A sample of the sirup was treated with aniline in ethanol[24] at the reflux temperature for 4 hr. On concentration, cooling, and nucleation, a crystalline precipitate was deposited which was gathered by filtration, washed with ether, and dried. The melting point, 162–165°, was undepressed on admixture with authentic aniline of 2-deoxy-D-*erythro*-pentose. The infrared spectra were indistinguishable. The yield of the anilide was 8% based on the amount of sirup oxidized by lead tetraacetate.

Hydrogenation of VII.—VII (100 mg.) rapidly consumed 2 moles of hydrogen per mole of VII when hydrogenated in methanol using Adams platinum catalyst. The n.m.r. spectrum of the product was in good agreement with that expected for a crude dideoxyhexose diacetate. Deacetylation using triethylamine in aqueous methanol gave a sirup which on paper chromatography showed two spots using the alkaline silver spray of about equal intensities and with R_f values relative to that of glucose of 6.6 and 9.3 after 21 hr. of development under the conditions described above for hydrogenated and deacetylated III.

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

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A series of synthetic transformations is described involving mixed acyclic C-1 derivatives of 3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose aldehydrol. The 1-bromo-1,1-dideoxy-1-ethylthio derivative I can be readily converted, by replacement of bromine by an acetoxy group, into the compound II. Treatment of the *O*-ethyl (or methyl) *S*-ethyl thioacetal derivative III with chlorine gives the corresponding 1-*O*-alkyl-1-deoxy chloride IV. The chlorine atom of the latter readily undergoes replacement by nucleophiles, for example, the acetoxy group (to give V) and the 6-acetamido-9-purinyl group (to give VI). The acyclic nucleoside derivatives VI are readily *N*-deacetylated to give the acyclic adenine 1-*O*-alkyl nucleoside derivatives (VIII) by the way of the picrate salts (VII); *O*-deacetylation was effected with methanolic ammonia. All isolated products were obtained crystalline and in high yield.

In the preceding paper[3] we reported the preparation of acyclic 1-halogeno derivatives in the fully blocked 2-amino-2-deoxy-D-glucose structure, by halogenation of appropriate diethyl dithioacetal derivatives. Replacement of halogen by alkoxide or 6-acetamido-9-purinyl groups afforded acyclic mixed monothioacetal or acylic nucleoside derivatives, respectively, all having an ethylthio group at C-1. The present work describes the conversion of acyclic mixed monothioacetals in the 3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose structure into the corresponding 1-alkoxy-1-chloro derivatives by replacement of the 1-ethylthio group by chlorine. The chlorine atom can be replaced by an acetoxy group, to give 1-*O*-acetyl-1-*O*-alkyl aldehydrol derivatives, and, by a 6-acetamido-9-purinyl group, to give acyclic nucleoside derivatives having an alkoxy group at C-1. The formation of a 1-*O*-acetyl-1-ethylthioaldehydrol derivative is also demonstrated.

The acyclic bromo sugar I, which is readily prepared from 3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose diethyl dithioacetal by treatment with bromine,[3] is smoothly converted by the action of mercuric acetate in acetic acid into 1,3,4,5,6-penta-*O*-acetyl-1,2-dideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose aldehydrol (II). Attempted replacement of the ethylthio group in this compound by halogen under the usual conditions[3,4] gave sirupy, unstable products which were not well suited for synthesis of acyclic nucleoside derivatives.

The acyclic monothioacetal derivative 3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose diethyl monothioacetal[3] (III, R = C_2H_5) underwent reaction in dichloromethane solution with an excess of chlorine to give 3,4,5,6-tetra-*O*-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose aldehydrol (IV, R = C_2H_5) in high yield as a stable, crystalline compound. The crystalline 1-*O*-methyl analog IV (R = CH_3) could be prepared by a corresponding procedure. Both compounds could be stored up to several months at room temperature in a desiccator before darkening and decomposing. Each compound underwent reaction with mercuric acetate in acetic acid to give the corresponding crystalline 1,3,4,5,6-penta-*O*-acetyl-1-*O*-alkyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose aldehydrol V (R = C_2H_5 or CH_3) in good yield.

Condensation of the chloro derivatives IV (R = C_2H_5 or CH_3) with 6-acetamido-9-chloromercuripurine, under the general conditions of Davoll and Lowy,[5] to give the fully blocked acyclic nucleoside derivatives VI (R = C_2H_5 or CH_3), followed by *N*-deacetylation[6] with picric acid in boiling methanol, gave the corresponding 3,4,5,6-tetra-*O*-acetyl-1-(9-adenyl)-1-*O*-alkyl-1,2-dideoxy-2-(2,4-dinitroanilino)-D-glucose aldehydrols as the crystalline picrate salts VII (R = C_2H_5 or CH_3), in good yield. Each of the picrate salts behaved as a single compound, was homogeneous by thin layer chromatography, exhibited a sharp melting point, and gave good elemental analytical values.

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(2) A preliminary report of a portion of this work has appeared in Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 3D.

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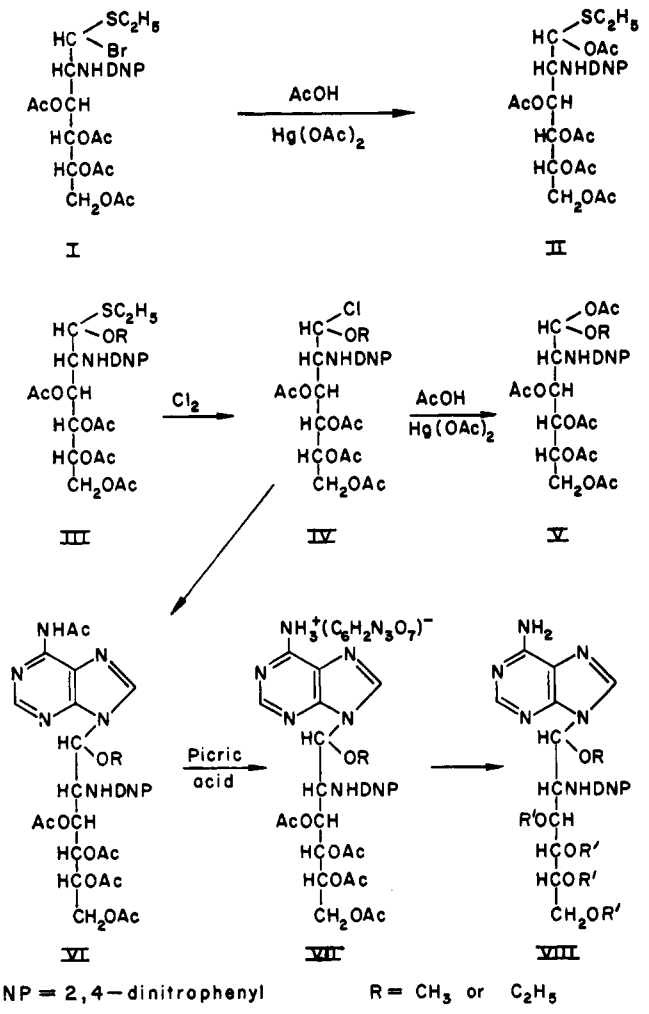

Treatment of the picrate salt of the 1-*O*-ethyl nucleoside derivative VII (R = C_2H_5) with Dowex-1 (CO_3^{-2}) ion-exchange resin gave the blocked acyclic nucleoside as the crystalline base VIII (R = C_2H_5; R′ = Ac) in excellent yield. The sharp melting point and chromatographic homogeneity indicated that this product was a single compound. Conversion of the picrate salt of the 1-*O*-methyl nucleoside derivative VII (R = CH_3) into the free base by treatment with Dowex-1 (CO_3^{-2}) ion-exchange resin gave VIII (R = CH_3; R′ = Ac) which crystallized in dimorphous forms (m.p. 141–143° and 216–219°) of high stability. Final deacetylation of VIII (R = CH_3 or C_2H_5; R′ = Ac) was effected with methanolic ammonia, to give VIII (R = CH_3 or C_2H_5; R′ = H).

Attempted removal of the 2,4-dinitrophenyl group from VIII (R = CH_3; R′ = H) was unsuccessful.

The products isolated in this work were all chromatographically homogeneous, and the high yields obtained are indicative of a high degree of stereoselectivity in the replacement reactions at C-1.

Further studies are in progress on routes for cyclization of the acyclic nucleoside derivatives.

Experimental[7]

1,3,4,5,6-Penta-*O*-acetyl-1,2-dideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose Aldehydrol (II).—Tetra-*O*-acetyl-1-bromo-1,-1,2-trideoxy-2-(2,4-dinitroanilino)-1-ethylthio-D-glucose aldehydrol[3] (I, 10 g.) was added to a solution of mercuric acetate (5.4 g.) in acetic acid (140 ml.). The solution was stirred for 7 hr. at room temperature, diluted with chloroform (250 ml.), washed several times with water, dried (magnesium sulfate), and evaporated. The sirup was dissolved in ether, and petroleum ether (b.p. 30–60°) was added, whereupon the product crystallized rapidly as plates, which were filtered after 24 hr. at room temperature: yield 6.8 g. (68%); m.p. 144–146°; $[\alpha]^{21}D$ −90 ± 2° (*c* 1, chloroform); λ_{max}^{KBr} 5.74 (OAc), 6.20, 6.30, 6.63 (aryl C=C), 7.48 (NO_2), 13.43, and 13.83 μ (substituted phenyl); $\lambda_{max}^{C_2H_5OH}$ 265 mμ (ε 14,200) and 399 mμ (ε 25,100); and X-ray powder diffraction data[7]: 10.05 w, 8.67 vs (1), 7.83 s (2,2), 6.92 s (2,2), 6.07 m, 5.61 m, 4.85 m (3,3), 4.48 vw, 4.17 w, 3.90 m, 3.62 m, and 3.45 m.

Anal. Calcd. for $C_{24}H_{31}N_3O_{14}S$: C, 46.69; H, 5.05; N, 6.80; S, 5.18. Found: C, 46.78; H, 4.73; N, 6.82; S, 5.03.

Chlorination of a methylene chloride solution of II gave rise to a sirupy product which contained at least two components as determined by thin layer chromatography.

3,4,5,6-Tetra-*O*-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose Aldehydrol (IV, R = C_2H_5).—Dry chlorine was passed for 10 min. through a chilled solution of 3,4,5,6-tetra-*O*-acetyl-1-deoxy-2-(2,4-dinitroanilino)-D-glucose diethyl monothioacetal[3] (III, R = C_2H_5, 0.9 g.) in dry dichloromethane (50 ml.). After 30 min. at room temperature, the solution was evaporated; the sirup was dissolved in ether and diluted with petroleum ether to give the crystalline product as fine needles which were filtered after 24 hr.: yield 0.6 g. (69%); m.p. 116–119° (softening at 96°); $[\alpha]^{23}D$ −43 ± 2° (*c* 0.9, chloroform); λ_{max}^{KBr} 5.73 (OAc), 6.20, 6.30, 6.59 (aryl), 7.52 (NO_2), and 13.43 μ (substituted phenyl); and X-ray powder diffraction data[7]: 13.19 w, 11.05 w, 9.03 m, 6.76 vs (1), 6.33 s, 5.57 w, 4.96 s (2,2), 4.37 s (2,2), 3.68 s (3), 3.53 m, 3.44 m, and 3.25 m.

Anal. Calcd. for $C_{22}H_{28}ClN_3O_{13}$: C, 45.71; H, 4.88; Cl, 6.13; N, 7.27. Found: C, 45.55; H, 5.15; Cl, 5.93; N, 7.35.

The compound was stable in a desiccator at room temperature for a period of several months, after which it gradually turned dark.

3,4,5,6-Tetra-*O*-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-methyl-D-glucose Aldehydrol (IV, R = CH_3).—A solution of 3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucose *S*-ethyl *O*-methyl monothioacetal[3] (III, R = CH_3, 0.6 g.) in dry dichloromethane (50 ml.) was treated with chlorine, and processed as in the preceding experiment to give IV (R = CH_3) as fine long needles: yield 0.3 g. (50%); m.p. 101–103° dec., softening at 96°; $[\alpha]^{20}D$ −29 ± 2° (*c* 0.6, chloroform); λ_{max}^{KBr} 5.75 (OAc), 6.16, 6.30, 6.60 (aryl C=C), 7.50 (NO_2), and 13.40 μ (substituted phenyl); and X-ray powder diffraction data[7]: 11.48 m, 9.03 w, 7.63 w, 7.08 vs (1), 5.13 s (2), 4.75 m, 4.23 m, 3.99 m, 3.79 w, 3.60 w, 3.49 m (3,3), and 3.18 m (3,3).

Anal. Calcd. for $C_{21}H_{28}ClN_3O_{13}$: C, 44.71; H, 4.60; Cl, 6.28; N, 7.45. Found: C, 44.77; H, 4.61; Cl, 6.19; N, 7.65.

The substance showed stability characteristics similar to those of the 1-*O*-ethyl analog.

1,3,4,5,6-Penta-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose Aldehydrol (V, R = C_2H_5).—A mixture of 3,4,5,6-tetra-*O*-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose aldehydrol (IV, R = C_2H_5, 0.3 g.) and mercuric acetate (0.3 g.) in acetic acid (10 ml.) was stirred for 5 hr. at room temperature. The solution was diluted with chloroform (50 ml.), washed with five 50-ml. portions of water, and the dried (magnesium sulfate) chloroform extract was evaporated. The product was crystallized from ether–petroleum ether as fine needles: yield 0.2 g. (64%); m.p. 118–119°; $[\alpha]^{21}D$ −29 ± 2° (*c* 0.75, chloroform); λ_{max}^{KBr} 5.73 (OAc), 6.20, 6.31, 6.63 (aryl C=C),

(7) 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. Microanalytical determinations were made by W. N. Rond. X-Ray powder diffraction data give interplanar spacings, in 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. Benzene–chloroform or chloroform–ether mixtures were used for development, except for VIII (R′ = H), where benzene–ethanol was used. All crystalline compounds described in this work were shown to be homogeneous by thin layer chromatography.

7.33 (NO_2), and 13.40 μ (substituted phenyl); $\lambda_{max}^{C_2H_5OH}$ 264 mμ (ϵ 10,000) and 340 mμ (ϵ 28,100); and X-ray powder diffraction data[7]: 12.63 s, 9.31 s, 7.03 vs, (1), 6.24 m, 5.47 vs (2), 5.10 w, 4.58 m, 4.25 m, 4.08 s, 3.77 m, 3.59 m (3), and 3.38 m.

Anal. Calcd. for $C_{24}H_{31}N_3O_{15}$: C, 47.91; H, 5.19; N, 6.78. Found: C, 47.80; H, 5.11; N, 7.11.

1,3,4,5,6-Penta-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-1-*O*-methyl-D-glucose Aldehydrol (V, R = CH_3).—A mixture of 3,4,5,6-tetra-*O*-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-methyl-D-glucose aldehydrol (IV, R = CH_3, 1.1 g.) and mercuric acetate (1.1 g.) in acetic acid (30 ml.) was stirred for 5 hr. at room temperature, and the solution was processed by the procedure used in the preceding experiment. The product (V, R = CH_3) was obtained as small needles: yield 0.8 g. (69%); m.p. 102–104°; $[\alpha]^{21}D$ −22 ± 2° (*c* 0.9, chloroform); λ_{max}^{KBr} 5.74 (OAc), 6.15, 6.27, 6.60 (aryl C=C), 7.50 (NO_2), 13.44, and 13.74 μ (substituted phenyl); $\lambda_{max}^{C_2H_5OH}$ 263 mμ (ϵ 9000), 341 mμ (ϵ 17,000); and X-ray powder diffraction data[7]: 13.81 vw, 12.11 vw, 9.21 w, 8.04 m (3), 7.25 s (1), 6.24 w, 5.79 w, 5.37 m (2), 5.01 w, 4.77 w, 4.27 w, and 3.97 w.

Anal. Calcd. for $C_{23}H_{29}N_3O_5$: C, 47.01; H, 4.97; N, 7.15. Found: C, 47.13; H, 4.79; N, 6.92.

3,4,5,6-Tetra-*O*-acetyl-1-(9-adenyl picrate)-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose Aldehydrol (VII, R = C_2H_5).—A mixture of 6-acetamido-9-chloromercuripurine[5] (2.0 g.), cadmium carbonate (0.16 g.), Celite[8] (2.0 g.), and toluene (400 ml.) was dried by distillation of toluene (100 ml.). To this suspension was added 3,4,5,6-tetra-O-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose aldehydrol (IV, R = C_2H_5, 2.0 g.). The mixture was stirred for 30 min. at room temperature, boiled under reflux with stirring for 3 hr., and then stirred overnight at room temperature. The mixture was filtered, the residue was extracted with hot chloroform (300 ml.), and the combined filtrate and extracts were washed twice with 30% aqueous potassium iodide and twice with water. The solution was dried (magnesium sulfate) and then evaporated to give 1-(6-acetamido-9-purinyl)-3,4,5,6-tetra-*O*-acetyl-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose aldehydrol (VI, R = C_2H_5) as a yellow glass. The latter was boiled for 5 min. with a solution of picric acid (0.8 g.) in ethanol (100 ml.). Concentration of the solution gave a crystalline solid which was filtered and washed several times with ether to remove picric acid: yield 2.2 g. (70%). Recrystallization from hot ethanol gave pure VII (R = C_2H_5): m.p. 196–198° dec.; $[\alpha]^{18}D$ −154 ± 4° (*c* 0.3, chloroform); λ_{max}^{KBr} 5.70 (OAc), 6.26, 6.45, 6.55 (NH_3^+, C=N), 7.45 (NO_2), and 13.40 μ (substituted phenyl); and X-ray powder diffraction data[7]: 10.05 m (3,3), 7.63 s (1), 5.47 m (3,3), 4.93 vw, 4.48 vw, 4.19 vw, 3.99 m (2), 3.82 vw, 3.60 w, 3.34 w, 3.18 w, and 2.67 w.

Anal. Calcd. for $C_{33}H_{35}N_{11}O_{20}$: C, 43.76; H, 3.89; N, 17.01. Found: C, 43.70; H, 4.23; N, 16.62.

3,4,5,6-Tetra-*O*-acetyl-1-(9-adenyl)-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose Aldehydrol (VIII, R = C_2H_5; R′ = Ac).—The crude picrate salt VII (R = C_2H_5; 1.0 g.) from the preceding preparation was dissolved in warm acetone (60 ml.) and water (20 ml.), an excess of Dowex-1 (CO_3^{-2}) ion-exchange resin was added, and the mixture was stirred for several minutes. The resin was removed by filtration and was thoroughly washed with acetone. The filtrate and washings were concentrated to remove acetone, and the aqueous suspension which remained was extracted with chloroform (200 ml.). The dried (magnesium sulfate) extract was evaporated, the resultant sirup was dissolved in ethanol and decolorized with activated carbon, and the concentrated solution was allowed to crystallize: yield 0.65 g. (87%); m.p. 183–185° dec.; $[\alpha]^{18}D$ −244 ± 4° (*c* 0.5, chloroform); λ_{max}^{KBr} 5.70 (OAc), 6.15, 6.25, 6.62 (aryl C=C, purine), 7.50 (NO_2), 13.45, and 13.80 μ (substituted phenyl); $\lambda_{max}^{C_2H_5OH}$ 260 mμ (ϵ 30,400), 340 mμ (ϵ 21,750); and X-ray powder diffraction data[7]: 12.28 w, 11.05 m, 8.85 m (3,3), 7.90 m, 7.14 m (2), 5.72 m (3,3), 5.34 w, 4.98 w, 4.82 w, 4.46 w, 4.21 m, and 3.90 s (1).

Anal. Calcd. for $C_{27}H_{32}N_8O_{13}$: C, 47.92; H, 4.76; N, 16.55. Found: C, 48.02; H, 5.13; N, 16.34.

3,4,5,6-Tetra-*O*-acetyl-1-(9-adenyl picrate)-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-methyl-D-glucose Aldehydrol (VII, R = CH_3).—This compound was prepared from 3,4,5,6-tetra-*O*-acetyl-1-chloro-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-methyl-D-glucose aldehydrol (IV, R = CH_3, 3.6 g.) and 6-acetamido-9-chloromercuripurine[5] (3.6 g.) in the presence of cadmium carbonate (0.24 g.) and Celite[8] (3.6 g.), by essentially the same procedure as that used for the 1-*O*-ethyl analog VII (R = C_2H_5). The product (VII, R = CH_3) was obtained crystalline: yield 4.05 g. (75%). This could be recrystallized from methanol with little loss: m.p. 175–177° dec.; $[\alpha]^{18}D$ −151 ± 6° (*c* 0.35, chloroform); λ_{max}^{KBr} 5.68 (OAc), 6.13, 6.23, 6.30, 6.40 (NH_3^+, C=N), 7.33 (NO_2), and 13.60 μ (substituted phenyl); and X-ray powder diffraction data[7]: 9.51 s (1), 8.27 w, 7.56 w, 5.22 m (3), 4.67 w, 4.33 w, 4.04 w, 3.87 s (2), 3.58 w, 3.25 w, 3.02 w, and 2.81 w.

Anal. Calcd. for $C_{32}H_{33}N_{11}O_{22}$: C, 43.10; H, 3.73; N, 17.27. Found: C, 42.83; H, 4.07; N, 16.90.

3,4,5,6-Tetra-*O*-acetyl-1-(9-adenyl)-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-methyl-D-glucose Aldehydrol (VIII, R = CH_3; R′ = Ac).—This compound was prepared from the crude picrate salt VII (R = CH_3; 3.0 g.) from the preceding preparation, by essentially the same procedure that was used for the 1-*O*-ethyl analog VIII (R = C_2H_5). The product (VIII, R = CH_3; R′ = Ac) was dissolved in hot methanol and allowed to crystallize slowly, to give yellow plates: yield 1.0 g. (45%), m.p. 138–140°. Further recrystallization from methanol gave a pure product: m.p. 141–143°; $[\alpha]^{18}D$ −250 ± 5° (*c* 0.5, chloroform); and X-ray powder diffraction data[7]: 9.94 s (3), 7.97 vs (1), 6.33 s (2), 5.16 vw, 4.96 m, 4.23 w, 4.02 w, 3.80 s, 3.53 w, 3.35 w, and 3.08 w.

Anal. Calcd. for $C_{26}H_{30}N_8O_{13}$: C, 47.12; H, 4.56; N, 16.90. Found: C, 46.85; H, 4.98; N, 16.36.

The filtrate from the above crystallization was evaporated and the residue was crystallized from methanol as shining yellow needles of a dimorphous form: yield 0.7 g. (31%); m.p. 216–219° dec.; $[\alpha]^{18}D$ −250 ± 5° (*c* 0.45, chloroform); and X-ray powder diffraction data[7]: 12.28 w, 9.83 m (3), 7.76 m, 6.92 vs (1,1), 6.07 vs (1,1), 5.64 w, 5.28 w, 4.96 m, 4.60 m, 4.00 m, 3.44 s (2), and 3.28 w.

Anal. Found: C, 47.05; H, 4.50; N, 17.00.

Both forms showed closely similar spectral properties: λ_{max}^{KBr} 5.77 (OAc), 6.05, 6.23, 6.35, 6.65 (aryl C=C, purine), 7.56 (NO_2), and 13.8 μ (substituted phenyl); and $\lambda_{max}^{C_2H_5OH}$ 261 mμ (ϵ 23,000), 340 mμ (ϵ 17,000). Both exhibited a low solubility in chloroform.

1-(9-Adenyl)-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-methyl-D-glucose Aldehydrol (VIII, R = CH_3; R′ = H).—Dry ammonia gas was passed for 30 min. at 0° through a solution of 3,4,5,6-tetra-*O*-acetyl-1-(9-adenyl)-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-methyl-D-glucose aldehydrol (VIII, R = CH_3; R′ = Ac; 0.6 g.) in methanol (200 ml.). After 1 hr. at room temperature the solution was evaporated and the glassy mass was crystallized from methanol: yield 0.35 g. (47%); m.p. 150–152°; $[\alpha]^{28}D$ −143 ± 2° (*c* 0.575, *N*,*N*-dimethylformamide); λ_{max}^{KBr} 3.00 (OH), 6.05, 6.15, 6.30 (aryl C=C, purine), 7.50 (NO_2), and 13.35 μ (substituted phenyl); $\lambda_{max}^{C_2H_5OH}$ 263 mμ (ϵ 12,390) and 351 mμ (ϵ 10,420); and X-ray powder diffraction data[7]: 11.79 m, 10.28 s, 8.42 s (1,1), 7.90 w, 7.14 m, 6.76 s (2), 6.19 w, 5.25 m, 4.85 s (1,1), 4.33 s (3), 4.10 m, and 3.93 m.

Anal. Calcd. for $C_{18}H_{22}N_8O_9$: C, 43.71; H, 4.48; N, 22.65. Found: C, 43.22; H, 5.26; N, 22.03.

Either dimorph of VIII (R = CH_3) gave the same product in this reaction.

Treatment of VIII (R = CH_3; R′ = H) in aqueous acetone with Dowex-1 (OH^-) resin, or with methanolic sodium methoxide at room temperature led to the return of predominantly starting material. Under vigorous conditions (refluxing with methanolic sodium methoxide) a chromatogram indicated a complex mixture of products.

1-(9-Adenyl)-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose Aldehydrol (VIII, R = C_2H_5; R′ = H).—This compound was prepared from 3,4,5,6-tetra-*O*-acetyl-1-(9-adenyl)-1,2-dideoxy-2-(2,4-dinitroanilino)-1-*O*-ethyl-D-glucose aldehydrol (VIII, R = C_2H_5; R′ = Ac) by the same procedure as was used for the methyl analog: yield 66%; m.p. 226–229°; $[\alpha]^{28}D$ −173 ± 4° (*c* 0.36, *N*,*N*-dimethylformamide); λ_{max}^{KBr} 3.10 (OH), 6.20, 6.27, 6.67 (aryl C=C, purine), 7.55 (NO_2), 13.45, and 13.85 μ (substituted phenyl); $\lambda_{max}^{C_2H_5OH}$ 260 mμ (ϵ 29,750) and 351 mμ (ϵ 22,490); and X-ray powder diffraction data[7]: 10.16 w, 7.31 s (1,1), 6.46 s (3), 5.87 s (2,2), 5.16 s, 4.85 w, 4.42 w, 4.17 s (2,2), 3.92 s (1,1), 3.71 s (1,1), 3.58 w, and 3.41 s.

Anal. Calcd. for $C_{19}H_{24}N_8O_9$: C, 44.88; H, 4.76; N, 22.03. Found: C, 45.27; H, 5.28; N, 22.29.

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