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SYNTHESIS AND CHARACTERIZATION OF PROPYL *O*-β-D-GALACTOPYRANOSYL-(1→4)-*O*-β-D-GALACTOPYRANOSYL-(1→4)-α-D-GALACTOPYRANOSIDE

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ABSTRACT

Allyl 4-*O*-(4-*O*-acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-galactopyranoside was *O*-deallylated to give the 1-hydroxy derivative, and this was converted into the corresponding 1-*O*-(*N*-phenylcarbamoyl) derivative, treatment of which with dry HCl produced the α-D-galactopyranosyl chloride. This was converted into the corresponding 2,2,2-trifluoroethanesulfonate, which was coupled to allyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-galactopyranoside, to give crystalline allyl 4-*O*-[4-*O*-(4-*O*-acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-galactopyranosyl]-2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-galactopyranoside (**15**) in 85% yield, no trace of the α anomer being found. The trisaccharide derivative **15** was de-esterified with 2% KCN in 95% ethanol, and the product *O*-debenzylated with H_2–Pd, to give the unprotected trisaccharide. Alternative sequences are discussed.

INTRODUCTION

4-*O*-β-D-Galactopyranosyl-D-galactopyranose was first identified in 1958 by Gillham and co-workers[1]. A few attempts have been made to synthesize the disaccharide or its derivatives[2,3]; in these attempts, it was obtained as one component of a mixture of regioisomers[2] or anomers[3]. Recently, we prepared the three β-(1→4)-linked D-galactopyranose disaccharides **7**, **8**, and **9** in reasonable yields and with complete stereoselectivity[4]. The chloroacetyl group was chosen to protect O-4 before further deprotection and coupling at O-4 of the disaccharide, but attempts to remove the chloroacetyl group by using thiourea led to cleavage of the β-D-galactosidic bond.

To prepare the trisaccharide, we had either to find a protecting group that could be selectively removed from O-4′ under non-basic conditions, or to deprotect the disaccharide at O-1, convert it into the corresponding 1-chloride, and then

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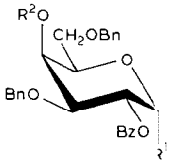
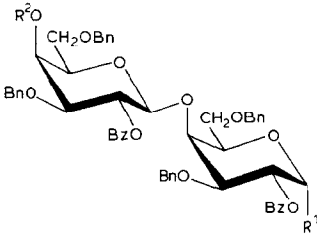


1 R^1 = OAll, R^2 = H
2 R^1 = OAll, R^2 = $MeO(CH_2)_2OCH_2$
3α R^1 = OH, R^2 = $MeO(CH_2)_2OCH_2$
4 R^1 = Cl, R^2 = $MeO(CH_2)_2OCH_2$
5α R^1 = OAc, R^2 = Ac
6 R^1 = Br, R^2 = Ac

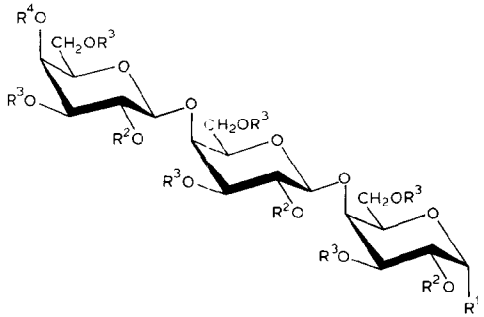
All = $H_2C{=}CHCH_2$
Bn = $PhCH_2$



7 R^1 = OAll, R^2 = Ac
8 R^1 = OAll, R^2 = $COCH_2Cl$
9 R^1 = OAll, R^2 = Bn
10α R^1 = OH, R^2 = Ac
11 R^1 = OAc, R^2 = Ac
12α R^1 = OCarb, R^2 = Ac
13 R^1 = Cl, R^2 = Ac
14 R^1 = OTres, R^2 = Ac

Carb = PhHNCO
Tres = $F_3CCH_2SO_2$

couple this to O-4 of D-galactose. In the present article, attempts to prepare trisaccharide **17** by both routes are reported, our purpose being to prepare this series of oligosaccharides for measurement of the binding constants of homogeneous, myeloma proteins[5].



15 R^1 = OAll, R^2 = Bz, R^3 = Bn, R^4 = Ac
16 R^1 = OAll, R^2 = H, R^3 = Bn, R^4 = H
17 R^1 = OPr, R^2 = H, R^3 = H, R^4 = H

RESULTS AND DISCUSSION

According to Corey *et al.*[6], the (2-methoxyethoxy)methyl (Mem) group can be selectively removed in the presence of allyl, benzyl, and benzoyl groups, and all can be removed in its presence. The conditions used to remove the Mem group are non-hydrolytic, and were not expected to cleave the disaccharide. Therefore, Mem

was used to protect O-4. Treatment of **1** with (2-methoxyethoxy)methyl chloride gave the 4-*O*-Mem derivative **2**. The ^{1}H-n.m.r. spectrum of **2** did not show any OH peaks, but showed Mem protons at δ 4.48 (OCH_2O), 3.80–3.54 (OCH_2-CH_2O), and 3.24 (OCH_3). Rearrangement of the allyl group of **2** with tris(triphenylphosphine)rhodium(I) chloride in the presence of diisopropylethylamine, followed by hydrolysis with $ZnCl_2$–ZnO in aqueous acetone, gave **3** without any detectable cleavage of the Mem group. ^{13}C-N.m.r. spectroscopy showed that **3** was actually a mixture of the α and β anomers in the ratio of 67:23 (see Table I). However, the Mem was lost in all attempts to convert **3** into the corresponding 1-chloride **4**. These attempts included the use[7] of Me_3SiCl, PCl_5–DMF, and $Th(OEt)_3$–$SOCl_2$.

The disaccharide **7** was *O*-deallylated to give the corresponding 1-hydroxy derivative **10**. ^{1}H-N.m.r. spectroscopy of **10** showed no allyl protons, and the ^{13}C-n.m.r. spectrum indicated that it was a mixture of the anomers; signals for C-1α, C-1β, and C-1′β appeared at 90.8, 96.1, and 101.8 p.p.m., respectively, and those of all other groups persisted (see Table I). Acetylation of **10** at O-1 gave the disaccharide derivative **11**. The structure of **11** was determined by ^{1}H-n.m.r. spectroscopy, which showed two acetyl peaks, at δ 2.10 and 1.95, and ^{13}C-n.m.r. spectroscopy, which showed two anomeric peaks, at 90.4 (C-1α) and 101.6 (C-1′β) p.p.m., in addition to all of the other protecting groups.

Treatment of **5** with[8] $TiBr_4$ produced a quantitative yield of the 1-bromide **6**. In the ^{1}H-n.m.r. spectrum of **6**, the C-1α resonance appeared at δ 6.85, $J_{1,2}$ 3.5 Hz, and that of OAc at δ 2.15. ^{13}C-N.m.r. spectroscopy showed a single anomeric peak, at 90.3 p.p.m., indicating that **6** was a pure α anomer, and also peaks for all of the other protecting groups (see Table I). The same procedure was applied to **11**, but, instead of obtaining the corresponding bromide, a D-galactopyranosyl bromide was obtained, the ^{13}C-n.m.r. spectrum of which matched that of **6**.

Because it was not possible to obtain the 1-bromide **13** by the $TiBr_4$ method, disaccharide **10** was converted into the 1-*O*-(*N*-phenylcarbamoyl) derivative **12** which, on treatment wth HCl in dichloromethane[9] for 5 min, gave **13**. The reaction was α-stereoselective, the yield was high, and no cleavage of the D-galactosidic bond was detected. Therefore, the reaction can be considered to be an alternative, and generally useful, method for the synthesis of sensitive glycosyl halides. The structure of **13** was proved by ^{1}H-n.m.r. spectroscopy, which showed the H-1α signal at δ 6.30 as a doublet, $J_{1,2}$ 3 Hz, and the presence of an acetyl group at δ 2.10. The two anomeric carbon atoms, C-1 and C-1′, appeared in the ^{13}C-n.m.r. spectrum at 93.2 and 101.8 p.p.m., respectively.

Reaction of **13** with silver 2,2,2-trifluoroethanesulfonate (silver tresylate) produced the 1-*O*-tresyl disaccharide **14**, which was coupled to **1** to afford trisaccharide derivative **15**. The yield was higher than that of the coupling reaction which led to disaccharide **7**. No other oligosaccharides were isolated. The reaction was stereoselective, and only the β anomer was obtained. The ^{13}C-n.m.r. spectrum of **15** showed one α-anomeric carbon signal, at 95.5, and two β-anomeric carbon signals, at 99.8 and 101.0 p.p.m., which proved the formation of a trisaccharide.

TABLE I

^{13}C-N.M.R SHIFTS (PROTON-DECOUPLED) IN p.p.m., FOR SOLUTIONS IN $CDCl_3$[a,b]

Carbon atom	*Compound*									
	2	**3**	**5**	**6**	**10**	**11**	**13**	**15**	**16**	**17**[c]
C-1	96.1	92.6 (β) 91.0 (α)	92.5 (β) 90.2 (α)	90.3	96.1 (β) 90.8 (α)	90.4	93.2	95.5	97.9	98.4
C-2	68.7	68.9	67.0[d]	66.7[d]	71.8 (α) 72.7 (β)	69.2[d]	68.9[d]	69.3[d]	68.8[d]	68.9
C-3	73.4	73.4	73.3	72.9	75.9 (β) 74.7 (α)	73.7	73.5	73.7	78.5	68.8
C-4	76.1	75.7	70.5	71.8	76.7	76.7	76.6	76.7	78.7	79.0
C-5	67.8	67.7	67.9[d]	67.4[d]	70.1 (α) 73.5 (β)	69.2[d]	71.1[d]	69.3[d]	69.2[d]	70.2
C-6	69.4	69.3	69.1	70.1	69.4	71.2[d]	71.1[d]	69.2[d]	69.2[d]	61.1
C-1′					101.8	101.6	101.8	101.0	106.3	104.5
C-2′					72.3[d]	72.5	72.4	72.4	69.7[d]	72.9
C-3′					73.8	73.8	73.8	73.9	79.1	72.1
C-4′					66.5	66.5	66.4	77.0	77.8	77.3
C-5′					73.1	73.1	73.2	72.8	72.5[d]	74.6
C-6′					68.2	68.2[d]	68.1[d]	68.4[d]	69.4	61.1
C-1″								99.8	106.3	104.7
C-2″								72.2	69.7[d]	71.5
C-3″								73.8	80.3	73.5
C-4″								67.0	67.2	70.2
C-5″								72.0[d]	73.8	75.9
C-6″								68.6[d]	68.8[d]	60.7
C=O	166.3	166.3	170.3 169.0 165.6	170.2 165.9	170.7 166.0 165.5	170.6 169.0 165.8 164.8	170.6 165.9 165.1	170.1 161.0 165.4		
CH=	134.1							134.3	133.9	
CH_2=	117.3							117.1	118.1	
Ac			20.7	20.7	20.9	20.9	20.9	20.9		

[a]These assignments are tentative, and are based on analogies[11]. [b]Benzyl and allyl CH_2 groups were partially identified, and the total number of carbon atoms was accounted for. [c]Spectrum was recorded for a solution in D_2O. [d]Assignments may have to be interchanged. Mem group of **2** and **3** gave peaks at 96.95 (OCH_2O), 71.78, 71.45 (OCH_2-CH_2O), and 58.99 p.p.m. (OCH_3). Trisaccharide **17** showed peaks at 22.05 (CH_2) and 9.91 p.p.m. (CH_3).

Disaccharides **7** and **8** were found to be base-sensitive, but were successfully de-esterified with KCN in 95% ethanol[10]. The same reagent was used to de-esterify trisaccharide **15**, to give trisaccharide **16**, which has free hydroxyl groups on C-2, C-2′, C-2″, and C-4″. No cleavage of D-galactosidic bonds was observed. ^{13}C-N.m.r. spectroscopy showed three anomeric carbon atoms, at 97.9 (C-1α) and 106.3 p.p.m. (C-1′β and C-1″β), but did not show any carbonyl peaks. The upfield shift of the C-2, C-2′, C-2″, and C-4″ signals, and the downfield shift of those of their neighboring carbon atoms is consistent with the ^{13}C-n.m.r. assignments made for **15**, and with removal of the ester groups from O-2, O-2′, O-2″, and O-4″. The

existence of two β-D-galactosidic bonds was also evident from the ^{1}H-n.m.r. spectrum, which showed H-1′ and H-1″ at δ 4.32 and 4.40, $J_{1',2'} = J_{1'',2''} = 8$ Hz.

Treatment of **16** with H_2–Pd afforded the disaccharide **17**. The structure of **17** was determined from its ^{13}C-n.m.r. spectrum, which showed no aromatic carbon atoms, but showed 18 sugar carbon atoms and 3 propyl carbon atoms (see Table I). Removal of the benzyl groups caused large upfield shifts of the C-3, C-6, C-3′, C-6′, C-3″, and C-6″ signals in the ^{13}C-n.m.r. spectrum of **17**. The chemical shifts of all of the carbon atoms of trisaccharide **17** were close to those of methyl α- and β-D-galactopyranoside, except for those of C-4 and C-4′, which appeared at higher values as a result of D-galactosidation at these atoms.

We conclude that conversion of the 1-hydroxy derivative **10** into the corresponding chloride **13** [*via* the 1-*O*-(*N*-phenylcarbamoyl) derivative **12**], and the de-esterification of the trisaccharide ester with KCN in 95% ethanol were two key reactions in the synthesis. Both reactions can be generally useful for the synthesis, involving sensitive intermediates, of oligosaccharides.

EXPERIMENTAL

General. — All instrumental procedures, chromatographic analyses, and preparations of materials were as described previously[12].

Allyl 2-O-benzoyl-3,6-di-O-benzyl-4-O-(2-methoxyethoxy)methyl-α-D-galactopyranoside (**2**). — Freshly prepared (2-methoxyethoxy)methyl chloride (1.1 g) was added to a solution of **1** (3 g) in chloroform (30 mL) containing diisopropylethylamine (1.2 g). The mixture was kept for 3 h at room temperature, washed with water, dried (magnesium sulfate), and evaporated under diminished pressure, to give 3.18 g (90%) of **2** as a clear syrup; ^{1}H-n.m.r. ($CDCl_3$): δ 8.19–7.95 (dd, 2 H, COC_6H_5, *o*), 7.68–7.19 (m, 13 H, 2 $CH_2C_6H_5$ and COC_6H_5, *m, p*), 6.02–5.60 (m, 1 H, CH=), 5.49 (dd, 1 H, $J_{2,3}$ 11, $J_{1,2}$ 4 Hz, H-2), 5.33–5.05 (m, 3 H, CH_2= and H-1), 4.90–4.62 (m, 4 H, 2 $CH_2C_6H_5$), 4.48 (s, 2 H, OCH_2O), 4.33–3.98 (m, 5 H, OCH_2CH=, H-3,4,5), 3.80–3.54 (m, 4 H, OCH_2CH_2O), and 3.43–3.24 (m, 5 H, 2 H-6 and OCH_3).

Anal. Calc. for $C_{34}H_{40}O_9$: C, 68.91; H, 6.80. Found: C, 68.58; H, 6.76.

2-O-Benzoyl-3,6-di-O-benzyl-4-O-(2-methoxyethoxy)methyl-D-galactopyranose (**3**). — A mixture of **2** (3 g) and tris(triphenylphosphine)rhodium(I) chloride (0.03 g) in 95% ethanol (50 mL) containing diisopropylethylamine (1 mL) was boiled under reflux for 2 h, cooled, and evaporated to a brown syrup which was dissolved in dichloromethane; the solution was washed with saline solution, dried (magnesium sulfate), and evaporated, and the yellow syrup was dissolved in 9:1 acetone-water containing mercuric oxide (3 g). Mercuric chloride (3 g) in 9:1 acetone-water was added dropwise, with continuous stirring, and, after 30 min, the solvent was evaporated, the syrup was dissolved in ether, and the solution was washed with saturated KI solution, and evaporated, giving 2.5 g (89%) of **3**; ^{1}H-n.m.r. ($CDCl_3$): δ 8.15–7.90 (m, 2 H, COC_6H_5, *o*), 7.54–7.10 (m, 13 H, 2

$C_6H_5CH_2$ and COC_6H_5, *m, p*), 5.4 (dd, 1 H, $J_{2,3}$ 10, $J_{1,2}$ 4 Hz, H-2), 5.15 (d, 1 H, $J_{1,2}$ 5 Hz, H-1α), 5.05–4.58 (m, 4 H, 2 $CH_2C_6H_5$), 4.49 (s, 2 H, OCH_2O), 4.28–3.88 (m, 3 H, H-3,4,5), and 3.80–3.20 (m, 9 H, OCH_2CH_2O, 2 H-6 and OCH_3).

Anal. Calc. for $C_{31}H_{36}O_9$: C, 67.39; H, 6.57. Found: C, 67.24; H, 6.30.

*1,4-Di-*O*-acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-*D*-galactopyranose* (**5**). — Acetylation of 4-*O*-acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-D-galactopyranose with Ac_2O–C_5H_5N produced **5** as a syrup in 92% yield; ^{1}H-n.m.r. ($CDCl_3$): δ 8.18–7.76 (m, 2 H, COC_6H_5, *o*), 7.60–7.00 (m, 13 H, 2 $CH_2C_6H_5$ and COC_6H_5, *m, p*), 6.48 (d, 0.7 H, $J_{1,2}$ 4 Hz, H-1α), 5.87–5.17 (m, 2 H, H-4,2, $J_{1,2}$ 4, $J_{2,3}$ 10 Hz), 4.75–4.05 (m, 5.3 H, $J_{1,2}$ 8 Hz, H-1β5, and 2 $CH_2C_6H_5$), 3.87 (dd, 1 H, $J_{3,4}$ 3 Hz), 3.5 (d, 2 H, 2 H-6), and 2.1 (t, 6 H, 2 Ac).

Anal. Calc. for $C_{31}H_{32}O_9$: C, 67.88; H, 5.86. Found: C, 67.52; H, 5.83.

*4-*O*-Acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-α-*D*-galactopyranosyl bromide* (**6**). — A solution of compound **5** (0.5 g) in dichloromethane (6 mL) containing ethyl acetate (0.6 mL) was poured onto $TiBr_4$ (0.4 g, 1.2 equiv.), and the mixture was kept for 90 min at room temperature. Dry acetonitrile (10 mL) was distilled into the mixture, anhydrous sodium acetate (1 g) was added, the mixture was kept at room temperature, and, after 10 min, toluene (10 mL) was added, and the mixture was filtered through Celite. The filtrate was concentrated to 5 mL, diluted with toluene (20 mL), and the suspension filtered through Celite. The filtrate was evaporated to dryness, giving syrupy **6** (0.44 g, 85%); ^{1}H-n.m.r. ($CDCl_3$): δ 8.25–7.90 (m, 2 H, COC_6H_5, *o*), 7.65–7.05 (m, 13 H, 2 $CH_2C_6H_5$ and COC_6H_5, *m, p*), 6.85 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1α), 5.80 (d, 1 H, H-4), 5.36 (dd, 1 H, $J_{2,3}$ 8 Hz, H-2), 4.9–4.40 (m, 5 H, 2 $CH_2C_6H_5$ and H-5), 4.2 (dd, 1 H, $J_{3,4}$ 3 Hz, H-3), 3.65 (d, 2 H, 2 H-6), and 2.15 (s, 3 H, Ac).

Anal. Calc. for $C_{29}H_{29}BrO_7$: C, 60.92; H, 5.52. Found: C, 61.14; H, 5.67.

*4-*O*-(4-*O*-Acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-*D*-galactopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*D*-galactopyranose* (**10**). — Treatment of disaccharide **7** (100 mg) with tris(triphenylphosphine)rhodium(I) chloride (10 mg), followed by hydrolysis of the product with $ZnCl_2$ (100 mg) in aqueous acetone containing[13] ZnO (100 mg) afforded **10** as white crystals (82 mg, 85.4%); m.p. 65–68°; ^{1}H-n.m.r. ($CDCl_3$): δ 8.0–7.55 (m, 4 H, 2 COC_6H_5, *o*), 7.55–6.84 (m, 26 H, 4 $CH_2C_6H_5$ and 2 COC_6H_5, *m, p*), 5.6–4.7 (m, 4 H, H-1,2,2′,4′), 4.6–4.3 (m, 9 H, H-2 and 4 $CH_2C_6H_5$), 4.3–3.9 (m, 3 H, H-3,3′,4), 3.75–3.30 (m, 6 H, H-5,5′, 2 H-6, 2 H-6′), 2.08 (s, 3 H, $COCH_3$), and 1.98 (s, 1 H, OH).

Anal. Calc. for $C_{56}H_{56}O_{14}$: C, 70.61; H, 5.88. Found: C, 70.43; H, 6.05.

*1-*O*-Acetyl-4-*O*-(4-*O*-acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-*D*-galactopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-α-*D*-galactopyranose* (**11**). — Acetylation of **10** with acetic anhydride in pyridine, followed by conventional processing, produced **11** in quantitative yield as syrup; ^{1}H-n.m.r. ($CDCl_3$): δ 8.1–7.55 (m, 4 H, 2 COC_6H_5, *o*), 7.55–6.9 (m, 26 H, 4 $CH_2C_6H_5$ and 2 COC_6H_5, *m, p*), 6.28 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1α), 5.7–5.1 (m, 2 H, H-4′,2), 4.95 (t, 1 H, $J_{1',2'} = J_{2',3'} = 9$ Hz, H-

2′), 4.65–4.15 (m, 9 H, 4 $CH_2C_6H_5$ and H-1′), 4.10–3.30 (m, 9 H, H-3,4,3′,5,5′, 2 H-6, and 2 H-6′), 2.06 (s, 3 H, $COCH_3$), and 1.94 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{58}H_{58}O_{14}$: C, 71.18; H, 5.93. Found: C, 71.34; H, 6.18.

4-O-(4-O-Acetyl-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactopyranosyl)-2-O-benzoyl-3,6-di-O-benzyl-α-D-galactopyranosyl chloride (**13**). — Compound **10** (50 mg) was converted into the corresponding 1-*O*-(*N*-phenylcarbamoyl) derivative **12** by the method of Kronzer and Schuerch[9]. The excess of isocyanate was decomposed with water, and the 1,3-diphenylurea crystallized from benzene. The solution was evaporated, giving a colorless syrup which was dissolved in dichloromethane (50 mL), and dry HCl was bubbled into the solution for 5 min. The suspension was filtered, and the filtrate was washed with water, dried (anhydrous magnesium sulfate), evaporated, and the product purified by ~12-MPa l.c. on silica gel using 1:3 ethyl acetate–hexane as the eluant. Compound **13** (41 mg, 80.4%) was obtained as white crystals; m.p. 56–58°, $[\alpha]_D^{24}$ +76.9° (*c* 0.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.00–7.64 (m, 4 H, 2 COC_6H_5, *o*), 7.55–6.80 (m, 26 H, 4 $CH_2C_6H_5$ and 2 COC_6H_5, *m, p*), 6.30 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.54 (d, 1 H, $J_{3',4'}$ 3.5 Hz, H-4′), 5.25 (dd, 1 H, $J_{2,3}$ 9 Hz, H-2), 4.86 (t, 1 H, $J_{1',2'} = J_{2',3'} = 8$ Hz, H-2′), 4.60–4.30 (m, 9 H, H-1′ and 4 $CH_2C_6H_5$), 4.20–3.30 (m, 9 H, H-3,4,3′,5,5′, 2 H-6, and 2 H-6′), and 2.10 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{56}H_{55}ClO_{13}$: C, 69.26; H, 5.66. Found: C, 69.63; H, 5.27.

Allyl 4-O-[4-O-(4-O-acetyl-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactopyranosyl)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactopyranosyl]-2-O-benzoyl-3,6-di-O-benzyl-α-D-galactopyranoside (**15**). — The reaction was conducted in an apparatus that consisted of a vertical tube having a glass joint and a stopcock at the top and three branches at the bottom. One of the branches was separated from the others by a glass filter, and a 10-mL, round-bottomed flask containing a small magnet was connected to each branch. The chloride **13** (25 mg), silver tresylate (5.5 mg, 1.2 equiv.), and the alcohol **1** (10.6 mg, 1.2 equiv.) were placed separately in the flasks. The apparatus was connected to a high-vacuum line, and kept on it for 12 h, to dry the materials. Acetonitrile (3 mL) was distilled under vacuum into the flasks. The stopcock was closed, and the silver tresylate solution was poured onto the chloride solution; then the suspension was filtered onto **1**, and the mixture was stirred for 10 min, and kept for 48 h in the dark at room temperature. The solution was diluted with dichloromethane, washed with a saturated solution of sodium hydrogencarbonate and sodium thiosulfate, dried (anhydrous magnesium sulfate), and evaporated, and the product was purified by ~12-MPa l.c. on silica gel with 1:3 ethyl acetate–hexane. Compound **15** was obtained as white crystals (31 mg, 85%); m.p. 126–127°, $[\alpha]_D^{24}$ +70.5° (*c* 0.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$, 360 MHz): δ 8.15 (d, 6 H, $J_{o,m}$ 7.4 Hz, 3 COC_6H_5, *o*), 7.85 (t, 6 H, $J_{o,m} = J_{m,p}$ = 9.5 Hz, 3 COC_6H_5, *m*), 7.56–7.00 (m, 33 H, 3 COC_6H_5, *p*, and 6 $CH_2C_6H_5$), 5.71–5.66 (m, 1 H, CH=), 5.61 (d, 1 H, $J_{3'',4''}$ 2.8 Hz, H-4″), 5.41 (t, 1 H, *J* 9.1 Hz, H-2″ or H-2′), 5.34–5.21 (m, 2 H, H-2 and H-2′ or H-2″), 5.14–5.86 (m, 3 H, CH_2= and H-1), 4.50–4.31 (m, 14 H, 6 $CH_2C_6H_5$, H-1′1″), 4.02 (dd, 1 H, $J_{2,3}$ 14.4, $J_{3,4}$ 5.6 Hz, H-3),

3.94 (d, 1 H, *J* 2.5 Hz, H-4 or H-4′), 3.91 (d, 1 H, *J* 2.4 Hz, H-4 or H-4′), 3.88–3.78 (m, 2 H, H-3′,3″), 3.76–3.64 (m, 3 H, H-5,5′5″), 3.56–3.21 (m, 4 H, 2 H-6′ and 2 H-6″), 3.20–3.12 (m, 2 H, 2 H-6), and 2.10 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{86}H_{86}O_{19}$: C, 72.74; H, 6.01. Found: C, 72.97; H, 6.32.

Propyl O-β-D-*galactopyranosyl-(1→4)*-O-β-D-*galactopyranosyl-(1→4)*-α-D-*galactopyranoside* (**17**). — Compound **15** (20 mg) was heated for 12 h at 55° with 2% KCN in 95% ethanol (10 mL). The solution was diluted with dichloromethane, washed with water, and dried (anhydrous magnesium sulfate). T.l.c. with 1:1 ethyl acetate–hexane showed a single spot, R_F 0.18. The solvent was evaporated under diminished pressure, to give **16** as a syrup; ^{1}H-n.m.r. ($CDCl_3$): δ 7.95–7.00 (m, 30 H, 6 $CH_2C_6H_5$), 6.2–5.7 (m, 1 H, CH=), 5.45–5.10 (m, 2 H, CH_2=), 4.96 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1). 4.90–4.42 (m, 12 H, 6 $CH_2C_6H_5$), 4.4, 4.32 (2 d, 2 H, $J_{1',2'} = J_{1'',2''}$ = 8 Hz, H-1′β and H-1″β), and 4.3–3.2 (m, 20 H, H-2,2′,2″,3,3′3″,4,4′,4″,5,5′5″, 2 H-6, 2 H-6′, 2 H-6″, and CH_2CH=).

Compound **16** was dissolved in 4:1 acetone–water (20 mL), treated with Pd–C, and kept under a hydrogen atmosphere, with stirring, for 72 h. The suspension was filtered through Celite, and the filtrate was evaporated under diminished pressure, to afford **17** (5.256 mg, 70% yield) as a white solid; the ^{1}H-n.m.r. spectrum (D_2O) showed no aromatic or acetyl protons; for ^{13}C-n.m.r. data see Table I. The trisaccharide was highly hygroscopic; therefore, melting point, optical rotation, and elemental analyses might not be accurate, and were not obtained.

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