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Synthesis of a phenylpropanoid glycoside, Osmanthuside B6[1]

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Abstract

2-Ac-Osmanthuside B6 [2-(4-hydroxyphenyl)ethyl 2-*O*-acetyl-3-*O*-(α-L-rhamnopyranosyl)-6-*O*-(4-hydroxycinnamoyl)-β-D-glucopyranoside, **8**], a derivative of Osmanthuside B6, was synthesized in 7 steps with the goal of preparing Osmanthuside B6. Surprisingly, it was found that the 2-acetyl group in the glucose ring of the compound **7**, 1-*O*-[2-(4-allyloxyphenyl)ethyl]-2-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-6-*O*-(4-acetoxycinnamoyl)-β-D-glucopyranoside, could not be removed by conventional deacetylation procedures.

Keywords: Phenylpropanoid glycosides; Osmanthuside B6; Synthesis

1. Introduction

Phenylpropanoid glycosides are natural glycosides acylated with a substituted cinnamoyl residue and having a substituted phenylethyl group as aglycon [1]. Many of them possess potent biological activities such as antiviral, antitumor, antifugal, and immunomodulatary agents [1–5]. To date, about one hundred of these glycosides have been isolated and identified by spectra and chemical conversions, but total syntheses have not yet been reported. In our previous paper [6], the total synthesis of a phenylpropanoid glycoside with a monosaccharide residue, Grayanoside A was reported. This present paper deals with the synthesis of a phenylpropanoid glycoside having a disaccharide residue, Osmanthuside B6 [7] (Fig. 1).

The designed synthetic route for Osmanthuside B6 was as shown in Scheme 1.

2. Results and discussion

Allyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**1**) was prepared as previously described [8] and Eby's [9] new method for selective acylation of the 2-OH group in methyl 4,6-*O*-benzylidene-α-D-glucopyranoside by forming a mercury complex was used to acetylate selectively the 2-OH group in compound **1**. Because the 2-OH group is more acidic than 3-OH, the reaction of the mercury complex with acetic anhydride favored regioselective 2-acetylation. In order to increase the selectivity and

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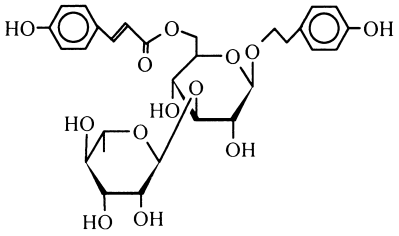
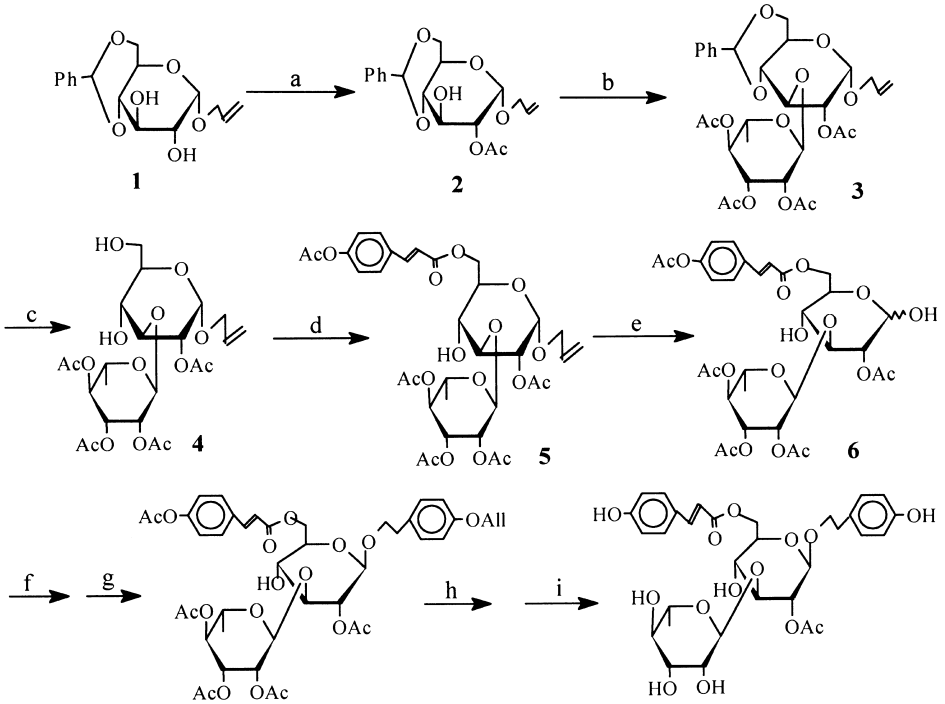


Fig. 1. The structure of Osmanthuside B6.

yield, the procedure was improved as follows: the reaction mixture was cooled to 0 °C, and after the mercury complex had been formed, acetic anhydride diluted with THF (~1:3, v/v) was added dropwise to afford compound **2** in 84% yield. The reaction of tri-*O*-acetyl-L-rhamnopyranosyl bromide with **2**, catalyzed by mercuric cyanide, gave disaccharide **3** in 80% yield. Removal of the benzylidene group from compound **3** was readily accomplished by refluxing **3** with catalytic amount of *p*-toluenesulfonic acid in refluxing methanol–water and **4** was obtained in 78% yield. Cinnamoylation of **4** was performed at 0 °C by using 4-acetoxycinnamoyl chloride as the acylation agent. The presence of a cinnamoyl group in compound **5** was confirmed by IR (1760,1631 cm^{-1}).

The trichloroacetoxy group, a new leaving group, has been used successfully in our laboratory to prepare certain glycosides and oligosaccharides [10–13]. Protected Osmanthuside B6 was also prepared by this method. By using an improved deprotection method [14], the allyl group in **5** was removed to give compound **6** in 94% yield. Compound **6** was converted into the syrupy trichloroacetate according to the previously reported procedure [11] in nearly quantitative yield. Without further purification, the trichloroacetate was treated with 4-allyloxyphenylethanol to give the protected disaccharide phenylpropanoid glycoside Osmanthuside B6 (**7**) with use of Me_3SiOTf as the glycosylation catalyst.

The allyl group on the aglycon in **7** was removed with the aid of $PdCl_2$/CuCl, reagents that do not need the presence of acid or base, and other functional groups in the glycosides were not affected. Compound **7** was dissolved in (10:1) THF–water, and one molar equivalent of $PdCl_2$/CuCl was added. The mixture was stirred vigorously. When TLC showed the disappearance of **7**, the crude product isolated was used directly for the attempted removal of acetyl groups by ammonia–methanol at 5–10 °C. The deacetylation product was purified by column chromatography to afford compound **8** in 53% yield (two steps). NMR showed that one acetyl group still remained, by comparison



Scheme 1. (a) $NaH/HgCl_2$, Ac_2O; (b) Tri-*O*-acetyl-L-rhamnopyranosyl bromide/$Hg(CN)_2$, anhydrous toluene, 4 h reflux; (c) MeOH-H_2O, *p*-TsOH, 2 h reflux; (d) 4-Acetoxycinnamoyl chloride/pyridine, THF, rt, 6 h; (e) $PdCl_2/CuCl/H_2O$, THF, 25–30 °C, 2 h; (f) $(Cl_3CCO)_2O/Cl_3CCO_2Na$, anhydrous $CHCl_3$, 5 h reflux; (g) 2-(4-Allyloxyphenyl)ethanol, DBMP, Me_3SiOTf, anhydrous CH_2Cl_2, -15 °C → rt, 48 ;h. (h) $PdCl_2/CuCl/H_2O$, THF, 25–30 °C, 6 h; (I) NH_3–MeOH (15%), 5–10 °C, 5 h.

of the ^{13}C NMR data of **8** with those of Osmanthuside B6 [7].

3. Experimental

General methods.—Melting points are uncorrected. Spectra were recorded with the following instruments: ^{1}H and ^{13}C NMR, Jeol FX-90Q (90 MHz) and Jeol GX-400 (400 MHz), ^{1}H-^{1}H COSY, HETCOR, NOESY, Jeol GX-400; mass spectra, VG 20-250 GLC–MS and VG ZAB GC GLC–MS. The ^{1}H NMR spectra were recorded with Me_4Si as the internal standard and ^{13}C NMR with $CDCl_3$ as solvent and internal standard. Optical rotations in $CHCl_3$ solutions were measured at 22–25 °C with a Perkin–Elmer 243 polarimeter. The progress of reactions was monitored by TLC on GF254 (Hai Yang Chemical Factory, Qingdao, Shandong, P. R. China). Column chromatography was performed on silica gel H (10–40 μm) (Hai Yang Chemical Factory, Qingdao, Shandong , P. R. China). The solvent system indicated are volume volume ratios. Components were detected by spraying the plates with 20% concd. H_2SO_4 in EtOH and heating. Elemental analyses were performed on Perkin–Elmer 240C instrument.

*Allyl 2-*O*-acetyl-4,6-*O*-benzylidene-*α*-*D*-glucopyranoside* (**2**).—To a dry THF solution of allyl 4,6-*O*-benzylidene-*α*-D-glucopyranoside (**1**) [8] (12.32 g, 40 mmol) (200 mL) was added NaH (2.4 g, 80 %, 80 mmol). The mixture was stirred at room temperature for 20 min. Anhydrous $HgCl_2$ (10.88 g, 40 mmol) was added, the mixture was stirred at room temperature for another 20 min. and then cooled to 0 °C in an ice–water bath. Acetic anhydride (6 mL, diluted with 20 mL THF) was added and the mixture was stirred for 2 h. Water (2 mL) and AcOH (2 drops) were added. The solvent was then evaporated off in vacuo. The residue was dissolved in the $CHCl_3$ (100 mL) and the solution was successively washed with water and brine, dried, and evaporated to syrup. The syrup was dissolved in EtOAc (15 mL), and petroleum ether (60 mL) was added. The solid (9.5 g) was collected by suction and further evaporation. Flash chromatography (15:1 benzene–ethyl acetate) of the filtrate gave additional **2** (2.2 g); yield: 83.6%, mp 96.0–97.0 °C; $[\alpha]_D$ +131.9° (*c* 0.27, $CHCl_3$); ^{1}H NMR (90 MHz, $CDCl_3$); δH (ppm): 7.60–7.80 (m, 5 H, ArH), 5.90 (m, 1 H, CH=C), 5.56 (s, 1 H, O-CHO), 5.30 (d, 1 H), 5.20 (d, 1 H, C=CH_2), 5.16 (d, 1 H, H-1), 4.82 (dd, 1 H, H-2), 4.36–3.50 (m, 7 H, H–3(6, -OCH_2-), 2.16 (s, 3 H, CH_3CO-).

*Allyl 2-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-4,6-*O*-benzylidene-α-D-glucopyranoside* (**3**).—A mixture of **2** (5.25 g, 15 mmol), tri-*O*-acetyl-L-rhamnopyranosyl bromide (8.8 g, 25 mmol), $Hg(CN)_2$ (6.3 g, 25 mmol) in anhydrous toluene (100 mL) was refluxed for 4 h. After cooling, the solid was removed by filtration and thoroughly washed with toluene. The filtrate and washings were combined and evaporated to dryness in vacuo. The residue was stirred in 80 mL of $CHCl_3$, the solid material that separated was filtered off, and the filtrate was evaporated to dryness. The residue was recrystallized from MeOH (60 mL) to give **3** (6.7 g) as a white needles. The filtrate was chromatographed on column of silica gel with 4:1 petroleum ether (60–90 °C)–EtOAc as eluent to give more **3** (0.8 g), yield 80.4%; mp 183.0–185.0 °C, $[\alpha]_D$ +29.4° (*c* 0.51, $CHCl_3$); IR: 1741, 1642 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), δH (ppm): Glc: 5.28 (d, 1 H, *J* 3.6 Hz, H-1), 4.80 (dd, 1 H, H-2), 4.24 (t, 1 H, H-3), 3.63 (t, 1 H, H-4), 4.12 (m, 1 H, H-5), 3.76 (m, 1 H, H-6a), 4.30 (m, 1 H, H-6e); Rha: 4.98 (s, 1 H, H-1'), 4.96 (dd, 1 H, H-2'), 5.22 (t, 1 H, H-3'), 5.07 (t, 1 H, H-4'), 3.98 (dd, 1 H, H-5'), 0.71 (d, 3 H, CH_3-6'), 1.96 (s, 3 H), 1.99 (s, 3 H), 2.11 (s, 3 H), 2.14 (s, 3 H) (4×CH_3CO-), 3.96 (dd,1 H), 4.16 (dd, 1 H), 5.81 (m, 1 H), 5.32 (m, 1 H), 5.11 (m, 1 H) (-OCH_2CH=CH_2), 5.56 (s, 1 H, -CH-, benzylidene), 7.33–7.48 (m, 5 H, Ar-H); ^{13}NMR (100 MHz, $CDCl_3$): δc (ppm) Glc: 95.7 (C-1), 73.5 (C-2), 74.0 (C-3), 79.5 (C-4), 62.8 (C-5), 68.6 (C-6), Rha.: 97.4 (C-1'), 71.2 (C-2'), 68.6 (C-3'), 70.2 (C-4'), 66.1 (C-5'), 16.5 (C-6'), aglycon: 68.8,133.3, 117.8; benzylidene: 101.9 (O-C-O) 137.0, 128.0, 126.3, 129.0 (Ar-C), 20.3, 20.5, 20.7, 20.8 (4×$\underline{C}H_3CO$), 169.7, 169.8, 170.2, 171.0 (4×$\underline{C}H_3CO$-). MS, *m*/*z*: 623 $(M+1)^+$, 563, 273; Anal. Calcd for $C_{30}H_{38}O_{14}$: C, 57.87; H, 6.15. Found: C, 57.62, H, 6.08.

*Allyl 2-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside* (**4**).—A mixture of **3** (0.9 g, 1.45 mmol), MeOH (30 mL), water (30 mL) and *p*-toluenesufonic acid (60 mg) was refluxed for 2 h and the solvent was evaporated under diminished pressure. The residue was dissolved in $CHCl_3$ (30 mL), and the solution was washed with saturated aqueous NaCl (30 mL), dried with Na_2SO_4, and concentrated. Purification of the residue by VLC (vacuum liquid chromatography) [eluent: petrolum ether (60–90 °C)–EtOAc 1:1→1:2 gave **4** (0.5 g, 78.1%) as a white amorphous

powder and **3** (0.15 g, recovered). IR (KBr): 3485, 1734, 1640 cm^{-1}.

*Allyl 6-*O*-(4-*O*-acetoxycinnamoyl)-2-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-rhamnopyranosyl)-α-*D*-glucopyranoside* (**5**).—To a mixture of **4** (1.4 g, 2.62 mmol), dry THF (20 mL) and dry pyridine (2 mL) cooled to 0 °C was added during 20 min a THF (10 mL) solution of 4-acetoxycinnamoyl chloride (0.62 g, 2.76 mmol). The mixture was stirred for 6 h (warming gradually to room temperature). After removal of THF from the mixture, $CHCl_3$ (30 mL) was added. The solution formed was washed with brine (2×30 mL), dried with anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the residue by VLC (eluent:5:1 benzene–EtOAc) gave **5** (1.7 g, 89.9%), mp 89.0–91.0 °C, $[\alpha]_D$ + 45.6 δ (*c* 0.32, $CHCl_3$); IR (KBr): 3474, 1741, 1706, 1631 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δH (ppm): Glc 5.24 (d, 1 H, *J* 3.4 Hz, H-1), 4.84 (dd, 1 H, H-2), 4.23 (t, 1 H, H-3), 3.53 (t, 1 H, H-4), 3.88 (t, 1 H, H-5), 4.37 (t, 1 H, H-6a), 4.68 (dd, 1 H, H-6e); Rha 4.96 (d, 1 H, *J* 2.20 Hz, H-1'), 5.07 (dd, 1 H, H-2'), 5.23 (dd, 1 H, H-3'), 5.09 (t, 1 H, H-4'), 4.03 (dd, 1 H, H-5'), 1.22 (d, 3 H, CH_3-6'), 4.17 (dd, 1 H), 3.98 (dd, 1 H), 5.87 (m, 1 H), 5.30 (m, 1 H), 5.15 (m, 1 H) (-$OCH_2CH=CH_2$), 6.48 (d, 1 H, *J* 16.1 Hz), 7.75 (d, 1 H, *J* 16.1 Hz) (Ar-CH=CH-CO-), 7.14–7.58 (m, 4 H, Ar-H), 1.95 (s, 3 H), 1.99 (s, 3 H), 2.11 (s, 3 H), 2.14 (s, 3 H), 2.21 (s, 3 H) (5×CH_3CO-); ^{13}CNMR (100 MHz, $CDCl_3$): δc (ppm) Glc. 95.2 (C-1), 72.0 (C-2), 80.0 (C-3), 69.2 (C-4), 70.0 (C-5), 62.9 (C-6); Rha: 98.8 (C-1'), 70.8 (C-2'), 68.5 (C-3'), 69.9 (C-4'), 67.3 (C-5'), 17.3 (C-6'); cinnamoyl: 131.9, 129.4 (2C), 122.1 (2C), 152.3 [Ar-C], 144.9, 118.0, 167.4 [$CH_2=CH-CH_2$-O], 20.3, 20.4, 20.8, 21.0, 21.7 (5×$\underline{C}H_3CO$), 168.9, 169.0, 169.8, 170.0, 171.7 (5×$\underline{C}H_3CO$); aglycon: 68.7, 133.2, 117.3; MS, *m/z*: 723 $(M+1)^+$, 655, 273, 189. Anal. Calcd for $C_{34}H_{42}O_{17}$: C, 56.50; H, 5.86. Found: C, 56.90; H, 5.81.

*6-*O*-(4-Acetoxycinnamoyl)-2-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-rhamnopyranosyl)-β-*D*-glucopyranose* (**6**).—To a THF (15 mL) solution of **5** (2.6 g, 3.6 mmol) were added $PdCl_2$ (0.64 g, 3.6 mmol), CuCl (0.35 g, 3.6 mol) and water (1.5 mL), and the solution was stirred vigorously for 2 h at 25–30 °C. The mixture was then diluted with $CHcl_3$ (40 mL), and filtered through a bed of Celite. The $CHcl_3$ solution was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated. Flash chromatography (3:1 benzene–EtOAc) of the residue gave **6** as a syrup (2.3 g, 93.5%).

*2-*O*-Acetyl-1-*O*[2-(4-allyloxyphenyl)ethyl]-6-*O*-(4-acetoxycinnamoyl)-3-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-rhamnopyranosyl)*β-*D*-glucopyranoside (**7**).—To a solution of **6** (2.3 g, 3.3 mmol) in $CHCl_3$ (15 mL) were added sodium trichloroacetate (0.6 g, 3.3 mmol) and trichloroacetic anhydride (1.35 g, 4.4 mmol). The solution was refluxed for 5 h. Chloroform (20 mL) was added after the mixture had been cooled to room temperature. The $CHCl_3$ solution was washed with ice–water (3×20 mL) and dried with anhydrous Na_2SO_4. Evaporation of the solvent gave a syrup (one spot on TLC). The syrup was dissolved in dry CH_2Cl_2 (50 mL) and 2-(4-allyloxyphenyl)ethanol (1.0 g) and 2,6-di-*tert*-butyl-4-methylpyridine (DBMP, 0.5 g) were added. The solution was cooled to −15 °C, and stirred for 48 h in the presence of Me_3SiOTf (10 drops) as catalyst, during which time the temperature was raised to room temperature. This mixture was diluted with $CHCl_3$ (50 mL), washed with water (50 mL), aqeous $NaHCO_3$ (5%, 50 mL) and water (50 mL), dried with Na_2SO_4 and concentrated. Flash chromatography (4:1 benzene–EtOAc) gave a white amorphous solid (1.85 g, 61% from **5**). mp 88.0–90.0 °C, $[\alpha]_D$ −35.0° (*c* 0.2, $CHCl_3$); IR(KBr): 3474, 1743, 1710, 1628 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δH (ppm): Glc 4.39 (d, 1 H, *J*7.93 Hz, H-1), 4.99 (dd, 1 H, H-2), 3.61 (t, 1 H, H-3), 3.55 (t, 1 H, H-4), 3.51 (m, 1 H, H-5), 4.62 (dd, 1 H, H-6a), 4.44 (t, 1 H, H-6e); Rha 4.87 (d, 1 H, *J*1.8 Hz, H-1'), 5.07 (dd, 1 H, H-2'), 5.26 (dd, 1 H, H-3'), 5.07 (t, 1 H, H-4'), 4.21 (dd, 1 H, H-5'), 1.21 (d, 3 H, CH_3-6'); 4.07 (m,1 H), 3.62 (m, 1 H) (-$O\underline{CH_2}$-CH_2Ar), 2.82 (t, 2 H, -$OCH_2\underline{CH_2}Ar$), 4.49 (m, 2 H), 6.04 (m, 1 H) , 5.42 (m, 1 H), 5.27 (m, 1 H) (-$OCH_2CH=CH_2$), 6.47 (d, 1 H, *J* 16.0 Hz), 7.73 (d, 1 H, *J* 16.0 Hz) (Ar-CH=CH-CO-), 6.81- 7.56 (m, 8 H, Ar-H), 1.95 (s, 3 H), 1.98 (s, 3 H), 2.11 (s, 3 H), 2.14 (s, 3 H), 2.21 (s, 3 H) (5×CH_3CO-); ^{13}C NMR (100 MHz, $CDCl_3$): δc (ppm) Glc.: 100.8 (C-1), 74.1 (C-2), 76.7 (C-3), 69.0 (C-4), 70.0 (C-5), 63.0 (C-6); Rha: 98.6 (C-1'), 71.7 (C-2'), 68.5 (C-3'), 70.8 (C-4'), 67.4 (C-5'), 17.3 (C-6'); cinnamoyl: 131.9, 129.4 (2C), 122.1 (2C), 152.3 [Ar-C], 144.8, 117.3, 67.0 [C=C-C=O]; aglycon: 70.7, 35.1 (O-C-C), 130.7, 129.9 (2C) 114.6 (2C), 157.1 [Ar-C], 68.8, 133.4, 117.5 (O-CH_2-CH=CH_2), 20.6, 20.7, 20.7, 20.8, 21.5 (5×$\underline{C}H_3CO$), 169.0, 169.9, 170.0, 170.5, 172.0 (5 ($CH_3\underline{C}O$). MS, *m/z*: 834 $(M+1)^+$, 655, 273, 189, 161. Anal. Calcd for $C_{42}H_{50}O_{18}$: C, 59.85; H, 5.98. Found: C, 60.07; H, 5.68.

*2-(4-Hydroxyphenyl)ethyl-2-*O*-acetyl-6-*O*-(4-hydroxycinnamoyl)-3-*O*-(α-*L*-rhamnopyranosyl)-β-*D*-glucopyranoside* (**8**, *2-*O*Ac Osmanthuside B6*).—To a THF (4 mL) solution of **7** (560 mg, 0.665 mmol) were added $PdCl_2$ (120 mg, 0.667 mmol), CuCl (66 mg, 0.667 mmol) and water (8 drops). The solution was stirred vigorously for 6 h at 25–30 °C. The mixture was then diluted with $CHCl_3$ (15 mL), and filtered on a bed of Celite. The filtrate was washed with water (10 mL×4) and dried over Na_2SO_4. Evaporation of the solvent gave a solid. To the solid was added an NH_4OH–MeOH mixture (15 mL, 15%, w/w) and the mixture was stirred for 5 h at 5–10 °C and refrigerated overnight. After evaporation of solvent, flash chromatography (10:5:1 EtOAc–benzene–MeOH) of the residue gave **8** (210 mg, 53.3%). ^{13}CNMR (100 MHz, $DOCD_3$), δc (ppm) Glc: 101.7 (C-1), 74.8 (C-2), 82.8 (C-3), 70.6 (C-4), 75.3 (C-5), 64.6 (C-6); Rha: 102.8 (C-1'), 72.4 (C-2'), 72.1 (C-3'), 73.9 (C-4'), 70.3 (C-5'), 17.6 (C-6'); cinnamoyl: 127.1,130.9 (2C), 116.9 (2C), 161.0 [Ar-C], 146.8, 115.0, 169.0 [C=C-C=O]; aglycon: 131.0, 116.2 (2C), 131.2 (2C), 156.5 [Ar-C], 36.1, 71.8 [O-$\underline{C}H_2$-$\underline{C}H_2$-Ar], 20.1 ($\underline{C}H_3$CO-), 170.2 ($CH_3\underline{C}$O-). MS, *m*/z: 843 $(M+K)^+$, 497, 147,121.

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