# Platanionosides D—J: Megastigmane Glycosides from the Leaves of *Alangium platanifolium* (Sieb. et Zucc.) Harms var. *platanifolium* Sieb. et Zucc.

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**From the leaves of *Alangium paltanifolium* var. *platanifolium*, collected in Fukuoka Prefecture, twelve further megastigmane glycosides were isolated. Seven of them, named platanionosides D—J (1—7), were found to be new compounds. Their structures were elucidated from spectroscopic evidence and their absolute structures were determined from β-D-glucosylation-induced shift trends of $^{13}$C-NMR and by application of a modified Mosher's method.**

**Key words** *Alangium platanifolium* var. *platanifolium*; Alangiaceae; megastigmane glycoside; modified Mosher's method

There are three Alangiaceous plants in Japan.[1] *Alangium premnifolium* grows in the southernmost part and *A. platanifolium* var. *trilobum* in wide areas of the northern to southern parts of Japan, and the title plant is restricted to the areas of western Yamaguchi and Fukuoka Prefectures. In a previous work, considerable numbers of megastigmane glycosides were isolated from the leaves of *A. premnifolium*.[2] At first, investigation of Alangiaceae plants was performed in order to isolate ipecac alkaloids.[3] However, this has not been successful so far, except for the isolation of alangiside.[4] Phytochemical isolation work on the title plant has afforded three megastigmane glycosides[5] and several phenolic glycosides.[6] Further investigation yielded seven new megastigmane glycosides (Fig. 1) along with five known compounds (Fig. 2). This paper deals with the structural elucidation of these new megastigmane glycosides.

## Results and Discussion

Air-dried leaves of *A. platanifolium* var. *platanifolium* were extracted with MeOH, followed by partitioning between solvents of increasing polarity, namely, *n*-hexane, EtOAc and *n*-BuOH. The *n*-BuOH-soluble fraction was purified using a highly porous synthetic resin, octadecyl silica (ODS), and silica gel column chromatographies, and then subjected to droplet counter-current chromatography (DCCC) to give 12 pure megastigmane glycosides. Five of them were known glycosides, being identified as (6*S*,9*R*)-roseoside,[7] alangionosides A,[8] H[7] and K,[7] and linarionoside C.[9]

Platanionoside D (**1**), $[\alpha]_D$ −25°, was isolated as an amorphous powder and its elemental composition, $C_{25}H_{44}O_{12}$, was deduced from the observation of a quasi-molecular ion peak in negative-ion high-resolution (HR) FAB-mass spectrometry. The IR spectrum indicated that **1** was a glycosidic compound. The $^1$H-NMR spectrum showed the presence of two singlet and two doublet methyls, and two doublet signals ($\delta_H$ 4.335, d, $J$=8 Hz and 4.338, d, $J$=8 Hz), which were assigned as two anomeric protons of sugar moieties. The $^{13}$C-NMR spectrum of **1** indicated the presence of two terminal β-glucopyranose units, and the remaining 13 signals were expected to present a megastigmane skeleton. These signals were assigned to four methyls, four methylenes, four methines, two of which were substituted by oxygen atoms ($\delta_C$ 75.8, 76.2), and one quaternary carbon. These functionalities and the relative arrangement of the ring protons, deduced

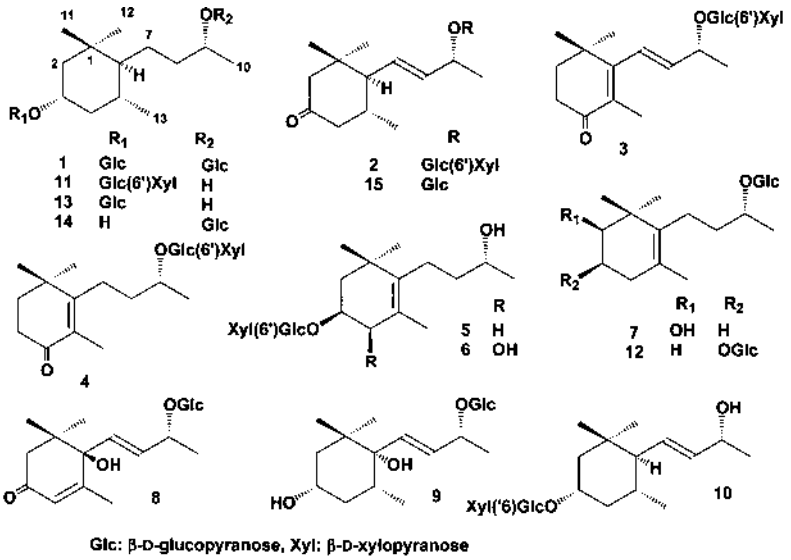


Fig. 1. Structures

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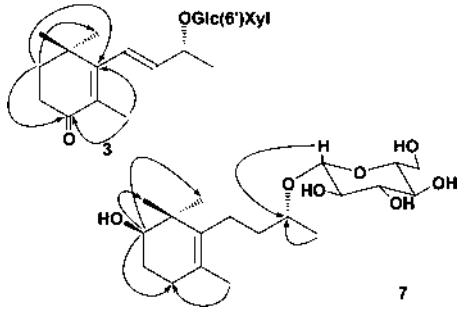


Fig. 2. Important HMBC Correlations of **3** and **7**

Arrowheads denote carbon atoms and arrow tails proton atom(s).

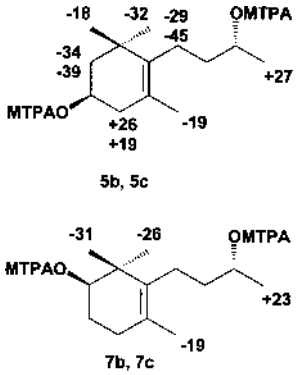


Fig. 3. Results with the Modified Mosher's Method for **5b** and **5c**, and **7b** and **7c**

The $\Delta\delta$ values are in Hz ($\delta S$-$\delta R$ at 400 MHz).

Table 1. $^{13}$C-NMR Data for Platanionosides D—J (**1**—**7**)

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| 1 | 36.8 | 39.4 | 36.7 | 37.7 | 38.8 | 39.0 | 41.4 |
| 2 | 48.5 | 56.7 | 38.3 | 38.5 | 47.5 | 40.0 | 77.0 |
| 3 | 75.8 | 214.0 | 35.2 | 35.1 | 73.5 | 76.2 | 28.0 |
| 4 | 44.8 | 50.1 | 201.8 | 201.6 | 39.8 | 70.6 | 31.5 |
| 5 | 35.0 | 34.8 | 130.8 | 131.7 | 125.1 | 127.3 | 127.1 |
| 6 | 54.4 | 57.9 | 163.7 | 168.7 | 138.6 | 144.2 | 137.5 |
| 7 | 26.0 | 131.7 | 127.7 | 28.0 | 25.6 | 25.9 | 25.9 |
| 8 | 40.7 | 137.6 | 140.3 | 37.3 | 40.7 | 40.3 | 39.0 |
| 9 | 76.2 | 77.7 | 77.4 | 76.0 | 69.2 | 69.2 | 76.3 |
| 10 | 19.7 | 21.4 | 21.1 | 20.0 | 23.3 | 23.3 | 19.8 |
| 11 | 21.4 | 21.6 | 27.8 | 27.3 | 29.0 | 28.0 | 21.9 |
| 12 | 31.4 | 31.3 | 27.8 | 27.4 | 30.3 | 29.9 | 26.5 |
| 13 | 21.5 | 21.8 | 13.8 | 11.9 | 20.1 | 18.5 | 19.9 |
| 1′,1″ | 102.7, 102.2 | 102.6 | 102.9 | 102.5 | 102.4 | 102.6 | 102.3 |
| 2′,2″ | 75.2, 75.1 | 75.4 | 75.3 | 75.2 | 75.1 | 75.3 | 75.3 |
| 3′,3″ | 78.2, 78.1 | 78.1 | 78.0 | 78.1 | 78.0 | 78.0 | 78.3 |
| 4′,4″ | 71.7, 71.9 | 71.4 | 71.4 | 71.7 | 71.5 | 71.5 | 71.9 |
| 5′,5″ | 77.9, 77.8 | 76.9 | 77.0 | 76.9 | 76.9 | 77.1 | 77.9 |
| 6′,6″ | 62.8, 63.0 | 69.6 | 69.7 | 70.0 | 69.9 | 69.9 | 63.0 |
| 1″ | | 105.5 | 105.5 | 105.6 | 105.5 | 105.6 | |
| 2″ | | 74.9 | 74.9 | 74.8 | 74.9 | 74.9 | |
| 3″ | | 77.8 | 77.7 | 77.7 | 77.6 | 77.7 | |
| 4″ | | 71.2 | 71.2 | 71.2 | 71.2 | 71.2 | |
| 5″ | | 66.9 | 66.9 | 66.9 | 66.9 | 66.9 | |

from the $^1$H-NMR spectral data, were the same as those of alangionoside J (**13**), which was isolated from *A. premnifolium*.[7] The $^{13}$C-NMR spectral data of the ring portion of **1** were also essentially the same as those of alangionoside J, and those of the side chain the same as those of dihydroalangionoside I (**14**). Since enzymatic hydrolysis of **1** gave D-glucose, the absolute configurations of the ring were determined to be 3*S*, 5*R* and 6*S*, and that of the side chain to be 9*R* from $\beta$-D-glucopyranosylation-induced shift-trends in the $^{13}$C-NMR spectroscopy [$\Delta\delta_{\text{glucoside–aglycone}}$ $|-2.0|$ (C-8)$<|-3.7|$ (C-10), thus the C-8 must be in the so-called pro-*R* position and the C-10 pro-*S*].[2c,10] Therefore, the structure of platanionoside D (**1**) was elucidated to be (3*S*,5*R*,6*S*,9*R*)-3,9-dihydroxymegastigmane di-*O*-$\beta$-D-glucopyranoside, namely dihydroplatanionoside A.[5]

Platanionoside E (**2**) was isolated as an amorphous powder and the elemental composition was analyzed to be $C_{24}H_{40}O_{11}$ by HR-FAB-MS. The IR spectrum indicated the presence of a ketone function, however, **2** was not UV active on TLC. All of the NMR spectral data for the aglycone moiety were indistinguishable from those of myrsinionoside A (**15**), isolated from *Myrsine seguinii*,[11] except for the presence of a terminal $\beta$-xylopyranose. The remaining sugar signals were assignable to 6-substituted $\beta$-glucopyranose. From the co-occurrence of D-glucose in **1**, the sugar moiety was presumed to be primeveroside [$\beta$-D-(6-*O*-$\beta$-D-xylopyranosyl)glucopyranoside]. The positive Cotton effect ([$\theta$] +650 at 290 nm) indicated that the absolute configuration of the 6-position was the same as **15** and that of the side chain was also the same that of **15** deduced from $\beta$-D-glucopyranosylation induced shift-trends on $^{13}$C-NMR spectroscopy. Finally, the structure of platanionoside E was elucidated to be (5*R*,6*R*,7*E*)-9-hydroxymegastigmen-7-en-3-one *O*-primeveroside, namely 6′-*O*-$\beta$-D-xylopyranoside of myrsinionoside A.

Platanionoside F (**3**) was also isolated as an amorphous powder and the elemental composition was analyzed to be $C_{24}H_{38}O_{11}$. The IR and UV spectra indicated the presence of a ketone functional group (1653 cm$^{-1}$), which was conjugated with double bond (s) (260 nm). The NMR spectrum showed the presence of a primeverose moiety, and other carbon signals included di- and tetra-substituted double bonds, three singlet methyls, one of which was obviously on the tetra-substitute double bond, one doublet methyl, two methylenes, and two quaternary carbons, such as one ketone and one $sp^3$ carbon with geminal methyls. The position of the ketone function was deduced from the results of heteronuclear multiple bond correlation (HMBC) spectroscopy, in which the 13-methyl protons ($\delta_H$ 1.79) crossed the carbonyl carbon ($\delta_C$ 201.8), and other diagnostic correlations were shown in Fig. 3. The absolute configuration of the 9 position was similarly assigned as *R* like that of (6*S*,9*R*)-roseoside from the $\delta$-D-glucopyranosylation-induced shift-trend. Therefore, the structure of platanionoside F (**3**) was established to be (9*R*,7*E*)-9-hydroxymengastigmane-5,7-dien-4-one *O*-primeveroside.

Platanionoside G (**4**) was also isolated as an amorphous powder and the elemental composition was analyzed to be $C_{24}H_{40}O_{11}$, which is two mass units more than in the case of **3**. The IR and UV spectra indicated the presence of a ketone functional group (1651 cm$^{-1}$), which was conjugated with a double bond (250 nm). The NMR spectra showed that **4** was a similar compound to **3**, except for the disappearance of the disubstituted double bond on the side chain. Therefore, the structure of **4** was elucidated to be (9*R*)-9-hydroxymengastigman-5-en-4-one *O*-primeveroside, namely 7,8-dihy-

droplatanionoside F.

Platanionoside H (**5**) was isolated as an amorphous powder and the spectroscopic data indicated that **5** was a derivative of a megastigmane glycoside. Primeveroside was found as a sugar moiety and the remaining carbon atoms were expected to form a megastigmane skeleton like the aglycone of linarionosides.[9] In the $^{13}$C-NMR spectrum, 11 signals were observed for the primeverose and the position of the sugar linkage was estimated to be the hydroxyl group on the ring, since the ring carbon signals were essentially the same as those of linarionoside A (**12**) and this was confirmed by the HMBC spectrum.[9] The absolute configuration of the chiral center on the ring was expected to be the same as that of **12** from the $\beta$-D-glucopyranosylation-induced shift-trend[10] and after enzymatic hydrolysis, that of the side chain was determined by a modified Mosher's method[12] to be *R*, as expected from the co-occurring compounds (Fig. 4). Thus, the structure of **5** was established to be (3*S*,9*R*)-3,9-dihydroxymegastigman-5-ene 3-*O*-primeveroside.

Platanionoside I (**6**) was isolated as an amorphous powder and also a derivative of megastigmane with primeverose as a sugar component. The aglycone portion was expected to be that of turpinionoside D, isolated from *Turpinia ternata*.[13] The absolute configuration of the ring moiety was the same as that of turpinionoside D, as ascertained with the aid of the sugar moiety. Finally, the structure of **6** was elucidated to be (3*S*,4*R*,9$\xi$)-3,4,9-trihydroxymegastigman-5-ene 3-*O*-primeveroside. Although the modified Mosher's method was not conducted to determine the absolute configuration of the side chain due to the low availability of the sample, it was assumed to most likely have the *R* configuration from the co-occurring compounds.

Platanionoside J (**7**) was also isolated as an amorphous powder and its elemental composition was analyzed to be $C_{19}H_{34}O_7$. The $^1$H- and $^{13}$C-NMR spectra showed three singlet methyls, one of which was on a double bond, one doublet methyl, four methylenes and two hydroxyl-carrying methines, a tetrasubstituted double bond and a quaternary carbon atom, along with a terminal glucose moiety. The hydroxyl group on the side chain was expected to carry the glucose moiety from the chemical shift ($\delta_C$ 76.3), and this was confirmed by the HMBC spectrum (Fig. 3). The position of the other hydroxyl group was determined to be C-2 from the HMBC spectrum, in which $\delta_H$ 3.40 (H-2) crossed both geminal methyls on C-1 ($\delta_C$ 21.9, 26.5) and a methylene at C-4 ($\delta_C$ 31.5), and olefinic methyl protons ($\delta_H$ 1.60) also crossed C-4 (Fig. 2). After enzymatic hydrolysis, the absolute configuration of the 2-position was analyzed similarly by the modified Mosher's method (Fig. 4). The protons on C-3, 4, 7 and 8 were not well resolved enough to ascertain the absolute configuration of C-2, however, from the apparent negative values of $H_3$-11 and 12, it was expected to have the *R* configuration. Thus, the structure of **7** was elucidated to be (2*R*,9*R*)-2,9-dihydroxymegastigman-5-ene 9-*O*-$\beta$-D-glucopyranoside.

Megastigmane was first isolated from *Boronia megastigma* (Rutaceae)[14] and its glycoside form was from *Catharanthus roseus* (=*Vinca rosea*) as roseoside.[15] Although this skeleton has only 13 carbons, several types of functionalization at the carbon atoms and glycosylation increase its variety. Some biological activities of megastigmanes have recently been reported.[16]

**Experimental**

Optical rotations were measured on a Union Giken PM-101 digital polarimeter. FT-IR spectra UV were recorded on Horiba FT-710 and JASCO V-520 spectrophotometers, respectively. $^1$H- and $^{13}$C-NMR spectra were recorded on a JEOL $\alpha$-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 as the calibration matrix. Circular dichroism (CD) spectra were 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 75$C_{18}$-OPN (Nacalai Tesque, Kyoto) [$\Phi$=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 DCCC (Tokyo Rikakikai, Tokyo) was equipped with 500 glass columns ($\Phi$=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 [$\Phi$=20 or 6 mm, L=250 mm; Inertsil, GL Science Co., Ltd. (Tokyo, 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 and hesperidinase were purchased from Sigma Chem. Co. (St. Louis, MO, U.S.A.), and (*R*)-(+)- and (*S*)-(−)-$\alpha$-methoxy-$\alpha$-trifluoromethylphenylacetic acids (MTPA) were from Nacalai Tesque Co., Ltd. (Kyoto, Japan). L-Glucose was commercially available from Kanto Chemical Co., Inc. (Tokyo, Japan).

**Plant Material** Leaves of *Alangium platanifolium* var. *paltanifolium* were collected in September 1994 in Amagi City, Fukuoka Prefecture, Japan, and a voucher specimen was deposited in the Herbarium of the Institute of Pharmaceutical Sciences, Hiroshima University Faculty of Medicine (No. 94-APP-Fukuoka-0918).

**Extraction and Isolation** Air-dried leaves (3.55 kg) of *A. platanifolium* var. *paltanifolium* were extracted with MeOH (12 l×2). To the concentrated MeOH extract (1.5 l) was added 75 ml of $H_2O$, followed by washing with *n*-hexane (1.5 l). The MeOH extract was concentrated to a dark green mass and then suspended in $H_2O$ (1.5 l). The suspension in 1.5 l of $H_2O$ was successively extracted with EtOAc (1.5 l) and *n*-BuOH (1.5 l) to give 65.9 g of a *n*-BuOH-soluble fraction. The fraction passed over a highly porous synthetic resin (Diaion HP-20; Mitsubishi Kagaku, Tokyo, Japan) column with 20% (6 l), 40% (6 l), 60% (6 l) and 80% (6 l) MeOH in $H_2O$, and MeOH (6 l) as eluents. Fractions of 2 l were collected. The residue (14.9 g in fractions 5—7) of the 40% MeOH eluate was subjected to silica gel (400 g) column chromatography with a stepwise increase of MeOH content in $CHCl_3$ [$CHCl_3$ (2 l) and $CHCl_3$–MeOH (99 : 1, 2 l), (49 : 1, 2 l), (24 : 1, 4 l), (93 : 7, 4 l), (9 : 1, 4 l), (17 : 3, 4 l), (4 : 1, 4 l), (3 : 1, 4 l) and (7 : 3, 4 l), fractions of 500 ml being collected]. The residue (1.52 g in fractions 31—37) of the 10% MeOH eluate was then subjected to RPCC. The residue (401 mg in fractions 79—94) was separated by DCCC to give 28 mg of **8** in fractions 54—64. The residue (3.75 g in fractions 38—44) of the 15% MeOH eluate was then subjected to RPCC. The residue (452 mg in fractions 97—120) was separated by DCCC to give a residue (118 mg in fractions in 32—43), which was then purified by HPLC to give 16 mg of **9**. The residue (1.71 g in fractions 45—58) of the 20% MeOH eluate was subjected to RPCC. The residue (124 mg in fractions 127—150) was separated by DCCC to give a residue (68 mg in fractions in 32—43), which was then purified by HPLC to give 19 mg of **11**, 34 mg of **1** and 4 mg of **6**.

The residue (9.20 g in fractions 8—10) of the 60% MeOH eluate on Diaion HP-20 CC was subjected to silica gel (300 g) column chromatography with a stepwise increase of MeOH content in $CHCl_3$ [$CHCl_3$ (2 l) and $CHCl_3$–MeOH (99 : 1, 2 l), (49 : 1, 2 l), (24 : 1, 2 l), (47 : 3, 2 l), (23 : 2, 2 l), (9 : 1, 2 l), (7 : 1, 2 l), (17 : 3, 2 l), (4 : 1, 2 l), (3 : 1, 2 l) and (7 : 3, 2 l), fractions of 500 ml being collected]. The residue (791 mg in fractions 24—29) of the 8—10% MeOH eluate was then subjected to RPCC. The residue (49 mg in fractions 163—174) was separated by DCCC to give 18 mg of a fraction, which was repeatedly purified by HPLC to afford 7 mg of **7**. The residue (772 mg in fractions 30—32) of the 12.5% MeOH eluate was then subjected to RPCC. The residue (147 mg in fractions 135—153) was purified by DCCC to give 74 mg of a fraction (75—89), followed by HPLC, which furnished three compounds, 13 mg of **2**, 20 mg of **3** and 20 mg of **4**. The residue (1.79 g in fractions 33—40) of the 15—20% MeOH eluate was separated by RPCC to give the residues (136 mg in fractions 149—156 and 157 mg in

fractions 163—170). The former was purified by DCCC (65 mg in 41—51) and then by HPLC to yield 22 mg of **10** and 20 mg of **5**. The latter was purified by DCCC to give 32 mg of **11** in fractions 53—62.

Platanionoside D (**1**): Amorphous powder, $[\alpha]_D^{20}$ −41.0° ($c$=0.61, MeOH). IR $\nu_{max}$ (KBr): 3461, 2930, 1373, 1074, 1032 cm$^{-1}$. $^1$H-NMR ($CD_3OD$): $\delta$ 0.55 (1H, br dd, $J$=11, 4 Hz, H-6), 0.82 (3H, s, $H_3$-12), 0.96 (3H, s, $H_3$-11), 0.98 (3H, d, $J$=6 Hz, $H_3$-13), 1.03 (1H, q, $J$=12 Hz, H-4ax), 1.13 (1H, t, $J$=12 Hz, H-2ax), 1.18 (3H, d, $J$=6 Hz, $H_3$-10), 1.80 (1H, ddd, $J$=12, 4, 2 Hz, H-2eq), 2.02 (1H, br dd, $J$=12, 4 Hz, H-4eq), 3.12, 3.15 (each 1H, each dd, $J$=9, 8 Hz, H-2′, 2″), 3.62, 3.63 (each 1H, each dd, $J$=12, 5 Hz, H-6′a, 6″a), 3.85 (2H, dd, $J$=12, 2 Hz, H-6′b, 6″b), 3.66 (1H, m, H-9), 3.82 (1H, m, H-3), 4.335, 4.338 (each 1H, each d, $J$=8 Hz, H-1′, 1″). $^{13}$C-NMR ($CD_3OD$): Table 1. HR-FAB-MS (negative-ion mode) $m/z$: 537.2893 $[M-H]^-$ (Calcd for $C_{25}H_{45}O_{12}$: 537.2911).

Platanionoside E (**2**): Amorphous powder, $[\alpha]_D^{20}$ −41.0° ($c$=0.61, MeOH). IR $\nu_{max}$ (KBr): 3459, 2965, 1703, 1645, 1373, 1165, 1074, 1044 cm$^{-1}$. $^1$H-NMR ($CD_3OD$): $\delta$ 0.82 (3H, s, $H_3$-11), 0.94 (3H, d, $J$=6 Hz, $H_3$-13), 1.01 (3H, s, $H_3$-12), 1.30 (3H, d, $J$=6 Hz, $H_3$-10), 1.90 (1H, m, H-5), 1.96 (1H, dd, $J$=11, 10 Hz, H-6), 2.03 (1H, dd, $J$=13, 2 Hz, H-2a), 2.16 (1H, t, $J$=13 Hz, H-4a), 2.30 (1H, ddd, $J$=13, 4, 2 Hz, H-4b), 2.42 (1H, br d, $J$=13 Hz, H-2b), 3.18 (1H, dd, $J$=11, 10 Hz, H-5″a), 3.19 (1H, dd, $J$=9, 8 Hz, H-2′), 3.21 (1H, dd, $J$=9, 7 Hz, H-2″), 3.48 (1H, ddd, $J$=10, 9, 5 Hz, H-5″), 3.72 (1H, dd, $J$=11, 5 Hz, H-6′a), 3.85 (1H, dd, $J$=11, 5 Hz, H-5″b), 4.04 (1H, dd, $J$=11, 2 Hz, H-6′b), 4.29 (1H, d, $J$=7 Hz, H-1″), 4.36 (1H, $J$=8 Hz, H-1′), 4.39 (1H, qd, $J$=6, 1 Hz, H-9), 5.45 (1H, ddd, $J$=16, 10, 1 Hz, H-7), 5.68 (1H, dd, $J$=16, 6 Hz, H-8). $^{13}$C-NMR ($CD_3OD$): Table 1. CD ($c$=0.0254, MeOH) [$\theta$] (nm): +650 (290). HR-FAB-MS (negative-ion mode) $m/z$: 503.2478 $[M-H]^-$ (Calcd for $C_{24}H_{39}H_{11}$: 503.2492).

Platanionoside F (**3**): Amorphous powder, $[\alpha]_D^{23}$ −17.6° ($c$=0.74, MeOH). IR $\nu_{max}$ (KBr): 3424, 2928, 1653, 1460, 1364, 1165, 1076, 1042 cm$^{-1}$. UV $\lambda_{max}$ (MeOH) nm (log $\varepsilon$): 204 (3.89), 260 (3.90). $^1$H-NMR ($CD_3OD$): $\delta$ 1.18 (3H, s, $H_3$-11), 1.19 (3H, s, $H_3$-12), 1.36 (3H, d, $J$=6 Hz, $H_3$-10), 1.79 (3H, d, $J$=1 Hz, $H_3$-13), 1.86 (2H, t, $J$=7 Hz, $H_2$-2), 2.49 (2H, t, $J$=7 Hz, $H_2$-3), 3.16 (1H, dd, $J$=11, 10 Hz, H-5″a), 3.19 (1H, dd, $J$=9, 8 Hz, H-2′), 3.22 (1H, dd, $J$=10, 7 Hz, H-1″), 3.27 (1H, t, $J$=9 Hz, H-3′), 3.39 (1H, m, H-5′), 3.47 (1H, ddd, $J$=10, 9, 5 Hz, H-4″), 3.72 (1H, dd, $J$=11, 5 Hz, H-6′a), 3.83 (1H, dd, $J$=11, 5 Hz, H-5″b), 4.04 (1H, dd, $J$=11, 2 Hz, H-6′b), 4.27 (1H, d, $J$=7 Hz, H-1″), 4.40 (1H, d, $J$=8 Hz, H-1′), 4.50 (1H, quintetd, $J$=6, 1 Hz, H-9), 5.77 (1H, dd, $J$=16, 6 Hz, H-8), 6.31 (1H, dquintet, $J$=16, 1 Hz, H-7). $^{13}$C-NMR ($CD_3OD$): Table 1. HR-FAB-MS (negative-ion mode) $m/z$: 501.2302 $[M-H]^-$ (Calcd for $C_{24}H_{37}H_{11}$: 501.2336).

Platanionoside G (**4**): Amorphous powder, $[\alpha]_D^{23}$ −32.8° ($c$=1.28, MeOH). IR $\nu_{max}$ (KBr): 3436, 2966, 1651, 1454, 1375, 1078, 1040 cm$^{-1}$. UV $\lambda_{max}$ (MeOH) nm (log $\varepsilon$): 205 (3.52), 250 (4.04). $^1$H-NMR ($CD_3OD$): $\delta$ 1.20 (6H, s, $H_3$-11, 12), 1.23 (3H, d, $J$=5 Hz, $H_3$-9), 1.67 (2H, m, $H_2$-8), 1.76 (3H, s, $H_3$-13), 1.81 (2H, t, $J$=7 Hz, $H_2$-2), 2.31 (1H, ddd, $J$=17, 10, 7 Hz, H-7a), 2.44 (2H, t, $J$=7 Hz, $H_2$-3), 2.54 (1H, ddd, $J$=17, 10, 8 Hz, H-7b), 3.16 (1H, dd, $J$=11, 10 Hz, H-5″a), 3.19 (1H, dd, $J$=9, 8 Hz, H-2′), 3.21 (1H, dd, $J$=9, 7 Hz, H-2″), 3.43 (1H, m, H-5′), 3.47 (1H, ddd, $J$=10, 9, 5 Hz, H-4″), 3.73 (1H, dd, $J$=11, 5 Hz, H-5″b), 3.84 (1H, dd, $J$=11, 5 Hz, H-6′a), 3.95 (1H, sextet, $J$=6 Hz, H-9), 4.08 (1H, dd, $J$=11, 2 Hz, H-6′b), 4.32 (1H, d, $J$=7 Hz, H-1″), 4.34 (1H, d, $J$=8 Hz, H-1′). $^{13}$C-NMR ($CD_3OD$): Table 1. HR-FAB-MS (negative-ion mode) $m/z$: 503.2474 $[M-H]^-$ (Calcd for $C_{24}H_{39}O_{11}$: 503.2492).

Platanionoside H (**5**): Amorphous powder, $[\alpha]_D^{20}$ −66.9° ($c$=1.30, MeOH). IR $\nu_{max}$ (KBr): 3393, 2928, 1372, 1167, 1076, 1040 cm$^{-1}$. $^1$H-NMR ($CD_3OD$): $\delta$ 1.06 (6H, s, $H_3$-11, 12), 1.17 (3H, d, $J$=6 Hz, $H_3$-10), 1.64 (3H, br s, $H_3$-13), 1.51 (1H, t, $J$=12 Hz, H-2), 1.52 (2H, m, $H_2$-8), 1.85 (1H, ddd, $J$=12, 3, 1 Hz, H-2eq), 1.92 (1H, dt, $J$=12, 6 Hz, H-7a), 2.01 (1H, dd, $J$=16, 10 Hz, H-4ax), 2.20 (1H, dt, $J$=12, 6 Hz, H-7b), 2.34 (1H, br dd, $J$=16, 5 Hz, H-4eq), 3.70 (1H, sextet, $J$=6 Hz, H-9), 3.76 (1H, dd, $J$=12, 6 Hz, H-6′a), 3.86 (1H, dd, $J$=11, 5 Hz, H-5b), 4.04 (1H, m, H-3), 4.05 (1H, dd, $J$=12, 2 Hz, H-6′b), 4.41 (1H, $J$=7 Hz, H-1″), 4.32 (1H, d, $J$=8 Hz, H-1′). $^{13}$C-NMR ($CD_3OD$): Table 1. HR-FAB-MS (negative-ion mode) $m/z$: 505.2631 $[M-H]^-$ (Calcd for $C_{24}H_{41}H_{11}$: 505.2649).

Platanionoside I (**6**): Amorphous powder, $[\alpha]_D^{20}$ −65.4° ($c$=0.26, MeOH). IR $\nu_{max}$ (KBr): 3355, 2961, 1591, 1373, 1074, 1032 cm$^{-1}$. $^1$H-NMR ($CD_3OD$): $\delta$ 1.08 (3H, s, $H_3$-12), 1.09 (3H, s, $H_3$-11), 1.17 (3H, d, $J$=6 Hz, $H_3$-10), 1.51 (2H, m, $H_2$-8), 1.53 (1H, ddd, $J$=13, 4, 2 Hz, H-2eq), 1.79 (3H, br s, $H_3$-13), 1.86 (1H, t, $J$=13 Hz, H-2ax), 1.97 (1H, ddd, $J$=13, 11, 6 Hz, H-7a), 2.23 (1H, ddd, $J$=13, 10, 7 Hz, H-7b), 3.19 (1H, dd, $J$=11, 10 Hz, H-5″a), 3.20 (1H, dd, $J$=8, 7 Hz, H-2″), 3.22 (1H, dd, $J$=8, 9 Hz, H-2′), 3.46 (1H, m, H-5′), 3.47 (1H, ddd, $J$=10, 9, 5 Hz, H-5″), 3.72 (1H, sextet, $J$=6 Hz, H-7b), 3.75 (1H, dd, $J$=12, 6 Hz, H-6′a), 3.85 (1H, dd, $J$=11, 5 Hz, H-5″b), 3.94 (1H, dt, $J$=13, 4 Hz, H-3), 3.98 (1H, br d, $J$=4 Hz, H-4), 4.06 (1H, dd, $J$=12, 2 Hz, H-6′b), 4.30 (1H, d, $J$=7 Hz, H-1″), 4.48 (1H, d, $J$=8 Hz, H-1′). $^{13}$C-NMR ($CD_3OD$): Table 1. HR-FAB-MS (negative-ion mode) $m/z$: 521.2584 $[M-H]^-$ (Calcd for $C_{24}H_{41}H_{12}$: 521.2598).

Platanionoside J (**7**): Amorphous powder, $[\alpha]_{405}^{20}$ −7.8° ($c$=0.51, MeOH). IR $\nu_{max}$ (KBr): 3378, 2961, 1373, 1074, 1032 cm$^{-1}$. $^1$H-NMR ($CD_3OD$): $\delta$ 0.95 (3H, s, $H_3$-11), 1.07 (3H, s, $H_3$-12), 1.20 (3H, d, $J$=6 Hz, $H_3$-10), 1.48—1.57 (1H, m, H-8a), 1.60 (3H, s, $H_3$-13), 1.63—1.78 (3H, m. H-3a, 3b, 7a), 1.93—2.10 (3H, m, H-4a, 4b, 7a), 2.17 (1H, td, $J$=13, 5 Hz, H-7b), 3.16 (1H, dd, $J$=8, 9 Hz, H-2′), 3.40 (1H, dd, $J$=10, 4 Hz, H-2), 3.68 (1H, dd, $J$=12, 5 Hz, H-6′a), 3.86 (1H, dd, $J$=12, 2 Hz, H-6′b), 3.87 (1H, sextet, $J$=6 Hz, H-9), 4.34 (1H, d, $J$=8 Hz, H-1′). $^{13}$C-NMR ($CD_3OD$): Table 1. HR-FAB-MS (negative-ion mode) $m/z$: 373.2230 $[M-H]^-$ (Calcd for $C_{19}H_{33}H_7$: 373.2227).]

**Known Compounds Isolated** (6*S*,9*R*)-Roseoside (**8**), $[\alpha]_D^{22}$ +117.6° ($c$=0.68, MeOH).[7] Alangionoside A (**9**), $[\alpha]_D^{22}$ −14.8° ($c$=0.81, MeOH).[8] Alangionoside H (**10**), $[\alpha]_D^{22}$ −52.8° ($c$=1.44, MeOH).[8] Alangionoside K (**11**), $[\alpha]_D^{22}$ −51.0° ($c$=0.51, MeOH).[8] Linariopnoside C (**12**), $[\alpha]_D^{22}$ −44.4° ($c$=1.17, MeOH).[9]

**Enzymatic Hydrolysis of 1** Compound **1** (9.6 mg) was hydrolyzed with the same amount of emulsin at 37 °C for 18 h in 2 ml of $H_2O$. The reaction mixture was evaporated to dryness. The resultants were taken up in methanol and evaporated. An $H_2O$ solution of the residue was applied to a Sep-Pak $C_{18}$ cartridge, twice. The pass-through eluate was collected and evaporated to yield 2.8 mg (46%) of D-glucose. D-Glucose, $[\alpha]_D^{26}$ +42.9° ($c$=0.21, $H_2O$, 24 h after being dissolved in the solvent).

**Enzymatic Hydrolysis of 5 to 5a** Compound **5** (20.0 mg) was hydrolyzed with crude hesperidinase (16.0 mg) at 37 °C for 18 h in 2 ml of $H_2O$. The reaction mixture was evaporated to dryness, and then a methanolic solution of the residue was absorbed on silica gel and subjected to silica gel (20 g, $\Phi$=15 mm, L=20 cm) column chromatography with $CHCl_3$ (100 ml), and $CHCl_3$–MeOH (19 : 1, 100 ml, 9 : 1, 100 ml, 17 : 3, 100 ml and 7 : 3, 300 ml), 20 g fractions being collected. The aglycone (**5a**), D-xylose and D-glucose were recovered in fractions 14—18 (6.2 mg, 74%), 33—38 (3.0 mg, 51%), and 41—46 (4.3 mg, 61%), respectively. Aglycone (**5a**): Colorless syrup, $[\alpha]_D^{26}$ −72.5° ($c$=0.41, MeOH). $^1$H-NMR ($CD_3OD$): $\delta$ 0.86 (3H, d, $J$=7 Hz, $H_3$-11), 0.90 (3H, s, $H_3$-12), 1.16 (3H, d, $J$=6 Hz, $H_3$-10), 1.38 (1H, q, $J$=12 Hz, H-2ax), 1.44—1.54 (2H, m, $H_2$-8), 1.63 (3H, s, $H_3$-13), (1H, ddd, $J$=12, 4, 2 Hz, H-2eq), 1.68 (1H, ddd, $J$=12, 4, 2 Hz, H-2eq), 1.89—1.95 (1H, m, H-7a), 1.93 (1H, dd, $J$=16, 10 Hz, H-4ax), 2.16—2.25 (2H, m, H-4eq, 7b), 3.70 (1H, sextet, $J$=6 Hz, H-9), 3.85 (1H, dddd, $J$=12, 10, 6, 4 Hz, H-3). $^{13}$C-NMR ($CD_3OD$): $\delta$ 20.0 (C-13), 23.3 (C-10), 25.6 (C-7), 28.9 (C-11), 30.4 (C-12), 38.8 (C-1), 40.8 (C-8), 43.0 (C-4), 49.6 (C-2), 65.7 (C-3), 69.2 (C-9), 125.5 (C-5), 138.3 (C-6). HR-FAB-MS (negative-ion mode) $m/z$: 211.1707 $[M-H]^-$ (Calcd for $C_{13}H_{23}O_2$: 211.1698). D-Xylose, $[\alpha]_D^{26}$ +15.0° ($c$=0.20, $H_2O$, 24 h after being dissolved in the solvent). D-Glucose, $[\alpha]_D^{26}$ +41.9° ($c$=0.28, $H_2O$, 24 h after being dissolved in the solvent).

**Preparation of (*R*)- and (*S*)-MTPA Diesters (5b, 5c) from 5a** A solution of **5a** (3.1 mg) in 1 ml of dehydrated $CH_2Cl_2$ was reacted with (*R*)-MTPA (47 mg) in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (37 mg) and 4-*N*,*N*-dimethylaminopyridine (DMAP) (18 mg), the mixture being occasionally stirred at 25 °C for 1 h. 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 $CHCl_3$–$(CH_3)_2CO$ (19 : 1) for 9 cm and eluted with $CHCl_3$–MeOH (9 : 1)) to furnish the ester, **5b** (7.9 mg, 84%). Through a similar procedure, **5c** (7.5 mg, 80%) was prepared from **5a** (3.3 mg) using (*S*)-MTPA (53 mg), EDC (37 mg) and 4-DMAP (20 mg).

(3*R*,9*R*)-3,9-Dihydroxymegastigman-5-ene Di-*O*-(*R*)-MTPA Ester (**5b**): Colorless syrup; $^1$H-NMR ($CDCl_3$): $\delta$: 1.01 (3H, s, $H_3$-11), 1.06 (3H, s, $H_3$-12), 1.29 (3H, d, $J$=6 Hz, $H_3$-10), 1.54 (3H, s, $H_3$-13), 1.58—1.69 (2H, m, $H_2$-8), 1.62 (1H, t, $J$=12 Hz, H-2ax), 1.82 (1H, ddd, $J$=12, 4, 2 Hz, H-2eq), 1.92 (1H, td, $J$=13, 5 Hz, H-7a), 2.08 (1H, br dd, $J$=16, 9 Hz, H-4a), 2.12 (1H, td, $J$=13, 5 Hz, H-7b), 2.30 (1H, br dd, $J$=16, 6 Hz, H-4b), 3.53 (3H, q, $J$=1 Hz, –$OCH_3$), 3.55 (3H, q, $J$=1 Hz, –$OCH_3$), 5.10 (1H, sextet, $J$=6 Hz, H-9), 5.25 (1H, dddd, $J$=12, 9, 6, 4 Hz, H-3), 7.38—7.41 (6H, m, aromatic protons), 7.52—7.54 (4H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) $m/z$: 667.2490 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_6F_6Na$: 667.2470).

(3*R*,9*R*)-3,9-Dihydroxymegastigman-5-ene Di-*O*-(*S*)-MTPA Ester (**5c**):

Colorless syrup, $^1$H-NMR ($CDCl_3$): $\delta$: 0.93 (3H, s, $H_3$-11), 1.02 (3H, s, $H_3$-12), 1.36 (3H, d, $J$=6 Hz, $H_3$-10), 1.50 (3H, s, $H_3$-13), 1.52 (1H, t, $J$=12 Hz, H-2ax), 1.55—1.67 (2H, m, $H_2$-8), 1.72 (1H, ddd, $J$=12, 4, 2 Hz, H-2eq), 1.85 (1H, td, $J$=13, 5 Hz, H-7a), 2.01 (1H, td, $J$=13, 5 Hz, H-7b), 2.15 (1H, br dd, $J$=16, 9 Hz, H-4a), 2.34 (1H, br dd, $J$=16, 6 Hz, H-4b), 3.54 (3H, q, $J$=1 Hz, –$OCH_3$), 3.57 (3H, q, $J$=1 Hz, –$OCH_3$), 5.13 (1H, sextet, $J$=6 Hz, H-9), 5.22 (1H, dddd, $J$=12, 9, 6, 4 Hz, H-3), 7.37—7.41 (6H, m, aromatic protons), 7.52—7.56 (4H, m, aromatic protons). HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) *m*/*z*: 667.2454 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_6F_6Na$: 667.2470).

**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 2.1 mg (56%) of the aglycone (**7a**) in fractions 13—16 and 1.5 mg (49%) of D-glucose in fractions 38—48. Aglycone (**7a**): Colorless syrup. $^1$H-NMR ($CD_3OD$): $\delta$: 0.96 (3H, s, $H_3$-11), 1.07 (3H, s, $H_3$-12), 1.17 (3H, d, $J$=6 Hz, $H_3$-10), 1.42—1.58 (2H, m, $H_2$-8), 1.60 (3H, s, $H_3$-13), 1.63—1.78 (2H, m. $H_2$-3), 1.97—2.05 (3H, m, H-4a, 4b, 7a), 2.15 (1H, td, $J$=13, 5 Hz, H-7b), 3.41 (1H, dd, $J$=10, 4 Hz, H-2), 3.71 (1H, sextet, $J$=6 Hz, H-9). $^{13}$C-NMR ($CD_3OD$): $\delta$ 19.8 (C-13), 21.9 (C-11), 23.3 (C-10), 26.1 (C-7), 26.5 (C-12), 28.0 (C-3), 31.5 (C-4), 40.8 (C-8), 41.4 (C-1), 69.3 (C-9), 77.0 (C-2), 127.1 (C-5), 137.4 (C-6). HR-FAB-MS (negative-ion mode) *m*/*z*: 211.1700 $[M-H]^-$ (Calcd for $C_{13}H_{23}O_2$: 211.1698).

**Preparation of *R*- and *S*-MPTA Diesters (7b, 7c) from 7a** In a similar manner to for the preparation of **5b** and **5c** from **5a**, **7b** and **7c** were prepared from **7a** (1.0 mg each) with the respective amounts of the reagents, (*R*)- and (*S*)-MPTA (25 mg and 29 mg), EDC (19 mg and 18 mg), and 4-DMAP (12 mg and 10 mg). The usual workup gave 1.1 mg (**7b**, 37%) and 0.7 mg (**7c**, 23%) of diesters, respectively.

(2*R*,9*R*)-2,9-Dihydroxymegastigman-5-ene Di-*O*-(*R*)-MTPA Ester (**7b**): Amorphous powder; $^1$H-NMR ($CDCl_3$): $\delta$: 0.89 (3H, s, $H_3$-11), 0.91 (3H, s, $H_3$-12), 1.29 (3H, d, $J$=6 Hz, $H_3$-10), 1.54 (3H, s, $H_3$-13), 3.50 (3H, q, $J$=1 Hz, –$OCH_3$), 3.52 (3H, q, $J$=1 Hz, –$OCH_3$), 4.22 (1H, t, $J$=6 Hz, H-2), 4.32 (1H, sextet, $J$=6 Hz, H-9), 7.24—7.53 (4H, m, aromatic protons), 7.52—7.53 (4H, m, aromatic protons), 7.69—7.71 (2H, m, aromatic protons), protons on C-3, 4, 7 and 8 were not identified, due to overlapping with each other. HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) *m*/*z*: 667.2460 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_6F_6Na$: 667.2470).

(2*R*,9*R*)-2,9-Dihydroxymegastigman-5-ene Di-*O*-(*S*)-MTPA Ester (**7c**): Amorphous powder; $^1$H-NMR ($CDCl_3$): $\delta$: 0.81 (3H, s, $H_3$-11), 0.84 (3H, s, $H_3$-12), 1.34 (3H, d, $J$=6 Hz, $H_3$-10), 3.55 (3H, q, $J$=1 Hz, –$OCH_3$), 3.57 (3H, q, $J$=1 Hz, –$OCH_3$), 4.23 (1H, t, $J$=6 Hz, H-2), 4.32 (1H, sextet, $J$=6 Hz, H-9), 7.26—7.34 (4H, m, aromatic protons), 7.51—7.53 (4H, m, aromatic protons), 7.69—7.71 (2H, m, aromatic protons), protons on C-3, 4, 7 and 8 were not identified, due to overlapping with each other. HR-FAB-MS (positive-ion mode, *m*-nitrobenzyl alcohol as a matrix) *m*/*z*: 667.2454 $[M+Na]^+$ (+NaI) (Calcd for $C_{33}H_{38}O_6F_6Na$: 667.2470).

**Determination of the Absolute Configuration of the Glucose Obtained on Hydrolysis of 7** Glucose (1.5 mg) was converted into a thiazolidine derivatives according to the reported procedure[14] and then analyzed by silica gel TLC (*Rf* 0.52 and 0.45, $CHCl_3$–MeOH–$H_2O$, 15 : 6 : 1). Authentic thiazolidine derivatives obtained from D- and L-glucoses gave spots at *Rf* 0.52 and 0.45, and 0.49, respectively.

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