Notes

New Naphthopyranone Glycosides from *Paepalanthus vellozioides* and *Paepalanthus latipes*

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Three new compounds—3,4-dihydro-10-hydroxy-7-methoxy-3-(*R*)-methyl-1H-3,4-dihydronaphtho-]2,3*c*]-pyran-1-one-9-*O*-*β*-D-glucopyranoside (**1**), 3,4-dihydro-10-hydroxy-7-methoxy-3-(*R*)-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one-9-*O*-*β*-D-glucopyranosyl-(1→6)-glucopyranoside (**2**), and 3,4-dihydro-10-dihydroxy-7-methoxy-3-(*R*)-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one-9-*O*-*β*-D-allopyranosyl (1→6)-glucopyranoside (**3**)—were isolated from the leaves of *Paepalanthus vellozioides* and *Paepalanthus latipes* and characterized by spectrometric methods, mainly electrospray mass spectrometry and 1D and 2D NMR experiments. These unusual glycosylated dihydronaphthopyranones may serve as taxonomic markers of the genus *Paepalanthus*, since these compounds were not detected in other genera belonging to the Eriocaulaceae family.

Several small shrubs called “sempre-vivas” (everlasting plants) grow wild in the Serra do Cipo, Minas Gerais, Brazil. This region is denominated “campos rupestres”, is about 800 m in altitude, and has a sandy soil. The Eriocaulaceae are the dominant herbal population of this region, together with Poaceae, Cyperaceae, and Xyridaceae.[1] According to Hensold and Giulietti, the monocotyledonous family Eriocaulaceae has about 1200 species, distributed in 10−14 genera.[2] It is a pantropical family with few species found in temperate regions.[3] Although this family has been botanically investigated for more than two decades, the taxonomic position of some genera has still been a matter of controversy.[4] On the other hand, little is known about the chemical composition of the plants from this family.[5,6] In previous reports,[7] we have described the isolation and structure determination of paepalantine, a new isocoumarin (naphthopyran-1-one) isolated from the chloroform extracts of the capitulae from *Paepalanthus bromelioides* as well as from *Paepalanthus vellozioides*, with potent antibiotic, cytotoxic, and mutagenic activities.[8] Other compounds belonging to this class of natural metabolites present antitumor, antileukemic, and even antiviral activities.[9] Now we have examined the constituents of the leaves from *P. vellozioides* and *P. latipes*, both belonging to the subgenus *Platycaulon*.

Compound **1** was obtained as a gummy solid. Under UV **1** showed a blue spot with R_f 0.80 (BuOH−AcOH−H_2O 12:3:5). The ES−MS (100 V, positive ion) gave the protonated molecular ion $[M + H]^+$ at *m*/*z* 437, corresponding to the molecular formula $C_{21}H_{24}O_{10}$, as well as the peak at *m*/*z* 459 corresponding to the sodium adduct $[M + Na]^+$. The loss of a hexose moiety (162 u) led to the protonated aglycon $[A + H]^+$ at *m*/*z* 275 and a sodium adduct $[A + Na]^+$ at *m*/*z* 297. Acid hydrolysis of **1** released D-glucose, identified by GC−MS. The complete structure of **1** could be elucidated by 1D and 2D NMR experiments at 600 MHz. The ^{13}C NMR and DEPT spectra showed 21 signals, six of which could be assigned to a glucopyranosyl moiety. The ^1H NMR spectrum displayed two signals of meta-coupled protons (J = 1.5 Hz) at δ 6.87 and 7.04 and one singlet at δ 6.99. Further signals appeared at δ 1.53 (d, 3H, J = 6.1 Hz), 2.97 (dd, 1H, J = 11.4, 16.2), 3.11 (dd, 1H, J = 2.6, 16.2 Hz), and 4.76 (m, 1H). The DQF−COSY spectrum indicated the sequence $-CH_2$(δ 2.97; 3.11)−CH(δ 4.76)−CH_3(1.53), typical of ring A of a naphthopyranone skeleton, and also provided the correlations of the glucose moiety. The anomeric signal appeared at δ 5.01 with J = 7.5 Hz, thus indicating the β-configuration of the sugar. A signal at δ 3.93 (s, 3H) corresponded to a methoxyl group. Assignments of all ^1H and ^{13}C NMR signals were based on HMBC, HSQC, and DQF−COSY experiments.

The HSQC spectrum, which correlated the ^1H resonances with those of the corresponding carbons, and the HMBC spectrum allowed us to deduce for the aglycon the structure 3,4-dihydro-9,10-dihydroxy-7-methoxy-3-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one. Diagnostic long-range correlations were observed between the proton signal at δ 7.04 (H-8) and the carbon resonances at δ 102.0 (C-6), 111.2 (C-9a), 159.4 (C-9), and 163.0 (C-7); the proton at δ 6.99 (H-5) and the carbon resonances at δ 102.0 (C-6), 111.2 (C-9a), and 142.2 (C-5a); the proton at δ 6.87 (H-6) and the carbon resonances at δ 104.6 (C-8), 111.2 (C-9a), 116.9 (C-5), and 163.0 (C-7); the proton signals at δ 2.97 and 3.11 (H_2-4) and the carbon resonances at δ 20.9 (C-11), 77.3 (C-3), 102.0 (C-10a), 116.9 (C-5), and 142.2 (C-4a); the methyl doublet at δ 1.53 (Me-11) and the carbon at δ 35.0 (C-4). Furthermore, the HMBC spectrum allowed us to confirm the position of the methoxyl group, showing a correlation between the ^1H signal at δ 3.93 and C-7 of the aglycon (δ 163.0), and to establish the position of the sugar residue,

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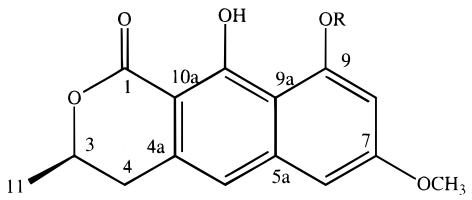
showing a correlation between the anomeric signal of the glucose (δ 5.01) and C-9 of the aglycon (δ 159.4). Thus, **1** was characterized as 3,4-dihydro-10-hydroxy-7-methoxy-3-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one-9-*O*-β-D-glucopyranoside.

Compound **2** was obtained as a white amorphous powder. It showed a blue spot on TLC in the same system described above, with a R_f value of 0.40 (BuOH−AcOH−H_2O 12:3:5). The ES−MS (100 V, positive ion) also gave the signal of a protonated aglycon $[A + H]^+$ at *m*/*z* 275 and its sodium adduct $[A + Na]^+$ at *m*/*z* 297, thus suggesting the same aglycon as in **1**. The protonated molecular ion $[M + H]^+$ occurred at *m*/*z* 599 and the adduct with sodium $[M + Na]^+$ at *m*/*z* 621, clearly indicating a disaccharide moiety linked to the aglycon. Loss of one hexose unit led to the fragment $[M - 162 + H]^+$ at *m*/*z* 437. Thus, the molecular formula could be deduced as $C_{27}H_{35}O_{15}$. Acid hydrolysis of **2** released only D-glucose, identified as mentioned above. The ^{1}H NMR spectrum was similar to that of **1**. The main difference was the presence of two anomeric protons at δ 5.06 (d, $J = 7.5$ Hz) and δ 4.41 (d, $J = 7.9$ Hz) as well as of the signals corresponding to two sugar units between δ 3.29 and δ 4.22. Complete assignment of all ^{1}H and ^{13}C resonances were performed by the 1D and 2D NMR experiments described above. In addition, a 1D TOCSY secured the assignments of the sugar spin system of each monosaccharide, thus confirming the two sugar residues as β-D-glucopyranosyl units. The location of the interglycosidic linkage could be deduced from the downfield shift of C-6′ (δ 70.2) when compared with the corresponding carbon in compound **1**. The interglycosidic linkage and the connecting point of the saccharide to the aglycon were established by the HMBC spectrum, which showed correlations between the proton at δ 5.06 (H-1 glc′) with C-9 of the aglycon at δ 159.4, between the proton at δ 4.41 (H-1 glc″) with C-6 glc′ at δ 70.2, and between the protons at δ 4.22 and 3.90 (H-6_a glc′ and H-6b glc′) with C-1 glc″ at δ 104.6. The β-configuration of both glucose moieties was deduced from their couplings constant of 7.5 Hz. Thus, the structure of **2** was defined as being 3,4-dihydro-10-hydroxy-7-methoxy-3-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one-9-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside.

Compound **3** was obtained as a gummy solid that showed a blue spot on TLC with an R_f value of 0.45 (BuOH−AcOH−H_2O 12:3:5). The ES−MS was fully similar to that of **2**, indicating an isomeric compound with molecular formula $C_{27}H_{35}O_{15}$. Acid hydrolysis of **3** afforded D-glucose and D-allose. Concerning the aglycon, λ, ^{1}H and ^{13}C NMR signals were almost superimposable on those of **1** and **2**. The main differences refer to the sugar moieties attached to the aglycon. The ^{1}H NMR spectrum exhibited two anomeric signals at δ 5.03 (d, $J = 7.9$ Hz) and 4.78 (d, $J = 7.4$ Hz), showing the β-configuration of both sugars. The complete sequence of the chemical shifts for each sugar was obtained by 1D TOCSY and DFQ−COSY experiments starting from the anomeric protons. Particularly characteristic of the allose moiety was the presence of only three signals after irradiating on $H_{1''}$ (δ 4.78), indicating the lack of transference of coherence between $H_{3''}$ and $H_{4''}$ due to the small coupling constant observed ($J_{H-3''-H4''} = 2.5$ Hz). The HMBC experiment showed correlations between the proton at 5.03 (H-1 glc′) and C-9 of the aglycon (δ 159.0), between the proton at δ 4.78 (H-1_{all}) and C-6 glc′ (δ 69.9), and between the protons at δ 3.91 and 4.26 (H-6a glc′ and H-6b glc′) with C-$1_{all''}$ (δ 102.5). Thus, compound **3** is 3,4-dihydro-10-hydroxy-7-methoxy-3-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one-9-*O*-β-D-allopyranosyl(1→6)-β-D-glucopyranoside.



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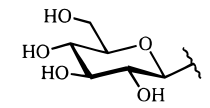
1



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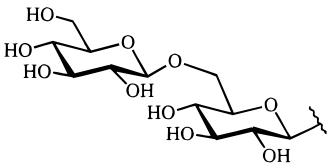

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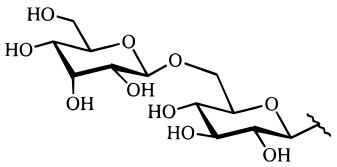

To define the absolute configuration at C-3 of the aglycon, the CD spectra of the hydrolyzed aglycons of compounds **2** and **3** were recorded. The CD curve showed negative Cotton effects at 268 and 222 nm, in good agreement with the CD measurements reported for 3,4-dihydro-9,10-dihydroxy-7-methoxy-3(*R*)-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one, which was previously named *semi*-vioxanthin, an isocoumarin with antibiotic properties isolated from *Penicillium citreo-viride* and identified by spectroscopic analysis.[10] This finding indicated the *R* configuration at C-3 and, together with the above data, allowed for the identification of the aglycon of **2** and **3** as 3,4-dihydro-9,10-dihydroxy-7-methoxy-3(*R*)-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one. Due to the lower amount, enzymatic hydrolysis of compound **1** was not performed. The absolute configuration at C-3 of the aglycon, however, is supposed, also in this case, to be *R*, and is also 3,4-dihydro-9,10-dihydroxy-7-methoxy-3(*R*)-methyl-1H-3,4-dihydronaphtho-[2,3*c*]-pyran-1-one.

Chemical studies of the Eriocaulaceae are scarce. The classic taxonomy of the family is rather complex. *Paepalanthus* is the largest genus and is the one that presents the most morphological variations. The species from the subgenus *Platycaulon* are characterized by having flat and joined scapes. Based on the morphology of the flowers, Giulietti has pointed out a relationship among the genera *Paepalanthus*, *Blastocaulon*, and *Syngonanthus*.[4] After studying the parafinic profile of some plants from the Eriocaulaceae family, Salatino et al. concluded that this class of compound could not afford a secure differentiation among the genera *Paepalanthus*, *Syngonanthus*, and *Leiothrix*.[11] The unusual glycosylated naphthopyranones herein

isolated may serve as a taxonomic marker of the genus *Paepalanthus*, because these compounds have not been reported in other genera of the Eriocaulaceae family. This is the first report of the occurrence of these compounds from this genus. Indeed, to our knowledge, naphthopyranones have never been used as taxonomic markers for any taxon. For a better understanding of the chemical interrelationships among the genera, however, it will be necessary to investigate many other species both from *Paepalanthus* as well as from other genera of the Eriocaulaceae family.

Experimental Section

General Experimental Procedures. NMR spectra in CD_3OD were obtained using a Bruker DRX-600 spectrometer,operating at 599.19 MHz for ^1H and 150.86 MHz for ^{13}C. 2D experiments: $^1H-^1H$ DQF−COSY[12] (double quantum filtered direct chemical shift correlation spectroscopy), inverse-detected $^1H-^{13}C$ HSQC[13] (heteronuclear single quantum coherence), HMBC[14] (heteronuclear multiple bond connectivity). The selective excitation spectra, 1D TOCSY[15] were acquired using waveform generator-based GAUSS shaped pulses, mixing time ranging from 100 to 120 ms and a MLEV-17 spin-lock field of 10 kHz preceded by a 2.5 ms trim pulse. Optical rotations were measured on a Perkin−Elmer 141 polarimeter using a sodium lamp operating at 589 nm in 1% w/v solutions in MeOH. ES−MS were performed in a Fisons Platform spectrometer in the positive mode (100 V). The samples were dissolved in MeOH and injected directly. UV spectra were obtained on a Beckman DU 670 spectrophotometer. CD measurement was performed on a JASCO J-7140 spectropolarimeter. HPLC separations were achieved on a Waters 590 system equipped with a Waters R401 refractive index detector and with a Waters μ-Bondapak RP_{18} columns and a U6K injector. GC−MS were run using a Hewlett−Packard 5890 gas chromatograph equipped with mass-selective detector MSD 5970 MS and a fused-silica column HP-5 (25 m × 0.2 mm; i.d. 0.33 mm film).

Plant Material. The leaves of *P. vellozioides* Ruhland (voucher number CFSC 13842) and *P. latipes* Silv. (voucher number CFSC 13840) were collected in January 1996, at the Serra do Cipo, State Minas Gerais, Brazil. Both species were authenticated by Prof. Paulo Takeo Sano from Instituto de Biociências, USP, Sao Paulo. Voucher specimens were deposited at the Herbarium of the IB−ISP.

Extraction and Isolation. The dried and powdered leaves of *P. vellozioides* (500 g) were macerated successively with 4 L $CHCl_3$ and then 4 L MeOH (one week each). Solvents were evaporated under vacuum. The crude MeOH extract (61 g) was dissolved in 5 L of H_2O and centrifuged. The supernatant was filtered on an Amberlite XAD-2 column (Aldrich, USA) eluted first with H_2O and then with MeOH, affording 6.0 g of the MeOH fraction. Of this MeOH fraction 2.0 g were chromatographed on a Sephadex LH-20 column (100 × 5 cm), with MeOH as eluent. Fractions (8 mL) were collected and checked by TLC [Si gel plates, *n*-BuOH−AcOH−H_2O (12:3:5)]. Fractions 32−40 (230 mg) containing the crude glycosidic mixture were further purified by reversed-phase HPLC (RP_{18}, MeOH−H_2O 2:3) to give pure compounds **1** (5 mg, t_R = 42.0 min), **2** (20 mg, t_R = 29.5 min), and **3** (1.5 mg, t_R = 33.0 min). *P. latipes* (500 g) was submitted to the same procedure affording 59 g of the crude MeOH extract, which, after filtering on XAD-2, led to 5.5 g of the MeOH fraction. After fractioning 2.0 g of this extract on Sephadex LH-20 and further purifying the fractions 29−40 in the same conditions described earlier, we obtained compounds **1** (1.5 mg), **2** (6.5 mg), and **3** (15 mg).

Acid Hydrolysis of Compounds 1−3, Glycosidic Constituents. A solution of each compound (4 mg) in 10% H_2SO_4−EtOH (1:1, 3.5 mL) was refluxed for 4 h. The reaction mixture was diluted with H_2O and then extracted with Et_2O. The Et_2O layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The H_2O layer was neutralized with Amberlite MB-3 ion-exchange resin and evaporated to dryness. The resulting monosaccharides were reacted with TRISIL-Z (Pierce) and analyzed by GC−MS. Retention times were identical to those of the authentic silylated sugars.

Enzymatic Hydrolysis of Compounds 2−3. The compound (ca. 6 mg) in citrate buffer (pH 5.0) (1.5 mL) was incubated with glycosidase mixture (6 mg) from *Charonia lampas* (Scikagaku Kogyo) at 40 °C for 24−48 h. The hydrolyzed aglycon was extracted with *n*-BuOH, and the extract was evaporated to dryness to give *semi*-vioxanthin.

Compound 1: $[\alpha]^{25}_D$ −121° (*c* 0.1, MeOH); UV λ_{max} (MeOH) (log ϵ) 360 (1.52), 306 (1.04), 261 (4.75), 216 (2.84), 204 (3.05); ^1H NMR data (CD_3OD, 600 MHz) δ 7.04 (1H, d, J = 1.5 Hz, H-8), 6.99 (1H, s, H-5), 6.87 (1H, d, J = 1.5 Hz, H-6), 5.01 (1H, d, J = 7.5 Hz, H-1 glc′), 4.76 (1H, m, H-3), 3.98 (1H, dd, J = 2.5, 11.0 Hz, H-6b glc′), 3.93 (3H, s, OMe), 3.77 (1H, dd, J = 5.0, 11.0 Hz, H-6a glc′), 3.67 (1H, dd, J = 7.5, 9.0 Hz, H-2 glc′), 3.55 (1H, dd, J = 9.0, 9.0 Hz, H-3 glc′), 3.55 (1H, m, H-5 glc′), 3.47 (1H, dd, J = 9.0, 9.0 Hz, H-4 glc′), 3.11 (1H, dd, J = 2.6, 16.2 Hz, H-4b), 2.97 (1H, dd, J = 11.4, 16.2 Hz, H-4a), 1.53 (3H, d, J = 6.1 Hz, Me-11); ^{13}C NMR data (CD_3OD, 600 MHz) δ 172.8 (C-1), 163.8 (C-10), 163.0 (C-7), 159.4 (C-9), 142.2 (C-5a), 136.0 (C-4a), 116.9 (C-5), 111.2 (C-9a), 104.6 (C-8), 103.6 (C-1 glc′), 102.0 (C-6, C-10a), 78.2 (C-5 glc′), 77.4 (C-3 glc′), 77.3 (C-3), 74.8 (C-2 glc′), 71.4 (C-4 glc′), 62.9 (C-6 glc′), 56.1 (OMe), 35.0 (C-4), 20.9 (C-11) ES−MS *m/z* 459 $[M + Na]^+$, *m/z* 437 $[M + H]^+$, *m/z* 297 $[M - 162 + Na]^+$, *m/z* 275 $[M - 162 + H]^+$.

Compound 2: $[\alpha]^{25}_D$ −80° (*c* 0.1, MeOH); UV λ_{max} (MeOH) (log ϵ) 360 (1.46), 304 (1.00), 260 (4.56), 216 (2.73), 202 (2.96); ^1H NMR data (CD_3OD, 600 MHz) δ 7.05 (1H, d, J = 1.5 Hz, H-8), 7.05 (1H, s, H-5), 6.90 (1H, d, J = 1.5 Hz, H-6), 5.06 (1H, d, J = 7.5 Hz, H-1 GLC′), 4.81 (1H, m, H-3), 4.41 (1H, d, J = 7.9 Hz, H-1 GLC″), 4.22 (1H, dd, J = 2.5, 11.4 Hz, H-6b GLC′), 3.95 (3H, s, OMe), 3.90 (1H, dd, J = 5.0, 11.4 Hz, H-6a GLC′), 3.90 (1H, dd, J = 2.5, 11.4 Hz, H-6b GLC″), 3.84 (1H, m, H-5 GLC′), 3.68 (1H, dd, J = 7.5, 9.0 Hz, H-2 GLC′), 3.68 (1H, dd, J = 5.0, 11.4 Hz, H-6a GLC″), 3.56 (1H, dd, J = 9.0, 9.0 Hz, H-3 GLC′), 3.48 (1H, dd, J = 9.0, 9.0 Hz, H-4 GLC′), 3.39 (1H, dd, J = 9.0, 9.0 Hz, H-4 GLC″), 3.35 (1H, dd, J = 9.0, 9.0 Hz, H-3 GLC″), 3.29 (1H, dd, J = 7.9, 9.0 Hz, H-2 GLC″), 3.29 (1H, m, H-5 GLC″), 3.10 (1H, dd, J = 2.6, 16.2 Hz, H-4b), 3.00 (1H, dd, J = 11.4, 16.2 Hz, H-4a), 1.53 (3H, d, J = 6.1 Hz, Me-11); ^{13}C NMR data (CD_3OD, 600 MHz) δ 172.8 (C-1), 163.9 (C-10), 163.0 (C-7), 159.4 (C-9), 142.0 (C-5a), 136.0 (C-4a), 116.8 (C-5), 111.0 (C-9a), 104.8 (C-8), 104.6 (C-1 GLC″), 103.5 (C-1 GLC′), 102.0 (C-6, C-10a), 77.8 (C-5 GLC″), 77.4 (C-3 GLC″), 77.3 (C-3, C-5 GLC′), 77.2 (C-3 GLC′), 75.0 (C-2 GLC″), 74.8 (C-2 GLC′), 71.8 (C-4 GLC″), 71.4 (C-4 GLC′), 70.2 (C-6 GLC′), 62.6 (C-6 GLC″), 56.1 (OMe), 35.0 (C-4), 20.9 (C-11); ES−MS *m/z* 621 $[M + Na]^+$, *m/z* 599 $[M + H]^+$, *m/z* 297 $[M - 162 + Na]^+$, *m/z* 437 $[M - 162 + H]^+$.

Compound 3: $[\alpha]^{25}_D$ −109° (*c* 0.1, MeOH); UV λ_{max} (MeOH) (log ϵ) 360 (1.50), 306 (1.02), 262 (4.68), 218 (2.86), 204 (3.01); ^1H NMR data (CD_3OD, 600 MHz) δ 6.97 (1H, d, J = 1.5 Hz, H-8), 6.96 (1H, s, H-5), 6.81 (1H, d, J = 1.5 Hz, H-6), 5.03 (1H, d, J = 7.5 Hz, H-1 GLC′), 4.78 (1H, d, J = 7.4 Hz, H-1 all), 4.76 (1H, m, H-3), 4.26 (1H, dd, J = 2.5, 11.4 Hz, H-6b GLC′), 4.13 (1H, dd, J = 2.8, 2.8 Hz, H-3 all), 3.93 (3H, s, OMe), 3.91 (1H, dd, J = 5.0, 11.4 Hz, H-6a GLC′), 3.89 (1H, dd, J = 3.0, 12.0 Hz, H-6b all), 3.84 (1H, m, H-5 GLC′), 3.76 (1H, m, H-5 all), 3.70 (1H, dd, J = 7.9, 9.0 Hz, H-2 GLC′), 3.69 (1H, dd, J = 5.0, 12.0 Hz, H-6a all), 3.59 (1H, dd, J = 9.0, 9.0 Hz, H-3 GLC′), 3.55 (1H, dd, J = 9.0, 9.0 Hz, H-4 GLC′), 3.55 (1H, dd, J = 2.8, 9.2 Hz, H-4 all), 3.45 (1H, dd, J = 2.8, 7.4 Hz, H-2 all), 3.07 (1H, dd, J = 11.4, 16.0 Hz, H-4a), 2.91 (1H, dd, J = 2.6, 16.0 Hz, H-4b), 1.53 (3H, d, J = 6.1 Hz, Me-11); ^{13}C NMR data (CD_3OD, 600 MHz): δ 172.8 (C-1), 163.9 (C-10), 162.8 (C-7), 159.0 (C-9), 142.4 (C-5a), 135.9 (C-4a), 117.0 (C-5), 111.2 (C-9a), 104.5 (C-8), 103.5 (C-1 GLC′), 102.5 (C-1 all), 102.2 (C-6), 101.9 (C-10a), 77.3 (C-3), 77.1 (C-3 GLC′, C-5 GLC′), 75.3 (C-5 all), 74.9 (C-2 GLC′), 72.6 (C-3 all), 72.1 (C-2 all), 71.2 (C-4 GLC′), 69.9 (C-6 GLC′), 68.6 (C-4 all), 62.7 (C-6 all), 55.9 (OMe), 35.3 (C-4), 20.9 (C-11) ^{13}C NMR data (CD_3OD, 600 MHz) ES−MS *m/z* 621 $[M + Na]^+$, *m/z* 599 $[M + H]^+$, *m/z* 297 $[M - 162 + Na]^+$, *m/z* 437 $[M - 162 + H]^+$.

Hydrolyzed Aglycon of Compounds 2 and 3 (*semi*-vioxanthin). CD curve (cyclohexan/5% dioxan: λ_{max} ($[\Theta]^{25}$) = 268 (−28 000), 246 (+ 5000), 222 nm (−27 000).

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References and Notes

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