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Note

Interaction of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosylamine with sulfhydryl compounds

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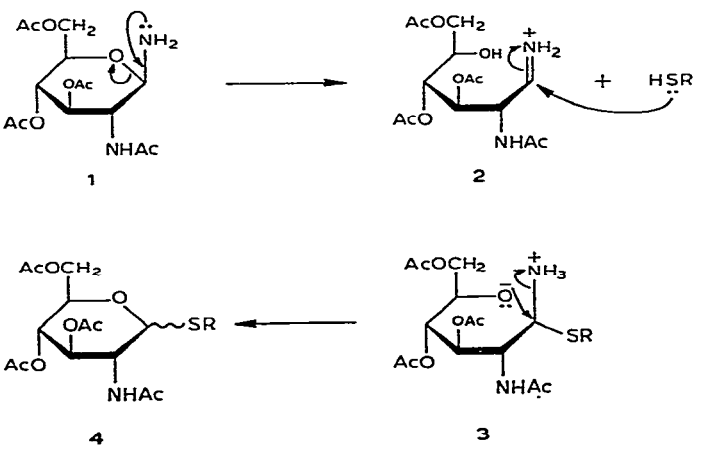
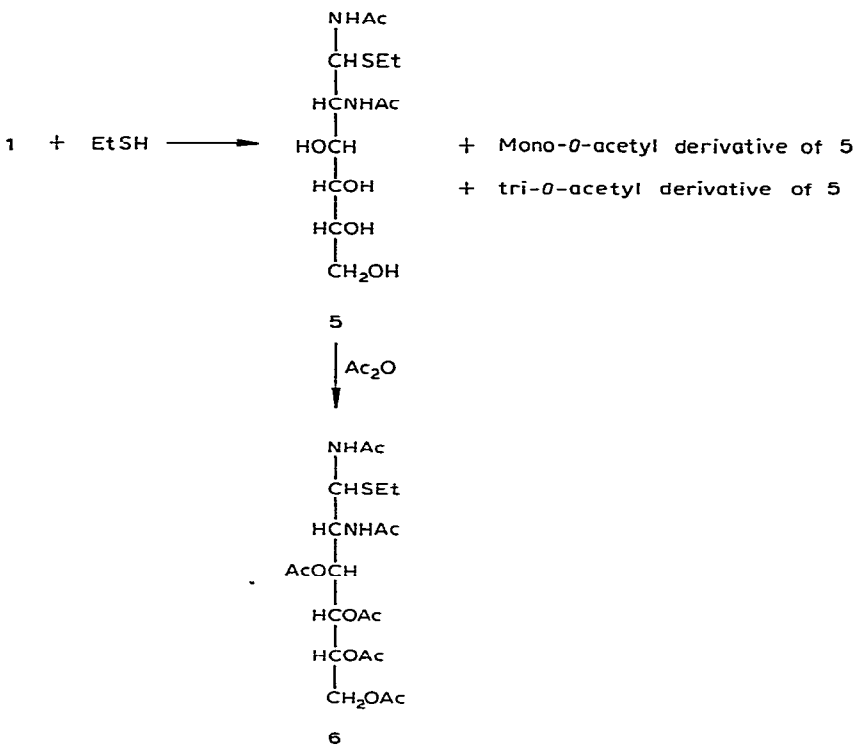
2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosylamine (**1**) has been recently used by us as an intermediate in the synthesis of analogs of 4-*N*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-L-asparagine (Glc*p*NAc-Asn), as potential inhibitors of glycopeptide biosynthesis. Tests in cell-culture systems show that **1** inhibits growth of mouse mammary adenocarcinoma (TA 3) cells and the incorporation of L-leucine and 2-amino-2-deoxy-D-glucose into glycoproteins of leukemic cells (P288)[1–4]. In order to elucidate the modes of biological activity of **1**, we have studied its reactivity. Initially, the formation of dimers was examined as a model for possible interactions with an amino group, such as the ε-amino group of L-lysine[1]. The dimerization reaction has been rationalized on the basis of formation of an acyclic, immonium-ion intermediate (**2**, Scheme 1) with which a second molecule of **1** reacts as a nucleophile, with subsequent elimination of ammonia, and ring closure[1].



Scheme 1

Another nucleophile common at the active site of enzymes is the sulfhydryl group of L-cysteine residues, and hence it was of interest to investigate the reaction of **1** with sulfhydryl compounds. It might be anticipated that such a reaction would proceed by an attack on the electron-deficient immonium ion (**2**), as has been postulated in the dimerization reaction, forming an adduct (**3**). This step is followed by ring closure, and elimination of ammonia, giving **4** (Scheme 1).

When **1** was treated with ethanethiol in methanol at room temperature during an extended time (2 months), the product displayed five spots in t.l.c. (1 :9 methanol–chloroform). Chromatography on a column of silica gel gave three major products, identified by elemental analysis and i.r., ^{1}H- and ^{13}C-n.m.r. spectroscopy as 1,2-diacetamido-1,2-dideoxy-1-*S*-ethyl-1-thio-D-glucitol (**5**) and its mono- and tri-*O*-acetyl derivatives (Scheme 2). The same products were obtained, as shown by t.l.c., when the reaction was conducted for 48 h at 60° in a sealed tube.



Scheme 2

The structure of **5** was confirmed by conversion into the hexacetyl derivative **6**. The ^{1}H-n.m.r. spectra of **5** and **6** (Figs. 1 and 2, respectively) show doubling of certain peaks, such as two superposed quartets caused by the ethyl protons, and may indicate that two epimers exist. On the other hand, the resonance of the methylene portion of an ethyl group attached to a chiral center might indeed be complex, and this complexity might be the result of a group projected into a chiral environment where two conformational species are contributing to the spectrum. As the two

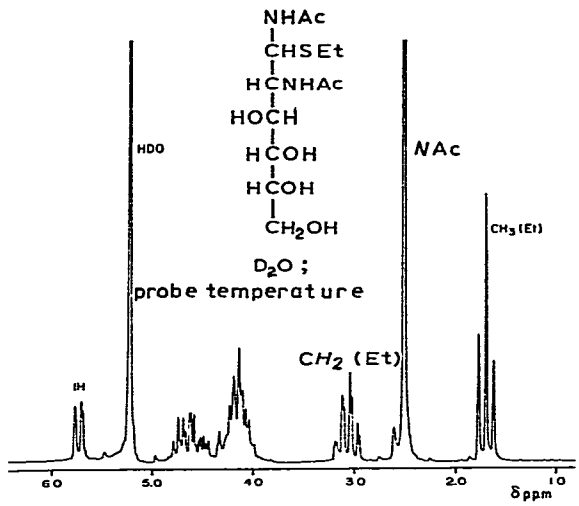


Fig. 1. ^{1}H-N.m.r. (100 MHz) spectrum of the ethylthiol adduct **5** in D_2O.

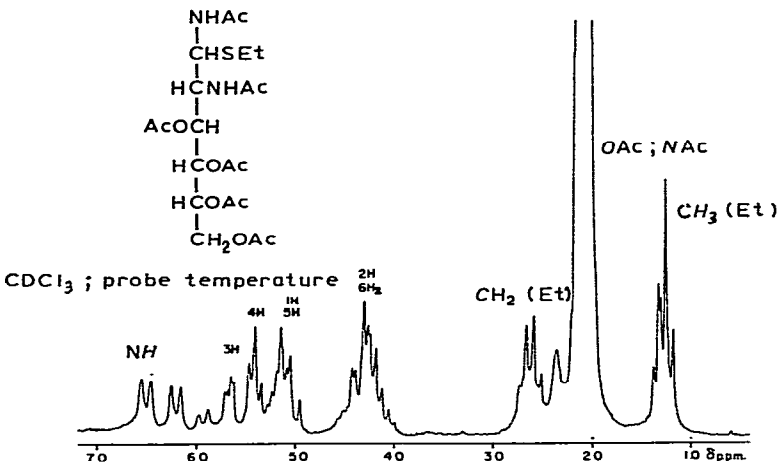


Fig. 2. ^{1}H-N.m.r. spectrum (100 MHz) of the acetylated ethylthiol adduct **6**.

possible epimers were not separated, the stereochemistry of the reaction is not established.

The mass spectrum (Fig. 3) of the hexaacetyl derivative **6** shows the expected molecule-ion peak at *m/e* 492 and a fragmentation pattern similar to that of fully acetylated diethyl dithioacetals[5]. The *m/e* 463 ion arises from fission of a carbon–sulfur bond in the molecule-ion and elimination of the ethyl group; a stabilized, five-membered ring may be drawn for this fragment. The fragment having *m/e* 431 is presumably obtained by the loss of ethanethiol. From this ion-species, *m/e* 431, acetic acid or protonated acetamide (*m/e* 60), acetamide (*m/e* 59), and ketene (*m/e* 42) are presumably eliminated; the position and the sequence of elimination of acetyl groups or ketene are not shown.

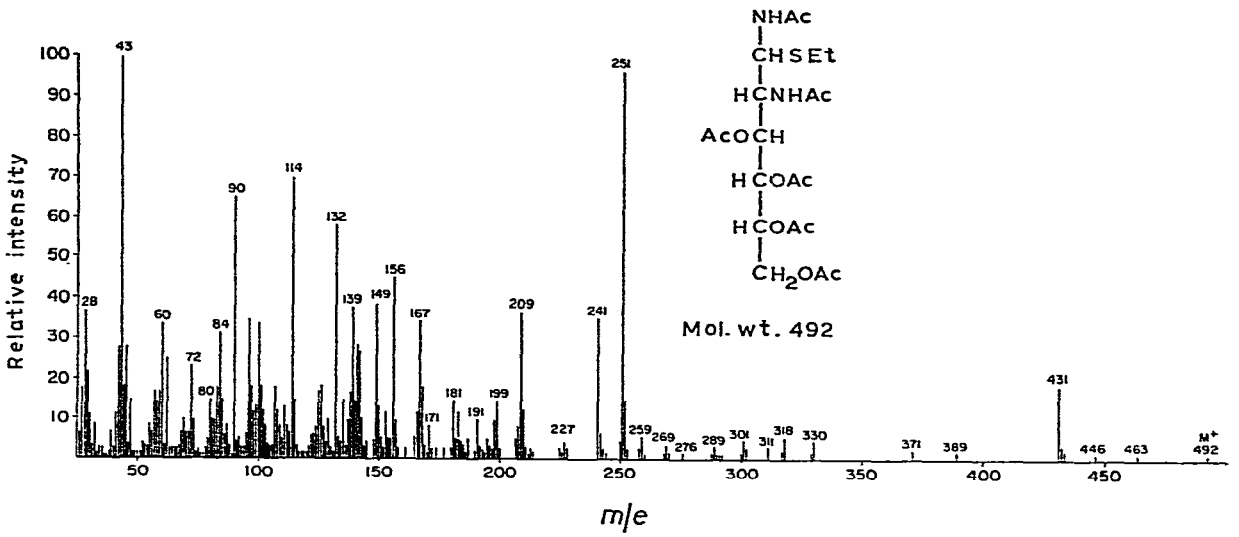
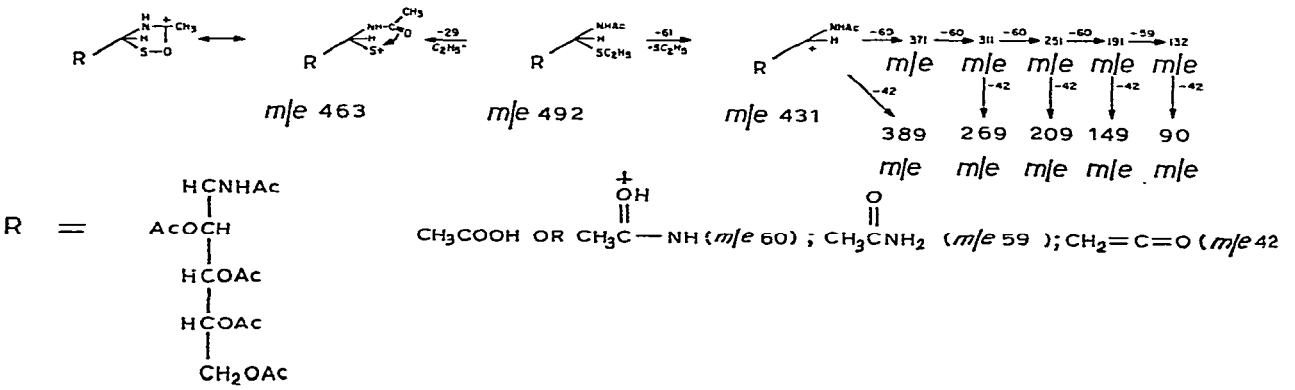
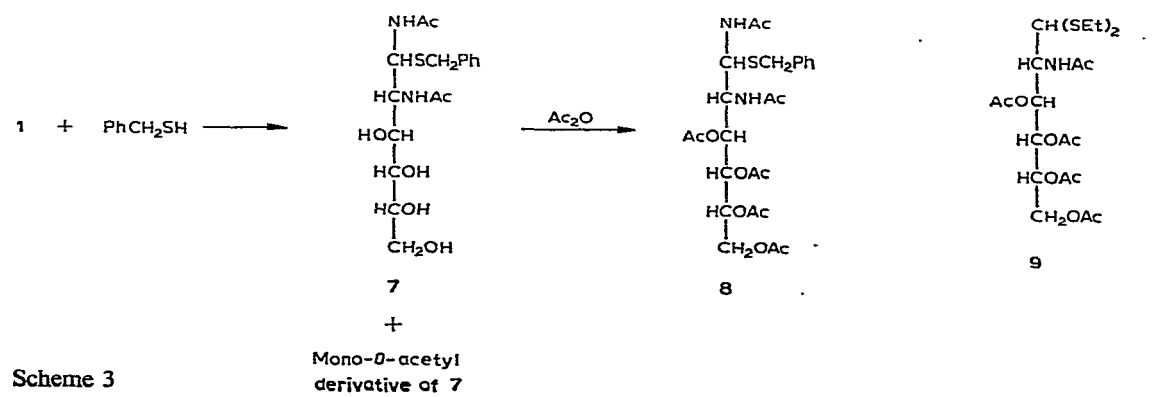


Fig. 3. Mass spectrum of **6**, determined with a DuPont 21-491 mass spectrometer, direct inlet, ionizing potential 70 eV, ionizing current 18 μA.





Scheme 3

TABLE I

^{1}H-N.M.R. PARAMETERS OF THE PERACETYLATED, THIOL ADDITION PRODUCTS IN $CDCl_3$

Compound	*^{1}H Chemical shifts (δ) and multiplicities of signals*									
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H_2-6*	*2-NH*	*1-NH*	*CH_3(ethyl)*	*CH_2(ethyl)*
9	4.08d	4.56m	5.62q	5.42q	5.16m	4.24m	5.80d		1.24t, 1.36t	2.69, 2.71
8	4.84d	4.33q	5.57q	5.31q	5.08m	4.2m	6.42d	6.20d		

Compound	*^{1}H Spin–spin coupling constants (Hz)*						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{6,6'}$	$J_{H-2,NH}$	$J_{H-1,NH}$
9	4.1	6.3	3.8	7.5	17.0	10.0	
8	9.4	2.6	6.4	5.2	—	10.0	9.0

Extending this reaction to other sulfhydryl compounds, compound **1** was treated with α-toluenethiol in methanol for two months. T.l.c. (1:9 methanol–chloroform) of the product showed four spots. Chromatography on a column of silica gel with methanolic chloroform as solvent (10–30%) gave three major products, identified as 1,2-diacetamido-1-*S*-benzyl-1,2-dideoxy-1-thio-D-glucitol (**7**), its mono-*O*-acetyl derivative, and dibenzyl disulfide (Scheme 3). The acyclic structure of **7** was confirmed by converting it into its hexaacetyl derivative **8**, by elemental analysis, and by i.r., ^{1}H-, ^{13}C-n.m.r., and mass-spectral data.

In order to assign ^{1}H and ^{13}C spectra to the amino thioacetals described here and to compare their conformations, 2-acetamido-3,4,5,6-tetra-*O*-acetyl-2-deoxy-D-glucose diethyl dithioacetal **9** was used as a model.

The 100-MHz, ^{1}H-n.m.r. spectrum of **9** was almost entirely first order, and resonances were assigned by spin-decoupling. The positions of the ^{1}H resonances (Table I) follow the general order established for the acetylated dithioacetals of neutral carbohydrates by Horton's group[6–8], except for H-2, which resonates upfield because of the acetamido group. The ethyl groups are magnetically nonequivalent, giving rise to separate methyl and methylene peaks. All coupling constants were measured, except for $J_{5,6}$, which was not determined because of the overlap of the C-6 methylene resonance with the H-1 signal. These coupling constants were used to assign probable conformations to the acetylated adducts, based on the principles developed by Horton *et al.* for open-chain carbohydrates[6,7]. These procedures have been checked in certain instances by X-ray crystallographic structure determination. Most vicinal coupling constants for **9** are of magnitude intermediate between those of pure antiparallel (~9 Hz) and pure gauche (~2 Hz) protons. Favorable conformers in which 1,3 interactions are avoided include the "sickle" forms in which either H-2,3 and/or H-4,5 are antiparallel and all of the carbon atoms, except C-1, are in the plane of the paper.

TABLE II

^{13}C CHEMICAL-SHIFTS OF THE PERACETYLATED, THIOL ADDITION PRODUCTS[a] IN $CDCl_3$

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*CH_3(NAc)*	*CH_3(OAc)*	*CH_3*	*CH_2*
9	51.9	52.1	69.8*	69.1*	68.8	61.5	22.9	20.7, 20.6	14.3, 14.6 (ethyl)	25.7, 25.9 (ethyl)
8	70.5	52.9	69.5	69.5	55.7	61.3	22.9	20.7		35.9 (benzyl)
6	70.2	53.1	69.4*,	69.2*	55.3	61.7	22.9	20.6	14.7(ethyl)	25.4 (ethyl)
	70.0		69.0*		55.0	61.4				

[a]Peaks indicated by * could be interchanged.

The intermediate values of $J_{3,4}$ and $J_{4,5}$ found for **8** likewise indicate sickle conformers. The most stable conformations appear to be those in which H-3 and H-4 are antiparallel, and C-1–C-4 are in the plane of the paper. This brings H-4 gauche with respect to H-5, and this conformation is consistent with the intermediate value observed for $J_{4,5}$. For a conformer having H-3 and 4 gauche, all three possible rotamers about C-4–C-5 lead to unfavorable 1,3-interactions, thus making them less stable than the conformer with H-3 and H-4 antiparallel.

In comparing the data for **8** and **9**, it appears that the introduction of a bulkier group at C-1 has a profound effect on the conformation of the whole molecule. A similar observation relating the bulk at C-1 with conformation has also been made for dithioacetals of D-ribose[8].

Assignments of ^{13}C resonances (Table II) to **6** and **9** have been deduced from ^{1}H spectra by plotting the ^{1}H off-resonance decoupling frequencies against ^{13}C resonances. The C-4 and C-5 resonances for **9** are very close and hence could be interchanged.

A difference of conformation of compound **8** as compared with **9** could also be determined from their different ^{13}C-n.m.r. spectra, especially upon considering the considerable upfield shift of the C-5 ^{13}C resonance for **8** (Table II). The ^{13}C-n.m.r. assignments for **6** are based on analogies with those for **8** and **9**, and are tentative; the complexity of the ^{1}H-n.m.r. spectrum of **6** precluded its detailed analysis.

The unexpected course of the reaction between **1** and ethane- or α-toluene-thiol may be rationalized as follows. Initially, the reaction proceeds as described in Scheme 1, namely, by the addition of ethanethiol to the acyclic immonium ion intermediate **2**. Subsequently, ring closure, followed by elimination of the amino group at position **1** is excluded because of *N*-acetylation, which could occur either by O→N acyl migration[9], or by an intermolecular mechanism in which the sulfhydryl reagent acts as both an *O*-deacetylating agent and an acyl donor to the NH_2 function[10]. The *O*-deacetylation observed may be effected either by the ammonia liberated during dimer formation in the initial stages of the reaction[1], or by the thiol reagent.

These model experiments thus show **1** to be a potential pseudoalkylating agent.

As has been found for many *O*-acetylated derivatives[2,3], compound **1** is probably *O*-deacetylated within the cell and then reacts with appropriate receptors.

EXPERIMENTAL

General methods. — Melting points (uncorrected) were determined by the capillary method, i.r. spectra with a Perkin–Elmer 457 spectrophotometer, and n.m.r. spectra with Varian A-60A and Varian XL-100 instruments. ^{1}H-N.m.r. spectra were obtained in the continuous-wave mode, and ^{13}C-n.m.r. spectra in the Fourier-transform mode; the positions of the peaks are expressed in δ (p.p.m.) from tetramethylsilane or 1,4-dioxane. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. T.l.c. was performed on plates of Merck HF-254 silica gel, and spots on chromatograms were detected with iodine vapor, by u.v. absorption, or by spraying with a ninhydrin solution.

Reaction of **1** *with ethanethiol.* — Ethanethiol (10 mL) was added to a methanolic solution of **1** (0.8 g in 10 mL) that was then kept for 2 months at room temperature. Methanol and the excess of ethanethiol were evaporated off at room temperature, and t.l.c. (1:9 methanol–chloroform) of the residual, oily gum showed five spots. The residue was chromatographed on a column of silicic acid (Bio-Sil A; 100–200 mesh), with 1:10 methanol–chloroform as eluent, followed by increasing concentrations of methanol (25–50%) in chloroform. Three fractions were collected. Evaporation of the first fraction gave an oil that solidified on trituration with ether–petroleum ether and the solid was washed with petroleum ether on the filter; yield 65 mg (6%); m.p. 88–90° (preshrinkage at 55°). The product was identified as the triacetate of **5** on the basis of the following data: ν_{max}^{KBr} 3540–3220 (broad, NH, OH), 1745 (C=O, acetoxyl), 1660, 1535, 1375 (C=O, amide), 1435 (S-CH_2), 2970, and 2940 cm^{-1} (CH_2); ^{1}H-n.m.r. ($CDCl_3$): δ 1.27 (t, *J* 7 Hz, C*H*$_3$ of ethyl), 2.04 (s, C*H*$_3$ of NHAc), 2.12 (s, C*H*$_3$ of OAc), 2.66 (q, *J* 7 Hz, C*H*$_2$ of ethyl), 5.26 (d, *J* 6 Hz, H-1), and 7.10 (d, *J* 8 Hz, N*H*Ac); $[\alpha]_D^{25}$ +9.3 (*c* 1.0, chloroform).

Anal. Calc. for $C_{18}H_{30}N_2O_9S \cdot 0.5\ H_2O$: C, 47.04; H, 6.80; N, 6.09; S, 6.97. Found: C, 47.02; H, 6.92; N, 6.28; S, 7.44.

The second fraction gave an oil, which solidified to a white powder on trituration with ether. This powder was filtered off, washed with ether, and dried; yield 210 mg (25%), m.p. 150–151°. The following data indicate that the compound is a mono-*O*-acetyl derivative of **5**: ν_{max}^{KBr} 3480–3380 (broad), 3290 (NH, OH), 1710 (C=O, acetoxyl), 1650, 1540, 1378 (C=O, amide), 1432 (S-CH_2), 2968, and 2935 cm^{-1} (CH_2); ^{1}H-n.m.r. (acetone-d_6): δ 1.24 (t, C*H*$_3$, *J* 7 Hz, ethyl), 2.04 (s, C*H*$_3$, of NHAc), 2.11 (s, CH_3 of OAc), 2.63 (q, *J* 7 Hz, C*H*$_2$ of ethyl), 5.41 (d, *J* 6 Hz, H-1); (D_2O): δ 1.17 (t, *J* 7 Hz, C*H*$_3$ of ethyl), 1.98 (s, CH_3 of NHAc), 2.09 (s, CH_3 of OAc), 2.55 (q, *J* 7 Hz, CH_2 of ethyl), and 5.22 (d, *J* 6 Hz, H-1); $[\alpha]_D^{23}$ +18.6 (*c* 1.0, methanol).

Anal. Calc. for $C_{14}H_{26}N_2O_7S$: C, 45.88; H, 7.15; N, 7.64; S, 8.75. Found: C, 45.86; H, 7.14; N, 7.36; S, 8.70.

The third fraction, on removal of the solvent, gave a solid that was crystallized

from methanol–ether, filtered off, washed with ether, and dried; m.p. 165–166°, yield 260 mg (35%). The following data suggest that the compound is **5**: ν_{max}^{KBr} 3460–3200 (broad, NH, OH), 1650, 1550, 1379 (C=O, amide), 1448 (S-CH_2), 2970, and 2950 cm^{-1} (CH_2); ^{1}H-n.m.r. (D_2O): δ 1.17, 1.22 (t × 2, 3, J 7 Hz, CH_3 of ethyl), 1.99 (s, 6, CH_3, NHAc), 2.53, 2.56 (q × 2, 2, J 7 Hz, CH_2 of ethyl), 3.65 (m, 4, H_2-6, H-5, H-2), 4.09 (m, 2, H-3, H-4), 5.19 (d, 1, J 6 Hz, H-1); ^{13}C-n.m.r. (D_2O): δ 175.2, 174.4 (C=O, NHAc), 73.0 (C-1), 72.5 (C-3), 69.8 69.4 (C-4), 63.9 (C-6), 56.1 (C-5), 55.8 (C-2), 25.5, 25.3 (CH_2 of ethyl), 23.3 (CH_3, NHAc), 15.5 (CH_3 of ethyl); $[\alpha]_D^{23}$ +21.9 (*c* 1.1, methanol).

Anal. Calc. for $C_{12}H_{24}N_2O_6S$: C, 44.42; H, 7.45; N, 8.63; S, 9.88. Found: C, 44.08; H, 7.28; N, 8.37; S, 9.51.

Reaction of **1** *with α-toluenethiol.* — α-Toluenethiol (10 mL) was added to a methanolic solution of **1** (0.8 g in 10 mL) and the mixture was kept for 2 months at room temperature. Methanol was allowed to evaporate at room temperature and the excess of α-toluenethiol was removed *in vacuo* at 40°. The residue was taken up in methanol (10 mL), whereupon a white precipitate separated out. This was filtered off, washed with cold methanol, and dried; m.p. 60–70°; ^{1}H-n.m.r. ($CDCl_3$): δ 3.60 (s, CH_2), 7.26 (C_6H_5) indicating that the material was dibenzyl disulfide (an oxidized product of α-toluenethiol, lit.[11] m.p. 69–70°). The filtrate was evaporated *in vacuo*, and the residue on t.l.c. (1:9 methanol–chloroform) indicated the presence of four spots. The residue was chromatographed on silicic acid (Bio-Sil A; 100–200 mesh) using methanolic chloroform (10%) as eluent. The first fraction solidified and was identified as dibenzyl disulfide, m.p. 69–70° (see foregoing). The column was then eluted with increasing concentrations of methanol (25–50%) in chloroform. The second fraction, an oil, on trituration with ether gave crystals that were washed on the filter with petroleum ether; m.p. 154–155°; yield 220 mg (22.4%). The following data indicate that the compound is a mono-*O*-acetyl derivative of **7**: ν_{max}^{KBr} 3520, 3440, 3358, 3300 (OH, NH), 1722 (C=O, acetoxyl), 1650, 1550 (C=O, amide), 2980, 2922 (CH_2), 1090, 1045, and 705 cm^{-1} (aromatic); ^{1}H-n.m.r. (CD_3OD); δ 1.90, 1.99 (s × 2, CH_3 of NHAc), 2.08 (s, CH_3 of OAc), 3.84 (s, CH_2 of benzyl), 5.36 (d, J 7 Hz, H-1), and 7.29 (C_6H_5, aromatic protons); ^{13}C-n.m.r. (CD_3OD): δ 173.5, 172.8, 172.5 (C=O), 139.3, 129.8, 129.2, 127.8 (aromatic C), 73.0 (C-1), 70.3 (C-3), 69.9 (C-4), 67.1 (C-6), 57.2 (C-5), 56.5 (C-2), 36.0 (CH_2 of benzyl), 22.7 (CH_3 of NHAc), and 20.8 (CH_3, OAc); $[\alpha]_D^{23}$ +2.2 (*c* 1.1, methanol).

Anal. Calc. for $C_{19}H_{28}N_2O_7S$: C, 53.25; H, 6.58; N, 6.53; S, 7.48. Found: C, 53.24; H, 6.50; N, 6.30; S, 7.69.

Evaporation of the third fraction gave a solid that was crystallized from methanol–ether; m.p. 167–169°; yield 290 mg (32%). The compound was identified as **7** on the basis of the following spectral data and elemental analysis: ν_{max}^{KBr} 3440–3240 (broad, NH, OH), 1650, 1530, 1373 (C=O, amide), 2958, 1920 (CH_2), 1437 (S-CH_2), 1075, 1028, and 700 cm^{-1} (aromatic); ^{1}H-n.m.r. (D_2O): δ 2.30, 2.37, 2.47, 2.50 (s × 4, 6, CH_3 of NHAc), 4.31 (s, 2, CH_2 of benzyl), 5.57 (d, 1, J 6 Hz, H-1), and 7.84 (s, 5, aromatic protons); ^{13}C-n.m.r. (D_2O): δ 175.1, 174.1 (C=O, NHAc), 138.9,

129.8, 128.3 (aromatic carbon atoms), 73.0 (C-1), 72.5 (C-3), 69.6 (C-4), 63.7 (C-6), 56.6 (C-5), 55.9 (C-2), 35.9 (CH_2, benzyl), 23.2 (CH_3, NHAc), and 23.0 (CH_3, NHAc); $[\alpha]_D^{23}$ +1.5 (*c* 1.0, methanol).

Anal. Calc. for $C_{17}H_{26}N_2O_6S$: C, 52.83; H, 6.78; N, 7.25; S, 8.29. Found: C, 53.10; H, 6.60; N, 7.12; S, 8.50.

Acetylation of **7**. *Formation of 1,2-diacetamido 3,4,5,6-tetra*-O-*acetyl-1*-S-*benzyl-1,2-dideoxy-1-thio*-D-*glucitol* (**8**). — Acetic anhydride (1 mL) was added slowly with stirring to a suspension of **7** (0.1 g) in dry pyridine (4 mL; dried over potassium hydroxide), cooled in ice. The suspension was stirred for 1 h at 0° and then for 4 h at room temperature and then evaporated *in vacuo*. The residue was taken up in ice-cold water (5 mL) and extracted with chloroform (25 mL × 2). The chloroform extract was washed with water (5 mL), dried (Drierite), and evaporated to an oil that solidified on trituration with ether–petroleum ether; m.p. 70–71° (shrinkage at 62°); yield 115 mg (80%); ν_{max}^{KBr} 3340 (broad, NH), 1755 (C=O, acetoxyl), 1670, 1525, 1373 (C=O, amide), 2970 (CH_2), 1430 (S-CH_2), 1040, and 706 cm^{-1} (aromatic); $[\alpha]_D^{23}$ +36.9 (*c* 1.0 chloroform).

Anal. Calc. for $C_{25}H_{34}N_2O_{10}S$: C, 54.13; H, 6.17; N, 5.05; S, 5.78. Found: C, 53.97; H, 6.40; N, 4.79; S, 5.55.

Acetylation of **5**. *Formation of 1,2-diacetamido-3,4,5,6-tetra*-O-*acetyl-1,2-dideoxy-1*-S-*ethyl-1-thio*-D-*glucitol* (**6**). — Compound **5** (0.1 g) in dry pyridine (4 mL) was acetylated with acetic anhydride (1 mL) under the same conditions as for **7**. After processing, the oil solidified on trituration with ether–petroleum ether; m.p. 62–63° (preshrinkage at 50°); yield 105 mg (79%); ν_{max}^{KBr} 3340 (broad, NH), 1756 (C=O, acetoxyl), 1670, 1530, 1371 (C=O, amide), 2980, 2940 (CH_2), 1434 (SCH_2) cm^{-1}, ^{1}H-n.m.r. ($CDCl_3$): δ 1.24, 1.30 (t × 2, 3, *J* 7 Hz, CH_3 of ethyl), 1.98–2.14 (m, 18, CH_3 s of OAc, NHAc), 2.62, 2.66 (q × 2, 2, *J* 7 Hz, CH_2 of ethyl), 4.15 (m, 2, H_2-6), 4.41 (m, 1, H-2), 5.09 (d, 1, *J* 10 Hz, H-1), 5.12 (m, 1, H-5), 5.40 (t, 1, *J* 6 Hz, H-4), 5.64, 5.70 (d × 2, 1, *J* 3 Hz, H-3), 4.93, 6.21, and 6.51 (d × 3, 2, N*H*Ac); ^{13}C-n.m.r. ($CDCl_3$): δ 170.8, 170.5, 170.3, 169.9, 169.7, 169.5 (C=O, NHAc and OAc), 70.2, 69.9 (C-1), 69.4, 69.2, 69.0 (C-3, C-4), 61.7, 61.4 (C-6), 55.3, 55.0 (C-5), 53.1 (C-2), 25.3, 24.7 (CH_2 of ethyl), 22.9 (CH_3 of NHAc), 20.6 (CH_3 of OAc), and 14.7 (CH_3 of ethyl); $[\alpha]_D^{23}$ +11.3 (*c* 1.0, chloroform).

Anal. Calc. for $C_{20}H_{32}N_2O_{10}S \cdot 0.5\ H_2O$: C, 47.89; H, 6.63; N, 5.58; S, 6.39. Found: C, 47.80; H, 6.40; N, 5.36; S, 6.18.

O-*Deacetylation of the mono*-O-*acetyl derivative of* **7**. — The mono-*O*-acetyl derivative of **7** (0.1 g) was dissolved in 10% Et_3N in 50% aqueous methanol (25 mL), and the mixture was stirred for 7 h at room temperature. The solution was evaporated *in vacuo*, and the residue dissolved in water (15 mL × 3), which was evaporated off to remove traces of triethylamine and methyl acetate. The residue crystallized from methanol–ether; m.p. 167–168°; yield 83 mg (91%). The product was identified as 1,2-diacetamido-1-*S*-benzyl-1,2-dideoxy-1-thio-D-glucitol (**7**) by mixed m.p., and identical i.r. and n.m.r. spectra with an authentic sample.

Under similar conditions, tri-*O*-acetyl and mono-*O*-acetyl derivatives of **5** gave

1,2-diacetamido-1,2-dideoxy-1-*S*-ethyl-1-thio-D-glucitol (**5**), identified by mixed m.p. and i.r. and n.m.r. spectra with an authentic sample.

*2-Acetamido-2-deoxy-*D*-glucose diethyl dithioacetal.* — This compound was prepared by the method of Wolfrom and Anno[12]: ν_{max}^{KBr} 3420–3300 (NH, OH), 2970, 2950, 2878 (CH), 1641, 1560 (C=O, amide), 1446 (CH_2); ^{13}C-n.m.r. (D_2O): δ 175.1 (C=O, NHAc), 72.9 (C-3), 72.5 (C-4), 70.1 (C-5), 63.9 (C-6), 55.9 (C-2), 53.5 (C-1), 26.8, 26.6 (CH_2 (ethyl)), 23.3 (CH_3, NHAc), and 15.1 (CH_3, ethyl).

2-Acetamido-3,4,5,6-tetra-*O*-acetyl-2-deoxy-D-glucose diethyl dithioacetal (**9**) was synthesized by the method of Wolfrom and Anno[12].

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