cyclopropane, crystallized from ethanol, m.p. 67–68°, was obtained in 83% yield.

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.70; H, 5.42; S, 12.40. Found: C, 69.44; H, 5.40; S, 12.52.

The infrared spectrum of *cis*-1-(phenylsulfonyl)-2-phenylcyclopropane showed peaks at following wave lengths in μ: 3.40 (s), 6.30 (m), 6.75 (s), 7.00 (s), 7.35 (w), 7.70 (s, broad), 8.30 (s), 8.80 (s, broad), 9.10 (m), 9.25 (s), 9.50 (w), 9.80 (w), 9.95 (w), 10.05 (w), 10.95 (s), 11.0 (s), 12.05 (s), and 14.50 (s, broad).

Isomerization of *cis*-1-(Phenylsulfonyl)-2-phenylcyclopropane (VII) to *trans*-1-(Phenylsulfonyl)-2-phenylcyclopropane (IV).—In a 50-ml., three-neck flask equipped with magnetic stirrer, dropping funnel, and nitrogen gas inlet tube was placed a solution of *cis*-1-(phenylsulfonyl)-2-phenylcyclopropane (1.3 g., 0.005 mole) in 10 ml. of dimethyl sulfoxide. Potassium *t*-butoxide (200 mg.) in 15 ml. of dimethyl sulfoxide was added dropwise with stirring to the above solution at room temperature. The reaction mixture developed a reddish brown color. After the addition was complete, the mixture was stirred at room temperature for 2 hr. It was then poured in 200 ml. of ice-cold water and stirred until the solid was precipitated. The solid was filtered, dried, and crystallized from ethanol, m.p. 96–97°, yield 1.2 g. The mixture melting point of this compound with *trans*-1-(phenylsulfonyl)-2-phenylcyclopropane, prepared through the sulfur ylid reaction, was not depressed. The infrared spectra were similar.

***trans*-1-(*p*-Tolylsulfonyl)-2-phenylcyclopropane.**—From *cis*- or *trans*-1-phenyl-2-(*p*-tolylsulfonyl)ethene (0.01 mole), *trans*-1-(*p*-tolylsulfonyl)-2-phenylcyclopropane was obtained according to general procedure in 45% yield. It crystallized from ethanol, m.p. 146–147°.

Anal. Calcd. for $C_{16}H_{16}O_2S$: C, 70.58; H, 5.88; S, 11.76; mol. wt., 272. Found: C, 70.87; H, 6.15; S, 11.58; mol. wt., 265.

1-(Phenylsulfonyl)-*cis*-1,2-diethylcyclopropane (XIV).—In a 200-ml., three-neck flask equipped with dropping funnel, magnetic stirrer, and nitrogen gas inlet tube were placed 4.48 g. (0.02 mole) of *trans*-3-phenylsulfonyl-3-hexene, 3.15 g. (0.02 mole) of trimethylsulfonium bromide, and 35 ml. of dimethyl sulfoxide. The mixture was stirred until a clear solution was obtained. The solution of potassium *t*-butoxide (2.24 g., 0.02 mole) in 25 ml. of dimethyl sulfoxide was added dropwise with stirring at room temperature. After the addition, the reaction mixture was stirred further for 1 hr. and diluted with 200 ml. of water. The oily layer was extracted with ether and the ethereal layer was washed twice with 100-ml. portions of water. The ethereal layer was dried over anhydrous magnesium sulfate and the ether was removed. The residue on distillation gave 2.1 g. (44%) of 1-(phenylsulfonyl)-*cis*-1,2-diethylcyclopropane, b.p. 135–137° at 0.55 mm., $n^{29}D$ 1.5302.

Anal. Calcd. for $C_{13}H_{18}O_2S$: C, 65.55; H, 7.55; S, 13.46. Found: C, 65.76; H, 7.78; S, 13.16.

Cleavage of 1-(Phenylsulfonyl)-*cis*-1,2-diethylcyclopropane by Lithium in Ammonia.—Liquid ammonia (25 ml.) was condensed into a three-neck flask equipped with a Dry Ice condenser and a magnetic stirrer. Lithium wire (0.180 g., 0.025 g.-atom) was cut into small pieces and added to ammonia. After all the lithium had completely dissolved, the flask and the contents were cooled to about −75° by means of a Dry Ice–acetone bath and 1-(phenylsulfonyl)-*cis*-1,2-diethylcyclopropane (2.36 g., 0.01 mole) was added dropwise. After all of the compound had been added, the mixture was stirred at −75° for about 15 min. and the excess of lithium metal was decomposed by the addition of 5–7 ml. of methanol followed by the addition of 75 ml. of distilled water. The cleavage mixture was stirred vigorously until all the sulfinate was dissolved. *n*-Nonane (Phillips Yellow Label, 10 ml.) was added to the cleavage mixture and stirred for five min. The upper organic layer was analyzed by vapor phase chromatography, using column R (Ucon polyglycol LB-550-x) at 80°.

1-(*p*-Tolylsulfonyl)-*cis*-1,2-dimethylcyclopropane.—This was prepared in 40% yield according to the general procedure from either *cis*-2-(*p*-tolylsulfonyl)-2-butene or *trans*-2-(*p*-tolylsulfonyl)-2-butene. 1-(*p*-Tolylsulfonyl)-*cis*-1,2-dimethylcyclopropane distilled at 149–151° at 0.55 mm.

Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 64.3; H, 7.14; S, 14.28. Found: C, 64.11; H, 7.20; S, 14.00.

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Halogen and Nucleoside Derivatives of Acyclic 2-Amino-2-deoxy-D-glucose.[1,2] I

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2-Acetamido-3,4,5,6-tetra-*O*-acetyl-2-deoxy-D-glucose diethyl dithioacetal (I), and its 2-(2,4-dinitroanilino) analog (III) react with a stoichiometric amount of bromine to give acyclic 1-bromo derivatives (II and VI, respectively) by replacement of one ethylthio group by bromine. An excess of chlorine converts (III), with replacement of one ethylthio group, into a trichloro derivative having the structure (IV). The acyclic 1-bromo derivative (VI) reacts with alcohols, with replacement of the bromine atom by an alkoxy group, to give mixed acyclic monothioacetals (VII). Reaction of VI with 6-acetamido-9-chloromercuripurine gives substituted acyclic nucleoside derivatives (V) in good yield.

Acyclic halogen derivatives of aldoses have been described by Wolfrom and co-workers.[3,4] Bromination of penta-*O*-acetyl-D-galactose diethyl dithioacetal provides a convenient synthetic route[5,6] to penta-*O*-acetyl-1-bromo-1,1-dideoxy-1-ethylthio-D-galactose aldehydrol,[4] and the latter, together with the sirupy D-glucose analog, has been used in preparation of acyclic sugar nucleoside analogs.[7] Related derivatives have also been prepared[8] from penta-*O*-acetyl-1-bromo-1-deoxy-1-*O*-methyl-D-galactose aldehydrol,[6] or the chloro analog.[3] The present work describes the bromination of two diethyl dithioacetal derivatives of 2-amino-2-deoxy-D-glucose to give crystalline acyclic 1-bromo derivatives which are, to the best of our knowledge, the first acyclic 1-halogen derivatives of an amino sugar to be described. One of them has been transformed, by alcoholysis, into acyclic mixed acetal derivatives, and, by a conventional procedure,[7,8] into acyclic sugar nu-

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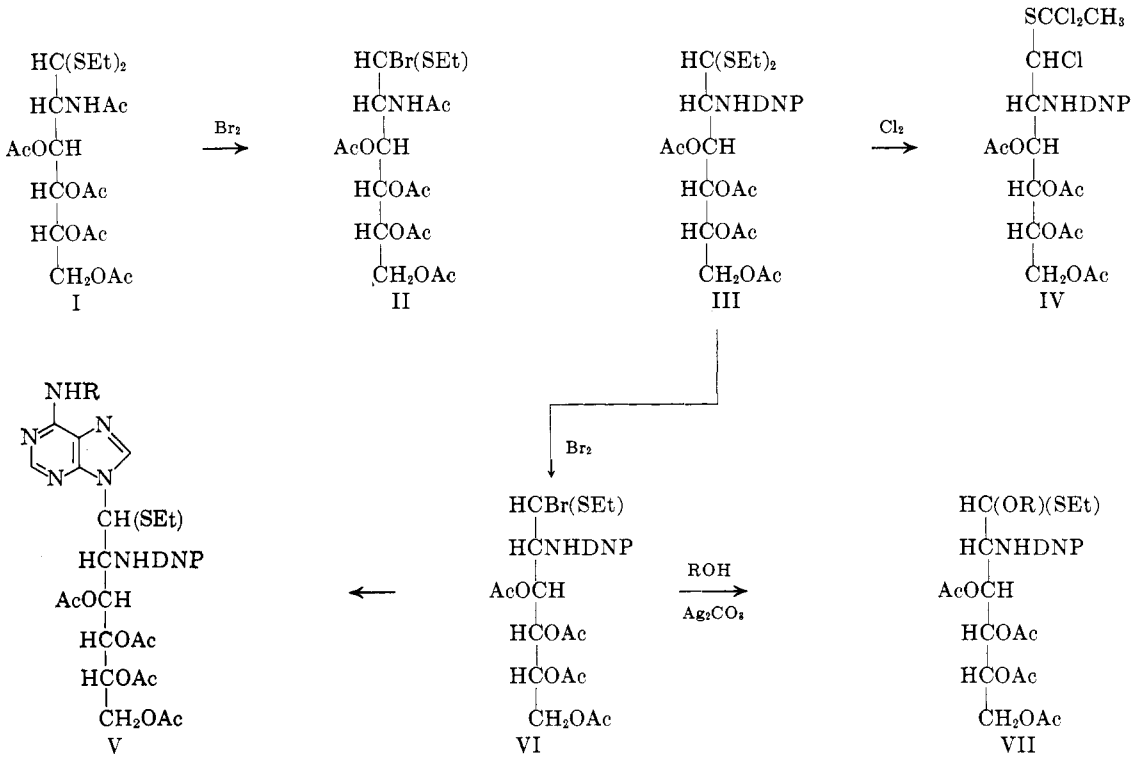

DNP = 2,4-dinitrophenyl

cleoside analogs. Chlorination of one of the diethyl dithioacetal derivatives gives a crystalline derivative of novel structure, in which three chlorine atoms have been introduced, with displacement of one ethylthio group.

Treatment of 2-acetamido-3,4,5,6-tetra-*O*-acetyl-2-deoxy-D-glucose diethyl dithioacetal[9] (I) in ether solution with 1 molar equiv. of bromine at room temperature gave a rapid reaction wherein a crystalline product separated directly in high yield; it was formulated as 2-acetamido-3,4,5,6-tetra-*O*-acetyl-1-bromo-1,1,2-trideoxy-1-ethylthio-D-glucose aldehydrol (II) on the basis of elemental analysis, presence of infrared spectral bands characteristic of the acetamido and acetoxy groups, and by analogy with the corresponding reaction product from penta-*O*-acetyl-D-galactose diethyl dithioacetal.[5,7] The presence of amide carbonyl absorption rules out a possible alternative formulation as an intramolecularly cyclized 2-bromooxazolidine derivative.

Compound II was unstable and decomposed on storage for a few days in a desiccator. It was highly reactive toward alcohols, but, since it did not appear to show the thermal stability required for nucleoside formation by the Davoll–Lowy[10] procedure, attention was directed toward synthesis of a more stable analog by the use of a more deactivating group, the 2,4-dinitrophenyl group, on the nitrogen atom.

N-Arylation of 2-amino-2-deoxy-D-glucose diethyl dithioacetal hydrochloride[9] with 1-fluoro-2,4-dinitrobenzene in aqueous ethanol gave the *N*-(2,4-dinitrophenyl) derivative as a sirup, which on acetylation with acetic anhydride in pyridine gave 3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose diethyl dithioacetal (III) in 77% yield, m.p. 94–96°, $[\alpha]^{24}D$ −153° (chloroform). This compound has been reported,[11] without preparative details or yield data, to have m.p. 87–88°, $[\alpha]^{21}D$ −108.5° (chloroform). A stream of chlorine was passed through a solution of III in methylene chloride, with a view to the replacement of one ethylthio group by chlorine. It was considered that the chloro derivative would possess an extra measure of stability over the bromo analog. The crystalline product isolated, however, gave analytical data corresponding to the displacement of one ethylthio group and the introduction of *three* chlorine atoms, and the product is formulated as 3,4,5,6-tetra-*O*-acetyl-1-chloro-1,1,2-trideoxy-1-[(1,1-dichloroethyl)thio]-2-(2,4-dinitroanilino)-D-glucose aldehydrol (IV). The analytical data would agree equally well with formulation as the 1-[ethyl(dichlorothio)] ($C_2H_5SCl_2$–) analog, but the n.m.r. spectrum of IV did not show the quartet in the τ 7.0–7.5 region and triplet in the 8.5–9.0 region expected for an ethyl group. The spectrum showed, in addition to the acetoxy resonances in the region τ 7.7–8.0, a singlet, τ 8.33, corresponding to the methyl protons of the CH_3CCl_2S group. The dichlorination of the α-carbon of the ethyl group would be analogous to the conversion of alkylsulfenyl chlorides (RCH_2SCl) to α-dihalogenosulfenyl chlorides ($RCCl_2SCl$), by way of alkylsulfur trichlorides (RCH_2SCl_3), in the presence of an excess of chlorine.[12]

A successful conversion of the dithioacetal III to a monohalogen derivative was achieved by treatment of III in ether solution with 1 equiv. of bromine, and a practically quantitative yield of a crystalline product formulated as 3,4,5,6-tetra-*O*-acetyl-1-bromo-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose aldehydrol (VI) was obtained. This substance was stable and could be stored in a desiccator for several

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(12) I. B. Douglass in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, Chapter 30.

months without decomposition. It reacted with methanol (or ethanol) in the presence of an acid acceptor (silver carbonate) to give the corresponding 3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-1-*S*-ethyl-1-*O*-methyl-(or ethyl-) D-glucose monothioacetal (VII, R = Me or Et) in high yield.

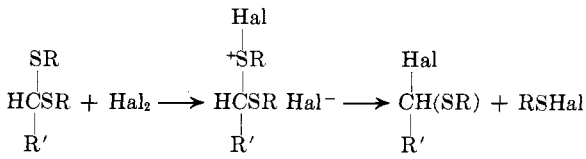
The acyclic 1-bromo derivative (VI) was condensed with 6-acetamido-9-chloromercuripurine by the general procedure of Davoll and Lowy,[10] as used in earlier syntheses of acyclic sugar nucleoside analogs,[7,8] and the product, 1-(6-acetamido-9-purinyl)-3,4,5,6-tetra-*O*-acetyl-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose aldehydrol (V, R = Ac), obtained as a glass, was *N*-deacetylated by boiling with methanolic picric acid,[13] to give the adenine nucleoside derivative (V, R = H) as the crystalline picrate salt. Treatment of the latter with Dowex-1 (CO_3^{-2}) ion-exchange resin gave the crystalline free base, 3,4,5,6-tetra-*O*-acetyl-1-(9-adenyl)-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose aldehydrol (V, R = H).

Further work is in progress on procedures for closure of the sugar ring in the acyclic sugar nucleoside analog (V).

The crystalline products II, IV, V (R = H), VI, and VII (R = Me and Et) all gave sharp melting points, indicative of each being a single isomer. Homogeneity was also demonstrated, in the last four of these derivatives, by thin layer chromatography. The stereochemical configuration at C-1 is unknown in all of these derivatives. The high yields obtained in the preparation of II, VI, and VII (R = Me and Et) would indicate that asymmetric induction exercises a considerable control over the steric course of the reaction.

The high reactivity of II, which has the acetamido group at C-2, contrasts with the low reactivity of the 2-(2,4-dinitroanilino) analog (VI). This behavior parallels that observed in cyclic glycosyl halide derivatives, where, for example, the high reactivity of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl bromide[14] may be contrasted with the stability of the 2-(2,4-dinitroanilino) analog,[15] or other derivatives having strongly electron-withdrawing groups at C-2.[16]

It is observed that dithioacetals react with halogen with replacement of only one of the ethylthio groups by halogen. A reasonable mechanistic rationalization of this reaction would involve attack on sulfur by a halonium ion, followed by cleavage of the C-1–sulfur bond and approach of halide ion, possibly synchronously, to C-1. This mechanism is similar to that proposed[17-19] for the conversion of 1-thioglycosides[17,18] and other 1-thio sugar derivatives[19,20] into glycosyl halide derivatives. The failure of the second alkylthio group to undergo displacement may be ascribed to the electron-withdrawing action of the C-1 halogen, which would render attack at sulfur by positive halogen more difficult, and would hinder the development of a positive charge at C-1, such as would occur in the heterolysis of the C-1–S bond by departure of the halogenated alkylthio group.



Experimental[21]

2-Acetamido-3,4,5,6-tetra-*O*-acetyl-1-bromo-1,1,2-trideoxy-1-ethylthio-D-glucose Aldehydrol (II).—A solution of 2-acetamido-3,4,5,6-tetra-*O*-acetyl-2-deoxy-D-glucose diethyl dithioacetal[9] (I, 1.0 g.) in anhydrous ether (60 ml.) was treated dropwise with stirring at room temperature with bromine (0.32 g.) in anhydrous ether (20 ml.). The precipitated product was filtered after 10 min. and washed several times with anhydrous ether: yield 0.95 g. (91.5%); m.p. 119–120° dec.; $[\alpha]^{22}D$ +165 (initial, extrapolated) → +32° (2.5 hr., *c* 1, chloroform[22]); λ_{max}^{KBr} 5.70 (OAc), 6.00, 6.70 (NHAc), and 7.95 μ (SEt); X-ray powder diffraction data,[21] 10.65 s (1), 8.27 s (2), 6.81 vw, 5.99 vw, 5.61 w, 5.34 m, 4.75 m, 4.35 m (3, 3), 4.13 m (3,3), 3.82 m, 3.63 m, and 3.35 m.

Anal. Calcd. for $C_{18}H_{28}BrNO_9S$: C, 42.06; H, 5.48; Br, 15.55; N, 2.72; S, 6.23. Found: C, 42.18; H, 5.63; Br, 16.01; N, 2.82; S, 6.02.

The compound was unstable, and developed an ethanethiol-like odor on storage in a desiccator for longer than 1 day.

3,4,5,6-Tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose Diethyl Dithioacetal (III).—A mixture of 2-amino-2-deoxy-D-glucose diethyl dithioacetal hydrochloride[11,23] (6.4 g.), water (30 ml.), sodium bicarbonate (3.3 g.), and ethanol (30 ml.) was stirred for 10 min., 1-fluoro-2,4-dinitrobenzene (3.72 g.) was added, and stirring was continued for 20 hr. at room temperature. The solution was evaporated at 40°, the residue was extracted with ethyl acetate, and the extract was washed with water, then dried (magnesium sulfate). Concentration of the extract gave 2-deoxy-2-(2,4-dinitroanilino)-D-glucose diethyl dithioacetal as a sirup, which was dissolved in pyridine (40 ml.) and treated with acetic anhydride (40 ml.). After 24 hr. at room temperature the mixture was poured into ice and water (200 ml.) and triturated until crystallization occurred; the product was filtered. Recrystallization from methanol gave III as needles: yield 9.5 g. (77%); m.p. 94–96°; $[\alpha]^{24}D$ −153 ± 5° (*c* 1.2, chloroform[22]); λ_{max}^{KBr} 6.70 (OAc), 6.15, 6.35, 6.60 (aryl C=C), 7.45 (NO_2), 7.95 (SEt), and 13.40 μ (substituted phenyl); λ_{max}^{EtOH} 263 (ε 7960) and 345 mμ (18,000); X-ray powder diffraction data,[21] 13.60 w, 10.28 w, 8.12 s (1), 7.38 w, 6.97 m, 6.51 m (2), 5.95 w, 5.40 w, 5.16 m, 4.58 m, 4.35 m (3,3), and 4.02 m (3,3).

Anal. Calcd. for $C_{24}H_{33}N_3O_{12}S_2$: C, 46.52; H, 5.36; N, 6.78; S, 10.35. Found: C, 46.29; H, 5.28; N, 7.24; S, 10.40.

For this compound the following constants have been reported,[11] without experimental details: m.p. 87–89°, $[\alpha]^{21}D$ −108.5° (chloroform).

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(19) D. Horton and D. H. Hutson, *Advan. Carbohydrate Chem.*, **18**, 123 (1963).

(20) D. Horton, M. L. Wolfrom, and H. G. Garg, *J. Org. Chem.*, **28**, 2992 (1963).

(21) Melting points were determined with a Hershberg-type apparatus [A. Thompson and M. L. Wolfrom, *Methods Carbohydrate Chem.*, **1**, 517 (1962)]. Specific rotations were determined in a 2-dm. polarimeter tube. Infrared spectra were measured with a Perkin-Elmer Infracord infrared spectrometer. Ultraviolet spectra were measured with a Bausch and Lomb Spectronic 505 spectrometer. Nuclear magnetic resonance (n.m.r.) spectra were measured in deuteriochloroform solution with a Varian A-60 spectrometer. Microanalytical determinations were made by W. N. Rond. X-Ray powder diffraction pattern data give interplanar spacings, Å., for Cu Kα radiation. Relative intensities were estimated visually: s, strong; m, medium; w, weak; v, very. The strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities. Thin layer chromatography was carried out with Desaga equipment, using silica gel G (E. Merck, Darmstadt, Germany) activated at 110°, with indication by sulfuric acid.

(22) Analytical reagent grade chloroform, Mallinckrodt Chemical Co., New York, N. Y.

(23) L. Hough and M. I. Taha, *J. Chem. Soc.*, 3564 (1957).

Reaction of 3,4,5,6-Tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose Diethyl Dithioacetal (III) with Chlorine.—Dry chlorine gas was passed for 15 min. through a chilled solution of III (1.0 g.) in methylene chloride (50 ml.). After 30 min. at room temperature the solution was evaporated and crystallized from ether–petroleum ether (b.p. 30–60°) to give a product formulated as 3,4,5,6-tetra-*O*-acetyl-1-chloro-1,1,2-trideoxy-1-[(1,1-dichloroethyl)thio]-2-(2,4-dinitroanilino)-D-glucose aldehydrol (IV): yield 0.35 g. (33%); m.p. 152–154°; $[\alpha]^{20}D$ −224 ± 4° (*c* 1.2, chloroform[22]); λ_{max}^{KBr} 5.60 (OAc), 6.10, 6.22, 6.55 (aryl C=C), 7.55 (NO_2), 13.60, and 14.05 μ (substituted phenyl); X-ray powder diffraction data,[21] 8.67 s (1), 8.12 m, 6.97 m, 6.28 w, 5.72 m (3), 4.85 s (2), 4.70 vw, 4.51 vw, 4.21 vw, 4.10 w, 3.85 w, 3.69 w; n.m.r. data,[21] τ 8.33 (singlet, 3 protons, CH_3CCl_2S–), 7.94 (singlet, 6 protons), 7.85 (singlet, 3 protons), 7.74 (singlet, 3 protons) (3,4,5,6-OAc), 3.65 (doublet, $J_{1,2}$ = 3.0 c.p.s., 1 proton, H-1), no absorption in the regions 7.0–7.5 and 8.5–9.0.

Anal. Calcd. for $C_{22}H_{26}Cl_3N_3O_{12}S$: C, 39.85; H, 3.92; Cl, 16.08; N, 6.34; S, 4.83. Found: C, 40.17; H, 4.10; Cl, 16.20; N, 6.27; S, 4.78.

3,4,5,6-Tetra-*O*-acetyl-1-bromo-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose Aldehydrol (VI).—A solution of 3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose diethyl dithioacetal (III) (1.2 g.) in anhydrous ether (100 ml.) was treated with bromine (0.32 g.) in ether for 10 min. at room temperature. Concentration of the solution gave the product (VI) as long needles; yield 1.2 g. (97%); m.p. 104–106° dec.; $[\alpha]^{23}D$ +35 (initial extrapolated) → −67° (3 hr., *c* 1.2, chloroform[22]); λ_{max}^{KBr} 5.68 (OAc), 6.13, 6.23, 6.55 (aryl C=C), 7.43 (NO_2), 7.73 (SEt), and 13.40 μ (substituted phenyl); X-ray powder diffraction data,[21] 11.19 s (1), 9.61 w, 8.85 vw, 7.25 vw, 6.51 m (2), 6.24 vw, 4.98 m (3), 4.72 vw, 4.48 w, 4.31 w, 3.97 w, and 3.77 w.

Anal. Calcd. for $C_{22}H_{28}BrN_3O_{12}S$: C, 41.38; H, 4.42; Br, 12.52; N, 6.58; S, 5.02. Found: C, 41.55; H, 4.59; Br, 12.78; N, 6.95; S, 5.15.

The product was homogeneous by thin layer chromatography with ethyl acetate as developer. No change in physical characteristics was observed after storage for 3 months in a desiccator.

3,4,5,6-Tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose *S*-Ethyl *O*-Methyl Monothioacetal (VII, R = Me).—A solution of 3,4,5,6-tetra-*O*-acetyl-1-bromo-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose aldehydrol (VI, 0.8 g.) in warm methanol (20 ml.) was shaken with silver carbonate (1.0 g.) for 24 hr. at room temperature. The mixture was filtered, the filter was washed with acetone, and the combined filtrates were treated with activated carbon. Evaporation of the solution gave a solid product which was recrystallized from methanol: yield 0.62 g. (84%); m.p. 122–124°; $[\alpha]^{25}D$ −111 ± 1° (*c* 0.75, chloroform[22]); λ_{max}^{KBr} 5.70 (OAc), 6.18, 6.30, 6.55 (aryl C=C), 7.48 (NO_2), 8.05 (SEt), 13.40, and 13.61 μ (substituted phenyl); λ_{max}^{EtOH} 266 (ε 4400) and 348 mμ (19,000); X-ray powder diffraction data,[21] 13.39 w, 9.12 m, 6.81 vs (1), 6.19 m, 5.04 s (3), 4.75 w, 4.42 m, 4.10 m, 3.69 m, 3.49 m, 3.40 s (2), and 3.24 m.

Anal. Calcd. for $C_{23}H_{31}N_3O_{13}S$: C, 46.87; H, 5.30; N, 7.12; S, 5.63. Found: C, 47.14; H, 5.28; N, 7.35; S, 5.73.

The product was homogeneous by thin layer chromatography with ethyl acetate as developer.

3,4,5,6-Tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose Ethyl *S*-Ethyl Monothioacetal (VII, R = Et).—This compound was prepared from VI (0.8 g.) and ethanol (30 ml.) by the same procedure used for the preceding methyl analog. The product (VII, R = Et) was obtained as needles from ethanol: yield 0.60 g. (79%); m.p. 104–105°; $[\alpha]^{23}D$ −127 ± 1° (*c* 0.5, chloroform[22]); λ_{max}^{KBr} 5.75 (OAc), 6.20, 6.32, 6.50 (aryl C=C), 7.50 (NO_2), 8.05 (SEt), and 13.40 μ (substituted phenyl); λ_{max}^{EtOH} 266 (ε 6000) and 346 mμ (16,000); X-ray powder diffraction data,[21] 14.26 w, 11.33 vw, 9.31 m, 7.56 m, 6.92 s (1), 6.19 w, 5.25 m (3, 3), 4.96 m (3, 3), 4.75 w, 4.46 w, 4.19 w, 3.99 w, 3.53 m (2), and 3.40 m.

Anal. Calcd. for $C_{24}H_{33}N_3O_{13}S$: C, 47.73; H, 5.51; N, 6.96; S, 5.31. Found: C, 47.76; H, 5.68; N, 7.20; S, 5.45.

The product was homogeneous by thin layer chromatography, with ethyl acetate as developer.

3,4,5,6-Tetra-*O*-acetyl-1-(9-adenyl picrate)-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose Aldehydrol (V, R = $C_6H_4N_3O_7$).—A mixture of 6-acetamido-9-chloromercuripurine[10] (1.7 g.), cadmium carbonate (1.0 g.), Celite[24] (1.0 g.), and toluene (300 ml.) was dried by distillation of toluene (100 ml.). To the suspension 3,4,5,6-tetra-*O*-acetyl-1-bromo-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose aldehydrol (VI) (2.5 g.) was added, and the stirred mixture was boiled under reflux for 2 hr. After a further hour at room temperature the mixture was filtered, and the filter was washed with chloroform (50 ml.). The filtrate was evaporated, the residue dissolved in chloroform (200 ml.), and the solution was washed twice with 20% aqueous potassium iodide and twice with water. The solution was dried (magnesium sulfate) and concentrated, to give the nucleoside derivative (V, R = Ac) as a yellow glass. The latter was boiled for several minutes with a solution of picric acid (2.01 g., 1 mole equiv. in ethanol; 50 ml.). The yellow crystalline picrate salt (V, R = $C_6H_4N_3O_7$) separated from the solution on cooling, yield 1.8 g. (50%). Recrystallization from methanol gave a pure product: m.p. 166–169°; $[\alpha]^{26}D$ −175 ± 1° (*c* 0.5, chloroform[22]); λ_{max}^{KBr} 6.20, 6.35 (NH_3^+, C=N), 5.70 (OAc), 7.45 (NO_2), 7.85 (SEt), 13.38, and 14.00 μ (substituted phenyl).

Anal. Calcd. for $C_{33}H_{35}N_{11}O_9S$: C, 42.99; H, 3.82; N, 16.72; S, 3.46. Found: C, 42.71; H, 3.76; N, 16.59; S. 3.53.

3,4,5,6-Tetra-*O*-acetyl-1-(9-adenyl)-1,1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose Aldehydrol (V, R = H).—The preceding picrate salt (V, R = $C_6H_4N_3O_7$, 0.7 g.) was dissolved in a warm mixture of acetone (35 ml.) and water (20 ml.) and stirred with an excess of Dowex-1 (CO_3^{-2}) ion-exchange resin for a few minutes. The mixture was filtered, the resin was washed with acetone until the washings were colorless and the filtrate was evaporated to remove the acetone. The remaining aqueous suspension was extracted with chloroform (100 ml.), and the dried (magnesium sulfate) extract was evaporated to a sirup which crystallized from methanol to give the nucleoside derivative (V, R = H): yield 0.25 g. (48%); m.p. 148–150° (softening at 141°); $[\alpha]^{24}D$ −255 ± 2° (*c* 0.42, chloroform[22]); λ_{max}^{KBr} 3.05 (NH), 5.70 (OAc), 6.13, 6.23, 6.33 (aryl C=C, purine), 7.40 (NO_2), 13.50, and 13.75 μ (substituted phenyl); λ_{max}^{EtOH} 263.5 (ε 15,400) and 341.5 mμ (11,700); X-ray powder diffraction data,[21] 9.72 m, 9.97 vs (1), 7.44 w, 6.28 s (2), 6.03 w, 5.57 w, 5.31 m (3), 5.07 w, 4.80 w, 4.46 w, 4.06 m, and 3.82 m.

Anal. Calcd. for $C_{27}H_{32}N_8O_{12}S$: C, 46.82; H, 4.65; N, 16.18; S, 4.62. Found: C, 46.34; H, 4.88; N, 15.87; S, 4.50.

The product was homogeneous by thin layer chromatography, with ethyl acetate as developer.

(24) Celite 535, a product of the Johns Manville Co., New York, N. Y.