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SYNTHESIS AND CHARACTERIZATION OF A TETRAMER, PROPYL 6-*O*-β-D-GALACTOPYRANOSYL-(1→6)-*O*-β-D-GALACTOPYRANOSYL-(1→6)-*O*-β-D-GALACTOPYRANOSYL-(1→6)-β-D-GALACTOPYRANOSIDE

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ABSTRACT

6-*O*-Acetyl-2-*O*-benzoyl-3,4-di-*O*-benzyl-α-D-galactopyranosyl chloride (**1a**) was converted into the 1-sulfonate (**1b**), which was allowed to react with allyl alcohol in acetonitrile to give allyl 6-*O*-acetyl-2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-galactopyranoside (**2**). Compound **2** was *O*-deacetylated with ammonium hydroxide in methanol to give **3**. Reaction of **1b** with **3** under the same conditions of glycosidation gave the corresponding disaccharide **4**. *O*-Deallylation of **4** gave **6**, which was chlorinated with methanesulfonyl chloride or (chloromethylene)dimethylimminium chloride in *N*,*N*-dimethylformamide, to form the 1-chloro derivative **7**. Compound **7** was converted into the 1-*O*-[(2,2,2-trifluoroethyl)sulfonyl] derivative (**8**). *O*-Deacetylation of **4** followed by glycosidation with **8** gave the corresponding tetrasaccharide derivative **9** in 77% yield. Appropriate deprotection sequences gave the title tetramer. The structures of the glycosides were determined with the aid of both ^{1}H- and ^{13}C-n.m.r. spectroscopy. No evidence of α-D linkages was found.

INTRODUCTION

Recently, we and others have reported the synthesis[1,1a] of methyl β-D-(1→6)- and[2] β-D-(1→2)-linked galactotrisaccharides. We used a stepwise glycosidation procedure developed in this laboratory[1–3]. Attempts to prepare tetrasaccharides[1,2] by this method failed, presumably because of steric factors. We now report our investigation of the synthesis of the β-D-(1→6)-linked tetrasaccharide, using the β-D-(1→6)-linked disaccharide as aglycon instead of the trisaccharide. The tetrasaccharide obtained is to be used to measure its binding constant with monoclonal myeloma immunoglobulins[4].

RESULTS AND DISCUSSION

The 1-*O*-sulfonyl-D-galactopyranose derivative **1b** was coupled with 1.2 equiv. of allyl alcohol in acetonitrile as described earlier[1], to afford, after liquid chromato-

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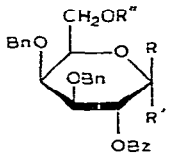
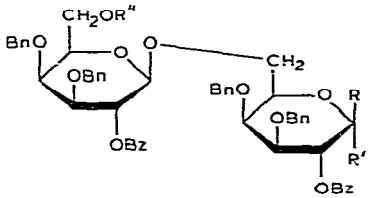
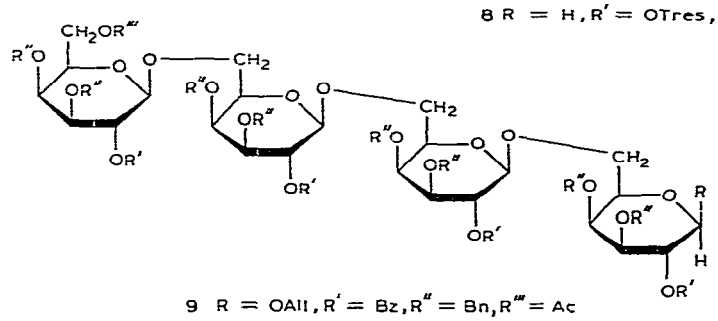
graphy on silica gel, allyl 6-*O*-acetyl-2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-galactopyranoside (**2**) in 85% yield. No α-D anomer could be detected. The ^{1}H-n.m.r. spectrum of **2** showed the H-2 signal at δ 5.74 ($J_{2,3}$ 10.5 Hz) and that of H-1β at 4.60 ($J_{1,2}$ 8.0 Hz). In the ^{13}C-n.m.r. spectrum of **2**, the signal for C-1 appeared at 100.42 p.p.m. The signal for C-1 in the allyl glycosides seems to appear upfield in comparison to the one for C-1 in corresponding methyl glycosides, where it is observed at 102–103 p.p.m.[1–3]. A similar relationship exists for C-1 in α-glycosides, as C-1 in allyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-chloroacetyl-α-D-galactopyranoside resonates at 95.97 p.p.m.[5], relatively upfield in comparison to the corresponding methyl glycoside[1–3].



1a R = H, R′ = Cl, R″ = Ac
1b R = H, R′ = OTs, R″ = Ac
2 R = OAll, R′ = H, R″ = Ac
3 R = OAll, R′ = H, R″ = H



4 R = OAll, R′ = H, R″ = Ac
5 R = OAll, R′ = H, R″ = H
6 R, R′ = H, OH, R″ = Ac
7 R = H, R′ = Cl, R″ = Ac
8 R = H, R′ = OTres, R″ = Ac



9 R = OAll, R′ = Bz, R″ = Bn, R‴ = Ac
10 R = OAll, R′ = Bz, R″ = Bn, R‴ = H
11 R = OAll, R′ = H, R″ = Bn, R‴ = H
12 R = OPr, R′ = H, R″ = H, R‴ = H

All = CH_2=CH—CH_2—
Bz = —CO—C_6H_5
Bn = —CH_2—C_6H_5
Pr = —CH_2—CH_2—CH_3
Tres = —SO_2—CH_2—CF_3

O-Deacetylation of **2** with ammonium hydroxide in methanol[1] gave crystalline allyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-galactopyranoside (**3**). Disaccharide **4** was prepared by glycosidation of **3** with **1b** in acetonitrile as described earlier. In this case also, no α-D linkage could be detected. *O*-Deacetylation of **4** was performed with ammonium hydroxide, to afford crystalline **5**. *O*-Deallylation of **4** was achieved in two steps. First, the allyl group was rearranged by treatment of **4** with tris(triphenylphosphine)rhodium(I) chloride[6] to the 1-propenyl derivative and in part converted into the deallylated disaccharide **6**. This mixture was treated with mercuric chloride and yellow mercuric oxide in acetone–water[7] to hydrolyze the remaining 1-*O*-

propenyl group and afford **6** as a crystalline compound. The 1-chloro-1-deoxy derivative (**7**) was prepared from the alcohol **6** by treatment with either methanesulfonyl chloride in *N*,*N*-dimethylformamide (DMF)[8], or (chloromethylene)dimethylimminium chloride in DMF[8]. The ^{1}H-n.m.r. spectrum of **7** showed a signal for H-1 at δ 6.38 ($J_{1,2}$ 3.8 Hz), confirming that **7** was the α anomer. Treatment of **7** with silver (2,2,2-trifluoroethyl)suifonate in acetonitrile gave the 1-*O*-tresyl derivative **8**, as described earlier[1]. Compound **8** was not isolated, but was treated directly with 1.1 equiv. of **5** to afford tetrasaccharide **9**. *O*-Deacetylation was effected with ammonium hydroxide to afford **10**. The ^{1}H-n.m.r. spectrum of **10** showed a broad singlet at δ 2.62 for an OH group and no resonances for an acetyl group. Debenzoylation of **10** with sodium methoxide in methanol gave almost no benzoylated tetrasaccharide **11**. Apparently, debenzoylation was followed immediately by decomposition of the tetrasaccharide because of glycosidic cleavage of the reducing end-group under the strongly basic conditions[2]. Similar observations have been reported in the literature[9,10],

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS[a] (IN P.P.M.)

Carbon atoms	*Compound*						
	2	**3**	**4**	**5**	**6**	**9**	**12**
					96.5β		
C-1	100.42	100.72	100.32	100.32	91.0α	100.36	104.8
C-2	72.53	72.45					
C-3	80.40	80.46	80.20[b]	80.25		80.25[b]	
C-4	74.43	74.38	74.58[b]				
C-5	72.53	75.26					
					68.74α		
C-6	63.28	62.05	68.60	68.42	67.76β	67.74	70.1
					102.21α		
C-1′			101.79	101.84	101.97β	101.67	104.8
C-3′			80.26[b]	80.25		80.25[b]	
C-4′			74.15[b]				
C-6′			63.22	62.02	63.3	67.15[b]	70.1
C-1″						101.67	104.8
C-3″						80.11[b]	
C-6″						66.72[b]	70.1
C-1‴						101.82	104.40
C-3‴						79.81[b]	
C-6‴						63.28	62.1
$COCH_3$	20.75		20.80		20.77	20.80	
C=O	170.74	165.61	170.80	165.51	170.80	170.80	
	165.56		165.50		166.21	165.51	
					165.55		

[a]These assignments are tentative, based on analogies, discussed in an earlier paper[1]. Additional assignments: C_6H_5CO and $C_6H_5CH_2$, 138.4–127.97; $C_6H_5CH_2$, 73.0–71.4 p.p.m.; CH_2-CH=CH_2, 134.2, 117.3 p.p.m. [b]Assignments not unequivocal.

namely, that β-D-galactopyranosyl groups may be cleaved at room temperature at pH >8.9. However, debenzoylation of **10** with dilute barium methoxide in methanol[2] for 36 h at room temperature gave the debenzoylated tetrasaccharide **11** in quantitative yield. No cleavage of glycosidic bonds was observed in this case. The ^{1}H-n.m.r. spectrum of **11** showed no aromatic resonances for *m*-benzoyl protons at δ 8.12–7.96.

The tetrasaccharide **11** was debenzylated by hydrogenolysis, with 5% palladium-on-carbon as the catalyst. The free tetrasaccharide **12** was purified on a column of Bio-Gel P-2 with water as eluant. The ^{1}H-n.m.r. spectrum of **12** showed no resonances for aromatic protons but did show a multiplet for -CH_2 (propyl) at δ 1.54 and a triplet for -CH_3 (propyl) at δ 0.92, indicating that the allyl group at C-1 had been reduced to a propyl group.

The ^{1}H-n.m.r. spectra of oligosaccharides **4** and **9** were used to determine the degree of polymerization of the product from the ratio of the aromatic protons (δ 7.55–7.0) to the acetyl-group (δ ~1.98) protons.

The ^{13}C-n.m.r. data (Table I) of the di- and tetra-saccharide derivatives are consistent with their β-D-linked structures. The C-1 atom bearing the β-*O*-allyl group, and C-1′, C-1″, and C-1‴, the β-D-galactosyl interresidue linkages, resonate at 100.32–101.84 p.p.m. in the 2-*O*-benzoylgalactoside derivatives **4**, **5**, and **9**. No signals were observed between 95–100 p.p.m., which is the region where C-1 atoms of 2-*O*-benzoyl-α-D-galactosides absorb[1,2,5]. In the fully deprotected tetrasaccharide **12**, the same anomeric carbon atoms resonate at 104.4–104.8 p.p.m.

Assignments of the other carbon resonances in the ^{13}C-n.m.r. spectra of the oligosaccharides were based on comparison with the chemical shifts shown by corresponding methyl β-D-galactopyranoside derivatives[1]. Evidence for ^{13}C-n.m.r. assignments are based on an earlier publication from this laboratory[1].

The success of this synthesis opens up a new method for synthesis of higher oligosaccharides by coupling two disaccharides *via* a 1-sulfonate leaving-group. The fact that a stepwise synthesis of a tetrasaccharide had failed earlier because of steric factors[1,2] is now confirmed, and suggests that this method may have potential for preparing higher oligosaccharides in such instances.

EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra were determined with a Varian A-60-A or XL-100-15 spectrometer for solutions of the appropriate compounds in chloroform-*d* with tetramethylsilane (Me_4Si) as an internal reference, or with a solution of the deprotected tetrasaccharide **12** in deuterium oxide with CH_3OD (δ 3.30) as the reference. ^{13}C-N.m.r. spectra were determined with a Varian XL-100-15 spectrometer in pulsed Fourier-transform, proton-noise-decoupled mode on similar solutions. Chemical shifts are reported downfield from Me_4Si, assuming the methyl carbon peak to be located at 49.8 p.p.m. in the deprotected tetrasaccharide **12**. Optical rotations were determined with a Perkin–Elmer Model 141 polarimeter for solutions in jacketed 1-dm cells. Melting points were determined with a "Meltemp" apparatus

and a 76-mm immersion thermometer. T.l.c. was performed on "Baker-Flex" silica gel 1B-F (2.5 × 7.5 cm) plates. High-pressure, liquid chromatography (l.c.) was performed with an apparatus having a Valvco septumless injector (1.0 mL), a Glenco pump model HPLPS-1, a Waters differential refractometer R-401, a stainless-steel column (25 × 1 cm, internal diameter) containing Silica gel (Whatman, Partisil M9 10/25), and a flow rate of 8.0 mL/min. The deprotected tetrasaccharide was purified on a jacketed column (1.9 × 73 cm, external diameter, jacketed with circulating water at 60°) containing Bio-Gel P-2, at a flow rate of 3.0 mL/min.

Spectrograde acetonitrile was dried with phosphorus pentaoxide, distilled, and stored over calcium hydride. Silver *p*-toluenesulfonate (Eastman Organic Chemicals, Rochester, N.Y. 14650) was recrystallized from acetonitrile and dried under high vacuum before use. Silver (2,2,2-trifluoroethyl)sulfonate[11] and (chloromethylene)-dimethylimminium chloride[12] were prepared by standard methods.

Allyl 6-O-acetyl-2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranoside (**2**). — The 1-*O*-tosyl derivative **1b** was prepared from the 1-chloro derivative **1a** (0.677 g) in acetonitrile as described earlier[1]. The 1-*O*-tosyl derivative **1b** was coupled with allyl alcohol (0.12 mL) in dry acetonitrile as described previously[1]. Separation by l.c. on a column of silica gel (1:2 ethyl acetate–hexane) gave 0.65 g (92%) of **2**. The product crystallized from ethyl acetate–hexane to give 0.60 g (85%) of **2**, m.p. 81–82°, $[\alpha]_D^{22}$ +11.4° (*c* 0.72, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.05 (m, 2H, *m*-Bz), 7.55–7.21 (m, 13H, *o*- and *p*-Bz and 2 $C_6H_5CH_2$), 6.11–5.55 [m, 2H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.5 Hz, H-2 (q, centered at 5.74) and -C*H*=CH_2], 4.60 (d, 1H, H-1), 4.03 (q, 1H, $J_{3,4}$ 3.0 Hz, H-3), 3.89 (q, 1H, $J_{4,5}$ 8.5 Hz, H-4), 3.60 (m, 1H, H-5), and 1.98 (s, 3H, OAc).

Anal. Calc. for $C_{32}H_{34}O_8$: C, 70.31; H, 6.27. Found: C, 70.20; H, 6.47.

Allyl 2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranoside (**3**). — Compound **2** (0.2 g) was *O*-deacetylated as described previously[1], to give 0.18 g (98%) of **3**. Crystallization from ether–hexane afforded **3** in pure form, m.p. 118–120°, $[\alpha]_D^{22}$ +8.3° (*c* 0.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.04 (m, 2H, *m*-Bz), 7.5–7.20 (m, 13H, *o*- and *p*-Bz and 2$C_6H_5CH_2$), 6.10–5.55 [m, 2H, $J_{1,2}$ 8.2, $J_{2,3}$ 10.5 Hz, H-2 (q centered at 5.72) and -C*H*=CH_2], 4.70 (d, 1H, H-1), and 1.56 (bs, 1H, OH).

Anal. Calc. for $C_{30}H_{31}O_7$: C, 71.55; H, 6.21. Found: C, 71.36; H, 6.47.

Allyl 6-O-(6-O-acetyl-2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranosyl)-2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranoside (**4**). — The glycosidation was conducted as described for **2**. The chloride **1a** (0.8 g) was converted into **1b** and the latter treated with alcohol **3** (0.75 g) to give 1.15 g (75%) of **4** as a crystalline compound (ethyl acetate–hexane), m.p. 140–141°, $[\alpha]_D^{24}$ +14.2° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.10–7.90 (m, 4H, *m*-Bz), 7.51–7.14 (m, 26H, *o*- and *p*-Bz and $C_6H_5CH_2$), 6.10–5.40 (m, 3H, H-2,2′, and -C*H*=CH_2), and 1.98 (s, 3H, OAc).

Anal. Calc. for $C_{59}H_{60}O_{14}$: C, 71.35; H, 6.09. Found: C, 71.13, H, 6.20.

Allyl 6-O-(2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranosyl)-2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranoside (**5**). — The acetyl group of disaccharide **4** (0.2 g) was removed with ammonium hydroxide as described previously[1] to afford crystalline

(from ethanol) disaccharide **5**; yield 0.18 g (95%); m.p. 70–71°, $[\alpha]_D^{24}$ +9.20° (*c* 0.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.11–7.90 (m, 4H, *m*-Bz), 7.50–7.15 (m, 26H, *o*- and *p*-Bz and $C_6H_5CH_2$), 6.11–5.42 (m, 3H, H-2,-2′, and -C*H*=CH_2), and 1.52 (bs, 1H, OH).

Anal. Calc. for $C_{57}H_{58}O_{13}$: C, 71.98; H, 6.15. Found: C, 71.47; H, 5.97.

6-O-(2-O-Benzoyl-3,4-di-O-benzyl-β-D-galactopyranosyl)-2-O-benzoyl-3,4-di-O-benzyl-D-galactopyranose (**6**). — Disaccharide **5** (0.30 g), tris(triphenylphosphine)-rhodium(I) chloride (50 mg) in ethanol (15 mL), and water (2 mL) were heated to boiling under reflux for 2 h. T.l.c. (2:3 EtOAc–hexane) showed the presence of two spots: the 1-propenyl ether (R_F 0.45) and 1-hydroxy disaccharide **6** (R_F 0.18). The mixture was filtered, the filtrate evaporated, and the dark brown residue passed through a small column (2 × 15 cm) of silica gel with 1:1 ethyl acetate–hexane to afford a light-yellow syrup. A solution of mercuric chloride (300 mg) in 10:1 acetone–water (5 mL) was added dropwise with stirring during 3 min to the foregoing mixture of disaccharides, plus yellow mercuric oxide (300 mg) and 10:1 acetone–water (10 mL). T.l.c. showed complete conversion of fast-moving 1-propenyl ether into **6**. The mixture was filtered through Celite and evaporated to a syrup. This syrup was dissolved in chloroform (20 mL), washed with a semisaturated, aqueous solution of potassium iodide (1 × 20 mL), and water (1 × 20 mL), and was then dried (anhydrous magnesium sulfate) and evaporated to a syrup.

This product was purified by l.c. with silica gel (1:2 ethyl acetate–hexane) to give **6** as a syrup, which crystallized from ethyl acetate–hexane to afford 0.245 g (85%) of pure **6**, m.p. 152–153°, $[\alpha]_D^{24}$ +45.4° (*c* 0.44, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 5.80–5.35 (m, 2H, H-2,-2′), 2.68 (bs, 1H, OH), and 1.98 (s, 3H, OAc).

Anal. Calc. for $C_{56}H_{56}O_{14}$: C, 70.57; H, 5.92. Found: C, 70.39; H, 6.06.

6-O-(2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranosyl)-2-O-benzoyl-3,4-di-O-benzyl-α-D-galactopyranosyl chloride (**7**). — (*a*) To a solution of **6** (0.1 g) in 2,6-lutidine (1.0 mL) was added methanesulfonyl chloride (0.5 mL) and the mixture was kept for 1 h at ~25° followed by 45 min at 50° ±5° to complete the reaction. The mixture was cooled and 10 mL of ice-cold water was added, and the whole extracted with chloroform (3 × 10 mL). The extract was washed with water (3 × 10 mL), dried (anhydrous magnesium sulfate), and evaporated to a syrup. Traces of 2,6-lutidine were removed by evaporation of toluene from the syrup. Separation by l.c. on silica gel (1:1 ethyl acetate–hexane) gave the 1-chloro derivative **7** as a solid, 0.06 g (60%); m.p. 58–60°, $[\alpha]_D^{24}$ +88.6° (*c* 0.4, chloroform), ^{1}H-n.m.r. ($CDCl_3$): δ 6.38 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 5.86–5.52 (m, 2H, H-2,-2′), and 1.95 (s, 3H, OAc).

Anal. Calc. for $C_{56}H_{55}ClO_{13}$: C, 69.23; H, 5.71; Cl, 3.65. Found: C, 69.04; H, 5.83; Cl, 3.52.

(*b*) A solution of (chloromethylene)dimethylimminium chloride (0.05 g) in *N*,*N*-dimethylformamide (3.0 mL) was added to disaccharide **6** (0.10 g). The mixture was heated for 2 h at 50° (±5°). The pale-yellow mixture was cooled, chloroform (10 mL) was added, and the solution was washed with aqueous, cold, saturated

hydrogencarbonate (2.0 mL), water (3 × 10 mL), and then dried and evaporated to a syrup. This was further purified as before to yield **7**, 0.09 g (89%).

Allyl 6-O-{6-O-[6-O-(6-O-acetyl-2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranosyl)-2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranosyl]-2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranosyl}-2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranoside (**9**). — The glycosidation was conducted as described for **3** except that the 1-*O*-tresyl derivative **8** was used instead of the 1-*O*-tosyl derivative. The chloride **7** (55 mg) and alcohol **5** (55 mg) gave 82 mg (77%) of tetrasaccharide **9** as a foam; $[\alpha]_D^{25}$ +25.8° (*c* 0.6, chloroform), ^{1}H-n.m.r. ($CDCl_3$): δ 8.10–7.85 (m, 8H, *m*-Bz), 7.51–7.11 (m, 52H, *o*- and *p*-Bz and $C_6H_5CH_2$), 6.10–5.40 (m, 5H, H-2,2′,2″,2‴, and -C*H*=CH_2), and 1.95 (s, 3H, OAc).

Anal. Calc. for $C_{113}H_{112}O_{26}$: C, 71.96; H, 5.99; Found: C, 71.66; H, 6.07.

Propyl 6-O-{6-O-[6-O-(6-O-β-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-galactopyranosyl}-β-D-galactopyranoside (**12**). — *O*-Deacetylation of tetrasaccharide **9** (75 mg) with ammonium hydroxide gave 63 mg (86%) of **10** as a foam, $[\alpha]_D^{24}$ +21.4° (*c* 0.8, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.12–7.96 (m, 8H, *m*-Bz), 7.52–7.24 (m, 52H, *o*- and *p*-Bz and $C_6H_5CH_2$), 6.12–5.40 (m, 5H, H-2,2′,2″,2‴, and -C*H*=CH_2), and 2.62 (bs, 1H, OH).

O-Debenzoylation of **10** (60 mg) with barium oxide (10 mg) in methanol (5 mL)[2] for 36 h at room temperature gave 40 mg (87%) of tetrasaccharide **11** as a foam, $[\alpha]_D^{24}$ −5.0° (*c* 0.38, chloroform); ^{1}H-n.m.r. ($CDCl_3$); δ 7.34–7.26 (m, 40H, $8C_6H_5CH_2$), and 2.40 (bs, 4H, OH).

The benzylated tetrasaccharide **11** (35 mg) was dissolved in methanol (4 mL) containing water (0.2 mL), and 10% palladium-on-carbon (35 mg) was added. The mixture was stirred under a hydrogen atmosphere for 80 h. Filtration of the catalyst followed by evaporation of the solvent gave a white solid (14 mg). This solid was dissolved in hot water and fractionated on a column of Bio-Gel P-2. The tetrasaccharide was collected and freeze-dried, to yield **12**, 12 mg (69%); $[\alpha]_D^{22}$ +37.2° (*c* 1.1, water). The tetrasaccharide **12** was very hygroscopic and became gummy when exposed to the atmosphere. For this reason, the optical rotation may not be very accurate and no elemental analysis could be obtained.

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