Chemistry and Stereochemistry of Iridoids, XX[+]

Preparation of Kingiside from Aucubin

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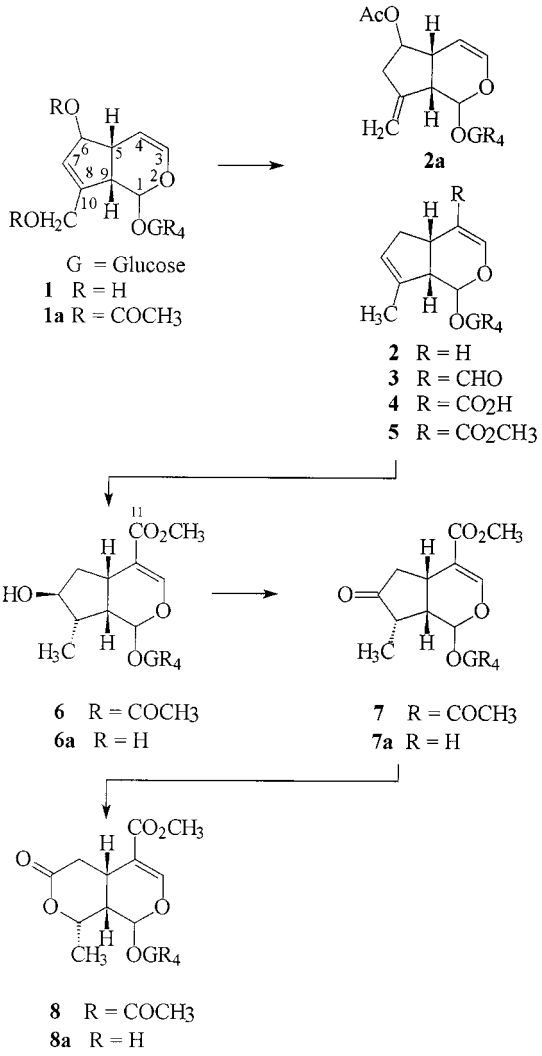
The tetraacetyl derivative **8** of the naturally occurring kingiside (**8a**) was prepared from aucubin (**1**). Intermediates in the synthesis were (8*S*)-tetraacetyl loganin (**6**) and (8*S*)-tetraacetyl-7-ketologanin (**7**), whose free (8*R*)-epimers occur in many different plants (Caprifoliaceae, Loganiaceae). The ^{13}C NMR spectrum allows the structure to be unequivocally identified.

Introduction

Kingiside (**8a**) was first isolated in 1969 by Souzu and Mitsuhashi[1] from *Lonicera morrowii* (Caprifoliaceae; Japanese name: Kingoboku) and belongs to the class Secoiridoides. Later **8a** was also identified in extracts from *Lonicera alpigena* (Caprifoliaceae; German name: Alpen-Heckenkirsche)[2] and *Gentiana pyrenaica* (Gentianaceae, gentian from the Pyrenees).[3]

For the preparation of kingiside (**8a**) we used aucubin (**1**), which can be isolated in 2–3% from the aqueous extract of *Aucuba japonica* (Carnaceae; German name: Goldblatt or Aucube). Alternatively, **8a** could be produced from catalpol, which can be isolated in large quantities from *Picrorhiza kurrooa* (Scrophulariaceae).[4] Compound **1** was acetylated to its hexaacetyl derivative **1a**. The two allyllic acetoxy groups of **1a** were reductively eliminated to **2** by Pd^0-catalyzed substitution with formic acid as the hydride donor; compound **2a** is formed as a by-product. The acetoxy groups on the glucose ring are not attacked under these reaction conditions. Since the 4-position in iridoids is activated toward electrophilic attack a formyl group was introduced by a Vilsmeier reaction to yield **3**. This route provides access to the series of C_{16} iridoid glucosides. Aldehyde **3** was oxidized to **4** in *tert*-butyl alcohol with sodium chlorite, followed by treatment with diazomethane in ether to yield **5**.

The double bond in the cyclopentane ring of **5** can be selectively hydroborated to **6** in the presence of the α/β-unsaturated methyl ester group. The attack of the borane is stereoselective from the 7*re*/8*re* face so that, after oxidative workup with hydrogen peroxide, the hydroxyl group on C-7 is trans to the methyl group on C-8, i.e. C-7 and C-8 have an *S*-configuration. A Zemplén saponification of **6** yields (8*S*)-loganin (**6a**), which has been isolated by Bianco et. al.[5] from the extract of *Odontites verna* (Scrophulariaceae; German name: Zahnkraut). (8*S*)-Loganin is an important iridoid glucoside, from which secologanin originates. Secologanin is a key intermediate in the biosynthesis of indole



Scheme 1. Structural determination of **2**–**8** from their ^{13}C NMR spectra

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alkaloids[6] and, accordingly, it is found primarily in plants that also contain indole alkaloids. (8*R*)-Loganin had already been isolated in 1883[7] from the fruit pulp of *Strychnos nux vomica* (Loganiaceae, German name: Brechnußbaum), a tree that is native to the tropical regions of India and Sri Lanka. In Europe (8*R*)-loganin is found in *Menyanthes trifoliata* (Menyanthaceae, German name: Fieberklee or Bitterklee).[8] However, the constitution of (8*R*)-loganin was first determined in 1961[9] and the absolute configuration in 1969 by an X-ray structural analysis.[10]

Oxidation of the free hydroxyl group in (8*S*)-tetraacetylloganin (**6**) with pyridinium chlorochromate (PCC) in anhydrous dichloromethane furnishes (8*S*)-tetraacetyl-7-ketologanin (**7**) in good yield. Whereas the free iridoid glucoside (**7a**) has not as yet been detected in plants, the epimer (8*R*)-7-ketologanin has been isolated from the extracts of *Lonicera coerulea*[11] (Caprifoliaceae, German name: Blaue Heckenkirsche) and *Strychnos nux-vomica* (Loganiaceae).[12]

Baeyer-Villiger oxidation of (8*S*)-tetraacetyl-7-ketologanin (**7**) yields (8*S*)-tetraacetyl-kingiside (**8**), whose melting point (164–166 °C) and specific rotation {[α] = –91 (*c* = 1, $CHCl_3$)} are identical (ref.[2]) to those of the tetraacetate of the naturally occurring kingiside. Inouye et. al.[13] have prepared (8*R*)-tetraacetylkingiside from the naturally occurring (8*R*)-tetraacetyl-7-ketologanin, whose physical properties {m.p. 114.5–115.5 °C, [α] = −55 ($CHCl_3$)} are distinctly different from **7**, implying that the naturally occurring kingiside **7a** has the 8*S* configuration.

Table 1. ^{13}C NMR spectroscopic data (δ, 50.32 MHz, 75.47 MHz, $CDCl_3$)

C-	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**8**[2]	**8**[3]
-1	92.8	96.1	97.1	95.6	94.5	93.2	92.6	92.6	92.6
-3	138.5	160.3	153.5	150.6	149.7	150.4	151.8	151.9	151.9
-4	108.7	125.1	112.6	112.6	113.9	110.9	110.6	110.6	110.7
-5	31.2	31.1	33.6	33.3	28.8	26.4	26.0	26.0	26.1
-6	38.2	37.1	38.9	38.3	39.9	41.9	33.1	33.0	33.1
-7	125.9	127.5	127.8	126.9	78.6	217.3	169	to	171[a]
-8	137.6	136.9	138.1	137.6	40.9	43.0	74.3	74.3	74.4
-9	49.9	48.9	49.7	49.1	43.3	45.0	38.5	38.5	38.6
-10	14.8	15.1	15.9	15.1	13.7	13.1	17.6	17.6	17.7
-11	–	190.4	173.2	167.2	167.1	166.5	165.9	165.9	165.9
OCH_3	–	–	–	50.9	51.2	51.4	51.4	51.4	51.5

[a] The signal for C-7 is found in the area of the carbonyl C-atoms of the acetyl groups. The signals for the carbon atoms of the glucose and acetyl groups are not cited since they do not give any evidence for the structure of the iridoid aglycons.

The ^{13}C NMR spectra (Table 1) of the acetylated iridoid glucosides **2–8** offer conclusive evidence of their structures since a large number of comparison spectra are available in our laboratory (see also ref.[14]) which allows the definite assignment of the carbon atoms. The ^{13}C chemical shifts of the (8*S*)-tetraacetylkingiside (**8**) are identical to those reported in the literature for the naturally occurring kingiside. There is currently no known ^{13}C NMR spectrum for the (8*R*)-tetraacetylkingiside, which was prepared from the naturally occurring (8*R*)-tetraacetyl-7-keto-loganin.[13]

Experimental Section

Melting points (uncorrected): Büchi melting point apparatus. – TLC: Polygram Sil G/UV_{254} (Macherey–Nagel); spray reagent hydroxylamine/iron(III) chloride according to Stahl.[15] – Optical rotation: polarimeter 241 (Perkin–Elmer). – NMR spectra: Bruker AC 200 and AC 300. – CC: Silica 32–63 (ICN Biomedicals).

Tetraacetyl-6,10-bisdeoxyaucubin (2): A mixture of formic acid (0.5 mL, 615 mg, 13.4 mmol) and triethylamine (1.87 mL, 1.36 g, 13.4 mmol) in 3 mL of dioxane was dripped slowly under stirring to a boiling mixture of hexaacetylaucubin (**1a**; 4.0 g, 6.68 mmol) and Pd on charcoal (10%, dry, 2 g) in dioxane (30 mL). When the addition was completed the black suspension was heated for another 1.5 h at 110 °C. After cooling to room temp. it was filtered by suction through a small quantity of silica gel and the residue washed carefully with chloroform. The combined filtrates were dried in vacuo. The TLC showed, besides the desired compound **2**, four other products. The yields of the fractions varied from set-up to set-up, and came to 25–35% for **2**. The mixture was separated by CC (toluene/acetone, 99:1 → 8:2).

2: Colourless crystals (ethanol), m.p. 137 °C, (yield 1.13 g, 35%), R_f = 0.70 (toluene/acetone, 8:2). – $[\alpha]_{589}^{20}$= −128; $[\alpha]_{578}^{20}$= −134; $[\alpha]_{546}^{20}$= −152 (*c* = 1, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$); signals for the aglycon: δ = 1.72 (s, 3 H, 10-Me), 1.97–2.05 (4s, 12 H, 4 $COCH_3$), 1.91–2.05 (m, 1 H, 6-H_B), 2.47–2.54 (m, 1 H, 6-H_A), 2.76–2.78 (m, 2 H, 5-H, 9-H), 4.61 (dd, $J_{3,4}$ = 6.1, $J_{4,5}$ = 1.6 Hz, 1 H, 4-H), 5.27 (s, 1 H, 1-H), 5.37 (s, 1 H, 7-H), 6.09 (d, 1 H, 3-H); signals for the glucose part: δ = 3.69 (ddd, $J_{4',5'}$ = 9.6, $J_{5',6'A}$ = 4.5, $J_{5',6'B}$ = 2.4 Hz, 1 H, 5′-H), 4.10 (dd, $J_{6'A,6'B}$ = 12.3 Hz, 1 H, 6′ H_B), 4.27 (dd, 1 H, 6′-H_A), 4.84 (d, $J_{1',2'}$ = 8.0 Hz, 1 H, 1′-H), 5.00 (dd, $J_{2',3'}$ = 9.4 Hz, 1 H, 2′-H), 5.07 (t, $J_{3'4'}$ = 9.4 Hz, 1 H, 4′-H), 5.21 (t, 1 H, 3′ H). – ^{13}C NMR: See Table 1. – $C_{23}H_{30}O_{11}$ (482.5): calcd. C 57.26, H 6.27; found C 57.24, H 6.37.

Pentaacetyl-10-deoxyexoaucubin (2a): Colourless crystals (ethanol), m.p. 120 °C, R_f = 0.58 (toluene/acetone, 8:2). – $[\alpha]_{589}^{20}$ = −125 (*c* = 1, $CHCl_3$). – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.97–2.07 (m, 15 H, 5 $COCH_3$), 2.37 (d, $J_{7A,7B}$ = 18.1 Hz, 1 H, 7-H_B), 2.71–2.83 (m, 2 H, 5-H, 7-H_A), 3.05–3.15 (m, 1 H, 9-H), 4.65 (dd, $J_{4,5}$ = 1.6, $J_{3,4}$ = 6.4 Hz, 1 H, 4-H), 5.45 (d, $J_{1,9}$ = 2.0 Hz, 1 H, 1-H), 6.13 (dd, 1 H, 3-H); the signals for the glucose are omitted since they are found in the usual areas (see **2** above). – ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 146.4 (C-8), 140.7 (C-3), 109.4 (C-10), 102.3 (C-4), 93.5 (C-1), 77.8 (C-6), 43.0 (C-9), 37.9 (C-5), 37.6 (C-7); the values for the acetyl groups and the glucose part are omitted. – $C_{25}H_{32}O_{13}$ (540.5): calcd. C 55.55, H 5.97; found C 55.52, H 6.12.

Tetraacetyl-6,10-bisdeoxy-4-formyl-aucubin (3): Dimethylformamide (4 mL, 52 mmol) was stirred for 1 h under argon with dichloromethane (4 mL) and powdered molecular sieves (4 Å, 0.7 g). After cooling to –25 °C, $POCl_3$ (2.4 mL, 25.8 mmol) was added dropwise through a septum. The cooling bath was removed and stirred for another 1 h while the mixture warmed to room temp. A solution of **2** (1.3 g, 2.6 mmol) in CH_2Cl_2 was then added and the mixture stirred under argon at 42 °C for another 24 h. When the reaction was finished (control by TLC), the reaction mixture was poured into a mixture of dichloromethane (50 mL), a saturated solution of $NaHCO_3$ (50 mL) and solid $NaHCO_3$ (10 g; **Caution**: violent production of carbon dioxide). After 1 h the mixture was filtered

over celite and the product extracted twice with CH_2Cl_2. The organic layer was washed with water and dried with Na_2SO_4. The solvent was removed in vacuo and the product purified by flash-CC (toluene/acetone 98:2). Colourless needles from ethanol (yield 89%), m.p. 130 °C, R_f = 0.49 (toluene/acetone, 8:2). – $[\alpha]_{589}^{20} = -38$; $[\alpha]_{578}^{20} = -40$; $[\alpha]_{546}^{20} = -44$ (c = 1, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.74 (s, 3 H, 10-Me), 1.91–2.10 (m, 1 H, 6-H_B), 2.65–2.85 (m, 2 H, 9-H, 6-H_A), 3.10–3.20 (m, 1 H, 5-H), 5.31 (d, $J_{1,9}$ = 4.5 Hz, 1 H, 1-H), 5.42 (s, 1 H, 7-H), 7.10 (s, 1 H, 3-H), 9.23 (s, 1 H, 11-H); the values for the acetyl groups and the glucose part are omitted. – ^{13}C NMR: See Table 1. – $C_{24}H_{30}O_{12}$ (510.5): calcd. C 56.47, H 5.92; found C 56.21, H 5.73.

Tetraacetyl-6,10-bisdeoxyaucubin-4-carbonic Acid (4): Aldehyde **3** (309 mg, 0.6 mmol) was put into *tert*-butyl alcohol (14 mL) and 3-methyl-butene (3.4 mL) was added as a chlorine trap. A solution of sodium chlorite (758 mg, 80%) and NaH_2PO_4 (605 mg) in 5 mL of water was added over ca. 30 min. with vigorous stirring. During the addition the aldehyde **3** dissolved. At the end of the reaction a clouding of the mixture occurred due to the separation of a second liquid layer. After stirring for 24 h, the solvent was evaporated and the residue extracted with ethyl acetate. The organic layer was washed with a saturated solution of ammonium chloride, dried with Na_2SO_4 and the solvent removed in vacuo. Purification by CC (toluene/acetone, 95:5) led to the amorphous solid product **4** (yield: 266 mg, 85%), R_f = 0.46 (toluene/acetone/formic acid, 4:1:0.01). – $[\alpha]_{589}^{20} = -24$; $[\alpha]_{578}^{20} = -25$; $[\alpha]_{546}^{20} = -27$ (c = 1, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, 10-Me), 2.08–2.30 (m, 1 H, 6-H_B), 2.70–2.73 (m, 2 H, 9-H, 6-H_A), 3.08–3.11 (m, 1 H, 5-H), 4.95–5.22 (m, 4 H, 1-H [and 2′,3′,4′-H]), 5.44 (s, 1 H, 7-H), 7.48 (d, $J_{3,5}$ = 0.6 Hz, 1 H, 3-H); the values for the acetyl groups and the rest of the glucose part are omitted. – ^{13}C NMR: See Table 1. – $C_{24}H_{30}O_{13}$ (526.5): calcd. C 54.75, H 5.74; found 54.59, H 6.01.

Tetraacetyl-6,10-bisdeoxyaucubin-4-carbonic-acid Methyl Ester (5): To a solution of **4** (1.90 g) in diethyl ether, cooled to ca. –70 °C, was added a solution of diazomethane in diethyl ether under stirring until the mixture remained yellow. Dilute acetic acid was then added in order to decompose the excess of diazomethane. The acidic solution was neutralized at room temp. with a saturated solution of $NaHCO_3$ and extracted several times with diethyl ether. The combined organic layers were washed with water and dried with Na_2SO_4. After removal of the solvent, the residue was crystallized from methanol. Colourless needles (yield: 1.50 g, 77%), m.p. 102 °C, R_f = 0.63 (toluene/acetone, 8:2). – $[\alpha]_{589}^{20} = -29$; $[\alpha]_{578}^{20} = -30$; $[\alpha]_{546}^{20} = -33$ (c = 0.55, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, 10-Me), 1.97–2.17 (m, 1 H, 6-H_B), 2.69–2.77* (m, 2 H, 5-H, 6-H_A), 3.11–3.17* (m, 1 H, 9-H), 3.70 (s, 3 H, OCH_3), 4.99–5.27 (m, 4 H, 1-H [and 2′,3′,4′-H]), 5.45 (s, 1 H, 7-H), 7.39 (d, $J_{3,5}$ = 0.9 Hz, 1 H, 3-H); the values for the acetyl groups and the rest of the glucose part are omitted. (The values marked with * are exchangeable). – ^{13}C NMR: See Table 1. – $C_{25}H_{32}O_{13}$ (540.5): calcd. C 55.55, H 5.97; found C 55.25, H 5.90.

8-*epi*-Tetraacetylloganin (6): Compound **5** (285 mg, 0.53 mmol) was dissolved in dry THF and cooled to 0 °C. Under nitrogen, borane dimethylsulfide complex (0.75 mL, 7.9 mmol) was dropped into the solution and the mixture stirred for 3 h. When the starting material was no longer visible on the TLC, H_2O_2 (30 mL) was added carefully. After gas formation stopped the cooling bath was removed, and the mixture was stirred for an additional hour. A saturated solution of Na_2SO_3 (50 mL) was then added and the product extracted with chloroform. The organic layer was washed with water and dried with Na_2SO_4. After removal of the solvent the product was purified by flash CC (toluene/acetone, 98:2 → 8:2). Colourless crystals from ethanol (yield 124 mg, 42%), m.p. 136 °C, R_f = 0.22 (toluene/acetone, 8:2). – $[\alpha]_{589}^{20} = -101$; $[\alpha]_{578}^{20} = -105$, $[\alpha]_{546}^{20} = -121$ (c = 1, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (d, $J_{9,10}$ = 7.4 Hz, 3 H, 10-Me), 1.76–2.14 (m, 4 H, 6-H, 8-H, OH), 2.71 (m_c, 1 H, 9-H), 2.94–3.02 (m, 1 H, 5-H), 3.68 (s, 3 H, OCH_3), 3.82 (m_c, 1 H, 7-H), 5.30 (d, $J_{1,9}$ = 2.6 Hz, 1 H, 1-H), 7.30 (s, 1 H, 3-H); the values for the acetyl groups and the rest of the glucose part are omitted. – ^{13}C NMR: See Table 1. $C_{25}H_{34}O_{14}$ (558.5): calcd. C 53.76, H 6.14; found C 53.63, H 6.17.

8-*epi*-Tetraacetyl-7-ketologanin (7): Compound **6** (124 mg) was dissolved in dichloromethane (3 mL) and stirred for 14 h at room temp. with pyridinium chlorochromate (500 mg) on aluminum oxide (neutral). Then the chromium salts were separated by filtration over a short column filled with silica gel. After removal of the solvent the product was purified by flash CC (toluene/acetone, 98:2 → 9.1). Colourless needles from ethanol (yield 90.4 mg, 73%), m.p. 151 °C, R_f = 0.39 (toluene/actone, 8:2). – $[\alpha]_{589}^{20} = -57$; $[\alpha]_{578}^{20} = -60$, $[\alpha]_{546}^{20} = -68$ (c = 1, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (d, $J_{8,10}$ = 6.7 Hz, 3 H, 10-Me), 2.04–2.13 (m, 1 H, 6-H_B), 2.55–2.65 (m, 2 H, 8-H, 9-H), 2.82 (m_c, 1 H, 6-H_A), 3.16 (m_c, 1 H, 5-H), 3.71 (s, 3 H, OCH_3), 5.05–5.12 (m, 2 H, 1-H with 4′-H), 7.44 (s, 1 H, 3-H); the values for the acetyl groups and the rest of the glucose part are omitted. – ^{13}C NMR: See Table 1. – $C_{25}H_{32}O_{14}$ (556.5): calcd. C 53.96, H 5.79; found C 53.88, H 5.67.

Tetraacetylkingiside (8): A mixture of **7** (174 mg, 0.31 mmol), $NaHCO_3$ (168 mg, 1.0 mmol) and *m*-chloroperbenzoic acid (80 mg) in dry dichloromethane (10 mL) was stirred for 21 h at room temp. For work-up, the excess of perbenzoic acid was destroyed by adding 50 mL of a saturated solution of Na_2SO_3. After addition of 20 mL of a saturated solution of $NaHCO_3$, the organic layer was separated and the aqueous phase extracted twice with dichloromethane. The combined organic phases were washed with a solution of $NaHCO_3$ and dried with Na_2SO_4. After removal of the solvent the product was purified by CC (toluene/acetone, 95:5 → 9.1). Colourless needles from ethanol (126 mg, 70%), m.p. 164–165 °C (ref.[1]: 165–166 °C; ref.[2]: 164–165 °C), R_f = 0.18 (toluene/acetone, 8:2). – $[\alpha]_{589}^{20} = -94$; $[\alpha]_{578}^{20} = -98$, $[\alpha]_{546}^{20} = -112$ (c = 1, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46, (d, $J_{8,10\text{-Me}}$ = 6.8 Hz, 3 H, 10-Me), 1.92–2.06 (4s, 12 H, 4 $COCH_3$), 2.29–2.35 (m, 1 H, 9-H), 2.65 (dd, $J_{5,6B}$ = 5.5, $J_{6A,6B}$ = 17.0 Hz, 1 H, 6-H_B), 2.86 (dd, $J_{5,6A}$ = 7.4 Hz, 1 H, 6-H_A), 3.18–3.20 (m, 1 H, 5-H), 3.67–3.75 (m, 1 H, 5′-H), 3.69 (s, 3 H, OCH_3), 4.08 (dd, $J_{5',6'B}$ = 2.3, $J_{6'A,6'B}$ = 12.4 Hz, 1 H, 6′-H_B), 4.27 (dd, $J_{5',6'A}$ = 4.8 Hz, 1 H, 6′-H_A), 4.56–4.61 (m, 1 H, 8-H), 4.84 (d, $J_{1',2'}$ = 8.1 Hz, 1 H, 1′-H), 4.97 (t, $J_{2',3'}$ = 8.8 Hz, 1 H, 2′-H), 5.06 (t, $J_{3',4'} = J_{4',5'}$ = 9.6 Hz, 1 H, 4′-H), 5.12 (t, 1 H, 3′-H), 5.41 (d, $J_{1,9}$ = 5.3 Hz, 1 H, 1-H), 7.40 (s, 1 H, 3-H). – ^{13}C NMR: See Table 1. – $C_{25}H_{32}O_{15}$ (572.5): calcd. C 52.45, H 5.63; found C 52.29, H 5.66.

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