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STUDIES ON THE SYNTHESIS OF PROPYL 4-*O*-β-D-GALACTO-PYRANOSYL-α-D-GALACTOPYRANOSIDE

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ABSTRACT

2-*O*-Benzoyl-3,6-di-*O*-benzyl-4-*O*-(chloroacetyl)-, 4-*O*-acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-, and 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride were converted into the corresponding 2,2,2-trifluoroethanesulfonates, and these were treated with allyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-galactopyranoside, to give allyl 2-*O*-benzoyl-4-*O*-[2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-(chloroacetyl)-β-D-galactopyranosyl]-3,6-di-*O*-benzyl-α-D-galactopyranoside (**26**; 41% yield), 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 (**27**; 62% yield), and allyl 2-*O*-benzoyl-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-3,6-di-*O*-benzyl-α-D-galactopyranoside (**28**; 65% yield). All disaccharides were free from their α anomers. Disaccharides **26** and **27** were found to be base-sensitive, and were de-esterified by KCN in aqueous ethanol, and debenzylated with H_2–Pd. Attempts to produce (1→4)-β-D-galactopyranosides from the coupling of a number of fully esterified D-galactopyranosyl sulfonates to allyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside were unsuccessful.

INTRODUCTION

4-*O*-β-D-Galactopyranosyl-D-galactopyranose was first identified in 1958, when Gillham *et al.*[1] isolated it by partial hydrolysis of an α-cellulose prepared from white birch *(Betula papyrifera)* wood. In 1965, Curtis and Jones[2] reported a nonregioselective synthesis of this disaccharide as a minor product in a mixture of (1→4)- and (1→6)-β-D-galacto-disaccharides that was obtained from the condensation of a mixture of 2,3:4,5- and 2,3:5,6-di-*O*-isopropylidene-D-galactose dimethyl acetals with tetra-*O*-acetyl-α-D-galactosyl bromide. Later, there was[3] reported a nonstereoselective synthesis of an anomeric mixture of (1→4)-D-galactopyranosides that contained more α than β anomer. Although coupling of different sugars to O-4 of D-galactopyranosides to form a β-linkage has been accomplished by different methods[4–8], stereoselective synthesis of the title compound (**30**) has not yet been reported.

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In continuation of our interest in the synthesis of β-D-galactopyranosides[9–11] for measurement of the binding constants of homogeneous myeloma proteins[12], we present the first stereoselective synthesis of propyl 4-*O*-β-D-galactopyranosyl-α-D-galactopyranoside (**30**).

RESULTS AND DISCUSSION

Allyl α-D-galactopyranoside (**1**) was prepared by a modification[13] of Fischer's glycosidation method. Benzoylation of **1** with 3.2 equiv. of benzoyl chloride in pyridine[14] produced a crystalline compound whose ^{13}C-n.m.r. spectrum showed an upfield shift of the signals of both C-1 and C-4 as a result of benzoylation at O-2 and O-3. Upfield shift of that of C-5 by 2.5 p.p.m., which is about half the shift reported for that of C-5 of fully acylated methyl α-D-galactopyranoside[15], indicated that the product had only one more benzoyl group, at either O-4 or O-6. Because OH-6 is known to be more reactive than OH-4, it was concluded that the product must have been allyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside (**2**). ^{1}H-N.m.r. spectroscopy of **2** confirmed the presence of three benzoyl groups, and showed the OH-4 peak at δ 3.0.

Treatment of **2** with chloroacetyl chloride[16] in ether–pyridine gave allyl 2,3,6-tri-*O*-benzoyl-4-*O*-(chloroacetyl)-α-D-galactopyranoside (**3**) in 94.4% yield. The ^{1}H-n.m.r. spectrum of **3** showed the chloroacetyl protons at δ 4.3–4.1, overlapping the OCH_2 signal of the allyl group, and a downfield shift of that of H-4. The chloroacetyl group was chosen as a temporary blocking-group that could be selectively removed from the disaccharide for further coupling at O-4'.

Compound **3** was rearranged to the corresponding propenyl glycoside **4** with tris(triphenylphosphine)rhodium(I) chloride[17], and **4** was hydrolyzed to the 1-hydroxy derivative **5**. The ^{1}H-n.m.r. spectrum of **5** showed the disappearance of the allyl protons, and the ^{13}C-n.m.r. spectrum showed two anomeric peaks, at 96.4 (C-1,β) and 91.4 p.p.m. (C-1,α). The ratio of the α to the β anomer was 37:13, based on the relative intensities of the anomeric peaks.

Compound **5** was very stable to HCl–ether, conditions that are used for the synthesis of glycosyl chlorides. Therefore, 2,3,6-tri-*O*-benzoyl-4-*O*-(chloroacetyl)-α-D-galactopyranosyl chloride (**6**) was prepared from **5** by treatment with thionyl chloride. The structure of **6** was proved by its ^{1}H-n.m.r. spectrum, which showed a large, downfield shift of the single, anomeric peak to δ 6.58 as a doublet, $J_{1,2}$ = 4 Hz. Formation of the α anomer only was also proved by its ^{13}C-n.m.r. spectrum, which showed a single, anomeric peak, at 91.8 p.p.m.

The chloride **6** was converted into the corresponding 1-*O*-(2,2,2-trifluoroethylsulfonyl) (tresyl) (**7**), 1-*O*-(trifluoromethylsulfonyl) (triflyl) (**8**), and 1-*O*-(*p*-tolylsulfonyl) (tosyl) (**9**) derivatives. Both **7** and **8** failed to react with methanol in acetonitrile at room temperature. Attempts to cause **9** to react with methanol at higher temperatures were also unsuccessful, and **9** was recovered unchanged; the ^{1}H-n.m.r. spectrum of the recovered compound showed the respec-

TABLE I

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

Carbon atom	*Compound*											
	1[c]	**2**	**5**	**6**	**10**[c]	**12**	**13**	**15**	**16**	**18**	**20**	**22**
C-1	100.0	96.1	91.4	91.8	100.2	96.1	96.2	96.0	96.0	92.5	96.1	92.7
C-2	69.0	68.8	69.7	68.8[d]	70.0	67.9	68.9	67.7	67.7	68.9[d]	67.9	67.6
C-3	70.6	69.3	68.3[d]	68.1[d]	71.5[d]	72.2	68.7	75.4	73.4	72.8[d]	73.6	73.0
C-4	70.1	68.5	71.0	69.9[d]	71.2[d]	73.9	70.1	69.0	69.9	72.8[d]	68.8	71.1
C-5	71.3	68.8	66.5	69.9[d]	71.0	70.0	70.7	71.0	68.0	70.7[d]	68.2	70.3
C-6	62.3	64.2	62.0	61.4	69.1	69.0	69.5	68.6	68.9	67.1	68.6	67.0
C=O		166.7	167.2	166.8		166.2		166.3	167.2	166.9	170.5	170.2
		166.5	166.5	166.1					166.2	165.8	166.3	165.9
		166.3	166.0	165.9								
				165.6								
CH=	136.8	133.9			136.8	133.6	134.1	134.1	133.8		134.0	
CH_2=	118.0	117.6			118.0	117.6	117.4	117.4	117.7		117.5	
CH_2Cl			40.6	40.4					40.8	40.7		
$COCH_3$											20.8	20.7

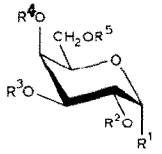
[a]These assignments are tentative, based on analogies. [b]Benzyl and allyl CH_2 were partially distinguished, and the total number of carbon atoms was accounted for. [c]Spectra for solution in Me_2SO-d_6, with Me_4Si as an external indicator. [d]Assignments may have to be reversed.

tive signals of the CH_3 of the tosyl group at δ 2.1 and of the anomeric proton at δ 6.7, and no OCH_3 peak.

Because the high stability of the D-galactopyranosyl derivatives **7, 8,** and **9** towards glycosidation was probably due to the electronic effects of both the benzoyl and the chloroacetyl groups, a different scheme for the synthesis of D-galactopyranosyl derivatives having fewer ester groups was examined.

Allyl 6-*O*-benzyl-α-D-galactopyranoside (**10**) was prepared from 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactose[18] by the glycosidation method used for the synthesis of allyl α-D-galactopyranoside (**1**). Compound **10** was converted into allyl 6-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (**11**), which was treated with benzoyl chloride in pyridine to produce the 2-benzoate **12**. Formation of **12** was evident from its ^{1}H-n.m.r. spectrum, which showed no OH peaks, but the addition of 5 protons to the aromatic peaks. The ^{13}C-n.m.r. spectrum of **12**, which was assigned in relation to the most recent chemical-shift values[15], showed the signals for C-3 and C-4 at 72.2 and 73.9 p.p.m. Acid hydrolysis of **12** produced allyl 2-*O*-benzoyl-6-*O*-benzyl-α-D-galactopyranoside (**13**), the ^{13}C-n.m.r. spectrum of which showed an upfield shift of the signals of both C-3 and C-4, to 68.7 and 70.1 p.p.m., as a result of the removal of the isopropylidene group.

Diol **13** was converted into allyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-galactopyranoside (**15**) by treatment of the 3,4-*O*-(dibutylstannylene) derivative **14** with benzyl bromide[19]. The selective benzylation at O-3 was proved from the ^{13}C-n.m.r.



1 R^1 = O-All, R^2 = R^3 = R^4 = R^5 = H
2 R^1 = O-All, R^2 = R^3 = R^5 = Bz, R^4 = H
3 R^1 = O-All, R^2 = R^3 = R^5 = Bz, R^4 = $COCH_2Cl$
4 R^1 = O-Pro, R^2 = R^3 = R^5 = Bz, R^4 = $COCH_2Cl$
5 R^1 = OH, R^2 = R^3 = R^5 = Bz, R^4 = $COCH_2Cl$
6 R^1 = Cl, R^2 = R^3 = R^5 = Bz, R^4 = $COCH_2Cl$
7 R^1 = O-Tres, R^2 = R^3 = R^5 = Bz, R^4 = $COCH_2Cl$
8 R^1 = O-Trif, R^2 = R^3 = R^5 = Bz, R^4 = $COCH_2Cl$
9 R^1 = O-Ts, R^2 = R^3 = R^5 = Bz, R^4 = $COCH_2Cl$
10 R^1 = O-All, R^2 = R^3 = R^4 = H, R^5 = Bn
11 R^1 = O-All, R^2 = H R^3, R^4 = Me_2C, R^5 = Bn
12 R^1 = O-All, R^2 = Bz, R^3, R^4 = Me_2C, R^5 = Bn
13 R^1 = O-All, R^2 = Bz, R^3 = R^4 = H, R^5 = Bn
14 R^1 = O-All, R^2 = Bz, R^3, R^4 = $(t\text{-Bu})_2Sn$, R^5 = Bn
15 R^1 = O-All, R^2 = Bz, R^3 = R^5 = Bn, R^4 = H
16 R^1 = O-All, R^2 = Bz, R^3 = R^5 = Bn, R^4 = $COCH_2Cl$
17 R^1 = OH, R^2 = Bz, R^3 = R^5 = Bn, R^4 = $COCH_2Cl$
18 R^1 = Cl, R^2 = Bz, R^3 = R^5 = Bn, R^4 = $COCH_2Cl$
19 R^1 = O-Tres, R^2 = Bz, R^3 = R^5 = Bn, R^4 = $COCH_2Cl$
20 R^1 = O-All, R^2 = Bz, R^3 = R^5 = Bn, R^4 = Ac
21 R^1 = OH, R^2 = Bz, R^3 = R^5 = Bn, R^4 = Ac
22 R^1 = Cl, R^2 = Bz, R^3 = R^5 = Bn, R^4 = Ac
23 R^1 = O-Tres, R^2 = Bz, R^3 = R^5 = Bn, R^4 = Ac
24 R^1 = Cl, R^2 = Bz, R^3 = R^4 = R^5 = Bn
25 R^1 = O-Tres, R^2 = Bz, R^3 = R^4 = R^5 = Bn

All = $CH_2CH{=}CH$, Bz = COPh, Bn = CH_2Ph
Pro = $CH{=}CHMe$, Tres = $F_3CCH_2SO_2$, Trif = F_3CSO_2, Ts = p-$H_3CC_6H_4SO_2$

spectrum of **15**, which showed a large downfield shift of the signal of C-3 (6.9 p.p.m.) and a smaller, upfield shift for C-2 and C-4 of −1.2 and −1.1 p.p.m., respectively; see Table I.

(Chloroacetyl)ation of **15** produced the 4-(chloroacetate) **16**. Rearrangement of **16** to the corresponding propenyl glycoside, followed by hydrolysis, gave 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-(chloroacetyl)-D-galactopyranose (**17**), and treatment of **17** with thionyl chloride produced 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-(chloroacetyl)-α-D-galactopyranosyl chloride (**18**) in 58% yield. A higher yield of **18** (70%) was obtained when **17** was treated with (chloromethylene)dimethylimminium chloride[11]. In the ^{1}H-n.m.r. spectrum of **18**, the anomeric-proton signal appeared at δ 6.45 as a doublet ($J_{1,2}$ 3.5 Hz); the ^{13}C-n.m.r. spectrum showed a signal for C-1,α at 92.5 p.p.m., and only a trace of one for C-1,β, at 97.0 p.p.m.

The D-galactopyranosyl chloride derivative **18** was converted into the corresponding 1-*O*-tresyl-D-galactopyranose **19** by treatment with silver tresylate in dry acetonitrile under diminished pressure. Compound **19** was not isolated, but was directly filtered onto 1.2 equiv. of the 4-hydroxy derivative **15**. After 48 h, the reaction was stopped, and the products were separated by ~12-MPa liquid chromatography (l.c.). Allyl 2-*O*-benzoyl-4-*O*-[2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-(chloroacetyl)-β-D-galactopyranosyl]-3,6-di-*O*-benzyl-α-D-galactopyranoside (**26**) was isolated as a clear syrup in 41% yield. The structure of disaccharide derivative **26** was

TABLE II

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

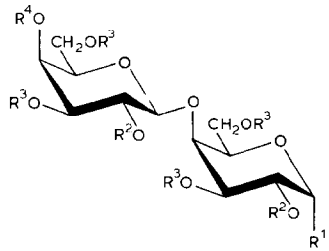
Carbon atom	*Compound*			
	26	**27**	**28**	**30**[c]
C-1	95.8	95.8	95.7	98.4
C-2	69.7	69.8	69.8	68.8
C-3	73.6	73.6	73.5	68.8
C-4	76.7	76.8	76.8	78.5
C-5	69.7	69.8	69.9	70.2
C-6	68.6	68.6	68.5[d]	61.1
C-1′	101.6	101.7	101.7	104.6
C-2′	71.8[d]	72.4	72.5	73.0
C-3′	74.1	74.0	74.7	75.3
C-4′	67.7	66.6	80.4	70.2
C-5′	71.6[d]	73.1	73.0	75.3
C-6′	68.6	68.2	68.9[d]	60.9
C=O	167.2	170.7	165.9	
	165.4	165.4	165.3	
		166.0		
CH=	134.2	132.4	134.2	
CH_2=	117.3	117.3	117.2	
CH_2Cl	40.9			
$COCH_3$		20.9		
Others				22.1(CH_2) 9.9(CH_3)

[a]These assignments are tentative, based on analogies. [b]Benzyl and allyl CH_2 carbon atoms were partially identified, and the total number of carbon atoms was accounted for. [c]Spectrum of a solution in D_2O, with Me_4Si as an external reference. [d]Assignments not unequivocal.

determined by ^{13}C-n.m.r. spectroscopy, which showed two anomeric peaks, at 95.8 (C-1,α) and 101.6 p.p.m. (C-1′,β), and a large downfield shift (7.7 p.p.m.) for C-4 (see Table II). A side product, identified from its ^{1}H- and ^{13}C-n.m.r. spectra as an α-D-galactopyranosyl α-D-galactopyranoside derivative (α,α-trehalose type), was also isolated.

The disaccharide **26** decomposed before *O*-de(chloroacetyl)ation[16] with thiourea was complete. Difficulty in removing the chloroacetyl group from O-4 of D-galactose had been reported in other studies[19]. Base decomposition of **26** and related β-D-galactopyranosides was also observed in this laboratory[10,11,20].

Acetylation of **15** gave the 4-*O*-acetyl derivative **20**. Rearrangement of the allyl group of **20**, followed by hydrolysis with $ZnCl_2$–ZnO in aqueous acetone, afforded the 1-hydroxy derivative **21** as a mixture of the α and β anomers in the ratio of 4:1 based on the relative integrations of the anomeric protons. Treatment of **21** with HCl–ether produced crystalline 4-*O*-acetyl-2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-galactopyranosyl chloride (**22**) in 89% yield. The ^{1}H-n.m.r. spectrum of **22** showed a signal for a single, α-anomeric peak, at δ 6.46, as a doublet, $J_{1,2}$ 3.9 Hz. Formation of the α anomer, only, was confirmed by the appearance of the signal for a single, anomeric peak, at 92.7 p.p.m., in the ^{13}C-n.m.r. spectrum.



26 R^1 = O-All, R^2 = Bz, R^3 = Bn, R^4 = $COCH_2Cl$
27 R^1 = O-All, R^2 = Bz, R^3 = Bn, R^4 = Ac
28 R^1 = O-All, R^2 = Bz, R^3 = R^4 = Bn
29 R^1 = O-All, R^2 = R^4 = H, R^3 = Bn
30 R^1 = O-Pr, R^2 = R^3 = R^4 = H

Chloride **22** was treated with silver tresylate, to form the 1-*O*-tresyl derivative **23**, which was then coupled to **15**, giving 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 (**27**) as a solidified foam in 62% yield. The structure of **27** was determined from its ^{1}H-n.m.r. spectrum, which showed the presence of both the allyl and the acetyl groups; also, from its ^{13}C-n.m.r. spectrum, in which two anomeric peaks appeared, at 95.8 (C-1,α) and 101.7 p.p.m. (C-1′,β), and a downfield shift of the C-4 resonance (7.8 p.p.m.) was observed (see Tables I and II).

Allyl 2-*O*-benzoyl-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-3,6-di-*O*-benzyl-α-D-galactopyranoside (**28**) was obtained in 65% yield from the reaction of 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride[21] (**24**) with silver tresylate, and of the product with D-galactoside **15**. Formation of **28** was proved by its ^{13}C-n.m.r. spectrum, which showed an α-anomeric peak at 95.7 p.p.m., a β-anomeric peak at 101.7 p.p.m., and a downfield shift (7.8 p.p.m.) of the C-4 signal, in addition to two carbonyl peaks, at 165.9 and 165.3 p.p.m.

Disaccharides **26** and **27** were de-esterified with 2% KCN in 95% ethanol, to give allyl 3,6-di-*O*-benzyl-4-*O*-(3,6-di-*O*-benzyl-β-D-galactopyranosyl)-α-D-galactopyranoside[20] (**29**). Reduction of **29** with H_2–Pd produced propyl 4-*O*-β-D-galactopyranosyl-α-D-galactopyranoside (**30**). Both ^{1}H- and ^{13}C-n.m.r. spectroscopy of **30** showed no signals for the benzyl groups; signals for C-1,α and C-1′,β appeared at 98.4 and 104.6 p.p.m. Chemical shifts of all carbon atoms were comparable to those of methyl α- and β-D-galactopyranoside, except for that of C-4, which showed a large downfield shift (8.3 p.p.m.), and those of C-3 and C-5, which showed a smaller, upfield shift (see Table II).

From the foregoing results, we conclude that it is important to minimize the number of ester groups on the D-galactosyl derivative for a successful coupling at O-4 of D-galactose, and that the yield from the coupling is affected by the type of substituent on O-4 of the D-galactosyl derivative. Benzyl and acetyl groups are preferable to the chloroacetyl group.

EXPERIMENTAL

Instrumental and chromatographic procedures, as well as preparation of materials, were the same as described previously[11]. L.c. was performed at 10.3–13.8 MPa.

Allyl α-D-galactopyranoside (**1**). — Dowex-50 X-8 (10 g) was heated under reflux in allyl alcohol (100 mL) for 30 min, filtered off, and washed with fresh allyl alcohol. A mixture of the treated resin, freshly distilled anhydrous allyl alcohol (200 mL), and anhydrous D-galactose (18 g) was boiled under reflux for 90 min, filtered while hot, in a warm system, and the filtrate allowed to cool to room temperature. Allyl α-D-galactopyranoside (10 g) crystallized from the filtrate as it cooled; it was collected, and the filtrate was diluted with allyl alcohol (50 mL), combined with the resin, and heated for 90 min. After filtration, another crop (3.9 g) of **1** was collected from the filtrate. The total yield was 13.9 g (62.6%); m.p. 145–146°, $[\alpha]_D^{24}$ +179.5° (*c* 1.6, water); lit.[13] yield 41%, m.p. 143–145°, $[\alpha]_D^{25}$ +181.3° (in H_2O); ^{1}H-n.m.r. (Me_2SO-d_6): δ 5.14–5.44 (m, 2 H, CH_2=), and 5.66–6.22 (m, 1 H, CH=).

*Allyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside* (**2**). — This compound was prepared from **1** by conventional benzoylation, using benzoyl chloride (3.2 equiv.) in pyridine. The product crystallized from chloroform as white crystals, yield 86%; m.p. 117–118°, $[\alpha]_D^{24}$ +146° (*c* 1.3, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.82–7.9 (m, 6 H, 3 COC_6H_5, *o*), 7.7–7.2 (m, 9 H, COC_6H_5, *m, p*), 6.2–5.7 (m, 2 H, CH=, H-2), 5.5–5.0 (m, 3 H, H-3, CH=), 4.8–4.65 (d, 1 H, $J_{1,2}$ 6 Hz, H-1), 4.65–4.40 (m, 4 H, H-4,5, 2 H-6), and 4.40–4.0 (m, 2 H, CH_2CH=).

Anal. Calc. for $C_{30}H_{28}O_9 \cdot 0.5\ H_2O$: C, 66.56; H, 5.35. Found: C, 66.60; H, 5.20.

*Allyl 2,3,6-tri-*O*-benzyl-4-*O*-(chloroacetyl)-α-D-galactopyranoside* (**3**). — (Chloroacetyl)ation of **2** by the method described by Bertolini and Glaudemans[16] produced **3** in 94.4% yield as a yellow syrup that showed a single spot in t.l.c. For analysis and n.m.r. spectroscopy, the product was purified by passage through a column of silica gel by l.c. with 1:4 ethyl acetate–hexane; ^{1}H-n.m.r. ($CDCl_3$): δ 8.3–7.95 (m, 6 H, 3 COC_6H_5, *o*), 7.8–7.2 (m, 9 H, 3 COC_6H_5, *m, p*), 6.3–5.65 (m, 3 H, CH=, H-2,4), 5.65-5.40 (d, 1 H, $J_{2,3}$ 6 Hz, H-3), 5.40–5.05 (m, 2 H, CH_2=), 4.9–4.4 (m, 4 H, H-1,5, and 2 H-6), and 4.3–4.1 (m, 4 H, CH_2CH= and CH_2Cl).

Anal. Calc. for $C_{32}H_{29}ClO_{10}$: C, 63.11; H, 4.80; Cl, 5.82. Found: C, 63.36; H, 4.69; Cl, 5.55.

*2,3,6-Tri-*O*-benzoyl-4-*O*-(chloroacetyl)-D-galactopyranose* (**5**). — A mixture of **3** (2.3 g), 95% ethanol (40 mL), and tris(triphenylphosphine)rhodium(I) chloride (0.3 g) was boiled under reflux for 2 h, cooled, and evaporated to dryness, giving a brown syrup. The ^{1}H-n.m.r. spectrum of the crude product showed the CH_3 of the propenyl group at δ 1.58 as a doublet of doublets equivalent to 3 protons, indicating full rearrangement of **3** to the corresponding propenyl D-galactoside **4**. Compound **4** was hydrolyzed by heating under reflux with M HCl in 95%

ethanol[17] for 30 min to give **5** as a dark-yellow syrup. Separation on silica gel by l.c. with 1:10 ethyl ether–toluene produced **5** as a white solid (1.5 g, 70%); m.p. 71°; ^{1}H-n.m.r. ($CDCl_3$): δ 8.25–7.8 (m, 6 H, COC_6H_5, *o*), 7.7–7.1 (m, 9 H, COC_6H_5, *m, p*), 6.25–5.5 (m, 3 H, H-2,3,4), 4.2 (d, 1 H, $J_{1,2}$ 8 Hz, H-1,α), and 4.6–4.0 (m, 5 H, 2 H-6, and CH_2Cl).

Anal. Calc. for $C_{29}H_{25}ClO_{10}$: C, 61.24; H, 4.40. Found: C, 61.32; H, 4.65.

*2,3,6-Tri-*O*-benzoyl-4-*O*-(chloroacetyl)-α-*D*-galactopyranosyl chloride* (**6**). — A mixture of **5** (0.5 g), thionyl chloride (1.5 mL), and chloroform (30 mL) was heated under reflux for 5 h, cooled, washed with cold water, dried (magnesium sulfate), and evaporated to dryness. After chromatographic separation by l.c. on silica gel with 1:1 ethyl acetate–hexane, **6** (0.39 g; 76%) was obtained as a solid; m.p. 53–55°, $[\alpha]_D^{24}$ +50.2° (*c* 0.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.15–7.80 (m, 6 H 3 COC_6H_5, *o*), 7.6–7.1 (m, 9 H, 3 COC_6H_5, *m, p*), 6.58 (d, 1 H, $J_{1,2}$ 4 Hz, H-1,α), 6.05–5.6 (m, 3 H, H-2,3,4), 5.1–4.4 (m, 3 H, H-5 and 2 H-6), and 4.14 (s, 2 H, CH_2Cl).

Anal. Calc. for $C_{29}H_{24}Cl_2O_9$: C, 59.32; H, 4.09. Found: C, 59.54; H, 4.07.

*Allyl 2-*O*-benzoyl-6-*O*-benzyl-3,4-*O*-isopropylidene-α-*D*-galactopyranoside* (**12**). — Allyl 6-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranoside[22] (**11**) was benzoylated conventionally. Separation on silica gel by l.c. with 1:2 ethyl acetate–hexane gave **12** as a clear, colorless syrup in 93% yield; $[\alpha]_D^{24}$ +110° (*c* 3.2, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.23–8.0 (m, 3 H, COC_6H_5, *o, p*), 7.65–7.25 (m, 7 H, COC_6H_5, *m,* and $CH_2C_6H_5$), 6.19–5.62 (m, 1 H, CH=), 5.5–5.03 (m, 4 H, CH_2=, H-1,2), 4.67 (s, 2 H, $CH_2C_6H_5$), 4.54–4.05 (m, 5 H, CH_2CH=, H-3,4,5), 4.0–3.74 (m, 2 H, 2 H-6), 1.55 (s, 3 H, CH_3), and 1.38 (s, 3 H, CH_3).

Anal. Calc. for $C_{26}H_{30}O_7$: C, 68.70; H, 6.65. Found: C, 68.94; H, 6.70.

*Allyl 2-*O*-benzoyl-6-*O*-benzyl-α-*D*-galactopyranoside* (**13**). — Hydrolysis of **12** with 0.5M HCl in methanol[18] gave a quantitative yield of **13**, which crystallized from ethyl acetate–hexane; m.p. 88°, $[\alpha]_D^{24}$ +113° (*c* 2.1, chloroform); lit.[19] m.p. 91–92°, $[\alpha]_D^{25}$ +116°; ^{1}H-n.m.r. ($CDCl_3$): δ 8.2–8.0 (m, 3 H, COC_6H_5, *o, p*), 7.67–7.20 (m, 7 H, COC_6H_5, *m,* and $CH_2C_6H_5$), 6.25–5.60 (m, 1 H, CH=), 5.5–5.0 (m, 4 H, H-1,2, and CH_2=), 4.62 (s, 2 H, $CH_2C_6H_5$), 4.5–4.0 (m, 5 H, H-3,4,5 and CH_2CH=), and 3.1 (d, 2 H, 2 OH).

Anal. Calc. for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.67; H, 6.41.

*Allyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-α-*D*-galactopyranoside* (**15**). — A suspension of **13** (3 g) and dibutyltin oxide (1.8 g) in methanol (150 mL) was boiled under reflux for 1.5 h, cooled, and evaporated; the 3,4-di-*O*-(dibutylstannylene) derivative **14** was obtained as a colorless syrup which was freed of traces of water by dissolving in *N,N*-dimethylformamide (DMF), and evaporating to dryness under vacuum.

A solution of compound **14** in DMF (30 mL) was treated with benzyl bromide (2.7 mL), heated on a steam bath for 2 h, cooled, and evaporated under vacuum, and the products were isolated on silica gel by l.c. with 1:3 ethyl acetate–hexane. Three compounds were isolated; the fastest-moving was a non-carbohydrate di-

butyltin derivative, the second was dibenzyl ether, and the slowest was the desired derivative **15**, contaminated with some dibenzyl ether; therefore, two more fractionations, using 1:4 ethyl acetate–hexane, were required. The yield was 3 g (83%); R_F 0.37 (1:1 ethyl acetate–hexane); $[\alpha]_D^{24}$ +117.2° (*c* 2.4, chloroform) (lit.[19] $[\alpha]_D^{25}$ +118°); ^{1}H-n.m.r. (360 MHz; $CDCl_3$): δ 8.05 (d, 2 H, COC_6H_5, $J_{o,m}$ 8.9 Hz, *o*), 7.57 (t, 1 H, COC_6H_5, $J_{m,p}$ 8.5, *p*), 7.44 (t, 2 H, COC_6H_5, *m*), 7.3 (m, 10 H, 2 $CH_2C_6H_5$), 5.82 (m, 1 H, CH=), 5.44 (dd, 1 H, $J_{2,3}$ 9.7, $J_{1,2}$ 4.8 Hz, H-2), 5.26 (m, 2 H, CH=), 5.1 (d, 1 H, H-1,α), 4.82–4.64 (m, 4 H, 2 $CH_2C_6H_5$), 4.18 (m, 2 H, CH_2CH=), 4.07 (m, 2 H, H-5,4), 4.0 (dd, 1 H, $J_{2,3}$ 10.9, $J_{3,4}$ 6.2 Hz, H-3), 3.75 (m, 2 H, 2 H-6), and 2.69 (s, 1 H, OH, exchangeable in D_2O).

Anal. Calc. for $C_{30}H_{32}O_7$: C, 71.40; H, 6.39. Found: C, 70.95; H, 6.72.

Allyl 2-O-benzoyl-3,6-di-O-benzyl-4-O-(chloroacetyl)-α-D-galactopyranoside (**16**). — Compound **15** was (chloroacetyl)ated by the procedure used for **3**, to give **16** as a colorless syrup in 78% yield after l.c. with 1:3 ethyl acetate–hexane; $[\alpha]_D^{24}$ +80° (*c* 1.7, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.06 (m, 2 H, COC_6H_5, *o*), 7.5 (m, 3 H, COC_6H_5, *m, p*), 7.3 (s, 5 H, $CH_2C_6H_5$), 7.23 (s, 5 H, $CH_2C_6H_5$), 6.2–5.9 (m, 1 H, CH=), 5.82 (dd, 1 H, H-4), 5.52 (dd, 1 H, $J_{2,3}$ 9, $J_{1,2}$ 4.5 Hz, H-2), 5.38–5.13 (m, 2 H, CH_2=), 5.05 (1 H, H-1), 4.73–4.5 (m, 4 H, 2 $CH_2C_6H_5$), 4.44–4.0 (m, 6 H, CH_2CH=, CH_2Cl, H-3,5), and 3.58 (d, 2 H, H-6).

Anal. Calc. for $C_{32}H_{33}ClO_8$: C, 66.14; H, 5.68; Cl. 6.1. Found: C, 65.86; H, 5.57; Cl. 6.8.

2-O-Benzoyl-3,6-di-O-benzyl-4-O-(chloroacetyl)-D-galactopyranose (**17**). — Rearrangement of **16** was conducted as for **5**. ^{1}H-N.m.r. spectroscopy of the crude product showed two doublets of doublets at δ 1.7 and 1.5, equivalent to 3 protons, indicating complete rearrangement to a *cis-trans* mixture of the corresponding propenyl D-galactoside. The product was hydrolyzed with 0.5M HCl in methanol, to give, in 78% yield, compound **17** as a colorless syrup that crystallized from diethyl ether at 0°; m.p. 148–150°, $[\alpha]_D^{24}$ +177° (*c* 0.8, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.0 (m, 2 H, COC_6H_5, *o*), 7.42 (m, 3 H, COC_6H_5, *m, p*), 7.3 (s, 5 H, $CH_2C_6H_5$), 7.2 (s, 5 H, $CH_2C_6H_5$), 5.72 (d, 1 H, $J_{3,4}$ 4 Hz, H-4), 5.58 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.32 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 4 Hz, H-3), 4.05 (s, 2 H, CH_2Cl), and 3.9–3.3 (m, 3 H, H-5, 2 H-6).

Anal. Calc. for $C_{29}H_{29}ClO_8$: C, 64.41; H, 5.36; Cl, 6.56. Found: C, 64.08; H, 5.44; Cl, 6.31.

2-O-Benzoyl-3,6-di-O-benzyl-4-O-(chloroacetyl)-α-D-galactopyranosyl chloride (**18**). — A solution of **17** (5 g) and (chloromethylene)dimethylimminium chloride[23] (3 g) in DMF (50 mL) was heated for 30 min at 60°, cooled, and evaporated under vacuum, to give a yellow syrup which was dissolved in chloroform, and the solution washed with sodium hydrogencarbonate solution, dried (anhydrous magnesium sulfate), and evaporated, and the product isolated by l.c. on silica gel with 1:3 ethyl acetate–hexane; yield 3.64 g (70.3%); $[\alpha]_D^{24}$ +182° (*c* 1.1, chloroform):^{1}H-n.m.r. ($CDCl_3$): δ 8.0 (m, 2 H, COC_6H_5, *o*), 7.68–7.39 (m, 3 H, COC_6H_5, *m, p*), 7.30 (s, 5 H, $CH_2C_6H_5$),), 6.45 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1,α), 5.84

(dd, 1 H, $J_{2,3}$ 10, $J_{2,1}$ 4 Hz, H-2), 4.75–4.45 (m, 4 H, 2 $CH_2C_6H_5$), 4.33 (dd, 1 H, $J_{3,2}$ 10, $J_{3,4}$ 3.5 Hz, H-3), 4.15-4.03 (m, 1 H, H-5), 4.07 (s, 2 H, CH_2Cl), and 3.6 (d, 2 H, 2 H-6).

Anal. Calc. for $C_{29}H_{28}Cl_2O_7$: C, 62.27; H, 5.00. Found: C, 62.60; H, 5.43.

Allyl 2-O-benzoyl-4-O-[2-O-benzoyl-3,6-di-O-benzyl-4-O-(chloroacetyl)-β-D-galactopyranosyl]-3,6-di-O-benzyl-α-D-galactopyranoside (**26**). — The reaction was conducted in an apparatus consisting of a vertical, glass tube having a glass joint and stopcock at the top and three branches at the bottom. Each branch ended with a glass joint, and one branch was separated from the other two by a glass filter. Chloride **18** (600 mg, 1.07 mmol), D-galactoside **15** (650 mg, 1.28 mmol), and silver tresylate (407 mg, 1.6 mmol) were each placed, separately, in a 25-mL, round-bottomed flask containing a small magnet. The flasks were connected to the three branches, and the other end was connected to a vacuum line. After 12 h, dry acetonitrile (5 mL) was distilled under vacuum into the flasks (to dissolve the reactants), the stopcock was closed, and the apparatus was disconnected from the vacuum line. The solution of silver tresylate was mixed with the solution of the chloride, with stirring, and kept in the dark at room temperature until precipitation of silver chloride was complete (30 min). The resulting 1-*O*-tresyl derivative **19** was filtered onto the **15**, stirred, and the solution kept for 48 h in the dark at room temperature, diluted with dichloromethane, washed with sodium hydrogencarbonate–sodium thiosulfate solution, dried (anhydrous magnesium sulfate), and evaporated; the products were isolated by l.c. on silica gel with 1:4 ethyl acetate–hexane.

The fastest-moving compound was allyl 2-*O*-benzoyl-4-*O*-[2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-(chloroacetyl)-α-D-galactopyranosyl]-3,6-di-*O*-benzyl-4-*O*-(chloroacetyl)-α-D-galactopyranoside; ^{1}H-n.m.r. ($CDCl_3$): δ 8.14–7.77 (m, 4 H, 2 COC_6H_5, *o*), 7.62–7.0 (m, 26 H, 4 $CH_2C_6H_5$, and 2 COC_6H_5, *m*, *p*), 5.85–4.95 (m, 6 H, 2 H-2, 2 H-4, and 2 H-1), 4.83–4.40 (m, 8 H, 4 $CH_2C_6H_5$), 4.32–3.90 (m, 6 H, 2 H-3, 2 H-5, and CH_2Cl), and 3.91–3.40 (m, 4 H, 4 H-6). The slowest-moving compound was unreacted D-galactoside **15**.

The second compound was the desired disaccharide **26**; 452 mg (41%); $[\alpha]_D^{24}$ +72° (*c* 2.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.15–7.77 (m, 4 H, 2 COC_6H_5, *o*), 7.61–7.05 (m, 26 H, 4 $CH_2C_6H_5$ and 2 COC_6H_5, *m*, *p*), 6.10–5.45 (m, 2 H, H-4 and CH=), 5.42–5.22 (m, 4 H, H-2,2′), 5.22–4.65 (m, 4 H, CH_2=, H-1,1′), 4.65–4.45 (m, 8 H, 4 $CH_2C_6H_5$), 4.25 (dd, 1 H, $J_{3,4}$ 2, $J_{4,5}$ 1 Hz, H-4), 4.16–3.87 (m, 6 H, CH_2Cl, CH_2CH=, H-3,3′), and 3.82–3.35 (m, 8 H, 2 H-6, 2 H-6′, H-5,5′).

Anal. Calc. for $C_{59}H_{59}ClO_{14}$: C, 68.93; H, 5.74. Found: C, 69.39; H, 5.90.

Allyl 4-O-acetyl-2-O-benzoyl-3,6-di-O-benzyl-α-D-galactopyranoside (**20**). — Acetylation of **15** with Ac_2O–C_5H_5N gave **20**, in 96% yield, as a colorless syrup pure enough to be used in the next step; $[\alpha]_D^{24}$ +172° (*c* 1.8, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.1 (m, COC_6H_5, *o*), 7.62–7.15 (m, 13 H, 2 $CH_2C_6H_5$ and COC_6H_5, *m*, *p*), 6.2–5.6 (m, 2 H, CH= and H-4), 5.45 (dd, 1 H, $J_{2,3}$ 8, $J_{2,1}$ 4 Hz, H-2), 5.32–4.70 (m, 3 H, CH_2= and H-1), 4.7–4.4 (m, 4 H, 2 $CH_2C_6H_5$), 4.4–3.9 (m, 4 H, CH_2CH=, H-3,5), 3.5 (d, 2 H, 2 H-6), and 2.08 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{32}H_{34}O_8$: C, 70.31; H, 6.27. Found: C, 69.85; H, 6.28.

4-O-Acetyl-2-O-benzoyl-3,6-di-O-benzyl-D-galactopyranose (**21**). — Rearrangement of **20** (2 g) to the corresponding propenyl D-galactoside was conducted as described for **5**. The allyl D-galactoside derivative was dissolved in 10:1 acetone–water containing mercuric oxide (2 g), and mercuric chloride (2 g) in 10:1 acetone–water was added dropwise during 15 min. After 8 h, the solution was evaporated, the residue dissolved in dichloromethane, and the solution successively washed with KI solution and water, dried (anhydrous magnesium sulfate), and evaporated, to yield 1.4 g (83%) of **21** as a syrup. Compound **21** was purified by l.c. on silica gel with 1:3 ethyl acetate–hexane; $[\alpha]_D^{24}$ +126° (*c* 2.3, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.0 (m, 2 H, COC_6H_5, *o*), 7.6–6.95 (m, 13 H, 2 $CH_2C_6H_5$ and COC_6H_5, *m, p*), 5.68 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 5.5–5.05 (m, 1.8 H, H-2 and 0.8 H-1,α), 4.85–4.39 (d, 4 H, 2 $CH_2C_6H_5$), 4.39–3.4 (m, 5.2 H, H-3,5,6, 0.2 H-1,β, and OH), and 2.08 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{29}H_{30}O_8$: C, 68.76; H, 5.97. Found: C, 69.12; H, 6.13.

4-O-Acetyl-2-O-benzoyl-3,6-di-O-benzyl-α-D-galactopyranosyl chloride (**22**). — A solution of **21** (0.5 g) in diethyl ether (100 mL) was saturated with HCl and kept in a tightly closed flask at room temperature. After 24 h, t.l.c. showed a single spot, and no trace of the starting material. The solution was evaporated, and the product was isolated by l.c. on silica gel with 1:4 ethyl acetate–hexane. Crystallization from ethyl acetate–hexane gave **22** as white crystals; 0.45 g (89%); m.p. 95°, $[\alpha]_D^{24}$ +156° (*c* 1.3, chloroform); ^{1}H-n.m.r. (360 MHz; $CDCl_3$): δ 8.80 (d, 2 H, $J_{o,m}$ 7.3 Hz, COC_6H_5, *o*), 7.59 (t, 1 H, $J_{m,p}$ 7.2 Hz, COC_6H_5, *p*), 7.45 (t, 2 H, $J_{o,m}$ = $J_{p,m}$ = 8.2 Hz, COC_6H_5, *m*), 7.38–7.11 (m, 10 H, 2 $CH_2C_6H_5$), 6.46 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1,α), 5.76 (d, 1 H, $J_{3,4}$ 2.4 Hz, H-4), 5.45 (dd, 1 H, $J_{1,2}$ 3.95, $J_{2,3}$ 10.28 Hz, H-2), 4.75–4.41 (m, 5 H, 2 $CH_2C_6H_5$, H-5), 4.13 (dd, 1 H, $J_{3,4}$ 2.9, $J_{2,3}$ 10.24 Hz, H-3), 3.61–3.35 (m, 2 H, 2 H-6), and 2.09 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{29}H_{29}ClO_7$: C, 66.34; H, 5.57; Cl, 6.75. Found: C, 66.06; H, 5.58; Cl, 6.86.

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 (**27**). — Compound **22** (0.2 g) was treated with silver tresylate (0.146 g), and then with **15** (0.23 g), as described for **26**, to produce disaccharide **27** as a solid foam (0.235 g, 62%); $[\alpha]_D^{24}$ +72° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.16–7.73 (m, 4 H, 2 COC_6H_5, *o*), 7.65–6.9 (m, 26 H, 4 $CH_2C_6H_5$ and 2 COC_6H_5, *m, p*), 5.94–5.5 (m, 2 H, H-4 and CH=), 5.35 (dd, 1 H, $J_{2',1'}$ 9, $J_{2',3'}$ 10 Hz, H-2'), 5.14 (dd, 1 H, $J_{2,1}$ 3, $J_{2,3}$ 10 Hz, H-2), 5.10–4.82 (m, 3 H, CH_2= and H-1), 4.75–4.38 (m, 8 H, 4 $CH_2C_6H_5$), 4.38–4.10 (m, 4 H, CH_2CH=, H-3,3'), and 3.83–3.35 (m, 6 H, H-5,5', 2 H-6, and 2 H-6').

Anal. Calc. for $C_{59}H_{60}O_{14}$: C, 71.35; H, 6.09. Found: C, 70.98; H, 5.85.

Allyl 2-O-benzoyl-4-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-3,6-di-O-benzyl-α-D-galactopyranoside (**28**). — The glycosidation was conducted as described for **26**. 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride[21] (0.1 g) was treated with silver tresylate (0.055 g), and then

15 (0.105 g) was added, to produce **28** (0.118 g, 65%); $[\alpha]_D^{24}$ +73° (*c* 1.4, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.93 (dd, 4 H, 2 COC_6H_5, *o*), 7.63–7.05 (m, 31 H, 5 $CH_2C_6H_5$ and 2 COC_6H_5, *m, p*), 5.77-5.11 (m, 1 H, CH=), 5.18–4.95 (m, 5 H, CH_2=, H-1,2,2′), 4.74–4.25 (m, 10 H, 5 $CH_2C_6H_5$), 4.13–3.96 (m, 5 H, H-1′,3,3′,4,4′), 3.91–3.76 (m, 2 H, H-5,5′), and 3.69–3.45 (m, 4 H, 2 H-6 and 2 H-6′).

Anal. Calc. for $C_{64}H_{64}O_{13}$: C, 73.83; H, 6.96. Found: C, 73.61; H, 6.82.

Propyl 4-O-β-D-galactopyranosyl-α-D-galactopyranoside (**30**). — The disaccharides **26** and **27** were de-esterified with 2% KCN in 95% ethanol, to give triol **29** in 67% yield[20]. The triol **29** (25 mg) was dissolved in 80% aqueous ethanol (5 mL), and 10% palladium-on-carbon (30 mg) was added. The mixture was stirred under a hydrogen atmosphere for 72 h. Filtration of the catalyst, followed by evaporation of the filtrate, gave a white solid (13 mg) which was dissolved in hot water, and fractionated on a column of Bio-Gel P-2. The disaccharide was collected and freeze-dried, to give **30** (11 mg, 85%); no aromatic-proton signal in the ^{1}H-n.m.r. spectrum; ^{13}C-n.m.r. data are listed in Table II. The disaccharide was very hygroscopic, and elemental analyses were not obtained.

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