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Note

Synthesis and conformation of 2,6-dioxabicyclo[3.1.1]heptanes: 1,3-anhydro-2,4,6-tri-*O*-benzyl-β-D-galactopyranose*

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A rationale for the study of 1,3-anhydroglycopyranoses was given previously in an article that described the synthesis of 1,3-anhydro-L-rhamnopyranose derivatives[1]. Earlier, 1,3-anhydro-D-gluco-[2,3] and -manno-pyranose[4,5] derivatives had been reported by Schuerch and collaborators. In the present communication, we report the synthesis and conformation of 1,3-anhydro-2,4,6-tri-*O*-benzyl-β-D-galactopyranose, which is of interest because its stereoregular polymerization and then deprotection can afford an α-(1→3)-linked D-galactopyranan, a useful model compound for immunology research.

Methyl α-D-galactopyranoside (**1**), prepared from D-galactose according to a reported method[6], was selectively 3-mono-*O*-allylated as the dibutyltin complex, following the method used for the preparation of allyl 3-*O*-crotyl-α-D-galactopyranoside[7], to afford methyl 3-*O*-allyl-α-D-galactopyranoside (**2**). Compound **2**, a readily crystallized compound after purification by column chromatography, was converted into the corresponding 2,4,6-tri-*O*-benzylated derivative (**3**) in the conventional way. Hydrolysis of **3** under acidic conditions gave 3-*O*-allyl-2,4,6-tri-*O*-benzyl-D-galactopyranose (**7**). Rearrangement of the allyl group to a propenyl group with tris(triphenylphosphine)chlororhodium furnished 2,4,6-tri-*O*-benzyl-3-*O*-propenyl-D-galactopyranose (**8**) that was converted, without isolation into 2,4,6-tri-*O*-benzyl-D-galactopyranose (**9**) under slightly acidic conditions. Acetylation with acetic anhydride–pyridine gave the 1,3-diacetate (**10**) quantitatively. 3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride (**11**) was obtained quantitatively from compound **10** with hydrogen chloride in ether by the method of

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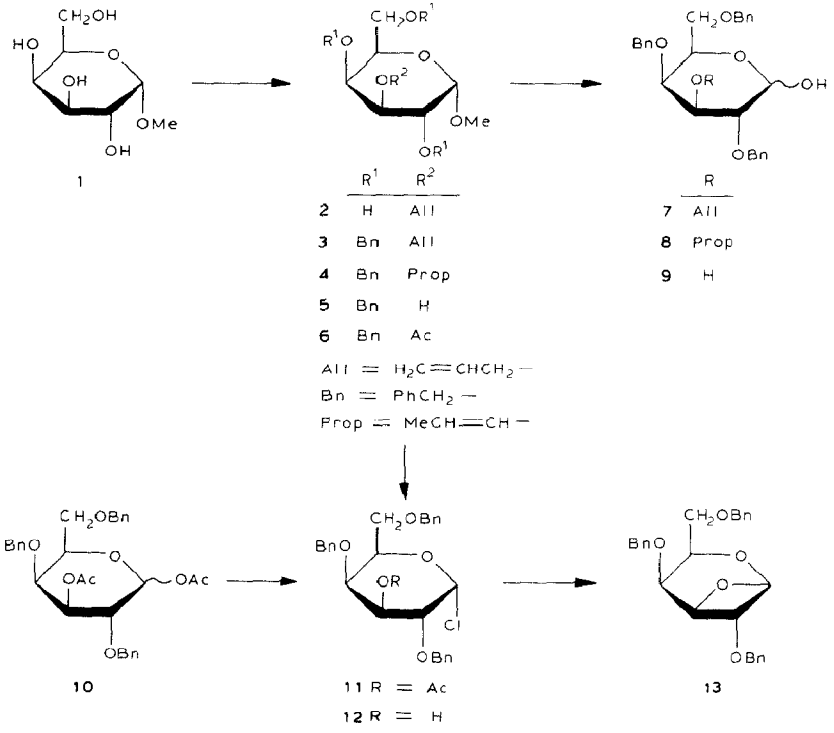
Micheel and Kreutzer[8]. Compound **11** was quite stable during storage for six months at 0°.

It had been reported that treatment of 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-α-D-glucopyranosyl chloride with potassium *tert*-butoxide in oxolane or 1,2-dimethoxyethane yields a glucal derivative as the main product[3], formed by *trans*-diaxial elimination of hydrogen chloride from C-1 and C-2. To avoid this side reaction, direct ring closure with potassium *tert*-butoxide was not used in the present research. Instead, the ring closure of **11** was performed in two steps. First, treatment of compound **11** in boiling oxolane with lithium methoxide, which was generated *in situ* from lithium hydride and absolute methanol, afforded crystalline 2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride (**12**) quantitatively. 1,3-Anhydro-2,4,6-tri-*O*-benzyl-β-D-galactopyranose (**13**) was then obtained in high yield by treatment of **12** in boiling oxolane with sodium hydride. No galactal was detected in the product from the ring closure. The 1,3-anhydro sugar ether **13** was acid-labile, but relatively stable in basic media.



An alternative method for the preparation of 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride was also used with satisfactory results; namely, rearrangement of methyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside gave the corresponding 3-*O*-propenyl derivative **4**, and hydrolysis of **4** afforded methyl 2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (**5**). Direct chlorination of **5** with

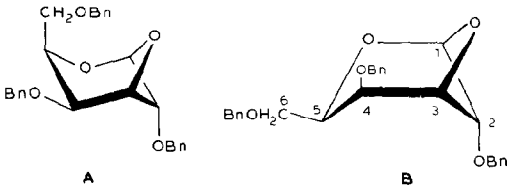


Fig. 1. Two possible conformations, A and B, for the 1,3-anhydro sugar ether **13**.

hydrogen chloride would cause[5] formation of disaccharide and other byproducts. Therefore, compound **5** was first acetylated, and the acetylated compound **6** was converted into the chloride **11** by the previously described method[5] with hydrogen chloride in acetic acid–dichloromethane. Although the chlorination reaction took 4 to 5 days, the yield was ~70%, and purification by chromatography was readily carried out.

The 1,3-anhydro sugar ether **13** was identified by its ^{1}H- and ^{13}C-n.m.r. and mass spectra, and its elemental analysis. The ^{1}H-n.m.r. spectrum showed a characteristic triplet for H-1 at δ 5.58, caused by a coupling between H-1 and H-2, and by a long-distance coupling between H-1 and H-3. The large value of $J_{1,3}$ (3.5 Hz) is probably caused by coupling through two W paths, as found in cyclobutane derivatives[9]. The ^{13}C-n.m.r. spectrum showed an anomeric carbon atom at δ 106.14. The mass spectrum of compound **13** showed a molecular-ion peak of moderate intensity at *m/z* 432.

A conformational analysis of the 1,3-anhydro sugar ether **13** was performed with the aid of a 400-MHz spectrometer in conjunction with calculations made by use of a modified Karplus equation[10]. First, the ^{1}H-n.m.r. spectrum of compound **13** was completely assigned by use of single-frequency decoupling and a two-dimensional homonuclear-correlated spectrum. Irradiation of H-1 identified a multiplet

TABLE I

H–H TORSION ANGLES AND ^{1}H–^{1}H COUPLING CONSTANTS FOR COMPOUND **13**

	$\phi_{1,2}$ *(degrees)*[a]	$\phi_{2,3}$	$\phi_{3,4}$	$\phi_{4,5}$
Measured from model of A	35	325	280	40
Measured from model of B	35	325	320	320
	$J_{1,2}$ *(values in Hz)*	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
Experimental value	3.5	5.5	2.3	1.2
Calculated, from model of A, by the modified Karplus equation[10]	5.3	7.2	0.8	6.6
Calculated, from model of B, by the modified Karplus equation[10]	5.3	7.2	4.8	2.9

[a]Torsion angles are defined as in ref. 10.

at δ 4.70 as H-3, because the multiplet collapsed to a doublet of doublets produced by coupling between H-2 and H-3, and by coupling between H-3 and H-4. A quartet at δ 4.52 was assigned as H-2, as it changed to a doublet given by coupling between H-2 and H-3. Irradiation of H-2 simplified the H-1 signal to a doublet and that of H-3 to a quartet. Irradiation of H-6 at δ 3.78 identified H-5, the signal of which changed to a doublet of very small coupling constant ($J_{4,5}$ 1.2 Hz) from a pseudoquartet at δ 5.03 ($J_{5,6}$ 10.8 Hz, $J_{5,6'}$ 5.1 Hz). Decoupling H-5 simplified only the H-6 signal, and did not affect those of H-3, H-2, and H-1 at all, and gave a non-observable change to that of H-4. Thus, H-5 and two H-6 comprise an ABX spin system. A broadened doublet at δ 4.67 was assigned as that of H-4.

Two conformations, A and B, may be considered for the 1,3-anhydro sugar ether **13**, as shown in Fig. 1. Torsion angles $\phi_{3,4}$ and $\phi_{4,5}$ are different in conformations A and B. Thus, the expected values of $J_{3,4}$ and $J_{4,5}$ would differ for the two conformations. When calculations are made by the modified Karplus equation[10], the differences are 3.7 Hz, or greater, for both couplings. Of particular interest is $J_{4,5}$ where the difference is due to a negative *gauche* effect[11] in B, and a positive *gauche* effect[11] in A. The experimental value (1.2 Hz) was close to the calculated value for the thermodynamically favored conformation B (2.9 Hz). Therefore, it was concluded that formula B depicts the conformation of compound **13**.

Single-frequency decoupling was also used to assign the signals in the spectrum of 2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride (**12**). The fact that $J_{4,5}$ (1.2 Hz) for **13** is very close to $J_{4,5}$ (1 Hz) for **12** indicated that the two compounds have a similar partial conformation in the moiety comprised of C-4, C-5, and C-6. This constitutes an alternative proof for the suggested conformation B. A large chemical-shift change of H-5 from δ 4.26 in **12** to δ 5.03 in **13** was perhaps caused by interaction between H-5 and O-2. A change of 0.21 p.p.m. to downfield for H-6 from the conversion of **12** to **13** is reasonable, and also a 0.41 p.p.m. shift to downfield for H-2 was expected for the transformation from the axial to the equatorial position. A change of the orientation of H-3 from the axial to the pseudo-equatorial orientation at the bridge-head caused a 0.71-p.p.m. shift to downfield. However, it is still not known why a large change to downfield for the H-4 signals occurred.

EXPERIMENTAL

General methods. — See ref. 1.

Methyl 3-O-allyl-α-D-galactopyranoside (**2**). — A mixture of methyl α-D-galactopyranoside monohydrate [**1**; 4.0 g, 18.9 mmol, m.p. 105°, $[\alpha]_D^{20}$ +169° (*c* 1.5, H_2O); lit.[7] m.p. 111°, $[\alpha]_D^{20}$ +177° (*c* 1.5, H_2O)] and dibutyltin oxide (5 g, 20 mmol) in toluene (250 mL) was boiled under reflux for 2 or 3 h with azeotropic removal of water. The brownish solution thus obtained was cooled to 60°, and tetrabutylammonium iodide (7.4 g, 20 mmol) and allyl bromide (20 mL, 23.1 mmol) were added. The reaction was carried out under stirring for 18 h at 60°. T.l.c. (ethyl

acetate) indicated that the ratio of di-*O*-allyl-, 3-*O*-allyl-α-D-galactopyranoside, and starting material were ~1:5:0.5. The reaction mixture was evaporated under diminished pressure, and the brown residue was purified by chromatography on a column (35 × 400 nm) with ethyl acetate as eluant, to give compound **2** from the main fraction. Concentration of the eluate afforded yellowish crystals of **2** (3.3 g, 70%, m.p. 83°) that were used directly for the next reaction. Recrystallization from ethyl acetate gave pure compound **2** as white needles, m.p. 95°, $[\alpha]_D^{20}$ +162° (*c* 0.94, CH_3OH); ^{1}H-n.m.r.: δ 5.82–5.72 (m, 1 H, CH_2=C*H*-), 5.18–5.05 (m, 2 H, CH_2=CH-), 4.63 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.03–3.42 (m, 8 H, CH_2=CH-CH_2-, H-2,3,4,5 and 2 H-6), 3.22 (s, 3 H, OCH_3); *m/z* 235 (M^+ + 1), 203 (M^+ − OCH_3), 185 (M^+ − OCH_3 − H_2O), and 144 (M^+ − OCH_3 − H_2O − allyl).

Anal. Calc. for $C_{10}H_{18}O_6$: C, 51.28; H, 7.69. Found: C, 50.92; H, 7.63.

Methyl 3-O-allyl-2,4,6-tri-O-benzyl-α-D-galactopyranoside (**3**). — The crude crystals of **2** (936 mg, 4 mmol) were dissolved in DMF (12 mL), the solution was stirred and cooled in an ice bath, and sodium hydride (80% in oil; 500 mg, 17.4 mmol) and benzyl bromide (1.5 mL, 12.7 mmol) were added. After 4 h at room temperature, the reaction was complete as indicated by t.l.c. (1:3 ethyl acetate–petroleum ether). The mixture was poured into ice–water and extracted with dichloromethane. The extracts were combined, washed with water, dried (anhydrous sodium sulfate), and evaporated, to give syrupy methyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside quantitatively; $[\alpha]_D^{20}$ +18.7° (*c* 1.6, chloroform); ^{1}H-n.m.r.: δ 7.49–7.26 (m, 15 H, Ph-H), 6.06–5.98 (m, 1 H, CH_2=C*H*-), 5.43–5.21 (m, 2 H, CH_2=CH-), 5.01–3.87 (m, 13 H, 3 CH_2Ph, H-1, CH_2=CH-CH_2-, H-2,3,4,5), 3.60 (d, 2 H, $J_{5,6}$ 6.5 Hz, 2 H-6), and 3.41 (s, 3 H, OCH_3); ^{13}C-n.m.r.: δ 137.9, 137.8, 137.2, 127.6, 127.4, 127.1 (Ph-C), 134.4 (CH_2=*C*H-), 115.7 (CH_2=CH-), 98.12 (C-1), 75.72, 75.40, 74.15, 73.93, 72.85, 72.75, 71.00 (3 CH_2-Ph, C-2,3,4,5), 68.32 (C-6), and 54.41 (OCH_3).

Anal. Calc. for $C_{31}H_{36}O_6$: C, 73.80; H, 7.15. Found: C, 73.68; H, 7.23.

3-O-*Allyl-2,4,6-tri-O-benzyl-D-galactopyranose* (**7**). — A mixture of methyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (**3**; 1.0 g, 2 mmol), acetic acid (80%, 6 mL), and M hydrochloric acid (2 mL) was boiled under reflux. After 5 h, the reaction was complete as indicated by t.l.c. in 1:3 ethyl acetate–petroleum ether. The mixture was evaporated under diminished pressure, washed with saturated sodium hydrogencarbonate, and extracted with diethyl ether. The extracts were combined, dried, and evaporated to a syrup. Column chromatography of the syrup with 1:2 ethyl acetate–petroleum ether, and evaporation of the main fraction, gave pure compound **4** as a syrup (750 mg, 77%); $[\alpha]_D^{20}$ +14.0° (*c* 2, chloroform); ^{1}H-n.m.r.: δ 7.37–7.28 (m, 15 H, 3 Ph-H), 5.93 (m, 1 H, CH_2=C*H*-), 5.45–3.48 (m, 17 H, CH_2=CH-, H-1, CH_2=CH-CH_2-, 3 CH_2Ph, H-2,3,4,5, and 2 H-6), and 1.30 (s, 1 H, O*H*).

Anal. Calc. for $C_{30}H_{34}O_6$: C, 73.47; H, 6.95. Found: C, 73.31; H, 7.06.

2,4,6-Tri-O-benzyl-D-galactopyranose (**9**). — To a solution of compound **7** (850 mg, 1.7 mmol) in ethanol (90%, 10 mL) was added tris(triphenylphosphine)-

chlororhodium (30 mg, 0.03 mmol) and the mixture was boiled under reflux for 7 h. As indicated by t.l.c. (1:3 ethyl acetate–petroleum ether), all of the starting material was converted into 2,4,6-tri-*O*-benzyl-3-*O*-propenyl-D-galactopyranose (**8**), of which about half was converted into 2,4,6-tri-*O*-benzyl-D-galactopyranose (**9**). To complete the reaction, M hydrochloric acid (1 mL) was added to the mixture and it was refluxed for 1 h. Most of the solvents were evaporated, the product taken up in dichloromethane, and the solution washed with brine, dried (anhydrous sodium sulfate), and evaporated. After separation by column chromatography with 1:2 ethyl acetate–petroleum ether as eluant, crystalline compound **9** was obtained on evaporation of the main fraction (687 mg, 90%); m.p. 125°, $[\alpha]_D^{20}$ +36.4° (*c* 0.95, chloroform, 2 h); lit.[12] m.p. 126–128°, $[\alpha]_D^{20}$ +40.3→+36.3° (*c* 1, chloroform); the ^{1}H-n.m.r. spectrum showed the presence of some β anomer[12].

*1,3-Di-*O*-acetyl-2,4,6-tri-*O*-benzyl-*D*-galactopyranose* (**10**). — Compound **9** (1.02 g, 2 mmol) was acetylated with acetic anhydride–pyridine by the standard procedure, to give **10** in theoretical yield; $[\alpha]_D^{20}$ +95.8° (*c* 1, chloroform); lit.[12] $[\alpha]_D^{25}$ +112° (*c* 1, chloroform, for α anomer); ^{1}H-n.m.r. spectrum was as described in ref. 12.

3-O-Acetyl-2,4,6-tri-O-benzyl-α-D-galactopyranosyl chloride (**11**). — Compound **10** (534 mg, 1 mmol) was dissolved in dry diethyl ether (10 mL), and hydrogen chloride was bubbled in to saturation, at 0°, under nitrogen protection. The mixture was kept at room temperature and the reaction monitored by t.l.c. (1:3 ethyl acetate–petroleum ether). After 3 h the reaction was complete. The yellowish solution was evaporated under diminished pressure to a syrup that was dissolved in dichloromethane (2 mL), and the solution evaporated. This procedure was repeated 7 or 8 times, to decrease the hydrogen chloride to the minimum. Purification of the brownish syrup by column chromatography (1:3 ethyl acetate–petroleum ether) yielded compound **11** (502 mg, 98%); $[\alpha]_D^{20}$ +117° (*c* 0.73, chloroform); ^{1}H-n.m.r.: δ 7.37–7.22 (m, 15 H, 3 Ph-H), 6.12 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.28 (q, 1 H, $J_{3,4}$ 3.6, $J_{2,3}$ 10.2 Hz, H-3), 4.70–4.46 (m, 6 H, 3 CH_2Ph), 4.34 (t, 1 H, $J_{5,6}$ 6.6 Hz, H-5), 4.17 (q, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.2 Hz, H-2), 4.11 (m, 1 H, H-4), 3.55 (d, 2 H, $J_{5,6}$ 6.8 Hz, 2 H-6), and 1.98 (s, 3 H, CH_3-CO-); ^{13}C-n.m.r.: δ 169.9 (CH$_3$-*C*O-), 137.7, 137.4, 128.4, 127.9, 127.8 (Ph-C), 93.84 (C-1), 75.28, 74.51, 73.66, 73.33, 72.72, 71.91, 71.55 (C-2,3,4,5, and 3 *C*H$_2$Ph), 67.22 (C-6), and 20.68 (*C*H$_3$-CO-).

Anal. Calc. for $C_{29}H_{31}ClO_6$: C, 68.17; H, 6.07. Found: C, 68.09; H, 6.11.

2,4,6-Tri-O-benzyl-α-D-galactopyranosyl chloride (**12**). — To a solution of compound **11** (153 mg, 0.3 mmol) in dry oxolane (10 mL) was added lithium hydride (18 mg, 2 mmol) and anhydrous methanol (45 μL, 1.1 mmol) and the mixture was boiled for 3 h under reflux with nitrogen protection. T.l.c. (1:3 ethyl acetate–petroleum ether) indicated that only one-third of the starting material was converted into **12**. Additional portions of lithium hydride and methanol were added, and the mixture was continuously boiled until the reaction was complete and only one spot was detected by t.l.c. The solid was separated by centrifuging, and compound **12** was obtained as a syrup on concentration of the supernatant

liquor and washings. Purification by column chromatography afforded crystalline **12** (132 mg, 93%); m.p. 112°, $[\alpha]_D^{20}$ +74.7° (*c* 1, chloroform); ^{1}H-n.m.r.: δ 7.37–7.22 (m, 15 H, 3 Ph-H), 6.19 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.86–4.45 (m, 6 H, 3 C*H*$_2$-Ph), 4.26 (t, 1 H, $J_{5,6}$ 6.8 Hz, H-5), 4.11 (q, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.1 Hz, H-2), 3.98 (m, 2 H, H-3,4), 3.57 (d, 2 H, $J_{5,6}$ 6.8 Hz, 2 H-6), and 1.41 (s, 1 H, O*H*); *m/z* 468 (M^+), 432 (M^+ − HCl), 377 (M^+ − CH_2Ph), and 341 (M^+ − CH_2Ph − HCl).

Anal. Calc. for $C_{27}H_{29}ClO_5$: C, 69.15; H, 6.23. Found: C, 69.03; H, 6.32.

*1,3-Anhydro-2,4,6-tri-*O*-benzyl-β-*D*-galactopyranose* (**13**). — To a solution of compound **12** (118 mg, 0.25 mmol) in dry oxolane (15 mL) was added sodium hydride (80% in oil; 50 mg, 1.7 mmol), the mixture was boiled under reflux, and the reaction was monitored by t.l.c. (1:3 ethyl acetate–petroleum ether). After 3 h, the reaction was complete as indicated by t.l.c. The solid was separated by centrifuging, and the residue was washed with oxolane. The supernatant liquor and washings were combined and evaporated to a syrup. Purification of the syrup by analytical l.c. with 1:3 ethyl acetate–petroleum ether as the eluant yielded the target 1,3-anhydro-2,4,6-tri-*O*-benzyl-β-D-galactopyranose (86 mg, 80%); $[\alpha]_D^{20}$ −2.7° (*c* 1.3, chloroform); ^{1}H-n.m.r.: δ 7.35–7.25 (m, 15 H, 3 Ph-H), 5.58 (t, 1 H, $J_{1,2}$ 3.5, $J_{1,3}$ 3.5 Hz, H-1), 5.03 (q, 1 H, $J_{5,6}$ 10.8, $J_{5,6'}$ 5.1 Hz, H-5), 4.70 (m, 1 H, $J_{1,3}$ 3.5, $J_{2,3}$ 5.5, $J_{3,4}$ 2.3 Hz, H-3), 4.67 (d, 1 H, $J_{3,4}$ 2.3 Hz, H-4), 4.51 (q, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 5.5 Hz, H-2), 4.64–4.34 (m, 6 H, 3 C*H*$_2$Ph), and 3.78 (m, 2 H, 2 H-6); ^{13}C-n.m.r.: δ 138.3, 137.9, 137.0, 128.7, 128.5, 128.3, 128.0, 127.9 (Ph-C), 106.1 (C-1), 83.28, 78.72, 74.23, 74.12, 73.63, 72.71, 72.10, and 70.87 (C-2,3,4,5,6 and 3 CH_2Ph); *m/z* 432 (M^+).

Anal. Calc. for $C_{27}H_{28}O_5$: C, 74.98; H, 6.53. Found: C, 75.12; H, 6.60.

*Methyl 2,4,6-tri-*O*-benzyl-α-*D*-galactopyranoside* (**5**). — To a solution of methyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (504 mg, 1 mmol) in ethanol (90%, 5 mL) was added tris(triphenylphosphine)chlororhodium (15 mg, 15 μmol) and the mixture was boiled for 7 h. As indicated by t.l.c. (1:3 ethyl acetate–petroleum ether), all of the starting material had disappeared, and partial hydrolysis of the 3-*O*-propenyl derivative (**4**) to **5** had occurred. M Hydrochloric acid (0.5 mL) was added, and the mixture was boiled for 1 h. The mixture was partitioned between dichloromethane and water, and the organic phase was evaporated to a syrup. Purification of the syrup by analytical l.c. (1:2 ethyl acetate–petroleum ether) afforded pure compound **5** (418 mg, 90%); $[\alpha]_D^{20}$ +45.8° (*c* 1.6, chloroform), lit.[13] $[\alpha]_D^{20}$ +44° (*c* 3.7, chloroform); lit.[14] $[\alpha]_D^{20}$ +46.6° (*c* 1.04, chloroform); ^{1}H-n.m.r.: δ 7.36–7.25 (m, 15 H, 3 Ph-H), 4.82–4.41 (m, 7 H, 3 C*H*$_2$-Ph, H-1), 4.04 (q, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.2 Hz, H-2), 3.90 (m, 2 H, H-4,5), 3.79 (q, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 10.4 Hz, H-3), 3.55 (d, 2 H, $J_{5,6}$ 6.8 Hz, 2 H-6), 3.33 (s, 3 H, OC*H*$_3$), and 2.27 (s, 1 H, O*H*); ^{13}C-n.m.r.: δ 138.3, 138.0, 137.8, 128.4, 128.2, 128.0, 127.9, 127.6 (Ph-C), 97.79 (C-1), 76.40, 74.94, 73.27, 72.82, 70.07 (3 CH_2-Ph, C-2,3,4,5), 68.86 (C-6), and 55.23 (OCH_3).

*3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-α-*D*-galactopyranosyl chloride* (**11**) *from compound* **5**. — Acetylation of **5** with acetic anhydride–pyridine gave methyl 3-*O*-

acetyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (**6**) quantitatively, $[\alpha]_D^{20}$ +55.5° (*c* 1.3, chloroform); lit.[13] no data; ^{1}H-n.m.r.: δ 7.33–7.23 (m, 15 H, 3 Ph-H), 5.25 (q, 1 H, $J_{2,3}$ 9.7, $J_{3,4}$ 3.2 Hz, H-3), 4.71 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.00 (m, 3 H, H-2,4,5), 3.54 (d, 2 H, $J_{5,6}$ 6.8 Hz, 2 H-6), 3.37 (s, 3 H, OCH_3), and 1.96 (s, 3 H, CH_3-CO-); ^{13}C-n.m.r.: δ 170.24 (CH_3CO), 138.1, 138.0, 137.7, 128.3, 128.0, 127.8, 127.7, 127.6 (Ph-C), 98.33 (C-1), 75.51, 75.08, 74.01, 73.29, 73.09, 72.36 (3 CH_2-Ph, C-2,3,4,5), 68.40 (C-6), 55.30 (OCH_3), and 20.91 (CH_3-CO-).

Compound **6** (253 mg, 0.5 mmol) was dissolved in a mixture of dichloromethane (10 mL) and acetic acid (10 mL), and hydrogen chloride was bubbled in to saturation under a nitrogen atmosphere and in an ice bath. After 4 days at room temperature, the reaction was 90% complete as indicated by t.l.c. (1:3 ethyl acetate–petroleum ether). The solvents were evaporated and the product purified by column chromatography. Pure, syrupy **11** (166 mg, 65%) was obtained. The physical data for **11** thus obtained were the same as those already described herein.

REFERENCES

1 E WU, F. KONG, AND B. SU, *Carbohydr. Res.*, 161 (1987) 235–246.
2 H. ITO, R. EBY, S. KRAMER, AND C. SCHUERCH, *Carbohydr. Res.*, 86 (1980) 193–202.
3 F. GOOD AND C. SCHUERCH, *Carbohydr. Res.*, 125 (1984) 165–172.
4 A. J. VARMA AND C. SCHUERCH, *J. Org. Chem.*, 96 (1981) 799–803.
5 F. KONG AND C. SCHUERCH, *Carbohydr. Res.*, 112 (1983) 141–147.
6 E. PACSU, *Ber.*, 62 (1929) 3011–3033.
7 A. K. M. ANISUZZAMAN, L. ANDERSON, AND J. L. NAVIA, *Carbohydr. Res.*, 174 (1988) 265–278.
8 F. MICHEEL AND O. KREUTZER, *Justus Liebigs Ann. Chem.*, 722 (1969) 228–231.
9 K. B. WIBERG, D. E. BARTH, AND W. E. PRATT, *J. Am. Chem. Soc.*, 99 (1977) 4286–4289.
10 C. A. G. HAASNOOT, F. A. A. M. DE LEEUW, AND C. ALTONA, *Bull. Soc. Chim. Belg.*, 89 (1980) 125–131.
11 H. BOOTH, *Tetrahedron Lett.*, (1965) 411–414.
12 M. A. NASHED AND L. ANDERSON, *Carbohydr. Res.*, 51 (1976) 65–72.
13 N. MORISHIMA, S. KOTO, M. OSHIMA, A. SUGIMOTO, AND S. ZEN, *Bull. Chem. Soc. Jpn.*, 56 (1983) 2849–2850.
14 H. M. FLOWERS, *Carbohydr. Res.*, 99 (1982) 170–174.