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POLYGALASAPONINS XLII–XLVI FROM ROOTS OF *POLYGALA GLOMERATA*

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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Key Word Index—*Polygala glomerata*; Polygalaceae; polygalasaponin; presenegenin; oleanane-type saponin.

Abstract—Five new oleanane-type saponins, polygalasaponins XLII–XLVI, along with two known saponins were isolated from the roots of *Polygala glomerata* Lour. The structures of polygalasaponins XLII–XLVI were elucidated as 3-*O*-β-D-glucopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1 → 4)-α-L-rhamnopyranosyl-(1 → 2)-{4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]}-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)-[α-L-arabinopyranosyl-(1 → 3)]-[4-*O*-(*E*)-*p*-methoxycinnamoyl]-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)-[β-D-glucopyranosyl-(1 → 3)]-{4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]}-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)-[6-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)]-{4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]}-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)-[6-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)]-{4-*O*-[(*Z*)-3,4-dimethoxycinnamoyl]}-β-D-fucopyranosyl ester, respectively, on the basis of spectroscopic and chemical evidence. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

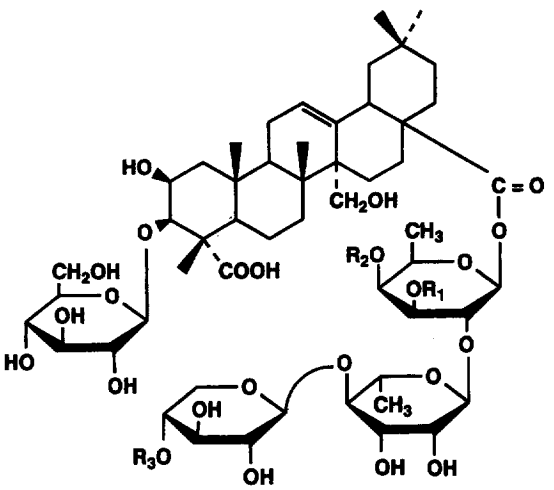
We previously reported the isolation and structural elucidation of sucrose and oligosaccharide esters called glomeratoses A–G, and four known sucrose and oligosaccharide esters from the roots of *Polygala glomerata* Lour. (= *Polygala chinesis* L.) (Polygalaceae) [1, 2]. We continued our investigation of the constituents of the roots of this plant, and isolated five new saponins called polygalasaponins XLII–XLVI (**1–5**), together with two known saponins, (*Z*)-senegin II (**6**) [3] and senegin II (**7**) [4]. This paper deals with the isolation and structural elucidation of these saponins.

RESULTS AND DISCUSSION

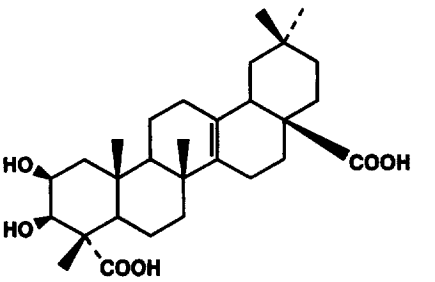
A 70% aqueous methanol extract of the roots of *P. glomerata* Lour. was concentrated and the residue was suspended in water and passed through a porous polymer gel, Mitsubishi Diaion HP-20, column and the adsorbed materials were eluted successively with 30 and 60% aqueous methanol and methanol. The methanol eluate were chromatographed on a octadecyl silica (ODS) column, followed by repeated semi-preparative HPLC on a reversed-phase (ODS, PhA-T) column to give seven saponins (**1–7**). On acid hydrolysis, saponins **1–5** afforded senegenic acid (**1a**) [5], which was well known as an artefact aglycone of presenegenin (**1b**) glycosides [6–8]. We therefore assumed that saponins **1–5** were presenegenin glycosides. Compounds **6** and **7** were assigned to be (*Z*)-senegin II [3] and senegin II [4] by comparison of their NMR data with reported data.

Polygalasaponin XLII (**1**) was obtained as an amorphous powder, and showed a $[M+Na]^+$ ion peak at *m/z* 1318 in the FAB-MS. The ^1H NMR spectrum suggested the presence of five singlet methyls (δ 0.79, 0.96, 1.14, 1.56 and 1.95), a pair of oxymethylene protons [δ 3.81 (*d*, *J* = 12 Hz) and 4.06 (*d*, *J* = 12 Hz)], a trisubstituted olefinic proton [δ 5.83 (*t*-like)] in the aglycone moiety, four anomeric proton signals [δ 5.05 (*d*, *J* = 8 Hz), 5.07 (*d*, *J* = 7 Hz), 6.17 (*d*, *J* = 8 Hz) and 6.38 (*br s*)] and one set of (*E*)-3,4-dimethoxycinnamoyl proton signals [δ 3.74 (3H, *s*), 3.80 (3H, *s*), 6.54 (1H, *d*, *J* = 16 Hz), 6.92 (1H, *d*, *J* = 8 Hz), 7.08 (1H, *dd*, *J* = 8, 2 Hz), 7.10 (1H, overlapping) and 7.94 (1H, *d*, *J* = 16 Hz)]. On acid

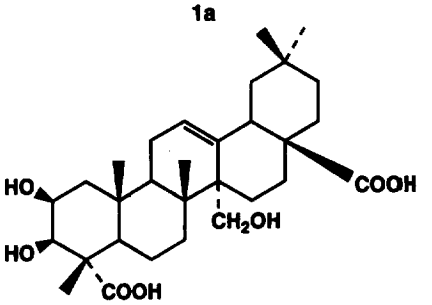
* Author to whom correspondence should be addressed.



	R_1	R_2	R_3
1	H	B	H
2	Ara	A	Gal
3	Glc	B	Gal
4	D	B	Gal
5	D	C	Gal
6	H	C	Gal
7	H	B	Gal



1a



1b

A (*E*)-*p*-methoxycinnamoyl
B (*E*)-3,4-dimethoxycinnamoyl
C (*Z*)-3,4-dimethoxycinnamoyl
D Glc$\overset{6}{}$Ac

hydrolysis, compound **1** afforded D-glucose, D-fucose, L-rhamnose and D-xylose as the sugar moieties, while on alkaline hydrolysis, it gave (*E*)-3,4-dimethoxycinnamic acid. Sugar proton and carbon signals in the NMR spectra (Tables 1 and 2) were assigned by ^1H–^1H correlation spectroscopy (COSY), homonuclear Hartmann–Hahn (HOHAHA), heteronuclear multiple bond coherence (HMBC) and heteronuclear single quantum coherence (HSQC) spectra. The sugar linkages were decided by nuclear Overhauser effect (NOE) difference and HMBC spectra. In the HMBC spectrum, long-range correlations ($^3J_{HCOC}$) were observed between the anomeric proton signal at δ 5.05 (H-1 of Glc) and the carbon signal at δ 86.0 due to C-3 of the aglycone, between the anomeric proton signal at δ 6.17 (H-1 of Fuc) and the carbon signal at δ 176.7 due to C-28 of the aglycone, between the anomeric proton signal at δ 6.38 (H-1 of Rha) and the carbon signal at δ 74.5 due to C-2 of fucose, between the anomeric proton signal at δ 5.07 (H-1 of Xyl) and the carbon signal at δ 85.0 due to C-4 of rhamnose, between the (*E*)-3,4-dimethoxycinnamoyl carbonyl carbon signal at δ 167.7 and the proton signal at δ 5.76 due to H-4 of focuse. When the signals at δ 5.05 (H-1 of Glc), 5.07 (H-1 of Xyl), 6.38 (H-1 of Rha) were irradiated, NOEs were observed at the signals of H-3 [δ 4.61 (*d*, J = 3 Hz)] of the aglycone, H-4 [δ 4.35 (*t*, J = 9.5 Hz)] of rhamnose, H-2 [δ 4.73 (*t*, J = 8.5 Hz)] of fucose, respectively. From these data, the structure of polygalasaponin XLII was elucidated as 3-*O*-β-D-glycopyranosyl presenegenin 28-*O*-β-D-xylopyranosyl-(1 → 4)-α-L-rhamnopyranosyl-(1 → 2)-{4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]}-β-D-fucopyranosyl ester.

Polygalasaponin XLIII (**2**) showed a $[M+Na]^+$ ion peak at m/z 1582 in the FAB-mass spectrum. Upon acid hydrolysis, compound **2** gave D-glucose, D-fucose, L-rhamnose, L-arabinose, D-xylose and D-galactose as a sugar moiety, while on alkaline hydrolysis, it afforded (*E*)-*p*-methoxycinnamic acid. The ^1H NMR spectrum of **2** exhibited six anomeric protons at δ 4.95 (*d*, J = 8 Hz), 4.98 (*d*, J = 7.5 Hz), 4.99 (*d*, J = 6.5 Hz), 5.03 (*d*, J = 8 Hz), 6.15 (*d*, J = 8 Hz), 6.27 (*br s*) and (*E*)-*p*-methoxycinnamoyl signals at δ 3.69 (3H, *s*), 6.48 (1H, *d*, J = 16 Hz), 7.00 (2H, *d*, J = 8.5 Hz), 7.40 (2H, *d*, J = 8.5 Hz), 7.84 (1H, *d*, J = 16 Hz). The ^{13}C NMR spectrum showed six anomeric carbons and *p*-methoxycinnamoyl carbon signals (see Table 2). Sugar linkages were decided by NOE difference and HMBC spectra. When the signals at δ 4.95 (H-1 of Gal), 4.98 (H-1 of Xyl), 4.99 (H-1 of Ara), 5.03 (H-1 of Glc), 6.27 (H-1 of Rha) were irradiated, NOEs were observed at the signals due to H-4 [δ 4.27 (*t*, J = 8.5 Hz)] of xylose, H-4 [δ 4.25 (*t*, J = 9 Hz)] of rhamnose, H-3 [δ 4.49 (*dd*, J = 9, 3.5 Hz)] of fucose, H-3 [δ 4.59 (*d*, J = 3 Hz)] of the aglycone, H-2 [δ 4.74 (*t*, J = 8.5 Hz) of fucose, respectively. In the HMBC spectrum, long-range correlations ($^3J_{HCOC}$) were observed between the following carbons and protons in the oligosaccharide moiety of **2**: C-3 and H-1 of Glc, C-28 and H-1 of

Table 1. ^{1}H NMR spectral data (400 MHz, pyridine-d_5) for saponins **1**–**5** from the roots of *Polygala glomerata*

	1	**2**	**3**	**4**	**5**
Aglycone					
2	4.71 *m*	4.70 *m*	4.70 *m*	4.71 *m*	4.71 *m*
3	4.61 *d* (3)	4.59 *d* (3)	4.59 *d* (3)	4.59 *d* (3)	4.61 *d* (3)
12	5.83 *t*-like	5.85 *t*-like	5.82 *t*-like	5.83 *t*-like	5.83 *t*-like
18	3.25 *dd* (14, 4)	3.24 *dd* (14, 4)	3.22 *dd* (14, 4)	3.22 *dd* (14, 4)	3.22 *dd* (14, 4)
24	1.95 *s*	1.95 *s*	1.97 *s*	1.95 *s*	1.95 *s*
25	1.56 *s*	1.52 *s*	1.52 *s*	1.52 *s*	1.53 *s*
26	1.14 *s*	1.15 *s*	1.13 *s*	1.14 *s*	1.15 *s*
27	3.81 *d* (12)	3.82 *d* (12)	3.82 *d* (12)	3.82 *d* (12)	3.82 *d* (12)
27	4.06 *d* (12)	4.06 *d* (12)	4.06 *d* (12)	4.06*	4.06*
29	0.79 *s*	0.79 *s*	0.78 *s*	0.78 *s*	0.79 *s*
30	0.96 *s*	0.94 *s*	0.92 *s*	0.92 *s*	0.93 *s*
C-3 sugar					
Glc-1	5.05 *d* (8)	5.03 *d* (8)	5.04 *d* (8)	5.04 *d* (8)	5.06 *d* (8)
2	3.92*	3.90*	3.91*	3.91*	3.92*
3	4.16*	4.14*	4.13 *t* (9)	4.15 *t* (9)	4.14*
4	4.14*	4.13*	4.14*	4.14*	4.13*
5	3.92 *m*	3.91 *m*	3.91 *m*	3.92 *m*	3.91 *m*
6	4.29 *dd* (12, 5)	4.28 *dd* (12, 5)	4.29 *dd* (12, 5)	4.28*	4.28*
6	4.46 *dd* (12, 2)	4.45*	4.45 *dd* (12, 2)	4.45*	4.45*
C-28 sugar					
Fuc-1	6.17 *d* (8)	6.15 *d* (8)	6.16 *d* (8)	6.18 *d* (8)	6.13 *d* (8)
2	4.73 *t* (8.5)	4.74 *t* (8.5)	4.78 *t* (8.5)	4.78 *t* (8.5)	4.66 *t* (8.5)
3	4.49 *dd* (9, 3.5)	4.49 *dd* (9, 3.5)	4.51 *dd* (9, 3.5)	4.48*	4.46*
4	5.76 *d* (3.5)	5.96 *d* (3.5)	6.10 *d* (3.5)	6.03 *d* (3.5)	5.95 *d* (3.5)
5	4.15*	4.11*	4.12*	4.21 *m*	4.18*
6	1.37 *d* (6)	1.31 *d* (6)	1.30 *d* (6)	1.39 *d* (6)	1.34 *d* (6)
Rha-1	6.38 *br s*	6.27 *br s*	6.45 *br s*	6.38 *br s*	6.30 *br s*
2	4.82 *br s*	4.82 *br s*	4.82 *br s*	4.81 *br s*	4.80 *br s*
3	4.70*	4.64 *dd* (9, 3)	4.65 *dd* (9, 3)	4.64 *dd* (9, 3.5)	4.63*
4	4.35 *t* (9.5)	4.25 *t* (9)	4.26 *t* (9)	4.25 *t* (9)	4.24 *t* (9)
5	4.55 *m*	4.45*	4.48*	4.46*	4.42*
6	1.82 *d* (6)	1.73 *d* (6)	1.74 *d* (6)	1.73 *d* (6)	1.74 *d* (6)
Ara-1		4.99 *d* (6.5)			
		4.41*			
		4.03*			
		4.26*			
		3.76 *br d* (12)			
		4.34 *dd* (12, 3)			
Glc-1			5.11 *d* (8)	5.05 *d* (8)	5.03 *d* (8)
2			3.95 *t* (8.5)	3.96 *t* (8.5)	3.95 *t* (8.5)
3			4.11 *t* (9)	4.08*	4.06*
4			4.02 *t* (9)	4.13*	4.12*
5			3.92 *m*	3.94*	3.94*
6			4.29 *dd* (12, 5)	4.73 *dd* (12, 5)	4.67 *dd* (12, 5)
6			4.50 *dd* (12, 2)	5.04*	5.01*
Ac				2.08 *s*	2.06 *s*
Xyl-1	5.07 *d* (7)	4.98 *d* (7.,5)	4.97 *d* (7.5)	4.97 *d* (7.5)	4.97 *d* (7)
2	4.04*	4.02 *t* (8)	4.02 *t* (8)	4.02 *t* (8)	4.03 *t* (8)
3	4.04*	4.04 *t* (8.5)	4.04 *t* (8.5)	4.05*	4.06 *t* (8.5)
4	4.16*	4.27*	4.28*	4.27*	4.29*
5	3.52 *t* (11)	3.44 *t* (11)	3.45 *t* (11)	3.44 *t* (11)	3.44 *t* (11)
5	4.24 *dd* (11, 5)	4.28*	4.29*	4.28*	4.28*

Table 1—*Continued.*

	1	2	3	4	5
Gal-1		4.95 *d* (8)	4.95 *d* (8)	4.95 *d* (8)	4.95 *d* (8)
2		4.45*	4.46*	4.46*	4.44*
3		4.08*	4.08*	4.10*	4.09*
4		4.47 *d* (3)	4.47*	4.47*	4.46 *d* (3)
5		4.13*	4.13*	4.12*	4.11*
6		4.34 *dd* (12, 5)	4.35 *dd* (12, 5)	4.36 *dd* (12, 5)	4.35*
6		4.42*	4.43*	4.43*	4.43*
Cinn.					
2	7.10*	7.40 *d* (8.5)	7.08 *d* (2)	7.08 *d* (2)	7.89 *d* (2)
3		7.00 *d* (8.5)			
5	6.92 *d* (8)	7.00 *d* (8.5)	6.91 *d* (8)	6.92 *d* (8)	6.93 *d* (8)
6	7.08 *dd* (8, 2)	7.40 *d* (8.5)	7.05 *dd* (8, 2)	7.06 *dd* (8, 2)	7.50 *dd* (8, 2)
7	7.94 *d* (16)	7.84 *d* (16)	7.93 *d* (16)	7.88 *d* (16)	6.82 *d* (13)
8	6.54 *d* (16)	6.48 *d* (16)	6.58 *d* (16)	6.54 *d* (16)	5.93 *d* (13)
MeO	3.80 *s*	3.69 *s*	3.80 *s*	3.80 *s*	3.85 *s*
	3.74 *s*		3.74 *s*	3.74 *s*	3.71 *s*

Assignments were based on ^{1}H–^{1}H Cosy, HOHAHA, NOE difference and HMBC spectra.
*Overlapping with other signals.

Fuc, C-2 of Fuc and H-1 of Rha, C-3 of Fuc and H-1 of Ara, C-4 of Rha and H-1 of Xyl, C-4 of Xyl and H-1 of Gal, and C-9 of *p*-methoxycinnamoyl and H-4 of Fuc. Based on the foregoing evidence, the structure of polygalasaponin XLIII has been concluded to be 3-*O*-*β*-D-glucopyranosyl presenegenin 28-*O*-*β*-D-galactopyransoyl-(1 → 4)-*β*-D-xylopyranosyl-(1 → 4)-α-L-rhamnpyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-[4-*O*-(*E*)-*p*-methoxycinnamoyl]-*β*-D-fucopyranosyl ester.

Polygalasaponin XLIV (**3**) was obtained as an amorphous powder, and it exhibited a $[M+Na]^+$ ion peak at *m/z* 1642 in the FAB-mass spectrum. The ^{1}H NMR spectrum showed the presence of six anomeric protons [*δ* 4.95 (*d*, *J* = 8 Hz), 4.97 (*d*, *J* = 7.5 Hz), 5.04 (*d*, *J* = 8 Hz), 5.11 (*d*, *J* = 8 Hz), 6.16 (*d*, *J* = 8 Hz), 6.45 (*br s*)] and (*E*)-3,4-dimethoxycinnamoyl signals [*δ* 3.74 (3H, *s*), 3.80 (3H, *s*), 6.58 (1H, *d*, *J* = 16 Hz), 6.91 (1H, *d*, *J* = 8 Hz), 7.05 (1H, *dd*, *J* = 8, 2 Hz), 7.08 (1H, *d*, *J* = 2 Hz), 7.93 (1H, *d*, *J* = 16 Hz)]. On acid hydrolysis, compound **3** afforded D-glucose, D-fucose, L-rhamnose, D-xylose and D-galactose, while on alkaline hydrolysis, it gave (*E*)-3,4-dimethoxycinnamic acid. The bonding sites of six monosaccharides and (*E*)-3,4-dimethoxycinnamoyl residue were decided by following observations of NOEs in the NOE difference and long-range correlations ($^3J_{HCOC}$) in the HMBC spectra (Fig. 1). Therefore, the structure of polygalasaponin XLIV was elucidated as 3-*O*-*β*-D-glucopyranosyl presenegenin 28-*O*-*β*-D-galactopyranosyl-(1 → 4)-*β*-D-xylopyranosyl-(1 → 4)-α-L-rhamnopyranosyl-(1 → 2)-[*β*-D-glucopyranosyl-(1 → 3)]-{4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]}-*β*-D-fucopyranosyl ester.

Polygalasaponin XLV (**4**) afforded D-glucose, D-fucose, L-rhamnose, D-xylose and D-galactose on acid hydrolysis, while on alkaline hydrolysis, it gave (*E*)-3,4-dimethoxycinnamic acid. The ^{1}H NMR spectrum of **4** exhibited acetyl signal at *δ* 2.08 (3H, *s*), (*E*)-3,4-dimethoxycinnamoyl signals at *δ* 3.74 (3H, *s*), 3.80 (3H, *s*), 6.54 (1H, *d*, *J* = 16 Hz), 6.92 (1H, *d*, *J* = 8 Hz), 7.06 (1H, *dd*, *J* = 8, 2 Hz), 7.08 (1H, *d*, *J* = 2 Hz), 7.88 (1H, *d*, *J* = 16 Hz) and six anomeric proton signals at *δ* 4.95 (*d*, *J* = 8 Hz), 4.97 (*d*, *J* = 7.5 Hz), 5.04 (*d*, *J* = 8 Hz), 5.05 (*d*, *J* = 8 Hz), 6.18 (*d*, *J* = 8 Hz), 6.38 (*br s*). The ^{1}H and ^{13}C chemical shifts of **4** were similar to those of **3** except for the signals due to the acetyl group. The bonding sites of six monosaccharides and acyl residues were determined by means of NOE, with irradiation at each anomeric proton signal, and the HMBC spectrum after assigning all proton signals due to a sugar moiety. The structure of polygalasaponin XLV was thus 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)-[6-*O*-acetyl-*β*-D-glucopyranosyl-(1 → 3)]-{4-*O*-[(*E*)-3,4-dimethoxycinnamoyl]}-*β*-D-fucopyranosyl ester.

Polygalasaponin XLVI (**5**) showed its $[M+Na]^+$ ion peak at *m/z* 1684 in the FAB-mass spectrum. The ^{1}H and ^{13}C NMR spectra of **5** exhibited six anomeric proton and carbon signals at *δ* 4.95 (*d*, *J* = 8 Hz), 4.97 (*d*, *J* = 7 Hz), 5.03 (*d*, *J* = 8 Hz), 5.06 (*d*, *J* = 8 Hz), 6.13 (*d*, *J* = 8 Hz), 6.30 (*br s*); 94.6, 101.7, 104.4, 105.3, 105.6, 106.9 and (*Z*)-3,4-dimethoxycinnamoyl signals at *δ* 3.71 (3H, *s*), 3.85 (3H, *s*), 5.93 (1H, *d*, *J* = 13 Hz), 6.82 (1H, *d*, *J* = 13 Hz), 6.93 (1H, *d*, *J* = 8 Hz), 7.50 (1H, *dd*, *J* = 8, 2 Hz), 7.89 (1H, *d*, *J* = 2 Hz); 55.7, 56.0, 111.6, 115.0, 117.0, 125.7, 128.1, 144.2, 149.9, 151.3, 165.8. The ^{1}H and ^{13}C chemical shifts of **5** were similar to those of **4** except for the appearance of the (*Z*)-3,4-dimethoxycinnamoyl group instead of one (*E*)-3,4-dimethoxycinnamoyl group. The site of linkage of (*Z*)-3,4-dimethoxycinnamoyl group was deter-

Table 2. ^{13}C NMR spectral data (100 MHz, pyridine-d_5) for compounds **1–5**

	1	**2**	**3**	**4**	**5**
Algycone					
1	44.3	44.2	44.3	44.3	44.3
2	70.3	70.3	70.3	70.3	70.4
3	86.0	86.0	86.0	86.0	86.0
4	52.9	52.9	52.9	52.9	52.9
5	52.5	52.5	52.5	52.5	52.5
6	21.5	21.5	21.6	21.6	21.6
7	33.6	33.6	33.6	33.6	33.6
8	41.2	41.2	41.2	41.2	41.2
9	49.4	49.3	49.3	49.3	49.3
10	37.1	37.0	37.0	37.0	37.0
11	23.7	23.7	23.6	23.6	23.7
12	127.8	127.8	127.8	127.8	128.1
13	138.9	138.9	138.9	138.9	139.0
14	48.0	48.1	48.1	48.1	48.1
15	24.5	24.5	24.5	24.5	24.6
16	24.0	24.0	24.0	24.0	24.0
17	47.0	47.1	47.1	47.1	47.1
18	42.0	42.0	42.1	42.1	42.0
19	45.4	45.4	45.4	45.4	45.5
20	30.8	30.8	30.8	30.8	30.7
21	33.9	33.9	33.9	33.9	33.9
22	32.4	32.4	32.4	32.4	32.4
23	180.8	180.8	180.8	180.8	180.8
24	14.2	14.2	14.2	14.2	14.3
25	17.5	17.5	17.5	17.5	17.5
26	18.8	18.8	18.8	18.8	18.8
27	64.5	64.4	64.4	64.5	64.4
28	176.7	176.7	176.7	176.7	176.7
29	33.1	33.0	33.0	33.0	33.0
30	24.0	24.0	24.0	24.0	24.0
C-3 sugar					
Glc-1	105.4	105.4	105.4	105.4	105.3
2	75.3	75.3	75.3	75.3	75.3
3	78.4	78.3	78.3	78.3	78.3
4	71.7	71.6	71.7	71.7	71.6
5	78.4	78.3	78.3	78.3	78.3
6	62.7	62.8	62.8	62.8	62.8
C-28 sugar					
Fuc-1	94.7	94.7	94.6	94.6	94.6
2	74.5	74.3	73.2	73.2	73.7
3	74.5	81.5	83.5	83.0	82.4
4	74.9	74.3	74.3	74.1	74.3
5	71.0	71.0	70.8	71.0	70.9
6	16.7	16.9	16.8	17.1	16.9
Rha-1	101.7	101.9	101.6	101.6	101.7
2	71.8	71.9	71.9	71.8	71.9
3	72.5	72.3	72.3	72.3	72.3
4	85.0	84.7	84.9	84.9	84.9
5	68.5	68.6	68.5	68.5	68.5
6	18.8	18.7	18.8	18.8	18.7
Ara-1		106.2			
2		72.4			
3		74.2			
4		69.0			
5		66.8			

Table 2—*Continued.*

	1	2	3	4	5
Glc-1			105.9	105.5	105.6
2			75.1	75.2	75.2
3			78.4	78.4	78.3
4			71.2	71.8	71.6
5			78.4	75.1	75.0
6			62.9	64.0	64.0
Ac (C-6 of Glc)				21.0	20.9
				171.0	170.8
Xyl-1	107.4	106.8	106.9	106.9	106.9
2	76.2	75.6	75.6	75.6	75.7
3	78.8	76.6	76.7	76.7	76.6
4	71.0	78.3	78.3	78.4	78.1
5	67.5	65.0	65.0	65.0	65.0
Gal-1		104.5	104.5	104.5	104.4
2		71.7	71.7	71.7	71.7
3		75.0	75.1	75.1	75.0
4		70.1	70.1	70.1	70.1
5		77.2	77.3	77.3	77.3
6		62.2	62.3	62.3	62.3
Cinn. 1	127.9	127.5	127.7	127.9	128.1
2	111.2	130.4	111.3	111.2	115.0
3	150.4	114.8	150.1	150.1	149.9
4	152.2	162.0	152.3	152.2	151.3
5	112.1	114.8	112.1	112.1	111.6
6	123.5	130.4	123.5	123.0	125.7
7	145.8	145.3	146.3	145.6	144.2
8	116.2	116.1	116.0	116.3	117.0
9	167.7	167.0	168.0	166.8	165.8
Meo	56.1	55.4	56.1	55.9	56.0
	55.9		55.9	55.8	55.7

Assigned by HSQC and HMBC spectra.

mined by the HMBC spectrum after assigning all proton and carbon signals in the oligosaccaride moiety of **5** by ^{1}H–^{1}H COSY, HOHAHA, NOE, HMBC and HSQC spectra. In the HMBC spectrum, long-range correlation ($^3J_{HCOC}$) was observed between the (*Z*)-3,4-dimethoxycinnamoyl carbonyl carbon signal at δ 165.8 and the proton signal at δ 5.95 (*d*, $J = 3.5$ Hz) due to H-4 of fucose. From these data, the structure of polygalasaponin XLVI was thus established as 3-*O*-β-D-glucopyranosyl presenengenin 28-*O*-β-D-galactopyranosyl-(1 → 4)-D-xylopyranosyl-(1 → 4)-α-L-rhamnopyranosyl-(1 → 2)-[6-*O*-acetyl-β-D-glucopyranosyl-(1→3)]-{4-*O*-[(*Z*)-3,4-dimethoxycinnamoyl]}-β-D-fucopyranosyl ester.

The anomeric configurations of glucose, fucose, xylose and galactose in these saponins were all determined to be β, and that of arabinose was determined to be α from the $^3J_{H1\text{-}H2}$ value of the anomeric proton signals, whereas that of rhamnose was determined to be α by comparison of the ^{13}C NMR data of C-3 and C-5 of rhamnose [9].

EXPERIMENTAL

General procedure. ^{1}H and ^{13}C NMR spectra were obtained with 400 MHz spectrometer at 35° and chemical shifts were given in δ ppm with tetramethylsilane as an int. standard. Prep. and semi-prep. HPLC were 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 glomerata Lour. was collected in Guangxi, China in Aug. 1994 and was identified by Prof. Deng Xi Qin, Guangxi Zhuangzu Zizhiqu Medicinal Botanical Garden, Nanning, China and a voucher specimen is deposited in the Herbarium of his institute. The dried roots (90 g) were extracted ×2 with 70% aq. MeOH. The extract (11 g) was

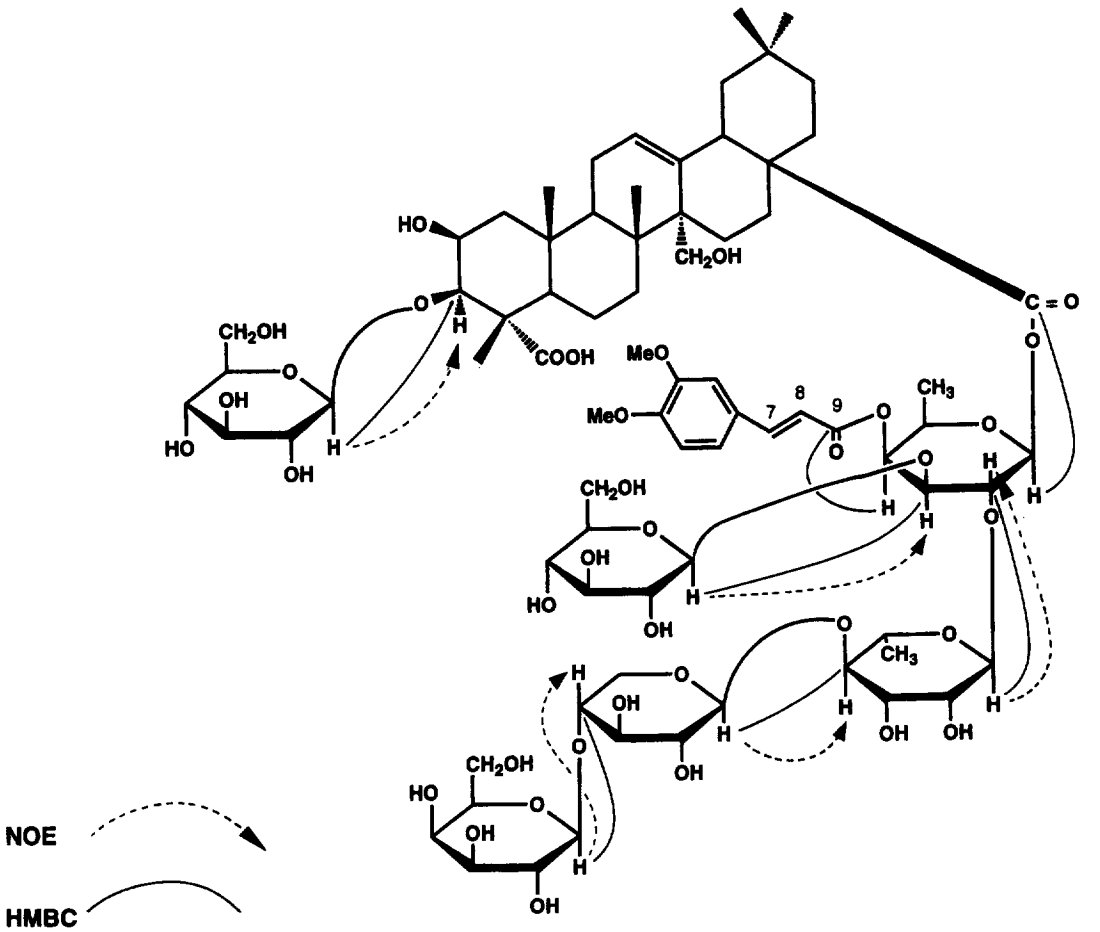


Fig. 1. HMBC and NOE correlations of compound **3**.

passed through a porous polymer gel, Mitsubishi Diaion HP-20, column. After the contents of the adsorbed materials were eluted successively with 30 and 60% aq. MeOH and MeOH. The MeOH eluate (2.2 g) was chromatographed on ODS column to give 28 frs (frs A–Z, a, b). From frs P (103 mg), R (94 mg), S (82 mg), T (102 mg), U (319 mg) and W (60 mg), compounds **1**–**7** were isolated by semi-prep. HPLC: **1** (13 mg), **2** (41 mg), **3** (19 mg), **4** (43 mg), **5** (6 mg), **6** (62 mg), **7** (118 mg).

Polygalasaponin XLII (**1**). Amorphous powder, $[\alpha]_D^{27}$ −1.3° (MeOH; *c* 0.49). UV λ_{max}^{MeOH} nm (log ε): 232 (4.06), 297 (4.09), 323 (4.20). FAB-MS *m/z*: 1318 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Polygalasaponin XLIII (**2**). Amorphous powder, $[\alpha]_D^{25}$ +11.9° (MeOH; *c* 1.29). UV λ_{max}^{MeOH} nm (log ε): 225 (4.12), 298 (4.26), 311 (4.32). FAB-MS *m/z*: 1582 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Polygalasaponin XLIV (**3**). Amorphous powder, $[\alpha]_D^{25}$ −1.7° (MeOH; *c* 0.52). UV λ_{max}^{MeOH} nm (log ε): 231 (4.08), 297 (4.09), 325 (4.21). FAB-MS *m/z*: 1642 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Polygalasaponin XLV (**4**). Amorphous powder, $[\alpha]_D^{25}$ +5.6° (MeOH; *c* 1.08). UV λ_{max}^{MeOH} nm (log ε): 233 (4.14), 296 (4.19), 323 (4.29). FAB-MS *m/z*: 1684 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Polygalasaponin XLVI (**5**). Amorphous powder, $[\alpha]_D^{25}$ −13.5° (MeOH; *c* 0.56). UV λ_{max}^{MeOH} nm (log ε): 231 (4.12), 297 (4.05), 321 (4.12). FAB-MS *m/z*: 1684 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Alkaline hydrolysis of **1**–**5**. Each compound (2 mg) was treated with 5% NaOH aq. (0.1 ml) for 3 hr at room temp. and the reaction mixt. was passed through a column filled with Amberlite IR-120B. The MeOH eluate was concd and subjected to HPLC [YMC R-ODS-7, 4.6 mm × 25 cm, CH_3CN–H_2O–TFA (32.5:67.5:0.05), 1.0 ml min^{-1}, UV 320 nm] to reveal a peak due to (*E*)-*p*-methoxycinnamic acid (R_t 12.4 min) from **2**, (*E*)-3,4-dimethoxycinnamic acid (R_t 8.2 min) from **1**, **3** and **4**, (*Z*)-3,4-dimethoxycinnamic acid (R_t 7.8 min) from **5**.

Acid hydrolysis of **1**–**5**. Each compound (1 mg) was heated at 100° with dioxane (0.05 ml) and 5% H_2SO_4 (0.05 ml) for 1 hr. After dilution with H_2O, the reaction mixt. was extracted ×2 with EtOAc and the H_2O layer was passed through an Amberlite IRA-60E column. The H_2O eluate was concd and the residue was treated with D-cysteine [10] (0.05 mg) in H_2O (0.03 ml) and pyridine (0.015 ml) at 60° for 1 hr with stirring. After the soln was concd and the reaction mixt. was dried, pyridine (0.015 ml), hexamethyldisilazane (0.015 ml) and trimethylsilylchloride (0.015 ml) were

added to the residue. The reaction mixt. was heated at 60° for 30 min. The supernatant was applied to GC. The EtOAc layer was concd and subject to HPLC to reveal a peak due to senegenic acid (**1a**) from saponins **1–5**. GC. conditions: column, Supelco SPB™-1, 0.25 mm × 27 m; column temp. 230°; carrier gas, N_2; R_t, D-xylose 10.40 min, L-xylose 9.69 min, D-arabinose 9.69 min, L-arabinose 10.40 min, D-rhamnose 11.80 min, L-rhamnose 11.97 min, D-fucose 12.91 min, L-fucose 11.91 min, D-glucose 17.49 min, L-glucose 16.89 min, D-galactose 19.20 in, L-galactose 18.01. The R_t for D-rhamnose and L-galactose were obtained from their enantiomers (L-rhamnose + L-cysteine and D-galactose + L-cysteine). D-Glucose, D-fucose, L-rhamnose and D-xylose were detected from **1–5**. L-Arabinose was detected from **2**. D-Galactose was detected from **2–5**. HPLC conditions: column, Develosil PhA-T-5, 4.6 mm × 25 cm; solvent, CH_3CN–H_2O–TFA (45:55:0.05); flow rate, 1.0 ml min^{-1}; UV 205 nm. R_t, senegenic acid 9.1 min.

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