Carbohydrate Research, 200 (1990) 227–235
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Convenient syntheses of 5-*O*- and 3,5-di-*O*-(β-D-galactofuranosyl)-D-galactofuranose

Rosa M. de Lederkremer, Carla Marino, and Oscar Varela
Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires (Argentina)

(Received May 27th, 1989; accepted for publication, August 18th, 1989)

ABSTRACT

Benzoylation of D-galactono-1,4-lactone with 2.2 mol of benzoyl chloride, at −23°, gave the 2,6-dibenzoate (**2**, 62%). Tin(IV) chloride-catalyzed glycosylation of **2** with 1,2,3,5,6-penta-*O*-benzoyl-α,β-D-galactofuranose (**1**) afforded 2,6-di-*O*-benzoyl-5-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl)-D-galactono-1,4-lactone (**4**, 70%), HO-3 of which was benzoylated to give **5**. The structure of **4** was confirmed by its conversion into crystalline β-D-Gal*f*-(1→5)-D-Gal-ol (**8**). Reduction of the lactone function of **5** with di-isoamylborane followed by debenzoylation gave β-D-Gal*f*-(1→5)-D-Gal*f* (**7**). A by-product of the condensation of **1** with **2** was characterized as 2,6-di-*O*-benzoyl-3,5-di-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl)-D-galactono-1,4-lactone (**9**), which was converted, as for **5**, into β-D-Gal*f*-(1→3)[β-D-Gal*f*-(1→5)]-D-Gal*f* (**13**).

INTRODUCTION

Galactofuranose has been described as the immunodominant sugar of bacterial[1], fungal[2–5], and protozoal[6,7] polysaccharides or glycoconjugates. In particular, (1→5)-linked β-D-galactofuranose oligosaccharides inhibited the reaction of extracellular polysaccharides of *Penicillium* and *Aspergillus* species with the antibodies[2]. The fact that galactofuranose residues have not been found in mammalian glycoconjugates has implications for the design and use of artificial antigens.

Glycosylaldono-1,4-lactones, which are useful precursors of disaccharides with furanoid reducing units, may be synthesized readily by stannic chloride ($SnCl_4$)-catalyzed condensation of appropriate derivatives of aldono-1,4-lactones with acylated sugar derivatives[8,9]. We have used this strategy to prepare[9] β-D-Gal*f*-(1→6)-D-Gal*f*, which is a unit of the highly immunogenic arabinogalactans of *Mycobacterium leprae* and *M. tuberculosis*[1].

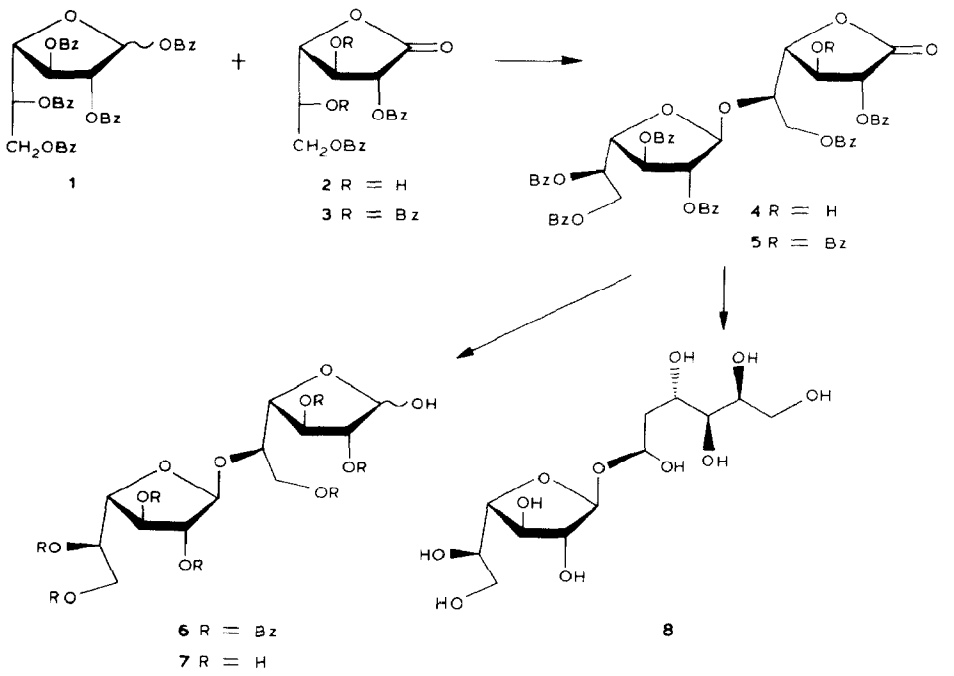
We now report the preparation of β-D-Gal*f*-(1→5)-D-Gal*f* (**7**), first isolated[10] from partial acid hydrolysates of galactocarolose, an extracellular polysaccharide from *Penicillium charlesii*, and also the branched trisaccharide, β-D-Gal*f*-(1→3)[β-D-Gal*f*-(1→5)]-D-Gal*f* (**13**), which could be a model for immunoassays since both (1→5)- and (1→3)-linked β-D-galactofuranosides are immunologically active.

0008-6215/90/$03.50

RESULTS AND DISCUSSION

Treatment of D-galactono-1,4-lactone at −23° with 2.2 mol of benzoyl chloride in pyridine afforded selectively the crystalline 2,6-dibenzoate **2** (62%). The higher reactivity of HO-6 (primary alcohol) and HO-2 (activated by the lactone group) is as expected. The structure of **2** was established on the basis of the n.m.r. data. The ^{1}H signals [$(CD_3)_2SO$] at δ 8.1–7.4 corresponded to 2 Ph groups, and that at δ 5.98 ($J_{2,3}$ 8.4 Hz) to H-2. The doublets at δ 6.22 and 5.78 disappeared on deuterium exchange and were assigned to HO-3 and HO-5, respectively ($J_{HO,3}$ 5.2, $J_{HO,5}$ 6.4 Hz). Also, the complex multiplets of H-3 (δ 4.69) and H-5 (δ 4.12) collapsed to a triplet and sextet, respectively, on deuterium exchange. The signals at lower field in the ^{13}C-n.m.r. spectrum of **2** were attributed to C-1 (169.7 p.p.m.) and Ph*C*O (163.5 and 164.4 p.p.m.). The signal for C-4 was shifted downfield (to 80.2 p.p.m.) with respect to those of the other sugar carbon atoms, as reported for other aldono-1,4-lactone derivatives[11]. The resonances for C-2,3,5,6 (75.3, 70.1, 65.4, and 64.9 p.p.m., respectively) were assigned by single-frequency decoupling experiments. Comparison of the ^{13}C-n.m.r. spectra of **2** and 2,3,5,6-tetra-*O*-benzoyl-D-galactono-1,4-lactone (**3**) showed that the signals for the α-carbon atoms (C-3 and C-5) were shifted downfield and those for the β-carbon atoms (C-2 and C-6) were shifted upfield on benzoylation of HO-3 and HO-5 in accord with established behavior[12].

Stannic chloride-catalyzed glycosylation of **2** with 1,2,3,5,6-penta-*O*-benzoyl-



α,β-D-galactofuranose[13] (**1**) resulted, as expected, in reaction of HO-5, which is more exposed than HO-3, to give the β-glycosyl-lactone **4** (70%). The reaction probably involves an intermediate 1,2-benzoxonium ion[14], generated from **1**, since this would explain the high β-stereoselectivity. Two by-products were isolated, namely, the trisaccharide derivative **9**, produced by glycosylation of both HO-3 and HO-5 of **2**, and the (1→1)-linked derivative 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranoside[9], formed by self-condensation of **1**.

The ^{1}H-n.m.r. spectrum of **4** contained signals (2 bs, $J_{1',2'} < 0.5$ Hz) for H-1′ and H-2′, which indicated H-1′,2′ to be *trans* and **4** to be a β-galactofuranoside[15] This assignment was confirmed by the ^{13}C resonance for C-1′ of **4**, which appeared at 105.5 p.p.m., as reported for related β-D-galactofuranosides[9,12]. Furthermore, the large downfield shift (~4.5 p.p.m.) for the signal of C-5 of **4** compared to the corresponding signal of **2**, and the small displacement (~1 p.p.m.) for the signal of C-3 in **4** as compared to that for **2**, indicated[12] that HO-5 in **2** had been glycosylated.

Benzoylation of **4** gave the crystalline heptabenzoate **5**, the ^{1}H-n.m.r. spectrum of which showed a strong downfield shift for the signal of H-3, indicating that HO-3 was benzoylated and confirming that HO-5 was involved in the glycosidic linkage. Also, as expected, on benzoylation of HO-3 of **4**, the signal for the α-carbon atom (C-3) was shifted to lower field, and those for the β-carbon atoms (C-2,4) to higher field.

Reduction[16] of the lactone group of **5** with di-isoamylborane gave (87% yield) the heptabenzoate (**6**) of β-D-Gal*f*-(1→5)-D-Gal*f* having HO-1 free. The n.m.r. spectra of **6** were complex because of the presence of both anomers. However, the region for anomeric carbons in the ^{13}C-n.m.r. spectrum contained signals for C-1′ and C-1 of the β (105.3 and 100.6 p.p.m., respectively), and α anomers (105.9 and 95.3 p.p.m., respectively). The assignments were made by comparison with the spectra of α- and β-D-galactofuranoses[12], and the αβ-ratio was 1:1.8.

O-Debenzoylation of **6** with MeOH–H_2O–Et_3N afforded the chromatographically pure disaccharide β-D-Gal*f*-(1→5)-D-Gal*f* (**7**), the ^{13}C-n.m.r. spectrum of which contained signals at 108.0 (C-1′) and 102.0 p.p.m. (C-1) corresponding to the β anomer, and at 107.7 (C-1′) and 96.2 p.p.m. (C-1) for the α anomer. Synthetic **7** had the same $[\alpha]_D$ value and chromatographic behavior as the products isolated from partial acid hydrolysates of galactocarolose, an extracellular polysaccharide of *P. charlesii*[10], and by condensation of partially protected galactofuranose derivatives with a 1,2-ortho-ester[17] or a 1-chloride[18] derivative of galactofuranose. The synthesis of **7** described above is more direct and efficient than those reported[17,18].

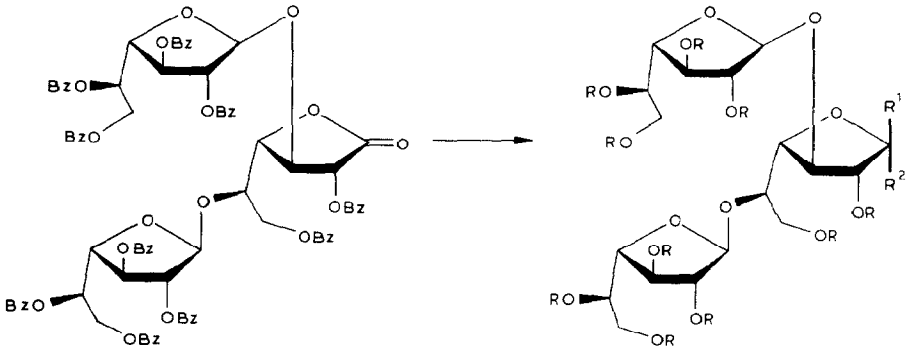
Borohydride reduction of **4** followed by *O*-debenzoylation gave crystalline 5-*O*-β-D-galactofuranosyl-D-galactitol (**8**), the ^{13}C-n.m.r. spectrum of which contained a single signal for an anomeric carbon (109.2 p.p.m.), corresponding to C-1′β. The signals for C-2′ for C-4′ appeared at low field (83.1 and 84.6 p.p.m., respectively) and the signals for the carbon atoms in the acyclic groups were shifted upfield (65.0, 64.5, and 63.4 p.p.m. for C-1,6,6′, respectively). Compound **8** had the same physical constants as reported[10,17].

The trisaccharide derivative **9**, formed as a by-product during the preparation of **4**, was synthesized (47%) by the $SnCl_4$-catalyzed condensation of **2** with 2 mol of **1**. The

^{13}C-n.m.r. spectrum of **9** contained signals for anomeric carbons (106.5 and 106.0 p.p.m.), which were attributed to the C-1′β and C-1″β. The signal for the lactone carbonyl group appeared at 168.1 p.p.m.

Reduction of **9** with di-isoamylborane[16] afforded crystalline 2,6-di-*O*-benzoyl-3,5-di-*O*-(2,3,5,6,-tetra-*O*-benzoyl-β-D-galactofuranosyl)-α,β-D-galactofuranose (**10**). After benzoylation of **10**, the perbenzoates could be isolated by column chromatography. The less polar product (R_F 0.45) was identified as the β anomer (**11**) on the basis of the signal at δ 6.68 (bs, $J_{1,2} < 1.0$ Hz) for H-1. The ^{13}C signals for C-1′ and C-1″ (105.6 and 105.3 p.p.m.) appeared at lower field than that of C-1 (99.8 p.p.m.), which was similar to that for C-1 of penta-*O*-benzoyl-β-D-galactofuranose[13]. The product having R_F 0.41 was characterized as the α anomer (**12**) on the basis of the signal at δ 6.86 (d, $J_{1,2}$ 4.5 Hz) for H-1 (*cf.* δ 6.86, $J_{1,2}$ 4.8 Hz for penta-*O*-benzoyl-α-D-galactofuranose[13]). The signal for C-1 (δ 94.2) of the latter compound was identical to that of C-1 of **12** (C-1′,1″ resonated at 106.0 and 105.7 p.p.m., respectively).

O-Debenzoylation of **10**, as for **6**, gave the branched trisaccharide β-D-Gal*f*-(1→3)[β-D-Gal*f*-(1→5)]-D-Gal*f* (**13**), the ^{13}C-n.m.r. spectrum of which contained signals for C-1α and C-1β at 96.4 and 102.4 p.p.m., which were comparable to those reported for α,β-D-galactofuranose[12] and **7**.



9

10 R = Bz, R^1, R^2 = H, OH
11 R = Bz, R^1 = OBz, R^2 = H
12 R = Bz, R^1 = H, R^2 = OBz
13 R = H, R^1, R^2 = H, OH

EXPERIMENTAL

General methods. — Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. The ^{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, for solutions in $CDCl_3$ (internal Me_4Si), unless otherwise indicated. A 250-MHz Bruker instrument was used for rec-

ording the ^{1}H-n.m.r. spectra of **4** and **9**. H.p.l.c. was performed with a Micromeritics liquid chromatograph equipped with a refractive-index detector and a Micromeritics 730 injector, using a column (25 × 0.4 cm i.d.) of Lichrosorb NH_2 (10 μm) and 4:1 MeCN–H_2O at 3 mL.min^{-1}. T.l.c. was carried out on Silica Gel $60F_{254}$ (Merck) with *A*, 2:1 PhMe–EtOAc; *B*, 9:1 PhMe–EtOAc; and *C*, 6:3:8:1 HOAc–EtOAc–BuOH–H_2O; and detection with u.v. light or charring with H_2SO_4. Descending p.c. was performed on Whatman No. 1 paper with *D*, 6:4:3 BuOH–C_5H_5N–H_2O; and *E*, 9:2:2 EtOAc–HOAc–H_2O. Column chromatography was performed on Silica Gel 60 (Merck).

*2,6-Di-*O*-benzoyl-*D*-galactono-1,4-lactone** (**2**). — To a solution of D-galactono-1,4-lactone (0.60 g, 3.37 mmol) in dry pyridine (5.5 mL) at −23° was added benzoyl chloride (0.3 mL every 0.5 h; total volume, 0.86 mL, 7.4 mmol). After stirring at −23° for 4 h, the mixture was allowed to reach room temperature, then poured into ice–water (300 mL), the resulting syrup was suspended in PhMe, and the solvent was evaporated in order to remove water and pyridine. The residue was dried overnight under vacuum to yield a solid, which was suspended in ether and then filtered off. The product (0.87 g, 62%), which showed a single spot in t.l.c. (R_F 0.39, solvent *A*), was recrystallized from ethanol to afford **2**, m.p. 194–195°, $[\alpha]_D$ +3° (*c* 0.8, acetone). N.m.r. data [$(CD_3)_2SO$]: ^{1}H, δ 8.1–7.4 (10 H, 2 Ph), 6.22 ($J_{OH,3}$ 5.2 Hz, HO-3), 5.98 ($J_{2,3}$ 8.4 Hz, H-2), 5.78 ($J_{OH,5}$ 6.4 Hz, HO-5), 4.69 ($J_{3,4}$ 8.4 Hz, H-3), 4.55–4.28 (H-4,6,6'), and 4.12 (H-5); ^{13}C, δ 169.7 (C-1), 165.3, 164.4 (Ph*C*O), 133.8–128.3 (C-aromatic), 80.2 (C-4), 75.3 (C-2), 70.1 (C-3), 65.4 (C-5), and 64.9 (C-6).

Anal. Calc. for $C_{20}H_{18}O_8$: C, 62.18; H, 4.70. Found: C, 62.28; H, 4.89.

*2,6-Di-*O*-benzoyl-5-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranosyl)-*D*-galactono-1,4-lactone* (**4**). — To a solution of **1**[13] (1.05 g, 1.5 mmol) in 1:1 CH_2Cl_2–MeCN (15 mL) at 0° was added $SnCl_4$ (0.18 mL, 1.5 mmol). The mixture was stirred for 10 min followed by the addition of a solution of **2** (1.16 g, 3.0 mmol) in 1:1 CH_2Cl_2–MeCN (35 mL). After stirring for 3 h at room temperature, t.l.c. (solvent *B*) of the mixture revealed three components (R_F 0.52, 0.43, and 0.22) but no **1**. The solvent was evaporated at 40°, a solution of the residue in CH_2Cl_2 (40 mL) was poured into saturated aq. $NaHCO_3$ and extracted with CH_2Cl_2 (3 x 40 mL), and the combined organic layers were washed with water (50 mL), dried ($MgSO_4$), and concentrated. Treatment of the syrupy residue with ether gave **2** (0.49 g) and column chromatography (19:1 PhMe–EtOAc) of the non-crystalline material gave, first, 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranoside (0.18 g, 10%), m.p. 79–81°, $[\alpha]_D$ −18° (*c* 1, chloroform), R_F 0.52; lit.[9] m.p. 79–82°, $[\alpha]_D$ −18° (chloroform).

Eluted next was 2,6-di-*O*-benzoyl-3,5-di-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl)-D-galactono-1,4-lactone (**9**; 0.07 g, 3%), R_F 0.43.

Eluted last was syrupy **4** (1.01 g, 70%), R_F 0.22, which, when dissolved in hot EtOH, yielded an amorphous solid upon cooling; $[\alpha]_D$ −42° (*c* 1, chloroform). N.m.r. data: ^{1}H (250 MHz), δ 8.10–7.20 (30 H, 6 Ph), 5.97 (H-5'), 5.75 (H-2), 5.70 ($J_{1',2'}$ < 0.5 Hz,

*First obtained by Lucio O. Jeroncic as a by-product, on partial benzoylation of D-galactono-1,4-lactone.

H-1'), 5.64 ($J_{2',3'}$ <0.5, $J_{3',4'}$ 4.4 Hz, H-3'), 5.53 (H-2'), 4.87–4.60 (H-3,4',6,6,6',6'), 4.55 ($J_{3,4}$ 7.6, $J_{4,5}$ 2.5 Hz, H-4), 4.32 ($J_{5,6a}$ 7.7, $J_{5,6b}$ 6.1 Hz, H-5); ^{13}C, δ 168.3 (x2), 167.0, 165.7, 165.5 (x2), 165.1 (C-1 and PhCO), 133.4–127.8 (C-aromatic), 105.5 (C-1'), 83.7 (C-4'), 81.8 (C-2'), 79.5 (C-4), 77.5 (C-3'), 75.6 (C-2), 71.8 (C-5), 71.5 (C-3), 70.5 (C-5'), and 63.4 and 62.8 (C-6,6').

Anal. Calc. for $C_{54}O_{17}H_{44}$: C, 67.22; H, 4.59. Found: C, 66.97; H, 4.50.

*2,3,6-Tri-*O*-benzoyl-5-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranosyl)-*D*-galactono-1,4-lactone* (**5**). — To a solution of **4** (0.90 g, 0.93 mmol) in CH_2Cl_2 (5 mL) and pyridine (1 mL) at 0° was added benzoyl chloride (1 mL). The mixture was stirred for 3 h at room temperature, the solvent was evaporated, and the residue was poured into ice–water to afford, after 16 h, a solid that was crystallized from EtOH to give **5** (0.92 g, 92%). Recrystallization gave material with m.p. 87–88°, $[\alpha]_D$ +6° (*c* 1, chloroform). N.m.r. data: ^{1}H, δ 8.15–7.00 (35 H, 7 Ph), 6.40–5.98 (H-2,3,5'), 5.78, 5.65 ($J_{1',2'}$ <1 Hz, H-1',2'), 5.76 (H-3'), 5.13–4.50 (H-4,4',5,6,6,6',6'); ^{13}C, δ 167.7 (C-1), 165.7 (x2), 165.5, 165.4, 165.0 (x2), 164.8 (PhCO), 133.8–127.7 (C-aromatic), 105.7 (C-1'), 83.5 (C-4'), 81.9 (C-2'), 78.8 (C-4), 77.4 (C-3'), 72.8, 72.5, 72.4 (C-2,3,5), 70.6 (C-5'), and 63.7 and 63.1 (C-6,6').

Anal. Calc. for $C_{61}H_{48}O_{18}$: C, 68.54; H, 4.53. Found: C, 68.25; H, 4.51.

*2,3,6-Tri-*O*-benzoyl-5-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranosyl)-α,β-*D*-galactofuranose* (**6**). — To a solution of freshly prepared bis(3-methyl-2-butyl)borane[16] (3.0 mmol) in tetrahydrofuran (2.5 mL) under nitrogen was added a solution of **5** (0.75 g, 0.70 mmol) in tetrahydrofuran (3 mL). The mixture was stirred for 48 h at room temperature under nitrogen, and then processed as described[16]. Boric acid was eliminated by successive evaporations with methanol. T.l.c. (solvent *B*) revealed a main component (R_F 0.27). Column chromatography (19:1 PhMe–EtOAc) gave syrupy **6** (0.65 g, 87%), $[\alpha]_D$ +6° (*c* 1, chloroform). ^{13}C-N.m.r. data: δ 105.3 and 100.6 (C-1'β and C-1β), 105.9 and 95.3 (C-1'α and C-1α), αβ-ratio 1:1.8.

Anal. Calc. for $C_{61}H_{50}O_{18}$: C, 68.40; H, 4.70. Found: C, 68.68; H, 4.90.

*5-*O*-β-*D*-Galactofuranosyl-*D*-galactofuranose* (**7**). — Compound **6** (0.16 g, 0.15 mmol) was treated with 5:2:1 MeOH–H_2O–Et_3N (50 mL) at room temperature for ~3 h; complete dissolution occurred. T.l.c. (solvent *C*) of the mixture showed a single product (R_F 0.20). The solvent was evaporated at 40°, and methyl benzoate and Et_3N were eliminated by three successive co-evaporations with MeOH–H_2O. A solution of the residue in water (20 mL) was extracted with ether (2 x 30 mL) and the aqueous layer was freeze-dried to afford chromatographically pure **7** (0.04 g, 78%), R_{Gal} 1.35 (solvent *C*) and 0.85 (solvent *D*), $[\alpha]_D$ −64° (*c* 1, water); in good agreement with literature data[10,17]. N.m.r. data: ^{1}H (D_2O), δ 5.32–5.20 (m, H-1,1'α and H-1,1'β); ^{13}C (1:1 D_2O–H_2O), δ 108.0 (C-1'β), 107.7 (C-1'α), 102.0 (C-1β), and 96.2 (C-1α).

*5-*O*-β-*D*-Galactofuranosyl-*D*-galactitol* (**8**). — A suspension of **4** (0.37 g, 0.38 mmol) in MeOH (15 mL) was stirred with $NaBH_4$ (0.15 g, 3.8 mmol) for 20 h at room temperature; no **4** then remained (t.l.c.). The solution was neutralized with Dowex 50W (H^+) resin, filtered, concentrated, and passed through a column of Amberlite MB3 resin. T.l.c. showed that the resulting solution had several components (partially

benzoylated products). The solvent was evaporated and the residue was debenzoylated in 5:2:1 MeOH–H_2O–Et_3N (40 mL) for 4 h at room temperature to give **8**, purified as described above for **7**. Chromatographically homogeneous syrupy **8** (R_{Gal} 0.72, solvent *D*) solidified upon addition of ether to give material (0.11 g, 84%) that crystallized from EtOH, to give **8**, m.p. 150–151°, $[\alpha]_D$ −65° (*c* 1, water); lit.[17] m.p. 148–150°, $[\alpha]_D$ −63° (water). N.m.r. data: ^1H (D_2O), δ 5.33 ($J_{1',2'}$ 1.8 Hz, H-1'); ^{13}C (1:1 D_2O–H_2O), δ 109.2 (C-1'), 84.6 (C-4'), 83.1 (C-2'), 78.3, 78.2 (C-3',5), 72.2, 71.8, 70.9 (C-2,3,4,5'), and 65.0, 64.5, and 63.4 (C-1,6,6').

*2,6-Di-*O*-benzoyl-3,5-di-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranosyl)-*D*-galactono-1,4-lactone* (**9**). — To a solution of **1** (0.89 g, 1.27 mmol) in 1:1 CH_2Cl_2–MeCN (10 mL) at 0° was added $SnCl_4$ (0.15 mL, 1.27 mmol), and the mixture was stirred at 0° for 10 min. A solution of **2** (0.49 g, 1.27 mmol) in 1:1 CH_2Cl_2–MeCN (15 mL) was then added slowly. After stirring at room temperature for 6 h, a freshly prepared solution of **1** (0.89 g, 1.27 mmol) and $SnCl_4$ (0.15 mL, 1.27 mmol) in 1:1 CH_2Cl_2–MeCN (15 mL) was added, stirring was continued for 16 h, and the solvent was evaporated at 40°. A solution of residue in CH_2Cl_2 (100 mL) was poured into aq. $NaHCO_3$, the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic solutions were washed with water, dried ($MgSO_4$), filtered, and concentrated. T.l.c. (solvent *B*) of the residue revealed a major (R_F 0.43) and two minor components (R_F 0.52 and 0.22). Column chromatography (19:1 PhMe–EtOAc) of the mixture gave 2,3,5,6,-tetra-*O*-benzoyl-β-*D*-galactofuranosyl 2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranoside[9] (0.25 g, 17%), R_F 0.52, and **2** (0.28 g, 23%), R_F 0.22. The product of R_F 0.43 was crystallized from EtOH to give **9** (1.01 g, 47%) which, after recrystallization, had m.p. 90–92°, $[\alpha]_D$ −1° (*c* 1, chloroform). N.m.r. data: ^1H (250 MHz), δ 8.10–7.10 (50 H, 10 Ph), 6.03–5.99 (H-2,5',5''), 5.75 ($J_{2'',3''}$ 1.5, $J_{3'',4''}$ 4.0 Hz, H-3''), 5.69 ($J_{1',2'}$ <0.5 Hz, H-1'), 5.66 ($J_{2',3'}$ <0.5, $J_{3',4'}$ 5.0 Hz, H-3'), 5.55–5.51 (H-1'',2',2''), 5.08 ($J_{2,3} = J_{3,4}$ = 7.1 Hz, H-3), 4.98 (H-4''), 4.82–4.53 (H-4,4',5,6,6,6',6',6'',6''); ^{13}C, δ 168.1 (C-1), 165.8, 165.7 (×2), 165.5, 165.3 (×2), 165.1, 165.0, 164.8 (Ph*C*O), 133.2–124.9 (C-aromatic), 106.5, 106.0 (C-1',1''), 82.6, 82.5, 82.2, 82.1 (C-2',2'',4',4'', 79.1, 77.8, 77.0, 76.9 (C-3',3'',4,5), 74.0, 73.6 (C-2,3), 70.6, 70.4 (C-5',5''), and 63.7, 63.4, and 63.3 (C-6,6',6'').

Anal. Calc. for $C_{88}H_{70}O_{26}$: C, 68.48; H, 4.57. Found: C, 68.27, H, 4.42.

*2,6-Di-*O*-benzoyl-3,5-di-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranosyl)-α,β-*D*-galactofuranose* (**10**). — Compound **9** (0.40 g, 0.25 mmol) was reduced with bis(3-methyl-2-butyl)borane (2.0 mmol) in tetrahydrofuran (1.7 mL) as described for the preparation of **6**. The reaction required 48 h for completion, and the syrupy product, obtained after elimination of boric acid, crystallized upon addition of EtOH, to afford **10** (0.37 g, 96%). Recrystallization from EtOH gave material with m.p. 87–89° $[\alpha]_D$ −3° (*c* 1, chloroform). ^{13}C-N.m.r. data: δ 107.1, 106.8, 106.3 (C-1,1',1''β), 95.7 (C-1α).

Anal. Calc. for $C_{88}H_{72}O_{26}$: C, 68.39; H, 4.69. Found: C, 68.28; H, 4.67.

*1,2,6-Tri-*O*-benzoyl-3,5-di-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranosyl)-β-*D*-galactofuranose* (**11**) *and 1,2,6-tri-*O*-benzoyl-3,5-di-*O*-(2,3,5,6-tetra-*O*-benzoyl-β-*D*-galactofuranosyl)-α-*D*-galactofuranose* (**12**). — To a solution of **10** (0.61 g, 0.39 mmol) in dry pyridine (5 mL) was added benzoyl chloride (3 mL). The mixture was stirred at room

temperature for 3 h and then poured slowly into ice–water to give a solid, t.l.c. (solvent *B*) of which revealed two components (R_F 0.41 and 0.45). Column chromatography (19:1 PhMe–EtOAc) of the mixture gave **11** (0.26 g, 40%), R_F 0.45; **12** (0.10 g, 16%), R_F 0.41; and a mixture (0.15 g).

Compound **11**, after recrystallization from EtOH, had m.p. 88–89°, $[\alpha]_D$ −21° (*c* 1, chloroform). N.m.r. data: ^{1}H, δ 6.68 ($J_{1,2}$ < 1.0 Hz, H-1); ^{13}C, δ 166.7–165.6 (Ph*C*O), 133.9–128.9 (C-aromatic), 105.6, 105.3 (C-1′,1″), 99.8 (C-1), 83.9, 82.2 (× 2), 81.7 (× 2), 81.6, 80.5 (C-2,2′,2″,3,4,4′,4″), 77.5, 77.0, 74.6 (C-3′,3″,5), 70.5 (× 2) (C-5′,5″), and 64.4, 63.9, and 63.4 (C-6,6′,6″).

Anal. Calc. for $C_{95}H_{76}O_{27}$: C, 69.24; H, 4.64. Found: C, 68.90; H, 4.87.

Compound **12**, after recrystallization from EtOH, had m.p. 78–80°, $[\alpha]_D$ +19° (*c* 1, chloroform). N.m.r. data: ^{1}H, δ 6.86 ($J_{1,2}$ 4.5 Hz, H-1); ^{13}C, δ 166.5–165.6 (Ph*C*O), 133.9–128.9 (C-aromatic), 106.0, 105.7 (C-1′,1″), 94.2 (C-1), 82.7, 82.3, 82.0, 81.2, 80.2 (C-2′,2″,4,4′,4″), 78.0, 77.8, 77.3, 77.0, 75.8 (C-2,3,3′,3″,5), 70.5, 70.1 (C-5′,5″), and 64.0, 63.7, and 63.5 (C-6,6′,6″).

Anal. Calc. for $C_{95}H_{76}O_{27}$: C, 69.24; H, 4.64. Found: C, 69.43; H, 4.87.

*3,5-Di-O-(β-*D*-galactofuranosyl)-*D*-galactofuranose* (**13**). — A suspension of **10** (0.22 g, 0.14 mmol) in 5:2:1 MeOH–H_2O–Et_3N (50 mL) was stirred at room temperature. After 20 h, complete dissolution had occurred, and t.l.c. (solvent *C*) of the mixture revealed a main component with R_F 0.22, and galactose (R_F 0.39). The solvent was evaporated, and the residue was washed with ether (2 x 5 mL) and then purified by h.p.l.c., to afford **13** (0.04 g, 53%), $[\alpha]_D$ −85° (*c* 1, water); R_{GAL} 1.1 (solvent *D*) and 0.51 (solvent *E*). N.m.r. data: ^{1}H (D_2O), δ 5.33 5.19 (m, H-1,1′,1″$\alpha\beta$); ^{13}C (1:1 D_2O–H_2O), δ 108.9, 108.8 (x2), 108.3 (C-1′,1″$\alpha\beta$), 102.4 (C-1β), and 96.4 (C-1α).

Anal. Calc. for $C_{18}H_{32}O_{16}$: C, 42.86; H, 6.39. Found: C, 42.51; H, 6.25.

ACKNOWLEDGMENTS

We thank CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), the University of Buenos Aires, and UNDP/World Bank/WHO Special Programme for Research and Training in Tropical Diseases for financial support, and UMYMFOR (CONICET–FCEN, Buenos Aires) for the microanalyses.

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