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SYNTHESIS OF 2-ACETAMIDO-2-DEOXY-5-THIO-D-GLUCOPYRANOSE*

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ABSTRACT

2-Acetamido-2-deoxy-5-thio-D-glucopyranose (**12**) has been synthesized from methyl 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (**1**). Benzoylation of **1**, followed by *O*-deisopropylidenation, gave methyl 2-acetamido-3-*O*-benzoyl-2-deoxy-β-D-glucofuranoside, which was converted, *via* selective benzoylation and mesylation, into methyl 2-acetamido-3,6-di-*O*-benzoyl-2-deoxy-5-*O*-mesyl-β-D-glucofuranoside (**5**). Treatment of **6**, formed by the action of sodium methoxide in chloroform on **5**, with thiourea gave methyl 2-acetamido-2,5,6-trideoxy-5,6-epithio-β-D-glucofuranoside (**7**), which was converted into the 5-thio compound **9** by cleavage of the epithio ring in **7** with potassium acetate. Alkaline treatment of **10**, derived from **9** by hydrolysis, afforded the title compound. Evidence in support of the structures assigned to the new derivatives is presented.

INTRODUCTION

There has been a great deal of activity in recent years in the synthesis of hetero-sugars, in which the ring-oxygen atom of aldoses has been replaced by sulfur or nitrogen. These sugars are interesting, not only from the point of view of the chemistry involved, but also for their various, biological activities. The synthesis and chemistry of 5-thio-D-xylose, 5-thio-D-ribose, 5-thio-D-glucose, and 4-thio-D- and -L-ribofuranose have been well studied[1-9], but only one report[10] has appeared on the synthesis of an amino sugar having sulfur in the ring, namely, 6-amino-6-deoxy-5-thio-D-glucopyranose.

In previous papers[11,12], we have shown that various *N*-substituted 2-amino-2-deoxy-D-aldohexoses react with 2,2-dialkoxypropane—*N*,*N*-dimethylformamide–*p*-toluenesulfonic acid at 80–90° to give 5,6-*O*-isopropylidene furanosides. The potential utility of this reagent for syntheses in the field of amino sugars was emphasized, and such biologically important, amino sugar derivatives as Prumycin, and Nojirimycin analogs, have been synthesized[13-15]. The present report describes a synthesis of 2-acetamido-2-deoxy-5-thio-D-glucose.

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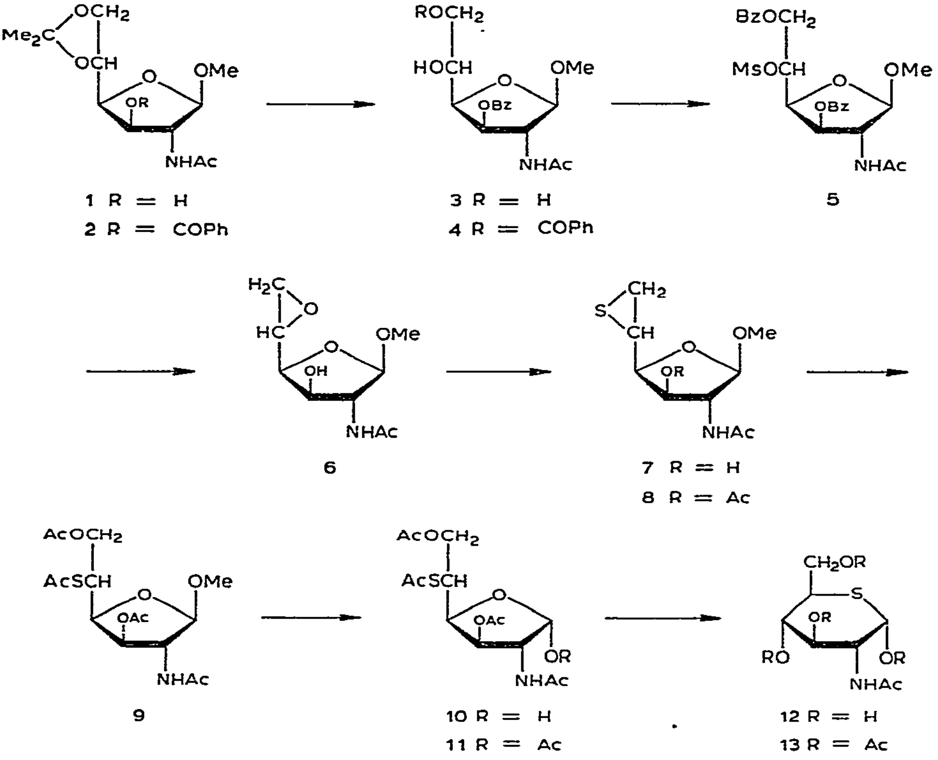
*Studies on Hetero Sugars, Part I.

RESULTS AND DISCUSSION

Benzoylation of methyl 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside[11] (**1**), and subsequent *O*-deisopropylidenation by mild, acid hydrolysis, gave methyl 2-acetamido-3-*O*-benzoyl-2-deoxy-β-D-glucofuranoside (**3**) in good yield. Selective benzoylation of the primary hydroxyl group on C-6 in **3** with benzoyl chloride in pyridine at −15° afforded the 3,6-dibenzoate (**4**) in 83% yield; **4** was mesylated with methanesulfonyl chloride in pyridine at 0° to afford the 5-*O*-mesyl derivative (**5**) in good yield. Compound **5** in dry chloroform was treated with methanolic sodium methoxide to give methyl 2-acetamido-5,6-anhydro-2-deoxy-β-D-glucofuranoside (**6**), which was treated with thiourea for 24 h at 40° to afford crystalline methyl 2-acetamido-2,5,6-trideoxy-5,6-epithio-β-D-glucofuranoside (**7**) (in 71% yield, from **5**). Formation of **7** involving inversion of C-5 in **6** was demonstrated by Hough *et al.*[16], and it was used for the synthesis of 5-thio-D-glucose by Nayak and Whistler[17]. Acetylation of **7** gave the 3-*O*-acetyl derivative **8**; significant signals in the n.m.r. spectrum were a one-proton doublet of doublets at τ 4.68 ($J_{2,3}$ 2.5 Hz, $J_{3,4}$ 6.5 Hz, H-3), a one-proton doublet at τ 5.13 ($J_{1,2}$ 2.5 Hz, H-1), and a high-field, three-proton multiplet at τ 6.70–7.88 (H-5,6,6′). Other n.m.r. data are given in the Experimental section, and are consistent with structure **8**. Nucleophilic ring-opening of



compound **7** with potassium acetate in acetic acid–acetic anhydride yielded methyl 2-acetamido-3,6-di-*O*-acetyl-5-*S*-acetyl-2-deoxy-5-thio-β-D-glucofuranoside (**9**), whose i.r. spectrum showed characteristic absorption at 1690 cm^{-1} (*S*-acetyl), and whose n.m.r. spectrum was consistent with structure **9**. Selective hydrolysis of **9** in 40:1 acetic acid–2M hydrochloric acid for 10 h at 40°, and acetylation of the product (**10**) yielded crystalline 2-acetamido-1,3,6-tri-*O*-acetyl-5-*S*-acetyl-2-deoxy-5-thio-D-glucofuranose (**11**), whose i.r. and n.m.r. spectra were consistent with structure **11**. In the n.m.r. spectrum of compound **11**, the value of $J_{2,3}$ is 5.9 Hz, and this seemed much larger than that of furanoid structures having a *trans* disposition of the adjacent groups on C-2 and C-3. However, we have recently observed that the $J_{2,3}$ value of furanose derivatives having a 1-*O*-acyl or -alkyl group *cis* to the group on C-2, such as 1,2,3-tri-*O*-acetyl-5,6-*O*-isopropylidene-α-D-glucofuranose (4.5 Hz)[18], 2-acetamido-1,2-di-*O*-acetyl-2-deoxy-5,6-*O*-isopropylidene-α-D-glucofuranose (7.4 Hz)[19], methyl 2-acetamido-3,6-di-*O*-acetyl-5-*S*-acetyl-2-deoxy-5-thio-α-D-glucofuranoside (5.0 Hz)[19], 1,3-di-*O*-acetyl-2-(benzyloxycarbonyl)amino-2-deoxy-5,6-*O*-isopropylidene-α-D-glucofuranose (5.4 Hz)[15], and 2,5-bis(acetamido)-1,3-di-*O*-acetyl-2,5-dideoxy-α-D-xylofuranose (6.8 Hz)[15], are generally large. It is presumed that, on account of the steric interaction between the substituents on C-1 and C-2, the furanose derivatives may adopt a distorted conformation.

On treatment with sodium methoxide in methanol for 1 h at 0°, compound **10** gave crystalline 2-acetamido-2-deoxy-5-thio-D-glucopyranose (**12**) in 74% yield. Acetylation of **12** afforded 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-5-thio-α-D-glucopyranose (**13**) in good yield. The i.r. spectrum of **13** did not exhibit *S*-acetyl absorption, and the n.m.r. data (see the Experimental section) were well resolved by use of decoupling techniques.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto micro melting-point apparatus, and are uncorrected. Specific rotations were determined with a Yanagimoto OR-50 polarimeter, and i.r. spectra were recorded with a Jasco IRA-1 spectrophotometer. N.m.r. spectra were recorded at 60 and 90 MHz with Hitachi R-24 and R-22 spectrometers for solutions in chloroform-*d*, unless otherwise noted. N.m.r. data were confirmed by use of decoupling techniques. Preparative chromatography was performed on silica gel (Waco Co.; 300 mesh) with the solvent systems specified. Evaporations were conducted *in vacuo*.

*Methyl 2-acetamido-3-*O*-benzoyl-2-deoxy-β-D-glucofuranoside* (**3**). — To a solution of **1** (ref. 11) (13.9 g) in pyridine (50 mL) was added benzoyl chloride (7.7 mL) at 0°. The mixture was kept for 1 h at 0°, and extracted with chloroform. The extract was successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and evaporated. The product (**2**) was used in the next reaction without further purification. A solution of **2** in 65% aqueous acetic acid (240 mL) was heated for 3 h at 40°, and then evaporated at 40° to a syrup which was chromatographed on a column of silica gel (150 g) with benzene, and then 30:1 benzene–methanol. With the latter eluant, compound 3 issued as the faster-moving component, and was obtained as needles (11.8 g, 69%) by recrystallization from ethanol–ether, m.p. 74.5–75.5°, $[\alpha]_D^{25}$ $-36.5°$ (*c* 0.5, methanol); ν_{max}^{Nujol} 3450–3240 (OH, NH), 1720 and 1265 (ester), 1670 and 1540 (amide), and 710 and 700 cm^{-1} (phenyl); n.m.r. data (methanol-d_4) at 60 MHz: τ 1.80–2.52 (5 H, COPh), 4.46 (d of d, 1 H, $J_{2,3}$ 1.2 Hz, $J_{3,4}$ 4.8 Hz, H-3), 5.08 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 6.57 (s, 3 H, OMe), and 8.00 (s, 3 H, AcN).

Anal. Calc. for $C_{16}H_{21}NO_7$: C, 56.63; H, 6.24; N, 4.13. Found: C, 56.61; H, 6.21; N, 3.98.

*Methyl 2-acetamido-3,6-di-*O*-benzoyl-2-deoxy-β-*D*-glucofuranose* (4). — To a stirred solution of 3 (6.0 g) in dry pyridine (24 mL) was added benzoyl chloride (3.6 mL) at −15°. The mixture was stirred for 30 min at −15°, and was then extracted with chloroform. The extract was successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and evaporated. The residue was chromatographed on a column of silica gel (80 g) with benzene, and then with 30:1 benzene–methanol. The latter eluate yielded 4 as a syrup (6.5 g; 83%), $[\alpha]_D^{25}$ $-21.5°$ (*c* 0.53, chloroform); ν_{max}^{film} 3500–3200 (OH, NH), 1720 and 1280 (ester), 1660 and 1540 (amide), and 750 and 700 cm^{-1} (phenyl).

Anal. Calc. for $C_{23}H_{25}NO_8$: C, 62.29; H, 5.68; N, 3.16. Found: C, 62.15; H, 5.72; N, 3.11.

*Methyl 2-acetamido-3,6-di-*O*-benzoyl-2-deoxy-5-*O*-mesyl-β-*D*-glucofuranoside* (5). — To an ice-cooled solution of 4 (9.6 g) in dry pyridine (27 mL) was added methanesulfonyl chloride (5.0 g), and the mixture was kept for 16 h at 0°. The mixture was evaporated, the residue extracted with chloroform, and the extract successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and evaporated to give a crystalline product. Recrystallization from ethanol–ether afforded 5 (9.44 g, 84%) as needles, m.p. 124°, $[\alpha]_D^{23}$ $-67.5°$ (*c* 0.5, methanol); ν_{max}^{Nujol} 3350 (NH), 1735, 1720, and 1265 (ester), 1665 and 1540 (amide), 1170 (SO_2), and 710 and 700 cm^{-1} (phenyl); n.m.r. data at 60 MHz: τ 1.80–2.55 (10 H, 2 COPh), 3.30 (d, 1 H, $J_{2,NH}$ 8.0 Hz, NH), 4.32 (d of d, 1 H, $J_{2,3}$ 1.5 Hz, $J_{3,4}$ 5.5 Hz, H-3), 4.60 (m, 1 H, H-5), 4.93 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.08–5.52 (m, 3 H, H-4,6,6′), 5.73 (near d, 1 H, $J_{2,NH}$ 8 Hz, H-2), 6.52 (s, 3 H, OMe), 7.10 (s, 3 H, SMe), and 8.00 (s, 3 H, AcN).

Anal. Calc. for $C_{24}H_{27}NO_{10}S$: C, 55.27; H, 5.22; N, 2.67. Found: C, 55.25; H. 5.30; N, 2.61.

*Methyl 2-acetamido-2,5,6-trideoxy-5,6-epithio-β-*D*-glucofuranoside* (7). — To a solution of 5 (5.0 g) in dry chloroform (20 mL), cooled to −15°, was added, with stirring, an ice-cooled solution of freshly prepared sodium methoxide in methanol (250 mg of sodium in 5 mL of methanol). The mixture was stirred for 5 h below 0°. Methanol (20 mL) was added to the mixture, which was then treated with Amberlite IRC-50 and Amberlite IR-45 ion-exchange resins; the resins were filtered off, and washed with methanol. The filtrate and washings were combined, and evaporated.

Water was added to the residue, and the solution was washed with benzene, and evaporated at 40° to give syrupy methyl 2-acetamido-5,6-anhydro-2-deoxy-α-L-idofuranoside (**6**). The crude 5,6-anhydro compound (**6**) was sufficiently pure for the next reaction. To a solution of compound **6** (1.8 g) in methanol (60 mL) was added thiourea (1.8 g), and the mixture was stirred for 24 h at 40°, and evaporated. The residue was chromatographed on a column of silica gel (30 g) with 50:1 chloroform–methanol to give compound **7** (1.6 g, 71%). Recrystallization from ethanol-ether gave needles, m.p. 163–164°, $[\alpha]_D^{23}$ $-175°$ (c 0.3, methanol); ν_{max}^{Nujol} 3400 (OH), 3260 (NH), and 1620 and 1570 cm^{-1} (amide).

Anal. Calc. for $C_9H_{15}NO_4S$: C, 46.33; H, 6.48; N, 6.00. Found: C, 46.22; H, 6.35; N, 5.98.

*Methyl 2-acetamido-3-*O*-acetyl-2,5,6-trideoxy-5,6-epithio-β-*D*-glucofuranoside* (**8**). — A sample of **7** (430 mg) was acetylated with acetic anhydride–pyridine overnight at room temperature. After recrystallization of the product from ethanol–ether, **8** was obtained as needles (442 mg, 87%), m.p. 143°, $[\alpha]_D^{23}$ $-76°$ (c 0.3, methanol); ν_{max}^{Nujol} 3230 (NH), 1730 and 1210 (ester), and 1640 and 1530 cm^{-1} (amide); n.m.r. data at 60 MHz: τ 3.27 (d, 1 H, $J_{2,NH}$ 8.5 Hz, NH), 4.68 (d of d, 1 H, $J_{2,3}$ 2.5 Hz, $J_{3,4}$ 6.5 Hz, H-3), 5.13 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.68 (near d, 1 H, $J_{2,NH}$ 8.5 Hz, H-2), 6.22 (d of d, 1 H, $J_{3,4}$ 6.5 Hz, $J_{4,5}$ 9.0 Hz, H-4), 6.58 (s, 3 H, OMe), 6.88 (m, 1 H, H-5), 7.40–7.90 (m, 2 H, H-6,6′), 7.87 (s, 3 H, AcO), and 8.02 (s, 3 H, AcN).

Anal. Calc. for $C_{11}H_{17}NO_5S$: C, 47.98; H, 6.22; N, 5.09. Found: C, 47.86; H, 6.29; N, 5.23.

*Methyl 2-acetamido-3,6-di-*O*-acetyl-5-*S*-acetyl-2-deoxy-5-thio-β-*D*-glucofuranoside* (**9**). — A mixture of **7** (100 mg), potassium acetate (500 mg), acetic acid (0.5 mL), and acetic anhydride (5 mL) was boiled under reflux for 8 h, and evaporated. Chloroform (20 mL) was added to the residue, the precipitate was removed by filtration, and the filtrate was successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and evaporated to a syrup. The product was purified by chromatography on a column of silica gel (5 g) with chloroform, and then 50:1 chloroform–methanol. The latter eluate gave compound **9** as a syrup (95 mg, 59%), $[\alpha]_D^{23}$ $-48°$ (c 0.36, chloroform); ν_{max}^{film} 3250 (NH), 1740 and 1220 (ester), 1690 (SAc), and 1650 and 1540 cm^{-1} (amide); n.m.r. data at 60 MHz: τ 2.67 (d, 1 H, $J_{2,NH}$ 7.5 Hz, NH), 4.68 (d of d, 1 H, $J_{2,3}$ 1.0 Hz, $J_{3,4}$ 5.2 Hz, H-3), 5.07 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 6.59 (s, 3 H, OMe), 7.72 (s, 3 H, SAc), 7.98 (s, 6 H, 2 Ac), and 8.04 (s, 3 H, AcN).

Anal. Calc. for $C_{15}H_{23}NO_8S$: C, 47.73; H, 6.14; N, 3.71. Found: C, 47.59; H, 6.32; N, 3.58.

*2-Acetamido-3,6-di-*O*-acetyl-5-*S*-acetyl-2-deoxy-5-thio-*D*-glucofuranose* (**10**). — A solution of **9** (400 mg) in 40:1 acetic acid–2M hydrochloric acid (15 mL) was heated for 10 h at 40°. Water (10 mL) was added to the mixture, which was then treated with Amberlite IR-45 resin; the resin was filtered off, and washed with methanol. The filtrate and washings were combined, and evaporated to a syrup which was chromatographed on a column of silicic acid (5 g) with chloroform, and then 30:1 chloroform–methanol. The latter eluate afforded **10** (220 mg, 57%) as a syrup, $[\alpha]_D^{23}$ +93.5° (equil., *c* 0.3, chloroform); ν_{max}^{film} 3350–3250 (OH, NH), 1740 and 1230 (ester), 1690 (SAc), and 1650 and 1530 cm^{-1} (amide).

Anal. Calc. for $C_{14}H_{21}NO_8S$: C, 46.27; H, 5.83; N, 3.85. Found: C, 46.06; H, 6.10; N, 3.58.

*2-Acetamido-1,3,6-tri-O-acetyl-5-S-acetyl-2-deoxy-5-thio-α-*D*-glucofuranose* (**11**). — Compound **10** (100 mg) was acetylated with acetic anhydride (1 mL)–pyridine (2 mL) overnight at 0° to yield, from ethanol–ether, 65 mg (59%) of **11**, m.p. 132–133°, $[\alpha]_D^{25}$ +65° (*c* 0.24, chloroform); ν_{max}^{Nujol} 3300 (NH), 1745 and 1220 (ester), 1690 (SAc), and 1650 and 1520 cm^{-1} (amide); n.m.r. data at 60 MHz: τ 3.60 (d, 1 H, $J_{1,2}$ 5.6 Hz, H-1), 3.80 (d, 1 H, $J_{2,NH}$ 8.0 Hz, NH), 4.88 (t, 1 H, $J_{2,3}$ and $J_{3,4}$ 5.9 Hz, H-3), 5.13–6.05 (m, 5 H, H-2,4–6), 7.65 (s, 3 H, AcS), 7.90 (s, 6 H, 2 AcO), 7.94 (s, 3 H, AcO), and 8.00 (s, 3 H, AcN).

Anal. Calc. for $C_{16}H_{23}NO_9S$: C, 47.40; H, 5.72; N, 3.46. Found: C, 47.53; H, 5.77; N, 3.51.

The final filtrate was evaporated to a syrup (40 mg, 36%), which was a mixture of **11** and its β anomer (α:β estimated at ~3:2 from ratio of the intensities of H-1α and H-1β in the n.m.r. spectrum).

*2-Acetamido-2-deoxy-5-thio-*D*-glucopyranose* (**12**). — To an ice-cooled solution of **10** (100 mg) in methanol (5 mL) was added 1M sodium methoxide (0.5 mL), and the mixture was kept for 1 h at 0°, and then treated with Amberlite IRC-50 resin to remove the base; the resin was filtered off, and washed with methanol. The filtrate and washings were combined, and evaporated, whereupon the residue crystallized. The solid was recrystallized from ethanol–ether, to give compound **12** (51 mg, 74%), m.p. 101–102°, $[\alpha]_D^{20}$ +61° (equil., *c* 0.3, methanol); ν_{max}^{Nujol} 3450–3300 (OH, NH), and 1620 and 1540 cm^{-1} (amide).

Anal. Calc. for $C_8H_{15}NO_5S$: C, 40.49; H, 6.37; N, 5.90. Found: C, 40.60; H, 6.48; N, 5.77.

*2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-5-thio-α-*D*-glucopyranose* (**13**). — Compound **12** (25 mg) was treated with acetic anhydride (1 mL)–pyridine (2 mL) overnight at room temperature. It was then evaporated to a syrup which was purified by chromatography on a column of silica gel (1 g) with chloroform. Compound **13** was obtained as needles, 36 mg (84%), m.p. 166–167°, $[\alpha]_D^{23}$ +178.5° (*c* 0.23, chloroform); ν_{max}^{Nujol} 3300 (NH), 1750 and 1230 (ester), and 1640 and 1540 cm^{-1} (amide); n.m.r. data at 90 MHz: τ 4.03 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.08 (d, 1 H, $J_{2,NH}$ 8.4 Hz, NH), 4.60 (t, 1 H, $J_{3,4} = J_{4,5} =$ 10.4 Hz, H-4), 4.82 (t, 1 H, $J_{2,3} = J_{3,4} =$ 10.4 Hz, H-3), 5.35 (m, 1 H, $J_{2,NH}$ 8.4 Hz, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 3.2 Hz, H-2), 5.63 (d of d, 1 H, $J_{6,6'}$ 11.6 Hz, $J_{5,6}$ 5.0 Hz, H-6), 5.94 (d of d, 1 H, $J_{6,6'}$ 11.6, $J_{5,6'}$ 3.0 Hz, H-6′), 6.49 (m, 1 H, H-5), 7.82, 7.94, and 7.96 (3 s, 9 H, 3 AcO), and 8.10 (s, 3 H, AcN).

Anal. Calc. for $C_{16}H_{23}NO_9S$: C, 47.40; H, 5.72; N, 3.46. Found: C, 47.45; H, 5.69; N, 3.46.

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