THIO SUGARS BY ISOMERIZATION OF CARBOHYDRATE THIONOCARBONATES*

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ABSTRACT

Certain thionocarbonate derivatives of sugars isomerize to the corresponding monothiolcarbonates in the presence of potassium iodide. Structural requirements for isomerization are that the thionocarbonate must include a primary carbon atom of the sugar in a ring and that there be no unprotected hydroxyl groups in the derivative. The 3-*O*-acetyl (**1**) and the 3-*O*-*p*-tolylsulfonyl (**2**) derivatives of 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-thionocarbonate gave the corresponding monothiolcarbonates (**3**) and (**4**) in excellent yields. In contrast, the parent compound unprotected at C-3 gave no monothiolcarbonate. Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-thionocarbonate (**5**) afforded the 4,6-monothiolcarbonate (**7**). With each isomerized product, thiolation occurred at the C-6 position. When treated under similar conditions, two carbohydrate cyclic thionocarbonates involving only secondary carbon atoms, and two acyclic thionocarbonates of fully protected sugars, underwent negligible isomerization.

INTRODUCTION

Isomerizations of the type $ROC(=S)XR' \rightarrow RSC(=O)XR'$ have found limited applicability as routes to thio sugars. With XR′ = SMe, thermal isomerization has given a thiohexose[1] and a thiopentose[2]. Photolysis of dimethylthiocarbamates (XR′ = NMe_2) of sugars gave deoxy derivatives[3], presumably via the isomeric thio sugar intermediates. In 1969, Jones and Andreades[4] reported the rearrangement of ethylene thionocarbonate into ethylene thiolcarbonate in good yield by a facile procedure with potassium iodide in acetonitrile. Since thionocarbonate derivatives of carbohydrates are readily available[5,6], we wished to determine whether thionocarbonates of sugars would rearrange to isomeric thio sugar derivatives in the presence of potassium iodide in acetonitrile.

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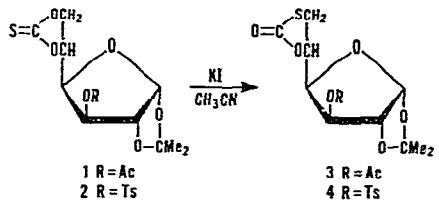
Two carbohydrates containing five-membered thionocarbonate rings, the 3-*O*-acetyl (**1**) and 3-*O*-*p*-tolylsulfonyl (**2**) derivatives of 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-thionocarbonate[7], isomerized completely to the monothiolcarbonates **3** and **4** on treatment with potassium iodide in acetonitrile at 125°. Evidence for this isomerization (Scheme I) was given by i.r. spectra of the products, in which

Scheme I



the strong C=S band (1290 cm^{-1}) shown by **1** and **2** was absent, and a strong C=O band (1760 cm^{-1}), as expected for structures **3** and **4**, was present. Similar spectral changes were reported for the transformation of ethylene thionocarbonate (1303 cm^{-1}, C=S) into ethylene thiolcarbonate (1739 cm^{-1}, C=O)[4,8]. N.m.r. spectral comparisons of **1** and **2** with the respective monothiolcarbonates **3** and **4** showed that the H-6,6′ resonances between τ 5.25 and 5.45 in the thionocarbonates had undergone upfield shifts to τ 6.30 and 6.50 in the monothiolcarbonates. Since proton resonances other than those at C-6 remained unchanged in the samples studied, the sulfur atom must have become attached preferentially to the 6-position in each product. Upfield shifts involving primary protons are known to occur when sulfur replaces oxygen at a primary carbon atom[4,9]. When **4** was treated with barium hydroxide[5], the monothiolcarbonate was converted into the known thiol[10], 1,2-*O*-isopropylidene-6-thio-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranose.

The parent compound, 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-thionocarbonate, when treated by this procedure, lost sulfur as hydrogen sulfide and gave a mixture of compounds. The major product was 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose. This component, a known transformation product of 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate, was identified by comparison of i.r. spectra and R_F values with a sample synthesized independently[11]. A minor product recovered was the 5,6-carbonate derivative. A second minor fraction isolated from the mixture showed strong i.r. bands near 1650 and 880 cm^{-1} and a u.v. band near 248–250 nm. These data support an acyclic dithiolcarbonate[8,12] structure, which indicates that a small amount of thiolation had occurred. The detrimental influence of hydroxyl groups on the rearrangement of thionocarbonates was also shown in the attempted isomerization of 3,4-*O*-isopropylidene-D-mannitol 1,2-thionocarbonate[6], when many products were observed by t.l.c., including cyclic and acyclic carbonates (i.r. spectral evidence).

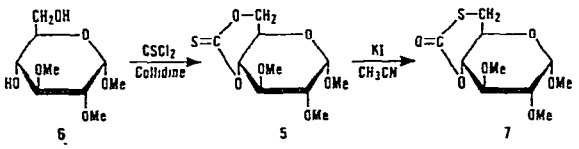
Two acyclic thionocarbonates, bis(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl) 6,6′-thionocarbonate and bis(methyl 6-deoxy-2,3,4-tri-*O*-

methyl-α-D-glucopyranosid-6-yl) 6,6′-thionocarbonate, were recovered essentially unchanged after treatment with potassium iodide, which result suggests that isomerization requires the thionocarbonate to be present in a ring form.

Another requirement for isomerization under the conditions described is that a primary carbon atom be part of the thionocarbonate ring. Thus methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate[5] and 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-thionocarbonate[6] underwent practically no change.

A novel, six-membered, cyclic thionocarbonate, methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-thionocarbonate (**5**), was synthesized from methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (**6**) and thiophosgene, to determine whether such a structure would undergo isomerization (Scheme II). Its structure was identified by

Scheme II



6 5 7

comparing its u.v. spectrum with the six-membered, cyclic thionocarbonate of neopentyl glycol[13] and by its conversion into the known methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-carbonate[14] with silver nitrate[7]. Treatment of **5** with potassium iodide gave methyl 2,3-di-*O*-methyl-6-thio-α-D-glucopyranoside 4,6-monothiolcarbonate (**7**) in 54% yield. N.m.r. spectral comparisons between **5** and **7** showed H-6,6′ signals between τ 5.3 and 6.1 for **5** and near τ 7.0 for **7**. Since the resonances of other corresponding protons in **5** and **7** were similar, preferential thiolation at C-6 was again indicated. The u.v. spectrum of **7** showed a maximum near 205 nm, whereas the u.v. spectrum of **5** displayed a maximum near 246–247 nm.

EXPERIMENTAL

General. — I.r. spectra were recorded, for films cast onto plates of silver chloride, with a Perkin–Elmer* Model 137 spectrophotometer. Wavelengths were calibrated with polystyrene film. N.m.r. spectra were recorded by means of a Varian HA-100 spectrometer, with tetramethylsilane (τ 10.00) as the internal reference standard. Melting points were determined in sealed capillaries and are uncorrected. Optical rotations were measured with a Rudolph polarimeter, and o.r.d. curves were recorded with a Cary Model 60 spectropolarimeter (26°, 0.1 dm). U.v. spectra were determined with Perkin–Elmer Model 202 and Beckman DK-2A recording spectrophotometers. Molecular weights were measured by mass spectroscopy and with a Mechrolab Model 301A vapor-pressure osmometer. T.l.c. was performed on

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2.5 × 7.5 cm plates sprayed with Silica Gel G (E. Merck, Germany). Detection was with 19:1 (v/v) methanol–sulfuric acid for charring. Large-scale separations were achieved by selective desorption from mixtures of silicic acid (Mallinckrodt, 100 mesh) and activated carbon (Darco). Celite was used as a filter aid.

3-O-Acetyl-1,2-O-isopropylidene-6-thio-α-D-glucofuranose 5,6-monothiolcarbonate (**3**). — A mixture of 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-thionocarbonate[7] (**1**) (1.0 g), acetonitrile (10 ml), and potassium iodide (1.0 g) was sealed in an evacuated glass tube and kept for 15 h at 125°. (The 60° temperature recommended for the isomerization of ethylene thionocarbonate[4] was too low to isomerize **1** and **2** completely, even after several days.) An i.r. spectrum of a film prepared from the mixture after heating revealed broadening of the C=O band (1760 cm^{-1}) and absence of the C=S band (1290 cm^{-1}), characteristic of **1**. T.l.c. [4:1 (v/v) carbon disulfide–ethyl acetate] gave a single component, R_F 0.28, and no **1** (R_F 0.15). After the solvent had been evaporated, the residue was extracted with chloroform (100 ml) and to remove iodine the extract was partitioned with that which contained sodium hydrogen sulfite. The chloroform layer was dried (sodium sulfate) and evaporated to a syrup, which crystallized from ethanol to give **3**, yield 0.84 g (84%). Recrystallization from ethanol gave m.p. 108–110°, $[\alpha]_D^{24}$ −58.8° (*c* 0.97, chloroform); $\lambda_{max}^{ethanol}$ 211–212 nm (ε 1,600); ν_{max}^{film} 1760 cm^{-1} (C=O); n.m.r. ($CDCl_3$): τ 4.11 (1-proton doublet, H-1), 5.45 (1-proton doublet, H-2), 4.75 (1-proton doublet, H-3), 5.59 (1-proton quartet, H-4), 5.15 (1-proton multiplet, H-5), 6.32, 6.39 (2-proton doublet, H-6, H-6'), 7.90 (3-proton singlet, OAc), 8.48, 8.68 (3-proton singlets, CMe_2).

Anal. Calc. for $C_{12}H_{16}O_7S$: C, 47.4; H, 5.3; S, 10.5. Found: C, 47.6; H, 5.3; S, 10.2.

1,2-O-Isopropylidene-6-thio-3-O-p-tolylsulfonyl-α-D-glucofuranose 5,6-monothiolcarbonate (**4**). — Treatment of 1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranose 5,6-thionocarbonate (**2**) as above at 125° required 64 h for complete conversion into a product having R_F 0.48 (**2** has R_F 0.41). A workup procedure as for **3** gave **4** as crystals from ethanol, yield 0.80 g (80%), m.p. 116–117°, $[\alpha]_D^{24}$ −106.3° (*c* 0.32, chloroform); ν_{max}^{film} 1760 cm^{-1} (C=O); n.m.r. ($CDCl_3$): τ 4.08 (1-proton doublet, H-1), 5.15 (1-proton doublet, H-2), 5.21 (1-proton doublet, H-3) 5.73 1-proton quartet, H-4), 5.42 (1-proton multiplet, H-5), 6.46, 6.51 (2-proton doublet, H-6, H-6'), 7.56 (3-proton singlet, Me of aryl), 8.52, 8.69 (3-proton singlets, CMe_2), 2.1–2.8 (4-proton multiplet, aryl).

Anal. Calc. for $C_{17}H_{20}O_8S_2$: C, 49.0; H, 4.8; S, 15.4. Found: C, 48.7; H, 5.1; S, 15.1.

1,2-O-Isopropylidene-6-thio-3-O-p-tolylsulfonyl-α-D-glucofuranose. — Compound **4** (0.10 g) in acetone (20 ml) was stirred at 60° under nitrogen and a saturated, aqueous solution of barium hydroxide (3 ml) was added. After 30 min the acetone was evaporated off and the residue was diluted with water (20 ml). The mixture was acidified with hydrochloric acid and extracted with chloroform (50 ml). The extract contained a product that decolorized iodine–azide reagent[15] on t.l.c. plates, and

which could be distinguished as a white spot upon spraying the treated plates with starch solution. The chloroform solution was washed with water (10 ml), dried (Na_2SO_4), and evaporated to a syrup; I.r. (CCl_4): ν_{max} 2590 (SH), 3550 (OH), 1180, 1370 cm^{-1} (OTs); n.m.r. (CCl_4): τ 4.25 (1-proton doublet, H-1), 7.1–7.5 (3-proton multiplet, H-6, H-6', OH), 7.55 (3-proton singlet, Me of aryl), 8.59, 8.79 (two 3-proton singlets, CMe_2), 8.61 (1-proton triplet, SH). The proton resonances of OH and SH disappeared upon exchange with deuterium oxide for 70 min. The i.r. and n.m.r. data are in agreement with those reported for 1,2-*O*-isopropylidene-6-thio-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranose by Heap and Owen[10].

Treatment of 1,2-O-isopropylidene-α-D-glucofuranose 5,6-thionocarbonate. — The title compound (0.5 g), acetonitrile (5.0 ml), and potassium iodide (0.5 g) were sealed in an evacuated glass tube. Upon being kept for 43 h at 125°, the title compound was completely converted into products. Hydrogen sulfide was detected with moistened lead acetate paper upon opening the tube. T.l.c. [1:1 (v/v) carbon disulfide–ethyl acetate] showed a major product (about 70%), R_F 0.34, and several minor products having R_F 0.5–1.0. In this system the tittle compound had R_F 0.40. The mixture was evaporated to a residue that was mixed with ethyl acetate and adsorbed onto a mixture of silicic acid (30 g) and activated carbon (2 g). Desorption with 4:1 (v/v) carbon disulfide–ethyl acetate (400 ml) removed most of the material (100 mg) having R_F 0.5–1.0, which was readsorbed on silicic acid (20 g). Elution with carbon disulfide–ethyl acetate in 100-ml portions gave a fraction (10 mg) containing a major component of R_F 0.51. The i.r. spectrum showed two C=O bands: 1650 cm^{-1} (major) and 1720 cm^{-1} (minor). A band near 880 cm^{-1} suggested that the major C=O band might be due to a dithiolcarbonate[8]. The u.v. spectrum (ethanol), which had maxima at 248–250 nm[12] and 219–221 nm, supported this suggestion. Continued desorption of the original reaction mixture with 1:1 (v/v) carbon disulfide–ethyl acetate (400 ml) removed products (300 mg) having lower R_F. Evaporation of solvent left a syrup, which was mixed with ether to give crystals (20 mg) identified as 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate by i.r., t.l.c., and m.p. comparison with an authentic sample[7]. The ether solution was mixed with hexane, filtered, and evaporated to a syrup, which contained a single component (R_F 0.34). This component was identical by i.r. spectrum and R_F value with 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose, prepared from 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate by reaction with sodium methoxide in *N,N*-dimethylformamide[11].

Treatment of 3,4-O-isopropylidene-D-mannitol 1,2-thionocarbonate. — This compound was treated as described in the preceding experiment. Hydrogen sulfide was detected upon opening the tube. T.l.c. (ethyl acetate) showed a mixture of at least five components in similar proportions. An i.r. spectrum of a film prepared from the mixture had C=O bands near 1800, 1730, and 1670 cm^{-1}. The strongest C=O band, near 1800 cm^{-1}, is characteristic of five-membered cyclic carbonates[7].

Preparation and treatment of bis(6-deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose) 6,6'-thionocarbonate. — This compound was prepared from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose and thiophosgene by a known method[7]. 1,2:3,4-

Di-*O*-isopropylidene-α-D-galactopyranose (2.36 g) in *p*-dioxane (10 ml) was stirred at 65°, and thiophosgene (0.4 ml) was added dropwise. After 10 min at 65°, pyridine (1.0 ml) was added. After being kept for an additional 20 min the mixture was cooled to 5°, diluted with ether (100 ml), filtered, and evaporated to a syrup.

The syrup was dissolved in chloroform and adsorbed onto a mixture of silicic acid (140 g) and activated carbon (20 g). Desorption with hexane (1 liter) removed impurities. Desorption with 1:1 (v/v) ether–hexane (500 ml) removed the product. Subsequent elutions with ether–hexane removed unreacted starting material. Repetition of this adsorption and desorption process from silicic acid (170 g) with 1:4 (v/v) ether–hexane (6 liters) gave the title compound, which crystallized from hexane, yield 1.12 g (44%), m.p. 140–142°; $[\alpha]_D^{24}$ −84° (*c* 1.19, chloroform); $\lambda_{max}^{ethanol}$ 306–310 (ε 20.1), 230–232 nm (9,040); ν_{max}^{film} 1280 cm^{-1} (C=S).

Anal. Calc. for $C_{25}H_{38}O_{12}S$: C, 53.4; H, 6.81; S, 5.70. Found: C, 53.4; H, 6.99; S, 5.48.

This compound (0.80 g), acetonitrile (100 ml), and potassium iodide (1.0 g) were heated for 70 h at 125° in a sealed tube. An i.r. spectrum of a film prepared from the mixture showed mainly starting material.

Preparation and treatment of bis(6-deoxy-methyl 2,3,4-tri-O-methyl-α-D-glucopyranosid-6-yl) 6,6'-thionocarbonate. — Methyl 2,3,4-tri-*O*-methyl-α-D-glucopyranoside[16] (1.20 g) in *p*-dioxane (5 ml) was stirred at 65° and thiophosgene (0.2 ml) was added dropwise, followed by the addition of pyridine (0.5 ml). T.l.c. [1:1 (v/v) carbon disulfide–ethyl acetate] showed mostly starting material, together with two other components. More thiophosgene (0.5 ml) and pyridine (1.0 ml) were added in alternate increments to bring about essentially complete conversion to two products. After 1 h at 65° the mixture was cooled, diluted with ether (50 ml), and filtered. The filtrate was shaken with three portions of water, and the ether layer was dried (sodium sulfate). T.l.c. revealed two major components, R_F 0.75 and 0.35, in similar proportions, distinct from the starting compound (R_F 0.25). The mixture was filtered and evaporated to a syrup, which was dissolved in chloroform and adsorbed onto a mixture of silicic acid (60 g) and activated carbon (10 g). Desorption with hexane (200 ml) removed impurities, 1:1 (v/v) ether–hexane (1 liter) removed the component (0.35 g) having R_F 0.75, and ether (1 liter) removed the component having R_F 0.35. The latter product was crystallized from ethanol to m.p. 140–143° and identified as the title compound, yield 0.54 g (41%), $[\alpha]_D^{24}$ +162.9° (*c* 0.70, ethanol); ν_{max}^{film} 1280 cm^{-1} (C=S); $\lambda_{max}^{ethanol}$ 230 nm (ε 9,740).

Anal. Calc. for $C_{21}H_{38}O_{12}S$: C, 49.0; H, 7.4; S, 6.2. Found: C, 48.5; H, 7.5; S, 6.4.

The component having R_F 0.75, a syrup, was methyl 6-chloro-6-deoxy-2,3,4-tri-*O*-methyl-α-D-glucopyranoside, identified by t.l.c. and i.r. spectral comparison with a sample synthesized independently through preparation of methyl 6-chloro-6-deoxy-α-D-glucopyranoside[17] followed by methylation with diazomethane and boron trifluoride[18].

The title compound (0.1 g), acetonitrile (1.0 ml), and potassium iodide (0.1 g)

were sealed in an evacuated glass tube and kept for 16 h at 125°. The i.r. spectrum of a film prepared from the reaction mixture was essentially identical with that of a film prepared from the original compound.

Treatment of methyl 4,6-O-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate and 1,2:5,6-di-O-isopropylidene-D-mannitol 3,4-thionocarbonate. — The title compounds (0.1 g), acetonitrile (1.0 ml), and potassium iodide (0.1 g) were sealed in evacuated glass tubes and kept for about 20 h at 125°. I.r. spectra of films prepared from the reaction mixtures were essentially identical with spectra of films prepared from the title compounds.

Methyl 2,3-di-O-methyl-α-D-glucopyranoside 4,6-thionocarbonate (**5**). — A solution of methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (**6**, 5.00 g) in 2,4,6-trimethylpyridine (40 ml) at 5° was stirred rapidly while thiophosgene was added dropwise (5.0 ml). After 30 min at room temperature, the mixture was dissolved in chloroform (80 ml), poured into ether (1 liter), and the suspension was filtered. The filtrate was shaken with hydrochloric acid and sodium hydrogen carbonate solutions saturated with sodium chloride. The combined aqueous extracts were re-extracted with ether (100 ml). The combined organic phases were dried over sodium sulfate, filtered, and evaporated to a syrup. The syrup was dissolved in chloroform and adsorbed onto a mixture of silicic acid (140 g) and activated carbon (20 g). The product was desorbed with 1:1 (v/v) ether–hexane (1 liter), ether (1 liter), and 1:4 (v/v) chloroform–ether (3 liters). T.l.c. [2:1 (v/v) carbon disulfide–acetone] showed nearly pure **5** in the ether and chloroform–ether eluates. Repetition of this adsorption and desorption process gave pure **5**, 2.90 g (49%), m.p. 120–122°; $[\alpha]_D^{22}$ +21.6° (*c* 0.97, ether); o.r.d. indicated a positive Cotton effect[9]: $[\alpha]_{358}$ +1070°, $[\alpha]_{341}$ 0°, $[\alpha]_{310}$ −2560°, $[\alpha]_{290}$ −2710° (*c* 0.195, ether); λ_{max}^{ether} 335–340 (ε 27), 246–247 nm (14,200); ν_{max}^{film} 1260 cm^{-1} (C=S); n.m.r. ($CDCl_3$): τ 5.06 (1-proton doublet, H-1), 6.69 (1-proton quartet, H-2), 6.29, 6.40, 6.49 (3-proton singlets, OMe), 5.3–6.1 (4-proton multiplets, H-4, H-5, H-6, H-6′).

Anal. Calc. for $C_{10}H_{16}O_6S$: C, 45.4; H, 6.10; S, 12.1; mol. wt. 264. Found: C, 45.3; H, 5.95; S, 12.1; mol. wt. (mass spectrum) 264.

Compound **5** was soluble in chloroform, moderately soluble in ether, and sparingly soluble in hexane. It was soluble with decomposition in water and ethanol. The u.v. spectrum of **5** closely resembled that of neopentyl glycol thionocarbonate[13], λ_{max}^{MeOH} 244 nm (ε 14,500). Compound **5** was converted into the known methyl 2,3-di-*O*-methyl-α-D-glucopyranoside 4,6-carbonate[14] with silver nitrate[7].

Methyl 2,3-di-O-methyl-6-thio-α-D-glucopyranoside 4,6-monothiolcarbonate (**7**). — Treatment of **5** (0.5 g) in acetonitrile (20 ml) with potassium iodide (3 g) in a sealed tube for 19 h at 70° gave a major product and two minor products (t.l.c.). Dilution with chloroform (100 ml), filtration, and evaporation gave a syrup that was dissolved in chloroform and adsorbed onto a mixture of silicic acid (80 g) and activated carbon (20 g). Desorption with 1:1 (v/v) ether–hexane (500 ml) and 6:4 (v/v) ether–hexane (500 ml) removed impurities, and then 7:3 (v/v) ether–hexane (2500 ml) removed the major product. Evaporation of solvent left 0.27 g (54%) of **7**, which

crystallized as needles. Several recrystallizations from ether gave 7, m.p. 127–128°, $[\alpha]_D^{25}$ +26.8° (*c* 0.64, chloroform); $\lambda_{max}^{ethanol}$ 205 nm (ε 3,560); ν_{max}^{film} 1680 cm^{-1}; n.m.r. ($CDCl_3$): τ 5.20 (1-proton doublet, H-1), 6.75 (1-proton quartet, H-2), 6.35, 6.50, 6.58 (3-proton singlets, OMe), 5.8–6.3 (3-proton multiplets, H-3, H-4, H-5), 7.00 (2-proton multiplets, H-6, H-6').

Anal. Calc. for $C_{10}H_{16}O_6S$: C, 45.4; H, 6.10; S, 12.1; mol. wt. 264. Found: C, 45.1; H, 6.28; S, 11.8; mol. wt. (Mechrolab, acetone) 259, 263. A mass spectrum showed a high-mass peak at 264.

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REFERENCES

1 K. FREUDENBERG AND A. WOLF, *Ber.*, 60 (1927) 232.
2 M. L. WOLFROM AND A. B. FOSTER, *J. Amer. Chem. Soc.*, 78 (1956) 1399.
3 R. H. BELL, D. HORTON, AND D. M. WILLIAMS, *Chem. Commun.*, (1968) 323.
4 F. N. JONES AND S. ANDREADES, *J. Org. Chem.*, 34 (1969) 3011.
5 E. I. STOUT, W. M. DOANE, B. S. SHASHA, C. R. RUSSELL, AND C. E. RIST, *Carbohyd. Res.*, 3 (1967) 354.
6 B. S. SHASHA, W. M. DOANE, C.R. RUSSELL, AND C. E. RIST, *Carbohyd. Res.*, 3 (1966) 121.
7 W. M. DOANE, B. S. SHASHA, C. R. RUSSELL, AND C. E. RIST, *J. Org. Chem.*, 30 (1965) 162.
8 R. A. NYQUIST AND W. J. POTTS, *Spectrochim. Acta*, 17 (1961) 679.
9 D. HORTON AND W. N. TURNER, *Carbohyd. Res.*, 1 (1966) 444.
10 J. M. HEAP AND L. N. OWEN, *J. Chem. Soc. (C)*, (1970) 707.
11 E. J. REIST, R. R. SPENCER, AND B. R. BAKER, *J. Org. Chem.*, 23 (1958) 1958.
12 D. HORTON AND H. S. PRIHAR, *Carbohyd. Res.*, 4 (1967) 115.
13 B. S. SHASHA, W. M. DOANE, C. R. RUSSELL, AND C. E. RIST, *Nature*, 211 (1966) 965.
14 D. TRIMNELL, W. M. DOANE, C. R. RUSSELL, AND C. E. RIST, *Carbohyd. Res.*, 13 (1970) 301.
15 F. FEIGL, *Spot Tests in Organic Analysis*, 6th edn., Elsevier, Amsterdam, 1960, p. 242.
16 J. LEHMANN, *Carbohyd. Res.*, 2 (1966) 1.
17 M. E. EVANS, L. LONG, AND F. W. PARRISH, *J. Org. Chem.*, 33 (1968) 1074.
18 D. TRIMNELL, W. M. DOANE, C. R. RUSSELL, AND C. E. RIST, *Carbohyd. Res.*, 11 (1969) 497.