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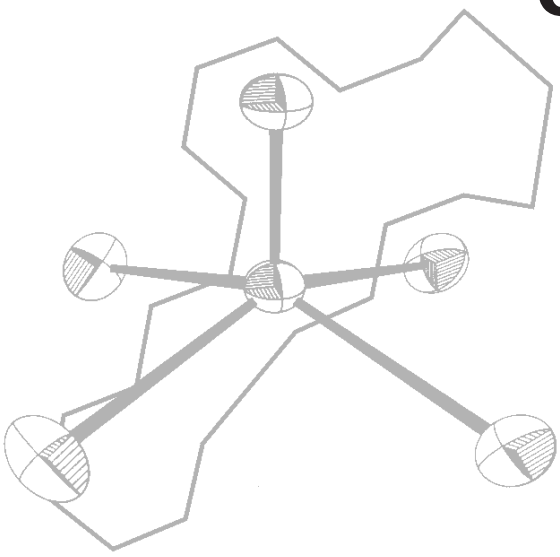

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# 1,6-Epithio- and 1,6-Episeleno-β-D-glucopyranose: Useful Adjuncts in the Synthesis of 6-Deoxy-β-D-glucopyranosides

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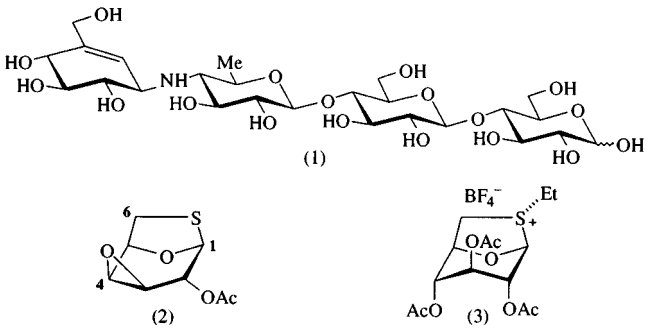
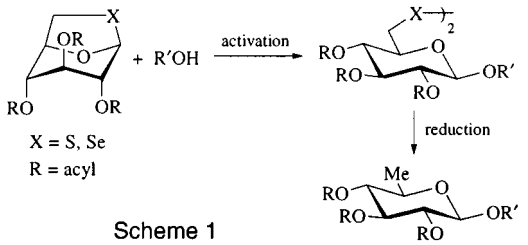
Derivatives of 1,6-dideoxy-1,6-epithio- and 1,6-dideoxy-1,6-episeleno-β-D-glucopyranose have been shown to be effective glycosyl donors toward carbohydrate alcohols under the agency of *N*-iodosuccinimide/trifluoromethanesulfonic acid. Reduction of the intermediate disulfides and diselenides affords 6-deoxy-β-D-glucopyranosides. The synthesis of a range of such 6′-deoxy disaccharide derivatives is reported.

Deoxy sugars are widely represented in Nature and, particularly, in oligosaccharides where they are frequently present as the terminal sugars necessary for mediation of recognition processes and trafficking of molecules within biological systems. Deoxy sugars such as L-fucose and L-rhamnose are present in biologically active molecules such as the $Le^a$, $Le^b$ and $Le^x$ blood group determinants[1] and sialyl $Lewis^x$,[2] as well as a range of carbohydrate-containing drugs such as the antibiotic cytovaricin and the antitumour compound calicheamycin γ[1]. Synthetic approaches to molecules such as these have been possible only recently owing to major advances in glycosidic bond-forming technology.[3,4]




Thioglycosides have gained deserved prominence as reliable glycosyl donors in the preparation of oligosaccharides.[5] Of particular appeal is the stability of thioglycosides to a broad range of reagents and conditions, making them ideal starting materials for the preparation of diversely functionalized glycosyl donors. One current interest in our laboratory is the synthesis of β-acarbose (1), a putative inhibitor of enzymes which process β-D-glucosidic linkages. One approach to the synthesis of this molecule centres on 2-*O*-acetyl-3,4-anhydro-1,6-dideoxy-1,6-epithio-β-D-galactose (2), a molecule beautifully arranged for the introduction of an amine (C 4), glycoside formation (C 1) and deoxygenation (C 6).

We have previously reported on model studies describing the introduction of nitrogen nucleophiles at C 4 into a sugar such as (2);[6] here, we disclose full details on the use of 1,6-dideoxy-1,6-epithio and 1,6-dideoxy-1,6-episeleno sugars as glycosyl donors for the synthesis of 6-deoxy sugars—the general approach is outlined in Scheme 1.[7] At this point, it is worth noting that Lundt and Skelbæk-Pedersen have reported the synthesis of the crystalline sulfonium salt (3) and have demonstrated that it has some utility as a glycosyl donor.[8] Our investigations here were aimed at taking advantage of more recent reagent systems developed for the activation of thio- and seleno-glycosides.[9]




Scheme 1

The 1,6-dideoxy-1,6-epithio sugar (4) was prepared according to known methods.[6] Initially, treatment of a mixture of the epithio sugar (4) and the commercially available alcohol (5) with *N*-iodosuccinimide/trifluoromethanesulfonic acid afforded only the acetate (6), in poor yield. To test the viability of our glycosylation procedure, the ethylthio D-glucoside (7) was treated in an identical manner to that above

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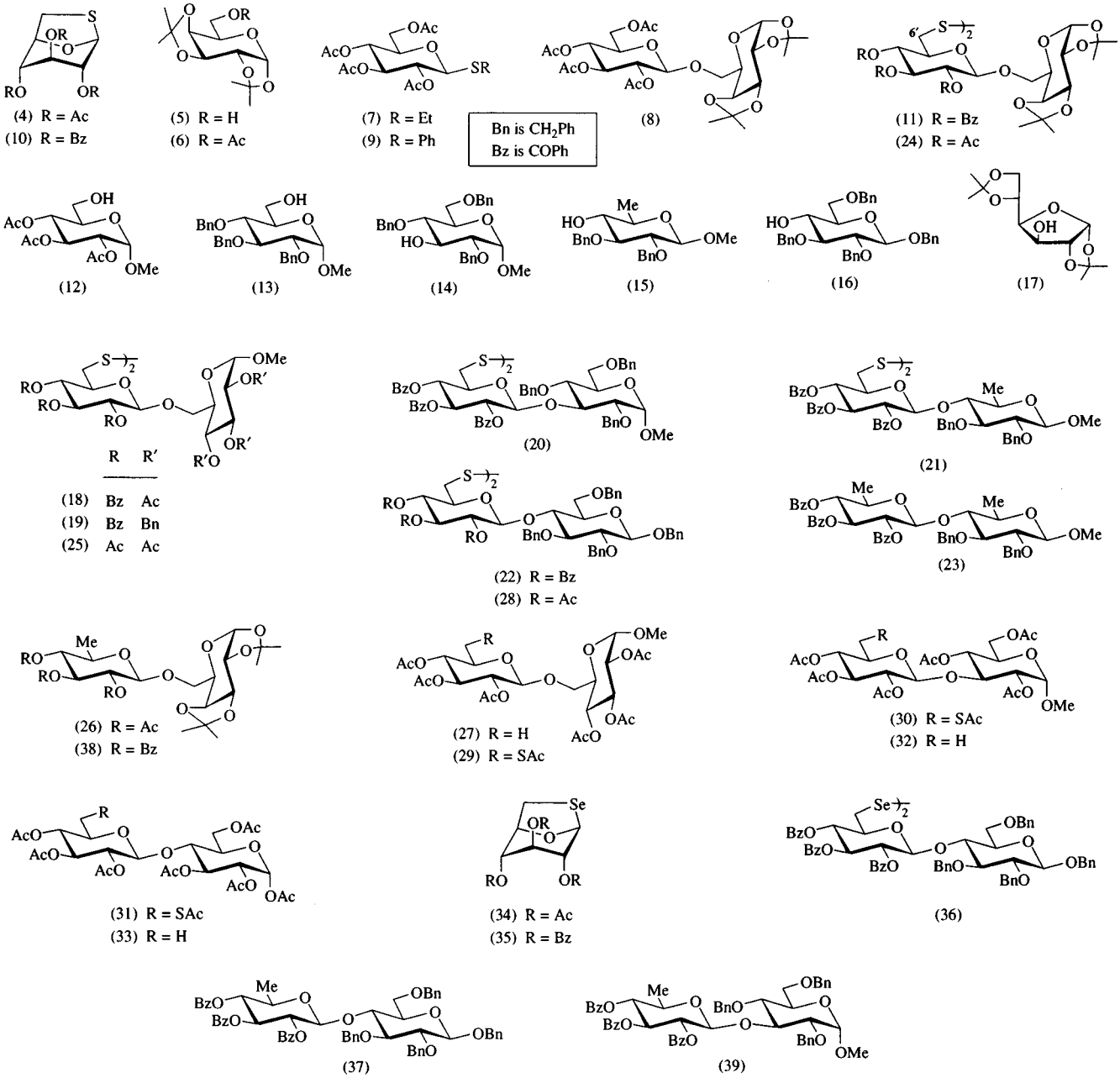
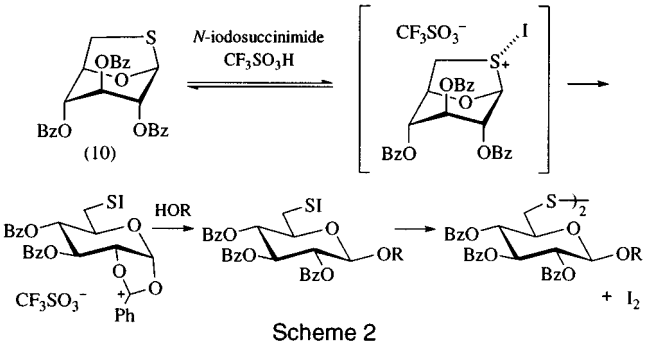
with the same alcohol (5). In our hands, the disaccharide (8) and the acetate (6) were formed, each in 32% yield. Furthermore, the phenylthio D-glucoside (9) was no more successful as a glycosyl donor, again affording both the disaccharide (8) and the acetate (6) in yields of 42% and 32%, respectively. The acetate (6) presumably arose from acetyl transfer from the donors to the alcohol (5). Transesterification of this sort has previously been noted with a number of acetylated glycosyl donors, such as glycosyl bromides[10] and thioglycosides.[11,12] In the case of the silver triflate-promoted reaction of tetra-*O*-acetyl-$\alpha$-D-galactopyranosyl bromide with methyl 2,4,6-tri-*O*-benzoyl-$\beta$-D-galactoside, a labelled donor was used to show that the acetyl group transferred to the acceptor originated from O 2 of the donor.[10] Despite such well established literature precendents, the observed transesterification nevertheless contrasts with the work of Fraser-Reid and coworkers who were able to effect glycosylation of the alcohol (5) with the acetylated donor (9) under the agency of *N*-iodosuccinimide/trifluoromethanesulfonic acid to afford (8) in 89% yield.[13] In both cases, our yields of the disaccharide (8) were substantially less than that quoted by Fraser-Reid and coworkers and the reactions were complicated by the formation of the acetate (6).

It is well known that benzoyl groups at O 2 direct 1,2-*trans*-glycosylation and, moreover, are less susceptible to transfer to an acceptor alcohol.[14] In addition, we were encouraged by our recent, successful work that used benzoylated thio-, seleno- and telluro-$\beta$-D-glucosides as glycosyl donors.[15] Therefore, the tribenzoate (10)



was prepared by treatment of the triacetate (4) with sodium methoxide in methanol and, subsequently, benzoyl chloride in pyridine.

Gratifyingly, treatment of a mixture of the tribenzoate (10) and the alcohol (5) with *N*-iodosuccinimide/trifluoromethanesulfonic acid afforded the disulfide (11) in an excellent yield. The identity of the disulfide (11) was supported by high-resolution mass spectrometry and by the presence of a signal at $\delta$ 40·63 in the $^{13}$C n.m.r. spectrum, assigned to C 6′. A rationale for the formation of the disulfide is presented in Scheme 2.




Scheme 2

To explore the generality of this reaction the alcohols (12),[16] (13),[17] (14),[18] (15),[19] (16)[20] and (17) were treated with the tribenzoate (10) in a manner similar to that above—the results of these reactions are presented in Table 1. Some aspects of these results deserve comment. Firstly, the only alcohol shown to be unreactive to the donor (10) was the di-*O*-isopropylidene-α-D-glucofuranose (17), a notoriously unreactive acceptor. Secondly, the yield of these glycosylations was dependent upon the scale of the reaction, with the best results being obtained on a larger scale—presumably, the variation in yield was due to a constant amount of adventitious water, the effect of which diminished with increasing scale.

**Table 1. Glycosylation reactions of the donors (4) and (10) with a range of carbohydrate alcohols**

| Reactants | Disulfide | | Reactants | Disulfide | |
|---|---|---|---|---|---|
| (4)+(5) | — | 0%[A] | (10)+(14) | (20) | 69% |
| (10)+(5) | (11) | 76% | (15) | (21) | 63% |
| (12) | (18) | 92% | (16) | (22) | 82% |
| (13) | (19) | 51% | (17) | — | 0% |

[A] Only the acetylated acceptor (6) was isolated.

The reductive desulfurization of these compounds was the next step to be investigated. Raney nickel is well known for its selective ability to remove sulfur from organosulfur compounds; however, treatment of the disulfides (11) and (18)–(22) with Raney nickel in ethanol was disappointing. Only the disulfide (21) was readily reduced by Raney nickel, affording the dideoxy sugar (23) in good yield (Table 2; method *A*). Chromatographic evidence (t.l.c.) otherwise was indicative of the formation of highly polar compounds—such compounds may have resulted from debenzoylation of the substrates, caused by basic residues present in the Raney nickel, under the prolonged treatment required for the desulfurization of the apparently unreactive disulfides. Alternatively, in the case of the disulfides (19), (20) and (22), some reductive debenzylation may have occurred. In a more successful approach, the disulfides (11) and (18) were deacylated by treatment with sodium methoxide in methanol and then acetylated to give the acetates (24) and (25), respectively. These compounds, upon treatment with Raney nickel in ethanol, rapidly and reliably gave the 6-deoxy-β-D-glucosides (26) and (27) (Table 2; method *B*).

**Table 2. Preparation of the various 6-deoxy-β-D-glucopyranosides**

Method *A*: Raney nickel, EtOH. Method *B*: (i) NaOMe, MeOH; (ii) $Ac_2O$, pyridine; (iii) Raney nickel, EtOH. Method *C*: (i) NaOMe, MeOH; (ii) Na, $NH_3$, tetrahydrofuran; (iii) $Ac_2O$, pyridine; (iv) Raney nickel

| Method used | Disulfide treated | Thioacetate/ disulfide | | 6-Deoxy-β-D-glucoside | |
|---|---|---|---|---|---|
| *B* | (11) | (24) | 81% | (26) | 69% |
| *B* | (18) | (25) | 77% | (27) | 75% |
| *C* | (19) | (29) | 60% | (27) | 67% |
| *C* | (20) | (30) | 57% | (32) | 85% |
| *A* | (21) | — | — | (23) | 84% |
| *C* | (22) | (31) | 59% | (33) | 85% |

Buoyed by these results, we converted the disulfide (22) into the acetate (28), and treated the acetate with Raney nickel in ethanol; however, again and disappointingly, a slow conversion into the deoxy sugar and a poor mass return was evident. Therefore, the remaining three compounds (19), (20) and (22) were debenzoylated, then treated with sodium in liquid ammonia and acetylated to afford the thioacetates (29), (30) and (31), respectively. Upon treatment with Raney nickel in ethanol, all three compounds cleanly afforded the various 6-deoxy-β-D-glucosides in good yield (Table 2; method *C*).

The preparation of hepta-*O*-acetyl-6′-deoxy-α-cellobiose (33) by acetolysis of methyl hepta-*O*-acetyl-6′-deoxy-β-cellobioside has been described by Ježo and Zemek.[21] However, the melting point and optical rotation reported for their material {m.p. 185–186° ($CHCl_3$/petrol), $[\alpha]_D$ +25·3° ($CHCl_3$)} do not agree with the values obtained here {m.p. 225·5–226° (EtOH), $[\alpha]_D$ +57·7° ($CHCl_3$)}. On the basis of a doublet at $\delta$ 6·22 ($J$ 3·8 Hz) in the $^1$H n.m.r. spectrum being assigned to H 1, the compound here was assigned the α-configuration. Ježo and Zemek fail to report any n.m.r. data for their material and it would appear likely that they, in fact, isolated the β-anomer, hepta-*O*-acetyl-6′-deoxy-β-cellobiose.

The results presented above for the desulfurization of the various disulfides are difficult to rationalize. In all cases, the Raney nickel was used within 1 month of preparation and thus retained high activity. The

disulfide (21) possesses both benzoyl and benzyl groups, yet was converted rapidly and in high yield into the dideoxy D-glucoside (23) upon treatment with Raney nickel. The remaining compounds were recalcitrant and required quite extensive manipulation to enable desulfurization.

The mixed and somewhat disappointing results in the glycosylation studies with the 1,6-dideoxy-1,6-epithio sugars (4) and (10) prompted investigations into glycosylations with 1,6-dideoxy-1,6-episeleno sugars. In a fashion similar to that of before, a solution of tri-*O*-acetyl-1,6-dideoxy-1,6-episeleno-$\beta$-D-glucopyranose (34)[6] and the di-*O*-isopropylidene-$\alpha$-D-galactose (5) was treated with *N*-iodosuccinimide/trifluoromethanesulfonic acid, to afford a mixture from which only the acetate (6) could be isolated. As before, protecting group exchange from acetyl to benzoyl afforded the tribenzoate (35). The tribenzoate (35) was treated with the alcohol (16) under the now standard conditions to afford, in an acceptable yield (54%), the diselenide (36).

The carbon–selenium bond is considerably weaker than the carbon–sulfur bond, and, consequently, allows for milder reagents to effect its reduction. Thus, the diselenide (36) was treated with tributylstannane and $\alpha,\alpha'$-azobisisobutyronitrile at reflux in toluene, resulting in the rapid and clean conversion into the 6-deoxy sugar (37) in an excellent yield (94%).

**Table 3. Glycosylation reactions of the donors (34) and (35) with a range of carbohydrate alcohols**

| Reactants used | 6-Deoxy-$\beta$-D-glucoside | | Reactants used | 6-Deoxy-$\beta$-D-glucoside | |
|---|---|---|---|---|---|
| (34)+(5) | — | 0%[A] | (35)+(14) | (39) | 55% |
| (35)+(5) | (38) | 73% | (16) | (37) | 64% |
| | | | (17) | — | 0% |

[A] Only the acetylated acceptor (6) was isolated.

The reduced yield of the glycosylation to form the diselenide (36), compared to the analogous disulfide (22), and the formation of very polar compounds (as shown by t.l.c.) believed to contain selenium prompted an approach involving the direct reduction of the reaction mixture after workup. Now, the tribenzoate (35) was treated with the alcohols (5), (14) and (16) as above to afford a mixture which, after aqueous workup, was treated directly with tributylstannane to provide the 6-deoxy-$\beta$-D-glucosides (38), (39) and (37), respectively, in excellent overall yields (Table 3). Unfortunately, but not entirely surprisingly, the treatment of a solution of the donor (35) and the alcohol (17) with *N*-iodosuccinimide/trifluoromethanesulfonic acid afforded no products of glycosylation.

## Experimental

General experimental procedures have been given previously.[22]

Raney nickel (W4) was prepared according to the procedure of Augustine and used within 1 month of preparation.[23]

### Epithio and Episeleno Sugars (10) and (35)

*2,3,4-Tri-*O*-benzoyl-1,6-dideoxy-1,6-epithio-$\beta$-D-glucose (10)*

2,3,4-Tri-*O*-acetyl-1,6-dideoxy-1,6-epithio-$\beta$-D-glucose (4)[6] (2·5 g, 8·2 mmol) was suspended in dry MeOH (25 ml) at room temperature and a small piece of sodium metal added. The mixture was stirred for 90 min and then resin (Dowex 50, $H^+$) was added until the solution became neutral. The mixture was filtered and evaporated under reduced pressure, then water (20 ml) was added. The water was evaporated and the residue freeze-dried to give a white powder. The solid was suspended in dry $CH_2Cl_2$ (10 ml) and dry pyridine (2·5 ml) and the suspension was treated with benzoyl chloride (4·0 ml, 4·8 g, 35 mmol) at 0° for 1 h and then stirred at room temperature for 4 h. T.l.c. analysis indicated complete conversion into a lower polarity compound. Water (1 ml) was added and the mixture was stirred for 20 min. The mixture was treated to the usual workup ($CH_2Cl_2$) to give an oil. The oil was taken up in ether and crystallization ensued upon the addition of petrol, affording the *tribenzoate* (10) as white cubes (3·60 g, 89%), m.p. 170–173° ($Et_2O$/petrol), $[\alpha]_D$ −31·2° (Found: C, 66·3; H, 4·7. $C_{27}H_{22}O_7S$ requires C, 66·1; H, 4·5%). $^1$H n.m.r. (300 MHz) $\delta$ 3·31, dd, $J_{5,6}$ 6·7, $J_{6,6}$ 10·2 Hz, H 6; 3·42, d, $J_{5,6} \approx 0$ Hz, H 6; 5·03–5·10, m, H 4,5; 5·16, m, H 2; 5·57, m, H 3; 5·77, br s, H 1; 7·38–8·15, m, 15H, Ph. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 53·94, C 6; 68·91, 71·66, 73·44, 78·92, 81·69, C 1,2,3,4,5; 128·42–129·98, 133·50, 133·57, Ph; 164·95, 165·34, 165·53, 3C, CO.

*2,3,4-Tri-*O*-benzoyl-1,6-dideoxy-1,6-episeleno-$\beta$-D-glucose (35)*

2,3,4-Tri-*O*-acetyl-1,6-dideoxy-1,6-episeleno-$\beta$-D-glucose (34)[6] (6·58 g, 18·8 mmol) was treated in the same manner as for the triacetate (4), yielding the *tribenzoate* (35) as colourless needles (7·09 g, 70%) in two crops, m.p. 175–176° ($CH_2Cl_2$/petrol), $[\alpha]_D$ −47·0° (Found: C, 60·1; H, 4·0. $C_{27}H_{22}O_7Se$ requires C, 60·3; H, 4·1%). $^1$H n.m.r. (300 MHz) $\delta$ 3·11–3·36, m, H 6; 3·61, br d, $J_{5,6}$ 9·4 Hz, H 6; 5·09, dd, $J_{3,4}$ 4·9, $J_{4,5}$ 1·9 Hz, H 4; 5·11, br d, H 5; 5·31, d, $J_{2,3}$ 3·7 Hz, H 2; 5·69, dd, H 3; 6·11, br s, H 1; 7·37–8·10, m, 15H, Ph. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 30·18, C 6; 68·89, 72·63, 75·17, 77·07, 80·70, C 1,2,3,4,5; 128·45–129·91, 133·43, Ph; 165·07, 165·47, 165·61, 3C, CO.

### Glycosylations with the Epithio and Episeleno Sugars

*Representative Procedures*

*(a)* A solution of *N*-iodosuccinimide (63 mg, 0·28 mmol) and trifluoromethanesulfonic acid (2–10 $\mu$l, 0·02–0·1 mmol) in dry $Et_2O$/1,2-dichloroethane (1 : 1, 4 ml) at 0° was added to a solution of the donors (4), (7), (10), (34) or (35) (0·24 mmol) and acceptor (0·20 mmol) in dry 1,2-dichloroethane (2 ml) at 0°. After completion of the reaction (t.l.c.), the solution was quenched with saturated aqueous $NaHCO_3$ (1 ml) and aqueous $Na_2S_2O_3$ (10%, 1 ml), the organic layer was separated, dried, the solvent evaporated and the residue purified by flash chromatography to give the various products.

*(b)* In the case of the 1,6-episeleno donor (35), after glycosylation and workup as in *(a)*, the crude residue was dissolved in dry toluene (4 ml) and treated with $Bu_3SnH$ (160 $\mu$l, 0·60 mmol) and $\alpha,\alpha'$-azobisisobutyronitrile (1 mg) at reflux. After completion of the reaction (t.l.c.), the solvent was evaporated and the residue partitioned between MeCN and petrol. The MeCN layer was separated and evaporated and the residue subjected to flash chromatography to give the various 6-deoxy-$\beta$-D-glucopyranosides.

*6-O-Acetyl-1,2:3,4-di-O-isopropylidene-α-D-galactose (6) and 1,2:3,4-Di-O-isopropylidene-6-O-(tetra-O-acetyl-β-D-glucosyl)-α-D-galactose (8)*

*(a)* Ethyl tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (7)[24,25] (470 mg, 1·20 mmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (5) (2·8 ml of 0·35 M in 1,2-dichloroethane, 1·0 mmol) were treated as described in procedure *(a)* above to give, after flash chromatography (25–40% EtOAc/petrol), the acetate (6) as a syrup (109 mg, 32%). This material gave an identical $^1$H n.m.r. (300 MHz) spectrum to the material prepared as outlined below.

Next to elute was the disaccharide (8) as a foam (186 mg, 32%). This material gave an identical $^1$H n.m.r. (300 MHz) spectrum to the material prepared as outlined below.

*(b)* Phenyl tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (9)[24,25] (440 mg, 1·00 mmol), 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (5) (3·1 ml of 0·362 M in $CH_2Cl_2$, 1·10 mmol), *N*-iodosuccinimide (270 mg, 1·2 mmol) and powdered molecular sieves (4 Å, 1 g) were suspended in dry $CH_2Cl_2$ (3 ml) at −5° under $N_2$. Trifluoromethanesulfonic acid (200 μl of 0·15 M in $CH_2Cl_2$, 0·03 mmol) was added, whereupon the suspension turned deep purple over 3 min. T.l.c. indicated the disappearance of the starting material, so saturated aqueous sodium bicarbonate solution (1 ml) and aqueous sodium thiosulfate solution (1 ml of 0·5 M) were added. The mixture was filtered, diluted with $CH_2Cl_2$ and the organic phase washed with saturated aqueous $NaHCO_3$, aqueous $Na_2S_2O_3$ and brine, then dried. The solvent was evaporated and the residue purified by flash chromatography (25–40% EtOAc/petrol) to give the acetate (6) as a white, crystalline solid (96 mg, 32%). This material crystallized as white needles, m.p. 109–110° (EtOH/$H_2O$; lit.[26] 109–110°), $[\alpha]_D$ −47·2° (lit.[26] −47·2°).

Next to elute was the disaccharide (8) as a white, crystalline solid (245 mg, 42%). This material crystallized as white needles, m.p. 140–141° (EtOH; lit.[14] 140–141°), $[\alpha]_D$ −58·2° (lit.[14] −56°).

*6-O-Acetyl-1,2:3,4-di-O-isopropylidene-α-D-galactose (6)*

*(a)* The triacetate (4) (168 mg, 554 μmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (5) (120 mg, 462 μmol) were treated as described in procedure *(a)* above to give, after flash chromatography (30–50% EtOAc/petrol), the unreacted triacetate (4) (12 mg).

Next to elute was the acetate (6) as a syrup (50 mg, 35%). This material gave an identical $^1$H n.m.r. (300 MHz) spectrum to the material prepared as outlined above. Finally, also recovered was some unreacted alcohol (5) (9 mg).

*(b)* The triacetate (34) (143 mg, 407 μmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (5) (88 mg, 340 μmol) were treated as described in procedure *(a)* above to give, after flash chromatography (25–50% EtOAc/petrol), the acetate (6) as a syrup (13 mg, 20% based on the alcohol consumed). This material gave an identical $^1$H n.m.r. (300 MHz) spectrum to the material prepared as outlined above.

Next to elute was some unreacted alcohol (5) (23 mg).

*6,6′-O-[6,6′-Dithiobis(2,3,4-tri-O-benzoyl-6-deoxy-β-D-glucosyl)]bis(1,2:3,4-di-O-isopropylidene-α-D-galactose) (11)*

The tribenzoate (10) (319 mg, 651 μmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (5) (141 mg, 542 μmol) were treated as described in procedure *(a)* above to give, after flash chromatography (5–15% EtOAc/toluene), the *disulfide* (11) as a syrup (311 mg, 76%), $[\alpha]_D$ +14·2° (Found: C, 62·1; H, 5·8; S, 4·4. $C_{78}H_{82}O_{26}S_2$ requires C, 62·5; H, 5·5; S, 4·3%). $^1$H n.m.r. (500 MHz) δ 1·19, 1·26, 1·42, 3s, 12H, Me; 2·88–2·99, 2H, m, H6′; 3·82, dd, $J_{5,6}$ 6·9, $J_{6,6}$ 10·9 Hz, H6; 3·87, ddd, $J_{4,5}$ 1·8, $J_{5,6}$ 4·4 Hz, H5; 3·97–4·00, m, H5′; 4·01, dd, H6; 4·15, dd, $J_{3,4}$ 7·9 Hz, H4; 4·20, dd, $J_{1,2}$ 5·0, $J_{2,3}$ 2·4 Hz, H2; 4·46, dd, H3; 4·90, d, $J_{1',2'}$ 7·9 Hz, H1′; 5·33, dd, $J_{3',4'}$ 9·6, $J_{4',5'}$ 9·6 Hz, H4′; 5·41, d, H1; 5·44, dd, $J_{2',3'}$ 9·6 Hz, H2′; 5·79, dd, H3′; 7·22–7·97, m, 15H, Ph. $^{13}$C n.m.r. (125·8 MHz) δ 24·42, 24·83, 25·66, 25·97, 4C, Me; 40·63, C6′; 67·43, C5; 68·32, C6; 70·33, C2; 70·53, C3; 70·95, C4; 71·80, C2′; 72·05, C4′; 72·85, C3′; 72·96, C5′; 96·12, C1; 101·22, C1′; 108·41, 109·33, 2C, **C**Me$_2$; 128·13–129·93, 132·95–133·51, Ph; 165·06, 165·34, 165·66, 3C, CO. High-resolution mass spectrum (f.a.b.) *m/z* 1498·01 [$C_{78}H_{82}O_{26}S_2$ ($M^{+\bullet}$) requires 1498·45].

*Dimethyl 6,6′-O-[6,6′-Dithiobis(2,3,4-tri-O-benzoyl-6-deoxy-β-D-glucosyl)]bis(2,3,4-tri-O-acetyl-α-D-glucoside) (18)*

The tribenzoate (10) (500 mg, 1·02 mmol) and methyl 2,3,4-tri-*O*-acetyl-α-D-glucoside (12)[16] (272 mg, 0·849 mmol) were treated as described in procedure *(a)* above to give, after flash chromatography (40–45% EtOAc/petrol), the *disulfide* (18) as a glass (631 mg, 92%), $[\alpha]_D$ +74·3° (Found: C, 59·1; H, 5·3. $C_{80}H_{82}O_{32}S_2$ requires C, 59·3; H, 5·1%). $^1$H n.m.r. (300 MHz) δ 1·93, 1·97, 2·00, 3s, 9H, Ac; 2·88–2·93, m, 2H, H6′; 2·96, s, OMe; 3·60, dd, $J_{5,6}$ 7·0, $J_{6,6}$ 10·9 Hz, H6; 3·87–4·00, m, H5,6,5′; 4·66, d, $J_{1,2}$ 3·6 Hz, H1; 4·71, dd, $J_{2,3}$ 10·0 Hz, H2; 4·80, d, $J_{1',2'}$ 7·9 Hz, H1′; 4·83, t, $J_{3,4} \approx J_{4,5}$ 9·7 Hz, H4; 5·33, dd, $J_{3',4'}$ 9·6, $J_{4',5'}$ 9·6 Hz, H4′; 5·38, dd, H3; 5·45, dd, $J_{2',3'}$ 7·9 Hz, H2′; 5·79, dd, H3′; 7·23–7·55, 7·77–7·94, 2m, 15H, Ph. $^{13}$C n.m.r. (75·5 MHz) δ 20·55, CO**Me**; 40·83, C6′; 54·74, OMe; 68·19, 69·02, 69·98, 70·74, 71·76, 71·98, 72·55, 73·16, C2,3,4,5,2′,3′,4′,5′; 68·47, C6; 96·00, C1; 101·24, C1′; 128·18–129·70, 133·07, 133·55, Ph; 164·97, 165·28, 165·60, 3C, **C**OPh; 169·65, 169·90, 169·96, 3C, **C**OMe. High-resolution mass spectrum (f.a.b.) *m/z* 1617·9960 [$C_{80}H_{82}O_{32}S_2$ ($M^{+\bullet}$) requires 1618·4229].

*Dimethyl 6,6′-O-[6,6′-Dithiobis(2,3,4-tri-O-benzoyl-6-deoxy-β-D-glucosyl)]bis(2,3,4-tri-O-benzyl-α-D-glucoside) (19)*

The tribenzoate (10) (127 mg, 257 μmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucoside (13)[17] (100 mg, 216 μmol) were treated as described in procedure *(a)* above to give, after flash chromatography (5% EtOAc/toluene), the *disulfide* (19) as a syrup (105 mg, 51%), $[\alpha]_D$ +51·8° (Found: C, 69·2; H, 5·6. $C_{110}H_{106}O_{26}S_2$ requires C, 69·2; H, 5·6%). $^1$H n.m.r. (500 MHz) δ 2·83, dd, $J_{5',6'}$ 2·8, $J_{6',6'}$ 14·2 Hz, H6′; 2·92, dd, $J_{5',6'}$ 8·8 Hz, H6′; 3·24, s, Me; 3·41, t, $J_{3,4} \approx J_{4,5}$ 9·4 Hz, H4; 3·45, dd, $J_{1,2}$ 3·5, $J_{2,3}$ 9·6 Hz, H2; 3·68–3·72, m, H5; 3·76, dd, $J_{5,6}$ 3·8, $J_{6,6}$ 10·3 Hz, H6; 3·89, dd, H3; 3·91, dd, $J_{4',5'}$ 9·3 Hz, H5′; 4·18, dd, $J_{5,6}$ 1·4 Hz, H6; 4·25–4·90, m, 6H, C**H**$_2$Ph; 4·53, d, H1; 4·69, d, $J_{1',2'}$ 7·8 Hz, H1′; 5·32, dd, $J_{3',4'}$ 9·6 Hz, H4′; 5·51, dd, $J_{2',3'}$ 9·8 Hz, H2′; 5·79, dd, H3′; 7·00–7·53, 7·77, 7·88, 2m, Ph. $^{13}$C n.m.r. (125·8 MHz) δ 40·58, C6′; 55·05, Me; 68·08, C6; 69·31, C5; 71·78, C2′; 71·99, C4′; 72·65, C3′; 73·16, C5′; 73·38, 74·61, 75·50, 3C, **C**H$_2$Ph; 77·14, C4; 79·69, C2; 81·86, C3; 99·97, C1; 100·88, C1′; 127·42–129·87, 133·11–133·64, 138·15, 138·78, Ph; 164·86, 165·34, 165·73, 3C, CO. Mass spectrum (f.a.b.) *m/z* 1906 (very weak) [$C_{110}H_{106}O_{26}S_2$ ($M^{+\bullet}$) requires 1906].

*Dimethyl 3,3′-O-[6,6′-Dithiobis(2,3,4-tri-O-benzoyl-6-deoxy-β-D-glucosyl)]bis(2,4,6-tri-O-benzyl-α-D-glucoside) (20)*

The tribenzoate (10) (89 mg, 181 μmol) and methyl 2,4,6-tri-*O*-benzyl-α-D-glucoside (14) (70 mg, 151 μmol) were treated as described in procedure *(a)* above to give, after flash chromatography (5% EtOAc/toluene), the *disulfide* (20) as a clear syrup (99 mg, 69%), $[\alpha]_D$ +13·8° (Found: C, 69·4; H, 5·7. $C_{110}H_{106}O_{26}S_2$ requires C, 69·2; H, 5·6%). $^1$H n.m.r. (300 MHz) δ 2·57, dd, $J_{5',6'}$ 7·6, $J_{6',6'}$ 14·1 Hz, H6′; 2·74, dd, $J_{5',6'}$ 3·1 Hz, H6′; 3·24, s, Me; 3·30, dd, $J_{1,2}$ 3·5, $J_{2,3}$ 9·6

Hz, H 2; 3·54–3·75, m, 4H, H 4,5,6; 3·95, ddd, $J_{4',5'}$ 10·1 Hz, H 5′; 4·07–5·12, m, 6H, C**H**$_2$Ph; 4·25, d, H 1; 4·34, t, $J_{2,3} \approx J_{3,4}$ 9·3 Hz, H 3; 5·33, dd, $J_{3',4'} \approx J_{4',5'}$ 9·6 Hz, H 4′; 5·39, d, $J_{1',2'}$ 7·9 Hz, H 1′; 5·54, dd, $J_{2',3'}$ 9·9 Hz, H 2′; 5·85, dd, H 3′; 7·00–8·01, m, Ph. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 40·50, C 6′; 54·92, Me; 68·49, C 6; 69·37, 72·05, 72·58, 73·00, 75·24, 79·18, 80·79, 8C, C 2,3,4,5,2′,3′,4′,5′; 73·41, 73·77, 74·27, 3C, **C**H$_2$Ph; 97·73, C 1; 100·59, C 1′; 127·24–129·77, 133·14, 133·31, 137·90–138·86, Ph; 165·13, 165·24, 165·70, 3C, CO. High-resolution mass spectrum (f.a.b.) *m/z* 1907·40 [$C_{110}H_{107}O_{26}S_2$ $(M+H)^{+\bullet}$ requires 1906·64].

*Dimethyl 4,4′-*O*-[6,6′-Dithiobis(2,3,4-tri-*O*-benzoyl-6-deoxy-β-*D*-glucosyl)]bis(2,3-di-*O*-benzyl-6-deoxy-β-*D*-glucoside) (21)*

The tribenzoate (10) (165 mg, 335 μmol) and methyl 2,3-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (15)[19] (100 mg, 279 μmol) were treated as described in procedure *(a)* above to give, after flash chromatography (5% EtOAc/toluene), the *disulfide* (21) as a clear oil (149 mg, 63%) which crystallized as flakes, m.p. 116–119° ($CH_2Cl_2$/petrol), $[\alpha]_D$ +60·5° (Found: C, 68·2; H, 5·5. $C_{96}H_{94}O_{24}S_2$ requires C, 68·1; H, 5·5%). $^1$H n.m.r. (500 MHz) $\delta$ 1·22, d, $J_{5,6}$ 6·2 Hz, 3H, H 6; 2·46, dd, $J_{5',6'}$ 7·5, $J_{6',6'}$ 14·2 Hz, H 6′; 2·59, dd, $J_{5',6'}$ 3·1 Hz, H 6′; 3·29, dq, $J_{4,5}$ 9·4 Hz, H 5; 3·42, dd, $J_{1,2}$ 7·9, $J_{2,3}$ 9·1 Hz, H 2; 3·51, s, OMe; 3·52, dd, $J_{3,4}$ 9·3 Hz, H 4; 3·63, dd, H 3; 3·81, ddd, $J_{4',5'}$ 9·6 Hz, H 5′; 4·25, d, $J_{1',2'}$ 7·8 Hz, H 1′; 4·69–5·06, m, 4H, C**H**$_2$Ph; 5·03, d, H 1; 5·29, dd, $J_{3',4'} \approx J_{4',5'}$ 9·6 Hz, H 4′; 5·48, dd, $J_{2',3'}$ 9·9 Hz, H 2′; 5·77, dd, H 3′; 7·16–7·55, 7·78–7·98, 2m, Ph. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 17·69, C 6; 40·11, C 6′; 56·87, OMe; 70·55, C 5; 71·70, C 4′; 72·63, C 2′; 72·92, C 5′; 72·94, C 3′; 74·59, 74·66, 2C, **C**H$_2$Ph; 82·12, C 2; 82·23, C 3; 82·92, C 4; 100·57, C 1′; 104·19, C 1; 127·00–129·63, 133·10–133·43, 138·54, 139·34, Ph; 164·89, 165·15, 165·63, 3C, CO.

*Dibenzyl 4,4′-*O*-[6,6′-Dithiobis(2,3,4-tri-*O*-benzoyl-6-deoxy-β-*D*-glucosyl)]bis(2,3,6-tri-*O*-benzyl-β-*D*-glucoside) (22)*

The tribenzoate (10) (436 mg, 888 μmol) and benzyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (16)[20] (400 mg, 741 μmol) were treated as described in procedure *(a)* above to give, after flash chromatography (5% EtOAc/toluene), the *disulfide* (22) as a syrup (623 mg, 82%), $[\alpha]_D$ +28·3° (Found: C, 71·0; H, 5·5. $C_{122}H_{114}O_{26}S_2$ requires C, 71·1; H, 5·6%). $^1$H n.m.r. (500 MHz) $\delta$ 2·40, dd, $J_{5',6'}$ 8·1, $J_{6',6'}$ 14·3 Hz, H 6′; 2·56, dd, $J_{5',6'}$ 2·7 Hz, H 6′; 3·24, m, H 5; 3·54, dd, $J_{1,2}$ 7·7, $J_{2,3}$ 9·1 Hz, H 2; 3·60, dd, $J_{3,4}$ 8·8 Hz, H 3; 3·61, dd, $J_{5,6}$ 1·8, $J_{6,6}$ 10·9 Hz, H 6; 3·71, dd, $J_{5,6}$ 3·6 Hz, H 6; 3·77, ddd, $J_{4',5'}$ 9·5 Hz, H 5′; 4·13, dd, $J_{4,5}$ 9·7 Hz, H 4; 4·41–5·06, m, 8H, C**H**$_2$Ph; 4·44, d, H 1; 4·85, d, $J_{1',2'}$ 8·0 Hz, H 1′; 5·20, dd, $J_{3',4'}$ 9·5 Hz, H 4′; 5·40, dd, $J_{2',3'}$ 9·8 Hz, H 2′; 5·60, dd, H 3′; 7·19–7·93, m, Ph. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 39·68, C 6′; 67·58, 70·83, 73·61, 74·72, 74·87, 5C, C 6, **C**H$_2$Ph; 71·98, 72·45, 72·80, 72·99, 74·37, 76·58, 81·60, 82·42, C 2,3,4,5,2′,3′,4′,5′; 99·66, C 1′; 102·44, C 1; 127·01–129·63, 133·05–133·43, 137·53–139·46, Ph; 164·73, 165·19, 165·56, 3C, CO. High-resolution mass spectrum (f.a.b.) *m/z* 2059·494 [$C_{122}H_{114}O_{26}S_2$ $(M^{+\bullet})$ requires 2058·704].

*Dibenzyl 4,4′-*O*-[6,6′-Diselenobis(2,3,4-tri-*O*-benzoyl-6-deoxy-β-*D*-glucosyl)]bis(2,3,6-tri-*O*-benzyl-β-*D*-glucoside) (36)*

The tribenzoate (35) (238 mg, 443 μmol) and benzyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (16) (200 mg, 370 μmol) were treated as described in procedure *(a)* above to give, after flash chromatography (0–5% EtOAc/toluene), the *diselenide* (36) as a yellow oil (214 mg, 54%), $[\alpha]_D$ +49·9° (Found: C, 67·9; H, 5·3. $C_{122}H_{114}O_{26}Se_2$ requires C, 68·0; H, 5·3%). $^1$H n.m.r. (300 MHz) $\delta$ 2·64, dd, $J_{5',6'}$ 8·5, $J_{6',6'}$ 13·0 Hz, H 6′; 2·74, dd, $J_{5',6'}$ 3·2 Hz, H 6′; 3·18–3·24, m, H 5; 3·43–3·71, m, 5H, H 2,3,6,5′; 4·08, t, $J_{3,4} \approx J_{4,5}$ 9·2 Hz, H 4; 4·38–5·02, m, 8H, C**H**$_2$Ph; 4·41, d, $J_{1,2}$ 7·2 Hz, H 1; 4·80, d, $J_{1',2'}$ 7·9 Hz, H 1′; 5·18, dd, $J_{3',4'}$ 9·6, $J_{4',5'}$ 9·6 Hz, H 4′; 5·37, dd, $J_{2',3'}$ 9·8 Hz, H 2′; 5·58, dd, H 3′; 7·07–8·11, m, Ph. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 31·42, C 6′; 67·66, 70·89, 73·63, 74·80, 74·90, 5C, C 6, **C**H$_2$Ph; 72·55, 72·98, 74·14, 74·40, 76·62, 81·69, 82·37, 8C, C 2,3,4,5,2′,3′,4′,5′; 99·73, C 1′; 102·46, C 1; 127·06–139·45, Ph; 164·78, 165·23, 165·62, 3C, CO.

*Benzyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzoyl-6-deoxy-β-*D*-glucosyl)-β-*D*-glucoside (37)*

*(a)* A solution of the diselenide (36) (32 mg, 15 μmol) in dry toluene (3 ml) was treated with $Bu_3SnH$ (25 μl, 26 mg, 89 μmol) and α,α′-azobisisobutyronitrite (2 mg) at reflux under $N_2$ for 3 h. The solvent was evaporated and the residue dissolved in MeCN and the solution washed (5×) with petrol. The solvent was evaporated from the acetonitrile layer and the residue purified by passage through a short plug of silica (0–10% EtOAc/toluene) to give the *deoxy sugar* (37) as a clear oil (28 mg, 94%). This oil crystallized as chunky crystals, m.p. 225·5–226·0° ($Et_2O$/petrol), $[\alpha]_D$ −17·6° (Found: C, 73·2; H, 6·1. $C_{61}H_{58}O_{13}$ requires C, 73·3; H, 5·9%). $^1$H n.m.r. (300 MHz) $\delta$ 1·19, d, $J_{5',6'}$ 6·2 Hz, 3H, H 6′; 3·18–3·25, m, H 5; 3·47–3·62, m, H 2,3,6,5′; 3·67, dd, $J_{5,6}$ 3·7, $J_{6,6}$ 11·0 Hz, H 6; 4·04, t, $J_{3,4} \approx J_{4,5}$ 9·2 Hz, H 4; 4·37–5·05, m, 8H, C**H**$_2$Ph; 4·41, d, $J_{1,2}$ 7·6 Hz, H 1; 4·92, d, $J_{1',2'}$ 8·0 Hz, H 1′; 5·25, t, $J_{3',4'} \approx J_{4',5'}$ 9·6 Hz, H 4′; 5·44, dd, $J_{2',3'}$ 9·8 Hz, H 2′; 5·64, dd, H 3′; 7·16–7·94, m, Ph. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 17·46, C 6′; 67·84, 70·99, 73·44, 74·88, 75·47, 5C, C 6, **C**H$_2$Ph; 70·37, 72·70, 73·13, 74·00, 74·46, 76·93, 81·79, 82·82, 8C, C 2,3,4,5,2′,3′,4′,5′; 100·16, C 1′; 102·46, C 1; 127·28–139·04, Ph; 164·85, 165·40, 165·76, 3C, CO.

*(b)* The tribenzoate (35) (119 mg, 222 μmol) and benzyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (16) (100 mg, 185 μmol) were treated as described in procedures *(a)* then *(b)* as above to give, after flash chromatography (0–5% EtOAc/toluene), the deoxy sugar (37) as a clear oil (118 mg, 64%). This material gave identical $^1$H (300 MHz) and $^{13}$C n.m.r. (75·5 MHz) spectra to the material prepared as outlined above.

*1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2,3,4-tri-*O*-benzoyl-6-deoxy-β-*D*-glucosyl)-α-*D*-galactose (38)*

The tribenzoate (35) (141 mg, 263 μmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (5) (57 mg, 220 μmol) were treated as described in procedures *(a)* then *(b)* as above to give, after flash chromatography (5–10% EtOAc/toluene), the *deoxy disaccharide* (38) as a clear oil (115 mg, 73%), $[\alpha]_D$ −33·0° (Found: C, 65·0; H, 6·0. $C_{39}H_{42}O_{13}$ requires C, 65·2; H, 5·9%). $^1$H n.m.r. (500 MHz) $\delta$ 1·21, 1·25, 1·42, 3s, 12H, $CMe_2$; 1·37, d, $J_{5',6'}$ 6·2 Hz, 3H, H 6′; 3·82, dd, $J_{5,6}$ 6·7, $J_{6,6}$ 11·1 Hz, H 6; 3·85–3·90, m, H 5,5′; 4·03, dd, $J_{5,6}$ 5·0 Hz, H 6; 4·14, dd, $J_{3,4}$ 7·9, $J_{4,5}$ 1·8 Hz, H 4; 4·21, dd, $J_{1,2}$ 5·0, $J_{2,3}$ 2·4 Hz, H 2; 4·44, dd, H 3; 4·93, d, $J_{1',2'}$ 8·0 Hz, H 1′; 5·33, dd, $J_{3',4'}$ 9·6, $J_{4',5'}$ 9·6 Hz, H 4′; 5·42, d, H 1; 5·49, dd, $J_{2',3'}$ 9·8 Hz, H 2′; 5·82, dd, H 3′; 7·23–8·00, m, 15H, Ph. $^{13}$C n.m.r. (125·8 MHz) $\delta$ 17·46, C 6′; 24·08, 24·73, 25·60, 25·80, 4C, C**Me**$_2$; 67·14, C 5; 67·94, C 6; 70·30, C 2; 70·39, C 3; 70·45, C 5′; 70·79, C 4; 71·92, C 2′; 72·94, C 3′; 73·88, C 4′; 96·06, C 1; 101·99, C 1′; 108·32, 109·09, 2C, **C**$Me_2$; 128·07–129·85, 132·87–133·22, Ph; 165·06, 165·34, 165·74, 3C, CO. High-resolution mass spectrum (f.a.b.) *m/z* 717·2567 [$C_{39}H_{41}O_{13}$ $(M-H)^{+\bullet}$ requires 717·2547].

*Methyl 2,4,6-Tri-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzoyl-6-deoxy-β-*D*-glucosyl)-α-*D*-glucoside (39)*

The tribenzoate (35) (132 mg, 246 μmol) and methyl 2,4,6-tri-*O*-benzyl-α-D-glucoside (14) (95 mg, 205 μmol) were treated as described in procedures *(a)* then *(b)* as above to give, after

flash chromatography (5% EtOAc/toluene), the *deoxy disaccharide* (39) as a clear syrup (103 mg, 55%), $[\alpha]_D$ −34·2° (Found: C, 71·4; H, 5·9. $C_{55}H_{54}O_{13}$ requires C, 71·6; H, 5·9%). $^1$H n.m.r. (300 MHz) δ 1·23, d, $J_{5',6'}$ 6·2 Hz, 3H, H6′; 3·16, s, OMe; 3·24, dd, $J_{1,2}$ 3·6, $J_{2,3}$ 9·5 Hz, H2; 3·44–3·64, m, 4H, H4,5,6; 3·76, dq, $J_{4',5'}$ 9·6 Hz, H5′; 4·05–5·06, m, 6H, C**H**$_2$Ph; 4·19, d, H1; 4·29, dd, $J_{3,4} \approx J_{4,5}$ 9·1 Hz, H3; 5·28, dd, $J_{3',4'}$ 9·6 Hz, H4′; 5·36, d, $J_{1',2'}$ 6·7 Hz, H1′; 5·50, dd, $J_{2',3'}$ 9·8 Hz, H2′; 5·79, dd, H3′; 7·00–7·95, Ph. $^{13}$C n.m.r. (75·5 MHz) δ 17·46, C6′; 54·94, OMe; 68·36, 73·50, 73·81, 75·07, C6, **C**H$_2$Ph; 69·48, 70·25, 72·95, 73·14, 74·15, 75·43, 78·44, 80·75, C2,3,4,5,2′,3′,4′,5′; 97·74, C1; 100·41, C1′; 127·62–129·78, 133·06–133·27, 137·82–138·38, Ph; 165·17, 165·49, 165·84, 3C, CO.

**Deprotection and Deoxygenation of the Disulfides**

*General Procedure for the Deacylation and Acetylation of the Tribenzoates (11), (18) and (22)*

A solution of the disulfide in the specified solvent was treated with a small piece of sodium metal overnight. The solvent was evaporated and the residue treated with pyridine (3 ml), $Ac_2O$ (2 ml) and 4-(dimethylamino)pyridine (5 mg). The solvent was evaporated and the residue subjected to the usual workup ($CH_2Cl_2$). The residue was purified by flash chromatography to afford the *per*-acetates.

*6,6′-O-[6,6′-Dithiobis(2,3,4-tri-O-acetyl-6-deoxy-β-D-glucosyl)]bis(1,2:3,4-di-O-isopropylidene-α-D-galactose) (24)*

The disulfide (11) (286 mg) dissolved in dry MeOH (5 ml) was treated as above to yield, after flash chromatography (40–50% EtOAc/petrol), the *disulfide* (24) as a clear syrup (175 mg, 81%), $[\alpha]_D$ −6·6° (Found: C, 51·3; H, 6·4. $C_{48}H_{70}O_{26}S_2$ requires C, 51·1; H, 6·3%). $^1$H n.m.r. (300 MHz) δ 1·26, 1·28, 1·40, 1·44, 4s, 12H, $CMe_2$; 1·99, 2·00, 2·01, 3s, 9H, Ac; 2·78, dd, $J_{5',6'}$ 7·6, $J_{6',6'}$ 13·8 Hz, H6′; 2·88, dd, $J_{5',6'}$ 3·3 Hz, H6′; 3·62–3·70, m, H5′; 3·64, dd, $J_{5,6}$ 7·6, $J_{6,6}$ 11·4 Hz, H6; 3·85–3·90, m, H5; 3·97, dd, $J_{5,6}$ 3·4 Hz, H6; 4·15, dd, $J_{3,4}$ 7·9, $J_{4,5}$ 1·8 Hz, H4; 4·24, dd, $J_{1,2}$ 5·0, $J_{2,3}$ 2·5 Hz, H2; 4·54, dd, H3; 4·56, d, $J_{1',2'}$ 7·9 Hz, H1′; 4·89, dd, $J_{3',4'}$ 9·5, $J_{4',5'}$ 9·5 Hz, H4′; 4·92, dd, $J_{2',3'}$ 9·6 Hz, H2′; 5·15, dd, H3′; 5·45, d, H1. $^{13}$C n.m.r. (75·5 MHz) δ 20·53, 20·59, 3C, CO**Me**; 24·35, 24·96, 25·91, 25·96, 4C, C**Me**$_2$; 41·06, C6′; 67·81, 70·37, 70·57, 71·16, 71·46, 72·10, 72·55, 8C, C2,3,4,5,2′,3′,4′,5′; 69·44, C6; 96·11, C1; 101·37, C1′; 108·54, 109·37, 2C, **C**Me$_2$; 169·44, 169·65, 170·07, 3C, CO.

*Dimethyl 6,6′-O-[6,6′-Dithiobis(2,3,4-tri-O-acetyl-6-deoxy-β-D-glucosyl)]bis(2,3,4-tri-O-acetyl-α-D-glucoside) (25)*

The disulfide (18) (163 mg) dissolved in dry MeOH (3 ml) was treated as above to yield, after flash chromatography (55–60% EtOAc/petrol), the *disulfide* (25) as a clear syrup (97 mg, 77%), $[\alpha]_D$ +106·5°. $^1$H n.m.r. (300 MHz) δ 1·93, 1·94, 1·97, 1·99, 2·00, 2·01, 6s, 18H, Ac; 2·77–2·84, m, 2H, H6′; 3·50, dd, $J_{5,6}$ 5·6, $J_{6,6}$ 10·8 Hz, H6; 3·65, m, H5′; 3·85–3·94, m, H5,6; 4·49, d, $J_{1',2'}$ 7·9 Hz, H1′; 4·79, dd, $J_{1,2}$ 3·6, $J_{2,3}$ 10·2 Hz, H2; 4·85–4·96, m, H1,4,2′,4′; 5·15, t, $J_{2',3'} \approx J_{3',4'}$ 9·5 Hz, H3′; 5·40, dd, $J_{3,4}$ 9·7 Hz, H3. $^{13}$C n.m.r. (75·5 MHz) δ 20·49, 20·58, 6C, CO**Me**; 40·99, C6′; 55·20, OMe; 67·75, C6; 68·04, 68·75, 70·11, 70·72, 71·19, 71·37, 72·36, 72·49, C2,3,4,5,2′,3′,4′,5′; 96·42, C1; 100·63, C1′; 169·25, 169·46, 169·60, 169·96, 6C, CO. High-resolution mass spectrum (f.a.b.) *m/z* 1246·3292 [$C_{50}H_{70}O_{32}S_2$ ($M^{+\bullet}$) requires 1246·3290].

*Dibenzyl 4,4′-O-[6,6′-Dithiobis(2,3,4-tri-O-acetyl-6-deoxy-β-D-glucosyl)]bis(2,3,6-tri-O-benzyl-β-D-glucoside) (28)*

The disulfide (22) (153 mg) dissolved in dry tetrahydrofuran/MeOH (1:1, 10 ml) was treated as above to yield, after flash chromatography (35% EtOAc/petrol), the *disulfide* (28) as a pale-yellow oil (113 mg, 90%), $[\alpha]_D$ +39·3° (Found: C, 65·6; H, 6·1. $C_{92}H_{102}O_{26}S_2$ requires C, 65·5; H, 6·1%). $^1$H n.m.r. (500 MHz) δ 1·88, 1·90, 1·93, 3s, 9H, OAc; 2·37, dd, $J_{5',6'}$ 7·0, $J_{6',6'}$ 13·9 Hz, H6′; 2·53, dd, $J_{5',6'}$ 3·7 Hz, H6′; 3·25, br d, $J_{4,5}$ 9·8 Hz, H5; 3·32–3·49, m, H2,3,5′; 3·62–3·70, m, 2H, H6; 3·89, dd, $J_{3,4}$ 8·7 Hz, H4; 4·39, d, $J_{1,2}$ 7·4 Hz, H1; 4·40–4·89, m, 8H, C**H**$_2$Ph; 4·50, d, $J_{1',2'}$ 8·0 Hz, H1′; 4·74–4·82, m, H2′,4′; 4·92, dd, $J_{2',3'} \approx J_{3',4'}$ 9·4 Hz, H3′; 7·14–7·36, m, Ph. $^{13}$C n.m.r. (75·5 MHz) δ 20·55, 20·71, 20·89, 3C, Me; 40·83, C6′; 67·62, 70·94, 72·97, 74·84, 74·88, 5C, C6, **C**H$_2$Ph; 71·24, 72·12, 72·97, 74·66, 76·68, 81·69, 82·30, 8C, C2,3,4,5,2′,3′,4′,5′; 127·10–128·64, 137·75–139·22, Ph; 169·08, 169·66, 170·11, 3C, CO.

*General Procedure for the Preparation of the Thioacetates (29)–(31)*

A solution of the disulfide in dry tetrahydrofuran/MeOH (1:1, 10 ml) was treated with a small piece of sodium metal. The solution was left to stand overnight under $N_2$. The solvent was evaporated and the residual oil was taken up in dry tetrahydrofuran (5 ml) and liquid ammonia (20 ml) added at −78°. Small pieces of sodium metal were added until the mixture went blue and remained so for 1 h. $NH_4OAc$ (0·5 g) was then added and the ammonia allowed to evaporate under a flow of $N_2$. The residue was treated with $Ac_2O$ (1 ml), pyridine (3 ml) and 4-(dimethylamino)pyridine (2 mg) at room temperature overnight. The solvent was evaporated and the residue was subjected to the usual workup ($CH_2Cl_2$) to give a residue which was purified by flash chromatography to give the various thioacetates in the indicated yield.

*Methyl 2,3,4-Tri-O-acetyl-6-O-(2,3,4-tri-O-acetyl-6-S-acetyl-6-thio-β-D-glucosyl)-α-D-glucoside (29)*

The disulfide (19) (203 mg) was treated according to the procedure above to give, after flash chromatography (40% EtOAc/petrol), the *thioacetate* (29) as a clear oil (85 mg, 60%), $[\alpha]_D$ +62·6° (Found: C, 48·7; H, 6·0. $C_{27}H_{38}O_{17}S$ requires C, 48·7; H, 5·8%). $^1$H n.m.r. (300 MHz) δ 1·94, 1·94, 1·98, 1·99, 2·01, 2·02, 6s, 18H, OAc; 2·29, s, SAc; 2·99, dd, $J_{5',6'}$ 7·0, $J_{6',6'}$ 14·3 Hz, H6′; 3·20, dd, $J_{5',6'}$ 2·9 Hz, H6′; 2·29, s, 3H, OMe; 3·48, dd, $J_{5,6}$ 4·7, $J_{6,6}$ 11·0 Hz, H6; 3·56, dd, $J_{4',5'}$ 9·9 Hz, H5′; 3·83, $J_{5,6}$ 2·1 Hz, H6; 3·90, m, H5; 4·46, d, $J_{1',2'}$ 8·0 Hz, H1′; 4·79, dd, $J_{1,2}$ 3·6, $J_{2,3}$ 10·2 Hz, H2; 4·86–4·95, H1,4,2′,4′; 5·12, t, $J_{2',3'} \approx J_{3',4'}$ 9·4 Hz, H3′; 5·40, dd, $J_{3,4}$ 9·3 Hz, H3. $^{13}$C n.m.r. (75·5 MHz) δ 20·49, 20·57, 6C, CO**Me**; 30·03, SCO**Me**; 30·30, C6′; 55·18, OMe; 67·92, C6; 68·16, 68·95, 70·11, 70·64, 70·77, 71·12, 72·57, 73·03, C2,3,4,5,2′,3′,4′,5′; 96·42, C1; 100·67, C1′; 169·22, 169·56, 169·64, 169·94, 170·02, 170·10, 6C, OCO; 194·48, SCO.

*Methyl 2,4,6-Tri-O-acetyl-3-O-(2,3,4-tri-O-acetyl-6-S-acetyl-6-thio-β-D-glucosyl)-α-D-glucoside (30)*

The disulfide (20) (225 mg) was treated according to the procedure above to give, after flash chromatography (40–50% EtOAc/petrol), the *thioacetate* (30) as a clear oil (90 mg, 57%), $[\alpha]_D$ +28·0° (Found: C, 48·6; H, 6·0. $C_{27}H_{38}O_{17}S$ requires C, 48·6; H, 5·8%). $^1$H n.m.r. (300 MHz) δ 1·91, 1·92, 2·02, 2·05, 2·13, 5s, 18H, OAc; 2·32, s, SAc; 2·99, dd, $J_{5',6'}$ 6·9, $J_{6',6'}$ 14·3 Hz, H6′; 3·20, dd, $J_{5',6'}$ 2·9 Hz, H6′; 3·37, s, OMe; 3·53, ddd, $J_{4',5'}$ 9·8 Hz, H5′; 3·89, ddd, $J_{4,5}$ 10·2, $J_{5,6}$ 2·4, 4·6 Hz, H5; 4·02–4·11, m, H3,6; 4·16, dd, $J_{6,6}$ 12·3 Hz, H6; 4·59, d, $J_{1',2'}$ 8·1 Hz, H1′; 4·78–4·86, m, H1,2,2′; 4·90, dd, $J_{3',4'}$ 10·0 Hz, H4′; 4·95, dd, $J_{3,4}$ 9·3 Hz, H4; 5·03, dd, $J_{2',3'}$ 9·4 Hz, H3′. $^{13}$C n.m.r. (75·5 MHz) δ 20·25, 20·50, 20·59, 20·70, 20·79, 20·92, 6C, OCO**Me**; 30·05, C6′; 30·37, SCO**Me**; 55·34, OMe; 62·04, C6; 67·34, 67·81, 70·31, 71·24, 72·83, 72·91, 75·95, C2,3,4,5,2′,3′,4′,5′; 96·67,

C 1; 100·41, C 1′; 168·98, 169·59, 169·75, 170·29, 170·68, 6C, OCO; 194·42, SCO.

*1,2,3,6-Tetra*-O-*acetyl-4*-O-*(2,3,4-tri*-O-*acetyl-6*-S-*acetyl-6-thio-β*-D-*glucosyl)-α*-D-*glucose (31)*

*(a)* The disulfide (22) (145 mg) was treated according to the procedure above to give, after flash chromatography (50% EtOAc/petrol), a clear oil (63 mg, 64%).

*(b)* A portion of the above mixture (49 mg) was treated with a solution of fused zinc chloride (100 mg) in $Ac_2O$ at 100° under Argon for 30 min. The brown solution was poured into ice-water and stirred for 10 min. The mixture was extracted with EtOAc and the organic extract washed with saturated aqueous $NaHCO_3$ and brine, then dried. The solvent was evaporated and the residue crystallized to give the *thioacetate* (31) as needles (29 mg, 59%), m.p. 216–218° (EtOAc/EtOH), $[\alpha]_D$ +23° (Found: C, 48·5; H, 5·5. $C_{28}H_{38}O_{18}S$ requires C, 48·4; H, 5·5%). $^1$H n.m.r. (300 MHz) $\delta$ 1·95, 1·99, 2·01, 2·04, 2·05, 2·11, 2·15, 7s, 21H, OAc; 2·35, s, SAc; 3·05, dd, $J_{5',6'}$ 6·9, $J_{6',6'}$ 14·5 Hz, H 6′; 3·22, dd, $J_{5',6'}$ 3·1 Hz, H 6′; 3·56, ddd, $J_{4',5'}$ 9·6 Hz, H 5′; 3·78, t, $J_{3,4} \approx J_{4,5}$ 9·7 Hz, H 4; 3·97, m, H 5; 4·09, dd, $J_{5,6}$ 4·3, $J_{6,6}$ 12·2 Hz, H 6; 4·45, d, $J_{1',2'}$ 7·9 Hz, H 1′; 4·44–4·48, m, H 6; 4·88, dd, $J_{2',3'}$ 9·3 Hz, H 2′; 4·95, dd, $J_{3',4'}$ 9·7 Hz, H 4′; 5·01, dd, $J_{1,2}$ 3·8, $J_{2,3}$ 10·3 Hz, H 2; 5·10, dd, H 3′; 5·42, dd, H 3; 6·24, d, H 1. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 20·53, 20·59, 20·65, 20·79, 20·93, 21·00, 7C, OCO**C**$H_3$; 29·99, C 6′; 30·44, SCO**C**$H_3$; 61·34, C 6; 69·19, 69·49, 70·19, 70·82, 71·72, 72·92, 73·45, 75·45, C 2,3,4,5,2′,3′,4′,5′; 88·97, C 1; 100·38, C 1′; 168·91, 169·04, 169·66, 169·95, 170·18, 7C, OCO; 194·24, SCO. High-resolution mass spectrum (f.a.b.) *m/z* 695·0897 [$C_{28}H_{39}O_{18}S$ $(M+H)^{+\bullet}$ requires 695·1856].

*General Procedure for the Reduction of the Disulfides (21), (24) and (25) and the Thioacetates (29)–(31) with Raney Nickel*

A solution of the thioacetate or disulfide in EtOH (5–10 ml) was treated with Raney nickel under reflux for the specified time. The reaction mixture was cooled and filtered through Celite and the filtrate evaporated. The residue was passed through a short plug of silica (EtOAc) and the solvent evaporated from the eluate to afford the deoxy disaccharides.

*Methyl 2,3-Di*-O-*benzyl-6-deoxy-4*-O-*(2,3,4-tri*-O-*benzoyl-6-deoxy-β*-D-*glucosyl)-β*-D-*glucoside (23)*

The disulfide (21) (88 mg) and Raney nickel (0·5 g; 1 h) yielded a clear residue which was purified by flash chromatography (5% EtOAc/toluene) to give the *dideoxy disaccharide* (23) as a clear oil (71 mg, 84%). A small portion was taken and crystallized to give flakes, m.p. 139–140° ($CH_2Cl_2$/petrol), $[\alpha]_D$ +7·5° (Found: C, 70·7; H, 6·0. $C_{48}H_{48}O_{12}$ requires C, 70·6; H, 5·9%). $^1$H n.m.r. (300 MHz) $\delta$ 1·16, d, $J_{5,6} \approx J_{5',6'}$ 6·0 Hz, 6H, H 6,6′; 3·27, dq, $J_{4,5}$ 9·4 Hz, H 5; 3·39, dd, $J_{1,2}$ 7·8, $J_{2,3}$ 9·0 Hz, H 2; 3·45, dd, $J_{3,4}$ 9·4 Hz, H 4; 3·49, s, OMe; 3·61, dd, H 3; 3·64, dq, $J_{4',5'}$ 9·9 Hz, H 5′; 4·22, d, H 1; 4·64–5·03, m, 4H, C**H**$_2$Ph; 5·08, d, $J_{1',2'}$ 8·0 Hz, H 1′; 5·28, dd, $J_{3',4'}$ 9·9 Hz, H 4′; 5·49, dd, $J_{2',3'}$ 9·9 Hz, H 2′; 5·75, dd, H 3′; 7·16–7·98, m, Ph. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 17·44, 17·69, C 6,6′; 56·99, OMe; 70·59, 70·62, 72·91, 73·09, 73·75, 82·32, 82·84, 83·53, C 2,3,4,5,2′,3′,4′,5′; 101·26, C 1′; 104·33, C 1; 127·08–129·69, 133·10–133·29, 138·48, 139·11, Ph; 165·01, 165·39, 165·82, 3C, CO.

*1,2:3,4-Di*-O-*isopropylidene-6*-O-*(2,3,4-tri*-O-*acetyl-6-deoxy-β*-D-*glucosyl)-α*-D-*galactose (26)*

The disulfide (24) (106 mg) and Raney nickel (2 g; 1·5 h) yielded the *deoxy disaccharide* (26) as a white, crystalline solid (69 mg, 69%). Recrystallization afforded needles, m.p. 163·5–165° (EtOH), $[\alpha]_D$ −62·8° (Found: C, 53·9; H, 6·6. $C_{24}H_{36}O_{13}$ requires C, 54·1; H, 6·8%). $^1$H n.m.r. (500 MHz) $\delta$ 1·20, d, $J_{5',6'}$ 8·0 Hz, 3H, H 6′; 1·29, 1·29, 1·41, 1·47, 4s, 12H, $CMe_2$; 1·96, 2·00, 2·03, 3s, 9H, Ac; 3·53, dq, $J_{4',5'}$ 9·7 Hz, H 5′; 3·63, dd, $J_{5,6}$ 7·4, $J_{6,6}$ 11·3 Hz, H 6; 3·89, m, H 5; 3·98, dd, $J_{5,6}$ 3·7 Hz, H 6; 4·15, dd, $J_{3,4}$ 7·9, $J_{4,5}$ 1·9 Hz, H 4; 4·25, dd, $J_{1,2}$ 5·0, $J_{2,3}$ 2·4 Hz, H 2; 4·53, d, $J_{1',2'}$ 8·0 Hz, H 1′; 4·55, dd, H 3; 4·57, dd, $J_{3',4'}$ 9·6 Hz, H 4′; 4·94, dd, $J_{2',3'}$ 9·8 Hz, H 2′; 5·13, dd, H 3′; 5·47, d, H 1. $^{13}$C n.m.r. (125·8 MHz) $\delta$ 17·31, C 6′; 20·65, 20·69, 3C, CO**Me**; 24·27, 25·01, 25·90, 26·01, 4C, C**Me**$_2$; 67·67, 69·88, 70·42, 70·59, 71·20, 71·39, 72·72, 73·52, C 2,3,4,5,2′,3′,4′,5′; 69·35, C 6; 96·17, C 1; 101·27, C 1′; 108·62, 109·33, 2C, **C**$Me_2$; 169·61, 169·70, 170·31, 3C, CO.

*Methyl 2,3,4-Tri*-O-*acetyl-6*-O-*(2,3,4-tri*-O-*acetyl-6-deoxy-β*-D-*glucosyl)-α*-D-*glucoside (27)*

*(a)* The thioacetate (29) (69 mg) and Raney nickel (1 g; 6 h) yielded the *deoxy disaccharide* (27) as a pale brown oil (43 mg, 67%) that crystallized as plates, m.p. 158–160° (EtOH), $[\alpha]_D$ +70·8° (Found: C, 50·4; H, 6·0. $C_{25}H_{36}O_{16}$ requires C, 50·7; H, 6·1%). $^1$H n.m.r. (300 MHz) $\delta$ 1·21, d, $J_{5',6'}$ 6·2 Hz, 3H, H 6′; 1·95, 1·96, 1·99, 2·00, 2·01, 2·03, 6s, 18H, Ac; 3·35, s, OMe; 3·51, dd, $J_{5,6}$ 6·9, $J_{6,6}$ 10·0 Hz, H 6; 3·53, dq, $J_{4',5'}$ 10·1 Hz, H 5′; 3·87, dd, $J_{5,6}$ 2·1 Hz, H 6; 3·91, m, H 5; 4·48, d, $J_{1',2'}$ 7·9 Hz, H 1′; 4·78, t, $J_{3,4} \approx J_{4,5}$ 9·5 Hz, H 4; 4·81, dd, $J_{1,2}$ 3·6, $J_{2,3}$ 10·2 Hz, H 2; 4·88, d, H 1; 4·89, dd, $J_{3',4'}$ 10·1 Hz, H 4′; 4·95, dd, $J_{2',3'}$ 9·6 Hz, H 2′; 5·12, dd, H 3′; 5·42, dd, H 3. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 17·26, C 6′; 20·63, 6C, CO**Me**; 55·22, OMe; 67·86, C 6; 68·13, 69·00, 70·07, 70·15, 70·82, 71·40, 72·75, 73·31, C 2,3,4,5,2′,3′,4′,5′; 96·43, C 1; 100·65, C 1′; 169·35, 169·62, 170·03, 170·29, 6C, CO.

*(b)* The disulfide (25) (47 mg) and Raney nickel (0·5 g; 1·5 h) yielded the deoxy disaccharide (27) as a pale yellow oil (35 mg, 75%). This material was identical by $^1$H n.m.r. (300 MHz) spectroscopy to that prepared above.

*Methyl 2,4,6-Tri*-O-*acetyl-3*-O-*(2,3,4-tri*-O-*acetyl-6-deoxy-β*-D-*glucosyl)-α*-D-*glucoside (32)*

The thioacetate (30) (71 mg) and Raney nickel (0·5 g; 2 h) yielded the *deoxy disaccharide* (32) as a light brown oil (56 mg, 85%). The colour was removed by careful flash chromatography (40% EtOAc/petrol) to give a clear oil which crystallized, m.p. 190–193° (EtOH), $[\alpha]_D$ +37·9° (Found: C, 50·4; H, 6·0. $C_{25}H_{36}O_{16}$ requires C, 50·7; H, 6·1%). $^1$H n.m.r. (300 MHz) $\delta$ 1·17, d, $J_{5',6'}$ 6·2 Hz, 3H, H 6′; 1·92, 1·93, 1·99, 2·00, 2·05, 2·13, 6s, 18H, Ac; 3·37, s, OMe; 3·48, dq, $J_{4',5'}$ 9·7 Hz, H 5′; 3·88, ddd, $J_{4,5}$ 10·3, $J_{5,6}$ 2·4, 4·4 Hz, H 5; 4·04–4·11, m, H 3,6; 4·16, dd, H 6; 4·56, d, $J_{1',2'}$ 8·1 Hz, H 1′; 4·74, dd, $J_{3',4'}$ 9·5 Hz, H 4′; 4·79–4·83, m, H 1,2′; 4·85, dd, $J_{1,2}$ 3·5, $J_{2,3}$ 9·9 Hz, H 2; 4·94, dd, $J_{3,4}$ 9·2 Hz, H 4; 5·03, dd, $J_{2',3'}$ 8·3 Hz, H 3′. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 17·43, C 6′; 20·34, 20·61, 20·72, 20·80, 20·94, 6C, CO**Me**; 55·34, OMe; 62·11, C 6; 67·33, 68·06, 69·78, 71·73, 72·65, 73·05, 73·26, 75·93, C 2,3,4,5,2′,3′,4′,5′; 96·78, C 1; 100·39, C 1′; 169·12, 169·56, 169·81, 170·41, 170·71, 6C, CO.

*1,2,3,6-Tetra*-O-*acetyl-4*-O-*(2,3,4-tri*-O-*acetyl-6-deoxy-β*-D-*glucosyl)-α*-D-*glucose (33)*

The thioacetate (31) (18·5 mg) and Raney nickel (0·5 g; 1 h) yielded the deoxy disaccharide (33) as a white, crystalline solid (14 mg, 85%). This material crystallized as white needles, m.p. 225·5–226° (EtOH; lit.[21] 185–186°), $[\alpha]_D$ +57·7° (lit.[21] +25·3°) (Found: C, 50·5; H, 5·7. Calc. for $C_{26}H_{36}O_{17}$: C, 50·3; H, 5·8%). $^1$H n.m.r. (300 MHz) $\delta$ 1·23, d, $J_{5',6'}$ 6·2 Hz, 3H, H 6′; 1·95, 1·98, 2·01, 2·02, 2·10, 2·15, 6s, 21H, Ac; 3·50, dq, $J_{4',5'}$ 9·7 Hz, H 5′; 3·76, t, $J_{3,4} \approx J_{4,5}$ 9·6 Hz, H 4; 3·96, ddd, $J_{5,6}$ 2·0, 4·2 Hz, H 5; 4·08, dd, $J_{6,6}$ 12·1 Hz, H 6; 4·45, d, $J_{1',2'}$ 8·0 Hz, H 1′; 4·45, dd, H 6; 4·78, dd, $J_{3',4'}$ 9·7

Hz, H 4′; 4·89, dd, $J_{2',3'}$ 9·5 Hz, H 2′; 4·99, dd, $J_{1,2}$ 3·8, $J_{2,3}$ 10·4 Hz, H 2; 5·08, dd, H 3′; 5·41, dd, H 3; 6·22, d, H 1. $^{13}$C n.m.r. (75·5 MHz) $\delta$ 17·54, C 6′; 20·47, 20·58, 20·81, 20·91, 21·05, 7C, CO**C**H$_3$; 61·41, C 6; 69·35, 69·61, 70·16, 70·76, 72·07, 72·95, 76·10, C 2,3,4,5,2′,3′,4′,5′; 88·99, C 1; 100·83, C 1′; 168·92, 169·18, 169·52, 169·58, 169·93, 170·29, 7C, CO.

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