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THIOLATION WITH INVERSION AT SECONDARY POSITIONS DURING FRAGMENTATION–REARRANGEMENT OF SUGAR DITHIOBIS(THIOFORMATES)*

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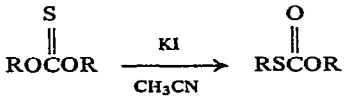
ABSTRACT

Cyclic dithiobis(thioformates) derived from vicinal *trans*-diols decomposed upon pyrolysis or upon treatment with methyl sulfoxide containing catalytic amounts of base to give *O*,*S*-dithiocarbonates with accompanying inversion at the site of thiolation. With derivatives of vicinal *cis*-diols, fragmentation led only to thionocarbonates and the parent diols. Cyclic dithiobis(thioformates) of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, 1,2:5,6-di-*O*-isopropylidene-D-mannitol, and *trans*-1,2-cyclohexanediol decomposed to *O*,*S*-dithiocarbonates; whereas the dithiobis(thioformates) of methyl 4,6-*O*-benzylidene-α-D-mannopyranoside and *cis*-1,2-cyclohexanediol decomposed only to thionocarbonates and the corresponding diols. The structures of the *O*,*S*-dithiocarbonates were confirmed by physical and chemical data.

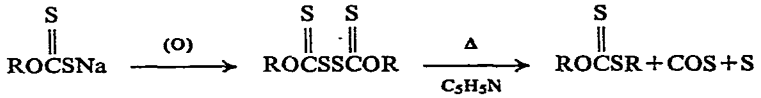
INTRODUCTION AND DISCUSSION

We have reported that thiol groups can be introduced at primary positions in sugars by rearrangement of thionocarbonates[1]



$$\mathrm{RO\overset{S}{\overset{\|}{C}}OR \xrightarrow[CH_3CN]{KI} RS\overset{O}{\overset{\|}{C}}OR}$$

and in aliphatic compounds[2,3] and sugars[4] by the reaction sequence:



$$\mathrm{RO\overset{S}{\overset{\|}{C}}SNa \xrightarrow{(O)} RO\overset{S}{\overset{\|}{C}}SS\overset{S}{\overset{\|}{C}}OR \xrightarrow[C_5H_5N]{\Delta} RO\overset{S}{\overset{\|}{C}}SR + COS + S}$$

Xanthate groups attached to carbon atoms in D-glucopyranosyl rings couple readily to dithiobis(thioformates) but give no thiol on subsequent treatment with pyridine.

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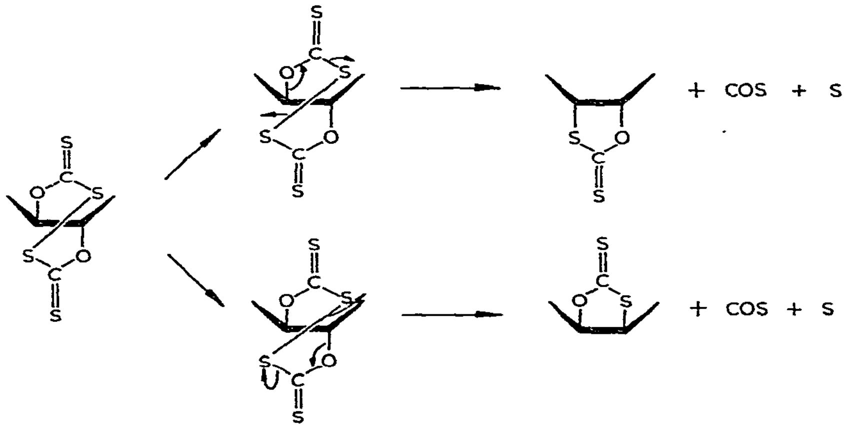
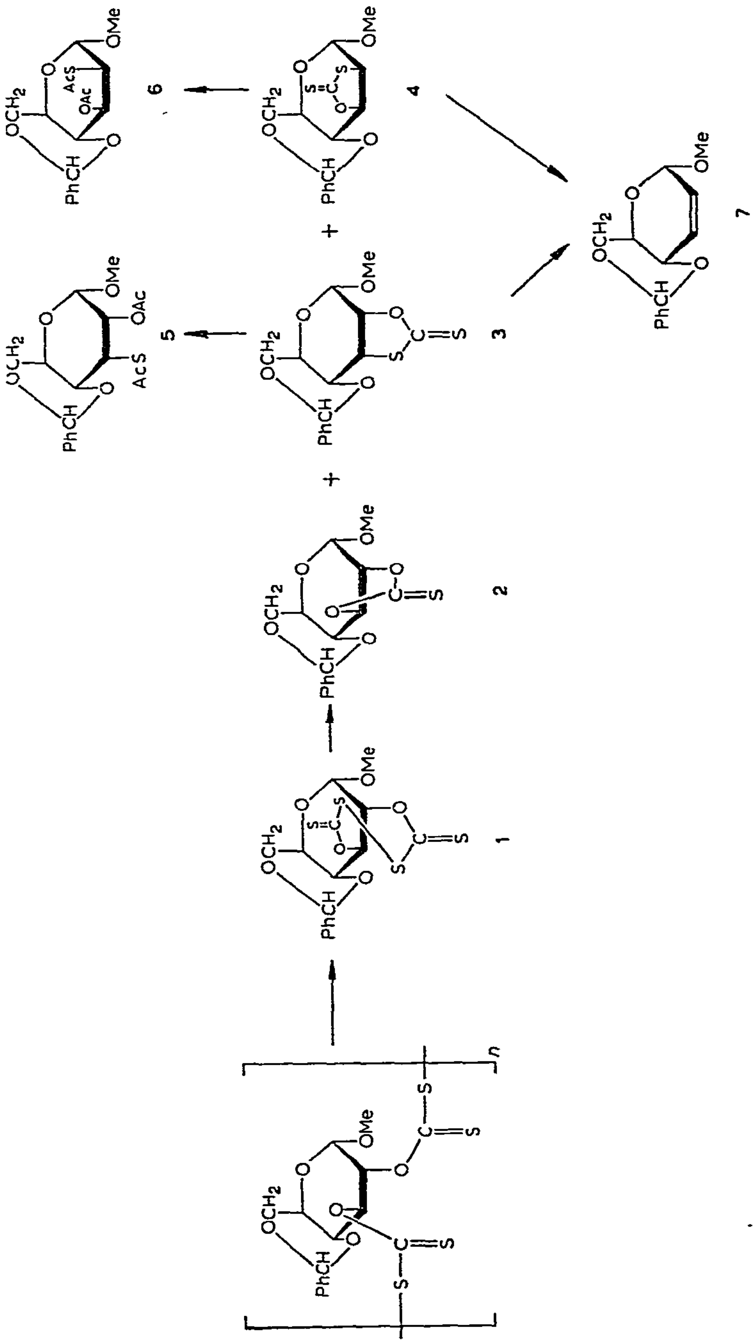
However, when an unsymmetrical dithiobis(thioformate), such as methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2-*O*-[*O*-ethyl dithiobis(thioformate)], is kept in tetrahydrofuran–pyridine, methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2-*O*-(*S*-ethyl dithiocarbonate) is obtained[3]. Thus with this compound, thiolation occurs on the alkyl carbon atom but not at a sugar carbon atom. These results are readily explained by a cyclic mechanism previously proposed[3], which involves nucleophilic displacement by sulfur from the rear side of the carbon atom bearing the dithiobis(thioformate) group. With secondary carbon atoms in glucopyranosyl rings, steric factors apparently impede such a nucleophilic attack.

In subsequent work[5], we applied the reaction sequence involving dithiobis(thioformate) groups with modification to various polysaccharides. The decomposition was conducted at higher temperatures than previously used and without pyridine. High degrees of thiolation were obtained with polysaccharides that were highly substituted with dithiobis(thioformate) groups. These results suggest that both primary and secondary positions were thiolated. Support for thiolation at secondary positions was also provided when xylan, a (1→4)-linked D-xylopyranosyl polymer, and dextran, a (1→6)-linked D-glucopyranosyl polymer, both of which contain essentially only secondary hydroxyl groups, readily gave thio derivatives. As these results with polysaccharides under the different reaction conditions appeared to be in disagreement with the results of monosaccharide studies, further consideration in model systems was given to this thiolation reaction.

A plausible explanation for thiolation at secondary positions in the polysaccharides is that the dithiobis(thioformate) groups involved are cyclic structures bridging vicinal carbon atoms. In such an eight-membered ring structure, an intramolecular nucleophilic displacement by one of the sulfur atoms on one of the sugar carbons in the ring might proceed readily. Such a displacement would result in an *O*,*S*-dithiocarbonate having the inverted configuration about the carbon atom bearing the thiol group.



Scheme 1.

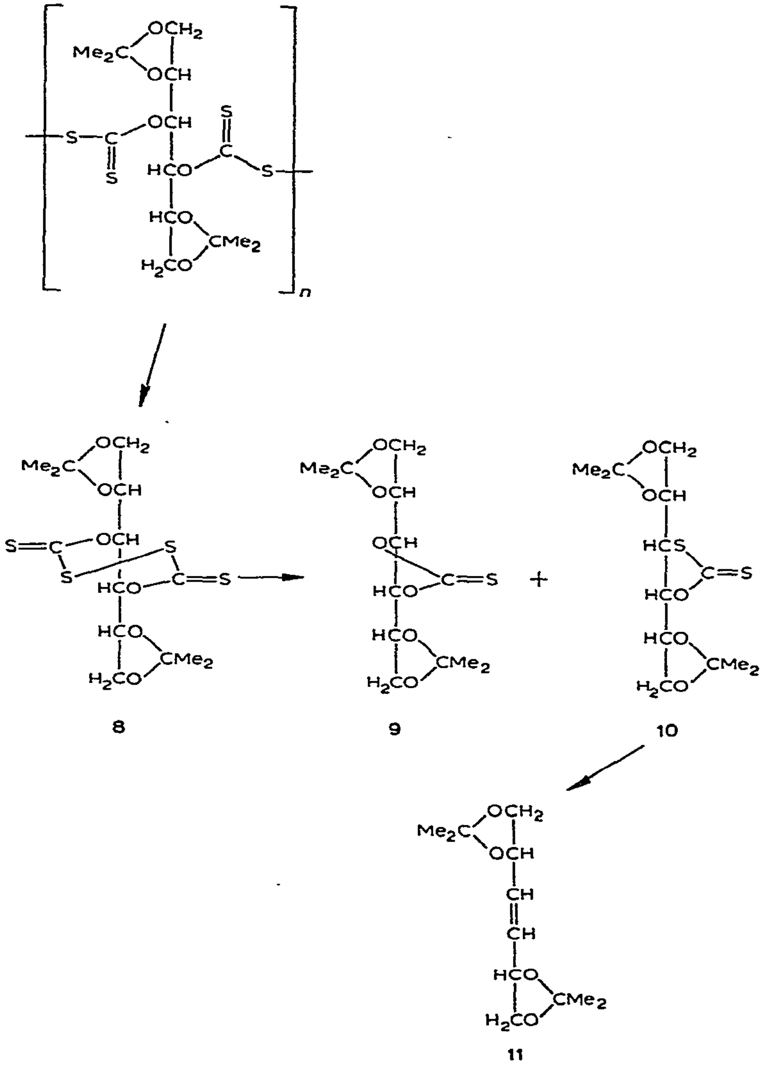


Scheme 2.

This paper presents data on preparation of cyclic dithiobis(thioformate) derivatives at secondary positions in a pyranoid ring, in a cyclohexane ring, and in an acyclic sugar, together with their subsequent decomposition to thiols by pyrolysis and by the use of methyl sulfoxide containing a catalytic amount of base.

Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was fully xanthated in methyl sulfoxide[4] and coupled[5] to give a polymeric dithiobis(thioformate). The polymeric material was then converted into the crystalline, monomeric, cyclic, dithiobis(thioformate) (**1**) on treatment with acetone or methyl sulfoxide. Pyrolysis of the polymeric material gave little thiolation, whereas methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-dithiobis(thioformate) (**1**) decomposed at 240° to give a mixture of *O*,*S*-dithiocarbonates and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate (**2**), as illustrated in Scheme 2. The preponderant *O*,*S*-dithiocarbonate, methyl 4,6-*O*-benzylidene-3-thio-α-D-allopyranoside 2,3-dithiocarbonate (**3**) was isolated in 20% yield. When **1** was heated at 140° in methyl sulfoxide–base, the preponderant *O*,*S*-dithiocarbonate formed (obtained in 47% yield) was methyl 4,6-*O*-benzylidene-2-thio-α-D-mannopyranoside 2,3-dithiocarbonate (**4**). The structures of these *O*,*S*-dithiocarbonates were deduced from i.r., u.v., and n.m.r. spectra (see Experimental), and from the properties of derivatives. The *O*,*S*-dithiocarbonate rings in **3** and **4** were cleaved with sodium hydroxide to the corresponding hydroxythiols, which were subsequently acetylated to crystalline methyl 2-*O*-acetyl-3-*S*-acetyl-4,6-*O*-benzylidene-3-thio-α-D-allopyranoside (**5**) and methyl 3-*O*-acetyl-2-*S*-acetyl-4,6-*O*-benzylidene-2-thio-α-D-mannopyranoside (**6**). The n.m.r. spectra of **5** and **6** were more easily interpreted than the spectra of **3** and **4** from which they were derived[6]. For example, the coupling constants of $J_{1,2}$ 3.5, $J_{2,3}$ 5.0, and $J_{3,4}$ 3.5 Hz in **5** are in fair agreement with the range of coupling constants reported for allopyranoside structures: $J_{1,2}$ 3.3–3.5, $J_{2,3}$ 3.9–4.4, and $J_{3,4}$ 3.9–4.2 Hz. In contrast, coupling constants for **3** were $J_{1,2}$ 5.3, $J_{2,3}$ 6.8, and $J_{3,4}$ 5.0 Hz. Evidently the five-membered *O*,*S*-dithiocarbonate ring structure in **3** distorted normal bond-angles. Both *O*,*S*-dithiocarbonates reacted with methyl phosphite to give the same alkene; namely, methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside[7] (**7**). This confirms the presence of *cis*-structures in both *O*,*S*-dithiocarbonates, based upon the anticipated mechanism[8] of *cis* elimination in this reaction. Methyl 2,3-anhydro-4,6-*O*-benzylidene α-D-allopyranoside, its 2,3-epithio analog, and methyl 4,6-*O*-benzylidene-α-D-mannopyranoside 2,3-thionocarbonate have all been transformed[7] into **7**.

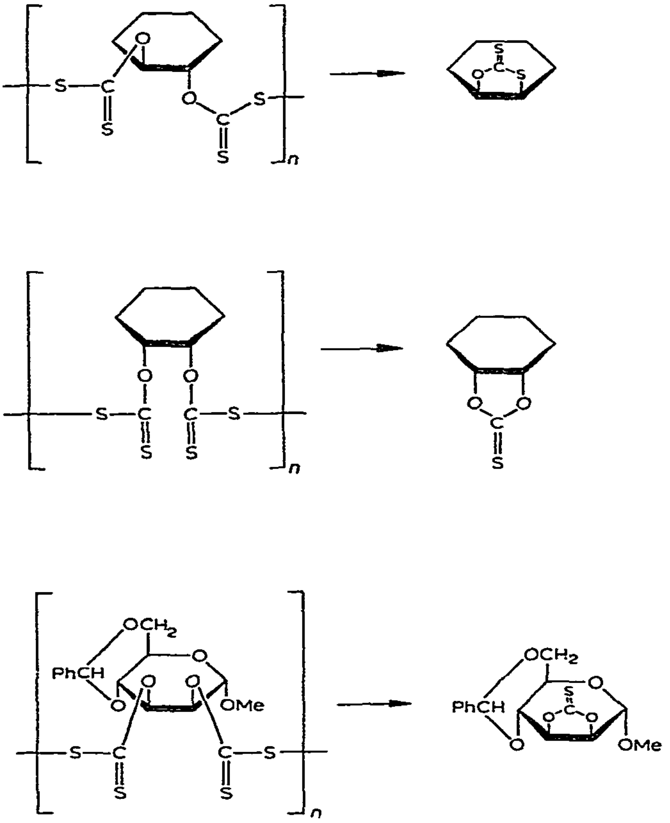
Crystalline 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-dithiobis(thioformate) (**8**) decomposed to a mixture of 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-thionocarbonate (**9**) and 1,2:5,6-di-*O*-isopropylidene-3-thio-D-altritol dithiocarbonate (**10**) upon heating to 220° or to 140° in (50:1) methyl sulfoxide–dicyclohexylamine (Scheme 3). The same *O*,*S*-dithiocarbonate was obtained under both sets of conditions and was identified by i.r., u.v., and n.m.r. spectroscopy, and conversion with methyl phosphite into the known[9] *cis*-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-D-*threo*-hex-3-enitol (**11**).



Scheme 3.

The polymeric 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-dithiobis(thioformate) gave good yields of **10** upon treatment with methyl sulfoxide–base. It is assumed that there was an initial rearrangement of the polymer to the cyclic dithiobis(thioformate) (**8**), followed by decomposition to the *O*,*S*-dithiocarbonate. In one experiment, heating a solution of the polymer in methyl sulfoxide containing 0.4% sodium acetate gave **10** in 93% yield. When the sodium acetate was eliminated, the major product was **9**. Other substances catalyzing the transformation to *O*,*S*-dithiocarbonate in methyl sulfoxide were triethylamine, dicyclohexylamine, sodium thiosulfate, sodium hydroxide, and sodium ethylxanthate. These substances greatly increased the rates of decomposition and lowered the decomposition temperatures. These results are in accord with the previous observations that the pyrolyses of starch dithiobis(thioformates) are influenced by various salts[5].

When polymeric *trans*-1,2-cyclohexanediol dithiobis(thioformate) was pyrolyzed alone, or in the presence of methyl sulfoxide containing triethylamine (50:1), the *O*,*S*-dithiocarbonate resulted (Scheme 4). Only thionocarbonate was obtained when polymeric *cis*-1,2-cyclohexanediol dithiobis(thioformate) was treated similarly. Likewise, decomposition of polymeric methyl 4,6-*O*-benzylidene-α-D-mannopyranoside 2,3-dithiobis(thioformate) gave only methyl 4,6-*O*-benzylidene-α-D-mannopyranoside 2,3-thionocarbonate. Apparently formation of the *O*,*S*-dithiocarbonate occurs only when the adjacent ring-hydroxyl groups involved have the *trans* relationship. Conversions have been reported of *trans*-diol systems in cyclopentane[10] and sugars[11] into *cis*-thio products via cyclizations of thiourethanes.



Scheme 4.

As expected for such dimeric derivatives as 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3,3′-dithiobis(thioformate) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose 6,6'-dithiobis(thioformate), no thiolation occurs on heating to 250° or upon treatment with methyl sulfoxide–base at 150°.

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*, carbon disulfide, and pyridine-d_5 as solvents and tetramethylsilane (τ 10.00) as the internal reference-standard. Spin-decoupling experiments were performed by using a Model 200 AB Hewlett–Packard audio frequency oscillator. Molecular weights were obtained by the Rast method. 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 was the spraying agent. Carbonyl sulfide and carbon disulfide were detected as previously described[5] in the gases liberated during decompositions. Chromatography was conducted with silicic acid (Mallinckrodt, 100 mesh) and activated carbon (Darco). Dithiobis(thioformates) were prepared by known methods[4] with sodium nitrite[5] as oxidant. Decompositions of dithiobis(thioformates) were performed in side-arm test tubes under nitrogen purified through sulfuric acid. The gas issuing from the reaction was passed through calcium chloride to remove moisture and then into a solution of hexane–piperidine (99:1 v/v) cooled to 5°. Pyrolysis temperatures were controlled by using a silicone oil-bath and a Rinco heating element.

Methyl 4,6-O-benzylidene-α-D-glucopyranoside 2,3-dithiobis(thioformate) (**1**). — The crude, polymeric methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-dithiobis-(thioformate) previously prepared[4], on treatment with hot acetone gave compound **1**, which crystallized on cooling. Alternatively, the crude material was dissolved in methyl sulfoxide and treated after 1 h with ethanol to give crystalline **1**, 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]; $\lambda_{\max}^{\text{tetrahydrofuran}}$ 367–370 (ε 129), 280–285 (8,880), 241 nm (16,000); n.m.r. in chloroform-*d*: τ 4.65 (1-proton doublet, $J_{1,2}$ 4.0 Hz, H-1), 4.43 (1-proton quartet, $J_{2,3}$ 10.0 Hz, H-2), 3.40 (1-proton triplet, $J_{3,4}$ 10.0 Hz, H-3).

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. 406 (Rast, in naphthalene).

Methyl 4,6-O-benzylidene-3-thio-α-D-allopyranoside 2,3-dithiocarbonate (**3**). — A suspension of **1** in sulfuric acid–ethanol (1:20 v/v) was filtered and the solid rinsed with ethanol until the washings were neutral. This acid treatment improved the yield of *O,S*-dithiocarbonates upon pyrolysis. Pyrolysis of **1** (2.90 g) at 240° for 5 min gave a mixture of carbonyl sulfide and carbon disulfide in a ratio of 1:1 and in amounts that indicated 72% of decomposition. T.l.c. of the pyrolyzate (4:1 carbon disulfide–ethyl acetate) showed five spots: R_F 0.80, which corresponded to **1**, R_F 0.65, 0.50, 0.45, and 0.0. The odor of benzaldehyde was detected. The pyrolyzate was chromatographed on a silicic acid-activated carbon (100 g, 9:1 w/w) column (3.5 × 30 cm). Elutions with ethyl acetate–hexane (1:9, 500 ml) removed sulfur and **1**, then elutions with ethyl acetate–hexane (1:4, 250 ml; 3:7, 500 ml; 2:3, 250 ml) removed the R_F 0.65, 0.50, and 0.45 components (1.19 g), and finally elution with ethyl acetate (500 ml) removed the R_F 0.0 component (0.44 g).

I.r. and u.v. suggested that the material having R_F 0.0 was a multicomponent mixture of *O*,*S*-dithiocarbonates and thionocarbonates derived from the loss of the benzylidene group from the components of higher R_F value. U.v. spectroscopy of solutions of the R_F 0.65 and 0.45 components eluted from qualitative t.l.c. plates indicated that they were *O*,*S*-dithiocarbonates. The R_F 0.5 component was identified as **2** by comparison with an authentic sample[12]. A solution of these components in ethyl acetate (50 ml) was shaken with sodium hydroxide solution (12.5M, 10 ml) for 5 min to decompose **2** to methyl 4,6-*O*-benzylidene-α-D-glucopyranoside and leave the *O*,*S*-dithiocarbonates intact. The ethyl acetate solution was neutralized by shaking with dilute acetic acid solution and dried. Evaporation of the solvent left a residue, that was chromatographed on a silicic acid (40 g) column (2.5 × 14 cm). Elution with 1:9 ethyl acetate–hexane (200 ml) removed the R_F 0.65 (0.07 g) and R_F 0.45 (0.46 g, 20%) components. The major component (R_F 0.45) was identified as **3** and it crystallized from ethyl acetate–hexane or ethanol, m.p. 183–184°, $[\alpha]_D^{23}$ +281° (*c* 1.2, chloroform); λ_{max}^{film} 1060, 1190 cm^{-1} [O(C=S)S]; $\lambda_{max}^{chloroform}$ 285–286 nm (ε 15,150); n.m.r. in pyridine-d_5: τ 4.95 (1-proton doublet, $J_{1,2}$ 5.3 Hz, H-1), 4.32 (1-proton quartet, $J_{2,3}$ 6.8 Hz, H-2), 4.72 (1-proton quartet, $J_{3,4}$ 5.0 Hz, H-3), 5.78 (1-proton quartet, $J_{4,5}$ 9.0 Hz, H-4).

Anal. Calc. for $C_{15}H_{16}O_5S_2$: C, 52.9; H, 4.74; S, 18.8; mol. wt. 340. Found: C, 53.1; H, 4.86; S, 18.5; mol. wt. 334 (Rast, in camphor).

When the crude, polymeric, methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-dithiobis(thioformate) (1.0 g, m.p. 170°, dec.) was heated for 5 min at 240°, carbonyl sulfide–carbon disulfide (3:7) was obtained. Decomposition was extensive, and t.l.c. showed only streaking where *O*,*S*-dithiocarbonates and thionocarbonates had previously been observed.

*Methyl 4,6-*O*-benzylidene-2-thio-α-D-mannopyranoside 2,3-dithiocarbonate* (**4**). — A mixture of **1** (1.0 g) in methyl sulfoxide (3 g) containing dicyclohexylamine (0.06 g) was heated for 3 min at 140° and carbonyl sulfide and carbon disulfide (1:1) were evolved. The solution was poured into ice–water and the resulting solid was filtered off and dried in air. The solid was dissolved in chloroform (5 ml) and adsorbed onto a column (4.5 × 11 cm) of silicic acid. Elution with hexane (1 l) gave sulfur, and with 1:9 ethyl acetate–hexane (first 250 ml) colored impurities, and the second 500 ml, **4** (0.35 g, 47%). Ester **4** was crystalline, m.p. 153–155° (ethanol), $[\alpha]_D^{25}$ −79° (*c* 0.9, chloroform); λ_{max}^{film} 1060, 1200 cm^{-1} [O(C=S)S]; $\lambda_{max}^{chloroform}$ 282–285 nm (ε 14,200); n.m.r. in pyridine-d_5: τ 4.97 (1-proton singlet, $J_{1,2}$ 0.0 Hz, H-1), 5.19 (1-proton doublet, $J_{2,3}$ 7.0 Hz, H-2), 4.39 (1-proton triplet, $J_{3,4}$ 8.0 Hz, H-3). These couplings corresponded to those of the known methyl 4,6-*O*-benzylidene-α-D-mannopyranoside 2,3-thionocarbonate[7,13].

Anal. Calc. for $C_{15}H_{16}O_5S_2$: C, 52.9; H, 4.74; S, 18.8; mol. wt. 340. Found: C, 52.7; H, 4.81; S, 18.5; mol. wt. 345 (Rast, in camphor).

*Methyl 2-O-acetyl-3-S-acetyl-4,6-O-benzylidene-3-thio-α-*D*-allopyranoside* (**5**). — A suspension of **3** (0.125 g) in ethanol (1 ml) and sodium hydroxide solution (12.5M, 2 ml) was warmed for 5 min on a steam bath until two phases formed. At this point the upper phase showed a positive thiol test[14]. The mixture was dissolved in ice–water (50 ml) and partitioned with chloroform (50 ml). The chloroform phase was shaken with 5% hydrochloric acid (10 ml), and then with water, and dried (Na_2SO_4). Evaporation of solvent gave a product that was treated with acetic anhydride (2 ml) and pyridine (2 ml) for 3 h at room temperature. The mixture was stirred with ice–water to precipitate a solid, which was filtered, air dried, and crystallized from ethanol to give **5**: 0.105 g (75%), m.p. 174–175°, $[\alpha]_D^{26}$ +31.4° (*c* 1.15, chloroform); λ_{max}^{film} 1700 (SAc), 1750 cm^{-1} (OAc); n.m.r. in pyridine-d_5: τ 5.05 (1-proton doublet, $J_{1,2}$ 3.5 Hz, H-1), 4.51 (1-proton triplet, $J_{2,3}$ 5.0 Hz, H-2), 4.90 (1-proton triplet, $J_{3,4}$ 3.5 Hz, H-3).

Anal. Calc. for $C_{18}H_{22}O_7S$: C, 56.5; H, 5.80; S, 8.38. Found: C, 56.6; H, 5.91; S, 8.23.

*Methyl 3-O-acetyl-2-S-acetyl-4,6-O-benzylidene-2-thio-α-*D*-mannopyranoside* (**6**). — The title compound was prepared from **4** (0.090 g) as **5** had been prepared from **3**; yield, 0.079 g (78%), m.p. 126–128°. Crystallization from alcohol gave m.p. 130–131°, $[\alpha]_D^{26}$ +31.6° (*c* 0.76, chloroform); λ_{max}^{film} 1705 (SAc), 1750 cm^{-1} (OAc); n.m.r. in pyridine-d_5: τ 5.09 (1-proton doublet, $J_{1,2}$ 1.5 Hz, H-1), 5.30 (1-proton quartet, $J_{2,3}$ 5.0 Hz, H-2), 4.01 (1-proton quartet, $J_{3,4}$ 9.5 Hz, H-3).

Anal. for $C_{18}H_{22}O_7S$. Found: C, 56.2; H, 5.94; S, 8.24.

*Methyl 4,6-O-benzylidene-2,3-dideoxy-α-*D-erythro-*hex-2-enopyranoside* (**7**). — Esters **3** (0.123 g) and **4** (0.108 g) were sealed under nitrogen in tubes with methyl phosphite (3 ml) and kept for 6 h at 120°. The products were isolated as described[7] and purified chromatographically; yields of **7**: 0.024 g (27%), m.p. 119° from **3**, and 0.047 g (60%), m.p. 119° from **4**; mixed m.p. 118–119°. The i.r. spectra were identical and the same as that of known **7**.

*1,2:5,6-Di-O-isopropylidene-*D*-mannitol 3,4-dithiobis(thioformate)* (**8**). — The polymeric 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-dithiobis(thioformate) was prepared under conditions described earlier[4] and pyrolyzed (1 g) in methyl sulfoxide (2 ml) containing 0.4% of sodium acetate for 15 min at 110° to give 720 mg (93%) of material characterized as 1,2:5,6-di-*O*-isopropylidene-3-thio-D-altritol 3,4-dithiocarbonate (**10**) (see next preparation). The crystalline title compound **8** was produced by treating the polymeric material with acetone–ethanol; yield 6.25 g (79%), m.p. 215° (dec.), $[\alpha]_D^{24}$ −372° (*c* 0.9, chloroform); λ_{max}^{film} 1040–1060, 1240 cm^{-1} [O(C=S)SS(C=S)O]; $\lambda_{max}^{ethanol}$ 280 nm (ε 7,500), 230–240 nm (ε 15,000); n.m.r. in chloroform-*d*: τ 3.92 (2-proton quartet, $J_{3,4}$ 9.0 Hz, H-3, H-4); 5.72 (2-proton quartet, $J_{2,3}$, $J_{4,5}$ 3.0 Hz, H-2, H-5).

Anal. Calc. for $C_{14}H_{20}O_6S_4$: C, 40.8; H, 4.89; S, 31.1; mol. wt. 412. Found: C, 40.9; H, 4.94; S, 30.7; mol. wt. 445 (Rast, in camphor).

*1,2:5,6-Di-O-isopropylidene-3-thio-*D*-altritol-3,4-dithiocarbonate* (**10**). — Pyrolysis of **8** (2.75 g) at 220° for 3 min gave 3:2 carbonyl sulfide–carbon disulfide. The pyrolyzate was mixed with carbon disulfide (100 ml) and filtered to remove some **9** (ref. 9) and impurities, and then diluted with hexane (100 ml) and adsorbed onto a silicic acid column (4.5 × 11 cm). Elution with carbon disulfide–hexane and hexane removed sulfur and yellow impurities, elution with (50:1) carbon disulfide–ethyl acetate removed **10** (0.55 g, 26%). Evaporation of solvent and crystallization of the residue from hexane gave pure **10**, m.p. 141–142°, $[\alpha]_D^{24}$ −94° (*c* 0.5, chloroform), λ_{max}^{film} 1060, 1200 cm^{-1}, $\lambda_{max}^{ethanol}$ 283 nm (ε 12,000); n.m.r. in CS_2: τ 6.47 (1-proton quartet, $J_{2,3}$ 8.5, $J_{3,4}$ 6.3 Hz, H-3).

Anal. Calc. for $C_{13}H_{20}O_5S_2$: C, 48.7; H, 6.29; S, 20.0; mol. wt. 320. Found: C, 48.6; H, 6.24; S, 20.2; mol. wt. 312 (Rast, in camphor).

Pyrolysis of **8** (0.200 g) in methyl sulfoxide (0.3 ml) at 200° for 10 min gave a major component (t.l.c.) that was precipitated by water and crystallized from ethanol to yield 0.100 g of **10**. When the experiment was repeated at 150°, two major spots, corresponding to **9** and **10** in about equal amounts, were revealed. When triethylamine, dicyclohexylamine, sodium acetate, sodium thiosulfate, sodium hydroxide, or sodium ethylxanthate was included in the methyl sulfoxide (1:50), the major component was **10**, even at 25° (3 h).

In another experiment, the polymeric 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-dithiobis(thioformate) (1 g), heated in methyl sulfoxide (2 ml) at 150° for 10 min, gave **9** (0.72 g) but inclusion of triethylamine in the methyl sulfoxide (1:50) gave **10** (0.72 g).

cis-*3,4-Dideoxy-1,2:5,6-di-*O*-isopropylidene-*D-threo-*hex-3-enitol* (**11**). — A solution of **10** (0.100 g) in methyl phosphite (1.5 ml) was kept in a sealed tube for 70 h at 120° under nitrogen. The reaction mixture was processed by a known method[9] and extracted with hexane. Evaporation of the hexane left a syrup (0.032 g, 45%), $[\alpha]_D^{25}$ −10.7° (*c* 2.9, chloroform); n.m.r. in CCl_4: τ 4.49 (2-proton multiplet, $J_{3,4}$ 10.9–11.0 Hz). Haines[9] reported $[\alpha]_D^{22}$ −8.1° (*c* 2.2, chloroform) and $J_{3,4}$ 10.95 Hz for this compound.

trans- *And* cis-*1,2-cyclohexanediol dithiobis(thioformates).* — Both of these polymeric dithiobis(thioformates) were prepared in 52% yield from the corresponding diols. The i.r. spectra of these products showed no hydroxyl or carbonyl absorption, but did absorb in the 1000–1200 cm^{-1} region characteristic of dithiobis(thioformate). For the *trans*-1,2-dithiobis(thioformate), the S content was 48.7%; for the *cis*-1,2-dithiobis(thioformate), the S content was 46.0%. (Calc. for $C_8H_{10}O_2S_4$: S, 48.1).

Suspensions of the *trans*- (6.7 mg) and *cis*- (4.4 mg) 1,2-dithiobis(thioformates) in methyl sulfoxide containing triethylamine (50:1, 2 drops) were heated for 3 min at 140°, cooled, and diluted to 100 ml with ethanol. With the *trans* product, a strong absorption maximum was found at 285 nm characteristic of *O,S*-dithiocarbonates. With the *cis* isomer, a strong maximum at 245 nm characteristic of thionocarbonates was observed.

Polymeric methyl 4,6-O-benzylidene-α-D-mannopyranoside 2,3-dithiobis(thioformate). — The polymer was prepared from methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (2.0 g) as described in the preparation of the corresponding polymer of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside[4]; yield 2.2 g (72%).

Anal. Calc. for $C_{16}H_{16}O_6S_4$: S, 29.7. Found: S, 29.2.

This material (0.3 g) in methyl sulfoxide–triethylamine (99:1, 2 ml) was heated for 3 min at 145° to give methyl 4,6-*O*-benzylidene-α-D-mannopyranoside 2,3-thionocarbonate[7,13], as shown by i.r., u.v., and t.l.c. No *O*,*S*-dithiocarbonate was detected; n.m.r. in pyridine-d_5: τ 4.80 (1-proton singlet, $J_{1,2}$ 0.0 Hz, H-1); 4.91 (1-proton doublet, $J_{2,3}$ 7.0 Hz, H-2); 4.53 (1-proton triplet, $J_{3,4}$ 7.0 Hz, H-3). The reported[7] $J_{1,2}$ value for this compound is 0.0 Hz. The abnormal coupling constants were similar to those found for **4**.

Decompositions of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose 3,3'-dithiobis-(thioformate)[15] *and 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose 6,6'-dithiobis-(thioformate)*[16]. — Samples of these compounds were heated for 10 min at >250°. Although the compounds darkened and some gas was evolved, t.l.c. showed mainly starting material and only small amounts of components of lower R_F value (carbon disulfide–ethyl acetate 4:1). When they were heated to >150° in methyl sulfoxide containing dicyclohexylamine (50:1) for a similar period, much gas was evolved (about 80% carbon disulfide). T.l.c. of the products showed mainly 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose.

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