Bioactive Constituents from Chinese Natural Medicines. XXII.[1] Absolute Structures of New Megastigmane Glycosides, Sedumosides E_1, E_2, E_3, F_1, F_2, and G, from *Sedum sarmentosum* (Crassulaceae)

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Six new megastigmane glycosides, sedumosides E_1, E_2, E_3, F_1, F_2, and G, were isolated from the whole plant of *Sedum sarmentosum* (Crassulaceae). The structures of new constituents including the absolute configuration were elucidated on the basis of chemical and physicochemical evidence.

Key words *Sedum sarmentosum*; sedumoside; sarmentol; megastigmane; Chinese natural medicine; Crassulaceae

In the course of our characterization studies on bioactive constituents from Chinese natural medicines,[1—15] we have reported the isolation and absolute stereostructure elucidation of two megastigmanes, sarmentoic acid and sarmentol A, and six megastigmane glycosides, sedumosides A_1, A_2, A_3, B, C, and D, from the whole plant of *Sedum sarmentosum* (Crassulaceae) together with eight known megastigmane constituents. As a continuation of the characterization studies on *S. sarmantosum*, we have isolated six new megastigmane glycosides, sedumosides E_1 (**1**), E_2 (**2**), E_3 (**3**), F_1 (**4**), F_2 (**5**), and G (**6**), from this herbal medicine together with 33 known compounds (**7**—**39**). In this paper, we describe the isolation and absolute stereostructure elucidation of these new megastigmane glycosides (**1**—**6**).

The hot water extract from the whole plant of *S. sarmentosum* was treated with methanol to give the methanol-soluble part (0.57% from the fresh plant). The methanol-soluble part was subjected to Diaion HP-20 column chromatography (H_2O→MeOH) to give the water- and methanol-eluted fractions (0.44 and 0.13%, respectively) as previously reported.[1] The methanol-eluted fraction was subjected to normal- and reversed-phase silica gel column chromatographies, and finally HPLC to give **1** (0.00005%), **2** (0.00018%), **3** (0.00001%), **4** (0.00015%), **5** (0.00018%), **6** (0.00001%), (−)-pinoresinol 4,4′-di-*O*-β-D-glucopyranoside[16] (**7**, 0.00005%), (+)-isolariciresinol[17] (**8**, 0.00012%), woorenoside XI[17] (**9**, 0.00015%), (+)-isolariciresinol 3a-*O*-β-D-glucopyranoside[18] (**10**, 0.00003%), secoisolariciresinol[19] (**11**, 0.00010%), **12**[20] (0.00005%), (+)-lariciresinol 4-*O*-β-D-glucopyranoside[21] (**13**, 0.00007%), (+)-lariciresinol 4,4′-bis-*O*-β-D-glucopyranoside[22] (**14**, 0.00031%), apigenin 7-*O*-β-D-glucopyranoside[23,24] (**15**, 0.00005%), luteolin 7-*O*-β-D-glucopyranoside[23,25,26] (**16**, 0.00006%), tricin 7-*O*-β-D-glucopyranoside[26] (**17**, 0.00002%), kaempferol 7-*O*-β-D-glucopyranoside[23,27] (**18**, 0.00004%), **19**[28] (0.00015%), grosvenorine[29] (**20**, 0.00010%), quercetin 3,7-di-*O*-α-L-rhamnopyranoside[23,24] (**21**, 0.00007%), **22**[30] (0.00004%), isorhamnetin 7-*O*-β-D-glucopyranoside[26] (**23**, 0.00009%), **24**[31] (0.00005%), isorhamnetin 3,7-di-*O*-β-D-glucopyranoside[26] (**25**, 0.00014%), **26**[32,33] (0.00005%), herbacetin 8-methyl ester 3,7-di-*O*-β-D-glucopyranoside[34] (**27**, 0.00003%), limocitrin 3-*O*-β-D-glucopyranoside[26] (**28**, 0.00008%), limocitrin 3,7-di-*O*-β-D-glucopyranoside[26] (**29**, 0.00057%), 2-phenylethyl β-D-glucopyranoside[35] (**30**, 0.00001%), 2-phenylethyl D-rutinoside[35] (**31**, 0.00003%), eugenyl β-D-glucopyranoside[36] (**32**, 0.00007%), 4*R*-*p*-menth-1-ene-7,8-diol 7-*O*-β-D-glucopyranoside[37] (**33**, 0.00006%), 4*R*-*p*-menth-1-ene-7,8-diol 8-*O*-β-D-glucopyranoside[37,38] (**34**, 0.00004%), (*R*)-α-terpinyl β-D-glucopyranoside[39] (**35**, 0.00012%), octa-1-en-3-yl α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside[40] (**36**, 0.00043%), 1-acetyl β-carboline[41] (**37**, 0.00001%), **38**[42] (0.00003%), and **39**[42] (0.00005%).

Absolute Stereostructures of Sedumosides E_1 (1), E_2 (2), E_3 (3), F_1 (4), F_2 (5), and G (6) Sedumoside E_1 (**1**) was isolated as an amorphous powder with negative optical rotation ($[\alpha]_D^{24}$ −33.9° in MeOH). The IR spectrum of **1** showed absorption bands at 3431, 1081, and 1046 cm^{-1} ascribable to hydroxyl and ether functions. In the positive-ion fast atom bombardment (FAB)-MS of **1**, a quasimolecular ion peak was observed at *m/z* 545 $(M+Na)^+$. The molecular formula $C_{25}H_{46}O_{11}$ of **1** was determined by high-resolution

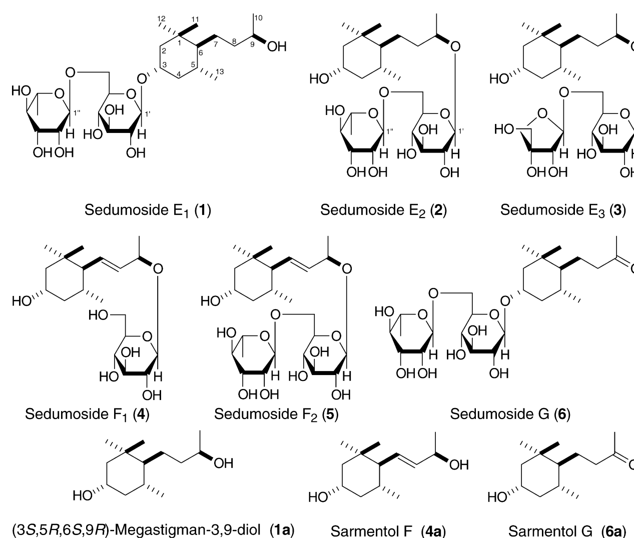

Chart 1

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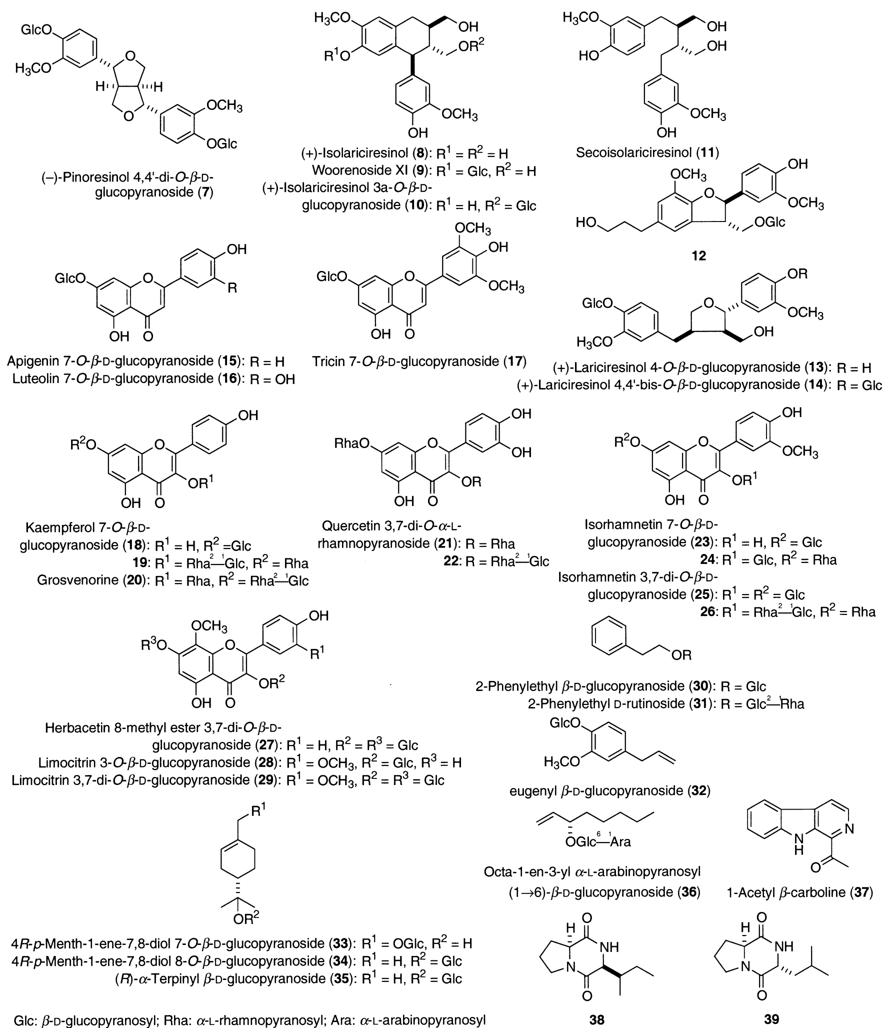

Chart 2

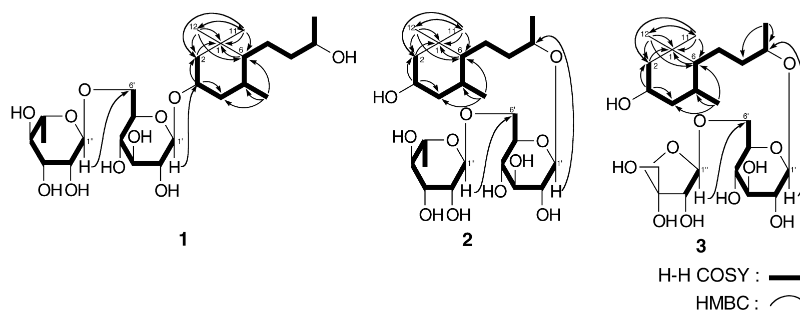

Fig. 1

positive-ion FAB-MS measurement. The acid hydrolysis of **1** with 1.0 M hydrochloric acid (HCl) liberated L-rhamnose and D-glucose, which were identified by HPLC analysis using an optical rotation detector.[1,2,4—6,9—12,14] The ^{1}H- (CD_3OD) and ^{13}C-NMR (Table 1) spectra[43] of **1** showed signals assignable to four methyls [δ 0.84, 0.96 (3H each, both s, 11, 12-H_3), 0.98, 1.14 (3H each, both d, J=6.4 Hz, 13, 10-H_3)], two methines bearing an oxygen function [δ 3.63 (1H, m, 9-H), 3.78 (1H, m, 3-H)], and a α-rhamnopyranosyl and a β-glucopyranosyl parts [δ 1.26 (3H, d, J=6.4 Hz, 6″-H_3), 4.32 (1H, d, J=8.0 Hz, 1′-H), 4.73 (1H, d, J=1.5 Hz, 1″-H)] together with four methylenes, two methines, and a quaternary carbon. Enzymatic hydrolysis of **1** with hesperidinase gave (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol (**1a**) as the aglycon, whose absolute stereostructure was determined by application of the modified Mosher's method.[44] The ^{1}H–^{1}H correlation spectroscopy (^{1}H–^{1}H COSY) experiment on **1** indicated the presence of three partial structures written in the bold lines as shown in Fig. 1. In the heteronuclear multiple bond correlations (HMBC) experiment of **1**, long-range correlations were observed between the following proton and carbon pairs (2-H_2 and 1-C; 6-H and 1-C; 3-H and 2, 4-C; 11-H_3 and 1, 2, 6, 12-C; 12-H_3 and 1, 2, 6, 11-C, 13-H_3 and 4, 5, 6-C; 1′-H and 3-C; 1″-H and 6′-C). Consequently, the structure

Table 1. ^{13}C-NMR Data for **1**—**6**, **4a**, and **6a**

Position	**1**$^{a)}$	**2**$^{a)}$	**3**$^{a)}$	**4**$^{a)}$	**4a**$^{b)}$	**5**$^{a)}$	**6**$^{a)}$	**6a**$^{b)}$
1	36.8	36.8	36.9	35.8	35.0	36.0	36.8	35.9
2	48.6	51.8	51.9	51.1	50.4	51.2	48.6	50.9
3	76.3	67.5	67.5	67.3	66.9	67.4	76.2	66.8
4	44.9	46.4	46.5	45.5	44.8	45.6	44.9	45.5
5	35.0	34.8	34.8	32.1	30.9	32.2	35.0	33.6
6	54.3	54.1	54.3	58.5	57.0	58.7	54.3	52.0
7	26.4	26.0	26.0	133.1	130.5	133.5	24.0	22.7
8	42.7	40.6	40.6	136.4	137.2	136.4	46.4	45.8
9	69.2	76.6	76.4	78.0	69.0	78.2	211.9	209.0
10	23.4	20.0	20.0	21.6	23.7	21.6	29.9	29.9
11	21.4	21.6	21.6	21.8	21.4	21.8	21.3	20.9
12	31.3	31.4	31.5	32.2	31.3	32.4	31.3	30.7
13	21.6	21.6	21.6	21.9	21.1	21.9	21.5	20.9
1′	103.0	102.3	102.3	102.2		102.4	103.1	
2′	75.2	75.1	75.2	75.3		75.4	75.2	
3′	78.1	78.1	78.2	78.0		78.3	78.1	
4′	71.7	71.5	71.8	71.2		71.5	71.8	
5′	76.7	76.7	76.9	77.9		76.8	76.7	
6′	68.0	68.5	68.7	62.4		67.9	68.0	
1″	102.2	102.3	111.0			102.2	102.2	
2″	72.3	72.2	78.0			72.2	72.3	
3″	72.4	72.4	80.6			72.4	72.4	
4″	74.3	74.0	75.0			74.1	74.3	
5″	69.8	69.7	65.8			69.8	69.8	
6″	18.2	18.2				18.2	18.1	

a) Measured in CD_3OD and *b*) $CDCl_3$ at 125 MHz.

and positions of oligosugar moieties in **1** was clarified and thus the absolute stereostructure of sedumoside E_1 was elucidated to be (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol 3-*O*-α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside (**1**).

Sedumoside E_2 (**2**) was obtained as an amorphous powder with a negative optical rotation ($[\alpha]_D^{22}$ $-38.6°$ in MeOH) and determined as the same molecular formula of **1** from the quasimolecular ion peak at *m/z* 545 $(M+Na)^+$ in the positive-ion FAB-MS and by high resolution positive-ion FAB-MS measurement. On the other hand, sedumoside E_3 (**3**) was also obtained as an amorphous powder with negative optical rotation ($[\alpha]_D^{21}$ $-41.5°$ in MeOH) and its molecular formula, $C_{24}H_{44}O_{11}$, was determined from the positive-ion FAB-MS [*m/z* 531 $(M+Na)^+$] and by high resolution positive-ion FAB-MS measurement. The IR spectra of **2** and **3** showed similar absorption bands (**2**: 3432, 1069, and 1046 cm^{-1}; **3**: 3339, 1089, and 1028 cm^{-1}) ascribable to hydroxyl and ether functions. Treatment of **2** and **3** with 1 M HCl liberated D-glucose (from **2**, **3**) and L-rhamnose (from **2**) or D-apiose[45—47] (from **3**), which were identified by HPLC analysis using an optical rotation detector.[1,2,4—6,9—12,14] Enzymatic hydrolysis of **2** and **3** with hesperidinase gave (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol (**1a**)[44] as the common aglycon. The ^{1}H-(CD_3OD) and ^{13}C-NMR (Table 1) spectra[43] of **2** showed signals assignable to an aglycon part {four methyls [δ 0.83, 0.94 (3H each, both s, 11, 12-H_3), 0.97, 1.17 (3H each, both d, J=6.4 Hz, 13, 10-H_3)] and two methines bearing an oxygen function [δ 3.69 (1H, m, 3-H), 3.77 (1H, m, 9-H)]} together with a α-rhamnopyranosyl and a β-glucopyranosyl parts [δ 1.26 (3H, d, J=6.1 Hz, 6″-H_3), 4.29 (1H, d, J=7.7 Hz, 1′-H), 4.73 (1H, d, J=1.6 Hz, 1″-H)]. The proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra of **3** were superimposable on those of **2**, except for the terminal β-D-apiofuranosyl part [δ 5.00 (1H, d, J=2.5 Hz, 1″-H)]. As shown in Fig. 1, the ^{1}H–^{1}H COSY experiment on **2** and **3** indicated the presence of partial structures written in bold lines, and in the HMBC experiment, long-range correlations were observed between the following protons and carbons (1′-H and 9-C; 1″-H and 6′-C, respectively). Consequently, the structures and positions of oligosugar moieties in **2** and **3** were clarified and thus the absolute stereostructures of sedumosides E_2 and E_3 were elucidated to be (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol 9-*O*-α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside (**2**) and (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol 9-*O*-β-D-apiofuranosyl(1→6)-β-D-glucopyranoside (**3**), respectively.

Sedumoside F_1 (**4**) was obtained as an amorphous powder with a negative optical rotation ($[\alpha]_D^{24}$ $-11.2°$ in MeOH). The molecular formula, $C_{19}H_{34}O_7$, of **4** was determined from the positive-ion FAB-MS [*m/z* 397 $(M+Na)^+$] and by high resolution positive-ion FAB-MS measurement. Sedumoside F_2 (**5**), $[\alpha]_D^{24}$ $-26.0°$ (MeOH), was also obtained as an amorphous powder and the molecular formula, $C_{25}H_{44}O_{11}$, of **5** was determined from the positive-ion FAB-MS data and by high resolution positive-ion FAB-MS measurement. Treatment of **4** and **5** with 1 M HCl liberated L-rhamnose (from **5**) and D-glucose (from **4**, **5**), which were identified by HPLC analysis using an optical rotation detector.[1,2,4—6,9—12,14] The ^{1}H- (CD_3OD) and ^{13}C-NMR (Table 1) spectra[43] of **4** showed signals assignable to four methyls [δ 0.82 (3H, d, J=6.4 Hz, 13-H_3), 0.88, 0.90 (3H each, both s, 11, 12-H_3), 1.28 (3H, d, J=6.4 Hz, 10-H_3)], two methines bearing an oxygen function [δ 3.73 (1H, m, 3-H), 4.35 (1H, m, 9-H)], an *trans*-olefin pair [δ 5.35 (1H, dd, J=9.8, 15.6 Hz, 7-H), 5.53 (1H, dd, J=7.0, 15.6 Hz, 8-H)] together with a β-glucopyranosyl moiety [δ 4.35 (1H, d, J=7.9 Hz, 1′-H)]. The proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra of **5** were superimposable on those of **4**, except for the signals

due to an additional α-L-rhamnopyranosyl moiety [δ 1.27 (3H, d, J=6.1 Hz, 6″-H$_3$), 4.71 (1H, d, J=1.5 Hz, 1″-H)]. Enzymatic hydrolysis of **4** with β-glucosidase gave a new megastigmane, sarmentol F (**4a**), as the aglycon. The aglycon (**4a**) was also obtained by the treatment of **5** with hesperidinase. The proton and carbon signals in the ^{1}H- (CDCl$_3$) and ^{13}C-NMR (Table 1) spectra[43] of **4a** indicated the presence of four methyls [δ 0.82 (3H, d, J=6.4 Hz, 13-H$_3$), 0.84, 0.88 (3H each, both s, 11, 12-H$_3$), 1.27 (3H, d, J=6.1 Hz, 10-H$_3$)] and two methines bearing an oxygen function [δ 3.79 (1H, m, 3-H), 4.30 (1H, m, 9-H)] together with *trans*-olefin pair [δ 5.29 (1H, dd, J=9.2, 15.6 Hz, 7-H), 5.50 (1H, dd, J=6.4, 15.6 Hz, 8-H)]. The ^{1}H–^{1}H COSY experiment on **4** and **5** indicated the presence of partial structures written in bold lines, and in the HMBC experiment, long-range correlations were observed between the following protons and carbons as shown in Fig. 2. Consequently, the planar structures of **4** and **5** including the positions of the glycosidic linkages were determined. Next, the relative stereostructures of **4** and **5** were elucidated using nuclear Overhauser enhancement spectroscopy (NOESY), which showed NOE correlations between the following proton pairs (2α-H and 6-H, 12-H$_3$; 2β-H and 3-H; 3-H and 4β-H; 4α-H and 6-H, 13-H$_3$; 6-H and 12-H$_3$; 7-H and 11-H$_3$). To clarify the absolute stereostructures of **4** and **5**, we carried out the conversion of **4a** into **1a**. Thus, hydrogenation of **4a** with 10% palladium carbon (Pd–C) under an H$_2$ atmosphere gave **1a**, so that the absolute stereostructures of sarmentol F was elucidated to be *trans*-(3*S*,5*R*,6*S*,9*R*)-megastigm-7-en-3,9-diol (**4a**). On the basis of above-mentioned evidence, the stereostructures of sedumosides F$_1$ and F$_2$ were determined to be sarmentol F 9-*O*-β-D-glucopyranoside (**4**) and sarmentol F 9-*O*-α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside (**5**).

Sedumoside G (**6**) was obtained as an amorphous powder and exhibited a negative optical rotation ($[\alpha]_D^{19}$ −35.7° in MeOH). The IR spectrum of **6** showed absorption bands at 3406, 1716, 1066, and 1047 cm^{-1} assignable to hydroxyl, carbonyl, and ether functions. In the positive-ion FAB-MS of **6**, a quasimolecular ion peak was observed at m/z 543 (M+Na)$^+$ and high-resolution FAB-MS analysis revealed the molecular formula of **6** to be $C_{25}H_{44}O_{11}$. The acid hydrolysis of **6** with 1.0 M HCl liberated L-rhamnose and D-glucose, which were identified by HPLC analysis using an optical rotation detector.[1,2,4—6,9—12,14] Enzymatic hydrolysis of **6** with hesperidinase gave a new megastigmane, sarmentol G (**6a**), as the aglycon. The proton and carbon signals in the ^{1}H-(CDCl$_3$) and ^{13}C-NMR (Table 1) spectra[43] of **6a** indicated the presence of four methyls [δ 0.95 (3H, d, J=6.9 Hz, 13-H$_3$), 0.82, 0.94 (3H each, both s, 11, 12-H$_3$), 2.14 (3H, s, 10-H$_3$)] and a methine bearing an oxygen function [δ 3.77 (1H, m, 3-H)] together with an carbonyl carbon [δ_C 209.0 (9-C)]. The ^{1}H- (CD$_3$OD) and ^{13}C-NMR (Table 1) spectra[43] of **6** showed signals assignable to an aglycon part [δ 0.85, 0.95 (3H each, both s, 11, 12-H$_3$), 0.97 (3H, d, J=6.5 Hz, 13-H$_3$), 2.12 (3H, s, 10-H$_3$), 3.78 (1H, m, 3-H)], together with a β-glucopyranosyl and a α-rhamnopyranosyl moieties [δ 1.26 (3H, d, J=6.3 Hz, 6″-H$_3$), 4.32 (1H, d, J=7.9 Hz, 1′-H), 4.73 (1H, d, J=1.8 Hz, 1″-H)]. The ^{1}H–^{1}H COSY experiment on **6** indicated the presence of partial structures written in bold lines, and in the HMBC experiment, long-range correlations were observed between the 1′-proton and the 3-carbon (δ_C 76.2) and between the 1″-proton and 6′-carbon (δ_C 68.0) as shown in Fig. 3. Consequently, the connectivity of oligosugar part in **6** was clarified to be the 3-position of **6a**. The relative

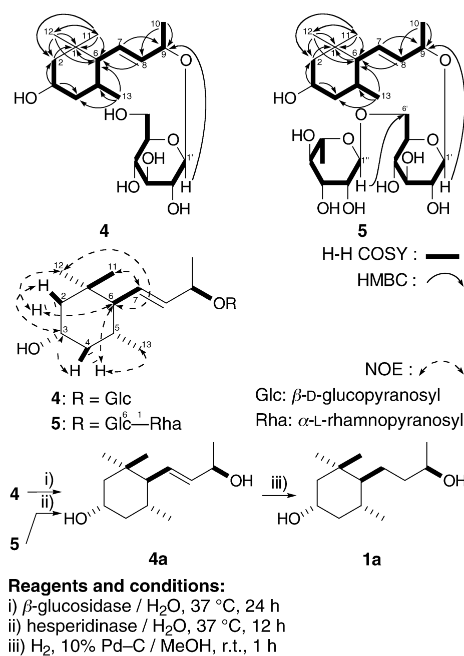

Fig. 2

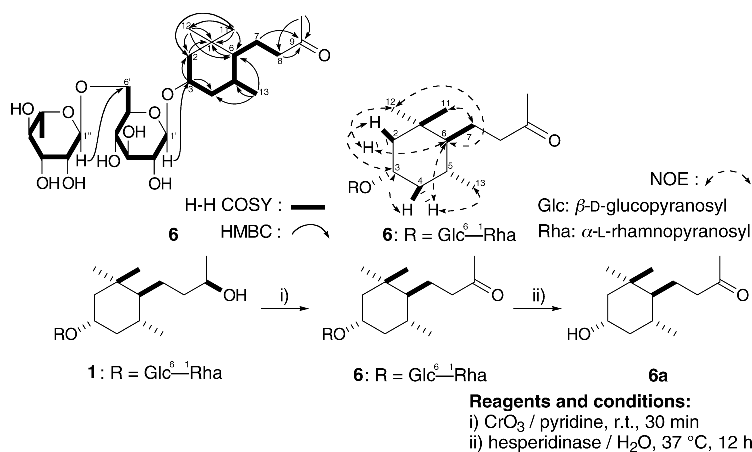

Fig. 3

stereostructure of **6** was characterized by NOESY experiment, which showed NOE correlations between the following proton pairs (2α-H and 12-H_3; 2β-H and 3-H; 3-H and 4β-H; 4α-H and 6-H, 13-H_3; 6-H and 12-H_3; 7-H_2 and 11-H_3). Finally, compound **6** was derived by selective oxidation of the aglycon part in **1** with chromium trioxide (CrO_3)–pyridine as shown in Fig. 3. Consequently, the absolute stereostructures of sarmentol G and sedumoside G were clarified to be (3*S*,5*R*,6*S*)-9-oxo-megastigman-3-ol (**6a**) and its 3-*O*-α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside (**6**).

Experimental

The following instruments were used to obtain physical data: specific rotations, Horiba SEPA-300 digital polarimeter (l=5 cm); CD spectra, JASCO J-720WI spectrometer; UV spectra, Shimadzu UV-1600 spectrometer; IR spectra, Shimadzu FTIR-8100 spectrometer; EI-MS, CI-MS and high-resolution MS, JEOL JMS-GCMATE mass spectrometer; FAB-MS and high-resolution MS, JEOL JMS-SX 102A mass spectrometer; ^{1}H-NMR spectra, JEOL EX-270 (270 MHz) and JNM-LA500 (500 MHz) spectrometers; ^{13}C-NMR spectra, JEOL EX-270 (68 MHz) and JNM-LA500 (125 MHz) spectrometers with tetramethylsilane as an internal standard; and HPLC detector, Shimadzu RID-6A refractive index and SPD-10A*vp* UV–VIS detectors. HPLC column, Cosmosil 5C_{18}-MS-II (Nacalai Tesque Inc., 250×4.6 mm i.d.) and (250×20 mm i.d.) columns were used for analytical and preparative purposes, respectively.

The following experimental conditions were used for chromatography: ordinary-phase silica gel column chromatography, Silica gel BW-200 (Fuji Silysia Chemical, Ltd., Aichi, Japan, 150—350 mesh); reversed-phase silica gel column chromatography, Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., Aichi, Japan, 100—200 mesh); TLC, precoated TLC plates with Silica gel 60F_{254} (Merck, 0.25 mm) (ordinary phase) and Silica gel RP-18 F_{254S} (Merck, 0.25 mm) (reversed phase); reversed-phase HPTLC, precoated TLC plates with Silica gel RP-18 WF_{254S} (Merck, 0.25 mm); and detection was achieved by spraying with 1% $Ce(SO_4)_2$–10% aqueous H_2SO_4 followed by heating.

Plant Material *S. sarmentosum* was cultivated at Huangshan, Anhui province, China and plant material was identified by one of authors (M. Y.). A voucher specimen (2005.01. Eishin-02) of this plant is on file in our laboratory.[1)]

Extraction and Isolation The hot water extract (1950 g) from the fresh whole plant of *S. sarmentosum* (Huangshan, Anhui province, China, 1.25% from this herbal medicine) was extracted three times with methanol under reflux for 3 h. Evaporation of the solvent under reduced pressure provided a methanolic extract (887.5 g, 0.57%), and an aliquot (398.6 g) was subjected to Diaion HP-20 column chromatography (4.0 kg, H_2O→MeOH, twice) to give H_2O- and MeOH-eluted fractions (305.0 and 93.6 g, respectively). The methanol-eluted fraction (72.0 g) was subjected to normal-phase silica gel column chromatography [2.0 kg, $CHCl_3$–MeOH–H_2O (10 : 3 : 0.5→7 : 3 : 1, v/v/v, lower layer)→MeOH] to give five fractions [Fr. 1 (12.1 g), Fr. 2 (19.2 g), Fr. 3 (10.4 g), Fr. 4 (8.7 g), and Fr. 5 (16.3 g)]. Fraction 1 (12.1 g) was subjected to reversed-phase silica gel column chromatography [300 g, MeOH–H_2O (5 : 95→10 : 90→20 : 80→30 : 70→50 : 50→70 : 30, v/v)→MeOH] to afford 13 fractions [Fr. 1-1 (550 mg), Fr. 1-2 (980 mg), Fr. 1-3 (1460 mg), Fr. 1-4 (1230 mg), Fr. 1-5 (1510 mg), Fr. 1-6 (1800 mg), Fr. 1-7 (540 mg), Fr. 1-8 (600 mg), Fr. 1-9 (710 mg), Fr. 1-10 (220 mg), Fr. 1-11 (1170 mg), Fr. 1-12 (1030 mg), and Fr. 1-13 (150 mg)], which were described previously.[1)] Fraction 1-5 (1510 mg) was purified by Sephadex LH-20 column chromatography [150 g, MeOH–H_2O (1 : 1, v/v)] and finally HPLC [MeOH–H_2O (35 : 65, v/v)] to furnish **38** (14.6 mg, 0.00003%), and **39** (24.5 mg, 0.00005%) together with sarmentol A (125.8 mg, 0.00023%), which was described previously.[1)] Fraction 1-6 (1800 mg) was purified by Sephadex LH-20 column chromatography [150 g, $CHCl_3$–MeOH (1 : 1, v/v)] and finally HPLC [MeOH–H_2O (42 : 58, v/v)] to furnish (+)-isolariciresinol (**8**, 64.7 mg, 0.00012%) and eugenyl β-D-glucopyranoside (**32**, 37.3 mg, 0.00007%). Fraction 1-7 (540 mg) was purified by Sephadex LH-20 column chromatography [150 g, $CHCl_3$–MeOH (1 : 1, v/v)] and finally HPLC [MeOH–H_2O (40 : 60, v/v)] to furnish secoisolariciresinol (**11**, 56.3 mg, 0.00010%) together with myrsinionoside A (48.5 mg, 0.00009%), which was described previously.[1)] Fraction 1-9 (710 mg) was purified by Sephadex LH-20 column chromatography [150 g, $CHCl_3$–MeOH (1 : 1, v/v)] and finally HPLC [MeOH–H_2O (50 : 50, v/v)] to furnish (*R*)-α-terpinyl β-D-glucopyranoside (**35**, 10.6 mg, 0.00002%) together with (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol (**1a**, 14.8 mg, 0.00003%), which was described previously.[1)] Fraction 1-12 (1030 mg) was crystallized in MeOH to give tricin 7-*O*-β-D-glucopyranoside (**17**, 295.3 mg, 0.00055%) and the mother liquid was purified by HPLC [MeOH–H_2O (60 : 40, v/v)] to furnish 1-acetyl β-carbolin (**37**, 3.6 mg, 0.00001%). Fraction 2 (19.2 g) was subjected to reversed-phase silica gel column chromatography [600 g, MeOH–H_2O (20 : 80→30 : 70→40 : 60→70 : 30, v/v)→MeOH] to afford 12 fractions [Fr. 2-1 (200 mg), Fr. 2-2 (4630 mg), Fr. 2-3 (1160 mg), Fr. 2-4 (1950 mg), Fr. 2-5 (3300 mg), Fr. 2-6 (650 mg), Fr. 2-7 (700 mg), Fr. 2-8 (1800 mg), Fr. 2-9 (810 mg), Fr. 2-10 (1360 mg), Fr. 2-11 (2270 mg), and Fr. 2-12 (770 mg)]. Fraction 2-4 (1950 mg) was subjected to normal-phase silica gel column chromatography [100 g, $CHCl_3$→$CHCl_3$–MeOH (50 : 1→20 : 1→10 : 1, v/v)→$CHCl_3$–MeOH–H_2O (20 : 3 : 1, v/v/v, lower layer)→MeOH] to give seven fractions [Fr. 2-4-1 (90.5 mg), Fr. 2-4-2 (50.1 mg), Fr. 2-4-3 (284.0 mg), Fr. 2-4-4 (153.8 mg), Fr. 2-4-5 (348.2 mg), Fr. 2-4-6 (721.1 mg), and Fr. 2-4-7 (300.0 mg)], which were described previously.[1)] Fraction 2-4-2 (50.1 mg) was further purified by HPLC [MeOH–H_2O (32 : 68, v/v)] to furnish 2-phynylethyl β-D-glucopyranoside (**30**, 5.0 mg, 0.00001%). Fraction 2-4-5 (348.2 mg) was further purified by HPLC [CH_3CN–MeOH–H_2O (10 : 8 : 82, v/v/v) and MeOH–H_2O (30 : 70 or 32 : 68, v/v)] to furnish 4*R*-*p*-menth-1-ene-7,8-diol 7-*O*-β-D-glucopyranoside (**33**, 31.3 mg, 0.00006%) and 4*R*-*p*-menth-1-ene-7,8-diol 8-*O*-β-D-glucopyranoside (**34**, 22.9 mg, 0.00004%) together with sedumoside D (43.0 mg, 0.00008%), staphylionoside D (3.2 mg, 0.00001%), and 3-hydroxy-5,6-epoxy-β-ionol 9-*O*-β-D-glucopyranoside (22.0 mg, 0.00004%), which were described previously.[1)] Fraction 2-4-6 (721.1 mg) was further purified by HPLC [MeOH–H_2O (32 : 68, v/v)] to give woorenoside XI (**9**, 58.7 mg, 0.00011%) together with sedumosides A_1 (162.5 mg, 0.00030%), A_2 (60.6 mg, 0.00011%), A_3 (29.2 mg, 0.00005%), and B (3.2 mg, 0.00001%), and alangioside A (52.8 mg, 0.00010%), which were described previously.[1)] Fraction 2-5 (3300 mg) was further separated by HPLC [CH_3CN–H_2O (15 : 85, v/v)] to furnish **9** (22.9 mg, 0.00004%), (+)-lariciresinol 4-*O*-β-D-glucopyranoside (**13**, 18.3 mg, 0.00003%), (+)-isolariciresinol 3a-*O*-β-D-glucopyranoside (**10**, 16.8 mg, 0.00003%), and 2-phenylethyl D-rutinoside (**31**, 5.5 mg, 0.00001%) together with sedumosides A_1 (34.0 mg, 0.00006%), A_2 (838.6 mg, 0.0016%), A_3 (200.9 mg, 0.00024%), and D (220.5 mg, 0.00041%), which were described previously.[1)] Fraction 2-8 (1800 mg) was purified by Sephadex LH-20 column chromatography [150 g, MeOH–H_2O (30 : 70, v/v)] and finally HPLC [CH_3CN–MeOH–H_2O (20 : 8 : 72, v/v/v) and MeOH–H_2O (40 : 60, v/v)] to furnish sedumosides F_1 (**4**, 82.5 mg, 0.00015%), F_2 (**5**, 22.6 mg, 0.00004%), G (**6**, 2.5 mg, 0.00001%), and **12** (25.1 mg, 0.00005%) together with sarmentoic acid (429.8 mg, 0.00080%), sarmentoic acid methyl ester (24.5 mg, 0.00005%), and alangioside J (80.9 mg, 0.00015%), which were described previously.[1)] Fraction 2-10 (1360 mg) was further separated by HPLC [CH_3CN–MeOH–H_2O (20 : 8 : 72, v/v/v) and MeOH–H_2O (40 : 60, v/v)] to furnish sedumosides E_1 (**1**, 5.1 mg, 0.00001%), E_2 (**2**, 21.7 mg, 0.00004%), and E_3 (**3**, 5.3 mg, 0.00001%), apigenin 7-*O*-β-D-glucopyranoside (**15**, 26.0 mg, 0.00005%), kaempferol 7-*O*-β-D-glucopyranoside (**18**, 20.6 mg, 0.00004%), **24** (28.9 mg, 0.00005%), and limocitrin 3-*O*-β-D-glucopyranoside (**28**, 43.3 mg, 0.00008%) together with myrsinionoside D (182.1 mg, 0.00034%) and alangioside J (21.2 mg, 0.00004%), which were described previously.[1)] Fraction 3 (10.4 g) was subjected to reversed-phase silica gel column chromatography [240 g, MeOH–H_2O (10 : 90→20 : 80→30 : 70→40 : 60, v/v)→MeOH] to afford 14 fractions [Fr. 3-1 (123.0 mg), Fr. 3-2 (675.1 mg), Fr. 3-3 (574.8 mg), Fr. 3-4 (1337 mg), Fr. 3-5 (797.8 mg), Fr. 3-6 (798.6 mg), Fr. 3-7 (230.3 mg), Fr. 3-8 (901.2 mg), Fr. 3-9 (645.6 mg), Fr. 3-10 (256.4 mg), Fr. 3-11 (511.7 mg), Fr. 3-12 (1238 mg), Fr. 3-13 (473.1 mg), and Fr. 3-14 (1320 mg)], which were described previously.[1)] Fraction 3-7 (230.3 mg) was purified by HPLC [MeOH–H_2O (29 : 71, v/v)] to give (−)-pinoresinol 4,4′-di-*O*-β-D-glucopyranoside (**7**, 25.6 mg, 0.00005%). Fraction 3-11 (512 mg) was purified by Sephadex LH-20 column chromatography [150 g, $CHCl_3$–MeOH (1 : 1, v/v)] and finally HPLC [MeOH–H_2O (40 : 60, v/v)] to furnish **5** (72.2 mg, 0.00013%). Fraction 3-12 (1238 mg) was purified by Sephadex LH-20 column chromatography [150 g, $CHCl_3$–MeOH (1 : 1, v/v)] and finally HPLC [MeOH–H_2O (45 : 55, v/v)] to give **1** (21.6 mg, 0.00004%) and **2** (73.8 mg, 0.00014%). Fraction 5 (8.7 g) was subjected to reversed-phase silica gel column chromatography [240 g, H_2O→MeOH–H_2O (10 : 90→20 : 80→30 : 70→40 : 60→50 : 50, v/v)→MeOH] to give 12 fractions [Fr. 5-1 (345.0 mg), Fr. 5-2 (408.3 mg), Fr. 5-3 (60.1 mg), Fr. 5-4 (318.3 mg), Fr. 5-5 (864.3 mg), Fr. 5-6 (664.5 mg), Fr. 5-7 (298.3 mg), Fr. 5-8 (672.4 mg), Fr. 5-9 (589.3 mg), Fr. 5-10 (1818 mg), Fr. 5-11 (388.1 mg), and Fr. 5-12

(1161 mg)]. Fr. 5-6 (664.5 mg) was purified by HPLC [CH_3CN–MeOH–H_2O (10 : 8 : 82, v/v/v)] to give (+)-lariciresinol 4,4′-bis-*O*-β-D-glucopyranoside (**14**, 167.7 mg, 0.00030%). Fr. 5-8 (229.8 mg) was crystallized in MeOH to give limocitrin 3,7-di-*O*-β-D-glucopyranoside (**29**, 295.3 mg, 0.00055%) and the mother liquid was purified by HPLC [CH_3CN–MeOH–H_2O (28 : 24 : 246, v/v/v)] to give herhacetin 8-methyl ester 3,7-di-*O*-β-D-glucopyranoside (**27**, 14.9 mg, 0.00003%). Fr. 5-9 (589.3 mg) was separated by Sephadex LH-20 column chromatography [150 g, $CHCl_3$–MeOH (1 : 1, v/v)] and finally HPLC [MeOH–H_2O (35 : 65, v/v)] to give isorhamnetin 3,7-di-*O*-β-D-glucopyranoside (**25**, 44.3 mg, 0.00008%) and limocitrin 3,7-di-*O*-β-D-glucopyranoside (**29**, 10.1 mg, 0.00002%). Fr. 5-10 (1818 mg) was separated by Sephadex LH-20 column chromatography [150 g, $CHCl_3$–MeOH (1 : 1, v/v)] and finally HPLC [MeOH–H_2O (35 : 65 or 40 : 60, v/v) or CH_3CN–MeOH–H_2O (15 : 8 : 77, v/v/v)] to give **19** (79.9 mg, 0.00015%), grosvenorine (**20**, 53.3 mg, 0.00010%), quercetin 3,7-di-*O*-β-D-glucopyranoside (**21**, 37.6 mg, 0.00007%), **22** (23.9 mg, 0.00004%), **25** (32.8 mg, 0.00006%), and **26** (26.8 mg, 0.00005%).

The known compounds were identified by comparison of their physical data ($[\alpha]_D$, IR, ^{1}H-, ^{13}C-NMR, MS) with reported values[16—22,24—32,34—42] or authentic samples.[23]

Sedumoside E_1 (**1**): An amorphous powder, $[\alpha]_D^{24}$ −33.9° (c=1.08, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{25}H_{46}O_{11}Na$ $(M+Na)^+$ 545.2938; Found 545.2933. IR (KBr, cm^{-1}): 3431, 2967, 2932, 1509, 1473, 1458, 1081, 1046. ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.54 (1H, ddd, J=2.4, 5.4, 11.3 Hz, 6-H), 0.84, 0.96 (3H each, both s, 11, 12-H_3), 0.98, 1.14 (3H each, both d, J=6.4 Hz, 13, 10-H_3), 1.02 (1H, ddd, J=11.6, 11.6, 11.6 Hz, 4α-H), 1.04, 1.43 (1H each, both m, 7-H_2), 1.14 (1H, dd, J=11.9, 11.9 Hz, 2α-H), 1.26 (3H, d, J=6.4 Hz, 6″-H_3), 1.46, 1.53 (1H each, both m, 8-H_2), 1.48 (1H, m, 5-H), 1.79 (1H, ddd, J=1.9, 3.7, 11.9 Hz, 2β-H), 2.04 (1H, m, 4β-H), 3.11 (1H, dd, J=8.0, 9.2 Hz, 2′-H), 3.26 (1H, dd, J=9.2, 9.2 Hz, 4′-H), 3.32 (1H, m, 3′-H), 3.35 (1H, m, 4″-H), 3.37 (1H, m, 5′-H), [3.59 (1H, dd, J=6.1, 11.0 Hz), 3.96 (1H, dd, J=1.8, 11.0 Hz), 6′-H_2], 3.63 (1H, m, 9-H), 3.64 (1H, m, 3″-H), 3.65 (1H, m, 5″-H), 3.78 (1H, m, 3-H), 3.82 (1H, dd, J=1.5, 3.7 Hz, 2″-H), 4.32 (1H, d, J=8.0 Hz, 1′-H), 4.73 (1H, d, J=1.5 Hz, 1″-H). ^{13}C-NMR (125 MHz, CD_3OD) δ_C: given in Table 1. Positive-ion FAB-MS m/z: 545 $(M+Na)^+$.

Sedumoside E_2 (**2**): An amorphous powder, $[\alpha]_D^{22}$ −38.6° (c=0.27, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{25}H_{46}O_{11}Na$ $(M+Na)^+$ 545.2938; Found 545.2932. IR (KBr, cm^{-1}): 3432, 2967, 2934, 1541, 1509, 1474, 1458, 1069, 1046. ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.51 (1H, ddd, J=2.5, 4.9, 11.1 Hz, 6-H), 0.83, 0.94 (3H each, both s, 11, 12-H_3), 0.90 (1H, ddd, J=11.9, 11.9, 11.9 Hz, 4α-H), 0.97, 1.17 (3H each, both d, J=6.4 Hz, 13, 10-H_3), 1.08, 1.55 (1H each, both m, 7-H_2), 1.08 (1H, dd, J=12.0, 12.0 Hz, 2α-H), 1.26 (3H, d, J=6.1 Hz, 6″-H_3), 1.55, 1.59 (1H each, both m, 8-H_2), 1.45 (1H, m, 5-H), 1.63 (1H, ddd, J=1.9, 3.7, 12.0 Hz, 2β-H), 1.87 (1H, m, 4β-H), 3.14 (1H, dd, J=7.7, 9.2 Hz, 2′-H), 3.25 (1H, dd, J=9.2, 9.2 Hz, 4′-H), 3.33 (1H, m, 3′-H), 3.37 (2H, m, 4″, 5′-H), [3.57 (1H, dd, J=6.4, 11.3 Hz), 3.97 (1H, dd, J=1.5, 11.3 Hz), 6′-H_2], 3.65 (1H, m, 5″-H), 3.67 (1H, m, 3″-H), 3.69 (1H, m, 3-H), 3.77 (1H, m, 9-H), 3.83 (1H, dd, J=1.6, 3.4 Hz, 2″-H), 4.29 (1H, d, J=7.7 Hz, 1′-H), 4.73 (1H, d, J=1.6 Hz, 1″-H). ^{13}C-NMR (125 MHz, CD_3OD) δ_C: given in Table 1. Positive-ion FAB-MS m/z: 545 $(M+Na)^+$.

Sedumoside E_3 (**3**): An amorphous powder, $[\alpha]_D^{21}$ −41.5° (c=0.35, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{24}H_{44}O_{11}Na$ $(M+Na)^+$: 531.2781. Found: 531.2774. IR (KBr, cm^{-1}): 3339, 2922, 1471, 1387, 1039, 1028. ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.51 (1H, ddd, J=2.4, 5.8, 11.0 Hz, 6-H), 0.83, 0.95 (3H each, both s, 11, 12-H_3), 0.90 (1H, ddd, J=12.2, 12.2, 12.2 Hz, 4α-H), 0.98 (3H, d, J=6.5 Hz, 13-H_3), 1.08, 1.54 (1H each, both m, 7-H_2), 1.08 (1H, dd, J=12.2, 12.2 Hz, 2α-H), 1.17 (3H, d, J=6.5 Hz, 10-H_3), 1.45 (1H, m, 5-H), 1.55, 1.59 (1H each, both m, 8-H_2), 1.63 (1H, ddd, J=2.4, 4.0, 12.2 Hz, 2β-H), 1.87 (1H, m, 4β-H), 3.14 (1H, dd, J=8.0, 9.2 Hz, 2′-H), 3.26 (1H, dd, J=9.2, 9.2 Hz, 4′-H), 3.33 (1H, m, 3′-H), 3.37 (1H, m, 5′-H), 3.57 (2H, s, 5″-H), [3.57 (1H, dd, J=6.1, 11.3 Hz), 3.97 (1H, dd, J=1.8, 11.3 Hz), 6′-H_2], 3.69 (1H, m, 3-H), 3.75, 3.94 (1H each, both d, J=9.8 Hz, 4″-H), 3.77 (1H, m, 9-H), 3.88 (1H, d, J=2.5 Hz, 2″-H), 4.29 (1H, d, J=8.0 Hz, 1′-H), 5.00 (1H, d, J=2.5 Hz, 1″-H). ^{13}C-NMR (125 MHz, CD_3OD) δ_C: given in Table 1. Positive-ion FAB-MS: m/z 531 $(M+Na)^+$.

Sedumoside F_1 (**4**): An amorphous powder, $[\alpha]_D^{24}$ −11.2° (c=1.14, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{19}H_{34}O_7Na$ $(M+Na)^-$: 397.2202. Found: 397.2206. IR (KBr, cm^{-1}): 3389, 2960, 2919, 1734, 1684, 1671, 1559, 1541, 1509, 1474, 1341, 1078, 1034. ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.82 (3H, d, J=6.4 Hz, 13-H_3), 0.88, 0.90 (3H each, both s, 11, 12-H_3), 0.90 (1H, ddd, J=12.2, 12.2, 12.2 Hz, 4α-H), 1.11 (1H, dd, J=12.2, 12.2 Hz, 2α-H), 1.32 (1H, dd, J=9.8, 10.4 Hz, 6-H), 1.28 (3H, d, J=6.4 Hz, 10-H_3), 1.53 (1H, m, 5-H), 1.69 (1H, ddd, J=2.2, 4.0, 12.2 Hz, 2β-H), 1.96 (1H, m, 4β-H), 3.17 (1H, m, 2′-H), 3.29 (1H, m, 4′-H), 3.30 (2H, m, 3′, 5′-H), [3.56 (1H, dd, J=4.6, 11.0 Hz), 3.79 (1H, dd, J=2.4, 11.0 Hz), 6′-H_2], 3.73 (1H, m, 3-H), 4.35 (1H, m, 9-H), 4.35 (1H, d, J=7.9 Hz, 1′-H), 5.35 (1H, dd, J=9.8, 15.6 Hz, 7-H), 5.53 (1H, dd, J=7.0, 15.6 Hz, 8-H). ^{13}C-NMR (125 MHz, CD_3OD) δ_C: given in Table 1. Positive-ion FAB-MS: m/z 397 $(M+Na)^+$.

Sedumoside F_2 (**5**): An amorphous powder, $[\alpha]_D^{24}$ −26.0° (c=1.08, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{25}H_{44}O_{11}Na$ $(M+Na)^+$: 543.2781. Found: 543.2776. IR (KBr, cm^{-1}): 3410, 2967, 2940, 1669, 1474, 1341, 1140, 1055, 968. ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.83 (3H, d, J=6.4 Hz, 13-H_3), 0.87, 0.91 (3H each, both s, 11, 12-H_3), 0.91 (1H, ddd, J=12.2, 12.2, 12.2 Hz, 4α-H), 1.12 (1H, dd, J=12.2, 12.2 Hz, 2α-H), 1.32 (1H, dd, J=9.8, 10.4 Hz, 6-H), 1.27 (3H, d, J=6.1 Hz, 6″-H_3), 1.28 (3H, d, J=6.1 Hz, 10-H_3), 1.54 (1H, m, 5-H), 1.69 (1H, ddd, J=1.9, 4.3, 12.2 Hz, 2β-H), 1.96 (1H, m, 4β-H), 3.16 (1H, dd, J=7.9, 8.6 Hz, 2′-H), 3.29 (1H, m, 4′-H), 3.30 (2H, m, 3′, 5′-H), 3.35 (1H, m, 4″-H), [3.56 (1H, dd, J=4.6, 11.0 Hz), 3.92 (1H, br d, J=*ca.* 11 Hz), 6′-H_2], 3.65 (1H, m, 5″-H), 3.68 (1H, dd, J=3.4, 9.8 Hz, 3″-H), 3.72 (1H, m, 3-H), 3.84 (1H, dd, J=1.5, 3.4 Hz, 2″-H), 4.31 (1H, m, 9-H), 4.32 (1H, d, J=7.9 Hz, 1′-H), 4.71 (1H, d, J=1.5 Hz, 1″-H), 5.35 (1H, dd, J=9.8, 15.6 Hz, 7-H), 5.52 (1H, dd, J=7.0, 15.6 Hz, 8-H). ^{13}C-NMR (125 MHz, CD_3OD) δ_C: given in Table 1. Positive-ion FAB-MS: m/z 543 $(M+Na)^+$.

Sedumoside G (**6**): An amorphous powder, $[\alpha]_D^{19}$ −35.7° (c=0.17, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{25}H_{44}O_{11}Na$ $(M+Na)^+$: 543.2781. Found: 543.2787. IR (KBr, cm^{-1}): 3406, 2932, 1716, 1456, 1368, 1066, 1047. ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.59 (1H, ddd, J=2.3, 5.3, 10.8 Hz, 6-H), 0.85, 0.95 (3H each, both s, 11, 12-H_3), 0.97 (3H, d, J=6.5 Hz, 13-H_3), 1.03 (1H, ddd, J=12.1, 12.1, 12.1 Hz, 4α-H), 1.15 (1H, dd, J=12.1, 12.1 Hz, 2α-H), 1.26 (3H, d, J=6.3 Hz, 6″-H_3), 1.31, 1.70 (1H each, both m, 7-H_2), 1.48 (1H, m, 5-H), 1.79 (1H, ddd, J=2.5, 4.4, 12.1 Hz, 2β-H), 2.05 (1H, m, 4β-H), 2.12 (3H, s, 10-H_3), [2.46 (1H, ddd, J=5.8, 11.0, 16.9 Hz), 2.59 (1H, ddd, J=5.2, 10.7, 16.9 Hz), 8-H_2], 3.11 (1H, dd, J=7.9, 9.2 Hz, 2′-H), 3.78 (1H, m, 3-H), 3.25 (1H, dd-like, 4′-H), 3.32 (1H, m, 3′-H), 3.35 (1H, m, 4″-H), 3.37 (1H, m, 5′-H), [3.59 (1H, dd, J=6.2, 11.1 Hz), 3.95 (1H, dd, J=1.7, 11.1 Hz), 6′-H_2], 3.65 (1H, m, 5″-H), 3.64 (1H, m, 3″-H), 3.82 (1H, dd, J=1.6, 3.5 Hz, 2″-H), 4.32 (1H, d, J=7.9 Hz, 1′-H), 4.73 (1H, d, J=1.8 Hz, 1″-H). ^{13}C-NMR (125 MHz, CD_3OD) δ_C: given in Table 1. Positive-ion FAB-MS: m/z 543 $(M+Na)^+$.

Acid Hydrolysis of 1—6 A solution of **1**—**6** (each 1.0 mg) in 1 M HCl (1.0 ml) was heated under reflux for 3 h. After cooling, the reaction mixture was extracted with EtOAc. The aqueous layers of **1**—**6** were subjected to HPLC analysis under the following conditions, respectively: HPLC column, Kaseisorb LC NH_2-60-5, 4.6 mm i.d.×250 mm (Tokyo Kasei Co., Ltd., Tokyo, Japan); detection, optical rotation [Shodex OR-2 (Showa Denko Co., Ltd., Tokyo, Japan); mobile phase, CH_3CN–H_2O (85 : 15, v/v); flow rate 0.8 ml/min]. Identification of D-apiose[45—47] (i) from **3**, L-rhamnose (ii) from **1**, **2**, **5**, or **6**, D-glucose (iii) from **1**—**6** present in the aqueous layer was carried out by comparison of its retention time and optical rotation with those of authentic samples, t_R: (i) 6.6 min (D-apiose, positive optical rotation), (ii) 7.8 min (L-rhamnose, negative optical rotation), and (iii) 13.9 min (D-glucose, positive optical rotation), respectively.

Enzymatic Hydrolysis of 1—3, 5, and 6 with Hesperidinase A solution of **1** (4.7 mg) in H_2O (1.0 ml) was treated with hesperidinase (11.6 mg, from *Aspergillus nigar*, Sigma) and the solution was stirred at 37 °C for 12 h. After EtOH was added to the reaction mixture, the solvent was removed under reduced pressure and the residue was purified by HPLC [MeOH–H_2O (55 : 45, v/v)] to furnish (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol (**1a**,[44] 1.3 mg, 64%). Through the similar procedure, a solution of **2** (17.3 mg), **3** (3.5 mg), **5** (21.0 mg), and **6** (3.2 mg) in H_2O (1.0 ml) was treated with hesperidinase (49.0, 45.0, 61.6, and 14.5 mg, respectively) and the solution was stirred at 37 °C for 12 h gave **1a** (5.0 mg, 70% from **2**, 0.6 mg, 42% from **3**), sarmentol F (**4a**, 5.2 mg, 61% from **5**), and sarmentol G (**6a**, 0.9 mg, 67% from **6**), respectively. Compound **1a** was identified by comparison of its physical data ($[\alpha]_D$ and ^{1}H- and ^{13}C-NMR) with reported values.[44]

Sarmentol F (**4a**): Colorless oil, $[\alpha]_D^{24}$ −12.1° (c=0.27, MeOH). High-resolution EI-MS: Calcd for $C_{13}H_{24}O_2$ (M^+): 212.1776. Found: 212.1769. IR (film, cm^{-1}): 3303, 2967, 2924, 1669, 1470, 1385, 1296, 1273, 1130, 1061, 976, 943, 916, 878, 756. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.82 (3H, d, J=6.4 Hz, 13-H_3), 0.84, 0.88 (3H each, both s, 11, 12-H_3), 0.92 (1H, ddd,

J=12.2, 12.2, 12.2 Hz, 4α-H), 1.21 (1H, dd, J=12.0, 12.0 Hz, 2α-H), 1.29 (1H, dd, J=9.2, 10.4 Hz, 6-H), 1.27 (3H, d, J=6.1 Hz, 10-H_3), 1.53 (1H, m, 5-H), 1.74 (1H, ddd, J=2.1, 4.0, 12.0 Hz, 2β-H), 2.01 (1H, m, 4β-H), 3.79 (1H, m, 3-H), 4.30 (1H, m, 9-H), 5.29 (1H, dd, J=9.2, 15.6 Hz, 7-H), 5.50 (1H, dd, J=6.4, 15.6 Hz, 8-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ_C: given in Table 1. EI-MS (%): m/z 212 (M^+, 1), 194 (M^+-H_2O, 18), 176 (18), 161 (10), 94 (100).

Sarmentol G (**6a**): Colorless oil, $[\alpha]_D^{23}$ +46.5° (c=0.05, MeOH). High-resolution CI-MS: Calcd for $C_{13}H_{24}O_2$ $(M+H)^+$: 213.1854. Found: 213.1858. IR (film, cm^{-1}): 3389, 2922, 1715, 1368, 1072, 1034. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.55 (1H, ddd, J=2.6, 4.8, 11.0 Hz, 6-H), 0.82, 0.94 (3H each, both s, 11, 12-H_3), 0.93 (1H, ddd, J=11.9, 11.9, 11.9 Hz, 4α-H), 0.95 (3H, d, J=6.9 Hz, 13-H_3), 1.10 (1H, dd, J=11.7, 11.7 Hz, 2α-H), 1.34, 1.70 (1H each, both m, 7-H_2), 1.46 (1H, m, 5-H), 1.70 (1H, m, 2β-H), 1.92 (1H, m, 4β-H), 2.14 (3H, s, 10-H_3), [2.42 (1H, ddd, J=5.5, 11.0, 17.2 Hz), 2.54 (1H, ddd, J=5.5, 11.6, 1.72 Hz), 8-H_2], 3.77 (1H, m, 3-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ_C: given in Table 1. CI-MS (%): m/z 213 [$(M+H)^+$, 6], 195 (100), 177 (66), 57 (54).

Enzymatic Hydrolysis of 4 with β-Glucosidase A solution of **4** (6.0 mg) in H_2O (1.0 ml) was treated with β-glucosidase (5.1 mg, from Almond, Oriental yeast Co., Ltd., Tokyo, Japan) and the solution was stirred at 37 °C for 24 h. After EtOH was added to the reaction mixture, the solvent was removed under reduced pressure and the residue was purified by HPLC [MeOH–H_2O (55 : 45, v/v)] to furnish **4a** (3.3 mg, 95%).

Hydrogenation of 4a A solution of **4a** (1.0 mg) in MeOH (1.0 ml) was treated with 10% palladium carbon (Pd–C, 2.1 mg) and the whole mixture was stirred at room temperature under an H_2 atmosphere for 1 h. The catalyst was filtered off, and the solvent from the filtrate was evaporated under reduced pressure to give a residue, which was purified by normal-phase silica gel column chromatography [100 mg, $CHCl_3$–MeOH–H_2O (10 : 3 : 1, v/v/v, lower layer)] to give **1a**[44] (0.6 mg, 60%).

CrO_3–Pyridine Oxidation of 1 A solution of **1** (3.3 mg) in pyridine (0.5 ml) was treated with chromium trioxide (CrO_3, 1.0 mg)–pyridine (0.5 ml) mixture, and whole mixture was stirred at room temperature for 30 min. The reaction mixture was poured into ice-water. Removal of the solvent under reduced pressure to give a residue, which was purified by HPLC [MeOH–H_2O (45 : 55, v/v)] to give **6** (1.1 mg, 33%).

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