($CHCl_3$) 1734, 1658 cm^{-1}; NMR ($CDCl_3$) 367 (s, 2, 6-H, 7-H), 340.5 (s, 1, 4-H), 221.5 (s, 3, CO_2CH_3), 68 (s, 3, 19-CH_3), 58.5 Hz (s, 3, 18-CH_3).

Anal. Calcd for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C, 74.26; H, 8.82.

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Registry No.—**1a,** 54498-03-2; **1b,** 54498-04-3; **2a,** 3460-93-3; **2b,** 54516-82-4; **2b** sodium salt, 54498-05-4; **3a,** 54498-06-5; **3b,** 54498-07-6; **4a,** 54498-08-7; **4b,** 54498-09-8; **5,** 54498-10-1; **8,** 976-71-6; **9,** 1176-21-2.

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Photolysis of Some Carbohydrate Dithiobis(thioformates)[1a]

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The photolysis of several oxidatively coupled xanthates of model sugar compounds has been investigated. The photolysis of bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)dithiobis(thioformate) (**2**) gave the xanthate ester, bis(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) 6-*O*,6′-*S*-dithiocarbonate (**5**), in 78% yield. In concentrated solutions, bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) tetrathiobis(thioformate) (**3**) was produced along with **5**. The photolysis of bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl) dithiobis(thioformate) (**14**) gave bis(3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl) 3-*O*,3′-*S*-dithiocarbonate (**15**), in which an oxygen atom on the sugar ring has been replaced with sulfur with retention of configuration. A cyclic mechanism in which either the excited thiocarbonyl sulfur or a sulfur of the disulfide linkage attacks the carbon giving a front-side displacement of oxygen has been proposed to account for the observed results.

The relatively high efficiency with which sulfur compounds absorb light, especially compounds which contain the thiocarbonyl group, has resulted in a large number of reports on the photochemistry of organic sulfur compounds.[2–4] The xanthate group [λ_{max} (H_2O) 305 nm (ϵ 12,000–17,000)] and derivatives thereof exhibit a very strong absorbance of uv light and, therefore, have the potential of photochemical transformations by direct irradiation. The photolyses of some xanthate esters have been reported. Okawara and coworkers subjected *O*-ethyl *S*-benzyl xanthate to uv irradiation and found benzyl mercaptan and carbonyl sulfide as major products, which were obtained in low yields.[5–7] When styrene or methyl methacrylate was added to the reaction mixture, polymerization occurred, indicating a free-radical mechanism for the photodecomposition of the xanthate ester. Photolysis of *O*-benzyl *S*-methyl xanthate in the presence of cyclohexene gave methyl mercaptan, carbonyl sulfide, 3-benzylcyclohexene, and 3-(2-cyclohexene-1-yl)cyclohexene (1). The xanthate ester, *O*-diphenylmethyl *S*-methyl xanthate, gave 1,1,2,2-tetraphenylethane and 1. The results suggested the formation of a carbene intermediate. In ethanol no decomposition of *O*-benzyl *S*-methyl xanthate occurred. However, addition of triethylamine gave methyl benzyl thioether, *S*-benzyl ethyl thiocarbonate, dibenzyl thioether, and dibenzyl disulfide.[8]

Acyl xanthate esters have been photolyzed and produced acyl radicals and xanthate radicals.[9] The acyl radical then loses carbon monoxide, and a recombination reaction occurs between the new alkyl radical and the xanthate radical to give a xanthate ester which is stable to Pyrex-filtered light. Shah, Singh, and George[10,11] observed that the photolytic decomposition of a dixanthate gave a mixture of dimeric compounds which appeared to be formed from a carbene intermediate. Another similar xanthate ester was prepared by Schonberg and Sodtke[12] and was photolyzed to produce a coupled product.

Xanthates have been used as photoinitiators in polymerization reactions[5,7,13–16] and incorporated in polymers for grafting sites.[15,16]

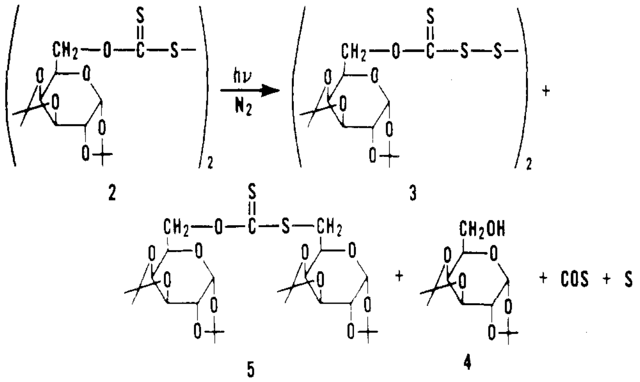
We have previously reported on the ground-state chemistry of the oxidatively coupled xanthate, dithiobis(thioformate), which is also called xanthide.[17]

Because of the strong absorption of light by the xanthide group [λ_{max} (EtOH) 230–240 nm (ϵ 15,800–18,900), 280–290 (6600–8900)],[18] the photoreactivity of xanthate derivatives, and the chemical reactivity of the xanthide group, a study of the photochemistry of some carbohydrate xanthides was undertaken.

Results

Photolysis of Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) Dithiobis(thioformate) (2). Photolysis of 2 through quartz (λ > 200 nm) in methanol gave a white solid (3), which was filtered off. Column chromatography of the filtrate afforded unreacted 2, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (4), sulfur, and a component (5) of R_f intermediate to that of 2 and 4 (Scheme I).

Scheme I



The uv spectrum of 5 showed absorption at 285 nm characteristic of a xanthate ester.[18]

From elemental analysis, 5 was formulated as bis(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) 6-*O*,6′-*S*-dithiocarbonate. Compound 5 was isolated in 35% yield. The NMR spectrum showed a two-proton absorption centered at τ 6.68, which is in the expected range for thiomethylene protons.[17]

Additional evidence for the structure of 5 was obtained by reductive cleavage with $LiAlH_4$[19] to give 4 and 1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactopyranose (6) (Scheme II). The structure of 6 was confirmed by NMR

Scheme II

$$\underset{5}{R{-}O{-}\overset{\overset{S}{\|}}{C}{-}S{-}R} \xrightarrow{LiAlH_4} \underset{4}{R{-}OH} + \underset{6}{RSH}$$

R = 1,2:3,4-di-O-ispropylidene-6-deoxy-α-D-galacopyranose

and elemental analysis. The NMR of this sample showed a one-proton doublet at τ 8.37, which slowly disappeared when kept with D_2O for 18 hr. The slow exchange and the position of the peak is indicative of a thiol group.[17] A two-proton multiplet centered at τ 7.31, assigned to the protons of the thiol-substituted methylene group, collapsed to a broad doublet when the deuterium exchange was complete.

The mass spectrum of 5 showed a high-mass peak at *m/e* 563 which corresponds to M − 15. Other mass peaks supporting the structure appeared at *m/e* 319, 303, and 275, which corresponds to $M - CH_3 - C_{12}H_{20}O_5$, $M - C_{12}H_{19}O_5S$, and the radical ion $C_{12}H_{19}O_5S$.

The white solid 3 showed a strong, continuous absorption from 350 to 220 nm with an ill-defined shoulder at approximately 315 nm (ε 7150) and a maximum at 240 nm (ε 21,000). From the NMR and elemental analysis, 3 was formulated as bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) tetrathiobis(thioformate). Although this compound had a fairly wide melting range, 160–164°, its physical properties were the same as those of an authentic sample prepared from the sodium xanthate salt of 4 and sulfur monochloride. Attempted recrystallization from hot methanol gave 2, free sulfur, and a component of mp 149–151° identified as bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) trithiobis(thioformate) (7). This decomposition might be expected, since polysulfides are known to readily lose sulfur to form disulfides.[20]

In addition to the products discussed above, COS was the major gas evolved, but after 3 hr CS_2 was also detected by the method of Brady.[21] This result suggests decomposition of the photoproduct.

Using cyclohexane solvent and similar reaction conditions, the same products were obtained in nearly the same yields when 2 was photolyzed in methanol. Longer irradiation in either solvent gave more complex mixtures, because 5 also undergoes photodecomposition under these reaction conditions and evolves CS_2. The yield of 3 was increased by photolyzing at 5° rather than at 25°. When Corex-filtered light (λ > 260 nm) was used, 5 did not react to any significant extent. Therefore, a cyclohexane solution (0.064 *M*) of 2 was irradiated for 22 hr with Corex-filtered light (λ > 260 nm) to yield 3 (37%), 5 (35%), 4 (13%), and COS, but no CS_2 could be detected. A more dilute solution (0.003 *M*) gave 5 in 74% yield and 3 could not be detected after 5.5 hr. However, when irradiation was stopped after 2 hr, an apparent mixture of polysulfides was obtained, based on mp 145–153° and elemental analysis.

The photolysis of the tetrasulfide 3 in cyclohexane resulted in the formation of the xanthate ester 5, but at a slower rate than from 2. For example, under similar conditions, a 9.2% yield of 5 was obtained from 3 compared to 35% from 2.

The effect of solvent on the reaction mixture is shown in Table I. The results show that the yield of 5 is highest in cyclohexane, and in the alcohol solvents more 4 is produced along with CS_2. In all cases, some 6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (8) was obtained. However, the yield of 8 was not greatly increased when 2-propanol was used.

Table I
Solvent Effect on Molar Yield of Products from Irradiation of 2[a]

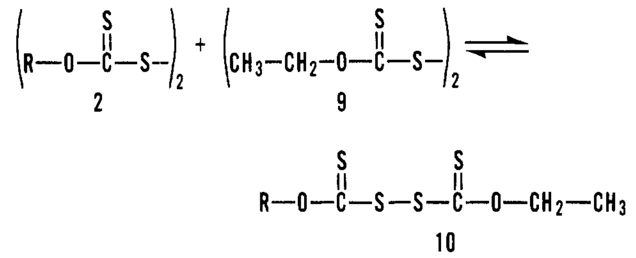
	Irradiation time, hr					
Product	13 Cyclohexane	23	19 Methanol	13 2-Propanol		5.5 Cyclohexane
Sulfur	0.80	0.75	0.88	0.34	0.34	0.33
8[b]	0.11	0.2	0.09	0.2	0.16	0.23
5[a]	0.74	0.5	0.57	0.31	0.27	0.74
4[a]	0.15	0.21	0.55	0.80	1.07	0.25
COS	0.34		0.25		0.81	
CS_2	0.0		0.27		0.81	

[a] See Scheme II. [b] 6-Deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose.

The photolysis of a solution of 2 and ethyl xanthide (9) in cyclohexane rapidly gave the mixed xanthide 10 (Scheme III). After 15–20 min, an apparent photostationary state of the three xanthides was established.

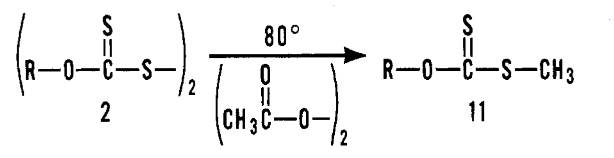
Compound 2 was found to react readily with methyl radicals generated by the thermal decomposition of acetyl peroxide. Using approximately 2 mol of acetyl peroxide per mole of 2, 1.1 mol of *S*-methyl xanthate ester 11 was obtained (Scheme IV). The structure of 11 was confirmed by

Scheme III



R = 1,2:3,4-di-O-isopropylidene-6-deoxy-α-D-galactopyranose

Scheme IV

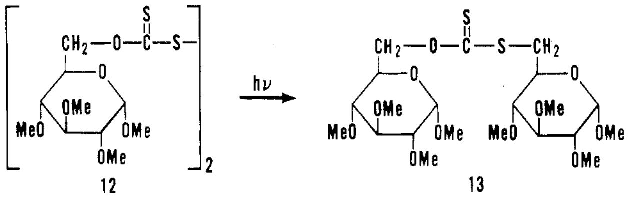


R = 1,2:3,4-di-O-isopropylidene-6-deoxy-α-D-galactopyranose

comparison of its properties to that of an authentic sample prepared from the sodium xanthate salt of 4 and methyl iodide.

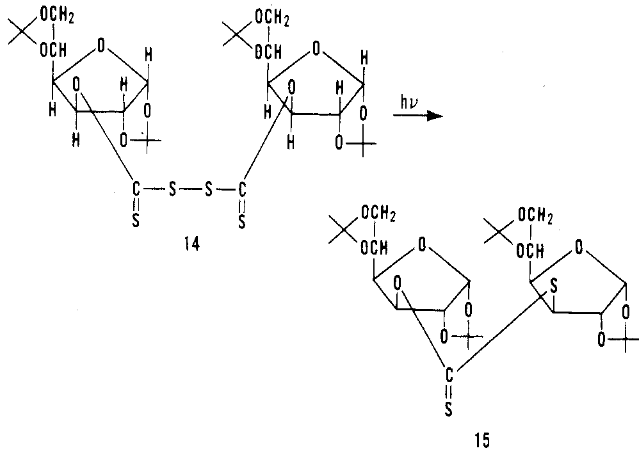
Photolysis of Bis(methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside) 6,6′-Dithiobis(thioformate) (12). The photolysis of 12 ($\lambda > 200$ nm) in cyclohexane resulted in the formation of the corresponding xanthate ester (13) in 47% yield (Scheme V). No attempt was made to identify any polysulfides similar to 3, and products having disulfide bonds were destroyed by reaction with thiophenol or *p*-chlorothiophenol.[22]

Scheme V



Photolysis of Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) 3,3′-Dithiobis(thioformate) (14). The photolysis of 14 with Corex-filtered light gave the xanthate ester, bis(3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl) 3-*O*,3′-*S*-dithiocarbonate (15) (Scheme VI), as a white, crystalline solid in 34% yield in which S has replaced O without inversion. Analysis of the original reaction mixture by measurement of the absorption of 283 nm showed that the total xanthate ester formed was 37%. Therefore, the xanthate ester formation occurred with at least 92% retention of configuration.

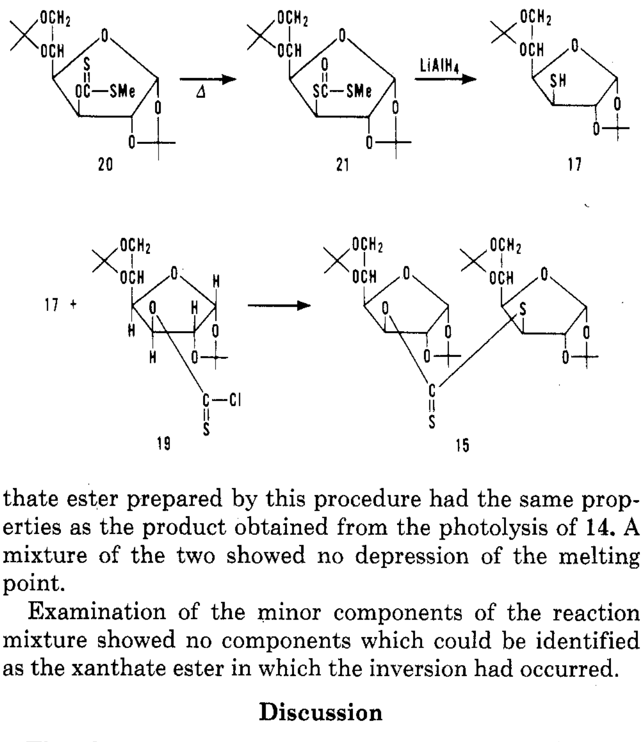
Scheme VI



This xanthate ester 15 was reduced with $LiAlH_4$ to give 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (16) and 1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-glucofuranose (17). The NMR spectrum of 17 was identical with that of the known 17 prepared by the method of Heap and Owen.[19] The thiol was also converted to the *S*-acetyl derivative (18) and exhibited properties identical with those previously reported for this compound.[19]

The xanthate ester 15 was independently synthesized by reaction of the 3-thiol 17, prepared by the method of Heap and Owen,[19] with the 3-chlorothioformate 19 of 16 described by Shasha and Doane[23] (Scheme VII). The xanthate ester prepared by this procedure had the same properties as the product obtained from the photolysis of 14. A mixture of the two showed no depression of the melting point.

Scheme VII



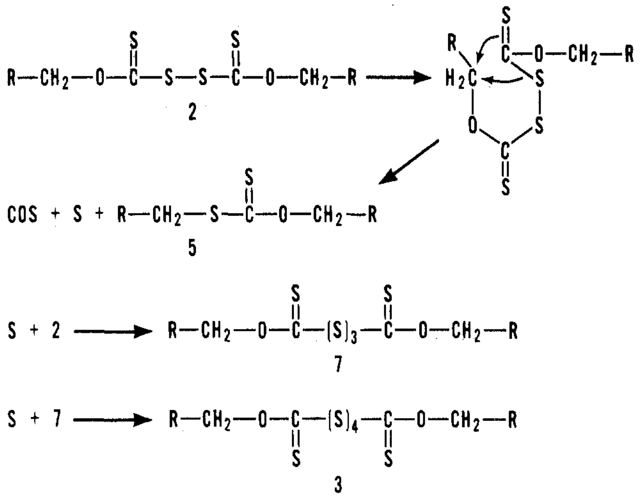
Examination of the minor components of the reaction mixture showed no components which could be identified as the xanthate ester in which the inversion had occurred.

Discussion

The photochemical transformation of 2 to 3 and 5 is in contrast to the pyrolysis reaction reported by Trimnell et al.[17] in which 2 gave only bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-thionocarbonate. However, on pyrolysis bis(methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside) 6,6′-dithiobis(thioformate) (12) rearranged to the corresponding dithiocarbonate 13.[17] They also reported that dithiocarbonates were not formed when xanthides attached to secondary positions were pyrolyzed. In the present work, photolyzing 14 gave the dithiocarbonate 15.

The mechanism proposed to account for the observed products is shown in Scheme VIII. This mechanism involves the attack of an excited sulfur atom on the methylene carbon, which requires a seven-membered cyclic transition state if it involves the thiocarbonyl sulfur, or a five-membered transition state if it involves a sulfur of the disulfide linkage. The reaction then proceeds with the elimination of carbonyl sulfide and free sulfur. This molecular sulfur may insert into a disulfide bond or possibly abstract another atom of sulfur to form S_2, which could insert into a disulfide bond. Gunning et al.[24,25] have shown that condensed-phase photolysis of COS yields long-chain sulfur biradicals and have proposed that either sulfur atoms or S_2 biradicals are the propagating species. These insertion reactions would account for the formation of the trisulfide and tetrasulfide products.

Scheme VIII



The proposed mechanism does not account for the apparent preference of tetrasulfide formation. However, Hoffmeister and Tarbell[26] found a similar preferential formation of a hexasulfide on pyrolysis of benzoyl cyclopentamethylene thiocarbamyl disulfide. The photolysis of benzoic pyrrolidine dithiocarbamic anhydride gave a hexasulfide, while photolysis of benzoic morpholine dithiocarbamic anhydride gave a tridecasulfide.[27] They suggested that the selective formation of the polysulfides is due to the lower solubilities of these polysulfides. This appears to be the most plausible explanation of the results presented here, for disulfide exchange would be expected to occur very rapidly to form many polysulfides based on the rapid exchange of ethyl xanthide and **2**.

The rapid exchange reaction of ethyl xanthide with **2** is assumed to proceed by a radical mechanism based on results of Siebert,[13] who has shown that photolysis of xanthide will catalyze the polymerization of butyl acrylate, and on results of Walling and Rabinowitz,[28] which showed that disulfides photolyze to thiyl radicals. The above results indicate the xanthate radical is relatively stable and does not readily abstract hydrogen atoms from cyclohexane, since **4** was obtained in low yield and carbon disulfide could not be detected in the reaction mixture when Corex-filtered light was used. However, methanol or 2-propanol appear to serve as a hydrogen source for the xanthate radical in dilute solution, since carbon disulfide and **4** are produced in larger quantities at the expense of **5** when photolysis is carried out in these solvents.

Although methyl radicals readily attacked the disulfide bond of the xanthide, which supports a free-radical mechanism, the stereoselectivity in the formation of **15**, the low yield of **5** from the tetrasulfide **3**, the high yield of **5** in dilute solution, and the low yield of the 6-deoxy derivative, **8**, in 2-propanol strongly favor the cyclic mechanism. If a free radical were formed on C_3 of the glucose, one would expect to obtain both the allo and the gluco configuration in the 3-thio sugar.

An initial isomerization similar to the thermal rearrangement of xanthate esters was considered unlikely, since, under the reaction conditions, no carbonyl-containing products could be detected by ir analysis of the reaction mixture.

The photolysis of either the mono- or the dixanthide of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside under similar reaction conditions did not give a xanthate ester. Likewise, the monoxanthide of *trans*-1,2-cyclohexanediol did not give a xanthate ester product.

Experimental Section

Melting points were determined with a Fisher-Johns[29] apparatus and are uncorrected. Optical rotations were determined in a 1-dm tube with a Rudolph polarimeter. Ir spectra were recorded with a Beckman IR-33 spectrophotometer. NMR spectra of $CDCl_3$ solutions were recorded on a Varian HA-100 spectrometer with tetramethylsilane as internal reference standard (τ 10.0). A Perkin-Elmer Model 202 spectrophotometer was used to record uv spectra. For TLC, silica gel G was used as the adsorbent and 19:1 (v/v) methanol–sulfuric acid as the spray reagent. Mallinckrodt silicic acid (100 mesh) was used for large-scale chromatography. All reagents were reagent grade and were used without further purification. The light source was a Hanovia high-pressure mercury arc lamp (450 W, No. 679A) in a quartz immersion well, with or without additional filters.

Preparation of Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) Dithiobis(thiformate) (2). Compound **2** was prepared by the procedure of Shasha et al.[30] and exhibited properties as reported by Doane et al.[31]

Photolysis of 2. A. Quartz, Methanol (0.016 *M*). A solution of **2** (2.5 g) in methanol (230 ml) was sparged with nitrogen for 10 min. The light yellow solution was then irradiated for 3 hr, while the flow of nitrogen continued. The insoluble solid present in the reaction mixture was collected to yield **3** (0.247 g): mp 160–164°; $[\alpha]^{23}\mathrm{D}$ 0.0° (*c* 1, $CHCl_3$); λ_{max} (ether) 315 nm (ϵ 7150) and 240 (21,000); λ_{max} (film) 1250 cm^{-1} [OC(S)SS]; NMR τ 4.49 (d, $J_{1,2}$ = 7 Hz, H-1), 5.20–5.44 (m), 5.60–5.84 (m), 8.43, 8.57, 8.68 (s, CMe_2).

Anal. Calcd for $C_{26}H_{38}O_{12}S_6$: C, 42.5; H, 5.3; S, 26.2; mol wt, 738. Found: C, 42.3; H, 5.5; S, 26.4; mol wt, 778 (vapor pressure osmometry, $CHCl_3$).

The methanol filtrate was concentrated and kept in an ice bath for 4 hr to yield a white precipitate. Recrystallization from methanol gave **2** (0.777 g), mp 130–134°.

Combining the methanol filtrates and evaporation of the solvent at 40° under reduced pressure gave a yellow syrup, which was chromatographed on silicic acid. The column was eluted with acetone–hexane (1:50). The first component eluted was free sulfur (0.005 g). Next eluted was a mixture of **2** and **5** (0.078 g) determined by TLC. Continued elution gave **5** (0.578 g, 27%) as a yellow syrup: $[\alpha]^{23}\mathrm{D}$ −55° (*c* 1, $CHCl_3$); λ_{max} (MeOH) 283 nm (ϵ 8200); NMR τ 4.50 (two-proton, four-line m, H-1, H-1′), 5.1–5.5 (four-proton m), 5.6–6.1 (six-proton m), 6.68 (two-proton m), 8.51, 8.59, 8.66 (24 protons, s, CMe_2).

Anal. Calcd for $C_{25}H_{38}O_{11}S_2$: C, 51.9; H, 6.6; S, 11.1; mol wt, 578. Found: C, 51.6; H, 6.6; S, 11.4; mol wt, 586 (vapor pressure osmometry, $CHCl_3$).

Next eluted was **4** (0.227 g). Compound **5** was recrystallized from hexane at −20° on long standing to give a crystalline product of mp 107–110°.

B. Quartz, 2-Propanol (0.016 *M*). A solution of **2** (2.5 g) in 2-propanol (230 ml) was irradiated under N_2 for 3 hr using the quartz immersion well. The reaction mixture was filtered and the solvent was evaporated at 40° under reduced pressure. TLC of the resulting light yellow syrup showed three components: one of R_f equal to the R_f of **2**, one of R_f equal to the R_f of **5**, and the other of R_f equal to the R_f of **4**. The syrup was dissolved in methanol (50 ml) and kept for 1.5 hr. A white precipitate (0.39 g) formed of mp 149–151°, which was formulated from elemental analysis as bis-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) trithiobis-(*thioformate*) (**7**).

Anal. Calcd for $C_{26}H_{38}O_{12}S_5$: C, 44.6; H, 5.32; S, 22.8. Found: C, 44.3; H, 5.14; S, 22.2.

The filtrate was kept for 72 hr at −20° and a second precipitate (0.50 g) formed of mp 130–152°. This precipitate was assumed to be a mixture of **2** and **7**, since TLC showed only one component. The methanol was evaporated and the remaining syrup was chromatographed to give free sulfur (0.024 g), **2** (0.25 g), **5** (0.30 g), and **4** (0.60 g).

C. Quartz, Cyclohexane (0.016 *M*). A solution of **2** (2.5 g) in cyclohexane (230 ml) was irradiated for 3 hr under N_2 using the quartz immersion well. The reaction mixture was concentrated at 40° under reduced pressure. The resulting syrup was dissolved in methanol (50 ml) and kept at −20°. A white precipitate formed, which was collected, washed with methanol, and dried (0.9 g), mp 130–162°, assumed to be a mixture of **2**, **3**, and other polysulfides.

The methanol was evaporated and the resulting syrup was chromatographed to give **2** (0.2 g), **5** (0.75 g), **4** (0.41 g), and sulfur (0.035 g).

D. Corex, Cyclohexane (0.064 *M*). A solution of **2** (10.0 g) in cyclohexane (230 ml) was irradiated under a continuous flow of N_2 for 24 hr using Corex-filtered light. The reaction mixture was filtered to remove the insoluble **3** (0.448 g) which had formed. The volatile components were then removed at room temperature. The resulting yellow syrup was dissolved in methanol (500 ml) and the methanol was slowly evaporated. As the solvent evaporated, a white precipitate formed (2.8 g, mp 152–158°). Recrystallization from methanol (250 ml) gave **3** (mp 159–163°). The remaining original methanol solution was kept at 5° for 18 hr to give **2** (2.8 g) as a white precipitate. Filtration of the supernatant liquid and concentration of the solvent at 40° under reduced pressure gave a yellow syrup, which was chromatographed on silica gel to give **2** (0.27 g), **5** (3.2 g), and **4** (0.53 g).

E. Pyrex, Cyclohexane (0.003 *M*). A solution of **2** (0.5 g) in cyclohexane (230 ml) was irradiated under a continuous flow of N_2 for 14 hr using Pyrex-filtered light. The volatile components were evaporated at room temperature. The resulting light yellow syrup was chromatographed to give sulfur (0.019 g), **8** (0.040 g), **5** (0.320 g), and **4** (0.030 g). No CS_2 could be detected in the effluent gases, but COS (0.25 mmol) was determined by uv analysis as a diethylamine complex in an ethanol (1 l.)–diethylamine (4.0 ml) solution.

F. Pyrex, 2-Propanol (0.003 *M*). A solution of **2** (0.5 g) in 2-propanol (230 ml) was irradiated under a continuous flow of N_2 for 23 hr. The volatiles were evaporated at room temperature. The resulting syrup was chromatographed to yield sulfur (0.008 g), **5** (0.14 g), and **4** (0.15 g). Compound **8** was obtained as a mixture (0.040 g). A mixture of CS_2 (0.62 mmol) and COS (0.60 mmol) was detected in the effluent gases by uv analysis of an ethanol (1 l.)–diethylamine (4.0 ml) solution into which the gases had been sparged.

G. Pyrex, Methanol (0.003 *M*). A solution of **2** (0.5 g) in methanol (230 ml) was irradiated under a continuous flow of N_2 for 19 hr using Pyrex-filtered light. The cloudy reaction mixture was kept at room temperature and the volatiles were allowed to evaporate. The resulting syrup was chromatographed to yield sulfur (0.021 g), a mixture containing mostly **8** (0.016 g), **5** (0.25 g), and **4** (0.107 g). Analysis of the effluent gases showed a mixture of COS (0.185 mmol) and CS_2 (0.205 mmol), determined by uv analysis after reaction with diethylamine.

H. Corex, Cyclohexane (0.003 *M*). A solution of **2** (0.5 g) in cyclohexane (230 ml) was irradiated with Corex-filtered light under a continuous flow of N_2 for 5.5 hr. The volatiles were removed at room temperature and the resulting syrup was chromatographed to yield sulfur (0.008 g), **5** (0.32 g), and **4** (0.087 g). Only COS could be detected in the effluent gases by uv analysis after reaction with diethylamine in ethanol.

Irradiation of Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) Tetrathiobis(thioformate) (3). A methanol (230 ml) suspension of **3** (2.4 g) was irradiated for 3 hr under N_2 using quartz-filtered light. The reaction mixture was filtered and unreacted **3** (1.3 g) was recovered. The solvent was removed from the filtrate and the resulting syrup was treated with pyridine (5 ml) and *p*-chlorothiophenol (1 g). After 30 min, the pyridine was evaporated and the sample was chromatographed to give **5** (0.197 g) and **4** (0.540 g).

Preparation of 1,2:3,4-Di-*O*-isopropylidene-6-thio-α-D-galactopyranose (6) from 5. Compound **5** (0.5 g) was dissolved in ether (20 ml), and $LiAlH_4$ (0.25 g) was added in portions over a 5-min period. The resulting black-gray mixture was then refluxed for 1 hr. TLC of the reaction mixture showed two components, one of R_f equal to that of **4** and the other of R_f greater than that of **5**. "Newcell" thiol spray reagent indicated that the component of higher R_f was a thiol. After the excess $LiAlH_4$ was destroyed by adding ethyl acetate, the reaction mixture was poured into 5% aqueous acetic acid (50 ml). The reaction flask was rinsed with acetic acid (2 ml) and the combined acetic acid solutions were extracted three times with ether (50-ml portions). The ether solution was kept over sodium bicarbonate until neutral, then washed with water and dried over sodium sulfate. Evaporation of the ether gave a colorless syrup, which was chromatographed on silica gel. Elution with hexane–$CHCl_3$ (4:1) gave **6** (0.165 g): NMR τ 4.51 (one-proton d, $J_{1,2}$ = 5 Hz, H-1), 5.40 (one-proton q, $J_{2,3}$ = 8, $J_{3,4}$ = 3 Hz, H-3), 5.70 (two-proton m, H-2,4), 6.25 (one-proton m, $J_{4,5}$ = 2, $J_{5,6}$ = 6 Hz, H-5), 7.31 (two-proton m, H-6), 8.37 (one-proton d, J = 9 Hz, H-thiol), 8.49, 8.60, 8.69, 8.76 (12 protons, s, CMe_2). The signal at τ 8.37 disappeared when kept with D_2O for 18 hr and the signal at τ 7.31 became a broad doublet.

Photolysis of 2 and Ethyl Xanthide. A solution of **2** (2.5 g) and ethyl xanthide (2.5 g) in cyclohexane (230 ml) was photolyzed under nitrogen (quartz). After 5 min, a new component was detected by TLC. This component had an R_f identical with that of an authentic sample of the mixed xanthide.[32] After 30 min, the mixed xanthide became a major component. Carbonyl sulfide was detected in the effluent gases by uv analysis of an ethanol solution containing piperidine.

Reaction of 2 with Acetyl Peroxide. Cyclohexane (50 ml) containing **2** (1.0 g) was warmed to 70°, and acetyl peroxide (0.2 ml) was added.[33] After 1 hr of gentle reflux, more acetyl peroxide (0.4 ml) was added. The reaction mixture was refluxed for 1 hr. After cooling, the solvent was removed by evaporation at 50° under reduced pressure to yield a light yellow syrup.

Chromatography gave a major component (0.58 g), which was identified as 1,2:3,4-di-*O*-isopropylidene-6-*O*-[methylthio(thiocarbonyl)]-α-D-galactopyranose (**11**). The uv, NMR, and mass spectra were identical with those of an authentic sample.

Anal. Calcd for $C_{14}H_{22}O_6S_2$: C, 48.0; H, 6.2; S, 18.3. Found: C, 47.9; H, 6.5; S, 17.8.

Preparation of 1,2:3,4-Di-*O*-isopropylidene-6-*O*-[methylthio(thiocarbonyl)]-α-D-galactopyranose (11). Dimethyl sulfoxide (DMSO, 5.0 ml), **4** (5.0 g), 5 *N* sodium hydroxide (5.0 ml), and carbon disulfide (7.5 ml) were stirred for 10 min. The reaction mixture was cooled to 5°, and methyl iodide (5.0 ml) was added. After 1 min, a precipitate formed; the mixture was kept for 15 min. Then water (100 ml) and $CHCl_3$ (50 ml) were added to the brown mixture, and the two phases were separated. The $CHCl_3$ solution was washed three times with H_2O (100 ml) and dried with Na_2SO_4 and the solvent was removed. The resulting dark brown syrup was dissolved in 1:1 hexane–chloroform and filtered through silica gel. Evaporation of the solvent gave a bright yellow syrup. This syrup was dissolved in methanol and treated with charcoal. The solvent was removed at 50° under reduced pressure to give a nearly colorless syrup.

Anal. Calcd for $C_{14}H_{22}O_6S_2$: C, 48.0; H, 6.3; S, 18.3. Found: C, 47.9; H, 6.2; S, 18.6.

Preparation of Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) Tetrathiobis(thioformate) (3). A mixture of **4** (4.5 g), DMSO (5 ml), 5 *N* NaOH (5.0 ml), and carbon disulfide (5 ml) was stirred for 10 min. After addition of acetic acid (0.6 ml), sulfur monochloride (1.0 ml) was added. A precipitate formed, which was collected and washed with acetone (30 ml) and ether (150 ml). The sample was dried and suspended in acetone (50 ml). The mixture was filtered and the filtrate was evaporated to give an off-white solid, mp 158–162°. The NMR of this sample was identical with that of **3** from the photolysis of **2**.

Anal. Calcd for $C_{26}H_{38}O_{12}S_6$: C, 42.6; H, 5.2; S, 26.2. Found: C, 42.0; H, 5.2; S, 25.8.

Preparation of Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl) 3,3′-Dithiobis(thioformate) (14). This compound was prepared according to the method of Shasha et al.[30]

Photolysis of Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl) 3,3′-Dithiobis(thioformate) (14). A. Corex, Cyclohexane (0.064 *M*). A solution of **14** (10.0 g) in cyclohexane (230 ml) was irradiated under N_2 for 27 hr using Corex-filtered light. The solution was kept at room temperature and the volatile components were evaporated. Hexane was added to the syrup and the resulting solution was filtered. The hexane filtrate was seeded with crystalline **15** and kept at 5°. A crystalline precipitate (2.02 g) of **15** formed, which was collected and washed with cold hexane. TLC of the supernatant showed considerable **15** in solution along with unreacted **14** and **16**.

B. Corex, Cyclohexane (0.016 *M*). A solution of **14** (2.5 g) in cyclohexane (230 ml) was irradiated under N_2 for 20 hr using Corex-filtered light. The volatile components were evaporated at room temperature and the yellow syrup was chromatographed to give sulfur (0.10 g), **14** (0.25 g), **14** and **15** (0.36 g), **15** (0.92 g), and **16** (0.56 g).

Compound **15** was recrystallized from hexane and exhibited the following properties: mp 133–135°; $[\alpha]^{23}D$ − 56° (*c* 1, acetone); λ_{max} (EtOH) 282 nm (ϵ 9600).

Anal. Calcd for $C_{25}H_{38}O_{11}S_2$: C, 52.0; H, 6.5; S, 11.1; mol wt, 578. Found: C, 51.6; H, 6.7; S, 11.6; mol wt, 550 (vapor pressure osmometry in $CHCl_3$).

NMR spectrum shows the following: τ 4.15 (three-proton m, H-1, H-1′, H-3′), 5.31 (two-proton d, H-2, H-2′), 5.6–6.1 (nine-proton m), 8.48, 8.60, 8.70 (24 protons, s, CMe_2).

C. Pyrex, Cyclohexane (0.003 *M*). A solution of 14 (0.5 g) in cyclohexane (230 ml) was irradiated under N_2 for 13.5 hr using Pyrex-filtered light. The volatile components of the reaction mixture were evaporated at room temperature and the remaining syrup was chromatographed to give sulfur (0.013 g), 1,2:5,6-di-*O*-isopropylidene-3-*O*-[cyclohexylthio(thiocarbonyl)]-α-D-glucofuranose (0.044 g), **14** (0.080 g), **15** (0.250 g), and **16** (0.066 g).

Reduction of 15 with $LiAlH_4$. Compound **15** (0.5 g) was dissolved in ether (20 ml) and $LiAlH_4$ (0.25 g) was added in small portions over a 5-min period. The resulting gray-black mixture was then refluxed for 1 hr. After the excess $LiAlH_4$ was destroyed with ethyl acetate, the reaction mixture was poured into 5% acetic acid (50 ml). The mixture was transferred to a separatory funnel, and the flask was rinsed with acetic aicd (2.0 ml). The ether layer was separated and the water layer was washed twice with ether (50 ml). The ether extracts were combined and washed with $NaHCO_3$ solution and with water. The ether layer was dried with Na_2SO_4. Evaporation of the ether and addition of hexane to the colorless syrup gave a crystalline precipitate, identified as **16** (0.291 g) by comparison with an authentic sample. The hexane solution was concentrated to a colorless syrup, which was purified by chromatography on silica gel. Elution with $CHCl_3$ gave a colorless syrup (0.188 g) which was identified as 1,2:5,6-di-*O*-isopropylidene-3-thiol-α-D-glucofuranose (**17**). The NMR spectrum of this sample was identical with that of an authentic sample prepared by the method of Heap and Owen.[19]

Anal. Calcd for $C_{12}H_{20}O_5S$: C, 52.2; H, 7.3; S, 11.6; mol wt, 276. Found: C, 52.1; H, 7.4; S, 11.5; mol wt, 312 (vapor pressure osmometry in $CHCl_3$).

Preparation of Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranos-3-yl) 3-*O*,3′-*S*-Dithiocarbonate (15) from 17 and 19. To a solution of 17 (1.0 g) in ether (10 ml) was added 19 (1.2 g).[23] Triethylamine (0.5 ml) was added dropwise to produce immediately a white precipitate. TLC indicated that nearly all **17** and **19** had reacted and gave a product of R_f equal to that of **15**. The white precipitate was removed by filtration. After evaporation of the ether, the syrup was dissolved in chloroform, washed with water, and dried with sodium sulfate, and the solvent was evaporated. After 10 days, the sample was chromatographed to give **15**, which crystallized from hexane, mp 133–134°. A portion of the product was mixed with **15** obtained from the photolysis of **14** and gave mp 132–134°; NMR, uv, and ir of both products were identical.

Preparation of 3-*S*-Acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (18) from 17. An ether solution (10 ml) containing 17 (0.125 g) was treated with acetic anhydride (2.5 ml) and pyridine (3.0 ml). The solution was kept for 3 days. The excess reagents were evaporated at room temperature (72 hr). The resulting syrup was dissolved in ether (20 ml) and the solution was extracted twice with water (10 ml). The ether solution was dried with sodium sulfate and the solvent was evaporated to give a colorless syrup (0.075 g), $[\alpha]^{23}D$ −47° (*c* 1, $CHCl_3$) (lit. $[\alpha]^{23}D$ − 46°).

Anal. Calcd for $C_{14}H_{22}O_6S$: C, 52.7; H, 6.95; S, 10.0. Found: C, 52.9; H, 7.19; S, 9.9.

Photolysis of Bis(methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside) 6,6′-Dithiobis(thioformate) (12). A solution of 12 (2.5 g) in methanol (230 ml) was irradiated under N_2 for 3 hr using a quartz immersion well. The solution was concentrated at 50° under reduced pressure to yield a yellow syrup. This syrup was treated with *p*-chlorothiophenol and pyridine to destroy unreacted **12** and polysulfides. The pyridine was evaporated and the remaining syrup was chromatographed to give **13** (0.970 g, 46%) and methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside.

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