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# Senegoses A—E, Oligosaccharide Multi-Esters from *Polygala senega* var. *latifolia* TORR. *et* GRAY

Hideki SAITOH, Toshio MIYASE* and Akira UENO

*School of Pharmaceutical Sciences, University of Shizuoka, 52-1, Yada, Shizuoka 422, Japan.* Received December 7, 1992

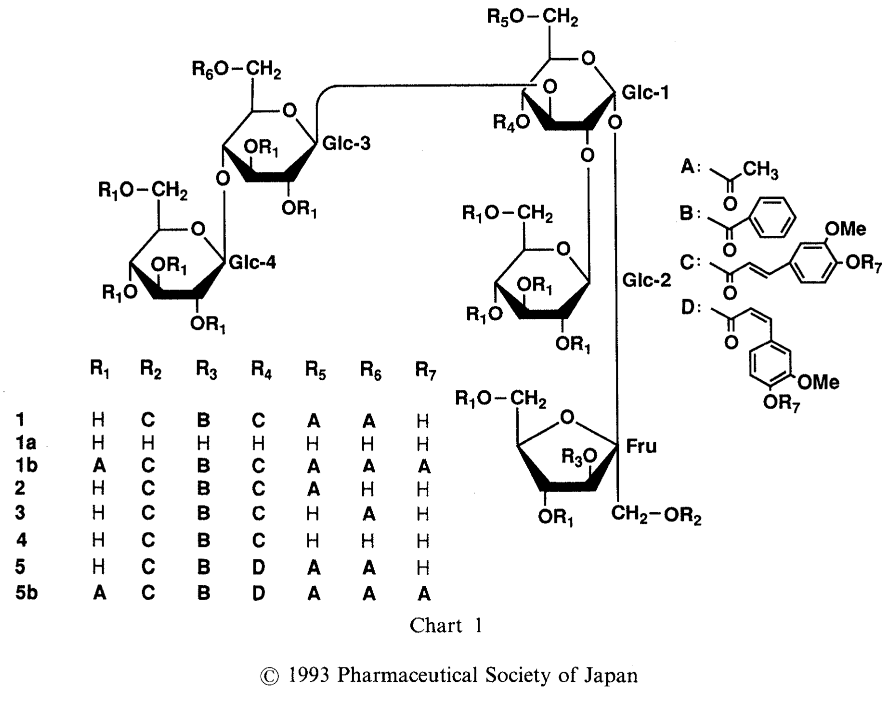
**From the roots of *Polygala senega* var. *latifolia* TORR. *et* GRAY five new oligosaccharides, called senegoses A—E, were isolated and their structures were elucidated by spectroscopic and chemical means. These oligosaccharides were esterified with acetic, benzoic, *trans*-ferulic and *cis*-ferulic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

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

The roots of *Polygala tenuifolia* WILLD. and *P. senega* var. *latifolia* TORR. *et* GRAY are well known crude drugs used as expectorants in China and Japan and the saponins they contain have been studied.[1] However, there are few studies of the other types constituents in these crude drugs. In a previous paper,[2,3] we reported the isolation and structural elucidation of rare oligosaccharide multi-esters, called tenuifolioses A—P from the roots of *P. tenuifolia*, and so we decided to search for similar constituents from *P. senega* var. *latifolia* belonging to the genus *Polygala*. We have been successful in isolating a number of new oligosaccharide multi-esters, structurally similar to the tenuifolioses. This paper reports the isolation and structural elucidation of these new oligosaccharides, called senegoses A—E.

Senegose A (**1**), $[\alpha]_D$ $-9.9°$, $C_{61}H_{76}O_{35}\cdot 9/2H_2O$ was obtained as an amorphous powder and it exhibited $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 1391 and 1369, respectively, under FAB-MS. On acid hydrolysis, compound **1** gave glucose and fructose in the ratio 4 : 1, while on alkaline hydrolysis, it gave a pentasaccharide **1a** and an acid mixture composed of benzoic and ferulic acids (see Experimental). On acetylation, **1** afforded a peracetate **1b** which exhibited two aromatic [$\delta$ 2.335, 2.343 (each 3H, s)] and fourteen aliphatic [$\delta$ 1.77, 1.95, 1.964, 1.99, 2.03, 2.05, 2.07, 2.080, 2.082, 2.10 (each 3H, s), 1.964, 2.06 (each 6H, s)] acetoxyl signals in the $^1$H-NMR spectrum. In the NMR spectrum of **1**, two acetyl [$\delta$ 1.57, 2.08 (each 3H, s)], one benzoyl and two feruloyl signals were observed (see Tables I and II). Detailed proton spin decoupling experiments which involved 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 presume that the sugar linkages and the acylated sites of senegose A (**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 2).[4] The carbon signals of the ester moiety were assigned from the HMBC (see Chart 2 and Table II). These data led us to assign the structure of **1** to senegose A. The glycosylation and acylation shifts in the $^{13}$C-NMR spectrum of senegose A supported this.

The $^1$H-NMR spectrum of senegose B (**2**), $[\alpha]_D$ $-10.2°$, $C_{59}H_{74}O_{34}\cdot H_2O$ and C (**3**), $[\alpha]_D$ $-16.0°$, $C_{59}H_{74}O_{34}\cdot 2H_2O$ showed that these two compounds were composed of a pentasaccharide **1a**, with acetic, benzoic and two ferulic acid moieties. On a acetylation these two compounds gave the same peracetate **1b** and a pentasaccharide **1a** on alkaline



| | R1 | R2 | R3 | R4 | R5 | R6 | R7 |
|---|---|---|---|---|---|---|---|
| **1** | H | C | B | C | A | A | H |
| **1a** | H | H | H | H | H | H | H |
| **1b** | A | C | B | C | A | A | A |
| **2** | H | C | B | C | A | H | H |
| **3** | H | C | B | C | H | A | H |
| **4** | H | C | B | C | H | H | H |
| **5** | H | C | B | D | A | A | H |
| **5b** | A | C | B | D | A | A | A |

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** | **5** |
|---|---|---|---|---|---|
| Glc-1 | | | | | |
| 1 | 5.86 (1H, d, $J$=3.5 Hz) | 5.88 (1H, d, $J$=3 Hz) | 5.87 (1H, d, $J$=3 Hz) | 5.85 (1H, d, $J$=3.5 Hz) | 5.84 (1H, d, $J$=3.5 Hz) |
| 2 | 3.82 (1H, dd, $J$=9.5, 3.5 Hz) | 3.85 [a] | 3.83 [a] | 3.82 (1H, dd, $J$=9.5, 3.5 Hz) | 3.81 (1H, dd, $J$=9.5, 3.5 Hz) |
| 3 | 3.95 (1H, t, $J$=9.5 Hz) | 4.01 (1H, t, $J$=9.5 Hz) | 3.99 (1H, t, $J$=9.5 Hz) | 4.00 (1H, t, $J$=9.5 Hz) | 3.89 [a] |
| 4 | 5.02 (1H, dd, $J$=10, 9.5 Hz) | 5.03 (1H, t, $J$=9.5 Hz) | 5.04 (1H, t, $J$=9.5 Hz) | 5.01 (1H, dd, $J$=10, 9.5 Hz) | 4.98 (1H, dd, $J$=10, 9.5 Hz) |
| 5 | 4.39 (1H, ddd, $J$=10, 5, 3 Hz) | 4.42 (1H, m) | 4.24 [a] | 4.23 (1H, m) | 4.37 (1H, m) |
| 6 | 4.14 [a]<br>4.18 (1H, dd, $J$=12, 3 Hz) | 4.15 [a]<br>4.15 [a] | 3.59 [a]<br>3.71 [a] | 3.60 [a]<br>3.71 [a] | 4.15 [a]<br>4.19 [a] |
| Glc-2 | | | | | |
| 1 | 4.61 (1H, d, $J$=8 Hz) | 4.63 (1H, d, $J$=8 Hz) | 4.63 (1H, d, $J$=8 Hz) | 4.61 (1H, d, $J$=8 Hz) | 4.61 (1H, d, $J$=8 Hz) |
| Glc-3 | | | | | |
| 1 | 4.56 (1H, d, $J$=8 Hz) | 4.48 (1H, d, $J$=8 Hz) | 4.55 (1H, d, $J$=8 Hz) | 4.46 (1H, d, $J$=8 Hz) | 4.50 (1H, d, $J$=8 Hz) |
| 2 | 3.08 (1H, dd, $J$=9.5, 8 Hz) | 3.13 (1H, t, $J$=8 Hz) | 3.13 (1H, t, $J$=8 Hz) | 3.11 (1H, dd, $J$=9.5, 8 Hz) | 3.10 (1H, t, $J$=8 Hz) |
| 3 | 3.35 (1H, t, $J$=9.5 Hz) | 3.38 [a] | 3.37 [a] | 3.35 (1H, t, $J$=9.5 Hz) | 3.36 [a] |
| 4 | 3.42 (1H, t, $J$=9.5 Hz) | 3.42 (1H, t, $J$=8 Hz) | 3.44 (1H, t, $J$=8 Hz) | 3.41 (1H, t, $J$=9.5 Hz) | 3.38 (1H, t, $J$=9.5 Hz) |
| 5 | 3.21 (1H, m) | 3.13 [a] | 3.22 (1H, m) | 3.11 [a] | 3.23 [a] |
| 6 | 4.14 [a]<br>4.14 [a] | 3.61 [a] | 4.16 [a] | 3.60 [a] | 4.09 [a]<br>4.15 [a] |
| Glc-4 | | | | | |
| 1 | 4.14 (1H, d, $J$=8 Hz) | 4.30 (1H, d, $J$=8 Hz) | 4.15 (1H, d, $J$=8 Hz) | 4.29 (1H, d, $J$=8 Hz) | 4.15 (1H, d, $J$=8 Hz) |
| Fru | | | | | |
| 1 | 4.18 (1H, d, $J$=12 Hz)<br>4.69 (1H, d, $J$=12 Hz) | 4.20 (1H, d, $J$=12 Hz)<br>4.73 (1H, d, $J$=12 Hz) | 4.15 (1H, d, $J$=12 Hz)<br>4.73 (1H, d, $J$=12 Hz) | 4.20 (1H, d, $J$=12 Hz)<br>4.73 (1H, d, $J$=12 Hz) | 4.17 [a]<br>4.69 (1H, d, $J$=12 Hz) |
| 3 | 5.74 (1H, d, $J$=8 Hz) | 5.77 (1H, d, $J$=8 Hz) | 5.76 (1H, d, $J$=8 Hz) | 5.74 (1H, d, $J$=8 Hz) | 5.75 (1H, d, $J$=8 Hz) |
| 4 | 4.43 (1H, t, $J$=8 Hz) | 4.46 (1H, t, $J$=8 Hz) | 4.54 (1H, t, $J$=8 Hz) | 4.51 (1H, t, $J$=8 Hz) | 4.42 (1H, t, $J$=8 Hz) |
| 5 | 4.08 (1H, ddd, $J$=8, 7, 3 Hz) | 4.11 (1H, m) | 4.08 (1H, m) | 4.05 (1H, m) | 4.09 [a] |
| 6 | 3.86 [a]<br>3.92 [a] | 3.88 [a]<br>3.94 [a] | 3.86 (1H, br d, $J$=12 Hz)<br>3.92 [a] | 3.85 [a]<br>3.90 [a] | 3.84 [a] |
| Ac ($R_5$) | | | | | |
| 2 | 2.08 (3H, s) | 2.06 (3H, s) | | | 2.05 (3H, s) |
| Ac ($R_6$) | | | | | |
| 2 | 1.57 (3H, s) | | 1.57 (3H, s) | | 1.83 (3H, s) |
| Bz ($R_3$) | | | | | |
| 2,6 | 8.19 (2H, dd, $J$=8, 1 Hz) | 8.18 (2H, dd, $J$=8, 1 Hz) | 8.21 (2H, dd, $J$=8, 1 Hz) | 8.19 (2H, dd, $J$=8, 1 Hz) | 8.14 (2H, dd, $J$=8, 1 Hz) |
| 3,5 | 7.62 (2H, t, $J$=8 Hz) | 7.57 (2H, t, $J$=8 Hz) | 7.62 (2H, t, $J$=8 Hz) | 7.57 (2H, t, $J$=8 Hz) | 7.58 (2H, t, $J$=8 Hz) |
| 4 | 7.72 (1H, tt, $J$=8, 1 Hz) | 7.63 (1H, tt, $J$=8, 1 Hz) | 7.72 (1H, tt, $J$=8, 1 Hz) | 7.67 (1H, tt, $J$=8, 1 Hz) | 7.74 (1H, tt, $J$=8, 1 Hz) |
| Fer ($R_2$) | | | | | |
| 2 | 7.20 (1H, d, $J$=2 Hz) | 7.18 (1H, d, $J$=2 Hz) | 7.20 (1H, d, $J$=2 Hz) | 7.19 (1H, d, $J$=2 Hz) | 7.20 (1H, d, $J$=2 Hz) |
| 5 | 6.81 (1H, d, $J$=8 Hz) | 6.82 (1H, d, $J$=8 Hz) | 6.82 (1H, d, $J$=8 Hz) | 6.81 (1H, d, $J$=8 Hz) | 6.78 (1H, d, $J$=8 Hz) |
| 6 | 6.99 (1H, dd, $J$=8, 2 Hz) | 7.10 (1H, dd, $J$=8, 2 Hz) | 6.99 (1H, dd, $J$=8, 2 Hz) | 7.02 (1H, dd, $J$=8, 2 Hz) | 6.99 (1H, dd, $J$=8, 2 Hz) |
| $\beta$ | 6.41 (1H, d, $J$=16 Hz) | 6.41 (1H, d, $J$=16 Hz) | 6.41 (1H, d, $J$=16 Hz) | 6.42 (1H, d, $J$=16 Hz) | 6.41 (1H, d, $J$=16 Hz) |
| $\gamma$ | 7.68 (1H, d, $J$=16 Hz) | 7.68 (1H, d, $J$=16 Hz) | 7.68 (1H, d, $J$=16 Hz) | 7.68 (1H, d, $J$=16 Hz) | 7.67 (1H, d, $J$=16 Hz) |
| OMe | 3.89 (3H, s) | 3.83 (3H, s) | 3.89 (3H, s) | 3.90 (3H, s) | 3.89 (3H, s) |
| Fer ($R_4$) | | | | | |
| 2 | 7.23 (1H, d, $J$=2 Hz) | 7.21 (1H, d, $J$=2 Hz) | 7.22 (1H, d, $J$=2 Hz) | 7.22 (1H, d, $J$=2 Hz) | 7.74 (1H, d, $J$=2 Hz) |
| 5 | 6.86 (1H, d, $J$=8.5 Hz) | 6.87 (1H, d, $J$=8 Hz) | 6.87 (1H, d, $J$=8 Hz) | 6.86 (1H, d, $J$=8 Hz) | 6.81 (1H, d, $J$=8 Hz) |
| 6 | 7.06 (1H, dd, $J$=8.5, 2 Hz) | 7.01 (1H, dd, $J$=8, 2 Hz) | 7.05 (1H, dd, $J$=8, 2 Hz) | 7.10 (1H, dd, $J$=8, 2 Hz) | 7.15 (1H, dd, $J$=8, 2 Hz) |
| $\beta$ | 6.24 (1H, d, $J$=16 Hz) | 6.34 (1H, d, $J$=16 Hz) | 6.25 (1H, d, $J$=16 Hz) | 6.34 (1H, d, $J$=16 Hz) | 5.67 (1H, d, $J$=13 Hz) |
| $\gamma$ | 7.58 (1H, d, $J$=16 Hz) | 7.58 (1H, d, $J$=16 Hz) | 7.59 (1H, d, $J$=16 Hz) | 7.59 (1H, d, $J$=16 Hz) | 6.82 (1H, d, $J$=13 Hz) |
| OMe | 3.97 (3H, s) | 3.93 (3H, s) | 3.96 (3H, s) | 3.93 (3H, s) | 3.85 (3H, s) |

[a] Overlapping with other signals.

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 $\delta$ 2.06, while the H-6 of Glc-3 was shifted upfield to $\delta$ 3.61 ($\Delta$ −0.53 ppm), the C-5 of Glc-3 was shifted downfield to $\delta$ 75.8 ($\Delta$ +2.7 ppm) and the C-6 of Glc-3 upfield to $\delta$ 62.2 ($\Delta$ −1.7 ppm) in **2**; an acetyl methyl signal was observed at $\delta$ 1.57, the $H_2$-6 of Glc-1 were shifted upfield to $\delta$ 3.59 ($\Delta$ −0.55 ppm) and 3.71 ($\Delta$ −0.47 ppm) the C-5 of Glc-1 downfield to $\delta$ 72.1 ($\Delta$ +2.5 ppm) and the C-6 of Glc-1 upfield to $\delta$ 62.0 ($\Delta$ −2.3 ppm) in **3**. Therefore, the structures of senegoses B and C were assigned as **2** and **3**, respectively.

Senegose D (**4**), $[\alpha]_D$ −6.9°, $C_{57}H_{72}O_{33}\cdot 2H_2O$ showed signals corresponding to a benzoyl and two feruloyl groups, but no acetyl group, in the $^1$H-NMR spectrum. A peracetate

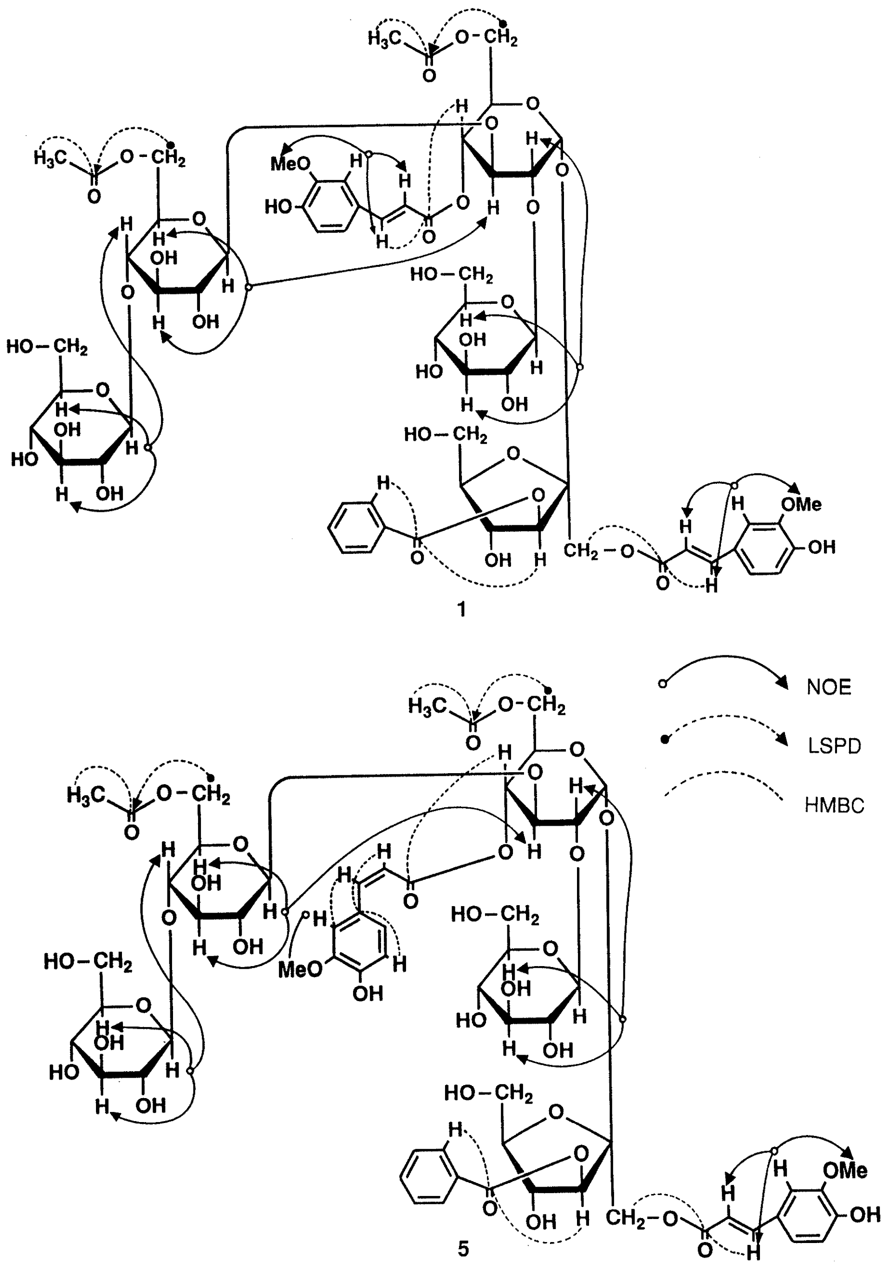


Chart 2

of this compound was identical to **1b**. Thus, the structure of senegose D was assigned as **4**.

Senegose E (**5**), $[\alpha]_D$ +64.5°, $C_{61}H_{76}O_{35} \cdot 3H_2O$ was obtained as an amorphous powder, and it exhibited $[M+Na]^+$ and $[M+H]^+$ ions at *m*/*z* 1391 and 1369, respectively, under FAB-MS. The $^1$H-NMR spectrum showed the presence of two acetyl groups, one benzoyl, one *trans*-feruloyl and one *cis*-feruloyl group (see Table I). Compound **5** gave glucose and fructose in the ratio 4 : 1 on acid hydrolysis, while alkaline hydrolysis gave a pentasaccharide **1a** and an acid mixture composed of benzoic, *trans*-ferulic and *cis*-ferulic acids (see Experimental). Compound **5** gave a peracetate **5b** and its $^1$H-NMR spectrum showed the presence of two aromatic and fourteen aliphatic acetoxyl signals. The detailed proton spin decoupling experiments which involved irradiation at each anomeric proton signal, the differential NOE experiments involving irradiation at each anomeric proton signal in the $^1$H-NMR spectra and the acylation shifts in the $^{13}$C-NMR spectrum showed that the acylated sites were identical to those of **1**. The position of each acyl residue was located by observation of $^3J_{(COCH)}$ using HMBC and LSPD methods (see Chart 2). These data led us to assign the structure, **5** to senegose E.

The anomeric configurations of Glc-1, Glc-2, Glc-3 and Glc-4 were determined to be $\alpha$, $\beta$, $\beta$ and $\beta$, respectively, from each $J_{H_1-H_2}$ value and that of the Fru moiety was determined to be $\beta$ from the NOE experiment described below. When the signal due to the H-3 of Fru was 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 in ref. 3.

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

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Glc-1 | | | | | |
| 1 | 92.7 | 92.7 | 93.0 | 93.1 | 92.9 |
| 2 | 81.3 | 80.8 | 81.5 | 81.3 | 81.2 |
| 3 | 78.7 | 79.6 | 78.9 | 79.9 | 79.6 |
| 4 | 70.2 | 70.9 | 70.0 | 70.8 | 70.0 |
| 5 | 69.6 | 69.5 | 72.1 | 72.2 | 69.5 |
| 6 | 64.3 | 64.4 | 62.0 | 62.1 | 64.4 |
| Glc-2 | | | | | |
| 1 | 105.2 | 105.2 | 105.2 | 105.3 | 105.3 |
| 2 | 75.2 | 75.1 | 75.2 | 75.2 | 75.2 |
| 3 | 78.3 | 78.2 | 78.3 | 78.3 | 78.5 |
| 4 | 71.5 | 71.5 | 71.5 | 71.6 | 71.6 |
| 5 | 77.9 | 77.8 | 77.9 | 77.9 | 78.0 |
| 6 | 63.0 | 63.0 | 63.0 | 63.1 | 63.0 |
| Glc-3 | | | | | |
| 1 | 103.9 | 104.4 | 103.7 | 104.5 | 104.2 |
| 2 | 75.0 | 75.1 | 75.0 | 75.2 | 75.2 |
| 3 | 76.2 | 76.0 | 76.2 | 76.2 | 76.2 |
| 4 | 80.5 | 81.4 | 80.5 | 81.1 | 80.8 |
| 5 | 73.1 | 75.8 | 73.1 | 75.8 | 73.1 |
| 6 | 63.9 | 62.2[a)] | 64.0 | 62.3 | 64.4 |
| Glc-4 | | | | | |
| 1 | 104.6 | 104.4 | 104.6 | 104.6 | 104.8 |
| 2 | 74.5 | 74.6 | 74.5 | 74.7 | 74.6 |
| 3 | 78.3 | 78.1 | 78.3 | 78.4 | 78.4 |
| 4 | 71.2 | 71.1 | 71.2 | 71.3 | 71.3 |
| 5 | 77.7 | 77.6 | 77.7 | 77.7 | 77.8 |
| 6 | 62.3 | 62.3[a)] | 62.3 | 62.4 | 62.4 |
| Fru | | | | | |
| 1 | 65.8 | 65.8 | 65.9 | 65.8 | 65.9 |
| 2 | 103.8 | 103.8 | 103.7 | 103.8 | 103.9 |
| 3 | 80.0 | 79.9 | 80.0 | 80.0 | 80.0 |
| 4 | 73.9 | 73.9 | 73.5 | 73.6 | 74.0 |
| 5 | 84.6 | 84.6 | 84.4 | 84.5 | 84.7 |
| 6 | 63.7 | 63.8 | 63.0 | 63.2 | 63.8 |
| Ac ($R_5$) | | | | | |
| 1 | 172.5 | 172.5 | | | 172.4 |
| 2 | 20.8 | 20.8 | | | 21.0 |
| Ac ($R_6$) | | | | | |
| 1 | 172.4 | | 172.4 | | 172.7 |
| 2 | 20.5 | | 20.5 | | 20.8 |
| Bz ($R_3$) | | | | | |
| 1 | 130.8 | 130.7 | 130.8 | 130.9 | 130.8 |
| 2,6 | 130.9 | 130.9 | 131.0 | 131.0 | 130.9 |
| 3,5 | 129.9 | 130.0 | 129.9 | 129.9 | 130.0 |
| 4 | 134.9 | 134.7 | 134.8 | 134.7 | 135.0 |
| α | 167.1 | 167.2 | 167.2 | 167.3 | 167.2 |
| Fer ($R_2$) | | | | | |
| 1 | 127.6 | 127.6 | 127.6[b)] | 127.7[h)] | 127.7 |
| 2 | 111.5 | 111.5 | 111.4[c)] | 111.8[i)] | 111.6 |
| 3 | 149.3 | 149.3 | 149.3 | 149.3 | 149.4 |
| 4 | 150.5 | 150.5 | 150.5[d)] | 150.7[j)] | 150.6 |
| 5 | 116.5 | 116.4 | 116.5 | 116.5[k)] | 116.5 |
| 6 | 124.6 | 124.3 | 124.6[e)] | 124.4[l)] | 124.3 |
| α | 168.3 | 168.8 | 168.4 | 168.4[m)] | 168.4 |
| β | 115.1 | 115.3 | 115.1[f)] | 115.6[n)] | 115.2 |
| γ | 147.2 | 147.2 | 147.0 | 147.3[o)] | 147.3 |
| OMe | 56.5 | 56.5 | 56.5[g)] | 56.5 | 56.5 |
| Fer ($R_4$) | | | | | |
| 1 | 127.4 | 127.5 | 127.4[b)] | 127.6[h)] | 127.8 |
| 2 | 111.5 | 111.7 | 111.5[c)] | 111.6[i)] | 115.3 |
| 3 | 149.3 | 149.2 | 149.3 | 149.3 | 148.4 |
| 4 | 150.7 | 150.6 | 150.7[d)] | 150.8[j)] | 149.7 |
| 5 | 116.5 | 116.5 | 116.5 | 116.6[k)] | 116.2 |
| 6 | 124.3 | 124.3 | 124.3[e)] | 124.3[l)] | 127.0 |
| α | 167.8 | 167.8 | 168.0 | 167.3[m)] | 166.7 |
| β | 115.0 | 115.0 | 115.1[f)] | 115.1[n)] | 115.7 |
| γ | 147.2 | 147.2 | 147.2 | 147.2[o)] | 145.9 |
| OMe | 56.4 | 56.5 | 56.4[g)] | 56.5 | 56.5 |

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

**Isolation** *Polygala senega* var. *latifolia* TORR. *et* GRAY (3 kg) were extracted twice with hot water (40 l). The extract was passed through a Mitsubishi Diaion HP-20 column (9 × 50 cm) and the adsorbed material 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). The 70% MeOH aq. eluate was chromatographed on a silica gel (250 g) column using $CHCl_3$–MeOH (75 : 25) as a mobile phase to give fractions 1 (81 mg), 2 (1.9 g), 3 (345 mg), 4 (390 mg), 5 (12.0 g), 6 (238 mg); in addition, $CHCl_3$–MeOH (72 : 28) was used to give fraction 7 (180 mg). From fraction 5, oligosaccharides were isolated by preparative HPLC [Develosil Lop-ODS 5 × 50 cm, $CH_3CN$–$H_2O$ (18 : 82)—(38 : 62) with linear gradient elution]: **1** (6.56 g), **2** (855 mg), **3** (1.08 g), **4** (192 mg), **5** (264 mg).

**Senegose A (1)** Amorphous powder. $[\alpha]_D^{23}$ $-9.9°$ ($c = 1.16$, MeOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log $\varepsilon$): 220 (4.52), 233 (4.52), 284 (sh 4.31), 299 (sh 4.42), 328 (4.59). *Anal.* Calcd for $C_{61}H_{76}O_{35} \cdot 9/2H_2O$: C, 50.52; H, 5.91. Found: C, 50.50; H, 5.93. FAB-MS *m/z*: 1391 $[M+Na]^+$, 1369 $[M+H]^+$. $^1$H- and $^{13}$C-NMR: Tables I and II.

**Senegose B (2)** Amorphous powder. $[\alpha]_D^{23}$ $-10.2°$ ($c = 1.17$, MeOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log $\varepsilon$): 220 (4.58), 233 (4.58), 284 (sh 4.39), 299 (sh 4.48), 327 (4.64). *Anal.* Calcd for $C_{59}H_{74}O_{34} \cdot H_2O$: C, 52.68; H, 5.69. Found: C, 52.43; H, 5.78. FAB-MS *m/z*: 1349 $[M+Na]^+$, 1327 $[M+H]^+$. $^1$H- and $^{13}$C-NMR: Tables I and II.

**Senegose C (3)** Amorphous powder. $[\alpha]_D^{23}$ $-16.0°$ ($c = 1.29$, MeOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log $\varepsilon$): 219 (4.52), 233 (4.53), 284 (sh 4.31), 297 (sh 4.43), 327 (4.61). *Anal.* Calcd for $C_{59}H_{74}O_{34} \cdot 2H_2O$: C, 51.98; H, 5.77. Found: C, 51.80; H, 5.78. FAB-MS *m/z*: 1349 $[M+Na]^+$, 1327 $[M+H]^+$. $^1$H- and $^{13}$C-NMR: Tables I and II.

**Senegose D (4)** Amorphous powder. $[\alpha]_D^{23}$ $-6.9°$ ($c = 1.01$, MeOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log $\varepsilon$): 220 (4.45), 233 (4.47), 284 (sh 4.25), 299 (sh 4.39), 325 (4.53). *Anal.* Calcd for $C_{57}H_{72}O_{33} \cdot 2H_2O$: C, 51.82; H, 5.80. Found: C, 51.82; H, 5.78. FAB-MS *m/z*: 1307 $[M+Na]^+$, 1285 $[M+H]^+$. $^1$H- and $^{13}$C-NMR: Tables I and II.

**Senegose E (5)** Amorphous powder. $[\alpha]_D^{23}$ $+64.5°$ ($c = 0.61$, MeOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log $\varepsilon$): 220 (4.55), 232 (4.55), 284 (sh 4.29), 301 (sh 4.41), 327 (4.56). *Anal.* Calcd for $C_{61}H_{76}O_{35} \cdot 3H_2O$: C, 51.48; H, 5.81. Found: C, 51.49; H, 5.80. FAB-MS *m/z*: 1391 $[M+Na]^+$, 1369 $[M+H]^+$. $^1$H- and $^{13}$C-NMR: Tables I and II.

**Acetylation of 1—5** 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**—**4**, **1b** was obtained as an amorphous powder. **1b**: $^1$H-NMR ($CDCl_3$) $\delta$: 1.77, 1.95, 1.964, 1.99, 2.03, 2.05, 2.07, 2.080, 2.082, 2.10 (each 3H, s, aliphatic OAc), 1.960, 2.06 (each 6H, s, aliphatic OAc), 2.335, 2.343 (each 3H, s, aromatic OAc), 3.90, 3.93 (each 3H, s, OMe), 4.65 (each 1H, d, $J = 8$ Hz, H-1 of Glc), 5.68 (1H, d, $J = 3.5$ Hz, H-1 of Glc-1), 6.29, 6.51 (each 1H, d, $J = 16$ Hz, H-$\beta$ of fer.), 7.07, 7.10 (each 1H, d, $J = 8$ Hz, H-5 of fer.), 7.14, 7.17 (each 1H, dd, $J = 8$, 2 Hz, H-6 of fer.), 7.19, 7.22 (each 1H, d, $J = 2$ Hz, H-2 of fer.), 7.49 (2H, t, $J = 8$ Hz, H-3, H-5 of benz.), 7.60 (1H, tt, $J = 8$, 1 Hz, H-4 of benz.), 7.64, 7.77 (each 1H, d, $J = 16$ Hz, H-$\gamma$ of fer.), 8.11 (2H, dd, $J = 8$, 1 Hz, H-2, H-6 of benz.). FAB-MS *m/z*: 1980 $[M+Na]^+$, 1958 $[M+H]^+$. From **5**, **5b** was obtained as an amorphous powder. **5b**: $^1$H-NMR ($CDCl_3$) $\delta$: 1.948, 1.954, 1.96, 1.98, 1.99, 2.02, 2.03, 2.05, 2.06, 2.07, 2.08, 2.09, 2.10, 2.16 (each 3H, s, aliphatic OAc), 2.326, 2.332 (each 3H, s, aromatic OAc), 3.91 (3H, s, OMe of fer.), 3.93 (3H, s, OMe of *cis*-fer.), 4.60 (each 1H, d, $J = 8$ Hz, H-1 of Glc), 5.68 (1H, d, $J = 3.5$ Hz, H-1 of Glc-1), 5.75 (1H, d, $J = 13$ Hz, H-$\beta$ of *cis*-fer.), 6.51 (1H, d, $J = 16$ Hz, H-$\beta$ of fer.), 6.83 (1H, d, $J = 13$ Hz, H-$\gamma$ of *cis*-fer.), 7.07 (1H, d, $J = 8$ Hz, H-5 of fer.), 7.09 (1H, d, $J = 8$ Hz, H-5 of *cis*-fer.), 7.18 (1H, dd, $J = 8$, 2 Hz, H-6 of fer.), 7.19 (1H, d, $J = 2$ Hz, H-2 of fer.), 7.23 (1H, dd, $J = 8$, 2 Hz, H-6 of *cis*-fer.), 7.49 (2H, t, $J = 8$ Hz, H-3, H-5 of benz.), 7.62 (1H, tt, $J = 8$, 1 Hz, H-4 of benz.), 7.78 (1H, d, $J = 16$ Hz, H-$\gamma$ of fer.), 7.84 (1H, d, $J = 2$ Hz, H-2 of *cis*-fer.), 8.08 (2H, dd, $J = 8$, 1 Hz, H-2, H-6 of benz.). FAB-MS *m/z*: 1980 $[M+Na]^+$, 1958 $[M+H]^+$.

**Alkaline Hydrolysis of 1** Compound **1** (100 mg) was treated with 5% NaOH aq. (*ca.* 2 ml) for 4 h at room temperature under on $N_2$ atmosphere and the reaction mixture was then passed through a column filled with Amberlite IR-120. The aqueous eluate of 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. **1a**: $^1$H-NMR ($D_2O$): $\delta$ 4.23 (1H, d, $J = 8$ Hz, H-1 of Glc-4), 4.44 (1H, d, $J = 8$ Hz, H-1 of Glc-3), 4.59 (1H, $J = 8$ Hz, H-1 of Glc-2), 5.28 (1H, $J = 3.5$ Hz, H-1 of Glc-1). $^{13}$C-NMR ($D_2O$): $\delta$ 60.9 (2C), 61.4, 61.7, 61.9, 63.2, 68.6, 70.3, 70.5, 72.9, 74.0, 74.2, 74.3, 74.8, 75.3, 75.6, 76.3, 76.7, 76.8 (3C), 79.5, 79.6, 80.2, 82.4, 92.8, 102.7, 103.4, 104.0, 104.8. Dioxane ($\delta$ 3.73, 67.3) was used as an internal standard. FAB-MS $m/z$: 851 $[M+Na]^+$. $[\alpha]_D^{25}$ +21.8° ($c$=1.40, $H_2O$).

**Alkaline Hydrolysis of 1—5** 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 aqueous eluate of the reaction mixture **1**—**5** a pentasaccharide **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[5] $t_R$ 8.0 min]. From the methanol eluate of the reaction mixture **1**—**4** benzoic and ferulic acids were identified and from that of the reaction mixture **5** benzoic, ferulic and *cis*-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, $t_R$ 9.9 min (ferulic acid); 10.4 min (*cis*-ferulic acid); 15.0 min (benzoic acid)].

**Acid Hydrolysis of 1—5** 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**—**5**, glucose and fructose were detected in the ratio 4 : 1 by HPLC [Asahipak NH2P-50 4.6 mm × 25 cm, $CH_3CN$–$H_2O$ (80 : 20), 1.0 ml/min, UV 195 nm, $t_R$ 8.1 min (fructose); 10.5 min (glucose)].

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