Stereoselective Thioglycoside Syntheses. Part 4.† A New Approach to 1,4-Linked 1-Thio-disaccharides and a Synthesis of Thiomaltose

By **Michèle Blanc-Muesser**, **Jacques Defaye**, and **Hugues Driguez**, Centre de Recherches sur les Macromolécules Végétales, Centre National de la Recherche Scientifique and Laboratoire Associé à l'Université Scientifique et Médicale de Grenoble, 53 X, 38041 Grenoble, France

Two approaches are devised for the preparation of thiomaltose (16). Condensation between the sodium salt of 1-thio-α-D-glucopyranose (3) and methyl 2,3,6-tri-*O*-benzoyl-4-*O*-trifluoromethylsulphonyl-α-D-galactopyranoside (5) in hexamethylphosphoramide, leads to the methyl α-thiomaltoside derivative (6). On the other hand, the displacement of the C-4 trifluoromethanesulphonate of 1,6-anhydro-D-galactopyranose diacetate (13) by the sodium salt (3) gave the 1,6-anhydro-thio-disaccharide (14). The precursor of (13), 2,3-di-*O*-acetyl-1,6-anhydro-β-D-galactopyranose (12) was obtained in near quantitative yield from the known 2-*O*-acetyl-1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose (9) by successive hydrolysis of the acetal group, orthoester formation (11), and selective opening of this intermediate through controlled acidic hydrolysis. Acetolysis of the methyl thio-maltoside (8) or the corresponding 1,6-anhydro-thio-disaccharide (14) followed by de-*O*-acylation afforded 4-*S*-α-D-glucopyranosyl-4-thio-D-glucopyranose [thiomaltose (16)] in excellent yields. 1,2,3,6-Tetra-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-4-thio-β-D-glucopyranose (15), a useful precursor of thiomaltotriosyloligosaccharides, is also prepared from the acetolysis reaction.

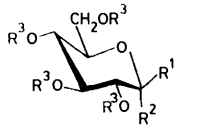
1-THIOGLYCOSES are well known as useful substrate analogues for the induction,[1,2] purification by affinity chromatography,[3] or study of the mechanism of action of glycosyl-hydrolases.[4] Such an approach is a major line of research in our laboratory for glycanases which need an oligosaccharide structure for the enzymic affinity. The synthesis of inter-anomerically sulphur-linked oligosaccharides as substrate analogues is thus a basic step of this programme.[5,6]

In a previous paper in this series,[7] the steric control in 1-thio-glycosidations for 1,4-linked 1-thio-disaccharide syntheses was achieved by a bimolecular S_N2 type of reaction at the anomeric carbon atom involving the displacement in hexamethylphosphoramide (HMPA) on a glycosyl halide by a thiolate anion generated at C-4 of another glycosyl moiety. The alternative approach involving the use of 1-thio-glycoses, which appears more suitable for further thio-oligosaccharide synthesis, has now been investigated.

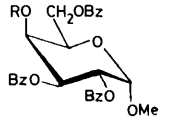
RESULTS AND DISCUSSION

A key compound for such a reaction scheme is 2,3,4,6-tetra-*O*-acetyl-1-*S*-acetyl-1-thio-α-D-glucopyranose (2), which has previously been prepared [7] by the action of sodium thioacetate on 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl chloride (1) in HMPA. A more convenient approach involves the action of tetrabutylammonium thioacetate, generated from thioacetic acid and tetrabutylammonium hydroxide on the β-chloride (1), using toluene as an easily removable solvent.

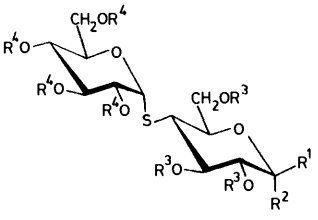
Two routes for the syntheses of thiomaltose from (2) were considered: these involved either an alkyl 4-*O*-trifluoromethylsulphonylgalactoside (5) or the corresponding 1,6-anhydrogalactose derivative (13). In the first pathway, the easily accessible methyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside [8] (4) was quantitatively esterified with trifluoromethanesulphonic anhydride in pyridine, and the resulting trifluoromethanesulphonate



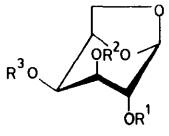
(1) R^1 = Cl, R^2 = H, R^3 = Ac
(2) R^1 = H, R^2 = SAc, R^3 = Ac
(3) R^1 = R^3 = H, R^2 = SNa



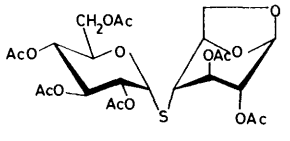
(4) R = H
(5) R = CF_3SO_2



(6) R^1 = H, R^2 = OMe, R^3 = Bz, R^4 = Ac
(7) R^1 = H, R^2 = OMe, R^3 = R^4 = H
(8) R^1 = H, R^2 = OMe, R^3 = R^4 = Ac
(15) R^1 = OAc, R^2 = H, R^3 = R^4 = Ac
(16) R^1, R^2 = H, OH, R^3 = R^4 = H



(9) R^1 = Ac, R^2,R^3 = $>C(Me)_2$
(10) R^1 = Ac, R^2 = R^3 = H
(11) R^1 = Ac, R^2,R^3 = $>C(OEt)Me$
(12) R^1 = R^2 = Ac, R^3 = H
(13) R^1 = R^2 = Ac, R^3 = CF_3SO_2



(14)

(triflate) (5) allowed to react smoothly at room temperature in HMPA with the sodium salt of 1-thio-α-D-glucopyranose (3), generated from (2). After the usual isolation procedure involving *O*-acetylation, the per-

† Part 3, M. Apparu, M. Blanc-Muesser, J. Defaye, and H. Driguez, *Can. J. Chem.*, 1981, **59**, 314. Part of a presentation at the Xth International Symposium on Carbohydrate Chemistry and Biochemistry, Sydney, Australia, 7—11 July, 1980, abstract IL3.

acylated thio-disaccharide (6) was obtained in 60% overall yield. Deacylation afforded the known methyl α-thiomaltoside [7] which could then be converted into the corresponding peracetylated derivative [7] (8). Acetolysis of (8) at room temperature for 24 h proceeded in 86% yield to give the mixture of anomeric 1,2,3,6-tetra-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-4-thio-D-glucopyranoses [α : β ratio 3.5 : 1, (^{1}H n.m.r.)], which could be either directly de-*O*-acylated into the thiomaltose (16), or converted *via* the corresponding α-halide, followed by the action of silver acetate in acetic acid–acetic anhydride into the peracetylated β-anomer (15), a key precursor for further chain lengthening into a thiomaltotriose derivative.[9]

The alternative pathway for (16) involves a 1,6-anhydro-4-*O*-trifluoromethylsulphonyl-β-D-galacto-pyranose derivative (13). 2,3-Di-*O*-acetyl-1,6-anhydro-β-D-galactopyranose (12) has previously been prepared [10] by selective acetylation of 1,6-anhydro-β-D-galactopyranose or its 2-acetate (10). This procedure leads to a mixture of the 2,3- and the 2,4-acetates which could not be readily separated owing to the ease of *O*-acetyl migration at the chromatographic purification stage,[11] which precludes any preparative scale application of this method. In 1975, one of us showed [12] that the acidic opening of an axial–equatorial orthoester in the *galacto*-series proceeds exclusively to the axial acetate and this selectivity found a recent confirmation in the *manno*-series.[13] Application of these results to the orthoester (11), prepared from the easily accessible 2-*O*-acetyl-1,6-anhydro-3,4-*O*-isopropylidene-β-D-galacto-pyranose [14] through selective hydrolysis of the isopropylidene acetal gave the 2,3-diacetate (12) in 82% overall yield; it could then smoothly be converted into the expected triflate (13). Condensation of (13) and the sodium salt of 1-thio-α-D-glucopyranose (3) in HMPA at room temperature leads, after *O*-acetylation, in a yield of 61%, to the expected 1,6-anhydro-1-thiomalto-disaccharide (14).

1,6-Anhydro-sugars are usually relatively resistant to acid hydrolysis but are readily opened by acetolysis.[10] When the 1,6-anhydro-disaccharide (14) was kept for 5 h in the acetolysis mixture as described for (8), a nearly quantitative yield of the above described, α,β-peracetylated thio-maltose was obtained; it was converted in the same way either into the thiomaltose (16) or into the corresponding β-peracetate (15).

All new compounds showed the expected proton magnetic resonance spectra and it is worth noting that, as in the thio-aryl series,[15] the anomeric coupling constants for α-D-1-thio-glycoses and -glycosides had values of 5—6 Hz *versus* 3—4 Hz found for their *O*-analogues, and H-1 for α-1-thio-glycosides was deshielded by *ca.* 0.3 p.p.m.

EXPERIMENTAL

Acylation reactions were followed by extraction with the solvent indicated. Usual work-up means successive washing of the non-aqueous phase with ice-cold solutions of potassium hydrogensulphate (10% w/v; 2 × 250 ml), sodium hydrogencarbonate (saturated), and water. Water washings were usually back-extracted. Solutions were dried (sodium sulphate) and evaporated *in vacuo* at temperatures below 45 °C. T.l.c. was performed on silica gel (Merck F 254, Merck, Darmstadt, Germany); preparative chromatography used silica gel (Merck 60, 70—230 mesh); in both cases, the following eluant systems were used (v/v): ether–hexane 3 : 1 (solvent A), ethyl acetate–hexane–dichloromethane 5 : 5 : 2 (solvent B), methanol–chloroform–water 25 : 65 : 4 (solvent C), ethyl acetate–hexane 1 : 1 (solvent D), ether (solvent E). Optical rotations were determined with a Quick polarimeter (Roussel and Jouan) at 20 °C. The ^{1}H n.m.r. spectra were recorded at 250 MHz with a Cameca spectrometer using deuteriochloroform as solvent. Assignments were confirmed by double irradiation or by the INDOR technique. Chemical shifts are reported relative to internal $SiMe_4$.

2,3,4,6-*Tetra*-O-*acetyl*-1-S-*acetyl*-1-*thio*-α-D-*glucopyranose* (2).[7]—To a solution in toluene–methanol of tetrabutylammonium hydroxide (0.1M 4 : 1 v/v; 500 ml) was added thioacetic acid (3.5 ml, 50 mmol) and the mixture was concentrated at 60 °C, then further co-evaporated with toluene (3 × 400 ml). To the resulting residue in toluene (500ml) was added 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylchloride (1) [prepared from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose [16] (18 g, 46 mmol)], and the mixture was stirred at room temperature for 12 h, then evaporated. The residue in dichloromethane (250 ml) was washed with water (3 × 250 ml). The combined organic extracts were dried and evaporated to dryness, and the residue was chromatographed on silica gel (350 g, 5 × 65 cm) using chloroform as eluant. 2 l of eluant gave the expected product (2) which crystallized in ether (8.5 g, 46%). Recrystallisation from ether gave a sample having m.p. 124—126 °C, $[\alpha]_D^{20}$ +140° (*c*, 1 in chloroform) {lit.,[7] m.p. 121—123 °C, $[\alpha]_D^{20}$ +128° (*c*, 0.92 in chloroform)}.

Methyl 2,3,6-*Tri*-O-*benzoyl*-4-O-*trifluoromethylsulphonyl*-α-D-*galactopyranoside* (5).—To a solution of methyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside [8] (4) (12.75 g, 25.5 mmol) in dichloromethane–pyridine (2.5 : 1 v/v; 91 ml), cooled to 0 °C, was added trifluoromethanesulphonic anhydride (10.2 ml, 62 mmol) and the solution was kept for 30 min at the same temperature, then left for 30 min at room temperature at which time t.l.c. (solvent A) showed complete conversion of the starting material (4) into the more mobile triflate (5). Extraction with dichloromethane (250 ml) followed by the usual work-up led, after evaporation, to a solid foam which was used without further purification in the next condensation step.

Methyl 2,3,6-*Tri*-O-*benzoyl*-4-S-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*glycopyranosyl*)-4-*thio*-α-D-*glucopyranoside* (6).—The per-*O*-acetylated 1-thio-α-D-glucopyranose (2) (5.2 g, 12.75 mmol) was dissolved in methanol (130 ml) containing sodium methoxide (1M, 12.75 ml). After standing overnight at room temperature the solution was evaporated. To the residue (3), dried under vacuum over phosphorus pentaoxide, were added successively the powdered triflate (5) and HMPA (55 ml). After standing for 5 h at room temperature, acetic anhydride–pyridine (4 : 3 v/v; 70 ml) was added to the reaction mixture which was then kept at 50 °C for 15 h. Extraction with chloroform (300 ml) followed by the usual work-up gave, after evaporation, a residue which was purified on silica gel (350 g) using solvent B as eluant. The pure *thio-disaccharide* (6) was obtained as a crystalline com-

pound (from ether) (6.4 g, 60%); further recrystallization gave a sample having m.p. 123—126 °C (from ether), $[\alpha]_D^{20}$ +156° (*c*, 0.64 in chloroform), δ 8.16—7.28 (15 H, 2 m, aryl-H), 6.05 (t, $J_{3,4}$ 10.0 Hz, H-3), 5.8 (d, $J_{1,2}$ 5.7 Hz, H-1′), 5.19 (dd, $J_{3,4}$ 9.5 Hz, H-3′), 5.18 (d, $J_{1,2}$ 3.5 Hz, H-1), 5.11 (dd, $J_{2,3}$ 10 Hz, H-2), 4.98 (t, $J_{4,5}$ 9.5 Hz, H-4′), 4.93 (dd, $J_{2,3}$ 10.0 Hz, H-2′), 4.86 (dd, $J_{a,b}$ 12 Hz, H-6a), 4.60 (dd, $J_{5,6b}$ 6 Hz, H-6b), 4.34 (2 H, m, H-5′, H-6′a), 4.22 (o, $J_{5,6a}$ 3 Hz, H-5), 3.94 (dd br, $J_{a,b}$ 13.0 Hz, H-6b′), 3.42 (3 H, s, OCH_3), 3.29 (t, $J_{4,5}$ 10.0 Hz, H-4), and 2.1, 2.00, 1.94, and 1.66 (12 H, 4 s, O*Ac*) (Found: C, 59.3; H, 5.25; S, 3.85. $C_{42}H_{44}O_{17}S$ requires C, 59.15; H, 5.20; S, 3.76%).

Methyl 4-S-(α-D-*Glucopyranosyl*)-4-*thio*-α-D-*glucopyranoside* (7).—The peracylated thio-disaccharide (6) (2.1 g, 2.46 mmol) was dissolved in methanol (120 ml), containing sodium methoxide in methanol (1M; 3 ml). After 15 h at room temperature, the reaction mixture was neutralized with Amberlite IRN 77 (H^+), then silica gel (6 g) was added and the suspension was evaporated. The resulting powder was applied to the top of a silica gel column (60 g) and eluted with solvent C to give pure (7), m.p. 165—168 °C then 201—205 °C, $[\alpha]_D^{20}$ +305° (*c*, 1 in water) {lit.,[7] $[\alpha]_D^{20}$ +270° (*c*, 0.19 in water) for the freeze-dried compound with 1 mol of water of crystallization * (Found: C, 41.95; H, 6.45; S, 8.05. Calc. for $C_{13}H_{24}O_{10}S$: C, 41.93; H, 6.50; S, 8.61%).

Methyl 2,3,6-*Tri*-O-*acetyl*-4-S-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-4-*thio*-α-D-*glucopyranoside* (8).—The peracylated thio-disaccharide (6) (2.1 g, 2.46 mmol), deacylated as above, was acetylated, after the Amberlite IRN 77 (H^+) neutralization step followed by concentration and drying of the methanolic solution, with acetic anhydride–pyridine (1 : 1 v/v; 30 ml). After extraction with chloroform and the usual work-up, the residue was applied to a silica gel column (80 g, solvent D), to give the peracetylated thio-disaccharide (8) (1.47 g, 90%), identical (^1H n.m.r.) with an authentic sample,[7] $[\alpha]_D^{20}$ +200° (*c*, 2.68 in chloroform); {lit.,[7] $[\alpha]_D^{20}$ +192° (*c*, 2 in chloroform)} (Found: C, 48.5; H, 5.7; S, 4.8. Calc. for $C_{27}H_{38}O_{17}S$: C, 48.64; H, 5.75; S, 4.81%).

2,3-*Di*-O-*acetyl*-1,6-*anhydro*-β-D-*galactopyranose* (12).—2-*O*-Acetyl-1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose [14] (9) (4 g, 16.3 mmol) was dissolved in aqueous trifluoroacetic acid (9 : 1 v/v; 40 ml). After 5 min at room temperature, concentration of the solution left oily (10) (t.l.c., R_F 0.17, solvent E) which was not further characterized but added to a mixture of dichloromethane (40 ml), triethyl orthoacetate (30 ml) and toluene-*p*-sulphonic acid monohydrate (10 mg). Reaction was complete (t.l.c.; solvent E) after stirring for 30 min at room temperature. Triethylamine (2 ml) was added, and the solution was poured into ice–water. Extraction with dichloromethane left a syrupy product which showed on t.l.c. (solvent E) a major spot (R_F 0.9), presumably the orthoester (11), together with a minor one (R_F 0.69). This crude product was dissolved in aqueous acetic acid (8 : 2 v/v; 60 ml) and the solution was kept at room temperature for 30 min, then evaporated under high vacuum at room temperature and dried by co-evaporation with toluene (3 × 20 ml). The resulting expected diacetate (12) (3.31 g, 82%) crystallized in ether–hexane, m.p. 106—112 °C. An analytical sample was obtained by further crystallization from propan-2-ol–ether (3.2 g, 79%), m.p. 108—112 °C, $[\alpha]_D^{20}$ +1.2° (*c*, 1.6 in chloroform); {lit.,[10] m.p. 113—115°, $[\alpha]_D$ −0.8°}.

* The value of +210.5° given in ref. 7 is probably a mistake.

2,3-*Di*-O-*acetyl*-1,6-*anhydro*-4-O-*trifluoromethylsulphonyl*-β-D-*galactopyranose* (13).—To the diacetate (12) (220 mg, 0.89 mmol) in pyridine (3 ml) at 0 °C, was added trifluoromethanesulphonic anhydride (0.3 ml, 1.76 mmol). After 30 min at 0 °C and then 2 h at room temperature, the solution was treated as described for the triflate (5). The crude product corresponding to the expected triflate (13) (329 mg, 92%) was not further characterized and was used as such in the next condensation step.

2,3-*Di*-O-*acetyl*-1,6-*anhydro*-4-S-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-4-*thio*-β-D-*glucopyranose* (14).—The sodium salt (3), prepared as described for (6) from the peracetylated 1-thioglucose (2) (300 mg, 0.73 mmol), was added to a solution of the foregoing triflate (13) (329 mg) in HMPA. After 4 h at room temperature, the reaction mixture was acetylated with pyridine–acetic anhydride (1 : 1 v/v; 2 ml). After 24 h at room temperature, the usual work-up gave a syrupy product, which was purified on a silica gel column (65 g, solvent E) leading to the *thio-anhydro-disaccharide* (14) (269 mg, 61%), m.p. 164—165 °C (from ethanol) $[\alpha]_D^{20}$ +104° (*c*, 0.96 in chloroform), δ 5.92 (d, $J_{1,2}$ 6 Hz, H-1′), 5.48 (m br, H-3), 5.35 (t, $J_{3,4}$ 9.5 Hz, H-3′), 5.07 (dd, $J_{2,3}$ 9.5 Hz, H-2′), 5.06 (t, $J_{4,5}$ 9.5 Hz, H-4′), 4.91 (d br, H-1), 4.68 (d br, $J_{5,6a}$ 5.5 Hz, H-6a), 4.62 (s br, H-2), 4.48 (o, $J_{5,6a}$ 5 Hz, H-5′), 4.24 (dd, $J_{a,b}$ 12 Hz, H-6′a), 4.12 (dd, $J_{5,6b}$ 2.5 Hz, H-6′b), 4.11 (d br, H-6b), 3.82 (dd, $J_{5,6b}$ 7.5 Hz, H-5), 2.92 (s br, H-4), and 2.16—2.02 (18 H, m, OAc) (Found: C, 48.5; H, 5.2; S, 5.55. $C_{24}H_{32}O_{15}S$ requires C, 48.64; H, 5.44; S, 5.41%).

1,2,3,6-*Tetra*-O-*acetyl*-4-S-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-4-*thio*-β-D-*glucopyranose* (15).—*From compound* (8). Methyl 2,3,6-tri-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-4-thio-α-D-glucopyranoside (8) (1.049 g, 1.57 mmol) in acetic anhydride–acetic acid–sulphuric acid (7 : 3 : 0.07 v/v; 42 ml) was stirred at room temperature for 24 h. Sodium acetate (1.049 g) was then added and the solution was concentrated. Dichloromethane (50 ml) was poured into the flask and the salts were removed by filtration and washed several times with the same solvent. Concentration of the solution gave a residue consisting mainly of (15) and its α-acetoxy-anomer (ratio α : β, 3.5 : 1). This syrupy product was converted into pure (15) as follows.

To the crude preceding mixture of anomers in dichloromethane (4 ml) at 0 °C was added hydrogen bromide in acetic acid (40% w/v; 8 ml). After standing overnight at 0 °C, the solution was poured into ice-cooled water (50 ml) and extracted with dichloromethane (150 ml). The organic layer was washed successively with an ice–cold saturated hydrogenocarbonate solution (50 ml), then water (2 × 50 ml), dried, and concentrated. The residue was dissolved in acetic anhydride (4 ml), and silver acetate (700 mg) in acetic anhydride (1 : 2 v/v; 12 ml) was added. After 2 h in the dark, the suspension was filtered on Celite and the solid was washed with dichloromethane (150 ml). Washing of the organic layer with water (2 × 50 ml) followed by drying and concentration left (15) as a *solid* (943 mg, 86%), m.p. 179—181 °C (from ethanol), $[\alpha]_D^{20}$ +127° (*c*, 0.44 in chloroform), δ 5.92 (d, $J_{1,2}$ 6 Hz, H-1′), 5.69 (d, $J_{1,2}$ 8.5 Hz, H-1), 5.32 (t, $J_{3,4}$ 10.5 Hz, H-3), 5.27 (t, $J_{3,4}$ 10.0 Hz, H-3′), 5.07 (t, $J_{4,5}$ 10.0 Hz, H-4′), 4.97 (dd, $J_{2,3}$ 10.5 Hz, H-2′), 4.95 (dd, $J_{2,3}$ 9.5 Hz, H-2), 4.63 (dd, $J_{a,b}$ 12.0 Hz, H-6a), 4.34 (dd, $J_{a,b}$ 12 Hz, H-6′a), 4.24 (o, $J_{5,6a}$ 2.0 Hz, H-5′), 4.22 (dd, $J_{5,6b}$ 6.5 Hz, H-6b), 4.11 (dd, $J_{5,6b}$ 4.0 Hz, H-6′b), 3.82 (o, $J_{5,6a}$ 2.5 Hz, H-5), 3.05 (t, $J_{4,5}$ 10.5 Hz, H-4), and

2.12—2.02 (24 H, m, OAc) (Found: C, 48.4; H, 5.6; S, 4.65. $C_{28}H_{38}O_{18}S$ requires C, 48.41; H, 5.51; S, 4.61%).

From compound (14). 2,3,Di-*O*-acetyl-1,6-anhydro-4-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-4-thio-β-D-glycopyranose (14) (580 mg, 0.98 mmol) was dissolved in the above acetolysis mixture (25 ml) which was then stirred at room temperature for 5 h. Sodium acetate (800 mg) was then added, the solution was concentrated, and the product was worked up as described above, including the glycosyl bromide step, to give (15) (540 mg, 79%).

4-S-α-D-*Glucopyranosyl*-4-*thio*-D-*glucopyranose* (16).—The peracetylated thio-disaccharide (15), or its anomeric mixture resulting from the direct acetolysis of either (8) or (14) (200 mg, 0.29 mmol), was dissolved in methanol (5 ml) containing sodium methoxide in methanol (1M; 0.1 ml). After 15 h, the solution was neutralized with Amberlite IR 120 (H^+) filtered, and concentrated to dryness. Freeze-drying of an aqueous solution of the residue left (16) as a foam (100 mg, 100%), $[\alpha]_D$ +162° (*c*, 0.16 in water) (Found: C, 39.1; H, 6.55; S, 8.55. Calc. for $C_{12}H_{22}O_{10}S \cdot 0.5H_2O$: C, 39.23; H, 8.31; S, 8.73%).

We acknowledge the skilful technical assistance of Mr. M. Paillet.

[1/533 *Received*, 6*th April*, 1981]

REFERENCES

[1] J. Monod, ' Enzymes, Units of Biological Structure and Function,' Academic Press, New York, 1956, p. S7; *ibid.*, *Angew. Chem.*, 1959, **71**, 685.

[2] W. Boos, P. Schaedel, and K. Wallenfels, *Eur. J. Biochem.*, 1967, **1**, 382.

[3] M. Claeyssens, H. Kersters-Hilderson, J. P. Van Wauwe, and C. K. De Bruyne, *FEBS Lett.*, 1970, **11**, 336; E. Steers, Jr., P. Cuatrecasas and H. B. Pollard, *J. Biol. Chem.*, 1971, **246**, 196; M. E. Rafestin, A. Obrenovitch, A. Oblin and M. Monsigny, *FEBS Lett.*, 1974, **40**, 62; L. Kiss and E. Laszlo, *Proc. Hung. Annu. Meet. Biochem.*, 1978, **18**, 217.

[4] J. Defaye, H. Driguez, B. Henrissat, and E. Bar-Guilloux, in ' Mechanism of Saccharide Polymerization and Depolymerization,' ed. J. J. Marshall, Academic Press, New York, 1980, p. 331; F. Deleyn, M. Claeyssens, and C. K. De Bruyne, *Can. J. Biochem.*, 1980, **58**, 5.

[5] M. Blanc-Muesser, J. Defaye, H. Driguez, and E. Ohleyer, in ' Energy from Biomass,' ed. W. Palz, P. Chartier, and D. O. Hall, Applied Science Publ., London 1981, p. 312.

[6] D. Rho, M. Desrochers, L. Jurasek, H. Driguez, and J. Defaye, *J. Bacteriol.*; J. Defaye, M. Desrochers, H. Driguez, L. Jurasek, and D. Rho, 14th FEBS Meeting, Edinburgh, 29 March—3 April, Abstract 87; *Biochem. Soc. Trans.*, 1981, 9. 168P.

[7] M. Blanc-Muesser, J. Defaye, and H. Driguez, *Carbohydr. Res.*, 1978, **67**, 305.

[8] J. M. Williams and A. C. Richardson, *Tetrahedron*, 1967, **23**, 1369.

[9] M. Blanc-Muesser, J. Defaye, H. Driguez, and E. Ohleyer, ' 10th International Symposium on Carbohydrate Chemistry and Biochemistry,' Sydney, 7—11 July 1980, abstract IL. 3.

[10] D. Shapiro, A. J. Acher, and E. S. Rachaman, *J. Org. Chem.*, 1967, **32**, 3767.

[11] M. E. Chaćon-Fuertes and M. Martin-Lomas, *Carbohydr. Res.*, 1975, **42**, C-4.

[12] R. U. Lemieux and H. Driguez, *J. Am. Chem. Soc.*, 1975, **97**, 4069.

[13] J. Defaye, A. Gadelle, and C. C. Wong, *Carbohydr. Res.*, 1981, **94**, 131.

[14] H. Masamune and S. Kamiyama, *Tohoku J. Exp. Med.*, 1957, **66**, 43.

[15] M. Apparu, M. Blanc-Muesser, J. Defaye, and H. Driguez, *Can. J. Chem.*, 1981, **59**, 314.

[16] I. Farkas, I. F. Szabó and R. Bognár, *Carbohydr. Res.*, 1976, **48**, 136.