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Carbohydrate Research 308 (1998) 207–211

Note

Synthesis of some galactofuranosyl disaccharides using a galactofuranosyl trichloroacetimidate as donor

Ambar Kumar Choudhury, Nirmolendu Roy*

Department of Biological Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Received 30 September 1997; accepted in revised form 4 March 1998

Abstract

2,3,5-Tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactofuranosyl trichloroacetimidate has been prepared for the first time and utilised as glycosyl donor for the synthesis of several disaccharides containing the β-linked galactofuranoside moiety.

Keywords: Galactofuranosyl trichloroacetimidate; Glycosidation; TMSOTf; Disaccharides

Synthesis of oligosaccharides containing furanose units is a topic of increasing interest in the field of glycobiology. D-Galactofuranoside moieties are the constituents of many polysaccharides of bacterial [1] and plant [2] origin as well as Kinetoplastid parasites [3] and they were claimed to be immunodominant in many bacterial antigens [4]. Although not many oligosaccharides having furanoside components have so far been prepared, reports of the synthesis of disaccharides utilising D-galactofuranose pentabenzoate [5] as donor are available. Synthesis of oligosaccharides containing galactofuranose have also been reported recently using acylic glycosyl donors [6]. *O*-Pentenyl galactofuranoside derivatives have been used for the synthesis of some disaccharides and glycolipids [7]. We have recently [8] reported some novel disaccharides using ethyl 2,3,5,6-tetra-*O*-benzoyl-1-thio-(methyl-β-D-galactofuranosiduronate) as donor. Although the preparation and glycosidation of a ribofuranosyl trichloroacetimidate derivative [9] and mannofuranosyl trichloroacetamidate [10] has been already reported, no trichloroacetimidate of galactofuranose derivatives have been described so far. Since there is wide utilisation of pyranose trichloroacetimidates as glycosyl donors, the possibility of using furanose trichloroacetimidate derivatives in glycosidation reactions seems to be highly promising. We report here the first synthesis of 2,3,5-tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactofuranosyl trichloroacetimidate and its use as glycosyl donor for the synthesis of disaccharides containing β-D-galactofuranoside.

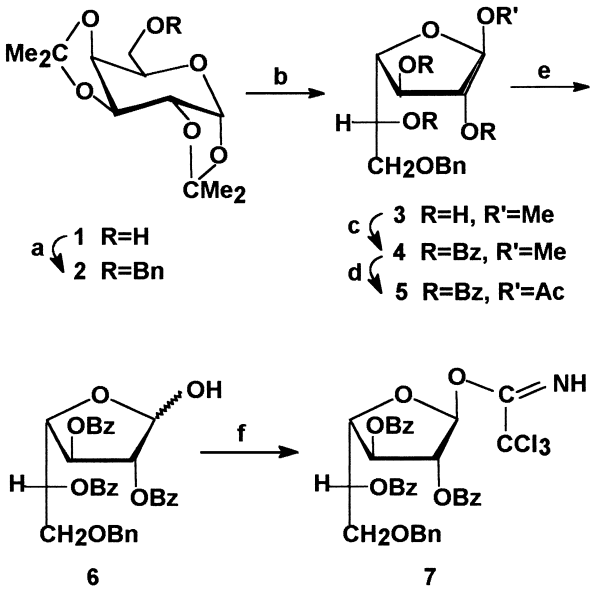
* Corresponding author.

0008-6215/98/$19.00
PII S0008-6215(98)00062-7

1. Results and discussion

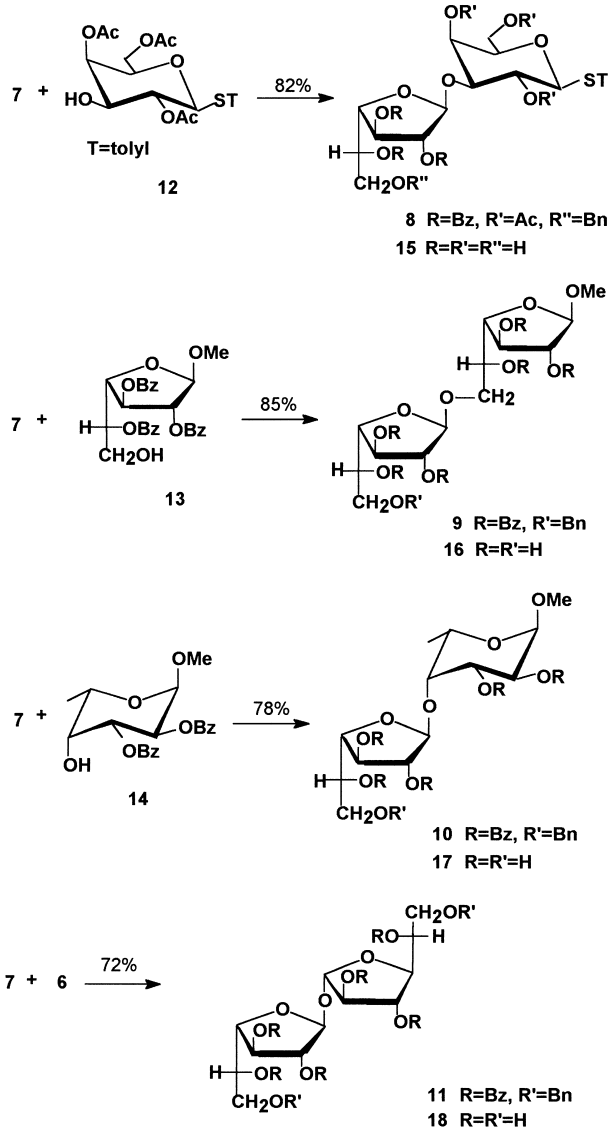
The known 1,2:3,4-di-*O*-isopropylidene-D-galactose (**1**, Scheme 1) [11] was benzylated in the usual way to give the 6-*O*-benzyl derivative **2**. Treatment of **2** with *p*-toluenesulfonic acid in methanol at 70 °C gave methyl-6-*O*-benzyl-β-D-galactofuranoside (**3**). The structure of **3** was confirmed by GLC and ^{1}H NMR spectroscopy. Benzoylation of **3** followed by acetolysis [12] of the product **4** furnished the β-acetate **5.** Treatment of **5** with hydrogen bromide in acetic acid–acetic anhydride [13] afforded exclusively 2,3,5-tri-*O*-benzoyl-6-*O*-benzyl-D-galactofuranose (**6**). No galactosyl bromide could be detected in the reaction mixture. Compound **6** was allowed to react in dichloromethane with trichloroacetonitrile in the presence of potassium carbonate [14] giving 2,3,5-tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactofuranosyl trichloroacetimidate (**7**) (85%) together with a small amount (8%) of its α-anomer.

The trichloroacetimidate donor **7** (1.2 mmol) was then allowed to react with 1 mmol each of the acceptors **12** [15], **13**, **14** [8] and **6**, having primary or secondary hydroxyl groups free and using trimethylsilyl trifluoromethanesulfonate [14] as promoter, giving the β-linked disaccharide derivatives **8**, **9**, **10** and **11** (Scheme 2).



Scheme 1. Reagents: (a) NaH, BnBr, DMF; (b) 0.1 M *p*-TsOH, MeOH, 70 °C, 6 h, 65%; (c) BzCl, pyridine, 3 h, quan; (d) 4:1:0.1 AcOH–Ac_2O–concd H_2SO_4, 0 °C→r.t., 2 h, 75%; (e) 33% HBr–AcOH, Ac_2O, CH_2Cl_2, 0 °C, 74%; (f) CH_2Cl_2, K_2CO_3, CCl_3CN, r.t., 85%.

The β-galactofuranoside nature of the residues in the disaccharide derivatives was confirmed by the presence of the characteristic ^{13}C NMR signals for C-1′ (δ 105–107), C-2′ (δ∼81.6) and C-4′ (δ 82.4–83.0); the only exception being the ^{13}C NMR signal of C-1 in the (1→1) disaccharide **11**, which appeared at a much higher field (δ 101.4). This deviation has, however, already been reported [5]. The reported ^{13}C NMR signals [16] of C-1 and C-2 in methyl α-D-galactofuranoside are δ 103.1 and 77.4, respectively, which are quite different from those of the methyl β-D-galactofuranoside. The β-selectivity in the glycoside formation may be explained by the participation of the C-2 benzoyl group. Moreover, steric interaction of two large groups in 1,2-*cis* configuration in α-galactofuranoside



Scheme 2.

may hinder their formation. This may explain the exclusive formation of the β-glycoside **11** although the acceptor contained 30% of α-galactofuranose derivative.

The disaccharide derivatives **8**, **9**, **10** and **11** were then hydrogenolysed and the products were treated with sodium methoxide to afford the desired disaccharides in the form of their glycosides, namely **15**, **16**, **17** and **18**. Compounds **16** and **18** had identical physical data as reported earlier and all (except **18**) have characteristic signals at δ∼109 (C-1′) and δ∼84 (C-4′) in their ^{13} NMR spectra [5].

2. Experimental

General.—All reactions were monitored by TLC on silica gel G (E. Merck). Column chromatography was performed on 100–200 mesh silica gel (SRL, India). All solvents were distilled and/or dried before use and all evaporations were conducted below 40 °C under reduced pressure unless stated otherwise. Optical rotations were measured with a Perkin-Elmer model 241 MC polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol FX-100 or Bruker 300 MHz spectrometer using $CDCl_3$ as solvent (internal standard Me_4Si) unless otherwise stated. Melting points were determined on a paraffin oil bath and are uncorrected.

Methyl 6-O-benzyl-β-D-galactofuranoside (**3**).—A soln of **2** (2 g, 5.7 mmol) and *p*-TsOH (760 mg) in MeOH (40 mL) was refluxed for 6 h. The soln was then neutralized with Et_3N and concentrated to a syrup. Column chromatography (EtOAc) gave **3** (1.05 g, 64.8%). $[\alpha]_D^{25}$ −76.2° (*c* 2.6, $CHCl_3$); ^{1}H NMR: δ 7.33 (s, 5 H, aromatic protons) 5.03 (s, 1 H, H-1), 3.36 (s, 3 H, OCH_3). Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 58.95; H, 7.18.

Methyl 2,3,5-tri-O-benzoyl-6-O-benzyl-β-D-galactofuranoside (**4**).—To a soln of **3** (500 mg, 1.76 mmol) in pyridine (20 mL), benzoyl chloride (1 mL, 8.6 mmol) was added dropwise at 0 °C and the mixture was stirred for 1 h. Water (1 mL) was added and stirring was continued for another 30 min. The mixture was concentrated to a small vol., diluted with CH_2Cl_2, washed with aq $NaHCO_3$ and water. The soln was filtered, dried and then concentrated. Column chromatography (10:1 toluene–EtOAc) gave **4** (1.03 g, 98%) as an amorphous solid. $[\alpha]_D^{25}$ −17° (*c* 5.2, $CHCl_3$); ^{1}H NMR: δ 7.20–8.06 (m, 20 H, aromatic protons), 5.66 (m, 1 H, H-5), 5.64 (d, 1 H, $J_{3,4}$ 5 Hz, H-3), 5.44 (s, 1 H, H-2), 5.22 (s, 1 H, H-1), 4.55 (dd, 1 H, $J_{3,4}$ 5 Hz, $J_{4,5}$ 4 Hz, H-4), 4.50 (s, 2 H, CH_2Ph), 3.80 (d, 2 H, $J_{5,6}$ 6 Hz, H-6), 3.42 (s, 3 H, OCH_3). Anal. Calcd for $C_{35}H_{32}O_9$: C, 70.45; H, 5.40. Found: C, 70.62; H, 5.57.

1-O-Acetyl-2,3,5-tri-O-benzoyl-6-O-benzyl-β-D-galactofuranose (**5**).—To a soln of **4** (500 mg, 0.84 mmol) in AcOH (4 mL) at 0 °C, Ac_2O (1 mL) and concd H_2SO_4 (0.1 mL) were added and the mixture was stirred for 30 min. The temperature was then allowed to rise to 25 °C, and after 90 min the reaction was quenched with crushed ice. The mixture was extracted with CH_2Cl_2 (3×10 mL) and the organic layer was washed successively with ice water, aq $NaHCO_3$ and water, dried and concentrated. Column chromatography (toluene–EtOAc 10:1) gave **5** (395 mg, 75.2%) as foam. $[\alpha]_D^{25}$ −4.8° (*c* 1.3, $CHCl_3$); ^{1}H NMR: δ 7.19–8.08 (m, 20 H, aromatic protons), 6.48 (s, 1 H, H-1), 5.81 (m, 1 H, H-5), 5.66 (d, 1 H, $J_{3,4}$ 4 Hz, H-3), 5.56 (bs, 1 H, H-2), 4.81 (t, 1 H, *J* 4 Hz, H-4), 4.56 (s, 2 H, CH_2Ph), 3.85 (d, 2 H, $J_{5,6}$ 6 Hz, H-6), 2.30 (s, 3H, OAc). Anal. Calcd for $C_{36}H_{32}O_{10}$: C, 69.22; H, 5.16. Found: C, 69.10; H, 5.38.

2,3,5-Tri-O-benzoyl-6-O-benzyl-D-galactofuranose (**6**).—To a soln of **5** (400 mg, 0.64 mmol) in CH_2Cl_2 (10 mL) at 0 °C, Ac_2O (0.5 mL) and 33% HBr in AcOH (3 mL) were added. The mixture was stirred for 2 h and then diluted with CH_2Cl_2 (15 mL), washed successively with ice-water, cold saturated $NaHCO_3$ and cold water. The organic layer was dried, filtered and then concentrated to a syrup. Column chromatography (5:1 toluene–EtOAc) gave pure **6** (277 mg, 74.2%) as a syrup. $[\alpha]_D^{25}$ +10.8° (*c* 0.4, $CHCl_3$); ^{1}H NMR: δ 7.23–8.00 (m, 20 H, aromatic protons), 6.14 (m, 1 H, H-5), 5.75 (d, 1 H, $J_{3,4}$ 4 Hz, H-3), 5.65 (d, 1 H, $J_{1,2}$ 6 Hz, H-2, α), 5.60 (bs, 1 H, H-2, β), 5.53 (d, 1 H, $J_{1,2}$ 6 Hz, H-1, α), 5.36 (s, 1 H, H-1), 4.75 (t, 1 H, *J* 4 Hz, H-4), 4.50 (s, 2 H, CH_2Ph), 3.82 (d, 2 H, $J_{5,6}$ 6 Hz, 6-H). ^{13}C NMR: δ 165.6–166.4 (*C*OPh) 127.6–137.7 (aromatic carbons), 100.8 (C-1, β, 75%), 95.8 (C-1, α, 25%), 83.0 (C-4), 81.6 (C-2), 78.8 (C-3), 76.6, 73.4, 71.5, 68.5 (C-6). Anal. Calcd for $C_{34}H_{30}O_9$: C, 70.09; H, 5.19. Found: C, 70.15; H, 5.32.

2,3,5-Tri-O-benzoyl-6-O-benzyl-β-D-galactofuranosyl trichloroacetimidate (**7**).—To a soln of **6** (375 mg, 0.64 mmol) in CH_2Cl_2 (3 mL), K_2CO_3 (450 mg) and trichloroacetonitrile (0.35 mL, 3.4 mmol) were added. The mixture was stirred at room temperature for 6 h, then filtered through

Celite. The filtrate was diluted with CH_2Cl_2, washed three times with water, dried and concentrated. Column chromatography of the resulting syrup (10:1 toluene–EtOAc) gave **7** (395 mg, 84.9%) together with its α-anomer (38 mg, 8.1%). $[\alpha]_D^{25}$ −30.7° (*c* 0.2, $CHCl_3$); ^{1}H NMR: δ 8.78 (s, 1 H, CON*H*CCl$_3$), 7.40–8.10 (m, 20 H, aromatic protons), 6.70 (s, 1 H, H-1), 5.86 (m, 1 H, H-5), 5.76 (d, 1 H, $J_{3,4}$ 4 Hz, H-3), 5.70 (s, 1 H, H-2), 4.88 (t, 1 H, *J* 4 Hz, H-4), 4.56 (s, 2 H, C*H*$_2$Ph), 3.84 (d, 2 H, $J_{5,6}$ 6 Hz, H-6). ^{13}C NMR: δ 166.2–165.6 (*C*OPh), 160.8 (*C*=NH), 125.8–138.2 (aromatic carbons), 103.5 (C-1), 85.0 (C-4), 81.5 (C-2), 77.7 (Ccl$_3$), 77.1 (C-3), 73.7 (C-5), 63.5 (C-6). Anal. Calcd for $C_{36}H_{30}O_9NCl_3$: C, 59.47; H, 4.16. Found: C, 59.66; H, 4.31. *α-Anomer of 7*: $[\alpha]_D^{25}$ +27.0° (*c* 0.44, $CHCl_3$); ^{1}H NMR: δ 8.56 (s, 1 H, CON*H*CCl$_3$), 7.50–8.08 (m, 20 H, aromatic protons) 6.86 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 6.30 (t, 1 H, *J* 6 Hz, H-3), 5.82 (dd, 1 H, $J_{1,2}$ 4 Hz, $J_{2,3}$ 6 Hz, H-2), 5.64 (m, 1 H, H-5), 4.82 (t, 1 H, *J* 6 Hz, H-4), 4.48 (s, 2 H, C*H*$_2$Ph), 3.92 (d, 2 H, $J_{5,6}$ 6 Hz, H-6). Anal. Calcd for $C_{36}H_{30}O_9NCl_3$: C, 59.47; H, 4.16. Found: C, 59.60; H, 4.27.

General procedure for glycosidation.—A mixture of donor **7** (0.22 mmol), the acceptor (0.18 mmol), 4 Å molecular sieves in CH_2Cl_2 (3 mL) was stirred for 3 h at 25 °C. The mixture was cooled to −20 °C and TMSOTf (0.10 mmol) was added upon stirring. After 20 min of continued stirring, the reaction mixture was diluted with CH_2Cl_2, filtered and washed successively with saturated $NaHCO_3$ and water. The organic layer was dried and then concentrated. Column chromatography (8:1 toluene–EtOAc) gave the pure disaccharide derivatives. The physical data of the compounds are given below.

1-S-p-*Tolyl 2,3,5-tri*-O-*benzoyl-6*-O-*benzyl*-β-D-*galactofuranosyl-(1→3)-2,4,6-tri*-O-*acetyl*-β-D-*galactopyranoside* (**8**).—144 mg, 82%; $[\alpha]_D^{25}$ +8.3° (*c* 1.4, $CHCl_3$); ^{1}H NMR: δ 7.10–8.13 (m, 24 H, aromatic protons), 5.46 (d, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 5.36 (d, 1 H, *J* 0.9 Hz, H-2′), 5.31 (t, 1 H, *J* 12 Hz, H-2), 5.26 (d, 1 H, $J_{1',2'}$ 0.9 Hz, H-1′), 4.89 (dd, 1 H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 5.1 Hz, H-4), 4.63 (dd, 2 H, C*H*$_2$C$_6$H$_5$), 4.55 (d, 1 H, $J_{1,2}$ 12 Hz, H-1), 2.34 (s, 3 H, SC$_6$H$_4$C*H*$_3$), 2.21, 2.08 and 2.05 (3 s, 9 H, 3 OAc). ^{13}C NMR: δ 170.2–165.3 (3 *C*OCH$_3$, 3 *C*OPh) 126.6–137.9 (aromatic carbons), 107.4 (C-1′), 87.0 (C-1), 82.8 (C-4′), 82.4 (C-2′), 77.5, 76.4, 74.8, 73.0, 71.2, 69.2, 68.8, 68.3 (C-6′), 62.3 (C-6), 21.0 (SC$_6$H$_4$*C*H$_3$), 20.8, 20.5 and 20.4 (3 CO*C*H$_3$). Anal. Calcd for $C_{53}H_{52}O_{16}S$: C, 65.15; H, 5.36. Found: C, 65.02; H, 5.50.

Methyl 2,3,5-tri-O-*benzoyl-6*-O-*benzyl*-β-D-*galactofuranosyl-(1→6)-2,3,5-tri*-O-*benzyl*-β-D-*galactofuranoside* (**9**).—164 mg, 85%; $[\alpha]_D^{25}$ −6.7° (*c* 1.6, $CHCl_3$); ^{1}H NMR: δ 7.25–8.06 (m, 20 H, aromatic protons), 5.80 (m, 2 H, H-5, H-5′), 5.75 (bs, 1 H, H-2′), 5.63 (d, 1 H, $J_{1',2'}$ 1.2 Hz, H-1′), 5.62 (bs, 1 H, H-2), 5.10 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 4.97 (t, 1 H, *J* 3 Hz, H-4′), 4.67 (t, 1 H, *J* 3.6 Hz, H-4), 3.79 (d, 2 H, $J_{5,6}$ 6 Hz, H-6′), 3.40 (s, 3 H, OC*H*$_3$). ^{13}C NMR: δ 166.3–165.8 (6 *C*OPh), 133.8–127.9 (aromatic carbons), 106.8 (C-1′), 105.5 (C-1), 82.3 (C-4′), 82.2 (C-4), 81.6 (2 C, C-2′, C-2), 77.5, 73.7, 73.1, 71.2 (C-6), 68.4 (C-6′), 54.9 (O*C*H$_3$). Anal. Calcd for $C_{62}H_{54}O_{17}$: C, 69.52; H, 5.08. Found: C, 69.35; H, 5.27.

Methyl 2,3,5-tri-O-*benzoyl-6*-O-*benzyl*-β-D-*galactofuranosyl-(1→4)-2,3-di*-O-*benzoyl*-α-D-*fucopyranoside* (**10**).—105 mg, 78%; $[\alpha]_D$ −79.5° (*c* 0.9, $CHCl_3$); ^{1}H NMR: δ 1.44 (7.10–8.00 (m, 20 H, aromatic protons), 5.75 (m, 1 H, H-5′), 5.69 (d, 1 H, $J_{3,4}$ 4 Hz, H-3′), 5.56 (bs, 1 H, H-2′), 5.39 (bs, 1 H, H-1′), 5.17 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1), 4.45 (t, 1 H, *J* 4 Hz, H-4′), 3.44 (s, 3 H, OC*H*$_3$), 1.44 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6). ^{13}C NMR: δ 165.8–165.3 (5 *C*OPh), 133.4–127.3 (aromatic carbons), 107.1 (C-1′), 97.5 (C-1), 83.1 (C-4′), 81.8 (C-2′), 77.3, 76.5, 72.6, 71.3, 70.2, 68.9, 68.7 (C-6′), 65.8 (C-6), 55.4 (O*C*H$_3$), 16.4 (C*C*H$_3$). Anal. Calcd for $C_{55}H_{50}O_{15}$: C, 69.46; H, 5.30. Found: C, 69.32; H, 5.41.

2,3,5-tri-O-*benzoyl-6*-O-*benzyl*-β-D-*galactofuranosyl-(1→1)-2,3,5-tri*--O-*benzoyl-6*-O-*benzyl*-β-D-*galactofuranoside* (**11**).—148 mg, 72%; $[\alpha]_D$ −16.4° (*c* 4.56, $CHCl_3$); ^{1}H NMR: δ 7.20–8.12 (m, 40 H, aromatic protons), 5.87 (m, 2 H, H-5, 5′), 5.73 (s, 2 H, H-2, 2′), 5.69 ((d, 2 H, $J_{3,4}$ 5.1 Hz, H-3, 3′), 5.57 (s, 2 H, H-1, 1′), 4.90 (t, 2 H, *J* 4.5 Hz, H-4, 4′), 4.56 (dd, 4 H, *J* 12 Hz, 2 C*H*$_2$C$_6$H$_5$), 3.90 (d, 4 H, *J* 6 Hz, H-6, 6′). ^{13}C NMR: δ 166.3–165.8 (*C*OPh), 128.0–138.2 (aromatic carbons), 101.4 (C-1, 1′), 82.9 (C-4, 4′), 82.6 (C-2, 2′), 73.8, 73.7, 71.8 (C-5, 5′), 69.0 (C-6, 6′). Anal. Calcd for $C_{68}H_{58}O_{17}$: C, 71.19; H, 5.09. Found: C, 71.11; H, 5.23.

1-S-p-*Tolyl* β-D-*galactofuranosyl-(1→3)*-β-D-*galactopyranoside* (**15**).—To a soln of **8** (75 mg, 0.08 mmol) in 2:1:1 1-propanol–AcOH–H_2O [17] (5 mL) was added 10% Pd/C (75 mg). The mixture was stirred at 80 °C for 20 h, then cooled, filtered through Celite, and concentrated to dryness. The product was purified by column chromatography (EtOAc) and then treated with 0.05 M MeONa in

MeOH (4 mL). After 2 h, the soln was made neutral by the addition of Amberlite IR-120 (H^+) resin, filtered and the solvent was evaporated to provide the product which was purified by column chromatography (19:1 EtOAc–EtOH) yielding pure **15** (23 mg, 67%) as an amorphous solid; $[\alpha]_D^{25}$ +25° (0.9, $CHCl_3$). ^1H NMR (D_2O): δ 5.30 (bs, 1 H, H-1′), 4.48 (d, 1 H, $J_{1,2}$ 12 Hz, H-1), 4.29 (bs, 1 H, H-4), 1.78 (s, 3 H, $SC_6H_4CH_3$). ^{13}C NMR (D_2O): δ 127–135 (aromatic carbons), 109.7 (C-1′), 88.4 (C-1), 84.6 (C-4′), 82.3 (C-2′), 77.1, 75.4, 73.5, 72.0, 71.0, 69.5, 63.4 (C-6, C-6′), 62.0, 20.7 ($SC_6H_4CH_3$). Anal. Calcd for $C_{19}H_{28}O_{10}S$: C,50.88; H, 6.29. Found: C, 50.62; H, 6.48.

Methyl β-D-*galactofuranosyl-(1→6)*-β-D-*galactofuranoside* (**16**).—A soln of **9** (83 mg, 0.08 mmol) in AcOH (3 mL), was hydrogenolysed over 10% Pd/C (60 mg) in a Paar apparatus overnight. The product was purified by column chromatography and debenzoylated with MeONa as described for the preparation of **15** giving pure **16** (19.8 mg, 72%) as colourless glass; $[\alpha]_D^{25}$ −87° (*c* 1, H_2O). ^1H NMR (D_2O): δ 5.43 (bs, 1 H, H-1′), 5.20 (bs, 1 H, H-1), 3.42 (s, 3 H, OCH_3). ^{13}C NMR (D_2O): δ 109.6 (C-1, 1′), 109.2, 84.5 (C-4, C-4′), 82.5 (C-2, C-2′), 82.2, 78.5, 78.2, 72.4, 71.1, 70.6 (C-6), 64.3 (C-6′), 56.5 (CH_3O). Anal. Calcd for $C_{13}H_{24}O_{11}$: C, 43.82; H, 6.79. Found: C, 44.15; H, 6.90. Lit [5] $[\alpha]_D$ −90° (H_2O).

Methyl β-D-*galactofuranosyl-(1→4)*-α-L-*fucopyranose* (**17**).—A soln of **10** (72 mg, 0.07 mmol) was hydrogenolysed and debenzoylated as described for the preparation of **16** to afford pure **17** (18 mg, 70%); $[\alpha]_D^{25}$ −18.8° (*c* 0.8, H_2O); ^1H NMR (D_2O): δ 5.32 (bs, 1 H, H-1′), 5.10 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1), 3.40 (s, 3 H, OCH_3), 1.42 (d, 3 H, $J_{5,6}$ 6 Hz, H-6). ^{13}C NMR (D_2O): δ 109.8 (C-1′) 98.1 (C-1), 84.1 (C-4′), 79.0, 75.9, 75.3, 71.5, 70.3, 70.1, 68.0, 64.2 (C-6′), 63.1 (C-6), 55.6 (OCH_3), 16.1 (CCH_3). Anal. Calcd for $C_{13}H_{24}O_{10}$: C, 45.88; H, 7.11. Found: C, 45.65; H, 7.32.

β-D-*galactofuranosyl-(1→1)*-β-D-*galactofuranoside* (**18**).—A soln of **11** (82 mg, 0.07 mmol) was hydrogenolysed and debenzoylated as described for the preparation of **16** to afford pure **18** (19.6 mg, 80%) as an amorphous solid which crystallised from MeOH; mp 203–205 °C; $[\alpha]_D^{25}$ −148° (*c* 0.9, H_2O). ^1H NMR (D_2O): δ 5.25 (s, 2 H, H-1, 1′), 3.88 (d, 4 H, *J* 6.5 Hz, H-6, 6′). ^{13}C NMR (D_2O): δ 104.7 (C-1, 1′), 84.4 (C-4, 4′), 82.2 (C-2, 2′), 78.0, 72.0, 64.1 (C-6, 6′). Anal. Calcd for $C_{12}H_{22}O_{11}$: C, 42.11; H, 6.48. Found: C, 41.82; H, 6.65. Lit [5] mp 206–208 °C (MeOH); $[\alpha]_D$ −150° (H_2O).

Acknowledgements

We thank the Department of Science and Technology, New Delhi (Project No. SP/S1/G14/95) for financial support.

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