

## New Dihydrophenanthrene and Phenylidihydroisocoumarin Constituents of *Trema orientalis*

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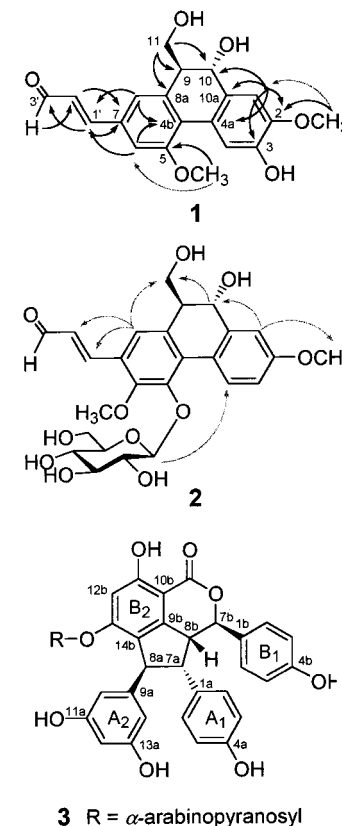
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In the course of the chemical investigation of extracts of the trunk bark and root bark of *Trema orientalis*, three new compounds were isolated, namely, (9*S*\*,10*S*\*)-3-[7-(3,10-dihydroxy-9-hydroxymethyl-2,5-dimethoxy)-9,10-dihydrophenanthrenyl]propenal (**1**), (9*S*\*,10*S*\*)-3-[7-(5-*O*-β-glucopyranosyl-10-hydroxy-9-hydroxymethyl-2,6-dimethoxy)-9,10-dihydrophenanthrenyl]propenal (**2**), and (3*R*\*,3*aR*\*,4*R*\*,5*S*\*)-6-*O*-α-arabinopyranosyl-3-(4-hydroxyphenyl)-4-(4-hydroxyphenyl)-5-(3,5-dihydroxyphenyl)-3,3*a*-dihydrocyclopenta[1,2,3-*de*]isobenzopyran-1-one (**3**, orientoside A). The structures of **1–3** were determined by spectral methods.

*Trema orientalis* L. (Ulmaceae) is a common shrub in Cameroon. Its bark is used in folk medicine as a treatment for hypertension.<sup>1</sup> Up to the present, only a few studies have been published on members of this genus, with triterpenoids,<sup>2,6</sup> sterols,<sup>2,4–7</sup> fatty acids,<sup>2,3,7</sup> phenols,<sup>7</sup> and flavonoid glycosides<sup>8,9</sup> having been reported. In the course of a chemical investigation on *T. orientalis* L. Blume, we previously isolated 16 known compounds, including, for the first time in the Ulmaceae, iridoids and xanthenes.<sup>10</sup> Further investigation of the same species has resulted in the isolation of three new compounds, identified as (9*S*\*,10*S*\*)-3-[7-(3,10-dihydroxy-9-hydroxymethyl-2,5-dimethoxy)-9,10-dihydrophenanthrenyl]propenal (**1**), (9*S*\*,10*S*\*)-3-[7-(5-*O*-β-glucopyranosyl-10-hydroxy-9-hydroxymethyl-2,6-dimethoxy)-9,10-dihydrophenanthrenyl]propenal (**2**), and (3*R*\*,3*aR*\*,4*R*\*,5*S*\*)-6-*O*-α-arabinopyranosyl-3-(4-hydroxyphenyl)-4-(4-hydroxyphenyl)-5-(3,5-dihydroxyphenyl)-3,3*a*-dihydrocyclopenta[1,2,3-*de*]isobenzopyran-1-one (**3**, orientoside A). This report deals with the identification of **1–3** on the basis of their spectral data (Figure 1).

Fractionation of the dichloromethane extract from the trunk bark of *Trema orientalis* by column chromatography on Si gel afforded compound **1**. The UV spectrum of **1** showed maxima at 343, 311 (sh), 278 (sh), 258 (sh), and 220 nm. The negative FABMS exhibited an ion [M – H]<sup>–</sup> at *m/z* 355 and fragment ions at *m/z* 337 [M – H – H<sub>2</sub>O]<sup>–</sup> and 325 [M – H – CH<sub>2</sub>O]<sup>–</sup>. The positive HRFABMS and <sup>13</sup>C NMR spectrum established its molecular formula as C<sub>20</sub>H<sub>20</sub>O<sub>6</sub> (11 degrees of unsaturation). The <sup>13</sup>C NMR spectrum displayed signals for all 20 carbons in the molecule, which were constituted by one methylene (δ 63.9) and one methine (δ 88.9), both bearing an oxygen, one aliphatic methine (δ 53.0), two olefinic methines (δ 153.0, 126.0), two methoxyls (δ 56.0, 56.1), and one aldehyde (δ 193.0), along with 12 aromatic carbons (δ 151.5–109.6). These data, together with the <sup>1</sup>H NMR and <sup>1</sup>H–<sup>1</sup>H COSY spectra, showed that **1** contained a substituted dihydro-



**Figure 1.** Structures of compounds **1–3**, with important HMBC (in black) and NOEs (in gray) correlations.

phenanthrene subunit with a multiplet at δ 3.66 (1H) due to H-9 coupled to both a doublet at δ 5.64 (H-10) (belonging to a CH(Ar)O– fragment) and a multiplet at δ 3.97 (2H, H-11) assigned to a CH<sub>2</sub>OH group. The substitution pattern of the aromatic rings was suggested by two *meta*-coupled protons observed at δ 7.04 (H-6) and 7.13 (H-8) and one singlet at δ 6.89 (H-1, H-4). Two methoxyl groups were characterized by two singlets at δ 3.87 and 3.93, located by NOEs at C-2 and C-5, respectively (Figure 1). Correlations between H-1 and C-4*a* and C-10 and between H-11 and C-9 and C-10 confirmed the substitution at C-9 and

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C-10 of the dihydrophenanthrene skeleton. Along with the dihydrophenanthrene moiety, **1** exhibited an AMX system at  $\delta$  9.64 (d,  $J = 7.6$  Hz, H-3'), 6.60 (dd,  $J = 7.6, 15.8$  Hz, H-2'), and 7.41 (d,  $J = 15.8$  Hz, H-1') due to an  $\alpha,\beta$ -unsaturated aldehyde group.<sup>11</sup> This was confirmed by the IR peaks at 1690, 1580, and 1480  $\text{cm}^{-1}$ , which supported the occurrence of an aromatic propenal side chain conjugated system.<sup>11</sup>

2D NMR experiments were used to establish the final structure of **1**. Long-range  $^1\text{H}$ - $^{13}\text{C}$  coupling established the linkage of the side chain to C-7 (Figure 1), with cross-peaks between H-1' and C-6, and H-6, H-8 and C-1', and NOEs between H-1' and H-6/H-8. The relative stereochemistry at C-9 and C-10 was deduced to be *trans* from the coupling constant ( $J = 7.0$  Hz) between H-9 and H-10.<sup>12,13</sup> Considering these data, two stereochemical arrangements of these carbons were possible: form **A** (9*R*,10*R*) and form **B** (9*S*,10*S*). To refine the conformation of the molecule, the theoretical coupling constants  $^3J_{\text{H9-H10}}$  were calculated for each minimized structure<sup>14,15</sup> by measuring the respective dihedral angles via the Karplus relationship.<sup>16</sup> The results of modeling calculations showed that only for both *trans* isomers (form **A** and form **B**) did the theoretical  $^3J_{\text{H9-H10}}$  values match well the experimental one, but no clear preference for **A** or **B** could be drawn,<sup>17</sup> as they are enantiomers.

A final analysis of NOEs data, coupling constants, and interatomic distances revealed that compound **1** has the structure (9*S*\*,10*S*\*)-3-[7-(3,10-dihydroxy-9-hydroxymethyl-2,5-dimethoxy)-9,10-dihydrophenanthrenyl]propenal.

Chromatographic purification of the EtOAc extract from the trunk bark of *T. orientalis* led to the isolation of compound **2** as a colorless resin. The UV spectrum exhibited the same maxima as in **1**. Positive HRFABMS established its elemental formula as  $\text{C}_{26}\text{H}_{30}\text{O}_{11}$  (12 degrees of unsaturation). The DCIMS showed peaks at  $m/z$  536 [ $\text{M} + \text{H} + \text{NH}_3$ ]<sup>+</sup>, 519 [ $\text{M} + \text{H}$ ]<sup>+</sup>, and 357 [ $\text{M} + \text{H} - 162$ ]<sup>+</sup>. The latter peak was characteristic of the loss of a hexosyl unit. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were closely related to those of compound **1**. In the  $^1\text{H}$  NMR spectrum, many similarities with **1** were detected such as the propenal side chain, two methoxy groups resonating at  $\delta$  3.83 (6H), and the subunit Ar-CH(CH<sub>2</sub>OH)-CH(OH)-Ar located at C-9-C-10. Two aromatic rings were represented by, on one side, three protons at  $\delta$  7.15 (d,  $J = 8.4$  Hz, H-4), 7.02 (d,  $J = 1.9$  Hz, H-1), and 6.93 (dd,  $J = 8.3, 1.9$  Hz, H-3) and, on the other side, a singlet at  $\delta$  7.14 (1H, H-8). The latter signal was shifted downfield to 7.31 ppm in DMSO-*d*<sub>6</sub>. Besides the aglycon signals, the  $^1\text{H}$  NMR spectrum showed the presence of a  $\beta$ -glucosyl unit with an anomeric proton at  $\delta$  4.88 (d,  $J = 6.9$  Hz) related to the signals between 3.80 and 3.20 ppm. These signals were assigned according to the correlations in the COSY NMR spectrum and were associated with exchangeable protons between 4.44 and 5.16 ppm. NOEs observed in CD<sub>3</sub>OD and in DMSO-*d*<sub>6</sub>, between H-1 and H-10 and CH<sub>3</sub>O-2, and between H-8 and H-1' and H-2' and H<sub>2</sub>-11, supported the placement of one of the methoxy groups at C-2 and of the propenal chain at C-7 (Figure 1). The glycoside could be attached at C-5 of the aglycon, with the NOEs observed between H-1'' and H-4. Thus, the second methoxy group was deduced to be attached to C-6.

The  $^{13}\text{C}$  NMR spectrum of **2** displayed signals for 26 carbons. The 18 carbons of the aglycon were assigned by comparison with compound **1** and literature values.<sup>20</sup> Together with these signals, the  $\beta$ -glucosyl unit was identified by five methines at  $\delta$  102.8, 78.2, 77.9, 74.9, 71.4, and one methylene at  $\delta$  62.5.<sup>21,22</sup> The relative stereochemistry of C-9 and C-10 was established to be *trans* because

of the large coupling constant  $J_{\text{H9-H10}}$  (6.9 Hz). Accordingly, compound **2** was assigned as (9*S*\*,10*S*\*)-3-[7-(5-*O*- $\beta$ -D-glucopyranosyl-10-hydroxy-9-hydroxymethyl-2,6-dimethoxy)-9,10-dihydrophenanthrenyl]propenal.

Chemical investigation of the EtOAc extract from the root bark led to the isolation of orientoside A (**3**). Its molecular formula was determined as  $\text{C}_{34}\text{H}_{30}\text{O}_{12}$ , with 20 degrees of unsaturation, using a combination of positive HRFABMS, negative FABMS ( $m/z$  629 [ $\text{M} - \text{H}$ ]<sup>-</sup>), and  $^{13}\text{C}$  NMR data. A peak was observed at  $m/z$  497, indicative of the loss of a pentosyl unit. The UV spectrum showed maxima at 309, 263, and 231 nm, with bathochromic effects observed after addition of specific reagents to show the presence of an aromatic structure with free hydroxyl groups. Addition of HCl to a MeOH + AlCl<sub>3</sub> solution of **3** induced a persistent bathochromic effect, indicative of a chelation in the molecule.<sup>23</sup>

The  $^1\text{H}$  NMR and  $^1\text{H}$ - $^1\text{H}$  COSY spectra exhibited three sets of aromatic protons: eight *ortho*-coupled protons at  $\delta$  6.90 (2H, d,  $J = 8.6$  Hz) and 6.73 (2H, d,  $J = 8.6$  Hz) and at  $\delta$  6.58 (2H, d,  $J = 8.7$  Hz) and 6.51 (2H, d,  $J = 8.6$  Hz); three *meta*-coupled protons at  $\delta$  6.15 (1H, t,  $J = 2.1$  Hz) and 6.10 (2H, d,  $J = 2.1$  Hz), and a singlet at  $\delta$  6.70 (brs, H-12b). They were indicative of two *para*-disubstituted, one *meta*-trisubstituted, and one pentasubstituted aromatic rings. The  $^1\text{H}$  NMR spectrum also showed an anomeric proton at 5.04 ppm (d,  $J = 6.7$  Hz, H-1'). The  $^1\text{H}$ - $^1\text{H}$  COSY spectrum showed five other sugar signals from 3.91 to 3.58 ppm belonging to the same spin system. The coupling constants were indicative of an  $\alpha$ -arabinopyranose<sup>22,24</sup> (Table 1). Besides the saccharide signals, the COSY experiment exhibited a set of four vicinally coupled methine signals at  $\delta$  4.80 (d,  $J = 12.3$  Hz, H-7b), 4.29 (brdd,  $J = 12.2, 7.7$  Hz, H-8b), 3.43 (d,  $J = 7.8$  Hz, H-7a), and 4.50 (brs, H-8a).

Well-resolved resonances for 28 carbons were observed in the  $^{13}\text{C}$  NMR spectrum of **3**: an ester at  $\delta$  168.3, 12 quaternary carbons ( $\delta$  159.9-101.3), seven aromatic methines ( $\delta$  129.4-100.5), one anomeric carbon at 100.5 ppm, seven aliphatic methines ( $\delta$  86.5-49.0), and one methylene ( $\delta$  65.5) (Table 1). The construction of the three aromatic rings (A<sub>1</sub>, A<sub>2</sub>, and B<sub>1</sub>) via  $^1\text{H}$ - $^1\text{H}$  COSY, HMQC, and HMBC experiments revealed that they are attached to a substructure corresponding to  $\text{C}_{11}\text{H}_6\text{O}_4$ , without considering the pentosyl unit. According to the DEPT data, these remaining structural elements were comprised of six quaternary carbons at  $\delta$  168.3, 162.0, 159.9, 149.7, 123.6, and 101.3 and five methines at  $\delta$  102.7, 86.5, 57.9, 57.7, and 45.9. HMQC experiments established that the methine protons at  $\delta$  4.80 (H-7b), 4.29 (H-8b), 3.43 (H-7a), and 4.50 (H-8a) were attached, respectively, to the carbons resonating at  $\delta$  86.5, 45.9, 57.7, and 57.9. The aromatic proton at  $\delta$  6.70 (H-12b) was assigned to the carbon resonating at 102.7 ppm.

The  $^1\text{H}$ - $^1\text{H}$  COSY experiment established that H-7b, H-8b, H-7a, and H-8a were vicinally coupled protons. HMBC data (Table 1) showed correlations between these four protons and C-9b, suggesting that C-8b was a juncture point for an O-CH(Ar) subunit, a fourth aromatic ring (B<sub>2</sub>), and a CH(Ar)-CH(Ar) fragment. Correlations between H-8a and C-14b and C-9b and C-13b suggested that C-8a was connected to C-14b, and C-14b to C-9b and C-13b. Altogether, they confirmed the occurrence of a bond between C-8b and C-9b. Cross-peaks between H-12b ( $\delta$  6.70) and C-14b and C-10b ( $\delta$  101.3) and C-13b ( $\delta$  159.9) completed the attachment of ring B<sub>2</sub> to the other fragments. Furthermore, these connectivities permitted the assign-

**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data of Compound **3** ( $\text{CD}_3\text{OD}$ , 500 and 125 MHz)<sup>a</sup>

position	$^1\text{H}$	$^{13}\text{C}$	HMBC	ROESY
1		168.3		
1a		131.6		
2a/6a	6.51 d (8.6)	128.4	C-4a, C-7a	H-7a, H-8a, H-8b
3a/5a	6.58 d (8.7)	114.5	C-1a, C-4a	
4a		156.2		
7a	3.43 d (7.8)	57.7	C-1a, C-2a, C-8a, C-9a, C-8b, C-9b, C-14b	H-2a, H-10a, H-8b
8a	4.50 brs	57.9	C-7a, C-9a, C-10a C-8b, C-9b, C-14b, C-13b	H-2a, H-10a
9a		145.3		
10a/14a	6.10 d (2.1)	105.0	C-8a, C-11a, C-12a	H-7a, H-8a, H-8b
11a/13a		158.5		
12a	6.15 t (2.1)	100.5		
1b		126.6		
2b/6b	6.90 d (8.6)	129.4	C-3b, C-4b, C-7b	H-7b, H-8b
3b/5b	6.73 d (8.6)	114.6	C-1b, C-4b	
4b		158.1		
7b	4.80 d (12.3)	86.5	C-1b, C-2b, C-8b, C-9b	H-2b
8b	4.29 brdd (12.2, 7.7)	45.9	C-1a, C-7a, C-1b, C-7b, C-9b	H-7a, H-10a, H-2b
9b		149.7		
10b		101.3		
11b		162.0		
12b	6.70 brs	102.7	C-10b, C-13b, C-14b	H-1'
13b		159.9		
14b		123.6		
1'	5.04 d (6.7)	100.5	C-13b	H-12b, H-3', H-5'
2'	3.72 dd (8.6, 6.8)	70.4	C-3'	
3'	3.58 brdd (8.6, 3.6)	72.3		H-1'
4'	3.86 m	67.7		
5'	3.91 dd (12.4, 3.2)	65.5		
	3.60 dd (12.0, 1.5)			

<sup>a</sup> *J* values (in Hz) are given in parentheses.

ment of every carbon of ring B<sub>2</sub>, among which C-11b and C-13b were substituted by an oxygen and C-10b by a carbonyl (C-1). The linkage between the  $\alpha$ -arabinopyranosyl and the aglycon was established by cross-peaks in the HMBC spectrum between H-1' ( $\delta$  5.04) and C-13b ( $\delta$  159.9) and in ROESY spectrum between H-1' and H-12b.

Dreiding models of **3** revealed a very rigid structure. The relative stereochemistry of C-7b, C-8b, C-7a, and C-8a was proposed to be *trans-cis-trans* with the protons in the axial position regarding their coupling constants and the ROESY experiment (Table 1). Thus, compound **3** was assigned structurally as (3*R*\*,3*aR*\*,4*R*\*,5*S*')-6-*O*- $\alpha$ -arabinopyranosyl-8-hydroxy-3-(4-hydroxyphenyl)-4-(4-hydroxyphenyl)-5-(3,5-dihydroxyphenyl)-3,3a-dihydrocyclopenta[1,2,3-*de*]isobenzopyrane-1-one (trivial name, orientoside A).

In conclusion, three new polyphenolic metabolites [**1**, **2**, and orientoside A (**3**)] have been isolated from the trunk bark and root bark of *Trema orientalis*. This is the first time that dihydrophenanthrene and isocoumarin derivatives have been reported in a species of the family Ulmaceae.

## Experimental Section

**General Experimental Procedures.** Optical rotations were recorded on a Perkin-Elmer 341 polarimeter at 589 nm (Na), at 20 °C. IR spectra were recorded on a Perkin-Elmer 1310 instrument. UV spectra were recorded on a Hitachi U2000 instrument. NMR spectra (in  $\text{CD}_3\text{OD}$  or  $\text{CDCl}_3$ ) were conducted on a Bruker AC-200 (200 MHz for proton and 50 MHz for carbon) and a Bruker Avance-500 (500 MHz for proton and 125 MHz for carbon). Mass spectra were recorded on a quadripolar mass spectrometer R210C coupled to a IPC (P2A) MSCAN Wallise computer.

**Molecular Modeling.** The molecular modeling program SYBYL (Version 6.3, Tripos, Inc., St. Louis, MO, on a Silicon Graphics O2 workstation) was used. Minimization was per-

formed by means of MOPAC, a program for semiempirical calculations. AM1 was used as the Hamiltonian. The resulting conformations were analyzed by measuring H-H dihedral angles and interatomic distances (Å).

**Plant Material.** The trunk bark and root bark of *Trema orientalis* L. Blume (Ulmaceae) were collected in September 1995 in Southern Cameroon, close to Nyamoko (5° 17' N, 11° 16' E) and identified by Dr. G. Achoundong (National Herbarium, Yaounde, Cameroon), and a voucher specimen (No. 3116: Achoundong) is preserved in the National Herbarium of Yaounde.

**Extraction and Isolation.** The dried trunk bark (3 kg) and root bark (1.2 kg) were ground. The trunk bark was extracted with boiling EtOH-H<sub>2</sub>O (1:1). On concentration, the aqueous phase was extracted successively with  $\text{CH}_2\text{Cl}_2$  and EtOAc to give 9.4 and 23.3 g of each crude extract, respectively. The root bark was extracted directly with boiling EtOAc and afforded 12.5 g of a crude extract.

A part of the  $\text{CH}_2\text{Cl}_2$  extract (9 g) from the trunk bark was subjected to column chromatography on Si gel using a gradient of hexane- $\text{CH}_2\text{Cl}_2$ -MeOH. Six fractions (A-F) were collected. Compound **1** (13 mg) was isolated from fraction D (40 mg) by preparative TLC on Si gel using hexanes-EtOAc (6:4) as solvent (*R<sub>f</sub>* = 0.4, after four developments).

The EtOAc extract (20 g) from the trunk bark was fractionated by column chromatography on Si gel with a gradient of hexane- $\text{CH}_2\text{Cl}_2$ -MeOH, affording eight fractions. Fraction 7 (3.7 g), eluted with  $\text{CH}_2\text{Cl}_2$ -MeOH (3:7), containing **2**, was subsequently purified by column chromatography on Si gel using a gradient of  $\text{CH}_2\text{Cl}_2$ -MeOH and then by centrifugal preparative TLC with  $\text{CH}_2\text{Cl}_2$ -acetone. The fraction containing **2** (82 mg) was finally purified by MPLC on Si gel using a gradient of EtOAc-MeOH as solvent. Compound **2** (6 mg) was obtained with 60% MeOH.

A portion of the root bark EtOAc extract (12 g) was fractionated by column chromatography on Si gel using hexane- $\text{CH}_2\text{Cl}_2$ -MeOH mixtures of increased polarity. Compound **3** (6 mg) was isolated from fraction F (1.5 g) by column chromatography on Si gel using a gradient of hexane-EtOAc-MeOH and finally by column chromatography on Si

gel using a gradient of  $\text{CH}_2\text{Cl}_2$ -MeOH. Compound **3** was eluted with 40% MeOH in  $\text{CH}_2\text{Cl}_2$ .

**Compound 1:** light yellow solid;  $[\alpha]_D^{20} +0.2^\circ$  ( $c$  0.56,  $\text{CHCl}_3$ ); IR (film)  $\nu_{\text{max}}$  3390, 2910, 2820, 1690, 1580, 1480, 1320, 1125, 1025, 960, 720  $\text{cm}^{-1}$ ; UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 343 (4.3), 311 (sh), 278 (sh), 258 (sh), 237 (sh), 219 (4.5) nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  9.64 (1H, d,  $J = 7.6$  Hz, H-3'), 7.41 (1H, d,  $J = 15.8$  Hz, H-1'), 7.13 (1H, brs, H-8), 7.04 (1H, d,  $J = 1.4$  Hz, H-6), 6.89 (2H, brs, H-1, H-4), 6.60 (1H, dd,  $J = 15.8, 7.6$  Hz, H-2'), 5.64 (1H, d,  $J = 7.0$  Hz, H-10), 3.97 (2H, m, H-11), 3.93 (3H, s,  $\text{CH}_3\text{O-5}$ ), 3.87 (3H, s,  $\text{CH}_3\text{O-2}$ ), 3.66 (1H, m, H-9);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  193.0 (C-3'), 153.0 (C-1'), 151.5 (C-4b), 146.8 (C-2), 145.9 (C-3), 144.5 (C-5), 132.2 (C-4a), 129.2 (C-10a, C-8a), 128.1 (C-7), 126.0 (C-2'), 119.4 (C-1), 118.0 (C-8), 112.0 (C-6), 108.8 (C-4), 88.9 (C-10), 63.9 (C-11), 56.1 ( $\text{CH}_3\text{O-5}$ ), 56.0 ( $\text{CH}_3\text{O-2}$ ), 53.0 (C-9); FABMS  $m/z$  355  $[\text{M} - \text{H}]^-$ , 337  $[\text{M} - \text{H} - \text{H}_2\text{O}]^-$ , 325  $[\text{M} - \text{H} - \text{CH}_2\text{O}]^-$ , 311  $[\text{325} - \text{CH}_3]^-$ , 295  $[\text{311} - \text{CH}_3]^-$ ; HRFABMS  $m/z$  357.1347  $[\text{M} + \text{H}]^+$  (calcd for  $\text{C}_{20}\text{H}_{20}\text{O}_6 + \text{H}$ , 357.1338).

**Compound 2:** colorless resin;  $[\alpha]_D^{20} + 0.8^\circ$  ( $c$  0.25, MeOH); IR (film)  $\nu_{\text{max}}$  3480, 2910, 2820, 1690, 1580, 1480, 1125, 1025  $\text{cm}^{-1}$ ; UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 343 (4.7), 311 (sh), 278 (sh), 258 (sh), 237 (sh), 219 (5.5) nm;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 200 MHz)  $\delta$  9.57 (1H, d,  $J = 7.8$  Hz, H-3'), 7.60 (1H, d,  $J = 15.7$  Hz, H-1'), 7.15 (1H, d,  $J = 8.4$  Hz, H-4), 7.14 (1H, s, H-8), 7.02 (1H, d,  $J = 1.9$  Hz, H-1), 6.93 (1H, dd,  $J = 8.3, 1.9$  Hz, H-3), 6.55 (1H, dd,  $J = 7.8, 15.7$  Hz, H-2'), 5.66 (1H, d,  $J = 6.1$  Hz, H-10), 4.88 (1H, d,  $J = 6.9$  Hz, H-1''), 3.88 (H-6''), 3.84 (H-11), 3.83 (6H, s,  $\text{CH}_3\text{O-2, 5}$ ), 3.65 (H-6''), 3.58 (H-9), 3.45 (H-2''), 3.39 (H-5''), 3.31 (H-3'', 4'');  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 50 MHz)  $\delta$  195.1 (C-3'), 156.0 (C-1'), 153.0 (C-6), 151.1 (C-4b), 148.5 (C-2), 146.4 (C-5), 137.5 (C-4a), 131.0 (C-7), 127.3 (C-8a, 10a), 120.0 (C-2'), 119.6 (C-8), 118.2 (C-3), 114.4 (C-1), 111.3 (C-4), 102.8 (C-1''), 89.6 (C-10), 78.2 (C-3''), 77.9 (C-5''), 74.9 (C-2''), 71.4 (C-4''), 64.7 (C-11), 62.5 (C-6''), 56.8 ( $\text{CH}_3\text{O-2,5}$ ), 54.9 (C-9); DCIMS  $m/z$  519  $[\text{M} + \text{H}]^+$ , 536  $[\text{M} + \text{H} + \text{NH}_3]^+$ , 357  $[\text{M} + \text{H} - 162]^+$ , 163 [hexosyl] $^+$ ; HRFABMS  $m/z$  541.1686  $[\text{M} + \text{Na}]^+$  (calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_{11} + \text{Na}$ , 541.1686).

**Orientoside A (3):** colorless amorphous powder;  $[\alpha]_D^{20} -86.6^\circ$  ( $c$  0.21, MeOH); IR (film)  $\nu_{\text{max}}$  3480, 2910, 1710, 1600, 1505, 1445, 1350, 1200, 1065  $\text{cm}^{-1}$ ; UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 309 (3.7), 263 (3.7), 231 (4.6) nm;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 500 MHz), see Table 1;  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 125 MHz), see Table 1; FABMS  $m/z$  629  $[\text{M} - \text{H}]^-$ , 497  $[\text{M} - \text{H} - \text{pentose}]^-$ , 453  $[\text{497} - \text{CO}_2]^-$ ; DCIMS  $m/z$  586, 454; positive HRFABMS  $m/z$  653.1628  $[\text{M} + \text{Na}]^+$  (calcd for  $\text{C}_{34}\text{H}_{30}\text{O}_{12} + \text{Na}$ , 653.1635).

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## References and Notes

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