Absolute Structures of New Megastigmane Glycosides, Foliasalaciosides E_1, E_2, E_3, F, G, H, and I from the Leaves of *Salacia chinensis*

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Following the investigation of foliasalaciosides A_1, A_2, B_1, B_2, C, and D, seven new megastigmane glycosides named foliasalaciosides E_1—I (1—7), together with four known constituents, were isolated from the leaves of *Salacia chinensis* LINN. collected in Thailand. The absolute stereostructures of the new compounds were characterized on the basis of chemical and physicochemical evidence, including the application of the modified Mosher's method.

Key words *Salacia chinensis*; foliasalacioside; megastigmane; Hippocrateaceae

In the course of our characterization studies on the bioactive constituents from *Salacia* species,[1—12] we reported the isolation and absolute stereostructural elucidation of six megastigmane glycosides, foliasalaciosides A_1, A_2, B_1, B_2, C, and D, from the leaves of *Salacia chinensis* LINN. (Hippocrateaceae), together with 16 known constituents.[13] As a continuing study on the leaves of *S. chinensis*, we have isolated seven new megastigmane glycosides, foliasalaciosides E_1 (**1**), E_2 (**2**), E_3 (**3**), F (**4**), G (**5**), H (**6**), and I (**7**) from this herbal medicine, together with four known megastigmane glycosides (**8**—**11**). In this paper, we describe the isolation and absolute stereostructural elucidation of these seven new megastigmane glycosides.

The dried leaves of *S. chinensis* were finely cut and extracted with MeOH to furnish a methanolic extract (13.0%). The MeOH extract was partitioned into an EtOAc–H_2O (1 : 1, v/v) mixture to furnish an EtOAc-soluble fraction (4.1%) and an aqueous phase. The aqueous phase was further extracted with *n*-BuOH to give an *n*-BuOH- and a H_2O-soluble fraction (2.4, 6.6%, respectively) as previously reported.[13] The *n*-BuOH-soluble fraction was subjected to Diaion HP-20 column chromatography (H_2O→MeOH→acetone) to give H_2O-, MeOH-, and acetone-eluted fractions (1.19, 0.93, 0.26%, respectively). From the MeOH-eluted fraction, foliasalaciosides E_1 (**1**, 0.00048%), E_2 (**2**, 0.00014%), E_3 (**3**, 0.00010%), F (**4**, 0.00028%), G (**5**, 0.00005%), H (**6**, 0.00063%), and I (**7**, 0.00008%) were isolated using normal- and reverse-phase silica gel column chromatography, and finally subjected to HPLC, together with myrsinionoside D[14] (**8**, 0.00005%), loliolide β-D-glucopyranoside[15] (**9**, 0.00012%), (+)-abscisyl β-D-glucopyranoside[16] (**10**, 0.00020%), and 1-[5-(8-hydroxy-1,5-dimethyl-3-oxo-6-oxabicyclo[3.2.1]oct-8-yl)-3-methyl-2,4-pentadienoate],[1*R*-[1α,5α,8*S**(2*Z*,4*E*)]]-β-D-glucopyranose[17] (**11**, 0.00036%) (Chart 1).

Absolute Stereostructures of Foliasalaciosides E_1 (1), E_2 (2), E_3 (3), F (4), G (5), H (6), and I (7) Foliasalacioside E_1 (**1**) was obtained as an amorphous powder with negative optical rotation ($[\alpha]_D^{26}$ −8.3° in MeOH). The IR spectrum of **1** showed absorption bands at 3420 and 1638 cm^{-1} ascribable to hydroxyl and double bond functions, respectively. In the positive- and negative-ion fast atom bombardment (FAB)-MS of **1**, quasimolecular ion peaks were observed at *m/z* 529 $(M+Na)^+$ and *m/z* 505 $(M-H)^-$, respectively. Its elemental composition was determined to be $C_{24}H_{42}O_{11}$ based on the results of high-resolution (HR) FAB-MS analysis. Acid hydrolysis of **1** with hydrochloric acid (HCl) 1 M liberated D-glucose and L-arabinose, which were identified in HPLC analysis using an optical rotation detector.[18,19] The ^{1}H-(CD_3OD) and ^{13}C-NMR spectra of **1** (Table 1), which were assigned based on the results of various NMR experiments,[20] showed signals assignable to four methyls [δ 1.05, 1.06, 1.64 (3H each, all s, H_3-11, 12, 13) and 1.16 (3H, d, J=6.4 Hz, H_3-10)], two methines bearing an oxygen function [δ 3.69 (1H, m, H-9), 3.95 (1H, m, H-3)], a tetrasubstituted double bond [δ_C 125.6 (C-5) and 138.3 (C-6)], four methylenes, and a quaternary carbon, together with a β-D-glucopyranosyl part [δ 4.38 (1H, d, J=7.9 Hz, H-1′)] and an α-L-arabinopyranosyl part [δ 4.32 (1H, d, J=6.7 Hz, H-1″)]. As shown in Fig. 1, a double-quantum filter correlation spectroscopy (DQF COSY) experiment on **1** indicated the presence of a partial structure shown in boldface lines. In a heteronuclear multiple-bond correlation (HMBC) experiment, long-range correlations were observed between the following protons and carbons: H_2-2 and C-6; H_2-4 and C-5, 6; H_2-7 and C-1, 5, 6; H_2-8 and C-6; H_3-10 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, 5, 6; and H-1′ and C-3, H-1″ and C-6′. Therefore the planar structure of the aglycon part and the positions of the glycoside linkages in **1** were characterized. The relative stereostructure of **1**, except for the 9-position, was characterized in a nuclear Overhauser enhancement spectroscopy (NOESY) experiment, which showed NOE correlations between the following proton pairs: H-2α and H_3-12; H-2β and H_3-11; H-3β and H_3-11, H-2β, H-4β; H_2-7 and H_3-12; and H_2-8 and H_3-11. Finally, the absolute configuration of **1** was characterized by the application of the modified Mosher's method.[21] The enzymatic hydrolysis of **1** with naringinase gave a new aglycon, foliasalaciol E (**1a**). Three pairs of (*R*)- and (*S*)-2-methoxy-2-trifluoromethylphenylacetic acid (MTPA) esters [3,9-MTPA diester (**1b**, **1c**), 3-MTPA ester (**1d**, **1e**), 9-MTPA ester (**1f**, **1g**)] were derived from **1a** upon reaction with (*R*)- and (*S*)-MTPA in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) and 4-(dimethylamino)pyridine (4-DMAP). As shown in Fig. 2, the protons at the 2- and 10-positions of the 3,9-(*S*)-MTPA diester (**1c**) resonated at lower fields than those of the 3,9-(*R*)-MTPA diester (**1b**)

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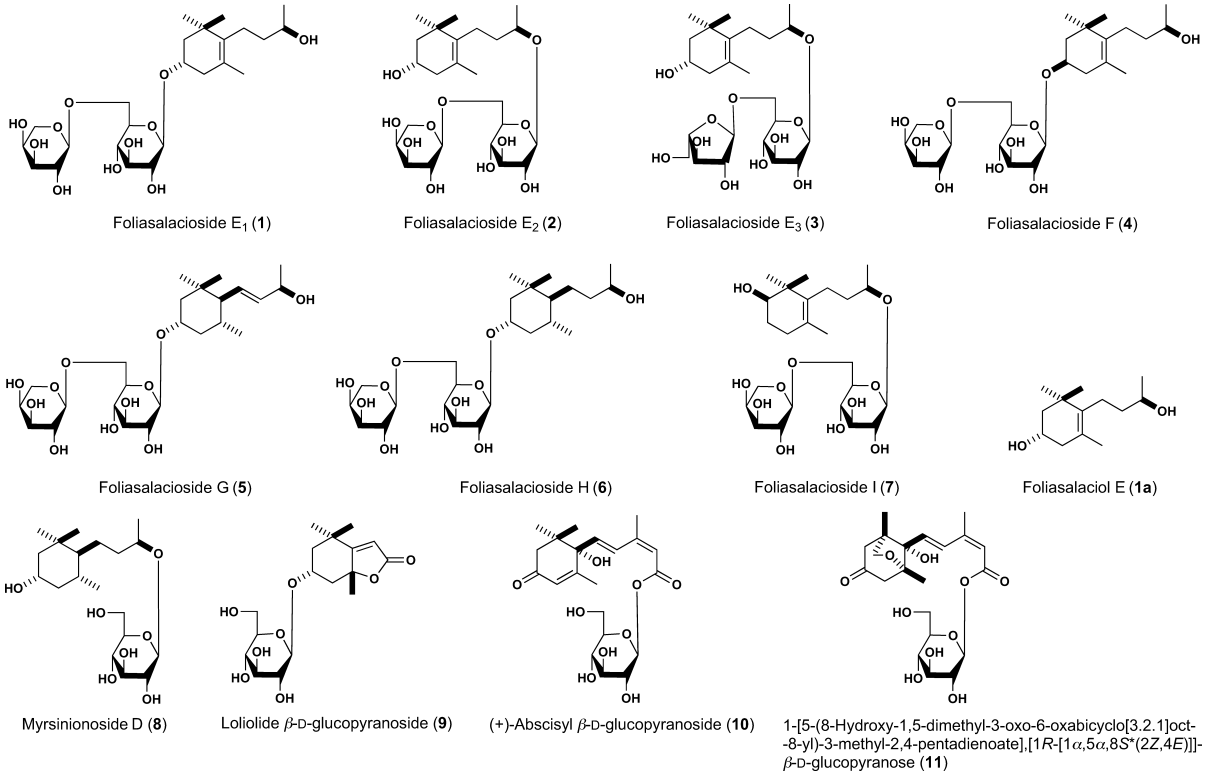

Chart 1. Chemical Strucutre of Constituents from the Leaves of *Salacia chinensis*

Table 1. ^{13}C-NMR (125 MHz) Data of **1**—**7** and Related Compound (**1a**)

Position	**1**[a]	**2**[a]	**3**[a]	**1a**[a]	**1a**[b]	**4**[a]	**5**[a]	**6**[a]	**7**[a]
1	38.7	38.9	38.9	38.8	37.9	38.8	35.9	36.8	41.4
2	46.3	49.5	49.5	49.5	48.6	47.5	48.1	48.6	77.0
3	74.5	65.7	65.7	65.7	65.3	73.3	76.1	76.1	28.0
4	41.5	43.0	43.0	43.0	42.3	39.8	44.0	44.8	31.6
5	125.6	125.5	125.4	125.5	124.1	125.1	32.0	35.0	127.1
6	138.3	138.5	138.6	138.3	136.9	138.5	58.7	54.3	137.5
7	25.6	25.5	25.4	25.6	24.4	25.6	131.3	26.4	26.0
8	40.8	39.0	38.9	40.7	39.7	40.7	138.5	42.7	39.0
9	69.2	76.3	76.4	69.2	68.8	69.2	69.4	69.2	76.2
10	23.3	19.9	19.9	23.3	23.4	23.3	24.1	23.4	19.9
11	28.9	29.0	29.0	28.9	28.6	30.3	21.8	21.4	21.9
12	30.3	30.4	30.4	30.4	29.7	29.0	32.2	31.3	26.6
13	20.1	20.2	20.2	20.0	19.7	20.0	21.8	21.5	19.95
1′	103.1	102.3	102.4			102.3	103.1	103.0	102.3
2′	75.2	75.2	75.2			75.2	75.1	75.1	75.2
3′	78.0	78.1	78.2			77.9	78.0	77.9	78.1
4′	71.6	71.8	72.2			71.6	71.7	71.6	71.9
5′	76.8	77.0	76.7			76.8	76.8	76.8	77.0
6′	69.4	69.7	68.2			69.3	69.3	69.3	69.7
1″	105.0	105.2	109.9			105.0	105.1	105.0	105.2
2″	72.4	72.4	83.1			72.4	72.4	72.4	72.4
3″	74.2	74.2	78.9			74.2	74.3	74.2	74.3
4″	69.4	69.5	86.0			69.4	69.4	69.4	69.4
5″	66.6	66.7	63.1			66.6	66.6	66.6	66.7

Measured in *a*) CD_3OD, *b*) $CDCl_3$.

($\Delta\delta$: positive), while the protons at the 4-, 7-, 8-, 11-, 12-, and 13-positions of **1c** were observed at higher fields compared with those of **1b** ($\Delta\delta$: negative). In addition, the protons at the 2-, 11-, and 12-positions of the 3-(*S*)-MTPA ester (**1e**) resonated at lower fields than those of the 3-(*R*)-MTPA ester (**1d**) ($\Delta\delta$: positive), while the protons at the 4- and 6-positions of **1e** were observed at higher fields compared with those of **1d** ($\Delta\delta$: negative). Furthermore, the protons of the 9-(*S*)-MTPA ester (**1g**), except for that at the 10-position, were observed at higher fields than those of the 9-(*R*)-MTPA ester (**1f**) ($\Delta\delta$: negative). Thus the absolute configurations at the 3- and 9-positions in **1** were elucidated to be 3*S* and 9*R*. Consequently, the structure of **1** was clarified to be (3*S*,9*R*)-3,9-dihydroxymegastigman-5-en 3-*O*-α-L-ara-

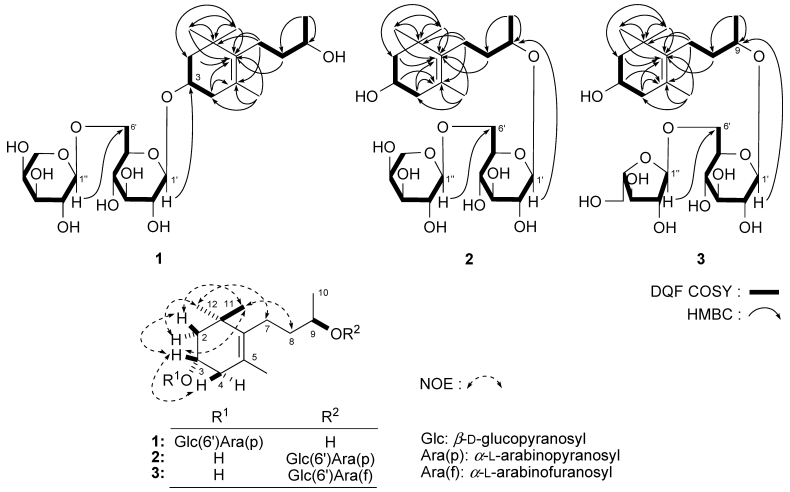

Fig. 1. Selected DQF COSY, HMBC and NOE Correlations of **1**—**3**

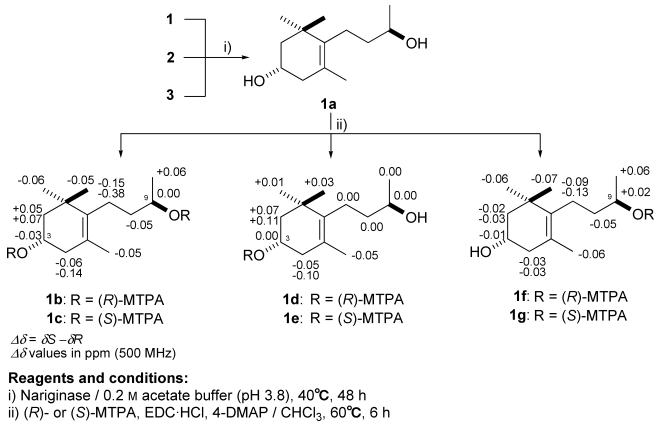

Fig. 2

binopyranosyl(1→6)-β-D-glucopyranoside.

Foliasalaciosides E_2 (**2**) and E_3 (**3**) were obtained as amorphous powders with positive optical rotation for **2** ($[\alpha]_D^{26}$ +1.6° in MeOH) and negative optical rotation for **3** ($[\alpha]_D^{26}$ −8.6° in MeOH), respectively. Both **2** and **3** were determined to have the same molecular formula as **1** from the positive- and negative-ion FAB-MS [*m/z* 529 $(M+Na)^+$, *m/z* 505 (M−H)] and the results of HR-FAB-MS measurement. The acid hydrolysis of **2** and **3** liberated D-glucose and L-arabinose, which were identified in HPLC analysis using an optical rotation detector.[18,19] Enzymatic hydrolysis of **2** and **3** with naringinase gave **1a** as the aglycon. The ^{1}H- (CD_3OD) and ^{13}C-NMR spectra (Table 1)[20] of **2** and **3** indicated the presence of the following functions: an aglycon part [**2**: δ 1.03, 1.06, 1.63 (3H each, all s, H_3-11, 12, 13), 1.19 (3H, d, J=6.2 Hz, H_3-10), 3.83 (1H, m, H-3), 3.87 (1H, m, H-9); **3**: δ 1.03, 1.06, 1.63 (3H each, all s, H_3-11, 12, 13), 1.19 (3H, d, J=6.1 Hz, H_3-10), 3.83 (1H, m, H-3), 3.87 (1H, m, H-9)]; a β-D-glucopyranosyl part and an α-L-arabinopyranosyl part for **2** [δ 4.32 (1H, d, J=7.6 Hz, H-1′), 4.34 (1H, d, J=6.8 Hz, H-1″); and a β-D-glucopyranosyl part and an α-L-arabinofuranosyl part for **3** [δ 4.32 (1H, d, J=7.6 Hz, H-1′), 4.97 (1H, d, J=1.2 Hz, H-1′)]. In the HMBC experiments on **2** and **3**, long-range correlations were observed between the 1′-proton and the 9-carbon (δ_C 76.3 for **2** and 76.4 for **3**) and between the 1″-proton and the 6′-carbon (δ_C 69.7 for **2** and 68.2 for **3**). On the basis of this evidence, the stereostructures of **2** and **3** were clarified to be (3*S*,9*R*)-3,9-dihydroxymegastigman-5-en 3-*O*-α-L-arabinopyranosyl(1→6)-β-D-glucopyranoside and (3*S*,9*R*)-3,9-dihydroxymegastigman-5-en 3-*O*-α-L-arabinofuranosyl(1→6)-β-D-glucopyranoside, respectively.

Foliasalacioside F (**4**) was obtained as an amorphous powder with negative optical rotation ($[\alpha]_D^{26}$ −44.2° in MeOH). The IR spectrum showed absorption bands at 3345, 1636, and 1078 cm^{-1} ascribable to hydroxyl, double-bond, and ether functions, respectively. The positive- and negative-ion FAB-MS of **4** showed quasimolecular ion peaks at *m/z* 529 $(M+Na)^+$ and 505 $(M-H)^-$, respectively. The molecular formula $C_{24}H_{42}O_{11}$ of **4** was determined based on the results of HR-FAB-MS measurement. Treatment of **4** with HCl 1 M liberated D-glucose and L-arabinose, which were identified in HPLC analysis using an optical rotation detector.[18,19] The ^{1}H- (CD_3OD) and ^{13}C-NMR spectra (Table 1)[20] of **4** showed signals assignable to an aglycon part {four methyls [δ 1.05, 1.06, 1.65 (3H each, all s, H_3-12, 11, 13)], 1.16 (1H, d, J=6.2 Hz, H_3-10)}, two methines bearing oxygen functions [3.69 (1H, m, H-9), and 4.03 (1H, m, H-3)], and one tetrasubstituted double bond [δ_C 125.1 (C-5) and 138.5 (C-6)], together with a β-D-glucopyranosyl part [δ 4.42 (1H, d, J=7.6 Hz, H-1′)] and an α-L-arabinopyranosyl part [δ 4.31 (1H, d, J=6.9 Hz, H-1″)]. The enzymatic hydrolysis of **4** with naringinase gave (3*R*,9*R*)-3,9-dihydroxymegastigman-5-ene[22] as the aglycon, of which the absolute stereostructure was determined by the application of the modified Mosher's method. As shown in Fig. 3, the DQF COSY experiment on **4** indicated the presence of a partial structure as shown in boldface lines, and in the HMBC experiment, long-range correlations between the 1′-proton and 3-carbon (δ_C 73.3) and between the 1″-proton and 6′-carbon (δ_C 69.3) were observed. Thus the absolute stereostructure of **4** was elucidated to be (3*R*,9*R*)-3,9-dihydroxymegastigman-5-en 3-*O*-α-L-arabinopyranosyl(1→6)-β-D-glucopyranoside.

Foliasalacioside G (**5**) was obtained as an amorphous powder with negative optical rotation ($[\alpha]_D^{26}$ −32.5° in MeOH). The IR spectrum of **5** showed absorption bands at 3420, 1638, and 1076 cm^{-1} assignable to hydroxyl, double bond, and ether functions, respectively. Its elemental composition

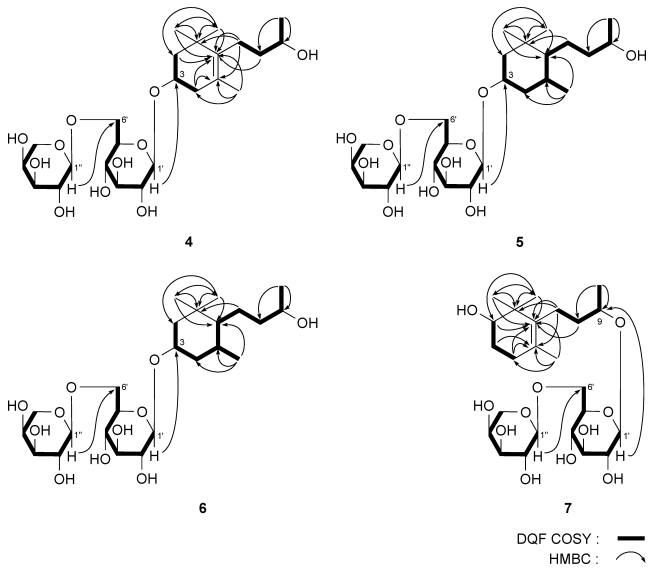

Fig. 3. Selected DQF COSY and HMBC Correlations of **4**—**7**

was determined to be $C_{24}H_{42}O_{11}$ based on the results of positive- and negative-ion FAB-MS [*m/z* 529 $(M+Na)^+$, *m/z* 505 $(M-H)^-$] and HR-FAB-MS analysis. The ^{1}H- (CD_3OD) and ^{13}C-NMR spectra (Table 1)[20] of **5** showed signals due to four methyls [δ 0.87, 0.91 (3H each, both s, H_3-11, 12), 0.83 (3H, d, J=6.7 Hz, H_3-13), and 1.21 (3H, d, J=6.4 Hz, H_3-10)] and two methines bearing an oxygen function [δ 3.84 (1H, m, H-3) and 4.22 (1H, m, H-9)], together with a β-D-glucopyranosyl part [δ 4.34 (1H, d, J=7.6 Hz, H-1′)] and an α-L-arabinopyranosyl part [δ 4.33 (1H, d, J=6.4 Hz, H-1″)]. The DQF COSY experiment on **5** indicated the presence of three partial structures shown in boldface lines, and in the HMBC experiment, important long-range correlations were observed between the following protons and carbons: H_3-10 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, 5, 6; and H-1′ and C-3; H-1″ and C-6′ (Fig. 3). Treatment of **5** with HCl 1 M liberated sarmentol F[23] as the aglycon, together with D-glucose and L-arabinose, which were identified in HPLC analysis using an optical rotation detector.[18,19] Thus the absolute configuration of **5** was clarified to be (3*S*,5*R*,6*S*,9*R*)-megastigman-7-en-3,9-diol 3-*O*-α-L-arabinopyranosyl(1→6)-β-D-glucopyranoside.

Foliasalacioside H (**6**) was isolated as an amorphous powder with negative optical rotation ($[\alpha]_D^{26}$ −28.0° in MeOH). The positive- and negative-ion FAB-MS [*m/z* 531 $(M+Na)^+$, *m/z* 507 $(M-H)^-$] and HR-FAB-MS revealed the molecular formula of **6** to be $C_{24}H_{44}O_{11}$, and the IR spectra indicated the presence of hydroxyl functions (3420 cm^{-1}) and ether functions (1073 cm^{-1}). The ^{1}H- (CD_3OD) and ^{13}C-NMR (Table 1) spectra[20] of **6** indicated the presence of four methyls [δ 0.84, 0.96 (3H each, both s, H_3-11, 12), 0.97 (3H, d, J=6.4 Hz, H_3-13), 1.14 (3H, d, J=6.1 Hz, H_3-10)], two methines bearing an oxygen function [δ 3.64 (1H, m, H-9), 3.79 (1H, m, H-3)], four methylenes, two methines, and a quaternary carbon, together with a β-D-glucopyranosyl part and an α-L-arabinopyranosyl part [δ 4.33 (1H, d, J=7.9 Hz, H-1′), 4.32 (1H, d, J=6.7 Hz, H-1″)]. The DQF COSY experiment on **6** revealed the presence of the three partial structures shown in boldface lines (Fig. 3). The positions of the β-glucopyranosyl and L-arabinopyranosyl moieties were determined based on the HMBC correlations (Fig. 3). The acid hydrolysis of **6** with HCl 1 M liberated D-glucose and L-arabinose, while the enzymatic hydrolysis of **6** with naringinase gave (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol[14] as the aglycon, of which the absolute stereostructure was determined by the application of the modified Mosher's method. Consequently, the absolute stereostructure of **6** was elucidated to be (3*S*,5*R*,6*S*,9*R*)-megastigman-3,9-diol 3-*O*-α-L-arabinopyranosyl(1→6)-β-D-glucopyranoside.

Foliasalacioside I (**7**) was isolated as an amorphous powder with negative optical rotation ($[\alpha]_D^{26}$ −18.4° in MeOH). The IR spectrum of **7** showed absorption bands at 3420, 1632, and 1078 cm^{-1} ascribable to hydroxyl, double bond, and ether functions, respectively. The molecular formula $C_{24}H_{42}O_{11}$ was determined from the results of HR-FAB-MS analysis. The proton and carbon signals in the ^{1}H- (CD_3OD) and ^{13}C-NMR spectra (Table 1)[20] of **7** indicated the presence of four methyls [δ 0.95, 1.06, 1.61 (3H each, all s, H_3-11, 12, 13), 1.19 (3H each, d, J=6.1 Hz, H_3-10)], two methines bearing an oxygen function [δ 3.40 (1H, dd, J=3.4, 10.1 Hz, H-2), and 3.87 (1H, m, H-9)], a tetrasubstituted double-bond function [δ_C 127.1 (C-5) and 137.5 (C-6)], four methylenes, and a quaternary carbon, together with a β-D-glucopyranosyl part [δ 4.33 (1H, d, J=7.9 Hz, H-1′)] and an α-L-arabinopyranosyl part [δ 4.34 (1H, d, J=6.7 Hz, H-1″)]. The proton and carbon signals due to the aglycon and the β-D-glucopyranosyl parts were superimposable on those of platanionoside J,[22] except for the signals due to the α-L-arabinopyranosyl moiety of **7**. The DQF COSY experiment on **7** indicated the presence of partial structures shown in boldface lines. In the HMBC experiment, long-range correlations were observed between the following protons and carbons: H-2 and C-6; H_2-3 and C-5; H_2-4 and C-5, 6; H_2-7 and C-1, 5, 6; H_2-8 and C-6; H_3-10 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, 5, 6; H-1′ and C-9; and H-1″ and C-6′. The structure of **7** was the same as that of the reported compound platanionoside J, except for the terminal oligosugar moiety of L-arabinopyranoside.[22] Treatment of **7** with HCl 1 M liberated D-glucose and L-arabinose, which were identified in HPLC analysis using an optical rotation detector.[18,19] On the basis of the above evidence, the stereostructure of **7** was elucidated to be (2*R*,9*R*)-megastigman-5-en-2,9-diol 9-*O*-α-L-arabinopyranosyl(1→6)-β-D-glucopyranoside.

Experimental

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; EI-MS and high-resolution MS, JEOL JMS-GCMATE mass spectrometer; FAB-MS and high-resolution MS, JEOL JMS-SX 102A mass spectrometer; ^{1}H-NMR spectra, JEOL EX-270 (270 MHz) and JNM-LA500 (500 MHz) spectrometers; ^{13}C-NMR spectra, JEOL EX-270 (68 MHz) and JNM-LA500 (125 MHz) spectrometers with tetramethylsilane as an internal standard; and HPLC detector, Shimadzu RID-6A refractive index and SPD-10A*vp* UV-VIS detectors. HPLC column, Cosmosil 5C_{18}-MS-II (Nacalai Tesque Inc., 250×4.6 mm i.d.) and (250×20 mm i.d.) columns were used for analytical and preparative purposes, respectively.

The following experimental conditions were used for chromatography: ordinary-phase silica gel column chromatography, Silica gel BW-200 (Fuji Silysia Chemical, Ltd., Aichi, Japan, 150—350 mesh); reversed-phase silica gel column chromatography, Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., Aichi, Japan, 100—200 mesh); TLC plates and precoated

TLC plates with Silica gel 60F_{254} (Merck, 0.25 mm) (ordinary phase) and Silica gel RP-18 F_{254S} (Merck, 0.25 mm) (reversed phase); reversed-phase HPTLC, with Silica gel RP-18 WF_{254S} (Merck, 0.25 mm); and detection was achieved by spraying with 1% $Ce(SO_4)_2$–10% aqueous H_2SO_4 followed by heating.

Plant Material The dried leaves of *S. chinensis* were collected at Thailand in 2006 and identified by one of authors (Rajamangala University of Technology Srivijaya, Pongpiriyadacha Y.). A voucher of the plant is on file in our laboratory (2006. Thai-06).

Extraction and Isolation The dried leaves of *S. chinensis* LINN. (5.8 kg) were finely cut and extracted 3 times with MeOH under reflux for 3 h. Evaporation of the solvent under reduced pressure provided a methanolic extract (756 g, 13.0%). The MeOH extract (712 g) was partitioned into an EtOAc–H_2O (1 : 1, v/v) mixture to furnish an EtOAc-soluble fraction (222 g, 4.1%) and an aqueous phase. The aqueous phase was further extracted with *n*-BuOH to give an *n*-BuOH-soluble fraction (130 g, 2.4%) and a H_2O-soluble fraction (361 g, 6.6%). The *n*-BuOH-soluble fraction (100.0 g) was subjected to Diaion HP-20 column chromatography (1.5 kg, H_2O→MeOH→acetone) to give H_2O-eluted fraction (49.8 g, 1.19%), MeOH-eluted fraction (39.2 g, 0.93%) and acetone-eluted fraction (11.0 g, 0.26%), respectively. The MeOH-eluted fraction (39.2 g) was subjected to ordinary-phase silica gel column chromatography {480 g, $CHCl_3$–MeOH (10 : 1, v/v)→$CHCl_3$–MeOH–H_2O [(10 : 3 : 1, v/v/v, lower layer)→(7 : 3 : 1, v/v/v, lower layer)→(6 : 4 : 1, v/v/v, lower layer)]→MeOH} to give ten fractions [Fr. 1 (0.5 g), Fr. 2 (0.6 g), Fr. 3 (1.3 g), Fr. 4 (7.3 g), Fr. 5 (3.0 g), Fr. 6 (6.7 g), Fr. 7 (1.6 g), Fr. 8 (2.4 g), Fr. 9 (9.3 g), Fr. 10 (3.5 g)] as reported previously.[13] Fraction 4 (7.3 g) was subjected to reversed-phase silica gel column chromatography [220 g, H_2O→MeOH–H_2O (10 : 90→20 : 80→30 : 70→40 : 60→60 : 40, v/v)→MeOH→$CHCl_3$] to give ten fractions [Fr. 4-1 (783 mg), Fr. 4-2 (821 mg), Fr. 4-3 (1122 mg), Fr. 4-4 (577 mg), Fr. 4-5 (288 mg), Fr. 4-6 (652 mg), Fr. 4-7 (1295 mg), Fr. 4-8 (413 mg), Fr. 4-9 (253 mg), Fr. 4-10 (760 mg)]. Fraction 4-3 (1122 mg) was isolated by HPLC [MeOH–H_2O (20 : 80, v/v)] to give fourteen fractions [Fr. 4-3-1 (5.8 mg), Fr. 4-3-2 (13.8 mg), Fr. 4-3-3 (21.4 mg), Fr. 4-3-4 (24.4 mg), Fr. 4-3-5 (131.9 mg), Fr. 4-3-6 (26.5 mg), Fr. 4-3-7 (58.1 mg), Fr. 4-3-8 (25.8 mg), Fr. 4-3-9 (28.6 mg), Fr. 4-3-10 (28.7 mg), Fr. 4-3-11 (139.2 mg), Fr. 4-3-12 (62.7 mg), Fr. 4-3-13 (97.2 mg), Fr. 4-3-14 (130.7 mg)]. Fraction 4-3-7 (58.1 mg) was purified by HPLC [CH_3CN–MeOH–H_2O (8 : 8 : 84, v/v/v)] to give 1-[5-(8-hydroxy-1,5-dimethyl-3-oxo-6-oxabicyclo[3.2.1]oct-8-yl)-3-methyl-2,4-pentadienoate], [1*R*-[1α,5α,8*S**(2*Z*,4*E*)]]-β-D-glucopyranose (**11**, 15.2 mg, 0.00036%). Fraction 4-3-13 (97.2 mg) was subjected to HPLC [MeOH–H_2O–CH_3CN (10 : 8 : 82, v/v/v)] to furnish loliolide β-D-glucopyranoside (**9**, 5.1 mg, 0.00012%). Fraction 4-6 (652 mg) was subjected to HPLC [MeOH–H_2O (30 : 70, v/v)] to give ten fractions [Fr. 4-6-1 (3.8 mg), Fr. 4-6-2 (13.6 mg), Fr. 4-6-3 (12.8 mg), Fr. 4-6-4 (15.2 mg), Fr. 4-6-5 (27.0 mg), Fr. 4-6-6 (13.9 mg), Fr. 4-6-7 (27.8 mg), Fr. 4-6-8 (35.2 mg), Fr. 4-6-9 (18.0 mg), Fr. 4-6-10 (44.6 mg)]. Fraction 4-6-10 (44.6 mg) was subjected to HPLC [CH_3CN–MeOH–H_2O (12 : 8 : 80, v/v/v)] to give (+)-abscisyl β-D-glucopyranoside (**10**, 8.2 mg, 0.00020%). Fraction 4-8 (413 mg) was subjected to HPLC [MeOH–H_2O (40 : 60, v/v)] to afford nine fractions [Fr. 4-8-1 (11.9 mg), Fr. 4-8-2 (22.2 mg), Fr. 4-8-3 (47.6 mg), Fr. 4-8-4 (16.2 mg), Fr. 4-8-5 (14.2 mg), Fr. 4-8-6 (11.4 mg), Fr. 4-8-7 (14.6 mg), Fr. 4-8-8 (16.8 mg), Fr. 4-8-9 (16.2 mg)]. Fraction 4-8-6 (11.4 mg) was further purified by HPLC [CH_3CN–MeOH–H_2O (15 : 8 : 77, v/v/v)] to give myrsinionoside D (**8**, 2.1 mg, 0.00005%). Fraction 5 (3.0 g) was subjected to reversed-phase silica gel column chromatography [90 g, H_2O→MeOH–H_2O (20 : 80→30 : 70→40 : 60→50 : 50, v/v)→MeOH] to afford seven fractions [Fr. 5-0 (812 mg), Fr. 5-1 (196 mg), Fr. 5-2 (212 mg), Fr. 5-3 (224 mg), Fr. 5-4 (158 mg), Fr. 5-5 (400 mg), Fr. 5-6 (624 mg)]. Fraction 5-5 (400 mg) was subjected to HPLC [MeOH–H_2O (40 : 60, v/v)] and HPLC [CH_3CN–MeOH–H_2O (15 : 8 : 75, v/v/v)] to give foliacalacioside E_3 (**3**, 4.5 mg, 0.00011%). Fraction 6 (6.7 g) was subjected to reversed-phase silica gel column chromatography [220 g, MeOH–H_2O (10 : 90→20 : 80→30 : 70→40 : 60→50 : 50→60 : 40, v/v)→MeOH→$CHCl_3$] to give eleven fractions [Fr. 6-1 (809 mg), Fr. 6-2 (859 mg), Fr. 6-3 (118 mg), Fr. 6-4 (103 mg), Fr. 6-5 (480 mg), Fr. 6-6 (300 mg), Fr. 6-7 (250 mg), Fr. 6-8 (1277 mg), Fr. 6-9 (239 mg), Fr. 6-10 (335 mg), Fr. 6-11 (1247 mg)]. Fraction 6-6 (300 mg) was isolated with HPLC [MeOH–H_2O (40 : 60, v/v)] to afford ten fractions [Fr. 6-6-1 (3.5 mg), Fr. 6-6-2 (7.6 mg), Fr. 6-6-3 (7.1 mg), Fr. 6-6-4 (45.6 mg), Fr. 6-6-5 (16.8 mg), Fr. 6-6-6 (10.8 mg), Fr. 6-6-7 (16.9 mg), Fr. 6-6-8 (14.6 mg), Fr. 6-6-9 (6.5 mg), Fr. 6-6-10 (12.8 mg)]. Fractions 6-6-3 (7.1 mg), 6-6-5 (16.8 mg) and 6-6-8 (14.6 mg) were purified by HPLC [CH_3CN–MeOH–H_2O (15 : 8 : 77, v/v/v)] to furnish foliasalacioside G (**5**, 2.2 mg, 0.00005%), foliasalacioside E_1 (**1**, 7.0 mg, 0.00016%), foliasalacioside H (**6**, 3.5 mg, 0.000083%) and foliasalacioside E_2 (**2**, 5.8 mg, 0.00014%), respectively. Fraction 6-6-4 (45.6 mg) was separated by HPLC [CH_3CN–MeOH–H_2O (13 : 8 : 79, v/v/v)] to give foliasalacioside F (**4**, 12.5 mg, 0.00028%) and foliasalacioside E_1 (**1**, 13.5 mg, 0.00032%). Fractions 6-6-7 were identified as foliasalacioside H (**6**, 16.9 mg, 0.00040%). Fraction 6-7 (250 mg) was subjected to HPLC [CH_3CN–MeOH–H_2O (15 : 8 : 77, v/v/v)] and HPLC [MeOH–H_2O (38 : 62, v/v)] to furnish foliasalacioside H (**6**, 5.8 mg, 0.00014%), and foliasalacioside I (**7**, 3.8 mg, 0.00008%).

Foliasalacioside E_1 (**1**): An amorphous powder; $[\alpha]_D^{26}$ −8.3° (*c*=0.28, MeOH); IR (KBr) ν_{max} 3420, 2928, 1638, 1458, 1375, 1078, 1046 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 1.05, 1.06, 1.64 (3H each, all s, H_3-11, 12, 13), 1.16 (3H, d, *J*=6.4 Hz, H_3-10), 1.42 (1H, dd, *J*=12.2, 12.2 Hz, H-2α), 1.48 (2H, m, H_2-8), 1.84 (1H, ddd, *J*=1.5, 2.8, 12.2 Hz, H-2β), 1.92, 2.21 (1H each, both m, H_2-7), 2.08 (1H, dd, *J*=10.1, 15.9 Hz, H-4α), 2.30 (1H, br dd, *J*=*ca.* 5, 16 Hz, H-4β), 3.15 (1H, dd, *J*=7.9, 8.9 Hz, H-2′), 3.34 (1H, m, H-4′), 3.35 (1H, m, H-3′), 3.44 (1H, m, H-5′), 3.51 (1H, dd, *J*=3.4, 8.8 Hz, H-3″), 3.53 (1H, dd, *J*=1.9, 12.4 Hz, H-5″a), 3.59 (1H, dd, *J*=6.7, 8.8 Hz, H-2″), 3.69 (1H, m, H-9), 3.74 (1H, dd, *J*=5.3, 11.3 Hz, H-6′a), 3.80 (1H, m, H-4″), 3.86 (1H, dd, *J*=3.4, 12.4 Hz, H-5″b), 3.95 (1H, m, H-3), 4.07 (1H, dd, *J*=2.4, 11.3 Hz, H-6′b), 4.32 (1H, d, *J*=6.7 Hz, H-1″), 4.38 (1H, d, *J*=7.9 Hz, H-1′); ^{13}C-NMR (125 MHz, CD_3OD) δ_C: see Table 1; positive-ion FAB-MS *m/z* 529 $(M+Na)^+$; negative-ion FAB-MS *m/z* 505 $(M-H)^-$; HR-FAB-MS: *m/z* 527.2620 (Calcd for $C_{24}H_{42}O_{11}Na$ $(M+Na)^+$, 529.2625).

Foliasalacioside E_2 (**2**): An amorphous powder; $[\alpha]_D^{26}$ +1.6° (*c*=0.22, MeOH); IR (KBr) ν_{max} 3420, 2929, 1635, 1456, 1375, 1074, 1042 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 1.03, 1.06, 1.63 (3H each, all s, H_3-11, 12, 13), 1.19 (3H, d, *J*=6.2 Hz, H_3-10), 1.37 (1H, dd, *J*=11.6, 11.6 Hz, H-2α), 1.53, 1.64 (1H each, both m, H_2-8), 1.67 (1H, m, H-2β), 1.92 (1H, br dd, *J*=*ca.* 10, 16 Hz, H-4α), 2.04, 2.15 (1H each, both m, H_2-7), 2.18 (1H, br dd, *J*=*ca.* 5, 16 Hz, H-4β), 3.16 (1H, dd, *J*=7.6, 8.9 Hz, H-2′), 3.30 (1H, m, H-4′), 3.35 (1H, m, H-3′), 3.42 (1H, m, H-5′), 3.50, 3.86 (1H each, both m, H_2-5″), 3.51 (1H, m, H-3″), 3.58 (1H, dd, *J*=6.7, 8.6 Hz, H-2″), 3.73 (1H, dd, *J*=5.5, 11.7 Hz, H-6′a), 3.79 (1H, m, H-4″), 3.83 (1H, m, H-3), 3.87 (1H, m, H-9), 4.06 (1H, dd, *J*=2.1, 11.7 Hz, H-6′b), 4.32 (1H, d, *J*=7.6 Hz, H-1′), 4.34 (1H, d, *J*=6.8 Hz, H -1″); ^{13}C-NMR (125 MHz, CD_3OD) δ_C: see Table 1; positive-ion FAB-MS *m/z* 529 $(M+Na)^+$; negative-ion FAB-MS *m/z* 505 $(M-H)^-$; HR-FAB-MS: *m/z* 529.2630 (Calcd for $C_{24}H_{42}O_{11}Na$ $(M+Na)^+$, 529.2625).

Foliasalacioside E_3 (**3**): An amorphous powder; $[\alpha]_D^{25}$ −8.6° (*c*=0.14, MeOH); IR (KBr) ν_{max} 3422, 2924, 1636, 1375, 1072, 1046 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 1.03, 1.06, 1.63 (3H each, all s, H_3-11, 12, 13), 1.19 (3H, d, *J*=6.1 Hz, H_3-10), 1.37 (1H, dd, *J*=11.9, 11.9 Hz, H-2α), 1.51, 1.64 (1H each, both m, H_2-8), 1.67 (1H, ddd, *J*=2.2, 3.4, 11.9 Hz, H-2β), 1.92 (1H, br dd, *J*=*ca.* 9, 16 Hz, H-4α), 2.05, 2.15 (1H each, both m, H_2-7), 2.18 (1H, br dd, *J*=*ca.* 5, 16 Hz, H-4β), 3.15 (1H, dd, *J*=7.6, 8.9 Hz, H-2′), 3.28 (1H, dd, *J*=8.9, 8.9 Hz, H-4′), 3.35 (1H, dd, *J*=8.9, 8.9 Hz, H-3′), 3.42 (1H, m, H-5′), 3.61 (1H, dd, *J*=5.8, 11.3 Hz, H-6′a), 3.63 (1H, dd, *J*=5.2, 11.9 Hz, H-5″a), 3.72 (1H, dd, *J*=3.4, 11.9 Hz, H-5″b), 3.82 (1H, dd, *J*=3.4, 5.8 Hz, H-3″), 3.83 (1H, m, H-3), 3.85 (1H, m, H-9), 3.95 (1H, m, H-4″), 3.98 (1H, dd, *J*=1.2, 3.4 Hz, H-2″), 4.00 (1H, dd, *J*=2.5, 11.3 Hz, H-6′a), 4.32 (1H, d, *J*=7.6 Hz, H-1′), 4.97 (1H, d, *J*=1.2 Hz, H-1″); ^{13}C-NMR (125 MHz, CD_3OD) δ_C: see Table 1; positive-ion FAB-MS *m/z* 529 $(M+Na)^+$; negative-ion FAB-MS *m/z* 505 $(M-H)^-$; HR-FAB-MS: *m/z* 529.2620 (Calcd for $C_{24}H_{42}O_{11}Na$ $(M+Na)^+$, 529.2625).

Foliasalacioside F (**4**): An amorphous powder; $[\alpha]_D^{26}$ −44.2° (*c*=0.52, MeOH); IR (KBr) ν_{max} 3345, 2930, 1636, 1456, 1373, 1078, 1045 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 1.05, 1.06, 1.65 (3H each, both s, H_3-12, 11, 13), 1.16 (3H, d, *J*=6.2 Hz, H_3-10), 1.48 (2H, m, H_2-8), 1.49 (1H, m, H-2β), 1.82 (1H, ddd, *J*=2.1, 2.1, 12.4 Hz, H-2α), 1.92, 2.21 (1H each, both m, H_2-7), 2.01 (1H, dd, *J*=9.6, 15.8 Hz, H-4β), 2.33 (1H, br dd, *J*=*ca.* 5, 16 Hz, H-4α), 3.15 (1H, m, H-2′), 3.35 (1H, m, H-4′), 3.36 (1H, m, H-3′), 3.44 (1H, m, H-5′), 3.52 (1H, m, H-3″), 3.53 (1H, dd, *J*=1.6, 12.4 Hz, H-5″a), 3.86 (1H, dd, *J*=3.4, 12.4 Hz, H-5″b), 3.59 (1H, dd, *J*=6.9, 8.2 Hz, H-2″), 3.69 (1H, m, H-9), 3.74 (1H, dd, *J*=5.5, 11.7 Hz, H-6′a), 4.03 (1H, m, H-3), 4.07 (1H, dd, *J*=2.1, 11.7 Hz, H-6′b), 3.79 (1H, m, H-4″), 4.31 (1H, d, *J*=6.9 Hz, H-1″), 4.42 (1H, d, *J*=7.6 Hz, H-1′); ^{13}C-NMR (125 MHz, CD_3OD) δ_C: see Table 1; positive-ion FAB-MS *m/z* 529 $(M+Na)^+$; negative-ion FAB-MS *m/z* 505 $(M-H)^-$. HR-FAB-MS: *m/z* 529.2631 (Calcd for $C_{24}H_{42}O_{11}Na$ $(M+Na)^+$, 529.2625).

Foliasalacioside G (**5**): An amorphous powder; $[\alpha]_D^{26}$ −32.5° (*c*=0.08, MeOH); IR (KBr) ν_{max} 3420, 2924, 1638, 1076, 1026 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 0.83 (3H, d, *J*=6.7 Hz, H_3-13), 0.87, 0.91 (3H each, both s, H_3-11, 12), 1.01 (1H, ddd, *J*=12.2, 12.2, 12.2 Hz, H-4α), 1.16 (1H,

dd, J=12.2, 12.2 Hz, H-2α), 1.21 (3H, d, J=6.4 Hz, H_3-10), 1.31 (1H, dd, J=9.8, 9.8 Hz, H-6), 1.57 (1H, m, H-5), 1.84 (1H, ddd, J=2.2, 4.3, 12.2 Hz, H-2β), 2.10 (1H, m, H-4β), 3.13 (1H, dd, J=7.6, 9.2 Hz, H-2′), 3.32 (1H, m, H-3′), 3.33 (1H, m, H-4′), 3.43 (1H, m, H-5′), 3.52 (1H, dd, J=3.2, 8.9 Hz, H-3″), 3.53 (1H, dd, J=1.9, 12.5 Hz, H-5″a), 3.86 (1H, dd, J=3.8, 12.5 Hz, H-5″b), 3.59 (1H, dd, J=6.4, 8.9 Hz, H-2″), 3.73 (1H, dd, J=5.5, 11.6 Hz, H-6′a), 3.80 (1H, m, H-4″), 3.84 (1H, m, H-3), 4.06 (1H, dd, J=2.5, 11.6 Hz, H-6′b), 4.22 (1H, m, H-9), 4.33 (1H, d, J=6.4 Hz, H-1″), 4.34 (1H, d, J=7.6 Hz, H-1′), 5.30 (1H, ddd, J=1.0, 9.8, 15.3 Hz, H-7), 5.45 (1H, dd, J=6.5, 15.3 Hz, H-8); ^{13}C-NMR (125 MHz, CD_3OD) δ_C: see Table 1; positive-ion FAB-MS m/z 529 $(M+Na)^+$; negative-ion FAB-MS m/z 505 $(M-H)^-$; HR-FAB-MS: m/z 529.2631 (Calcd for $C_{24}H_{42}O_{11}Na$ $(M+Na)^+$, 529.2625).

Foliasalacioside H (**6**): An amorphous powder; $[\alpha]_D^{26}$ −28.0° (c=0.81, MeOH); IR (KBr) ν_{max} 3420, 2934, 1373, 1073 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 0.54 (1H, ddd, J=2.5, 4.9, 10.7 Hz, H-6), 0.84, 0.96 (3H each, both s, H_3-11, 12), 0.97 (3H, d, J=6.4 Hz, H_3-13), 1.01, 1.55 (1H each, both m, H_2-7), 1.02 (1H, ddd, J=12.2, 12.2, 12.2 Hz, H-4α), 1.14 (1H, m, H-2α), 1.14 (3H, d, J=6.1 Hz, H_3-10), 1.40, 1.52 (1H each, both m, H_2-8), 1.45 (1H, m, H-5), 1.79 (1H, ddd, J=2.1, 4.0, 12.8 Hz, H-2β), 2.02 (1H, m, H-4β), 3.12 (1H, dd, J=7.9, 9.2 Hz, H-2′), 3.33 (1H, m, H-3′), 3.34 (1H, m, H-4′), 3.43 (1H, m, H-5′), 3.51 (1H, m, H-3″), 3.54 (1H, dd, J=1.9, 12.5 Hz, H-5″a), 3.59 (1H, dd, J=6.7, 8.6 Hz, H-2″), 3.64 (1H, m, H-9), 3.73 (1H, dd, J=5.5, 11.6 Hz, H-6′a), 3.79 (1H, m, H-3), 3.80 (1H, m, H-4″), 3.86 (1H, dd, J=3.4, 12.5 Hz, H-5″b), 4.05 (1H, dd, J=2.1, 11.6 Hz, H-6′b), 4.32 (1H, d, J=6.7 Hz, H-1″), 4.33 (1H, d, J=7.9 Hz, H-1′). ^{13}C-NMR (125 MHz, CD_3OD) δ_C: see Table 1; positive-ion FAB-MS m/z 531 $(M+Na)^+$; negative-ion FAB-MS m/z 507 $(M-H)^-$; HR-FAB-MS: m/z 531.2778 (Calcd for $C_{24}H_{44}O_{11}Na$ $(M+Na)^+$, 531.2781).

Foliasalacioside I (**7**): An amorphous powder; $[\alpha]_D^{26}$ −18.4° (c=0.15, MeOH); IR (KBr) ν_{max} 3430, 2932, 1632, 1456, 1379, 1078, 1040 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 0.95, 1.06, 1.61 (3H each, both s, H_3-11, 12, 13), 1.19 (3H, d, J=6.1 Hz, H_3-10), 1.60 (2H, m, H_2-8), 1.70 (2H, m, H_2-3), 1.97 (1H, ddd, J=5.2, 12.8, 12.8 Hz, H-7a), 2.02 (2H, m, H_2-4), 2.25 (1H, dd, J=4.0, 12.8, 12.8 Hz, H-7b), 3.16 (1H, dd, J=7.9, 8.9 Hz, 2′-H), 3.34 (1H, m, H-4′), 3.35 (1H, m, H-3′), 3.40 (1H, dd, J=3.4, 10.1 Hz, H-2), 3.42 (1H, m, H-5′), 3.51 (1H, dd, J=1.9, 12.5 Hz, H-5″a), 3.52 (1H, dd, J=3.5, 8.9 Hz , H-3″), 3.59 (1H, dd, J=6.7, 8.9 Hz, H-2″), 3.74 (1H, dd, J=5.8, 11.6 Hz, H-6′a), 3.79 (1H, m, H-4″), 3.85 (1H, dd, J=3.4, 12.5 Hz, H-5″b), 3.87 (1H, m, H-9), 4.07 (1H, dd, J=2.1, 11.6 Hz, H-6′b), 4.33 (1H, d, J=7.9 Hz, H-1′), 4.34 (1H, d, J=6.7 Hz, H-1″); ^{13}C-NMR (125 MHz, CD_3OD) δ_C: see Table 1; positive-ion FAB-MS m/z 529 $(M+Na)^+$; negative-ion FAB-MS m/z 505 $(M-H)^-$; HR-FAB-MS: m/z 529.2620 (Calcd for $C_{24}H_{42}O_{11}Na$ $(M+Na)^+$, 529.2625).

Acid Hydrolysis of 1—4, 6, and 7 A solution of foliasalaciosides E_1 (**1**), E_2 (**2**), E_3 (**3**), F (**4**), H (**6**) and I (**7**) (each 1.0 mg) in 1 M HCl (1.0 ml) were heated under reflux for 3 h. After cooling, each reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and filtrated, and the solution was partitioned with EtOAc. The aqueous layer was evaporated and then subjected to HPLC analysis using Kaseisorb LC NH_2-60-5 column (4.6 mm×250 mm i.d., Tokyo Kasei Co., Ltd., Tokyo, Japan) and an optical rotation detector (Shodex OR-2, Showa Denko Co., Ltd., Tokyo, Japan). D-glucose and L-arabinose from **1**—**7** were confirmed by comparison of the retention times with the authentic samples (Wako Pure Chemicals Ltd., Osaka, Japan) [mobile phase: CH_3CN–H_2O (85 : 15, v/v), flow rate: 0.8 ml/min, t_R: 10.2 min (L-arabinose, positive optical rotation); t_R: 12.8 min (D-glucose, positive optical rotation)].

Acid Hydrolysis of 5 A solution of foliasalacioside G (**5**, 2.0 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 EtOAc extract was neutralized with Amberlite IRA-400 (OH^- form) and filtrated, the solvent was removed under reduced pressure to give a residue, which was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give sarmentol F (0.5 mg, 59.5%). From the aqueous layer, D-glucose and L-arabinose from **5** were confirmed by using the same method as described above.

Enzymatic Hydrolysis of 1—4 and 6 A solution of **1**—**4** and **6** (12.8, 2.1, 1.6, 5.0, 8.2 mg, respectively) in 0.2 M acetate buffer (pH 3.8, 1.0 ml) was treated with naringinase (55.2, 18.9, 16.3, 10.2, 20.2 mg, respectively) and the solution was stirred at 40 °C for 48 h. After cooling, the reaction mixture was extracted with EtOAc. The EtOAc solvent was removed under reduced pressure and the residue was purified by HPLC [MeOH–H_2O (50 : 50 for **1**—**4**; 60 : 40 for **6**, v/v)] to furnish **1a** (4.6 mg, 85.8% from **1**, 0.6 mg, 68.1% from **2** and 0.5 mg, 74.6% from **3**), (3R,9R)-3,9-dihydroxymegastigman-5-ene (1.7 mg, 81.4% from **4**), and (3S,5R,6S,9R)-3,9-dihydroxymegastigman (3.2 mg, 91.4% from **6**), respectively.

Foliasalaciol E (**1a**): Colorless oil; $[\alpha]_D^{26}$ +45.9° (c=0.21, MeOH); IR (film) ν_{max} 3372, 2926, 1625, 1456, 1362, 1123, 1042, 756 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.03, 1.06, 1.62 (3H each, all s, H_3-11, 12, 13), 1.22 (3H, d, J=6.1 Hz, H_3-10), 1.43 (1H, dd, J=11.9, 11.9 Hz, H-2α), 1.51 (2H, m, H_2-8), 1.71 (1H, ddd, J=2.1, 3.7, 11.9 Hz, H-2β), 1.96 (1H, br dd, J=*ca.* 10, 16 Hz, H-4α), 2.02, 2.08 (1H each, both m, H_2-7), 2.24 (1H, m, H-4β), 3.80 (1H, m, H-9), 3.94 (1H, m, H-3); ^{1}H-NMR (500 MHz, CD_3OD) δ 1.03, 1.06, 1.63 (3H each, all s, H_3-11, 12, 13), 1.17 (3H, d, J=6.2 Hz, H_3-10), 1.37 (1H, dd, J=12.0, 12.0 Hz, H-2α), 1.48 (2H, m, H_2-8), 1.67 (1H, ddd, J=2.1, 3.5, 12.0 Hz, H-2β), 1.92 (1H, br dd, J=*ca.* 10, 16 Hz, H-4α), 2.05, 2.14 (1H each, both m, H_2-7), 2.21 (1H, m, H-4β), 3.70 (1H, m, H-9), 3.84 (1H, m, H-3). ^{13}C-NMR (125 MHz, $CDCl_3$ and CD_3OD) δ_C: see Table 1. EI-MS (%): m/z 212 (M^+, 6), 194 (7), 176 (3), 161 (35), 121 (100). HR-EI-MS: m/z 212.1781 (Calcd for $C_{13}H_{24}O_2$ $(M)^+$, 212.1776).

Preparation of the (*R*)-MTPA Ester and (*S*)-MTPA Esters from 1a A solution of foliasalaciol E (**1a**, 2.3 mg) in dehydrated $CHCl_3$ (1.0 ml) was treated with (*R*)-2-methoxy-2-trifluoromethylphenylacetic acid [(*R*)-MTPA, (38.6 mg)] in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, 31.7 mg) and 4-dimethylaminopyridine (4-DMAP, 13.5 mg), and the mixture was stirred under reflux at 60 °C for 6 h. After cooling, the reaction mixture was poured into ice-water and extracted with EtOAc. The EtOAc extract was washed successively with 5% HCl, $NaHCO_3$-saturated H_2O and brine and dried over Na_2SO_4 and filtered. Removal of the solvent from the filtrate under reduced pressure to afford a residue, which was subjected to normal-phase silica gel CC [500 mg, *n*-hexane–EtOAc (100 : 0→10 : 1→5 : 1→3 : 1, v/v)] to furnish **1b** (1.2 mg, 17.2%), **1d** (1.1 mg, 23.7%) and **1f** (1.0 mg, 21.6%). Using a similar procedure, (*S*)-MTPA ester **1c** (1.4 mg, 20.0%), **1e** (0.9 mg, 19.4%) and **1g** (0.9 mg, 19.4%) were obtained from **1a** (2.3 mg) with (*S*)-MTPA (38.5 mg), EDC·HCl (32.1 mg) and 4-DMAP (14.2 mg).

Compound **1b**: Colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.98, 1.03, 1.55 (3H each, all s, H_3-11, 12, 13), 1.30 (3H, d, J=6.2 Hz, H_3-10), 1.52 (1H, dd, J=11.9, 11.9 Hz, H-2α), 1.61 (2H, m, H_2-8), 1.74 (1H, ddd, J=2.3, 4.1, 11.9 Hz, H-2β), 2.03, 2.31 (1H each, both m, H_2-7), 2.18 (1H, br dd, J=*ca.* 10, 15 Hz, H-4α), 2.36 (1H, br dd, J=*ca.* 5, 15 Hz, H-4β), 3.56, 3.58 (3H each, both s, –COOC$\underline{H}_3$), 5.13 (1H, m, H-9), 5.26 (1H, m, H-3), 7.40—7.53 (10H, m, Ph-H).

Compound **1c**: Colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.93, 0.97, 1.50 (3H each, all s, H_3-11, 12, 13), 1.36 (3H, d, J=6.2 Hz, H_3-10), 1.56 (2H, m, H_2-8), 1.59 (1H, dd, J=11.7, 11.7 Hz, H-2α), 1.79 (1H, ddd, J=2.1, 3.4, 11.7 Hz, H-2β), 1.88, 1.93 (1H each, both m, H_2-7), 2.04 (1H, br dd, J=*ca.* 10, 17 Hz, H-4α), 2.28 (1H, br dd, J=*ca.* 5, 17 Hz, H-4β), 3.56, 3.58 (3H each, both s, –COOC$\underline{H}_3$), 5.13 (1H, m, H-9), 5.23 (1H, m, H-3), 7.40—7.53 (10H, m, Ph-H).

Compound **1d**: Colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.05, 1.10, 1.66 (3H each, all s, H_3-11, 12, 13), 1.22 (3H, d, J=6.2 Hz, H_3-10), 1.52 (2H, m, H_2-8), 1.53 (1H, dd, J=11.7, 11.7 Hz, H-2α), 1.76 (1H, ddd, J=2.1, 3.7, 11.7 Hz, H-2β), 2.03, 2.09 (1H each, both m, H_2-7), 2.19 (1H, br dd, J=*ca.* 10, 16 Hz, H-4α), 2.37 (1H, br dd, J=*ca.* 5, 16 Hz, H-4β), 3.56 (3H, s, –COOC$\underline{H}_3$), 3.80 (1H, m, H-9), 5.27 (1H, m, H-3), 7.40—7.54 (5H, m, Ph-H).

Compound **1e**: Colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.08, 1.11, 1.61 (3H each, all s, H_3-11, 12, 13), 1.22 (3H, d, J=6.2 Hz, H_3-10), 1.52 (2H, m, H_2-8), 1.64 (1H, dd, J=11.7, 11.7 Hz, H-2α), 1.83 (1H, ddd, J=2.1, 4.1, 11.7 Hz, H-2β), 2.03, 2.09 (1H each, both m, H_2-7), 2.09 (1H, m, H-4α), 2.32 (1H, br dd, J=*ca.* 6, 17 Hz, H-4β), 3.56 (3H, s, –COOC$\underline{H}_3$), 3.80 (1H, m, H-9), 5.23 (1H, m, H-3), 7.40—7.54 (5H, m, Ph-H).

Compound **1f**: Colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.97, 0.99, 1.58 (3H each, all s, H_3-11, 12, 13), 1.30 (3H, d, J=6.2 Hz, H_3-10), 1.40 (1H, dd, J=11.9, 11.9 Hz, H-2α), 1.61 (2H, m, H_2-8), 1.69 (1H, ddd, J=2.1, 4.1, 11.9 Hz, H-2β), 1.95 (1H, br dd, J=*ca.* 10, 15 Hz, H-4α), 2.01 (2H, m, H_2-7), 2.23 (1H, br dd, J=*ca.* 5, 15 Hz, H-4β), 3.58 (3H, s, –COOC$\underline{H}_3$), 3.91 (1H, m, H-3), 5.12 (1H, m, H-9), 7.40—7.54 (5H, m, Ph-H).

Compound **1g**: Colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.90, 0.93, 1.52 (3H each, all s, H_3-11, 12, 13), 1.36 (3H, d, J=6.1 Hz, H_3-10), 1.37 (1H, dd, J=11.9, 11.9 Hz, H-2α), 1.56 (2H, m, H_2-8), 1.67 (1H, ddd, J=1.8, 3.5, 11.9 Hz, H-2β), 1.92 (1H, m, H-4α), 1.88, 1.92 (1H each, both m, H_2-7), 2.20 (1H, br dd, J=*ca.* 5, 15 Hz, H-4β), 3.58 (3H, s, –COOC$\underline{H}_3$), 3.90 (1H, m, H-3), 5.14 (1H, m, H-9), 7.40—7.54 (5H, m, Ph-H).

(3R,9R)-3,9-Dihydroxymegastigman-5-ene: Colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.03, 1.06, 1.63 (3H each, all s, H_3-12, 11, 13), 1.21 (3H, d, J=6.1 Hz, H_3-10), 1.43 (1H, dd, J=11.9, 11.9 Hz, H-2β), 1.51 (2H, m, H_2-8), 1.71 (1H, ddd, J=2.1, 3.4, 11.9 Hz, H-2α), 1.96 (1H, m, H-4β), 1.90,

2.19 (1H each, both m, H_2-7), 2.24 (1H, m, H-4α), 3.80 (1H, m, H-9), 3.94 (1H, m, H-3); ^{1}H-NMR (500 MHz, CD_3OD) δ: 1.03, 1.05, 1.63 (3H each, all s, H_3-12, 11, 13), 1.16 (3H, d, J=6.3 Hz, H_3-10), 1.37 (1H, dd, J=12.0, 12.0 Hz, H-2β), 1.48 (2H, m, H_2-8), 1.67 (1H, ddd, J=2.1, 3.5, 12.0 Hz, H-2α), 1.95 (1H, m, H-4β), 1.91, 2.20 (1H each, both m, H_2-7), 2.18 (1H, m, H-4α), 3.70 (1H, m, H-9), 3.84 (1H, m, H-3).

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