Two New Galloylglucosides from the Leaves of *Mallotus furetianus*

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Two new galloylglucosides, mallophenols A (1) and B (2), were isolated from the leaves of *Mallotus furetianus* (Euphorbiaceae), together with seven known compounds, (6*S*,9*R*)-roseoside (3), aviculin (4), (+)-lyoniresinol-3α-*O*-α-L-rhamnopyranoside (5), (*Z*)-3-hexenyl-β-D-glucopyranoside (6), 3,3,8,9,10-pentahydroxydibenzo[*b*,*d*]pyran-6-one (7), 3-hydroxy-4,5(*R*)-dimethyl-2(5*H*)-furanone (8) and gallic acid (9). The stereostructures of 1 and 2 were elucidated on the basis of spectroscopic analysis and chemical evidence.

Key words *Mallotus furetianus*; Euphorbiaceae; galloylglucoside; mallophenol

Mallotus furetianus (Bail.) Muell-Arg. (Euphorbiaceae), a kind of tropical plant, is a herb indigenous to Hainan Island of China. Its leaves, commonly called "Shan Ku Cha", have been used as a popular aromatic beverage for indigestion. For medicinal purposes, it is used as a folk medicine for the treatment of cholecystitis disease. To our best knowledge, no previous phytochemical studies have been published on its chemical constituents to date. Thus, the title plant was chemically investigated as part of our current interest in the medicinal plants in Hainan Island, resulting in the isolation of two new compounds, mallophenols A (**1**) and B (**2**), together with seven known compounds. This paper describes the isolation and structural elucidation of the new compounds on the basis of spectroscopic data and chemical evidence.

Air-dried leaves of *M. furetianus* were extracted with ethanol, and the ethanolic extracts were combined and evaporated under vacuum to afford a dark brownish residue. The residue was subjected to Diaion HP-20 column chromatography (CC) eluted with a gradient of methanol and water. The 50% methanolic fraction was chromatographed on a combination of successive normal and reversed-phase (RP) silica gel CC and RP preparative HPLC to afford compounds **1**—**9**. The compounds **3**—**9** were identified as (6*S*,9*R*)-roseoside (**3**),[1] aviculin (**4**),[2] (+)-lyoniresinol-3α-*O*-α-L-rhamno-pyranoside (**5**),[3] (*Z*)-3-hexenyl-β-D-glucopyranoside (**6**),[4] 3,3,8,9,10-pentahydroxydibenzo[*b*,*d*]pyran-6-one (**7**),[5] 3-hydroxy-4,5(*R*)-dimethyl-2(5*H*)-furanone (**8**)[6] and gallic acid (**9**)[7] by comparison of their spectral data with the reported values.

Mallophenol A (**1**) was obtained as an amorphous powder. Its high resolution (HR)-FAB-MS exhibited a *pseudo* molecular ion peak at *m*/*z* 533.1259 $[M+Na]^+$ (calculated as 533.1272), consistent with the molecular formula $C_{23}H_{26}O_{13}$ and eleven degrees of unsaturation. Its IR spectrum suggested the presence of hydroxyl (3438 cm^{-1}) and conjugated ester (1695, 1225, 1041 cm^{-1}). The ^{1}H-NMR spectrum showed the presence of a two-proton singlet signal at δ 7.10 which suggested a galloyl group, supported by five characteristic carbon signals (δ 168.3, 146.6, 139.9, 121.4, 110.3) in the ^{13}C-NMR spectrum. Also, in the ^{1}H-NMR spectrum, signals assignable to protons of one 1,3,4-trisubstituted phenyl group were observed at δ 6.78 (1H, d, J=8.0 Hz), 6.85 (1H, dd, J=8.0, 1.8 Hz) and 6.99 (1H, d, J=1.8 Hz) as well as a methoxyl proton signal at δ 3.86 and the protons of a β-glucopyranosyl group with the anomeric proton signal resonating at δ 4.63 (1H, d, J=7.8 Hz) (Table 1). The position of the methoxyl was determined from NOE difference experiment. Namely, upon irradiation of the methyl signal at δ 3.86, NOE was observed at δ 6.99 corresponding to H-2, which suggested that the methoxyl is located at C-3. In addition, the analysis of double quantum filter correlation spectroscopy (DQF-COSY) and heteronuclear multiple quantum coherence (HMQC) spectra assigned the remaining proton signals as a three-carbon unit from C-7 to C-9. The connections of

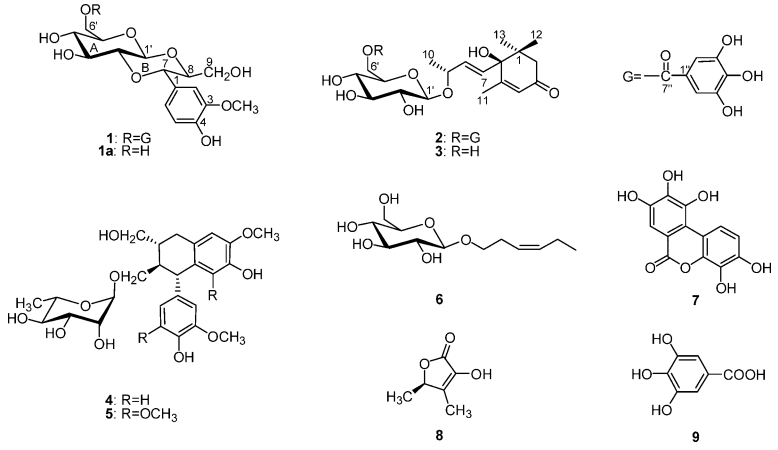

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Table 1. ^{1}H- (500 MHz) and ^{13}C-NMR (125 MHz) Spectral Data of **1** and **2** in Methanol-d_4

Position	**1**		**2**	
	δ ^{1}H (mult, J in Hz)	δ ^{13}C	δ ^{1}H (mult, J in Hz)	δ ^{13}C
1		130.1		42.3
2a	6.99 d (1.8)	112.5	2.09 d (16.9)	50.6
2b			2.42 d (16.9)	
3		149.0		201.3
4		148.1	5.80 d (1.4)	127.1
5	6.78 d (8.0)	116.2		167.0
6	6.85 dd (8.0, 1.8)	122.0		79.9
7	4.46 d (9.6)	80.3	5.78 d (15.6)	134.8
8	3.80 ddd (9.6, 5.3, 2.1)	82.2	5.83 dd (15.6, 6.2)	131.5
9a	3.38 dd (12.1, 5.3)	62.1	4.37 m	77.0
9b	3.46 dd (12.1, 2.1)			
10			1.28 d (6.4)	21.2
11			1.84 d (1.4)	19.6
12			0.99 s	23.4
13			0.95 s	24.6
1′	4.63 d (7.8)	99.8	4.40 d (7.8)	103.0
2′	3.20 dd (9.7, 7.8)	80.8	3.22 dd (8.8, 7.8)	75.2
3′	3.65 dd (9.7, 8.9)	75.0	3.38 dd (9.2, 8.8)	77.9
4′	3.55 dd (9.8, 8.9)	72.0	3.44 t (9.2)	71.5
5′	3.78 ddd (9.8, 5.5, 2.1)	77.3	3.51 ddd (9.2, 5.0, 2.0)	75.4
6′a	4.43 dd (12.1, 5.5)	64.6	4.36 dd (11.8, 5.0)	64.7
6′b	4.61 dd (12.1, 2.1)		4.47 d dd (11.8, 2.0)	
3-OCH_3	3.86 s	56.6		
1″		121.4		121.4
2″,6″	7.10 s	110.3	7.11 s	110.3
3″,5″		146.6		146.4
4″		139.9		139.8
7″		168.3		168.3

the above-described structural units were determined by the ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) data. In the HMBC spectrum, the ^{3}J-correlations between δ_H 4.46 (H-7) and δ_C 80.8 (C-2′), δ_H 3.80 (H-8) and δ_C 99.8 (C-1′), and δ_H 4.46 (H-7) and δ_C 112.5 (C-2), 122.0 (C-6) suggested that these positions between C-1′ and C-8 and between C-2′ and C-7 were connected by oxygen atoms and a 1,3,4-trisubstituted phenyl group was located on C-7 (Fig. 1). Furthermore, mild alkaline hydrolysis of **1** with 0.5% $NaHCO_3$ gave **1a**. Detailed NMR spectral analysis of **1a** led to the identification of junipetrioloside A.[8] Also, in comparison of the ^{1}H- and ^{13}C-NMR data of **1** and **1a**, the downfield shift of H-6′ ($\Delta\delta_H$ 0.71 ppm) of **1**, corresponding to C-6′ ($\Delta\delta_C$ 2.0 ppm), together with the HMBC correlation between δ_H 4.43 (H-6′a), 4.61 (H-6′b) and δ_C 168.3 (C-7″), are in agreement with a galloyl group substitution of the position at C-6′ of the glucose.

The relative stereostructure of **1** was deduced by ^{1}H–^{1}H coupling constants. The large coupling constants between H-7/H-8 (9.6 Hz), H-1′/H-2′ (7.8 Hz), H-2′/H-3′ (9.7 Hz), H-3′/H-4′ (8.9 Hz) and H-4′/H-5′ (9.7 Hz) suggested that the relationship of those protons are all *trans*-axial and the A-ring and B-ring are both chair conformation. A modified Mosher method was used to elucidate the absolute configuration of **1**.[9] In order to obtain a secondary alcohol, **1a** was treated with $PhCH(OMe)_2$ to give the protected derivative **1b** at the positions of C-4′ and C-6′,[10,11] followed by esterification with (*R*)-(−)- and (*S*)-(+)-α-methoxy-α-trifluoromethylphenyl acetatyl chlororide (MTPACl) in dry pyridine to give the 3′-(*S*)-MTPA ester (**1c**) and the 3′-(*R*)-MTPA ester (**1d**), respectively (Chart 1). $\Delta\delta$ values ($\delta_S-\delta_R$) obtained from ^{1}H-NMR data of **1c** and **1d** are shown in Fig. 2. The $\Delta\delta$ values for the proton signals at C-1′, C-2′ and C-3′ are positive, while negative $\Delta\delta$ values are observed for the proton signals at C-4′, C-5′ and C-6′, indicating an *S* configuration of C-3′. Furthermore, in combination with the above

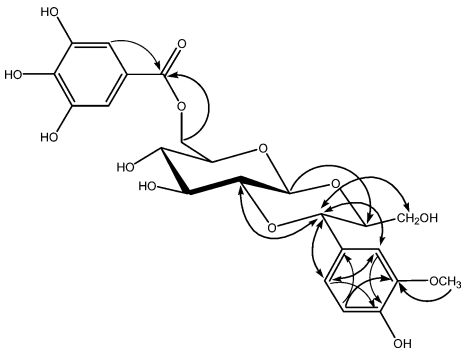
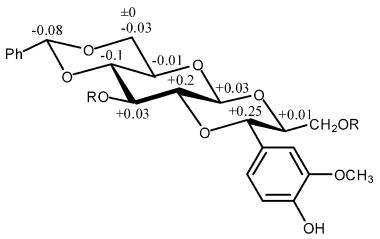
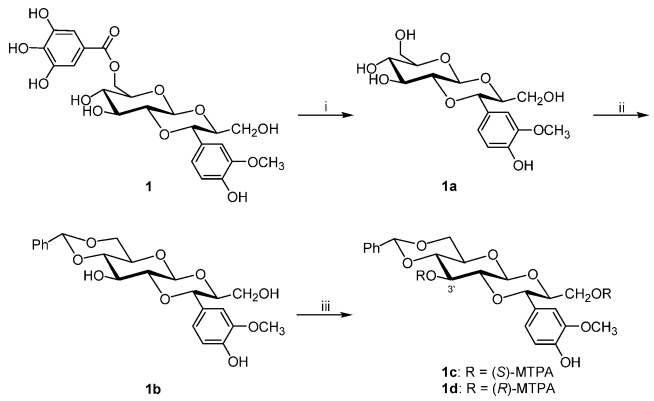


Fig. 1. Important HMBC Correlations of **1**



R = MTPA

Fig. 2. $\Delta\delta$ Values [$\Delta\delta$ (in ppm)$=\delta_S-\delta_R$] Obtained for the 3′,9-di-(*S*)- and (*R*)-MTPA Esters (**1c** and **1d**, Respectively) of the Derivative (**1b**) of **1**



i) 0.5% $NaHCO_3$; ii) $PhCH(OMe)_2$, DMF, CSA, 60 °C; iii) (*R*)- or (*S*)-MTPA-Cl, pyridine(dehydrated)

Chart 1

analysis of relative stereochemistry, the glucose in **1** was determined to be β-D-glucose and the absolute configurations at C-7 and C-8 were both assigned as *S*. On the basis of the above evidence, the structure of mallophenol A (**1**) was established as (7*S*,8*S*)-3-methoxy-4-hydroxyphenylpropane-7,8-[2′,1′-*O*-(6-*O*-galloyl)-β-D-glucopyranosyl]-7,8,9-triol.

Mallophenol B (**2**) was obtained as an amorphous powder with a molecular formula of $C_{26}H_{34}O_{12}$, as determined by HR-FAB-MS analysis (*m/z* 561.1938 $[M+Na]^+$, calculated as 561.1947), implying the presence of ten degrees of unsaturation in the molecule. On acid hydrolysis, **2** afforded D-glucose as a component sugar, which was identified by gas–liquid chromatography (GLC) analysis of its trimethylsilyl thiazolidine derivative. In the ^{1}H-NMR spectrum, an anomeric proton signal at δ 4.40 (1H, d, J=7.8 Hz) was observed. The large $^3J_{H1,H2}$ coupling constant (7.8 Hz) suggested the β-configuration of the anomeric proton of the glucose. Furthermore, analysis of the ^{1}H-NMR spectrum showed the presence of a galloyl group due to the proton signals at δ 7.11 (2H, s), corresponding to the carbon signals at δ 110.3, 121.4, 139.8, 146.4 and 168.3 in the ^{13}C-NMR spectrum. In addition to the signals due to the galloyl group and a sugar moiety, the remaining proton signals, corresponding to 13 carbons, were assignable to the aglycone, which include two *trans*-coupled olefinic protons at δ 5.78 (1H, d, J=15.6 Hz) and 5.83 (1H, dd, J=15.6, 6.2 Hz), an olefinic proton at δ 5.80 (1H, d, J=1.4 Hz) located on α-position of an α,β-unsaturated ketone, and four methyls at δ 0.95, 0.99, 1.28 and 1.84. The deshielded methyl signal at δ 1.84 (H-11) and the olefinic proton at δ 5.80 (H-4) indicated that the methyl directly attached to an olefinic carbon, supported by the HMBC correlation between δ_H 1.84 (H-11) and δ_C 127.1 (C-4). Analysis of the DQF-COSY spectrum, in which the methyl at δ 1.28 (H-10) showed cross-peak with a methine proton at δ 4.37 (H-9) which, in turn, exhibited cross-peaks with two olefinic protons at δ 5.78 (H-7) and 5.83 (H-8), displayed a four-carbon spin system from C-7 to C-10. In addition, two methyls at δ 0.95 (H-13) and 0.99 (H-12) were combined with the carbon at δ 42.3 (C-1), confirmed by the HMBC correlations between H-13/C-12, H-12/C-13, H-12/C-1 and H-13/C-1. Furthermore, the analysis of the HMBC spectrum allowed all three parts containing methyls to be connected by a methylene at δ_C 50.6 (C-2) and a sp^3-hybridized quaternary carbon at δ_C 79.9 (C-6) (Fig. 3). These spectral data clearly indicated that the aglycone of **2** was blumenol A,[12] of which the position at C-9 was connected with the glucose, confirmed by the HMBC correlation between δ_H 4.40 (H-1′) and δ_C 77.0 (C-9). Also, mild alkaline hydrolysis of **2** with 0.5% $NaHCO_3$ gave (6*S*,9*R*)-roseoside (**3**). Analysis of the ^{1}H- and ^{13}C-NMR spectral comparison of **2** and **3**, the downfield shift of H-6′ ($\Delta\delta_{Ha}$ 0.74 and $\Delta\delta_{Hb}$ 0.63 ppm) of **2**, corresponding to C-6′ ($\Delta\delta_C$ 1.9 ppm), suggested that the galloyl group was connected with the position at C-6′ of the glucose, supported by the HMBC correlations between δ_H 4.36 (H-6′a), 4.47 (H-6′b) and δ_C 168.3 (C-7″). Based on the above spectral analysis, the structure of mallophenol B (**2**) was determined to be 6*S*,9*R*-ionone 9-*O*-(6-*O*-galloyl)-β-D-glucopyranoside.

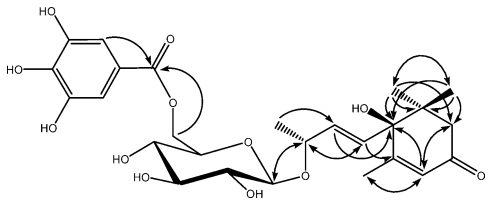


Fig. 3. Important HMBC Correlations of **2**

Experimental

General Experimental Procedures The UV spectra were obtained with a Shimadzu UV-160 spectrophotometer, whereas the IR spectra were measured with a JASCO FT/IR-300E (by a KBr disk method) spectrometer. Optical rotations were measured with a JASCO DIP-370 digital polarimeter in a 0.5-dm cell. The FAB-MS was taken on a JEOL JMS-AX505HA spectrometer. The HR-FAB-MS was taken on a JEOL JMS-700 MStation spectrometer. The ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL ECP-500 or JEOL AL-400 spectrometer in the solution with TMS as the internal reference, and chemical shifts are expressed in δ (ppm). RP HPLC separations were carried out with a JASCO PU-2080 HPLC system, equipped with a Shodex RI-101 Differential Refractometer detector and a Senshu Pak RP-C_{18} column (20×150 mm i.d.), at a flow rate of 5.0 ml/min. RP CC was accomplished with RP-C_{18} silica gel (100—200 mesh, Chromatorex DM1020T ODS, Fuji Silysia Chemical Ltd.). Silica gel CC was carried out with Kieselgel 60 (E. Merck). TLC was conducted in Kieselgel 60 F_{254} plates (E. Merck).

Extraction and Isolation The leaves of *Mallotus furetianus* used in this study were collected in Hainan Island of China. The air-dried powdered leaves (3 kg) were extracted three times with EtOH. Evaporation of the solvent under reduced pressure provided an EtOH extract (50 g). The extract was subjected to Diaion HP-20 CC with a gradient of MeOH and H_2O (30 : 70, 50 : 50, 70 : 30, 100 : 0, v/v) to give four fractions (A—D). Fr. B (18.4 g) was separated by RP CC eluted with a gradient of MeOH and H_2O (30 : 70, 50 : 50, 70 : 30, 100 : 0, v/v) to afford four subfractions (B1—B4). Fr. B1 (12.6 g) was subjected to silica gel CC eluted with $CHCl_3$–MeOH–H_2O (9 : 1 : 0, 60 : 20 : 3, 60 : 29 : 6, 6 : 4 : 1) to give four subfractions (B1a—B1d). Fr. B1a (1.26 g) was further separated by RP CC (MeOH–H_2O, 30 : 70) and RP-HPLC (MeOH–H_2O, 20 : 80) to yield **8** (103 mg) and **9** (348 mg). Fr. B1b (2.96 g) was further separated on RP CC (MeOH–H_2O, 40 : 60) and RP-HPLC (MeOH–H_2O, 25 : 75) to give **1** (85 mg), **2** (27 mg), **3** (203 mg), and **5** (13 mg). Fr. B3 (2.2 g) was subjected to silica gel CC eluted with $CHCl_3$–MeOH–H_2O (9 : 1 : 0, 60 : 20 : 3, 60 : 29 : 6, 6 : 4 : 1) and divided into four subfractions (B3a—B3d). Fr. B3b (0.703 g) was further separated by RP CC (MeOH–H_2O, 40 : 60) and RP-HPLC (MeOH–H_2O, 35 : 65) to yield **4** (22 mg), **6** (21 mg) and **7** (11 mg).

Mallophenol A (**1**): Colorless oil; $[\alpha]_D^{25}$ +19.4° (c=0.968, MeOH); UV (MeOH) λ_{max} nm (log ε): 217 (4.51), 276 (4.11); IR ν_{max} (KBr) cm^{-1}: 3438 (–OH), 1710 (C=O), 1569, 1449, 1351; ^{1}H-NMR (CD_3OD, 500 MHz) and ^{13}C-NMR (CD_3OD, 125 MHz) (see Table 1); HR-FAB-MS *m/z* 533.1259 $[M+Na]^+$ (Calcd for 533.1272); FAB-MS *m/z* 533 $[M+Na]^+$.

Mallophenol B (**2**): Colorless oil; $[\alpha]_D^{25}$ +54.1° (c=1.127, MeOH); UV (MeOH) λ_{max} nm (log ε): 219 (4.50), 274 (4.04); IR ν_{max} (KBr) cm^{-1}: 3424 (–OH), 2925 (C–H), 2858 (C–H), 1647 (C=O), 1569, 1517, 1350, 1222; ^{1}H-NMR (CD_3OD, 500 MHz) and ^{13}C-NMR (CD_3OD, 125 MHz) (see Table 1); HR-FAB-MS *m/z* 561.1938 $[M+Na]^+$ (Calcd for 561.1947); FAB-MS

m/z 561 $[M+Na]^+$.

Hydrolysis of 1 with 0.5% $NaHCO_3$ A solution of **1** (16 mg) in 1% $NaHCO_3$–EtOH (1 : 1, 6 ml) was refluxed for 45 min. The reaction solution was passed through Diaion HP-20 column eluted with H_2O and MeOH. The MeOH eluate was purified by silica gel CC to give **1a** (7 mg). **1a**: colorless amorphous powder; $[\alpha]_D^{25}$ +33.9° (c=0.7, MeOH); ^{1}H- and ^{13}C-NMR data were consistent with those reported in the literature.[9]

Preparation of 4′,6′-*O*-Benzylidine (1b) from 1a **1a** (6 mg), benzaldehyde dimethyl acetal (8 μl) and 10-camphorsulfonic acid (0.078 mg) were dissolved in DMF (4 μl) and the mixture was put into a rotary evaporator at 65 °C and 260—280 mbar. The procedure of reaction was supervised by TLC ($CHCl_3$–MeOH, 9 : 1). After 2.5 h, the reaction mixture was diluted with $CHCl_3$, washed with saturated aqueous $NaHCO_3$, dried (anhydrous Na_2SO_4) and concentrated. The residue was purified by silica gel CC ($CHCl_3$–MeOH, 98 : 2) to give the product **1b** (2 mg): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.44 (1H, dd, J=9.3, 7.8 Hz, H-2′), 3.47 (1H, dd, J=12.1, 4.4 Hz, H-9), 3.59 (1H, dd, J=12.3, 2.6 Hz, H-9), 3.70 (1H, m, H-4′), 3.83 (1H, m, H-8), 3.88 (1H, m, H-5′), 3.92 (3H, s, OCH_3), 4.02 (1H, t, J=9.2 Hz, H-3′), 4.27 (1H, m, H-6′), 4.43 (1H, dd, J=10.3, 2.0 Hz, H-6′), 4.56 (1H, d, J=9.5 Hz, H-7), 4.74 (1H, d, J=7.9 Hz, H-1′), 5.58 (1H, s, H-1″), 6.89 (1H, d, J=8.2 Hz, H-4), 6.89 (1H, dd, J=8.2, 1.8 Hz, H-5), 6.90 (1H, d, J=1.8 Hz, H-1), 7.37 (2H, m, H-4″, H-6″), 7.39 (1H, m, H-5″), 7.50 (2H, m, H-3″, H-7″).

(*S*)-MTPA Ester 1c To a solution of **1b** (1 mg) in pyridine (0.1 ml) was added (*R*)-(−)-MTPACl (10 μl) at room temperature. The reaction mixture was stirred at room temperature for 4 h. After addition of methanol and evaporation of the solvent, the oily residue was purified by RP-HPLC (MeOH–H_2O, 90 : 10) to give (*S*)-MTPA ester **1c** (0.8 mg) as a white powder. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.38 (3H, s, OCH_3–MTPA), 3.49 (1H, dd, J=9.5, 7.8 Hz, H-2′), 3.57 (3H, s, OCH_3–MTPA), 3.73 (3H, s, OCH_3), 3.76 (1H, t, J=9.5 Hz, H-4′), 3.78 (1H, dd, J=10.3, 4.3 Hz, H-6′a), 3.87 (1H, d, J=10.3 Hz, H-6′b), 3.92 (1H, dd, J=12.4, 4.4 Hz, H-9a), 3.96 (1H, dt, J=9.3, 2.7 Hz, H-8), 4.46 (1H, dd, J=9.5, 4.3 Hz, H-5′), 4.55 (1H, d, J=9.3 Hz, H-7), 4.72 (1H, dd, J=12.2, 1.7 Hz, H-9b), 4.80 (1H, d, J=7.8 Hz, H-1′), 5.48 (1H, s, Ph–CH), 5.68 (1H, t, J=9.5 Hz, H-3′), 6.76 (1H, dd, J=8.3, 2.0 Hz, H-6), 6.91 (1H, d, J=2.0 Hz, H-2), 6.96 (1H, d, J=8.3 Hz, H-5), 6.88 (2H, Ph), 7.21—7.48 (13H, Ph).

(*R*)-MTPA Ester 1d **1b** (1 mg) was treated with (*S*)-(+)-MTPACl (10 μl) by the same procedure as above described to afford the (*R*)-MTPA ester **1d** (0.5 mg). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.29 (1H, dd, J=9.8, 7.8 Hz, H-2′), 3.47 (3H, s, OCH_3–MTPA), 3.53 (3H, s, OCH_3–MTPA), 3.78 (1H, m, H-6′a), 3.82 (3H, s, OCH_3), 3.86 (1H, t, J=10.2 Hz, H-4′), 3.90 (1H, d, J=10.3 Hz, H-6′b), 3.95 (1H, ddd, J=9.3, 4.0, 2.0 Hz, H-8), 4.07 (1H, dd, J=12.4, 4.0 Hz, H-9a), 4.30 (1H, d, J=9.3 Hz, H-7), 4.47 (1H, dd, J=10.5, 4.6 Hz, H-5′), 4.58 (1H, dd, J=12.2, 2.0 Hz, H-9a), 4.77 (1H, d, J=7.6 Hz, H-1′), 5.56 (1H, s, Ph–CH), 5.65 (1H, t, J=9.5 Hz, H-3′), 6.87 (1H, dd, J=8.1, 2.0 Hz, H-6), 6.99 (1H, d, J=2.0 Hz, H-2), 7.03 (1H, d, J=8.1 Hz, H-5), 6.84 (2H, Ph), 7.19—7.48 (13H, Ph).

Acid Hydrolysis and Determination of the Absolute Configuration of Sugar in 2 **2** (1 mg), in 1 M HCl (dioxane–H_2O, 1 : 1, 200 μl) was heated at 100 °C for 1 h under an Ar atmosphere. After dioxane was removed, the solution was extracted with EtOAc (1 ml×3) to remove the aglycon. The aqueous layer was neutralized by passing through an ion-exchange resin (Amberlite MB-3, Organo, Tokyo, Japan) column, concentrated under reduced pressure to dryness, to give a residue of the sugar fraction. The residue was dissolved in pyridine (1 ml), to which 0.1 M L-cysteine methyl ester hydrochloride in pyridine (2 ml) was added. The mixture was kept at 60 °C for 1.5 h. After the reaction mixture was dried *in vacuo*, the residue was trimethylsilylated with 1-trimethylsilylimidazole (0.2 ml) for 2 h. The mixture was partitioned between hexane and H_2O (0.3 ml each) and the hexane extract was analyzed by GLC under the following conditions: capillary column, EQUITY^{TM}-1 (30 m×0.25 mm×0.25 μm, Supelco), column temperature, 230 °C; injection temperature, 250 °C; carrier N_2 gas. In the acid hydrolysate of **2**, D-glucose was confirmed by comparison of the retention times of their derivatives with those of D-glucose and L-glucose derivatives prepared in a similar way, which showed retention times of 11.79 and 11.33 min, respectively.

Hydrolysis of 2 with 0.5% $NaHCO_3$ A solution of **2** (12 mg) in 1% $NaHCO_3$–EtOH (1 : 1, 2 ml) was refluxed for 45 min. The reaction solution was passed through Diaion HP-20 column eluted with H_2O and MeOH. The MeOH eluate was purified by silica gel CC to furnish **3** (6 mg), which was identified by comparison of the physical data (^{1}H- and ^{13}C-NMR, $[\alpha]_D^{25}$) with literature data.[2]

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