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O-BENZYLATED THIO SUGARS: 2,3,4- AND 2,4,6-TRI-*O*-BENZYL-1-THIO-β-D-GALACTOPYRANOSE

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ABSTRACT

The 2,3,4- (**9**) and 2,4,6-tribenzyl (**19**) ethers of 1-thio-β-D-galactopyranose were prepared from the corresponding *O*-benzylated normal (1-hydroxyl) sugars **4** and **15** via the sequence: normal sugar → diacetate → *O*-acetylglycosyl bromide → *O*-acetylglycosyl ethylxanthate → 1-thio sugar. 2,3,4-Tri-*O*-benzyl-α-D-galactopyranose (**4**) is most advantageously made from allyl 6-*O*-allyl-α-D-galactopyranoside (**2**) by a published synthesis. An improved synthesis of 2,4,6-tri-*O*-benzyl-D-galactopyranose (**15**) was devised; it involves the selective 3-*O*-benzoylation of allyl 2,6-di-*O*-benzyl-α-D-galactopyranoside (**10**).

INTRODUCTION

For work now in progress in this laboratory on the solid-phase synthesis of oligosaccharides having D-galactose as the reducing group, three of the isomeric tri-*O*-benzyl-1-thio-D-galactoses were needed. As described in previous papers[1,2], a benzylated 1-thio sugar is readily made from the corresponding benzylated normal sugar via the acetate, 1-halide, and 1-ethylxanthate (as shown for the 6-hydroxyl isomer in Scheme I). More specifically, then, our task was to prepare the 2,3,4-, the 2,4,6-, and the 2,3,6-tri-*O*-benzyl-D-galactoses having free or potentially free hydroxyl groups in the 1 and 6, 1 and 3, and 1 and 4 positions, respectively. Both the 1,6-dihydroxy derivative (**4**) and the 1,3-dihydroxy derivative (**15**) are already known, but it was necessary to choose between alternative routes to the 1,6-diacetate **5**, and it appeared that an improved synthesis of **15** could be devised. This paper presents our solutions to these problems, and the preparation of 2,3,4-tri-*O*-benzyl-1-thio- (**9**, 6-OH) and 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranose (**19**, 3-OH). 2,3,6-Tri-*O*-benzyl-1-thio-D-galactopyranose poses a special problem in that the hydroxyl group at position 4 must be kept protected at all times. Derivatives of this thio sugar will be described in a forthcoming paper.

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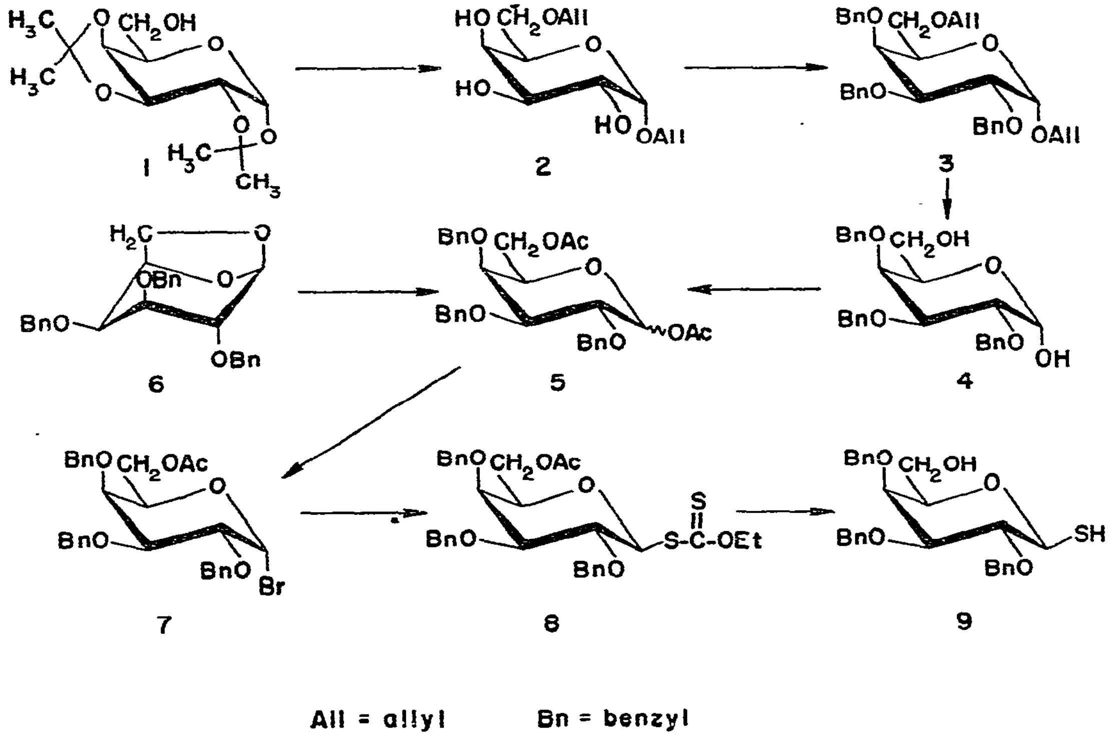
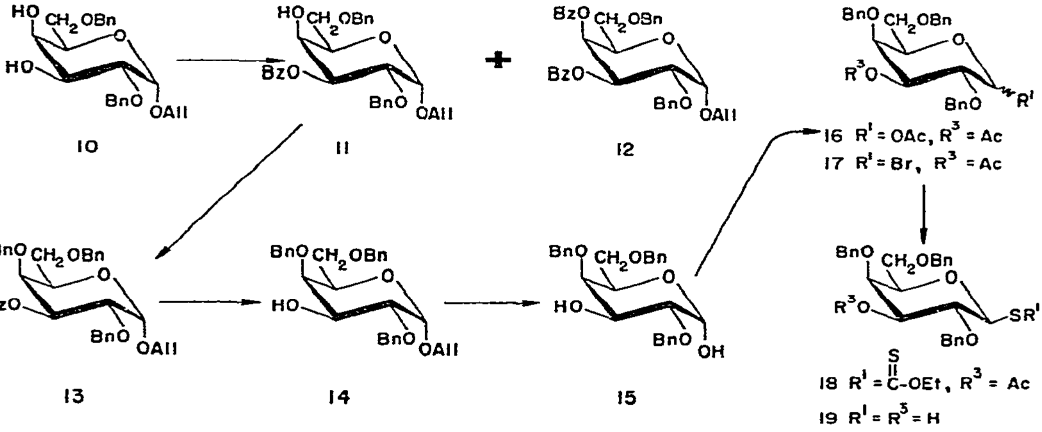


Scheme I.

RESULTS AND DISCUSSION

2,3,4-Tri-*O*-benzyl-D-galactose (**4**) has been made in two ways: from the allyl 6-*O*-allylgalactoside[3] **3** and from the 1,6-anhydro derivative[4] **6**. In the preparation from **6**, the 1,6-diacetate **5** was an intermediate, but this compound was not characterized. Of these two syntheses, we found the first to be considerably more practical. It is three steps shorter than the route via the anhydride, gives excellent yields in all but one of the steps, and readily furnishes crystalline 2,3,4-tri-*O*-benzyl-D-galactose (**4**). The formation of allyl 6-*O*-allyl-α-D-galactopyranoside (**2**) from 1,2:3,4-di-*O*-isopropylidene-D-galactose (**1**) is the least satisfactory step, but even here, yields of 60% may be obtained by recycling incompletely converted material, as recommended by Gigg and Warren[3]. The two-step procedure used for removal of the allyl groups from **3** (isomerization to 1-propenyl groups with potassium *t*-butoxide, followed by mild, acid hydrolysis of the 1-propenyl derivative[5]) avoids the strongly acidic conditions that might cause partial cleavage of the benzyl ether groups. As pointed out by Gigg and Gigg[5] this capability makes the allyl group a very attractive protecting group for use in synthetic operations with benzyl ethers. When testing the alternative route to **5**, we experienced difficulty in converting phenyl β-D-galactopyranoside into crystalline 1,6-anhydro-β-D-galactopyranose[6], and obtained poor yields or impure products in the subsequent steps.

The 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-D-galactopyranose (**5**) derived from the dihydroxy compound **4** was a syrup. Its p.m.r. spectrum showed it to be a mixture of α- and β-anomers in about equal proportions. Conversion into the ethylxanthate **8**, also a syrup, was accomplished without isolation of the intermediate bromide **7**. The p.m.r. spectrum of **8** showed only one anomeric-proton signal, a doublet at τ 4.66 having a large spacing (10 Hz), indicating that the compound has the expected[7] β-configuration. As was the case with the related tri-*O*-benzyl-1-thio-D-glucoses[2], the anomeric configuration of the crystalline 2,3,4-tri-*O*-benzyl-1-thio-D-galactopyranose (**9**) could not be ascertained from its p.m.r. spectrum. However, the initial product of saponification from the ethylxanthate must surely have been the sodium salt of the 1-thio-β-D-aldose. If the sodium salts of 1-thioaldoses do not anomerize, and the free –SH forms anomerize only slowly[8], the assignment of the β-configuration to **9** is reasonable. The low specific rotation (+15.8°) of the compound, and its upward mutarotation is acidic methanol, substantiate this assignment.



Scheme II.

2,4,6-Tri-*O*-benzyl-D-galactose (**15**) was described by Gent *et al.*[9] in 1972. Using a series of blocking groups, these authors converted allyl α-D-galactopyranoside into the 3-*O*-allyl-2-*O*-benzyl derivative in ~50% overall yield. Further benzylation and deallylation gave **15**. In seeking an alternative synthesis of **15**, we wished primarily to avoid any route involving allyl α-D-galactopyranoside, as we have not found a satisfactory preparation of this compound. Attention was directed to allyl 2,6-di-*O*-benzyl-α-D-galactopyranoside (**10**), which can be made from 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (**1**) in satisfactory yield by a five-step procedure[5,9]. Compound **10** has two secondary hydroxyl groups, one equatorially disposed (position 3) and one axially disposed (position 4), and it is the axial group that must be benzylated to afford the desired product **15**. The direct benzylation of **10** was considered, as Flowers[10] found that the direct benzylation of methyl 2,6-di-*O*-benzyl-α-D-galactopyranoside gave primarily the 2,4,6-tribenzyl ether. However, the yield in this reaction was rather low (40%), and the product had to be purified by chromatography. Hence a scheme involving prior protection of the 3-hydroxyl group seemed preferable.

Direct allylation of the 3-position in **10** was attempted by Gent *et al.*[9], but the reaction was not regioselective under their conditions. On the other hand, we found, that partial benzoylation[11] of **10** at low temperature is highly selective, giving a single monobenzoate (**11**) as the major product, together with ~15% of 3,4-dibenzoate (**12**). The two benzoyl derivatives were readily separated by chromatography on silica gel, and the monobenzoate **11** was converted into 2,4,6-tri-*O*-benzyl-D-galactose (**15**). This transformation established the 3-*O*-benzoyl structure for **11**. The conversion was accomplished by benzylation of the 4-hydroxyl group with benzyl bromide and silver oxide in benzene[12], followed by debenzoylation and deallylation.

The further transformation of **15** into 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranose (**19**) closely paralleled the corresponding transformation in the 6-hydroxyl series. On the same basis as in that series, the β configuration was assigned to the intermediate ethylxanthate (**18**) and the final product (**19**). Satisfactory yields of **19** could be obtained from the crude benzoylation product (**11**+**12**); the 2,6-dibenzyl ether formed from **12** separated out during the final crystallization.

EXPERIMENTAL

General methods. — Instrumental and chromatographic procedures were as described in earlier papers of this series[1,2,7]. The following solvent combinations (v/v) were utilized for thin-layer and column chromatography: A, 4:1 benzene–ethyl acetate; B, 9:1 chloroform–ethyl acetate; C, 19:1 chloroform–methanol; and D, 19:1 chloroform–acetone.

2,3,4-Tri-O-benzyl-D-galactose derivatives

1,6-Di-O-acetyl-2,3,4-tri-O-benzyl-D-galactopyranose (**5**). — A solution of 2,3,4-tri-*O*-benzyl-α-D-galactopyranose[3] (**4**, 5.0 g, 11 mmol) in dry pyridine (20 ml) was treated with acetic anhydride (5 ml) for ~10 h at room temperature. The mixture was poured into 100 ml of water, and the product recovered by conventional chloroform extraction. Evaporation of the dried extract gave 5.5 g (93%) of **5** as a colorless syrup; $[\alpha]_D^{25}$ +31.7°, $[\alpha]_{436}^{25}$ +62.9° (*c* 1.4, chloroform); p.m.r. ($CDCl_3$): τ 2.65 (ps, 15, Ph-*H*), 3.57 (d, 0.57, *J* 3.0 Hz, H-1α), 4.40 (d, 0.43, *J* 8.0 Hz, H-1β), 4.85–5.5 (m, 6, PhC*H*$_2$), 5.65–6.55 (m, 6, H-2,3,4,5,6,6′), 7.93, 7.98, and 8.05 (3 s, 6 total, COC*H*$_3$). Found: C, 69.70; H, 6.53. $C_{31}H_{34}O_8$ (534.58) requires C, 69.65; H, 6.41.

6-O-Acetyl-2,3,4-tri-O-benzyl-β-D-galactopyranosyl ethylxanthate (**8**). — Compound **5** was dissolved in ~15 volumes of dry dichloromethane saturated with hydrogen bromide, and the solution was kept for 15–30 min at room temperature.

The solvent was evaporated under diminished pressure, and residual hydrogen bromide was removed by the addition and evaporation of several portions of dry dichloromethane. The resulting *6-O-acetyl-2,3,4-tri-O-benzyl-D-galactopyranosyl bromide* (7) [τ ($CDCl_3$) 3.48 (H-1 α)] was further dried under oil-pump vacuum before use.

To 0.90 g (1.62 mmol) of the bromide in 25 ml of dry benzene was added 0.35 g (2.2 mmol) of potassium ethylxanthate[1,*] in 25 ml of abs. ethanol. The solution was stirred for 5 h at room temperature and then washed with water. Evaporation of the dried benzene layer left a yellow syrup. Material prepared in this way was suitable for conversion into the 1-thio sugar. Chromatography of the syrup on silica gel, with solvent B as eluant, afforded 0.73 g (75%) of the title compound **8**; $[\alpha]_D^{25}$ +12° (c 1, chloroform); p.m.r.[†] ($CDCl_3$): τ 4.70 (d, 1, $J_{1,2}$ 10 Hz, H-1), 4.9–6.55 now 14 H (addition of CH_2CH_3), 8.04 (s, 3, $COCH_3$), and 8.64 (t, 3, J 7.0 Hz, CH_2CH_3). Found: C, 64.91; H, 5.99; S, 10.76. $C_{32}H_{36}O_7S_2$ (596.74) requires C, 64.40; H, 6.08; S, 10.75.

2,3,4-Tri-O-benzyl-1-thio-β-D-galactopyranose (**9**). — A few small pieces of sodium were added over a 10-min period to a solution of 1.26 g (2.1 mmol) of pure **8** in 30 ml of abs. methanol. At this point, t.l.c. (solvent B) indicated disappearance of the starting material. The mixture was made neutral with dilute acetic acid, whereupon the product separated as an oil. The product was recovered by extraction with chloroform and the extract was washed with sodium hydrogencarbonate and water. Evaporation of the dried chloroform solution left a yellow syrup that crystallized from benzene–Skellysolve B. The product was recrystallized from methanol; yield 0.82 g (83%). A lower yield (57%) was realized when crude ethylxanthate was used as starting material. The product was obtained as needles, m.p. 139–140, $[\alpha]_D^{25}$ +15.8°, $[\alpha]_{436}^{25}$ +35.7° (c 2, chloroform); $[\alpha]_D^{30}$ in 3mM methanolic hydrogen chloride (c 1) +15.4° (initial) → +68.1° (140 h); p.m.r. ($CDCl_3$): τ 7.73 (d, 1, D_2O exchangeable, J 8.0 Hz, SH) and 7.90 (bs, 1, D_2O exchangeable, OH), no signals at 4.7, 8.0, or 8.6. Found: C, 69.76; H, 6.44; S, 6.79. $C_{27}H_{30}O_5S$ (466.51) requires C, 69.50; H, 6.48; S, 6.87.

2,4,6-Tri-O-benzyl-D-galactose derivatives

Selective benzoylation of allyl 2,6-di-O-benzyl-α-D-galactopyranoside (**10**). — Compound **10** was prepared as described by Gent *et al.*[9]; p.m.r. ($CDCl_3$): τ 2.63 (ps, 10, Ph-H), 3.65–4.4 (m, 1, –CH=) 4.5–4.95 (m, 2, =CH_2), 5.07 (d, 1, $J_{1,2}$ 3 Hz, H-1), 5.33 and 5.41 (2 s, 2 ea., PhCH_2), 5.8–6.5 (m, 8, H-2,3,4,5,6,6′, OCH_2CH=), 7.07 (bs, 1, OH-4), and 7.25 (bs, 1, OH-3). A magnetically stirred solution of **10** (49.0 g, 0.12 mol) in anhydrous pyridine (450 ml) was cooled in a Dry Ice–acetone bath to −30°. Benzoyl chloride (17.35 ml, 0.151 mol), was added dropwise during 0.5 h, with exclusion of moisture, and the bath temperature was kept below −25° for an additional 0.5 h. After this period, t.l.c. (solvent A) showed one major and one

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[*] See also ref. 13.

[†] For this and further compounds of the 2,3,4-tri-O-benzyl series, the p.m.r. spectrum is described in terms of differences from the spectrum of the compound's precursor.

minor product, and traces of starting material. The mixture was treated with a few drops of water, and most of the pyridine was removed by evaporation below 40°. The remainder was diluted with water and the crude, syrupy product (62.4 g) isolated by chloroform extraction. Most of this product was used, without purification, for synthesis of **19** or its precursor **15**, as described at the end of the Experimental section.

Chromatography of a sample (4.3 g) on silica gel (solvent A) separated the product into its components. First eluted from the column was the minor component (0.7 g after crystallization from ethanol, 14% yield from **10**), which was *allyl 3,4-di-O-benzoyl-2,6-di-O-benzyl-α-D-galactopyranoside* (**12**), needles, m.p. 73–74°, $[\alpha]_D^{25}$ +113° (*c* 1.5, chloroform); p.m.r.* ($CDCl_3$): τ 1.80–2.35 (m, ~4, 2 PhCO, 2 ea), 2.4–3.1 now ~16 H (including ~6 H of PhCO), 3.6–5.0 now 6 H and 5.65–6.6 now 6 H (downfield shift of H-3,4), no O*H* signals. Found: C, 73.23; H, 5.88. $C_{37}H_{36}O_8$ (608.66) requires C, 73.01; H, 5.96.

The major component (3.16 g, 74%) was *allyl 3-O-benzoyl-2,6-di-O-benzyl-α-D-galactopyranoside* (**11**), syrup, $[\alpha]_D^{25}$ +95° (*c* 3, chloroform); p.m.r. ($CDCl_3$): τ 1.65–2.2 (m, ~2, PhCO) and 7.07 (bs, 1, D_2O exchangeable, O*H*-4), 2.25–2.95 now ~13 H, 3.60–5.05 now 5 H and 5.5–6.45 now 7 H (downfield shift of H-3). Found: C, 71.31; H, 6.27. $C_{30}H_{32}O_7$ (504.56) requires C, 71.41; H, 6.39.

Allyl 2,4,6-tri-O-benzyl-α-D-galactopyranoside (**14**). — Pure allyl 3-*O*-benzoyl-2,6-di-*O*-benzyl-α-D-galactopyranoside (**11**) (2.0 g, 4.0 mmol), freshly prepared, powdered, dry silver oxide (4.0 g), and ground Drierite (3.0 g) were stirred in dry benzene (20 ml) for 30 min in the dark at room temperature with exclusion of moisture. The mixture was then cooled to ~15°, benzyl bromide (3 ml, 25 mmol) was added, and stirring was continued for 10 h at room temperature. T.l.c. (solvent A) indicated that the reaction was complete. The mixture was filtered, the salts were washed with benzene, and the filtrate and washings were combined and evaporated. Chromatography on silica gel (solvent C) gave 1.65 g (70%) of a syrup whose p.m.r. spectrum was consistent with its formulation as *allyl 3-O-benzoyl-2,4,6-tri-O-benzyl-α-D-galactopyranoside* (**13**), $[\alpha]_D^{25}$ +72° (*c* 1, chloroform); p.m.r. ($CDCl_3$): τ 2.35–3.0 now ~18 H, 4.0–5.05 now 6 H and 5.25–6.65 now 12 H (addition of PhCH_2 and downfield shift of 1 sugar-ring H), no O*H* signal.

A few small pieces of sodium were added to the foregoing sample of **13** in 25 ml of abs. methanol, and the solution was boiled under reflux. The debenzoylation was monitored by t.l.c. (solvent C), which indicated disappearance of the starting material after 1 h. Water was added to the cooled solution, and the product was isolated by chloroform extraction. Chromatography on silica gel (solvent C) afforded the syrupy title-compound **14**; yield 1.2 g (88%); p.m.r. ($CDCl_3$): τ 7.70 (bs, 1, D_2O exchangeable, O*H*-3), no signal at 1.9–2.2, 2.63 now ps, 15 H; 3.7–5.2 now 5 H and 5.2–6.55 now 13 H (upfield shift of 1 sugar-ring H). Found: C, 73.74; H, 7.26. $C_{30}H_{34}O_6$ (490.57) requires C, 73.44; H, 6.99. Crystallization was eventually

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*For this and further compounds of the 2,4,6-tri-*O*-benzyl series the p.m.r. spectrum is described in terms of differences from the spectrum of the compound's precursor.

achieved by adding methanol to the spontaneously nucleated residue from an abandoned chloroform solution of the compound. Two recrystallizations from ether–Skellysolve B gave blades having m.p. 67–68°, $[\alpha]_D^{25}$ +62.3°, $[\alpha]_{436}^{25}$ +122.5° (*c* 0.81, chloroform).

*2,4,6-Tri-O-benzyl-*D*-galactopyranose* (**15**). — Allyl 2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (**14**, 0.4 g, 0.8 mmol) and potassium *tert*-butoxide (0.4 g) in dry methyl sulfoxide (5 ml) were heated for 20 min at 100°. At this time t.l.c. (solvent C) showed complete conversion of the starting material into 1-propenyl 2,4,6-tri-*O*-benzyl-α-D-galactopyranoside. The solution was cooled and extracted with ether, and the ether extract dried over sodium sulfate. The syrup obtained by evaporation of the ether was refluxed for 15 min in acetone (18 ml) and M hydrochloric acid (2 ml). Neutralization of the cooled mixture with 5% sodium hydrogencarbonate caused the product to separate as an oil. It was isolated by conventional chloroform extraction, crystallized from benzene–Skellysolve B, and recrystallized from methanol; yield 0.25 g (68%); m.p. 126–128°, $[\alpha]_D^{25}$ +40.3° (2 min) → +36.3° (20 h) (*c* 1, chloroform). Lit.[9] m.p. 123–124°; $[\alpha]_D$ +40.4° → +37.6°; lit.[10] m.p. 125–127°, $[\alpha]_D^{24}$ +41.7° → +39.4°. The p.m.r. spectrum ($CDCl_3$) suggested the presence of some β-anomer: τ 4.67 (d, $J_{1,2}$ 2 Hz after D_2O exchange, H-1α) only ~0.85 H; D_2O-exchangeable signal at 8.35 (~0.25 H) as well as at 6.73 (O*H*-1α) and 7.72 (O*H*-3).

*1,3-Di-O-acetyl-2,4,6-tri-O-benzyl-*D*-galactopyranose* (**16**) was prepared from **15** as already described for the conversion of **4** into **5**. The product, a colorless syrup, was a mixture of the α- and β-anomers in various proportions. One batch composed of nearly pure α-anomer had $[\alpha]_D^{25}$ +112°, $[\alpha]_{436}^{25}$ +222° (*c* 1, chloroform); p.m.r. ($CDCl_3$): τ 3.58 (d, 1, $J_{1,2}$ 3.5 Hz, H-1), 4.73 (dd, 1, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 3.0 Hz, H-3), 7.93 (s, 3, 1-COCH_3), and 8.05 (s, 3, 3-COCH_3). Samples containing β-anomer also showed τ 4.35 (d, *J* 7.5 Hz, H-1), 5.02 (dd, *J* 10.0 and 3.0 Hz, H-3), 8.00 and 8.13 (COCH_3). Found: C, 70.04; 69.17; H, 6.60, 6.20. $C_{31}H_{34}O_8$ (534.58) requires C, 69.65; H, 6.41.

*3-O-Acetyl-2,4,6-tri-O-benzyl-β-*D*-galactopyranosyl ethylxanthate* (**18**). — The foregoing diacetate (0.52 g, 0.97 mmol) was converted into *3-O-acetyl-2,4,6-tri-O-benzyl-α,β-*D*-galactopyranosyl bromide* (**17**) [p.m.r. ($CDCl_3$): τ 3.45 (d, ~0.65, $J_{1,2}$ 4.0 Hz, H-1α), 1 major COCH_3 signal at τ 8.03] and thence into the title compound as already described for the transformation **5**→**7**→**8**. Chromatography on silica gel (solvent D) afforded 0.4 g (69%) of **18**; syrup, $[\alpha]_D^{25}$ +63°, $[\alpha]_{436}^{25}$ +186° (*c* 1, chloroform); p.m.r. ($CDCl_3$): τ 4.58 (d, 1, $J_{1,2}$ 10.0 Hz, H-1), 4.95 (dd, 1, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.0 Hz, H-3), 5.05–6.55 now 13 H (addition of CH_2CH$_3$), 8.14 (s, 3, COCH_3), and 8.67 (t, 3, *J* 7.0 Hz, CH$_2$CH_3). Found: C, 64.55; H, 6.13; S, 11.07. $C_{32}H_{36}O_7S_2$ (596.74) requires C, 64.40; H, 6.08; S, 10.75.

*2,4,6-Tri-O-benzyl-1-thio-β-*D*-galactopyranose* (**19**) was prepared from **18** as already described for the conversion of **8** into **9**. The compound was crystallized from benzene–Skellysolve B and recrystallized from methanol; yield, 84%; needles, m.p. 122–122.5°, $[\alpha]_D^{25}$ +28.4°, $[\alpha]_{436}^{25}$ +61.1° (*c* 1, chloroform); $[\alpha]_D^{30}$ in 3mM methanolic hydrogen chloride (*c* 0.66) +17.8° (initial) → +79.9° (96 h); p.m.r.

($CDCl_3$): no signals from τ 3.0–5.0, 13 H from 4.85–6.6 (upfield shift of H-1 and H-3, loss of CH_2CH_3), 7.68 (d, 1, D_2O-exchangeable, J 8.0 Hz, S*H*), and 7.78 (bs, 1, D_2O-exchangeable, O*H*). Found: C, 69.64; H, 6.35; S, 6.61. $C_{27}H_{30}O_5S$ (466.58) requires C, 69.50; H, 6.48; S, 6.87.

Preparation of thio sugar **19** *from allyl 2,6-di-*O*-benzyl-α-*D*-galactopyranoside* (**10**) *with minimal purification of intermediates.* — For preparative purposes, the conversion of **10** into **19** was carried out without chromatographic purification of any of the intermediates. All operations were otherwise as just described for the successive steps. The crude product of the partial benzoylation of **10**, containing several percent of the dibenzoate **12**, was in some runs not fully benzylated after reaction with benzyl bromide and silver oxide. In these cases, the treatment was repeated with half quantities of the reagents. Debenzoylation and deallylation gave crystalline 2,4,6-tri-*O*-benzyl-D-galactose (**15**) containing some 2,6-di-*O*-benzyl-D-galactose. This product was successively converted into the diacetate (**16**), glycosyl bromide (**17**), and ethylxanthate (**18**). After saponification of the ethylxanthate, the pure thio sugar **19** was readily crystallized.

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REFERENCES

1 S. A. Holick and L. Anderson, *Carbohydr. Res.*, 34 (1974) 208–213.
2 S. A. Holick, S.-H. L. Chiu, and L. Anderson, *Carbohydr. Res.*, 50 (1976) 215–225.
3 R. Gigg and C. D. Warren, *J. Chem. Soc.*, (1965) 2205–2210.
4 T. J. Lucas and C. Schuerch, *Carbohydr. Res.*, 39 (1975) 39–45.
5 J. Gigg and R. Gigg, *J. Chem. Soc. (C)*, (1966) 82–86.
6 T. Uryu, H. Libert, J. Zachoval, and C. Schuerch, *Macromolecules*, 3 (1970) 345–349.
7 P. J. Pfäffli, S. H. Hixson, and L. Anderson, *Carbohydr. Res.*, 23 (1972) 195–206.
8 W. Schneider, R. Gille, and K. Eisfeld, *Ber.*, 61 (1928) 1244–1259.
9 P. A. Gent, R. Gigg, and R. Conant, *J. Chem. Soc. Perkin Trans. 1*, (1972) 1535–1542.
10 H. M. Flowers, *Carbohydr. Res.*, 39 (1975) 245–251.
11 J. M. Williams and A. C. Richardson, *Tetrahedron*, 23 (1967) 1369–1378.
12 J. M. Berry and G. G. S. Dutton, *Carbohydr. Res.*, 38 (1974) 339–345.
13 A. I. Vogel, *Practical Organic Chemistry*, 3rd ed., John Wiley, New York, 1956, p. 499.