Studies on the Constituents of *Solidago virga-aurea* L. III. Structures of Solidagosaponins XXI—XXIX

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From the most polar fractions of *Solidago virga-aurea* L. (Compositae), 9 oleanane-type triterpene saponins named solidagosaponins XXI—XXIX (1—9) were isolated, together with a known saponin, virgaureasaponin 2 (10). These saponins are bisdesmosidic glycosides having two monosaccharides at C-3 and four or five monosaccharides at C-28. Their structures were established on the basis of spectroscopic and chemical evidence.

Keywords *Solidago virga-aurea*; solidagosaponin; polygalacic acid; Compositae; trimeric β-hydroxy butyrate; dimeric β-hydroxy butyrate

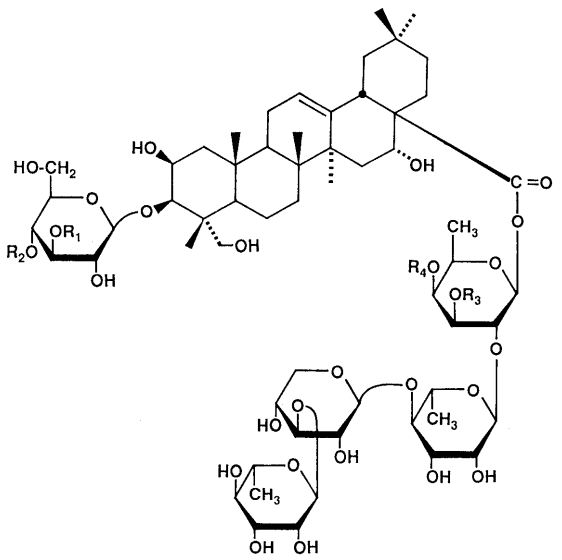
In the previous paper,[1,2] we reported the isolation and structure elucidation of 20 new oleanane-type triterpene saponins named solidagosaponins I—XX, together with two known saponins, virgaureasaponin 1[3] and bellissaponin BA2[4] from the less polar and more polar fractions of a methanol eluate of the water extract of *Solidago virga-aurea* L. (Compositae). Further investigation of the most polar fraction has led to the isolation of 9 new saponins, named solidagosaponins XXI—XXIX (**1**—**9**), together with a known saponin, virgaureasaponin 2 (**10**).[5] This paper deals with the isolation and structure elucidation of these saponins.

A water extract of the whole plants was passed through a porous polymer gel Mitsubishi Diaion HP-20 column and the adsorbed materials were eluted with 50% aqueous methanol and methanol, successively. The methanol eluate was chromatographed on a silica gel column and octadecyl silica (ODS) column, followed by repeated semi-preparative HPLC on a reversed phase column [ODS, phenyl alkyl (PhA)]. As a result, we have isolated 10 polar saponins, and the structures of nine new saponins were established and a known saponin was identified as virgaureasaponin 2 by comparison of our spectral data with reported data.[5]

Solidagosaponin XXI (**1**) revealed a $[M+Na]^+$ ion peak at *m/z* 1650 in the FAB-MS, and elemental analysis data was consistent with $C_{76}H_{122}O_{37}\cdot 6H_2O$. On acid hydrolysis, **1** afforded polygalacic acid as an aglycone, and D-glucose, D-xylose, D-fucose and L-rhamnose in the ratio of 1:2:1:2 as a sugar moiety. In the ^{1}H-NMR spectrum, all proton signals due to a sugar moiety were assigned (Table I) by using a detailed proton spin decoupling experiment, ^{1}H–^{13}C correlated spectroscopy (COSY) and a *J*-resolved 2D-NMR spectra. While the ^{13}C-NMR spectrum exhibited six anomeric carbon signals and four ester carbonyl carbon signals (Table II), the ^{1}H-NMR spectrum showed three sets of signals due to β-hydroxy butyrate. Glycosylation shifts at C-2 (−1.2 ppm), C-3 (+9.9 ppm) and C-28 (−3.8 ppm) of the aglycone indicated that **1** was a 3,28-bisdesmoside. Since the anomeric carbon signal (δ 94.5) due to fucose showed an ester-type glycoside linkage, fucose was found to be linked at the C-28 of polygalacic acid. The binding sites of five other monosaccharides were determined by the nuclear Overhauser effect (NOE) method. When the signals at δ 4.99 (the H-1 of xylose), 5.11 (the H-1 of glucose), 5.14 (the H-1 of xylose), 6.10 and 6.19 (the H-1 of each rhamnose) were irradiated, NOEs were observed at signals due to the H-4 of rhamnose, the H-3 of the aglycone, the H-3 of glucose, the H-3 of xylose and the H-2 of fucose, respectively. In the ^{1}H-NMR spectrum, the H-4 of fucose (δ 5.48) and the H-3 of two out of three β-hydroxy butyrates (δ 5.52, 5.53) appeared lower in the field than usual (δ 3.9, 4.5, respectively). Furthermore, no other signals in the sugar and aglycone moieties shifted to a relatively lower field. Judging from these results, we assumed that a trimeric β-hydroxy butyrate attached to the C-4 of fucose, as in the case of solidagosaponin XIV.[2] Based upon the above evidence, the structure of salidagosaponin XXI was characterized as **1**.

Solidagosaponin XXII (**2**) has the same molecular formula, ester and sugar side chains as those of **1** according to the elemental analysis and NMR spectral data, including the NOE experiment involving irradiation at each anomeric proton signal. In the ^{1}H-NMR spectrum of **2**, the H-3 of fucose was shifted downfield by 1.25 ppm compared with that of bellissaponin BA2[2,4] which had no acyl residue in the fucose moiety. The acylation shifts were observed at C-2 (−4.6 ppm), C-3 (+1.7 ppm) and C-4 (−1.0 ppm) of the fucose moiety by comparison with those of bellissaponin BA2 in the ^{13}C-NMR spectrum. These data led to the proposed structure **2** for solidagosaponin XXII.

Solidagosaponin XXIII (**3**) revealed a $[M+Na]^+$ ion peak at *m/z* 1824 in the FAB-MS, and elemental analysis data was consistent with $C_{83}H_{132}O_{42}\cdot 5H_2O$. On acid hydrolysis, **3** afforded polygalacic acid as an aglycone moiety, and D-glucose, D-xylose, D-fucose and L-rhamnose in the ratio of 1:2:1:2 as a sugar moiety. On mild acid hydrolysis, D-apiose was detected. The ^{1}H- and ^{13}C-NMR spectra showed the presence of acetyl and trimeric β-hydroxy butyroyl residues. In the ^{1}H-NMR spectrum, all proton signals due to a sugar and ester moieties were assigned (Table I) by using a detailed proton spin decoupling experiment and NOEs with irradiation at each anomeric proton signal. The hetero nuclear multiple bond coherrence (HMBC) spectrum (J=8 Hz) showed the connections of individual monosac-



	R_1	R_2	R_3	R_4
1	Xyl	H	H	**A**
2	Xyl	H	**A**	H
3	Xyl	H	Api(5)—Ac	**A**
4	Xyl	H	H	**B**
5	Xyl	H	H	H
6	Glc	H	H	**A**
7	H	Glc	H	H
8	Glc	H	Api	Ac
9	H	Glc	Api	Ac
10	Glc	H	H	H

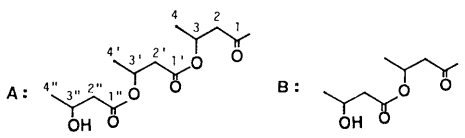


Chart 1

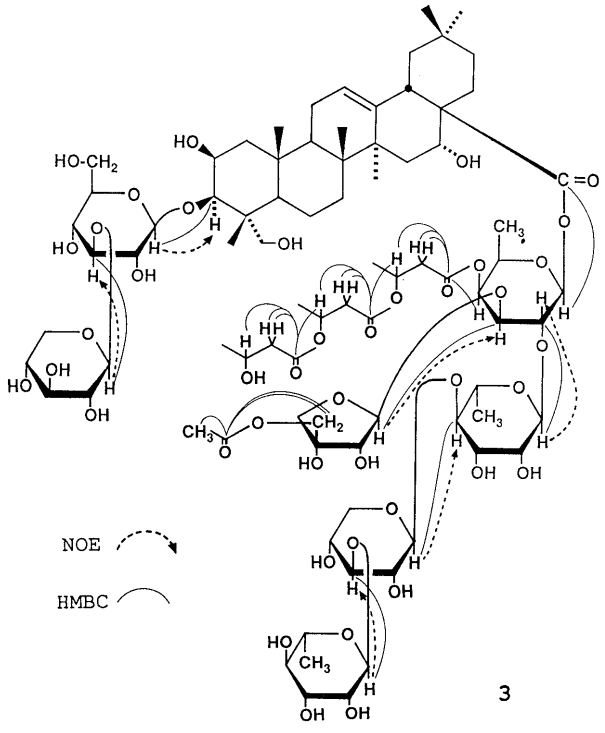


Chart 2

charide and acyl residues, as shown in Chart 2.

Solidagosaponin XXIV (**4**) revealed a $[M+Na]^+$ ion peak at *m/z* 1564 in the FAB-MS, and elemental analysis data was consistent with $C_{72}H_{116}O_{35}\cdot 6H_2O$. 4 afforded D-glucose, D-xylose, D-fucose, L-rhamnose (1:2:1:2) and polygalacic acid on acid hydrolysis. In the ^{1}H-NMR spectrum, two sets of signals due to β-hydroxy butyrate were observed. The H-4 of fucose (δ 5.48) and the H-3 of a β-hydroxy butyrate (δ 5.54) appeared lower in the field than usual. So, a dimeric β-hydroxy butyric acid was attached to the C-4 of fucose. The sugar linkages were determined to be as shown (Chart 1) by means of NOE with irradiation at each anomeric proton signal after assignment of the sugar proton signal by spin decoupling experiments. These data led to the proposed structure **4** for solidagosaponin XXIV.

Solidagosaponin XXV (**5**) revealed a $[M+Na]^+$ ion peak at *m/z* 1392 in the FAB-MS, and had a molecular formula $C_{64}H_{104}O_{31}\cdot 5H_2O$ by elemental analysis. The ^{1}H- and ^{13}C-NMR spectra were similar to those of **4** except for the lack of a dimeric β-hydroxy butyrate. The binding sites of each monosaccharide were determined by the NOE method. When the signals at δ 5.01 (the H-1 of xylose), 5.10 (the H-1 of glucose), 5.17 (the H-1 of xylose), 6.14, 6.33 (the H-1 of each rhamnose) were irradiated, NOEs were observed at signals due to the H-4 of rhamnose, the H-3 of an aglycone, the H-3 of glucose, the H-3 of xylose and the H-2 of fucose, respectively. From these data, the structure of solidagosaponin XXV was determined to be **5**.

Solidagosaponin XXVI (**6**) afforded D-glucose, D-xylose, D-fucose, L-rhamnose (2:1:1:2) and polygalacic acid on acid hydrolysis. The ^{1}H- and ^{13}C-NMR spectra showed the presence of a trimeric β-hydroxy butyrate (Tables I and II). The H-4 of fucose was shifted downfield to δ 5.48 (1H, d, J=3.5 Hz) suggesting that the acyl residue was attached to the C-4 of fucose. The sugar sequences were decided by the NOE method. When the signal at δ 5.01 (the H-1 of xylose), 5.08, 5.20 (the H-1 of each glucose), 6.14, 6.22 (the H-1 of each rhamnose) were irradiated, NOEs were observed at signals due to the H-4 of rhamnose, the H-3 of an aglycone, the H-3 of glucose, the H-3 of xylose and the H-2 of fucose, respectively. So, the structure of solidagosaponin XXVI was determined to be **6**.

Solidagosaponin XXVII (**7**) has the same molecular formula, $C_{65}H_{106}O_{32}\cdot 6H_2O$ as that of virgaureasaponin 2 (**10**).[5] Acid hydrolysis gave D-glucose, D-xylose, D-fucose and L-rhamnose (2:1:1:2) as a sugar moiety. In the ^{13}C-NMR spectrum of **7**, the C-4 (δ 81.2) of glucose shifted downfield by +9.6 ppm, and the C-3 (δ 76.8) and C-5 (δ 76.3) of glucose shifted upfield by 1.8 and 2.0 ppm, respectively, compared with those of bellissaponin BA2.[4] So, the terminal glucose was attached to the C-4 of the

TABLE I. ^{1}H-NMR Spectral Data of Saponins in C_5D_5N

Proton No.	1	2	3	4
Aglycone moiety				
2	4.78 (1H, br q, J=3 Hz)	4.76 (1H, br q, J=3 Hz)	4.76 (1H, br q, J=3 Hz)	4.75 [a]
3	4.27 [a]	4.31 [a]	4.30 (1H, d, J=3 Hz)	4.29 (1H, d, J=3 Hz)
12	5.65 (1H, t-like)	5.62 (1H, t-like)	5.64 (1H, t-like)	5.65 (1H, t-like)
16	5.16 (1H, br s)	5.12 (1H, br s)	5.12 (1H, br s)	5.18 (1H, br s)
18	3.40 (1H, dd, J=14, 4 Hz)	3.38 (1H, dd, J=13.5, 4.5 Hz)	3.38 (1H, dd, J=14, 3 Hz)	3.40 [a]
23	3.69 (1H, d, J=11 Hz)	3.70 (1H, d, J=11 Hz)	3.72 (1H, d, J=11 Hz)	3.72 (1H, d, J=11 Hz)
	4.25 (1H, d, J=11 Hz)	4.30 [a]	4.29 [a]	[b]
24	1.31 (3H, s)	1.33 (3H, s)	1.34 (3H, s)	1.33 (3H, s)
25	1.54 (3H, s)	1.57 (3H, s)	1.57 (3H, s)	1.55 (3H, s)
26	1.17 (3H, s)	1.17 (3H, s)	1.17 (3H, s)	1.17 (3H, s)
27	1.77 (3H, s)	1.75 (3H, s)	1.76 (3H, s)	1.76 (3H, s)
29	0.93 (3H, s)	0.95 (3H, s)	0.95 (3H, s)	0.93 (3H, s)
30	1.04 (3H, s)	1.02 (3H, s)	1.06 (3H, s)	1.04 (3H, s)
Ester moiety				
Ac			1.99 (3H, s)	
2	2.68 (1H, dd, J=14.5, 6 Hz)	2.64 (1H, dd, J=15, 5.5 Hz)	2.73 (1H, dd, J=15.5, 6 Hz)	2.64 (1H, dd, J=15.5, 6 Hz)
	2.79 (1H, dd, J=14.5, 7 Hz)	2.80 (1H, dd, J=15, 7.5 Hz)	2.93 (1H, dd, J=15.5, 6.5 Hz)	2.77 (1H, dd, J=15.5, 7 Hz)
3	5.52 [a]	5.49 (1H, m)	5.51 (1H, m)	5.54 (1H, m)
4	1.32 (3H, d, J=6 Hz)	1.20 (3H, d, J=6 Hz)	1.36 (3H, d, J=6 Hz)	1.32 (1H, d, J=6 Hz)
2′	2.70 (1H, dd, J=14.5, 6 Hz)	2.67 (1H, dd, J=15, 5.5 Hz)	2.72 (1H, dd, J=15.5, 6 Hz)	2.62 (1H, dd, J=15, 5.5 Hz)
	2.81 (1H, dd, J=14.5, 7 Hz)	2.81 (1H, dd, J=15, 7.5 Hz)	2.83 (1H, dd, J=15.5, 7.5 Hz)	2.76 (1H, dd, J=15, 7.5 Hz)
3′	5.53 [a]	5.52 (1H, m)	5.56 (1H, m)	4.52 [a]
4′	1.35 (3H, d, J=6 Hz)	1.29 (3H, d, J=6 Hz)	1.36 (3H, d, J=6.5 Hz)	1.38 (3H, d, J=6 Hz)
2″	2.62 (1H, dd, J=14.5, 6 Hz)	2.60 (1H, dd, J=14.5, 5.5 Hz)	2.61 (1H, dd, J=14.5, 5.5 Hz)	
	2.78 (1H, dd, J=14.5, 7 Hz)	2.75 (1H, dd, J=14.5, 7.5 Hz)	2.76 (1H, dd, J=14.5, 7.5 Hz)	
3″	4.54 (1H, m)	4.53 (1H, m)	4.54 [a]	
4′	1.40 (3H, d, J=6 Hz)	1.38 (3H, d, J=6 Hz)	1.39 (3H, d, J=6 Hz)	
Sugar moiety				
C-3 (Inner)				
Glc-1	5.11 (1H, d, J=8 Hz)	5.10 (1H, d, J=8 Hz)	5.09 (1H, d, J=8 Hz)	5.09 (1H, d, J=8 Hz)
Glc-2	4.03 (1H, t, J=8.5 Hz)	4.00 (1H, t, J=8.5 Hz)	3.99 (1H, t, J=8 Hz)	3.98 (1H, t, J=8 Hz)
Glc-3	4.09 (1H, t, J=9 Hz)	4.06 (1H, t, J=9 Hz)	4.06 (1H, t, J=8 Hz)	4.05 (1H, t, J=8.5 Hz)
Glc-4	4.04 (1H, t, J=9 Hz)	4.11 (1H, t, J=9 Hz)	4.09 [a]	[b]
Glc-5	3.85 (1H, m)	3.82 (1H, m)	3.81 (1H, m)	3.81 (1H, m)
Glc-6	4.20 (1H, dd, J=12, 5 Hz)	4.24 [a]	4.24 (1H, dd, J=11.5, 5.5 Hz)	4.23 [a]
	4.37 (1H, dd, J=12, 2 Hz)	4.39 (1H, dd, J=11.5, 2 Hz)	4.38 (1H, dd, J=11.5, 1.5 Hz)	4.38 (1H, dd, J=11.5, 2 Hz)
(Terminal)				
Xyl-1	5.14 (1H, d, J=8 Hz)	5.17 (1H, d, J=8 Hz)	5.16 (1H, d, J=8 Hz)	5.16 (1H, d, J=8 Hz)
Xyl-2	3.99 (1H, dd, J=8.5, 8 Hz)	4.00 (1H, t, J=8.5 Hz)	3.99 (1H, t, J=8 Hz)	3.98 (1H, t, J=8 Hz)
Xyl-3	4.11 (1H, t, J=8.5 Hz)	4.12 [a]	4.11 (1H, t, J=8 Hz)	4.10 (1H, t, J=8 Hz)
Xyl-4	4.13 [a]	4.15 [a]	4.13 [a]	[b]
Xyl-5	3.65 (1H, br t, J=11 Hz)	3.68 (1H, br t, J=10 Hz)	3.67 (1H, br t, J=11 Hz)	3.67 (1H, br t, J=11 Hz)
	4.27 (1H, br d, J=11 Hz)	4.30 [a]	4.29 [a]	[b]
C-28 Fuc-1	5.99 (1H, d, J=8 Hz)	6.05 (1H, d, J=8 Hz)	5.95 (1H, d, J=8 Hz)	6.00 (1H, d, J=8 Hz)
Fuc-2	4.48 (1H, dd, J=9.5, 8 Hz)	4.73 (1H, dd, J=9.5, 8 Hz)	4.40 (1H, dd, J=9.5, 8 Hz)	4.48 (1H, t, J=8.5 Hz)
Fuc-3	4.32 (1H, dd, J=9.5, 3.5 Hz)	5.36 (1H, dd, J=9.5, 3 Hz)	4.20 (1H, dd, J=9.5, 3 Hz)	4.31 [a]
Fuc-4	5.48 (1H, d, J=3.5 Hz)	[b]	5.67 (1H, d, J=3 Hz)	5.48 (1H, d, J=3 Hz)
Fuc-5	4.04 [a]	3.94 (1H, q, J=6 Hz)	3.97 [a]	[b]
Fuc-6	1.25 (3H, d, J=6 Hz)	1.40 (3H, d, J=6 Hz)	1.18 (3H, d, J=6 Hz)	1.24 (3H, d, J=6.5 Hz)
(Inner)				
Rham-1	6.19 (1H, br s)	5.68 (1H, br s)	5.84 (1H, br s)	6.19 (1H, br s)
Rham-2	4.73 [a]	4.53 (1H, m)	4.65 (1H, m)	4.73 [a]
Rham-3	4.59 (1H, dd, J=9.5, 3 Hz)	4.46 (1H, dd, J=9, 3 Hz)	4.54 [a]	4.61 (1H, dd, J=9.5, 3 Hz)
Rham-4	4.29 (1H, t, J=9 Hz)	4.25 (1H, t, J=9.5 Hz)	4.27 (1H, t, J=9 Hz)	4.30 (1H, t, J=9.5 Hz)
Rham-5	4.46 (1H, m)	4.32 (1H, m)	4.34 (1H, m)	4.46 [a]
Rham-6	1.74 (3H, d, J=6 Hz)	1.63 (1H, d, J=6 Hz)	1.70 (3H, d, J=6 Hz)	1.73 (3H, d, J=6 Hz)
Xyl-1	4.99 (1H, d, J=8 Hz)	4.99 (1H, d, J=8 Hz)	4.97 (1H, d, J=8 Hz)	5.00 (1H, d, J=8 Hz)
Xyl-2	4.02 (1H, t, J=8.5 Hz)	4.00 (1H, t, J=8.5 Hz)	4.02 (1H, t, J=8.5 Hz)	4.03 (1H, t, J=8.5 Hz)
Xyl-3	4.16 (1H, t, J=8.5 Hz)	4.15 [a]	4.16 (1H, t, J=8 Hz)	4.15 (1H, t, J=8.5 Hz)
Xyl-4	4.07 [a]	4.14 [a]	4.07 [a]	[b]
Xyl-5	3.45 (1H, br t, J=11 Hz)	3.43 (1H, br t, J=11 Hz)	3.43 (1H, br t, J=11 Hz)	3.43 (1H, br t, J=11 Hz)
	4.15 (1H, d, J=11 Hz)	[b]	4.15 [a]	[b]
(Terminal)				
Rham-1	6.10 (1H, br s)	6.10 (1H, br s)	6.13 (1H, br s)	6.12 (1H, br s)
Rham-2	4.74 [a]	4.70 (1H, m)	4.73 (1H, m)	4.72 (1H, m)
Rham-3	4.56 (1H, dd, J=9.5, 3 Hz)	4.51 (1H, dd, J=9.5, 3 Hz)	4.53 [a]	4.52 [a]
Rham-4	4.26 (1H, t, J=9 Hz)	4.26 (1H, t, J=9.5 Hz)	4.26 (1H, t, J=9 Hz)	[b]
Rham-5	4.85 (1H, m)	4.86 (1H, m)	4.87 (1H, m)	4.86 (1H, m)
Rham-6	1.64 (3H, d, J=6 Hz)	1.64 (3H, d, J=6 Hz)	1.64 (3H, d, J=6 Hz)	1.63 (3H, d, J=6 Hz)
Api-1			5.69 (1H, d, J=2 Hz)	
Api-2			4.51 (1H, d, J=2 Hz)	
Api-4			4.32, 4.47 (each 1H, d, J=10 Hz)	
Api-5			4.46, 4.59 (each 1H, d, J=11.5 Hz)	

Recorded at 500 MHz at 35 °C. *a*) Obscured by other signals, therefore, couplings could not be determined. *b*) Not assigned.

TABLE I. (continued)

Proton No.	5	6	7	8
Aglycone moiety				
2	4.76 [a]	4.76 [a]	4.70 (1H, m)	4.76 [a]
3	4.30 [a]	4.30 (1H, d, J=3 Hz)	4.22 (1H, d, J=3 Hz)	4.31 (1H, d, J=3 Hz)
12	5.62 (1H, t-like)	5.66 (1H, t-like)	5.62 (1H, t-like)	5.63 (1H, t-like)
16	5.16 (1H, br s)	5.19 [a]	5.16 (1H, br s)	5.13 (1H, br s)
18	3.39 (1H, dd, J=14, 4 Hz)	3.41 (1H, dd, J=14, 4 Hz)	3.39 (1H, dd, J=14, 4 Hz)	3.38 (1H, dd, J=14, 3 Hz)
23	3.71 (1H, d, J=11 Hz)	3.73 (1H, d, J=11 Hz)	3.71 (1H, d, J=11 Hz)	3.72 (1H, d, J=11 Hz)
	[b]	4.27 [a]	4.28 [a]	4.29 [a]
24	1.32 (3H, s)	1.33 (3H, s)	1.33 (3H, s)	1.35 (3H, s)
25	1.56 (3H, s)	1.56 (3H, s)	1.54 (3H, s)	1.58 (3H, s)
26	1.17 (3H, s)	1.18 (3H, s)	1.17 (3H, s)	1.18 (3H, s)
27	1.74 (3H, s)	1.77 (3H, s)	1.75 (3H, s)	1.77 (3H, s)
29	0.93 (3H, s)	0.94 (3H, s)	0.93 (3H, s)	0.94 (3H, s)
30	1.00 (3H, s)	1.05 (3H, s)	1.00 (3H, s)	1.05 (3H, s)
Ester moiety				
Ac				2.00 (3H, s)
2		2.63 (1H, dd, J=15.5, 6 Hz)		
		2.75 (1H, dd, J=15.5, 7 Hz)		
3		5.52 (1H, m)		
4		1.31 (3H, d, J=6.5 Hz)		
2′		2.67 (1H, dd, J=15.5, 6 Hz)		
		2.78 (1H, dd, J=15.5, 7.5 Hz)		
3′		5.54 (1H, m)		
4′		1.34 (3H, d, J=6.5 Hz)		
2″		2.60 (1H, dd, J=15, 5.5 Hz)		
		2.74 (1H, dd, J=15, 7.5 Hz)		
3″		4.54 [a]		
4″		1.38 (3H, d, J=6.5 Hz)		
Sugar moiety				
C-3 (Inner)				
Glc-1	5.10 (1H, d, J=8 Hz)	5.08 (1H, d, J=8 Hz)	5.06 (1H, d, J=8 Hz)	5.09 (1H, d, J=8 Hz)
Glc-2	4.00 (1H, t, J=8 Hz)	3.99 (1H, t, J=8 Hz)	3.98 (1H, t, J=8.5 Hz)	4.01 [a]
Glc-3	4.06 (1H, t, J=8.5 Hz)	4.07 (1H, t, J=8 Hz)	4.18 (1H, t, J=9 Hz)	4.07 [a]
Glc-4	4.10 (1H, t, J=8.5 Hz)	[b]	4.29 [a]	4.07 [a]
Glc-5	3.82 (1H, m)	3.80 (1H, m)	3.85 (1H, m)	3.80 (1H, m)
Glc-6	4.24 (1H, dd, J=11.5, 5 Hz)	4.21 [a]	4.37 (1H, dd, J=12, 2 Hz)	4.21 [a]
	4.39 (1H, br d, J=11.5 Hz)	4.36 (1H, dd, J=11.5, 2 Hz)	4.48 [a]	4.37 (1H, br d, J=12 Hz)
(Terminal)				
Xyl-1	5.17 (1H, d, J=8 Hz)	5.20 (1H, d, J=8 Hz)	5.15 (1H, d, J=8 Hz)	5.21 (1H, d, J=8 Hz)
Xyl-2	4.00 (1H, t, J=8 Hz)	4.04 (1H, t, J=8.5 Hz)	4.06 (1H, d, J=8.5 Hz)	4.05 [a]
Xyl-3	4.12 (1H, t, J=8 Hz)	4.23 (1H, t, J=8.5 Hz)	4.18 [a]	4.23 (1H, t, J=8.5 Hz)
Xyl-4	[b]	[b]	[b]	[b]
Xyl-5	3.68 (1H, br t, J=11 Hz)	4.00 (1H, m)	3.98 (1H, m)	4.01 [a]
	[b]	[b]	4.28 [a]	[b]
		[b]	4.51 (1H, dd, J=12, 2 Hz)	4.52 (1H, dd, J=12, 1 Hz)
C-28 Fuc-1	5.97 (1H, d, J=8 Hz)	6.02 (1H, d, J=8 Hz)	5.98 (1H, d, J=8 Hz)	5.96 (1H, d, J=8 Hz)
Fuc-2	4.59 (1H, t, J=9 Hz)	4.49 (1H, t, J=8.5 Hz)	4.60 (1H, t, J=8.5 Hz)	4.42 (1H, t, J=8.5 Hz)
Fuc-3	4.10 (1H, dd, J=9, 3 Hz)	4.32 [a]	4.11 (1H, dd, J=8.5, 3 Hz)	4.20 [a]
Fuc-4	3.92 (1H, d, J=3 Hz)	5.48 (1H, d, J=3.5 Hz)	3.92 (1H, d, J=3 Hz)	5.68 (1H, d, J=3 Hz)
Fuc-5	3.88 (1H, q, J=6.5 Hz)	4.00 [a]	3.88 (1H, m)	3.97 [a]
Fuc-6	1.46 (3H, d, J=6.5 Hz)	1.24 (3H, d, J=6.5 Hz)	1.45 (3H, d, J=6 Hz)	1.18 (3H, d, J=6 Hz)
(Inner)				
Rham-1	6.33 (1H, br s)	6.22 (1H, s)	6.34 (1H, br s)	5.87 (1H, br s)
Rham-2	4.76 (1H, m)	4.73 [a]	4.77 (1H, m)	4.71 [a]
Rham-3	4.64 (1H, dd, J=9.5, 3 Hz)	4.62 (1H, dd, J=9.5, 3 Hz)	4.65 (1H, dd, J=9.5, 3 Hz)	4.56 [a]
Rham-4	4.30 (1H, t, J=9.5 Hz)	4.31 (1H, t, J=9.5 Hz)	4.30 (1H, t, J=9.5 Hz)	4.28 [a]
Rham-5	4.45 (1H, m)	4.49 [a]	4.87 (1H, m)	4.34 [a]
Rham-6	1.61 (3H, d, J=6.5 Hz)	1.75 (3H, d, J=6.5 Hz)	1.61 (3H, d, J=6 Hz)	1.70 (3H, d, J=6 Hz)
Xyl-1	5.01 (1H, d, J=8 Hz)	5.01 (1H, d, J=8 Hz)	5.01 (1H, d, J=8 Hz)	4.99 (1H, d, J=8 Hz)
Xyl-2	4.03 (1H, t, J=8 Hz)	4.05 (1H, t, J=8 Hz)	4.04 (1H, t, J=8.5 Hz)	4.02 (1H, t, J=8 Hz)
Xyl-3	4.17 (1H, t, J=8.5 Hz)	4.17 (1H, t, J=8 Hz)	4.16 [a]	4.18 [a]
Xyl-4	[b]	[b]	4.15 [a]	[b]
Xyl-5	3.45 (1H, br t, J=11 Hz)	3.44 (1H, br t, J=11 Hz)	3.43 (1H, br t, J=11 Hz)	3.45 (1H, br t, J=11 Hz)
	[b]	[b]	4.16 [a]	[b]
(Terminal)				
Rham-1	6.14 (1H, br s)	6.14 (1H, br s)	6.13 (1H, br s)	6.15 (1H, br s)
Rham-2	4.74 (1H, m)	4.74 [a]	4.74 (1H, m)	4.75 [a]
Rham-3	4.53 (1H, dd, J=9.5, 3 Hz)	4.54 (1H, dd, J=9.5, 3 Hz)	4.55 (1H, dd, J=9.5, 3 Hz)	4.56 [a]
Rham-4	4.26 (1H, t, J=9.5 Hz)	4.26 (1H, t, J=9.5 Hz)	4.28 [a]	4.30 [a]
Rham-5	4.86 (1H, m)	4.88 (1H, m)	4.46 (1H, m)	4.90 (1H, m)
Rham-6	1.64 (3H, d, J=6.5 Hz)	1.64 (3H, d, J=6.5 Hz)	1.64 (3H, d, J=6 Hz)	1.66 (3H, d, J=6 Hz)
Api-1				5.72 (1H, d, J=2 Hz)
Api-2				4.71 [a]
Api-4				4.32, 4.61 (each 1H, d, J=10 Hz)
Api-5				[b], [b]

TABLE I. (continued)

Proton No.	9	10
Aglycone moiety		
2	4.70 [a]	[b]
3	4.24 (1H, d, J=3 Hz)	4.30 [a]
12	5.63 (1H, t-like)	5.62 (1H, t-like)
16	5.13 (1H, br s)	5.16 (1H, br s)
18	3.38 (1H, dd, J=14, 3 Hz)	3.39 (1H, dd, J=14, 4 Hz)
23	3.73 (1H, d, J=11 Hz)	3.71 (1H, d, J=11 Hz)
	4.30 [a]	4.28 [a]
24	1.36 (3H, s)	1.32 (3H, s)
25	1.56 (3H, s)	1.56 (3H, s)
26	1.18 (3H, s)	1.17 (3H, s)
27	1.77 (3H, s)	1.74 (3H, s)
29	0.94 (3H, s)	0.93 (3H, s)
30	1.05 (3H, s)	1.00 (3H, s)
Ester moiety		
Ac	2.00 (3H, s)	
2		
3		
4		
2′		
3′		
4′		
2″		
3″		
4″		
Sugar moiety		
C-3 (Inner)		
Glc-1	5.07 (1H, d, J=8 Hz)	5.08 (1H, d, J=8 Hz)
Glc-2	3.98 (1H, t, J=8 Hz)	4.00 [a]
Glc-3	4.19 [a]	4.06 [a]
Glc-4	4.29 [a]	4.06 [a]
Glc-5	3.85 (1H, m)	3.79 (1H, m)
Glc-6	[b]	4.20 [a]
	4.37 (1H, dd, J=11, 1.5 Hz)	4.37 (1H, br d, J=12 Hz)
(Terminal)		
Xyl-1	5.16 (1H, d, J=8 Hz)	5.20 (1H, d, J=8 Hz)
Xyl-2	4.06 [a]	4.05 [a]
Xyl-3	4.18 [a]	4.23 (1H, t, J=9 Hz)
Xyl-4	[b]	[b]
Xyl-5	3.98 (1H, m)	4.02 [a]
	[b]	4.30 [a]
	[b]	4.52 (1H, br d, J=12 Hz)
C-28 Fuc-1	5.97 (1H, d, J=8 Hz)	5.98 (1H, d, J=8.5 Hz)
Fuc-2	4.42 (1H, t, J=9 Hz)	4.59 (1H, t, J=8.5 Hz)
Fuc-3	4.19 (1H, dd, J=9.5, 3 Hz)	4.11 [a]
Fuc-4	5.68 (1H, d, J=3 Hz)	3.92 (1H, d, J=3 Hz)
Fuc-5	3.97 [a]	3.88 (1H, q, J=6.5 Hz)
Fuc-6	1.17 (3H, d, J=6 Hz)	1.46 (3H, d, J=6 Hz)
(Inner)		
Rham-1	5.88 (1H, br s)	6.34 (1H, br s)
Rham-2	4.70 [a]	4.76 [a]
Rham-3	4.55 [a]	4.63 (1H, dd, J=9.5, 3.5 Hz)
Rham-4	4.28 [a]	4.31 (1H, t, J=9.5 Hz)
Rham-5	4.34 (1H, m)	4.45 (1H, m)
Rham-6	1.70 (3H, d, J=6 Hz)	1.61 (3H, d, J=6 Hz)
Xyl-1	4.98 (1H, d, J=8 Hz)	5.02 (1H, d, J=8 Hz)
Xyl-2	4.05 [a]	4.04 [a]
Xyl-3	4.16 [a]	4.17 [a]
Xyl-4	4.06 [a]	4.15 [a]
Xyl-5	3.44 (1H, br t, J=11 Hz)	3.44 (1H, br t, J=11 Hz)
	4.16 [a]	4.14 [a]
(Terminal)		
Rham-1	6.14 (1H, br s)	6.15 (1H, br s)
Rham-2	4.75 (1H, m)	4.74 [a]
Rham-3	4.56 [a]	4.54 (1H, dd, J=9.5, 3.5 Hz)
Rham-4	4.28 [a]	4.26 (1H, t, J=9.5 Hz)
Rham-5	4.88 (1H, m)	4.87 (1H, m)
Rham-6	1.66 (3H, d, J=6 Hz)	1.63 (3H, d, J=6 Hz)
Api-1	5.72 (1H, d, J=2 Hz)	
Api-2	4.70 [a]	
Api-4	4.32, 4.61 (each 1H, d, J=10 Hz)	
Api-5	[b], [b]	

inner glucose. The NOE irradiation at each anomeric proton signal showed the sugar linkage as shown in Chart 1.

Solidagosaponins XXVIII (**8**) and XXIX (**9**) revealed a $[M+Na]^+$ ion peaks at m/z 1596 in the FAB-MS, and ^{1}H- and ^{13}C-NMR spectra very similar to each other, with an acetyl (δ 2.00; 20.6; 170.6) and an apiosyl residue (δ 65.2; 75.5; 78.6; 80.5; 112.8). Both compounds afforded D-glucose, D-xylose, D-fucose and L-rhamnose (2:1:1:2) and polygalacic acid on acid hydrolysis, while D-apiose was detected on mild acid hydrolysis. The H-4 of fucose was shifted downfield to δ 5.68 in **8** and **9**, suggesting that the acetyl group was attached to the C-4 of fucose. When the signal due to the H-1 of each glucose (δ 5.09, 5.21), the H-1 of apiose (δ 5.72), the H-1 of each rhamnose (δ 5.87, 6.15) and the H-1 of xylose (δ 4.99) were irradiated, NOEs were observed at signals due to the H-3 of an aglycone, the H-3 of glucose, the H-3 of fucose, the H-2 of fucose, the H-3 of xylose and the H-4 of rhamnose, respectively, in the ^{1}H-NMR spectrum of **8**. While the signal due to the H-1 of each glucose (δ 5.07, 5.16), the H-1 of apiose (δ 5.72), the H-1 of each rhamnose (δ 5.88, 6.14) and the H-1 of xylose (δ 4.98) were irradiated, NOEs were observed at signals due to the H-3 of an aglycone, the H-4 of glucose, the H-3 of fucose, the H-2 of fucose, the H-3 of xylose and the H-4 of rhamnose, respectively in **9**. These data led to the proposed structures **8** and **9** for solidagosaponins XXVIII and XXIX, respectively.

Hiller *et al.* reported the isolation of virgaureasaponins 1—3 belonging to the 3,28-bisdesmoside of polygalacic acid after partial alkaline hydrolysis of a saponin fraction of European *S. virga-aurea* L.[3,5] On the other hand, we reported the isolation of 3-mono-, 16-mono-, 16,28-bis- and 3,16,28-tridesmosides other than 3,28-bisdesmoside from the intact saponin fraction of Japanese *S. virga-aurea* L. We cannot explain these difference as yet.

The anomeric configurations of glucose, fucose and xylose in these saponins were determined to be all β from the J value of its anomeric proton signal, and those of rhamnose and apiose were decided to be α and β, respectively, by comparison of the ^{13}C-NMR data of C-3 and C-5 of rhamnose[6] and C-1 and C-2 of apiose.[7] The absolute configuration of the ester side chain attached to the C-4 of fucose could not be determined.

Experimental

General Procedure ^{1}H- and ^{13}C-NMR spectra were obtained with a JEOL GSX 270 and GSX 500 FT NMR, and chemical shifts were given in ppm with tetramethylsilane as an internal standard. FAB-MS was recorded on a JEOL JMS SX102 mass spectrometer. Optical rotations were measured with a JASCO DIP-360 digital polarimeter. Gas chromatography (GC) was run on a Hitachi G-3000 gas chromatograph. Preparative and semi-preparative HPLC was carried out on a column of Develosil Lop-ODS (5 cm × 50 cm) and YMC D-ODS-7 (2 cm × 25 cm) or Develosil PhA-7 (2 cm × 25 cm), respectively.

Extraction and Isolation *Solidago virga-aurea* L. was collected in Shizuoka, Japan in October, 1989. The fresh whole plants (*ca.* 17 kg) were extracted twice with hot water. The extract was passed through a porous polymer gel Mitsubishi Diaion HP-20 column. After the content of the column was washed with water, the adsorbed materials were eluted with 50% aqueous methanol and methanol, successively. The methanol eluate (113 g) was rechromatographed on silica gel with $CHCl_3$–MeOH–EtOAc–H_2O (40:20:27:3) to afford 17 fractions,

TABLE II. ^{13}C-NMR Spectral Data of Saponins XXI—XXIX in C_5D_5N

Carbon No.	1	2	3	4	5	6	7	8	9	10
Aglycone										
1	44.3	44.3	44.4	44.3	44.3	44.3	44.2	44.4	44.3	44.3
2	70.4	70.7	70.4	70.4	70.6	70.4	70.5	70.5	70.5	70.7
3	83.3	83.2	83.3	83.3	83.3	83.3	83.9	83.3	83.8	83.7
4	42.9	42.9	42.9	42.9	42.9	42.9	42.8	42.9	42.8	42.9
5	47.9	47.9	48.0	48.0	47.9	48.0	48.2	48.0	48.2	48.0
6	18.3	18.3	18.4	18.4	18.3	18.4	18.4	18.3	18.4	18.3
7	33.3	33.3	33.4	33.4	33.3	33.4	33.4	33.4	33.4	33.3
8	40.3	40.3	40.3	40.3	40.3	40.3	40.3	40.3	40.4	40.3
9	47.6	47.6	47.6	47.7	47.6	47.6	47.6	47.6	47.7	47.6
10	37.1	37.1	37.1	37.1	37.1	37.1	37.1	37.1	37.1	37.1
11	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1
12	122.8	122.8	122.7	122.8	122.7	122.8	122.7	122.8	122.8	122.8
13	144.4	144.3	144.4	144.4	144.4	144.4	144.5	144.4	144.4	144.4
14	42.4	42.3	42.4	42.4	42.3	42.4	42.4	42.4	42.4	42.4
15	36.0	36.0	36.1	36.1	36.0	36.1	36.1	36.0	36.0	36.1
16	74.0	74.0	74.1	74.1	74.0	74.1	74.0	74.1	74.1	74.1
17	49.5	49.4	49.6	49.6	49.4	49.6	49.4	49.6	49.6	49.4
18	41.7	41.7	41.7	41.7	41.7	41.7	41.7	41.7	41.7	41.7
19	47.4	47.4	47.5	47.5	47.4	47.5	47.4	47.5	47.5	47.4
20	30.8	30.8	30.8	30.8	30.8	30.8	30.9	30.8	30.8	30.8
21	36.3	36.3	36.3	36.3	36.3	36.3	36.3	36.3	36.2	36.3
22	32.0	31.9	31.9	32.0	31.9	32.0	32.0	31.8	31.9	32.0
23	65.7	65.5	65.7	65.7	65.6	65.7	66.2	65.7	66.2	65.7
24	15.0	15.1	15.1	15.1	15.0	15.1	15.0	15.1	15.0	15.1
25	17.5	17.5	17.6	17.6	17.5	17.6	17.5	17.6	17.6	17.5
26	17.6	17.6	17.7	17.7	17.6	17.7	17.6	17.7	17.7	17.6
27	27.1	27.2	27.2	27.2	27.1	27.2	27.1	27.2	27.1	27.2
28	176.2	175.9	176.1	176.2	176.1	176.2	176.2	176.1	176.1	176.2
29	33.1	33.2	33.1	33.2	33.2	33.1	33.2	33.2	33.2	33.2
30	24.6	24.6	24.7	24.7	24.6	24.7	24.6	24.7	24.7	24.6
Sugar at C-3										
Inner Glc										
1	105.3	105.4	105.4	105.3	105.3	105.3	105.3	105.3	105.3	105.3
2	74.4	74.4	74.4	74.4	74.4	74.1	75.0	74.1	75.0	74.1
3	87.7	87.7	87.7	87.7	87.7	88.8	76.8	88.7	76.8	88.8
4	69.4	69.4	69.4	69.4	69.4	69.7	81.2	69.7	81.2	69.7
5	78.2	78.2	78.2	78.2	77.9	77.9	76.3	77.9	76.2	77.9
6	62.2	62.3	62.3	62.3	62.2	62.3	62.1	62.3	62.1	62.2
Terminal Xyl or Glc										
1	106.3	106.3	106.3	106.3	106.2	105.9	105.0	105.9	105.0	105.9
2	75.3	75.3	75.3	75.3	75.2	75.5	74.8	75.5	74.8	75.5
3	77.9	78.0	78.0	78.0	78.1	78.8	78.3	78.3	78.3	78.3
4	70.9	70.9	70.9	70.9	70.9	71.7	71.7	71.7	71.6	71.7
5	67.4	67.4	67.4	67.4	67.4	78.3	78.5	78.7	78.5	78.8
6						62.6	62.5	62.6	62.5	62.6
Sugar at C-28										
Fuc										
1	94.5	94.5	94.4	94.5	94.8	94.5	94.8	94.5	94.4	94.8
2	74.5	69.7	74.4	74.7	74.3	74.5	74.3	74.7	74.7	74.3
3	73.8	78.3	80.6	73.8	76.6	73.9	76.6	80.3	80.5	76.6
4	74.9	72.1	74.1	74.9	73.1	75.0	73.2	73.8	73.8	73.2
5	70.6	72.3	70.7	70.7	72.4	70.7	72.4	70.7	70.5	72.5
6	16.5	16.6	16.5	16.5	16.9	16.5	16.9	16.5	16.5	16.9
Inner Rham										
1	101.8	101.8	102.3	101.9	101.3	101.8	101.4	102.5	102.5	101.4
2	71.8	71.6	71.6	71.8	71.9	71.9	71.9	71.6	71.6	71.9
3	72.5	72.4	72.3	72.5	72.5	72.5	72.5	72.3	72.3	72.7
4	84.5	84.1	84.0	84.6	84.4	84.6	84.5	84.0	84.1	84.5
5	68.6	68.9	69.1	68.7	68.4	68.7	68.4	69.1	69.1	68.4
6	18.6	18.5	18.6	18.6	18.5	18.6	18.5	18.6	18.6	18.5
Xyl										
1	107.1	106.9	107.0	107.1	107.0	107.1	107.1	107.0	107.1	107.1
2	76.3	76.1	76.2	76.3	76.4	76.4	76.4	76.3	76.4	76.4
3	83.7	83.8	83.6	83.8	83.6	83.8	83.6	83.6	83.6	83.3
4	69.3	69.3	69.3	69.3	69.3	69.3	69.3	69.3	69.3	69.3
5	67.5	67.3	67.3	67.3	67.3	67.5	67.3	67.4	67.3	67.3

TABLE II. (continued)

Carbon No.	1	2	3	4	5	6	7	8	9	10
Terminal Rham										
1	102.6	102.7	102.6	102.6	102.6	102.7	102.7	102.6	102.7	102.6
2	72.5	72.5	72.5	72.5	72.5	72.5	72.5	72.5	72.5	72.7
3	72.6	72.6	72.7	72.6	72.6	72.7	72.6	72.7	72.6	72.9
4	74.0	74.0	74.1	74.1	74.0	74.1	74.1	74.1	74.1	74.1
5	69.9	69.9	69.9	69.9	69.9	69.9	70.0	69.9	70.0	69.9
6	18.6	18.6	18.6	18.7	18.6	18.7	18.6	18.6	18.6	18.6
Api										
1			112.4					112.8	112.8	
2			78.8					78.6	78.6	
3			78.4					80.5	80.5	
4			75.4					75.5	75.6	
5			67.3					65.2	65.2	
Ester										
Butyrate										
1	170.6	170.0	170.2	170.8		170.7				
2	40.6	40.8	40.5	40.8		40.6				
3	67.8	67.8	67.8	67.5		67.9				
4	19.7	19.7	19.8	19.9		19.8				
1′	169.7	170.0	169.7	171.3		169.7				
2′	41.3	41.1	41.3	45.2		41.3				
3′	67.6	67.7	67.6	64.5		67.6				
4′	19.9	19.9	20.0	23.9		20.0				
1″	171.4	171.4	171.4			171.4				
2″	45.1	45.1	45.1			45.1				
3″	64.4	64.4	64.5			64.4				
4″	23.9	23.9	23.9			23.9				
Acetyl										
1			170.8					170.6	170.6	
2			20.7					20.6	20.6	

Recorded at 67.8 MHz or 125.6 MHz at 35 °C.

frs. A—Q. Fraction K (4.7 g) was chromatographed on a silica gel (Fuji gel 2061) column with $CHCl_3$–MeOH–EtOAc–H_2O (34:25:36:4) to give 7 fractions, frs. a—g. Repeated chromatography of fr. d (1.6 g) on a D-ODS-7 and PhA-7 column yielded **1** (21 mg) and **2** (8 mg). Fraction L (1.2 g, 1/2 of total fraction) was chromatographed on a Lop-ODS column with aqueous methanol (50→80%, linear gradient) to give **3** (50 mg). Fractions N (1.7 g, 1/3 of total fraction) and P (1.8 g, 1/4 of total fraction) were separated to give **4** (94 mg), **6** (265 mg) and **5** (44 mg), respectively, under the same condition as fr. L. Fraction Q (2.0 g, 1/3 of total fraction) was chromatographed on a Lop-ODS column with aqueous methanol (50→80%, linear gradient) to give 16 fractions, frs. a′—p′. Repeated chromatography of frs. g′ (93 mg), i′ (166 mg), k′(96 mg) and l′ (150 mg) on a PhA-7 column yielded **7** (32 mg), **10** (60 mg), **9** (20 mg) and **8** (25 mg), respectively.

Solidagosaponin XXI (**1**): Amorphous powder, $[\alpha]_D^{20}$ −20.1° (c= 0.83, MeOH). *Anal.* Calcd for $C_{76}H_{122}O_{37}\cdot 6H_2O$: C, 52.59; H, 7.78. Found: C, 52.64; H, 7.76. FAB-MS *m/z*: 1650 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Solidagosaponin XXII (**2**): Amorphous powder, $[\alpha]_D^{20}$ −3.8° (c= 0.31, MeOH). *Anal.* Calcd for $C_{76}H_{122}O_{37}\cdot 10H_2O$: C, 50.49; H, 7.92. Found: C, 50.38; H, 7.56. FAB-MS *m/z*: 1650 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Solidagosaponin XXIII (**3**): Amorphous powder, $[\alpha]_D^{22}$ −25.0° (c= 0.98, MeOH). *Anal.* Calcd for $C_{72}H_{116}O_{35}\cdot 6H_2O$: C, 52.42; H, 7.82. Found: C, 52.46; H, 7.82. FAB-MS *m/z*: 1564 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Solidagosaponin XXIV (**4**): Amorphous powder, $[\alpha]_D^{20}$ −25.0° (c= 0.98, MeOH). *Anal.* Calcd for $C_{72}H_{116}O_{35}\cdot 6H_2O$: C, 52.42; H, 7.82. Found: C, 52.46; H, 7.82. FAB-MS *m/z*: 1564 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Solidagosaponin XXV (**5**): Amorphous powder, $[\alpha]_D^{20}$ −25.8° (c= 1.23, MeOH). *Anal.* Calcd for $C_{64}H_{104}O_{31}\cdot 5H_2O$: C, 52.66; H, 7.87. Found: C, 52.79; H, 7.85. FAB-MS *m/z*: 1392 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Solidagosaponin XXVI (**6**): Amorphous powder, $[\alpha]_D^{20}$ −22.2° (c= 1.04, MeOH). *Anal.* Calcd for $C_{77}H_{124}O_{38}\cdot 5H_2O$: C, 52.91; H, 7.73. Found: C, 52.68; H, 7.81. FAB-MS *m/z*: 1680 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Solidagosaponin XXVII (**7**): Amorphous powder, $[\alpha]_D^{25}$ −31.5° (c= 1.62, MeOH). *Anal.* Calcd for $C_{65}H_{106}O_{32}\cdot 6H_2O$: C, 51.78; H, 7.89. Found: C, 51.68; H, 7.81. FAB-MS *m/z*: 1422 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Solidagosaponin XXVIII (**8**): Amorphous powder, $[\alpha]_D^{25}$ −28.6° (c= 1.75, MeOH). *Anal.* Calcd for $C_{72}H_{116}O_{37}\cdot 15/2H_2O$: C, 50.61; H, 7.73. Found: C, 50.44; H, 7.64. FAB-MS *m/z*: 1596 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Solidagosaponin XXIX (**9**): Amorphous powder, $[\alpha]_D^{25}$ −28.2° (c= 1.56, MeOH). *Anal.* Calcd for $C_{72}H_{116}O_{37}\cdot 7H_2O$: C, 50.88; H, 7.71. Found: C, 50.91; H, 7.78. FAB-MS *m/z*: 1596 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Acid Hydrolysis of Saponins 1—10 Each saponin (1 mg) was heated with dioxane (0.05 ml) and 5% H_2SO_4 in water (0.05 ml) at 100 °C for 1 h. After dilution with water, the reaction mixture was extracted with ethyl acetate twice, and the water layer was passed through an Amberlite IRA-60E column. The water eluate was concentrated and the residue was treated with D-cysteine (0.2 mg)[8] in pyridine (0.2 ml) at 60 °C for 1 h. After evaporation of the solvent, hexamethyl disilazane–trimethyl silylchloride–pyridine (2:1:10) (0.02 ml) was added to the residue and the reaction mixture was heated at 60 °C for 1 h. The supernatant was applied to GC. The ethyl acetate layer was concentrated and subjected to HPLC to reveal a peak due to polygalacic acid from every saponin. GC conditions: column, Supelco SPB™-1, 0.25 mm × 27 m; column temperature, 220 °C; carrier gas, N_2; t_R, D-xylose 13.8 min, L-xylose 12.5 min, D-rhamnose 16.2 min[9] L-rhamnose 16.4 min, L-fucose 15.9 min, D-fucose 17.6 min, L-glucose 22.4 min, D-glucose 24.6 min. D-Glucose, D-xylose, D-fucose and L-rhamnose were detected from **1**—**5** at the ratio 1:2:1:2 and from **6**—**10** at the ratio 2:1:1:2. HPLC conditions : column, Develosil OSD-7, 4.6 mm × 25 cm; solvent, MeCN–H_2O (55:45) + 0.05% trifluoroacetic acid (TFA); flow rate, 1.0 ml/min; UV 207 nm; t_R, polygalacic acid 10.1 min.

Mild Acid Hydrolysis of 3, 8 and 9 Each saponin (1 mg) was dissolved in 2 N HCl (0.1 ml) and the solution was stirred for 24 h at room

temperature. The reaction mixture was passed through a column equipped with a Mitsubishi Diaion HP-20 (2 ml) and Amberlite IRA-60E (2 ml). The water eluate was concentrated and the residue was treated with D-cysteine (0.2 mg) in pyridine (0.3 ml) at 60 °C for 1 h. After evaporation of the solvent, *N*-trimethylsilylimidazole-pyridine (1 : 1) (0.04 ml) was added to the solution and the reaction mixture was left for 1 h at room temperature. The solution was applied to GC directly. D-Apiose was detected from every saponin under the same GC conditions mentioned above. t_R, D-apiose 13.3 min, L-apiose 12.4 min.[9]

References and Notes

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