Carbohydrate Research 436 (2016) 50–53

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Short synthesis of phenylpropanoid glycoside grayanoside-A and analogues

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ARTICLE INFO

Article history:
Received 2 November 2016
Accepted 12 November 2016
Available online 14 November 2016

Keywords:
Phenylpropanoid glycosides
Grayanoside-A
Regioselective acylation
Me_2SnCl_2

ABSTRACT

A short synthesis of phenylethyl glycosides grayanoside-A **1**, **2** and analogues **3**–**4** in high 43–65% overall yields is described. The main synthetic step involved regioselective *O*-6 acylation of unprotected 2-phenylethyl-β-D-glucoside **7** with cinnamoyl chlorides **8a-d** using Me_2SnCl_2 as catalyst. The acylation at *O*-6 is regioselective regardless of the type of cinnamoyl chloride used. Protection/deprotection steps of the glucoside core were not necessary. The synthetic route is generally applicable for the synthesis of phenylpropanoid glycoside class of compounds acylated at *O*-6.

1. Introduction

Phenylpropanoid glycosides (PhGs) are natural compounds distributed in plants and show antioxidation, antiproliferation, antibacterial, antiviral, anti-inflammatory and hepatoprotection activities [1]. PhGs have 2-phenylethyl-β-D-glucoside core acylated with a (substituted) cinnamoyl moiety mainly at *O*-4 or *O*-6 and may have additional one or two saccharide units bonded to the glucoside core through glycosidic bonds (Fig. 1).

Total synthesis of PhGs has attracted significant interests due to their diverse bioactivities. The conventional approach for their synthesis has mainly relied on tedious, low-yielding and multistep protection-deprotection strategies [2]. Our group has been interested in developing short and convenient synthesis of PhGs that eliminate unnecessary protection/deprotection steps. To this end, we focused our attention at synthesizing PhG class of compounds acylated at *O*-6 since they represent the vast majority of the reported PhGs. We recently communicated the synthesis of calceolarioside-B and eutigoside-A [3]. It was natural for us to extend our synthetic efforts to grayanoside-A **1**, [4] PhG **2** [5] (no name was given to this reported PhG) and test the general applicability of the approach by synthesizing PhGs analogues **3**–**4** having cinnamoyl moieties at *O*-6 (Fig. 1). The reported synthesis of grayanoside-A **1** involved acylation of the glucoside core at *O*-6 with feruloyl acid chloride in pyridine [2g] or protection-deprotection strategies [2a]. The use of feruloyl, coumaroyl and cinnamoyl acid chlorides/pyridine system for selective acylation of primary hydroxyl groups of sucrose has been employed in our lab for the synthesis of various phenylpropanoid sucrose esters [6]. It usually resulted in unpredictable mixtures of acylated products that were tedious to purify. Therefore, a general selective and more predictable approach is needed to prepare the phenylpropanoid glycoside class of compounds acylated at *O*-6.

Herein, we report a short synthetic route for grayanoside-A **1** and demonstrate its general applicability for the synthesis of *O*-6 acylated PhGs analogues **2**–**4**. This route relies on direct *O*-6 acylation of unprotected glucoside core in high selectivity and yield without protection/deprotection steps. The route is general for the synthesis of phenylpropanoid glycosides class of compounds acylated at *O*-6.

2. Results and discussion

Our synthesis of grayanoside-A **1**, PhG **2** and analogues **3**–**4** is depicted in Scheme 1. Direct 1,2-*tran*-β-glycosylation between excess peracetate D-glucose **5** and 2-(4-allyloxyphenyl)ethanol **6** followed by deacetylation using NaOMe/MeOH gave 2-(4-allyloxyphenyl)ethyl-β-D-glucopyranoside **7** in 82% yield [3]. We noted that the use of excess rather than stoichiometric amount of peracetate D-glucose **5** was beneficial as it gave higher yield of glucopyranoside **7** [2a]. The glycosylation reaction proceeded through neighboring group participation mechanism [7].

Next, direct regioselective *O*-6 acylation of 2-(4-allyloxyphenyl)

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http://dx.doi.org/10.1016/j.carres.2016.11.010
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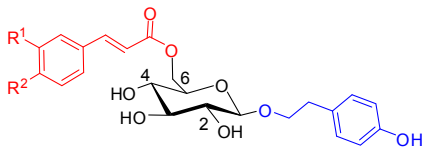


R^1 = OMe, R^2 = OH grayanoside-A **1**
R^1 = R^2 = OH **2**
R^1 = R^2 = H **3**
R^1 = R^2 = OMe **4**

Fig. 1. Structures of grayanoside-A **1**, PhG **2** and analogues **3**–**4**.

ethyl-β-D-glucopyranoside **7** with acid chlorides **8a-d** [8] using catalytic amount of Me_2SnCl_2 [9] gave the desired *O*-6 acylated glucosides **9a-d** in 79–86% yield (Scheme 1). The preferential acylation of cinnamoyl chloride at O-6 is due to the higher intrinsic reactivity of 6-OH [10] and the increased acidity of 6-OH after complexation with Me_2SnCl_2 [9].

Finally, removal of the allyl groups of the acylated glucosides **9a, c-d** using Pd/C proceeded smoothly to give grayanoside-A **1** in 74% yield and analogues **3** and **4** in 92% and 89% yields, respectively. Removal of the *tert*-butyldimethylsilyl (TBS) groups of acylated glucoside **9b** using tetra-*n*-butylammonium fluoride (TBAF) followed by removal of the allyl group using Pd/C gave PhG **2** in 67% yield. In all cases, no migration and/or hydrolysis [2g,h] of the cinnamoyl moieties occurred as the allyl and TBS groups were removed selectively. The structures of grayanoside-A **1** and PhG **2** were confirmed by ^{1}H NMR and ^{13}C NMR and matched with the reported data [2a,g,5].

3. Conclusion

We have developed a short synthesis of grayanoside-A **1** and PhG **2** and analogues 3–**4** in high 43–65% overall yields without protection-deprotection steps. The first key step involved 1,2-*trans*-β-glycosylation of peracetylated D-glucose **5** with 2-(4-allyloxyphenyl)ethanol **6** to give 2-(4-allyloxyphenyl)ethyl-β-D-glucopyranoside **7**. The second key step involved regioselective *O*-6 acylation of unprotected 2-phenylethyl-β-D-glucoside **7** with cinnamoyl chlorides **8a-d** using Me_2SnCl_2 as catalyst. Acylation at *O*-6 is regioselective regardless of the type of cinnamoyl chloride used. No migration and/or hydrolysis of the cinnamoyl moieties were observed at any stage. Because of convenience and high yields, this work serves as a model for the direct synthesis of phenylpropanoid glycoside class of compounds acylated at *O*-6.

4. Experimental

4.1. General procedures

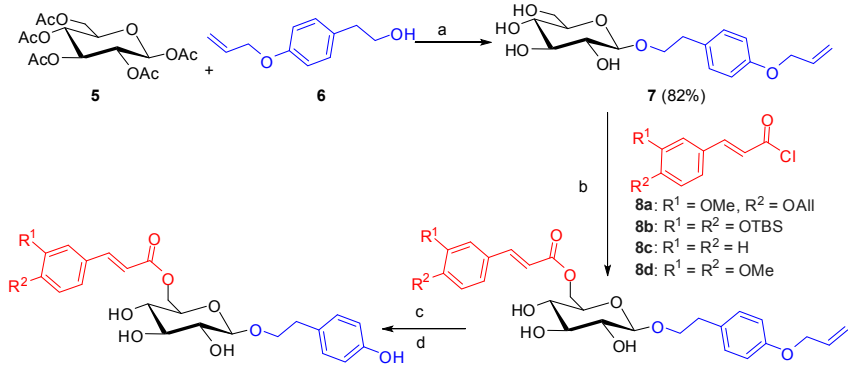
Chemical reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received without further purification. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker Avance DPX 300. Unless stated otherwise, data refer to solutions in $CDCl_3$ with TMS as an internal reference. ^{13}C NMR spectra were recorded at 75.47 MHz on a Bruker Avance DPX 300. HRMS were recorded on Qstar XL MS/MS system. FTIR spectra were recorded on Perkin Elmer FTIR system Spectrum BX. Analytical TLC was performed using Merck 60 F_{254} precoated silica gel plates (0.2 mm thickness) and visualized using UV radiation (254 nm). Flash chromatography was performed using Merck silica gel 60 (230–400 mesh).

4.2. General procedure for O-6 acylation of 2-(4-allyloxyphenyl) ethyl β-D-glucopyranoside 7 with cinnamoyl chloride 8a-d

To a solution of glucopyranoside **7** (85 mg, 0.25 mmol) in THF (2.5 mL) was added Me_2SnCl_2 (2.75 mg, 5 mol%), cinnamoyl chloride **8** (0.375 mmol), DIPEA (87 μL, 0.5 mmol) under strong stirring. The reaction was stirred for ~18 h (TLC) before diluting with deionized H_2O (10 mL). The mixture was extracted with EtOAc (10 mL x 3), the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and evaporated. The crude residue was purified by flash column chromatography to give the respective *O*-6 acylated products. The general method was used to prepare compounds **9a-d**.

4.2.1. 2-(4-Allyloxyphenyl)ethyl 6-O-(E)-(3-methoxy-4-allyloxy) cinnamoyl β-D-glucopyranoside 9a

The crude product was purified by flash column chromatography (EtOAc: DCM = 3: 1) to give 120 mg (85% yield) as amorphous solid. $[\alpha]_D$ − 25° (*c* 0.023, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ: 2.80 (t, *J* = 7.2 Hz, 2H), 3.32–3.43 (m, 3H), 3.50–3.56 (m, 1H), 3.62 (q, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 4.00 (q, *J* = 7.9 Hz, 1H), 4.25 (d,



5 + **6** → **7** (82%)

8a: R^1 = OMe, R^2 = OAll
8b: R^1 = R^2 = OTBS
8c: R^1 = R^2 = H
8d: R^1 = R^2 = OMe

R^1 = OMe, R^2 = H grayanoside-A **1** (74%)
R^1 = R^2 = OH PhG **2** (67%)
R^1 = R^2 = H **3** (92%)
R^1 = R^2 = OMe **4** (89%)

9a: R^1 = OMe, R^2 = OAll (85%)
9b: R^1 = R^2 = OTBS (79%)
9c: R^1 = R^2 = H (86%)
9d: R^1 = R^2 = OMe (82%)

Reagents and conditions: a) BF_3OEt_2, CH_2Cl_2, MS 4Å, rt, 12 h then NaOMe, MeOH, rt, 1 h; b) **8a-d**, Me_2SnCl_2, THF, rt, 18 h; c) Pd/C, *p*-TsOH, MeOH-H_2O, 80 °C, 16 h (for **9a, 9c-d**) d) TBAF, THF, 0 °C - rt, 2 h then Pd/C, *p*-TsOH, MeOH-H_2O, 80 °C, 16 h (for **9b**)

Scheme 1. Synthesis of grayanoside-A **1**, PhG **2** and analogues **3**–**4**.

J = 3.75 Hz, 1H), 4.32–3.38 (m, 3H), 4.51–4.55 (m, 3H), 5.16–5.37 (m, 4H), 5.88–6.04 (m, 2H), 6.27 (d, J = 16.0 Hz, 1H), 6.69–6.76 (m, 3H), 6.92–7.02 (m, 4H), 7.56 (d, J = 16.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 35.2, 55.93, 63.3, 68.8, 69.7,70.0, 71.2, 73.6, 74.2, 75.9, 102.9, 110.1, 112.7, 114.7, 115.0, 117.6, 118.5, 122.8, 127.3, 129.8, 130.3, 132.7, 133.3, 145.9, 149.5, 150.3, 157.2, 168.0. HRMS (ESI+): m/z $[M+H]^+$ calcd for $C_{30}H_{37}O_{10}$: 577.3952; found: 577.3948.

4.2.2. 2-(4-Allyloxyphenyl)ethyl 6-O-(E)-3,4-bis(tert-butyldimethylsilyloxy)caffeoyl β-D-glucopyranoside **9b**

The crude product was purified by flash column chromatography (EtOAc: DCM = 3: 1) to give 144 mg (79% yield) as amorphous solid. $[\alpha]_D$ − 66^o (c 0.030, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ: −0.01 (s, 6H), 0.00 (s, 6H), 0.768 (s, 9H), 0.772 (s, 9H), 2.67 (t, J = 7.05 Hz, 2H), 3.25–3.53 (m, 5H), 3.87 (q, J = 9.3 Hz, 1H), 4.10 (d, J = 7.8 Hz, 1H), 4.18–4.25 (m, 3H), 4.37–4.42 (m, 1H), 5.03 (dd, J = 1.2, 10.5 Hz, 1H), 5.16 (dd, J = 1.5, 17.4 Hz, 1H), 5.74–5.83 (m, 1H), 6.07 (d, J = 15.9 Hz, 1H), 6.57–6.60 (m, 3H), 6.75–6.90 (m, 4H), 7.40 (d, J = 15.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: −5.44, −5.41, 17.06, 17.12, 24.51, 24.54, 33.9, 62.0, 67.4, 68.6, 69.8, 72.2, 72.9, 103.0, 113.4, 113.5, 116.2, 119.2, 119.8, 121.2, 126.4, 128.5, 129.0, 132.0, 144.7, 145.8, 148.3, 155.8, 166.8. HRMS (ESI+): m/z $[M+H]^+$ calcd for $C_{38}H_{59}O_{10}Si_2$: 731.3647; found: 731.3643.

4.2.3. 2-(4-Allyloxyphenyl)ethyl 6-O-(E)-cinnamoyl β-D-glucopyranoside **9c**

The crude product was purified by flash column chromatography (EtOAc: DCM = 3: 1) to give 101 mg (86% yield) as amorphous solid. $[\alpha]_D$ − 63^o (c 0.022, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ: 2.81 (t, J = 8.1 Hz, 2H), 3.32–3.67 (m, 5H), 4.01 (q, J = 8.0 Hz, 1H), 4.25 (d, J = 7.5 Hz, 1H), 4.34–4.39 (m, 3H), 4.51–4.56 (m, 1H), 5.22 (dd, J = 1.5, 10.5 Hz, 1H), 5.31 (dd, J = 1.5, 17.1, 1H), 5.88–6.01 (m, 1H), 6.40 (d, J = 15.9 Hz, 1H), 6.71 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 7.26–7.30 (m, 3H), 7.39–7.42 (m, 2H), 7.63 (d, J = 15.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 32.8, 61.4, 66.2, 67.9, 68.8, 70.1, 71.5, 73.8, 100.3, 112.2, 115.0, 115.1, 125.8, 126.4, 127.4, 127.7, 127.9, 130.9, 131.7, 143.1, 154.6, 164.9. HRMS (ESI+): m/z $[M+H]^+$ calcd for $C_{26}H_{31}O_8$: 471.2019; found: 471.2020.

4.2.4. 2-(4-Allyloxyphenyl)ethyl 6-O-(E)-3,4-dimethoxycaffeoyl β-D-glucopyranoside **9d**

The crude product was purified by flash column chromatography (EtOAc: DCM = 3: 1) to give 108 mg (82% yield) as amorphous solid. $[\alpha]_D$ − 34^o (c 0.023, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ: 2.87 (t, J = 6.9 Hz, 2H), 3.43–3.71 (m, 5H + O*H*), 3.90 (s, 6H), 4.06 (q, J = 7.8 Hz, 1H), 4.32–4.34 (m, 2H), 4.38–4.44 (m, 2H), 4.57–4.60 (m, 1H), 5.27 (d, J = 10.5 Hz, 1H), 5.39 (d, J = 17.1 Hz, 1H), 5.96–6.01 (m, 1H), 6.37 (d, J = 15.9 Hz, 1H), 6.82–6.88 (m, 3H), 7.05–7.14 (m, 4H), 7.68 (d, J = 15.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 35.0, 55.88, 55.94, 63.4, 68.7, 70.0, 71.2, 73.6, 74.2, 76.0, 102.9, 109.7, 111.0, 114.7, 114.9, 117.6, 123.0, 127.1, 129.8, 130.3, 133.3, 145.9, 149.2, 151.3, 157.2, 168.0. HRMS (ESI+): m/z $[M+H]^+$ calcd for $C_{28}H_{35}O_{10}$: 531.2230; found: 531.2234.

4.3. General procedure for deprotection of allyl groups

To a solution of *O*-Allyl protected glucopyranoside **9a, c-d** (0.1 mmol) in MeOH: H_2O (20:1 v:v, 10 mL) was added *p*-TsOH (1.72 mg), Pd/C (100 mg of Pd/C per 0.1 mmol of allyl group). The reaction mixture was heated at 80 °C for ~12 h whereby TLC analysis showed complete consumption of starting material. The reaction mixture was filtered through a pad of Celite® and the filtrates were evaporated to dryness. The crude residue was purified by column chromatography using pure EtOAc as eluent to give PhGs **1, 3–4**.

4.3.1. 2-(4-Hydroxyphenyl)ethyl 6-O-(E)-(3-methoxy-4-hydroxy) cinnamoyl β-D-glucopyranoside (grayanoside-A) **1**

The crude mixture was purified by flash column chromatography to give 35 mg (74% yield) as amorphous solid. $[\alpha]_D$ − 15^o (c 0.032, *MeOH*). ^{1}H NMR (MeOD) δ: 2.75 (t, J = 7.35 Hz, 2H), 3.12 (t, J = 8.55 Hz, 1H), 3.25–3.29 (m, 2H), 3.41–3.43 (m, 1H), 3.57–3.66 (m, 1H), 3.75 (s, 3H), 3.71–3.88 (m, 2H), 4.21–4.27 (m, 2H), 4.38–4.42 (m, 1H), 6.27 (d, J = 15.9 Hz, 1H), 6.51–6.57 (m, 2H), 6.70 (d, J = 8.1 Hz, 1H), 6.89–6.94 (m, 3H), 7.04 (d, J = 1.8 Hz, 1H), 7.52 (d, J = 15.9 Hz, 1H). ^{13}C NMR (MeOD) δ: 38.0, 57.9, 66.2, 73.3, 74.0, 76.6, 76.9, 79.4, 106.1, 113.1, 116.8, 117.7, 118.0, 125.8, 129.2, 132.1, 132.4, 148.6, 150.9, 152.1, 158.3, 170.6. HRMS (ESI+): m/z $[M+H]^+$ calcd for $C_{24}H_{29}O_{10}$: 477.1761; found: 477.1760. ^{1}H NMR and ^{13}C NMR are in agreement with the reported values [2g].

4.3.2. 2-(4-Hydroxyphenyl)ethyl 6-O-(E)-cinnamoyl β-D-glucopyranoside **3**

The crude mixture was purified by flash column chromatography to give 40 mg (92% yield) as amorphous solid. $[\alpha]_D$ − 28^o (c 0.030, *MeOH*). ^{1}H NMR (MeOD) δ: 2.73 (t, J = 7.35 Hz, 2H), 3.11 (t, J = 7.8 Hz, 1H), 3.25–3.27 (m, 3H), 3.44 (t, J = 7.8 Hz, 1H), 3.62 (q, J = 8.7 Hz, 1H), 3.84 (q, J = 9.3 Hz, 1H), 4.22–4.28 (m, 2H), 4.41–4.45 (m, 1H), 6.44 (d, J = 16.2 Hz, 1H), 6.54 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 7.8 Hz, 2H), 7.22–7.31 (m, 3H), 7.40–7.46 (m, 2H), 7.59 (d, J = 15.6 Hz, 1H). ^{13}C NMR (MeOD) δ: 38.0. 66.4, 73.3, 74.0, 76.6, 76.9, 79.5, 106.1, 117.6, 117.7, 120.2, 130.7, 131.5, 132.1, 132.4, 133.1, 137.2, 148.0, 158.3, 169.9. HRMS (ESI+): m/z $[M+H]^+$ calcd for $C_{23}H_{27}O_8$: 431.1706; found: 431.1712.

4.3.3. 2-(4-Hydroxyphenyl)ethyl 6-O-(E)-3,4-dimethoxycinnamic β-D-glucopyranoside **4**

The crude mixture was purified by flash column chromatography to give 43 mg (89% yield) as amorphous solid. $[\alpha]_D$ − 28^o (c 0.030, *MeOH*). ^{1}H NMR (MeOD) δ: 2.73 (t, J = 7.2 Hz, 2H), 3.11 (t, J = 7.35 Hz, 1H), 3.20–3.30 (m, 2H), 3.34–3.48 (m, 1H), 3.62 (q, J = 7.8 Hz, 1H), 3.74 (s, 3H), 3.77 (s, 3H), 3.77–3.88 (m, 1H), 4.22–4.26 (m, 2H), 4.40–4.44 (m, 1H), 6.32 (d, J = 15.6 Hz, 1H), 6.53 (d, J = 6.9 Hz, 2H), 6.84–6.98 (m 4H), 7.08 (s, 1H), 7.53 (d, J = 15.3 Hz, 1H). ^{13}C NMR (MeOD) δ: 36.6, 56.49, 56.55, 64.8, 72.0, 72.6, 75.1, 75.5, 78.1, 104.7, 111.4, 112.7, 116.2, 116.3, 124.3, 128.8, 130.6, 131.0, 146.8, 150.9, 153.0, 156.9, 169.0. HRMS (ESI+): m/z $[M+H]^+$ calcd for $C_{25}H_{31}O_{10}$: 491.1917; found: 491.1910.

4.4. 2-(4-Hydroxyphenyl)ethyl 6-O-(E)-caffeoyl β-D-glucopyranoside **PhG 2**

A solution of TBAF (1M in THF, 0.4 mL) was added dropwise to an ice-cold solution of glucoside **9b** (73 mg, 0.1 mmol) in THF (6 mL). The reaction mixture was stirred for 2 h, evaporated to dryness, and then dissolved in H_2O (5 mL). The aqueous solution was extracted with EtOAc (5 mL x 5), the combined organic extracts were dried over $MgSO_4$, filtered and evaporated to dryness. The crude mixture obtained was redissolved in MeOH: H_2O (1.8 mL: 0.2 mL). Pd/C (10 wt%, 50 mg) and *p*-TsOH (2 mg) were then added to the solution which was stirred at 80 °C for 8 h. The reaction mixture was then filtered through a pad of Celite®, and evaporated to dryness. The residue was purified by flash column chromatography (CH_2Cl_2–MeOH = 15: 1) to afford 31 mg (67% yield after two steps) as amorphous solid. $[\alpha]_D$ − 28^o (c 0.020, *MeOH*). ^{1}H NMR (MeOD) δ: 2.73 (t, J = 7.5 Hz, 2H), 3.14 (t, J = 8.1 Hz, 1H), 3.24–3.28 (m, 1H), 3.40–3.44 (m, 1H), 3.58–3.66 (m, 1H), 3.73–3.89 (m, 2H), 4.20–4.28 (m, 2H), 4.37–4.41 (m, 1H), 6.28 (d, J = 15.6 Hz, 1H), 6.49–58 (m, 2H), 6.62 (d, J = 8.4 Hz, 1H), 6.78–6.81 (m, 1H), 6.85–6.92 (m, 3H), 7.58 (d, J = 15.6 Hz, 1H). ^{13}C NMR (MeOD) δ:38.0, 66.1, 73.3, 73.9, 76.6, 76.9, 79.4, 106.1, 116.4, 116.5, 117.6, 118.0, 124.6,

129.2, 132.1, 132.4, 148.3, 148.7, 151.1, 158.3, 170.7. HRMS (ESI+): m/z $[M+H]^+$ calcd for $C_{23}H_{27}O_{10}$: 463.1604; found: 463.1609. The spectra was in agreement with the literature values [5].

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carres.2016.11.010.

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