Turpinionosides A—E: Megastigmane Glucosides from Leaves of *Turpinia ternata* NAKAI

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From leaves of *Turpenia ternata* (Staphylaceae), one megastigmane and seven of its glucosides (1—8) were isolated. Megastigmane and two of the glucosides were found to be known compounds, namely, 3*S*,5*R*,6*R*,9*S*-tetrahydroxymegastigmane (1), corchoionoside C (2), and icariside B_4 (3). The structures of compounds 4—8 (turpinionosides A—E, respectively) were elucidated by means of spectroscopic analyses, and then their absolute structures were determined by the modified Mosher's method to be (3*S*,5*R*,6*S*,9*S*)-3,6,9-trihydroxymegastigman-7-ene 3-*O*- and 9-*O*-β-D-glucopyranosides (4, 5, respectively), (1*S*,3*S*,5*R*,6*S*,9*R*)-3,9,12-trihydroxymegastigmane 3-*O*-β-D-glucopyranoside (6), (3*S*,4*R*,9*R*)-3,4,6-trihydroxymegastigman-5-ene 3-*O*-β-D-glucopyranoside (7), and (2*S*,9*R*)-2,9-dihydroxymegastigman-5-en-4-one 2-*O*-β-D-glucopyranoside (8).

Key words *Turpinia ternata*; Staphylaceae; turpinionosides A—E; megastigmane glucoside; modified Mosher's method

Megastigmane glycosides are now an expanding class of compounds and their relatively wide distribution in plant kingdom has been reported. In a previous work,[1] a megastigmane was isolated as a non-glycosidic form from *Euscaphis japonica* and its absolute configuration was determined by the modified Mosher's method. Leaves of *Turpinia ternate* collected in Okinawa also afforded one megastigmane (**1**) and seven megastigmane glycosides (**2**—**8**). The structure of the megastigmane (**1**) was elucidated to be the same as that of that isolated from *E. japonica*, including absolute configurations. Compounds **2** and **3** were found to be known compounds, corchoionoside C[2] and icariside B_4,[3] respectively. The structures of the remaining megastigmane glucosides were elucidated by NMR spectroscopic analyses and the absolute configurations of turpinionosides A—E (**4**—**8**) were elucidated in this work by the modified Mosher's method.

Results and Discussion

Megastigamane (**1**) and megastigamane glucosides (**2**—**8**) were isolated from the *n*-BuOH-soluble fraction of a MeOH extract of leaves of *Turpinia ternata* by means of a combination of several kinds of chromatographic methods, and details being given in the experimental section. The structures of other known compounds (**2**, **3**) were identified by comparison of spectroscopic data with those reported.

Compound **1**, $C_{13}H_{24}O_4$, was isolated as a syrup and its planar structure was elucidated to be the same as that of the megastigamane isolated from a related plant, *Euscaphis japonica*.[1] On comparison of the optical rotation values of **1** from both sources, the absolute configurations were presumed to be the same. This was confirmed by that compound **1** from the title plant was also determined with the modified Mosher's method[4] to have the 3*S*, 5*R*, 6*R* and 9*S* configurations (Fig. 1).

Turpenionoside A (**4**), $[\alpha]_D^{22}$ −38.4°, was isolated as an amorphous powder and its elemental composition was determined to be $C_{19}H_{34}O_8$ by negative-ion high-resolution (HR) FAB-MS. The IR spectrum of **4** showed a strong absorption band at 3401 cm^{-1} suggestive of a glycosidic structure. The ^{1}H- and ^{13}C-NMR spectra of **4** showed signals attributable to a β-glucopyranosyl unit, and two tertiary methyls at a geminal position, two secondary methyls, two methylenes, one methine without and two methines with hydroxyl groups, one disubstituted *trans* double bond, and two quarternary carbon atoms with and without a hydroxyl group, respectively. These functionalities were the same as those of megastigmane glucoside, dendranthemoside A (**9**) ($[\alpha]_D^{22}$ −44.2°), isolated from *Dendranthema shiwogiku*,[5] and the NMR spectroscopic data of **4** and **9** were essentially indistinguishable from each other. The absolute structure for **9** has been determined by X-crystallographic analysis of its pentaacetate to have the 3*S*, 5*R*, 6*S* and 9*R* configurations.[6] Since most glucose in Nature is of the D-series, the β-D-glucosylation-induced shift-trend in the ^{13}C-NMR spectroscopy was applied for the elucidation of absolute configuration.[7] On β-D-glucosylation onto the

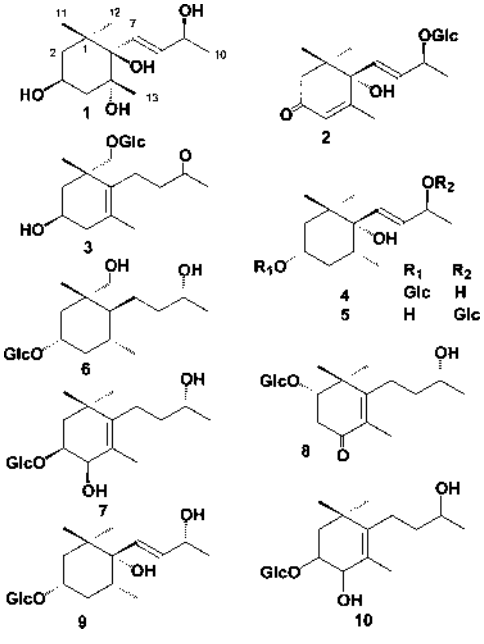

Fig. 1. Structures

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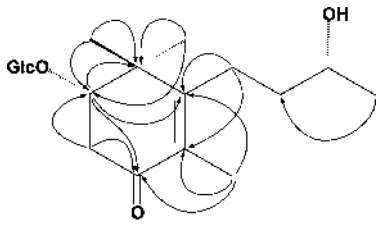

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Fig. 2. Diagnostic HMBC Correlations of Turpinionoside E (**8**)
Arrowheads denote carbon atoms and arrow tails proton atom(s).

secondary alcohol, ^{13}C-NMR chemical shift values of adjacent carbon atoms shift up in different magnitudes, so-called pro-*R* carbon by around 2 ppm and so-called pro-*S* carbon by around 4 ppm. When the adjacent carbon atoms show the same chemical shifts in two compounds, which have the same relative structure, the absolute configurations of the secondary alcohols are unambiguously presumed to be the same. Therefore, the absolute structure of the ring system of **4** must be the same as that of **9**. However, the co-occurrence of compound **1** and corchoionoside C (**2**), whose configurations of the 9-position are opposite to that of **9**, prompted us to analyze the absolute configuration of that position. Thus, turpinioside A was enzymatically hydrolyzed to afford an aglycone and D-glucose and the aglycone formed was subjected to β-D-glucosylation-induced shift-trend analysis and then the aglycone was converted to the (*R*)- and (*S*)-α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) esters. The modified Mosher's method[4] clearly demonstrated that turpinioside A has the 9-*S* configuration, like compounds **1** and **2** (Fig. 2). Therefore, the structure of turpinionoside A (**4**) was elucidated to be (3*S*,5*R*,6*S*,9*S*)-3,6,9-trihydroxymegastigman-7-ene 3-*O*-β-D-glucopyranoside, namely 9-*epi*-dendranthemoside A (Fig. 1).

Turpinoionoside B (**5**), $[\alpha]_D^{22}$ −76.3°, was isolated as an amorphous powder and its elemental composition was the same as that of **4**. The ^{1}H- and ^{13}C-NMR spectra also indicated that the planar structure of the aglycone portion was the same as that of **4**, and the position of sugar linkage was deduced to be the hydroxyl group at the 9-position from the upfield shift of the C-3 carbon atom (−8.2 ppm) and the down field shift of the C-9 carbon atom (+6.0 ppm). The absolute configuration of the 9-position was deduced to be *S* from the β-D-glucosylation-induced shift-trend (C-8 shifted up by 2.9 ppm and C-10 by 1.6 ppm). The absolute configuration of the ring portion was most likely the same as that of **4**. However, to confirm this, **5** was hydrolyzed and the modified Mosher's method was applied to the aglycone. As expected, the structure of turpinionoside B (**5**) was elucidated to be (3*S*,5*R*,6*S*,9*S*)-3,6,9-trihydroxymegastigman-7-ene 9-*O*-β-D-glucopyranoside (Figs. 1, 2).

Turpinionoside C (**6**), $[\alpha]_D^{22}$ −17.3°, was also isolated as an amorphous powder. Its elemental composition was determined to be $C_{19}H_{36}O_8$ by negative-ion HR-FAB-MS. NMR spectroscopic data also revealed that **6** possessed a β-glucopyranosyl unit, and the remaining 13 carbons comprised the megastigmane carbon skeleton. Since only three methyl groups, two doublet signals and one singlet signal were observed in the ^{1}H-NMR spectrum, and one primary alcohol signal in the ^{13}C-NMR spectrum, one of the geminal methyl carbons at the 1-position was suspected to be oxidized. Since, on ^{1}H–^{1}H correlation spectroscopy (COSY), the singlet methyl (δ_H 0.99) at the 1-position crossed the axial proton signal (δ_H 1.37, t, J=12 Hz) on C-2, the equatorial methyl (C-12) must bear the alcoholic functional group. The large coupling value of the H-4ax with H-5 (J=12 Hz) implied that, although H-5 was not observed clearly, it must be in the axial position. The orientation of the side chain was deduced to be in an equatorial position from the coupling constant of H-5 and H-6 (δ_H 0.90, J=11 Hz), which indicated that H-6 was in the axial position. The absolute configurations of the chiral centers were similarly determined by the modified Mosher's method to be 1*S*, 3*R*, 5*R*, 6*S* and 9*R* (Fig. 2). The sugar linkage was determined to be on the hydroxyl group at the 3-position, on comparison of the ^{13}C-NMR chemical shifts of the glucoside (**6**, δ_C 75.2) and aglycone (**6a**, δ_C 67.6). Finally, the structure of turpinionoside C (**6**) was elucidated to be (1*S*,3*S*,5*R*,6*S*,9*R*)-3,9,12-trihydroxymegastigmane 3-*O*-β-D-glucopyranoside (Fig. 1).

Turpinionoside D (**7**) was isolated as an amorphous powder and its elemental composition was determined to be $C_{19}H_{34}O_8$. All the spectroscopic and physical data suggested that **7** was also a megastigmane glucoside, whose ring system bore two hydroxy substitutents at C-3 and C-4 like plucheoside B (**10**), isolated from *Pluchea indica*[8] and *Alangium* premnifolium.[9] However, the double bond on the side chain was reduced to methylenes. The orientations of the two hydroxy substituents were deduced to be equatorial and axial, respectively, from the coupling constants of H-3 (δ_H 3.99, dt, $J_{H2ax\text{-}H3}$=13 Hz and $J_{H3\text{-}H4\ and\ H2eq}$=4 Hz) and H-4 ($\delta_H$ 4.05, br d, $J_{H3\text{-}H4}$=4 Hz). To determine the absolute structure of **7**, the modified Mosher's method was applied. On esterification, under the conditions employed, only 3,9-di-*O*-MTPA esters were formed. This favored elucidation of the absolute configurations of the chiral carbons on the ring system. As a result, the structure of turpinionoside D was elucidated to be (3*S*,4*R*,9*R*)-3,4,9-trihydroxymegastigman-5-ene 3-*O*-δ-D-glucopyranoside.

Turpinionoside E (**8**) was isolated as an amorphous powder and the elemental composition was determined to be $C_{19}H_{32}O_8$. The NMR spectral data also suggested that **8** was a megastigmane glucoside with a tetrasubstituted double bond and a ketone functional group. The tetrasubstituted double bond must be between C-5 and C-6, and from the UV absorption band at 248 nm, the ketone functional group was placed adjacent to the double bond such as C-4 or C-7. One of the two hydroxyl groups was presumed to be at the 9-position from the COSY spectrum and the other one was at the 2- or 3-position. To determine the positions of the ketone and hydroxyl groups, two-dimensional NMR spectra were examined. In the heteronuclear multiple bond correlation (HMBC) spectrum (Fig. 3), the 13-methyl protons (δ_H 1.76) and the methylene protons on the ring (δ_H 2.75, 2.90) crossed the carbonyl carbon atom (δ_C 200.4). Thus, the ketone functional group must be placed at the 4-position. The correlation between both geminal methyl protons at the 1-position and the hydroxyl-bearing carbon atom (δ_C 85.1) on the ring was indicative that the hydroxyl group was at the 2-position. The absolute stereochemistry of glucose was revealed to be of the D-series on analysis as its thiazolidine derivatives by TLC.[10] Since the proton at the 2-position was in the pseudo-axial

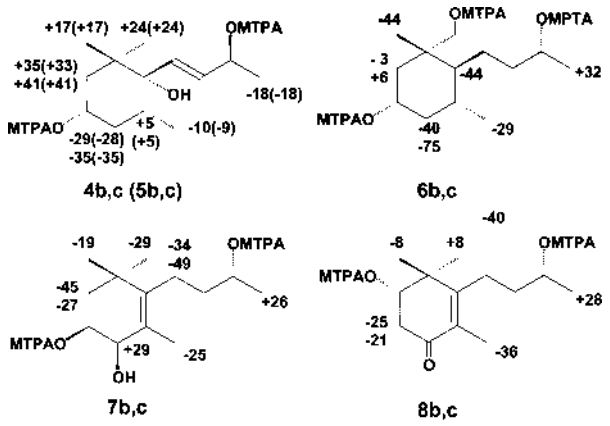

Fig. 3. Results with the Modified Mosher's Method for Turpinionosides A—E (**4**—**8**)

The $\Delta\delta$ values are in Hz (δS-δR, at 400 MHz).

Table 1. ^{13}C-NMR Data (CD_3OD) for Compounds **1** and Turpinionosides A—E (**4**—**8**)

C No.	**1**	**4**	**5**	**6**	**7**	**8**
1	40.8	40.5	40.4	41.5	38.8	43.3
2	46.6	42.6	45.9	42.7	40.0	85.1
3	65.3	75.8	67.6	75.8	76.2	42.7
4	45.8	38.2	39.9	44.6	70.6	200.4
5	77.6	35.6	35.6	34.7	127.3	131.9
6	79.0	78.3	78.3	47.4	144.2	166.4
7	131.1	133.8	138.7	26.1	25.9	28.0
8	136.1	135.6	132.7	41.7	40.3	38.8
9	69.6	69.3	75.3	69.5	69.2	68.9
10	24.1	24.1	22.5	23.5	23.3	23.3
11	27.6	25.1	25.2	17.3	27.8	22.1
12	26.2	25.9	25.8	71.3	29.9	25.4
13	27.1	16.5	16.9	21.5	18.5	11.6
1′		102.7	100.6	102.7	102.7	106.2
2′		75.2	75.1	75.2	75.4	75.5
3′		78.1	78.4	78.3	78.1	78.3
4′		71.8	71.8	71.7	71.7	71.8
5′		77.9	78.1	77.9	78.1	77.9
6′		62.9	62.9	62.9	62.9	62.8

orientation, as deduced from the coupling constants, the β-D-glucopyranosylation-induced upfield shifts of adjacent carbons gave relatively small differences. Thus, the absolute structure of the aglycone was also determined by the modified Mosher's method (Fig. 2). The $\Delta\delta_{S\text{-}R}$ values of geminal methyls were small and showed opposite signs, probably due to being counterbalanced by two MTPAs at the 2- and 9-positions. From the reliable negative values of H-3 protons obtained with the modified Mosher's method, the structure of **8** was elucidated to be (2*S*,9*R*)-2,9-dihydroxymegastigman-5-en-4-one 2-*O*-β-D-glucopyranoside, as shown in Fig. 1.

Experimental

Optical rotations were measured on a Union Giken PM-101 digital polarimeter. FT-IR and UV spectra were recorded on Horiba FT-710 and JASCO V-520 spectrophotometers, respectively. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL α-400 spectrometer (400 and 100 MHz, respectively) with tetramethylsilane (TMS) as the internal standard. HR-FAB-MS analyses were carried out on a JEOL SX-102 mass spectrometer with PEG-400 or -600 as the calibration matrix. CD spectrum was measured on a JASCO J-720 spectropolarimeter. Silica gel and reversed-phase octadecyl silica (ODS) gel open column chromatographies (RPCC) were performed on silica gel 60 (Merck, 70—230 mesh) and Cosmosil 75C_{18}-OPN (Nacalai Tesque Co., Ltd., Kyoto, Japan) [Φ=50 mm, L=25 cm, linear gradient: MeOH–H_2O (1 : 9, 1.5 l)→(7 : 3, 1.5 l), fractions of 10 g being collected]. The droplet counter-current chromatograph (DCCC) (Tokyo Rikakikai, Tokyo) was equipped with 500 glass columns (Φ=2 mm, L=40 cm), and the lower and upper layers of the solvent, $CHCl_3$–MeOH–H_2O–*n*-PrOH (9 : 12 : 8 : 2), were used as the stationary and mobile phases, respectively. Five-gram fractions were collected and numbered according to the order of elution of the mobile phase. HPLC was performed on an ODS column [Φ=20 or 6 mm, L=250 mm; Inertsil, GL Science Co. Ltd. (Tokyo, Japan, Japan)] with UV at 254 or 210 nm and refractive index monitors. Precoated silica gel 60 F_{254} TLC plates (Merck, 0.25 mm in thickness) were used for identification and preparative purification. Emulsin was purchased from Sigma Chem. Co. (St. Louis, MO, U.S.A.), and (*R*)-(+)- and (*S*)-(−)-MTPAs were from Nacalai Tesque Co., Ltd. L-Glucose was commercially available from Kanto Chemical Co., Inc. (Tokyo, Japan).

Plant Material Leaves of *Turpinia ternata* were collected in Okinawa prefecture, Japan in July 1994 and the plant material was identified by Anki Takushi of the Okinawa Prefectural Experimental Station of Forestry. A voucher specimen was deposited in the Herbarium of the Institute of Pharmaceutical Sciences, Hiroshima University Faculty of Medicine (No. 94-TT-Okinawa-0713).

Extraction and Isolation Dried leaves (3.43 kg) of *T. ternata* were extracted with MeOH (40 l×3) and then the MeOH extract was concentrated to 2 l. The concentrated MeOH layer was washed with *n*-hexane (1 l×2, *n*-hexane-soluble fraction, 43.2 g), and the MeOH layer was concentrated to yield a viscous gummy material. The latter was suspended in H_2O (3 l), and then extracted with EtOAc (3 l) and *n*-BuOH (3 l) successively to give EtOAc- and *n*-BuOH-soluble fractions (120 g and 82.5 g, respectively). The remaining H_2O layer was concentrated to furnish an H_2O-soluble fraction (180 g).

The *n*-BuOH-soluble fraction (82.0 g) was separated first by column chromatography (CC) on a highly porous synthetic resin, Diaion HP-20 (Φ=5.5 cm. L=50 cm) (Mitsubishi Chemical Co., Ltd., Tokyo, Japan), with MeOH–H_2O [(1 : 4, 3.5 l), (2 : 3, 3 l), (3 : 2, 3 l), (4 : 1, 3 l) and MeOH (3 l)], and 500 ml fractions were collected. The residue (18.6 g in fractions 6—9) of the 40% MeOH eluate obtained on HP-20 CC was subjected to silica gel (400 g) CC with $CHCl_3$ (2 l), and $CHCl_3$–MeOH (99 : 1, 3 l), (39 : 1, 3 l), (19 : 1, 3 l), (37 : 3, 3 l), (9 : 1, 3 l), (7 : 1, 3 l), (17 : 3, 3 l), (33 : 7, 3 l), (4 : 1, 3 l) and (3 : 1, 3 l), fractions of 500 ml being collected. The residue (1.03 g in fractions 27—34) of the 10% MeOH in $CHCl_3$ eluate was then subjected to RPCC. The residue (62 mg in fractions 59—65) was separated by DCCC to give a compound **1**-enriched fraction, which was then purified by HPLC (MeOH–H_2O, 1 : 4) to give 14.1 mg of **1**.

The residue (1.66 g in fractions 35—45) of the 10% MeOH eluate on silica gel CC was then subjected to RPCC. The residue (132 mg in fractions 85—91) was separated by DCCC to give 25 mg of a fraction enriched with compound **2**, which was then purified by HPLC to give 10.6 mg of **2**. The residue (285 mg in fractions 102—116) was then subjected to DCCC to give 155 mg of **4**.

The residue (142 mg in fractions 126—144) obtained on RPCC was separated by DCCC. The residue (46 mg) in fractions 23—32 was purified by HPLC (MeOH–H_2O, 1 : 4) to give **5** (6.2 mg). The residues of DCCC fractions (30 mg in 40—50 and 13 mg in 51—65) were also subjected to HPLC. The former gave 3.1 mg of **8** and 6.4 mg of **7**, and the latter 13 mg of **3**.

The residue (63 mg in fractions 145—162) obtained on RPCC was similarly separated by DCCC and HPLC to afford 7.0 mg of **6**.

Known Compounds Isolated (3*S*,5*R*,6*R*,9*S*)-3,5,6,9-Tetrahydroxymegastigmane (**1**), amorphous powder, $[\alpha]_D^{26}$ −25.1° (*c*=0.99, MeOH) ($[\alpha]_D^{26}$ −25.7°[1]). Corchoionoside C (**2**), amorphous powder, $[\alpha]_D^{22}$ +50.7° (*c*=0.71, MeOH), CD $\Delta\varepsilon$ (nm) +14.5 (242), −0.73 (331) (7.21×10^{-5} M, MeOH). Icariside B_4 (**3**), amorphous powder, $[\alpha]_D^{22}$ −58.6° (*c*=0.43, MeOH).

Turpinionoside A (4) Amorphous powder, $[\alpha]_D^{22}$ −38.4° (*c*=0.86, MeOH). IR ν_{max} (KBr): 3401, 2929, 1455, 1369, 1076, 1033 cm^{-1}. ^{1}H-NMR (CD_3OD): δ 0.83 (3H, d, *J*=7 Hz, H_3-13), 0.88 (3H, s, H_3-12), 0.97 (3H, s, H_3-11), 1.25 (3H, d, *J*=6 Hz, H_3-10), 1.48 (1H, q, *J*=12 Hz, H-4_{ax}), 1.56 (1H, ddd, *J*=12, 4, 2 Hz, H-2_{eq}), 1.68 (1H, t, *J*=12 Hz, H-2_{ax}), 1.83 (1H, br d, *J*=13 Hz, H-4_{eq}), 1.95 (1H, m, H-5), 3.13 (1H, dd, *J*=9, 8 Hz, H-2′), 3.66 (1H, dd, *J*=12, 5 Hz, H-6′a), 3.86 (1H, dd, *J*=12, 2 Hz, H-6′b), 3.95 (1H, tt, *J*=12, 4 Hz, H-3), 4.29 (1H, quid, *J*=6, 1 Hz, H-9), 4.35 (1H, d, *J*=8 Hz, H-1′), 5.55 (1H, dd, *J*=16, 1 Hz, H-7), 5.73 (1H, dd, *J*=16, 6 Hz, H-8). ^{13}C-NMR (CD_3OD): Table 1. HR-FAB-MS (negative-ion mode) *m*/*z*: 389.2198 $[M-H]^-$ (Calcd for $C_{19}H_{33}O_8$: 389.2175).

Turpinionoside B (5) Amorphous powder, $[\alpha]_D^{22}$ −76.3° (*c*=0.77, MeOH). ^{1}H-NMR (CD_3OD): δ 0.87 (3H, s, H_3-12), 0.88 (3H, d, *J*=7 Hz,

H_3-13), 0.95 (3H, s, H_3-11), 1.29 (3H, d, J=6 Hz, H_3-10), 1.48 (1H, q, J=12 Hz, H-4_{ax}), 1.56 (1H, m, H-2_{eq}), 1.66 (1H, t, J=12 Hz, H-2_{ax}), 1.69 (1H, br d, J=12 Hz, H-4_{eq}), 1.97 (1H, m, H-5), 3.65 (1H, dd, J=12, 5 Hz, H-6′a), 3.80 (1H, tt, J=12, 5 Hz, H-3), 3.86 (1H, dd, J=12, 2 Hz, H-6′b), 4.50 (1H, qd, J=6, 1 Hz, H-9), 4.35 (1H, d, J=8 Hz, H-1′), 5.67 (1H, d, J=16 Hz, H-7), 5.73 (1H, dd, J=16, 6 Hz, H-8). ^{13}C-NMR (CD_3OD): Table 1. HR-FAB-MS (negative-ion mode) m/z: 389.2194 $[M-H]^-$ (Calcd for $C_{19}H_{33}O_8$: 389.2175).

Turpinionoside C (6) Amorphous powder, $[\alpha]_D^{22}$ −17.3° (c=0.87, MeOH). ^{1}H-NMR (CD_3OD): δ 0.77 (3H, s, H_3-11), 0.90 (1H, ddd, J=11, 5, 2 Hz, H-6), 0.99 (3H, d, J=6 Hz, H_3-13), 1.14 (3H, d, J=6 Hz, H_3-10), 1.04 (1H, br q, J=12 Hz, H-4_{ax}), 1.37 (1H, t, J=12 Hz, H-2_{ax}), 1.78 (1H, ddd, J=12, 4, 2 Hz, H-2_{eq}), 2.02 (1H, td, J=12, 2 Hz, H-4_{eq}), 3.18 (1H, dd, H-2′), 3.27 (1H, t, J=9 Hz, H-4′), 3.65 (1H, m, H-9), 3.67 (1H, dd, J=12, 5 Hz, H-6′a), 3.87 (1H, dd, J=12, 2 Hz, H-6′b), 3.90 (1H, tt, J=12, 4 Hz, H-3), 4.20 (1H, d, J=8 Hz, H-1′). ^{13}C-NMR (CD_3OD): Table 1. HR-FAB-MS (negative-ion mode) m/z: 391.2328 $[M-H]^-$ (Calcd for $C_{19}H_{35}O_8$: 391.2332).

Turpinionoside D (7) Amorphous powder, $[\alpha]_D^{22}$ −58.6° (c=0.43, MeOH). ^{1}H-NMR (CD_3OD): δ 1.07 (3H, s, H_3-12), 1.08 (3H, s, H_3-11), 1.22 (3H, d, J=7 Hz, H_3-10), 1.49—1.56 (3H, m, H-2_{eq}, 8a and 8b), 1.79 (3H, s, H_3-13), 1.91 (1H, t, J=13 Hz, H-2_{ax}), 1.97 (1H, ddd, J=15, 11, 6 Hz, H-7a), 2.23 (1H, ddd, J=15, 11, 6 Hz, H-7b), 3.22 (1H, dd, J=9, 8 Hz, H-2′), 3.72 (1H, sextet, J=6 Hz, H-9), 3.72 (1H, dd, J=12, 6 Hz, H-6′a), 3.86 (1H, dd, J=12, 2 Hz, H-6′b), 3.99 (1H, dt, J=13, 4 Hz, H-3), 4.05 (1H, br d, J=3 Hz, H-4), 4.49 (1H, d, J=8 Hz, H-1′). ^{13}C-NMR (CD_3OD): Table 1. HR-FAB-MS (negative-ion mode) m/z: 389.2163 $[M-H]^-$ (Calcd for $C_{19}H_{33}O_8$: 389.2175).

Turpinionoside E (8) Amorphous powder, $[\alpha]_D^{22}$ −9.7° (c=0.21, MeOH). UV λ_{max} (MeOH) nm (log ε) 248 (4.23). ^{1}H-NMR (CD_3OD): δ 1.21 (3H, d, J=6 Hz, H_3-10), 1.26 (3H, s, H_3-11), 1.29 (3H, s, H_3-12), 1.57—1.63 (2H, m, H-8a and 8b), 1.76 (3H, s, H_3-13), 2.30 (1H, m. H-7a), 2.48 (1H, m, H-7b), 2.75 (1H, dd, J=7, 8 Hz, H-3a), 2.90 (1H, dd, J=17, 4 Hz, H-3b), 3.18 (1H, dd, J=9, 8 Hz, H-2′), 3.30 (1H, sextet, J=6 Hz, H-9), 3.66 (1H, dd, J=12, 5 Hz, H-6′a), 3.80 (1H, dd, J=8, 4 Hz, H-2), 3.85 (1H, dd, J=12, 2 Hz, H-6′b), 4.35 (1H, d, J=8 Hz, H-1′). ^{13}C-NMR (CD_3OD): Table 1. HR-FAB-MS (negative-ion mode) m/z: 387.2023 $[M-H]^-$ (Calcd for $C_{19}H_{32}O_8$: 387.2019).

Enzymatic Hydrolysis of 4 to 4a Compound **4** (18.0 mg) was hydrolyzed with emulsin (16.0 mg) for 18 h at 37 °C. The reaction mixture was evaporated to dryness and methanolic solution of the residue was absorbed on silica gel and subjected to silica gel (20 g, Φ=15 mm, L=20 cm) column chromatography with $CHCl_3$ (100 ml), $CHCl_3$–MeOH (19 : 1, 100 ml, 9 : 1, 100 ml, 17 : 3, 100 ml, 7 : 3, 300 ml), 10 ml fractions being collected. The aglycone and (**4a**) and D-glucose were recovered in fractions 23—28 (6.5 mg, 78%) and 40—48 (5.7 mg, 54%), respectively. Aglycone (**4a**): amorphous powder, $[\alpha]_D^{24}$ −14.0° (c=0.43, MeOH). ^{1}H-NMR (CD_3OD): δ 0.84 (3H, d, J=7 Hz, H_3-13), 0.86 (3H, s, H_3-12), 0.96 (3H, s, H_3-11), 1.24 (3H, d, J=6 Hz, H_3-10), 1.39 (1H, q, J=12 Hz, H-4_{ax}), 1.40 (1H, ddd, J=12, 4, 2 Hz, H-2_{eq}), 1.66 (1H, t, J=12 Hz, H-2_{ax}), 1.68 (1H, m, H-4_{eq}), 1.94 (1H, dqd, J=12, 7, 4 Hz, H-5), 3.80 (1H, tt, J=12, 4 Hz, H-3), 4.29 (1H, quid, J=6, 1 Hz, H-9), 5.55 (1H, dd, J=16, 1 Hz, H-7), 5.73 (1H, dd, J=16, 6 Hz, H-8). ^{13}C-NMR (CD_3OD): δ 16.5 (C-13), 24.2 (C-10), 25.2 (C-11), 25.9 (C-12), 35.5 (C-5), 40.0 (C-4), 40.5 (C-1), 67.5 (C-3), 69.3 (C-9), 78.1 (C-6), 133.9 (C-7), 135.6 (C-8). HR-FAB-MS (negative-ion mode) m/z: 227.1660 $[M-H]^-$ (Calcd for $C_{13}H_{23}O_3$: 227.1647). D-glucose, $[\alpha]_D^{26}$ +34.2° (c=0.38, H_2O, 24 h after being dissolved in the solvent).

Preparation of (*R*)- and (*S*)-MTPA Diesters (4b and 4c) from 4a A solution of **3a** (3.3 mg) in 1 ml of dehydrated CH_2Cl_2 was reacted with (*R*)-MTPA (47 mg) in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) (39 mg) and 4-*N*,*N*-dimethylaminopyridine (DMAP) (19 mg), and the mixture was occasionally stirred at 25° for 30 min. After the addition of 1 ml of CH_2Cl_2, the solution was washed with H_2O (1 ml), 5% HCl (1 ml), $NaHCO_3$-saturated H_2O (1 ml), and brine (1 ml), successively. The organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure. The residue was purified by prep. TLC [silica gel (0.25 mm thickness, applied for 18 cm and developed with $CHCl_3$–$(CH_3)_2CO$ (9 : 1) for 9 cm and eluted with $CHCl_3$–MeOH (9 : 1)) to furnish the ester, **4b** (8.6 mg, 91%). Through a similar procedure, **4c** (7.5 mg, 80%) was prepared from **4a** (3.3 mg) using (*S*)-MTPA (48 mg), DCC (37 mg), and 4-DMAP (18 mg).

(3*S*,5*R*,6*S*,9*S*)-3,6,9-Trihydroxymegastigman-7-ene 3,9-Di-*O*-(*R*)-MTPA Ester (**4b**): Amorphous powder; ^{1}H-NMR ($CDCl_3$): δ 0.77 (3H, d, J=7 Hz, H_3-13), 0.82 (3H, s, H_3-12), 0.97 (3H, s, H_3-11), 1.44 (3H, d, J=6 Hz, H_3-10), 1.51 (1H, ddd, J=12, 4, 2 Hz, H-2_{eq}), 1.58 (1H, q, J=12 Hz, H-4_{ax}), 1.77 (1H, t, J=12 Hz, H-2_{ax}), 1.86 (1H, m, H-4_{eq}), 1.99 (1H, dqd, J=12, 7, 4 Hz, H-5), 3.53 (3H, q, J=1 Hz, –OCH_3), 3.54 (3H, q, J=1 Hz, –OCH_3), 5.20 (1H, tt, J=12, 4 Hz, H-3), 5.60—5.80 (3H, m, H-7, 8 and 9), 7.50—7.53 (6H, m, aromatic protons), 7.56—7.58 (4H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) m/z: 683.2396 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_7F_6Na$: 683.2419).

(3*S*,5*R*,6*S*,9*S*)-3,6,9-Trihydroxymegastigman-7-ene 3,9-Di-*O*-(*S*)-MTPA Ester (**4c**): Amorphous powder; ^{1}H-NMR ($CDCl_3$): δ 0.75 (3H, d, J=7 Hz, H_3-13), 0.87 (3H, s, H_3-12), 1.02 (3H, s, H_3-11), 1.39 (3H, d, J=7 Hz, H_3-10), 1.49 (1H, q, J=12 Hz, H-4_{ax}), 1.60 (1H, ddd, J=12, 4, 2 Hz, H-2_{eq}), 1.79 (1H, m, H-4_{eq}), 1.87 (1H, t, J=12 Hz, H-2_{ax}), 2.01 (1H, dqd, J=12, 7, 4 Hz, H-5), 3.52 (3H, q, J=1 Hz, –OCH_3), 3.55 (3H, q, J=1 Hz, –OCH_3), 5.21 (1H, tt, J=12, 4 Hz, H-3), 5.65 (1H, m, H-9), 5.745—5.754 (2H, m, H-7 and 8), 7.35—7.43 (6H, m, aromatic protons), 7.51—7.60 (4H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) m/z: 683.2428 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_7F_6Na$: 683.2419).

Enzymatic Hydrolysis of 5 to 5a Compound **5** (11.6 mg) was hydrolyzed with emulsin (18 mg) for 18 h at 37 °C. A similar chromatographic workup to in case of compound **4** gave 3.8 mg (56%) of an aglycone (**5a**) and 3.4 mg (64%) of D-glucose. Aglycone (**5a**): amorphous powder. The ^{1}H- and ^{13}C-NMR spectra were essentially the same as those of **4a**. HR-FAB-MS (negative-ion mode) m/z: 227.1640 $[M-H]^-$ (Calcd for $C_{13}H_{23}O_3$: 227.1647). D-glucose, $[\alpha]_D^{22}$ +44.1° (c=0.23, H_2O, 24 h after being dissolved in the solvent).

Preparation of *R*- and *S*-MPTA Diesters (5b, 5c) from 5a In a similar manner to for the preparation of **4b** and **4c** from **4a**, **5b** and **5c** were prepared from **5a** (1.9 mg each) with the respective amounts of the reagents, (*R*)- and (*S*)-MPTA (48 mg and 41 mg), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (29 mg and 30 mg), and 4-DMAP (16 mg and 15 mg). The usual workup gave 4.5 mg (**5b**, 84%) and 4.3 mg (**5c**, 80%) of diesters, respectively. (3*R*,5*R*,6*S*,9*S*)-3,6,9-Trihydroxymegastigman-7-ene 3,9-di-*O*-(*R*)-MTPA ester (**5b**) and (3*R*,5*R*,6*S*,9*S*)-3,6,9-trihydroxymegastigman-7-ene 3,9-di-*O*-(*R*)-MTPA ester (**5c**), amorphous powders. The ^{1}H-NMR spectra were essentially the same as those of 3b and 3c, respectively. HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) m/z: 683.2426 and 683.2415, respectively $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_7F_6Na$: 683.2419).

Enzymatic Hydrolysis of 6 to 6a Compound **6** (6.7 mg) was hydrolyzed with emulsin (10 mg) for 18 h at 37 °C. A similar chromatographic workup to in the case of compound **4** gave 2.4 mg (61%) of an aglycone (**6a**) and 2.1 mg (68%) of D-glucose. Aglycone (**6a**): syrup. ^{1}H-NMR (CD_3OD): δ 0.77 (3H, s, H_3-11), 0.88 (1H, ddd, J=11, 5, 2 Hz, H-6), 0.92 (1H, q, J=12 Hz, H-4_{ax}), 0.99 (3H, s, H_3-13), 1.06 (1H, m, H-7a), 1.14 (3H, d, J=6 Hz, H_3-10), 1.34 (1H, t, J=12 Hz, H-2_{ax}), 1.42—1.58 (4H, m, H-5, 7b, 8a and 8b), 1.62 (1H, ddd, J=12, 4, 2 Hz, H-2_{eq}), 1.88 (1H, ddd, J=12, 4, 2 Hz, H-4_{eq}), 3.21 (1H, d, J=11 Hz, H-12a), 3.41 (1H, d, J=11 Hz, H-12b), 3.64 (1H, sextet, J=6 Hz, H-9), 3.73 (1H, tt, J=12, 4 Hz, H-3). ^{13}C-NMR (CD_3OD): δ 17.4 (C-11), 21.5 (C-13), 23.6 (C-10), 26.1 (C-7), 34.7 (C-5), 41.6 (C-1), 41.7 (C-8), 46.0 (C-2), 46.4 (C-4), 47.6 (C-6), 67.6 (C-3), 69.6 (C-10), 71.3 (C-12). HR-FAB-MS (negative-ion mode) m/z: 229.1805 $[M-H]^-$ (Calcd for $C_{13}H_{25}O_3$: 229.1804). D-glucose, $[\alpha]_D^{22}$ +33.9° (c=0.14, H_2O, 24 h after being dissolved in the solvent).

Preparation of *R*- and *S*-MPTA Triesters (6b, 6c) from 6a Using a similar manner to for the preparation of **4b** and **4c** from **4a**, **6b** and **6c** were prepared from **6a** (1.9 mg each) with the respective amounts of the reagents, (*R*)- and (*S*)-MPTA (48 mg and 41 mg), EDC (29 mg and 30 mg), and 4-DMAP (16 mg and 15 mg). The usual workup gave 3.5 mg (**6b**, 76%) and 3.8 mg (**6c**, 83%) of triesters, respectively.

(1*S*,3*S*,5*R*,6*S*,9*R*)-3,9,12-Trihydroxymegastigmane Tri-*O*-(*R*)-MTPA Ester (**6b**): Amorphous powder; ^{1}H-NMR ($CDCl_3$): δ 0.73 (1H, ddd, J=11, 5, 3 Hz, H-6), 0.84 (3H, s, H_3-11), 0.91 (3H, d, J=6 Hz, H_3-13), 1.04 (1H, q, J=12 Hz, H-4_{ax}), 1.22 (3H, d, J=6 Hz, H_3-10), 1.29 (1H, t, J=12 Hz, H-2_{ax}), 1.69 (1H, ddd, J=12, 4, 2 Hz, H-2_{eq}), 1.98 (1H, m, H-4_{eq}), 3.48 (3H, q, J=1 Hz, –OCH_3), 3.50 (3H, q, J=1 Hz, –OCH_3), 3.55 (3H, q, J=1 Hz, –OCH_3), 3.91 (1H, d, J=11 Hz, H-12a), 3.94 (1H, d, J=11 Hz, H-12b), 4.99 (1H, m, H-9), 5.10 (1H, tt, J=12, 4 Hz, H-3), 5.20 (1H, tt, J=12, 4 Hz, H-3), 7.30—7.54 (15H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) m/z: 901.3018 $[M+Na]^+$ (+NaI) (Calcd for $C_{43}H_{47}O_9F_9Na$: 901.2974).

(1*S*,3*S*,5*R*,6*S*,9*S*)-3,9,12-Trihydroxymegastigmane Tri-*O*-(*S*)-MTPA Ester (**6c**): Amorphous powder; ^{1}H-NMR ($CDCl_3$): δ 0.62 (1H, ddd, J=11, 5, 3 Hz, H-6), 0.73 (3H, s, H_3-11), 0.84 (3H, d, J=6 Hz, H_3-13), 0.85 (1H, q, J=12 Hz, H-4_{ax}), 1.29 (1H, t, J=12 Hz, H-2_{ax}), 1.30 (3H, d, J=7 Hz, H_3-10), 1.70 (1H, ddd, J=12, 4, 2 Hz, H-2_{eq}), 1.88 (1H, m, H-4_{eq}), 3.45 (3H, q,

J=1 Hz, –OCH_3), 3.49 (3H, q, J=1 Hz, –OCH_3), 3.52 (3H, q, J=1 Hz, –OCH_3), 3.64 (1H, d, J=11 Hz, H-12a), 4.02 (1H, d, J=11 Hz, H-12b), 5.21 (1H, tt, J=12, 4 Hz, H-3), 4.99 (1H, m, H-9), 5.05 (1H, tt, J=12, 4 Hz, H-3), 7.30—7.53 (15H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) *m/z*: 901.2953 $[M+Na]^+$ (+NaI) (Calcd for $C_{43}H_{47}O_9F_9Na$: 901.2974).

Enzymatic Hydrolysis of 7 to 7a Compound **7** (6.3 mg) was hydrolyzed with emulsin (7 mg) for 18 h at 37 °C. A similar chromatographic workup gave 3.0 mg (82%) of an aglycone (**7a**) and 2.5 mg (86%) of D-glucose. Aglycone (**7a**): Syrup. ^{1}H-NMR (CD_3OD): δ 1.06 (3H, s, H_3-12), 1.07 (3H, s, H_3-11), 1.19 (3H, d, J=6 Hz, H_3-10), 1.39 (1H, ddd, J=13, 3, 1 Hz, H-2_{eq}), 1.48—1.55 (2H, m, H-8a and 8b), 1.75 (1H, t, J=13 Hz, H-2_{ax}), 1.78 (3H, s, H_3-13), 1.96 (1H, ddd, J=13, 11, 6 Hz, H-7a), 2.23 (1H, ddd, J=13, 11, 6 Hz, H-7b), 3.68—3.75 (3H, m, H-3, 4 and 9). ^{13}C-NMR (CD_3OD): δ 18.4 (C-13), 23.3 (C-10), 25.9 (C-7), 27.9 (C-11), 29.9 (C-12), 38.8 (C-1), 40.1 (C-8), 42.1(C-2), 68.1 (C-3), 69.2 (C-9), 73.1 (C-4), 128.3 (C-5), 143.6 (C-6). HR-FAB-MS (negative-ion mode) *m/z*: 227.1640 $[M-H]^-$ (Calcd for $C_{13}H_{23}O_3$: 227.1647). D-glucose, $[\alpha]_D^{25}$ +60.0° (c=0.17, H_2O, 24 h after being dissolved in the solvent).

Preparation of *R*- and *S*-MPTA Diesters (7b, 7c) from 7a Using a similar manner to for the preparation of **4b** and **3c** from **4a**, **7b** and **7c** were prepared from **7a** (1.4 mg each) with the respective amounts of the reagents, (*R*)- and (*S*)-MPTA (41 mg and 44 mg), EDC (29 mg and 28 mg), and 4-DMAP (14 mg and 13 mg). The usual workup gave 1.9 mg (**7b**, 47%) and 2.0 mg (**7c**, 50%) of diesters, respectively.

(3*S*,4*R*,9*R*)-3,4,9-Trihydroxymegastigman-5-ene 3,9-Di-*O*-(*R*)-MTPA Ester (**7b**): Amorphous powder; ^{1}H-NMR one drop of ($CDCl_3$+D_2O): δ 1.04 (3H, s, H_3-12), 1.10 (3H, s, H_3-11), 1.30 (3H, d, J=6 Hz, H_3-10), 1.52 (1H, ddd, J=13, 4, 1 Hz, H-2_{eq}), 1.71 (3H, s, H_3-13), 1.96 (1H, td, J=13, 6 Hz, H-7a), 2.01 (1H, t, J=3 Hz, H-2_{ax}), 2.12 (1H, td, J=13, 6 Hz, H-7b), 3.52 (3H, q, J=1 Hz, –OCH_3), 3.58 (3H, q, J=1 Hz, –OCH_3), 3.95 (1H, br d, J=4 Hz, H-4), 5.12 (1H, sextet, J=6 Hz, H-9), 5.16 (1H, dt, J=13, 4 Hz, H-3), 7.26—7.44 (6H, m, aromatic protons), 7.52—7.55 (4H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) *m/z*: 683.2425 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_7F_6Na$: 683.2419).

(3*S*,4*R*,9*R*)-3,4,9-Trihydroxymegastigman-5-ene 3,9-Di-*O*-(*S*)-MTPA Ester (**7c**): Amorphous powder; ^{1}H-NMR ($CDCl_3$+one drop of D_2O): δ 0.97 (3H, s, H_3-12), 1.05 (3H, s, H_3-11), 1.36 (3H, d, J=6 Hz, H_3-10), 1.59 (1H, ddd, J=13, 4, 1 Hz, H-2_{eq}), 1.65 (3H, s, H_3-13), 1.87 (1H, td, J=13, 6 Hz, H-7a), 1.90 (1H, t, J=13 Hz, H-2_{ax}), 2.01 (1H, td, J=13, 6 Hz, H-7b), 3.55 (3H, br s, –OCH_3), 3.57 (3H, br d, J=1 Hz, –OCH_3), 4.02 (1H, br d, J=4 Hz, H-4), 5.12 (1H, dt, J=13, 4 Hz, H-3), 5.14 (1H, sextet, J=6 Hz, H-9), 7.26—7.42 (6H, m, aromatic protons), 7.53—7.57 (4H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) *m/z*: 683.2415 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_7F_6Na$: 683.2419).

Enzymatic Hydrolysis of 8 to 8a Compound **8** (2.9 mg) was hydrolyzed with emulsin (8 mg) for 18 h at 37 °C and then with 5 mg of crude hesperidinase for 2 h. A similar chromatographic workup gave 1.6 mg (95%) of an aglycone (**8a**) and 1.0 mg (74%) of D-glucose. Aglycone (**8a**): Syrup. ^{1}H-NMR (CD_3OD): δ 1.16 (3H, s, H_3-11), 1.21 (3H, d, J=6 Hz, H_3-10), 1.24 (3H, s, H_3-12), 1.77 (1H, s, H_3-13), 1.55—1.61 (2H, m, H-8a and 8b), 2.29 (1H, m, H-7a), 2.49 (1H, m, H-7b), 2.51 (1H, dd, J=17, 9 Hz, H-2_{ax}), 2.67 (1H, dd, J=17, 4 Hz, H-2_{eq}), 3.74 (1H, dd, J=9, 4 Hz, H-2), 3.79 (1H, sextet, J=6 Hz, H-9). ^{13}C-NMR (CD_3OD): δ 11.6 (C-13), 21.3 (C-11), 23.3 (C-11), 25.4 (C-12), 28.2 (C-7), 38.8 (C-9), 43.5 (C-1 and 3), 42.1 (C-2), 68.9 (C-9), 74.8 (C-2), 131.8 (C-5), 166.5 (C-6), 200.0 (C-4). HR-FAB-MS (negative-ion mode) *m/z*: 225.1492 $[M-H]^-$ (Calcd for $C_{13}H_{21}O_3$: 225.1491).

Preparation of *R* and *S*-MPTA Diesters (8b and 8c) from 8a In a similar manner to for the preparation of **4b** and **4c** from **4a**, **8b** and **9c** were prepared from **8a** (0.8 mg each) with the respective amounts of the reagents, (*R*)- and (*S*)-MPTA (34 mg and 35 mg), EDC (23 mg and 22 mg), and 4-DMAP (10 mg and 11 mg). The usual workup gave 1.0 mg (**6b**, 43%) and 0.7 mg (**6c**, 30%) of diesters, respectively.

(2*S*,9*R*)-2,9-Dihydroxymegastigman-4-on-5-ene Di-*O*-(*R*)-MTPA Ester (**8b**): Amorphous powder, ^{1}H-NMR (CD_3OD): δ 0.99 (3H, s, H_3-11), 1.10 (3H, s, H_3-12), 1.31 (3H, d, J=6 Hz, H_3-10), 1.61—1.67 (1H, m, H-7a), 1.71 (3H, s, H_3-13), 2.18—2.22 (1H, m, H-7b), 2.69 (1H, dd, J=17, 7 Hz, H-$2_{pseudo\text{-}ax}$), 2.87 (1H, dd, J=17, 4 Hz, H-$2_{pseudo\text{-}eq}$), 3.49 (6H, br s, –OCH_3×2), 5.13 (1H, sextet, J=6 Hz, H-9), 5.18 (1H, dd, J=7, 4 Hz, H-2), 7.37—7.42 (6H, m, aromatic protons), 7.44—7.46 (2H, m, aromatic protons), 7.51—7.55 (2H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) *m/z*: 681.2291 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{36}O_7F_6Na$: 681.2263).

(2*S*,9*R*)-2,9-Dihydroxymegastigman-4-on-5-ene Di-*O*-(*S*)-MTPA Ester (**8c**): Amorphous powder, ^{1}H-NMR (CD_3OD): δ 1.01 (3H, s, H_3-11), 1.09 (3H, s, H_3-12), 1.38 (3H, d, J=6 Hz, H_3-10), 1.62 (3H, s, H_3-13), 2.07—2.13 (1H, m, H-7b), 2.63 (1H, dd, J=17, 7 Hz, H-$2_{pseudo\text{-}ax}$), 2.82 (1H, dd, J=17, 4 Hz, H-$2_{pseudo\text{-}eq}$), 3.43 (3H, q, J=1 Hz, –OCH_3), 3.58 (3H, q, J=1 Hz, –OCH_3), 5.13 (1H, dd, J=7, 4 Hz, H-2), 5.16 (1H, sextet, J=6 Hz, H-9), 7.36—7.44 (6H, m, aromatic protons), 7.45—7.46 (2H, m, aromatic protons), 7.51—7.55 (2H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) *m/z*: 681.2311 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{36}O_7F_6Na$: 681.2263).

Determination of the Absolute Structure of the Glucose Obtained on Hydrolysis of 8 Glucose (1.0 mg), obtained on hydrolysis, was reacted with cysteine methyl ester in pyridine to yield thiazolidine derivatives according to the reported procedure,[10,11] and the resultants were analyzed by silica gel TLC (*Rf* 0.51 and 0.46, $CHCl_3$–MeOH–H_2O, 15 : 6 : 1). Authentic thiazolidine derivatives obtained from D- and L-glucoses gave spots at *Rf* 0.51 and 0.46, and 0.49, respectively.

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