New Antioxidant *C*-Glucosylxanthones from the Stems of *Arrabidaea samydoides*

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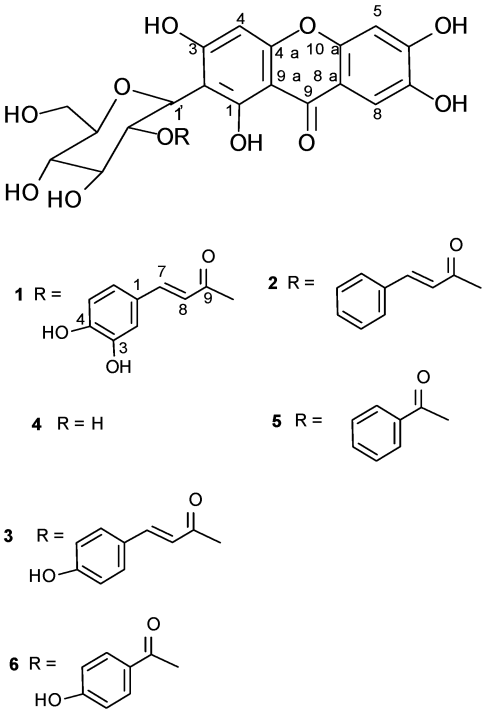
Three new *C*-glucosylxanthones, 2-(2′-*O*-*trans*-caffeoyl)-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**1**), 2-(2′-*O*-*trans*-cinnamoyl)-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**2**), and 2-(2′-*O*-*trans*-coumaroyl)-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**3**), were isolated from the stems of *Arrabidaea samydoides*, in addition to three known *C*-glucosylxanthones, mangiferin (**4**), 2-(2′-*O*-benzoyl)-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**5**), and muraxanthone (**6**). Their chemical structures were assigned on the basis of MS and 1D and 2D NMR experiments. Xanthones **1**−**6** showed moderate free radical scavenging activity against 1,1-diphenyl-2-picrylhydrazyl (DPPH) as well as antioxidant activity evidenced by redox properties measured on ElCD-HPLC.

As part of our bioprospecting program Biota-FAPESP (The Virtual Institute of Biodiversity), whose main goal is to discover potential antitumoral, antifungal, and antioxidant agents from plants of the Cerrado and Atlantic forest, we have screened hundreds of plants collected in the State of São Paulo. Among these, *Arrabidaea samydoides* was chosen for detailed chemical investigation due to prior antioxidant activity revealed on a TLC autographic assay sprayed with *β*-carotene solution, and to our knowledge there are no previous reports on chemical and biological studies. This species belongs to the family Bignoniaceae, which contains about 120 genera and 800 species distributed throughout tropical regions of South America and Africa.[1] Species from the genus *Arrabidaea* have been used in traditional medicine for wound asepsis and treating intestinal disorders.[2] In northeast Brazil, *Arrabidaea chica* is used in tattoos by Indians due to the pigments carajurin and carajurone.[2,3] A literature review indicated that this genus is a source of anthocyanins, flavonoids, and tannins.[3−7] The ethanolic extract from the stems showed promising antioxidant activity and led to the isolation of three new *C*-glucopyranosylxanthones, 2-(2′-*O*-*trans*-caffeoyl)-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**1**), 2-(2′-*O*-*trans*-cinnamoyl)-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**2**), and 2-(2′-*O*-*trans*-coumaroyl)-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**3**), and the known mangiferin (**4**),[8] 2-(2′-*O*-benzoyl)-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (**5**),[9] and muraxanthone (**6**).[10] In this paper, we report the isolation, structure elucidation, and antioxidant properties of these *C*-glucopyranosylxanthones.

Compounds **4** and **6** were identified by comparison with previously published NMR and other physical data.[8,10] Compound **5** was described previously as a mixture of three isomers from *Hymenophyllum recurvum*.[9] Only a few ^{13}C NMR data were analyzed and discussed. In this paper we describe the complete ^{1}H, ^{13}C NMR and ES-MS/MS data for this compound.



Compound **1** was shown to have the molecular formula $C_{28}H_{23}O_{14}$ $[M - H]^-$ *m*/*z* 583.1008, by analysis of the negative-ion HRESIMS. The IR spectrum showed bands at 3370, 1615, and 1474 cm^{-1} accounting for hydroxyl, conjugated carbonyl, and aromatic groups, respectively. The ^{13}C NMR spectrum showed six signals for hydroxymethine carbons, suggesting the presence of a sugar moiety, and 22 signals for sp^2 carbons, which could be assigned to three aromatic rings, and also two carbonyls and one additional olefinic function. In the ^{1}H NMR spectrum (Table 1) of **1**, a caffeoyl moiety was identified by signals at *δ* 6.79 (1H, d, *J* = 2.0 Hz, H-2″), 6.58 (1H, d, *J* = 8.0 Hz, H-5″), and 6.67 (1H, br d, *J* = 8.0 Hz, H-6″),

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Table 1. ^{1}H NMR Data for Compounds **1**−**3** and **5**[a,b]

position	1	2	3	5
OH-1		13.82 s		13.81 s
4	6.15 s	6.29 s	6.17 s	6.25 s
5	6.61 s	6.79 s	6.64 s	6.77 s
8	7.22 s	7.33 s	7.24 s	7.30 s
1′	5.01 d (10.0)	4.85 d (10.0)	5.02 d (10.0)	4.95 d (9.0)
2′	5.58 m	5.67 m	5.58 m	5.73 m
3′	3.66 t (9.2)	3.49 m	3.65 t (9.2)	3.55 m
4′	3.53 t (9.2)	3.26 m	3.51 t (9.0)	3.29 m
5′	3.43 m	3.26 m	3.41 m	3.29 m
6′	3.85 dd (12.0, 2.5)	3.38 m	3.83 br d (11.0)	3.47 m
	3.71 dd (12.0, 5.5)	3.74 br d (11.0)	3.70 dd (12.0, 5.2)	3.75 br d (11.0)
2″	6.79 d (2.0)	7.34 m	7.18 d (8.0)	7.75 dd (7.8, 1.3)
3″		7.56 m	6.61 d (8.0)	7.39 dd (7.8, 7.8)
4″		7.34 m		7.52 dd (7.8, 7.8)
5″	6.58 d (8.0)	7.56 m	6.61 d (8.0)	7.39 dd (7.8, 7.8)
6″	6.67 br d (8.0)	7.34 m	7.18 d (8.0)	7.75 dd (7.8, 1.3)
7″	7.23 d (16.0)	7.39 d (15.5)	7.29 d (16.0)	
8″	5.93 d (16.0)	6.37 d (15.5)	5.99 d (16.0)	

[a] Compounds **5** and **2** recorded in DMSO-d_6; **1** and **3** in CD_3OD, 500 MHz. [b] Chemical shifts are expressed in δ values. J values (Hz) are in parentheses.

Table 2. ^{13}C NMR Data of Compounds **1**−**3** and **5**[a]

position	1	2	3	5
1	162.8	161.7	162.6	161.8
2	106.0	105.7	106.7	105.6
3	165.0	163.9	165.0	163.7
4	95.0	93.9	94.0	93.0
4a	158.8	156.4	158.7	156.4
5	103.4	102.5	103.4	102.5
6	155.3	154.3	155.6	154.4
7	144.8	143.9	144.8	143.9
8	109.1	107.9	108.8	107.8
8a	113.6	111.5	113.4	111.5
9	181.1	179.9	181.0	179.1
9a	102.9	102.0	102.8	102.5
10a	153.0	150.8	153.0	150.8
1′	73.2	70.6	73.1	70.6
2′	73.9	72.3	73.8	72.8
3′	78.0	76.4	78.0	76.4
4′	71.7	70.6	71.7	70.6
5′	82.7	81.8	82.7	81.9
6′	62.8	61.4	62.7	61.5
1″	127.6	133.9	127.1	130.2
2″	115.0	128.9	131.0	129.0
3″	146.8	128.2	116.6	128.5
4″	149.3	130.3	161.0	133.0
5″	116.3	128.2	116.6	128.5
6″	122.9	128.9	131.0	129.0
7″	146.5	143.9	146.4	164.7
8″	114.8	118.3	115.0	
9″	168.3	164.9	168.3	

[a] Compounds **5** and **2** recorded in DMSO-d_6; **1** and **3** in CD_3OD, 125 MHz δ (ppm).

along with the olefinic protons in a *trans* arrangement at δ 7.23 (1H, d, J = 16.0 Hz, H-7″) and 5.93 (1H, d, J = 16.0 Hz, H-8″). In addition, the ^{1}H NMR spectrum also displayed singlets at δ 7.22, 6.61, and 6.15, which showed correlation with signals at δ 109.1, 103.4, and 95.0, respectively, in the HMQC spectrum. These data, analyzed with their corresponding ^{13}C NMR data (Table 2), and further information from ESI-MS/MS (*m*/*z* 405), and analogues published in the literature,[10] suggested a xanthone skeleton linked to a caffeoyl-glucose moiety for compound **1**. TOCSY experiments showed a complete sequence of five correlated signals of the sugar moiety at δ 3.4−3.9. In addition a doublet at δ 5.01 (J = 10.0 Hz) and one multiplet at δ 5.58 were assigned to H-1′ and H-2′, respectively, on the basis of COSY, ^{13}C NMR, and HMQC spectral analysis. The unusual downfield chemical shift of the H-2′ signal suggested an acyl moiety at C-2′,[12] which was corroborated by the values from C-1′, C-2′, and C-3′ (Table 2) and observation of a cross-peak between the H-2′ and C-9″ (δ 168.3) signals in the HMBC spectrum. Additional correlations between H-1′ (δ 5.01) and C-1 (δ 162.8), C-2 (δ 106.0), and C-3 (δ 165.0) evidenced the linkage of the glucose moiety at C-2. This spectrum also showed correlations of the signals at δ 6.15 (H-4) to C-2 (δ 106.0), C-3 (δ 165.0), C-4a (δ 158.8), and C-9a (δ 102.9); δ 6.61 (H-5) to C-10a (δ 153.0), C-6 (δ 155.3), C-7 (δ 144.8), and C-8a (δ 113.6), and δ 7.22 (H-8) to C-10a (δ 153.0), C-6 (δ 155.3), C-7 (δ 144.8), C-9a (δ 102.9), and C-9 (δ 181.1), supporting the substitution pattern proposed for the aglycone. The UV spectra recorded in MeOH and shift reagents ($AlCl_3$, HCl, KOH, NaOAc, and H_3BO_3) confirmed the presence of free hydroxy groups at C-1 and C-3 and an *ortho*-dihydroxylation pattern for the B ring of compound **1**.[11] Finally, the positive-ion electrospray tandem mass spectra ESI(+)-MS/MS (Table 3) completely established the proposed structure for **1**. The fragment at *m*/*z* 585 (a) is rather simple and structurally characteristic, as it shows two major fragment ions of *m*/*z* 405 (b) and 285 (c), which can be clearly related to the proposed *C*-glucosylxanthone, as well as the fragment at *m*/*z* 163 (d), confirming the caffeoyl moiety for this xanthone.

Table 3. Positive-Ion Electrospray Tandem Mass Spectra ESI(+)-MS/MS of the Isolated C-Glucosylxanthones **1**−**6** in Their Protonated Forms

	major ion fragments (*m*/*z*)			
compound	a	b	c	d
1	585	405	285	163
2	553	405	285	131
3	569	405	285	147
4	423	405	285	
5	527	405	285	105
6	543	405	285	121

Compound **2** was assigned the empirical formula $C_{28}H_{23}O_{12}$, $[M - H]^-$ *m*/*z* 551.1241, by accurate negative-ion HRESIMS. The UV and IR spectra were nearly identical to those obtained for **1**. Direct comparison of ^{1}H data (Table 1) of **1** and **2** showed that the signals for the caffeoyl moiety from **1** were replaced in **2** by a pair of multiplets at δ 7.56 and 7.34. The hydrogens corresponding to the two olefinic protons were similar and appeared as doublets with a coupling constant of 15.5 Hz at δ 7.39 (H-7″) and 6.37 (H-8″), revealing a cinnamoyl moiety with a *trans* stereochemistry. The remaining ^{1}H NMR of this compound was

Table 4. Negative-Ion Electrospray Tandem Mass Spectra ESI(−)-MS/MS of the Isolated Compounds **1**−**6** in Their Negative Ion Mode

	major ion fragments (*m*/*z*)			
compound	a	b	c	d
1	583	463	403	283
2	551	431	403	283
3	567	447	403	283
4	421	301		
5	525	405	403	283
6	541	421	403	283

Table 5. Radical Redox Potentials (V) and Scavenging Activity of Compounds **1**−**6** for DPPH

compound	IC_{50} (μmol)[a]	$E_{ox}(+)$	$E_{red}(-)$
1	17.81	0.90	0.05
2	31.36	0.60	0.40
3	25.45	0.80	0.35
4	35.02	0.50	0.45
5	32.66	0.60	0.40
6	30.72	0.65	0.40
standard (rutin)	12.34	0.90	0.10

[a] Concentration in μmol required to scavenge 50% DPPH free radical.

identical with those of **1**, and the ^{13}C NMR and mass spectrum also corroborated these findings. The ESI(+)-MS/MS tandem mass spectrum of the protonated ion at *m*/*z* 553 (a) was analyzed and also corroborated the proposed structure for this compound (Table 3). It showed two major ion fragments at *m*/*z* 405 (b) and 285 (c), which revealed the *C*-glucosylxanthone backbone, whereas the unique acylium ion fragment at *m*/*z* 131 (d) corroborated the cinnamoyl group.

Compound **3** was assigned the molecular formula $C_{28}H_{23}O_{12}$, $[M - H]^-$ *m*/*z* 567.1183, by accurate negative-ion HRESIMS. The UV and IR spectra were very similar to those of **1** and **2**. A comparison of the ^1H NMR spectrum (Table 1) of **3** with those of **1** revealed that the only noticeable difference was related to the aromatic moiety substituent at C-2′. The caffeoyl moiety in **1** was replaced by a coumaroyl residue in compound **3**. The coumaroyl moiety was evidenced in the ^1H NMR spectrum by two doublets at δ 7.18 (2H, $J = 8.0$ Hz) and 6.61 (2H, $J = 8.0$ Hz), characteristic of an AA′XX′ system, and by two olefinic protons in a *trans* arrangement at δ 7.29 (1H, d, $J = 16.0$ Hz, H-7″) and 5.99 (1H, d, $J = 16.0$ Hz, H-8″). These data were also supported by ^{13}C NMR (Table 2) and mass spectral data. The ESI(+)-MS/MS tandem mass spectrum of the protonated ion at *m*/*z* 569 (a) registered for **3** is also diagnostic for a xanthone with these characteristic features (Table 3). The distinct peaks showed the common and major *C*-glucosylxanthone fragment ions at *m*/*z* 405 (b) and 285 (c), whereas the unique acylium ion fragment at *m*/*z* 147 (d) confirmed the coumaroyl moiety.

The scavenging effects obtained for compounds **1**−**6** are shown in Table 5. Compounds **1** and **3** showed the best scavenging activities, taking as the reference the flavonoid rutin (IC_{50} 12.34 μg/mL), revealing a moderate antioxidant activity, while compounds **6**, **2**, and **5** showed lower activities and similar IC_{50} values. This result indicates that the moderate free radical scavenging activity of the xanthones is due to their hydrogen-donating ability, so increasing the number of hydroxyls or catechol groups results in a more efficient radical scavenging effect.[13] The electrochemical behavior displayed by these compounds showed a good correlation with the radical scavenging effect measured in the DPPH assay. This observation clearly indicates that substances with oxidative peaks below +1.2 V (Table 5) and a large oxidative capacity have more promising radical scavenging properties than those that are oxidized at higher potentials.[14]

Experimental Section

General Experimental Procedures. Optical rotations were determined at room temperature using a Perkin-Elmer 241 polarimeter. IR and UV spectra were recorded on a Perkin-Elmer 1710 spectrometer and a Perkin-Elmer UV−vis 14P spectrometer. Melting points were measured on a Microquimica MQAPF-301. ^1H and ^{13}C NMR spectra and *g*HMBC and *g*HMQC, *g*COSY, and TOCSY experiments were recorded on a Varian Unity 500 NMR, with TMS as internal standard. Electrospray mass and tandem mass spectra in both positive- and negative-ion modes were recorded on a Q-Tof (Micromass) mass spectrometer with a quadrupole (Qq) and high-resolution orthogonal time-of-flight (o-TOF) configuration. The sample introduction was performed using a syringe pump (Harvard Apparatus, Pump 11) set to 10 μL/min pumped through an uncoated fused-silica capillary. All samples were dissolved in MeOH−H_2O (1:1). The HRESI-MS mass spectra were acquired using an ESI capillary voltage of 3 kV and a cone voltage of 10 V. ESI-MS/MS spectra of mass-selected ions were acquired using 10−20 eV collisions with argon. For column chromatography purification, RP-18 (230−400 mesh, Merck) and Sephadex LH-20 (Pharmacia) were used as solid supports. TLC analysis was carried out on precoated silica gel 60 F_{254} plates (Merck). Spots were visualized spraying anisaldehyde 5% in H_2SO_4 followed by heating. Scavenging activities were measured using a Varian Star 9090 ElCD composed of a glassy carbon working electrode and an Ag/AgCl reference electrode. A Rheodyne injector, with a 20 μL loop and a Varian 210 HPLC pump as solvent delivery module, was used. Separation of the micromolecules was carried out on a Phenomenex ODS LUNA, 5 μm (250 × 4.60 mm) column. The isocratic phase used was MeOH−H_2O (85:15) (HPLC grade, Mallinckrodt, and ultrapure water, obtained by passing redistilled water through a Milli-Q system, Millipore). All separations were carried out at 30 °C.

Plant Material. The stems of *Arrabidaea samydoides* were collected in Campininha Farm, Mogi-Guaçú, SP, Brazil, by M.C.M.Y. in April 2000. A voucher specimen (Moraes 43) has been deposited in the herbarium of the Botanic Garden of São Paulo, Brazil.

Extraction and Isolation. Dried and pulverized stems (0.837 kg) from *A. samydoides* were exhaustively extracted with ethanol at room temperature to give a crude extract (32.86 g). The resultant extract was diluted with MeOH−H_2O (8:2) and then partitioned with hexane, $CHCl_3$, and EtOAc to afford dried hexane (0.46 g), $CHCl_3$ (2.50 g), EtOAc (4.77 g), stable emulsion (3.77 g), and hydroalcoholic (6.46 g) extracts. Compound **4** (3.03 g) was derived from the emulsion extract (3.77 g) and purified by successive crystallization using MeOH. The EtOAc extract was diluted in *n*-BuOH and partitioned with H_2O. After the removal of the solvent, each extract yielded 3.40 and 0.37 g, respectively. The *n*-BuOH extract was further purified using Sephadex LH-20 gel, eluting isocratically with MeOH, to afford 189 fractions. Fractions 160−167 (138.2 mg) yielded compound **1**. Fractions 109−114 (186.7 mg) were combined, and further purification using a silica gel RP-18 column, eluted with gradient mixtures of H_2O−MeOH (95:5 to 100), led to the isolation of **5** (14.8 mg) and **2** (21.0 mg). Fractions 115−122 (288.8 mg) were combined and subjected to silica gel RP-18 column chromatography using gradient mixtures of H_2O−MeOH (95:5 to 100) to yield **6** (27.4 mg). Fractions 123−136 (294.0 mg) were combined and subjected to a silica gel RP-18 column eluted with gradient mixtures of H_2O−MeOH (95:5 to 100) to afford **3** (25.3 mg).

Determination of the Radical Scavenging Activity. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was used as a stable radical in methanol (200 μmol, 2 mL). The reagent was added to a 1 mL aliquot of the compounds, previously dissolved in

methanol, to yield final concentrations of 100, 80, 40, 20, 10, and 5 μmol. Each mixture was shaken and held for 30 min at room temperature, in the dark. Rutin was used as a reference compound. DPPH solution (2 mL) in methanol (1 mL) served as a control. The evaluation of the reduced form of DPPH generated in situ was performed measuring the decrease in the current (*I*) on the electrochemical cell of the ElCD.[15] The areas obtained in each chromatogram were normalized and compared with the one obtained for the blank. The radical scavenging activity of the samples was expressed in terms of IC_{50} (concentration in μmol required for a 50% decrease in current (*I*) by the reduced form of DPPH). Rutin was used as reference compound.

Redox Potential. The determination of the optimal potential (E_{ox}) required to apply on each sample was obtained by means of a hydrodynamic voltammogram generated for each compound (Table 5).

2-(2′-*O*-*trans*-Caffeoyl)-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (1): orange powder (MeOH); $[\alpha]^{25}_D$ −185.46° (*c* 5.0, MeOH); UV (MeOH) λ_{max} (log ϵ) 242 (4.48), 257 (4.46), 318 (4.35), 387 (sh) (4.10) nm; (MeOH + $AlCl_3$) 235.5 (4.58), 265.5 (4.57), 355 (4.45), 408.5 (sh) (4.34) nm; (MeOH + $AlCl_3$ + HCl) 233 (4.54), 265 (4.47), 337 (4.52), 406.5 (4.05) nm; (MeOH + KOH) 248 (4.62), 272 (4.49), 392 (4.65); (MeOH + NaOAc) 241 (4.54), 332 (4.32), 376 (4.28) nm; (MeOH + H_3BO_3 + NaOAc) 261.5 (4.57), 357 (4.42); IR (KBr) ν_{max} 3370, 1615, 1474, 1287, 1176, 1072, 813, 704 cm^{-1}; ^1H NMR and ^{13}C NMR (CD_3OD), see Tables 1 and 2; ESI-MS/MS, see Tables 3 and 4; HRESI-MS *m*/*z* 583.1008 $[M - H]^-$ (calcd for $C_{28}H_{23}O_{14}$, 583.1088).

2-(2′-*O*-*trans*-Cinnamoyl)-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (2): yellow powder (MeOH); $[\alpha]^{25}_D$ −125.66° (*c* 2.65, MeOH); UV (MeOH) λ_{max} (log ϵ) 243 (sh) (4.63), 258 (4.78), 315 (sh) (4.20), 364.5 (4.18) nm; (MeOH + $AlCl_3$) 237 (4.66), 264 (4.81), 325.5 (4.23), 378.5 (4.34) nm; (MeOH + $AlCl_3$ + HCl) 241 (4.64), 260 (4.76), 340 (sh) (4.27), 375 (sh) (4.20) nm; (MeOH + KOH) 240 (4.60), 273 (4.74), 340 (sh) (4.20), 391 (4.61) nm, (MeOH + NaOAc) 242 (4.70), 260 (4.72), 374 (4.38) nm; (MeOH + H_3BO_3 + NaOAc) 262 (4.85), 314 (4.31), 371 (4.36) nm; IR (KBr) ν_{max} 3378, 2925, 1628, 1473, 1286, 1186, 1074, 827, 765 cm^{-1}; ^1H NMR and ^{13}C NMR (CD_3OD), see Tables 1 and 2; ESI-MS/MS, see Tables 3 and 4; HRESI-MS *m*/*z* 551.1241 $[M - H]^-$ (calcd for $C_{28}H_{23}O_{12}$, 551.1190).

2-(2′-*O*-*trans*-Coumaroyl)-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (3): yellow powder (MeOH); $[\alpha]^{25}_D$ −189.0° (*c* 2.7, MeOH); UV (MeOH) λ_{max} (log ϵ) 237.5 (4.41), 258.5 (4.43), 314.5 (4.42), 367 (4.02) nm; (MeOH + $AlCl_3$) 235 (4.57), 268.5 (4.52), 321.5 (4.42), 416 (4.26) nm; (MeOH + $AlCl_3$ + HCl) 232.5 (4.53), 265.5 (4.46), 322.5 (4.49), 405.5 (4.00) nm; (MeOH + KOH) 251 (4.45), 272 (sh) (4.31), 283 (4.38) nm; (MeOH + NaOAc) 236.5 (4.48), 260 (4.35), 315.5 (4.35), 374.5 (4.21) nm; (MeOH + H_3BO_3 + NaOAc) 230 (4.46), 262 (4.52), 317 (4.41), 373 (4.09) nm; IR (KBr) ν_{max} 3390, 2924, 1614, 1473, 1286, 1168, 1000, 819 cm^{-1}; ^1H NMR and ^{13}C NMR (CD_3OD), see Tables 1 and 2; ESI-MS/MS, see Tables 3 and 4; HRESI-MS *m*/*z* 567.1183 $[M - H]^-$ (calcd for $C_{28}H_{24}O_{13}$, 567.1139).

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