and the mixture was further sonicated at room temperature for 1 h. Then CH_3I was removed by blowing N_2 gas under heating. The solution was diluted with H_2O under cooling and was passed through a SEP-PAK C_{18} cartridge and eluted with H_2O and MeOH. The MeOH eluate was hydrolyzed with 2 M trifluoroacetic acid at 120 °C for 1 h in a sealed tube. The reaction mixture was neutralized with Amberlite IRA-93 (OH^- form) and converted into alditol acetate under the same

conditions as described above. The partially methylated alditol acetate mixture obtained in this way was analyzed by GC-MS. GC-MS was performed on a JEOL JMS DX-300 spectrometer equipped with a glass column (2.3 mm × 2 m) packed with 1% OV-225 on Uniport HP at 170 °C, and operated at an ionization voltage of 70 eV. Relative retention times (Rt_R) of partially methylated alditol acetates were recorded on the basis of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylglucitol ($Rt_R = 1.00$, $t_R = 15.8$ min) as the standard. The Rt_R values of partially methylated alditol acetates are summarized in Table IV.

Hydrolysis of 2 with 0.5% $NaHCO_3$ A solution of **2** (30.6 mg) in 1% $NaHCO_3$–EtOH (1 : 1, 6 ml) was refluxed for 45 min. The reaction mixture was worked up in the same manner as described above to give **15** (4.2 mg) and **12** (21.2 mg). **15**: White powder, $[\alpha]_D^{27}$ −17.9° ($c = 0.39$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3370, 1730. Positive ion FAB-MS *m/z*: 459 $(M+Na)^+$. ^{1}H-NMR (C_5D_5N) δ: 3.61 (1H, dd, $J = 11.5$, 9.5 Hz, Xyl-5H_{ax}), 3.74 (2H, t, $J = 6.0$ Hz, 16-H), 4.01 (1H, dd, $J = 8.5$, 7.0 Hz, Xyl-2), 4.24 (1H, dd, $J = 11.5$, 5.0 Hz, Xyl-5H_{eq}), 4.60 (1H, dd, $J = 6.3$, 6.3 Hz, 2-H), 4.88 (1H, d, $J = 7.0$ Hz, Xyl-1). **12**: White powder, $[\alpha]_D^{27}$ −18.6° ($c = 2.12$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740. Positive ion FAB-MS *m/z*: 1539 $(M+Na)^+$, 821 (aglycone − Gly − Ara + Na)$^+$, 741.

Preparation of TMS Ether (13) from 15 Hesperidinase (4.0 mg) was added to a solution of **15** (0.3 mg) in H_2O (0.2 ml). The reaction mixture was incubated at 37 °C for 2 d, applied to a SEP-PAK C_{18} cartridge and eluted with H_2O and MeOH. The MeOH eluate was esterified by treatment with excess diazomethane in ether–MeOH. The methyl ester in pyridine (0.2 ml) was treated with BSA (50 μl) to give the TMS ether (**13**). Compound **13** was subjected to GC-MS analysis under the same conditions as described above. Retantion time of **13** (min): 22.5. **13**: EI-MS *m/z* (%): 519 (M − 15, 5), 475 (4), 347 (100), 289 (68), 103 (23).

Hydrolysis of 3 with 0.5% $NaHCO_3$ A solution of **3** (32.9 mg) in 1% $NaHCO_3$–EtOH (1 : 1, 6 ml) was refluxed for 85 min. The reaction mixture was neutralized with Dowex 50W-X8 (H^+ form), and evaporated to remove EtOH. The solution was extracted with EtOAc to give the EtOAc extract. The aqueous layer was passed through a Diaion HP-20 column and eluted with H_2O and MeOH. The MeOH eluate was subjected to HPLC to give **12** (14.9 mg). Conditions of HPLC: column, Senshu Pak NP-118; solvent, 60% MeOH: flow rate, 3 ml/min. The EtOAc extract was methylated with excess diazomethane and was subjected to HPLC to give **16** (0.9 mg). Conditions of HPLC: column, Senshu Pak NP-118; solvent, 70% MeOH; flow rate, 3 ml/min. **16**: White powder, $[\alpha]_D^{20}$ −5.6° ($c = 0.09$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3400, 1745. Positive ion FAB-MS *m/z*: 341 $(M+Na)^+$. ^{1}H-NMR (C_5D_5N) δ: 3.68 (3H, s, carbomethoxy), 3.78 (1H, m, 9-H), 3.84 (2H, t, $J = 6.0$ Hz, 16-H), 4.52 (1H, ddd, $J = 6.0$, 6.0, 6.0 Hz, 2-H). **12**: White powder, $[\alpha]_D^{27}$ −18.5° ($c = 1.49$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3420, 1740. Positive ion FAB-MS *m/z*: 1539 $(M+Na)^+$, 821 (aglycone − Glc − Ara + Na)$^+$, 741.

Preparation of TMS Ether (13) from 16 Compound **16** in pyridine (0.2 ml) was treated with BSA (50 μl) to give the TMS ether (**13**). Compound **13** was subjected to GC-MS analysis under the same conditions as described above. Retention time of **13** (min): 22.5. **13**: EI-MS *m/z* (%): 519 (M − 15, 5), 475 (4), 347 (100), 289 (68), 103 (23).

Enzymatic Hydrolysis of 4 with Naringinase Naringinase (67.3 mg, Sigma Co., Ltd.) was added to a solution of **4** (41.7 mg) in H_2O (5.5 ml), and the mixture was incubated at 37 °C for 20 h. The reaction mixture was passed through a Diaion HP-20 column and eluted with H_2O and MeOH. The MeOH eluate was subjected to HPLC to give **3** (32.9 mg). Conditions of HPLC: column, Senshu Pak Aquasil (20 × 300 nm); solvent, $CHCl_3$–MeOH–H_2O (60 : 33 : 7); flow rate, 7 ml/min. **3**: White powder, $[\alpha]_D^{21}$ −13.9° ($c = 0.59$, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3410, 1740, 1640. Positive ion FAB-MS *m/z*: 1825 $(M+Na)^+$. The hydrolyzate (**3**) was identical with a naturally occurring specimen on the basis of $[\alpha]_D$, FAB-MS, ^{1}H- and ^{13}C-NMR spectral data. The H_2O eluate was converted into 1-(L(−)-*N*-acetyl-α-methylbenzylamino)-1-deoxyalditol acetate in the same manner as described above, and was analyzed by normal- and reversed-phase HPLC. Conditions of normal-phase HPLC: column, Senshu Pak Silica-4301-N (10 × 300 mm); solvent, hexane–EtOH (92 : 8); flow rate, 4 ml/min; detection, UV (230 nm). Retention times (min) of 1-(L(−)-*N*-acetyl-α-methylbenzylamino)-1-deoxyalditol acetates: L-rhamnose 20.8, (reference: D-rhamnose 19.0). Conditions of reversed-phase HPLC: column, Senshu Pak NP-118; solvent, 40% CH_3CN; flow rate, 3 ml/min; detection, UV (230 nm). Retention times (min) of 1-(L(−)-*N*-acetyl-α-methylbenzylamino)-1-deoxyalditol acetates: L-rhamnose 33.4, (reference: D-rhamnose 33.4).

Preparation of TMS Ether (13) from 5 A solution of **5** (2.3 mg) in 1% $NaHCO_3$–EtOH (1 : 1, 1 ml) was refluxed for 1.5 h. The reaction mixture was neutralized with Dowex 50W-X8 (H^+ form), and evaporated to dryness. The reaction mixture was hydrolyzed with hesperidinase (15.2 mg) in H_2O (0.3 ml) at 37 °C for 2 d. The hydrolyzate was passed through a SEP-PAK C_{18} cartridge and eluted with H_2O and MeOH. The MeOH eluate was reduced with $NaBH_3CN$ (15.2 mg) in MeOH–AcOH (9 : 1, 2 ml) at room temperature for 3 h. The solution was evaporated to dryness and the residue was esterified by treatment with excess diazomethane in ether–MeOH. The methyl ester in pyridine (0.2 ml) was treated with BSA (50 μl) to give the TMS ether (**13**). Compound **13** was subjected to GC-MS analysis under the same conditions as described above. Retention time of **13** (min): 22.5. **13**: EI-MS *m/z* (%): 519 (M − 15, 5), 475 (4), 347 (100), 289 (68), 103 (23).

Enzymatic Hydrolysis of 5 with Naringinase Naringinase (25.0 mg) was added to a solution of **5** (16.0 mg) in H_2O (2 ml), and the mixture was incubated at 37 °C for 7 d. The reaction mixture was passed through a SEP-PAK C_{18} cartridge and eluted with H_2O and MeOH. The MeOH eluate was subjected to HPLC to give **1** (10.7 mg). Conditions of HPLC: column, μBondapak C_{18} (19 × 150 mm); solvent, dioxane–CH_3CN–H_2O (15 : 15 : 40); flow rate, 5 ml/min. **1**: White powder, $[\alpha]_D^{20}$ −16.0° ($c = 0.35$, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3410, 1740, 1710. Positive ion FAB-MS *m/z*: 1955 $(M+Na)^+$. The hydrolyzate (**1**) was identical with a naturally occurring specimen on the basis of $[\alpha]_D$, FAB-MS, ^{1}H- and ^{13}C-NMR spectral data. The H_2O eluate was converted into 1-(L(−)-*N*-acetyl-α-methylbenzylamino)-1-deoxyalditol acetate and analyzed under the same conditions as described above.

Hydrolysis of 4 with 2 N HCl A solution of **4** (32.5 mg) in 2 N HCl (3 ml) was left for 23 h at room temperature. After being diluted with H_2O, the reaction mixture was passed through a SEP-PAK C_{18} cartridge and eluted with H_2O and MeOH. The MeOH eluate was purified by HPLC to give **6** (25.6 mg). Conditions of HPLC: column, Senshu Pak NP-118; solvent, MeOH–H_2O–dioxane (65 : 35 : 5); flow rate, 3 ml/min. **6**: $[\alpha]_D^{20}$ −8.6° ($c = 0.35$, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3410, 1735. The hydrolyzate (**6**) was identical with a naturally occurring specimen on the basis of $[\alpha]_D$, FAB-MS, ^{1}H- and ^{13}C-NMR spectral data. The H_2O eluate was neutralized with Amberlite IRA-93 (OH^- form) and concentrated to dryness. The residue was subjected to HPLC to give D-apiose (1.1 mg). Conditions of HPLC: column, ERC-NH-1171 (6 × 200 mm); solvent, 85% CH_3CN; flow rate, 2 ml/min. Retention time (min) of apiose: 3.6, $[\alpha]_D^{20}$ +3.7° ($c = 0.11$, H_2O).

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