

Megastigmanes and Their Glucosides from the Whole Plant of *Sedum sarmentosum*¹

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Two new megastigmanes, sarmentoic acid (**1**) and sarmentol A (**2**), and six new megastigmane glucosides, sedumosides A₁ (**3**), A₂ (**4**), A₃ (**5**), B (**6**), C (**7**), and D (**8**), were isolated from the whole plant of *Sedum sarmentosum* together with eight known megastigmanes (**9**–**16**). The absolute stereostructures of **1**–**8** were elucidated on the basis of chemical and physicochemical evidence, including the application of the modified Mosher's method.

The plant *Sedum sarmentosum* (Crassulaceae) is a perennial herb widely distributed on the mountain slopes in China (e.g., Anhui, Hebei, Jiangxi, and Jiangsu Provinces). The whole plant of *S. sarmentosum* has been used for the treatment of chronic viral hepatitis in Chinese and Korean traditional medicines.^{2,3} In previous studies, several flavonoid,^{4–7} sterol,^{5,8} triterpene,^{5,9} and cyanogenic constituents^{10,11} were isolated from this herbal medicine. During the course of our studies on bioactive constituents from Chinese natural medicines,^{1,12–24} two new megastigmanes, sarmentoic acid (**1**) and sarmentol A (**2**), and six new megastigmane glucosides, sedumosides A₁ (**3**), A₂ (**4**), A₃ (**5**), B (**6**), C (**7**), and D (**8**), were isolated from the whole plant of *S. sarmentosum* together with eight known megastigmanes (**9**–**16**). This paper deals with the isolation and structure elucidation, including the absolute configuration, of **1**–**8**.

Results and Discussion

The fresh whole plant of *S. sarmentosum* was extracted with hot H₂O, and the H₂O extract was further treated with MeOH to give a MeOH-soluble extract (0.57% from the fresh plant). The MeOH-soluble extract was subjected to Diaion HP-20 column chromatography (H₂O → MeOH) to give H₂O- and MeOH-eluted fractions (0.44 and 0.13%, respectively). The MeOH-eluted fraction was subjected to normal- and reversed-phase column chromatographies and finally HPLC to give **1**–**8** together with (3*S*,5*R*,6*S*,9*R*)-megastigmane-3,9-diol²⁵ (**9**), staphylionoside D²⁶ (**10**), myrsiniosides A²⁵ (**11**) and D²⁵ (**12**), alangiosides A²⁷ (**13**) and J²⁵ (**14**), 3-hydroxy-5,6-epoxy-β-ionol 9-*O*-β-D-glucopyranoside²⁸ (**15**), and platanionoside D²⁹ (**16**).

Sarmentoic acid (**1**) was obtained as an amorphous powder ([α]_D²⁷ −3.3 in MeOH). The IR spectrum of **1** showed absorption bands at 3364 and 1713 cm^{−1} ascribable to hydroxyl and carboxyl functions. In the positive-ion FABMS of **1**, a quasimolecular ion peak was observed at *m/z* 267 [M + Na]⁺, and HRFABMS analysis revealed the molecular formula of **1** to be C₁₃H₂₄O₄. The ¹H (pyridine-*d*₅, Table 1) and ¹³C NMR (Table 2) spectra of **1**, which were assigned by various NMR experiments,³⁰ showed signals assignable to three methyls [δ 1.03, 1.34 (both s, H₃-12, 11), 1.07 (d, *J* = 6.7 Hz, H₃-13)], two methines bearing an oxygen function [δ 4.29 (m, H-3), 4.73 (dd, *J* = 4.0, 7.6 Hz, H-9)], and a carboxyl carbon [δ_C 178.2 (C-10)] together with four methylenes, two methines, and a quaternary carbon. As shown in Figure S1 (Supporting Information), the ¹H–¹H COSY experiment on **1** indicated the presence of a partial structure, written in bold lines,

and in the HMBC experiment, long-range correlations were observed between the following: H₂-2 and C-1; H-6 and C-1; H-9 and C-7, 8, 10; H₃-11 and C-1, 2, 6, 12; H₃-12 and C-1, 2, 6, 11; H₃-13 and C-4–6. The relative stereostructure of **1** except for the 9-position was characterized by the NOESY experiment, which showed NOE correlations between Hα-2 and H-3, H-6, H₃-12; H-3 and Hα-4; Hα-4 and H-6, H₃-13; H-6 and H₃-12; and H₂-7 and H₃-11, as shown in Figure S1. Finally, the absolute configuration of **1** was characterized by the application of the modified Mosher's method.³¹ Namely, methyl ester **1a**, which was derived from **1** upon reaction with trimethylsilyldiazomethane (TMSCHN₂), gave the 3-(*R*)-MTPA ester (**1b**), 9-(*R*)-MTPA ester (**1d**), and 3,9-di-(*R*)-MTPA ester by treatment with (*R*)-2-methoxy-2-trifluoromethylphenylacetic acid [(*R*)-MTPA] in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) and 4-dimethylaminopyridine (4-DMAP). On the other hand, the 3-(*S*)- and 9-(*S*)-MTPA esters (**1c**, **1e**) and 3,9-di-(*S*)-MTPA ester were obtained from **1a** using (*S*)-MTPA in the presence of EDC·HCl and 4-DMAP. As shown in Figure 1, the signals due to protons attached to the 4-, 5-, and 13-positions in the 3-(*S*)-MTPA ester (**1c**) were observed at lower fields compared with those of the 3-(*R*)-MTPA ester (**1b**) [Δδ: positive], while the signals due to protons on the 2-, 11-, and 12-positions in **1c** were observed at higher fields compared with those of **1b** [Δδ: negative]. Thus, the absolute configuration at the 3-position of **1a** was determined to be *R*. The signals due to protons attached to the 5–8- and 11–13-positions in the 9-(*S*)-MTPA ester (**1e**) were observed at lower fields compared with those of the 9-(*R*)-MTPA ester (**1d**) [Δδ: positive], while the signal of the 10-carboxy methyl proton in **1e** was observed at higher field compared with that of **1d** [Δδ: negative]. Consequently, the absolute configuration at the 9-position of **1a** was determined to be *R* and the absolute configurations of **1** and **1a** were elucidated as shown.

Sarmentol A (**2**) was obtained as colorless oil ([α]_D²⁷ −7.4 in MeOH). The molecular formula, C₁₃H₂₆O₃, of **2** was determined from the positive-ion FABMS (*m/z* 253 [M + Na]⁺) and by HRFABMS. The ¹H (CD₃OD, Table 1) and ¹³C NMR (Table 2) spectra³⁰ of **2** showed signals assignable to three methyls [δ 0.83, 0.96 (both s, H₃-11, 12), 0.98 (d, *J* = 6.5 Hz, H₃-13)] and a methylene and two methines bearing an oxygen function [δ 3.41 (dd, *J* = 6.7, 11.0 Hz), 3.46 (dd, *J* = 4.6, 11.0 Hz), H₂-10], 3.53 (m, H-9), 3.69 (m, H-3)] together with four methylenes, two methines, and a quaternary carbon. The proton and carbon signals in the ¹H and ¹³C NMR spectra of **2** resembled those of **1f**, which was derived from **1a** by reduction with sodium borohydride (NaBH₄). As shown in Figure S1, the ¹H–¹H COSY experiment on **2** indicated the partial structure written in bold lines, and the carbon skeleton and the positions of functional groups were characterized by the HMBC experiment, which showed long-range correlations between the following: H₂-2 and C-1; H-3 and C-2,

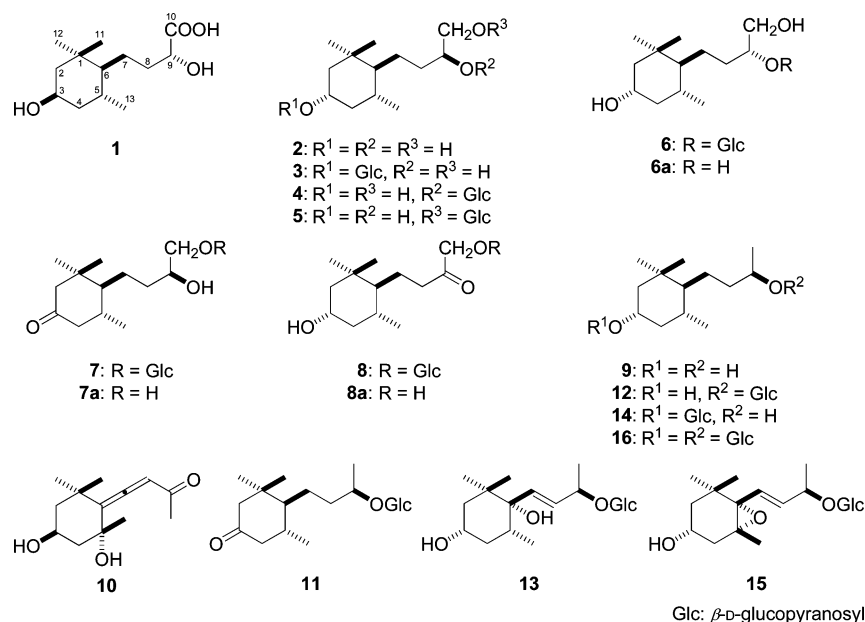
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Chart 1

Table 1. ^1H NMR (500 MHz) Data of **1** and **2** and Related Compounds (**1a** and **1f**)

	1 ^a	1a ^a	1a ^b	1f ^b	2 ^b	2 ^c
position	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)
2 α	1.42 (br dd, ca. 3, 14)	1.42 (br dd, ca. 3, 14)	1.38 (br dd, ca. 3, 15)	1.39 (br dd, ca. 3, 14)	1.10 (dd, 11.9, 11.9)	1.08 (dd, 11.6, 11.6)
2 β	1.81 (m)	1.82 (ddd, 2.0, 2.0, 14.3)	1.58 (m)	1.59 (ddd, 2.0, 2.0, 13.7)	1.69 (ddd, 2.8, 4.3, 11.9)	1.63 (m)
3	4.29 (m)	4.29 (m)	4.08 (m)	4.09 (m)	3.76 (m)	3.69 (m)
4 α	1.28 (ddd, 2.8, 13.2, 14.7)	1.28 (ddd, 2.8, 13.2, 14.7)	1.24 (m)	1.24 (m)	0.93 (ddd, 12.2, 12.2, 12.2)	0.90 (ddd, 12.1, 12.1, 12.1)
4 β	1.97 (ddd, 3.1, 5.5, 14.7)	1.97 (ddd, 3.1, 5.5, 14.7)	1.75 (ddd, 2.8, 5.5, 13.7)	1.73 (ddd, 2.8, 5.5, 13.7)	1.92 (m)	1.89 (m)
5	2.12 (m)	2.13 (m)	1.80 (m)	1.80 (m)	1.46 (m)	1.45 (m)
6	0.78 (ddd, 2.2, 5.8, 10.8)	0.72 (ddd, 2.1, 5.8, 10.8)	0.62 (ddd, 2.2, 5.8, 10.8)	0.62 (ddd, 2.1, 4.6, 9.2)	0.55 (ddd, 1.9, 4.9, 10.7)	0.54 (ddd, 2.1, 5.2, 12.6)
7	1.72 (m)	1.57 (m)	1.20 (m)	1.31 (m)	1.05 (m)	1.03 (m)
	2.05 (m)	1.94 (m)	1.60 (m)	1.46 (m)	1.57 (m)	1.65 (m)
8	2.19 (m)	2.03 (m)	1.72 (m)	1.37 (m)	1.40 (m)	1.32 (m)
	2.22 (m)	2.15 (m)	1.79 (m)	1.68 (m)	1.55 (m)	1.61 (m)
9	4.73 (dd, 4.0, 7.6)	4.59 (dd, 4.0, 7.7)	4.17 (dd, 4.0, 7.7)	3.69 (m)	3.67 (m)	3.53 (m)
10				3.45 (dd, 5.7, 10.3)	3.44 (dd, 8.2, 11.6)	3.41 (dd, 6.7, 11.0)
				3.66 (dd, 2.3, 10.3)	3.67 (dd, 3.1, 11.6)	3.46 (dd, 4.6, 11.0)
11	1.34 (s)	1.32 (s)	1.02 (s)	1.03 (s)	0.81 (s)	0.83 (s)
12	1.03 (s)	0.99 (s)	0.90 (s)	0.89 (s)	0.95 (s)	0.96 (s)
13	1.07 (d, 6.7)	1.01 (d, 6.7)	0.92 (d, 6.7)	0.95 (d, 6.9)	0.98 (d, 6.5)	0.98 (d, 6.5)
COOMe		3.75 (s)	3.80 (s)			

^a Measured in pyridine-*d*₅. ^b Measured in CDCl₃. ^c Measured in CD₃OD.

4; H-6 and C-1; H₂-8 and C-9, 10; H-9 and C-8, 10; H₂-10 and C-8, 9; H₃-11 and C-1, 2, 6, 12; H₃-12 and C-1, 2, 6, 11; H₃-13 and C-4–6. On the basis of this evidence, the planar structure of **2** was the same as that of **1f**. Next, the relative stereostructure of **2** was determined by a NOESY experiment, in which correlations were observed between H α -2 and H-6, H₃-12; H β -2 and H-3; H-3 and H β -4; H α -4 and H-6, H₃-13; H-6 and H₃-12; and H₂-7 and H₃-11. Finally, the absolute configuration of **2** was clarified by a modified Mosher's method.³¹ As shown in Figure 2, treatment of **2** with pivaloyl chloride in pyridine yielded the 10-pivaloyl and 3,10-dipivaloyl esters (**2a**, **2b**). The 10-pivaloyl ester (**2a**) selectively gave the 3-MTPA esters (**2c**, **2d**) by steric hindrance due to the 10-pivaloyl group. In contrast, the 9-MTPA esters (**2e**, **2f**) were obtained from **2b** in low yields. The protons on the 2-, 11-, and 12-positions of the 3-(*S*)-MTPA ester (**2d**) resonated at lower fields than those of the 3-(*R*)-MTPA ester (**2c**) [$\Delta\delta$: positive], while the protons on the 4-, 5-, and 13-positions of **2d** were observed at higher fields compared to those of **2c** [$\Delta\delta$: negative]. On the other hand,

the 10-proton and pivaloyl methyl protons of the 9-(*S*)-MTPA ester (**2f**) resonated at lower fields than those of the 9-(*R*)-MTPA ester (**2e**) [$\Delta\delta$: positive], while the protons on the 5–8- and 11–13-positions of **2f** were observed at higher fields compared to those of **2e** [$\Delta\delta$: negative]. Consequently, the absolute configurations at the 3- and 9-positions in **2** were elucidated to be 3*S* and 9*S*.

Sedumoside A₁ (**3**) was obtained as an amorphous powder ($[\alpha]_{\text{D}}^{25}$ –28.3 in MeOH). HRFABMS revealed the molecular formula of **3** to be C₁₉H₃₆O₈, and the IR spectrum showed absorption bands at 3389 and 1078 cm^{–1}, ascribable to hydroxyl and ether functions. The ^1H NMR (pyridine-*d*₅, Table 3) and ^{13}C NMR (Table 4) spectra³⁰ of **3** showed the presence of the following functions: three methyls [δ 0.75, 0.92 (both s, H₃-11, 12), 0.92 (d, J = 6.1 Hz, H₃-13)], a methylene and two methines bearing an oxygen function [δ 3.52 (dd, J = 5.8, 11.9 Hz), 3.65 (dd, J = 3.4, 11.9 Hz), H₂-10], 4.05 (m, H-9), 4.12 (m, H-3)], and a β -glucopyranosyl part [δ 5.02 (d, J = 7.6 Hz, H-1')]. The acid hydrolysis of **3** with 1 M HCl liberated D-glucose, which was identified by HPLC analysis

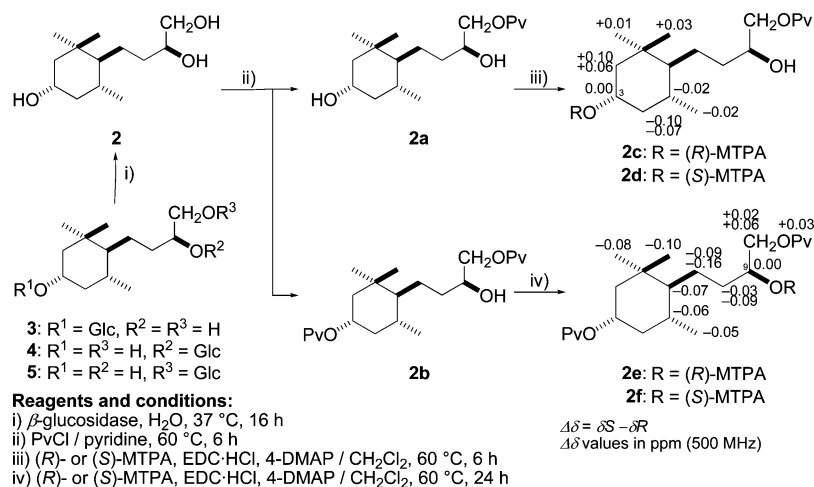


Figure 2.

Table 3. ¹H NMR (500 MHz) Data of 3–5

	3 ^a	3 ^b	4 ^a	4 ^b	5 ^a	5 ^b
position	δ_H (J Hz)	δ_H (J Hz)	δ_H (J Hz)	δ_H (J Hz)	δ_H (J Hz)	δ_H (J Hz)
2 α	1.29 (dd, 12.2, 12.2)	1.14 (dd, 11.9, 11.9)	1.36 (dd, 12.0, 12.0)	1.08 (dd, 11.9, 11.9)	1.39 (dd, 12.0, 12.0)	1.09 (dd, 12.0, 12.0)
2 β	2.03 (ddd, 1.9, 3.5, 12.2)	1.79 (ddd, 2.2, 4.1, 11.9)	1.90 (m)	1.63 (m)	1.92 (ddd, 2.8, 4.5, 12.0)	1.64 (ddd, 2.5, 4.5, 12.0)
3	4.12 (m)	3.84 (m)	3.97 (m)	3.69 (m)	4.02 (m)	3.69 (m)
4 α	1.20 (ddd, 11.3, 11.3, 11.3)	1.03 (ddd, 12.2, 12.2, 12.2)	1.17 (m)	0.91 (ddd, 12.2, 12.2, 12.2)	1.21 (ddd, 11.3, 11.3, 11.3)	0.90 (ddd, 12.2, 12.2, 12.2)
4 β	2.21 (m)	2.01 (m)	2.10 (m)	1.89 (m)	2.12 (m)	1.89 (m)
5	1.28 (m)	1.45 (m)	1.35 (m)	1.44 (m)	1.35 (m)	1.43 (m)
6	0.57 (ddd, 2.2, 4.6, 10.7)	0.56 (ddd, 2.1, 5.2, 11.0)	0.53 (ddd, 2.2, 5.3, 11.7)	0.53 (ddd, 2.1, 5.2, 12.6)	0.53 (ddd, 2.5, 5.0, 11.0)	0.53 (ddd, 2.8, 4.0, 10.7)
7	1.18 (m)	1.03 (m)	1.18 (m)	1.08 (m)	1.16 (m)	1.06 (m)
8	1.83 (m)	1.65 (m)	1.89 (m)	1.65 (m)	1.82 (m)	1.63 (m)
9	1.65 (m)	1.33 (m)	1.77 (m)	1.57 (m)	1.60 (m)	1.41 (m)
10	1.89 (m)	1.61 (m)	1.85 (m)	1.64 (m)	1.75 (m)	1.57 (m)
11	4.05 (m)	3.52 (m)	4.10 (m)	3.69 (m)	4.14 (m)	3.71 (m)
12	3.52 (dd, 5.8, 11.9)	3.41 (dd, 6.7, 11.0)	3.79 (2H, m)	3.52 (dd, 5.8, 11.9)	3.89 (dd, 8.6, 10.1)	3.37 (dd, 7.8, 10.1)
13	3.65 (dd, 3.4, 11.9)	3.46 (dd, 4.3, 11.0)		3.65 (dd, 3.4, 11.9)	4.27 (dd, 3.7, 10.1)	3.92 (dd, 2.7, 10.1)
Glc-1'	0.75 (s)	0.84 (s)	0.83 (s)	0.83 (s)	0.80 (s)	0.83 (s)
2'	0.92 (s)	0.97 (s)	0.93 (s)	0.97 (s)	0.94 (s)	0.96 (s)
3'	0.92 (d, 6.1)	0.98 (d, 6.1)	0.97 (d, 6.2)	0.98 (d, 6.5)	0.96 (d, 6.1)	0.97 (d, 6.4)
4'	5.02 (d, 7.6)	4.34 (d, 7.6)	5.12 (d, 7.6)	4.42 (d, 7.7)	5.00 (d, 7.6)	4.27 (d, 7.6)
5'	4.05 (m)	3.12 (dd, 7.6, 9.2)	4.03 (m)	3.20 (dd, 7.7, 9.2)	4.09 (dd, 7.6, 9.0)	3.21 (dd, 7.6, 9.2)
6'	4.30 (m)	3.35 (dd, 9.2, 9.2)	4.20 (m)	3.33 (dd, 9.2, 9.2)	4.24 (m)	3.33 (m)
7'	4.28 (m)	3.25 (m)	4.19 (m)	3.27 (m)	4.24 (m)	3.27 (m)
8'	4.00 (m)	3.27 (m)	3.90 (m)	3.27 (m)	3.99 (m)	3.25 (m)
9'	4.33 (dd, 4.9, 11.9)	3.65 (dd, 4.9, 11.6)	4.34 (dd, 4.8, 11.6)	3.64 (m)	4.37 (dd, 5.5, 11.9)	3.64 (m)
10'	4.58 (dd, 3.1, 11.9)	3.86 (dd, 2.1, 11.6)	4.48 (dd, 2.1, 11.6)	3.85 (dd, 2.2, 12.0)	4.56 (br d, ca. 12)	3.86 (dd, 1.6, 10.1)

^a Measured in pyridine-*d*₅. ^b Measured in CD₃OD.

respectively. The protons on the 2-, 11-, and 12-positions of the (S)-MTPA ester (**8c**) resonated at lower fields than those of the (R)-MTPA ester (**8b**) [$\Delta\delta$: positive], while the protons on the 4-, 5-, and 13-positions of **8c** were observed at higher fields compared to those of **8b** [$\Delta\delta$: negative]. Finally, reduction of the 9-carbonyl group in **8** with NaBH₄ gave **5** and its 9-diastereoisomer (**8d**) in an approximate 1:1 ratio. Enzymatic hydrolysis of **8d** with β -glucosidase gave **6a**, and thus the absolute configuration of **6a** was also clarified. On the basis of this evidence, the absolute configurations of **6** and **8** were elucidated to be as shown.

Experimental Section

General Experimental Procedures. 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; ¹H NMR spectra, JEOL JNM-

LA500 (500 MHz) spectrometer; ¹³C NMR spectra, JEOL JNM-LA500 (125 MHz) spectrometer with tetramethylsilane as an internal standard; EIMS, CIMS, HREIMS, and HRCIMS, JEOL JMS-GCMATE mass spectrometer; FABMS and HRFABMS, JEOL JMS-SX 102A mass spectrometer; HPLC detector, Shimadzu RID-6A refractive index and SPD-10A UV-vis detectors; HPLC, Cosmosil 5C₁₈-MS-II columns (Nacalai Tesque Inc., 250 × 4.6 mm i.d. and 250 × 20 mm i.d. for analytical and preparative purposes, respectively).

The following experimental conditions were used for chromatography: normal-phase silica gel column chromatography (CC), silica gel BW-200 (Fuji Silysia Chemical, Ltd., 150–350 mesh); reversed-phase silica gel CC, Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., 100–200 mesh); Diaion HP-20 CC (Nippon Rensui); Sephadex LH-20 CC (Amersham Biosciences K. K.); preparative TLC, precoated TLC plates with silica gel 60F₂₅₄ (Merck, 0.25 mm) (normal-phase); TLC, precoated TLC plates with silica gel 60F₂₅₄ (Merck, 0.25 mm) (normal-phase) and silica gel RP-18 F_{254s} (Merck, 0.25 mm) (reversed-phase); reversed-phase HPTLC, precoated TLC plates with silica gel

Table 4. ^{13}C NMR (125 MHz) Data of **3**–**5**

	3^a	3^b	4^a	4^b	5^a	5^b
position	δ_{C}	δ_{C}	δ_{C}	δ_{C}	δ_{C}	δ_{C}
1	35.8	36.7	36.0	36.8	35.9	36.8
2	48.1	48.4	51.9	51.8	52.1	51.8
3	74.2	75.7	66.0	67.4	66.0	67.4
4	44.3	44.7	46.6	46.5	46.8	46.5
5	33.9	34.9	33.9	34.9	34.0	34.9
6	53.1	54.3	53.3	54.4	53.1	54.2
7	25.7	26.3	25.3	26.1	25.5	26.1
8	36.9	36.9	35.0	35.2	36.5	36.8
9	73.3	73.9	82.8	82.5	71.4	72.4
10	67.5	67.2	65.0	64.8	75.8	75.5
11	21.0	21.3	21.2	21.4	21.3	21.3
12	30.9	31.3	31.0	31.4	31.0	31.4
13	21.1	21.5	21.3	21.5	21.3	21.5
Glc-1'	103.0	102.6	104.5	103.9	105.5	104.8
2'	75.4	75.0	75.7	75.6	75.4	75.2
3'	78.7	78.0	78.4	78.1	78.6	77.9
4'	71.8	71.7	71.7	71.7	71.7	71.6
5'	78.5	77.8	78.2	77.9	78.6	78.0
6'	62.9	62.8	62.8	62.9	62.8	62.7

^a Measured in pyridine-*d*₅. ^b Measured in CD₃OD.

RP-18 WF_{254S} (Merck, 0.25 mm); 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 the authors (M.Y.). A voucher specimen (2005.01. Eishin-02) of this plant is on file in our laboratory.

Extraction and Isolation. The hot H₂O 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 MeOH under reflux for 3 h. Evaporation of the solvent under reduced pressure provided a MeOH extract (887.5 g, 0.57%), and an aliquot (398.6 g) was subjected to Diaion HP-20 CC (4.0 kg, H₂O → MeOH, twice) to give H₂O- and MeOH-eluted fractions (305.0 and 93.6 g, respectively). The MeOH-eluted fraction (72.0 g) was subjected to normal-phase silica gel CC [2.0 kg, CHCl₃–MeOH–H₂O (10:3:0.5 → 7:3:1, v/v/v, lower layer) → MeOH] to give five fractions [1 (12.1 g), 2 (19.2 g), 3 (10.4 g), 4 (8.7 g), and 5 (16.3 g)]. Fraction 1 (12.1 g) was subjected to reversed-phase silica gel CC [300 g, MeOH–H₂O (5:95 → 10:90 → 20:80 → 30:70 → 50:50 → 70:30, v/v) → MeOH] to afford 13 fractions [1-1 (550 mg), 1-2 (980 mg), 1-3 (1460 mg), 1-4 (1230 mg), 1-5 (1510 mg), 1-6 (1800 mg), 1-7 (540 mg), 1-8 (600 mg), 1-9 (710 mg), 1-10 (220 mg), 1-11 (1170 mg), 1-12 (1030 mg), and 1-13 (150 mg)]. Fraction 1-5 (1510 mg) was purified by Sephadex LH-20 CC [150 g, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (35:65, v/v)] to furnish sarmentol A (**2**, 125.8 mg, 0.00023%). Fraction 1-7 (540 mg) was purified by Sephadex LH-20 CC [150 g, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (40:60, v/v)] to furnish myrsinioside A (**11**, 48.5 mg, 0.00009%). Fraction 1-9 (710 mg) was purified by Sephadex LH-20 CC [150 g, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (50:50, v/v)] to furnish (3*S*,5*R*,6*S*,9*R*)-megastigmane-3,9-diol (**9**, 14.8 mg, 0.00003%). Fraction 2 (19.2 g) was subjected to reversed-phase silica gel CC [600 g, MeOH–H₂O (20:80 → 30:70 → 40:60 → 70:30, v/v) → MeOH] to afford 12 fractions [2-1 (200 mg), 2-2 (4630 mg), 2-3 (1160 mg), 2-4 (1950 mg), 2-5 (3300 mg), 2-6 (650 mg), 2-7 (700 mg), 2-8 (1800 mg), 2-9 (810 mg), 2-10 (1360 mg), 2-11 (2270 mg), and 2-12 (770 mg)]. Fraction 2-4 (1950 mg) was subjected to normal-phase silica gel CC [100 g, CHCl₃ → CHCl₃–MeOH (50:1 → 20:1 → 10:1, v/v) → CHCl₃–MeOH–H₂O (20:3:1, v/v/v, lower layer) → MeOH] to give seven fractions [2-4-1 (90.5 mg), 2-4-2 (50.1 mg), 2-4-3 (284.0 mg), 2-4-4 (153.8 mg), 2-4-5 (348.2 mg), 2-4-6 (721.1 mg), and 2-4-7 (300.0 mg)]. Fraction 2-4-5 (348.2 mg) was further purified by HPLC [CH₃–CN–MeOH–H₂O (10:8:82, v/v/v) and MeOH–H₂O (30:70 or 32:68, v/v)] to furnish sedumoside D (**8**, 43.0 mg, 0.00008%), staphylionoside D (**10**, 3.2 mg, 0.00001%), and 3-hydroxy-5,6-epoxy-β-ionol 9-*O*-β-D-glucopyranoside (**15**, 22.0 mg, 0.00004%). Fraction 2-4-6 (721.1 mg) was further purified by HPLC [MeOH–H₂O (32:68, v/v)] to give sedumosides A₁ (**3**, 162.5 mg, 0.00030%), A₂ (**4**, 60.6 mg, 0.00011%), A₃ (**5**, 29.2 mg, 0.00005%), and B (**6**, 3.2 mg, 0.00001%) and alangioside A (**13**, 52.8 mg, 0.00010%). Fraction 2-5 (3300 mg) was

further separated by HPLC [CH₃CN–H₂O (15:85, v/v)] to furnish **3** (34.0 mg, 0.00006%), **4** (838.6 mg, 0.0016%), **5** (200.9 mg, 0.00024%), sedumoside C (**7**, 24.1 mg, 0.00005%), and **8** (220.5 mg, 0.00041%). Fraction 2-8 (1800 mg) was purified by Sephadex LH-20 CC [150 g, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [CH₃CN–MeOH–H₂O (20:8:72, v/v/v) and MeOH–H₂O (40:60, v/v)] to furnish sarmentoic acid (**1**, 429.8 mg, 0.00080%), **1a** (24.5 mg, 0.00005%), and alangioside J (**14**, 80.9 mg, 0.00015%). Fraction 2-10 (1360 mg) was further separated by HPLC [CH₃CN–MeOH–H₂O (20:8:72, v/v/v) and CHCl₃–MeOH (40:60, v/v)] to furnish myrsinioside D (**12**, 182.1 mg, 0.00034%) and **14** (21.2 mg, 0.00004%). Fraction 3 (10.4 g) was subjected to reversed-phase silica gel CC [240 g, MeOH–H₂O (10:90 → 20:80 → 30:70 → 40:60, v/v) → MeOH] to afford 14 fractions [3-1 (123.0 mg), 3-2 (675.1 mg), 3-3 (574.8 mg), 3-4 (1337 mg), 3-5 (797.8 mg), 3-6 (798.6 mg), 3-7 (230.3 mg), 3-8 (901.2 mg), 3-9 (645.6 mg), 3-10 (256.4 mg), 3-11 (511.7 mg), 3-12 (1238 mg), 3-13 (473.1 mg), and 3-14 (1320 mg)]. Fraction 3-9 (645.6 mg) was purified by Sephadex LH-20 CC [150 g, CHCl₃–MeOH (1:1, v/v)] and finally HPLC [MeOH–H₂O (32:68, v/v)] to give plantaninoside D (**16**, 17.7 mg, 0.00003%). The known compounds were identified by comparison of their physical data ([α]_D, IR, ¹H NMR, ¹³C NMR, MS) with reported values.^{25–29}

Sarmentoic acid (1): amorphous powder; [α]_D²⁷ –3.3 (c 1.02, MeOH); IR (KBr) ν_{max} 3364, 2971, 2922, 2512, 1713, 1470, 1294, 1267, 1192, 1113, 1080, 1042, 948, 793, 650 cm^{–1}; ¹H NMR data, see Table 1; ¹³C NMR data, see Table 2; positive-ion FABMS *m/z* 267 [M + Na]⁺; HRFABMS *m/z* 267.1579 (calcd for C₁₃H₂₄O₄Na [M + Na]⁺, 267.1572).

Sarmentol A (2): colorless oil; [α]_D²⁷ –7.4 (c 0.10, MeOH); IR (film) ν_{max} 3389, 2926, 2874, 1472, 1387, 1026, 756 cm^{–1}; ¹H NMR data, see Table 1; ¹³C NMR data, see Table 2; positive-ion FABMS *m/z* 253 [M + Na]⁺; HRFABMS *m/z* 253.1774 (calcd for C₁₃H₂₆O₃Na [M + Na]⁺, 253.1780).

Sedumoside A₁ (3): amorphous powder; [α]_D²⁷ –28.3 (c 1.64, MeOH); IR (KBr) ν_{max} 3389, 2930, 2876, 1474, 1368, 1163, 1078, 1022 cm^{–1}; ¹H NMR data, see Table 3; ¹³C NMR data, see Table 4; positive-ion FABMS *m/z* 415 [M + Na]⁺; HRFABMS *m/z* 415.2313 (calcd for C₁₉H₃₆O₈Na [M + Na]⁺, 415.2308).

Sedumoside A₂ (4): amorphous powder; [α]_D²⁷ –6.2 (c 1.69, MeOH); IR (KBr) ν_{max} 3410, 2918, 1508, 1474, 1377, 1165, 1076, 1022 cm^{–1}; ¹H NMR data, see Table 3; ¹³C NMR data, see Table 4; positive-ion FABMS *m/z* 415 [M + Na]⁺; HRFABMS *m/z* 415.2313 (calcd for C₁₉H₃₆O₈Na [M + Na]⁺, 415.2308).

Sedumoside A₃ (5): amorphous powder; [α]_D²⁷ –16.9 (c 0.95, MeOH); IR (KBr) ν_{max} 3389, 2940, 1561, 1522, 1474, 1175, 1085, 1032 cm^{–1}; ¹H NMR data, see Table 3; ¹³C NMR data, see Table 4; positive-ion FABMS *m/z* 415 [M + Na]⁺; HRFABMS *m/z* 415.2303 (calcd for C₁₉H₃₆O₈Na [M + Na]⁺, 415.2308).

Sedumoside B (6): amorphous powder; [α]_D²³ –15.7 (c 0.16, MeOH); IR (KBr) ν_{max} 3390, 2928, 2876, 1474, 1078, 1022 cm^{–1}; ¹H NMR data, see Table 5; ¹³C NMR data, see Table 6; positive-ion FABMS *m/z* 415 [M + Na]⁺; HRFABMS *m/z* 415.2313 (calcd for C₁₉H₃₆O₈Na [M + Na]⁺, 415.2308).

Sedumoside C (7): amorphous powder; [α]_D²⁷ –0.8 (c 0.82, MeOH); CD (MeOH) λ_{max} (Δε) 284 (+0.08); IR (KBr) ν_{max} 3432, 2958, 1702, 1653, 1474, 1100, 1061 cm^{–1}; ¹H NMR data, see Table 5; ¹³C NMR data, see Table 6; positive-ion FABMS *m/z* 413 [M + Na]⁺; HRFABMS *m/z* 413.2153 (calcd for C₁₉H₃₄O₈Na [M + Na]⁺, 413.2151).

Sedumoside D (8): amorphous powder; [α]_D²⁷ –1.4 (c 2.01, MeOH); IR (KBr) ν_{max} 3432, 2961, 1719, 1655, 1647, 1561, 1541, 1474, 1079, 1051 cm^{–1}; ¹H NMR data, see Table 5; ¹³C NMR data, see Table 6; positive-ion FABMS *m/z* 413 [M + Na]⁺; HRFABMS *m/z* 413.2147 (calcd for C₁₉H₃₄O₈Na [M + Na]⁺, 413.2151).

Methylation of 1.¹⁸ A solution of **1** (20.0 mg) in Et₂O–MeOH (1:1, v/v, 1.0 mL) was treated with trimethylsilyldiazomethane (TM-SCHN₂, 10% in hexane, ca. 0.3 mL), and the whole was stirred at room temperature for 16 h. Removal of the solvent under reduced pressure furnished a residue, which was purified by normal-phase silica gel CC [2.0 g, hexane → hexane–CHCl₃ (1:1, v/v) → CHCl₃] to give **1a** (18.0 mg, 85%).

Compound 1a: colorless oil; [α]_D²⁷ –6.4 (c 2.01, MeOH); IR (film) ν_{max} 3432, 2953, 2940, 1717, 1541, 1472, 1259, 1165, 1076, 1038, 899, 752 cm^{–1}; ¹H NMR data, see Table 1; ¹³C NMR data, see Table 2; EIMS *m/z* 258 [M]⁺ (1), 240 (8), 225 (20), 123 (100); HREIMS *m/z* 258.1825 (calcd for C₁₄H₂₆O₄, 258.1831).

Table 5. ^1H NMR (500 MHz) Data of **6–8** and Related Compounds (**6a–8a** and **8d**)

position	6^a	6a^a	6a^b	7^a	7a^b
	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)
2 α	1.08 (dd, 11.6, 11.6)	1.09 (dd, 11.9, 11.9)	1.10 (dd, 11.9, 11.9)	2.38 (d, 13.2)	2.28 (d, 13.1)
2 β	1.64 (m)	1.64 (ddd, 2.5, 4.3, 11.9)	1.64 (ddd, 2.5, 4.3, 11.9)	1.97 (dd, 2.4, 13.2)	2.07 (dd, 2.5, 13.1)
3	3.69 (m)	3.69 (m)	3.77 (m)		
4 α	0.92 (ddd, 12.2, 12.2, 12.2)	0.90 (ddd, 12.2, 12.2, 12.2)	0.93 (ddd, 12.1, 12.1, 12.1)	2.15 (ddd, 0.9, 14.1, 14.1)	2.04 (m)
4 β	1.88 (m)	1.88 (m)	1.92 (m)	2.21 (ddd, 2.4, 4.6, 14.1)	2.31 (ddd, 2.5, 4.6, 14.1)
5	1.44 (m)	1.45 (m)	1.45 (m)	1.78 (m)	1.81 (m)
6	0.53 (ddd, 3.1, 4.9, 11.3)	0.54 (ddd, 2.7, 5.8, 11.3)	0.54 (ddd, 2.5, 5.2, 11.0)	1.16 (ddd, 2.5, 4.9, 11.3)	1.09 (m)
7	1.32 (m)	1.28 (m)	1.24 (m)	1.20 (m)	1.17 (m)
	1.47 (m)	1.47 (m)	1.46 (m)	1.67 (m)	1.65 (m)
8	1.50 (m)	1.49 (2H, m)	1.37 (m)	1.47 (m)	1.51 (m)
	1.69 (m)		1.58 (m)	1.65 (m)	1.63 (m)
9	3.65 (m)	3.53 (m)	3.69 (m)	3.75 (m)	3.73 (m)
10	3.59 (2H, d-like)	3.42 (dd, 6.4, 11.0)	3.47 (dd, 6.4, 11.0)	3.40 (dd, 8.0, 10.5)	3.47 (dd, 8.0, 11.0)
		3.45 (dd, 4.6, 11.0)	3.66 (dd, 4.6, 11.0)	3.93 (dd, 3.4, 10.5)	3.69 (dd, 3.3, 11.0)
11	0.83 (s)	0.83 (s)	0.81 (s)	0.77 (s)	0.78 (s)
12	0.96 (s)	0.96 (s)	0.95 (s)	1.08 (s)	1.06 (s)
13	0.99 (d, 6.4)	0.99 (d, 6.4)	0.97 (d, 6.4)	1.09 (d, 6.1)	1.07 (d, 6.1)
Glc-1'	4.33 (d, 8.0)			4.28 (d, 7.7)	
2'	3.19 (dd, 8.0, 9.2)			3.22 (dd, 7.7, 9.5)	
3'	3.33 (dd, 9.2, 9.2)			3.36 (dd, 8.9, 9.5)	
4'	3.28 (m)			3.26 (m)	
5'	3.28 (m)			3.28 (m)	
6'	3.64 (m)			3.66 (dd, 4.9, 11.9)	
	3.86 (dd, 2.2, 12.0)			3.84 (dd, 1.6, 11.9)	

position	8^a	8^c	8a^a	8a^b	8d^b
	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)	δ_{H} (J Hz)
2 α	1.09 (dd, 11.9, 11.9)	1.36 (dd, 12.2, 12.2)	1.09 (dd, 12.0, 12.0)	1.11 (dd, 11.9, 11.9)	1.09
2 β	1.64 (ddd, 2.4, 4.0, 11.9)	1.91 (ddd, 2.5, 4.3, 12.2)	1.64 (ddd, 2.5, 4.0, 12.0)	1.70 (ddd, 2.8, 4.3, 11.9)	1.64
3	3.69 (m)	3.97 (m)	3.69 (m)	3.76 (m)	3.69
4 α	0.92 (ddd, 12.2, 12.2, 12.2)	1.16 (ddd, 12.1, 12.1, 12.1)	0.91 (ddd, 11.9, 11.9, 11.9)	0.94 (ddd, 11.9, 11.9, 11.9)	0.90
4 β	1.88 (m)	2.08 (m)	1.88 (m)	1.94 (m)	1.89
5	1.35 (m)	1.35 (m)	1.35 (m)	1.48 (m)	1.43
6	0.60 (ddd, 2.8, 5.5, 11.0)	0.53 (ddd, 2.7, 5.2, 11.0)	0.59 (ddd, 2.5, 5.2, 10.7)	0.57 (ddd, 2.8, 5.2, 11.0)	0.54
7	1.47 (m)	1.41 (m)	1.48 (m)	1.41 (m)	1.26
	1.74 (m)	1.80 (m)	1.74 (m)	1.76 (m)	1.46
8	2.54 (ddd, 6.1, 10.4, 16.8)	2.64 (ddd, 5.8, 11.3, 17.7)	2.43 (ddd, 6.1, 10.4, 16.8)	2.40 (ddd, 6.1, 11.0, 16.5)	1.48
	2.62 (ddd, 5.5, 11.6, 16.8)	2.70 (ddd, 5.8, 11.5, 17.7)	2.54 (ddd, 5.2, 11.0, 16.8)	2.51 (ddd, 5.2, 11.3, 16.5)	1.57
9					
10	4.28 (d, 17.4)	4.57 (d, 16.8)	4.17 (2H, s)	4.23 (2H, s)	3.58
	4.51 (d, 17.4)	4.74 (d, 16.8)			3.77
11	0.83 (s)	0.78 (s)	0.83 (s)	0.83 (s)	0.83
12	0.95 (s)	0.89 (s)	0.95 (s)	0.94 (s)	0.96
13	0.97 (d, 6.4)	0.87 (d, 6.4)	0.97 (d, 6.4)	0.96 (d, 6.4)	0.99
Glc-1'	4.29 (d, 7.1)	4.95 (d, 7.1)			4.27
2'	3.27 (m)	4.13 (dd, 7.1, 8.8)			3.21
3'	3.35 (m)	4.25 (dd, 8.8, 8.8)			3.36
4'	3.27 (m)	4.23 (dd, 8.8, 9.0)			3.27
5'	3.27	3.94 (m)			3.27
6'	3.64 (m)	4.38 (dd, 5.5, 11.9)			3.64
	3.86 (dd, 2.2, 11.9)	4.53 (br, d, ca. 12)			3.86

^a Measured in CD₃OD. ^b Measured in CDCl₃. ^c Measured in pyridine-*d*₅.

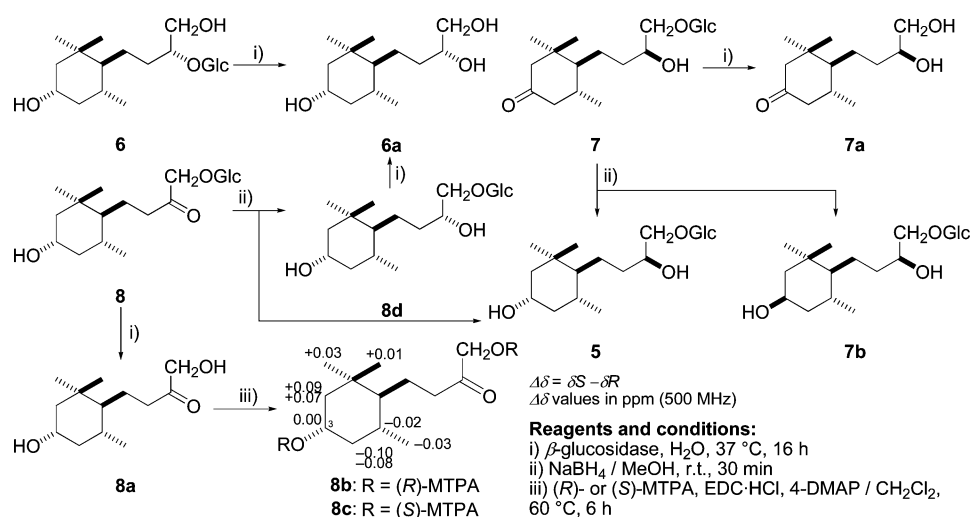
Preparation of the (R)-MTPA Esters (1b, 1d) and (S)-MTPA Esters (1c, 1e) from 1a. A solution of **1a** (9.3 mg) in CH₂Cl₂ (2.0 mL) was treated with (R)-2-methoxy-2-trifluoromethylphenylacetic acid [(R)-MTPA, 45.6 mg] in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, 37.1 mg) and 4-dimethylaminopyridine (4-DMAP, 15.7 mg), and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into ice–water and extracted with EtOAc. The EtOAc extract was successively washed with 5% aqueous HCl, saturated aqueous NaHCO₃, and brine, then dried over MgSO₄ powder and filtered. Removal of the

solvent from the filtrate under reduced pressure furnished a residue, which was purified by preparative TLC [CHCl₃–acetone (20:1, v/v)] to give **1b** (1.2 mg, 7%), **1d** (2.0 mg, 11%), and 3,9-di-(R)-MTPA ester derivative of **1a** (trace). Using a similar procedure, **1c** (0.6 mg, 4%), **1e** (1.8 mg, 12%), and 3,9-di-(S)-MTPA ester derivative of **1a** (trace) were obtained from **1a** (7.7 mg) using (S)-MTPA (35.1 mg), EDC·HCl (32.9 mg), and 4-DMAP (13.4 mg).

Compound 1b: colorless oil; ^1H NMR (pyridine-*d*₅, 500 MHz) δ 0.61 (ddd, *J* = 1.6, 5.2, 10.4 Hz, H-6), 0.85, 0.91 (3H each, both s, H₃-12, 11), 0.85 (3H, d, *J* = 5.8 Hz, H₃-13), 1.18 (1H, ddd, *J* = 3.1,

Table 6. ^{13}C NMR (125 MHz) Data of **6–8** and Related Compounds (**6a–8a** and **8d**)

	6^a	6a^a	6a^b	7^a	7a^b	8^a	8^c	8a^a	8a^b	8d^b
position	δ_{C}	δ_{C}	δ_{C}	δ_{C}	δ_{C}	δ_{C}	δ_{C}	δ_{C}	δ_{C}	δ_{C}
1	36.8	36.8	35.3	40.4	39.3	36.8	35.9	36.8	35.9	36.8
2	51.9	51.9	51.0	57.1	56.3	51.8	52.0	51.8	50.9	51.9
3	67.4	67.4	66.9	214.2	211.1	67.3	65.8	67.3	66.7	67.4
4	46.5	46.5	45.6	50.9	50.1	46.4	46.6	46.4	45.5	46.5
5	34.8	35.2	33.8	37.7	36.1	34.9	33.8	34.9	33.5	35.1
6	54.4	54.1	52.5	52.2	52.6	53.4	52.2	53.5	52.2	54.1
7	25.9	26.2	24.8	26.1	25.0	23.4	22.6	23.7	22.7	26.2
8	35.0	36.7	35.3	36.5	35.2	41.6	41.2	41.0	40.3	36.6
9	83.2	73.7	72.5	72.2	72.6	210.9	208.6	212.4	209.4	71.8
10	65.9	67.4	66.9	75.4	66.6	74.7	74.5	68.8	68.1	75.0
11	21.4	21.4	20.9	21.1	20.7	21.3	21.1	21.3	20.9	21.4
12	31.4	31.3	30.7	30.3	29.9	31.4	30.9	31.3	30.7	31.4
13	21.6	21.5	21.0	21.5	21.0	21.4	21.7	21.4	20.9	21.5
Glc-1'	104.0			104.9		104.3	104.6			104.5
2'	75.2			75.1		75.0	75.0			75.2
3'	78.2			77.9		77.8	78.4			78.0
4'	71.7			71.6		71.6	71.6			71.8
5'	77.9			78.0		78.2	78.7			78.0
6'	62.7			62.7		62.8	62.8			62.9

^a Measured in CD_3OD . ^b Measured in CDCl_3 . ^c Measured in pyridine- d_5 .**Figure 3.**

12.5, 13.7 Hz, $\text{H}\alpha$ -4), 1.35 (1H, m, H-5), 1.37, 1.77 (1H each, both m, H_2 -7), 1.42 (1H, br d, $J \approx 4$, 15 Hz, $\text{H}\alpha$ -2), 1.77 (1H, ddd, $J = 2.1$, 2.1, 14.7 Hz, $\text{H}\beta$ -2), 1.86 (1H, ddd, $J = 3.1$, 6.1, 13.7 Hz, $\text{H}\beta$ -4), 1.93, 2.02 (1H each, both m, H_2 -8), 3.62, 3.74 (3H each, both s, $-\text{COOCH}_3$), 4.53 (1H, m, H-9), 5.43 (1H, m, H-3), [7.41–7.45 (3H, m), 7.76 (2H, dd-like), Ph-H].

Compound 1c: colorless oil; ^1H NMR (pyridine- d_5 , 500 MHz) δ 0.62 (ddd, $J = 1.8$, 5.8, 10.7 Hz, H-6), 0.62, 0.85 (3H each, both s, H_3 -12, 11), 0.93 (3H, d, $J = 5.8$ Hz, H_3 -13), 1.26 (1H, ddd, $J = 3.2$, 12.7, 14.4 Hz, $\text{H}\alpha$ -4), 1.37 (1H, br d, $J = 4$, 15 Hz, $\text{H}\alpha$ -2), 1.40, 1.78 (1H each, both m, H_2 -7), 1.64 (1H, ddd, $J = 2.5$, 2.5, 14.7 Hz, $\text{H}\beta$ -2), 1.67 (1H, m, H-5), 1.91 (1H, ddd, $J = 2.5$, 4.9, 14.4 Hz, $\text{H}\beta$ -4), 1.95, 2.04 (1H each, both m, H_2 -8), 3.65, 3.74 (3H each, both s, $-\text{COOCH}_3$), 4.55 (1H, m, H-9), 5.43 (1H, m, H-3), [7.42–7.46 (3H, m), 7.78 (2H, dd-like), Ph-H].

Compound 1d: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.54 (ddd, $J = 1.8$, 5.7, 10.6 Hz, H-6), 0.78, 0.93 (3H each, both s, H_3 -12, 11), 0.78 (3H, d, $J = 6.4$ Hz, H_3 -13), 1.04, 1.42 (1H each, both m, H_2 -7), 1.19 (1H, ddd, $J = 3.2$, 12.4, 14.5 Hz, $\text{H}\alpha$ -4), 1.33 (1H, br d, $J \approx 4$, 15 Hz, $\text{H}\alpha$ -2), 1.54 (1H, m, $\text{H}\beta$ -2), 1.58, 1.81 (1H each, both m, H_2 -8), 1.68 (1H, ddd, $J = 2.5$, 4.8, 14.5 Hz, $\text{H}\beta$ -4), 2.00 (1H, m, H-5), 3.66, 3.79 (3H each, both s, $-\text{COOCH}_3$), 4.05 (1H, m, H-3), 5.16 (1H, dd, $J = 3.4$, 8.3 Hz, H-9), 7.39–7.69 (5H, m, Ph-H).

Compound 1e: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.61 (ddd, $J = 1.8$, 5.8, 10.7 Hz, H-6), 0.84, 0.98 (3H each, both s, H_3 -12, 11), 0.88 (3H, d, $J = 6.7$ Hz, H_3 -13), 1.22, 1.53 (1H each, both m,

H_2 -7), 1.25 (1H, ddd, $J = 3.2$, 12.7, 14.4 Hz, $\text{H}\alpha$ -4), 1.36 (1H, br d, $J \approx 4$, 15 Hz, $\text{H}\alpha$ -2), 1.56 (1H, ddd, $J = 2.7$, 2.7, 14.7 Hz, $\text{H}\beta$ -2), 1.64, 1.87 (1H each, both m, H_2 -8), 1.73 (1H, ddd, $J = 2.5$, 4.9, 14.4 Hz, $\text{H}\beta$ -4), 2.08 (1H, m, H-5), 3.65, 3.76 (3H each, both s, $-\text{COOCH}_3$), 4.08 (1H, m, H-3), 5.16 (1H, dd, $J = 3.4$, 8.3 Hz, H-9), 7.39–7.61 (5H, m, Ph-H).

NaBH_4 Reduction of 1a. A solution of **1a** (18.9 mg) in MeOH –pyridine (2:1, v/v, 1.5 mL) was treated with NaBH_4 (4.0 mg), and the mixture was stirred at room temperature for 3 h. The reaction mixture was quenched in acetone, and then removal of the solvent under reduced pressure gave a residue, which was purified by normal-phase silica gel CC [hexane– EtOAc (5:1 \rightarrow 1:1, v/v)] to give **1f** (10.7 mg, 64%).

Compound 1f: colorless oil; $[\alpha]_{\text{D}}^{27} +37.2$ (c 1.30, MeOH); IR (film) ν_{max} 3375, 2922, 2874, 1473, 1387, 1026, 756 cm^{-1} ; ^1H NMR data, see Table 1; ^{13}C NMR data, see Table 2; positive-ion FABMS m/z 253 $[\text{M} + \text{Na}]^+$; HRFABMS m/z 253.1789 (calcd for $\text{C}_{13}\text{H}_{26}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$, 253.1780).

Pivaloylation of 2. A solution of **2** (36.8 mg) in pyridine (1.0 mL) was treated with pivaloyl chloride (50 μL), and the mixture was stirred at 60°C for 6 h. The reaction mixture was poured into ice–water, and the whole was extracted with EtOAc . The EtOAc extract was successively washed with 5% aqueous HCl , saturated aqueous NaHCO_3 , and brine, then dried over MgSO_4 powder and filtered. Removal of the solvent under reduced pressure furnished a residue, which was

purified by normal-phase silica gel CC [1.5 g, hexane–EtOAc (20:1 → 10:1 → 5:1 → 3:1, v/v)] to give **2a** (16.4 mg, 32%) and **2b** (8.3 mg, 13%).

Compound 2a: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.56 (ddd, $J = 2.5, 4.6, 11.1$ Hz, H-6), 0.81, 0.95 (3H each, both s, H₃-11, 12), 0.94 (1H, ddd, $J = 12.2, 12.2, 12.2$ Hz, H α -4), 0.96 (3H, d, $J = 6.7$ Hz, H₃-13), 1.07, 1.60 (1H each, both m, H₂-7), 1.11 (1H, dd, $J = 12.0, 12.0$ Hz, H α -2), 1.22 [9H, s, $-\text{OCOC}(\text{CH}_3)_3$], 1.45 (1H, m, H-5), 1.45, 1.59 (1H each, both m, H₂-8), 1.69 (1H, ddd, $J = 2.5, 4.3, 12.0$ Hz, H β -2), 1.93 (1H, m, H β -4), 3.76 (1H, m, H-3), 3.79 (1H, m, H-9), [3.98 (1H, dd, $J = 6.7, 11.3$ Hz), 4.15 (1H, dd, $J = 3.4, 11.3$ Hz), H₂-10], ^{13}C NMR (CDCl_3 , 125 MHz) δ 35.9 (C-1), 50.9 (C-2), 66.8 (C-3), 45.6 (C-4), 33.5 (C-5), 52.6 (C-6), 24.7 (C-7), 35.6 (C-8), 70.7 (C-9), 68.2 (C-10), 20.8 (C-11), 30.6 (C-12), 20.9 (C-13), 178.7 [$-\text{OCOC}(\text{CH}_3)_3$], 38.9 [$-\text{OCOC}(\text{CH}_3)_3$], 27.2 [$-\text{OCOC}(\text{CH}_3)_3$]; EIMS m/z 314 [M^+ , (1)], 296 (5), 257 (1), 212 (2), 200 (1), 57 (100); HREIMS m/z 314.2458 (calcd for $\text{C}_{18}\text{H}_{34}\text{O}_4$ [M^+], 314.2457).

Compound 2b: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.59 (ddd, $J = 2.1, 4.9, 11.0$ Hz, H-6), 0.87, 0.95 (3H each, both s, H₃-11, 12), 0.95 (3H, d, $J = 6.4$ Hz, H₃-13), 1.00 (1H, ddd, $J = 12.3, 12.3, 12.3$ Hz, H α -4), 1.08, 1.61 (1H each, both m, H₂-7), 1.16, 1.22 [9H each, both s, $-\text{OCOC}(\text{CH}_3)_3$], 1.26 (1H, dd, $J = 12.0, 12.0$ Hz, H α -2), 1.46, 1.59 (1H each, both m, H₂-8), 1.52 (1H, m, H-5), 1.67 (1H, ddd, $J = 2.5, 4.3, 12.0$ Hz, H β -2), 1.93 (1H, m, H β -4), 3.79 (1H, m, H-9), [3.98 (1H, dd, $J = 6.7, 11.3$ Hz), 4.15 (1H, dd, $J = 3.4, 11.3$ Hz), H₂-10], 4.83 (1H, m, H-3); ^{13}C NMR (CDCl_3 , 125 MHz) δ 35.9 (C-1), 46.5 (C-2), 69.6 (C-3), 41.1 (C-4), 33.3 (C-5), 52.7 (C-6), 24.6 (C-7), 35.5 (C-8), 70.7 (C-9), 68.2 (C-10), 20.6 (C-11), 30.5 (C-12), 20.7 (C-13), 178.2, 178.8 [$-\text{OCOC}(\text{CH}_3)_3$], 38.6, 38.9 [$-\text{OCOC}(\text{CH}_3)_3$], 27.1, 27.2 [$-\text{OCOC}(\text{CH}_3)_3$]; positive-ion CIMS m/z 399 [$\text{M} + 1$] $^+$, (9), 381 (3), 297 (100), 279 (14); HRCIMS m/z 399.3106 (calcd for $\text{C}_{23}\text{H}_{42}\text{O}_5$ [$\text{M} + 1$] $^+$, 399.3110).

Preparation of the (R)-MTPA Esters (2c, 2e) and (S)-MTPA Esters (2d, 2f) from 2a and 2b. A solution of **2a** (7.6 mg) in CH_2Cl_2 (1.0 mL) was treated with (R)-MTPA (68.3 mg) in the presence of $\text{EDC}\cdot\text{HCl}$ (48.5 mg) and 4-DMAP (21.6 mg), and the mixture was stirred under reflux for 6 h. Workup of the reaction mixture as described above gave a residue, which was purified by normal-phase silica gel CC [800 mg, hexane–EtOAc (40:1 → 10:1 → 5:1 → 2:1, v/v)] to give **2c** (1.3 mg, 10%). Using a similar procedure, (S)-MTPA ester derivative of **2a** (**2d**, 1.2 mg, 10%) was obtained from **2a** (7.2 mg) using (S)-MTPA (62.5 mg), $\text{EDC}\cdot\text{HCl}$ (53.4 mg), and 4-DMAP (21.6 mg). Through the similar procedure, a solution of **2b** (4.2 mg) in CH_2Cl_2 (1.0 mL) was treated with (R)-MTPA (50.7 mg) in the presence of $\text{EDC}\cdot\text{HCl}$ (32.5 mg) and 4-DMAP (17.2 mg), and the mixture was stirred under reflux for 6 h. Workup of the reaction mixture as described above gave a residue, which was purified by normal-phase silica gel CC [580 mg, hexane–EtOAc (20:1 → 10:1, v/v)] to give **2e** (0.3 mg, 5%). Using a similar procedure, (S)-MTPA ester derivative of **2b** (**2f**, 0.2 mg, 4%) was obtained from **2b** (3.4 mg) using (S)-MTPA (45.8 mg), $\text{EDC}\cdot\text{HCl}$ (31.2 mg), and 4-DMAP (15.5 mg).

Compound 2c: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.61 (ddd, $J = 2.5, 4.6, 11.1$ Hz, H-6), 0.89, 0.95 (3H each, both s, H₃-12, 11), 0.98 (3H, d, $J = 6.7$ Hz, H₃-13), 1.09, 1.60 (1H each, both m, H₂-7), 1.17 (1H, ddd, $J = 12.2, 12.2, 12.2$ Hz, H α -4), 1.22 [9H, s, $-\text{OCOC}(\text{CH}_3)_3$], 1.25 (1H, dd, $J = 12.2, 12.2$ Hz, H α -2), 1.45, 1.59 (1H each, both m, H₂-8), 1.55 (1H, m, H-5), 1.73 (1H, ddd, $J = 2.5, 4.3, 12.2$ Hz, H β -2), 2.05 (1H, m, H β -4), 3.56 (3H, s, $-\text{COOCH}_3$), 3.78 (1H, m, H-9), [3.98 (1H, dd, $J = 6.7, 11.3$ Hz), 4.14 (1H, dd, $J = 3.4, 11.3$ Hz), H₂-10], 5.14 (1H, m, H-3), 7.39–7.53 (5H, m, Ph–H).

Compound 2d: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.60 (ddd, $J = 2.5, 4.6, 11.1$ Hz, H-6), 0.90, 0.98 (3H each, both s, H₃-12, 11), 0.96 (3H, d, $J = 6.5$ Hz, H₃-13), 1.07 (1H, ddd, $J = 12.3, 12.3, 12.3$ Hz, H α -4), 1.09, 1.60 (1H each, both m, H₂-7), 1.22 [9H, s, $-\text{OCOC}(\text{CH}_3)_3$], 1.35 (1H, dd, $J = 11.9, 11.9$ Hz, H α -2), 1.45, 1.58 (1H each, both m, H₂-8), 1.53 (1H, m, H-5), 1.79 (1H, ddd, $J = 2.5, 4.3, 11.9$ Hz, H β -2), 1.98 (1H, m, H β -4), 3.55 (3H, s, $-\text{COOCH}_3$), 3.78 (1H, m, H-9), [3.97 (1H, dd, $J = 6.7, 11.3$ Hz), 4.14 (1H, dd, $J = 3.4, 11.3$ Hz), H₂-10], 5.14 (1H, m, H-3), 7.40–7.53 (5H, m, Ph–H).

Compound 2e: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.56 (ddd, $J = 2.1, 4.9, 11.0$ Hz, H-6), 0.81, 0.88 (3H each, both s, H₃-12, 11), 0.92 (3H, d, $J = 6.4$ Hz, H₃-13), 0.99 (1H, ddd, $J = 12.0, 12.0, 12.0$ Hz, H α -4), 1.10, 1.49 (1H each, both m, H₂-7), 1.14, 1.16 [9H

each, both s, $-\text{OCOC}(\text{CH}_3)_3$], 1.19 (1H, dd, $J = 12.0, 12.0$ Hz, H α -2), 1.51 (1H, m, H-5), 1.60, 1.78 (1H each, both m, H₂-8), 1.66 (1H, ddd, $J = 2.8, 4.0, 12.0$ Hz, H β -2), 1.91 (1H, m, H β -4), 3.55 (3H, s, $-\text{COOCH}_3$), [4.06 (1H, dd, $J = 6.1, 12.5$ Hz), 4.31 (1H, dd, $J = 3.1, 12.5$ Hz), H₂-10], 4.80 (1H, m, H-3), 5.23 (1H, m, H-9), 7.39–7.55 (5H, m, Ph–H).

Compound 2f: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.49 (ddd, $J = 1.8, 4.2, 10.7$ Hz, H-6), 0.73, 0.78 (3H each, both s, H₃-12, 11), 0.87 (3H, d, $J = 6.4$ Hz, H₃-13), 0.96 (1H, ddd, $J = 11.9, 11.9, 11.9$ Hz, H α -4), 1.01, 1.33 (1H each, both m, H₂-7), 1.15, 1.17 [9H each, both s, $-\text{OCOC}(\text{CH}_3)_3$], 1.15 (1H, dd, $J = 12.1, 12.1$ Hz, H α -2), 1.45 (1H, m, H-5), 1.57, 1.69 (1H each, both m, H₂-8), 1.65 (1H, ddd, $J = 2.5, 4.3, 12.1$ Hz, H β -2), 1.90 (1H, m, H β -4), 3.55 (3H, s, $-\text{COOCH}_3$), [4.08 (1H, dd, $J = 6.7, 12.2$ Hz), 4.37 (1H, dd, $J = 3.1, 12.2$ Hz), H₂-10], 4.81 (1H, m, H-3), 5.23 (1H, m, H-9), 7.34–7.56 (5H, m, Ph–H).

Acid Hydrolysis of 3–8. A solution of **3–8** (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 layer was subjected to 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-glucose present in the aqueous layer was carried out by comparison of its retention time and optical rotation with those of an authentic sample.

Enzymatic Hydrolysis of 3–8 with β -Glucosidase. A solution of **3–6** (3.0, 7.6, 5.0, and 2.0 mg, respectively) in H_2O (1.0 mL) was treated with β -glucosidase (2.0, 2.0, 2.6, 2.0 mg, respectively). The solution was stirred at 37 $^\circ\text{C}$ for 16 h, EtOH was added to the reaction mixture, the solvent was removed under reduced pressure, and the residue was purified by HPLC [$\text{MeOH}-\text{H}_2\text{O}$ (40:60, v/v)] to furnish sarmentol A (**2**, 1.5 mg, 91% from **3**; 3.8 mg, 85% from **4**; 2.9 mg, 95% from **5**) and sarmentol B (**6a**, 1.0 mg, 85% from **6**). A solution of **7** (12.1 mg) or **8** (25.1 mg) in H_2O (2.0 mL) was treated with β -glucosidase (8.0, 18.2 mg, respectively), and the solution was stirred at 37 $^\circ\text{C}$ for 16 h. The residue was purified by HPLC [$\text{MeOH}-\text{H}_2\text{O}$ (40:60, v/v)] to give sarmentols C (**7a**, 6.3 mg, 89% from **7**) and D (**8a**, 12.1 mg, 82% from **8**), respectively.

Sarmentol B (6a): colorless oil; $[\alpha]_D^{25} +5.6$ (c 0.05, MeOH); IR (film) ν_{max} 3372, 2924, 2874, 1474, 1387, 1026, 754 cm^{-1} ; ^1H NMR data, see Table 5; ^{13}C NMR data, see Table 6; positive-ion FABMS m/z 253 [$\text{M} + \text{Na}$] $^+$; HRFABMS m/z 253.1771 (calcd for $\text{C}_{13}\text{H}_{26}\text{O}_3\text{Na}$ [$\text{M} + \text{Na}$] $^+$, 253.1780).

Sarmentol C (7a): colorless oil; $[\alpha]_D^{25} +11.9$ (c 0.22, MeOH); CD (MeOH) λ_{max} ($\Delta\epsilon$) 286 (+0.19); IR (film) ν_{max} 3432, 2955, 2876, 1700, 1653, 1472, 1391, 1285, 1100, 1063 cm^{-1} ; ^1H NMR data, see Table 5; ^{13}C NMR data, see Table 6; positive-ion CIMS m/z 229 [$\text{M} + 1$] $^+$ (57), 211 (41), 197 (64), 138 (64), 95 (100); HRCIMS m/z 229.1801 (calcd for $\text{C}_{13}\text{H}_{25}\text{O}_3$ [$\text{M} + 1$] $^+$, 229.1804).

Sarmentol D (8a): colorless oil; $[\alpha]_D^{25} +1.2$ (c 0.42, MeOH); IR (film) ν_{max} 3346, 2955, 2876, 1717, 1473, 1073, 1026 cm^{-1} ; ^1H NMR data, see Table 1; ^{13}C NMR data, see Table 2; EIMS m/z 228 [M] $^+$ (1), 210 (15), 200 (2), 197 (61), 179 (67), 161 (100); HREIMS: m/z 228.1723 (calcd for $\text{C}_{13}\text{H}_{24}\text{O}_3$, 228.1725).

NaBH_4 Reduction of 7 and 8. A solution of **7** (5.1 mg) in MeOH (1.5 mL) was treated with NaBH_4 (1.2 mg), and the mixture was stirred at room temperature for 30 min. The reaction mixture was quenched in acetone, and then removal of the solvent under reduced pressure gave a residue, which was purified by HPLC [$\text{MeOH}-\text{H}_2\text{O}$ (34:66, v/v)] to give **5** (0.7 mg, 14%) and **7b** (0.2 mg, 4%). Through the similar procedure, a solution of **8** (20.0 mg) in MeOH (2.0 mL) was treated with NaBH_4 (3.0 mg) and the mixture was stirred at room temperature for 30 min. Workup of the reaction mixture as described above gave a residue, which was purified by HPLC [$\text{MeOH}-\text{H}_2\text{O}$ (25:75, v/v)] to give **5** (6.3 mg, 31%) and **8d** (6.3 mg, 31%).

Compound 7b: ^1H NMR (CD_3OD , 500 MHz) δ 0.53 (1H, ddd, $J = 2.1, 5.0, 11.0$ Hz, H-6), 0.83, 0.95 (3H each, both s, H₃-12, 11), 0.98 (3H, d, $J = 6.2$ Hz, H₃-13), 1.60 (1H, m, H-5), [3.52 (1H, dd, $J = 5.5, 11.2$ Hz), 3.68 (1H, dd, $J = 3.1, 11.2$ Hz), H₂-10], [3.64 (1H, m), 3.86 (1H, dd, $J = 1.6, 10.1$ Hz), H₂-6'], 3.96 (1H, m, H-3), 4.41 (1H, d, $J = 7.6$ Hz, H-1'); positive-ion FABMS m/z 415 [$\text{M} + \text{Na}$] $^+$; HRFABMS m/z 415.2316 (calcd for $\text{C}_{19}\text{H}_{36}\text{O}_8\text{Na}$ [$\text{M} + \text{Na}$] $^+$, 415.2308).

Compound 8d: amorphous powder; $[\alpha]_D^{25} -20.2$ (c 2.50, MeOH); IR (KBr) ν_{max} 3422, 2940, 1565, 1475, 1078 cm^{-1} ; ^1H NMR data, see

Table 5; ^{13}C NMR data, see Table 6; positive-ion FABMS m/z 415 $[\text{M} + \text{Na}]^+$; HRFABMS m/z 415.2301 (calcd for $\text{C}_{19}\text{H}_{36}\text{O}_8\text{Na}$ $[\text{M} + \text{Na}]^+$, 415.2308).

Enzymatic Hydrolysis of 8d with β -Glucosidase. A solution of **8d** (5.0 mg) in H_2O (1.0 mL) was treated with β -glucosidase (3.0 mg), and the solution was stirred at 37 °C for 16 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 (40:60, v/v)] to give **6a** (2.7 mg, 92%).

Preparation of the (R)-MTPA Ester (8b) and (S)-MTPA Ester (8c) from 8a. A solution of **8a** (6.4 mg) in CH_2Cl_2 (1.0 mL) was treated with (R)-MTPA (78.6 mg) in the presence of EDC·HCl (62.1 mg) and 4-DMAP (30.5 mg), and the mixture was stirred at room temperature for 6 h. Workup of the reaction mixture as described above gave a residue, which was purified by normal-phase silica gel CC [1.0 g, hexane–EtOAc (30:1 \rightarrow 10:1, v/v)] to give **8b** (10.4 mg, 61%). Using a similar procedure, the (S)-MTPA ester **8c** (8.3 mg, 62%) was obtained from **8a** (4.7 mg) using (S)-MTPA (78.5 mg), EDC·HCl (60.1 mg), and 4-DMAP (23.9 mg).

Compound 8b: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.60 (ddd, $J = 2.8, 5.5, 11.0$ Hz, H-6), 0.89, 0.93 (3H each, both s, H₃-11, 12), 0.96 (3H, d, $J = 6.4$ Hz, H₃-13), 1.17 (1H, ddd, $J = 11.9, 11.9, 11.9$ Hz, H α -4), 1.25 (1H, dd, $J = 12.5, 12.5$ Hz, H α -2), 1.42, 1.77 (1H each, both m, H₂-7), 1.57 (1H, m, H-5), 1.73 (1H, ddd, $J = 2.8, 4.6, 12.5$ Hz, H β -2), 2.05 (1H, m, H β -4), [2.40 (1H, ddd, $J = 5.8, 11.0, 17.4$ Hz), 2.52 (1H, ddd, $J = 4.9, 11.6, 17.4$ Hz), H₂-8], 3.54, 3.64 (3H each, both s, $-\text{COOCH}_3$), 4.78, 4.89 (1H each, both d, $J = 16.5$ Hz, H₂-10), 5.13 (1H, m, H-3), 7.39–7.64 (10H, m, Ph-H).

Compound 8c: colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.60 (ddd, $J = 2.5, 5.2, 10.7$ Hz, H-6), 0.90, 0.96 (3H each, both s, H₃-11, 12), 0.93 (3H, d, $J = 6.4$ Hz, H₃-13), 1.07 (1H, ddd, $J = 11.9, 11.9, 11.9$ Hz, H α -4), 1.34 (1H, dd, $J = 12.2, 12.2$ Hz, H α -2), 1.40, 1.76 (1H each, both m, H₂-7), 1.55 (1H, m, H-5), 1.80 (1H, ddd, $J = 2.2, 4.3, 12.2$ Hz, H β -2), 1.97 (1H, m, H β -4), [2.40 (1H, ddd, $J = 6.1, 10.4, 16.8$ Hz), 2.51 (1H, ddd, $J = 5.2, 11.0, 16.8$ Hz), H₂-8], 3.54, 3.64 (3H each, both s, $-\text{COOCH}_3$), 4.78, 4.89 (1H each, both d, $J = 16.5$ Hz, H₂-10), 5.13 (1H, m, H-3), 7.39–7.64 (10H, m, Ph-H).

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Supporting Information Available: ^1H – ^1H COSY, HMBC, and NOE correlations of **1**–**8** (Figure S1). This information is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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