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

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Received October 24, 2006

Two new megastigmanes, sarmentoic acid (**1**) and sarmentol A (**2**), and six new megastigmane glucosides, sedumosides A_1 (**3**), A_2 (**4**), A_3 (**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 A_1 (**3**), A_2 (**4**), A_3 (**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 H_2O, and the H_2O 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 ($H_2O \rightarrow$ MeOH) to give H_2O- 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-diol[25] (**9**), staphylionoside D[26] (**10**), myrsinionosides A[25] (**11**) and D[25] (**12**), alangiosides A[27] (**13**) and J[25] (**14**), 3-hydroxy-5,6-epoxy-β-ionol 9-*O*-β-D-glucopyranoside[28] (**15**), and platanionoside D[29] (**16**).

Sarmentoic acid (**1**) was obtained as an amorphous powder ($[\alpha]^{27}_D$ −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 $C_{13}H_{24}O_4$. The ^1H (pyridine-d_5, Table 1) and ^{13}C 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, H_3-12, 11), 1.07 (d, J = 6.7 Hz, H_3-13)], 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: H_2-2 and C-1; H-6 and C-1; H-9 and C-7, 8, 10; H_3-11 and C-1, 2, 6, 12; H_3-12 and C-1, 2, 6, 11; H_3-13 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, H_3-12; H-3 and Hα-4; Hα-4 and H-6, H_3-13; H-6 and H_3-12; and H_2-7 and H_3-11, 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 ($TMSCHN_2$), 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**) [$\Delta\delta$: 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** [$\Delta\delta$: 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**) [$\Delta\delta$: positive], while the signal of the 10-carboxy methyl proton in **1e** was observed at higher field compared with that of **1d** [$\Delta\delta$: 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 ($[\alpha]^{27}_D$ −7.4 in MeOH). The molecular formula, $C_{13}H_{26}O_3$, of **2** was determined from the positive-ion FABMS (*m*/*z* 253 $[M + Na]^+$) and by HRFABMS. The ^1H (CD_3OD, Table 1) and ^{13}C NMR (Table 2) spectra[30] of **2** showed signals assignable to three methyls [δ 0.83, 0.96 (both s, H_3-11, 12), 0.98 (d, J = 6.5 Hz, H_3-13)] 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), H_2-10], 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 ^{13}C NMR spectra of **2** resembled those of **1f**, which was derived from **1a** by reduction with sodium borohydride ($NaBH_4$). 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: H_2-2 and C-1; H-3 and C-2,

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10.1021/np068059s CCC: $37.00
Published on Web 02/10/2007

Chart 1

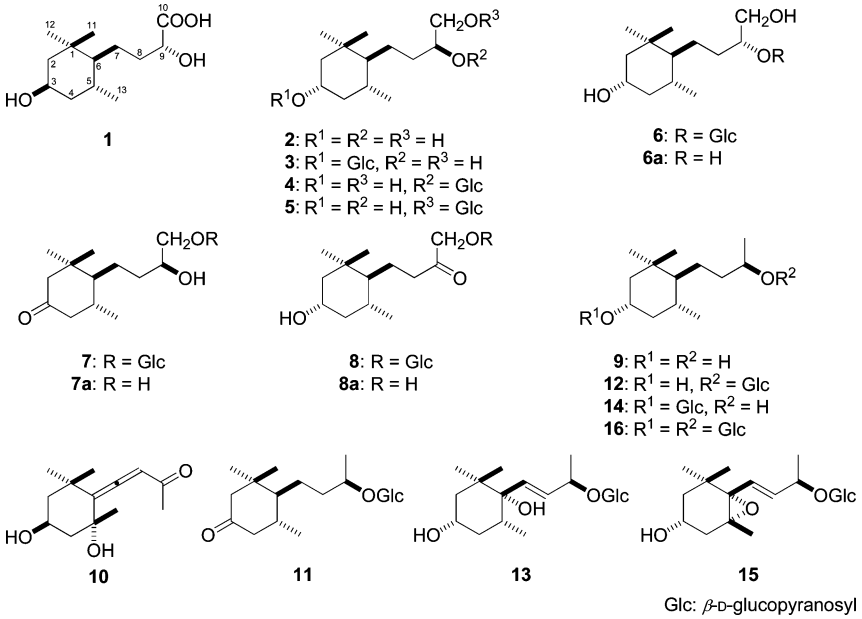

Table 1. ^{1}H NMR (500 MHz) Data of **1** and **2** and Related Compounds (**1a** and **1f**)

	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)
2α	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)
4α	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 $CDCl_3$. [c]Measured in CD_3OD.

4; H-6 and C-1; H_2-8 and C-9, 10; H-9 and C-8, 10; H_2-10 and C-8, 9; H_3-11 and C-1, 2, 6, 12; H_3-12 and C-1, 2, 6, 11; H_3-13 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 Hα-2 and H-6, H_3-12; H*β*-2 and H-3; H-3 and H*β*-4; Hα-4 and H-6, H_3-13; H-6 and H_3-12; and H_2-7 and H_3-11. 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**) [Δ*δ*: positive], while the protons on the 4-, 5-, and 13-positions of **2d** were observed at higher fields compared to those of **2c** [Δ*δ*: 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**) [Δ*δ*: positive], while the protons on the 5−8- and 11−13-positions of **2f** were observed at higher fields compared to those of **2e** [Δ*δ*: negative]. Consequently, the absolute configurations at the 3- and 9-positions in **2** were elucidated to be 3*S* and 9*S*.

Sedumoside A_1 (**3**) was obtained as an amorphous powder ($[\alpha]^{22}_D$ −28.3 in MeOH). HRFABMS revealed the molecular formula of **3** to be $C_{19}H_{36}O_8$, and the IR spectrum showed absorption bands at 3389 and 1078 cm^{-1}, ascribable to hydroxyl and ether functions. The ^{1}H NMR (pyridine-d_5, Table 3) and ^{13}C NMR (Table 4) spectra[30] of **3** showed the presence of the following functions: three methyls [*δ* 0.75, 0.92 (both s, H_3-11, 12), 0.92 (d, *J* = 6.1 Hz, H_3-13)], 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), H_2-10], 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

Table 2. ^{13}C NMR (125 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_C	δ_C	δ_C	δ_C	δ_C	δ_C
1	34.8	34.8	34.2	34.2	35.9	36.8
2	48.0	48.0	47.4	47.4	51.0	51.8
3	66.7	66.7	67.8	67.8	66.9	67.3
4	44.4	44.3	43.1	43.1	45.6	46.5
5	29.7	29.7	28.8	28.8	33.6	34.9
6	53.7	53.6	53.1	53.3	52.7	54.2
7	25.5	25.3	24.1	24.9	24.9	26.3
8	37.6	37.3	36.3	35.3	35.5	36.9
9	71.7	71.5	70.7	72.6	72.8	73.9
10	178.2	176.0	175.8	66.9	66.7	67.3
11	23.5	23.5	23.1	23.1	21.0	21.4
12	31.9	31.8	31.4	31.4	30.7	31.3
13	21.2	21.1	20.6	20.8	21.5	21.5
COOMe		51.6	52.5			

[a] Measured in pyridine-d_5. [b]Measured in $CDCl_3$. [c]Measured in CD_3OD.

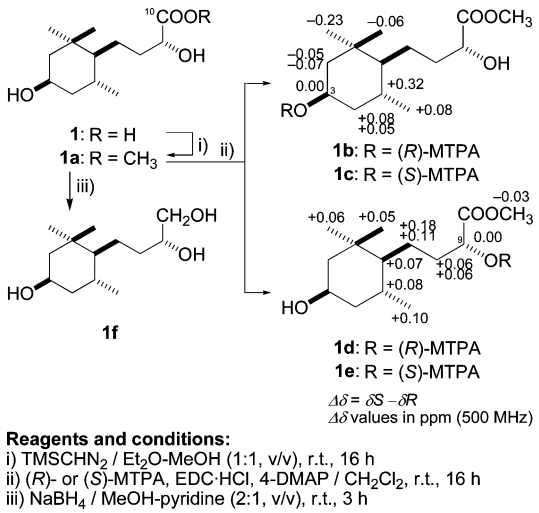

Figure 1.

using an optical rotation detector.[12,14−16,19−22,24] Enzymatic hydrolysis of **3** with β-glucosidase gave **2** as an aglycon. The position of the β-D-glucopyranosyl moiety in **3** was determined by the HMBC experiment, in which a long-range correlation was observed between the 1′-proton and the 3-carbon. Consequently, the structure of **3** was elucidated as sarmentol A 3-*O*-β-D-glucopyranoside.

Sedumosides A_2 (**4**) and A_3 (**5**) were obtained as amorphous powders (**4**: $[\alpha]^{27}_D$ −6.2; **5**: $[\alpha]^{27}_D$ −16.9, both in MeOH). The same molecular formula, $C_{19}H_{36}O_8$, for both **4** and **5** was determined individually from the positive-ion FABMS (*m*/*z* 415 $[M + Na]^+$) and by HRFABMS. Acid hydrolysis of **4** and **5** with 1 M HCl liberated D-glucose. Enzymatic hydrolysis of **4** and **5** with β-glucosidase both gave **2** as the aglycon. The ^1H (pyridine-d_5, Table 3) and ^{13}C NMR (Table 4) spectra[30] of **4** and **5** indicated the presence of the following functions: an aglycon part {**4**: δ 0.83, 0.93 (both s, H_3-11, 12), 0.97 (d, J = 6.2 Hz, H_3-13), 3.79 (2H, m, H_2-10), 3.97 (m, H-3), 4.10 (m, H-9); **5**: δ 0.80, 0.94 (both s, H_3-11, 12), 0.96 (d, J = 6.4 Hz, H_3-13), [3.89 (dd, J = 8.6, 10.1 Hz), 4.27 (dd, J = 3.7, 10.1 Hz), H_2-10], 4.02 (m, H-3), 4.14 (m, H-9)} and a β-glucopyranosyl part [**4**: δ 5.12 (d, J = 7.6 Hz, H-1′); **5**: δ 5.00 (d, J = 7.6 Hz, H-1′)]. In the HMBC experiment of **4**, a long-range correlation was observed between the 1′-proton and the 9-carbon, while a long-range correlation in the HMBC experiment of **5** was observed between the 1′-proton and the 10-carbon. Thus, **4** and **5** were elucidated as sarmentol A 9-*O*-β-D-glucopyranoside and sarmentol A 10-*O*-β-D-glucopyranoside, respectively.

Sedumoside B (**6**), $[\alpha]^{23}_D$ −15.7 (MeOH), was also obtained as an amorphous powder. The molecular formula, $C_{19}H_{36}O_8$, of **6** was determined from the positive-ion FABMS and by HRFABMS. The proton and carbon signals in the ^1H (CD_3OD, Table 5) and ^{13}C NMR (Table 6) spectra[30] of **6** were very similar to those of **4**, except for the signals around the 9-position: three methyls [δ 0.83, 0.96 (both s, H_3-11, 12), 0.99 (d, J = 6.4 Hz, H_3-13)], a methylene and two methines bearing an oxygen function [δ 3.59 (2H, d-like, H_2-10), 3.65 (m, H-9), 3.69 (m, H-3)], and a β-glucopyranosyl part [δ 4.33 (d, J = 8.0 Hz, H-1′)]. Acid hydrolysis of **6** liberated D-glucose. The enzymatic hydrolysis of **6** with β-glucosidase gave a new megastigmane, sarmentol B (**6a**), the 9*R* isomer of **2**, as determined by the chemical correlation with **8** (*vide infra*). The linkage of the β-D-glucopyranosyl moiety in **6** was clarified by the HMBC experiment, which showed long-range correlation between the 1′-proton and 9-carbon (Figure S1). Consequently, **6** was elucidated to be sarmentol B 9-*O*-β-D-glucopyranoside.

Sedumoside C (**7**) was obtained as an amorphous powder ($[\alpha]^{27}_D$ −0.8 in MeOH). The IR spectrum of **7** showed absorption bands at 3432, 1702, and 1061 cm^{-1}, ascribable to hydroxyl, carbonyl, and ether functions. The molecular formula, $C_{19}H_{34}O_8$, of **7** was from FABMS (*m*/*z* 413 $[M + Na]^+$) and HRFABMS. Sedumoside D (**8**), $[\alpha]^{27}_D$ −1.4 (MeOH), was also obtained as an amorphous powder ($C_{19}H_{34}O_8$). Treatment of **7** and **8** with 1 M HCl liberated D-glucose. The ^1H (CD_3OD, Table 5) and ^{13}C NMR (Table 6) spectra[30] of **7** showed signals assignable to three methyls [δ 0.77, 1.08 (both s, H_3-11, 12), 1.09 (d, J = 6.1 Hz, H_3-13)], a methylene and a methine bearing an oxygen function {δ [3.40 (dd, J = 8.0, 10.5 Hz), 3.93 (dd, J = 3.4, 10.5 Hz), H_2-10], 3.75 (m, H-9)}, and a β-glucopyranosyl moiety [δ 4.28 (d, J = 7.7 Hz, H-1′)] together with four methylenes, two methines, and two quaternary carbons including an carbonyl carbon (δ_C 214.2, C-3). The ^1H and ^{13}C NMR spectra of **7** were superimposable on those of **5**, except for signals due to the 3-position. The $^1H-^1H$ COSY experiment on **7** indicated the presence of partial structures, written in bold lines, and in the HMBC experiment, long-range correlations were observed between H_2-2 and C-1, 3; H_2-4 and C-3; H-6 and C-1; H-9 and C-7, 8, 10; H_3-11 and C-1, 2, 6, 12; H_3-12 and C-1, 2, 6, 11; H_3-13 and C-4−6; and H-1′ and C-10. In the NOESY experiment on **7**, NOE correlations were observed between the following: Hα-2 and H_3-12; Hβ-2 and H_3-11; Hα-4 and H-6, H_3-13; H-5 and H_3-11; H-6 and H_3-12; H_2-7 and H_3-11. Enzymatic hydrolysis of **7** with β-glucosidase gave a new megastigmane, sarmentol C (**7a**), as the aglycon. By the application of the octant rule for **7** and **7a**, the absolute configurations of the 5-positions were confirmed to be *R*. That is, the circular dichroic (CD) spectra of **7** and **7a** showed a positive Cotton effect [**7**: 284 nm ($\Delta\epsilon$ +0.08); **7a**: 286 nm ($\Delta\epsilon$ +0.19), both in MeOH].[25,32] Finally, reduction of **7** with $NaBH_4$ yielded **5** and **7b** in an approximate 7:2 ratio, so that the configuration of the 9-position in **7** was clarified to be *S*.

The ^1H (CD_3OD, Table 5) and ^{13}C NMR (Table 6) spectra[30] of **8** indicated the same functional groups as those of **7**. Enzymatic hydrolysis of **8** with β-glucosidase gave a new megastigmane, sarmentol D (**8a**), as the aglycon. The $^1H-^1H$ COSY experiment on **8** indicated the partial structures written in bold lines, and the carbon skeleton and the positions of functional groups were determined by the HMBC experiment, which showed long-range correlations between H_2-2 and C-1; H-3 and C-2, 4; H-6 and C-1; H_2-7 and C-9; H_2-8 and C-9; H_2-10 and C-9; H_3-11 and C-1, 2, 6, 12; H_3-12 and C-1, 2, 6, 11; H_3-13 and C-4−6; and H-1′ and C-10. Consequently, the β-glucopyranosyl group in **8** was at the 10-position of **8a**. The relative structure of **8** was characterized by the NOESY experiment, which showed NOE correlations between Hα-2 and H-6, H_3-12; Hβ-2 and H-3; H-3 and Hβ-4; Hα-4 and H-6, H_3-13; H-6 and H_3-12, H_3-13; and H_2-7 and H_3-11. The (*R*)- and (*S*)-MTPA esters (**8b**, **8c**) were obtained from **8a** using (*R*)- and (*S*)-MTPA in the presence of EDC·HCl and 4-DMAP,

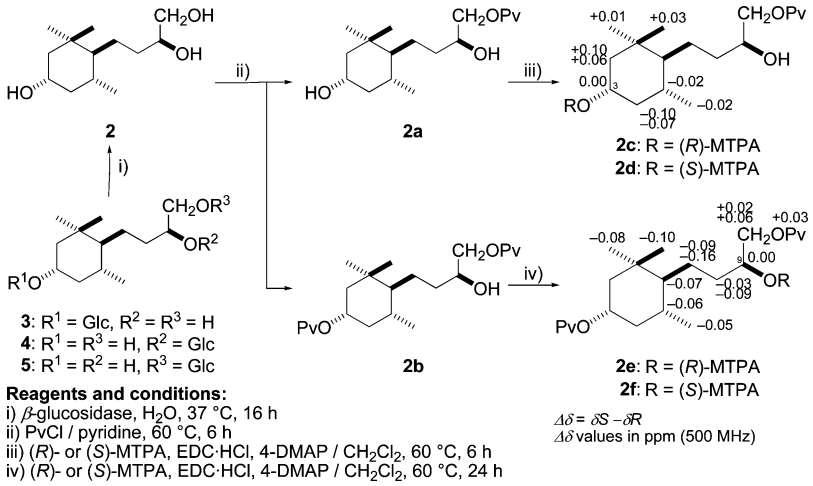

Figure 2.

Table 3. ^{1}H 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)
2α	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)
4α	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)
	1.83 (m)	1.65 (m)	1.89 (m)	1.65 (m)	1.82 (m)	1.63 (m)
8	1.65 (m)	1.33 (m)	1.77 (m)	1.57 (m)	1.60 (m)	1.41 (m)
	1.89 (m)	1.61 (m)	1.85 (m)	1.64 (m)	1.75 (m)	1.57 (m)
9	4.05 (m)	3.52 (m)	4.10 (m)	3.69 (m)	4.14 (m)	3.71 (m)
10	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)
	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)
11	0.75 (s)	0.84 (s)	0.83 (s)	0.83 (s)	0.80 (s)	0.83 (s)
12	0.92 (s)	0.97 (s)	0.93 (s)	0.97 (s)	0.94 (s)	0.96 (s)
13	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)
Glc-1′	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)
2′	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)
3′	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)
4′	4.28 (m)	3.25 (m)	4.19 (m)	3.27 (m)	4.24 (m)	3.27 (m)
5′	4.00 (m)	3.27 (m)	3.90 (m)	3.27 (m)	3.99 (m)	3.25 (m)
6′	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)
	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 CD_3OD.

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 $NaBH_4$ 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; ^{1}H NMR spectra, JEOL JNM-LA500 (500 MHz) spectrometer; ^{13}C 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 5C_{18}-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 60F_{254} (Merck, 0.25 mm) (normal-phase); TLC, precoated TLC plates with silica gel 60F_{254} (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 CD_3OD.

RP-18 WF_{254S} (Merck, 0.25 mm); 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 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 H_2O 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, H_2O → MeOH, twice) to give H_2O- 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, $CHCl_3$−MeOH−H_2O (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−H_2O (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, $CHCl_3$−MeOH (1:1, v/v)] and finally HPLC [MeOH−H_2O (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, $CHCl_3$−MeOH (1:1, v/v)] and finally HPLC [MeOH−H_2O (40:60, v/v)] to furnish myrsinionoside A (**11**, 48.5 mg, 0.00009%). Fraction 1-9 (710 mg) was purified by Sephadex LH-20 CC [150 g, $CHCl_3$−MeOH (1:1, v/v)] and finally HPLC [MeOH−H_2O (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−H_2O (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, $CHCl_3$ → $CHCl_3$−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 [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 [CH_3CN−MeOH−H_2O (10:8:82, v/v/v) and MeOH−H_2O (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−H_2O (32:68, v/v)] to give sedumosides A_1 (**3**, 162.5 mg, 0.00030%), A_2 (**4**, 60.6 mg, 0.00011%), A_3 (**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 [CH_3CN−H_2O (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, $CHCl_3$−MeOH (1:1, 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 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 [CH_3CN−MeOH−H_2O (20:8:72, v/v/v) and $CHCl_3$−MeOH (40:60, v/v)] to furnish myrsinionoside 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−H_2O (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, $CHCl_3$−MeOH (1:1, v/v)] and finally HPLC [MeOH−H_2O (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, ^{13}C NMR, MS] with reported values.[25−29]

Sarmentoic acid (1): amorphous powder; $[\alpha]^{27}_D$ −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; ^{13}C NMR data, see Table 2; positive-ion FABMS *m/z* 267 $[M + Na]^+$; HRFABMS *m/z* 267.1579 (calcd for $C_{13}H_{24}O_4Na$ $[M + Na]^+$, 267.1572).

Sarmentol A (2): colorless oil; $[\alpha]^{27}_D$ −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; ^{13}C NMR data, see Table 2; positive-ion FABMS *m/z* 253 $[M + Na]^+$; HRFABMS *m/z* 253.1774 (calcd for $C_{13}H_{26}O_3Na$ $[M + Na]^+$, 253.1780).

Sedumoside A_1 (3): amorphous powder; $[\alpha]^{22}_D$ −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; ^{13}C NMR data, see Table 4; positive-ion FABMS *m/z* 415 $[M + Na]^+$; HRFABMS *m/z* 415.2313 (calcd for $C_{19}H_{36}O_8Na$ $[M + Na]^+$, 415.2308).

Sedumoside A_2 (4): amorphous powder; $[\alpha]^{27}_D$ −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; ^{13}C NMR data, see Table 4; positive-ion FABMS *m/z* 415 $[M + Na]^+$; HRFABMS *m/z* 415.2313 (calcd for $C_{19}H_{36}O_8Na$ $[M + Na]^+$, 415.2308).

Sedumoside A_3 (5): amorphous powder; $[\alpha]^{27}_D$ −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; ^{13}C NMR data, see Table 4; positive-ion FABMS *m/z* 415 $[M + Na]^+$; HRFABMS *m/z* 415.2303 (calcd for $C_{19}H_{36}O_8Na$ $[M + Na]^+$, 415.2308).

Sedumoside B (6): amorphous powder; $[\alpha]^{23}_D$ −15.7 (*c* 0.16, MeOH); IR (KBr) ν_{max} 3390, 2928, 2876, 1474, 1078, 1022 cm^{-1}; ^1H NMR data, see Table 5; ^{13}C NMR data, see Table 6; positive-ion FABMS *m/z* 415 $[M + Na]^+$; HRFABMS *m/z* 415.2313 (calcd for $C_{19}H_{36}O_8Na$ $[M + Na]^+$, 415.2308).

Sedumoside C (7): amorphous powder; $[\alpha]^{27}_D$ −0.8 (*c* 0.82, MeOH); CD (MeOH) λ_{max} ($\Delta\epsilon$) 284 (+0.08); IR (KBr) ν_{max} 3432, 2958, 1702, 1653, 1474, 1100, 1061 cm^{-1}; ^1H NMR data, see Table 5; ^{13}C NMR data, see Table 6; positive-ion FABMS *m/z* 413 $[M + Na]^+$; HRFABMS *m/z* 413.2153 (calcd for $C_{19}H_{34}O_8Na$ $[M + Na]^+$, 413.2151).

Sedumoside D (8): amorphous powder; $[\alpha]^{27}_D$ −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; ^{13}C NMR data, see Table 6; positive-ion FABMS *m/z* 413 $[M + Na]^+$; HRFABMS *m/z* 413.2147 (calcd for $C_{19}H_{34}O_8Na$ $[M + Na]^+$, 413.2151).

Methylation of 1.[18] A solution of **1** (20.0 mg) in Et_2O−MeOH (1:1, v/v, 1.0 mL) was treated with trimethylsilyldiazomethane (TMSCHN_2, 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−$CHCl_3$ (1:1, v/v) → $CHCl_3$] to give **1a** (18.0 mg, 85%).

Compound 1a: colorless oil; $[\alpha]^{27}_D$ −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; ^{13}C NMR data, see Table 2; EIMS *m/z* 258 $[M]^+$ (1), 240 (8), 225 (20), 123 (100); HREIMS *m/z* 258.1825 (calcd for $C_{14}H_{26}O_4$, 258.1831).

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

	6[a]	**6a**[a]	**6a**[b]	**7**[a]	**7a**[b]
position	δ_H (*J* Hz)	δ_H (*J* Hz)	δ_H (*J* Hz)	δ_H (*J* Hz)	δ_H (*J* Hz)
2α	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)		
4α	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)	

	8[a]	**8**[c]	**8a**[a]	**8a**[b]	**8d**[b]
position	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
2β	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
4α	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	060 (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 CD_3OD. [b] Measured in $CDCl_3$. [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 CH_2Cl_2 (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 $NaHCO_3$, and brine, then dried over $MgSO_4$ powder and filtered. Removal of the solvent from the filtrate under reduced pressure furnished a residue, which was purified by preparative TLC [$CHCl_3$−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; ^{1}H 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, H_3-12, 11), 0.85 (3H, d, J = 5.8 Hz, H_3-13), 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.

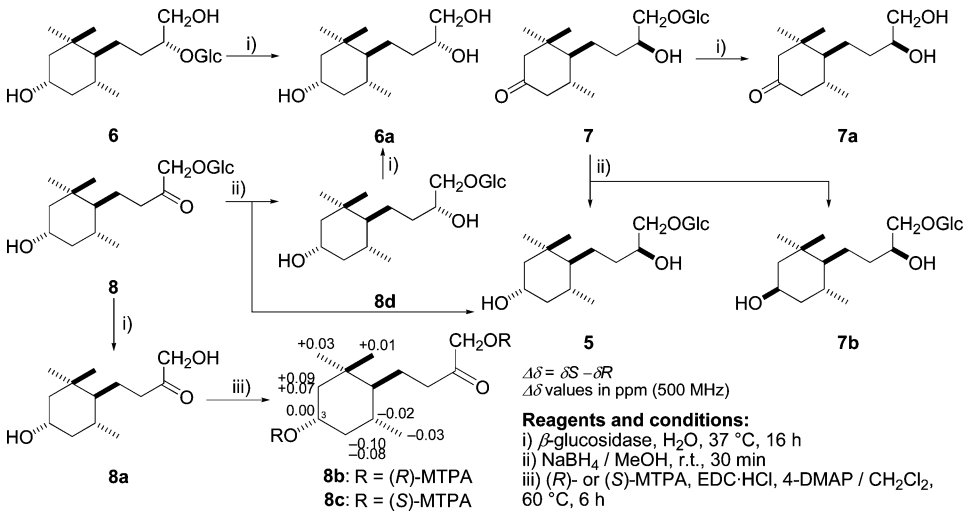

Figure 3.

12.5, 13.7 Hz, Hα-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, Hα-2), 1.77 (1H, ddd, $J = 2.1$, 2.1, 14.7 Hz, Hβ-2), 1.86 (1H, ddd, $J = 3.1$, 6.1, 13.7 Hz, Hβ-4), 1.93, 2.02 (1H each, both m, H_2-8), 3.62, 3.74 (3H each, both s, −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; ^{1}H 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, Hα-4), 1.37 (1H, br d, $J = 4$, 15 Hz, Hα-2), 1.40, 1.78 (1H each, both m, H_2-7), 1.64 (1H, ddd, $J = 2.5$, 2.5, 14.7 Hz, Hβ-2), 1.67 (1H, m, H-5), 1.91 (1H, ddd, $J = 2.5$, 4.9, 14.4 Hz, Hβ-4), 1.95, 2.04 (1H each, both m, H_2-8), 3.65, 3.74 (3H each, both s, −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; ^{1}H 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, Hα-4), 1.33 (1H, br d, $J \approx 4$, 15 Hz, Hα-2), 1.54 (1H, m, Hβ-2), 1.58, 1.81 (1H each, both m, H_2-8), 1.68 (1H, ddd, $J = 2.5$, 4.8, 14.5 Hz, Hβ-4), 2.00 (1H, m, H-5), 3.66, 3.79 (3H each, both s, −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; ^{1}H 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, Hα-4), 1.36 (1H, br d, $J \approx 4$, 15 Hz, Hα-2), 1.56 (1H, ddd, $J = 2.7$, 2.7, 14.7 Hz, Hβ-2), 1.64, 1.87 (1H each, both m, H_2-8), 1.73 (1H, ddd, $J = 2.5$, 4.9, 14.4 Hz, Hβ-4), 2.08 (1H, m, H-5), 3.65, 3.76 (3H each, both s, −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 → 1:1, v/v)] to give **1f** (10.7 mg, 64%).

Compound 1f: colorless oil; $[\alpha]^{27}_D$ +37.2 (*c* 1.30, MeOH); IR (film) ν_{max} 3375, 2922, 2874, 1473, 1387, 1026, 756 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 2; positive-ion FABMS *m*/*z* 253 [M + Na]$^+$; HRFABMS *m*/*z* 253.1789 (calcd for $C_{13}H_{26}O_3Na$ [M + 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 resudue, 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; ^{1}H 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, H_3-11, 12), 0.94 (1H, ddd, J = 12.2, 12.2, 12.2 Hz, Hα-4), 0.96 (3H, d, J = 6.7 Hz, H_3-13), 1.07, 1.60 (1H each, both m, H_2-7), 1.11 (1H, dd, J = 12.0, 12.0 Hz, Hα-2), 1.22 [9H, s, −OCOC(CH_3)$_3$], 1.45 (1H, m, H-5), 1.45, 1.59 (1H each, both m, H_2-8), 1.69 (1H, ddd, J = 2.5, 4.3, 12.0 Hz, Hβ-2), 1.93 (1H, m, Hβ-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), H_2-10]; ^{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 [−O*C*OC(CH$_3$)$_3$], 38.9 [−OCO*C*(CH$_3$)$_3$], 27.2 [−OCOC(*C*H$_3$)$_3$]; EIMS m/z 314 [M$^+$, (1)], 296 (5), 257 (1), 212 (2), 200 (1), 57 (100); HREIMS m/z 314.2458 (calcd for $C_{18}H_{34}O_4$ [M$^+$], 314.2457).

Compound 2b: colorless oil; ^{1}H 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, H_3-11, 12), 0.95 (3H, d, J = 6.4 Hz, H_3-13), 1.00 (1H, ddd, J = 12.3, 12.3, 12.3 Hz, Hα-4), 1.08, 1.61 (1H each, both m, H_2-7), 1.16, 1.22 [9H each, both s, −OCOC(CH_3)$_3$], 1.26 (1H, dd, J = 12.0, 12.0 Hz, Hα-2), 1.46, 1.59 (1H each, both m, H_2-8), 1.52 (1H, m, H-5), 1.67 (1H, ddd, J = 2.5, 4.3, 12.0 Hz, Hβ-2), 1.93 (1H, m, Hβ-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), H_2-10], 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 [−O*C*OC(CH$_3$)$_3$], 38.6, 38.9 [−OCO*C*-(CH$_3$)$_3$], 27.1, 27.2 [−OCOC(*C*H$_3$)$_3$]; positive-ion CIMS m/z 399 [M + 1]$^+$, (9), 381 (3), 297 (100), 279 (14); HRCIMS m/z 399.3106 (calcd for $C_{23}H_{42}O_5$ [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 EDC·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), EDC·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 EDC·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), EDC·HCl (31.2 mg), and 4-DMAP (15.5 mg).

Compound 2c: colorless oil; ^{1}H 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, H_3-12, 11), 0.98 (3H, d, J = 6.7 Hz, H_3-13), 1.09, 1.60 (1H each, both m, H2−7), 1.17 (1H, ddd, J = 12.2, 12.2, 12.2 Hz, Hα-4), 1.22 [9H, s, −OCOC(C*H*$_3$)$_3$], 1.25 (1H, dd, J = 12.2, 12.2 Hz, Hα-2), 1.45, 1.59 (1H each, both m, H_2-8), 1.55 (1H, m, H-5), 1.73 (1H, ddd, J = 2.5, 4.3, 12.2 Hz, Hβ-2), 2.05 (1H, m, Hβ-4), 3.56 (3H, s, −COOC*H*$_3$), 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), H_2-10], 5.14 (1H, m, H-3), 7.39−7.53 (5H, m, Ph−H).

Compound 2d: colorless oil; ^{1}H 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, H_3-12, 11), 0.96 (3H, d, J = 6.5 Hz, H_3-13), 1.07 (1H, ddd, J = 12.3, 12.3, 12.3 Hz, Hα-4), 1.09, 1.60 (1H each, both m, H_2-7), 1.22 [9H, s, −OCOC(C*H*$_3$)$_3$], 1.35 (1H, dd, J = 11.9, 11.9 Hz, Hα-2), 1.45, 1.58 (1H each, both m, H_2-8), 1.53 (1H, m, H-5), 1.79 (1H, ddd, J = 2.5, 4.3, 11.9 Hz, Hβ-2), 1.98 (1H, m, Hβ-4), 3.55 (3H, s, −COOC*H*$_3$), 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), H_2-10], 5.14 (1H, m, H-3), 7.40−7.53 (5H, m, Ph−H).

Compound 2e: colorless oil; ^{1}H 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, H_3-12, 11), 0.92 (3H, d, J = 6.4 Hz, H_3-13), 0.99 (1H, ddd, J = 12.0, 12.0, 12.0 Hz, Hα-4), 1.10, 1.49 (1H each, both m, H_2-7), 1.14, 1.16 [9H each, both s, −OCOC(C*H*$_3$)$_3$], 1.19 (1H, dd, J = 12.0, 12.0 Hz, Hα-2), 1.51 (1H, m, H-5), 1.60, 1.78 (1H each, both m, H_2-8), 1.66 (1H, ddd, J = 2.8, 4.0, 12.0 Hz, Hβ-2), 1.91 (1H, m, Hβ-4), 3.55 (3H, s, −COOC*H*$_3$), [4.06 (1H, dd, J = 6.1, 12.5 Hz), 4.31 (1H, dd, J = 3.1, 12.5 Hz), H_2-10], 4.80 (1H, m, H-3), 5.23 (1H, m, H-9), 7.39−7.55 (5H, m, Ph−H).

Compound 2f: colorless oil; ^{1}H 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, H_3-12, 11), 0.87 (3H, d, J = 6.4 Hz, H_3-13), 0.96 (1H, ddd, J = 11.9, 11.9, 11.9 Hz, Hα-4), 1.01, 1.33 (1H each, both m, H_2-7), 1.15, 1.17 [9H each, both s, −OCOC(C*H*$_3$)$_3$], 1.15 (1H, dd, J = 12.1, 12.1 Hz, Hα-2), 1.45 (1H, m, H-5), 1.57, 1.69 (1H each, both m, H_2-8), 1.65 (1H, ddd, J = 2.5, 4.3, 12.1 Hz, Hβ-2), 1.90 (1H, m, Hβ-4), 3.55 (3H, s, −COOC*H*$_3$), [4.08 (1H, dd, J = 6.7, 12.2 Hz), 4.37 (1H, dd, J = 3.1, 12.2 Hz), H_2-10], 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 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-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 °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 [MeOH−H_2O (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 °C for 16 h. The residue was purified by HPLC [MeOH−H_2O (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; $[\alpha]^{25}_D$ +5.6 (*c* 0.05, MeOH); IR (film) ν_{max} 3372, 2924, 2874, 1474, 1387, 1026, 754 cm^{-1}; ^{1}H NMR data, see Table 5; ^{13}C NMR data, see Table 6; positive-ion FABMS m/z 253 [M + Na]$^+$; HRFABMS m/z 253.1771 (calcd for $C_{13}H_{26}O_3Na$ [M + Na]$^+$, 253.1780).

Sarmentol C (7a): colorless oil; $[\alpha]^{23}_D$ +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}; ^{1}H NMR data, see Table 5; ^{13}C NMR data, see Table 6; positive-ion CIMS m/z 229 [M + 1]$^+$ (57), 211 (41), 197 (64), 138 (64), 95 (100); HRCIMS m/z 229.1801 (calcd for $C_{13}H_{25}O_3$ [M + 1]$^+$, 229.1804).

Sarmentol D (8a): colorless oil; $[\alpha]^{21}_D$ +1.2 (*c* 0.42, MeOH); IR (film) ν_{max} 3346, 2955, 2876, 1717, 1473, 1073, 1026 cm^{-1}; ^{1}H 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 $C_{13}H_{24}O_3$, 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 [MeOH−H_2O (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 [MeOH−H_2O (25:75, v/v)] to give **5** (6.3 mg, 31%) and **8d** (6.3 mg, 31%).

Compound 7b: ^{1}H 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, H_3-12, 11), 0.98 (3H, d, J = 6.2 Hz, H_3-13), 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), H_2-10], [3.64 (1H, m), 3.86 (1H, dd, J = 1.6, 10.1 Hz), H_2-6′], 3.96 (1H, m, H-3), 4.41 (1H, d, J = 7.6 Hz, H-1′); positive-ion FABMS m/z 415 [M + Na]$^+$; HRFABMS m/z 415.2316 (calcd for $C_{19}H_{36}O_8Na$ [M + Na]$^+$, 415.2308).

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

Table 5; ^{13}C NMR data, see Table 6; positive-ion FABMS *m*/*z* 415 [M + Na]$^+$; HRFABMS *m*/*z* 415.2301 (calcd for $C_{19}H_{36}O_8Na$ [M + 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 → 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, H_3-11, 12), 0.96 (3H, d, *J* = 6.4 Hz, H_3-13), 1.17 (1H, ddd, *J* = 11.9, 11.9, 11.9 Hz, Hα-4), 1.25 (1H, dd, *J* = 12.5, 12.5 Hz, Hα-2), 1.42, 1.77 (1H each, both m, H_2-7), 1.57 (1H, m, H-5), 1.73 (1H, ddd, *J* = 2.8, 4.6, 12.5 Hz, Hβ-2), 2.05 (1H, m, Hβ-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), H_2-8], 3.54, 3.64 (3H each, both s, −COOCH_3), 4.78, 4.89 (1H each, both d, *J* = 16.5 Hz, H_2-10), 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, H_3-11, 12), 0.93 (3H, d, *J* = 6.4 Hz, H_3-13), 1.07 (1H, ddd, *J* = 11.9, 11.9, 11.9 Hz, Hα-4), 1.34 (1H, dd, *J* = 12.2, 12.2 Hz, Hα-2), 1.40, 1.76 (1H each, both m, H_2-7), 1.55 (1H, m, H-5), 1.80 (1H, ddd, *J* = 2.2, 4.3, 12.2 Hz, Hβ-2), 1.97 (1H, m, Hβ-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), H_2-8], 3.54, 3.64 (3H each, both s, −COOCH_3), 4.78, 4.89 (1H each, both d, *J* = 16.5 Hz, H_2-10), 5.13 (1H, m, H-3), 7.39−7.64 (10H, m, Ph−H).

Acknowledgment. Part of this work was supported by the 21st COE program and Academic Frontier Project from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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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NP068059S