Nine New Triterpene Saponins, Polygalasaponins XXXIII—XLI from the Roots of *Polygala fallax* HEMSL.

Dongming ZHANG, Toshio MIYASE,* Masanori KUROYANAGI, Kaoru UMEHARA, and Hiroshi NOGUCHI

School of Pharmaceutical Sciences, University of Shizuoka, 52-1, Yada, Shizuoka 422, Japan.

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Nine new oleanane-type saponins, polygalasaponins XXXIII—XLI, along with seven known saponins were isolated from the roots of *Polygala fallax* HEMSL. Polygalasaponins XXXIII—XLI were elucidated as 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(4-*O*-acetyl)-β-D-fucopyranosyl ester, 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(4-*O*-acetyl)-β-D-fucopyranosyl ester, 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(3,4-di-*O*-acetyl)-β-D-fucopyranosyl ester, 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-[(5-*O*-acetyl)-β-D-apiofuranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-(3,4-di-*O*-acetyl)-β-D-fucopyranosyl ester, 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(3-*O*-acetyl)-β-D-fucopyranosyl ester, 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(4-*O*-acetyl)-β-D-fucopyranosyl ester, 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→3)]-(4-*O*-acetyl)-β-D-fucopyranosyl ester, 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-[β-D-apiofuranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-(3,4-di-*O*-acetyl)-β-D-fucopyranosyl ester and 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-[(5-*O*-acetyl)-β-D-apiofuranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-(3,4-di-*O*-acetyl)-β-D-fucopyranosyl ester, respectively, on the basis of spectroscopic and chemical evidence.

Key words *Polygala fallax*; Polygalaceae; polygalasaponin; oleanane-type saponin; presenegenin

Polygala fallax HEMSL. (Polygalaceae) is widely distributed in southern China, and is used as a tonic and antihepatitis agent.[1] The constituents of *P. fallax* have not been reported. We previously reported the isolation and structural elucidation of 32 new triterpene glycosides called polygalasaponins I—XXXII isolated from *P. japonica* HOUTT.[2] We continued our investigation of the constituents of *Polygala* genus and isolated nine new saponins (**1**—**9**) and seven known saponins, 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranosyl ester (**10**), reiniosides B (**11**), C (**12**), D (**13**), E (**14**), F (**15**) and senegin III (**16**), from the roots of *P. fallax* HEMSL. Compounds **10**—**16** were identified by comparison of the ^{1}H- and ^{13}C-NMR data with reported data.[3,4]

A 70% aqueous methanol extract of the roots of *P. fallax* HEMSL. was passed through a porous polymer gel, Mitsubishi Diaion HP-20, column and the adsorbed materials were eluted successively with 30%, 60% aqueous methanol and methanol. The methanol eluate was chromatographed on silica-gel and octadecyl silica (ODS)-gel columns, followed by repeated semi-preparative HPLC on a reversed phase column [ODS, phenylalkyl (PhA-T)] to give compounds **1**—**16**. On acid hydrolysis, saponins **1**—**9** afforded senegenic acid (**1a**)[2] which is a well known artifactual aglycone of presenegenin (**1b**) glycoside.[5—7] We, therefore, assumed that saponins **1**—**9** were presenegenin glycosides.

Polygalasaponin XXXIII (**1**) revealed a $[M+Na]^+$ ion peak at *m/z* 1170 in FAB-MS and elemental analysis data are consistent with $C_{55}H_{86}O_{25}$. On acid hydrolysis, **1** afforded D-glucose, D-fucose, L-rhamnose and D-xylose as sugar components. The ^{1}H-NMR spectrum suggested the presence of six tertiary methyl protons (δ 0.79, 0.95, 1.13, 1.57, 1.96, 1.96), a pair of oxymethylene protons [δ 3.80 (d, $J=12$ Hz), 4.06 (d, $J=12$ Hz)], a trisubstituted olefinic proton [δ 5.82 (t-like)] in the aglycone moiety and four anomeric proton signals [δ 5.06 (d, $J=8$ Hz), 5.06 (d, $J=8$ Hz), 6.10 (d, $J=8$ Hz), 6.31 (d, $J=1$ Hz)]. The ^{13}C-NMR spectrum suggested the presence of a carboxylic carbon (δ 180.8), two ester carbonyl carbon (δ 171.1, 176.7) and four anomeric carbon signals (δ 94.6, 101.8, 105.4, 107.4). The ester carbonyl carbon signal at δ 171.1 was assigned to an acetyl carbonyl carbon following observation of a ^{1}H–^{13}C long-range correlation with a methyl proton signal at δ 1.96. As far as the nuclear Overhauser effect (NOE) difference was concerned, when the signal at δ 5.06 (d, $J=8$ Hz) (H-1 of Glu) was irradiated, NOEs were observed at the signals of the H-3 [δ 4.61 (d, $J=3$ Hz)] of the aglycone moiety, the H-3 [δ 4.15 (t, $J=9$ Hz)] and H-5 [δ 3.93 (m)] of glucose; when the signal at δ 5.06 (d, $J=8$ Hz) (H-1 of Xyl) was irradiated, NOEs were observed at the signals of the H-4 [δ 4.34 (t, $J=9.5$ Hz)] of rhamnose and H-3 [δ 4.04 (t, $J=8.5$ Hz)], H-5 [δ 3.52 (t, $J=11$ Hz)] of xylose; when the signal at δ 6.10 (d, $J=8$ Hz) (H-1 of Fuc) was irradiated, NOEs were observed at the signals of the H-3 [δ 4.38 (dd, $J=9.5$, 3 Hz)] and H-5 [δ 4.03 (m)] of fucose; when the signal at δ 6.31 (d, $J=1$ Hz) (H-1 of Rha) was irradiated, NOEs were observed at the signals of the H-2 [δ 4.58 (t, $J=8.5$ Hz)] of fucose and H-2 [δ 4.79 (m)] of

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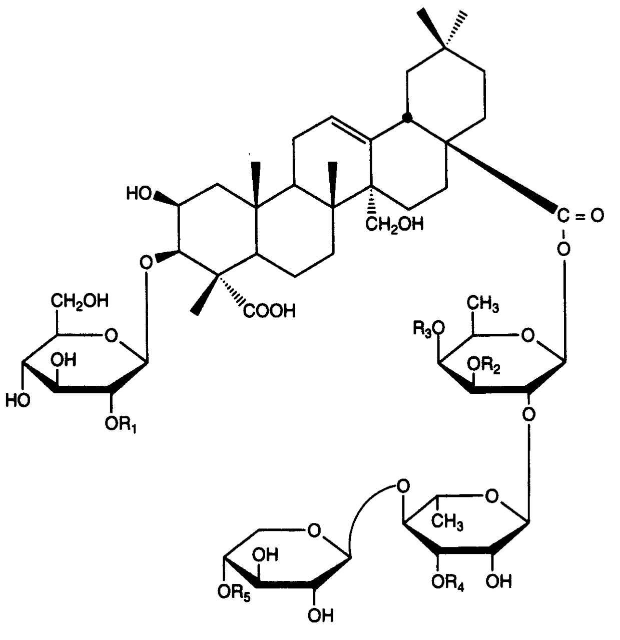
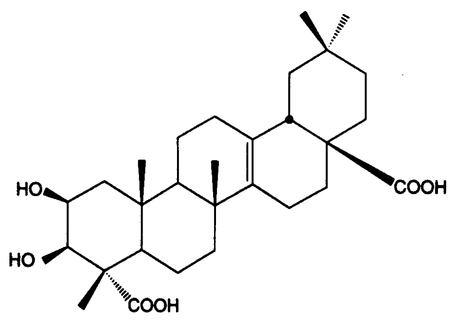
* To whom correspondence should be addressed.



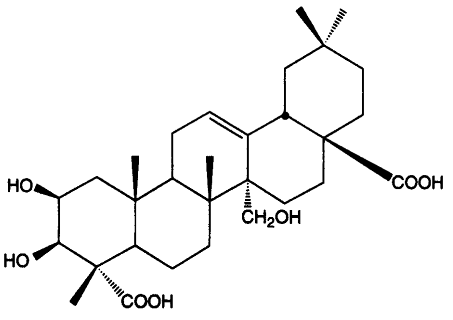
	R_1	R_2	R_3	R_4	R_5
1	H	H	Ac	H	H
2	H	H	Ac	H	Gal
3	H	Ac	Ac	H	Gal
4	H	Ac	Ac	Api$\overset{5}{-}$Ac	Gal
5	Glc	Ac	H	H	H
6	Glc	H	Ac	H	Gal
7	Glc	Rha	Ac	H	H
8	Glc	Ac	Ac	Api	Gal
9	Glc	Ac	Ac	Api$\overset{5}{-}$Ac	Gal
10	Glc	H	H	H	H
11	Glc	H	Ac	H	H
12	Glc	Ac	Ac	H	H
13	Glc	Ac	Ac	H	Gal
14	Glc	Ac	Ac	Api	H
15	Glc	Ac	Ac	Api$\overset{5}{-}$Ac	H
16	H	Rha	**A**	H	Gal

A : *p*-methoxycinnamoyl

Chart 1



1a



1b

Chart 2

rhamnose. In the heteronuclear multiple bond coherence (HMBC) spectrum, long-range couplings ($^3J_{HCOC}$) were observed between the anomeric proton signal at δ 5.06 (H-1 of Glc) and the carbon signal at δ 86.0 due to the C-3 of the aglycone, between the anomeric proton signal at δ 6.10 (H-1 of Fuc) and the carbon signal at δ 176.7 due to the C-28 of the aglycone, between the anomeric proton signal at δ 6.31 (H-1 of Rha) and the carbon signal at δ 74.1 due to the C-2 of fucose, between the anomeric proton signal at δ 5.06 (H-1 of Xyl) and the carbon signal at δ 85.0 due to the C-4 of rhamnose, between the anomeric carbon signal at δ 107.4 (C-1 of Xyl) and the proton signal at δ 4.34 (t, J=9.5 Hz) due to the H-4 of rhamnose, between the acetyl carbonyl carbon signal at δ 171.1 and the proton signal at δ 5.53 (d, J=3 Hz) due to the H-4 of fucose. Sugar proton and carbon signals in the NMR spectra (Tables 1, 2) were assigned by ^{1}H–^{1}H correlation spectroscopy (COSY), the NOE difference, HMBC spectrum and heteronuclear single quantum coherence (HSQC) spectrum. The sugar linkages were decided by NOE difference and the HMBC spectrum. From these data, the structure of polygalasaponin XXXIII was elucidated as 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(4-*O*-acetyl)-β-D-fucopyranosyl ester.

Polygalasaponins XXXIV (**2**), $C_{61}H_{96}O_{30}$ and XXXV (**3**), $C_{63}H_{98}O_{31}$ furnished D-glucose, D-fucose, L-rhamnose, D-xylose, D-galactose as a sugar component on acid hydrolysis. In the NMR spectra, **2** and **3** showed five anomeric proton and carbon signals (see Tables 1, 2), compound **2** exhibited an acetyl methyl signal at δ 1.97, and compound **3** revealed two acetyl methyl signals at δ 2.05 ($2 \times CH_3$). The sugar proton and carbon signals in the NMR spectra were assigned by the ^{1}H–^{1}H COSY, homonuclear Hartmann-Hahn (HOHAHA) spectrum, NOE and HSQC spectra (Tables 1, 2). The data of NOE and HMBC spectra of **2** and **3** suggested those have the same binding sites for the sugar moieties. The position of the acetyl group of **2** was determined to be the C-4 of the fucose moiety by comparison of the ^{1}H-NMR data of the fucose moiety in **2** with those of the fucose moiety in **1**. Comparing the ^{1}H-NMR spectrum of **3** with that of **2**,

Table 1. ^{1}H-NMR Data of Compounds **1**—**9** in Pyridine-d_5

	1	**2**	**3**	**4**	**5**
Aglycone					
2	4.72 (1H, m)	4.72 (1H, m)	4.72 (1H, m)	4.73 (1H, m)	4.70 (1H, m)
3	4.61 (1H, d, *J*=3 Hz)	4.60 (1H, d, *J*=3 Hz)	4.61 (1H, d, *J*=3 Hz)	4.63 (1H, d, *J*=3 Hz)	4.60 (1H, d, *J*=3 Hz)
12	5.82 (1H, t-like)	5.83 (1H, t-like)	5.81 (1H, t-like)	5.79 (1H, t-like)	5.81 (1H, t-like)
18	3.23 (1H, dd, *J*=14, 4 Hz)	3.24 (1H, dd, *J*=14, 4 Hz)	3.21 (1H, dd, *J*=14, 4 Hz)	3.22 (1H, dd, *J*=14, 4 Hz)	3.21 (1H, dd, *J*=14, 4 Hz)
24	1.96 (3H, s)	1.97 (3H, s)	1.97 (3H, s)	2.00 (3H, s)	1.98 (3H, s)
25	1.57 (3H, s)	1.53 (3H, s)	1.55 (3H, s)	1.60 (3H, s)	1.55 (3H, s)
26	1.13 (3H, s)	1.13 (3H, s)	1.12 (3H, s)	1.10 (3H, s)	1.12 (3H, s)
27	3.80 (1H, d, *J*=12 Hz)	3.81 (1H, d, *J*=12 Hz)	3.81 (1H, d, *J*=12 Hz)	3.82 (1H, d, *J*=12 Hz)	3.76 (1H, d, *J*=12 Hz)
27	4.06 (1H, d, *J*=12 Hz)	4.06 (1H, d, *J*=12 Hz)	4.06 (1H, d, *J*=12 Hz)	4.06 (1H, d, *J*=12 Hz)	4.01 (1H, d, *J*=12 Hz)
29	0.79 (3H, s)	0.79 (3H, s)	0.80 (3H, s)	0.80 (3H, s)	0.79 (3H, s)
30	0.95 (3H, s)	0.94 (3H, s)	0.95 (3H, s)	1.00 (3H, s)	0.94 (3H, s)
C-3 sugar					
Glc-1 (inn.)	5.06 (1H, d, *J*=8 Hz)	5.05 (1H, d, *J*=8 Hz)	5.05 (1H, d, *J*=8 Hz)	5.07 (1H, d, *J*=8 Hz)	5.09 (1H, d, *J*=8 Hz)
2	3.92[a)]	3.91[a)]	3.91 (1H, t, *J*=8.5 Hz)	3.92 (1H, t, *J*=8.5 Hz)	4.00[a)]
3	4.15[a)]	4.15[a)]	4.15[a)]	4.15[a)]	4.19 (1H, t, *J*=9 Hz)
4	4.15[a)]	4.15[a)]	4.13[a)]	4.16[a)]	4.10 (1H, t, *J*=9 Hz)
5	3.93 (1H, m)	3.91 (1H, m)	3.91 (1H, m)	3.93 (1H, m)	3.85 (1H, m)
6	4.29 (1H, dd, *J*=12, 5 Hz)	4.29[a)]	4.29[a)]	4.29[a)]	4.23 (1H, dd, *J*=12, 5 Hz)
6	4.46 (1H, dd, *J*=12, 2 Hz)	4.47[a)]	4.46[a)]	4.47[a)]	4.42 (1H, dd, *J*=12, 2 Hz)
Glc-1 (ter.)					5.20 (1H, d, *J*=8 Hz)
2					3.96 (1H, t, *J*=8.5 Hz)
3					4.15 (1H, t, *J*=8.5 Hz)
4					4.08 (1H, t, *J*=8.5 Hz)
5					4.03[a)]
6					4.34 (1H, dd, *J*=12, 5 Hz)
6					4.61[a)]
C-28 sugar					
Fuc-1	6.10 (1H, d, *J*=8 Hz)	6.09 (1H, d, *J*=8 Hz)	6.16 (1H, d, *J*=8 Hz)	6.16 (1H, d, *J*=8 Hz)	6.14 (1H, d, *J*=8 Hz)
2	4.58 (1H, t, *J*=8.5 Hz)	4.56 (1H, t, *J*=8.5 Hz)	4.56 (1H, t, *J*=8.5 Hz)	4.53 (1H, t, *J*=8.5 Hz)	4.80 (1H, dd, *J*=9.5, 8 Hz)
3	4.38 (1H, dd, *J*=9.5, 3 Hz)	4.35 (1H, dd, *J*=9.5, 3 Hz)	5.56 (1H, dd, *J*=9.5, 3 Hz)	5.56 (1H, dd, *J*=9.5, 3 Hz)	5.40 (1H, dd, *J*=9.5, 3 Hz)
4	5.53 (1H, d, *J*=3 Hz)	5.52 (1H, d, *J*=3 Hz)	5.58[a)]	5.61 (1H, d, *J*=3 Hz)	4.26 (1H, d, *J*=3 Hz)
5	4.03[a)]	4.02[a)]	4.11[a)]	4.13[a)]	3.96[a)]
6	1.27 (3H, d, *J*=6 Hz)	1.26 (3H, d, *J*=6 Hz)	1.19 (3H, d, *J*=6 Hz)	1.22 (3H, d, *J*=6 Hz)	1.44 (3H, d, *J*=6 Hz)
Ac at C-3			2.05 (3H, s)	2.11 (3H, s)	1.99 (3H, s)
Ac at C-4	1.96 (3H, s)	1.97 (3H, s)	2.05 (3H, s)	2.07 (3H, s)	
Rha-1 (C-2 of Fuc)	6.31 (1H, d, *J*=1 Hz)	6.27 (1H, br s)	5.67 (1H, br s)	5.64 (1H, d, *J*=1.5 Hz)	5.73 (1H, d, *J*=1.5 Hz)
2	4.79 (1H, m)	4.79 (1H, br s)	4.53 (1H, br s)	4.64[a)]	4.60[a)]
3	4.68 (1H, dd, *J*=9.5, 3 Hz)	4.66 (1H, dd, *J*=9.5, 3 Hz)	4.46[a)]	4.37[a)]	4.53 (1H, dd, *J*=9.5, 3 Hz)
4	4.34 (1H, t, *J*=9.5 Hz)	4.27 (1H, t, *J*=9.5 Hz)	4.22 (1H, t, *J*=9.5 Hz)	4.38[a)]	4.29 (1H, t, *J*=9.5 Hz)
5	4.52[a)]	4.48[a)]	4.31[a)]	4.27[a)]	4.37[a)]
6	1.80 (3H, d, *J*=6 Hz)	1.74 (3H, d, *J*=6 Hz)	1.69 (3H, d, *J*=6 Hz)	1.65 (3H, d, *J*=6 Hz)	1.70 (3H, d, *J*=6 Hz)
Rha-1 (C-3 of Fuc)					
2					
3					
4					
5					
6					
Xyl-1	5.06 (1H, d, *J*=8 Hz)	4.99 (1H, d, *J*=7.5 Hz)	4.97 (1H, d, *J*=7.5 Hz)	5.23 (1H, d, *J*=8 Hz)	5.05 (1H, d, *J*=7.5 Hz)
2	4.04[a)]	4.01[a)]	3.98 (1H, t, *J*=8 Hz)	3.90 (1H, t, *J*=8.5 Hz)	4.02[a)]
3	4.04[a)]	4.05[a)]	4.06[a)]	4.10[a)]	4.01[a)]
4	4.14[a)]	4.28[a)]	4.27[a9]	4.24[a)]	4.17[a)]
5	3.52 (1H, t, *J*=11 Hz)	3.46 (1H, t, *J*=11 Hz)	3.45 (1H, t, *J*=11 Hz)	3.45 (1H, t, *J*=11 Hz)	3.51 (1H, t, *J*=11 Hz)
5	4.24 (1H, dd, *J*=11, 5 Hz)	4.28[a)]	4.28[a)]	4.24[a)]	4.22[a)]
Api-1				5.98 (1H, d, *J*=4 Hz)	
2				4.44 (1H, d, *J*=4 Hz)	
4				4.17[a)]	
4				4.29[a)]	
5				4.44 (1H, d, *J*=11 Hz)	
5				4.54 (1H, d, *J*=11 Hz)	
Ac at C-5				1.89 (3H, s)	

Table 1. (continued)

	1	2	3	4	5
Gal-1		4.94 (1H, d, $J=8$ Hz)	4.94 (1H, d, $J=8$ Hz)	4.93 (1H, d, $J=8$ Hz)	
2		4.44[a]	4.45[a]	4.47[a]	
3		4.13[a]	4.10[a]	4.12[a]	
4		4.47[a]	4.47 (1H, d, $J=3$ Hz)	4.49[a]	
5		4.12[a]	4.11[a]	4.11[a]	
6		4.30[a]	4.34[a]	4.37[a]	
6		4.42[a]	4.41[a]	4.43[a]	

Table 1. (continued)

	6	7	8	9
Aglycone				
2	4.69 (1H, m)	4.71 (1H, m)	4.71 (1H, m)	4.70 (1H, m)
3	4.60 (1H, d, $J=3$ Hz)	4.60 (1H, d, $J=3$ Hz)	4.62 (1H, d, $J=3$ Hz)	4.62 (1H, d, $J=3$ Hz)
12	5.82 (1H, t-like)	5.82 (1H, t-like)	5.78 (1H, t-like)	5.78 (1H, t-like)
18	3.23 (1H, dd, $J=14$, 4 Hz)	3.20 (1H, dd, $J=14$, 4 Hz)	3.21 (1H, dd, $J=14$, 4 Hz)	3.20 (1H, dd, $J=14$, 4 Hz)
24	1.97 (3H, s)	1.98 (3H, s)	2.01 (3H, s)	2.00 (3H, s)
25	1.52 (3H, s)	1.54 (3H, s)	1.58 (3H, s)	1.57 (3H, s)
26	1.11 (3H, s)	1.10 (3H, s)	1.08 (3H, s)	1.08 (3H, s)
27	3.79 (1H, d, $J=12$ Hz)	3.76 (1H, d, $J=12$ Hz)	3.78 (1H, d, $J=12$ Hz)	3.77 (1H, d, $J=12$ Hz)
27	4.01[a]	4.01[a]	4.01[a]	4.01 (1H, d, $J=12$ Hz)
29	0.79 (3H, s)	0.78 (3H, s)	0.80 (3H, s)	0.80 (3H, s)
30	0.94 (3H, s)	0.96 (3H, s)	1.00 (3H, s)	1.00 (3H, s)
C-3 sugar				
Glc-1 (inn.)	5.09 (1H, d, $J=8$ Hz)	5.09 (1H, d, $J=8$ Hz)	5.10 (1H, d, $J=8$ Hz)	5.10 (1H, d, $J=8$ Hz)
2	4.05 (1H, t, $J=8.5$ Hz)	4.02[a]	4.03[a]	4.03[a]
3	4.19 (1H, t, $J=9$ Hz)	4.19 (1H, t, $J=9$ Hz)	4.20 (1H, t, $J=9$ Hz)	4.19 (1H, t, $J=9$ Hz)
4	4.10[a]	4.10[a]	4.11[a]	4.10[a]
5	3.85 (1H, m)	3.85 (1H, m)	3.85 (1H, m)	3.84 (1H, m)
6	4.24 (1H, dd, $J=12$, 5 Hz)	4.23[a]	4.24[a]	4.24[a]
6	4.43[a]	4.43 (1H, dd, $J=12$, 2 Hz)	4.43[a]	4.43[a]
Glc-1 (ter.)	5.22 (1H, d, $J=8$ Hz)	5.20 (1H, d, $J=8$ Hz)	5.22 (1H, d, $J=8$ Hz)	5.21 (1H, d, $J=8$ Hz)
2	3.99 (1H, t, $J=8.5$ Hz)	3.97 (1H, t, $J=8.5$ Hz)	3.98 (1H, t, $J=8.5$ Hz)	3.98 (1H, t, $J=8.5$ Hz)
3	4.15 (1H, t, $J=8.5$ Hz)	4.15[a]	4.15[a]	4.15[a]
4	4.07[a]	4.07[a]	4.07[a]	4.07[a]
5	4.07[a]	4.03[a]	4.05[a]	4.06[a]
6	4.35[a]	4.34 (1H, dd, $J=12$, 5 Hz)	4.35 (1H, dd, $J=12$, 5 Hz)	4.35[a]
6	4.62[a]	4.61 (1H, dd, $J=12$, 2 Hz)	4.60 (1H, dd, $J=12$, 2 Hz)	4.61[a]
C-28 sugar				
Fuc-1	6.09 (1H, d, $J=8$ Hz)	6.06 (1H, t, $J=8$ Hz)	6.15 (1H, d, $J=8$ Hz)	6.15 (1H, d, $J=8$ Hz)
2	4.57 (1H, t, $J=8.5$ Hz)	4.54 (1H, t, $J=8.5$ Hz)	4.53 (1H, t, $J=8.5$ Hz)	4.51 (1H, t, $J=8.5$ Hz)
3	4.38[a]	4.41 (1H, dd, $J=9.5$, 3 Hz)	5.56 (1H, dd, $J=9.5$, 3 Hz)	5.55 (1H, dd, $J=9.5$, 3 Hz)
4	5.22 (1H, d, $J=3$ Hz)	5.66 (1H, d, $J=3$ Hz)	5.61 (1H, d, $J=3$ Hz)	5.60 (1H, d, $J=3$ Hz)
5	4.02[a]	4.04[a]	4.12[a]	4.11[a]
6	1.26 (3H, t, $J=6$ Hz)	1.24 (3H, d, $J=6$ Hz)	1.22 (3H, d, $J=6$ Hz)	1.22 (3H, d, $J=6$ Hz)
Ac at C-3			2.11 (3H, s)	2.11 (3H, s)
Ac at C-4	1.96 (3H, s)	1.94 (3H, s)	2.06 (3H, s)	2.07 (3H, s)
Rha-1 (C-2 of Fuc)	6.29 (1H, d, $J=1$ Hz)	5.89 (1H, br s)	5.65 (1H, br s)	5.63 (1H, br s)
2	4.77[a]	4.64 (1H, br s)	4.66 (1H, br s)	4.63[a]
3	4.66 (1H, dd, $J=9.5$, 3 Hz)	4.57 (1H, dd, $J=9.5$, 3 Hz)	4.37[a]	4.37[a]
4	4.27 (1H, t, $J=9.5$ Hz)	4.28 (1H, t, $J=9.5$ Hz)	4.37[a]	4.37[a]
5	4.49[a]	4.37[a]	4.26[a]	4.24[a]
6	1.73 (3H, d, $J=6$ Hz)	1.74 (3H, d, $J=6$ Hz)	1.65 (3H, d, $J=6$ Hz)	1.64 (3H, d, $J=6$ Hz)
Rha-1 (C-3 of Fuc)		5.64 (1H, br s)		
2		4.81 (1H, br s)		
3		4.41 (1H, dd, $J=9$, 3 Hz)		
4		4.26 (1H, t, $J=9$ Hz)		
5		4.29[a]		
6		1.69 (3H, d, $J=6$ Hz)		
Xyl-1	4.99 (1H, d, $J=7.5$ Hz)	5.04 (1H, d, $J=7$ Hz)	5.24 (1H, d, $J=7.5$ Hz)	5.23 (1H, d, $J=8$ Hz)
2	3.97 (1H, t, $J=8$ Hz)	4.03[a]	3.89 (1H, t, $J=8$ Hz)	3.89 (1H, t, $J=8.5$ Hz)
3	4.06[a]	4.02[a]	4.07[a]	4.10[a]
4	4.23[a]	4.16[a]	4.24[a]	4.24[a]
5	3.45 (1H, t, $J=11$ Hz)	3.51 (1H, t, $J=11$ Hz)	3.39 (1H, t, $J=11$ Hz)	3.45 (1H, t, $J=11$ Hz)
5	4.27[a]	4.23[a]	4.24[a]	4.25[a]

Table 1. (continued)

	6	7	8	9
Api-1			5.98 (1H, d, J=4.5 Hz)	5.98 (1H, d, J=4 Hz)
2			4.68 (1H, d, J=4.5 Hz)	4.44$^{a)}$
3			4.19 (1H, d, J=9.5 Hz)	4.16$^{a)}$
4			4.54 (1H, d, J=9.5 Hz)	4.29$^{a)}$
5			4.01$^{a)}$	4.45 (1H, d, J=11 Hz)
5			4.05$^{a)}$	4.55 (1H, d, J=11 Hz)
Ac at C-5				1.89 (3H, s)
Gal-1	4.94 (1H, d, J=8 Hz)		4.92 (1H, d, J=8 Hz)	4.92 (1H, d, J=8 Hz)
2	4.45$^{a)}$		4.47$^{a)}$	4.46 (1H, t, J=8.5 Hz)
3	4.15$^{a)}$		4.13$^{a)}$	4.15$^{a)}$
4	4.48$^{a)}$		4.49$^{a)}$	4.49 (1H, d, J=3 Hz)
5	4.12$^{a)}$		4.11$^{a)}$	4.11$^{a)}$
6	4.36$^{a)}$		4.35$^{a)}$	4.37$^{a)}$
6	4.44$^{a)}$		4.44$^{a)}$	4.44$^{a)}$

Recorded at 400 MHz at 35 °C. Assignments were based on ^{1}H–^{1}H COSY, HOHAHA, NOE difference and detailed proton spin decoupling experiments. $a)$ Overlapping with other signals.

Table 2. ^{13}C-NMR Spectral Data of Compounds **1**—**9** in Pyridine-d_5

	1	2	3	4	5	6	7	8	9
Aglycone									
1	44.3	44.3	44.3	44.3	44.1	44.1	44.2	44.2	44.1
2	70.4	70.4	70.4	70.3	70.2	70.1	70.2	70.0	70.2
3	86.0	86.0	86.0	86.0	85.5	85.4	85.5	85.3	85.3
4	52.9	52.5	52.9	52.9	52.7	52.6	52.6	52.7	52.6
5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5
6	21.4	21.5	21.5	21.3	21.2	21.2	21.2	21.1	21.1
7	33.6	33.6	33.5	33.7	33.5	33.6	33.6	33.7	33.6
8	41.2	41.2	41.2	41.2	41.1	41.1	41.1	41.1	41.2
9	49.3	49.4	49.3	49.3	49.4	49.3	49.3	49.3	49.3
10	37.1	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0
11	23.7	23.7	23.7	23.6	23.6	23.6	23.8	23.6	23.6
12	127.9	127.9	127.8	127.8	127.9	127.8	127.8	127.9	127.9
13	138.9	139.0	138.9	138.8	138.8	138.9	138.9	138.9	138.8
14	48.0	48.1	48.0	47.9	48.0	48.0	48.0	47.9	47.9
15	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5
16	24.0	24.0	23.9	23.9	24.1	24.0	24.0	23.9	23.9
17	47.0	47.0	47.1	47.0	47.0	47.0	47.0	47.0	47.0
18	42.0	42.0	41.9	41.9	41.9	42.0	42.0	41.9	42.0
19	45.4	45.4	45.4	45.4	45.4	45.4	45.5	45.4	45.4
20	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8
21	33.8	33.9	33.9	33.9	33.8	33.9	33.9	33.8	33.8
22	32.4	32.4	32.4	32.3	32.3	32.4	32.3	32.3	32.4
23	180.8	180.8	180.7	180.8	180.4	180.4	180.4	180.4	180.4
24	14.3	14.2	14.2	14.3	14.2	14.1	14.2	14.2	14.2
25	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
26	18.9	18.7	18.6	19.0	18.7	18.7	18.9	18.9	18.9
27	64.5	64.5	64.4	64.5	64.4	64.4	64.4	64.5	64.5
28	176.7	176.7	176.4	176.4	176.4	176.7	176.6	176.3	176.4
29	33.1	33.1	33.0	33.1	33.1	33.0	33.0	33.1	33.1
30	24.1	24.0	23.9	24.1	24.0	24.0	24.0	24.1	24.1
C-3 sugar									
Glc-1 (inn.)	105.4	105.4	105.4	105.4	102.8	102.6	102.9	102.7	102.7
2	75.3	75.3	75.3	75.3	83.9	83.6	83.8	83.7	83.7
3	78.4	78.3	78.3	78.4	78.1	78.2	78.3	78.1	78.1
4	71.7	71.7	71.7	71.6	71.1	71.2	71.1	71.1	71.2
5	78.4	78.3	78.3	78.4	78.3	78.1	78.1	78.3	78.3
6	62.8	62.8	62.8	62.8	62.6	62.5	62.6	62.6	62.5
Glc-1 (ter.)					106.2	106.1	106.2	106.1	106.1
2					76.9	76.9	76.9	76.9	76.9
3					77.9	77.9	77.9	77.9	77.9
4					71.2	71.2	71.2	71.1	71.2
5					78.3	78.5	78.3	78.3	78.3
6					62.6	62.7	62.6	62.6	62.6

Table 2. (continued)

	1	2	3	4	5	6	7	8	9
C-28 sugar									
Fuc-1	94.6	94.6	94.2	94.3	94.6	94.6	94.7	94.3	94.3
2	74.1	74.1	73.0	74.5	72.6	74.3	74.8	74.6	74.6
3	74.4	74.7	74.6	74.1	78.1	74.0	80.6	74.0	74.0
4	74.8	74.8	71.2	71.2	69.8	74.8	73.7	71.2	71.2
5	70.6	70.6	70.1	70.2	72.1	70.6	70.9	70.2	69.9
6	16.5	16.5	16.1	16.1	16.7	16.5	16.8	16.1	16.1
Ac at C-3			20.6	20.6	20.9			20.6	20.7
			170.1	170.1	170.4			170.2	170.2
Ac at C-4	20.8	20.7	20.4	20.4		20.8	20.6	20.4	20.4
	171.1	171.1	170.8	170.8		171.1	170.6	170.8	170.8
Rha-1 (C-2 of Fuc)	101.8	101.8	102.1	102.3	101.9	101.7	102.0	102.3	102.4
2	71.8	71.8	71.4	71.5	71.5	71.7	71.7	71.4	71.5
3	72.5	72.5	72.4	81.8	72.4	72.4	72.5	82.0	81.8
4	85.0	85.2	84.7	78.1	84.7	85.0	84.6	78.0	78.1
5	68.6	68.5	69.0	69.1	68.9	68.4	68.8	69.1	69.1
6	18.7	18.8	18.8	18.8	18.7	18.7	18.6	18.8	18.8
Rha-1 (C-3 of Fuc)							104.8		
2							72.3		
3							72.6		
4							73.6		
5							70.9		
6							18.6		
Xyl-1	107.4	107.0	106.8	104.8	107.2	106.9	107.2	104.7	104.8
2	76.2	75.7	75.6	75.0	76.1	75.7	76.1	75.0	75.0
3	78.8	76.7	76.6	76.5	78.7	76.7	78.7	76.5	76.5
4	71.0	78.3	78.2	78.5	70.9	78.4	70.6	78.5	78.5
5	67.5	65.0	65.0	64.8	67.5	65.0	67.5	64.8	64.8
Api-1				111.3				111.7	111.2
2				78.1				77.5	78.1
3				77.4				79.5	77.4
4				74.3				74.4	74.5
5				67.0				64.5	67.0
Ac at C-5				20.6					20.7
				170.7					170.7
Gal-1		104.5	104.5	104.4		104.5		104.4	104.4
2		71.8	71.8	71.7		71.8		71.8	71.8
3		75.1	75.1	75.0		75.0		75.0	75.0
4		70.1	70.0	70.0		70.2		70.2	70.2
5		77.3	77.3	77.6		77.3		77.4	77.6
6		62.3	62.3	62.3		62.3		62.3	62.3

Recorded at 100 MHz at 35 °C. Assignments of carbon signals of the sugar moiety were based on the HSQC spectrum.

the H-3 signal of the fucose moiety in **3** was shifted downfield at δ 5.56 ($\Delta + 1.21$ ppm). The position of the acetyl groups were thus decided to be the C-3 and C-4 of the fucose moiety. Based on the foregoing evidence, the structures of polygalasaponins XXXIV and XXXV were characterized as 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(4-*O*-acetyl)-β-D-fucopyranosyl ester and 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(3,4-di-*O*-acetyl)-β-D-fucopyranosyl ester.

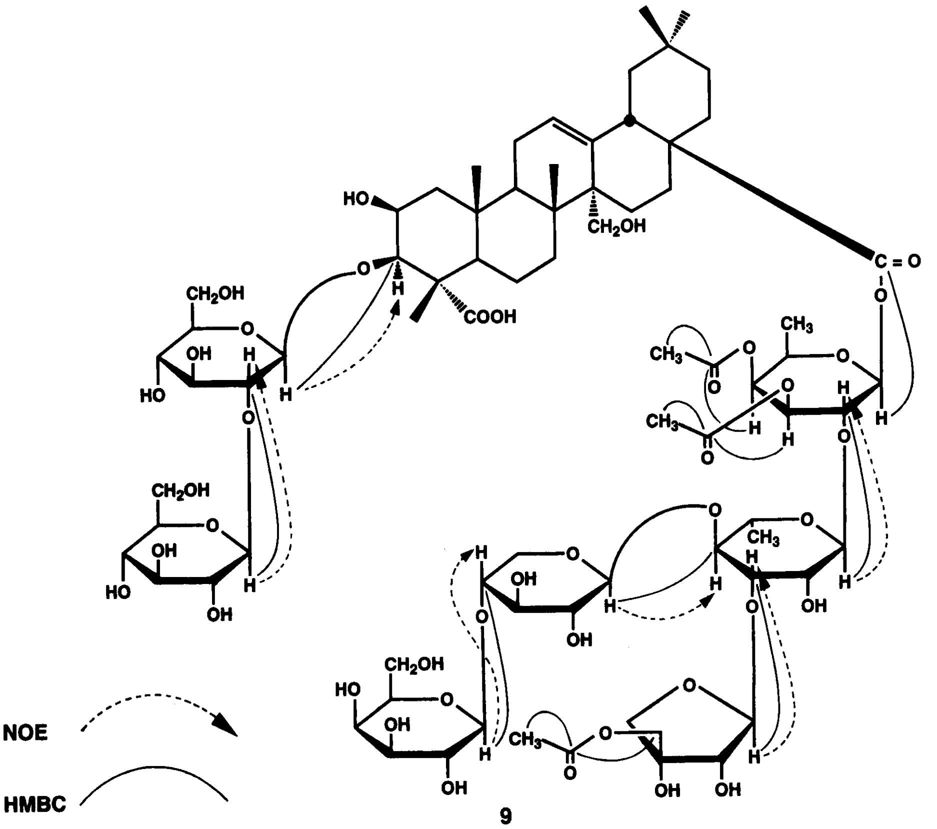
Polygalasaponin XXXVI (**4**) showed a $[M+Na]^+$ ion peak at m/z 1547.6549 in the high-resolution (HR) positive FAB-MS, suggesting the molecular formula of **4** was $C_{70}H_{108}O_{36}$. Compound **4** afforded D-glucose, D-fucose, L-rhamnose, D-xylose, D-galactose and D-apiose as the sugar components on acid hydrolysis. The NMR spectra were like those of **3** except for the presence of another acetyl (δ_H 1.89, δ_C 170.7) and apiose signals. The binding sites of the acetyl group and apiose were determined by an HMBC and NOE method. In the HMBC spectrum, long-range couplings ($^3J_{HCOC}$) were observed between the acetyl carbonyl carbon signal at δ 170.7 and the proton signals at δ 4.44 (d, $J=11$ Hz), 4.54 (d, $J=11$ Hz) due to the H_2-5 of apiose, between the anomeric proton at δ 5.98 (d, $J=4$ Hz) (H-1 of Api) and the carbon signal at δ 81.8 due to the C-3 of rhamnose. In the NOE difference spectrum of **4**, when the signal at δ 5.98 (H-1 of Api) was irradiated, NOE was observed at δ 4.37 (H-3 of Rha). The structure of **4** was, therefore, determined to be 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-[(5-*O*-acetyl)-β-D-apiofuranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-(3,4-di-*O*-acetyl)-β-D-fucopyranosyl ester.

Polygalasaponin XXXVII (**5**) showed an $[M+Na]^+$ ion peak at m/z 1332 in the FAB-MS. Combined with the result of the elemental analysis, its molecular formula was deduced to be $C_{61}H_{96}O_{30}$. The ^{1}H-NMR spectrum suggested the presence of an acetyl methyl proton (δ 1.99) and five anomeric proton signals at δ 5.05 (d, $J=7.5$ Hz), 5.09 (d, $J=8$ Hz), 5.20 (d, $J=8$ Hz), 5.73 (d, $J=1.5$ Hz), 6.14 (d, $J=8$ Hz) in addition to the signals due to the aglycone moiety. On acid hydrolysis, compound **5** afforded D-glucose, D-fucose, L-rhamnose and D-xylose. The position of the acetyl group was the C-3 of the fucose moiety by comparison of the NMR data with those of compounds **2**—**3** (see Tables 1 and 2). The data of the NOE experiments and the HMBC spectrum enabled us to identify the structure of **5** as 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(3-*O*-acetyl)-β-D-fucopyranosyl ester.

Polygalasaponin XXXVIII (**6**) afforded D-glucose, D-fucose, L-rhamnose, D-xylose and D-galactose on acid hydrolysis. Its molecular formula is $C_{67}H_{106}O_{35}$ from the FAB-MS and elemental analysis. The ^{1}H- and ^{13}C-NMR spectra of **6** disclosed acetyl signals at δ_H 1.96; δ_C 171.1, and six anomeric proton and carbon signals at δ 4.94 (d, $J=8$ Hz), 4.99 (d, $J=7.5$ Hz), 5.09 (d, $J=8$ Hz), 5.22 (d, $J=8$ Hz), 6.09 (d, $J=8$ Hz), 6.29 (d, $J=1$ Hz); 94.6, 101.7, 102.6, 104.5, 106.1, 106.9. The ^{1}H- and ^{13}C-chemical shifts of **6** were similar to those of **2** except for the signals due to the terminal glucose moiety. The binding sites of six monosaccharides and an acetyl group were determined by means of NOE, with irradiation at each anomeric proton signal, and the HMBC spectrum. Therefore, polygalasaponin XXXVIII was elucidated as 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-(4-*O*-acetyl)-β-D-fucopyranosyl ester.

The ^{1}H-NMR spectrum of polygalasaponin XXXIX (**7**), $C_{67}H_{106}O_{34}$, showed acetyl signals at δ_H 1.94; δ_C 170.6, six anomeric proton signals at δ 5.04 (d, $J=7$ Hz), 5.09 (d, $J=8$ Hz), 5.20 (d, $J=8$ Hz), 5.64 (br s), 5.89 (br s) and 6.06 (d, $J=8$ Hz). On acid hydrolysis, compound **7** afforded D-glucose, D-fucose, L-rhamnose and D-xylose as sugar components. Sugar linkages were decided by NOE and the HMBC spectrum. When the signals at δ 5.09, 5.20 (H-1 of each Glc), 5.64, 5.89 (H-1 of each Rha), 5.04 (H-1 of Xyl) were irradiated, NOEs were observed at the signals due to the H-3 [δ 4.60 (d, $J=3$ Hz)] of the aglycone, the H-2 [δ 4.02 (t, $J=8.5$ Hz)] of the glucose bound to the C-3 of the aglycone, the H-3 [δ 4.41 (dd, $J=9$, 3 Hz)] and the H-2 [δ 4.54 (t, $J=8.5$ Hz)] of the fucose and the H-4 [δ 4.28 (t, $J=9.5$ Hz)] of rhamnose (C-2 of Fuc). HMBC correlations were observed between the following carbons and protons in the oligosaccharide moieties of **7**: C-3 and H-1 of Glc(inn.), C-2 of Glc(inn.) and H-1 of Glc(ter)., C-28 and H-1 of Fuc, C-2 of Fuc and H-1 of Rha (C-2 of Fuc), C-3 of Fuc and H-1 of Rha (C-3 of Fuc), C-4 of Rha (C-2 of Fuc) and H-1 of Xyl, carbonyl carbon of acetyl group and H-4 of Fuc. Based on this evidence, the structure of polygalasaponin XXXIX was elucidated as 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→3)]-(4-*O*-acetyl)-β-D-fucopyranosyl ester.

Polygalasaponins XL (**8**), $C_{74}H_{116}O_{40}$ and XLI (**9**), $C_{76}H_{118}O_{41}$, afforded D-glucose, D-fucose, L-rhamnose, D-xylose, D-apiose, and D-galactose on acid hydrolysis. In the ^{1}H-NMR spectra of **8** and **9**, seven anomeric proton signals (δ 4.92, 5.10, 5.22, 5.24, 5.65, 5.98, 6.15; 4.92, 5.10,



9

Chart 3

5.21, 5.23, 5.63, 5.98, 6.15, respectively) were observed. Compound **8** showed two acetyl signals at δ 2.06, 2.11, while compound **9** showed three acetyl signals at δ 1.89, 2.07, 2.11. The NOE experiment with irradiation at the anomeric proton signal of each and the HMBC spectrum showed both the connection among individual glycosyl residues and the position of the acetyl groups (see Chart 3). Therefore, the structures of polygalasaponins XL and XLI were characterized as 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-[β-D-apiofuranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-(3,4-di-*O*-acetyl)-β-D-fucopyranosyl ester and 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl presenegenin 28-*O*-β-D-galactopyranosyl-(1→4)-β-D-xylopyranosyl-(1→4)-[(5-*O*-acetyl)-β-D-apiofuranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-(3,4-di-*O*-acetyl)-β-D-fucopyranosyl ester.

All anomeric configurations of glucose, fucose, xylose and galactose in these saponins were determined to be β from the J values of the anomeric proton signals, and those of rhamnose and apiose were determined to be α and β, respectively, by comparison of the ^{13}C-NMR data of the C-3 and C-5 of rhamnose[8] and the C-1 and C-2 of apiose.[9]

Experimental

General Procedure ^{1}H- and ^{13}C-NMR spectra were obtained with a JEOL α-400 spectrometer at 35 °C 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-1000 digital polarimeter. Gas chromatography (GC) was carried out 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 ODS-7 (2 cm × 25 cm) or Develosil PhA-T-5 (2 cm × 25 cm), respectively.

Extraction and Isolation *Polygala fallax* HEMSL. was collected in Guangxi, China in Aug. 1994, and dried roots (960 g) were extracted twice with 70% aqueous MeOH. The extract was passed through a porous polymer gel, Mitsubishi Diaion HP-20, column after evaporation of MeOH. After the contents of the column were washed with water, the adsorbed materials were eluted successively with 30% and 60% aqueous methanol and methanol. The methanol eluate (25 g) was chromatographed on silica-gel with $CHCl_3$–MeOH–H_2O (85 : 14 : 1), increasing the proportion of MeOH to give 18 fractions (frs. A—R). From frs. L, N and P, compounds **1**—**16** were isolated by preparative and semi-preparative HPLC [solvent: MeCN–H_2O system +0.05% trifluoroacetic acid (TFA)]. **1** (120 mg), **2** (43 mg), **3** (156 mg), **4** (32 mg), **5** (51 mg), **6** (39 mg), **7** (36 mg), **8** (16 mg), **9** (60 mg), **10** (78 mg), **11** (144 mg), **12** (301 mg), **13** (108 mg), **14** (240 mg), **15** (131 mg), **16** (8 mg).

Polygalasaponin XXXIII (**1**): Amorphous powder, $[\alpha]_D^{25}$ $-4.9°$ (c=0.44, MeOH). *Anal.* Calcd for $C_{55}H_{86}O_{25} \cdot 5H_2O$: C, 53.39; H, 7.82. Found: C, 53.20; H, 7.50. FAB-MS m/z: 1170 $[M+Na]^+$. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Polygalasaponin XXXIV (**2**): Amorphous powder, $[\alpha]_D^{25}$ $+1.6°$ (c=0.64, MeOH). *Anal.* Calcd for $C_{61}H_{96}O_{30} \cdot 15/2H_2O$: C, 50.67; H, 7.75. Found: C, 50.67; H, 7.46. FAB-MS m/z: 1332 $[M+Na]^+$. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Polygalasaponin XXXV (**3**): Amorphous powder, $[\alpha]_D^{25}$ $-2.1°$ (c=0.74, MeOH). *Anal.* Calcd for $C_{63}H_{98}O_{31} \cdot 5H_2O$: C, 52.49; H, 7.55. Found: C, 52.73; H, 7.44. FAB-MS m/z: 1374 $[M+Na]^+$. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Polygalasaponin XXXVI (**4**): Amorphous powder, $[\alpha]_D^{25}$ $-12.1°$ (c=0.40, MeOH). HR-FAB-MS m/z: 1547.6549 (Calcd for $C_{70}H_{108}NaO_{36}$: 1547.6511). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Polygalasaponin XXXVII (**5**): Amorphous powder, $[\alpha]_D^{25}$ $+19.2°$ (c=0.46, MeOH). *Anal.* Calcd for $C_{61}H_{96}O_{30} \cdot 4H_2O$: C, 53.03; H, 7.59. Found: C, 52.95; H, 7.67. FAB-MS m/z: 1332 $[M+Na]^+$. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Polygalasaponin XXXVIII (**6**): Amorphous powder, $[\alpha]_D^{25}$ $+3.7°$ (c=0.50, MeOH). *Anal.* Calcd for $C_{67}H_{106}O_{35} \cdot 6H_2O$: C, 50.94; H, 7.53. Found: C, 50.77; H, 7.44. FAB-MS m/z: 1494 $[M+Na]^+$. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Polygalasaponin XXXIX (**7**): Amorphous powder, $[\alpha]_D^{25}$ $-0.8°$ (c=0.55, MeOH). *Anal.* Calcd for $C_{67}H_{106}O_{34} \cdot 7H_2O$: C, 50.88; H, 7.65. Found: C, 50.86; H, 7.50. FAB-MS m/z: 1478 $[M+Na]^+$. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Polygalasaponin XL (**8**): Amorphous powder, $[\alpha]_D^{25}$ $-6.9°$ (c=0.45, MeOH). *Anal.* Calcd for $C_{74}H_{116}O_{40} \cdot 8H_2O$: C, 49.66; H, 7.43. Found: C, 49.50; H, 7.22. FAB-MS m/z: 1668 $[M+Na]^+$. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Polygalasaponin XLI (**9**): Amorphous powder, $[\alpha]_D^{25}$ $-6.5°$ (c=0.54, MeOH). *Anal.* Calcd for $C_{76}H_{118}O_{41} \cdot 8H_2O$: C, 49.83; H, 7.37. Found: C, 49.77; H, 7.08. FAB-MS m/z: 1710 $[M+Na]^+$. ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 2.

Acid Hydrolysis of Saponins (1—9) Each saponin (2 mg) was heated at 100 °C with dioxane (0.05 ml) and 5% H_2SO_4 (0.05 ml) 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[10] (0.05 mg) in water (0.03 ml) and pyridine (0.015 ml) at 60 °C for 1 h with stirring. After the solution was evaporated and the reaction mixture was dried, pyridine (0.015 ml), hexamethyldisilazane (0.015 ml) and trimethylsilylchloride (0.015 ml) were added to the residue. The reaction mixture was heated at 60 °C for 30 min. The supernatant was applied to GC. The ethyl acetate layer was concentrated and subjected to HPLC to reveal a peak from every saponin due to senegenic acid. GC conditions: column, Supelco SPB™-1, 0.25 mm × 27 m; column temperature, 230 °C; carrier gas, N_2; t_R: D-apiose 10.4 min, L-apiose 9.8 min,[11] D-xylose 10.7 min, L-xylose 9.8 min, L-rhamnose 12.4 min, D-rhamnose 12.0 min,[11] D-fucose 13.3 min, L-fucose 12.3 min, D-glucose 18.0 min, L-glucose 17.4 min, D-galactose 19.6 min, L-galactose 18.6 min.[11] D-Glucose, D-fucose, L-rhamnose, D-xylose were detected from **1**—**9**. D-Apiose was detected from **4**, **8** and **9**. D-Galactose was detected from **2**, **3**, **4**, **6**, **8** and **9**. HPLC conditions: column, Develosil PhA-T-5, 4.6 mm × 25 cm; solvent, MeCN–H_2O (45 : 55) +0.05% TFA; flow rate, 1.0 ml/min; UV 205 nm; t_R, senegenic acid 9.7 min.

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