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AN APPROACH TO REGIOSELECTIVE ALKYLATION OF ALKYL β-D-GALACTOPYRANOSIDES THROUGH (TRIALKYLSTANNYL)ATION*

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ABSTRACT

Regioselective preparation of methyl 3,6-di-*O*-benzyl-β-D-galactopyranoside, methyl 2,4-di-*O*-benzyl-β-D-galactopyranoside, and methyl 3,4-di-*O*-benzyl-β-D-galactopyranoside by the stannyl method is described.

INTRODUCTION

Partially benzylated D-galactopyranosides play key roles in the synthesis of such biologically important oligosaccharides as blood-group substances[2]. At present, methods available for the regioselective introduction of benzyl groups into carbohydrate molecules are as follows: (*i*) hydrogenolytic cleavage of the benzylidene group[3], (ii) selective activation of a *vic.*-diol with a stannylidene group[4], (*iii*) phase-transfer catalysis[5], and (*iv*) activation of hydroxyl groups by partial stannylation[6]. Employing methods (*i*), (*ii*), and (*iii*), several di- and tri-*O*-benzyl-D-galactopyranosides have been synthesized[7]. We now describe an approach to the partial benzylation of alkyl β-D-galactopyranosides by the stannylation method, using methyl β-D-galactopyranoside as a model compound.

RESULTS AND DISCUSSION

Partial stannylation and acylation[6] of methyl β-D-galactopyranoside (**1**) and its α anomer showed that hydroxyl groups were activated toward the electrophile in a regioselective way in the case of **1**, but not for its α anomer, and that **1** was transformed into the 3,6-dibenzoate **5** in high yield. From these observations, alkylation of partially stannylated **1** was also expected to proceed at O-3 and O-6.

(Tributylstannyl)ation of **1** with 1.5 molar equivalents of $(Bu_3Sn)_2O$, and subsequent alkylation in benzyl bromide for 3 days at 85°, afforded the 3,6-dibenzyl

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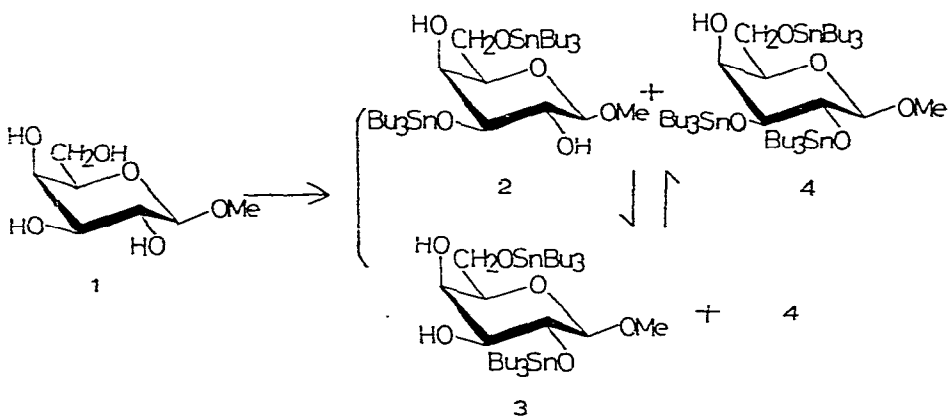
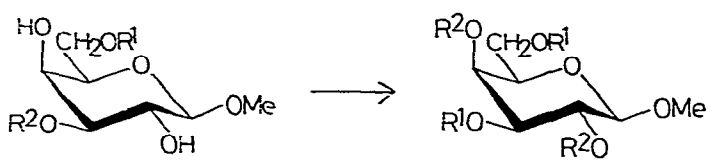
TABLE I

^{13}C CHEMICAL-SHIFTS OF PARTIALLY ALKYLATED METHYL β-D-GALACTOPYRANOSIDES IN $CDCl_3$

Structure	$^1J_{CH}$							
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Me*	OCH_2R
1 (D_2O)	103.9	70.8	72.9	68.8	75.2	61.1	57.3	
6	103.8 (159.9)	70.8	80.3	66.4	73.4	69.0	56.9	73.6 (O-6)
(3,6-Bn_2)								71.9 (O-3)
7	104.0 (158.3)	71.6	73.6	69.2	73.6	69.3	67.1	73.6 (O-6)
(6-Bn)								
11	104.6 (156.3)	79.3	74.0	74.5	74.5	61.9	56.8	74.6 (O-4)
(2,4-Bn_2)								74.6 (O-2)
15	104.3 (159.7)	71.4	82.1	74.9	72.4	62.0	57.0	74.2 (O-4)
(3,4-Bn_2)								72.7 (O-3)
8	103.7 (158.2)	70.5	80.0	66.1	73.3	68.8	56.8	72.4 (O-6)
(3,6-A_2)								70.7 (O-3)
9	103.9 (158.2)	71.0	73.5	69.0	73.5	69.0	57.0	72.3 (O-6)
(6-A)								
12	103.9 (158.3)	74.6	73.1	68.5	73.7	62.4	55.9	88.1
(2,6-Tr_2)								86.7





5 $R^1 = R^2 =$ Bz
6 $R^1 = R^2 =$ Bn
7 $R^1 =$ Bn, $R^2 =$ H
8 $R^1 = R^2 =$ allyl
9 $R^1 =$ allyl, $R^2 =$ H

10 $R^1 =$ allyl, $R^2 =$ Bn
11 $R^1 =$ H, $R^2 =$ Bn

ether **6** in 47.8% yield, together with the 6-monobenzyl ether **7** in 23.9% yield. The regiochemistry of **6** and **7** was assigned by ^{13}C-n.m.r. spectroscopy (see Table I): the spectrum of **6** contained two deshielded signals, for C-3 and C-6, at δ 80.3 and 69.0, and that of **7** contained only one deshielded signal, for C-6, at δ 69.3, in agreement with the previous observation for partially methylated β-D-galactopyranosides[8]. As no alternative approach for the regioselective introduction of two ether linkages directly at O-3 and O-6 seems to be available, this approach may be of preparative significance, despite its moderate yield. The formation of **6** as the major product may be explained in terms of the reactive intermediates of partially stannylated structures **2** or **4**, or both.

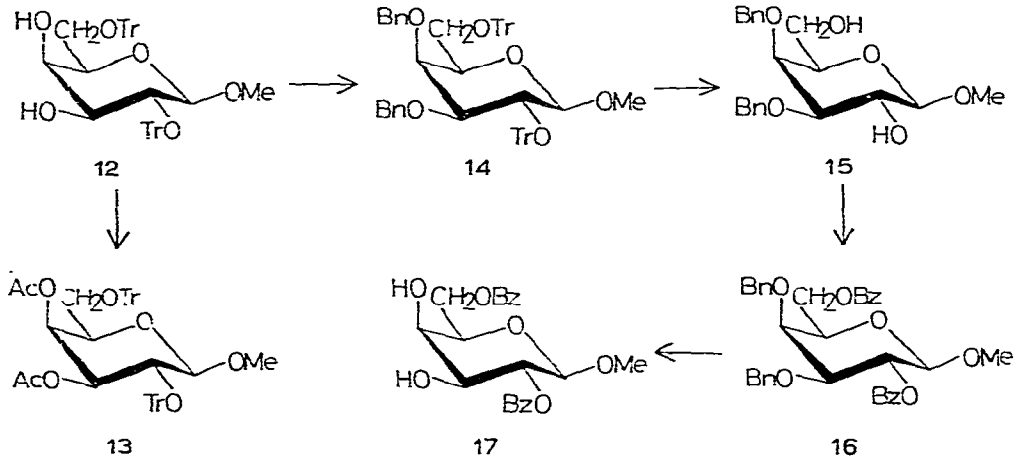
In 1973, a 2,4-dibenzyl ether derivative of a D-galactopyranoside was first prepared[9] as the intermediate for the synthesis of branching oligosaccharides of blood-group substances. From the viewpoint of the crucial importance of such 2,4-dibenzyl ether derivatives in the synthesis of oligosaccharides containing D-galactopyranosides having branching at both O-3 and O-6, the preparation of methyl 2,4-di-*O*-benzyl-β-D-galactopyranoside **11** has now been studied by the stannyl approach.

A similar stannylation–alkylation process, using allyl bromide instead of benzyl bromide, gave the expected 3,6-diallyl ether **8** and the 6-allyl ether **9** in 50.7 and 11.3% yield, respectively. These structures were again assignable by ^{13}C-n.m.r. spectroscopy. The deshielded signals for C-3 and C-6 of **8** appeared at δ 80.0 and 68.8, and that for C-6 of **9** at δ 69.0. Benzylation of **8** to the diallyl dibenzyl ether **10**, and deallylation[10] with 10% Pd–C in EtOH–AcOH–H_2O at 75°, gave a 60.0% yield of **11**, the overall yield of **11**, in 3 steps from **1**, being 30%.

These experiments, as well as a previous observation[6], demonstrated that partial stannylation of **1** leads to the formation of **2** or **4** (or both), which reacts with benzyl bromide and allyl bromide preferentially at O-6 and O-3, to afford the observed regiochemistry.

However, trityl chloride, a sterically demanding electrophile, showed different regioselectivity. Thus, treatment of partially stannylated **1** with trityl chloride for 35 h at 55–60° afforded a 71.6% yield of the crystalline 2,6-ditrityl ether **12**. The diacetate (**13**) of **12** showed, in its ^{1}H-n.m.r. spectrum, two deshielded signals, for H-3 and H-4, at δ 5.12 as a quartet with $J_{2,3}$ 9.4 and $J_{3,4}$ 3 Hz, and at δ 5.46 as a doublet with $J_{3,4}$ 3 Hz, indicating that the two trityl groups in **12** were situated at O-2 and O-6. ^{13}C-N.m.r. spectroscopy of **12** disclosed the signals for two trityl methine carbon atoms, at δ 88.1 and 86.7, but showed only a small deshielding effect for the chemical shifts of C-2 and C-6 compared with those of allyl and benzyl derivatives (see Table I). In order to confirm the structure of **12**, the following chemical transformation was performed. Benzylation of **12** gave the crystalline dibenzyl ditrityl ether **14**, which was hydrolyzed in aqueous AcOH to give the 3,4-dibenzyl ether **15**, the overall yield of **15** from **1** being 49.6% (in 3 steps). The ^{13}C-n.m.r. spectrum of **15** supported the structure assigned, as it contained two deshielded signals, for C-3 and C-4, at δ 82.1 and 74.9, respectively. It may be noted (see Table I) that the chemical shifts of the methylene carbon atoms of benzyl groups linked to O-3

were the most shielded and appeared at δ 71.9–72.7, those linked to O-6 appeared at δ 73.6, and those linked to O-2 or O-4 were the most deshielded and appeared at δ 74.2–74.6. A similar trend in the relative value of the chemical shifts was also observed for the methylene carbon atoms of allyl groups.



Finally, dibenzyl ether **15** was transformed into the crystalline dibenzoate **17** *via* benzoylation of **15** to **16**, and catalytic hydrogenolysis of **16**. The structure of **17** was clearly demonstrated by the ^{1}H-n.m.r. data, which contained a deshielded signal for C-2, at δ 5.26, as a quartet with $J_{1,2}$ 8 and $J_{2,3}$ 9.6 Hz. From these chemical transformations, the structure of the 2,6-dityrityl ether **12** was firmly established.

The different regioselectivity observed for the alkylating reagents suggested the presence of an equilibrium between such partially stannylated species as **2**, **3**, and **4** under these reaction conditions. In the case of allylation and benzylation, O–Sn linkages at C-3 and C-6 of **2** or **4** (or both) should react preferentially to give 3,6-diethers. In contrast, with (bulky) trityl chloride, O–Sn linkages at C-2 and C-6 of **3** or **4** (or both) preferentially react to give the 2,6-diether **12**.

In conclusion, successful introduction of allyl, benzyl, and trityl groups on two hydroxyl groups of methyl β-D-galactopyranoside was achieved in a regioselective way *via* the intermediacy of partially stannylated derivatives.

EXPERIMENTAL

General. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 141 polarimeter for solutions in $CHCl_3$ at 25°, unless otherwise noted. Column chromatography was performed in columns of Silica Gel Merck (70–230 mesh; E. Merck, Darmstadt, Germany). Thin-layer chromatography was conducted on precoated plates (layer thickness, 0.25 mm; E. Merck, Darmstadt,

Germany) of Silica Gel 60 F_{254}. I.r. spectra were recorded with an EPI-G2 Hitachi spectrophotometer, as KBr discs for the crystalline samples, and as neat films for the liquid samples. ^{1}H-N.m.r. spectra were recorded with a Varian HA-100 n.m.r. spectrometer, using tetramethylsilane as the internal standard. ^{13}C-N.m.r. spectra were recorded with a JNM-FX 100FT n.m.r. spectrometer operated at 25.05 MHz. The values of δ_C and δ_H are expressed in p.p.m. downwards from the internal standard for the solutions in $CDCl_3$, unless otherwise noted.

Methyl 3,6-di-O-benzyl-β-D-galactopyranoside (**6**) *and methyl 6-O-benzyl-β-D-galactopyranoside* (**7**). — Methyl β-D-galactopyranoside (**1**; 485 mg, 2.5 mmol) was stannylated with $(Bu_3Sn)_2O$ (2.25 g, 3.75 mmol) in toluene (20 mL) for 3.5 h at 130°. The toluene was evaporated *in vacuo*, and a solution of the residue in benzyl bromide (15 mL) was stirred for 3 days at 85° under argon, evaporated *in vacuo*, and the residue chromatographed on SiO_2 (100 g) with 1:3 toluene–EtOAc, to afford **6** (447 mg, 47.8%); $[\alpha]_D$ −1.9° (*c* 1.575); R_F 0.47 in 1:3 toluene–EtOAc; δ_H: 7.4–7.1 (m, 10 H, 2 benzyl), 4.71 (s, 2 H, C*H*$_2$Ph), 4.57 (s, 2 H, C*H*$_2$Ph), 4.16 (d, 1 H, *J* 8 Hz, H-1), and 3.52 (s, 3 H, OMe).

Anal. Calc. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.12; H, 7.12.

Further elution, with 10:1 $CHCl_3$–MeOH, afforded **7** (170 mg, 23.9%); m.p. 85–90° (EtOAc–i-Pr$_2$O), $[\alpha]_D$ −26.1° (*c* 0.46); R_F 0.06 in 3:1 EtOAc–toluene; δ_H: 7.28 (s, 5 H, benzyl), 4.54 (s, 2 H, C*H*$_2$Ph), 4.13 (d, 1 H, *J* 6 Hz, H-1), and 3.50 (s, 3 H, OMe).

Anal. Calc. for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 58.72; H, 6.96.

Methyl 3,6-di-O-allyl-β-D-galactopyranoside (**8**) *and methyl 6-O-allyl-β-D-galactopyranoside* (**9**). — Compound **1** (3.84 g, 20 mmol) was stannylated with $(Bu_3Sn)_2O$ (18 g, 30 mmol) in toluene (100 mL). The clear solution was evaporated *in vacuo*, and a solution of the residue in allyl bromide (50 mL) was stirred for 8 days at 80° under argon, evaporated *in vacuo*, and the residue chromatographed on SiO_2 (200 g) with 1:1 toluene–EtOAc, to give **8** (2.748 g, 50.7%); $[\alpha]_D$ +1.3° (*c* 0.60); R_F 0.25 in 1:3 toluene–EtOAc; δ_H: 6.1–5.6 (m, 2 H, 2 CH_2-*CH*=CH_2), 5.5–5.1 (m, 4 H, CH_2-CH=*C*H_2), and 3.54 (s, 3 H, OMe).

Anal. Calc. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 56.47; H, 7.93.

Further elution, with 10:1 $CHCl_3$–MeOH, afforded **9** (525 mg, 11.3%); $[\alpha]_D$ −23.0° (*c* 0.895), R_F 0.30 in 10:1 $CHCl_3$–MeOH; δ_H: 6.1–5.7 (m, 1 H, CH_2-C*H*=CH_2), 5.4–5.1 (m, 2 H, CH_2-CH=C*H*$_2$), and 3.52 (s, 3 H, OMe).

Anal. Calc. for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 50.72; H, 7.63.

Methyl 3,6-di-O-allyl-2,4-di-O-benzyl-β-D-galactopyranoside (**10**). — To a solution of **8** (2.748 g, 10 mmol) in $HCONMe_2$ (20 mL) was added NaH (50%, 1.2 g, 25 mmol) portionwise, and the mixture was stirred for 30 min at 15–20°. To the cooled mixture was added, dropwise, benzyl bromide (3.0 mL, 25 mmol) during 15 min at −5° to 0°. The mixture was stirred under nitrogen for 2 h at 20°, and then MeOH (2 mL) was added dropwise at −5°. The usual processing, and chromatography on SiO_2 (100 g) with 5:1 toluene–EtOAc, afforded **10** (4.5 g, 98.2%); $[\alpha]_D$ −9.9° (*c* 0.90); R_F 0.75 in 3:1 toluene–EtOAc; δ_H: 7.4–7.2 (m, 10 H, 2 benzyl), 6.1–

5.6 (m, 2 H, 2 CH_2-C*H*=CH_2), 5.4–5.1 (m, 4 H, 2 CH_2-CH=C*H*$_2$), 4.94 and 4.62 (AB q, 2 H, *J* 11 Hz, C*H*$_2$Ph), 4.87 and 4.71 (AB q, 2 H, *J* 9 Hz, C*H*$_2$Ph), 4.25 (d, 1 H, *J* 7 Hz, H-1), and 3.52 (s, 3 H, OMe).

Anal. Calc. for $C_{27}H_{34}O_6$: C, 71.34; H, 7.54. Found: C, 71.29; H, 7.49.

*Methyl 2,4-di-*O*-benzyl-β-*D*-galactopyranoside* (**11**). — A mixture of **10** (4.3 g, 9.46 mmol) and 10% Pd–C (0.5 g) in EtOH (30 mL)–AcOH (15 mL)–H_2O (15 mL) was stirred for 68 h at 75°. Filtration of the suspension, and evaporation of the filtrate *in vacuo*, afforded crystalline solid which was triturated with EtOAc–i-Pr_2O, to afford **11** (1.9 g, 53.8%). The mother liquor was evaporated, and the residue was chromatographed on SiO_2 (70 g) with 1 : 1 toluene–EtOAc, to give further **11** (220 mg, 6.2%); combined yield, 60.0%, m.p. 144–146° (from CH_2Cl_2–i-Pr_2O), $[\alpha]_D$ −10.6° (*c* 0.405); R_F 0.25 in 3 : 1 toluene–EtOAc; δ_H: 7.4–7.2 (m, 10 H, 2 benzyl), 4.95 and 4.63 (AB q, 2 H, *J* 11 Hz, C*H*$_2$Ph), 4.84 and 4.63 (AB q, 2 H, *J* 11 Hz, C*H*$_2$Ph), 4.27 (d, 1 H, *J* 7 Hz, H-1), and 3.54 (s, 3 H, OMe).

Anal. Calc. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.19; H, 6.96.

*Methyl 2,6-di-*O*-trityl-β-*D*-galactopyranoside* (**12**). — Compound **1** (4.8 g, 25 mmol) was stannylated with $(Bu_3Sn)_2O$ (23 g, 38 mmol) in toluene (100 mL). To the resulting, clear solution was added TrCl (21 g, 76 mmol) in one portion at 20°. The mixture was stirred for 35 h at 55–60°, and poured into 3 : 1 i-Pr_2O–hexane (400 mL), to give crystalline product (12.0 g, 71.6%); m.p. 134–136° (from i-Pr_2O), $[\alpha]_D$ +2.0° (*c* 1.0); R_F 0.5 in 5 : 1 toluene–EtOAc: δ_H: 7.6–7.2 (m, 30 H, 2 trityl), 4.22 (d, 1 H, *J* 6 Hz, H-1), 2.98 (s, 3 H, OMe), 2.10 (d, 1 H, *J* 4 Hz, OH), and 1.97 (d, 1 H, *J* 4 Hz, OH).

Anal. Calc. for $C_{45}H_{42}O_6$: C, 79.62; H, 6.24. Found: C, 79.77; H, 6.31.

*Methyl 3,4-di-*O*-acetyl-2,6-di-*O*-trityl-β-*D*-galactopyranoside* (**13**). — A solution of **12** (240 mg) in pyridine (4 mL) and Ac_2O (2 mL) was stirred for 40 h at 15°. The usual processing gave **13**; δ_H: 5.46 (d, 1 H, *J* 3 Hz, H-4), 5.12 (q, 1 H, *J* 3, *J* 9.4 Hz, H-3), 4.50 (d, 1 H, *J* 7.2 Hz, H-1), 3.85 (m, 1 H, H-5), 3.47–3.28 (m, 2 H, H-6,6'), 3.28 (s, 3 H, OMe), 3.01 (t, 1 H, *J* 8 Hz, H-2), 1.63 (s, 3 H, Ac), and 1.53 (s, 3 H, Ac).

*Methyl 3,4-di-*O*-benzyl-2,6-di-*O*-trityl-β-*D*-galactopyranoside* (**14**). — To a stirred mixture of **12** (3.4 g, 5 mmol) and NaH (0.4 g, 17 mmol) in $HCONMe_2$ (25 mL) was added benzyl bromide (1.4 mL) dropwise at 0°, and the mixture was stirred for 12 h at 15–20°. The excess of NaH was decomposed by the addition of MeOH, and the mixture was poured into ice–water, and extracted with EtOAc. The extract was washed with H_2O, dried ($MgSO_4$), and evaporated *in vacuo*, to afford an oily product which crystallized from EtOH, to give **14** (3.6 g, 84%); m.p. 80–82°, $[\alpha]_D$ −24.0° (*c* 0.95); R_F 0.49 in 40 : 1 toluene–EtOAc; δ_H: 7.56–6.77 (m, 40 H, aromatic), 3.02 (s, 3 H, OMe); δ_C: 104.1 (C-1, $^1J_{CH}$ 158.3 Hz), 88.3 and 86.7 (two *C*Ph$_3$), 82.0 (C-3), 73.5 (*C*H$_2$Ph), 73.1 (C-2,4,5), 72.0 (*C*H$_2$Ph), 62.6 (C-6), and 56.0 (OMe).

Anal. Calc. for $C_{59}H_{54}O_6$: C, 82.49; H, 6.33. Found: C, 82.51; H, 6.38.

*Methyl 3,4-di-*O*-benzyl-β-*D*-galactopyranoside* (**15**). — A mixture of **14** (0.90 g, 1.0 mmol), AcOH (6.5 mL), and H_2O (1.5 mL) was stirred for 2 h at 50–60°, and

evaporated *in vacuo*, and the residue was partitioned between water (40°) and i-Pr_2O. The aqueous layer was concentrated *in vacuo*, the concentrate extracted with EtOAc, and the extract dried ($MgSO_4$), and evaporated, to give crystalline **15** (0.32 g, 82% yield); m.p. 147–149°, $[\alpha]_D$ −22.7° (*c* 0.64); R_F 0.69 in 10:1 $CHCl_3$–MeOH; δ_H: 7.36–7.25 (m, 10 H, aromatic), 4.94 and 4.63 (AB q, 2 H, *J* 12 Hz, CH_2Ph), 4.75 (s, 2 H, CH_2Ph), 4.20 (d, 1 H, *J* 7.2 Hz, H-1), 3.58 (s, 3 H, OMe), 2.56 (bs, 1 H, OH), and 1.72 (bs, 1 H, OH).

Anal. Calc. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 66.91; H, 7.00.

Methyl 2,6-di-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranoside (**16**). — To a solution of **15** (50 mg) in pyridine (0.2 mL) was added benzoyl chloride (0.1 mL), and the mixture was stirred for 15 h at 0–5°. The usual processing, and chromatography on SiO_2 (4.5 g) with 10:1 toluene–EtOAc, afforded **16** (76 mg, 96%); $[\alpha]_D$ +19.5° (*c* 0.68); R_F 0.45 in 10:1 toluene–EtOAc; δ_H 8.18–7.80 (m, 4 H, benzoyl), 7.68–7.08 (m, 16 H, benzoyl and benzyl), 5.65 (q, 1 H, *J* 8.0, 9.6 Hz, H-2), and 3.48 (s, 3 H, OMe).

Anal. Calc. for $C_{35}H_{34}O_8$: C, 72.15; H, 5.88. Found: C, 72.12; H, 5.87.

Methyl 2,6-di-O-benzoyl-β-D-galactopyranoside (**17**). — A mixture of **16** (50 mg, 0.09 mmol) and 10% Pd–C (20 mg) in EtOH (2 mL) was stirred under H_2 for 3 days at 30–40°. The usual processing, and chromatography on SiO_2 (2 g) with 10:1 CH_2Cl_2–acetone, gave crystalline **17** (32 mg, 93%); m.p. 145–147°, $[\alpha]_D$ +0.7° (*c* 1.13); R_F 0.38 in 10:1 CH_2Cl_2–acetone; δ_H: 8.23–7.94 (m, 4 H, benzoyl), 7.68–7.08 (m, 6 H, benzoyl), 5.26 (q, 1 H, *J* 8.0, *J* 9.6 Hz, H-2), 4.87–4.44 (m, 2 H, H-6,6'), 4.52 (d, 1 H, *J* 8 Hz, H-1), 4.10–3.72 (m, 3 H, H-3,4,5), and 3.55 (s, 3 H, OMe).

Anal. Calc. for $C_{21}H_{22}O_8 \cdot 0.5\ H_2O$: C, 61.30; H, 5.63. Found: C, 61.10; H, 5.50.

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