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Nucleosides XXVIII. 3'-Amino-3'-deoxyhexopyranosyl Nucleosides. Part III. Synthesis of 3'-Amino-3'-deoxyhexopyranosyl Adenines (1)

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Treatment of adenosine with metaperiodate followed by condensation with nitromethane yielded a mixture or 3'-deoxy-3'-nitrohexopyranosyl adenines which were converted to 3'-amino-3'-deoxyhexopyranosyl nucleosides. Separation of this mixture followed by acetylation yielded three crystalline isomeric 9-(3'-acetamido-3'-deoxy-2',4',6'-tri-*O*-acetyl-β-D-hexosyl)adenines which were proved by chemical and n.m.r. studies to be the *manno* (VII), *galacto* (X) and *gluco* (XIII) derivatives.

The previous paper in this series (2) described a facile synthesis of 3'-amino-3'-deoxyglucopyranosyl pyrimidines (uracils and cytosine) by use of the "periodate-nitromethane" procedure previously described (3) in the carbohydrate field. In the present communication, we describe the synthesis of several 3'-amino-3'-deoxyhexopyranosyl adenines from the readily available purine nucleoside, adenosine (I).

Treatment of adenosine (I) in suspension in water with one equivalent of sodium metaperiodate yielded the dialdehyde (II) (4) which was separated from salts and condensed directly with an excess of nitromethane in the presence of sodium hydroxide in aqueous ethanol at room temperature. The reaction mixture was neutralized with acetic acid and after removal of solvents a sirup was obtained which contained a mixture of nitro compounds (III) (5). Treatment of this mixture with Raney nickel and hydrogen gave a mixture of 3'-amino-3'-deoxyglycosyl adenines.

It was expected that this mixture contained the gluco derivative (VI) based on the work of Baer and Fischer (3) with glycosides and of Watanabe and Fox (2) with nucleosides. Methanolysis of this mixture followed by acetylation with acetic anhydride in pyridine gave a 20% yield of methyl-3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucoside in crystalline form. These data establish the gluco derivative VI as one of the components of the mixture obtained by reduction of III. The mixture of amino compounds was fractionated by use of a strongly basic ion exchange resin(Dowex 1-X2, OH^- form) (6) and elution with water. The effluents were monitored spectrophotometrically (adenosine-like spectrum, λ max at 258 mμ) and by paper electrophoresis (borate buffer, *p*H 9, 900 v., 6 hrs.). The early fractions (8-14) showed mainly one spot by paper electrophoresis and yielded, after crystallization from water, pure manno derivative (IV) in ~ 10% overall yield from adenosine (I). Fractions 15-26 afforded mainly the galacto nucleoside V as an amorphous powder in ~ 30% yield from I. Subsequent fractions (27-64) yielded the amorphous gluco nucleoside VI in ~ 28% overall yield. The amorphous compounds (V and VI) were slightly "cross-contaminated". Rechromatography of V and VI in the same manner (Dowex-1 OH^-) gave pure fractions.

Proof of the configuration of these isomers were obtained as follows: Compounds IV, V and VI were converted to their respective crystalline tetraacetyl derivatives (VII, X and XIII) by acetylation with acetic anhydride in pyridine. These crystalline derivatives were subjected to n.m.r. analysis.

Compounds X and XIII gave n.m.r. spectra (see Table I) for the anomeric proton at $\tau = 3.90$ and $\tau = 3.91$ respectively and $J_{H_1'H_2'}$ of ~ 9 c.p.s. indicative of an axial-axial orientation of the C1' and C2' protons (7). Such data are consonant with the galacto or gluco configurations for X and XIII. The nucleoside derivative (VII) showed a doublet for the anomeric proton at $\tau = 3.45$ with $J_{H_1', H_2'}$ ~ 2 c.p.s. diagnostic for an axial-equatorial arrangement of the C1' and C2' protons. Compound VII is therefore of the manno or talo configuration (8, 9).

Compound VII, X and XIII showed four sharp peaks for acetate resonances (10). Assignment of conformation (axial or equatorial) to these peaks on the basis of τ values (see Table) is not without hazard. Also, further work is necessary to determine the *N*-acetate *vs.* *O*-acetate resonances in these compounds.

Conclusive proof of the configuration of each of the nucleosides was obtained from further chemical studies. Nucleoside VI was treated with methanolic hydrogen chloride to afford the glycoside mixture XIV (sirup) which after acetylation yielded crystalline XV identical (with respect to melting point, mixed melting point, optical rotation and infrared spectrum) with methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucoside (2, 11). These data unequivocally establish VI as 9-(3'-amino-3'-deoxy-β-D-glucopyranosyl)adenine.

Methanolysis of nucleoside V gave a mixture (XI) which was converted in a three step process according to Baer (8) to crystalline XII which was identical with a sample of 3-acetamido-3-deoxy-β-D-galactose

(kindly furnished by Dr. H. H. Baer) with respect to melting point, optical (and mutarotational) behavior and infrared spectrum. Nucleoside V is therefore 9-(3'-amino-3'-deoxy-β-D-galactopyranosyl)adenine.

Methanolysis of IV also gave a mixture (VIII) which upon acetylation afforded a crystalline derivative IX which was identical with respect to melting point, optical rotation and infrared spectrum with a sample of methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-mannoside (12) prepared from a sample of methyl 3-amino-3-deoxy-α-D-mannoside hydrochloride (kindly provided by Dr. A. C. Richardson) according to the reported procedure (12a). The structure of nucleoside IV is thus established as 9-(3'-amino-3'-deoxy-β-D-mannopyranosyl)adenine.

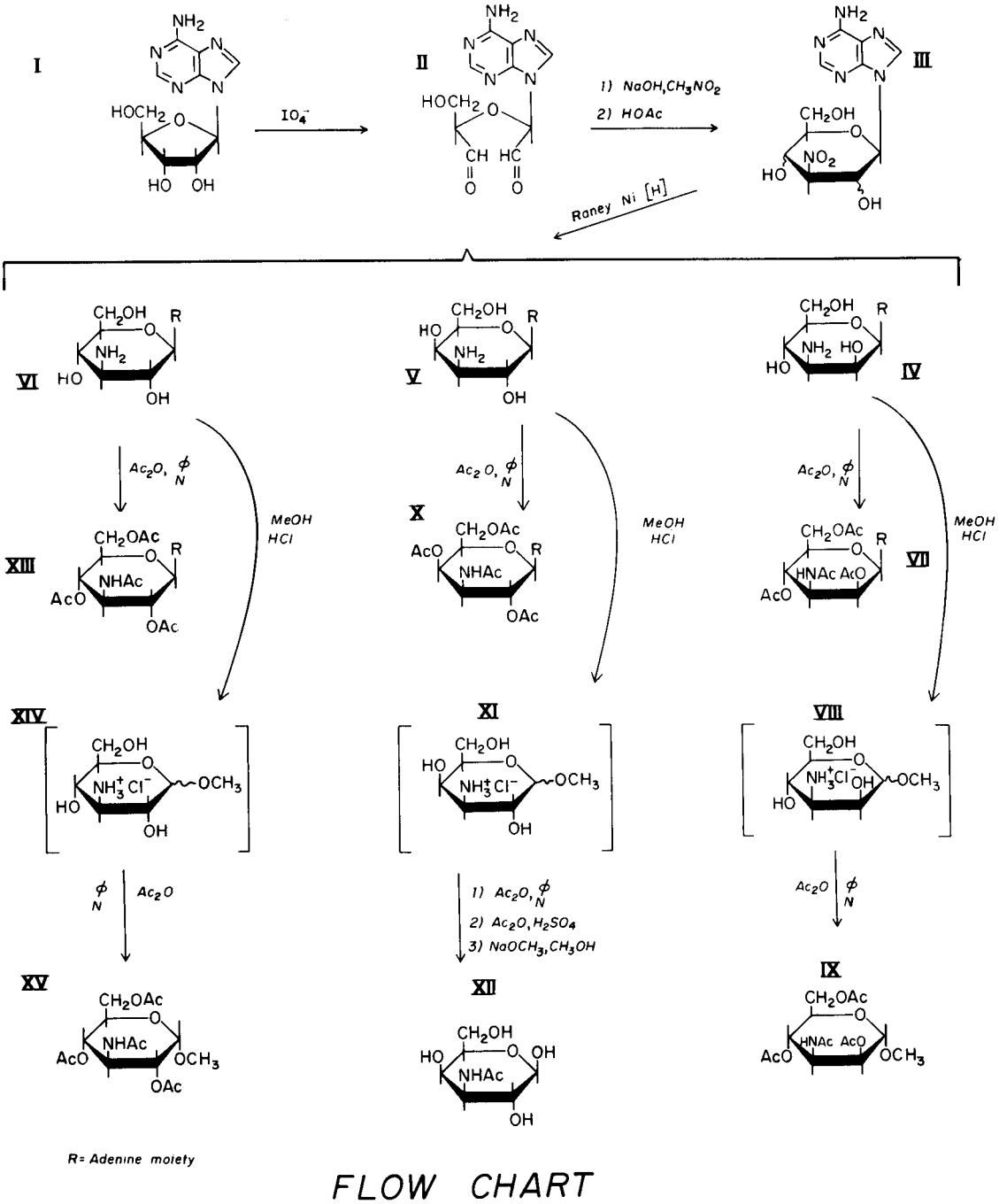

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TABLE I

NMR Data for 9-(3'-Acetamido-3'-deoxy-2',4',6'-tri-*O*-acetyl-β-D-hexosyl)adenines (a)

τ Values

Nucleoside	Acetyl Resonances	H_1'	$J_{H_1', H_2'}$
VII (manno)	8.20	3.45	~ 2 c.p.s.
	8.00		
	7.94		
	7.92		
X (galacto)	8.30	3.90	~ 9 c.p.s.
	8.17		
	8.01		
	7.75		
XIII (gluco)	8.30	3.91	~ 9 c.p.s.
	8.21		
	8.08		
	8.00		

(a) N.M.R. spectra were run on a Varian A-60 spectrometer. Dimethylsulfoxide-d_6 was used as solvent and tetramethylsilane as an internal reference. The authors are indebted to Dr. Earl B. Whipple of the Union Carbide Research Institute for the determination of the n.m.r. spectra.

EXPERIMENTAL (13)

Synthesis of Mixed 9-(3'-deoxy-3'-nitro-β-D-hexopyranosyl)adenines.

Sodium periodate (4.28 g.) was added portion-wise over a 5 minute period to a stirred suspension of 5.34 g. of adenosine in 80 ml. of water. The reaction temperature was kept at 20-25° with the aid of external cooling. During the course of the reaction complete solution took place. Following an additional 10 minutes of stirring the solution was poured into 300 ml. of ethanol and the resultant mixture was stirred for an additional hour. The precipitated inorganic salts were removed by filtration and twice washed with 40 ml. portions of ethanol.

To a solution of 2.2 ml. of nitromethane in the above filtrate, 24 ml. of N sodium hydroxide in 15 ml. of ethanol was added at room temperature dropwise over a 5 minute period. Stirring was continued for an additional 3 hours. Following acidification of the solution with 3 ml. of acetic acid, the solvent was removed *in vacuo* and the residue was dissolved in 100 ml. of water. The evaporation was repeated one more time. An amber sirup was obtained containing a mixture of 3'-nitro nucleosides.

Synthesis of Mixed 9-(3'-Amino-3'-deoxy-β-D-hexopyranosyl)adenines.

The residue from the above procedure was dissolved in 90 ml. of water. Raney nickel in methanol (5 g.) was added and the mixture was hydrogenated at an initial pressure of 3 atm. Following completion of the hydrogenation, the catalyst was filtered and washed 4 times with 50 ml. portions of water. Evaporation of the filtrate *in vacuo* yielded a residue containing sodium acetate and a mixture of 3'-amino-3'-deoxyhexopyranosyl adenines.

Chromatographic Separation of Amino-nucleosides, IV, V and VI.

The residue from the above procedure was dissolved in 10 ml. of water and was applied to a column (3 x 34 cm.) containing the ion exchange resin Dowex 1-X2, 100-200 mesh (OH^- form). The reaction flask was washed with 2-5 ml. portions of water and the washings were added to the column. The column was eluted with water at a flow rate of 3 ml./min. and the effluent was collected in 60 ml. portions. The separation was followed by measuring optical density units in the effluent.

By this procedure, 3 fractions were obtained. Fraction A (760 mg., 13%, tubes 8-14) gave an electrophoretic migration (0.1 M borate buffer, *p*H 9.0, at 900 v, 6 hrs.) of - 2.2 cm. (main spot). Fraction B (1.8 g., 30%, tubes 15-26) gave an electrophoretic mobility of the main spot of + 2.5 cm. Fraction C (1.7 g., 28%, tubes 27-64) gave an electrophoretic migration of the main spot of - 2.2 cm.

9-(3'-Amino-3'-deoxy-β-D-mannopyranosyl)adenine (IV).

Fraction A was crystallized from 7 ml. of water to yield 564 mg. of amino-nucleoside (IV), m.p. 272-275°. Two recrystallizations from water raised its m.p. to 278-279°, $[\alpha]_D^{25}$ + 42° (c., 0.8 in water). Ultraviolet absorption data in water showed λ max 258 mμ, λ min. 224.5 mμ. Under the same conditions adenosine showed λ max 258.5 mμ and λ min. 225.5 mμ.

Anal. Calcd. for $C_{11}H_{16}N_6O_4 \cdot H_2O$: C, 42.04; H, 5.77; N, 26.74. Found: C, 42.03; H, 5.75; N, 26.97.

9-(3'-Acetamido-3'-deoxy-2',4',6'-tri-*O*-acetyl-β-D-mannopyranosyl)-adenine (VII).

Compound IV (165 mg.) dissolved in 6 ml. of anhydrous pyridine was allowed to react with 0.8 ml. of acetic anhydride. The solution was allowed to stand overnight in a refrigerator. Following evaporation of the solution *in vacuo*, three portions of dioxane-benzene (1:1) were added and the mixture evaporated to dryness each time. The residue was crystallized, first from benzene and then from ethyl acetate, to yield 269 mg. of VII, m.p. 203-204° (slight sintering at ~ 135°), $[\alpha]_D^{25}$ -28° (c., 0.9 in chloroform). Ultraviolet absorption data in ethanol showed λ max, 258 mμ, λ min. 225.5 mμ.

Nuclear magnetic resonance and ultraviolet absorption spectroscopy indicated the presence of 4 acetyl groups. Elemental analyses and n.m.r. spectrum indicated solvent of crystallization.

Anal. Calcd. for $C_{19}H_{24}N_6O_8 \cdot 1/4CH_3CO_2C_2H_5$: C, 49.37; H, 5.39; N, 17.28. Found: C, 49.34; H, 5.24; N, 16.96.

Structural Proof of the Sugar Moiety of IV. Conversion of IV to methyl 3-Acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-mannopyranoside (IX).

A cooled suspension of 300 mg. of compound IV in 40 ml. of methanol was saturated with *ca.* 4 g. of anhydrous hydrogen chloride. The reaction mixture was placed in a glass-lined steel bomb and heated at 95° for 14 hours. After cooling, the contents of the bomb were removed and evaporated *in vacuo*. Two portions each of methanol and dioxane and one of benzene were added. Evaporation of the solvent followed each addition.

Acetic anhydride (4 ml.) was added to the residue dissolved in 10 ml. of pyridine. The resulting solution was allowed to stand overnight in a refrigerator and the solvent subsequently removed *in vacuo*. Three portions of ethanol-dioxane (1:1) and one of dioxane-benzene (1:1) were added and evaporated each time. The residue was dissolved in 10 ml. of chloroform and applied to a column (2.5 x 19 cm.) of aluminum oxide (acid washed). Elution of the column was effected with ethyl acetate. The initial 250 ml. of solvent afforded 235 mg. of IX which crystallized upon standing in the refrigerator. After washing with a small amount of ether, IX showed m.p. of 144-147° and $[\alpha]_D^{24}$ + 27° (c., 1.3 in chloroform). Compound IX was recrystallized twice from ethanol and then washed with a 1:1 mixture of ethanol-ether, m.p. 151-153° and $[\alpha]_D^{24}$ + 27° (c., 0.9 in chloroform). [Lit. values for IX are as follows: m.p. 153°, $[\alpha]_D$ + 41° (water) (12a); m.p. 151-152°, $[\alpha]_D$ + 40.2 ± 1.2° (water) (12b); von Saltza (12c) reports m.p. 152-153°, $[\alpha]_D$ + 26.8° (in $CHCl_3$)]. An authentic sample prepared from methyl 3-amino-3-deoxy-β-D-mannoside hydrochloride (12a) had a m.p. 152-153° and $[\alpha]_D^{24}$ + 27° (c., 1.2 in chloroform). A mixed melting point of the two compounds was without depression. Infrared spectra of the two compounds were superimposable.

9-(3'-Amino-3'-deoxy-β-D-galactopyranosyl)adenine (V).

A portion (1.12 g.) of fraction B, from the chromatographic fractionation of the amino-nucleosides described above, was re-chromatographed on the same column by elution with water at a flow rate of 3 ml./min. in 60 ml. fractions. The first fraction (tubes 22-29, yielding 212 mg. of compound) consisted mainly of the mannoside IV. The second fraction (tubes 31-49) yielded 713 mg. of an amorphous powder (V) which gave a single spot upon subjection to paper electrophoresis (borate buffer, *p*H 9.0, 900 v for 6 hours). The compound exhibited an $[\alpha]_D^{24}$ + 26.6° (c., 0.8 in water). Ultraviolet absorption data in water showed λ max 258.5 mμ and λ min. 225 mμ. The product was fairly pure and was used directly in the ensuing reactions.

Anal. Calcd. for $C_{11}H_{16}N_6O_4$: C, 44.59; H, 5.44; N, 28.37. Found: C, 44.29; H, 5.70; N, 26.60.

9-(3'-Acetamido-3'-deoxy-2',4',6'-tri-*O*-acetyl-β-D-galactopyranosyl)-adenine (X).

The aminogalactoside V (210 mg.) was shaken with 5 ml. of anhydrous pyridine and 0.8 ml. of acetic anhydride until solution was complete. The mixture was then allowed to stand in a refrigerator overnight. After evaporation of the reaction mixture to dryness, dioxane was added to the residue and solvent removed *in vacuo*. This process was repeated twice. Crystallization of the residue from 7 ml. of ethanol afforded 229 mg. of compound X. An analytical sample, m.p. 153-155° and $[\alpha]_D^{24}$ + 29.5 (c., 0.8 in chloroform) was obtained by recrystallization of the compound from the same solvent. Ultraviolet absorption data in ethanol showed λ max 258 mμ and λ min. 225.5 mμ. The n.m.r. spectrum indicated ethanol of crystallization (Triplet at 8.9 τ).

Anal. Calcd. for $C_{19}H_{24}N_6O_8 \cdot C_2H_5OH$: C, 49.41; H, 5.92; N, 16.46. Found: C, 49.18; H, 5.62; N, 16.40.

Proof of the Structure of the Sugar Moiety in Amino-nucleoside V. Conversion of V to 3-Acetamido-3-deoxy-β-D-galactose (XII).

A cooled solution of 322 mg. of the aminogalactoside V in 40 ml. of methanol was saturated with 6 g. of hydrogen chloride. The mixture was heated in a glass-lined steel bomb at 95° for 14 hours. After cooling the bomb, the reaction product was removed and evaporated *in vacuo*. Methanol was added twice to the residue and evaporated, followed by two additions of a methanol-dioxane (1:1) mixture and evaporation of solvent. Finally, a dioxane-benzene (1:1) mixture was added and evaporated.

Acetic anhydride (4 ml.) was added to a solution of the above residue in 10 ml. of pyridine and the mixture was allowed to stand overnight in a refrigerator. After evaporation of the solvent *in vacuo* a mixture of ethanol-dioxane (1:1) was added and evaporated to dryness three times followed by similar treatment with one portion of a dioxane-benzene (1:1) mixture. The residue was dissolved in 10 ml. of chloroform and the solution applied to a column (2.5 x 19 cm.) of aluminum oxide (acid washed). Elution was accomplished with 500 ml. of ethyl acetate. The residue (285 mg.), after evaporation of the solvent, was non-crystalline, as expected (8a).

A solution of the above residue (260 mg.) in 6 ml. of acetic anhydride and 0.12 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 21 hours. Sodium bicarbonate (0.6 g.) was added to the cooled reaction mixture. The mixture was stirred for 30 minutes and then evaporated *in vacuo*. The residue was extracted with a mixture of 70 ml. of chloroform and 5 ml. of a saturated solution of sodium bicarbonate. The aqueous layer was extracted with an additional 30 ml. of chloroform. Filtration and evaporation of the combined chloroform layers yielded 241 mg. of non-crystalline material.

The above residue was dissolved in 3 ml. of methanol containing a catalytic amount of sodium methylate (corresponding to 10 mg. of sodium). The reaction solution was allowed to stand in an ice-bath for 2.5 hours. Methanol (25 ml.) was added and the solution was deionized by stirring with 1 ml. of cation exchange resin Dowex-50, H^+ form (methanol washed). The resin was filtered and washed with 25 ml. of methanol. The combined filtrate was evaporated *in vacuo* yielding 100 mg. of a residue which was crystallized from 2 ml. of a methanol-ethyl acetate (2:3) mixture. The compound (XII) melted at 168-170°, $[\alpha]_D^{24}$ + 91.7° ⟶ 117° (C., 0.6, in water, final, 2.5 hours). [Lit. (8) 173°, $[\alpha]_D^{23}$ + 92.5 ⟶ 118° (final, 2.5 hours)]. A mixed melting point of this compound with an authentic sample (8) was without depression. Infrared spectra of both compounds were superimposable.

9-(3'-Amino-3'-deoxy-β-D-glucopyranosyl)adenine (VI).

A portion (1.0 g.) of fraction C from the chromatographic fractionation of the mixture of amino-nucleosides (described above) was rechromatographed in the same fashion as described for compound V. The main fraction (tubes 51-79) gave a single spot (- 2.2 cm.) when subjected to paper electrophoresis (borate buffer, *p*H 9, 900 v for 6 hours). Evaporation of the solvent *in vacuo* gave 690 mg. of a white amorphous powder (VI) $[\alpha]_D^{24}$ - 0.7 (c., 0.9 in water). Ultraviolet absorption data in water showed λ max 258 and λ min. 224.5 mμ. This product (VI) was used in ensuing steps.

9-(3'-Acetamido-3'-deoxy-2',4',6'-tri-*O*-acetyl-β-D-glucopyranosyl)-adenine (XIII).

Amorphous compound VI (175 mg.) was dissolved in 5 ml. of pyridine and 0.6 ml. of acetic anhydride. The solution was kept overnight in a refrigerator. After evaporation of the solvent *in vacuo*, three portions of dioxane-ethyl acetate (1:1) were added followed by evaporation of the solvent after each addition. The residue was crystallized from 7 ml. of ethyl acetate to give 211 mg. of material melting at 183-185°, $[\alpha]_D^{24}$ - 36° (c., 0.1 in chloroform). Ultraviolet absorption data in water showed λ max 258 mμ and λ min. 225.5 mμ.

Anal. Calcd. for $C_{19}H_{24}N_6O_8$: C, 49.14; H, 5.21; N, 18.10. Found: C, 49.10; H, 5.22; N, 17.62.

The Proof of the Structure of the Sugar Moiety of VI. Conversion of VI to methyl 3-acetamido-3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (XV).

A cooled suspension of 397 mg. of amino-nucleoside VI dissolved in 40 ml. of methanol was saturated with 4 g. of anhydrous hydrogen chloride. The reaction mixture was heated in a glass-lined steel bomb at 95° for 10 hours. After cooling the bomb its contents were removed and the solution evaporated *in vacuo*. A mixture of methanol-ethanol (1:1) was added three times and evaporated after each addition, followed by one addition of methanol-benzene (1:1) and evaporation to dryness.

Acetic anhydride (3 ml.) was added to a cooled solution of the above residue in 5 ml. of pyridine. The mixture was kept overnight in a refrigerator and then evaporated to dryness *in vacuo*. Ethanol-dioxane (1:1) was added in three portions and evaporated after each addition. The residue was dissolved in 10 ml. of chloroform and chromatographed on a column (2.5 x 19 cm.) containing aluminum oxide (acid washed). Elution was accomplished with 500 ml. of ethyl acetate. The material obtained (456 mg.) by evaporation of the solvent was crystallized twice from 2.5 ml. of ethanol. The filtered crystals were washed with ether; m.p. 179-180°, $[\alpha]_D^{24}$ + 106° (c., 0.9 in chloroform). The infrared spectrum of this compound was superimposable with that of an authentic sample (2) and the mixed melting point of the two compounds was without depression. The literature reports m.p. 179-180° (8a), 172.5-173°, 178° (11), 175-176° (2) and $[\alpha]_D^{20}$ + 110° (chloroform) (8a), + 105.5° (chloroform), + 101.8° (chloroform) (11), + 101° (chloroform) (2) for this compound.

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REFERENCES

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(2) K. A. Watanabe and J. J. Fox, *Chem. Pharm. Bull.*, (Japan) 12, 975 (1964); K. A. Watanabe, J. Beránek, H. A. Friedman, and J. J. Fox, *J. Org. Chem.*, in press.

(3) H. H. Baer and H. O. L. Fischer, *J. Am. Chem. Soc.*, 81, 5184 (1959).

(4) J. Davoll, B. Lythgoe, and A. R. Todd, *J. Chem. Soc.*, 833 (1946); J. X. Khym and W. E. Cohn, *J. Am. Chem. Soc.*, 82, 6380 (1960).

(5) As this manuscript was being prepared, a brief communication appeared [F. W. Lichtenthaler, H. P. Albrecht, and G. Olferman, *Angew. Chem.*, 77, 131 (1965)] which reports isolation of a crystalline 9-(3'-deoxy-3'-nitro-hexopyranosyl)adenine by the dialdehydenitromethane reaction. They assign the gluco configuration to this crystalline nitro derivative.

(6) P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley, *J. Chem. Soc.*, 5350 (1963); Y. Matsushima and T. Miyazaki, *J. Biochem.*, 55, 464 (1964); Y. Matsushima, T. Miyazaki, and J. T. Park, *ibid.*, 54, 109 (1963).

(7) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, 80, 6098 (1958).

(8) From the work (a) of H. H. Baer, *J. Am. Chem. Soc.*, 84, 83 (1962) and (b) of H. H. Baer and F. Kienzle, *Can. J. Chem.*, 41, 1606 (1963) with glycosides it would be expected that, in the application of their reaction to the nucleoside series, a maximum of four isomers would form. These should be the gluco, galacto, manno and talo nucleosides.

(9) The rationale assumes the C1 conformation for compounds XIII, X and VII which is most probable.

(10) L. D. Hall, "Advances in Carbohydrate Chemistry," 19, 51 (1964) and leading references therein.

(11) M. J. Cron, D. L. Evans, F. M. Palermiti, D. F. Whitehead, I. R. Hooper, P. Chu, and R. U. Lemieux, *J. Am. Chem. Soc.*, 80, 4741 (1958); S. Peat and L. F. Wiggins, *J. Chem. Soc.*, 1810 (1938).

(12a) A. C. Richardson, *ibid.*, 373 (1962); (b) M. L. Wolfrom, H. G. Grag and D. Horton, *J. Org. Chem.*, 28, 2989 (1963); (c) M. H. von Saltza, private communication.

(13) Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. Microanalyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tennessee, and by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

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