Senegoses F—I, Oligosaccharide Multi-Esters from the Roots of *Polygala senega* var. *latifolia* TORR. *et* GRAY

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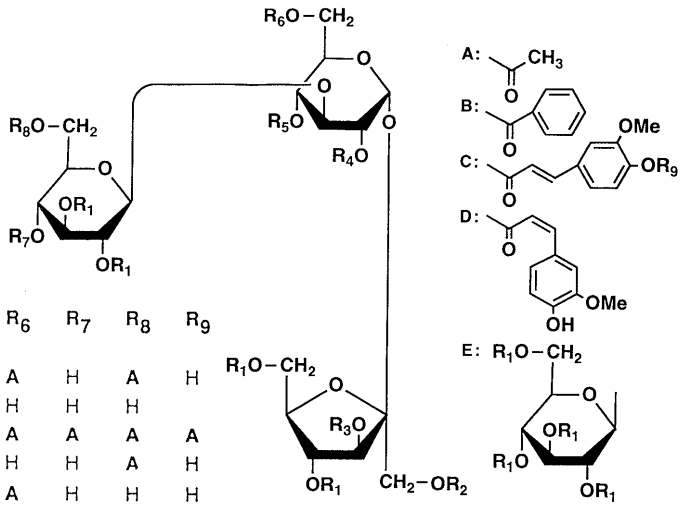
From the roots of *Polygala senega* var. *latifolia* TORR. *et* GRAY four new oligosaccharides, called senegoses F—I, were isolated and their structures were elucidated by spectroscopic and chemical means. These oligosaccharides were esterified with acetic, benzoic and ferulic acids.

Keywords *Polygala senega* var. *latifolia*; Polygalaceae; senegose; acylated oligosaccharide; tetrasaccharide

We earlier reported[1] the isolation and structural elucidation of five new oligosaccharide multi-esters called senegoses A—E from the roots of *Polygala senega* var. *latifolia* TORR. *et* GRAY (see Chart 1). The rarity of the structure prompted us to investigate further for additional oligosaccharide constituents of this medical plant and we have been successful in isolating other new oligosaccharide mutli-esters. This paper reports the isolation and structural elucidation of these rare oligosaccharides called senegoses F—I.

Senegose F (**1**), $[\alpha]_D$ −11.5°, $C_{55}H_{66}O_{30}\cdot 3H_2O$ was obtained as an amorphous powder and it exhibited $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 1229 and 1207, respectively, under FAB-MS. On acid hydrolysis compound **1** gave glucose and fructose in the ratio 3 : 1, while on alkaline hydrolysis it gave a tetrasaccharide **1a** and acid mixture composed of benzoic and ferulic acid (see Experimental). On acetylation, **1** afforded a peracetate **1b** which exhibited two aromatic [δ 2.33 (6H, s)] and eleven aliphatic [δ 1.69, 1.98, 2.03, 2.083, 2.100, 2.102, 2.12 (each 3H, s), 1.95, 2.079 (each 6H, s)] acetoxyl signals in the ^{1}H-NMR spectrum. In the NMR spectrum of **1**, two acetyl, one benzoyl and two feruloyl signals were observed (see Tables I and II). Detailed proton spin decoupling experiments which started from the irradiation at each anomeric proton signal and differential nuclear Overhauser effect (NOE) experiments involving irradiation at each anomeric proton signal enabled us to assign all proton signals of the Glc-1 and Glc-3 moieties (see Chart 2 and Table I). The C–H correlation spectroscopy) (COSY) spectrum and above mentioned ^{1}H-NMR data led us to assume that the sugar linkage and the acylated sites of senegose F (**1**) are as shown. The position of each acyl residue was allocated by observation of $^3J_{(COCH)}$ using ^{1}H detected heteronuclear multiple bond connectivity (HMBC) and long-range selective proton decoupling (LSPD) methods (see Chart 3).[2] The carbon signals of the ester moiety were assigned from the HMBC (see Chart 3 and Table II). These data led us to assign the structure of **1** to senegose F. The glycosylation and acylation shifts in the ^{13}C-NMR spectrum of senegose F supported this conclusion.

The ^{1}H-NMR spectrum of senegoses G (**2**), $[\alpha]_D$ +1.2°, $C_{53}H_{64}O_{29}\cdot 3H_2O$ and H (**3**), $[\alpha]_D$ −3.0°, $C_{53}H_{64}O_{29}\cdot 5/2H_2O$ showed that these two compounds were composed of a tetrasaccharide **1a**, an acetic, a benzoic and two ferulic acid moieties. On acetylation, these two compounds gave



	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	
1	H	C	B	E	C	A	H	A	H	
1a	H	H	H	E	H	H	H	H		
1b	A	C	B	E	C	A	A	A	A	
2	H	C	B	E	C	H	H	A	H	
3	H	C	B	E	C	A	H	H	H	
4	H	C	B	H	C	A	E	A	H	
5	H	C	B	E	C	A	E	A	H	senegose A
6	H	C	B	E	C	A	E	H	H	senegose B
7	H	C	B	E	C	H	E	A	H	senegose C
8	H	C	B	E	C	H	E	H	H	senegose D
9	H	C	B	E	D	A	E	A	H	senegose E

Chart 1

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

	1	2	3	4
Glc-1				
1	5.88 (1H, d, J=3.5 Hz)	5.84 (1H, d, J=3.5 Hz)	5.86 (1H, d, J=3.5 Hz)	5.57 (1H, d, J=3.5 Hz)
2	3.82 (1H, dd, J=9.5, 3.5 Hz)	3.73 (1H, dd, J=9.5, 3.5 Hz)	3.82 (1H, dd, J=9.5, 3.5 Hz)	3.73 (1H, dd, J=9.5, 3.5 Hz)
3	3.95 (1H, t, J=9.5 Hz)	3.90 (1H, t, J=9.5 Hz)	4.02 (1H, t, J=9.5 Hz)	3.85 (1H, t, J=9.5 Hz)
4	5.03 (1H, dd, J=10, 9.5 Hz)	5.02 (1H, t, J=10 Hz)	5.00 (1H, dd, J=10, 9.5 Hz)	4.97 (1H, dd, J=10, 9.5 Hz)
5	4.41 (1H, ddd, J=10, 5, 3 Hz)	4.15 (1H, m)	4.40 (1H, m)	4.36 (1H, m)
6	4.15 (1H, dd, J=12, 5 Hz)	3.52 (1H, dd, J=12, 5 Hz)	4.14 (1H, dd, J=12, 5 Hz)	3.90 [a]
	4.20 (1H, dd, J=12, 3 Hz)	3.64 (1H, dd, J=12, 2 Hz)	4.20 (1H, dd, J=12, 3 Hz)	4.11 [a]
Glc-2				
1	4.63 (1H, d, J=8 Hz)	4.61 (1H, d, J=8 Hz)	4.60 (1H, d, J=8 Hz)	
3	3.35 [a]			
5	3.35 [a]			
Glc-3				
1	4.51 (1H, d, J=8 Hz)	4.42 (1H, d, J=8 Hz)	4.46 (1H, d, J=8 Hz)	4.20 (1H, d, J=8 Hz)
2	3.03 (1H, dd, J=8.5, 8 Hz)	2.96 (1H, dd, J=8.5, 8 Hz)	3.02 (1H, dd, J=8.5, 8 Hz)	3.14 (1H, t, J=8 Hz)
3	3.20 (1H, t, J=8.5 Hz)	3.13 (1H, t, J=8.5 Hz)	3.16 (1H, t, J=8.5 Hz)	3.23 (1H, t, J=8 Hz)
4	3.23 (1H, t, J=8.5 Hz)	3.17 (1H, t, J=8.5 Hz)	3.20 (1H, t, J=8.5 Hz)	3.36 (1H, t, J=8 Hz)
5	3.11 (1H, m)	3.01 (1H, m)	3.03 (1H, m)	3.04 (1H, m)
6	3.99 (1H, dd, J=12, 2 Hz)	3.93 (1H, dd, J=12, 2 Hz)	3.44 (1H, dd, J=12, 5 Hz)	4.12 [a]
	4.07 (1H, dd, J=12, 4 Hz)	4.01 (1H, dd, J=12, 4 Hz)	3.61 (1H, dd, J=12, 3 Hz)	
Glc-4				
1				4.12 (1H, d, J=8 Hz)
3				3.25 (1H, t, J=8 Hz)
5				3.25 (1H, m)
Fru				
1	4.21 (1H, d, J=12 Hz)	4.15 (1H, d, J=12 Hz)	4.18 (1H, d, J=12 Hz)	4.33 (1H, d, J=12 Hz)
	4.73 (1H, d, J=12 Hz)	4.73 (1H, d, J=12 Hz)	4.73 (1H, d, J=12 Hz)	4.41 (1H, d, J=12 Hz)
3	5.76 (1H, d, J=8 Hz)	5.73 (1H, d, J=8 Hz)	5.76 (1H, d, J=8 Hz)	5.72 (1H, d, J=8 Hz)
4	4.46 (1H, t, J=8 Hz)	4.46 (1H, t, J=8 Hz)	4.45 (1H, t, J=8 Hz)	4.48 (1H, t, J=8 Hz)
5	4.09 (1H, m)	4.00 (1H, m)	4.08 (1H, m)	4.09 (1H, m)
6	3.88 (1H, dd, J=12, 3 Hz)	3.78 (1H, dd, J=12, 3 Hz)	3.84 (1H, dd, J=12, 3 Hz)	3.88 (1H, dd, J=12, 3 Hz)
	3.95 [a]	3.82 [a]	3.90 (1H, dd, J=12, 7 Hz)	
Ac (R_5)				
2	2.08 (3H, s)		2.07 (3H, s)	2.05 (3H, s)
Ac (R_6)				
2	1.59 (3H, s)	1.53 (3H, s)		1.72 (3H, s)
Bz (R_3)				
2, 6	8.20 (2H, dd, J=8, 1 Hz)	8.20 (2H, dd, J=8, 1 Hz)	8.16 (2H, dd, J=8, 1 Hz)	8.21 (2H, dd, J=8, 1 Hz)
3, 5	7.62 (2H, t, J=8 Hz)	7.59 (2H, t, J=8 Hz)	7.58 (2H, t, J=8 Hz)	7.59 (2H, t, J=8 Hz)
4,	7.71 (1H, tt, J=8, 1 Hz)	7.69 (1H, tt, J=8, 1 Hz)	7.63 (1H, tt, J=8, 1 Hz)	7.67 (1H, tt, J=8, 1 Hz)
Fer (R_2)				
2	7.21 (1H, d, J=2 Hz)	7.19 (1H, d, J=2 Hz)	7.20 (1H, d, J=2 Hz)	7.13 (1H, d, J=2 Hz)
5	6.83 (1H, d, J=8 Hz)	6.81 (1H, d, J=8 Hz)	6.81 (1H, d, J=8 Hz)	6.76 (1H, d, J=8 Hz)
6	7.03 (1H, dd, J=8, 2 Hz)	7.02 (1H, dd, J=8, 2 Hz)	7.04 (1H, dd, J=8, 2 Hz)	6.82 (1H, dd, J=8, 2 Hz)
β	6.43 (1H, d, J=16 Hz)	6.42 (1H, d, J=16 Hz)	6.42 (1H, d, J=16 Hz)	6.30 (1H, d, J=16 Hz)
γ	7.69 (1H, d, J=16 Hz)	7.68 (1H, d, J=16 Hz)	7.68 (1H, d, J=16 Hz)	7.62 (1H, d, J=16 Hz)
OMe	3.92 (3H, s)	3.84 (3H, s)	3.90 (3H, s)	3.88 (3H, s)
Fer (R_4)				
2	7.23 (1H, d, J=2 Hz)	7.21 (1H, d, J=2 Hz)	7.25 (1H, d, J=2 Hz)	7.22 (1H, d, J=2 Hz)
5	6.87 (1H, d, J=8 Hz)	6.85 (1H, d, J=8 Hz)	6.85 (1H, d, J=8 Hz)	6.85 (1H, d, J=8 Hz)
6	7.07 (1H, dd, J=8, 2 Hz)	7.05 (1H, dd, J=8, 2 Hz)	7.10 (1H, dd, J=8, 2 Hz)	7.05 (1H, dd, J=8, 2 Hz)
β	6.27 (1H, d, J=16 Hz)	6.27 (1H, d, J=16 Hz)	6.36 (1H, d, J=16 Hz)	6.25 (1H, d, J=16 Hz)
γ	7.58 (1H, d, J=16 Hz)	7.57 (1H, d, J=16 Hz)	7.59 (1H, d, J=16 Hz)	7.56 (1H, d, J=16 Hz)
OMe	3.97 (3H, s)	3.90 (3H, s)	3.93 (3H, s)	3.95 (3H, s)

a) Overlapping with other signals.

the same peracetate **1b** and a tetrasaccharide **1a** on alkaline hydrolysis as in the case of **1**; therefore, the positions of the benzoyl and two feruloyl groups were the same as in **1**. Comparing the ^{1}H- and ^{13}C-NMR spectra with those of **1**, an acetyl methyl signal was observed at δ 1.53, while the H_2-6 of Glc-1 were shifted upfield to δ 3.52 (Δ −0.63 ppm) and δ 3.64 (Δ −0.56 ppm), the C-5 of Glc-1 was shifted downfield to δ 72.3 (Δ +2.6 ppm) and the C-6 of Glc-1 upfield to δ 62.1 (Δ −2.2 ppm) in **2**; an acetyl methyl signal was observed at δ 2.07, the H_2-6 of Glc-3 were shifted upfield to δ 3.44 (Δ −0.55 ppm) and 3.61 (Δ −0.46 ppm), C-5 of Glc-3 downfield to δ 77.3 (Δ +2.7 ppm) and the C-6 of Glc-3 upfield δ 62.9 (Δ −1.3 ppm) in **3**. Therefore, the structures of senegoses G and H were assigned as **2** and **3**, respectively.

Senegose I (**4**), $[\alpha]_D$ −29.1°, $C_{55}H_{66}O_{30}\cdot 5/2H_2O$ was obtained as an amorphous powder and it exhibited $[M+Na]^+$ and $[M+H]^+$ ions at m/z 1229 and 1207, respectively, under FAB-MS. On acid hydrolysis compound **4** gave glucose and fructose in the ratio 3 : 1, while on alkaline hydrolysis it gave an acid mixture composed of benzoic and ferulic acids (see Experimental). In the NMR spectrum of

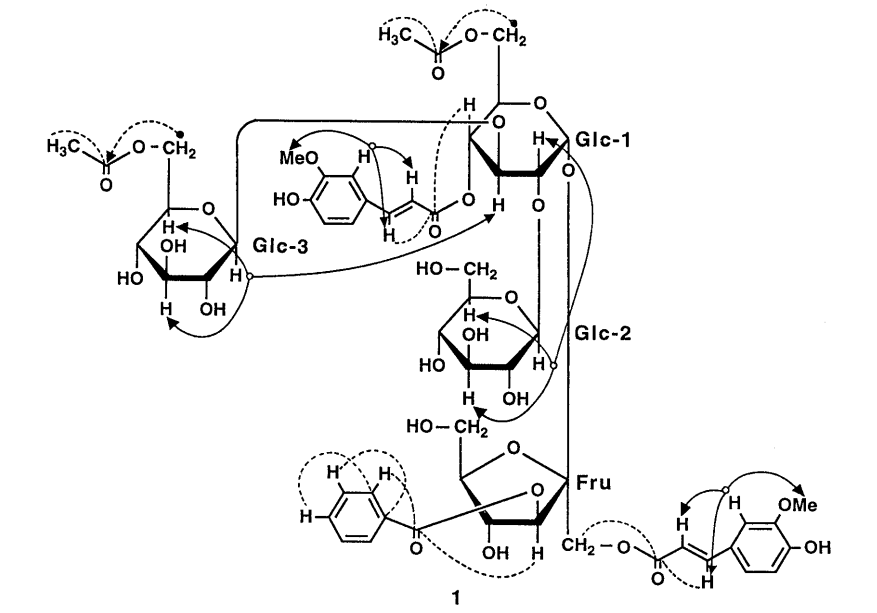


Chart 2

4, two acetyl [δ 1.72, 2.05 (each 3H, s)], one benzoyl and two feruloyl signals were observed (see Tables I and II). Detailed proton spin decoupling experiments which started from the irradiation at each anomeric proton signal and differential NOE experiments involving irradiation at each anomeric proton signal enabled us to assign all proton signals of the Glc-1 and Glc-3 moieties (see Chart 3 and 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 of senegose I (**4**) were as shown. The position of each acyl residue was allocated by observation of $^3J_{(COCH)}$ using HMBC and LSPD methods (see Chart 3). The carbon signals of the ester moiety were assigned from the HMBC (see Chart 3 and Table II). These data led us to assign the structure of **4** to senegose I. The glycosylation and acylation shifts in the ^{13}C-NMR spectrum of senegose I supported this conclusion.

The anomeric configurations of Glc-1, Glc-2 and Glc-3 were determined to be α, β and β, respectively, from each $J_{H_1-H_2}$ value, and that of the Fru moiety was determined to be β from the NOE experiment described below. When the signals due to the H-3 of Fru were irradiated, NOEs were observed at the signals due to the H_2-1 of Fru. The absolute configuration of each monosaccharide was not determined.

Experimental

General Procedure Instrumental analyses were carried out as described previously.[3)]

Isolation *Polygala senega* var. *latifolia* TORR. *et* GRAY (3 kg) was extracted twice with hot water (40 l). 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 77 g, 70% MeOH aq. eluate 40 g and MeOH eluate 88 g). MeOH eluate was chromatographed on a silica gel (900 g) column using $CHCl_3$–MeOH–H_2O (74 : 24 : 2) as a mobile phase to give fractions 1 (8.4 g), 2 (3.8 g), 3 (1.9 g), 4 (16.2 g), 5 (33.5 g), 6 (14.9 g). From fraction 2, oligosaccharides were isolated by preparative HPLC [Develosil Lop-ODS 5 cm × 50 cm, MeOH–H_2O (40 : 60)—(55 : 45) with linear gradient elution]: **1** (667 mg), **2** (217 mg), **3** (35 mg), **4** (19 mg).

Senegose F (1) Amorphous powder, $[\alpha]_D^{22}$ −11.5° (c = 1.21, MeOH).

TABLE II. ^{13}C-NMR Data for Oligosaccharides from the Roots of *Polygala senega* var. *latifolia* in MeOH-d_4

	1	2	3	4
Glc-1				
1	92.9	93.1	92.9	93.0
2	81.3	81.5	81.0	72.7
3	79.0	79.2	79.5	82.5
4	70.3	70.2	70.9	70.2
5	69.7	72.3	69.6	70.2
6	64.3	62.1	64.4	64.3
Glc-2				
1	105.3	105.3	105.4	
2	75.2	75.3	75.2	
3	78.4	78.4	78.4	
4	71.6	71.6	71.6	
5	77.9	77.9	77.8	
6	63.0	63.0	63.0	
Glc-3				
1	104.4	104.4	104.6	104.8
2	75.5	75.4	75.6	75.2
3	78.5	78.4	78.5	76.0
4	71.0	71.3	71.8	80.5
5	74.6	74.6	77.3	73.5
6	64.2	64.3	62.9	63.8
Glc-4				
1				105.6
2				74.7
3				78.1
4				71.3
5				77.8
6				62.4
Fru				
1	65.8	65.8	65.6	66.6
2	103.9	103.8	104.4	103.7
3	80.0	80.1	79.8	80.7
4	73.9	73.5	73.9	74.7
5	84.6	84.5	84.6	84.6
6	63.8	63.0	63.8	63.6
Ac (R_5)				
1	172.6		172.5	172.5
2	20.8		20.8	20.8
Ac (R_6)				
1	172.5	172.6		172.4
2	20.5	20.5		20.5
Bz (R_3)				
1	130.9	131.1	130.9	131.1
2, 6	131.0	131.2	131.0	131.1
3, 5	129.9	129.9	129.9	130.0
4	134.8	134.8	134.7	134.8
α	167.2	167.3	167.3	167.1
Fer (R_2)				
1	127.6	127.6	127.7	127.6
2	111.6	111.7[a]	111.8[h]	111.5
3	149.4	149.4	149.4	149.5
4	150.7	150.7[b]	150.7[i]	150.7
5	116.5	116.5	116.5[j]	116.5
6	124.6	124.5[c]	124.4	124.3
α	168.4	168.4[d]	168.4[k]	168.4
β	115.2	115.4[e]	115.5[l]	115.2
γ	147.3	147.3[f]	147.3	147.2
OMe	56.5	56.6[g]	56.5	56.5
Fer (R_4)				
1	127.5	127.6	127.7	127.5
2	111.5	111.5[a]	111.6	111.6
3	149.4	149.4	149.4[h]	149.4
4	150.9	150.8[b]	150.8	150.9
5	116.5	116.5	116.4[i]	116.5
6	124.4	124.4[c]	124.4[j]	124.6
α	167.9	168.0[d]	168.1	167.8
β	115.1	115.1[e]	115.1[k]	115.2
γ	147.2	146.9[f]	147.3[l]	147.2
OMe	56.4	56.5[g]	56.5	56.5

a—*l*) Assignments may be interchanged in each column.

UV λ_{max}^{MeOH} nm (log ε): 219 (4.58), 233 (4.58), 285 (sh, 4.36), 299 (sh, 4.46), 327 (4.64). *Anal.* Calcd for $C_{55}H_{66}O_{30}\cdot 3H_2O$: C, 52.38; H, 5.91. Found: C, 52.29; H, 5.59. FAB-MS *m/z*: 1229 $[M+Na]^+$, 1207 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Senegose G (2) Amorphous powder, $[\alpha]_D^{22}$ +1.2° (*c*=1.21, MeOH). UV λ_{max}^{MeOH} nm (log ε): 220 (4.47), 233 (4.48), 285 (sh, 4.24), 299 (sh, 4.36), 327 (4.54). *Anal.* Calcd for $C_{53}H_{64}O_{29}\cdot 3H_2O$: C, 52.22; H, 5.78. Found: C, 52.03; H, 5.60. FAB-MS *m/z*: 1187 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Senegose H (3) Amorphous powder, $[\alpha]_D^{22}$ −3.0° (*c*=0.66, MeOH). UV λ_{max}^{MeOH} nm (log ε): 219 (4.58), 233 (4.58), 286 (sh, 4.35), 301 (sh, 4.47), 328 (4.64). *Anal.* Calcd for $C_{53}H_{64}O_{29}\cdot 5/2H_2O$: C, 52.60; H, 5.75. Found: C, 52.54; H, 5.88. FAB-MS *m/z*: 1187 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Senegose I (4) Amorphous powder, $[\alpha]_D^{22}$ −29.1° (*c*=0.79, MeOH). UV λ_{max}^{MeOH} nm (log ε): 220 (4.55), 234 (4.55), 287 (sh, 4.34), 300 (sh, 4.43), 328 (4.61). *Anal.* Calcd for $C_{55}H_{66}O_{30}\cdot 5/2H_2O$: C, 52.76; H, 5.72. Found: C, 52.99; H, 5.84. FAB-MS *m/z*: 1229 $[M+Na]^+$, 1207 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Acetylation of 1—3 A sample of each compound (3 mg) was treated with acetic anhydride–pyridine (1 : 1) (3 drops) overnight at 35 °C and the reagents were then evaporated to give a residue. From **1**—**3**, **1b** was obtained as an amorphous powder. **1b**: ^{1}H-NMR ($CDCl_3$) δ: 1.69, 1.98, 2.03, 2.083, 2.100, 2.102, 2.12 (each 3H, s, aliphatic OAc), 1.95, 2.079 (each 6H, s, aliphatic OAc), 2.33 (6H, s, aromatic OAc), 3.89, 3.91 (each 3H, s, OMe), 4.38 (1H, d, *J*=8 Hz, H-1 of Glc-3), 4.66 (1H, d, *J*=8 Hz, H-1 of Glc-2), 5.71 (1H, d, *J*=3.5 Hz, H-1 of Glc-1), 6.27, 6.52 (each 1H, d, *J*=16 Hz, H-β of fer.), 7.07, 7.08 (each 1H, d, *J*=8 Hz, H-5 of fer.), 7.12, 7.16 (each 1H, dd, *J*=8, 2 Hz, H-6 of fer.), 7.14, 7.20 (each 1H, d, *J*=2 Hz, H-2 of fer.), 7.50 (2H, t, *J*=8 Hz, H-3, H-5 of benz.), 7.59 (1H, tt, *J*=8, 1 Hz, H-4 of benz.), 7.63, 7.78 (each 1H, d, *J*=16 Hz, H-γ of fer.), 8.13 (2H, dd, *J*=8, 1 Hz, H-2, H-6 of benz.). FAB-MS *m/z*: 1691 $[M+Na]^+$, 1669 $[M+H]^+$.

Alkaline Hydrolysis of 1 Compound **1** (100 mg) was treated with 5% NaOH aq. (*ca.* 2 ml) for 4 h at room temperature in N_2 atmosphere and the reaction mixture was then passed through a column filled with Amberlite IR-120. The reaction mixture **1** was concentrated to give a residue, which was purified by HPLC [Asahipak NH2P-50 20 mm × 25 cm, CH_3CN–H_2O (75 : 25)]. From **1**, **1a** was obtained as an amorphous powder (20 mg). **1a**: ^{1}H-NMR (D_2O) δ: 4.68 (1H, *J*=8 Hz, H-1 of Glc-3), 4.79 (1H, *J*=8 Hz, H-1 of Glc-2), 5.28 (1H, *J*=3.5 Hz, H-1 of Glc-1). ^{13}C-NMR (D_2O) δ: 60.9, 61.6, 61.7, 61.9, 63.2, 68.6, 70.5, 70.6, 72.9, 74.3, 74.4, 74.8, 76.7, 76.8 (4C), 79.6, 80.3, 82.4, 92.8, 102.9, 104.0, 104.8. Dioxane (δ 3.73, 67.3) was used as an internal standard. FAB-MS *m/z*: 689 $[M+Na]^+$. $[\alpha]_D^{22}$ +21.0° (*c*=0.62, H_2O).

Alkaline Hydrolysis of 1—4 Each compound (2 mg) was treated with 2% NaOH aq. (3 drops) for 4 h at room temperature and the reaction mixture was passed through a column filled with Amberlite IR-120. From the water eluate of the reaction mixture of **1**—**3** a tetrasaccharide **1a** 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,[4] t_R 6.9 min]. From the methanol eluate of the reaction mixture of **1**—**4** benzoic and ferulic acids were identified 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 9.6 min (ferulic acid); 14.8 (benzoic acid)].

Acid Hydrolysis of 1—4 A solution of each compound (2 mg) in 5% H_2SO_4 (3 drops) was heated in a boiling water bath for 30 min. The solution was passed through a column filled with Amberlite IR-45 and the residue was concentrated. From **1**—**4**, glucose and fructose were detected in the ratio 3 : 1 by HPLC [Asahipak NH2P-50 4.6 mm × 25 cm, CH_3CN–H_2O (80 : 20), 1.0 ml/min, UV 195 nm, t_R 8.2 min (Fru); 10.6 min (Glc)].

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