Tenuifolioses G—P, Oligosaccharide Multi-Esters from the Roots of *Polygala tenuifolia* WILLD.[1)]

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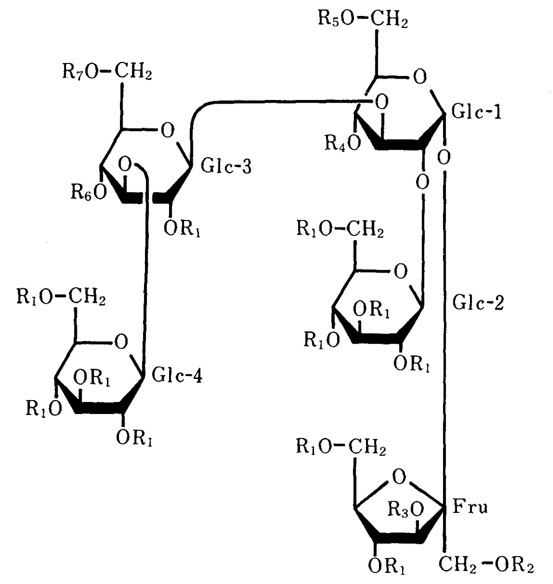
From the roots of *Polygala tenuifolia* WILLD. ten new oligosaccharides, called tenuifolioses G—P, were isolated and their structures were elucidated by spectroscopic data and chemical evidence. These oligosaccharides were esterified with acetic, benzoic, *p*-coumaric and/or ferulic acid.

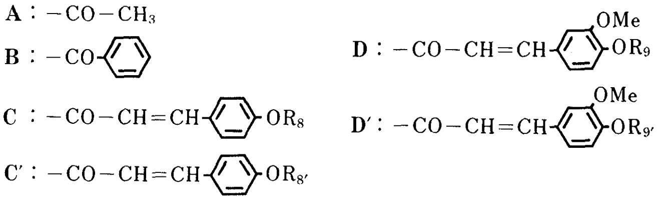
Keywords *Polygala tenuifolia*; Polygalaceae; tenuifoliose; acylated oligosaccharide; pentasaccharide

In a previous communication[1)] we reported the isolation and structural elucidation of six new oligosaccharide multi-esters, called tenuifolioses A—F from the roots of *Polygala tenuifolia* WILLD. The rarity of the structure prompted us to investigate further for additional oligosaccharide constituents of this medicinal plant and we have been successful in isolating other new oligosaccharide multi-esters. This paper reports the isolation and structural elucidation of these rare oligosaccharides called tenuifolioses G—P. All of them gave the same pentasaccharide **1b** which was identical to the deacyl compound of tenuifolioses A—F on alkaline hydrolysis, suggesting that tenuifolioses G—P were homologous to tenuifolioses A—F.

Tenuifoliose G (**1**), $[\alpha]_D$ −22.2°, $C_{66}H_{84}O_{38} \cdot 4H_2O$ was obtained as an amorphous powder and it showed $[M+Na]^+$ ion at *m/z* 1507 in the fast atom bombardment mass spectrum (FAB-MS). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum was very similar to that of tenuifoliose F (**12**).[1)] Results of the proton spin decoupling experiments which started from the irradiation at each anomeric proton signal showed one acetyl methyl signal and a downfield shifted oximethine proton signal assigned to H-4 of Glc-3, which were observed in the ^{1}H-NMR spectrum of **12**, were absent in that of **1**. In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum, C-3 and C-5 of Glc-3 were shifted downfield by 3.9 ppm and 2.0 ppm, respectively, compared with those of tenuifoliose F (**12**) (see Table II). On acetylation, **1** gave a peracetate **1a** which was identical to the peracetate of tenuifoliose F (**12**). Therefore, the structure of tenuifoliose G was concluded to be as shown in Chart 1.

Tenuifoliose H (**2**), $[\alpha]_D$ −26.3°, $C_{61}H_{74}O_{34} \cdot 2H_2O$ was obtained as an amorphous powder and it showed $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 1373 and 1351, respectively, in the FAB-MS. **2** gave glucose and fructose in the ratio 4:1 on acid hydrolysis, while it gave a pentasaccharide **1b** and an acid mixture composed of benzoic and *p*-coumaric acid on alkaline hydrolysis (see Experimental). On acetylation, **2** afforded a peracetate **2a** which had two aromatic [δ 2.32 (6H, s)] and fourteen aliphatic [δ 1.77, 1.96, 1.97, 2.00, 2.01, 2.051, 2.054, 2.08, 2.10, 2.13 (each 3H, s), 1.996, 2.076 (each 6H, s)] acetoxyl signals in the ^{1}H-NMR spectrum. In the NMR spectrum of **2**, three acetyl, one benzoyl and two *p*-coumaroyl signals were observed (see Tables I and II). Detailed proton spin decoupling experiments which started from the irradiation at each anomeric proton signal and difference nuclear Overhauser effect (NOE) experiments on irradiation at each anomeric proton signal enabled us to assign all proton signals of Glc-1 and Glc-3 (see Chart 2, Table I). The C–H COSY spectrum and above mentioned ^{1}H-NMR data led us to presume that the sugar linkages and the acylated sites





	R1	R2	R3	R4	R5	R6	R7	R8	R8′	R9	R9′
1	H	C	B	D′	A	H	A	H			Rham
1a	A	C	B	D′	A	A	A	A			Rham(OAc)3
1b	H	H	H	H	H	H	H				
2	H	C	B	C	A	A	A	H			
2a	A	C	B	C	A	A	A	A			
3	H	C	B	C	A	H	A	H			
4	H	C	B	C	H	A	A	H			
5	H	C	B	C	H	H	A	H			
6	H	C	B	C′	A	A	A	H	Rham		
6a	A	C	B	C′	A	A	A	A	Rham(OAc)3		
7	H	C	B	C′	A	H	A	H	Rham		
8	H	D	B	D	A	A	A			H	
8a	A	D	B	D	A	A	A			A	
9	H	D	B	D	H	A	A			H	
10	H	D	B	D	H	H	A			H	
11	H	C	B	D	A	A	A			H	
12	H	C	B	D′	A	A	A				Rham

Chart 1

TABLE I. ^{1}H-NMR Data for Oligosaccharides from the Roots of *Polygala tenuifolia* in MeOH-d_4

	1	2	3	4
Glc-1				
1	5.88 (1H, d, J=3.5 Hz)	5.90 (1H, d, J=3.5 Hz)	5.88 (1H, d, J=3.5 Hz)	5.87 (1H, d, J=3.5 Hz)
2	3.82 a)	3.82 (1H, dd, J=9, 3.5 Hz)	3.82 (1H, dd, J=9, 3.5 Hz)	3.79 (1H, dd, J=9.5, 3.5 Hz)
3	3.97 (1H, t, J=9 Hz)	3.97 (1H, t, J=9 Hz)	3.97 (1H, t, J=9 Hz)	3.97 (1H, t, J=9.5 Hz)
4	5.03 (1H, t, J=9.5 Hz)	5.02 (1H, t, J=9.5 Hz)	5.02 (1H, dd, J=9.5, 9 Hz)	5.02 (1H, t, J=9.5 Hz)
5	4.40 (1H, m)	4.43 (1H, m)	4.39 (1H, m)	4.29 (1H, ddd, J=10, 5, 2 Hz)
6	4.15 (1H, dd, J=12.5, 5.5 Hz)	4.15 (1H, dd, J=12.5, 6 Hz)	4.14 (1H, dd, J=12, 5.5 Hz)	3.58 (1H, dd, J=12.5, 5 Hz)
	4.19 (1H, dd, J=12.5, 3 Hz)	4.20 (1H, dd, J=12.5, 2 Hz)	4.18 (1H, dd, J=12, 2.5 Hz)	3.69 (1H, dd, J=12.5, 2 Hz)
Glc-2				
1	4.59 (1H, d, J=8 Hz)	4.60 (1H, d, J=8 Hz)	4.59 (1H, d, J=8 Hz)	4.58 (1H, d, J=8 Hz)
Glc-3				
1	4.53 (1H, d, J=8 Hz)	4.52 (1H, d, J=8 Hz)	4.52 (1H, d, J=8 Hz)	4.50 (1H, d, J=8 Hz)
2	3.21 (1H, t, J=8.5 Hz)	3.30 (1H, t, J=8.5 Hz)	3.22 (1H, t, J=9 Hz)	3.29 (1H, t, J=9 Hz)
3	3.38 (1H, t, J=9.5 Hz)	3.61 (1H, t, J=9 Hz)	3.33 a)	3.60 (1H, t, J=9 Hz)
4	3.3 a)	4.73 (1H, t, J=9.5 Hz)	3.31 a)	4.72 (1H, t, J=9.5 Hz)
5	3.12 (1H, m)	3.20 (1H, td, J=3, 9.5 Hz)	3.13 (1H, ddd, J=9.5, 3.5, 2 Hz)	3.19 (1H, td, J=2, 10 Hz)
6	4.00 (1H, dd, J=12, 2 Hz)	3.64 (1H, dd, J=12, 2 Hz)	3.98 (1H, dd, J=12, 2 Hz)	3.62 a)
	4.07 a)	4.00 (1H, dd, J=12, 3.5 Hz)	4.05 (1H, dd, J=12, 4 Hz)	4.00 (1H, dd, J=12.5, 3.5 Hz)
Glc-4				
1	4.47 (1H, d, J=8 Hz)	4.46 (1H, d, J=8 Hz)	4.48 (1H, d, J=8 Hz)	4.46 (1H, d, J=8 Hz)
Fru				
1	4.22 (1H, d, J=12 Hz)	4.29 (1H, d, J=12 Hz)	4.22 (1H, d, J=12 Hz)	4.29 (1H, d, J=12 Hz)
2	4.68 (1H, d, J=12 Hz)	4.61 (1H, d, J=12 Hz)	4.69 (1H, d, J=12 Hz)	4.63 (1H, d, J=12 Hz)
3	5.73 (1H, d, J=8 Hz)	5.75 (1H, d, J=8 Hz)	5.73 (1H, d, J=8 Hz)	5.72 (1H, d, J=8 Hz)
4	4.42 (1H, t, J=8 Hz)	4.43 (1H, t, J=8 Hz)	4.43 (1H, t, J=8 Hz)	4.51 (1H, t, J=8 Hz)
5	4.06 (1H, m)	4.10 (1H, ddd, J=8, 7, 3 Hz)	4.07 (1H, ddd, J=8, 6, 3 Hz)	4.05 (1H, ddd, J=8, 6, 3 Hz)
6	3.85 a)	3.85 (1H, dd, J=12, 3 Hz)	3.84 (1H, dd, J=12, 3 Hz)	3.84 a)
	3.87 a)	3.89 (1H, dd, J=12, 6 Hz)	3.88 (1H, dd, J=12, 6 Hz)	3.94 a)
Rham				
1	5.48 (1H, d, J=1.5 Hz)			
2	4.08 (1H, dd, J=3.5, 1.5 Hz)			
3	3.90 (1H, dd, J=9.5, 3.5 Hz)			
4	3.47 (1H, t, J=9.5 Hz)			
5	3.73 a)			
6	1.23 (3H, d, J=6 Hz)			
Ac (R_5)				
2	2.07 (3H, s)	2.07 (3H, s)	2.06 (3H, s)	
Ac (R_6)				
2		1.99 (3H, s)		1.99 (3H, s)
Ac (R_7)				
2	1.56 (3H, s)	1.55 (3H, s)	1.61 (3H, s)	1.55 (3H, s)
Bz (R_3)				
2, 6	8.19 (2H, dd, J=8, 1 Hz)	8.20 (2H, dd, J=8, 1 Hz)	8.18 (2H, dd, J=8, 1 Hz)	8.23 (2H, dd, J=8, 1 Hz)
3, 5	7.61 (2H, t, J=8 Hz)	7.60 (2H, t, J=8 Hz)	7.59 (2H, t, J=8 Hz)	7.60 (2H, t, J=8 Hz)
4	7.70 (1H, tt, J=8, 1 Hz)	7.70 (1H, tt, J=8, 1 Hz)	7.71 (1H, tt, J=8, 1 Hz)	7.70 (1H, tt, J=8, 1 Hz)
Cinn (R_2)				
2	7.41 (1H, d, J=8.5 Hz)	7.35 (1H, d, J=8.5 Hz)	7.41 (1H, d, J=8.5 Hz)	7.37 (1H, d, J=8.5 Hz)
3	6.80 (1H, d, J=8.5 Hz)	6.81 (1H, d, J=8.5 Hz)	6.81 (1H, d, J=8.5 Hz)	6.80 (1H, d, J=8.5 Hz)
5	6.80 (1H, d, J=8.5 Hz)	6.81 (1H, d, J=8.5 Hz)	6.81 (1H, d, J=8.5 Hz)	6.80 (1H, d, J=8.5 Hz)
6	7.41 (1H, d, J=8.5 Hz)	7.35 (1H, d, J=8.5 Hz)	7.41 (1H, d, J=8.5 Hz)	7.37 (1H, d, J=8.5 Hz)
β	6.34 (1H, d, J=16 Hz)	6.32 (1H, d, J=16 Hz)	6.36 (1H, d, J=16 Hz)	6.33 (1H, d, J=16 Hz)
γ	7.67 (1H, d, J=16 Hz)	7.65 (1H, d, J=16 Hz)	7.67 (1H, d, J=16 Hz)	7.65 (1H, d, J=16 Hz)
OMe				
Cinn (R_4)				
2	7.27 (1H, d, J=2 Hz)	7.44 (1H, d, J=8.5 Hz)	7.45 (1H, d, J=8.5 Hz)	7.44 (1H, d, J=8.5 Hz)
3		6.85 (1H, d, J=8.5 Hz)	6.85 (1H, d, J=8.5 Hz)	6.85 (1H, d, J=8.5 Hz)
5	7.19 (1H, d, J=8 Hz)	6.85 (1H, d, J=8.5 Hz)	6.85 (1H, d, J=8.5 Hz)	6.85 (1H, d, J=8.5 Hz)
6	7.14 (1H, dd, J=8, 2 Hz)	7.44 (1H, d, J=8.5 Hz)	7.45 (1H, d, J=8.5 Hz)	7.44 (1H, d, J=8.5 Hz)
β	6.34 (1H, d, J=16 Hz)	6.22 (1H, d, J=16 Hz)	6.23 (1H, d, J=16 Hz)	6.23 (1H, d, J=16 Hz)
γ	7.60 (1H, d, J=16 Hz)	7.57 (1H, d, J=16 Hz)	7.56 (1H, d, J=16 Hz)	7.57 (1H, d, J=16 Hz)
OMe	3.93 (3H, s)			

a) Overlapped with other signals.

were identical to those of tenuifoliose A (**11**).[1] The position of each acyl residue was decided by observation of $^3J_{(\mathrm{COCH})}$ using a long-range selective proton decoupling (LSPD) method (see Chart 2).[2] The carbon signal of the ester moiety was assigned from the long-range C—H COSY spectrum (see Chart 2, Table II). These data led us to determine the structure of **2** for tenuifoliose H.

The ^{1}H-NMR spectra of tenuifolioses I (**3**), $[\alpha]_D$ −9.1°, $C_{59}H_{72}O_{33}\cdot 3/2H_2O$ and J (**4**), $[\alpha]_D$ −35.9°, $C_{59}H_{72}O_{33}\cdot 2H_2O$ showed that these two compounds were composed of

TABLE I. (continued)

	5	**6**	**7**	**8**
Glc-1				
1	5.85 (1H, d, *J*=3.5 Hz)	5.90 (1H, d, *J*=3.5 Hz)	5.88 (1H, d, *J*=3.5 Hz)	5.89 (1H, d, *J*=3.5 Hz)
2	3.78 (1H, dd, *J*=9.5, 3.5 Hz)	3.83 (1H, dd, *J*=9.5, 3.5 Hz)	3.82 a)	3.83 (1H, dd, *J*=9, 3.5 Hz)
3	3.97 (1H, t, *J*=9.5 Hz)	3.97 (1H, t, *J*=9.5 Hz)	3.95 (1H, t, *J*=9 Hz)	3.98 (1H, t, *J*=9 Hz)
4	5.01 (1H, dd, *J*=9.5, 9 Hz)	5.03 (1H, t, *J*=9.5 Hz)	5.02 (1H, dd, *J*=9.5, 9 Hz)	5.02 (1H, t, *J*=9.5 Hz)
5	4.21 (1H, m)	4.43 (1H, m)	4.40 (1H, m)	4.43 (1H, m)
6	3.56 (1H, dd, *J*=12.5, 5 Hz)	4.16 (1H, dd, *J*=12, 5.5 Hz)	4.15 (1H, dd, *J*=12, 5.5 Hz)	4.15 (1H, dd, *J*=12.5, 6 Hz)
	3.68 (1H, dd, *J*=12.5, 2 Hz)	4.20 (1H, dd, *J*=12, 3 Hz)	4.18 (1H, dd, *J*=12, 3 Hz)	4.20 (1H, dd, *J*=12.5, 2 Hz)
Glc-2				
1	4.57 (1H, d, *J*=8 Hz)	4.60 (1H, d, *J*=8 Hz)	4.58 (1H, d, *J*=8 Hz)	4.59 (1H, d, *J*=8 Hz)
Glc-3				
1	4.49 (1H, d, *J*=8 Hz)	4.52 (1H, d, *J*=8 Hz)	4.52 (1H, d, *J*=8 Hz)	4.54 (1H, d, *J*=8 Hz)
2	3.23 (1H, t, *J*=9 Hz)	3.29 (1H, t, *J*=9 Hz)	3.22 (1H, t, *J*=9 Hz)	3.30 (1H, dd, *J*=9, 8 Hz)
3	3.37 (1H, t, *J*=9 Hz)	3.61 (1H, t, *J*=9 Hz)	3.37 (1H, t, *J*=9 Hz)	3.61 (1H, t, *J*=9 Hz)
4	3.32 a)	4.72 (1H, t, *J*=9.5 Hz)	3.3 a)	4.72 (1H, t, *J*=9.5 Hz)
5	3.10 (1H, ddd, *J*=9, 3, 1.5 Hz)	3.21 (1H, td, *J*=2, 9.5 Hz)	3.13 (1H, ddd, *J*=9, 4, 2 Hz)	3.20 (1H, td, *J*=3, 9.5 Hz)
6	4.03 a)	3.62 a)	3.96 (1H, dd, *J*=12, 2 Hz)	3.68 (1H, dd, *J*=12, 2 Hz)
	4.05 (1H, dd, *J*=12, 4 Hz)	4.00 (1H, dd, *J*=12.5, 3.5 Hz)	4.04 a)	3.98 (1H, dd, *J*=12, 3.5 Hz)
Glc-4				
1	4.47 (1H, d, *J*=8 Hz)	4.46 (1H, d, *J*=8 Hz)	4.47 (1H, d, *J*=8 Hz)	4.46 (1H, d, *J*=8 Hz)
Fru				
1	4.22 (1H, d, *J*=12 Hz)	4.29 (1H, d, *J*=12 Hz)	4.21 (1H, d, *J*=12 Hz)	4.27 (1H, d, *J*=12 Hz)
2	4.71 (1H, d, *J*=12 Hz)	4.61 (1H, d, *J*=12 Hz)	4.68 (1H, d, *J*=12 Hz)	4.61 (1H, d, *J*=12 Hz)
3	5.71 (1H, d, *J*=8 Hz)	5.74 (1H, d, *J*=8 Hz)	5.72 (1H, d, *J*=8 Hz)	5.74 (1H, d, *J*=8 Hz)
4	4.50 (1H, t, *J*=8 Hz)	4.43 (1H, t, *J*=8 Hz)	4.42 (1H, t, *J*=8 Hz)	4.42 (1H, t, *J*=8 Hz)
5	4.03 (1H, m)	4.10 (1H, ddd, *J*=8, 7, 3.5 Hz)	4.07 (1H, m)	4.08 (1H, ddd, *J*=8, 7, 3 Hz)
6	3.84 a)	3.84 (1H, dd, *J*=12.5, 3.5 Hz)	3.83 a)	3.83 (1H, dd, *J*=12, 4 Hz)
	3.88 a)	3.88 a)	3.86 a)	3.84 (1H, dd, *J*=12, 3 Hz)
Rham				
1		5.55 (1H, d, *J*=1.5 Hz)		
2		4.04 (1H, dd, *J*=3.5, 1.5 Hz)		
3		3.87 (1H, dd, *J*=9.5, 3.5 Hz)		
4		3.49 (1H, t, *J*=9 Hz)		
5		3.62 a)		
6		1.24 (3H, d, *J*=6 Hz)		
Ac (R_5)				
2		2.07 (3H, s)	2.07 (3H, s)	2.07 (3H, s)
Ac (R_6)				
2		1.99 (3H, s)		1.98 (3H, s)
Ac (R_7)				
2	1.62 (3H, s)	1.52 (3H, s)	1.59 (3H, s)	1.53 (3H, s)
Bz (R_3)				
2, 6	8.20 (2H, dd, *J*=8, 1 Hz)	8.20 (2H, dd, *J*=8, 1 Hz)	8.18 (2H, dd, *J*=8, 1 Hz)	8.20 (2H, dd, *J*=8, 1 Hz)
3, 5	7.59 (2H, t, *J*=8 Hz)	7.60 (2H, t, *J*=8 Hz)	7.60 (2H, t, *J*=8 Hz)	7.61 (2H, t, *J*=8 Hz)
4	7.71 (1H, tt, *J*=8, 1 Hz)	7.71 (1H, tt, *J*=8, 1 Hz)	7.71 (1H, tt, *J*=8, 1 Hz)	7.69 (1H, tt, *J*=8, 1 Hz)
Cinn (R_2)				
2	7.42 (1H, d, *J*=8.5 Hz)	7.36 (1H, d, *J*=8.5 Hz)	7.42 (1H, d, *J*=8.5 Hz)	7.19 (1H, d, *J*=2 Hz)
3	6.81 (1H, d, *J*=8.5 Hz)	6.81 (1H, d, *J*=8.5 Hz)	6.81 (1H, d, *J*=8.5 Hz)	
5	6.81 (1H, d, *J*=8.5 Hz)	6.81 (1H, d, *J*=8.5 Hz)	6.81 (1H, d, *J*=8.5 Hz)	6.79 (1H, d, *J*=8 Hz)
6	7.42 (1H, d, *J*=8.5 Hz)	7.36 (1H, d, *J*=8.5 Hz)	7.42 (1H, d, *J*=8.5 Hz)	6.91 (1H, dd, *J*=8, 2 Hz)
β	6.36 (1H, d, *J*=16 Hz)	6.32 (1H, d, *J*=16 Hz)	6.36 (1H, d, *J*=16 Hz)	6.37 (1H, d, *J*=16 Hz)
γ	7.67 (1H, d, *J*=16 Hz)	7.65 (1H, d, *J*=16 Hz)	7.67 (1H, d, *J*=16 Hz)	7.65 (1H, d, *J*=16 Hz)
OMe				3.90 (3H, s)
Cinn (R_4)				
2	7.45 (1H, d, *J*=8.5 Hz)	7.55 (1H, d, *J*=8.5 Hz)	7.56 (1H, d, *J*=8.5 Hz)	7.17 (1H, d, *J*=2 Hz)
3	6.84 (1H, d, *J*=8.5 Hz)	7.15 (1H, d, *J*=8.5 Hz)	7.15 (1H, d, *J*=8.5 Hz)	
5	6.84 (1H, d, *J*=8.5 Hz)	7.15 (1H, d, *J*=8.5 Hz)	7.15 (1H, d, *J*=8.5 Hz)	6.85 (1H, d, *J*=8 Hz)
6	7.45 (1H, d, *J*=8.5 Hz)	7.55 (1H, d, *J*=8.5 Hz)	7.56 (1H, d, *J*=8.5 Hz)	7.05 (1H, dd, *J*=8, 2 Hz)
β	6.23 (1H, s, *J*=16 Hz)	6.31 (1H, d, *J*=16 Hz)	6.32 (1H, d, *J*=16 Hz)	6.25 (1H, d, *J*=16 Hz)
γ	7.57 (1H, d, *J*=16 Hz)	7.60 (1H, d, *J*=16 Hz)	7.59 (1H, d, *J*=16 Hz)	7.56 (1H, d, *J*=16 Hz)
OMe				3.93 (3H, s)

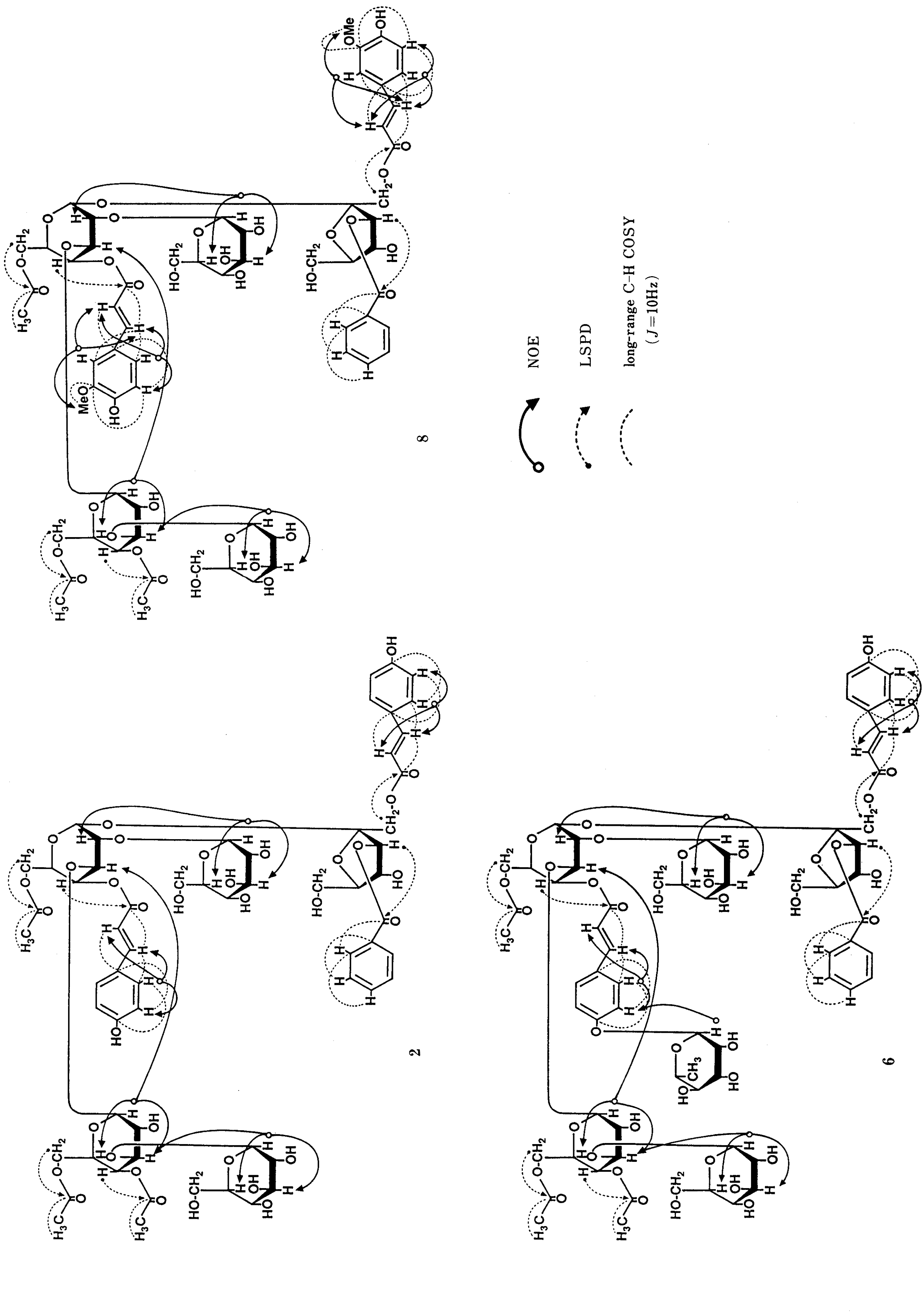
a pentasaccharide **1b**, two acetic, a benzoic and two *p*-coumaric acids. Comparing the ^{1}H- and ^{13}C-NMR spectra with those of **2**, H-4 of Glc-3 was shifted upfield to δ 3.31 ($\Delta-1.42$ ppm) and C-3 and C-5 of Glc-3 were shifted downfield to δ 87.0 ($\Delta+3.6$ ppm) and 74.3 ($\Delta+1.9$ ppm), respectively, in **3**; H_2-6 of Glc-1 were shifted upfield to δ 3.58 ($\Delta-0.57$ ppm) and 3.69 ($\Delta-0.51$ ppm), C-5 of Glc-1 downfield to δ 72.2 ($\Delta+2.6$ ppm) and C-6 of Glc-1 upfield to δ 62.0 ($\Delta-2.4$ ppm) in **4**. On acetylation these two compounds gave the same peracetate **2a**. Therefore, the

TABLE I. (continued)

	9	**10**	**11**	**12**
Glc-1				
1	5.87 (1H, d, J=3.5 Hz)	5.86 (1H, d, J=3.5 Hz)	5.90 (1H, d, J=3.5 Hz)	5.90 (1H, d, J=3.5 Hz)
2	3.78 (1H, dd, J=9, 3.5 Hz)	3.79 (1H, dd, J=9.5, 3.5 Hz)	3.83 (1H, dd, J=9, 3.5 Hz)	3.85 a)
3	3.97 (1H, t, J=9 Hz)	3.96 (1H, t, J=9.5 Hz)	3.98 (1H, t, J=9 Hz)	3.98 (1H, t, J=9 Hz)
4	5.02 (1H, dd, J=9.5, 8.5 Hz)	5.02 (1H, t, J=9.5 Hz)	5.03 (1H, t, J=9.5 Hz)	5.03 (1H, t, J=9 Hz)
5	4.23 (1H, m)	4.21 (1H, m)	4.43 (1H, m)	4.43 (1H, m)
6	3.57 (1H, dd, J=12, 5 Hz)	3.58 (1H, dd, J=12.5, 5 Hz)	4.15 (1H, dd, J=12.5, 6 Hz)	4.16 (1H, dd, J=12.5, 5.5 Hz)
	3.68 (1H, dd, J=12, 2 Hz)	3.68 (1H, dd, J=12.5, 2 Hz)	4.20 (1H, dd, J=12.5, 2 Hz)	4.21 (1H, dd, J=12.5, 2 Hz)
Glc-2				
1	4.58 (1H, d, J=8 Hz)	4.58 (1H, d, J=8 Hz)	4.59 (1H, d, J=8 Hz)	4.60 (1H, d, J=8 Hz)
Glc-3				
1	4.50 (1H, d, J=8 Hz)	4.50 (1H, d, J=8 Hz)	4.53 (1H, d, J=8 Hz)	4.53 (1H, d, J=8 Hz)
2	3.27 a)	3.22 (1H, t, J=8.5 Hz)	3.30 (1H, dd, J=9, 8 Hz)	3.31 a)
3	3.60 (1H, t, J=9 Hz)	3.37 (1H, t, J=9 Hz)	3.61 (1H, t, J=9 Hz)	3.61 (1H, t, J=9 Hz)
4	4.73 (1H, t, J=9.5 Hz)	3.32 a)	4.73 (1H, t, J=9.5 Hz)	4.73 (1H, t, J=9 Hz)
5	3.17 (1H, td, J=3, 9.5 Hz)	3.11 (1H, m)	3.20 (1H, td, J=3. 9.5 Hz)	3.20 (1H, td, J=2, 10 Hz)
6	3.66 (1H, dd, J=12, 2 Hz)	4.01 (1H, dd, J=12, 2 Hz)	3.68 (1H, dd, J=12, 2 Hz)	3.66 (1H, dd, J=12, 2 Hz)
	3.98 (1H, dd, J=12, 3 Hz)	4.07 (1H, dd, J=12, 3.5 Hz)	3.98 (1H, dd, J=12, 3.5 Hz)	3.98 (1H, dd, J=12, 3.5 Hz)
Glc-4				
1	4.46 (1H, d, J=8 Hz)	4.47 (1H, d, J=8 Hz)	4.46 (1H, d, J=8 Hz)	4.47 (1H, d, J=8 Hz)
Fru				
1	4.28 (1H, d, J=12 Hz)	4.23 (1H, d, J=12 Hz)	4.29 (1H, d, J=12 Hz)	4.30 (1H, d, J=12 Hz)
2	4.64 (1H, d, J=12 Hz)	4.72 (1H, d, J=12 Hz)	4.60 (1H, d, J=12 Hz)	4.61 (1H, d, J=12 Hz)
3	5.72 (1H, d, J=8 Hz)	5.72 (1H, d, J=8 Hz)	5.75 (1H, d, J=8 Hz)	5.75 (1H, d, J=8 Hz)
4	4.50 (1H, t, J=8 Hz)	4.52 (1H, t, J=8 Hz)	4.43 (1H, t, J=8 Hz)	4.43 (1H, t, J=8 Hz)
5	4.05 (1H, ddd, J=9, 6, 3 Hz)	4.04 (1H, m)	4.09 (1H, ddd, J=8, 7, 3 Hz)	4.09 (1H, m)
6	3.84 a)	3.85 (1H, dd, J=12.5, 3 Hz)	3.84 (1H, dd, J=12, 3 Hz)	3.83 a)
	3.86 a)	3.89 a)	3.89 (1H, dd, J=12, 6 Hz)	3.87 (1H, dd, J=12.5, 6 Hz)
Rham				
1				5.49 (1H, d, J=1.5 Hz)
2				4.11 (1H, dd, J=3.5, 1.5 Hz)
3				3.93 a)
4				3.49 (1H, t, J=9.5 Hz)
5				3.75 (1H, m)
6				1.24 (3H, d, J=6.5 Hz)
Ac (R_5)				
2			2.02 (3H, s)	2.08 (3H, s)
Ac (R_6)				
2	1.99 (3H, s)		1.99 (3H, s)	1.99 (3H, s)
Ac (R_7)				
2	1.53 (3H, s)	1.60 (3H, s)	1.53 (3H, s)	1.50 (3H, s)
Bz (R_3)				
2, 6	8.22 (2H, dd, J=8, 1 Hz)	8.20 (2H, dd, J=8, 1 Hz)	8.21 (2H, br d, J=8 Hz)	8.21 (2H, br d, J=8 Hz)
3, 5	7.60 (2H, t, J=8 Hz)	7.60 (2H, t, J=8 Hz)	7.61 (2H, t, J=8 Hz)	7.62 (2H, t, J=8 Hz)
4	7.68 (1H, tt, J=8, 1 Hz)	7.69 (1H, tt, J=8, 1 Hz)	7.69 (1H, br t, J=8 Hz)	7.69 (1H, tt, J=8, 1.5 Hz)
Cinn (R_2)				
2	7.19 (1H, d, J=2 Hz)	7.20 (1H, d, J=2 Hz)	7.35 (1H, d, J=8.5 Hz)	7.35 (1H, d, J=8.5 Hz)
3			6.80 (1H, d, J=8.5 Hz)	6.80 (1H, d, J=8.5 Hz)
5	6.79 (1H, d, J=8 Hz)	6.81 (1H, d, J=8 Hz)	6.80 (1H, d, J=8.5 Hz)	6.80 (1H, d, J=8.5 Hz)
6	6.92 (1H, dd, J=8, 2 Hz)	7.01 (1H, dd, J=8, 2 Hz)	7.35 (1H, d, J=8.5 Hz)	7.35 (1H, d, J=8.5 Hz)
β	6.38 (1H, d, J=16 Hz)	6.41 (1H, d, J=16 Hz)	6.31 (1H, d, J=16 Hz)	6.31 (1H, d, J=16 Hz)
γ	7.65 (1H, d, J=16 Hz)	7.68 (1H, d, J=16 Hz)	7.64 (1H, d, J=16 Hz)	7.64 (1H, d, J=16 Hz)
OMe	3.90 (3H, s)	3.90 (3H, s)		
Cinn (R_4)				
2	7.17 (1H, d, J=2 Hz)	7.20 (1H, d, J=2 Hz)	7.17 (1H, d, J=2 Hz)	7.23 (1H, d, J=2 Hz)
3				
5	6.84 (1H, d, J=8 Hz)	6.84 (1H, d, J=8 Hz)	6.85 (1H, d, J=8 Hz)	7.19 (1H, d, J=8 Hz)
6	7.04 (1H, d, J=8 Hz)	7.04 (1H, dd, J=8, 2 Hz)	7.05 (1H, dd, J=8, 2 Hz)	7.13 (1H, dd, J=8, 2 Hz)
β	6.26 (1H, d, J=16 Hz)	6.26 (1H, d, J=16 Hz)	6.26 (1H, d, J=16 Hz)	6.34 (1H, d, J=16 Hz)
γ	7.57 (1H, d, J=16 Hz)	7.57 (1H, d, J=16 Hz)	7.61 (1H, d, J=16 Hz)	7.60 (1H, d, J=16 Hz)
OMe	3.93 (3H, s)	3.95 (3H, s)	3.93 (3H, s)	3.92 (3H, s)

structures of tenuifolioses I and J were determined as **3** and **4**, respectively.

Tenuifoliose K (**5**), $[\alpha]_D$ −3.2°, $C_{57}H_{70}O_{32}\cdot 2H_2O$ showed only one signal [δ 1.62 (3H, s)] for an acetyl group in the ^{1}H-NMR spectrum. H_2-6 of Glc-1 and H-4 of Glc-3 were shifted upfield to δ 3.56 (Δ −0.59 ppm); 3.68 (Δ −0.52 ppm) and 3.32 (Δ −1.41 ppm), respectively, compared with those of **2**. The ^{13}C-NMR chemical shifts supported that the acetyl group was located at C-6 of Glc-3. A peracetate of this compound was identical to **2a**.



8

2

6

Chart 2

TABLE 11. ^{13}C-NMR Data for Oligosaccharides from the Roots of *Polygala tenuifolia* in MeOH-d_4

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Glc-1												
1	92.9	92.7	92.7	92.9	93.1	92.7	92.4	92.8	93.0	93.1	92.7	92.7
2	81.4	81.3	81.2	81.3	81.4	81.3	81.3	81.4	81.5	81.5	81.3	81.3
3	79.1	79.3	79.0	79.4	79.3	79.3	79.1	79.3	79.5	79.3	79.3	79.2
4	70.6	70.4	70.3	70.2	70.3	70.5	70.5	70.4	70.2	70.3	70.3	70.4
5	69.7	69.6	69.6	72.2	72.2	69.6	69.6	69.7	72.3	72.3	69.6	69.6
6	64.6	64.4	64.3	62.0	62.1	64.3	64.3	64.4	62.1	62.1	64.4	64.3
Glc-2												
1	105.4	105.3	105.2	105.3	105.3	105.3	105.4	105.4	105.4	105.4	105.4	105.3
2	75.4[a]	75.2	75.2	75.2	75.3	75.3	75.4[i]	75.3	75.3	75.4	75.2	75.3
3	78.4	78.3	78.3	78.3	78.4	78.5	78.4	78.5	78.5	78.5	78.5	78.4
4	71.6	71.5	71.4	71.4	71.5	71.5	71.6	71.6	71.6	71.5	71.5	71.5
5	77.8	77.7	77.9	77.6	77.7	77.7	78.0	77.8	77.8	77.7	77.7	77.7
6	63.0	63.0	63.0	63.0	63.0	63.1	63.0	63.1	63.1	63.1	63.0	63.0
Glc-3												
1	104.2	104.1	104.1	104.1	104.2	104.1	104.2	104.2	104.1	104.1	104.1	104.1
2	74.8	75.3	74.6	75.3	74.7	75.4	74.7	75.2	75.5	74.7	75.4	75.2
3	87.3	83.4	87.0	83.4	87.1	83.4	87.2	83.5	83.4	87.3	83.4	83.4
4	69.5	69.6	69.6	69.6	70.0	69.6	69.6	69.7	69.7	69.6	69.6	69.6
5	74.4	72.4	74.3	72.3	74.3	72.4	74.4	72.4	72.4	74.3	72.3	72.4
6	64.2	63.0	64.2	63.0	64.2	63.1	64.3	63.1	62.9	64.2	63.0	63.0
Glc-4												
1	105.1	105.3	104.9	105.3	105.0	105.3	105.1	105.4	105.4	105.0	105.4	105.3
2	75.3[a]	75.7	75.2	75.7	75.3	75.7	75.3[i]	75.8	75.8	75.4	75.4	75.3
3	78.1	78.4	78.3	78.3	78.4	78.4	78.6	78.6	78.5	78.5	78.4	78.4
4	71.6	71.5	71.4	71.4	71.5	71.5	71.6	71.6	71.6	71.5	71.5	71.5
5	77.8	77.8	77.6	77.8	78.0	77.9	77.7	78.0	78.0	78.0	77.9	77.8
6	62.7	62.8	62.5	62.8	62.6	62.8	62.6	62.9	62.6	62.6	62.8	62.8
Fru												
1	66.0	66.3	66.0	66.4	66.0	66.3	66.0	66.3	66.3	65.9	66.3	66.3
2	103.9	103.7	103.8	103.6	103.8	103.7	103.9	103.8	103.7	103.8	103.7	103.7
3	80.2	80.4	80.1	80.4	80.2	80.4	80.1	80.4	80.4	80.1	80.4	80.4
4	73.8	74.0	73.9	73.6	73.5	74.0	73.7	74.1	73.7	73.5	74.0	74.0
5	84.6	84.7	84.5	84.5	84.5	84.7	84.7	84.8	84.6	84.5	84.7	84.6
6	63.8	63.8	63.7	63.1	63.2	63.9	63.8	63.9	63.2	63.1	63.9	63.8
Rham												
1	100.8					99.5	99.6					100.7
2	72.0					71.8	71.9					71.9
3	72.2					72.1	72.2					72.1
4	73.8					73.7	73.7					73.7
5	71.0					70.9	70.9					71.0
6	18.0					18.1	18.1					18.0
Ac (R_5)												
1	172.5	172.5	172.6[b]			172.5	172.4	172.5			172.5	172.5
2	20.8	20.8	20.8			20.8	20.8	20.8			20.8	20.8
Ac (R_6)												
1		171.9		172.0		172.0		172.0	172.0		171.9	171.9
2		21.1		21.0		21.1		21.1	21.1		21.1	21.1
Ac (R_7)												
1	172.5	172.3	172.5[b]	172.3	172.5	172.2	172.4	172.3	172.3	172.5	172.3	172.2
2	20.4	20.4	20.5	20.4	20.5	20.4	20.5	20.4	20.3	20.4	20.3	20.3
Bz (R_3)												
1	131.0	130.9	130.8	130.9	131.0	131.0	131.0	131.1	131.1	131.0	131.1	131.1
2, 6	131.1	131.1	131.0	131.1	131.1	131.0	131.1	131.2	131.2	131.1	131.1	131.1
3, 5	130.0	129.9	129.9	129.9	130.0	130.0	130.0	130.0	129.9	129.9	130.0	129.9
4	134.9	134.8	134.9	134.8	135.0	134.9	134.9	134.9	134.8	134.8	134.8	134.8
α	167.3	167.1	167.2	167.1	167.3	167.1	167.2	167.1	167.2	167.3	167.1	167.1
Cinn (R_2)												
1	127.1	127.1	127.0[c]	127.0[e]	127.0	127.1	127.1	127.7	127.7	127.6	127.0	127.0
2	131.3	131.2	131.2	131.2	131.2[g]	131.2	131.3	111.6	111.6	111.6[l]	131.2	131.2
3	116.9	116.9	116.8	116.8	116.8	116.9	116.9	149.5	149.5	149.5[m]	116.9	116.9
4	161.4	161.2	161.2	161.2[f]	161.4[h]	161.3	161.4	151.0[j]	150.9[k]	150.9[n]	161.3	161.3
5	116.9	116.9	116.8[d]	116.8	116.8	116.9	116.9	116.5	116.5	116.5	116.9	116.9
6	131.3	131.2	131.2	131.2	131.2[g]	131.2	131.3	124.4	124.4	124.4	131.2	131.2
α	168.4	168.3	168.4	168.4	168.4	168.3	168.4	168.4	168.4	168.4	168.3	168.3
β	114.8	114.9	114.7	114.9	114.8	114.9	114.9	115.3	115.4	115.3	114.9	114.9
γ	147.0	146.8	147.0	146.9	147.0	146.9	147.0	147.2	147.2	147.3	146.8	146.8
OMe								56.6	56.6	56.5		

TABLE 11. (continued)

	1	2	3	4	5	6	7	8	9	10	11	12
Cinn (R_4)												
1	130.6	126.9	126.9[c]	126.9[e]	127.0	129.5	129.6	127.5	127.5	127.5	127.5	130.9
2	112.4	131.2	131.2	131.2	131.3[g]	131.1	131.1	111.6	111.6	111.5[l]	111.5	112.4
3	152.4	116.9	117.0	117.0	117.0	117.9	117.9	149.5	149.5	149.4[m]	149.4	152.0
4	149.1	161.4	161.4[d]	161.3[f]	161.3[h]	159.7	159.8	150.8[j]	150.8[k]	150.8[n]	150.9	149.1
5	118.8	116.9	117.0	117.0	117.0	117.9	117.9	116.6	116.6	116.6	116.6	118.7
6	123.2	131.2	131.2	131.2	131.3[g]	131.1	131.1	124.4	124.4	124.5	124.4	123.5
α	167.5	167.8	167.8	168.0	168.0	167.5	167.5	167.9	168.0	168.0	167.8	167.4
β	116.9	114.9	114.8	115.0	115.0	116.7	116.9	115.2	115.2	115.1	115.1	117.0
γ	146.6	146.8	146.8	146.6	146.7	146.1	146.1	147.2	147.0	147.0	147.1	146.4
OMe	56.6							56.5	56.5	56.5	56.4	56.6

a—n) Assignments are interchangeable within each column.

The FAB-MS of tenuifoliose L (**6**), $[\alpha]_D$ $-59.2°$, $C_{67}H_{84}O_{38}\cdot 7/2\ H_2O$ showed quasi-molecular ion at *m/z* 1519 $[M+Na]^+$. The ^{1}H-NMR spectrum showed the presence of three acetyl [δ 1.52, 1.99, 2.07 (each 3H, s)], a benzoyl [δ 7.60 (2H, t, $J=8$ Hz), 7.71 (1H, tt, $J=8$, 1 Hz), 8.20 (2H, dd, $J=8$, 1 Hz)] and two *p*-coumaroyl [δ 6.31 (1H, d, $J=16$ Hz), 7.15 (2H, d, $J=8.5$ Hz), 7.55 (2H, d, $J=8.5$ Hz), 7.60 (1H, d, $J=16$ Hz), 6.32 (1H, d, $J=16$ Hz), 6.81 (2H, d, $J=8.5$ Hz), 7.36 (2H, d, $J=8.5$ Hz), 7.65 (1H, d, $J=16$ Hz)] residues. **6** gave glucose, fructose and rhamnose in the ratio 4 : 1 : 1 on acid hydrolysis, while **6** giving a pentasaccharide **1b** and an acid mixture composed of benzoic and *p*-coumaric acid on alkaline hydrolysis (see Experimental). The ^{13}C-NMR spectrum revealed the presence of rhamnose other than **2**. **6** gave a peracetate **6a** and its ^{1}H-NMR spectrum showed the presence of one aromatic and seventeen aliphatic acetoxyl signals [δ 2.32 (3H, s), 1.80, 1.96, 1.97, 1.995, 1.998, 2.001, 2.01, 2.04, 2.051, 2.057, 2.068, 2.074, 2.078, 2.082, 2.098, 2.12, 2.21 (each 3H, s)]. An NOE was observed at δ 7.15 (2H, d, $J=8.5$ Hz) due to H-3 and H-5 of *p*-coumaroyl residue by irradiation at the anomeric proton signal of rhamnose, suggesting **6** to be a phenolic rhamnoside. The position of each acyl residue was recognized to be identical in the case of **2** by observation of $^3J_{(COCH)}$ using LSPD method (see Chart 2). NOEs were observed at the signals δ 6.31 (1H, d, $J=16$ Hz), 7.15 (2H, d, $J=8.5$ Hz) and 7.60 (1H, d, $J=16$ Hz) on irradiation at the signal δ 7.55 (2H, d, $J=8.5$ Hz), suggesting these signals were assigned to 4-*O*-rhamnosyl-*p*-coumaroyl residue (see Chart 2). The $^3J_{(CCCH)}$[3] was observed between an ester carbonyl carbon signal (δ 167.5) and an olefinic γ-proton signal (δ 7.60), and $^3J_{(COCH)}$ between the carbon signal and an oxymethine proton signal (δ 5.03) which was assigned to H-4 of Glc-1 by detailed proton spin decoupling experiments (see Chart 2). So, 4-*O*-rhamnosyl-*p*-coumaroyl residue was located at C-4 of Glc-1. The rhamnosyl anomeric configuration was α from the $J_{C1\text{-}H1}$ (171.3 Hz).[4] These data led us to conclude the structure of **6** for tenuifoliose L.

The ^{1}H-NMR spectrum of tenuifoliose M (**7**), $[\alpha]_D$ $-29.2°$, $C_{65}H_{82}O_{37}\cdot 5H_2O$ showed two acetyl methyl signals at δ 1.59 and 2.07, while H-4 of Glc-3 shifted upfield to δ 3.3 compared with that of **6**. The ^{13}C-NMR signals at C-3 and C-5 of Glc-3 supported that **7** was lacking an acetyl group at C-4 of Glc-3. On acetylation **7** gave a peracetate which was identical to the peracetate of **6**.

Tenuifoliose N (**8**), $[\alpha]_D$ $-26.6°$, $C_{63}H_{78}O_{36}\cdot 3/2\,H_2O$ showed similar ^{1}H- and ^{13}C-NMR spectra to those of **2** except for the presence of two feruloyl residues instead of two *p*-coumaroyl residues. On acetylation **8** gave a peracetate **8a**, which had two aromatic and fourteen aliphatic acetoxyl methyl signals in the ^{1}H-NMR spectrum [δ 2.33 (6H, s), 1.77, 1.96, 1.97, 1.98, 1.997, 2.002, 2.009, 2.052, 2.054, 2.097, 2.014 (each 3H, s), 2.08 (9H, s)], while **8** gave a pentasaccharide **1b** and an acid mixture composed of benzoic and ferulic acids on alkaline hydrolysis. The location of each acyl residue was decided by observation of $^3J_{(COCH)}$ as in the case of **2** (see Chart 2). We therefore propose the structure **8** for tenuifoliose N.

The ^{1}H-NMR spectra of tenuifolioses O (**9**), $[\alpha]_D$ $-17.4°$, $C_{61}H_{76}O_{35}\cdot 3/2H_2O$ and P (**10**), $[\alpha]_D$ $-7.7°$, $C_{59}H_{74}O_{34}\cdot 3H_2O$ showed that these two compounds were composed of a pentasaccharide **1b**, a benzoic, two ferulic and two acetic acids in **9** and one acetic acid in **10**. H_2-6 of Glc-1 of **9** were shifted upfield to δ 3.57 ($\Delta -0.58$ ppm) and 3.68 ($\Delta -0.52$ ppm) and H_2-6 of Glc-1 and H-4 of Glc-3 of **10** were shifted upfield to δ 3.58 ($\Delta -0.57$ ppm); 3.68 ($\Delta -0.52$ ppm) and 3.32 ($\Delta -1.50$ ppm) compared with those of **8**. On acetylation these two compounds gave the same peracetate **8a**. So, the structure of tenuifolioses O and P were determined as **9** and **10**, respectively.

Experimental

General Procedure Optical rotations were measured with a Jasco DIP-360 digital polarimeter. UV spectra were taken on a Hitachi U-3410 spectrophotometer. FAB-MS were measured on a Jeol JMS-SX102 mass spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Jeol GSX-500 and GSX-270. Chemical shifts are given on the δ scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad). High performance liquid chromatography (HPLC) was done on a Jasco model 800 instrument.

Isolation Dried roots of *Polygala tenuifolia* WILLD. (5 kg) were extracted twice with hot water. The extract was passed through a Mitsubishi Diaion HP-20 column (9 cm × 50 cm) and the adsorbed material was eluted with 50% MeOH aq., 70% MeOH aq. and MeOH successively to give a pale yellow powder (50% MeOH aq. eluate 215 g, 70% MeOH aq. eluate 128 g and MeOH eluate 169 g). The 70% MeOH aq. eluate was chromatographed on a silica gel (700 g) column using $CHCl_3$–MeOH (75 : 25) to give fractions 1 (22.7 g), 2 (17.7 g), 3 (21.3 g), and using $CHCl_3$–MeOH (72 : 28) to give fraction 4 (32.1 g). From fractions 2 and 3, oligosaccharides were isolated by preparative HPLC [Develosil Lop-ODS, 5 cm × 50 cm, CH_3CN–H_2O (22 : 78)—(32 : 68) linear gradient]: **1** (0.00057%), **2** (0.066%), **3** (0.022%), **4** (0.027%), **5** (0.0036%), **6** (0.018%), **7** (0.00033%), **8** (0.0017%), **9** (0.0016%) and **10** (0.0014%).

Tenuifoliose G (1) Amorphous powder, $[\alpha]_D^{24}$ $-22.2°$ ($c=0.45$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 229 (4.54), 298 (sh 4.49), 314 (4.52). *Anal.* Calcd for $C_{66}H_{84}O_{38} \cdot 4H_2O$: C, 50.90; H, 5.95. Found: C, 50.92; H, 5.95. FAB-MS *m/z*: 1507 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose H (2) Amorphous powder, $[\alpha]_D^{24}$ −26.3° ($c=1.86$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 229 (4.55), 301 (sh 4.60), 315 (4.67). *Anal.* Calcd for $C_{61}H_{74}O_{34} \cdot 2H_2O$: C, 52.81; H, 5.67. Found: C, 52.90; H, 5.90. FAB-MS *m/z*: 1373 $[M+Na]^+$, 1351 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose I (3) Amorphous powder, $[\alpha]_D^{24}$ −9.1° ($c=1.05$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 229 (4.54), 296 (sh 4.55), 315 (4.64). *Anal.* Calcd for $C_{59}H_{72}O_{33} \cdot 3/2\,H_2O$: C, 53.03; H, 5.66. Found: C, 53.06; H, 5.92. FAB-MS *m/z*: 1311 $[M+Na]^+$, 1309 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose J (4) Amorphous powder, $[\alpha]_D^{24}$ −35.9° ($c=1.38$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 229 (4.45), 300 (sh 4.61), 314 (4.67). *Anal.* Calcd for $C_{59}H_{72}O_{33} \cdot 2H_2O$: C, 52.68; H, 5.69. Found: C, 52.81; H, 5.67. FAB-MS *m/z*: 1331 $[M+Na]^+$, 1309 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose K (5) Amorphous powder, $[\alpha]_D^{24}$ −3.2° ($c=0.74$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 229 (4.58), 299 (sh 4.63), 314 (4.70). *Anal.* Calcd for $C_{57}H_{70}O_{32} \cdot 2H_2O$: C, 52.53; H, 5.72. Found: C, 52.33; H, 5.73. FAB-MS *m/z*: 1289 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose L (6) Amorphous powder, $[\alpha]_D^{24}$ −59.2° ($c=0.92$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 228 (4.57), 299 (4.64), 309 (4.67). *Anal.* Calcd for $C_{67}H_{84}O_{38} \cdot 7/2\,H_2O$: C, 51.57; H, 5.88. Found: C, 51.36; H, 5.78. FAB-MS *m/z*: 1519 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose M (7) Amorphous powder, $[\alpha]_D^{24}$ −29.2° ($c=0.53$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 226 (4.69), 299 (sh 4.64), 309 (4.66). *Anal.* Calcd for $C_{65}H_{82}O_{37} \cdot 5H_2O$: C, 50.52; H, 6.00. Found: C, 50.64; H, 5.83. FAB-MS *m/z*: 1477 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose N (8) Amorphous powder, $[\alpha]_D^{24}$ −26.6° ($c=0.62$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 230 (4.53), 299 (sh 4.45), 322 (4.55). *Anal.* Calcd for $C_{63}H_{78}O_{36} \cdot 3/2\,H_2O$: C, 52.61; H, 5.68. Found: C, 52.69; H, 5.80. FAB-MS *m/z*: 1433 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose O (9) Amorphous powder, $[\alpha]_D^{24}$ −17.4° ($c=0.86$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 232 (4.54), 297 (sh 4.44), 326 (4.59). *Anal.* Calcd for $C_{61}H_{76}O_{35} \cdot 3/2H_2O$: C, 52.47; H, 5.70. Found: C, 52.42; H, 5.96. FAB-MS *m/z*: 1391 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Tenuifoliose P (10) Amorphous powder, $[\alpha]_D^{24}$ −7.7° ($c=0.92$, MeOH). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 232 (4.54), 299 (sh 4.44), 326 (4.60). *Anal.* Calcd for $C_{59}H_{74}O_{34} \cdot 3H_2O$: C, 51.30; H, 5.84. Found: C, 51.44; H, 5.76. FAB-MS *m/z*: 1349 $[M+Na]^+$, 1327 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Acetylation of 1—10 Each compound (3 mg) was treated with acetic anhydride–pyridine (1 : 1) (0.5 ml) overnight at 35 °C and the reagents were evaporated off to give a residue, which was purified by HPLC [YMC A-232 ODS, 10 mm × 25 cm, CH_3CN–H_2O (60 : 40)]. From **1**, **1a** was obtained as an amorphous powder. **1a**: ^{1}H-NMR and FAB-MS were identical to those of tenuifoliose F. 1) From **2—5**, **2a** was obtained as an amorphous powder. **2a**: ^{1}H-NMR ($CDCl_3$) δ: 1.77, 1.96, 1.97, 2.00, 2.01, 2.051, 2.054, 2.08, 2.10, 2.13 (each 3H, s, aliphatic OAc), 1.996, 2.076 (each 6H, s, aliphatic OAc), 2.32 (6H, s, aromatic OAc), 4.49, 4.75, 4.54 (each 1H, d, $J=8$ Hz, H-1 of Glc), 5.66 (1H, d, $J=3.5$ Hz, H-1 of Glc-1), 6.26, 6.49 (each 1H, d, $J=16$ Hz, H-β), 7.14, 7.17 (each, 2H, d, $J=8.5$ Hz, H-3, H-5 of *p*-coum.), 7.48 (2H, t, $J=8$ Hz, H-3, H-5 of benz.), 7.53, 7.58 (each 2H, d, $J=8.5$ Hz, H-2, H-6 of *p*-coum.), 7.58 (1H, tt, $J=8$, 1 Hz, H-4 of benz.), 7.64, 7.78 (each 1H, d, $J=16$ Hz, H-γ of *p*-coum.), 8.11 (2H, dd, $J=8$, 1 Hz, H-2, H-6 of benz.). FAB-MS *m/z*: 1919 $[M+Na]^+$. From **6** and **7**, **6a** was obtained as an amorphous powder. ^{1}H-NMR ($CDCl_3$): δ: 1.22 (3H, d, $J=6$ Hz, H_3-6 of Rham), 1.80, 1.96, 1.97, 1.995, 1.998, 2.001, 2.01, 2.04, 2.051, 2.057, 2.068, 2.074, 2.078, 2.082, 2.098, 2.12 (each 3H, s, aliphatic OAc), 2.21, 2.32 (each 3H, s, aromatic OAc), 4.50, 4.53, 4.75 (each 1H, d, $J=8$ Hz, H-1 of Glc), 5.53 (1H, d, $J=1.5$ Hz, H-1 of Rham), 5.66 (1H, d, $J=3.5$ Hz, H-1 of Glc-1), 6.20, 6.50 (each 1H, d, $J=16$ Hz, H-β of *p*-coum.). 7.12, 7.58 (each 2H, d, $J=8.5$ Hz, H-2, H-5 of *p*-coum.), 7.14, 7.47 (each 2H, d, $J=8.5$ Hz, H-3, H-5 of *p*-coum.), 7.49 (2H, t, $J=8$ Hz, H-3, H-5 of benz.), 7.59 (1H, tt, $J=8$, 1 Hz, H-5 of benz.), 7.60, 7.78 (each 1H, d, $J=16$ Hz, H-γ of *p*-coum.), 8.11 (2H, dd, $J=8$, 1 Hz, H-2, H-6 of benz.). FAB-MS *m/z*: 2128 $[M+H]^+$. From **8—10**, **8a** was obtained as an amorphous powder. **8a**: ^{1}H-NMR ($CDCl_3$) δ: 1.77, 1.96, 1.97, 1.98, 1.997, 2.002, 2.009, 2.052, 2.054, 2.097, 2.014 (each 3H, s, aliphatic OAc), 2.08 (9H, s, aliphatic OAc), 2.33 (6H, s, aromatic OAc), 3.90, 3.93 (each 3H, s, OMe), 4.49, 4.54, 4.75 (each 1H, d, $J=8$ Hz, H-1 of Glc), 6.27, 6.50 (each 1H, d, $J=16$ Hz, H-β of fer.), 7.06, 7.11 (each 1H, d, $J=8$ Hz, H-5 of fer.), 7.12 (2H, m, H-6 of fer.), 7.17 (2H, br s, H-2 of fer.), 7.63, 7.76 (each 1H, d, $J=16$ Hz, H-γ of fer.). FAB-MS *m/z*: 1980 $[M+Na]^+$.

Alkaline Hydrolysis of 1—10 Each compound (2 mg) was treated with 2% NaOH aq. (3 drops) for 2 h at room temperature in N_2 atmosphere and the reaction mixture was passed through a column equipped with Amberlite IR-120 on Mitsubishi Diaion HP-20. From the water eluate of **1—10** a pentasaccharide **1b** was detected by HPLC [Asahipak NH2P-50, 4.6 mm × 25 cm, CH_3CN–H_2O (65 : 35), 1.0 ml/min, UV 195 nm,5) t_R 11.5 min]. From the methanol eluate of **1** benzoic, *p*-coumaric and ferulic acid, from that of **2—7** benzoic and *p*-coumaric acid and from that of **8—10** benzoic and ferulic acid were detected by HPLC [YMC R-ODS-7, 4.6 mm × 25 cm, CH_3CN–H_2O–trifluoroacetic acid (22.5 : 77.5 : 0.05), 1.0 ml/min, UV 270 nm, t_R 9.0 min (*p*-coumaric acid); 10.0 min (ferulic acid); 15.3 min (benzoic acid)].

Acid Hydrolysis of 1—10 A solution of each compound (2 mg) in 5% H_2SO_4 (2 drops) was heated in a boiling water bath for 1 h. The solution was passed through a column equipped with Amberlite IR-45 on Mitsubishi Diaion HP-20 and the residue was concentrated. From **1**, **6** and **7**, glucose–fructose–rhamnose were detected in the ratio 4 : 1 : 1 and from **2—5** and **8—10** glucose–fructose in the ratio 4 : 1 by HPLC [Asahipak NH2P-50, 4.6 mm × 25 cm, CH_3CN–H_2O (75 : 25), 1.0 ml/min, UV 195 nm, t_R 6.0 min (rhamnose); 8.1 min (fructose); 10.1 min (glucose)].

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