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ACETALATION OF 1,6-ANHYDRO-1(6)-THIO-D-GLUCITOL*

JÁNOS KUSZMANN, PÁL SOHÁR, AND GYULA HORVÁTH
Research Institute for Pharmaceutical Chemistry, Budapest 4 (Hungary)
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ABSTRACT

Acetalation of 1,6-anhydro-1(6)-thio-D-glucitol (**1a**) with acetone, formaldehyde, or benzaldehyde afforded 2,3:4,5-diacetals (**2a**, **2b**, and **2c**) whose structure, after desulfurization, was proved by mass spectrometry. Upon partial hydrolysis of **2a**, one of the isopropylidene groups was split off, and the other migrated to O-3,O-4 to give **4b**. In **4b**, in the stable conformation, OH-2 occupies an equatorial position, whereas OH-5 is axially oriented. Accordingly, OH-2 reacts faster than OH-5 on methylation of **4b**, giving **4e**. Hydrolysis of the isopropylidene group of the 2,5-di-*O*-methyl derivative **4d** and subsequent mesylation afforded the corresponding 3,4-di-*O*-mesyl compound **1c**, which showed significant ulcerostatic activity.

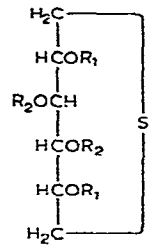
INTRODUCTION

Recently, we described[1] the synthesis of 1,6-anhydro-1(6)-thio-D-glucitol [1,6-(thioanhydro)-D-glucitol] (**1a**), which was needed for studying the structure–activity relationships of 1,6:2,5-dianhydro-3,4-di-*O*-(methylsulfonyl)-1(6)-thio-D-glucitol[2–4]. To establish the role of the 2,5-anhydro ring, it was decided to attempt the synthesis of the corresponding 2,5-di-*O*-methyl derivative **1c**. Consequently, the possibility of selectively protecting two of the four hydroxyl groups in **1a** by acetalation, either at C-2 and C-5, or at C-3 and C-4, was investigated.

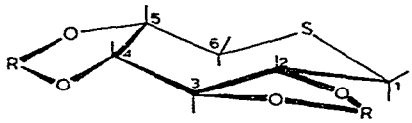
RESULTS AND DISCUSSION

When compound **1a** was treated with acetone in the presence of sulfuric acid, only the 2,3:4,5-diacetal **2a** was formed. On using formaldehyde or benzaldehyde for acetalation, similar diacetals (**2b** and **2c**, respectively) having 2,3:4,5-situated 1,3-dioxolane rings were obtained. For **2c**, due to the chirality of the benzylidene group, a mixture of isomers might be expected, but the n.m.r. spectrum of the isolated and recrystallized dibenzylidene derivative **2c** showed two distinct benzylidene signals, at

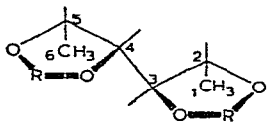
*1,6-Anhydro-1(6)-thiohexitols VII. For Part VI, see ref. 1.



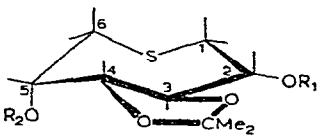
1a $R_1 = R_2 = H$
1b $R_1 = Me, R_2 = H$
1c $R_1 = Me, R_2 = Ms$



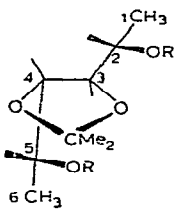
2a $R = CMe_2$
2b $R = CH_2$
2c $R = CHPh$



3a $R = CMe_2$
3b $R = CH_2$
3c $R = CHPh$



4a $R_1 = R_2 = Ac$
4b $R_1 = R_2 = H$
4c $R_1 = R_2 = Ms$
4d $R_1 = R_2 = Me$
4e $R_1 = Me, R_2 = H$
4f $R_1 = Me, R_2 = Ac$
4g $R_1 = Me, R_2 = Ms$



5a $R = H$
5b $R = Ac$

δ 5.80 and 6.01, each of one-proton intensity, indicating the presence of one isomer only. The 2,3:4,5-positions of the acetal groups (that is, the presence of two 1,3-dioxolane rings) was proved by using reductive desulfurization with Raney nickel. The mass spectra of the 1,6-dideoxyhexitol derivatives **3a**, **3b**, and **3c** thus obtained all showed an abundant ion corresponding to half of the molecule, as follows: **3a**: *m/e* 115, 100%; **3b**: *m/e* 87, 100%; and **3c**: *m/e* 163, 80%. This cleavage between the 1,3-dioxolane rings is favored in similar systems[5].

According to these results, it is very probable that 1,6-anhydro-di-*O*-benzylidene-D-glucitol, which is the only analog of compounds of type **2** thus far described in the literature[6], contains benzylidene groups in a similar 2,3:4,5 arrangement.

It may be mentioned that, when acyclic, 1,6-disubstituted D-glucitol derivatives are treated with aldehydes, 2,4:3,5-bis-1,3-dioxane derivatives are formed[7,8]. In this way was synthesized 1,6-dideoxy-2,4:3,5-di-*O*-methylene-D-glucitol, which differed significantly in its optical rotation[7] ($[\alpha]_D^{20}$ +35.6°) from the 2,3:4,5-di-*O*-methylene isomer **3b**, which has $[\alpha]_D^{20}$ −76°.

We next investigated the possibility of selectively removing the *trans* (2,3) or the *cis* (4,5) situated 1,3-dioxolane ring by hydrolysis. When **2a** was treated with methanolic hydrogen chloride, a mono-*O*-isopropylidene derivative was formed; this was isolated as its diacetate **4a** in good yield. In the n.m.r. spectrum of compound **4a**, the signals of H-2 and H-5 (δ 5.50 and 5.05) appeared downfield of those of H-3 and H-4 (δ 4.70 and 4.00), whereas the isopropylidene methyl groups were isochronic (δ 1.38); consequently, a structure having acetoxyl groups on C-2 and C-5 and a central 1,3-dioxolane ring had to be taken into consideration. That means that, under the acidic conditions, one of the 1,3-dioxolane rings is split off, but, simultaneously, migration of the other isopropylidene group to O-3,O-4 occurs, yielding compound **4b**. Mesylation of **4b** afforded the di-*O*-mesyl derivative **4c**, having similarly isochronic isopropylidene and mesyl methyl groups (δ 1.45 and 3.45, respectively), and only in the spectrum of the di-*O*-methyl derivative **4d** were isopropylidene methyl groups having different shifts (δ 1.42 and 1.45) observed.

The structure of the compound obtained by reductive desulfurization of **4b** was proved as follows. The mass spectrum of the resulting 1,6-dideoxy derivative **5a** showed an abundant ion at *m/e* 145 (26%), which corresponds to the loss of $\cdot CHOH{-}CH_3$ from the molecular ion. This type of cleavage, and the other abundant ions in the spectrum (*m/e* 59; $M - \cdot CH_3$, etc.) formed directly by the fragmentation of the acetal group, are characteristic for compounds containing that group[9].

The n.m.r. data for the acetate (**5b**) of **5a** were also in full accordance with the structure proposed. The terminal methyl groups are, by chance, isochronic, and give a doublet at δ 1.25 (J 6 Hz). The geminal-partner protons of the acetoxyl groups (H-2,5) give a complex multiplet at δ 4.9, resembling a quartet (with a splitting of 6 Hz), but each line is further split to give a quintet. The two protons of the 1,3-dioxolane ring (H-3,4) give a much simpler multiplet at δ 3.7, and the isopropylidene methyl groups appear as a singlet at δ 1.35.

The stability of the 3,4-*O*-isopropylidene ring towards acids depends on the substituents at C-2 and C-5. Hydrolysis of the 2,5-dihydroxy compound **4b** to **1a** was a slower process than conversion of the di-*O*-methyl derivative **4d** into **1b**. The 2,5-di-*O*-mesyl derivative **4c** was completely resistant towards hydrolysis in 0.1M aqueous trifluoroacetic acid at 100°, and, when more drastic conditions were applied, gave only decomposition products. The dihydroxy-dimethyl derivative **1b** was converted into the desired 3,4-di-*O*-mesyl compound **1c**, which showed biological properties similar to those of the corresponding 2,5-anhydro derivative[2-4] in significantly inhibiting the secretion of gastric acid.

During methylation of **4b** with dimethyl sulfate, besides **4d**, a variable amount of a mono-*O*-methyl derivative (**4e**) could be isolated, depending on the reaction conditions used. Location of the methoxyl group at C-2 was established by n.m.r. spectroscopy, the spectra of the acetate (**4f**) and methanesulfonate (**4g**) being compared. In the spectrum of **4f**, the signal of the proton geminal to the acetoxyl group appeared at δ 5.50, whereas, in that of the 2,5-di-*O*-acetyl derivative **4a**, the corresponding protons, H-2_a and H-5_e, gave signals at δ 5.05 and 5.50, respectively.

That means that the signal of **4f** at δ 5.50 is that of an *equatorial* proton, and, consequently, the acetoxyl group is attached *axially* at C-5, and the methoxyl group *equatorially* at C-2. Similarly, in the spectrum of the mesyl-methyl derivative **4g**, H-5 gives a multiplet at δ 5.22, proving the *axial* arrangement of the mesyloxy group; in the spectrum of the corresponding di-*O*-mesyl derivative **4c**, H-2_a and H-5_e appear at δ 4.85 and 5.27, respectively. This major conformation of these molecules, with equatorial C-2 and axial C-5 substituents, is confirmed by the values of the coupling constants $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$, namely, ~7, 9, and 2.5 Hz, respectively, which are in agreement with the *trans* diaxial arrangement of H-2,3 and H-3,4 and the *cis* axial–equatorial arrangement of H-4,5, respectively.

Formation of the 2-*O*-methyl derivative **4e** suggests that the dihydroxy compound **4b** has the same conformation as its derivatives (**4e**–**4g**), with *equatorial* OH-2 and *axial* OH-5 groups, as OH-2 reacts faster than OH-5 on methylation.

The ready formation of the 3,4-*O*-isopropylidene derivative **4b** suggested a new, simple synthesis for this useful intermediate, starting from 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-glucitol[10]. Treatment of the latter with sodium sulfide gave, besides some polymeric material, **4b** as the main component. As separation of **4b** therefrom was difficult, the crude mixture was acetylated, affording pure **4a**, which, on deacetylation, gave **4b**. Instead of the 1,2:5,6-dianhydride, its precursor, 3,4-*O*-isopropylidene-1,6-di-*O*-tosyl-D-glucitol[10], could be used in the same reaction.

EXPERIMENTAL

General methods. — Melting points are uncorrected. T.l.c. was effected on Kieselgel G with ethyl acetate (*A*), and with ethyl acetate–carbon tetrachloride 1:1 (*B*), 1:3 (*C*), and 1:5 (*D*). For detection, 0.1M potassium permanganate–M sulfuric acid (1:1) at 105° was used. Column chromatography was performed on Kieselgel 40 (63–200 μm). N.m.r. spectra (60 MHz) were recorded at room temperature with a JEOL 60-HL spectrometer for solutions in chloroform-*d* with tetramethylsilane as the internal standard. Mass spectra were recorded with a Varian MAT SM-1 instrument.

All evaporations were performed in a rotary evaporator under diminished pressure, after the organic solutions had been dried with sodium sulfate. Light petroleum refers to the fraction having b.p. 60–80°. Optical rotations were determined in chloroform (*c* 1). Reaction mixtures containing sodium methoxide were made neutral with carbon dioxide.

*1,6-Anhydro-2,5-di-*O*-methyl-1(6)-thio-*D*-glucitol* (**1b**). — A solution of compound **4d** (1.5 g) in 0.1M aqueous trifluoroacetic acid solution (15 ml) was boiled under reflux for 2 h, cooled, and evaporated; the residue was dissolved in water, and the solution was treated with charcoal, and evaporated. Two portions of ethanol were added to, and evaporated from, the residue, to give **1b** as a colorless syrup (1.15 g, 91.3%) that crystallized on storage, but could not be recrystallized; $[\alpha]_D^{20}$ −44°; R_F 0.55 (*A*), 0.15 (*B*).

Anal. Calc. for $C_8H_{16}O_4S$: C, 46.13; H, 7.74; S, 15.40. Found: C, 45.98; H, 7.92; S, 15.22.

*1,6-Anhydro-2,5-di-*O*-methyl-3,4-di-*O*-(methysulfonyl)-1(6)-thio-*D*-glucitol* (**1c**). — A solution of **1b** (10 g) in pyridine (50 ml) was treated with methanesulfonyl chloride (12 ml) at 0°. After 5 h at room temperature, the mixture was processed to give crude **1c** (11.2 g, 62%) which was crystallized from chloroform–methanol (9.2 g, 51%), m.p. 146–148°, $[\alpha]_D^{20}$ −8°, R_F 0.70 (*B*).

Anal. Calc. for $C_{10}H_{20}O_8S_3$: C, 32.95; H, 5.53; S, 26.40. Found: C, 32.92; H, 5.52; S, 26.36.

*1,6-Anhydro-2,3:4,5-di-*O*-isopropylidene-1(6)-thio-*D*-glucitol* (**2a**). — *Method a.* A slurry of 1,6-anhydro-1(6)-thio-D-glucitol[1] (**1a**, 0.9 g) in acetone (50 ml) containing concentrated sulfuric acid (0.5 ml) was stirred at room temperature until complete dissolution occurred (10 min). After 20 h, the mixture was made neutral with solid sodium carbonate, the suspension was filtered, and the filtrate was evaporated to dryness. The residue was crystallized from methanol–water, to give pure **2a** (0.90 g, 69%), m.p. 121–123°, $[\alpha]_D^{20}$ +8°; R_F 0.70 (*D*).

Anal. Calc. for $C_{12}H_{20}O_4S$: C, 55.35; H, 7.74; S, 12.32. Found: C, 55.37; H, 7.86; S, 12.22.

Method b. A solution of 2,3,4,5-tetra-*O*-acetyl-6-*S*-acetyl-6-thio-1-*O*-*p*-tolylsulfonyl-D-glucitol[1] (28 g) in chloroform (500 ml) and methanol (250 ml) was treated with 4.3M methanolic sodium methoxide (25 ml). After 30 min, the mixture was made neutral, and evaporated. The residue was treated with acetone (500 ml) and concentrated sulfuric acid (6 ml) to give, after processing as described for route *a*, pure **2a** (4.4 g, 33.8%), identical with that obtained *via* route *a*.

Hydrolysis of **2a**. — A slurry of **2a** (5.2 g) in 0.1M aqueous trifluoroacetic acid (52 ml) was stirred on a steam bath until complete dissolution occurred (4 h). The solution was then heated for 2 h, and evaporated. Ethanol was added to, and evaporated from, the residue, which was then crystallized from ethanol, to give **1a** (2.3 g, 64%), m.p. 130–131° (alone or in admixture with authentic material[1]).

*1,6-Anhydro-2,3:4,5-di-*O*-methylene-1(6)-thio-*D*-glucitol* (**2b**). — A solution of **1a** (0.36 g) in 37% aqueous formaldehyde (2 ml) and concentrated hydrochloric acid (2 ml) was kept in a desiccator over concentrated sulfuric acid for 3 days. The solid residue was dissolved in ethyl acetate, and was purified by column chromatography using solvent *D*. The fraction having R_F 0.45 (*D*) was evaporated, and the residue was crystallized from acetone–light petroleum, yielding **2b** (0.22 g, 54%), m.p. 93–95°, $[\alpha]_D^{20}$ +49.3°.

Anal. Calc. for: $C_8H_{12}O_4S$: C, 47.04; H, 5.92; S, 15.70. Found: C, 46.92; H, 6.11; S, 15,62.

*1,6-Anhydro-2,3:4,5-di-*O*-benzylidene-1(6)-thio-*D*-glucitol* (**2c**). — To a solution of **1a** (0.9 g) in concentrated hydrochloric acid (2.5 ml) was added benzaldehyde (2.5 ml), and the mixture was vigorously stirred for 15 h, and diluted with chloroform; the organic layer was successively washed with 5% aqueous sodium hydrogen carbonate and water, dried, and evaporated, and the residue was crystallized from methanol–chloroform to give pure **2c** (1.12 g, 63%), m.p. 166–168°, $[\alpha]_D^{20}$ +22.7°; R_F 0.70 (*D*),

Anal. Calc. for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66; S, 9.00. Found: C, 67.71; H, 5.72; S, 8.92.

Desulfurization of acetals **2a**, **2b**, *and* **2c**. — A solution of the corresponding thioether (1 mmole) in ethanol (10 ml) was boiled under reflux with Raney nickel (~3 g) for 2 h. The mixture was cooled, and filtered, and the filtrate was repeatedly heated with fresh Raney nickel (~3 g) for 2 h. The suspension was filtered, the filtrate was evaporated, and the residue was treated with chloroform. The extract was washed with water, and evaporated, and the residue was purified by column chromatography (solvent *D*). The fractions containing the desulfurized compound were combined, and evaporated, and the residue was freed of traces of solvents at 10^{-2} torr, yielding (*a*) **3a** as a syrup (0.15 g, 79%), $[\alpha]_D^{20}$ −60°; R_F 0.40 (*D*); mass spectral data: peaks at *m/e* 230 ($[M^+]$, 3% of base peak at *m/e* 115) and 215 (55, $[M-\cdot CH_3]$); (*b*) **3b** as a syrup (0.12 g, 62.5%), $[\alpha]_D^{20}$ −76°; R_F 0.45 (*D*); mass spectral data: peaks at *m/e* 174 ($[M^+]$, 1% of base peak at *m/e* 87) and 144 (4, $[M-CH_2=O]$); and (*c*) **3c** as a solid that was recrystallized from methanol–water and then from ether–light petroleum, yield 0.08 g (24.8%), m.p. 75–80°, $[\alpha]_D^{20}$ 0°; R_F 0.65 (*D*); mass spectral data: a peak at *m/e* 326 ($[M^+]$, 67% of base peak at *m/e* 105).

1,6-Anhydro-2,5-di-O-acetyl-3,4-O-isopropylidene-1(6)-thio-D-glucitol (**4a**). — *Method a.* A solution of **2a** (2.6 g) in M methanolic hydrogen chloride (120 ml) was kept for 24 h at room temperature, and then made neutral with solid sodium hydrogen carbonate. The mixture was filtered, the filtrate was evaporated, and then ethanol and chloroform were successively added to, and evaporated from, the residue. The dry, solid residue was treated with pyridine (30 ml) and acetic anhydride (20 ml), and the mixture was kept overnight, and processed, to give, after recrystallization from ether–light petroleum, compound **4a** (2 g). The mother liquor was evaporated, and the residue was repeatedly methanolyzed, to yield a second crop of **4a** (1 g). Recrystallization of the combined materials from 1:1 methanol–water afforded pure **4a** as needles (2.6 g, 85.5%), m.p. 131–132°, $[\alpha]_D^{20}$ −19°; R_F 0.45 (*C*).

Anal. Calc. for $C_{13}H_{20}O_6S$: C, 51.30; H, 6.62; S, 10.53. Found: C, 51.41; H, 6.65; S, 10.51.

Method b. Sodium sulfide nonahydrate (2.4 g) was added to a solution of 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-glucitol[10] (18.6 g) in ethanol (200 ml) and water (50 ml). The mixture was stirred for 1 h at room temperature, made neutral with acetic acid (phenolphthalein as internal indicator), and evaporated. Ethanol was twice added to, and evaporated from, the residue, and then chloroform was added and evaporated, and the residue was treated with pyridine (100 ml) and acetic anhydride (100 ml). After the usual processing, compound **4a** (17.3 g, 75%) was obtained, identical with that prepared *via* route *a*.

Method c. A slurry of 3,4-*O*-isopropylidene-1,6-di-*O*-*p*-tolylsulfonyl-D-glucitol[10] (53 g) and sodium sulfide nonahydrate (26.5 g) in ethanol (220 ml) and water (55 ml) was stirred for 1 h at room temperature. The mixture was then made neutral with carbon dioxide, and evaporated, to give (after processing as described for route *b*) compound **4a** (20.8 g, 68.5%), identical with that already described.

1,6-Anhydro-3,4-O-isopropylidene-1(6)-thio-D-glucitol (**4b**). — A solution of **4a** (15.2 g) in chloroform (15 ml) and methanol (60 ml) was treated with 4M methanolic sodium methoxide (0.2 ml). After 2 days at room temperature, the solution was made neutral and evaporated. The residue was dissolved in acetone, to give (after treatment with charcoal and evaporation) a syrup that, on treatment with ether–light petroleum, afforded pure **4b** (8.7 g, 79%), m.p. 80–81°, $[\alpha]_D^{20}$ −36°; R_F 0.40 (*B*).

Anal. Calc. for $C_9H_{16}O_4S$: C, 49.07; H, 7.32; S, 14.56. Found: C, 49.20; H, 7.39; S, 14.38.

Mesylation of compound **4b** (4.4 g) afforded the di-*O*-mesyl derivative **4c** (6.7 g, 89%), m.p. 167–169°, $[\alpha]_D^{20}$ −18.6°; R_F 0.55 (*B*).

Anal. Calc. for $C_{11}H_{20}O_8S_3$: C, 35.10; H, 5.36; S, 25.55. Found: C, 34.99; H, 5.32; S, 25.52.

2,5-Di-O-acetyl-1,6-dideoxy-3,4-O-isopropylidene-D-glucitol (**5b**). — A solution of **4b** (1.1 g, 5 mmoles) was treated with Raney nickel as described for the desulfurization of **2a**. The resulting, semi-solid **5a** (0.6 g) had $[\alpha]_D^{20}$ −13°; R_F 0.40 (*B*). After acetylation, and column chromatography (solvent *D*), it gave pure **5b** (0.29 g, 21.2%) as a colorless syrup, $[\alpha]_D^{20}$ +11°; R_F 0.55 (*D*); mass-spectral data: peaks at *m/e* 259 ([M − ·CH_3], 68% of base peak at *m/e* 129) and 187 (22, [M − ·CHOAc − CH_3]).

1,6-Anhydro-3,4-O-isopropylidene-2,5-di-O-methyl-1(6)-thio-D-glucitol (**4d**) *and 1,6-anhydro-3,4-O-isopropylidene-2-O-methyl-1(6)-thio-D-glucitol* (**4e**). — Crude, syrupy **4b** obtained by deacetylation of **4a** (30.4 g) was dissolved in water (50 ml) and, during 1 h, a solution of sodium hydroxide (36 g) in water (70 ml) and dimethyl sulfate (37 ml) were simultaneously added dropwise, with stirring, the temperature of the mixture being kept below 20° by cooling in ice. Stirring was continued for 1 h at room temperature, and the di-*O*-methyl derivative that separated started to solidify. The mixture was extracted several times with chloroform, and the extracts were combined, washed with the minimal volume of water, dried, evaporated, and the residue re-evaporated with methanol, to give a solid mixture of **4d** and **4e**. On recrystallization from methanol–water, the pure di-*O*-methyl derivative **4d** (12.9 g, 52%) was obtained; m.p. 74–75°, $[\alpha]_D^{20}$ −41°; R_F 0.75 (*B*).

Anal. Calc. for $C_{11}H_{20}O_4S$: C, 53.20; H, 8.12; S, 12.91. Found: C, 53.31; H, 7.93; S, 13.05.

Evaporation of the mother liquor, followed by column chromatography (solvent *B*), afforded a further crop of **4d** (0.7 g, 2.9%), together with the 2-*O*-methyl derivative **4e**, which was recrystallized from carbon tetrachloride–light petroleum; yield 4.4 g (18.8%), m.p. 87–89°, $[\alpha]_D^{20}$ −29°; R_F 0.55 (*B*).

Anal. Calc. for $C_{10}H_{18}O_4S$: C, 51.26; H, 7.74; S, 13.68. Found: C, 51.31; H, 7.72; S, 13.84.

Acetylation of **4e** (1.17 g) with pyridine–acetic anhydride afforded (after recrystallization from ether–light petroleum) compound **4f** (1.18 g, 85.5%), m.p. 100–101°, $[\alpha]_D^{20}$ −83°; R_F 0.75 (*B*).

Anal. Calc. for $C_{12}H_{20}O_5S$: C, 52.15; H, 7.30; S, 11.60. Found: C, 52.37; H, 7.35; S, 11.62.

Mesylation of **4e** (1.17 g) with pyridine–methanesulfonyl chloride gave, after recrystallization from acetone–light petroleum, compound **4g** (1.2 g, 77%), m.p. 124–125°, $[\alpha]_D^{20}$ −54.6°; R_F 0.70 (*B*).

Anal. Calc. for $C_{11}H_{20}O_6S_2$: C, 42.30; H, 6.45; S, 20.52. Found: C, 42.24; H, 6.42; S, 20.40.

REFERENCES

1 J. KUSZMANN AND P. SOHÁR, *Carbohydr. Res.*, 48 (1976) 23–32.
2 J. KUSZMANN AND P. SOHÁR, *Carbohydr. Res.*, 27 (1973) 157–168.
3 J. KUSZMANN AND P. SOHÁR, *Carbohydr. Res.*, 35 (1974) 97–102.
4 J. KUSZMANN, P. SOHÁR, J. BORSY, AND F. ANDRÁSI, *Hung. Pat. Appl.*, GO 1265 (1974).
5 O. S. CHIZOV, L. S. GOLOVKINA, AND N. S. WULFSON, *Carbohydr. Res.*, 6 (1968) 143–149; I. J. BURDEN AND J. F. STODDART, *J. Chem. Soc.*, (1975) 675–682.
6 L. VARGHA AND E. KASZTREINER, *Chem. Ber.*, 93 (1960) 1608–1616.
7 R. M. HANN, J. K. WOLFE, AND C. S. HUDSON, *J. Am. Chem. Soc.*, 66 (1944) 1898–1901.
8 L. VARGHA, *Ber.*, 68 (1935) 1377–1384.
9 *Cf.*, J. A. MCCLOSKEY, *Methods Enzymol.*, 14 (1969) 416–417.
10 L. VARGHA AND E. KASZTREINER, *Chem. Ber.*, 92 (1959) 2506–2515.