Bioactive Constituents from Chinese Natural Medicines. XXII.¹⁾ Absolute Structures of New Megastigmane Glycosides, Sedumosides E₁, E₂, E₃, F₁, F₂, and G, from *Sedum sarmentosum* (Crassulaceae)

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Six new megastigmane glycosides, sedumosides E₁, E₂, E₃, F₁, F₂, 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*; sedumside; 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 A₁, A₂, A₃, 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. sarmentosum*, we have isolated six new megastigmane glycosides, sedumosides E₁ (**1**), E₂ (**2**), E₃ (**3**), F₁ (**4**), F₂ (**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 (H₂O→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** (0.0005%), **2** (0.00018%), **3** (0.00001%), **4** (0.00015%), **5** (0.00018%), **6** (0.00001%), (–)-pinoresinol 4,4′-di-*O*-β-D-glucopyranoside¹⁶⁾ (**7**, 0.00005%), (+)-isolariciresinol¹⁷⁾ (**8**, 0.00012%), woorenoside XI¹⁷⁾ (**9**, 0.00015%), (+)-isolariciresinol 3*a*-*O*-β-D-glucopyranoside¹⁸⁾ (**10**, 0.00003%), secoisolariciresinol¹⁹⁾ (**11**, 0.00010%), **12**²⁰⁾ (0.00005%), (+)-lariciresinol 4-*O*-β-D-glucopyranoside²¹⁾ (**13**, 0.00007%), (+)-lariciresinol 4,4′-bis-*O*-β-D-glucopyranoside²²⁾ (**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%), tricetin 7-*O*-β-D-glucopyranoside²⁶⁾ (**17**, 0.00002%), kaempferol 7-*O*-β-D-glucopyranoside^{23,27)} (**18**, 0.00004%), **19**²⁸⁾ (0.00015%), grosvenorine²⁹⁾ (**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-glucopyranoside²⁶⁾ (**23**, 0.00009%), **24**³¹⁾ (0.00005%), isorhamnetin 3,7-di-*O*-β-D-glucopyranoside²⁶⁾ (**25**, 0.00014%), **26**^{32,33)} (0.00005%), herbacetin 8-methyl ester 3,7-di-*O*-β-D-glucopyranoside³⁴⁾ (**27**,

0.00003%), limocitrin 3-*O*-β-D-glucopyranoside²⁶⁾ (**28**, 0.00008%), limocitrin 3,7-di-*O*-β-D-glucopyranoside²⁶⁾ (**29**, 0.00057%), 2-phenylethyl β-D-glucopyranoside³⁵⁾ (**30**, 0.00001%), 2-phenylethyl D-rutinoside³⁵⁾ (**31**, 0.00003%), eugenyl β-D-glucopyranoside³⁶⁾ (**32**, 0.00007%), 4*R*-*p*-menth-1-ene-7,8-diol 7-*O*-β-D-glucopyranoside³⁷⁾ (**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-glucopyranoside³⁹⁾ (**35**, 0.00012%), octa-1-en-3-yl α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside⁴⁰⁾ (**36**, 0.00043%), 1-acetyl β-carboline⁴¹⁾ (**37**, 0.00001%), **38**⁴²⁾ (0.00003%), and **39**⁴²⁾ (0.00005%).

Absolute Stereostructures of Sedumosides E₁ (1**), E₂ (**2**), E₃ (**3**), F₁ (**4**), F₂ (**5**), and G (**6**)** Sedumside E₁ (**1**) was isolated as an amorphous powder with negative optical rotation ([α]_D²⁴ –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 C₂₅H₄₆O₁₁ 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 ^1H - (CD_3OD) and ^{13}C -NMR (Table 1) spectra⁴³ 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 ^1H - ^1H correlation spectroscopy (^1H - ^1H 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 ($[\alpha]_{\text{D}}^{22}$ –38.6° in MeOH) and determined as the same molecular formula of **1** from the quasi-molecular ion peak at m/z 545 ($\text{M}+\text{Na}$)⁺ 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 ($[\alpha]_{\text{D}}^{21}$ –41.5° in MeOH) and its molecular formula, $\text{C}_{24}\text{H}_{44}\text{O}_{11}$, was determined from the positive-ion FAB-MS [m/z 531 ($\text{M}+\text{Na}$)⁺] 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 ^1H - (CD_3OD) and ^{13}C -NMR (Table 1) spectra⁴³ 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 ^1H - 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 ^1H - ^1H 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 ($[\alpha]_{\text{D}}^{24}$ –11.2° in MeOH). The molecular formula, $\text{C}_{19}\text{H}_{34}\text{O}_7$, of **4** was determined from the positive-ion FAB-MS [m/z 397 ($\text{M}+\text{Na}$)⁺] and by high resolution positive-ion FAB-MS measurement. Sedumoside **F**₂ (**5**), $[\alpha]_{\text{D}}^{24}$ –26.0° (MeOH), was also obtained as an amorphous powder and the molecular formula, $\text{C}_{25}\text{H}_{44}\text{O}_{11}$, 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 ^1H - (CD_3OD) and ^{13}C -NMR (Table 1) spectra⁴³ 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 ^1H - 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''-H₃), 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 ^1H - (CDCl_3) and ^{13}C -NMR (Table 1) spectra⁴³ of **4a** indicated the presence of four methyls [δ 0.82 (3H, d, $J=6.4$ Hz, 13-H₃), 0.84, 0.88 (3H each, both s, 11, 12-H₃), 1.27 (3H, d, $J=6.1$ Hz, 10-H₃)] 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 ^1H - ^1H 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 (2 α -H and 6-H, 12-H₃; 2 β -H and 3-H; 3-H and 4 β -H; 4 α -H and 6-H, 13-H₃; 6-H and 12-H₃; 7-H and 11-H₃). 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 H₂ 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 F₁ and F₂ were determined to be sarmentol F 9-*O*- β -D-glucopyranoside (**4**) and sarmentol F 9-*O*- α -L-rhamnopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranoside (**5**).

Sedumoside G (**6**) was obtained as an amorphous powder and exhibited a negative optical rotation ($[\alpha]_D^{19} -35.7^\circ$ 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 ($M+\text{Na}$)⁺ and high-resolution FAB-MS analysis revealed the molecular formula of **6** to be C₂₅H₄₄O₁₁. 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 ^1H - (CDCl_3) and ^{13}C -NMR (Table 1) spectra⁴³ of **6a** indicated the presence of four methyls [δ 0.95 (3H, d, $J=6.9$ Hz, 13-H₃), 0.82, 0.94 (3H each, both s, 11, 12-H₃), 2.14 (3H, s, 10-H₃)] 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 ^1H - (CD_3OD) and ^{13}C -NMR (Table 1) spectra⁴³ of **6** showed signals assignable to an aglycon part [δ 0.85, 0.95 (3H each, both s, 11, 12-H₃), 0.97 (3H, d, $J=6.5$ Hz, 13-H₃), 2.12 (3H, s, 10-H₃), 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''-H₃), 4.32 (1H, d, $J=7.9$ Hz, 1'-H), 4.73 (1H, d, $J=1.8$ Hz, 1''-H)]. The ^1H - ^1H 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 -H₃; 2β -H and 3 -H; 3 -H and 4β -H; 4α -H and 6 -H, 13 -H₃; 6 -H and 12 -H₃; 7 -H₂ and 11 -H₃). Finally, compound **6** was derived by selective oxidation of the aglycon part in **1** with chromium trioxide (CrO₃)–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 $\rightarrow$ 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; ¹H-NMR spectra, JEOL EX-270 (270 MHz) and JNM-LA500 (500 MHz) spectrometers; ¹³C-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 5C₁₈-MS-II (Nacalai Tesque Inc., 250 $\times$ 4.6 mm i.d.) and (250 $\times$ 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 60F₂₅₄ (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(SO₄)₂–10% aqueous H₂SO₄ 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, H₂O $\rightarrow$ MeOH, twice) to give H₂O- 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, CHCl₃–MeOH–H₂O (10:3:0.5 $\rightarrow$ 7:3:1, v/v/v, lower layer) $\rightarrow$ 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–H₂O (5:95 $\rightarrow$ 10:90 $\rightarrow$ 20:80 $\rightarrow$ 30:70 $\rightarrow$ 50:50 $\rightarrow$ 70:30, v/v) $\rightarrow$ 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–H₂O (1:1, v/v)] and finally HPLC [MeOH–H₂O (35:65, v/v)] to furnish **38** (14.6 mg, 0.0003%), and **39** (24.5 mg, 0.0005%) 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, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (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, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (40:60, v/v)] to furnish secoisolariciresinol (**11**, 56.3 mg, 0.00010%) together with myrsinonide 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, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (50:50, v/v)] to furnish (*R*)- α -terpinyl β -D-glucopyra-

noside (**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 triclin 7-*O*- β -D-glucopyranoside (**17**, 295.3 mg, 0.00055%) and the mother liquid was purified by HPLC [MeOH–H₂O (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–H₂O (20:80 $\rightarrow$ 30:70 $\rightarrow$ 40:60 $\rightarrow$ 70:30, v/v) $\rightarrow$ 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, CHCl₃ $\rightarrow$ CHCl₃–MeOH (50:1 $\rightarrow$ 20:1 $\rightarrow$ 10:1, v/v) $\rightarrow$ CHCl₃–MeOH–H₂O (20:3:1, v/v/v, lower layer) $\rightarrow$ 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–H₂O (32:68, v/v)] to furnish 2-phenylethyl β -D-glucopyranoside (**30**, 5.0 mg, 0.00001%). Fraction 2-4-5 (348.2 mg) was further purified by HPLC [CH₃CN–MeOH–H₂O (10:8:82, v/v/v) and MeOH–H₂O (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–H₂O (32:68, v/v)] to give woerenoside XI (**9**, 58.7 mg, 0.00011%) together with sedumosides A₁ (162.5 mg, 0.00030%), A₂ (60.6 mg, 0.00011%), A₃ (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 [CH₃CN–H₂O (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 A₁ (34.0 mg, 0.00006%), A₂ (838.6 mg, 0.0016%), A₃ (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–H₂O (30:70, v/v)] and finally HPLC [CH₃CN–MeOH–H₂O (20:8:72, v/v/v) and MeOH–H₂O (40:60, v/v)] to furnish sedumosides F₁ (**4**, 82.5 mg, 0.00015%), F₂ (**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 [CH₃CN–MeOH–H₂O (20:8:72, v/v/v) and MeOH–H₂O (40:60, v/v)] to furnish sedumosides E₁ (**1**, 5.1 mg, 0.00001%), E₂ (**2**, 21.7 mg, 0.00004%), and E₃ (**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 myrsinonide 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–H₂O (10:90 $\rightarrow$ 20:80 $\rightarrow$ 30:70 $\rightarrow$ 40:60, v/v) $\rightarrow$ 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–H₂O (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, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (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, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (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, H₂O $\rightarrow$ MeOH–H₂O (10:90 $\rightarrow$ 20:80 $\rightarrow$ 30:70 $\rightarrow$ 40:60 $\rightarrow$ 50:50, v/v) $\rightarrow$ 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 [$\text{CH}_3\text{CN}-\text{MeOH}-\text{H}_2\text{O}$ (10:8:82, v/v/v)] to give (+)-larisiresinol 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 [$\text{CH}_3\text{CN}-\text{MeOH}-\text{H}_2\text{O}$ (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, $\text{CHCl}_3-\text{MeOH}$ (1:1, v/v)] and finally HPLC [$\text{MeOH}-\text{H}_2\text{O}$ (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, $\text{CHCl}_3-\text{MeOH}$ (1:1, v/v)] and finally HPLC [$\text{MeOH}-\text{H}_2\text{O}$ (35:65 or 40:60, v/v) or $\text{CH}_3\text{CN}-\text{MeOH}-\text{H}_2\text{O}$ (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, ^1H -, ^{13}C -NMR, MS) with reported values^{16–22,24–32,34–42} or authentic samples.²³

Sedumside E_1 (**1**): An amorphous powder, $[\alpha]_D^{24} -33.9^\circ$ ($c=1.08$, MeOH). High-resolution positive-ion FAB-MS: Calcd for $\text{C}_{25}\text{H}_{46}\text{O}_{11}\text{Na}$ ($\text{M}+\text{Na}^+$): 545.2938; Found 545.2933. IR (KBr, cm^{-1}): 3431, 2967, 2932, 1509, 1473, 1458, 1081, 1046. ^1H -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, dd, $J=11.6, 11.6, 11.6$ Hz, 4 α -H), 1.04, 1.43 (1H each, both m, 7- H_2), 1.14 (1H, dd, $J=11.9, 11.9$ Hz, 2 α -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, 2 β -H), 2.04 (1H, m, 4 β -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 ($\text{M}+\text{Na}^+$).

Sedumside E_2 (**2**): An amorphous powder, $[\alpha]_D^{22} -38.6^\circ$ ($c=0.27$, MeOH). High-resolution positive-ion FAB-MS: Calcd for $\text{C}_{25}\text{H}_{46}\text{O}_{11}\text{Na}$ ($\text{M}+\text{Na}^+$): 545.2938; Found 545.2932. IR (KBr, cm^{-1}): 3432, 2967, 2934, 1541, 1509, 1474, 1458, 1069, 1046. ^1H -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, 4 α -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, 2 α -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, 2 β -H), 1.87 (1H, m, 4 β -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 ($\text{M}+\text{Na}^+$).

Sedumside E_3 (**3**): An amorphous powder, $[\alpha]_D^{21} -41.5^\circ$ ($c=0.35$, MeOH). High-resolution positive-ion FAB-MS: Calcd for $\text{C}_{24}\text{H}_{44}\text{O}_{11}\text{Na}$ ($\text{M}+\text{Na}^+$): 531.2781. Found: 531.2774. IR (KBr, cm^{-1}): 3339, 2922, 1471, 1387, 1039, 1028. ^1H -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, 4 α -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, 2 α -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, 2 β -H), 1.87 (1H, m, 4 β -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 ($\text{M}+\text{Na}^+$).

Sedumside F_1 (**4**): An amorphous powder, $[\alpha]_D^{24} -11.2^\circ$ ($c=1.14$, MeOH). High-resolution positive-ion FAB-MS: Calcd for $\text{C}_{19}\text{H}_{34}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}^+$): 397.2202. Found: 397.2206. IR (KBr, cm^{-1}): 3389, 2960, 2919, 1734, 1684, 1671, 1559, 1541, 1509, 1474, 1341, 1078, 1034. ^1H -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, 4 α -H), 1.11 (1H, dd, $J=12.2, 12.2$ Hz, 2 α -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, 2 β -H), 1.96 (1H, m, 4 β -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 ($\text{M}+\text{Na}^+$).

Sedumside F_2 (**5**): An amorphous powder, $[\alpha]_D^{24} -26.0^\circ$ ($c=1.08$, MeOH). High-resolution positive-ion FAB-MS: Calcd for $\text{C}_{25}\text{H}_{44}\text{O}_{11}\text{Na}$ ($\text{M}+\text{Na}^+$): 543.2776. Found: 543.2776. IR (KBr, cm^{-1}): 3410, 2967, 2940, 1669, 1474, 1341, 1140, 1055, 968. ^1H -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, 4 α -H), 1.12 (1H, dd, $J=12.2, 12.2$ Hz, 2 α -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, 2 β -H), 1.96 (1H, m, 4 β -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 ($\text{M}+\text{Na}^+$).

Sedumside G (**6**): An amorphous powder, $[\alpha]_D^{19} -35.7^\circ$ ($c=0.17$, MeOH). High-resolution positive-ion FAB-MS: Calcd for $\text{C}_{25}\text{H}_{44}\text{O}_{11}\text{Na}$ ($\text{M}+\text{Na}^+$): 543.2781. Found: 543.2787. IR (KBr, cm^{-1}): 3406, 2932, 1716, 1456, 1368, 1066, 1047. ^1H -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, 4 α -H), 1.15 (1H, dd, $J=12.1, 12.1$ Hz, 2 α -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, 2 β -H), 2.05 (1H, m, 4 β -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 ($\text{M}+\text{Na}^+$).

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 NH₂-60-5, 4.6 mm i.d. $\times$ 250 mm (Tokyo Kasei Co., Ltd., Tokyo, Japan); detection, optical rotation [Shodex OR-2 (Showa Denko Co., Ltd., Tokyo, Japan); mobile phase, $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (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 niger*, 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 [$\text{MeOH}-\text{H}_2\text{O}$ (55:45, v/v)] to furnish (3S,5R,6S,9R)-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 ^1H - and ^{13}C -NMR) with reported values.⁴⁴

Sarmentol F (**4a**): Colorless oil, $[\alpha]_D^{24} -12.1^\circ$ ($c=0.27$, MeOH). High-resolution EI-MS: Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ (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. ^1H -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-H₃), 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 ($\text{M}^+ - \text{H}_2\text{O}$, 18), 176 (18), 161 (10), 94 (100).

Sarmentol G (**6a**): Colorless oil, $[\alpha]_{\text{D}}^{25} +46.5^\circ$ ($c=0.05$, MeOH). High-resolution CI-MS: Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 213.1854. Found: 213.1858. IR (film, cm^{-1}): 3389, 2922, 1715, 1368, 1072, 1034. ^1H -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-H₃), 0.93 (1H, ddd, $J=11.9, 11.9, 11.9$ Hz, 4α -H), 0.95 (3H, d, $J=6.9$ Hz, 13-H₃), 1.10 (1H, dd, $J=11.7, 11.7$ Hz, 2α -H), 1.34, 1.70 (1H each, both m, 7-H₂), 1.46 (1H, m, 5-H), 1.70 (1H, m, 2β -H), 1.92 (1H, m, 4β -H), 2.14 (3H, s, 10-H₃), [2.42 (1H, ddd, $J=5.5, 11.0, 17.2$ Hz), 2.54 (1H, ddd, $J=5.5, 11.6, 17.2$ Hz), 8-H₂], 3.77 (1H, m, 3-H). ^{13}C -NMR (125 MHz, CDCl_3) δ_{C} : given in Table 1. CI-MS (%): m/z 213 [$(\text{M}+\text{H})^+$, 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 [$\text{MeOH}-\text{H}_2\text{O}$ (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 [$\text{MeOH}-\text{H}_2\text{O}$ (45 : 55, v/v)] to give **6** (1.1 mg, 33%).

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