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A NEW APPROACH TO THE SYNTHESIS OF DISACCHARIDE DERIVATIVES HAVING A FURANOSE AS THE REDUCING UNIT

CECILE DU MORTIER, OSCAR VARELA*, AND ROSA M. DE LEDERKREMER*

Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires (Argentina)

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ABSTRACT

The lactonic disaccharide 2,3,5-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-D-galactono-1,4-lactone (**7**) was prepared by condensing 6-*O*-trityl-2,3,5-tri-*O*-benzoyl-D-galactono-1,4-lactone (**2**) with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**4**) or with 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**6**). The reaction was carried out using various catalysts. In the presence of silver trifluoromethanesulfonate or tin(IV) chloride, formation of the 1,2-*trans* glycosidic bond took place stereoselectively, to afford compound **7** in good yields. However, condensation of 2,3,5-tri-*O*-benzoyl-D-galactono-1,4-lactone (**3**) with **4** catalyzed by mercuric salts gave 3,4,6-tri-*O*-acetyl-1,2-*O*-[1(*S*)-(2,3,5-tri-*O*-benzoyl-D-galactono-1,4-lacton-6-yloxy)ethylidene]-α-D-glucopyranose (**5**) as the main product. Reduction of the lactone function of **7** with bis(3-methyl-2-butyl)borane led to 2,3,5-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-galactofuranose (**8**).

INTRODUCTION

Aldonolactones have been widely used as chiral starting compounds in the synthesis of carbohydrate and non-carbohydrate natural products[1,2]. In our laboratory, selectively protected aldonolactones have been employed as intermediates for the preparation of different molecules[3,4]. Glycosyl-aldono-1,4-lactones would be useful precursors of disaccharides having the reducing end in a furanoid ring structure; specifically, a glycosyl-galactono-1,4-lactone would be a good precursor for a disaccharide having galactofuranose as the reducing end. This sugar has been identified, among others, in a glycopeptide from *Penicillium charlesii*[5] and in a glycoconjugate from *Trypanosoma cruzi*[6].

As we have found no examples in the literature on the use of selectively substituted aldonolactones as glycosidating agents of monosaccharides, we first explored the condensation of readily available tetra-*O*-acetyl-α-D-glucopyranosyl

*Research members of the National Research Council of Argentina (CONICET).

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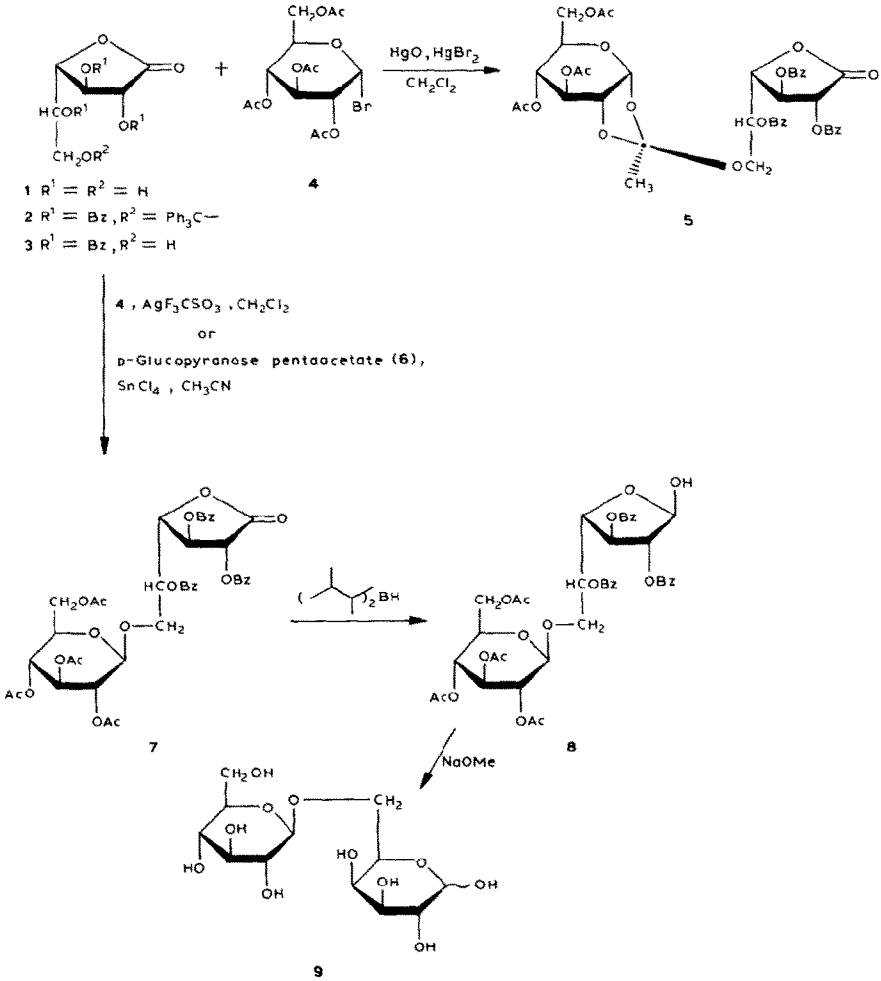
bromide (**4**) with the more reactive HO-6 of galactono-1,4-lactone derivatives **2** and **3**. We report here an efficient synthesis of the 6-*O*-β-D-glucopyranosyl-D-galactono-1,4-lactone derivative **7**. The conversion of **6** into a disaccharide having a furanose reducing unit was also studied.

RESULTS AND DISCUSSION

Tritylation of D-galactono-1,4-lactone (**1**) with chlorotriphenylmethane, followed by benzoylation, gave 2,3,5-tri-*O*-benzoyl-6-*O*-trityl-D-galactono-1,4-lactone (**2**) in 90% yield. Detritylation of **2** with $BF_3 \cdot OEt_2$ took place cleanly to afford 2,3,5-tri-*O*-benzoyl-D-galactono-1,4-lactone (**3**). The ^{1}H-n.m.r. spectrum of compound **3** showed a downfield shift for H-6,6′ of 0.46 p.p.m. and for H-5 of 0.12 p.p.m. with respect to the corresponding signals in the tritylated derivative **2**. Detritylation of the acetylated analog of **3** was reported[3] to occur with O-5→O-6 acetyl migration, which was not observed in the detritylation of **3**. This result agrees with the fact that benzoyl groups do not migrate as readily as acetyl groups[7]. Compound **3** was condensed with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**4**) in CH_2Cl_2 in the presence of HgO and $HgBr_2$ to give a main product that was isolated by column chromatography in good yield. The 100-MHz ^{1}H-n.m.r. spectrum of this compound was quite complex, showing besides 15 aromatic protons (3 benzoyl groups) and 12 aliphatic protons (4 acetyl groups), a neat triplet at δ 5.16 p.p.m. (*J* 2.9 Hz) which did not match either with the glucopyranose or the lactone portion of the molecule. In order to establish the structure of the product, a 2D ^{1}H-chemical-shift-correlated n.m.r. spectroscopy[8,9] (2D-COSY) experiment was carried out. The protons of the lactone moiety were readily assigned by comparison with the spectra of compounds **2** and **3**, and confirmed by their connectivities starting from H-2. The connectivities for the protons in the glucopyranoid ring were made starting with the resonance of the anomeric proton, which appeared as a doublet at 5.72 p.p.m. The signal at 5.16 p.p.m. corresponded to H-3′, and the double doublet at 4.34 p.p.m. was attributable to H-2′. The large value for the H-1′–H-2′ coupling constant ($J_{1',2'}$ 5.2 Hz) and the small values for $J_{2',3'}$ (3.1 Hz) and $J_{3',4'}$ (2.6 Hz) would indicate a distortion of the $^4C_1$ conformation of the glucopyranose ring, as established for *cis*-fused bicyclic systems[10]. This fact, together with the anomalously high chemical shift of H-1′ (5.72 p.p.m.) compared with the values for glucosides, suggested an 1,2-orthoester structure for product **5** from the Koenigs–Knorr condensation. Compound **5** would consist of a pyranoid ring in a skew or in a flattened-chair conformation[10], *cis*-fused to a five-membered ring ethylidene orthoester. The ^{13}C-n.m.r. spectrum of **5** showed the orthoester carbon at 121.2 p.p.m. C-1′ at 97.0 p.p.m., these values being similar to those reported[11] for analogous derivatives. Furthermore, comparison of the ^{1}H-n.m.r. data of **5** with chemical shifts and coupling constants described[11–13] for glycopyranose 1,2-orthoesters, would suggest the *S*-(*exo*) configuration at the orthoester carbon. Thus, the diagnostic signal[11,13] of the orthoacetate methyl group of compound **5** (δ 1.74



p.p.m.) lies within the range observed for *exo* isomers. The preference for the *exo* diastereoisomer may be explained on the basis of the mechanism of orthoester formation[12,14]. A more facile approach of the bulky lactone derivative **3** to the 1,2-acetoxonium ion intermediate to the less-hindered side, opposite the glucopyranose ring, would produce the exo-isomer.

Orthoesters are rather common side-products in Koenigs–Knorr condensations of acetylated glycosyl halides with alcohols[14,15]. The use of appropriate catalyst–solvent and catalyst–acid acceptor systems[13,16] can lead preferentially to orthoesters. Conversely, orthoester formation can be decreased by modifying the polarity of the solvent; for instance, by replacing CH_2Cl_2 by $CHCl_3$ or CCl_4[11]. However, when the condensation of **3** with **4** was carried out in those solvents instead

of CH_2Cl_2, considerable amounts of **5** were detected by t.l.c. In view of these results, we decided to conduct the reaction in the presence of silver trifluoromethanesulfonate (silver triflate), which has shown to be effective for the synthesis of 1,2-*trans* disaccharides[17]. The 6-*O*-trityl derivative (**2**) was used as the glycosidating agent, as it has been reported that trityl ethers reacted with the acyloxonium intermediates, generated from glycosyl halides and silver perchlorate[15], or from 1,2-*O*-(1-cyanoethylidene) derivatives[18,19], to produce 1,2-*trans*-glycosides. This procedure has the advantage that no strong acids are liberated, and acid acceptors in the reaction medium are not required. Condensation of the glucosyl bromide **4** with the trityl ether **2**, in CH_2Cl_2 with silver triflate as catalyst, gave a main product, which was isolated by column chromatography in 50% yield. Its ^{1}H-n.m.r. spectrum showed a doublet at 4.59 p.p.m. (J 8.0 Hz) characteristic of H-1′ of 1,2-*trans* glucopyranosides[20]. The connectivities for the protons in a 2D-COSY experiment allowed the complete assignment of the spectrum. The ^{13}C-n.m.r. spectrum of **7** showed a single signal in the anomeric region (δ 100.8 p.p.m.), which is in accordance with the β configuration at C-1′.

The glycosyl-lactone **7** was also obtained by using $SnCl_4$ as catalyst. Stannic chloride has been successfully used in the synthesis of 1,2-*trans* glycosides, starting from readily available per-*O*-acetyl sugar derivatives[21,22]. 1,2,3,4,6-Penta-*O*-acetyl-β-D-glucopyranose (**6**), was allowed to react with $SnCl_4$ in order to activate the anomeric center. The trityl group of **2** would attack the intermediate acyloxonium ion, to give the crystalline compound **7**, which was isolated in 77% yield.

Disiamylborane reduction[23] of **7** gave the β-D-Glc*p*-(1→6)-β-D-Gal*f* disaccharide derivative **8** in 73% yield. The ^{13}C-n.m.r. spectrum of **8** showed two signals in the anomeric region (100.5 and 99.9 p.p.m.), which correspond to C-1′ of the β-glucopyranosyl and C-1 of the β-galactofuranose units[24]. Reduction of the lactone function to the lactol caused a downfield shift of C-4 and C-2 (82.8 and 80.9 p.p.m.), as observed for other galactofuranose systems[4,25]. The ^{1}H-n.m.r. spectrum of **8** showed the H-1′ signal at 4.67 p.p.m. ($J_{1',2'}$ 8.0 Hz) and two broad singlets at 5.69 and 5.50 p.p.m. ($J_{1,2}$ <1.0 Hz) attributable to H-1 and H-2. The small value observed for $J_{1,2}$ confirms the β-configuration assigned to the galactofuranose ring[26].

Compound **8** was deacylated in order to obtain the disaccharide 6-*O*-(β-D-glucopyranosyl)-α,β-D-galactopyranose (**9**), which has also been isolated from hydrolyzates of a polysaccharide from *Xanthomonas stewartii*[27] and of arabinogalactans from Mountain and European larch[28]. The optical rotation at equilibrium of the deacylated product **9** was in good agreement with the value reported for the natural compound. The ^{13}C-n.m.r. spectrum of **9** showed three signals in the anomeric region. The signal at 103.5 p.p.m. was attributed to C-1′ of the glucopyranosyl moiety, and it had an intensity equal to the sum of the other two signals located at 97.3 and 93.2 p.p.m., which would correspond respectively, to the β- and α-anomeric carbons of the galactopyranose moiety. These assignments were made by comparison with known spectral data for disaccharides having glucose or galactose as constituents[24].

The procedures described here constitute a ready route of access to lactonic disaccharides, which could otherwise be obtained from the parent disaccharides in a synthesis that would sometimes include a difficult step of lactonization[29].

EXPERIMENTAL

General methods. — Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. ^{1}H- and ^{13}C-n.m.r. spectra were recorded with a Varian XL-100 spectrometer at 100.1 and 25.2 MHz respectively, with solutions in chloroform-*d*. Chemical shifts refer to an internal standard of tetramethylsilane (δ 0.00). The 2D COSY ^{1}H-n.m.r. spectra were performed with a Bruker 500-MHz spectrometer. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter. Silica gel 60 (230–400 mesh, E. Merck, Darmstadt, G.F.R.) was used for column chromatography. T.l.c. was performed on silica gel 60F precoated aluminum sheets (E. Merck), with 1:1 EtOAc–hexane as solvent. Detection was effected by spraying the plates with 5% H_2SO_4 in EtOH with subsequent heating.

2,3,5-Tri-O-benzoyl-6-O-trityl-D-galactono-1,4-lactone (**2**). — The procedure previously described[4] was essentially followed. To a solution of D-galactono-1,4-lactone (**1**, 1.78 g, 10.0 mmol) in anhydrous C_5H_5N (15 mL), chlorotriphenylmethane (3.0 g, 10.7 mmol) was added. The mixture was kept in the dark for two days at room temperature. Benzoyl chloride (12 mL) was added, with external cooling (ice–water). The solution was stirred for 3 h at room temperature and poured into ice–water (300 mL). After 2 h, the product was extracted with CH_2Cl_2 (2 × 150 mL), and the extract was washed successively with saturated aqueous $NaHCO_3$ and water until pH 7, dried ($MgSO_4$) and evaporated. The syrup crystallized (6.6 g, 90%) upon addition of EtOH. Compound **2** was recrystallized from EtOH and had m.p. 145–146°, $[\alpha]_D^{20}$ +8° (*c* 1, $CHCl_3$), R_F 0.70.

Anal. Calc. for $C_{46}H_{36}O_9$: C, 75.41; H, 4.92. Found: C, 75.71; H, 4.88.

2,3,5-Tri-O-benzoyl-D-galactono-1,4-lactone (**3**). — To a solution of compound **2** (1.56 g, 2 mmol) in dichloromethane (80 mL), $BF_3 \cdot OEt_2$ (0.25 mL) and MeOH (0.8 mL) were added. The solution was stirred for 3 h at room temperature, diluted with CH_2Cl_2 (40 mL) and successively extracted with water, saturated aqueous $NaHCO_3$, and water; dried ($MgSO_4$) and evaporated. The residue showed two spots by t.l.c. (R_F 0.94 and 0.60). The faster-migrating component had the same R_F value as triphenylmethanol. The slower-moving component was dissolved in Et_2O and purified by precipitation with hexane, affording a chromatographically homogeneous compound **3** (0.87 g, 83%); it had $[\alpha]_D^{20}$ +6° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. ($CDCl_3$): δ 8.2–7.2 (15 H-aromatic), 6.08 (d, $J_{2,3}$ 5.6 Hz, H-2), 5.88 (t, $J_{3,4}$ 5.3 Hz, H-3), 5.65 (m, H-5), 5.10 (dd, $J_{4,5}$ 2.5 Hz, H-4), 4.04 (m, 2 H-6), and 2.15 (bs, OH); ^{13}C-n.m.r. ($CDCl_3$): δ 169.1 (C-1), 165.6 (×2), 164.9 (PhCO), 133.8–127.1 (C-aromatic), 79.1 (C-4), 74.3, 72.8, 72.6 (C-2,3,5), and 60.3 (C-6).

Anal. Calc. for $C_{27}H_{22}O_9$: C, 66.12; H, 4.49. Found: C, 66.44; H, 4.74.

3,4,6-Tri-O-acetyl-1,2-O-[1(S)-(2,3,5-tri-O-benzoyl-D-galactono-1,4-lactone-

6-yloxy)ethylidene]-α-D-*glucopyranose* (**5**). — A mixture of compound **3** (1 g, 2 mmol), $HgBr_2$ (0.4 g), HgO (2.5 g) and molecular sieves (4 Å, 15 g) in CH_2Cl_2 (70 mL) was rapidly stirred for 15 min and then 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide[31] (**4**, 1.0 g, 2.2 mmol) was added. After 16 h, with continuous stirring, the mixture was filtered, and the solid was washed with CH_2Cl_2. The organic solutions were pooled and extracted with saturated aqueous $NaHCO_3$, 5% aqueous KI and water, dried ($MgSO_4$) and evaporated. The syrup was dissolved in hot EtOH and, upon cooling, an essentially pure product was obtained. It was purified by dissolution in hot EtOH and cooling, affording chromatographically pure compound **5** (R_F 0.8) as an amorphous solid (0.9 g, 50%); it had $[\alpha]_D^{20}$ +13° (*c* 1, $CHCl_3$); 2D-COSY ^{1}H-n.m.r. ($CDCl_3$): δ 8.2–7.2 (m, 15 H, aromatic), 6.08 (d, $J_{2,3}$ 5.8 Hz, H-2), 5.85 (t, $J_{3,4}$ 5.6 Hz, H-3), 5.72 (d, $J_{1',2'}$ 5.2 Hz, H-1'), 5.68 (m, H-5), 5.16 (t, $J_{3',4'}$ 2.6 Hz, H-3'), 5.00 (dd, $J_{4,5}$ 2.4 Hz, H-4), 4.89 (dd, $J_{4',5'}$ 9.5 Hz, H-4'), 4.34 (d, $J_{2',3'}$ 3.1 Hz, H-2'), 4.21–4.15 (m, 2H-6'), 3.96–3.85 (m, H-5', 2H-6), 2.09, 2.08, 2.07 (s, 3 CH_3CO), and 1.74 (s, CH_3CO_3); ^{13}C-n.m.r. ($CDCl_3$): δ 170.2, 169.3, 168.8, 168.7 (C-1, 3 CH_3CO), 165.2, 164.9, 164.7 (3 PhCO), 133.7–127.9 (C-aromatic), 121.2 (CH_3CO_3), 97.0 (C-1'), 78.6 (C-4), 74.0, 73.4, 72.5, 70.6, 70.0, 68.0, 67.2 (C-2,3,5,2',3',4',5'), 63.0, 60.7 (C-6,6'), and 20.7, 20.6 (CH_3CO, and CH_3CO_3).

Anal. Calc. for $C_{41}H_{40}O_{18}$: C, 60.00; H, 4.88. Found: C, 60.08; H, 4.83.

*2,3,5-Tri-*O-*benzoyl-6-*O-*(2,3,4,6-tetra-*O-*acetyl-β-*D-*glucopyranosyl)-*D-*galactono-1,4-lactone* (**7**). — (*a*) To a solution of compound **2** (0.8 g, 1.1 mmol) in dry CH_2Cl_2 (40 mL), silver trifluoromethanesulfonate (0.32 g, 1.2 mmol) was added, in the dark. After complete dissolution of the silver salt, compound **4** (0.6 g, 1.2 mmol) was added. The strongly yellow suspension was stirred for 2 h at room temperature in the dark. The mixture was filtered, diluted with CH_2Cl_2 (60 mL), and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and water, dried ($MgSO_4$) and evaporated. The residue obtained was purified by column chromatography on silica gel and eluted with 2:3 EtOAc–hexane. Fractions containing the product (R_F 0.6) were pooled and evaporated. The syrup crystallized from EtOH, yield 0.42 g (47%). Compound **7**, recrystallized from the same solvent, had m.p. 134–136°, $[\alpha]_D^{20}$ −13° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. ($CDCl_3$): δ 8.2–7.2 (m, 15 H-aromatic), 6.10 (d, $J_{2,3}$ 5.8 Hz, H-2), 5.77–5.70 (m, H-3,5), 5.19 (t, $J_{3',4'}$ 9.6 Hz, H-3'), 5.05 (dd, $J_{4',5'}$ 9.7 Hz, H-4'), 4.99 (dd, $J_{3,4}$ 5.6, $J_{4,5}$ 2.4 Hz, H-4), 4.98 (dd, $J_{2',3'}$ 9.4 Hz, H-2'), 4.59 (d, $J_{1',2'}$ 8.0 Hz, H-1'), 4.19 (m, 2H-6'), 4.18 (dd, H-6a), 3.99 (dd, H-6b), 3.69 (m, H-5'), and 2.08, 2.02, 1.97 and 1.81 (4 CH_3CO); ^{13}C-n.m.r. ($CDCl_3$): δ 170.4, 169.9, 169.2, 169.0, 168.8 (C-1, 4 CH_3CO), 165.3, 164.9, 164.7 (3 PhCO), 133.8–127.8 (C-aromatic), 100.8 (C-1'), 78.9 (C-4), 74.1, 72.6, 72.4, 72.0, 70.9, 70.4, 68.2 (C-2,3,5,2',3',4',5'), 66.6, 61.6 (C-6,6'), and 20.7, 20.6 (×2), 20.3 (4 CH_3CO).

Anal. Calc. for $C_{41}H_{40}O_{18}$: C, 60.00; H, 4.88. Found: C, 60.02; H, 4.80.

(*b*) A solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**6**, 0.2 g, 0.51 mmol) in MeCN (6 mL) was chilled at 0° (ice–water bath) and $SnCl_4$ (0.06 mL, 0.5 mmol) was added. The solution was stirred for 10 min at 0°, and compound **2** (0.37

g, 0.5 mmol) was added. After 24 h no starting material was detected by t.l.c. The mixture was diluted with CH_2Cl_2 (50 mL) and processed as described in (*a*). After evaporation of the solvent, the product was dissolved in Et_2O and precipitated by addition of hexane. The resulting syrup was dissolved in hot EtOH, and compound **7** crystallized upon cooling by seeding with crystals of **7**, yield 0.32 g (77%). Recrystallization from EtOH gave pure **7**, which had the same constants as the product from (*a*).

*2,3,5-Tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-galactofuranose* (**8**). — To a solution containing 4.8 mmol of freshly prepared bis-(3-methyl-2-butyl)borane[23] in tetrahydrofuran under a nitrogen atmosphere, compound **7** (0.5 g, 0.6 mmol) in tetrahydrofuran (3 mL) was added. After stirring for 20 h at room temperature, the mixture was cooled in ice–water and water (3 mL) was added dropwise. The solution was stirred for 0.5 h and 30% H_2O_2 (1.5 mL) was slowly added. The pH of the solution was kept between 7 and 8 with 3M NaOH. Tetrahydrofuran was removed from the mixture by evaporation, and the residue was extracted with CH_2Cl_2 (3 × 50 mL). The extract was washed with water, dried ($MgSO_4$) and evaporated. The resulting syrup was purified by column chromatography on silica gel, using 1:1 EtOAc–hexane as eluant. Fractions containing the product of R_F 0.47 were pooled and evaporated, affording compound **8** as a syrup (0.37 g, 73%), homogeneous by t.l.c. It had $[\alpha]_D^{20}$ −17° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. ($CDCl_3$): δ 8.2–7.2 (m, 15 H-aromatic), 5.81 (m, H-5), 5.69, 5.50 (bs, $J_{1,2}$ <1.0 Hz, H-1,2), 5.52 (d, $J_{3,4}$ 3.0 Hz, H-3), 5.30–4.90 (m, H-2′,3′,4′), 4.77 (dd, H-4), 4.67 (d, $J_{1',2'}$ 8.0 Hz, H-1′), 4.35–3.60 (H-5′, 2H-6, 2-H6′), and 2.10–1.90 (4 CH_3CO); ^{13}C-n.m.r. ($CDCl_3$): δ 170.6, 169.9, 169.4, 169.0 (4 CH_3CO), 165.5, 165.4, 165.2 (3 PhCO), 133.3–128.2 (C-aromatic), 100.5, 99.9 (C-1,1′), 82.8 (C-4), 80.9 (C-2), 77.7, 72.7, 71.5, 71.0, 70.8, 68.3 (C-3,5,2′,3′,4′,5′), 67.0, 60.7 (C-6,6′), and 20.6, 20.5 (4 CH_3CO).

Anal. Calc. for $C_{41}H_{42}O_{18}$: C, 59.85; H, 5.11. Found: C, 59.55; H, 5.16.

*6-*O*-(β-*D*-Glucopyranosyl)-*D*-galactose* (**9**). — To a solution of compound **8** (60 mg) in $CHCl_3$ (1 mL), NaOMe in MeOH (1 mL, 0.2M) was added. After stirring for 0.5 h at 0°, the mixture was diluted with $CHCl_3$ (20 mL) and extracted with water (3 × 10 mL). The aqueous solution was decationized with Dowex-50 (H^+ form) and evaporated to a syrup, which was redissolved in water and freeze dried, to give compound **9** (17 mg, 68%). It showed a single spot by paper chromatography, (R_{Glc} 0.47, 6:4:3 butanol–pyridine–water), detected with both $AgNO_3$–NaOH[32] or *p*-anisidine hydrochloride[33]. Compound **9** had $[\alpha]_D^{20}$ +14.5° (*c* 1, H_2O) in good agreement with data from the literature[27,34]; ^{13}C-n.m.r. (D_2O): δ 103.5 (C-1′), 97.3 (C-1, β anomer), 93.2 (C-1, α anomer), 76.8, 76.6 (C-3′,5′), 74.0 (C-2′), 70.6 (C-4′), 61.7 (C-6′), and 74.6, 73.6, 72.7, 70.4, 70.1, 69.9, 69.8, and 69.2 (C-2,3,4,5,6 of α and β anomers).

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