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OLIGOSACCHARIDE POLYESTERS FROM ROOTS OF *POLYGALA GLOMERATA*

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Key Word Index—*Polygala glomerata*; Polygalaceae; roots; glomeratose; sucrose esters; oligosaccharide esters.

Abstract—Seven new sucrose and oligosaccharide esters, glomeratoses A–G, together with four known compounds, 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2 → 1)-(6-*O*-benzoyl)-α--D-glucopyranoside, 3-*O*-(*E*)-sinapoyl-β-D-fructofuranosyl-(2 → 1)-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside, tenuifoliside C and reiniose G were isolated from the roots of *Polygala glomerata*. Glomeratoses A–G were elucidated as 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2 → 1)-α-D-glucopyranoside, 3-*O*-(*E*)-sinapoyl-β-D-fructofuranosyl-(2 → 1)-[6-*O*-(*E*)-*p*-coumaroyl]-α-D-glucopyranoside, 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2 → 1)-[6-*O*-(*E*)-*p*-coumaroyl]-α-D-glucopyranoside, 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2 → 1)-[6-*O*-(*E*)-3,4,5-trimethoxycinnamoyl]-α-D-glucopyranoside, 1-*O*-{6-*O*-[3-*O*-(*E,E*)-(β,β′-bis-sinapoyl)-β-D-fructofuranosyl]}-α-D-glucopyranoside intramolecular ester, 1-*O*-(*E*)-*p*-coumaroyl-(3-*O*-benzoyl)-β-D-fructofuranosyl-(2→1)-[β-D-glucopyranosyl-(1→2)]-[6-*O*-acetyl-β-D-glucopyranoysl-(1 → 3)]-[4-*O*-(*E*)-feruloyl]-(6-D-acetyl)-α-D-glucopyranoside, 1-*O*-(*E*)-*p*-coumaroyl-(3-*O*-benzoyl)-β-D-fructofuranosyl-(2 → 1)-[β-D-glucopyranosyl-(1 → 2)]-[6-*O*-acetyl-β-D-glucopyranoside-(1 →3)]-{4-*O*-[4-*O*-β-D-glucopyranosyl-(*E*)-feruloyl]}-[6-*O*-(*E*)-*p*-coumaroyl]-α-D-glucopyranosyl, respectively, on the basis of chemical and spectral evidence. © 1997 Elsevier Science Ltd

INTRODUCTION

Polygala glomerata (Chinese name Jin Bu Huan) is widely distributed in southern China, and is used as a remedy for coughs and hepatitis [1]. The constituents of this species have been investigated and the presence of saponins [2], lignans [3–5] and flavonol glycosides [6] have been reported. We have continued our investigations on the constituents of the genus *Polygala* and have isolated seven new sucrose and oligosaccharide esters, designated glomeratoses A (**1**), B (**3**), C (**4**), D (**7**), E (**8**), F (**10**) and G (**11**), together with four known compounds, 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2 → 1)-(6-*O*-benzoyl)-α-D-glucopyranoside (**2**) [7], 3-*O*-(*E*)-sinapoyl-β-D-fructofuranosyl-(2 → 1)-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside (**5**) [8], tenuifoliside C (**6**) [8–9] and reiniose G (**9**) [10] from the roots of *Polygala glomerata*. The present paper deals with the isolation and structural elucidation of these compounds.

RESULTS AND DISCUSSION

A 70% aqueous methanol extract of the roots of *P. glomerata* was concentrated and the residue suspended in water and passed through a porous polymer gel (Mitsubishi Diaion HP-20) column and the adsorbed materials eluted successively with 30%, 60% aqueous methanol and methanol. The 60% methanol and methanol eluate were chromatographed on octadecyl silica (ODS) columns, respectively, followed by repeated semi-preparative HPLC on a reversed-phase (ODS, PhA-T) column to give compounds **1**–**11**. Compounds **2**, **5**, **6** and **9** were identified as 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2 → 1)-(6-*O*-benzoyl)-α-D-glucopyranoside, 3-*O*-(*E*)-sinapoyl-β-D-fructofuranosyl-(2 → 1)-[6-*O*-(*E*)-sinapoyl]-α-D-glucopyranoside, tenuifoliside C and reiniose G, respectively, by comparison of their ^{1}H and ^{13}C NMR data with reported ones.

Glomeratose A (**1**) was obtained as an amorphous powder, and showed a $[M+Na]^+$ ion peak at *m/z* 585 in the FAB mass spectrum. On acid hydrolysis, compound **1** afforded D-glucose and D-fructose, while on alkaline hydrolysis, it gave sucrose and (*E*)-3,4,5-trimethoxycinnamic acid. The ^{1}H NMR spectrum of **1** suggested the presence of one set of glucose, one set of fructose and one set of (*E*)-3,4,5-trimethoxycinnamoyl proton signals (Table 1). The ^{13}C NMR spectrum exhibited one set of sucrose [δ 93.3 (C-1 of Glc), 73.1 (C-2 of Glc), 75.0 (C-3 of Glc), 71.2

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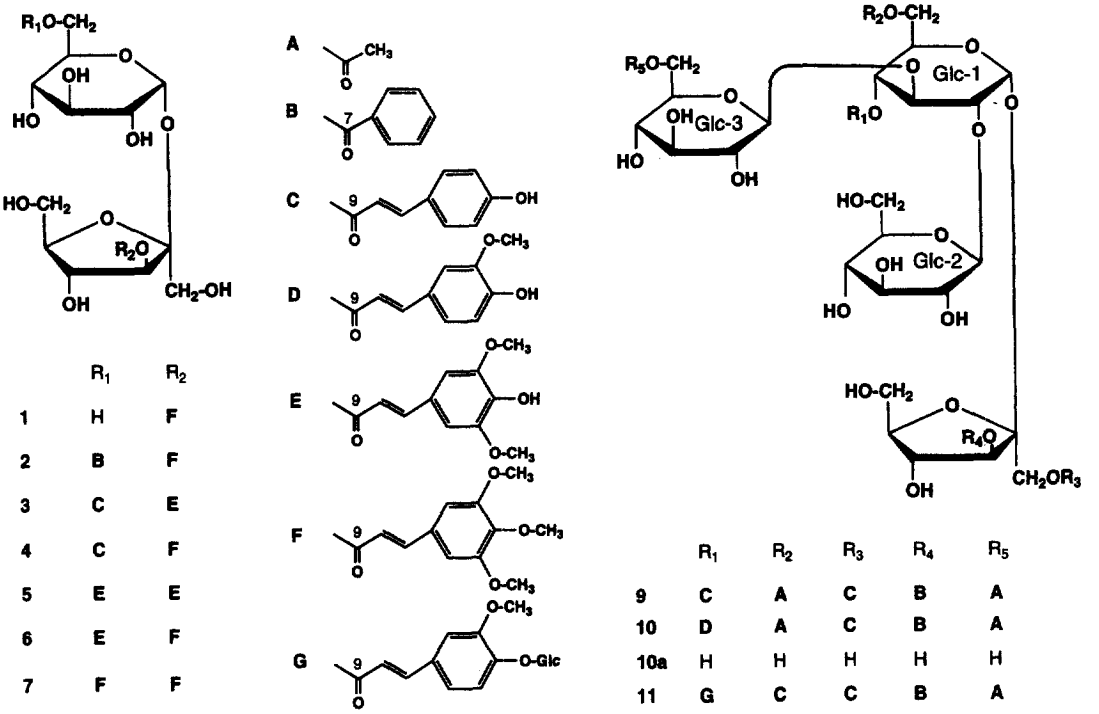
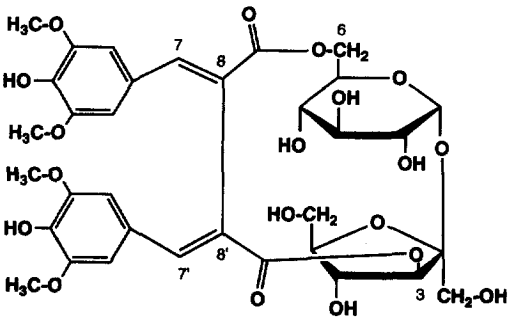


	R_1	R_2
1	H	F
2	B	F
3	C	E
4	C	F
5	E	E
6	E	F
7	F	F

	R_1	R_2	R_3	R_4	R_5
9	C	A	C	B	A
10	D	A	C	B	A
10a	H	H	H	H	H
11	G	C	C	B	A



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(C-4 of Glc), 74.6 (C-5 of Glc), 62.4 (C-6 of Glc); 65.4 (C-1 of Fru), 104.8 (C-2 of Fru), 79.8 (C-3 of Fru), 74.6 (C-4 of Fru), 84.2 (C-5 of Fru), 62.9 (C-6 of Fru)] and one set of (*E*)-3,4,5-trimethoxycinnamoyl carbon signals [δ 131.5 (C-1), 107.0 (C-2,6), 154.8 (C-3,5), 141.3 (C-4), 147.2 (C-7), 117.9 (C-8), 167.7 (C-9), 56.8 ($2\times$C of OCH_3), 61.2 (C of OCH_3)]. All 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 band coherence (HMBC) and heteronuclear single quantum coherence (HSQC) experiments. The position of the (*E*)-3,4,5-trimethoxycinnamoyl group in the sucrose moiety of **1** was deduced from the HMBC experiment. In this spectrum, long-range correlations ($^3J_{HCOC}$) were observed between the (*E*)-3,4,5-trimethoxycinnamoyl carbonyl carbon signal at δ 167.7 and the proton signal at δ 5.47 due to H-3 of fructose, and between the anomeric proton signal at δ 5.44 (H-1 of Glc) and the anomeric carbon signal at δ 104.8 (C-2 of Fru). From these data, the structure of glomeratose A was elucidated as 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl-(2 → 1)-α-D-glucopyranoside.

Glomeratose B (**3**) showed a $[M+Na]^+$ ion peak at *m/z* 717 in the FAB mass spectrum. The ^1H NMR spectrum exhibited signals belonging to a (*E*)-*p*-coumaroyl group [δ 6.41 (1H, *d*, J = 16 Hz), 6.79 (2H, *d*, J = 8.5 Hz), 7.45 (2H, *d*, J = 8.5 Hz), 7.62 (1H, *d*, J = 16 Hz)] and a (*E*)-sinapoyl group [δ 3.88 (6H, *s*), 6.45 (1H, *d*, J = 16 Hz), 6.95 (2H, *s*), 7.69 (1H, *d*, J = 16 Hz)], in addition to the signals due to the sucrose moiety. On acid hydrolysis, **3** afforded D-glucose and D-fructose, while on alkaline hydrolysis, it gave (*E*)-*p*-coumaric, (*E*)-sinapic acid and sucrose. The position of each acyl residue was determined by an HMBC experiment after assigning all proton and carbon signals. In this spectrum, long-range correlations ($^3J_{HCOC}$) were observed between the (*E*)-*p*-coumaroyl carbonyl carbon signal at δ 169.2 and the proton signals at δ 4.26 and 4.63, due to the H_2-6 of glucose, and between the (*E*)-sinapoyl carbonyl carbon signal at δ 168.2 and the proton signal at δ 5.47 due to the H-3 of fructose. Based on the foregoing evidence, the structure of glomeratose B was established as 3-*O*-(*E*)-sinapoyl-β-D-fructofuranosyl-(2 → 1)-[6-*O*-(*E*)-*p*-coumaroyl]-α-D-glucopyranoside.

Glomeratoses C (**4**), $C_{33}H_{40}O_{17}$ and D (**7**), $C_{36}H_{46}O_{19}$ showed one set of sucrose proton and carbon signals (Tables 1 and 2) in their NMR spectra, and gave D-glucose and D-fructose as a sugar moieties on acid hydrolysis. On alkaline hydrolysis, **4** yielded (*E*)-*p*-coumaric, (*E*)-3,4,5-trimethoxycinnamic acid and sucrose, whereas **7** gave (*E*)-3,4,5-trimethoxycinnamic

Table 1. ^{1}H NMR spectral data (in CD_3OD) for sucrose and oligosaccharide esters from *Polygala glomerata*

	1	**3**	**4**	**7**	**8**	**10**	**11**
Glc-1							
1	5.44 *d* (3.5)	5.49 *d* (4)	5.49 *d* (3.5)	5.52 *d* (3.5)	5.48 *d* (4)	5.86 *d* (3.5)	5.89 *d* (3.5)
2	3.44 *dd* (9.5, 3.5)	3.47 *dd* (9.5, 4)	3.47 *dd* (9.5, 3.5)	3.48 *dd* (9.5, 3.5)	3.40 *dd* (9.5, 4)	3.81 *dd* (9.5, 3.5)	3.84 *dd* (9.5, 3.5)
3	3.67 *t* (9.5)	3.67 *t* (9.5)	3.67 *t* (9.5)	3.67 *t* (9.5)	3.51 *dd* (9.5, 9)	3.97 *t* (9.5)	3.98 *t* (9.5)
4	3.40 *dd* (10, 9)	3.34 *t* (9.5)	3.34 *t* (9.5)	3.31 *t* (9.5)	3.16 *dd* (10, 9)	5.02 *dd* (10, 9.5)	5.09 *t* (9.5)
5	3.94 *m*	4.24 *m*	4.24 *m*	4.29 *m*	3.83 *m*	4.39 *m*	4.49 *m*
6	3.77 *dd* (12, 5)	4.26 *dd* (11, 6)	4.25 *dd* (11, 6)	4.22 *dd* (12, 7)	4.04 *dd* (12, 2)	4.13 *dd* (12, 5)	4.29 *dd* (12, 7)
6	3.86 *dd* (12, 2)	4.63 *br d* (11)	4.63 *br d* (11)	4.70 *dd* (12, 2)	4.98 *dd* (12, 10)	4.19 *dd* (12, 2)	4.32 *dd* (12, 5)
Ac						2.06 *s*	
Glc-2							
1						4.60 *d* (8)	4.60 *d* (8)
2						3.33*	3.31*
3						3.33*	3.33*
4						3.33*	3.32*
5						3.33*	3.33*
6						3.72 *dd* (12, 6)	3.72 *dd* (12, 5)
6						3.93 *dd* (12, 1)	3.91*
Glc-3							
1						4.50 *d* (8)	4.51 *d* (8)
2						3.01 *t* (8.5)	3.01 *t* (8.5)
3						3.18 *t* (9)	3.20 *t* (9)
4						3.22 *t* (9)	3.19 *t* (9)
5						3.09 *m*	3.10 *m*
6						3.99 *dd* (12, 2)	3.99 *dd* (12, 2)
6						4.06 *dd* (12, 5)	4.05 *dd* (12, 5)
Ac						1.60 *s*	2.09 *s*
Glc-4							
1							5.01 *d* (8)
2							3.55 *t* (8.5)
3							3.51 *t* (9)
4							3.48 *t* (9)
5							3.48 *m*
6							3.72 *dd* (12, 5)
6							3.94*
Fru							
1	3.59 *d* (12)	3.59 *d* (12)	3.59 *d* (12)	3.59 *d* (12)	3.69 *d* (12)	4.22 *d* (12)	4.23 *d* (12)
1	3.67 *d* (12)	3.65 *d* (12)	3.65 *d* (12)	3.64 *d* (12)	3.84 *d* (12)	4.69 *d* (12)	4.68 *d* (12)
3	5.47 *d* (8)	5.47 *d* (8)	5.49 *d* (8)	5.51 *d* (8)	5.35 *d* (8)	5.73 *d* (8)	5.73 *d* (8)
4	4.39 *t* (8)	4.43 *t* (8)	4.44 *t* (8)	4.50 *t* (8)	4.17 *t* (8)	4.43 *t* (8)	4.51 *t* (8)
5	3.94 *m*	3.96 *m*	3.97 *m*	3.98 *m*	3.65 *m*	4.07 *m*	4.08 *m*
6	3.80*	3.81 *dd* (12, 5)	3.82 *dd* (12, 4)	3.83 *dd* (12, 4)	3.62 *dd* (12, 4)	3.84 *dd* (12, 3)	3.84*
6	3.83*	3.88 *dd* (12, 7)	3.89 *dd* (12, 6)	3.89 *dd* (12, 6)	3.78*	3.87 *dd* (12, 6)	3.88 *dd* (12, 6)
Benzoyl (C-3 of Fru)							
2, 6						8.18 *dd* (8, 1)	8.19 *dd* (8, 1)
3, 5						7.60 *t* (8)	7.57 *t* (8)
4						7.69 *tt* (8, 1)	7.66 *tt* (8, 1)
Cinn.	C-3 of Fru	C-3 of Fru	C-3 of Fru	C-3 of Fru	C-3 of Fru	C-4 of Glc-1	C-4 of Glc-1
2	6.98 *s*	6.95 *s*	6.96 *s*	6.95 *s*	6.78 *s*	7.20 *d* (2)	7.22 *d* (2)
3							
5						6.85 *d* (8)	7.18 *d* (8)
6	6.98 *s*	6.95 *s*	6.96 *s*	6.95 *s*	6.78 *s*	7.05 *dd* (8, 2)	7.09 *dd* (8, 2)
7	7.72 *d* (16)	7.69 *d* (16)	7.71 *d* (16)	7.68 *d* (16)	7.82 *br s*	7.57 *d* (16)	7.58 *d* (16)
8	6.54 *d* (16)	6.45 *d* (16)	6.54 *d* (16)	6.53 *d* (16)		6.25 *d* (16)	6.34 *d* (16)
MeO	3.88 *s*	3.88 *s*	3.84 *s*	3.87 *s*	3.73 *s*	3.95 *s*	3.90 *s*
	3.88 *s*	3.88 *s*	3.84 *s*	3.87 *s*	3.73 *s*		
	3.80 *s*		3.79 *s*	3.79 *s*			
Cinn. (C-6 of Glc-1)							
2, 6		7.45 *d* (8.5)	7.44 *d* (8.5)	6.90 *s*	6.82 *s*		7.31 *d* (8.5)
3, 5		6.79 *d* (8.5)	6.79 *d* (8.5)				6.70 *d* (8.5)
7		7.62 *d* (16)	7.62 *d* (16)	7.60 *d* (16)	7.81 *br s*		7.67 *d* (16)
8		6.41 *d* (16)	6.40 *d* (16)	6.54 *d* (16)			6.35 *d* (16)
MeO				3.85 *s*	3.73 *s*		
				3.85 *s*	3.73 *s*		
				3.78 *s*			

Table 1.—*Continued.*

1	3	4	7	8	10	11
Cinn. (C-1 of Fru)						
2, 6					7.42 *d* (8.5)	7.41 *d* (8.5)
3, 5					6.81 *d* (8.5)	6.81 *d* (8.5)
7					7.67 *d* (16)	7.58 *d* (16)
8					6.35 *d* (16)	6.27 *d* (16)

Recorded at 400 MHz at 35°. Assignments were based on ^{1}H–^{1}H COSY, HOHAHA, NOE difference and HMBC spectra.
* Overlapping with other signals.

acid and sucrose. The position of each acyl residue was decided by an HMBC experiment. In the HMBC spectrum of **4**, long-range correlations ($^3J_{HCOC}$) were observed between the (*E*)-*p*-coumaroyl carbonyl carbon signal at δ 169.2 and the proton signals at δ 4.25 and 4.63, due to the H_2-6 of glucose, and between the (*E*)-3,4,5-trimethoxycinnamoyl carbonyl carbon signal at δ 167.8 and the proton signal at δ 5.49, due to the H-3 of fructose. In the HMBC spectrum of **7**, long-range correlations ($^3J_{HCOC}$) were observed between the two (*E*)-3,4,5-trimethoxycinnamoyl carbonyl carbon signals at δ 167.8 and 168.7 and the proton signals at δ 5.51, due to the H-3 of fructose, and δ 4.22, 4.70 due to the H_2-6 of glucose, respectively. From these data, the structures of glomeratoses C and D were determined as 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl(2 → 1)-[6-*O*-(*E*)-*p*-coumaroyl]-α-D-glucopyranoside and 3-*O*-[(*E*)-3,4,5-trimethoxycinnamoyl]-β-D-fructofuranosyl(2 → 1)-[3-*O*-(*E*)-3,4,5-trimethoxycinnamoyl]-α-D-glucopyranoside, respectively.

Glomeratose E (**8**), $C_{34}H_{40}O_{19}$ showed a $[M+Na]^+$ ion peak at *m/z* 775 in the FAB mass spectrum. On acid hydrolysis, it afforded D-glucose and D-fructose, while on alkaline hydrolysis, it gave sucrose and (*E*,*E*)-β,β'-bis-sinapic acid. The ^{1}H NMR spectrum of **8** exhibited two trisubstituted olefinic protons [δ 7.81 (1H, *br s*) and 7.82 (1H, *br s*)], four aromatic protons [δ 6.78 (2H, *s*) and 6.82 (2H, *s*)] and four methoxyl signals [δ 3.73 (12H, *s*)], in addition to the signals due to sucrose. The ^{13}C NMR spectrum of **8** suggested the presence of one set of bis-sinapoyl [δ 56.8 (2C), 109.1 (2C), 125.6, 126.7, 139.2, 144.6, 149.1 (2C), 169.3; 56.8 (2C), 108.8 (2C), 126.2, 126.7, 138.9, 144.7, 149.1 (2C), 169.7] and one set of sucrose carbon signals [δ 92.9 (C-1 of Glc), 73.8 (C-2 of Glc), 75.6 (C-3 of Glc), 72.3 (C-4 of Glc), 73.8 (C-5 of Glc), 65.3 (C-6 of Glc); 66.7 (C-1 of Fru), 105.6 (C-2 of Fru), 80.8 (C-3 of Fru), 72.7 (C-4 of Fru), 82.3 (C-5 of Fru), 61.2 (C-6 of Fru)]. All proton and carbon signals were assigned by ^{1}H–^{1}H COSY, NOE, HMBC and HSQC spectra. Comparing the ^{13}C NMR spectrum of **8** with that of **5** (Table 2), the C-8 signals of the two sinapoyl groups in **8** were shifted downfield at δ 125.6 (Δ+10.1 ppm) and 126.2 (Δ+10.3 ppm), respectively. In the HMBC spectrum, long-range correlations ($^3J_{HCOC}$) were observed between the olefinic proton signal at δ 7.81 (1H, *br s*, H-7 of acyl) and the carbon signal at δ 126.2 due to C-8′ of the acyl group, and between the olefinic proton signal at δ 7.82 (1H, *br s*, H-7′ of acyl) and the carbon signal at δ 125.6 due to C-8 of the acyl group. We assumed that two sinapoyl residues were connected as a dimeric group by the C-8 of each sinapoyl group. The stereochemistry of this dimeric group was decided as (*E*,*E*)-β,β'-bis-sinapoyl group by comparing the chemical shifts of the two olefinic protons of compound **8** with those of dimethyl (*E*)- and (*Z*)-α-benzyl-α'-benzylidenesuccinates [11]. The linkage between this dimeric group and sucrose was decided by an HMBC experiment. In this spectrum, long-range correlations ($^3J_{HCOC}$) were observed between two carbonyl carbon signals at δ 169.3 and 169.7 of the dimeric group and the proton signals at δ 4.04 and 4.98, due to the H_2-6 of glucose, and δ 5.35 due to the H-3 of fructose, respectively. Based on the above data, the structure of glomeratose E was determined as 1-*O*-{6-*O*-[3-*O*-(*E*,*E*)-(β,β'-bis-sinapoyl)-β-D-fructofuranosyl]}-α-D-glucopyranoside intramolecular ester.

Glomeratose F (**10**) was obtained as an amorphous powder, and it revealed a $[M+Na]^+$ ion peak at *m/z* 1199 in the FAB mass spectrum. The ^{1}H NMR spectrum suggested the presence of three anomeric proton signals [δ 4.50 (1H, *d*, *J* = 8 Hz), 4.60 (1H, *d*, *J* = 8 Hz) and 5.86 (1H, *d*, *J* = 3.5 Hz)] and the ^{13}C NMR spectrum suggested the presence of four anomeric carbons (δ 93.0, 103.9, 104.4 and 105.4), two sets of acetyl carbons (δ 20.5 and 172.5; 20.8 and 172.6), one set of benzoyl carbons [δ 129.9 (2C), 131.1 (3C), 134.8 and 167.3], one set of (*E*)-*p*-coumaroyl carbons [δ 114.9, 116.9 (2C), 127.1, 131.2 (2C), 147.0, 161.4 and 168.4] and one set of (*E*)-feruloyl carbons [δ 56.5, 111.7, 115.2, 116.6, 124.6, 127.5, 147.2, 149.5, 151.0 and 167.9). On acid hydrolysis, **10** gave D-glucose and D-fructose as sugar moieties, while on alkaline hydrolysis, it afforded tetrasaccharide **10a** [12] (see Experimental) and a mixture of benzoic, (*E*)-*p*-coumaric, (*E*)-ferulic and acetic acids. All proton and carbon signals in the NMR spectra (Tables 1 and 2) were assigned by ^{1}H–^{1}H COSY, HOHAHA, NOE, HMBC and HSQC spectra. The position of each acyl residue was decided by NOE difference and HMBC spectra. When the signals at δ 4.50 (H-1 of Glc-3) and 4.60 (H-1 of Glc-2) were irradiated, NOEs were observed at the signals due to the H-3 [δ 3.97 (*t*, *J* = 9.5 Hz)] and H-2 [δ 3.81 (*dd*, *J* = 9.5, 3.5 Hz) of Glc-1, respectively. In the HMBC spectrum, long-range cor-

Table 2. ^{13}C NMR data (in CD_3OD) for sucrose and oligosaccharide esters from *Polygala glomerata*

	1	**3**	**4**	**5**	**7**	**8**	**10**	**11**
Glc-1								
1	93.3	92.9	92.9	92.7	92.7	92.9	93.0	92.9
2	73.1	73.2	73.1	73.2	73.2	73.8	81.4	81.5
3	75.0	75.0	75.1	75.1	75.1	75.6	79.0	79.0
4	71.2	71.9	71.9	72.0	72.0	72.3	70.4	71.8
5	74.6	72.5	72.5	72.5	72.6	73.8	69.7	69.1
6	62.4	65.4	65.4	65.6	65.7	65.3	64.3	64.9
Ac							20.8	
							172.6	
Glc-2								
1							105.4	105.4
2							75.3	75.3
3							78.5	78.5
4							71.7	71.7
5							78.5	78.5
6							63.1	63.1
Glc-3								
1							104.4	104.4
2							75.6	75.6
3							77.9	77.9
4							71.1	71.1
5							74.7	74.7
6							64.3	64.3
Ac							20.5	20.5
							172.5	172.6
Glc-4								
1								102.4
2								74.9
3								77.9
4								71.3
5								78.3
6								62.5
Fru								
1	65.4	65.7	65.7	65.8	65.7	66.7	65.9	66.0
2	104.8	105.0	105.0	104.9	104.9	105.6	103.9	103.9
3	79.8	79.6	79.7	79.5	79.5	80.8	80.2	80.3
4	74.6	74.3	74.3	74.3	74.3	72.7	74.0	74.0
5	84.2	84.4	84.4	84.4	84.4	82.3	84.7	84.7
6	62.9	63.7	63.7	63.8	63.8	61.2	63.8	64.0
Benzoyl (C-3 of Fru)								
1							131.1	131.0
2, 6							131.1	131.1
3, 5							129.9	129.9
4							134.8	134.8
7							167.3	167.3
Cinn.	C-3 of Fru	C-3 of Fru	C-3 of Fru	C-3 of Fru	C-3 of Fru	C-3 of Fru	C-4 of Glc-1	C-4 of Glc-1
1	131.5	126.6	131.5	126.7	131.5	126.7	127.5	130.4
2	107.0	107.3	107.1	107.2	107.1	108.8	111.7	112.4
3	154.8	149.5	154.8	149.4	154.8	149.1	149.5	151.2
4	141.3	139.5	141.5	139.6	141.5	138.9	151.0	150.4
5	154.8	149.5	154.8	149.4	154.8	149.1	116.6	117.6
6	107.0	107.3	107.1	107.2	107.1	108.8	124.6	124.0
7	147.2	147.9	147.2	147.9	147.2	144.7	147.2	146.4
8	117.9	115.5	117.8	115.9	117.8	126.2	115.2	117.3
9	167.7	168.2	167.8	168.2	167.8	169.7	167.9	167.7
MeO	56.8	57.0	56.8	56.9	56.8	56.8	56.5	56.8
	56.8	57.0	56.8	56.9	56.8	56.8		
	61.2		61.2		61.2			

Table 2.—*Continued.*

	1	3	4	5	7	8	10	11
Cinn. (C-6 of Glc-1)								
1		127.2	127.2	126.6	131.4	126.7		127.0
2, 6		131.3	131.3	107.0	106.9	109.1		131.2
3, 5		116.8	116.8	149.4	154.8	149.1		116.8
4		161.3	161.3	139.7	141.4	139.2		161.3
7		146.9	146.9	147.3	146.6	144.6		147.0
8		115.1	115.1	115.5	118.2	125.6		114.9
9		169.2	169.2	169.1	168.7	169.3		168.4
MeO				57.0	56.8	56.8		
				57.0	56.8	56.8		
					61.2			
Cinn. (C-1 of Fru)								
1							127.1	127.2
2, 6							131.2	131.2
3, 5							116.9	116.9
4							161.4	161.4
7							147.0	147.2
8							114.9	114.7
9							168.4	168.7

Recorded at 100 MHz at 35°. Assigned by HSQC and HMBC spectra.

relations ($^3J_{HCOC}$) were observed between the anomeric proton signals at δ 4.50 (H-1 of Glc-3) and 4.60 (H-1 of Glc-2), and the carbon signals at δ 79.0 (C-3 of Glc-1) and 81.4 (C-2 of Glc-1), respectively, between the anomeric proton signal at δ 5.86 (H-1 of Glc-1) and the anomeric carbon signal at δ 103.9 (C-2 of Fru), between the two acetyl carbonyl carbon signals at δ 172.5 and 172.6 and the proton signals at δ 3.99 and 4.06, due to the H_2-6 of Glc-3, and δ 4.13 and 4.19, due to the H_2-6 of Glc-1, respectively, between the (*E*)-feruloyl carbonyl carbon signal at δ 167.9 and the proton signal at δ 5.02, due to the H-4 of Glc-1, between the (*E*)-*p*-coumaroyl carbonyl carbon signal at δ 168.4 and the proton signals at δ 4.22 and 4.69 due to the H_2-1 of fructose, and between the benzoyl carbonyl carbon signal at δ 167.3 and the proton signal at δ 5.73, due to the H-3 of fructose. These data led us to assign the structure of glomeratose F as 1-*O*-(*E*)-*p*-coumaroyl-(3-*O*-benzoyl)-β-D-fructofuranosyl-(2 → 1)-[β-D-glucopyranosyl-(1 → 2)]-[6-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)]-[4-*O*-(*E*)-feruloyl]-(6-*O*-acetyl)-α-D-glucopyranoside.

Glomeratose G (**11**) was obtained as an amorphous powder, and it exhibited a $[M+Na]^+$ ion peak at *m/z* 1465 in the FAB-mass spectrum. The ^{1}H NMR spectrum showed the presence of one acetyl [δ 2.09 (3H, *s*)], one benzoyl [δ 7.57 (2H, *t*, J = 8 Hz), 7.66 (1H, *tt*, J = 8, 1 Hz), 8.19 (2H, *dd*, J = 8 Hz), two (*E*)-*p*-coumaroyls [δ 6.35 (1H, *d*, J = 16 Hz), 6.70 (2H, *d*, J = 8.5 Hz), 7.31 (2H, *d*, J = 8.5 Hz), 7.67 (1H, *d*, J = 16 Hz)]; 6.27 (1H, *d*, J = 16 Hz), 6.81 (2H, *d*, J = 8.5 Hz), 7.41 (2H, *d*, J = 8.5 Hz), 7.58 (1H, *d*, J = 16)], one (*E*)-feruloyl [δ 3.90 (3H, *s*), 6.34 (1H, *d*, J = 16 Hz), 7.09 (1H, *dd*, J = 8, 2 Hz), 7.18 (1H, *d*, J = 8 Hz), 7.22 (1H, *d*, J = 2 Hz), 7.58 (1H, *d*, J = 16 Hz)] and the sugar moiety signals. On acid hydrolysis, **11** afforded D-glucose and D-fructose, whilst on alkaline hydrolysis, it gave glucose, tetrasaccharide **10a** and a mixture of benzoic, (*E*)-*p*-coumaric and (*E*)-ferulic acids. The positions of the acyl residue and sugar were deduced from observation of NOEs in the NOE difference spectrum and long-range correlations ($^3J_{HCOC}$) in the HMBC spectrum (Fig. 1). Therefore, the structure of glomeratose G was elucidated as 1-*O*-(*E*)-*p*-coumaroyl-(3-*O*-benzoyl)-β-D-fructofuranosyl-(2 → 1)-[β-D-glucopyransoyl-(1 → 2)]-[6-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)]-{4-*O*-[4-*O*-β-D-glucopyranosyl-(*E*)-feruloyl]-[6-*O*-(*E*)-*p*-coumaroyl]-α-D-glucopyranoside. The anomeric configurations of Glc-1, Glc-2, Glc-3 and Glc-4 were determined to be α, β, β and β, respectively, from their corresponding J_{H1-H2} values.

EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were measured at 400 MHz at 35°C; chemical shifts are given in δ with TMS as int. standard. Prep. and semi-prep. 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 glomerata Lour. was collected in Guangxi, Peoples Republic of China, in August 1994 and identified by Prof. Deng Xi Qin, Guangxi Zhuangzu Zizhiqu Medicinal Botanical Garden, Nan Ning, Peoples Republic of China. A voucher specimen (No. 9971) is deposited in the Herbarium of this institute. Dried roots (90 g) were extracted × 2 with 70% aq. MeOH. The extract (11 g) was passed through a porous polymer gel (Mitsubishi

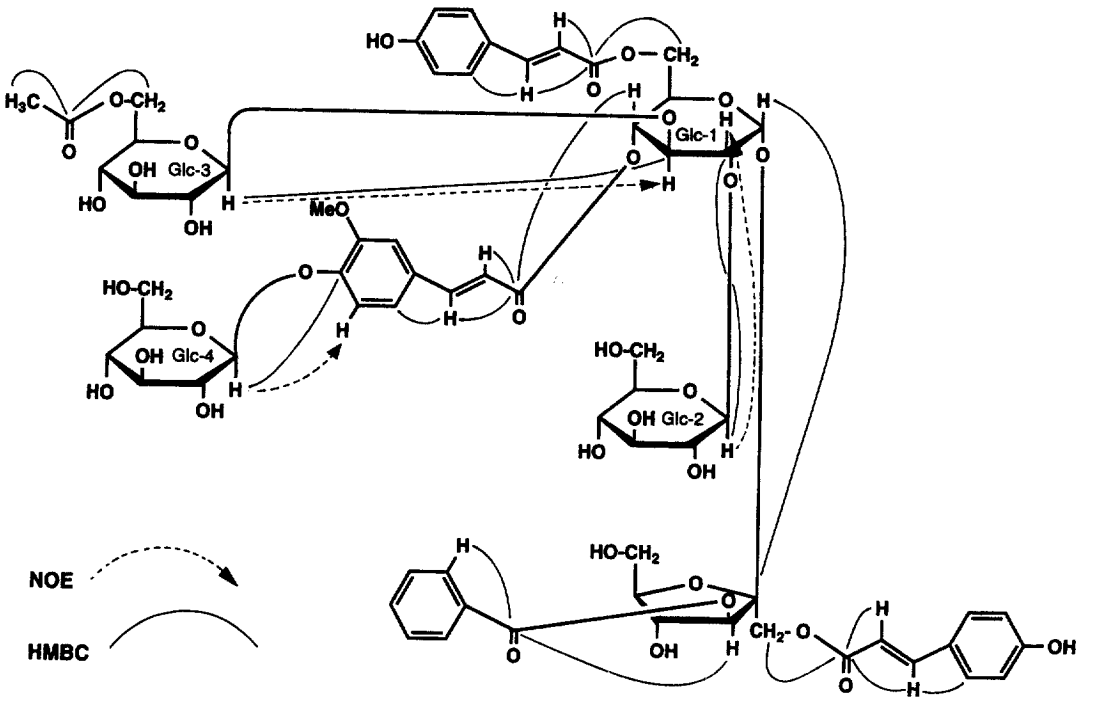

Fig. 1. HMBC and NOE correlations of compound **11**.

Diaion HP-20) column. After the contents of the column were washed with H_2O, the adsorbed materials were eluted successively with 30 and 60% aq. MeOH and MeOH. The 60% MeOH eluate (1.3 g) and MeOH eluate (2.2 g) were chromatographed on an octadecyl silica column (Develosil Lop-ODS 5 cm × 50 cm × 2), respectively, to give 16 frs (A_1–P_1) from the 60% MeOH eluate and 28 frs (A_2–Z_2, a_2 and b_2) from the MeOH eluate. From frs C_1, D_1, K_1, L_1 and C_2–G_2, compounds **1**–**11** were isolated by semi-prep. HPLC (MeCN–H_2O or MeOH–H_2O systems). **1** (14.0 mg), **2** (7.4 mg), **3** (3.2 mg), **4** (5.6 mg), **5** (40.8 mg), **6** (7.7 mg), **7** (5.3 mg), **8** (3.3 mg), **9** (5.1 mg), **10** (61.2 mg), **11** (4.2 mg).

Glomeratose A (**1**). Amorphous powder. $[\alpha]_D^{25}$ +5.7° (MeOH; *c* 1.39). UV λ_{max}^{MeOH} nm (log ε): 207 (4.12), 230 (4.21), 307 (4.15). FAB-MS *m/z*: 585 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Glomeratose B (**3**). Amorphous powder. $[\alpha]_D^{27}$ −51.6° (MeOH: *c* 0.43). UV λ_{max}^{MeOH} nm (log ε): 207 (4.34), 227 (4.32), 315 (4.42). FAB-MS *m/z*: 717 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Glomeratose C (**4**). Amorphous powder. $[\alpha]_D^{28}$ −71.2° (MeOH; *c* 0.56). UV λ_{max}^{MeOH} nm (log ε): 207 (4.20), 230 (4.35), 310 (4.37). FAB-MS *m/z*: 731 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Glomeratose D (**7**). Amorphous powder. $[\alpha]_D^{28}$ −55.8° (MeOH; *c* 0.53). UV λ_{max}^{MeOH} nm (log ε): 210 (4.63), 230 (4.76), 310 (4.69). FAB-MS *m/z*: 805 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Glomeratose E (**8**). Amorphous powder. $[\alpha]_D^{27}$ −133.0° (MeOH; *c* 0.33). UV λ_{max}^{MeOH} nm (log ε): 207 (4.52), 241 (4.34), 326 (4.33). FAB-MS *m/z*: 775 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Glomeratose F (**10**). Amorphous powder. $[\alpha]_D^{27}$ −5.9° (MeOH; *c* 1.26). UV λ_{max}^{MeOH} nm (log ε): 209 (sh 4.39), 231 (4.49), 319 (4.49). FAB-MS *m/z*: 1199 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Glomeratose G (**11**). Amorphous powder. $[\alpha]_D^{28}$ −15.5° (MeOH; *c* 0.42). UV λ_{max}^{MeOH} nm (log ε): 209 (4.75), 229 (4.70), 296 (sh 4.67), 312 (4.71). FAB-MS *m/z*: 1465 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Preparation of (E,E)-β,β′-bis-sinapic acid. 4-*O*-Benzyl-3,4-dimethoxyl-benzaldehyde (544 mg) and diethyl succinate (174 mg) in dry THF (1 ml) were added dropwise to a stirred suspension of NaH (dry 50 mg) in dry THF (2 ml) overnight at room temp. The reaction mixt. was diluted with MeOH and H_2O, and passed through an Amberlite IR-120B column. After evapn of solvent, the eluate (663 mg) in THF (10 ml) was hydrogenated over 5% Pd-C (20 mg) for 1.5 hr. The catalyst was removed by filtration and the solvent evapd. The residue (446 mg) was chromatographed on HPLC (PhA-T column) to give (*E,E*)-β,β′-bis-sinapic acid (110 mg). UV λ_{max}^{MeOH} nm (log ε): 225 (4.37), 239 (4.40), 324 (4.44). FAB-MS *m/z*: 469 $[M+Na]^+$, 446 $[M]^+$. ^1H NMR (400 MHz, CD_3OD): δ 3.76 (12H, *s*), 6.89 (4H, *s*), 7.84 (2H, *s*). ^{13}C NMR (100 MHz, CD_3OD): δ 56.8 (4C), 108.9 (4C), 127.1 (4C), 138.9 (2C), 143.8 (2C), 149.1 (4C), 170.6 (2C).

Alkaline hydrolysis of **1**, **3**–**4**, **7**–**8**, **10** and **11**. Each compound (2 mg) was treated with 5% aq. NaOH

(0.1 ml) for 3 hr at room temp. and the reaction mixt. passed through a column of Amberlite IR-120B. From the aq. eluate of the reaction mixt., sugars were detected by HPLC {Asahipak NH2P-50, 4.6 mm × 25 cm, MeCN–H_2O (17:7), 1 ml min^{-1}, UV 195 nm [13]} as follows: (R_t min) glucose (4.9) from **11**; sucrose (5.4) from **1**, **3**, **4**, **7** and **8**; tetrasaccharide **10a** (7.3) [12] from **10** and **11**. The MeOH eluate was concd and subjected to HPLC [YMC R-ODS-7, 4.6 mm × 25 cm, MeCN–H_2O–TFA (450:1550:1), 1 ml min^{-1}, UV 270 nm] to reveal peaks (R_t min) due to benzoic acid (12.8) from **10** and **11**, (*E*)-*p*-coumaric acid (7.8) from **3**, **4**, **10** and **11**, (*E*)-ferulic acid (8.5) from **10** and **11**, (*E*)-sinapic acid (8.0) from **3** and (*E*)-3,4,5-trimethoxycinnamic acid (21.5) from **1**, **4** and **7**, and (*E,E*)-β,β′-bis-sinapic acid (6.8) from **8**.

Acid hydrolysis of **1**, **3**, **4**, **7**, **8**, **10** and **11**. 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 passed through an Amberlite IRA-60E column. The H_2O eluate was concd and the residue treated with D-cysteine [14] (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. dried, pyridine (0.015 ml), hexamethyldisilazane (0.015 ml) and trimethylsilylchloride (0.015 ml) were added to the residue. The reaction mixt. was then heated at 60° for 30 min and supernatant analysed by GC. GC conditions: column, Supelco SPB™-1, 0.25 mm × 27 m; column temp. 230°; carrier gas, N_2; R_t (min) D-fructose (14.5), L-fructose (15.1) D-glucose (18.8) and L-glucose (17.7). The R_t for L-fructose was obtained from its enantiomer (D-fructose + L-cysteine). D-Glucose and D-fructose were detected from **1**, **3**, **4**, **7**, **8**, **10** and **11**.

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