THIO SUGARS BY DECOMPOSITION OF CARBOHYDRATE DITHIOBIS(THIOFORMATES)

D. Trimnell, W. M. Doane, and C. R. Russell
Northern Regional Research Laboratory, Peoria, Illinois 61604 (U. S. A.)*

(Received August 4th, 1971; accepted in revised form November 11th, 1971)

ABSTRACT

When certain primary dithiobis(thioformates) are decomposed, yields of 6-thio sugars are moderate to good. Bis(methyl 2,3-di-*O*-methyl-α-D-glucopyranoside) 6,6′-[dithiobis(thioformate)], bis(methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside) 6,6′-[dithiobis(thioformate)], and methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-[dithiobis(thioformate)] on treatment with pyridine gave corresponding dithiocarbonates in which thiolation at C-6 had occurred. Structures of the dithiocarbonates were deduced from spectral data, conversion into known compounds, and, with one, by independent synthesis. Dithiobis(thioformates) on secondary positions gave no thio sugar.

INTRODUCTION AND DISCUSSION

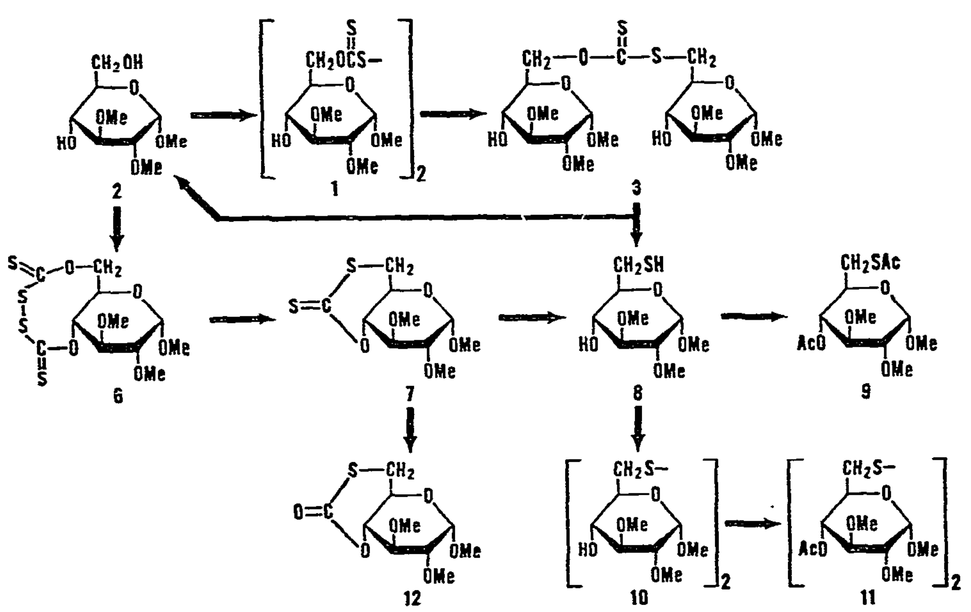
Recently we reported[1] that thio sugars can be prepared by treating certain cyclic thionocarbonates with potassium iodide in acetonitrile. Another route for preparing thio sugars is through transformation of sugar dithiobis(thioformates), since certain aliphatic[2] and mixed sugar–aliphatic[3] dithiobis(thioformates) rearrange in pyridine to dithiocarbonates. An attempt to form a 1-substituted dithiobis(thioformate) of a sugar led to a thio sugar[4] in low yield.

This report describes the products of decomposition of methyl α-D-glucopyranosides containing dithiobis(thioformate) groups at various positions. With certain of these derivatives, decomposition by pyridine gave dithiocarbonates as thio sugar products. The dithiocarbonates were identified through spectral data, conversion into known compounds, and by independent synthesis for one. Byproducts of this decomposition were carbonyl sulfide[5,6] and sulfur.

Bis(methyl 2,3-di-*O*-methyl-α-D-glucopyranoside) 6,6′-[dithiobis(thioformate)] (**1**), obtained as a solid from the xanthation of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (**2**) followed by oxidative coupling, decomposed to give methyl 2,3-di-*O*-methyl-α-D-glucopyranoside methyl 2′,3′-di-*O*-methyl-6′-thio-α-D-glucopyranoside 6,6′-dithiocarbonate (**3**) in 40% yield (Scheme 1). Higher yields of dithiocarbonate were realized when the C-4 hydroxyl group was protected. Thus, bis(methyl 2,3,4-tri-

---

*This is a laboratory of the Northern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.



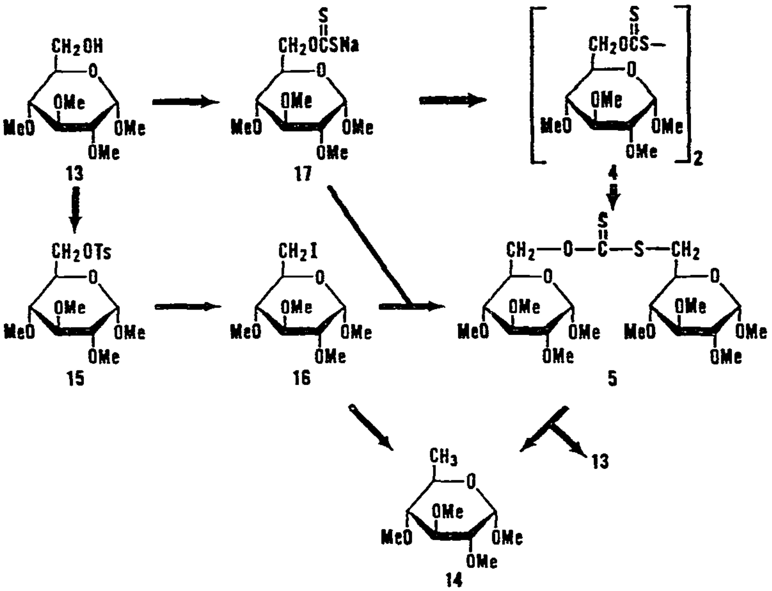
Scheme 1

O-methyl-α-D-glucopyranoside) 6,6′-[dithiobis(thioformate)] (4) gave the corresponding 6,6′-dithiocarbonate (5) in 78% yield and methyl 2,3-di-O-methyl-α-D-glucopyranoside 4,6-[dithiobis(thioformate)] (6) gave the cyclic dithiocarbonate 7 in 80% yield.

When 7 was treated with barium hydroxide solution and then neutralized, methyl 2,3-di-O-methyl-6-thio-α-D-glucopyranoside (8) resulted, as shown by chromatographic detection[7]and n.m.r. spectroscopy[1]. This thiol was further identified by acetylation to methyl 4-O-acetyl-6-S-acetyl-2,3-di-O-methyl-6-thio-α-D-glucopyranoside (9) and by oxidation to the disulfide **10**, which was converted into bis(methyl 4-O-acetyl-2,3-di-O-methyl-6-thio-α-D-glucopyranoside) disulfide (**11**). Treatment of 7 with mercuric acetate[8] converted it into the known methyl 2,3-di-O-methyl-6-thio-α-D-glucopyranoside 4,6-monothiolcarbonate[1] (**12**).

Dithiocarbonate 3 on treatment with sodium hydroxide in methanol, gave the parent diol 2 and the 6-thiol 8. A small proportion of **10** was also formed through oxidation of 8.

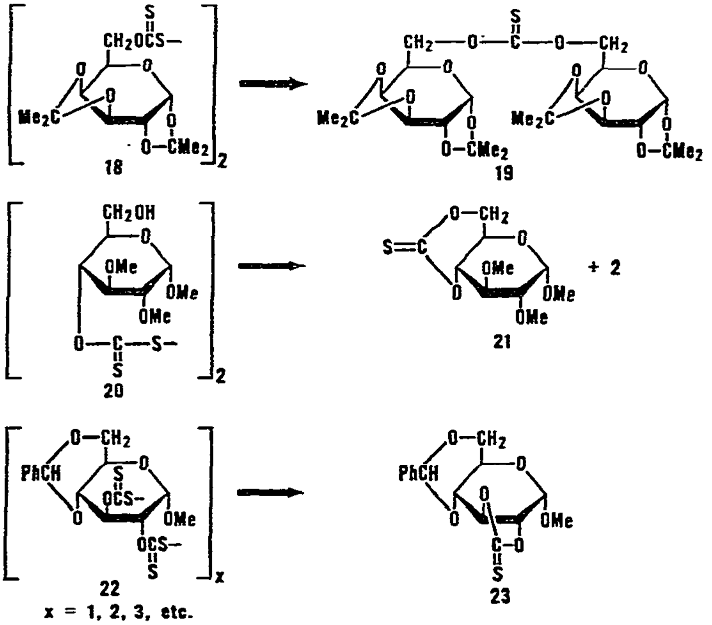
Desulfurization of 5 with Raney nickel gave a mixture of methyl 2,3,4-tri-O-methyl-α-D-glucopyranoside (**13**) and methyl 2,3,4-tri-O-methyl-α-D-quinovoside (**14**) (Scheme 2). The structure of **14** was confirmed by comparison of its mass spectrum with that of the known compound[9], and by independent synthesis through tosylation of **13** to give methyl 6-O-(p-tolylsulfonyl)-2,3,4-tri-O-methyl-α-D-glucopyranoside (**15**), iodination of **15** to give methyl 6-deoxy-6-iodo-2,3,4-tri-O-methyl-α-D-glucopyranoside (**16**), and by hydrogenation of **16** with Raney nickel. Compound 5 was



Scheme 2

synthesized independently from **16** and methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside 6-*O*-(*S*-sodium dithiocarbonate) (**17**) (Scheme 2).

Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-[dithiobis(thio-



Scheme 3

formate)] (**18**) failed to give a thio sugar derivative but in pyridine decomposed to many products, yielding mainly 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose. By diluting the pyridine with toluene and refluxing for 14 days, the known bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-thionocarbonate[1] (**19**) was obtained (Scheme 3).

Decomposition of dithiobis(thioformate) groups at secondary hydroxyl groups gave thionocarbonates but no thio sugars. Bis(methyl 2,3-di-*O*-methyl-α-D-glucopyranoside) 4,4′-[dithiobis(thioformate)] (**20**), prepared from **2** by the sequence of tritylation, xanthation, oxidative coupling, and detritylation, gave methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-thionocarbonate (**21**), previously obtained by treating **2** with thiophosgene[1]. Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-[dithiobis(thioformate)] (**22**) decomposed to the known 2,3-*trans* thionocarbonate[10] (**23**) in good yield.

EXPERIMENTAL

General. — I.r. spectra were recorded for solutions and films with a Perkin–Elmer* Model 137 spectrophotometer. U.v. spectra were determined with a Perkin–Elmer Model 202 spectrophotometer. N.m.r. spectra were recorded with a Varian HA-100 n.m.r. spectrometer, with chloroform-*d* or carbon tetrachloride as the solvent and tetramethylsilane (τ 10.00) as the internal reference standard. Mass spectra were determined with a Nuclide 12-90-DF mass spectrometer operating at probe temperatures between 115–250°. Molecular weights were obtained by the Rast method and with a Mechrolab Model 301A vapor-pressure osmometer. Melting points were determined in sealed capillaries and are uncorrected. Optical rotations were measured with a Rudolph polarimeter. Silica Gel G was used as the adsorbent for t.l.c., and sulfuric acid (5%) in methanol, as the spraying agent. For preparative t.l.c., plates were covered with a slurry of 0.5 to 1.0 mm thickness of adsorbent, containing Rhodamine 6G as the indicator, and dried. Gases evolved from decompositions of dithiobis(thioformates) in pyridine were swept with nitrogen into a solution of 1% piperidine in hexane to form the piperidine complexes of carbonyl sulfide and carbon disulfide[5]. The proportions of these complexes in mixtures were more accurately determined by measuring their i.r.[6] rather than u.v. spectra relative to known standards.

*Bis(methyl 2,3-di-*O*-methyl-α-D-glucopyranoside) 6,6′-[dithiobis(thioformate)]* (**1**). — The title compound was prepared by a reported procedure[11] with stoichiometric quantities of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (**2**) and sodium hydroxide solution. The crude product was a multicomponent mixture by t.l.c. [1:4 tetrahydrofuran (THF)–ether]. The major component, R_F 0.55, was isolated by desorption from silicic acid[1] with ether. Addition of hexane to the ether solution precipitated a solid (30%); m.p. 65–75°, $[\alpha]_D^{22}$ $-60.8°$ (*c* 1.14, chloroform), $+149.5°$ (*c* 0.91, ether);

---

*Mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

λ_{max}^{film} 1050, 1260 [O(C=S)SS(C=S)O], 3500 cm^{-1} (OH); $\lambda_{max}^{ethanol}$ 291–293 (ε 8,640), 243–247 nm (19,700); n.m.r. in $CDCl_3$: τ 4.78, 4.91 (two 1-proton doublets, H-6′), 5.40, 5.51 (two 1-proton doublets, H-6).

Anal. Calc. for $C_{20}H_{34}O_{12}S_4$: C, 40.6; H, 5.8; S, 21.6; mol. wt. 595. Found: C, 40.6; H, 6.0; S, 21.6; mol. wt. 580 (Mechrolab, in chloroform).

*Methyl 2,3-di-*O*-methyl-α-*D*-glucopyranoside methyl 2′,3′-di-*O*-methyl-6′-thio-α-*D*-glucopyranoside 6,6′-dithiocarbonate* (**3**). — A solution of **1** (3.0 g) in pyridine[2,3] (15 ml) was stirred for 1 h at 55° under nitrogen. Carbonyl sulfide and carbon disulfide[5,6] (1:1) were evolved. Sulfur precipitated from a methanol solution of the residue after the pyridine had been evaporated. The methanol was evaporated and the residue taken up in ether. Extraction of the ether solution with saturated sodium chloride solution containing sodium hydrogen carbonate took out much dark material. The major product in the multicomponent mixture (R_F 0.4, 2:1 carbon disulfide–acetone) was isolated by desorption from a silicic acid-activated carbon mixture[1] with 1:4 THF–chloroform. Evaporation of solvent left **3** (1.0 g, 40%); m.p. 50–60° (ether–hexane), $[\alpha]_D^{22}$ +243.8° (*c* 1.46, chloroform); λ_{max}^{film} 1220 cm^{-1} [O(C=S)S]; $\lambda_{max}^{ethanol}$ 280–282 (ε 9,060), 222–225 nm (6,930); n.m.r. in $CDCl_3$: τ 6.39, 6.51, 6.52, 6.58, 6.61 (OMe), 7.40 (OH), disappears upon D_2O exchange.

Anal. Calc. for $C_{19}H_{34}O_{11}S_2$: C, 45.4; H, 6.8; S, 12.8; mol. wt. 503. Found: C, 45.4; H, 6.6; S, 12.5; mol. wt. 456 (Rast, in camphor).

*Bis(methyl 2,3,4-tri-*O*-methyl-α-*D*-glucopyranoside) 6,6′-[dithiobis(thioformate)]* (**4**). — Methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside (**13**) (13.5 g) was converted[11] into **4** (89%); m.p. 130–132°, $[\alpha]_D^{22}$ +230.1° (*c* 0.97, chloroform); λ_{max}^{film} 1040, 1260 cm^{-1} [O(C=S)SS(C=S)O]; $\lambda_{max}^{ethanol}$ 358–362 (ε 97), 290–292 (8,610), 243–247 nm (19,500); n.m.r. in $CDCl_3$: τ 5.35 (4-proton multiplet, H-6, H-6′), 6.42, 6.60 (6-proton singlets, OMe), 6.50 (12-proton singlet, OMe).

Anal. Calc. for $C_{22}H_{38}O_{12}S_4$: C, 42.4; H, 6.2; S, 20.6; mol. wt. 623. Found: C. 42.2; H, 6.2; S, 21.0; mol. wt. 621 (Rast, in camphor).

*Methyl 2,3,4-tri-*O*-methyl-6-thio-α-*D*-glucopyranoside methyl 2′,3′,4′-tri-*O*-methyl-α-*D*-glucopyranoside 6,6′-dithiocarbonate* (**5**). — (*a*) *From the decomposition of* **4**. Treatment of **4** (1.0 g) in pyridine for 10 h at 55° gave carbonyl sulfide, sulfur, and **5** (78%) (compare preparation of **3**). Product **5** was a solid, m.p. 53–58°, $[\alpha]_D^{23}$ +161.3° (*c* 0.93, chloroform); λ_{max}^{film} 1060, 1210 cm^{-1} [O(C=S)S]; $\lambda_{max}^{ethanol}$ 280–282 (ε 12,400), 221–224 nm (7,700); n.m.r. in $CDCl_3$: τ 5.25 (H-1, H-6′ of O moiety), 7.00 (2-proton quartet, H-6 of S moiety) 6.40, 6.41, 6.42, 6.51, 6.52, 6.53, 6.60, 6.63 (OMe).

Anal. Calc. for $C_{21}H_{38}O_{11}S_2$: C, 47.5; H, 7.2; S, 12.1; mol. wt. 531. Found: C, 47.3; H, 7.4; S, 12.3; mol. wt. 515 (Rast, in camphor).

(*b*) *From methyl 6-deoxy-6-iodo-2,3,4-tri-*O*-methyl-α-*D*-glucopyranoside* (**16**) *and methyl 2,3,4-tri-*O*-methyl-α-*D*-glucopyranoside 6-*O*-(*S*-sodium dithiocarbonate)* (**17**). Compound **16** was prepared from **13** by *p*-toluenesulfonylation to methyl 6-*O*-(*p*-tolylsulfonyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (**15**), (yield 81%); i.r. 1600 (OAc), 1360 ($ROSO_2R$), 1100 cm^{-1} (OMe), and no OH, followed by displacement of the *p*-tolylsulfonyloxy group by iodide following common procedures[12]. Compound **16** was recovered in 87% yield and had m.p. 46–48° (hexane), $[\alpha]_D^{24}$ +126.5° (*c* 1.02, chloroform).

Anal. Calc. for $C_{10}H_{19}O_5I$: C, 34.7; H, 5.5; I, 36.7. Found: C, 34.8; H, 5.7; I, 36.4.

Salt **17** was prepared by xanthation[11] of **13** (0.71 g). After 5 min, **16** (1.00 g) was added to the xanthation mixture and kept overnight at room temperature. Excess **17** was destroyed by adding hydrochloric acid. Compound **13** from the decomposition of **17** was removed by extracting an ether solution of the acidified mixture with water, and the resulting mixture of **16** and **5** was separated by desorption from silicic acid[1]. Hexane and chloroform removed **16** and ethyl acetate removed **5**. Yield of **5**: 0.56 g (37%), m.p. 57–59° (hexane). A mixed melting point with the ester obtained in part (*a*) showed no depression. Optical rotations and i.r. and u.v. spectra were comparable.

Methyl 2,3-di-O-methyl-α-D-glucopyranoside 4,6-[dithiobis(thioformate)] (**6**). — The title compound was prepared[11] from **2** (1.0 g) and excess sodium hydroxide (5M, 2.7 ml). The initial, crude dithiobis(thioformate) was kept for 25 h at room temperature in THF containing 1% of pyridine[3] (10 ml). The most mobile component of this mixture (R_F 0.82, 4:1 carbon disulfide–ethyl acetate) was isolated by desorption from silicic acid[1] with 9:1 carbon disulfide–ethyl acetate; yield 0.55 g (33%); m.p. 205–207° dec. (hexane), $[\alpha]_D^{22}$ −322.6° (*c* 1.09, chloroform); λ_{max}^{film} 1020, 1040, 1060 and 1240, 1260 cm^{-1} [O(C=S)SS(C=S)O]; $\lambda_{max}^{ethanol}$ 359–363 (ε 91), 293–296 (8,120), 240–244 nm (19,900) based upon mol. wt. 373 for the monomer; n.m.r. in $CDCl_3$: τ 5.85–6.30 (3-proton multiplet, H-3, H-5, H-6), 4.52 (1-proton triplet, H-4), 5.42 (1-proton quartet, H-6′).

Anal. Calc. for $C_{11}H_{16}O_6S_4$: C, 35.5; H, 4.3; S, 34.4; mol. wt. 373. Found: C, 35.2; H, 4.4; S, 34.5; mol. wt. 409 (Rast, in camphor), 792 (Mechrolab, acetone: a dimer), 1171 (Mechrolab, chloroform: a trimer).

Methyl 2,3-di-O-methyl-6-thio-α-D-glucopyranoside 4,6-dithiocarbonate (**7**). — Treatment of **6** (0.5 g) in pyridine for 1 h at 55° (compare preparations of **3** and **5**) gave carbonyl sulfide, sulfur, and **7**, 0.30 g (80%); m.p. 141–142° (hexane), $[\alpha]_D^{25}$ +27.6° (*c* 0.98, chloroform); λ_{max}^{film} 1040, 1190 cm^{-1} [O(C=S)S]; $\lambda_{max}^{ethanol}$ 375–380 (ε 92), 295–297 (12,700), 224–226 nm (5,240); n.m.r. in $CDCl_3$: τ 5.8–6.4 (3-proton multiplet, H-3, H-4, H-5) 7.00 (2-proton multiplet, H-6, H-6′), 6.35, 6.50, 6.58 (three 3-proton singlets, OMe).

Anal. Calc. for $C_{10}H_{16}O_5S_2$: C, 42.8; H, 5.8; S, 22.9; mol. wt. 280. Found: C, 42.6; H, 6.0; S, 23.2; mol. wt. 255 (Mechrolab, chloroform), 298 (Mechrolab, acetone).

Amorphous **6** also gave **7** in 68% yield when kept for 70 h at room temperature in THF containing 1% of pyridine[3]. Compound **7** was identical with a minor component identified in the isomerization of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-thionocarbonate[1] (**21**).

Methyl 2,3-di-O-methyl-6-thio-α-D-glucopyranoside (**8**). — (*a*) *From* **7**. Ester **7** (0.080 g) was saponified with barium hydroxide[1] to give thiol **8** (0.067 g). Compound **8** gave a positive test on t.l.c. with a thiol spray reagent[7]. The product had $\lambda_{\max}^{\mathrm{CCl_4}}$ 2590 (SH), and 3450, 3600 cm^{-1} (OH, H-bonded and free); n.m.r. in CCl_4: τ 8.5 (quartet, disappearing upon D_2O exchange after 15 min[1]). The quartet may arise from unequal coupling of the thiol proton with H-6 and H-6′ and indicates a primary thiol.

(*b*) *From* **3**. A solution of **3** (0.22 g) in methanol (5 ml) was warmed with sodium hydroxide (0.10 g) at 50° under nitrogen. After 15 min, t.l.c. showed complete decomposition to **2** and **8** in similar proportions, and a small proportion of **10** arising from the oxidation of **8**.

*Methyl 4-*O*-acetyl-6-*S*-acetyl-2,3-di-*O*-methyl-6-thio-α-*D*-glucopyranoside* (**9**). — A solution of **8** (0.35 g) in acetic anhydride (5 ml) was mixed with sulfuric acid (5 μl). After 5 min, the mixture was diluted with ice–water and kept for 1 h. The solution was extracted with ether and the ether extract washed with sodium hydrogen carbonate solution. After drying and evaporating the ether, the product was isolated by desorption from silicic acid[1] with 1:1 chloroform–hexane; yield 0.27 g (57%), m.p. 67–69° (hexane), $[\alpha]_D^{25}$ +111.2° (*c* 1.34, chloroform); $\lambda_{\max}^{\mathrm{film}}$ 1750 (OAc), 1690 cm^{-1} (SAc); n.m.r. in $CDCl_3$: τ 5.25 (1-proton triplet, H-4), 6.85 (1-proton quartet, H-6), 7.15 (1-proton quartet, H-6′), 7.70 (3-proton singlet, SAc), 7.89 (3-proton singlet, OAc).

Anal. Calc. for $C_{13}H_{22}O_7S$: C, 48.4; H, 6.9; S, 10.0; mol. wt. 322. Found: C, 48.6; H, 6.5; S, 10.1; mol. wt. 315 (Rast, in camphor).

*Bis(methyl 4-*O*-acetyl-2,3-di-*O*-methyl-6-thio-α-*D*-glucopyranoside) disulfide* (**11**). — A solution of **8** (0.48 g) in water was treated with iodine and neutralized with sodium hydrogen carbonate. The disulfide **10** was extracted with chloroform. After drying, the chloroform was evaporated, and **10** was converted into **11** (compare preparation of **9**); yield 0.50 g (89%), m.p. 117–119°, $[\alpha]_D^{24}$ +238.2° (*c* 0.55, ethanol); $\lambda_{\max}^{\mathrm{film}}$ 1750 cm^{-1} (OAc); $\lambda_{\max}^{\mathrm{ethanol}}$ 250–254 nm (ε 670); n.m.r. in $CDCl_3$: τ 5.25 (2-proton triplet, H-4), 7.20 (4-proton multiplet, H-6, H-6′), 7.90 (6-proton singlet, OAc).

Anal. Calc. for $C_{22}H_{38}O_{12}S_2$: C, 47.3; H, 6.9; S, 11.5; mol. wt. 559. Found: C, 47.2; H, 6.9; S, 11.8; mol. wt. 546 (Rast, in camphor).

*Methyl 2,3-di-*O*-methyl-6-thio-α-*D*-glucopyranoside 4,6-monothiolcarbonate* (**12**). — Compound **7** (0.047 g) was converted into **12** with mercuric acetate in aqueous *p*-dioxane[8]; yield 0.021 g (48%). A mixed melting point with authentic **12** showed no depression, and the i.r. spectra were identical.

*Methyl 2,3,4-tri-*O*-methyl-α-*D*-quinovoside* (**14**). — (*a*) *From* **5**. A solution of **5** (0.10 g) in ethanol (20 ml) was refluxed for 1 h with activated Raney nickel (2 g). T.l.c. (ethyl acetate) showed complete conversion into similar amounts of components having R_F 0.36 (**13**) and 0.70. The solution was filtered and the ethanol evaporated. The component having R_F 0.70 was isolated as a syrup after desorption from silicic acid[1] (ethyl acetate) and identified as **14**: b.p. 95° at 0.65 torr, $[\alpha]_D^{23}$ +151.1° (*c* 1.80, chloroform); $\lambda_{\max}^{\mathrm{film}}$ 1100 cm^{-1} (OMe), 1380, 1440 cm^{-1} (CCH_3); n.m.r. data: τ 8.75 (3-proton doublet, CCH_3), 6.40, 6.45, 6.50, 6.61 (3-proton singlets, OMe); mass spectral data: *m/e* (I): 88 (100), 101 (30), 119 (6), 129 (4), 176 (7), 189 (2) at 200–213°. Reported[9] for the 3-OCD_3 isotope of this compound: *m/e* 91 (100), 101 (30), 122 (13), 129 (6), 179 (18), 192 (2).

(*b*) *From* **16**. A solution of **16** (1.44 g) in methanol (50 ml) was treated with activated Raney nickel (20 g) overnight at room temperature. The solution was diluted with methanol (1 liter), filtered through Celite, and evaporated to give 0.74 g (81%). The i.r. spectrum of this product was identical with that obtained from the desulfurization of **5**.

*Bis(1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose) 6,6'-thionocarbonate* (**19**). — A solution of bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6'-[dithiobis-(thioformate)][13] (**18**) (1.0 g) in toluene (10 ml) and pyridine (0.1 ml) was refluxed for 14 days. The solution was cooled and diluted with toluene (100 ml). Subsequently, it was shaken with hydrochloric acid, sodium hydrogen carbonate solution, and water. After drying, the solution was passed through activated carbon (10 g) and evaporated to a syrup. Preparative t.l.c. on Silica Gel G using 1:3 ethyl acetate–carbon disulfide revealed a multicomponent mixture. Elution of the upper section of the plate with ether gave a fraction which crystallized from hexane, 0.17 g (20%), m.p. 141-143°, shown to be **19** by comparison with an authentic sample[1].

*Bis(methyl 2,3-di-*O*-methyl-α-*D*-glucopyranoside) 4,4'-[dithiobis(thioformate)]* (**20**). — Crude bis(methyl 2,3-di-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside) 4,4'-[dithiobis(thioformate)] (88.3 g) was prepared[11] from methyl 2,3-di-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside[14] (76.7 g). Detritylation[15] of this crude material (10 g) with hydrochloric acid in methanol gave a mixture of **2** and **20**. Compound **2** was removed by extracting an ether solution of this mixture with water. Evaporation of the dried ether extract gave **20**, yield 2.80 g, $\lambda_{\max}^{\text{film}}$ 1020, 1050, and 1255 [O(C=S)SS(C=S)O], 3500 cm^{-1} (OH); $\lambda_{\max}^{\text{ethanol}}$ 270–290 (ε 8,750), 233–238 nm (19,050); n.m.r. in $CDCl_3$: τ 4.43 (2-proton triplet, H-4), 7.60 (2-protons, OH), 6.50 (6-proton singlet, OMe), 6.60 (12-proton singlet, OMe).

Anal. Calc. for $C_{20}H_{34}O_{12}S_4$: S, 21.6. Found: S, 21.8.

*Methyl 2,3-di-*O*-methyl-α-*D*-glucopyranoside 4,6-thionocarbonate* (**21**). — A solution of **20** (2.03 g) in pyridine (2.5 ml) was stirred at 5° and powdered iodine[16] (0.85 g) added. After 30 min, ether (100 ml) was added and the mixture filtered. The filtrate was shaken with hydrochloric acid (10M, 4 ml) saturated with sodium chloride, and then with a saturated sodium chloride solution (10 ml). The product was isolated by desorption from silicic acid[1] with ether; yield 0.37 g (20%), m.p. 121° (chloroform–ether). A mixed m.p. with authentic[1] **21** showed no depression; i.r. and u.v. spectra were also consistent with the proposed structure.

*Methyl 4,6-*O*-benzylidene-α-*D*-glucopyranoside 2,3-[dithiobis(thioformate)]* (**22**). — Crude **22** was prepared[11] from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (2.00 g) (*cf.* preparation of **6**) and stirred in THF containing 1% of pyridine[3] (100 ml) for 2 h at 70°. Evaporation of solvent and extraction of the residue with ethanol left insoluble material, R_F 0.8 (4:1 carbon disulfide–ethyl acetate), 3.03 g (50%), m.p. 245–250° dec., $[\alpha]_D^{23}$ −903.3° (*c* 0.76, chloroform); $\lambda_{\max}^{\text{chloroform}}$ 1040 and 1210 cm^{-1} [O(C=S)SS(C=S)O]; $\lambda_{\max}^{\text{THF}}$ 367–370 (ε 129), 280–285 (8,880), 241 nm (16,000) based upon mol. wt. 433 for the monomer; n.m.r. in $CDCl_3$: τ 3.40 (1-proton triplet, H-3), 4.43 (1-proton quartet, H-2).

Anal. Calc. for $C_{16}H_{16}O_6S_4$: C, 44.4; H, 3.7; S, 29.7; mol. wt. 433. Found: C, 44.3; H, 3.9; S, 29.8; mol. wt. 600–800 (Rast, in camphor), 908 (Mechrolab, chloroform: a dimer).

Methyl 4,6-O-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate (**23**). — Treatment of **22** (1.00 g) in pyridine for 5 h at 55° gave carbon disulfide, sulfur, and **23** (0.65 g, 87%). The physical properties were comparable with those of authentic[10] **23**.

ACKNOWLEDGMENTS

We thank C. A. Glass and Dr. D. Weisleder for n.m.r. measurements; Dr. W. K. Rohwedder for mass spectroscopic measurements; and C. E. McGrew, B. R. Heaton, and K. A. Jones for microanalyses and determinations of molecular weights.

REFERENCES

1 D. Trimnell, W. M. Doane, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, 17 (1971) 319.
2 B. S. Shasha, W. M. Doane, C. R. Russell, and C. E. Rist, *Nature* (London), 211 (1966) 965.
3 B. S. Shasha, W. M. Doane, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, 10 (1969) 449.
4 W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *J. Org. Chem.*, 32 (1967) 1080.
5 L. J. Brady, *Anal. Chem.*, 20 (1948) 512.
6 D. A. Andrews, F. G. Hurtubise, and H. Krässig, *Can. J. Chem.*, 38 (1960) 1381.
7 D. R. Grassetti and J. F. Murray, *J. Chromatogr.*, 41 (1969) 121.
8 J. J. Willard and E. Pacsu, *J. Amer. Chem. Soc.*, 82 (1960) 4347.
9 H. Ripperger and K. Schreiber, *Chem. Ber.*, 101 (1968) 2450.
10 E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, 3 (1967) 354.
11 B. S. Shasha, W. M. Doane, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, 7 (1968) 99.
12 R. L. Whistler and M. L. Wolfrom, *Methods Carbohyd. Chem.*, 2 (1963) 244.
13 W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *J. Org. Chem.*, 30 (1965) 3071.
14 D. Trimnell, W. M. Doane, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, 11 (1969) 497.
15 D. Trimnell, W. M. Doane, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, 13 (1970) 301.
16 B. S. Shasha, W. M. Doane, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, 6 (1968) 34.