Studies on the Constituents of *Solidago virga-aurea* L. II. Structures of Solidagosaponins X—XX

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After further investigation of more polar fractions of *Solidago virga-aurea* L. (Compositae), 11 new oleanane-type saponins named solidagosaponins X—XX (1—11) were isolated, together with two known saponins, virgaureasaponin 1 (12) and bellissaponin BA_2 (13). These new saponins contain various acyl groups, and four of them were tridesmosidic glycoside. Their structures were established on the basis of spectroscopic and chemical evidence.

Keywords *Solidago virga-aurea*; Compositae; β-hydroxy butyric acid; crotonic acid; polygalacic acid 3,16,28-*O*-tridesmoside; polygalacic acid; oleanane-type saponin; solidagosaponin

In the preceding paper,[1] we reported the isolation and structure elucidation of solidagosaponins I—IX, oleanane-type triterpene glycosides isolated from the less polar saponin fraction of a 100% MeOH eluate of the *Solidago virga-aurea* L. (Compositae). Further investigating the eluate's more polar fraction, we obtained 11 new saponins, designated as solidagosaponins X—XX (**1**—**11**), together with two known saponins, virgaureasaponin 1 (**12**)[2] and bellissaponin BA_2 (**13**).[3] This paper deals with the isolation and structure elucidation of these saponins.

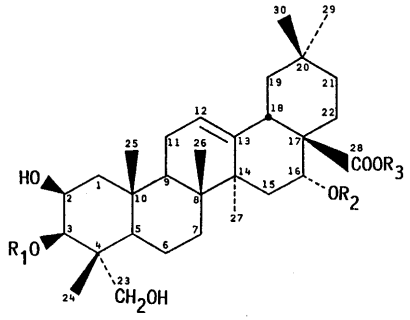
A water extract of the whole plants was passed through a Diaion HP-20 column, and the absorbed materials were eluted with 50% aqueous methanol and 100% methanol, successively. The 100% methanol eluate was chromatographed on a silica gel and an ODS column, followed by repeated semi-preparative high performance liquid chromatography (HPLC) on a reversed phase column (ODS, PhA). We identified all 11 saponins.

Solidagosaponin X (**1**) revealed an $[M+Na]^+$ ion peak at *m/z* 1285 in the fast atom bombardment mass spectrum (FAB-MS) and elemental analysis data was consistent with $C_{60}H_{94}O_{28}\cdot 6H_2O$. On mild methanolysis with AcCl–MeOH (1:10), **1** afforded polygalacic acid. Subsequent acid hydrolysis of the methanolysate yielded glucose and arabinose in a ratio of 1:1. The ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum of **1** showed four anomeric carbon signals (δ 95.3, 98.6, 105.3, 105.7), one set of signals due to a β-hydroxy butyroyl group (δ 24.2, 45.2, 64.5, 172.2) and two sets of signals due to an acetyl group (δ 20.6, 20.9, 170.2, 170.4). When the ^{13}C-NMR data of **1** was compared with that of authentic polygalacic acid,[4] glycosylation shifts[5] were observed at C-2 (−1.0 ppm), C-3 (+9.2 ppm), C-15 (−6.4 ppm), C-16 (+2.6 ppm) and C-28 (−4.5 ppm). This characteristic data suggested that **1** should be a 3,16,28-tridesmoside of polygalacic acid having two glucose, two arabinose, two acetyl groups and one β-hydroxy butyroyl group. The proton signals of **1** were assigned by a detailed proton spin decoupling experiment (Table III). Based on this assignment, the carbon signals of that were identified by carbon-13–proton correlation spectroscopy (^{13}C–^1H COSY) (Tables I and II). For the purpose of investigating the binding site of four monosaccharides, we employed a difference nuclear Overhauser effect (NOE) spectral experiment.[6] When the signals at δ 4.81, 5.14 (the H-1 of each glucose) and 5.45 (the H-1 of one arabinose) were irradiated, NOEs were observed at signals due to the H-16 and H-3 of the aglycone and the H-2 of C-16 glucose (abbreviation for "glucose belongs to the C-16 sugar chain"), respectively. Because an anomeric carbon signal (δ 95.3) of another arabinose was peculiar to an ester-type-glycoside linkage, this sugar attached to the C-28 of the aglycone. Then, in the ^1H-NMR spectrum, the H-3 (δ 5.72) and H-4 (δ 5.71) of C-28 arabinose, and the H-4 (δ 5.47) of C-16 arabinose appeared at so much lower a field than usual that we thought three acyl groups attached to these positions. In order to confirm the binding site of three acyl groups, we used the long range selective proton decoupling (LSPD) method. As the chemical shifts of the H-3 and H-4 of C-28 arabinose were very close to each other, these protons were decoupled selectively at the same time. Owing to the disappearance of long range coupling with these protons, the splitting pattern of two carbonyl carbons (δ 170.4 and 170.2) belonging to each acyl group was a quartet. On the other hand, the H-4 of C-16 arabinose was decoupled selectively, and the splitting pattern of a carbonyl carbon (δ 172.2) belonging to β-hydroxy butyrate was simplified for the same reason. Therefore, solidagosaponin X can be formulated as **1** shown in Chart 1.

Solidagosaponin XI (**2**) gave the same FAB-MS and elemental analysis data as **1**. Mild methanolysis and subsequent acid hydrolysis of **2** yielded polygalacic acid, glucose and arabinose. The ^1H- and ^{13}C-NMR spectra of **2** remarkably resembled those of **1** except for the chemical shifts of C-28 arabinose. Instead of the H-3 of C-28 arabinose in **1**, the H-2 of that in **2** was displaced low-field (δ 5.78) and the anomeric carbon signal of C-28 arabinose (δ 93.0) of **2** shifted higher-field by 2.3 ppm, compared with that of **1**. The linkage sites of three acyl groups (β-hydroxy butyroyl group, 2 × acetyl groups) were confirmed by the LSPD method. It follows that the structure of solidagosaponin XI can be assigned as **2** in Chart 1.

Solidagosaponin XII (**3**) and XIII (**4**) gave polygalacic acid, glucose and arabinose on mild methanolysis and subsequent acid hydrolysis. Except for the absence of the signals due to a β-hydroxy butyrate, the ^1H- and ^{13}C-NMR data of **3** and **4** were almost superimposable on those of **1** and **2**, respectively. In the FAB-MS, **3** and **4** revealed an $[M+Na]^+$ ion peak at *m/z* 1199. This value was 86 mass units less, ($C_4H_7O_2$) corresponding to a β-hydroxy butyrate than that of **1** and **2**. Solidagosaponins XII and XIII can be formulated as **3** and **4**, respectively, in Chart 1.

Solidagosaponin XIV (**5**) revealed at $[M+Na]^+$ ion peak at *m/z* 1517 in the FAB-MS. Elemental analysis data were compatible with $C_{71}H_{114}O_{33}\cdot 3H_2O$. Methanolysis of **5** under mild conditions afforded a polygalacic acid, and subsequent acid hydrolysis of the methanolysate yielded



A : -C(=O)-CH2-CH(OH)-CH3

B : -C(=O)-CH2-CH(O-C(=O)-CH2-CH(OH)-CH3)-CH3

C : -C(=O)-CH2-CH(O-C(=O)-CH2-CH(OH)-CH3)-CH3

D : -C(=O)-CH2-CH(O-C(=O)-C(H)=C(H)-CH3)-CH3

E : -C(=O)-C(H)=C(H)-CH3

Ac : -C(=O)-CH3

	R_1	R_2	R_3
1	-glc	-glc(2)-ara(4)-A	-ara(3)-Ac, (4)-Ac
2	-glc	-glc(2)-ara(4)-A	-ara(2)-Ac, (4)-Ac
3	-glc	-glc(2)-ara	-ara(3)-Ac, (4)-Ac
4	-glc	-glc(2)-ara	-ara(2)-Ac, (4)-Ac
5	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham, (4)-B
6	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham, (4)-Ac
7	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham, (4)-A
8	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham, (4)-A(3)-Ac
9	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham, (4)-C
10	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham, (4)-D
11	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham, (4)-Ac, (3)-api(5)-Ac
12	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham, (4)-E
13	-glc	-H	-fuc(2)-rham(4)-xyl(3)-rham

Chart 1

glucose, fucose, xylose and rhamnose in a ratio of 1 : 1 : 1 : 2. The assignment of this compound was achieved by analysis of a detailed proton spin decoupling experiment and ^{13}C–^{1}H COSY spectrum. While the ^{13}C-NMR spectrum of **5** exhibited five anomeric carbon signals and four ester carbonyl carbon signals (Tables I and II), the ^{1}H-NMR spectrum showed three sets of signals due to β-hydroxy butyrate. Glycosylation shifts[5] at C-2 (−1.2 ppm), C-3 (+10.2 ppm) and C-28 (−3.8 ppm) of the aglycone indicated that **5** was a 3,28-*O*-bisdesmoside. Since the anomeric carbon signal (δ 94.5 ppm) due to fucose showed an ester-type-glycoside linkage, fucose was found to link at the C-28 of the polygalacic acid. The binding sites of four other monosaccharides were determined by the NOE method. When the signal at δ 5.01 (the H-1 of xylose), 5.11 (the H-1 of glucose), 6.13 and 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 the aglycone, the H-3 of xylose and the H-2 of fucose, respectively. The last problem to resolve was where three β-hydroxy butyrate attached. In the ^{1}H-NMR spectrum, the H-4 of fucose (δ 5.48) and the H-3s of two β-hydroxy butyrates out of three (δ 5.52 and 5.54) appeared in the lower field than usual. Furthermore, no other signals in sugar and aglycone moieties shifted to a relatively lower field. Judging from these factors, we assumed that a trimeric β-hydroxy butyrate like B (Chart 1) attached to the H-4 of fucose. Then, in order to investigate acylation shifts in 3-OH of β-hydroxy butyrate, we prepared methyl β-acetoxy butyrate in the usual manner. While the H-3 signal of methyl β-acetoxy butyrate (δ 5.41, m) shifted downfield by 0.86 ppm compared with that of β-hydroxy butyric acid (δ 4.55, m), the C-2,

TABLE I. ^{13}C-NMR Spectral Data of Aglycone and Ester Moieties in C_5D_5N

Carbon No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Aglycone moiety													
1	44.1	44.1	44.0	44.0	44.2	44.2	44.2	44.2	44.2	44.2	44.3	44.1	44.2
2	70.6	70.6	70.6	70.6	70.4	70.4	70.4	70.4	70.4	70.4	70.4	70.4	70.4
3	83.0	83.0	83.0	83.0	83.4	83.6	83.6	83.6	83.5	83.6	83.6	83.6	83.6
4	42.8	42.8	42.8	42.8	42.8	42.8	42.8	42.8	42.8	42.8	42.8	42.8	42.8
5	47.9	47.9	47.8	47.9	48.1	48.2	48.2	48.2	48.2	48.2	48.2	48.1	48.2
6	18.0	18.0	18.0	18.0	18.4	18.4	18.5	18.4	18.4	18.5	18.4	18.4	18.4
7	33.1	33.1	33.0	33.2	33.3	33.3	33.3	33.3	33.3	33.4	33.4	33.3	33.3
8	40.1	40.0	40.1	40.0	40.3	40.3	40.3	40.3	40.3	40.3	40.8	40.3	40.3
9	47.6	47.6	47.5	47.5	47.6	47.6	47.6	47.6	47.6	47.6	47.6	47.6	47.6
10	37.0	37.0	36.9	37.0	37.1	37.1	37.1	37.1	37.1	37.1	37.1	37.1	37.1
11	24.0	24.0	24.0	24.0	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1
12	122.9	122.9	122.9	122.9	122.8	122.8	122.8	122.7	122.8	122.8	122.7	122.8	122.8
13	144.4	144.3	144.1	144.0	144.4	144.4	144.4	144.4	144.4	144.4	144.4	144.4	144.4
14	41.4	41.4	41.4	41.4	42.4	42.4	42.4	42.4	42.4	42.4	42.4	42.4	42.3
15	29.9	29.7	29.8	30.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.1
16	77.5	77.4	77.2	77.0	74.0	74.0	74.0	74.0	74.0	74.0	74.1	74.0	74.0
17	48.8	48.7	48.9	48.8	49.5	49.5	49.5	49.5	49.5	49.5	49.6	49.4	49.5
18	41.0	40.6	41.1	40.7	41.7	41.7	41.7	41.7	41.7	41.7	41.7	41.7	41.7
19	45.0	45.0	45.0	45.2	47.4	47.4	47.4	47.4	47.4	47.4	47.5	47.4	47.4
20	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.7	30.8	30.8
21	36.1	36.2	36.2	36.3	36.2	36.3	36.4	36.3	36.3	36.3	36.3	36.3	36.3
22	32.0	31.9	31.8	31.7	32.1	32.0	32.0	32.0	32.0	32.0	31.9	32.0	32.0
23	65.9	65.9	65.9	65.9	66.2	66.4	66.4	66.4	66.4	66.4	66.3	66.3	66.3
24	15.0	15.0	15.0	15.0	15.1	15.1	15.1	15.0	15.1	15.1	15.1	15.0	15.0
25	17.3	17.3	17.3	17.3	17.5	17.5	17.5	17.5	17.6[e]	17.5	17.6[f]	17.5	17.5
26	17.6	17.5	17.6	17.5	17.6	17.6	17.6	17.6	17.7[e]	17.7	17.7[f]	17.7	17.6
27	27.0	26.9	27.0	26.8	27.1	27.1	27.1	27.1	27.1	27.1	27.1	27.1	27.1
28	175.7	175.2	175.7	175.2	176.2	176.2	176.2	176.2	176.2	176.3	176.1	176.2	176.2
29	33.1	33.2	33.2	33.2	33.1	33.1	33.1	33.1	33.1	33.1	33.1	33.1	33.1
30	25.1	24.8	25.1	24.9	24.6	24.6	24.6	24.7	24.6	24.7	24.7	24.6	24.6
Ester moiety													
$CH_3\underline{C}O$	170.4	170.4	170.4	170.4		171.0		170.7			170.6		
	170.2	170.0	170.2	170.0							170.8		
$\underline{C}H_3CO$	20.9	21.0	20.9	21.0		20.7		21.1			20.7		
	20.6	20.7	20.6	20.7							20.6		
	A	A			B		A	A	C	D		E	
1	172.2	172.2			170.7[a]		172.3	170.0	170.8	170.8		166.5	
2	45.2	45.2			40.5[b]		45.0	40.7	40.7	40.9		[g]	
3	64.5	64.5			67.8[c]		64.9	67.4	67.5	67.4		145.1	
4	24.2	24.2			19.7[d]		24.0	19.8	19.8	19.9		17.7	
1′					169.7[a]				171.3	165.6			
2′					41.2[b]				45.2	[g]			
3′					67.6[c]				64.4	144.9			
4′					19.9[d]				23.9	17.7			
1″					171.4								
2″					45.1								
3″					64.4								
4″					24.0								

Recorded at 67.80 MHz. *a—f*) These values may be interchangeable in each column. *g*) Obscured by signals of C_5D_5N.

C-3 and C-4 signals of methyl β-acetoxy butyrate were observed at δ 40.5 (−4.2 ppm), 67.6 (+2.9 ppm) and 19.8 (−3.7 ppm), respectively. This data sustained our assumption (see Table I ester moiety). Based upon the above evidence, the structure of solidagosaponin XIV was characterized as **5**.

Solidagosaponins XV (**6**), XVI (**7**), XVII (**8**), XVIII (**9**), XIX (**10**), saponins **12** and **13** afforded glucose, fucose, xylose, rhamnose (1 : 1 : 1 : 2) and polygalacic acid on mild methanolysis and subsequent acid hydrolysis. The ^{13}C- and ^{1}H-NMR spectrum due to the aglycone and sugar moieties of these seven saponins were almost superimposable on those of **5**. These facts led us to the conclusion that these saponins partially shared the same structure as **5** and differed only in the structures of an acyl group binding at the 4-OH of fucose. According to the NMR data, **6** and **7** contained one acetyl group and one β-hydroxy butyroyl group, respectively. As the ^{1}H-NMR spectrum of an authentic crotonic acid showed signals at δ 1.71 (3H, d, J=6.5 Hz), 7.14 (1H, m) and 6.11 (1H, br d, J=16.5 Hz), **12** had one crotonoyl group. On the other hand, **8**, **9** and **10** had one acetate, one β-hydroxy butyrate and one crotonate, together with one common β-hydroxy butyrate, respectively. The H-3s of the common β-hydroxy butyrate in **8**, **9** and **10** showed acylation shifts (**8**; δ 5.48, **9**; δ 5.55, **10**; δ 5.56). So acyl moieties in **8**, **9** and **10** were determined as shown in Chart 1. In the NMR spectra of **13**, no signal due to an acyl moiety and no acylation shift in the H-4 of fucose were observed. This evidence led to the formulation of solidagosaponins XV, XVI, XVII, XVIII and XIX as **6**, **7**,

TABLE II. ^{13}C-NMR Spectral Data of Sugar Moiety in C_5D_5N

Carbon No.	1	2	3	4		5	6	7	8	9	10	11	12	13
Sugar moiety														
C-3														
Glc-1	105.7	105.7	105.8	105.8		105.7	105.6	105.6	105.6	105.6	105.6	105.6	105.6	105.6
Glc-2	75.5	75.5	75.5	75.5		75.5	75.5	75.5	75.5	75.5	75.5	75.5	75.5	75.5
Glc-3	78.6	78.6	78.6	78.6		78.6	78.6	78.6	78.6	78.6	78.6	78.6	78.5	78.6
Glc-4	71.7	71.7	71.7	71.7		71.6	71.6	71.6	71.6	71.6	71.6	71.6	71.6	71.6
Glc-5	78.2	78.3	78.3	78.4		78.3	78.3	78.3	78.3	78.3	78.3	78.3	78.3	78.3
Glc-6	62.7	62.7	62.8	62.8		62.6	62.7	62.7	62.7	62.7	62.7	62.7	62.6	62.7
C-16					C-28									
Glc-1	98.6	98.8	98.4	98.5	Fuc-1	94.5	94.5	94.5	94.5	94.5	94.5	94.4	94.6	94.8
Glc-2	80.5	80.6	82.8	82.9	Fuc-2	74.3	74.6	74.6	74.6	74.7	74.7	74.7	74.4	74.3
Glc-3	79.6	79.7	79.4	79.5	Fuc-3	73.8	74.0	74.0	73.9	73.8	73.8	80.3	74.1	76.6
Glc-4	72.2	72.4	71.9	72.3	Fuc-4	74.9	74.7	75.0	74.9	74.9	74.9	73.7	74.9	73.1
Glc-5	78.1	78.2	78.1	78.3	Fuc-5	70.5	70.5	70.6	70.4	70.4	70.4	70.4	70.7	72.4
Glc-6	62.9	62.9	62.9	62.8	Fuc-6	16.5	16.5	16.5	16.5	16.5	16.5	16.4	16.5	16.4
					(Inner)									
Ara-1	105.3	105.3	106.3	106.4	Rham-1	101.9	101.9	101.9	101.9	101.9	101.9	102.4	102.0	101.4
Ara-2	73.4	73.5	73.6	73.6	Rham-2	71.8	71.8	71.8	71.8	71.8	71.8	71.6	71.8	71.9
Ara-3	72.7	72.7	74.9	74.9	Rham-3	72.5	72.6[a]	72.5[b]	72.5[d]	72.5[e]	72.5[g]	72.3	72.5[i]	72.5[k]
Ara-4	72.6	72.6	69.6	69.6	Rham-4	84.6	84.6	84.7	84.6	84.6	84.8	84.1	84.6	84.5
Ara-5	64.2	64.3	67.5	67.5	Rham-5	68.6	68.6	68.6	68.6	68.6	68.6	69.0	68.6	68.4
C-28					Rham-6	18.7	18.6	18.6[c]	18.6	18.6[f]	18.6[h]	18.6	18.6[j]	18.6[l]
Ara-1	95.3	93.0	95.4	93.0	Xyl-1	107.1	107.1	107.1	107.1	107.1	107.1	107.0	107.1	107.1
Ara-2	68.6	72.0	68.6	71.7	Xyl-2	76.3	76.2	76.2	76.2	76.2	76.2	76.1	76.2	76.3
Ara-3	72.9	70.9	72.9	70.9	Xyl-3	83.9	84.0	84.0	84.0	84.0	84.0	83.8	83.9	83.9
Ara-4	67.8	68.9	67.8	68.9	Xyl-4	69.3	69.3	69.3	69.3	69.3	69.3	69.3	69.3	69.3
Ara-5	63.0	63.5	62.9	63.6	Xyl-5	67.3	67.3	67.3	67.3	67.3	67.3	67.3	67.3	67.3
					(Terminal)									
					Rham-1	102.7	102.7	102.7	102.7	102.7	102.7	102.7	102.7	102.6
					Rham-2	72.5	72.5[a]	72.5[b]	72.5[d]	72.5[e]	72.5[g]	72.5	72.5[i]	72.5[k]
					Rham-3	72.5	72.6[a]	72.6[b]	72.6[d]	72.6[e]	72.6[g]	72.6	72.6[i]	72.6[k]
					Rham-4	74.0	74.0	74.0	74.0	74.0	74.0	74.0	74.0	74.0
					Rham-5	70.0	69.9	70.0	69.9	70.0	70.0	69.9	69.9	69.9
					Rham-6	18.7	18.6	18.7[c]	18.6	18.7[f]	18.7[h]	18.6	18.7[j]	18.5[l]
					Api-1							112.3		
					Api-2							78.6		
					Api-3							78.4		
					Api-4							75.4		
					Api-5							67.3		

Recorded at 67.80 MHz. *a—l*) These values may be interchangeable in each column.

8, **9** and **10**, respectively, as shown in Chart 1. Saponins **12** and **13** were identified as bellissaponin BA_2[3] and virgaureasaponin 1,[2] respectively, because their NMR data (in methanol-d_4) were consistent with the reference data reported by Hiller *et al.* (see Experimental). They had already isolated the former from *Bellis perennis* and the latter from *Solidago virga-aurea* L. But they derived virgaureasaponin 1 after partial alkaline hydrolysis of saponin fraction. So we don't know whether or not they obtained this compound as a natural product.

Solidagosaponin XX (**11**) gave glucose, fucose, xylose, rhamnose, apiose (1 : 1 : 1 : 2 : 1) and polygalacic acid as the sugar and aglycone moieties. The ^{13}C-NMR spectrum of **11** confirmed that this compound had the same sugar sequence as **5**—**13**. Not only these monosaccharides (glc, fuc, xyl and 2 × rham), but also one apiose and two acetyl groups, were contained by **11**. According to the NOE method, the binding site of the apiose was determined to be at 3-OH of fucose. The binding sites of two acetyl groups were proved to be at 4-OH of fucose and 5-OH of apiose, respectively. Because of acylation,[5] the H-4 of fucose appeared at a lower field (δ 5.64) and the H_2-5 of apiose also did (δ 4.43 and 4.55). The analysis of the latter was accomplished by the combination of *J*-resolution and a decoupling experiment. Moreover, by comparing the reference data of apiose[7] and employing ^{13}C–^{1}H COSY spectrum, we could assign the C-3 (δ 78.4, +2.0 ppm) and C-5 (δ 67.3, −2.0 ppm) of apiose. It follows that the structure of solidagosaponin XX can be assigned as **11**, as shown in Chart 1.

The anomeric configurations of glucose, fucose, xylose and C-16 arabinose in these saponins were determined to be β, β, β, and α, respectively, from the *J* values of its anomeric proton signals.

As far as we know, solidagosaponins X—XIII (**1**—**4**) represent the first examples of tridesmosidic saponins. The other original saponins (**5**—**11**) were full of a variety of acyl groups binding at a sugar moiety.

Experimental

General Procedures ^{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. Semi-preparative HPLC was carried out on a column of YMC ODS-7

(20 mm × 25 cm) and Develosil PhA-7 (phenyl alkyl) (20 mm × 25 cm).

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 Diaion HP-20 column. After the content of the column was washed with water, the absorbed materials were eluted with 50% aqueous methanol and 100% methanol, successively. The 100% methanol eluate (113 g) was rechromatographed on a silica gel with $CHCl_3$–MeOH–AcOEt–H_2O (40:20:37:3) to afford 17 fractions, frs. A—Q. Fraction H (3.5 g) was chromatographed on a silica gel (Fuji gel, 2061) column with $CHCl_3$–MeOH–AcOEt–H_2O (40:20:37:3) to give six fractions, frs. a—f. Repeated chromatography of fr. e (1.749 g) on an ODS-7 and PhA column yielded **9** (9 mg), **10** (6 mg) and **12** (5 mg). Fraction I (2.1 g) was separated by silica gel column chromatography with $CHCl_3$–MeOH–AcOEt–H_2O (40:20:37:3) to give six fractions, frs. a′—f′. Repeated chromatography of fr. e′ (1.131 g) on an ODS-7 and PhA column yielded **8** (15 mg), **11** (11 mg) and **13** (48 mg). Fraction K (4.7 g) was separated by a silica gel column chromatography with $CHCl_3$–MeOH–AcOEt–H_2O (35:25:36:4) to give seven fractions, frs. a″—g″. Repeated chromatography of fr. d″ (1.681 g) and fr. e″ (0.855 g) on an ODS-7 and PhA column yielded **1** (15 mg), **2** (12 mg), **3** (12 mg), **4** (13 mg), **6** (11 mg) and **7** (10 mg).

Solidagosaponin X (**1**): White amorphous powder, $[\alpha]_D^{21}$ −2.2° (c=0.51, MeOH). *Anal.* Calcd for $C_{60}H_{94}O_{28}\cdot 6H_2O$: C, 52.55; H, 7.79. Found: C, 52.75; H, 7.90. FAB-MS m/z: 1285 $[M+Na]^+$, ^{1}H- and ^{13}C-NMR: Tables I—III.

Solidagosaponin XI (**2**): White amorphous powder, $[\alpha]_D^{21}$ −2.7° (c=0.43, MeOH). *Anal.* Calcd for $C_{60}H_{94}O_{28}\cdot 4H_2O$: C, 53.96; H, 7.70. Found: C, 54.09; H, 7.77. FAB-MS m/z: 1285 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Solidagosaponin XII (**3**): White amorphous powder, $[\alpha]_D^{21}$ −10.3° (c=0.69, MeOH). *Anal.* Calcd for $C_{56}H_{88}O_{26}\cdot 4H_2O$: C, 53.84; H, 7.75. Found: C, 53.94; H, 7.88. FAB-MS m/z: 1199 $[M+Na]^+$. ^{1}H- and

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

Proton No.	1	2	3	4
Aglycone moiety				
2	4.79 (1H, br q, J=3.5 Hz)	4.80 (1H, br q, J=3 Hz)	4.76 (1H, br q, J=3 Hz)	4.76 (1H, br q, J=3 Hz)
3	4.31 (1H, d, J=3.5 Hz)	4.32 (1H, d, J=3 Hz)	4.27 (1H, d, J=3 Hz)	4.28 (1H, d, J=3 Hz)
12	5.56 (1H, t-like)	5.57 (1H, t-like)	5.53 (1H, t-like)	5.54 (1H, t-like)
16	5.31 (1H, br s)	5.22 (1H, br s)	5.37 (1H, br s)	5.28 (1H, br s)
18	3.47 (1H, dd, J=14, 4 Hz)	3.42 (1H, dd, J=14, 4 Hz)	3.45 (1H, dd, J=14, 4.5 Hz)	3.41 (1H, dd, J=14, 4 Hz)
19α	2.86 (1H, t, J=14 Hz)	2.82 (1H, t, J=14 Hz)	2.86 (1H, t, J=14 Hz)	2.83 (1H, t, J=14 Hz)
23	3.67 (1H, d, J=11 Hz)	3.69 (1H, d, J=10.5 Hz)	3.67 (1H, d, J=11 Hz)	3.69 (1H, d, J=11 Hz)
23	4.35 (1H, d, J=11 Hz)	4.36 (1H, d, J=10.5 Hz)	4.33 (1H, d, J=11 Hz)	4.34 (1H, d, J=11 Hz)
24	1.36 (3H, s)	1.37 (3H, s)	1.34 (3H, s)	1.35 (3H, s)
25	1.57 (3H, s)	1.59 (3H, s)	1.54 (3H, s)	1.57 (3H, s)
26	1.01 (3H, s)	1.04 (3H, s)[a]	1.00 (3H, s)[b]	1.03 (3H, s)[c]
27	1.72 (3H, s)	1.73 (3H, s)	1.73 (3H, s)	1.74 (3H, s)
29	1.07 (3H, s)	1.05 (3H, s)[a]	1.07 (3H, s)[b]	1.08 (3H, s)[c]
30	1.07 (3H, s)	1.07 (3H, s)[a]	1.11 (3H, s)[b]	1.10 (3H, s)[c]
Ester moiety				
CH_3CO	1.91 (3H, s)	1.82 (3H, s)	1.93 (3H, s)	1.83 (3H, s)
	2.13 (3H, s)	2.09 (3H, s)	2.13 (3H, s)	2.09 (3H, s)
	A	A		
2	2.70 (1H, dd, J=15, 5.5 Hz)	2.69 (1H, dd, J=15.5, 5.5 Hz)		
2	2.82 (1H, dd, J=15, 7.5 Hz)	2.82 (1H, dd, J=15.5, 7 Hz)		
3	4.59 (1H, m)	4.59 (1H, m)		
4	1.48 (3H, d, J=6 Hz)	1.47 (3H, d, J=6 Hz)		
Sugar moiety				
C-3				
Glc-1	5.14 (1H, d, J=8 Hz)	5.15 (1H, d, J=8 Hz)	5.18 (1H, d, J=8 Hz)	5.19 (1H, d, J=8 Hz)
Glc-2	4.00 (1H, t, J=8 Hz)	4.01 (1H, t, J=8 Hz)	4.01 (1H, t, J=8 Hz)	4.01 (1H, t, J=8 Hz)
Glc-3	4.13 (1H, t, J=8 Hz)	4.13 (1H, t, J=8 Hz)	4.16[h]	4.16 (1H, t, J=8 Hz)
Glc-4	4.18 (1H, t, J=8 Hz)	4.18 (1H, t, J=8 Hz)	4.19[h]	4.18 (1H, t, J=8 Hz)
Glc-5	3.88 (1H, m)	3.89 (1H, m)	3.94 (1H, m)	3.94 (1H, m)
Glc-6	4.29 (1H, dd, J=11.5, 5 Hz)	4.29 (1H, dd, J=11.5, 5 Hz)	4.31 (1H, dd, J=11.5, 5.5 Hz)	4.32 (1H, dd, J=11, 5 Hz)
Glc-6	4.44 (1H, dd, J=11.5, 2.5 Hz)	4.44 (1H, dd, J=11.5, 2.5 Hz)	4.46 (1H, dd, J=11.5, 2.5 Hz)	4.47 (1H, dd, J=11, 2 Hz)
C-16				
Glc-1	4.81 (1H, d, J=8.5 Hz)	4.86 (1H, d, J=8 Hz)	4.88 (1H, d, J=8 Hz)	4.93 (1H, d, J=8 Hz)
Glc-2	4.22 (1H, t, J=8.5 Hz)	4.23 (1H, t, J=8 Hz)	4.16 (1H, t, J=8 Hz)	4.16 (1H, t, J=8.5 Hz)
Glc-3	4.36 (1H, t, J=8.5 Hz)	4.39[h]	4.36 (1H, t, J=8.5 Hz)	4.38 (1H, t, J=9 Hz)
Glc-4	4.15 (1H, t, J=8.5 Hz)	4.24 (1H, t, J=8.5 Hz)	4.18 (1H, t, J=8 Hz)	4.26 (1H, t, J=9 Hz)
Glc-5	3.82 (1H, m)	3.92 (1H, m)	3.83 (1H, m)	3.92 (1H, m)
Glc-6	4.30 (1H, dd, J=11.5, 5.5 Hz)	4.41 (1H, dd, J=11.5, 5 Hz)	4.30[h]	4.41 (1H, dd, J=12, 5 Hz)
Glc-6	4.51 (1H, dd, J=11.5, 2.5 Hz)	4.64 (1H, dd, J=11.5, 2.5 Hz)	4.51 (1H, dd, J=11.5, 2.5 Hz)	4.65 (1H, dd, J=12, 2.5 Hz)
Ara-1	5.45 (1H, d, J=7.5 Hz)	5.44 (1H, d, J=7.5 Hz)	5.28 (1H, d, J=7.5 Hz)	5.26 (1H, d, J=8 Hz)
Ara-2	4.30 (1H, dd, J=9.5, 7.5 Hz)	4.31 (1H, dd, J=9.5, 7.5 Hz)	4.45 (1H, dd, J=9.5, 7.5 Hz)	4.45 (1H, dd, J=9.5, 8 Hz)
Ara-3	4.17 (1H, dd, J=9.5, 3 Hz)	4.17 (1H, br d, J=9.5 Hz)	4.09 (1H, dd, J=9.5, 3.5 Hz)	4.09 (1H, dd, J=9.5, 3.5 Hz)
Ara-4	5.47 (1H, br s)	5.48 (1H, br s)	4.20[h]	4.19 (1H, br s)
Ara-5	3.61 (1H, d, J=13 Hz)	3.62 (1H, d, J=13.5 Hz)	3.66 (1H, d, J=13 Hz)	3.66 (1H, d, J=12.5 Hz)
Ara-5	4.23 (1H, br d, J=13 Hz)	4.22 (1H, br d, J=13.5 Hz)	4.26[h]	4.24 (1H, dd, J=12.5, 2.5 Hz)
C-28				
Ara-1	6.31 (1H, d, J=5.5 Hz)	6.08 (1H, d, J=6.5 Hz)	6.30 (1H, d, J=5.5 Hz)	6.08 (1H, d, J=6.5 Hz)
Ara-2	4.47 (1H, dd, J=6.5, 5.5 Hz)	5.78 (1H, dd, J=8, 6.5 Hz)	4.48[h]	5.78 (1H, dd, J=8, 6.5 Hz)
Ara-3	5.72 (1H, d, J=6.5 Hz)	4.52 (1H, dd, J=8, 3.5 Hz)	5.72 (1H, d, J=5.5 Hz)	4.51 (1H, dd, J=8, 3.5 Hz)
Ara-4	5.71 (1H, br s)	5.56 (1H, br s)	5.71 (1H, br s)	5.55[h]
Ara-5	3.96 (1H, dd, J=12.5, 2.5 Hz)	3.97 (1H, br d, J=12.5 Hz)	3.96 (1H, br d, J=12.5 Hz)	3.96 (1H, br d, J=12 Hz)
Ara-5	4.27[h]	4.38 (1H, dd, J=12.5, 2.5 Hz)	4.27[h]	4.37[h]

TABLE III. (continued)

Proton No.	5	6	7	8	9
Aglycone moiety					
2	4.78 (1H, brq, J=3 Hz)	4.78 (1H, brq, J=3 Hz)	4.78 (1H, brq, J=3 Hz)		4.78 (1H, brq, J=3 Hz)
3	4.29[h]	4.29[h]	4.29[h]	4.29[h]	4.29[h]
12	5.66 (1H, t-like)	5.64 (1H, t-like)	5.64 (1H, t-like)	5.66 (1H, t-like)	5.65 (1H, t-like)
16	5.19 (1H, brs)	5.18 (1H, brs)	5.17 (1H, brs)	5.19 (1H, brs)	5.19 (1H, brs)
18	3.42 (1H, dd, J=14, 4 Hz)	3.42[h]	3.42[h]	3.42[h]	3.42 (1H, dd, J=14, 4 Hz)
19α	2.74[h]	2.74 (1H, t, J=14 Hz)	2.73 (1H, t, J=14 Hz)	2.74 (1H, t, J=14 Hz)	2.73 (1H, t, J=14 Hz)
23	3.74 (1H, d, J=11 Hz)	3.74 (1H, d, J=11 Hz)	3.74 (1H, d, J=10.5 Hz)	3.74 (1H, d, J=11 Hz)	3.74 (1H, d, J=11 Hz)
23	4.31[h]	4.31[h]	4.30 (1H, d, J=10.5 Hz)	4.31[h]	4.31[h]
24	1.36 (3H, s)	1.36 (3H, s)	1.36 (3H, s)	1.36 (3H, s)	1.36 (3H, s)
25	1.55 (3H, s)	1.55 (3H, s)	1.55 (3H, s)	1.56 (3H, s)	1.55 (3H, s)
26	1.18 (3H, s)	1.18 (3H, s)	1.18 (3H, s)	1.19 (3H, s)	1.18 (3H, s)
27	1.76 (3H, s)	1.76 (3H, s)	1.76 (3H, s)	1.77 (3H, s)	1.77 (3H, s)
29	0.94 (3H, s)	0.93 (3H, s)	0.94 (3H, s)	0.94 (3H, s)	0.93 (3H, s)
30	1.04 (3H, s)	1.04 (3H, s)	1.03 (3H, s)	1.05 (3H, s)	1.04 (3H, s)
Ester moiety					
CH_3CO		1.94 (3H, s)		2.00 (3H, s)	
	B		A	A	C
2	2.64 (1H, dd, J=15.5, 6 Hz)[d]		2.62 (1H, dd, J=14.5, 5 Hz)	2.63 (1H, dd, J=15.5, 6 Hz)	2.64 (1H, dd, J=15.5, 6 Hz)
2	2.75 (1H, dd, J=15.5, 7 Hz)[e]		2.72 (1H, dd, J=14.5, 7.5 Hz)	2.73 (1H, dd, J=16.5, 7 Hz)	2.77 (1H, dd, J=14, 7 Hz)
3	5.52[f,h]		4.51[h]	5.48 (1H, m)	5.55 (1H, m)
4	1.31 (3H, d, J=6 Hz)[g]		1.37 (3H, d, J=6 Hz)	1.27 (3H, d, J=6 Hz)	1.33 (3H, d, J=6 Hz)
2′	2.68 (1H, dd, J=15.5, 6 Hz)[d]				2.62 (1H, dd, J=15.5, 5.5 Hz)
2′	2.78 (1H, dd, J=15.5, 7 Hz)[e]				2.77 (1H, dd, J=15.5, 7 Hz)
3′	5.54[f,h]				4.53 (1H, m)
4′	1.34 (3H, d, J=6 Hz)[g]				1.38 (3H, d, J=6 Hz)
2″	2.61 (1H, dd, J=15, 5.5 Hz)				
2″	2.74 (1H, dd, J=15, 7 Hz)				
3″	4.53[h]				
4″	1.38 (3H, d, J=6 Hz)				
Sugar moiety					
C-3					
Glc-1	5.11 (1H, d, J=8 Hz)	5.12 (1H, d, J=8.5 Hz)	5.11 (1H, d, J=8 Hz)	5.11 (1H, d, J=8 Hz)	5.11 (1H, d, J=8 Hz)
Glc-2	3.99 (1H, t, J=8 Hz)	3.99 (1H, t, J=8.5 Hz)	3.99 (1H, t, J=8 Hz)	3.99 (1H, t, J=8 Hz)	3.99 (1H, t, J=8 Hz)
Glc-3	4.15 (1H, t, J=8 Hz)	4.15 (1H, t, J=8.5 Hz)	4.15 (1H, t, J=8.5 Hz)	4.15 (1H, t, J=8 Hz)	4.15 (1H, t, J=8 Hz)
Glc-4	4.19 (1H, t, J=8 Hz)	4.19 (1H, t, J=8.5 Hz)	4.20 (1H, t, J=8.5 Hz)	4.19 (1H, t, J=9 Hz)	4.19 (1H, t, J=8 Hz)
Glc-5	3.89 (1H, m)	3.89 (1H, m)	3.89 (1H, m)	3.89 (1H, m)	3.89 (1H, m)
Glc-6	4.32[h]	4.31 (1H, dd, J=12, 4 Hz)	4.31 (1H, dd, J=11, 4.5 Hz)	4.31[h]	4.31[h]
Glc-6	4.44 (1H, dd, J=12, 2 Hz)	4.45 (1H, dd, J=11.5, 2 Hz)	4.44 (1H, dd, J=11.5, 2 Hz)	4.45 (1H, dd, J=11.5, 2.5 Hz)	4.44 (1H, dd, J=12, 2 Hz)
C-28					
Fuc-1	6.02 (1H, d, J=8 Hz)	6.03 (1H, d, J=8 Hz)	6.02 (1H, d, J=8 Hz)	6.02 (1H, d, J=8 Hz)	6.02 (1H, d, J=8 Hz)
Fuc-2	4.49 (1H, t, J=8.5 Hz)	4.51 (1H, t, J=8.5 Hz)	4.50 (1H, t, J=8.5 Hz)	4.49 (1H, t, J=8.5 Hz)	4.49 (1H, t, J=8.5 Hz)
Fuc-3	4.32[h]	4.31[h]	4.29[h]	4.31[h]	4.31[h]
Fuc-4	5.48 (1H, d, J=3.5 Hz)	5.48 (1H, d, J=3.5 Hz)	5.54 (1H, d, J=3.5 Hz)	5.49 (1H, d, J=4 Hz)	5.48 (1H, d, J=3.5 Hz)
Fuc-5	3.99[h]	3.99[h]	4.02[h]	3.99[h]	3.99[h]
Fuc-6	1.24 (3H, d, J=6 Hz)	1.23 (3H, d, J=6 Hz)	1.30 (3H, d, J=6 Hz)	1.24 (3H, d, J=6 Hz)	1.26 (3H, d, J=6 Hz)
(Inner)					
Rham-1	6.22 (1H, brs)	6.24 (1H, brs)	6.20 (1H, brs)	6.23 (1H, brs)	6.21 (1H. brs)
Rham-2	4.73 (1H, dd, J=3, 1.5 Hz)	4.74 (1H, d, J=3 Hz)	4.74 (1H, d, J=3.5 Hz)	4.74[h]	4.74 (1H, d, J=3 Hz)
Rham-3	4.62 (1H, dd, J=9.5, 3 Hz)	4.62 (1H, dd, J=9.5, 3.5 Hz)	4.62 (1H, dd, J=9.5, 3.5 Hz)	4.62 (1H, dd, J=9.5, 3 Hz)	4.62 (1H, dd, J=9.5, 3 Hz)
Rham-4	4.32[h]	4.32[h]	4.31 (1H, t, J=9 Hz)	4.31[h]	4.31 (1H, t, J=9 Hz)
Rham-5	4.50[h]	4.48[h]	4.47[h]	4.49[h]	4.49[h]
Rham-6	1.74 (3H, d, J=6 Hz)	1.73 (3H, d, J=6 Hz)	1.71 (3H, d, J=6 Hz)	1.75 (3H, d, J=6 Hz)	1.74 (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)	5.01 (1H, d, J=8 Hz)	5.01 (1H, d, J=8 Hz)
Xyl-2	4.05 (1H, t, J=8 Hz)	4.05 (1H, t, J=8.5 Hz)	4.05 (1H, t, J=8 Hz)	4.05 (1H, t, J=8 Hz)	4.05 (1H, t, J=8 Hz)
Xyl-3	4.16 (1H, t, J=8 Hz)	4.16 (1H, t, J=8 Hz)	4.16 (1H, t, J=8 Hz)	4.16 (1H, t, J=8 Hz)	4.16 (1H, t, J=8 Hz)
Xyl-4	4.07[h]	4.07[h]	4.07[h]	4.07[h]	4.07[h]
Xyl-5	3.44 (1H, brt, J=11 Hz)	3.44 (1H, brt, J=11 Hz)	3.44 (1H, brt, J=11 Hz)	3.44 (1H, brt, J=11 Hz)	3.44 (1H, brt, J=11 Hz)
Xyl-5	4.13 (1H, d, J=11 Hz)	4.13 (1H, d, J=11 Hz)	4.13 (1H, d, J=11 Hz)	4.14 (1H, d, J=11 Hz)	4.14 (1H, d, J=11 Hz)
(Terminal)					
Rham-1	6.13 (1H, brs)	6.13 (1H, brs)	6.13 (1H, brs)	6.13 (1H, brs)	6.13 (1H, brs)
Rham-2	4.75 (1H, dd, J=3, 1.5 Hz)	4.75 (1H, d, J=3.5 Hz)	4.75 (1H, d, J=3.5 Hz)	4.74[h]	4.74 (1H, d, J=3 Hz)
Rham-3	4.55 (1H, dd, J=9.5, 3 Hz)	4.55 (1H, dd, J=9.5, 3.5 Hz)	4.55 (1H, dd, J=9, 3.5 Hz)	4.55 (1H, dd, J=9.5, 3 Hz)	4.55 (1H, dd, J=9.5, 3 Hz)
Rham-4	4.27 (1H, t, J=9.5 Hz)	4.27 (1H, t, J=9.5 Hz)	4.27 (1H, t, J=9 Hz)	4.27 (1H, t, J=9.5 Hz)	4.27 (1H, t, J=9 Hz)
Rham-5	4.87 (1H, m)	4.87 (1H, m)	4.87 (1H, m)	4.87 (1H, m)	4.87 (1H, m)
Rham-6	1.65 (3H, d, J=6 Hz)	1.65 (3H, d, J=6 Hz)	1.65 (3H, d, J=6.5 Hz)	1.65 (3H, d, J=6 Hz)	1.65 (3H, d, J=6 Hz)

^{13}C-NMR: Tables I—III.

Solidagosaponin XIII (**4**): White amorphous powder, $[\alpha]_D^{21}$ −6.5° (c=0.50, MeOH). *Anal.* Calcd for $C_{56}H_{88}O_{26}\cdot 5H_2O$: C, 53.07; H, 7.79. Found: C, 53.09; H, 7.69. FAB-MS m/z: 1199 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Solidagosaponin XIV (**5**): White amorphous powder, $[\alpha]_D^{21}$ −23.6° (c=1.13, MeOH). *Anal.* Calcd for $C_{71}H_{114}O_{33}\cdot 3H_2O$: C, 55.0; H, 7.81. Found: C, 54.84; H, 8.03. FAB-MS m/z: 1517 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Solidagosaponin XV (**6**): White amorphous powder, $[\alpha]_D^{21}$ −33.3° (c=0.19, MeOH). *Anal.* Calcd for $C_{61}H_{98}O_{28}\cdot 5H_2O$: C, 53.50; H, 7.95. Found: C, 53.43; H, 7.82. FAB-MS m/z: 1301 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Solidagosaponin XVI (**7**): White amorphous powder, $[\alpha]_D^{21}$ −20.1° (c=0.24, MeOH). *Anal.* Calcd for $C_{63}H_{102}O_{29}\cdot 5H_2O$: C, 53.53; H, 7.75. Found: C, 53.20; H, 7.75. FAB-MS m/z: 1345 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Solidagosaponin XVII (**8**): White amorphous powder, $[\alpha]_D^{21}$ −21.6° (c=0.17, MeOH). *Anal.* Calcd for $C_{65}H_{104}O_{30}\cdot 6H_2O$: C, 52.98; H, 7.93. Found: C, 53.07; H, 7.71. FAB-MS m/z: 1387 $[M+Na]^+$. ^{1}H- and

TABLE III. (continued)

Proton No.	10	11	12	13
Aglycone moiety				
2		4.79 (1H, br q, J=3 Hz)	4.78[h]	4.78[h]
3	4.29[h]	4.29 (1H, d, J=3 Hz)	4.29[h]	4.21[h]
12	5.66 (1H, t-like)	5.62 (1H, t-like)	5.65 (1H, t-like)	5.62 (1H, t-like)
16	5.19 (1H, br s)	5.12 (1H, br s)	5.20 (1H, br s)	5.14 (1H, br s)
18	3.42[h]	3.37 (1H, dd, J=14, 3.5 Hz)	3.43[h]	3.38 (1H, dd, J=14, 4 Hz)
19α	2.74 (1H, t, J=14 Hz)	2.72 (1H, t, J=14 Hz)	2.74 (1H, t, J=13 Hz)	2.72 (1H, t, J=13.5 Hz)
23	3.74 (1H, d, J=11 Hz)	3.72 (1H, d, J=11 Hz)	3.73 (1H, d, J=11 Hz)	3.68 (1H, d, J=11 Hz)
23	4.31[h]	4.31 (1H, d, J=11 Hz)	4.30[h]	4.25 (1H, d, J=11 Hz)
24	1.36 (3H, s)	1.36 (3H, s)	1.35 (3H, s)	1.29 (3H, s)
25	1.55 (3H, s)	1.57 (3H, s)	1.55 (3H, s)	1.52 (3H, s)
26	1.18 (3H, s)	1.17 (3H, s)	1.19 (3H, s)	1.16 (3H, s)
27	1.77 (3H, s)	1.76 (3H, s)	1.76 (3H, s)	1.76 (3H, s)
29	0.94 (3H, s)	0.94 (3H, s)	0.93 (3H, s)	0.92 (3H, s)
30	1.05 (3H, s)	1.05 (3H, s)	1.05 (3H, s)	1.00 (3H, s)
Ester moiety				
CH_3CO		1.95 (3H, s) 2.09 (3H, s)		
	D		E	
2	2.68 (1H, dd, J=15.5, 6 Hz)		5.77 (1H, br d, J=16 Hz)	
2	2.81 (1H, dd, J=15.5, 7.5 Hz)			
3	5.56 (1H, m)		6.99 (1H, m)	
4	1.34 (3H, d, J=6 Hz)		1.56 (3H, d, J=6 Hz)	
2′	5.88 (1H, br d, J=6 Hz)			
3′	7.00 (1H, m)			
4′	1.65 (3H, d, J=6 Hz)			
Sugar moiety				
C-3				
Glc-1	5.11 (1H, d, J=8 Hz)	5.11 (1H, d, J=8 Hz)	5.11 (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)	3.99 (1H, t, J=8 Hz)	4.01 (1H, t, J=8 Hz)
Glc-3	4.15 (1H, t, J=8.5 Hz)	4.14 (1H, t, J=9 Hz)	4.15 (1H, t, J=8 Hz)	4.14 (1H, t, J=8 Hz)
Glc-4	4.19 (1H, t, J=8.5 Hz)	4.19 (1H, t, J=9 Hz)	4.19 (1H, t, J=8.5 Hz)	4.12 (1H, t, J=8 Hz)
Glc-5	3.89 (1H, m)	3.83 (1H, m)	3.89 (1H, m)	3.91 (1H, m)
Glc-6	4.31[h]	4.30 (1H, dd, J=12.5, 5.5 Hz)	4.29[h]	4.22[h]
Glc-6	4.44 (1H, dd, J=11.5, 2 Hz)	4.44 (1H, dd, J=12.5, 3 Hz)	4.44 (1H, dd, J=12, 1.5 Hz)	4.42 (1H, br d, J=11.5 Hz)
C-28				
Fuc-1	6.02 (1H, d, J=8 Hz)	5.96 (1H, d, J=8 Hz)	6.05 (1H, d, J=8 Hz)	5.93 (1H, d, J=8 Hz)
Fuc-2	4.50 (1H, t, J=8.5 Hz)	4.40 (1H, dd, J=10, 9 Hz)	4.54 (1H, t, J=8.5 Hz)	4.57 (1H, t, J=8 Hz)
Fuc-3	4.31[h]	4.19 (1H, dd, J=10, 4 Hz)	4.34[h]	4.11[h]
Fuc-4	5.49 (1H, d, J=3 Hz)	5.64 (1H, d, J=3 Hz)	5.57 (1H, d, J=3 Hz)	4.25 (1H, d, J=4 Hz)
Fuc-5	4.00[h]	3.97 (1H, m)	3.99[h]	3.90[h]
Fuc-6	1.24 (3H, d, J=6 Hz)	1.16 (3H, d, J=6 Hz)	1.25 (3H, d, J=6 Hz)	1.47 (3H, d, J=6 Hz)
(Inner)				
Rham-1	6.22 (1H, br s)	5.83 (1H, br s)	6.26 (1H, br s)	6.25 (1H, br s)
Rham-2	4.75 (1H, d, J=2.5 Hz)	4.65 (1H, d, J=3 Hz)	4.75[h]	4.77 (1H, d, J=2 Hz)
Rham-3	4.62 (1H, dd, J=9.5, 2.5 Hz)	4.52 (1H, dd, J=9, 3 Hz)	4.63 (1H, dd, J=9.5, 2.5 Hz)	4.61 (1H, dd, J=9.5, 2 Hz)
Rham-4	4.31[h]	4.28[h]	4.32[h]	4.25 (1H, t, J=9.5 Hz)
Rham-5	4.48[h]	4.31[h]	4.51 (1H, m)	4.41[h]
Rham-6	1.74 (3H, d, J=5.5 Hz)	1.68 (3H, d, J=6 Hz)	1.75 (3H, d, J=6 Hz)	1.65 (3H, d, J=6 Hz)
Xyl-1	5.00 (1H, d, J=8 Hz)	4.97 (1H, d, J=8 Hz)	5.01 (1H, d, J=8 Hz)	4.98 (1H, d, J=7.5 Hz)
Xyl-2	4.05 (1H, t, J=8 Hz)	4.03 (1H, t, J=8 Hz)	4.04 (1H, t, J=8 Hz)	4.01[h]
Xyl-3	4.16[h]	4.16 (1H, t, J=9 Hz)	4.17 (1H, t, J=8 Hz)	4.21 (1H, t, J=8 Hz)
Xyl-4	4.07[h]	4.07 (1H, m)	4.07[h]	4.05[h]
Xyl-5	3.44 (1H, br t, J=11 Hz)	3.44 (1H, br t, J=11 Hz)	3.44 (1H, br t, J=11 Hz)	3.46 (1H, br t, J=11 Hz)
Xyl-5	4.15 (1H, d, J=11 Hz)	4.16 (1H, d, J=11 Hz)	4.14 (1H, d, J=11.5 Hz)	4.15[h]
(Terminal)				
Rham-1	6.13 (1H, br s)	6.12 (1H, br s)	6.13 (1H, br s)	6.07 (1H, br s)
Rham-2	4.75 (1H, d, J=3 Hz)	4.74 (1H, br d, J=2.5 Hz)	4.77[h]	4.74 (1H, d, J=2 Hz)
Rham-3	4.55 (1H, dd, J=9.5, 3 Hz)	4.57 (1H, dd, J=9, 3 Hz)	4.56 (1H, dd, J=9.5, 3 Hz)	4.56 (1H, dd, J=9, 1.5 Hz)
Rham-4	4.28 (1H, t, J=9.5 Hz)	4.27 (1H, t, J=9.5 Hz)	4.28 (1H, t, J=9.5 Hz)	4.27 (1H, t, J=9.5 Hz)
Rham-5		4.88 (1H, m)		4.83 (1H, m)
Rham-6	1.65 (3H, d, J=6 Hz)	1.65 (3H, d, J=6 Hz)	1.65 (3H, d, J=6 Hz)	1.65 (3H, d, J=6 Hz)
Api-1		5.70 (1H, br s)		
Api-2		4.49 (1H, br s)		
Api-4		4.30 (1H, d, J=10 Hz)		
Api-4		4.49 (1H, d, J=10 Hz)		
Api-5		4.43 (1H, d, J=12.5 Hz)		
Api-5		4.55 (1H, d, J=12.5 Hz)		

Recorded at 500 MHz. *a—g*) These values may be interchangeable in each column. *h*) Obscured by other signals; therefore, couplings could not be determined accurately.

^{13}C-NMR: Tables I—III.

Solidagosaponin XVIII (**9**): White amorphous powder, $[\alpha]_D^{21}$ −29.0° (c=1.11, MeOH). *Anal.* Calcd for $C_{67}H_{108}O_{31}\cdot 3H_2O$: C, 54.98; H, 7.85. Found: C, 55.13; H, 8.04. FAB-MS m/z: 1431 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Solidagosaponin XIX (**10**): White amorphous powder, $[\alpha]_D^{21}$ −15.6° (c=0.04, MeOH). *Anal.* Calcd for $C_{67}H_{106}O_{30}\cdot 7H_2O$: C, 53.02; H, 7.97. Found: C, 52.70; H, 7.82. FAB-MS m/z: 1413 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Solidagosaponin XX (**11**): White amorphous powder, $[\alpha]_D^{21}$ −37.1° (c=0.53, MeOH). *Anal.* Calcd for $C_{68}H_{108}O_{33}\cdot 6H_2O$: C, 52.30; H, 7.75. Found: C, 52.18; H, 7.79. FAB-MS m/z: 1475 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Saponin **12**: White amorphous powder, $[\alpha]_D^{21}$ −28.0° (c=0.25, MeOH). *Anal.* Calcd for $C_{63}H_{100}O_{28}\cdot 6H_2O$: C, 53.52; H, 7.99. Found: C, 53.52; H, 7.70. FAB-MS m/z: 1327 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables I—III. ^{13}C-NMR (methanol-d_4) δ: aglycone moiety: 44.5 (C_1), 71.9 (C_2), 84.0 (C_3), 43.2 (C_4), 18.9 (C_6), 33.6 (C_7), 40.9 (C_8), 37.6 (C_{10}), 24.6 (C_{11}), 123.5 (C_{12}), 144.7 (C_{13}), 43.0 (C_{14}), 36.5 (C_{15}), 74.6 (C_{16}), 50.3 (C_{17}), 42.4 (C_{18}), 31.3 (C_{20}), 36.3 (C_{21}), 31.9 (C_{22}), 65.9 (C_{23}), 14.9 (C_{24}), 18.0 (C_{25}), 17.8 (C_{26}), 27.2 (C_{27}), 177.3 (C_{28}), 33.4 (C_{29}), 25.0 (C_{30}); glucose moiety: 105.5 (C_1), 75.4 (C_2), 77.7 (C_3), 71.1 (C_4), 78.2 (C_5), 62.3 (C_6); fucose moiety: 95.0 (C_1), 75.4 (C_2), 74.7 (C_3), 74.9 (C_4), 71.2 (C_5), 16.6 (C_6); inner rhamnose moiety: 101.7 (C_1), 72.2 (C_2), 72.2 (C_3), 84.6 (C_4), 69.9 (C_5), 18.4 (C_6); xylose moiety; 107.2 (C_1), 76.5 (C_2), 84.3 (C_3), 69.0 (C_4), 67.2 (C_5); outer rhamnose moiety: 102.5 (C_1), 72.3 (C_2), 72.3 (C_3), 74.0 (C_4), 70.0 (C_5), 17.9 (C_6); crotoyl moiety: 168.0 (C_1), 123.4 (C_2), 147.0 (C_3), 18.2 (C_4).

Saponin **13**: White amorphous powder, $[\alpha]_D^{21}$ −29.9° (c=0.24, MeOH). *Anal.* Calcd for $C_{59}H_{96}O_{27}\cdot 4H_2O$: C, 54.12; H, 8.01. Found: C, 54.03; H, 7.93. FAB-MS m/z: 1259 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables I—III. ^{13}C-NMR (methanol-d_4) δ: aglycone moiety: 44.5 (C_1), 69.9 (C_2), 84.6 (C_3), 43.0 (C_4), 48.5 (C_5), 17.8 (C_6), 33.7 (C_7), 40.9 (C_8), 48.0 (C_9), 37.6 (C_{10}), 24.6 (C_{11}), 123.5 (C_{12}), 144.7 (C_{13}), 43.2 (C_{14}), 36.6 (C_{15}), 74.8 (C_{16}), 50.1 (C_{17}), 42.4 (C_{18}), 46.1 (C_{19}), 31.3 (C_{20}), 36.6 (C_{21}), 31.8 (C_{22}), 67.2 (C_{23}), 14.9 (C_{24}), 23.0 (C_{25}), 17.7 (C_{26}), 27.2 (C_{27}), 177.3 (C_{28}), 33.4 (C_{29}), 24.8 (C_{30}); glucose moiety: 105.5 (C_1), 76.5 (C_2), 78.2 (C_3), 72.2 (C_4), 77.7 (C_5), 62.3 (C_6); fucose moiety: 95.1 (C_1), 76.8 (C_2), 74.5 (C_3), 72.3 (C_4), 71.2 (C_5), 16.5 (C_6); inner rhamnose moiety: 101.4 (C_1), 72.0 (C_2), 72.7 (C_3), 84.1 (C_4), 68.8 (C_5), 17.9 (C_6); xylose moiety: 107.2 (C_1), 75.4 (C_2), 84.3 (C_3), 70.0 (C_4), 66.1 (C_5); outer rhamnose moiety: 102.5 (C_1), 72.3 (C_2), 73.6 (C_3), 74.0 (C_4), 71.1 (C_5), 18.4 (C_6).

Mild Methanolysis and Subsequent Acid Hydrolysis of 1—13 Compound **11** (*ca.* 0.05 mg) was refluxed with AcCl–MeOH (1 : 10) (1 ml) for 1 h. The reaction mixture was concentrated to afford a residue. Next, part of the residue was subjected to column chromatography to reveal one peak due to polygalacic acid. The retention time of this material was in accordance with that of authentic polygalacic acid. The residue left was heated at 100 °C with 3 drops of 5% H_2SO_4 for 20 min. The reaction mixture was diluted with H_2O and passed through an Amberlite IR-45 column. The eluate was concentrated to give a residue, which was reduced with $NaBH_4$ (*ca.* 1 mg) in water (0.2 ml) for 1 h at room temperature and passed through an Amberlite IR-120 column. The eluate was concentrated to dryness under reduced pressure and then the reaction mixture was heated at 100 °C with acetic anhydride (2 drops) and pyridine (2 drops) for 1 h. The acetylated mixture was subjected to GC, which revealed five peaks for derivatives of glucose, fucose, rhamnose, xylose and apiose (1 : 1 : 2 : 1 : 1, respectively). Mild methanolysis and subsequent acid hydrolysis of the other compounds (**1**—**10**, **12** and **13**) was performed by the same method used for **11**, and the sugar components of each saponin were confirmed by the same method employed for **11**.

HPLC Conditions: column, Develosil ODS-10 (4.6 × 250 mm); solvent, [CH_3CN–H_2O (42.5 : 57.5) + 0.05% TFA]; flow rate, 1.3 ml/min; UV absorption, 207 nm; t_R, polygalacic acid 11.5 min.

GC Conditions: column, Supelco SP-2380 capillary column (0.25 mm × 30 m); column temperature, 250 °C; carrier gas, N_2; t_R, rhamnitol acetate 5.0 min, fucitol acetate 5.2 min, arabinitol acetate 6.2 min, xylitol acetate 7.3 min, apinitol acetate 10.2 min, glucitol acetate 11.2 min).

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