Desacylsaponins, Desacylmasonosides 1, 2 and 3, from the Corms of *Crocosmia masonorum*

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Three novel triterpene saponins named desacylmasonosides 1 (1), 2 (2) and 3 (3) have been isolated from the weak alkaline hydrolyzate of the crude saponin obtained from the corms of *Crocosmia masonorum*. On the basis of spectral and chemical evidence, their structures were characterized 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)-β-D-fucopyranosyl}polygalacic acid (1), 3-*O*-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 (2) and 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)-β-D-fucopyranosyl}polygalacic acid (3).

Keywords *Crocosmia masonorum*; Iridaceae; triterpene saponin; desacylmasonoside 1; desacylmasonoside 2; desacylmasonoside 3; polygalacic acid; enzymatic hydrolysis

Crocosmia masonorum (Iridaceae), indigenous to South Africa, has recently been cultivated as a garden plant in Japan. No phytochemical study has been reported on this plant. We have already isolated polygalacic acid as a main aglycone on acidic hydrolysis of crude saponin of its corms.[1] In this paper, we report the isolation and structural elucidation of three novel desacylsaponins obtained by mild alkaline hydrolysis of the crude saponin.

The butanol-soluble fraction of the methanolic extract of *C. masonorum* corms was treated with $NaHCO_3$. Desacylsaponin mixture was repeatedly separated by normal- and reversed-phase high-performance liquid chromatography (HPLC) to give desacylmasonosides 1 (**1**), 2 (**2**) and 3 (**3**).

Acidic hydrolysis of desacylmasonoside 1 (**1**) gave D-apiose, D-fucose, D-glucose, D-xylose, L-arabinose and L-rhamnose.[2] The D-L series of these component sugars in **1** were determined using the method of Oshima *et al.*[3] as follows: 1-(*N*-acetyl-L-α-methylbenzylamino)-1-deoxyalditol acetates derived from component sugars of **1** were identified by comparison of their retention times with those of authentic sugars in the normal- and reversed-phase HPLC. The infrared (IR) spectrum of **1** showed absorption bands due to hydroxyl and ester groups at 3400 and 1740 cm^{-1}, respectively. The positive ion fast atom bombardment mass spectrum (FAB-MS) of **1** revealed an $(M+Na)^+$ ion peak at *m/z* 1539 and a fragment ion peak at *m/z* 821 assigned to (aglycone-Glc-Ara + Na)$^+$ on the basis of evidence described hereinafter. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed signals due to six tertiary methyl groups at δ 0.81, 0.83, 1.08, 1.20, 1.42, 1.60 and two secondary methyl groups at δ 1.23 (1H, d, *J* = 6.5 Hz) and 1.47 (1H, d, *J* = 6.0 Hz). It also showed seven anomeric proton signals at δ 4.68 (1H, d, *J* = 6.5 Hz), 4.89 (1H, d, *J* = 8.0 Hz), 4.97 (1H, d, *J* = 7.2 Hz), 5.00 (1H, d, *J* = 7.8 Hz), 5.59 (1H, d, *J* = 3.0 Hz), 5.86 (1H, d, *J* = 8.0 Hz) and 6.31 (1H, br s). The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum showed seven anomeric carbon signals at δ 95.0, 101.3, 105.1, 105.6, 105.8, 106.6, 109.1 and an ester carbon signal at δ 176.3 (Tables I and II). On methylation followed by successive hydrolysis, reduction and acetylation, **1** afforded partially methylated alditol acetates attributable to 6-linked glucopyranoside, terminal arabinopyranoside, 2,3-linked fucopyranoside, 4-linked rhamnopyranoside, 2- or 4-linked xylopyranoside, terminal apiofuranoside and terminal glucopyranoside. Their partially methylated alditol acetates were identified by comparison of retention times and MS fragmentation patterns with those of authentic specimens[4] in gas chromatography-mass spectrometry (GC-MS). On treatment with anhydrous LiI, 2,6-lutidine and anhydrous methanol,[5] **1** yielded a hydrolyzate (**4**) and a methyl glycoside (**5**). The positive ion FAB-MS of **4** showed a pseudo-molecular ion peak at *m/z* 821 $(M+Na)^+$. The ^{1}H-NMR spectrum of **4** exhibited signals due to six tertiary methyl groups at δ 0.92, 0.97, 1.05, 1.22, 1.45, 1.66, a hydroxymethyl group at δ 3.53, 4.19 (each 1H, d, *J* = 10.5 Hz, 23-H), three methine protons at δ

TABLE I. ^{13}C-NMR Chemical Shifts of Aglycone Moieties of Desacylmasonosides 1 (**1**), 2 (**2**), 3 (**3**) and Related Compounds in C_5D_5N

Carbon No.	1	2	3	4	6	7	8	9
1	44.4	44.5	44.4	44.3	45.3	45.3	44.5	44.5
2	70.1	70.7	70.1	70.2	71.8	71.8	70.8	70.8
3	84.5	83.3	84.4	84.2	73.5	73.5	83.1	83.1
4	43.0	43.0	43.0	43.0	42.6	42.6	43.0	43.0
5	48.0	48.2	47.9	47.8	48.7	48.7	48.2	48.1
6	18.5	18.4	18.5	18.4	18.8	18.8	18.3	18.3
7	33.5	33.5	33.5	33.4	33.5	33.6	33.6	33.5
8	40.4	40.4	40.4	40.2	40.4	40.4	40.4	40.4
9	47.7	47.7	47.7	47.7	47.8	47.8	47.7	47.7
10	37.2	37.2	37.2	37.2	37.5	37.5	37.2	37.2
11	24.2	24.2	24.2	24.2	24.2	24.2	24.2	24.2
12	122.8	122.7	122.8	122.8	122.7	122.7	122.7	122.7
13	144.6	144.7	144.6	145.2	144.7	144.7	144.7	144.7
14	42.5	42.5	42.5	42.4	42.5	42.5	42.5	42.5
15	36.4	36.4	36.4	36.3	36.4	36.5	36.4	36.4
16	74.1	74.0	74.1	74.9	74.2	74.0	74.1	73.8
17	49.6	49.5	49.5	49.0	49.5	49.6	49.5	49.6
18	41.9	41.9	41.9	41.6	41.8	41.9	41.8	41.8
19	47.7	47.6	47.7	47.4	47.6	47.7	47.8	47.8
20	30.9	30.9	30.9	31.2	30.9	30.9	30.9	30.9
21	36.2	36.2	36.2	36.4	36.2	36.2	36.2	36.2
22	32.0	32.0	32.0	33.0	32.1	32.0	32.0	31.8
23	66.3	65.9	66.3	66.0	68.2	68.2	65.8	65.7
24	15.4	15.2	15.4	15.4	14.8	14.8	15.3	15.2
25	17.8	17.7	17.7	17.7	17.7	17.7	17.7	17.7
26	17.7	17.6	17.7	17.6	17.7	17.7	17.6	17.6
27	27.3	27.3	27.2	27.4	27.3	27.3	27.3	27.2
28	176.3	176.2	176.2	180.2	176.2	176.2	176.2	176.3
29	33.3	33.3	33.3	33.5	33.3	33.3	33.3	33.3
30	24.6	24.6	24.6	24.9	24.6	24.6	24.6	24.6

Table II. ^{13}C-NMR Chemical Shifts of Sugar Moieties of Desacylmasonosides 1 (**1**), 2 (**2**), 3 (**3**) and Related Compounds in C_5D_5N

Sugar		1	2	3	4	6	7	8	9
C-3									
Glc	1	105.6	105.8	105.6	105.7			105.9	105.9
Glc	2	75.5	75.6	75.4	75.5			75.7	75.7
Glc	3	78.7	78.7[a]	78.7	78.7			78.7[a]	78.7[a]
Glc	4	72.2	71.7	72.2	72.2			71.7	71.7
Glc	5	76.7	78.4[a]	76.7	76.7			78.4[a]	78.4[a]
Glc	6	69.8	62.7	69.7	69.7			62.7	62.8
Ara	1	105.1		105.0	105.1				
Ara	2	72.6		72.6	72.6				
Ara	3	74.4		74.3	74.4				
Ara	4	69.2		69.2	69.2				
Ara	5	66.6		66.5	66.5				
C-28									
Fuc	1	95.0	94.9	94.9		95.0	94.9	94.9	95.0
Fuc	2	72.5	72.5	72.4		73.7	72.7	72.4	73.1
Fuc	3	85.6	85.5	85.6		76.9	85.6	85.6	85.2
Fuc	4	72.5	72.4	72.4		73.4	72.4	72.6	72.5
Fuc	5	72.2	72.1	72.1		72.7	72.1	72.1	72.1
Fuc	6	17.0	17.0	17.0		17.1	17.0	17.0	17.0
Rha	1	101.3	101.3	101.3		101.3	101.4	101.3	101.9
Rha	2	72.1	72.2	72.3		72.1	72.2	72.3	72.5
Rha	3	72.6	72.5	72.5		72.7	72.5	72.5	72.5
Rha	4	83.7	83.6	83.4		83.7	83.9	83.3	74.0
Rha	5	68.5	68.5	68.6		68.3	68.5	68.6	70.2
Rha	6	18.7	18.6	18.7		18.6	18.7	18.7	18.9
Xyl	1	106.6	106.6	106.8		106.5	106.7	106.8	
Xyl	2	76.1	76.0	76.2		76.2	76.1	76.2	
Xyl	3	76.4[b]	76.4[b]	78.7		76.4[b]	76.4[b]	78.7	
Xyl	4	76.5[b]	76.5[b]	71.1		76.6[b]	76.5[b]	71.2	
Xyl	5	64.5	64.5	67.5		64.5	64.4	67.5	
Api	1	109.1	109.1			109.1	109.1		
Api	2	77.7	77.7			77.7	77.7		
Api	3	80.5	80.4			80.4	80.5		
Api	4	65.3	65.3			65.3	65.3		
Api	5	75.4	75.3			75.4	75.4		
Glc′	1	105.8	105.7	105.7			105.7	105.8	105.7
Glc′	2	75.1	75.1	75.1			75.1	75.1	75.1
Glc′	3	78.7	78.7	78.7			78.7	78.7	78.7
Glc′	4	71.7	71.7	71.7			71.7	71.7	71.7
Glc′	5	78.7	78.7	78.7			78.7	78.7	78.7
Glc′	6	62.7	62.7	62.7			62.7	62.7	62.7

a, 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.

Table III. ^{1}H-NMR Chemical Shifts and Coupling Constants of Anomeric Protons in the Methyl Glycoside (**5**)

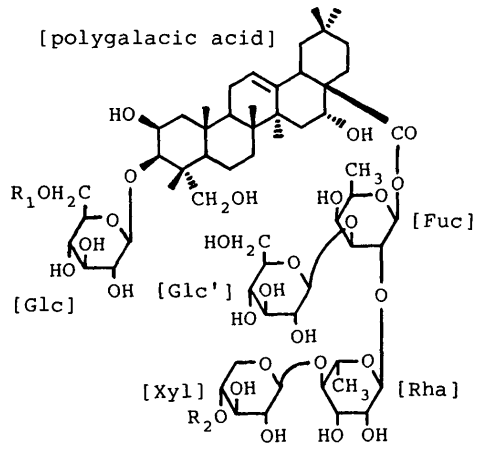
	α-Glycoside	β-Glycoside
Fuc	5.05 (2/3H, d, J=2.5 Hz)	4.35 (1/3H, d, J=8.0 Hz)
Rha	5.42 (2/3H, d, J=1.0 Hz)	5.93 (1/3H, d, J=1.0 Hz)
Xyl	4.97 (2/3H, d, J=8.0 Hz)	5.00 (1/3H, d, J=8.0 Hz)
Api	5.63 (2/3H, d, J=3.0 Hz)	5.63 (1/3H, d, J=3.0 Hz)
Glc	5.09 (2/3H, d, J=8.0 Hz)	5.09 (1/3H, d, J=8.0 Hz)
OMe	3.20 (2H, s)	3.37 (1H, s)

Table IV. ^{13}C-NMR Chemical Shifts of the Methyl Glycoside (**5**) in C_5D_5N[a]

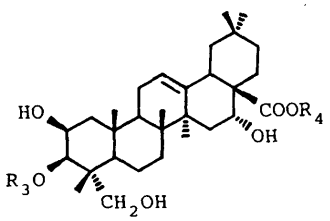
Sugar moiety	α-Glycoside	β-Glycoside	Sugar moiety	α-Glycoside	β-Glycoside
Fuc 1	100.7	103.7	Xyl 1	107.0	107.0
Fuc 2	77.9	76.1	Xyl 2	76.1	76.2
Fuc 3	78.4	84.4	Xyl 3	76.5[b]	76.6
Fuc 4	73.0	72.5	Xyl 4	76.6[b]	76.6
Fuc 5	66.6	71.0	Xyl 5	64.6	64.6
Fuc 6	17.0	17.1	Api 1	109.2	109.2
OMe	54.9	56.1	Api 2	77.7	77.7
Rha 1	104.6	102.7	Api 3	80.5	80.5
Rha 2	71.6	72.2	Api 4	65.3	65.3
Rha 3	72.8	73.0	Api 5	75.4	75.4
Rha 4	84.6	85.2	Glc 1	106.2	106.3
Rha 5	68.1	67.8	Glc 2	75.3	75.0
Rha 6	18.6	18.3	Glc 3	78.5[c]	78.6[c]
			Glc 4	71.7	71.7
			Glc 5	78.3[c]	78.2[c]
			Glc 6	62.7	62.7

a) Assignments of signals were achieved by analyses of the HH- and CH-COSY spectra and by comparison with reference data. *b—c*) Assignments may be interchangeable within the same column.

4.17 (1H, d, J=3.0 Hz, 3-H), 4.73 (1H, ddd, J=3.5, 3.0, 3.0 Hz, 2-H), 5.12 (1H, br s, 16-H) and an olefinic proton at δ 5.55 (1H, dd, J=3.0, 3.0 Hz, 12-H). It also showed two anomeric proton signals at δ 4.71 (1H, d, J=6.5 Hz, Ara-1-H) and 4.92 (1H, d, J=8.0 Hz, Glc-1-H). In the ^{13}C-NMR spectrum, a downfield shift of the C-6 signal of glucose to δ 69.7 was observed, indicating that arabinopyranose is linked to C-6 of the glucopyranosyl moiety (Table II). The hydrolyzate (**4**) was identical with 3-*O*-[α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl]polygalacic acid obtained from montbretia.[6] A comparison of the ^{13}C-NMR spectrum of **1** with that of **4** revealed that the 28-ester carbon signal was shifted upfield by 3.9 ppm,[7] suggesting that **1** is polygalacic acid 3,28-*O*-bisglycoside. The positive ion FAB-MS of **5** revealed a pseudo-molecular ion peak at m/z 773 $(M+Na)^+$. The ^{1}H-NMR spectrum of the methyl glycoside (**5**) showed signals of two anomeric protons due to α- and β-methyl fucopyranoside moieties at δ 5.05 (2/3H, d, J=2.5 Hz) and 4.35 (1/3H, d, J=8.0 Hz), suggesting that **5** is an α- and β-anomeric mixture in a ratio of 2:1 (Table III). Then, the result of methylation analysis of **5** indicated the presence of 2,3-linked fucopyranoside, 4-linked rhamnopyranoside, 2- or 4-linked xylopyranoside, terminal apiofuranoside and terminal glucopyranoside. In the ^{13}C-NMR spectrum, carbon signals attributable to α- and β-methyl glycosides were observed in a ratio of 2:1, respectively. The differences of chemical shifts between these carbons, induced by α- and β-methoxyl groups, decreased in the order of fucoside, rhamnoside and xyloside or glucoside moieties, but they were not observed any longer in the apioside moiety (Table IV). Assignments of carbon signals in **5** were achieved by analyses of the ^{1}H–^{1}H homonuclear and ^{13}C–^{1}H heteronuclear shift correlation 2D spectra (HH- and CH-COSY) and by comparison of the spectral data with those of partial hydrolyzates of **1** described hereinafter and reference data.[8] On the other hand, enzymatic hydrolysis of **1** with hesperidinase[9] gave two hydrolyzates (**6**), m/z 1083 $(M+Na)^+$ and **7**, m/z 1245 $(M+Na)^+$. The result of methylation analysis of **6** indicated the presence of 2-linked fucopyranoside, 4-linked rhamnopyranoside, 4-linked xylopyranoside and terminal apiofuranoside. The ^{1}H-NMR spectrum of **6** showed two secondary methyl groups at δ 1.24 (1H, d, J=6.5 Hz), 1.47 (1H, d, J=6.0 Hz) and four anomeric proton signals at δ 5.03 (1H, d, J=7.2 Hz), 5.60 (1H, d, J=3.0 Hz), 5.89 (1H, d, J=8.0 Hz) and 6.35 (1H, d, J=1.5 Hz). The ^{13}C-NMR spectrum of **6** also exhibited four anomeric carbon signals

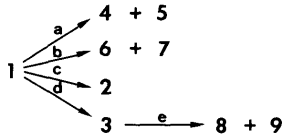


desacylmasonoside 1 (**1**):R_1=-Ara, R_2=-Api
desacylmasonoside 2 (**2**):R_1=-H, R_2=-Api
desacylmasonoside 3 (**3**):R_1=-Ara, R_2=-H



4:R_3=-Glc^6-Ara, R_4=-H
6:R_3=-H, R_4=-Fuc^2-Rha^4-Xyl^4-Api
7:R_3=-H, R_4=-Fuc^2(Glc'^{3})-Rha^4-Xyl^4-Api
8:R_3=-Glc, R_4=-Fuc^2(Glc'^{3})-Rha^4-Xyl
9:R_3=-Glc, R_4=-Fuc^2(Glc'^{3})-Rha
5:MeO-Fuc^2(Glc^3)-Rha^4-Xyl^4-Api

Chart 1. Structures of Desacylmasonosides 1, 2, 3 and Related Compounds



a: LiI, dry MeOH, 2,6-lutidine
b: hesperidinase
c: emulsin
d: 2 N HCl
e: emulsin

Chart 2. Degradation of Desacylmasonoside 1 (**1**)

and suggested that **6** is polygalacic acid 28-*O*-glycoside (Tables I and II). On the basis of these results, **6** is identical with 28-*O*-{2-*O*-[β-D-apio-D-furanosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl]-β-D-fucopyranosyl}polygalacic acid[10] obtained from crocosmioside A. In the ^{13}C-NMR spectrum of **7**, five anomeric anomeric carbon signals were observed. In a comparison of the ^{13}C-NMR spectrum of **7** with that of **6**, the glycosylation shifts[11] were observed for the carbon signals due to C-2 (−1.0 ppm), C-3 (+8.7 ppm) and C-4 (−1.0 ppm) of the fucopyranosyl moiety, suggesting that the glucopyranose in **7** is linked to the C-3 position of the fucopyranosyl moiety. The ^{1}H-NMR spectrum of **7** showed five anomeric proton signals which are larger by one anomeric proton signal than that of **6** and the signals at δ 5.00 (1H, d, J= 7.8 Hz) was assigned to the anomeric proton of β-glucopyranose on the basis of analyses of the HH- and CH-COSY spectra and a comparison of ^{1}H-NMR spectra of **6** and **7** as described in Experimental. Consequently, the structure of **7** was elucidated as shown in Chart 1. On the other hand, a comparison of the ^{13}C-NMR spectra of **1** and **7** showed glycosylation shifts for the carbon signals due to C-2 (−1.7 ppm), C-3 (+11.0 ppm) and C-4 (+0.4 ppm) among the aglycone carbons, supporting the view that the arabinosyl glucoside moiety in **1** is linked to the C-3 hydroxyl group of the aglycone as in the case of **4**.

Based on the above evidence, the structure of desacylmasonoside 1 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)-β-D-fucopyranosyl}polygalacic acid (**1**).

Desacylmasonoside 2 (**2**) revealed an ion peak at m/z 1407 $(M+Na)^+$ which is less by 132 mass units than that of **1** and a fragment ion peak at m/z 689 (aglycone-Glc + Na)$^+$ in the positive ion FAB-MS. The ^{1}H-NMR spectrum of **2** showed signals due to six tertiary methyl groups at δ 0.80, 0.83, 1.10, 1.21, 1.46, 1.63 and two secondary methyl groups at δ 1.23 and 1.47. It also showed six anomeric proton signals at δ 4.98 (1H, d, J=7.0 Hz), 5.00 (1H, d, J= 7.8 Hz), 5.05 (1H, d, J=8.0 Hz), 5.59 (1H, d, J=3.0 Hz), 5.87 (1H, d, J=8.0 Hz) and 6.31 (1H, d, J=1.0 Hz). The ^{13}C-NMR spectrum showed six anomeric carbon signals at δ 94.9, 101.3, 105.7, 105.8, 106.6, 109.1 and an ester carbon signal at δ 176.2. Detailed comparison of the ^{13}C-NMR spectrum of **2** with that of **1** showed that the carbon signals due to C-5 and C-6 of the glucopyranosyl moiety were shifted by +1.7 and −7.1 ppm, respectively, while the other signals were almost unchanged, suggesting that arabinopyranose attached to C-6 of the glucopyranosyl moiety of **1** is absent in **2** (Tables I and II). The structure of **2** deduced by analysis of the ^{13}C-NMR data was well supported by comparison of the result of methylation analysis of **1** with that of **2**. Namely, the result of methylation analysis suggested that **2** has terminal glucopyranoside, 2,3-linked fucopyranoside, 4-linked rhamnopyranoside, 4-linked xylopyranoside and terminal apiofuranoside.

Enzymatic hydrolysis of **1** with emulsin[12] afforded a hydrolyzate (**2**) which was identical with desacylmasonoside 2.

Consequently, the structure of desacylmasonoside 2 was formulated as 3-*O*-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 (**2**).

On acidic hydrolysis, desacylmasonoside 3 (**3**) gave D-fucose, D-glucose, D-xylose, L-arabinose and L-rhamnose. The positive ion FAB-MS of **3** revealed the same $(M+Na)^+$ ion peak as that of **2** at m/z 1407 and a fragment ion peak at m/z 821 (aglycone-Glc-Ara + Na)$^+$. The ^{1}H-NMR spectrum showed signals due to six tertiary methyl groups and two secondary methyl groups in analogy with

that of **1**. It also showed six anomeric proton signals at δ 4.70 (1H, d, J=6.5 Hz), 4.90 (1H, d, J=8.0 Hz), 5.01 (1H, d, J=7.8 Hz), 5.07 (1H, d, J=7.2 Hz), 5.87 (1H, d, J=8.0 Hz) and 6.35 (1H, d, J=1.0 Hz). The ^{13}C-NMR spectrum showed six anomeric carbon signals at δ 94.9, 101.3, 105.0, 105.6, 105.7, 106.8 and an ester carbon signal at δ 176.2. On careful comparison of the ^{13}C-NMR spectrum of **1** with that of **3**, glycosylation shifts were observed for the carbon signals due to C-3 (−2.3 ppm), C-4 (+5.4 ppm) and C-5 (−3.0 ppm) of the xylopyranosyl moiety, indicating that **3** is deficient in apiofuranose attached to C-4 of the xylopyranosyl moiety of **1** (Tables I and II). The structure of **3** presumed from the analysis of the ^{13}C-NMR data was well supported by comparison of the result of methylation analysis of **1** with that of **3**. Namely, the result of methylation analysis of **3** suggested the presence of the 6-linked glucopyranoside, terminal arabinopyranoside, 2,3-linked fucopyranoside, 4-linked rhamnopyranoside, terminal xylopyranoside and terminal glucopyranoside.

Acidic hydrolysis of **1** with 2 N HCl gave a hydrolyzate (**3**) which was identical with desacylmasonoside 3. Furthermore, the structure of **3** was confirmed by enzymatic hydrolysis with emulsin, which afforded two hydrolyzates (**8** and **9**). The hydrolyzate (**8**) exhibited an ion peak at m/z 1275 $(M+Na)^+$ and a fragment ion peak at m/z 689 (aglycone-Glc+Na)$^+$ in the positive FAB-MS. Comparison of the ^{13}C-NMR spectra of **3** and **8** showed glycosylation shifts for the carbon signals due to C-5 (−1.7 ppm) and C-6 (+7.0 ppm) of glucopyranosyl moiety, supporting the view that the arabinopyranose in **3** is linked to the C-6 position of the glucopyranosyl moiety. The hydrolyzate (**9**) revealed an ion peak at m/z 1143 $(M+Na)^+$ and a fragment ion peak at m/z 689 (aglycone-Glc+Na)$^+$ in the positive FAB-MS. When the ^{13}C-NMR spectrum of **8** was compared with that of **9**, the glycosylation shifts were observed for the carbon signals due to C-4 (+9.3 ppm) and C-5 (−1.6 ppm) of the rhamnopyranosyl moiety, indicating that the xylopyranose in **8** is linked to the C-4 position of the rhamnopyranosyl moiety. From these results, the linkage sites of the arabinopyranose and xylopyranose in **3** were ascertained.

Based on the above evidence, the structure of desacylmasonoside 3 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)-β-D-fucopyranosyl}polygalacic acid (**3**).

The structures of the three novel desacylmasonosides 1, 2 and 3 were thus determined as **1**, **2**, and **3**, respectively. The saponin composition of *C. masonorum* appears to be very complex, consisting of desacylsaponins with several palmitic acid derivatives as acyl moieties.[13] Their structural elucidation is in progress.

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. HH-COSY and CH-COSY spectra were measured for all samples. EI-MS and positive ion FAB-MS were taken on a JEOL JMS DX-300. For gas liquid chromatography (GLC), a Shimadzu GC-9A was used. Thin layer chromatography was performed on precoated Silica gel 60 F_{254} plates (Merck) [solvents: $CHCl_3$–MeOH–H_2O (6:4:1), EtOAc–EtOH–H_2O (8:3:3), BuOH–HOAc–H_2O (4:1:5, upper layer)] and RP-18 F_{254}s plates (Merck) [solvent: 65% MeOH].

Extraction of Crude Saponin The commercial corms of *C. masonorum* (fresh weight, 600 g) purchased from Yamato-noen Co., Ltd. in 1985 were extracted with MeOH. The concentrated methanolic extract (104.7 g), was dissolved in H_2O and extracted with EtOAc and BuOH successively. The BuOH layer was evaporated *in vacuo* to give the crude saponin (37.7 g).

Alkaline Hydrolysis of Crude Saponin A solution of crude saponin (2 g) in 1% $NaHCO_3$–EtOH (1:1, 80 ml) was refluxed for 40 min. The reaction mixture was neutralized with Dowex 50W-X8 (H^+ form) and filtered. The filtrate was concentrated and extracted with EtOAc. The aqueous layer was evaporated *in vacuo* to give a residue (1.580 g). The residue was subjected to HPLC to give five fractions, fractions 1 (164 mg), 2 (129 mg), 3 (275 mg), 4 (952 mg) and 5 (10 mg). Conditions of normal phase HPLC: column, Senshu Pak Aquasil, 5 μm (10×300 mm); solvent, $CHCl_3$–MeOH–H_2O (60:33:7); flow rate, 3 ml/min; detection, refraction index. Fractions 2 and 3 were further subjected to normal- and reversed-phase HPLC to give **2** (16 mg) and **3** (91 mg). Conditions of normal-phase HPLC: column, Senshu Pak Aquasil; solvent, $CHCl_3$–MeOH–H_2O (60:33:7) and EtOAc–MeOH–H_2O (80:17:15); flow rate, 3 ml/min, reversed-phase HPLC: column, Senshu Pak NP-118, 7 μm (10×300 mm); solvent, 60% MeOH; flow rate, 4 ml/min. Fraction 4 was subjected to reversed-phase HPLC to give **1** (788 mg). Conditions of HPLC: column, Senshu Pak NP-118; solvent, 60% MeOH; flow rate, 4 ml/min.

Desacylmasonoside 1 (1) White powder. $[\alpha]_D^{22}$ −20.8° (c=0.97, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740. *Anal.* Calcd for $C_{69}H_{112}O_{36}\cdot 6H_2O$: C, 50.97; H, 7.68. Found: C, 51.21; H, 7.44. Positive ion FAB-MS m/z: 1539 $(M+Na)^+$, 843, 821, 741, 609. ^{1}H-NMR (C_5D_5N) δ: 0.81, 0.83, 1.08, 1.20, 1.42, 1.60 (each 3H, s), 1.23 (3H, d, J=6.5 Hz, Fuc-6-H), 1.47 (3H, d, J=6.0 Hz, Rha-6-H), 2.64 (1H, dd, J=13.5, 13.5 Hz, 19-H_{ax}), 3.25 (1H, dd, J=13.5, 3.5 Hz, 18-H), 4.68 (1H, d, J=6.5 Hz, Ara-1-H), 4.89 (1H, d, J=8.0 Hz, Glc-1-H), 4.97 (1H, d, J=7.2 Hz, Xyl-1-H), 5.00 (1H, d, J=7.8 Hz, Glc′-1-H), 5.08 (1H, br s, 16-H), 5.47 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.59 (1H, d, J=3.0 Hz, Api-1-H), 5.86 (1H, d, J=8.0 Hz, Fuc-1-H), 6.31 (1H, br s, Rha-1-H).

Desacylmasonoside 2 (2) White powder. $[\alpha]_D^{22}$ −25.4° (c=0.89, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3420, 1735. *Anal.* Calcd for $C_{64}H_{104}O_{32}\cdot 5H_2O$: C, 52.09; H, 7.79. Found: C, 51.92; H, 7.57. Positive ion FAB-MS m/z: 1407 $(M+Na)^+$, 741, 711, 689. ^{1}H-NMR (C_5D_5N) δ: 0.80, 0.83, 1.10, 1.21, 1.46, 1.63 (each 3H, s), 1.23 (3H, d, J=6.5 Hz, Fuc-6-H), 1.47 (3H, d, J=6.0 Hz, Rha-6-H), 2.59 (1H, dd, J=13.5, 13.5 Hz, 19-H_{ax}), 3.26 (1H, dd, J=13.5, 3.5 Hz, 18-H), 4.98 (1H, d, J=7.0 Hz, Xyl-1-H), 5.00 (1H, d, J=7.8 Hz, Glc′-1-H), 5.05 (1H, d, J=8.0 Hz, Glc-1-H), 5.09 (1H, br s, 16-H), 5.51 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.59 (1H, d, J=3.0 Hz, Api-1-H), 5.87 (1H, d, J=8.0 Hz, Fuc-1-H), 6.31 (1H, d, J=1.0 Hz, Rha-1-H).

Desacylmasonoside 3 (3) White powder. $[\alpha]_D^{22}$ −4.7° (c=0.90, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3410, 1740. *Anal.* Calcd for $C_{64}H_{104}O_{32}\cdot 6H_2O$: C, 51.46; H, 7.83. Found: C, 51.32; H, 7.56. Positive ion FAB-MS m/z: 1407 $(M+Na)^+$, 843, 821, 609. ^{1}H-NMR (C_5D_5N) δ: 0.80, 0.83, 1.10, 1.21, 1.44, 1.60 (each 3H, s), 1.23 (3H, d, J=6.5 Hz, Fuc-6-H), 1.51 (3H, d, J=6.0 Hz, Rha-6-H), 2.61 (1H, dd, J=13.5, 13.5 Hz, 19-H_{ax}), 3.26 (1H, dd, J=13.5, 3.5 Hz, 18-H), 4.70 (1H, d, J=6.5 Hz, Ara-1-H), 4.90 (1H, d, J=8.0 Hz, Glc-1-H), 5.01 (1H, d, J=7.8 Hz, Glc′-1-H), 5.07 (1H, d, J=7.2 Hz, Xyl-1-H), 5.11 (1H, br s, 16-H), 5.42 (1H, dd, J=3.0, 3.0 Hz, 12-H), 5.87 (1H, d, J=8.0 Hz, Fuc-1-H), 6.35 (1H, d, J=1.0 Hz, Rha-1-H).

Determination of D-L Series of Component Sugars by HPLC A solution of each of **1** and **3** (1 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 neutralized with Amberlite IRA-93 (OH^- form) and passed through a SEP-PAK C_{18} cartridge to give a sugar fraction. A solution of the 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 dissolved in Ac_2O–C_5H_5N (1:1, 2 ml) was treated with 4-(dimethylamino)pyridine (DMAP) (20 mg), and the whole mixture was left at room temperature overnight. After removal of excess Ac_2O and C_5H_5N, the residue dissolved in 20% CH_3CN was loaded into a SEP-PAK C_{18} cartridge and eluted with 20% CH_3CN (total 7 ml) and 100% CH_3CN. The fraction eluted with 100% CH_3CN 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, ultraviolet (UV) (230 nm). t_R (min) of 1-(*N*-acetyl-L-α-methylbenzylamino)-1-deoxyalditol acetates were as follows. **1**; L-rhamnose 25.9, D-fucose 28.7, L-arabinose

36.1, D-apiose 41.2, D-xylose 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. ODS-H-4301; solvent, 40% CH_3CN; flow rate, 3 ml/min; detection, UV (230 nm). t_R (min) of 1-(*N*-acetyl-L-α-methylbenzylamino)-1-deoxyalditol acetates: L-arabinose 24.0, D-apiose 25.2, D-xylose 25.2, D-fucose 28.9, D-glucose 33.0, L-rhamnose 38.0 (D-arabinose 24.8, L-apiose 25.2, L-xylose 24.4, L-fucose 31.2, L-glucose 30.7, D-rhamnose 38.0). 1-(*N*-Acetyl-L-α-methylbenzylamino)-1-deoxyalditol acetates were identified by direct comparison with authentic specimens. **3**; normal-phase HPLC: L-rhamnose 25.9, D-fucose 28.7, L-arabinose 36.1, D-xylose 41.2, D-glucose 41.2; reversed-phase HPLC: L-arabinose 24.0, D-xylose 25.2, D-fucose 28.9, D-glucose 33.0, L-rhamnose 38.0.

Methylation Analysis of 1, 2 and 3 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 mixture of desacylmasonoside (2 mg) in DMSO (1 ml) and the solution was sonicated at room temperature for 1 h. Methyl iodide (1 ml) was added to this solution under cooling and the mixture was further sonicated at room temperature for 1 h. After excess methyl iodide 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 (Waters) and eluted with H_2O and MeOH. The permethylated product eluted with MeOH was hydrolyzed with 2 M trifluoroacetic acid (TFA) at 120 °C for 1 h in a sealed tube. The reaction mixture was neutralized with Amberlite IRA-93 (OH^- form) and concentrated to about 2 ml. To this solution, $NaBH_4$ (25 mg) was added. After being stirred at room temperature for 2 h, the solution was acidified with Dowex 50W–X8 (H^+ form) and concentrated to dryness. Boric acid in the residue was removed by repeated co-distillation with MeOH. The resulting methylated alditol mixture was acetylated with Ac_2O–C_5H_5N (1:1, 2 ml) at room temperature overnight. The reagent was removed by co-distillation with toluene. 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 (*T*) of partially methylated alditol acetates were recorded on the basis of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylglucitol ($T=1.00$, t_R 18.2 min) as the standard. The following abbreviations are used: t = terminal, 2 = 2-linked, 4 = 4-linked, 6 = 6-linked, 2,3 = 2,3-linked. The *T* values of partially methylated alditol acetates were as follows. **1**; t-Api (0.49), t-Ara (0.55), 4-Rha (0.91), t-Glc (1.00), 4-Xyl (1.17), 2,3-Fuc (1.76), 6-Glc (2.23). **2**; t-Api (0.49), 4-Rha (0.91), t-Glc (1.00), 4-Xyl (1.18), 2,3-Fuc (1.76). **3**; t-Ara and t-Xyl (0.55), 4-Rha (0.91), t-Glc (1.00), 2,3-Fuc (1.75), 6-Glc (2.23). EI-MS of partially methylated alditol acetates *m/z*: 6-Glc; 223, 189, 161, 117, t-Ara; 161, 117, 2,3-Fuc; 261, 113, 4-Rha; 203, 161, 117, 4-Xyl; 189, 117, t-Api; 233, 205, 161, 117, t-Glc; 205, 161, 145, 117, t-Xyl; 161, 117.

Cleavage of Ester-Glycoside Linkage of 1 A solution of **1** (150 mg), anhydrous LiI (453 mg), and 2,6-lutidine (4 ml) in anhydrous MeOH (4 ml) was refluxed for 7 h. The solution was deionized by passing it through a column of Amberlite MB-3 and concentrated to dryness. The residue was subjected to HPLC to give **4** (46.3 mg) and crude **5**. Conditions of HPLC: column, Senshu Pak Aquasil; solvent, $CHCl_3$–MeOH–H_2O (60:29:6); flow rate, 3 ml/min. Crude **5** was further purified by reversed-phase HPLC to give **5** (50.4 mg). **4**: white powder. $[\alpha]_D^{22}$ +13.3° ($c=0.98$, MeOH). *Anal.* Calcd for $C_{41}H_{66}O_{15}\cdot 3.5H_2O$: C, 57.12; H, 8.53. Found: C, 57.21; H, 8.26. IR ν_{max}^{KBr} cm^{-1}: 3400, 1690. Positive ion FAB-MS *m/z*: 821 $(M+Na)^+$. ^{1}H-NMR (C_5D_5N) δ: 0.92, 0.97, 1.05, 1.22, 1.45, 1.66 (each 3H, s), 2.70 (1H, dd, $J=13.5$, 13.5 Hz, 19-H_{ax}), 3.50 (1H, dd, $J=13.5$, 3.5 Hz, 18-H), 3.53 (1H, d, $J=10.5$ Hz, 23-H_a), 3.63 (1H, dd, $J=12.0$, 1.0 Hz, Ara-5-H_{ax}), 3.92 (1H, dd, $J=9.0$, 3.5 Hz, Glc-6-H_a), 4.06 (1H, dd, $J=8.5$, 3.5 Hz, Ara-3-H), 4.17 (1H, d, $J=3.0$ Hz, 3-H), 4.18 (1H, ddd, $J=3.5$, 3.5, 1.0 Hz, Ara-4-H), 4.33 (1H, dd, $J=8.5$, 6.5 Hz, Ara-2-H), 4.67 (1H, d, $J=9.0$ Hz, Glc-6-H_b), 4.71 (1H, d, $J=6.5$ Hz, Ara-1-H), 4.73 (1H, ddd, $J=3.5$, 3.0, 3.0 Hz, 2-H), 4.92 (1H, d, $J=8.0$ Hz, Glc-1-H), 5.12 (1H, br s, 16-H), 5.55 (1H, dd, $J=3.0$, 3.0 Hz, 12-H). Hydrolyzate (**4**) was identical with **4** obtained from montbretia on the basis of $[\alpha]_D$, FAB-MS, ^{1}H- and ^{13}C-NMR spectral data. **5**: white powder. $[\alpha]_D^{22}$ −23.1° ($c=0.52$, C_5H_5N). *Anal.* Calcd for $C_{29}H_{50}O_{22}\cdot 3H_2O$: C, 43.27; H, 7.01. Found: C, 42.99; H, 6.79. IR ν_{max}^{KBr} cm^{-1}: 3420. Positive ion FAB-MS *m/z*: 773 $(M+Na)^+$. ^{1}H-NMR spectral data are summarized in Table III. Methylation analysis of **5** was carried out in the same manner as described for desacylmasonosides. The *T* values of partially methylated alditol acetates were as follows; t-Api (0.49), 4-Rha (0.91), t-Glc (1.00), 4-Xyl (1.17), 2,3-Fuc (1.75).

Enzymatic Hydrolysis of 1 with Hesperidinase Hesperidinase (352 mg) was added to a solution of **1** (136 mg) in H_2O (10 ml), and the mixture was incubated at 37 °C for 4 d. The reaction mixture was passed through a SEP-PAK C_{18} cartridge (Waters) and eluted with H_2O and MeOH. The MeOH eluate was subjected to HPLC to give **6** (11 mg) and **7** (51 mg). Conditions of HPLC: column, Senshu Pak Aquasil; solvent, $CHCl_3$–MeOH–H_2O (60:29:6); flow rate, 3 ml/min. **6**: white powder. $[\alpha]_D^{22}$ −24.0° ($c=0.36$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3410, 1740. Positive ion FAB-MS *m/z*: 1083 $(M+Na)^+$, 579. ^{1}H-NMR (C_5D_5N) δ: 0.81, 0.84, 1.10, 1.24, 1.51, 1.63 (each 3H, s), 1.24 (3H, d, $J=6.5$ Hz, Fuc-6-H), 1.47 (3H, d, $J=6.0$ Hz, Rha-6-H), 2.65 (1H, dd, $J=13.5$, 13.5 Hz, 19-H_{ax}) 3.29 (1H, dd, $J=13.5$, 3.5 Hz, 18-H), 5.03 (1H, d, $J=7.2$ Hz, Xyl-1-H), 5.12 (1H, br s, 16-H), 5.53 (1H, dd, $J=3.0$, 3.0 Hz, 12-H), 5.60 (1H, d, $J=3.0$ Hz, Api-1-H), 5.89 (1H, d, $J=8.0$ Hz, Fuc-1-H), 6.35 (1H, d, $J=1.5$ Hz, Rha-1-H). The hydrolyzate (**6**) was identical with **6** obtained from crocosmioside A on the basis of $[\alpha]_D$, FAB-MS, ^{1}H- and ^{13}C-NMR spectral data. **7**: white powder. $[\alpha]_D^{22}$ −24.9° ($c=0.89$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740. *Anal.* Calcd for $C_{58}H_{94}O_{27}\cdot 2H_2O$: C, 55.31; H, 7.84. Found: C, 55.51; H, 7.84. Positive ion FAB-MS *m/z*: 1245 $(M+Na)^+$, 741. ^{1}H-NMR (C_5D_5N) δ: 0.80, 0.83, 1.14, 1.24, 1.50, 1.65 (each 3H, s), 1.23 (3H, d, $J=6.5$ Hz, Fuc-6-H), 1.48 (3H, d, $J=6.0$ Hz, Rha-6-H), 2.62 (1H, dd, $J=13.5$, 13.5 Hz, 19-H_{ax}), 3.28 (1H, dd, $J=13.5$, 3.5 Hz, 18-H), 4.96 (1H, d, $J=7.0$ Hz, Xyl-1-H), 5.00 (1H, d, $J=7.8$ Hz, Glc-1-H), 5.10 (1H, br s, 16-H), 5.54 (1H, dd, $J=3.0$, 3.0 Hz, 12-H), 5.60 (1H, d, $J=3.0$ Hz, Api-1-H), 5.88 (1H, d, $J=8.0$ Hz, Fuc-1-H), 6.32 (1H, br s, Rha-1-H).

Methylation Analysis of 6 Hydrolyzate (**6**) was methylated by Hakomori's method as described above. The partially methylated alditol acetate mixture obtained from the permethylated derivative of **6** was analyzed by GC-MS in the same manner as described for desacylmasonosides. Their partially methylated alditol acetates were identified by comparison with authentic specimens. The *T* values of partially methylated alditol acetates were as follows; t-Api (0.49), 4-Rha (0.91), 2-Fuc (1.13), 4-Xyl (1.17). EI-MS of 1,2,5-tri-*O*-acetyl-3,4-di-*O*-methylfucitol; *m/z*: 189, 131.

Enzymatic Hydrolysis of 1 with Emulsin Emulsin (from almonds, G-8625, Sigma Co., 120 mg) was added to a solution of **1** (41 mg) in H_2O (6 ml) and the mixture was incubated at 37 °C for 4 d. 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 **2** (24.7 mg). Conditions of HPLC: column, Senshu Pak Aquasil; solvent, $CHCl_3$–MeOH–H_2O (60:29:6); flow rate, 3 ml/min. **2**: white powder. $[\alpha]_D^{22}$ −23.3° ($c=0.5$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3410, 1740. Positive ion FAB-MS *m/z*: 1407 $(M+Na)^+$. The hydrolyzate (**2**) was identical with desacylmasonoside 2 on the basis of $[\alpha]_D$, FAB-MS, ^{1}H- and ^{13}C-NMR spectral data.

Hydrolysis of 1 with 2N HCl A solution of **1** (30.5 mg) in 2 N HCl (6 ml) was left for 48 h at room temperature. After being diluted with H_2O, the reaction mixture was passed through a SEP-PAK C_{18} cartridge (Waters) and eluted with H_2O and MeOH. The MeOH eluate was purified by HPLC to give **3** (8 mg) and **4** (4.5 mg). Conditions of HPLC: column, Senshu Pak Aquasil; solvent, $CHCl_3$–MeOH–H_2O (60:29:6); flow rate, 3 ml/min. **3**: white powder. $[\alpha]_D^{21}$ −4.6° ($c=0.78$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3440, 1740. The hydrolyzate (**3**) was identical with desacylmasonoside 3 on the basis of $[\alpha]_D$, FAB-MS, ^{1}H- and ^{13}C-NMR spectral data.

Enzymatic Hydrolysis of 3 with Emulsin Emulsin (82 mg) was added to a solution of **3** (35.7 mg) in H_2O (7 ml), and the mixture was incubated at 37 °C for 2 d. The reaction mixture was passed through a SEP-PAK C_{18} cartridge (Waters) and eluted with H_2O and MeOH. The MeOH eluate was subjected to HPLC to give **8** (14.2 mg) and **9** (5.8 mg). Conditions of HPLC: column, μ-Bondasphere C_{18}, 5 μm (19 × 150 mm); solvent, 60% MeOH; flow rate, 5 ml/min. **8**: white powder. $[\alpha]_D^{21}$ −6.2° ($c=1.39$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3410, 1735. Positive ion FAB-MS *m/z*: 1275 $(M+Na)^+$, 711 (aglycone-Glc + 2Na−H)$^+$, 689 (aglycone-Glc + Na)$^+$, 609. ^{1}H-NMR (C_5D_5N) δ: 0.79, 0.82, 1.12, 1.22, 1.48, 1.63 (each 3H, s), 1.23 (3H, d, $J=6.5$ Hz, Fuc-6–H), 1.52 (3H, d, $J=6.0$ Hz, Rha-6-H), 2.60 (1H, dd, $J=13.5$, 13.5 Hz, 19-H_{ax}), 3.26 (1H, dd, $J=13.5$, 3.5 Hz, 18-H), 5.01 (1H, d, $J=7.8$ Hz, Glc′-1-H), 5.06 (1H, d, $J=8.0$ Hz, Glc-1-H), 5.07 (1H, d, $J=7.0$ Hz, Xyl-1-H), 5.12 (1H, br s, 16-H), 5.51 (1H, dd, $J=3.0$, 3.0 Hz, 12-H), 5.88 (1H, d, $J=8.0$ Hz, Fuc-1-H), 6.35 (1H, d, $J=1.0$ Hz, Rha-1-H). **9**: white powder. $[\alpha]_D^{21}$ −1.1° ($c=0.55$, C_5H_5N). IR ν_{max}^{KBr} cm^{-1}: 3410, 1735. Positive ion FAB-MS *m/z*: 1143 $(M+Na)^+$, 711 (aglycone-Glc + 2Na-H)$^+$, 689 (aglycone-Glc + Na)$^+$, 477. ^{1}H-NMR (C_5D_5N) δ: 0.80, 0.84, 1.15, 1.22, 1.53, 1.66 (each 3H, s), 1.23 (3H, d, $J=6.5$ Hz, Fuc-6-H), 1.47 (3H, d, $J=6.0$ Hz, Rha-6-H), 2.61 (1H, dd, $J=13.5$, 13.5 Hz, 19-H_{ax}), 3.27 (1H, dd, $J=13.5$, 3.5 Hz, 18-H), 5.05 (1H, d, $J=7.8$ Hz, Glc′-1-H), 5.07 (1H, d, $J=8.0$ Hz, Glc-1-H), 5.12 (1H, br s, 16-H), 5.51 (1H, dd,

J=3.0, 3.0 Hz, 12-H), 5.88 (1H, d, J=8.0 Hz, Fuc-1-H), 6.31 (1H, d, J= 1.0 Hz, Rha-1-H).

Acknowledgement We are grateful to Dr. T. Mizoguchi (Tanabe Seiyaku Co., Ltd.) for supplying the crude hesperidinase.

References and Notes

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