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Quercetagetin 7-methyl ether glycosides from *Paepalanthus vellozioides* and *Paepalanthus latipes*

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Abstract

Several new quercetagetin 7-methyl ether glycosides were characterized from the ethanolic extracts of scapes and leaves of *Paepalanthus vellozioides* and *P. latipes*. Their structures were determined mainly by 600 MHz NMR spectroscopy.

Keywords: *Paepalanthus vellozioides*; *Paepalanthus latipes*; Eriocaulaceae; Quercetagetin 7-methyl ether glycosides

1. Introduction

The genus *Paepalanthus* (Eriocaulaceae) contains ca. 400 species found mostly in Brazil (Ruhland, 1903). *P. vellozioides* and *P. latipes* are small shrubs native to the 'campos rupestres' of Serra do Cipò, in Southwest Brazil, and are members of the subgenus *Platycaulon* (Giulietti & Pirani, 1988). Plants from the Eriocaulaceae are important world wide as ornamental plants (Teixeira, 1987). Botanical aspects of the family have been widely investigated but phytochemical investigations are scarce and limited to a small number of species. Thus some napthopyrones and flavonols have been reported (Vilegas et al., 1988; Vilegas, Roque, Salatino, Giesbrecht, & Davino, 1990; Vilegas, Dokkeddal, Rastrelli, Piacente, & Pizza, 1998) and Bate-Smith and Harborne have identified quercetagetin and its 6-methyl ether, patuletin, as characteristic constituents in *Eriocaulon* species (Bate-Smith & Harborne, 1969). In this work we describe the isolation and structured elucidation of the leaf flavonoids of *P. vellozioides* and *P. latipes*.

2. Results and discussion

A TLC examination and treatment with NP:PEG reagent (Wagner, Bladt, & Zgainski, 1984) demonstrated that the MeOH fraction of the leaves of both *P. vellozioides* and *P. Latipes* contained several flavonol glycosides based upon their R_f values and orange colour under UV light (345 nm). After isolation by gel permeation chromatography and further purification by HPLC (see Section 3) the structures of the compounds were elucidated through the combined use of 600 MHz NMR techniques (DEPT, DFQ-COSY, 1D-TOCSY, HMBC, and HSQC), mass spectrometry (Electrospray-MS) and UV spectral analysis. The chemical shift values of all the protons and carbons were unambiguously assigned. All six flavonols isolated were quercetagetin 7-methyl ether glycosides. Of these, only **1** had been reported previously in the literature where its identification was based solely on UV-spectroscopy

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with no NMR data given (Bohm & Choy, 1987). We have performed a series of 1D and 2D NMR experiments in order to fully characterize **1** and the other five glycosides (**2**–**6**).

The ES–MS spectrum (100 V, positive mode) of **1** showed a pseudo molecular ion $[M+H]^+$ at m/z 333, consistent with a molecular formula $C_{16}H_{12}O_8$. The adducts with sodium $[M+Na]^+$ at m/z 355 and with potassium $[M+K]^+$ at m/z 371 were also observable. Loss of the CH_3 group led to the ion $[(M+H)\text{-}15]^+$ at m/z 318, while loss of the OCH_3 group afforded the ion $[(M+H)\text{-}30]^+$ at m/z 302. The peak at m/z 182 was due to the ion with formula $C_8H_6O_5$, resulting from the retro-Diels–Alder fragmentation of **1**, and suggested the location of the methoxyl at the A ring of a flavonol. The ^{1}H NMR spectrum (see Section 3) showed a doublet at δ 7.79 (1H, $J=1.8$ Hz), a double doublet at δ 7.68 (1H, $J=1.8$ and 8.3 Hz) and a doublet at δ 6.91 (1H, $J=8.3$ Hz), due to the B ring of a 3′,4′ dioxygenated flavonol (Markham & Geiger, 1996). The intense signal at δ 4.00 (3H) related to one OMe group. The ^{13}C NMR spectrum showed 16 carbons (see Section 3). The HSQC spectrum showed a correlation between the singlet at δ 6.74 (H-8) with the signal at δ 91.3 (C-8). The HMBC spectrum gave correlations between H-8 and C-6 and C-10 and between OMe (δ 4.00) and C-6, C-7 and C-8. Further confirmation was obtained through a NOED experiment, by irradiating the protons of the OMe group which showed a correlation with the H-8 proton. These data are compatible with the location of the methoxyl at the position 7 (Agrawal, 1989). Thus **1** is quercetagetin 7-methyl ether, previously isolated from *Balsamorrhiza deltoideae* (Bohm & Choy, 1987).

The ES–MS (100 V, positive ion) of **2** exhibited the protonated ion $[M+H]^+$ at m/z 495, indicating the molecular formula $C_{22}H_{22}O_{13}$. Loss of a hexose moiety (162 u) led to the protonated aglycone $[A+H]^+$ at m/z 333. The ^{1}H NMR spectrum of the aglycone portion of **2** was almost superimposable on that of **1** revealing the same flavonoid nucleus. Acid hydrolysis of **2** furnished **1** and methanolysis furnished D-glucose. The glucose moiety was confirmed by the presence of an anomeric proton at δ 5.26 ($J=7.5$ Hz) as well as from six other signals between δ 3.25 and δ 3.93 in the ^{1}H NMR. The coupling constant of 7.5 Hz indicated the β-configuration of the sugar and the downfield shift of the C-2 resonance (δ 159.1) in **2** when compared to **1** indicate that the glucose moiety was bonded to position 3 of the aglycone (Agrawal, 1989). The HMBC spectrum confirmed the location of the glucose at C-3 by showing connectivity between the anomeric signal of glucose and the carbon at δ 135.3 (C-3). The HSQC spectrum furnished all the direct correlations between

Table 1
^{1}H NMR data (CD_3OD, 600 MHz) of sugar portion of compounds **1**–**6**[a]

H	**2**	**3**	**4**	**5**	**6**
	glucose	glucose	glucose	glucose	glucuronic acid
1″	5.26 d (7.5)	4.94 d (7.5)	5.32 d (7.5)	5.80 d (7.5)	5.27 d (7.5)
2″	3.52 dd (7.5;9.5)	3.59 dd (7.5;9.5)	3.60 dd (7.5;9.5)	3.70 dd (7.5;9.5)	3.57 dd (7.5;9.5)
3″	3.46 dd (9.5;9.5)	3.59 dd (9.5;9.5)	3.64 dd (9.5;9.5)	3.60 dd (9.5;9.5)	3.53 dd (9.5;9.5)
4″	3.38 dd (9.5;9.5)	3.48 dd (9.5;9.5)	3.67 dd (9.5;9.5)	3.38 dd (9.5;9.5)	3.64 dd (9.5;9.5)
5″	3.25 ddd (9.5;5.0;3.0)	3.54 ddd (9.5;5.0;3.0)	3.41 ddd (9.5;5.0;3.0)	3.26 ddd (9.5;5.0;3.0)	3.28 d (9.5)
6a″	3.73 dd (12.0;3.0)	3.77 dd (12.0;3.0)	3.63 dd (12.0;3.0)	3.58 dd (12.0;3.0)	
6b″	3.93 dd (12.0;5.0)	3.92 dd (12.0;5.0)	3.68 dd (12.0;5.0)	3.76 dd (12.0;5.0)	
			glucose	rhamnose	glucose
1‴			4.43 d (7.5)	5.26 d (1.5)	4.70 d (7.5)
2‴			3.25 dd (7.5;9.5)	4.04 dd (1.5;3.5)	4.88 dd (7.5;9.5)
3‴			3.39 dd (9.5;9.5)	3.81 dd (3.5;9.5)	3.62 dd (9.5;9.5)
4‴			3.34 dd (9.5;9.5)	3.36 dd (9.5;9.5)	3.44 dd (9.5;9.5)
5‴			3.36 ddd (9.5;5.0;3.0)	4.08 dd (9.5;6.0)	3.45 ddd (9.5;5.0;3.0)
6a‴			3.70 dd (12.0;3.0)	0.98 d (6.0)	3.74 dd (12.0;3.0)
6b‴			3.92 dd (12.0;5.0)		3.95 dd (12.0;5.0)
					caffeoyl
2					7.04 d (1.5)
5					6.77 d (7.5)
6					6.95 dd (1.5;7.5)
α					6.30 d (16.0)
β					7.60 d (16.0)

[a] Assignments confirmed by DQF-COSY and 1D-TOCSY experiments, J values in Hz presented in parentheses.

Table 2
^{13}C NMR (CD_3OD) assignments for compounds **1**–**6**[a]

Position	**2**	**3**	**4**	**5**	**6**
	glucose	glucose	glucose	glucose	glucuronic
1″	104.1	102.6	104.1	100.2	104.2
2″	75.4	74.5	75.6	80.0	75.1
3″	78.0	77.2	76.5	78.6	78.1
4″	71.0	71.0	80.5	71.5	80.0
5″	78.1	77.8	77.1	78.1	76.5
6″	62.2	62.0	61.8	62.2	176.0
			glucose	rhamnose	glucose
1‴			104.5	102.6	102.5
2‴			75.0	72.2	75.0
3‴			77.7	72.2	76.2
4‴			71.2	73.8	71.3
5‴			78.3	69.7	78.2
6‴			62.2	17.5	62.2
					caffeoyl
1					127.7
2					115.2
3					146.7
4					149.7
5					116.5
6					123.1
α					146.7
β					114.8
C=O					168.2

[a] Assignments confirmed by HSQC and HMBC experiments.

protons and carbons (Tables 1 and 2). Thus, the structure of **2** could be deduced as being quercetagetin 7-methyl ether-3-*O*-β-D-glucopyranoside.

The ES–MS spectrum of **3** was identical to that of **2**, indicating an isomeric compound of formula $C_{22}H_{22}O_{13}$. Methanolysis of **3** afforded D-glucose. The ^1H NMR spectrum of **3** was similar to those of **1** and **2**. Inspection of the NMR data (see Section 3) showed that the main difference was a downfield shift of +0.4 of the H-5′ resonance in **3** (δ 7.31) suggesting that the glucose moiety was attached to the B ring. The constant coupling $J=7.5$ Hz of the anomeric proton (δ 4.94) established the β configuration of the sugar. The HMBC spectrum showed the coupling of the H-1″ of glucose to C-4′, confirming that the sugar is bonded to C-4′; of H-2′ to C-4′, C-6′ and C-2; of H-5′ to C-3′ and C-1′; and of H-6′ to C-2, C-2′ and C-4′. Consequently, **3** was determined to be quercetagetin 7-methyl ether 4′-*O*-β-D-glucopyranoside (see Section 3, Tables 1 and 2).

The ES–MS (100 V, positive ion) of **4** ($C_{28}H_{32}O_{18}$) exhibited a protonated ion $[M+H]^+$ at m/z 657, and peaks at m/z 495 $[(M+H)\text{-}162]^+$ and 333 $[(M+H)\text{-}162\times2]^+$ due to the subsequent losses of 2 hexose units. Compound **4** showed ^1H and ^{13}C NMR spectra for the aglycone moiety almost superimposable on those of **2**. The ^1H NMR spectrum presented two doublets at δ 5.32 (d, $J=7.5$ Hz) and at δ 4.43 (d, $J=7.5$ Hz) as well as protons corresponding to two saccharidic moieties between δ 3.25 and 3.92. In the ^{13}C NMR spectrum, 12 additional signals also indicated the presence of two sugar moieties. Methanolysis of **4** gave only D-glucose. The chemical shift of C-2 (δ 159.3) showed that the disaccharidic unity was bonded to position 3 of the aglycone. 1D-TOCSY combined to DFQ-COSY experiments afforded the spin sequences of the two glucose moieties. The HMBC spectrum showed a correlation between the proton at δ 5.32 (H-1″-glc) with the C-3 of the aglycone (δ 135.5) and between the proton at δ 4.42 (H-1‴-glc) with the C-4″ of the inner glucose (δ 80.5). From these observations we deduced the existence of a β-D-glucopyranosyl-(1->4)-β-D-glucopyranoside (cellobioside) moiety bonded to position 3 of the aglycone. Thus, **4** is quercetagetin 7-methyl ether 3-*O*-cellobioside.

The ES–MS (100 V, positive ion) of **5** ($C_{28}H_{32}O_{17}$) showed the protonated ion $[M+H]^+$ at m/z 641 and peaks ascribable to the subsequent losses of one deoxyhexose unit at m/z 495 $[(M+H)\text{-}146]^+$ and one hexose unit at m/z 333 $[(M+H)\text{-}146\text{–}162]^+$. Methanolysis of **5** gave D-glucose and L-rhamnose. The ^1H and ^{13}C NMR spectra of **5** showed that its aglycone was again quer-

cetagetin. Concerning the sugars, the ^{1}H NMR spectrum clearly showed one doublet with $J=7.5$ Hz at δ 5.80. Another doublet with smaller coupling constant ($J=1.5$ Hz) at δ 5.26 and an intense doublet integrating for three protons with $J=6.0$ Hz strongly suggested the presence of a rhamnose unity. From the DFQ-COSY and 1D TOCSY spectra we could assign all the spin sequences of the two sugars. The connecting point of the saccharidic moiety with the aglycone and the interglycosidic linkage were determined from the HMBC spectrum, that showed connectivity between the H-1″ of glucose and C-3 and between the H-1‴ of rhamnose and the C-2″ of the glucose. Therefore, we determined **5** as quercetagetin 7-methyl ether 3-*O*-neohesperidoside.

The ES–MS (100 V, positive ion) of **6** ($C_{37}H_{36}O_{22}$) showed the protonated ion $[M+H]^+$ at m/z 833, and peaks at m/z 671 $[M\text{-}162+H]^+$ and 509 $[M\text{-}162\times 2+H]^+$. Accurate observation of the ^{1}H and ^{13}C NMR signals of **6** revealed the same chemical shifts as for the aglycone of **1** in quercetagetin 7-methyl ether (see Section 3). Acid hydrolysis of **6** released **1** and caffeic acid. Methanolysis of **6** afforded glucose and glucuronic acid. In the ^{1}H NMR spectrum, the doublets at δ 7.60 (H-β) and δ 6.30 (H-α) ($J=16.0$ Hz), the doublets at δ 7.04 ($J=1.5$ Hz), and δ 6.77($J=7.5$ Hz) and the double doublet at δ 6.95 ($J=7.5$ Hz and 1.5 Hz) were consistent with the presence of a caffeoyl moiety (Table 1). The signals at δ 5.27 ($J=7.5$ Hz) and δ 4.70 ($J=7.5$ Hz) in the ^{1}H NMR spectrum clearly indicated the presence of two sugar moieties. The DFQ-COSY and 1D-TOCSY spectra afforded the sequences of the protons of each sugar (Table 1). The HSQC spectrum established all the correlations between protons and carbons of **6** (Table 2 and Section 3). The HMBC spectrum showed connectivities for H-1″-glucA/C-3, H-1‴-glc/C-4″-glucA, H-2‴-glc/C=O of the caffeoyl moiety. Thus, **6** is identified as quercetagetin 7-methyl ether 3-*O*-[2-*O*-caffeoyl-β-D-glucopyranosyl (1-2)-*O*-β-D-glucuronopyranoside].

The presence of quercetagetin 7-methyl ether glycosides in the leaves of *Paepalanthus* species (Fig. 1) is of taxonomic interest since species in the related genera *Leiothix* and *Syngonanthus* genus mainly produce luteolin *O*- and *C*-glycosides but no 7-methoxyflavonol derivatives. Thus, these 7-methoxy flavonols may be considered as taxonomic markers for *Paepalanthus* species.

3. Experimental

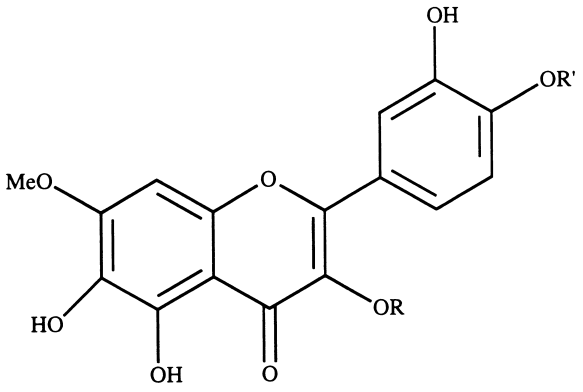
ESMS spectra were performed in a Fisons Platform spectrometer in the positive mode (100 V), the samples were dissolved in MeOH and injected directly. NMR spectra in CD_3OD were obtained using a Brucker DRX-600 spectrometer, operating at 599.19 MHz for ^{1}H and 150.86 MHz for ^{13}C. The DEPT (distortionless enhancement by polarization transfer) experiments were performed using a transfer pulse of 135°. Polarization transfer delays were adjusted to average CH coupling of 135 Hz. ^{1}H–^{1}H DFQ-COSY (Bodenhausen, Freeman, Morrois, Neidermeyer, & Turner, 1977), ^{1}H–^{13}C HSQC (Bodenhausen & Ruben, 1980), HMBC (Martin & Crouch, 1991) and 1D-TOCSY (Davis & Bax, 1985) experiments were obtained using conventional pulse sequences. HPLC separations were achieved on a Waters 590 system equipped with a Waters R401 refractive index detector, a Waters-Bondapak RP18 column and a UK6 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).

3.1. Plant material

Fresh leaves and scapes of *P. vellozioides* and *P. latipes* were collected at Serra do Cipò-MG, Brazil in January 1997. Authentication of the plant material was carried out by Professor Paulo Takeo Sano. Voucher specimens were deposited at the Herbarium of the Instituto de Botanica da USP (*P. vellozioides* Ruhland CFSC 13842; *P. latipes* Silveira CFSC 13846).

3.2. Extraction and isolation

The separated scapes and powdered leaves (100 g each) of *P. vellozioides* and *P. latipes* were extracted ×2 with $CHCl_3$ and then ×2 with 80% MeOH (maceration at room temp., 1 week each solvent). The solvents were evaporated in vacuo yielding black syrups. The concd MeOH 80% extracts of each plant were redissolved in H_2O, filtered and submitted to XAD-2 CC eluted with 3 l H_2O and then 1 l of MeOH. A portion (1.2 g) of the MeOH residue of *P. latipes* was submitted to CC on Sephadex LH-20 (80× 2 cm). Frs (8 ml) were eluted with MeOH and checked by TLC on silica gel in BuOH:HOAc:H_2O (13:3:5). Frs 31–36 (116 mg) were further purified by HPLC on a Waters (μ-Bondapak RP-18 column (30 cm×7.6 mm i.d.) using MeOH:H_2O (9:11) as eluent to afford pure **4** (5 mg, R_t 13 min) and **2** (9 mg, R_t 16 min). Frs 41–44 (55 mg) contained pure **6** (12 mg, R_t 10 min), frs 51–56 (88 mg) contained pure **3** (10 mg, R_t 17 min) and frs 67–70 (35 mg) contained pure **1** (9 mg, R_t 24 min). The MeOH extract (1.2 g) of *P. vellozioides* was submitted to the same procedure to Sephadex LH-20 and to HPLC to afford from frs 33–40 (143 mg) pure **4** (11 mg, R_t 13 min) and **2** (6 mg, R_t 16 min), from frs



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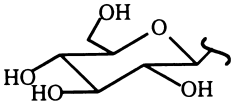
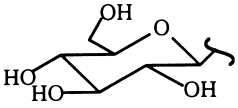
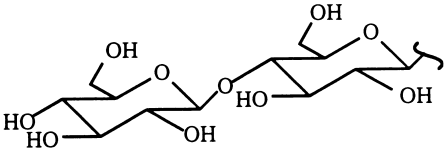
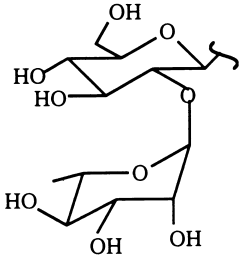
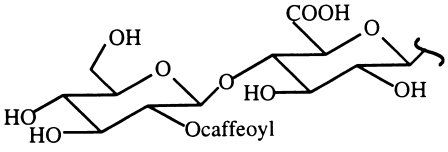
2		H
3	H	
4		H
5		H
6		H

Fig. 1. New quercetagetin 7-methyl ether glycosides from *P. vellozioides* and *P. latipes* leaves.

48–52 (90 mg) pure **5** (16 mg, R_t 14 min) and from frs 64–69 (45 mg) pure **1** (4.5 mg, R_t 24 min).

3.3. Acid hydrolysis of compounds 2–6

A solution of each compound (3 mg) in 10% HCl (3.5 ml) was refluxed for 2 h. The reaction mixture was diluted with H_2O and then extracted with EtOAc. The resulting aglycones were identified by their ^{1}H NMR spectra.

3.4. Methanolysis of compounds 2–6

Each compound (1.0 mg) was heated in a vial for 24 h at 80°C in MeOH–2% HCl (2 ml). After MeOH and HCl distillation in a N_2 stream, Ag_2CO_3 and MeOH were added until CO_2 production stopped. The mixture was centrifuged and the centrifugate was dried over P_2O_5. The resulting monosaccharides were treated with Trisil-Z (pierce) and analyzed by GC–MS. Retention times were identical to those of the authentic trisil-sugars.

3.5. Compound 1

$[\alpha]_D^{25} = -128.6$ (MeOH; *c* 0.1); UV λ_{max} (MeOH): 360, 280, 2.62, 2.10; EI–MS in positive ion mode: *m/z* 333 $[M+H]^+$, 355 $[M+Na]^+$, 371 $[M+K]^+$, 318 $[M-15+H]^+$, 302 $[M-31+H]^+$; ^{1}H NMR (CD_3OD) δ 7.79 (d, $J=1.8$ Hz, H-2′), 7.68 (dd, $J=1.8$, 8.3 Hz, H-6′), 6.91 (d, $J=8.3$ Hz, H-5′), 6.74 (s, H-8), 4.00 (s, OMe); ^{13}C NMR (CD_3OD) δ 177.1 (C-4), 155.7 (C-7), 150.7 (C-9), 148.5 (C-5, C-4′), 145.8 (C-2, C-3′), 136.9 (C-3), 130.1 (C-6), 124.1 (C-1′), 121.9 (C-6′), 116.3 (C-5′), 116.1 (C-2′), 105.5 (C-10), 91.3 (C-8), 57.0 (OCH_3).

3.6. Compound 2

$[\alpha]_D^{25} = -12.5$ (MeOH; *c* 0.1); UV λ_{max} (MeOH): 360, 282, 2.64, 2.10; EI–MS in positive ion mode: *m/z* 495 $[M+H]^+$, 333 $[A+H]^+$; ^{1}H NMR (CD_3OD) aglycone moiety δ 7.76 (d, $J=1.8$ Hz, H-2′), 7.63 (dd, $J=1.8$, 8.3 Hz, H-6′), 6.92 (d, $J=8.3$ Hz, H-5′), 6.79 (s, H-8), 4.01 (s, OCH_3); ^{13}C NMR (CD_3OD) aglycone moiety δ 179.0 (C-4), 159.2 (C-2), 155.6 (C-7), 150.9 (C-9), 149.8 (C-4′), 146.2 (C-5), 145.8 (C-3′), 135.3 (C-3), 131.0 (C-6), 123.4 (C-1′), 122.9 (C-6′), 117.4 (C-2′), 115.9 (C-5′), 106.7 (C-10), 91.1 (C-8), 56.9 (OCH_3); for the ^{1}H NMR and ^{13}C NMR data of the glucose unit see Tables 1 and 2.

3.7. Compound 3

$[\alpha]_D^{25} = -7.4$ (MeOH; *c* 0.1); UV λ_{max} (MeOH): 361, 280, 2.61, 2.10; EI–MS in positive ion mode: *m/z* 495 $[M+H]^+$, 333 $[A+H]^+$; ^{1}H NMR (CD_3OD) aglycone moiety δ 7.79 (d, $J=1.8$ Hz, H-2′), 7.73 (dd, $J=1.8$, 8.3 Hz, H-6′), 7.31 (d, $J=8.3$ Hz, H-5′), 6.72 (s, H-8), 4.00 (s, OCH_3); ^{13}C NMR (CD_3OD) aglycone moiety δ 177.0 (C-4), 155.7 (C-7), 150.7 (C-9), 147.8 (C-5), 147.1 (C-4′), 146.9 (C-3′), 145.3 (C-2), 137.3 (C-3), 129.9 (C-6), 127.0 (C-1′), 121.5 (C-6′), 116.9 (C-5′), 116.3 (C-2′), 105.3 (C-10), 91.3 (C-8), 57.0 (OCH_3); for the ^{1}H NMR and ^{13}C NMR data of the glucose unit see Tables 1 and 2.

3.8. Compound 4

$[\alpha]_D^{25} = -11.4$ (MeOH; *c* 0.1); UV λ_{max} (MeOH): 362, 281, 2.64, 2.12; EI–MS in positive ion mode: *m/z* 657 $[M+H]^+$, 495 $[M-162+H]^+$, 333 $[A+H]^+$; ^{1}H NMR (CD_3OD) aglycone moiety δ 7.75 (d, $J=1.8$ Hz, H-2′), 7.60 (dd, $J=1.8$, 8.3 Hz, H-6′), 6.90 (d, $J=8.3$ Hz, H-5′), 6.72 (s, H-8), 3.97 (s, OCH_3); ^{13}C NMR (CD_3OD) aglycone moiety δ 179.5 (C-4), 159.3 (C-2), 155.9 (C-7), 151.1 (C-9), 149.8 (C-4′), 146.6 (C-5), 145.8 (C-3′), 135.5 (C-3), 131.1 (C-6), 123.1 (C-1′, C-6′), 117.6 (C-2′), 116.0 (C-5′), 106.9 (C-10), 91.5 (C-8), 56.9 (OCH_3); for the ^{1}H NMR and ^{13}C NMR data of the sugar units see Tables 1 and 2.

3.9. Compound 5

$[\alpha]_D^{25} = -47.2$ (MeOH; *c* 0.1); UV λ_{max} (MeOH): 360, 281, 2.62, 2.12; EI–MS in positive ion mode: *m/z* 641 $[M+H]^+$, 495 $[M-146+H]^+$, 333 $[A+H]^+$; ^{1}H NMR (CD_3OD) aglycone moiety δ 7.68 (d, $J=1.8$ Hz, H-2′), 7.61 (dd, $J=1.8$, 8.3 Hz, H-6′), 6.90 (d, $J=8.3$ Hz, H-5′), 6.76 (s, H-8), 3.99 (s, OCH_3); ^{13}C NMR (CD_3OD) aglycone moiety 179.6 (C-4), 158.9 (C-2), 155.7 (C-7), 151.1 (C-9), 149.6 (C-4′), 147.0 (C-5), 146.1 (C-3′), 134.5 (C-3), 131.0 (C-6), 123.6 (C-1′), 123.2 (C-6′), 117.3 (C-2′), 116.0 (C-5′), 107.3 (C-10), 91.4 (C-8), 57.0 (OCH_3); for the ^{1}H NMR and ^{13}C NMR data of the sugar units see Tables 1 and 2.

3.10. Compound 6

$[\alpha]_D^{25} = -30.6$ (MeOH; *c* 0.1); UV λ_{max} (MeOH): 335, 284, 2.56, 2.14; EI–MS in positive ion mode: *m/z* 833 $[M+H]^+$, 671 $[M-162+H]^+$, 509 $[M-162\times 2+H]^+$, 333 $[A+H]^+$; ^{1}H NMR (CD_3OD) aglycone moiety δ 7.72 (d, $J=1.8$ Hz, H-2′), 7.59 (dd, $J=1.8$, 8.3 Hz, H-6′), 6.88 (d, $J=8.3$ Hz, H-5′), 6.72 (s, H-8), 3.99 (s, OCH_3); ^{13}C NMR (CD_3OD) aglycone moiety δ 179.6 (C-4), 159.3 (C-2), 156.0 (C-7), 151.1 (C-9), 149.9 (C-4′), 146.7 (C-5), 145.9 (C-3′), 135.6 (C-3), 131.2 (C-6), 123.2 (C-6′), 123.1 (C-1′), 117.7 (C-2′), 116.0 (C-5′), 106.9 (C-10), 91.6 (C-8), 57.0 (OCH_3); for the ^{1}H NMR and ^{13}C NMR data of the sugar units see Tables 1 and 2.

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