nol (25 ml) nearly saturated at 0° with ammonia. After keeping the solution for 8 hr at room temperature, the crystalline product obtained on solvent removal was recrystallized from ethanol to yield 300 mg (40%): mp 281–283° dec; $[\alpha]^{22}D$ +23° (*c* 2.69, ethanol); λ_{max}^{EtOH} 264 mμ (ε 8800); λ_{max}^{KB} 2.9–3.1 (OH, NH), 5.85, 5.9 (thymine), 6.5, 6.8, 7.8, 8.1, 8.8, 9.1, 10.9, 11.9, and 12.2 μ; X-ray powder diffraction data 9.51 (vs, 2), 8.35 (vs, 3), 7.03 (m), 5.22 (vs, 1), 4.6 (s), 4.44 (s), 4.1 (s), 3.79 (s), 3.53 (s), 3.28 (s), 3.13 (s), 2.98 (s), 2.69 (s), and 2.58 (s).

Anal. Calcd for $C_{13}H_{16}Cl_3N_3O_7$: C, 36.19; H, 3.71; Cl, 24.36; N, 9.74. Found: C, 35.98; H, 4.04; Cl, 24.62; H, 9.73.

This substance was also obtained (35% yield) of treating the tri-*O*-acetyl derivative with methanolic hydrogen chloride as described above for the analogous acetylated trifluoroacetamido derivative.

1-(2-Amino-2-deoxy-D-glucopyranosyl)thymine (and Hydrochloride) from 3 (F = Cl).—1-(Tri-*O*-acetyl-2-trichloroacetamido-2-deoxy-β-D-glucopyranosyl)thymine (0.5 g) was refluxed with water (6.2 ml) and concentrated hyrochloric acid (6.2 ml) in an oil bath for 1.5 hr. The solution was evaporated to dryness and the residue was crystallized from methanol to yield 210 mg (75%) of **4**-HCl, mp 320–304° dec; X-ray powder diffraction data were identical with those of the product obtained through the *N*-trifluoroacetyl derivative.

A mixture of 1-(tri-*O*-acetyl-2-trichloroacetamido-2-deoxy-D-glucopyranosyl)thymine (**3**, F = Cl, 0.5 g), barium hydroxide octahydrate (3.0 g), and water (100 ml) was refluxed for 30 min. After cooling, the solution was treated with 1 *N* sulfuric acid to pH 3.0 and the barium sulfate formed was removed by filtration. The filtrate was evaporated to dryness and the residue was treated with ether to remove trichloroacetic acid. The residue, separated by decantation, was dissolved in water (25 ml) and stirred with barium carbonate (1.0 g) to pH 8.0. The solution was filtered through Celite and the filtrate was evaporated to dryness. The syrupy residue was chromatographed on two silica gel G plates using ethyl acetate–methanol (1:1, v/v) as developer and sulfuric acid guideline indication. The band at R_f 0.5 was extracted with 95% ethanol. Evaporation of the solvent yielded a colorless residue which was readily crystallized from methanol to yield 170 mg (80%) of **4**, mp 240–242°; the mixture melting point with **4** was undepressed.

Registry No.—**1**, 7139-63-1; **1** (F = Cl), 10353-00-1; **2**, 6736-63-6; **3**, 7057-54-7; **3** (F = Cl), 10385-54-3; **4**, 10353-03-4; **4** hydrochloride, 7111-40-2; 1-(trichloroacetamido-2-deoxy-D-glucopyranosyl)thymine, 10380-83-3.

Acknowledgment.—This work was supported by Grants No. CA-03232-09 and CA-03232-10 from the Department of Health, Education, and Welfare, U. S. Public Health Service, National Institutes of Health, Bethesda, Md. (The Ohio State Univesity Research Foundation Projects 759 H and 759 I). We are pleased to acknowledge the counsel of P. McWain, W. A. Szarek, and M. W. Winkley.

Anomeric Purine Nucleosides of the Furanose Form of 2-Amino-2-deoxy-D-ribose[1]

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Received December 28, 1966

Ethyl 2-deoxy-2-(2,4-dinitroanilino)-1-thio-α-D-ribofuranoside (**1**) was converted into the acetylated glycosyl chloride (**3**) which was coupled with chloromercuriadenine to give, when purified through the picrate, an essentially equal mixture of the anomeric forms of 9-(2-amino-2-deoxy-D-ribofuranosyl)adenine. Evidence was adduced that this crystalline mixture was a molecular compound. Anomeric separation was achieved by elution from a column of ion-exchange resin and each of the anomers was obtained in crystalline form.

This laboratory has been interested in devising and applying methods for the synthesis of nucleosides of 2-amino-2-deoxyaldoses, preferably in their furanose forms. In this communication we report the synthesis of the anomeric forms of 9-(2-amino-2-deoxy-D-ribofuranosyl)adenine. 2-Amino-2-deoxy-D-ribose was first synthesized in this laboratory[2] and we later reported a synthesis of this rare sugar from 2-amino-2-deoxy-D-glucose which involved the synthesis of ethyl 2-acetamidodi-*O*-acetyl-2-deoxy-1-thio-α-D-ribofuranoside as a step in the process; from this latter compound there was obtained the crystalline ethyl 2-deoxy-2-(2,4-dinitroanilino)-1-thio-α-D-ribofuranoside (**1**).[3] The 1-thiofuranoside **1** was acetylated to the syrupy diacetate **2**. Treatment of **2** with chlorine[4] in dichloromethane produced the glycosyl chloride **3** which was immediately brought into reaction with 6-acetamido-9-chloromercuripurine in refluxing toluene. The crude product from this reaction was purified by preparative thin layer chromatography on silica gel and the major product was converted into a crystalline picrate in order to *N*-deacetylate the adenine moiety according to the method of Burger and co-workers.[5] Removal of the *O*-acetyl and the *N*-(2,4-dinitroanilino) groups in **4** was effected with basic ion-exchange resin to obtain **5**. The nmr spectrum of **5**, measured in deuterium oxide at ambient temperature, revealed a pair of clearly defined doublets in the anomeric region of the spectrum. These doublets, of essentially equal areas, were at δ 6.05 ($J_{1,2}$ = 7.9 cps) and 6.51 ($J_{1,2}$ = 6.6 cps). Compound **5** was, therefore, a mixture of essentially equal amounts of each anomer. This was attested to also by the optical rotatory power of the mixture, $[\alpha]D$ +17 ± 3°, compared with the mean, +12 ± 2°, of that of the components, $[\alpha]D$ +90 ± 2° and −66 ± 2°, as later isolated. The optical rotatory data, obtained in methanol, were not precise owing to the low solubility of the compounds. Furthermore, the X-ray powder diffraction pattern of the anomeric mixture was distinctly not indicative of a crystalline mixture of essentially equal amounts of the anomers, when com-

(1) Preliminary communication: M. L. Wolfrom and M. W. Winkley, *Chem. Commun.*, 533 (1966). In this communication there was reported a successful separation of the β-D anomer **7** through isolative silica gel chromatography of the anomeric mixture **4** with subsequent removal of all blocking groups. This procedure was very laborious, did not lead to the isolation of the α-D anomer, and was abandoned in favor of the separation method herein described.

(2) M. L. Wolfrom, F. Shafizadeh, R. K. Armstrong, and T. M. Shen Han, *J. Am. Chem. Soc.*, **81**, 3716 (1959).

(3) M. L. Wolfrom and M. W. Winkley, *J. Org. Chem.*, **31**, 1169 (1966).

(4) M. L. Wolfrom and W. Groebke, *ibid.*, **28**, 2986 (1963).

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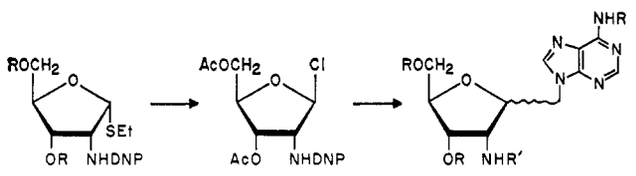
pared with like data obtained from each of the pure, crystalline components. It is, therefore, probable that **5** was a molecular compound between the two anomers of essentially a 1:1 composition. Molecular compounds have been previously found in the sugar series by Hockett and Hudson.[6]

A separation of the anomers was achieved quite elegantly by the general method of Dekker[7] by methanol elution from a basic ion-exchange resin. The



1, R = H
2, R = Ac

3

4, R = Ac; R′ = DNP, α,β
5, R = R′ = H, α,β
6, R = R′ = H, α-D
7, R = R′ = H, β-D

nmr spectrum of the anomer assigned to the β-D series, measured in deuterium oxide at ambient temperature, revealed a lone doublet (H-1′) at δ 6.05 ($J_{1,2}$ = 7.9 cps). The nmr spectrum of the anomer allocated to the α-D series, measured in deuterium oxide at 98° because of its relative insolubility, revealed a well-isolated doublet at δ 6.52 ($J_{1,2}$ = 6.6 cps, H-1′). The anomeric mixture, measured at 98°, displayed well-isolated doublets at δ 6.07 ($J_{1,2}$ = 8.0 cps, H-1′-β-D) and 6.52 ($J_{1,2}$ = 6.6 cps, H-1′-α-D). It was noted that on heating or on prolonged standing of the deuterium oxide solutions, the H-2 or H-8 protons of the purine ring were partially deuterated and the size of the two singlet signals at lower magnetic field decreased.[8] These nmr data clearly demonstrate the effective separation of the anomers. Since both anomers were obtained, the nmr data allow an assured assignment of anomeric form,[9] which assignment is also in agreement with the polarimetric data. The relative sizes of the first-order coupling constants ($J_{1,2}$ = 6.6 cps, H-1′-α-D; $J_{1,2}$ = 7.9 cps, H-1-β-D) for the H-1′ protons of the α-D- and β-D-nucleosides represent another exception[10] to results predicted by application of the Karplus equation[11] and further support the statement of Hall[12] that "The desirability of caution in applying the Karplus equation cannot be overstressed." The same view is expressed by Karplus.[11b]

An analog of our β-D anomer, 9-(2-amino-2-deoxy-β-D-ribofuranosyl)-6-dimethylaminopurine, has been reported by Baker and co-workers[13] as "a non-crystalline substance of somewhat doubtful purity." Nevertheless, their specific rotation, $[\alpha]^{25}D$ −62° (*c* 0.8, methanol), agrees well with that, $[\alpha]^{22}D$ −66 ± 2° (*c* 1, methanol), reported by us for the β-D anomer with an unsubstituted amino group on the purine ring. Their synthesis involved a 14-step synthesis from an aminated derivative of D-altrose.

Experimental Section[14]

9-[3,5-Di-*O*-acetyl-2-deoxy-(2,4-dinitroanilino)-α,β-D-ribofuranosyl]adenine Picrate.—Ethyl 2-deoxy-2-(2,4-dinitroanilino)-1-thio-α-D-ribofuranoside[3] (**1**, 6.94 g) was dissolved in pyridine (75 ml) and acetic anhydride (75 ml) and the mixture was kept at room temperature overnight, then poured into ice and water and extracted with dichloromethane. The extract was washed consecutively with water, cold, saturated, aqueous sodium hydrogen carbonate solution, and water. The dried (magnesium sulfate) extract was evaporated to a syrup under diminished pressure, the residual pyridine was removed by repeated evaporation with toluene, and the syrup was dried under oil pump vacuum to give the acetylated thiofuranoside **2** in a yield of 9.01 g.

Dry chlorine was passed into a solution of **2** (9.01 g) in dried (Drierite) dichloromethane (100 ml) for 10 min at 0°. The residual syrup obtained on solvent removal was dissolved in dichloromethane (50 ml) and added to a hot, vigorously stirred, azeotropically dried suspension of 6-acetamido-9-chloromercuripurine (20 g) and Celite (8 g) in toluene (300 ml). The dichloromethane was removed by distillation and the mixture was heated for 6 hr under reflux with vigorous stirring. The cooled suspension was filtered and the filter cake was washed thoroughly with hot chloroform and then with dichloromethane. The filtrate was evaporated to dryness and the residue was extracted with dichloromethane. The extract was washed consecutively with 30% aqueous potassium iodide solution, cold, saturated, aqueous sodium hydrogen carbonate solution, and water. The dried (magnesium sulfate) solution was evaporated to yield 7.9 g of a syrup. Thin layer chromatography, with ethyl acetate as developer, revealed a major component with R_f 0.30. Preparative thin layer chromatography on plates 200 × 200 × 1 mm of silica gel (100 mg of material per plate), with ethyl acetate as developer, was employed to purify the nucleosidic material. The zones with R_f 0.3 were excised and eluted with acetone. The acetone was removed and the residue was extracted with dichloromethane. Resultant solvent removal gave crude **4** in a yield of 5.9 g (55% from **1**).

The above syrup was dissolved in ethyl acetate (60 ml) and methanol (440 ml). To this solution was added picric acid (6 g) and the mixture was refluxed for 15 min. The crystalline picrate which separated on cooling was removed by filtration and washed with cold methanol to yield 6.6 g (84%): mp 190–192°; $[\alpha]^{25}D$ −70 ± 1° (*c* 1.20, acetone); λ_{max}^{KBr} 5.70 (OAc), 5.87, 6.17, 6.35, 6.45 (picrate, aryl C=C, purine), 7.58 (NO_2), 12.65, and 13.40 μ (substituted benzene). This crystalline picrate anomeric mixture exhibited a distinct X-ray powder diffraction diagram.

Anal. Calcd for $C_{26}H_{23}N_{11}O_{16}$: C, 41.88; H, 3.11; N, 20.66. Found: C, 41.60; H, 3.33; N, 20.68.

9-(2-Amino-2-deoxy-α,β-D-ribofuranosyl)adenine.—To a stirred solution, in acetone (650 ml) and water (150 ml), of the above picrate of the anomeric mixture (5.0 g) was added, at 45–50°, Bio Rad AG 1-X2 (OH^-, 50–100 mesh) resin portionwise until the solution became colorless. The resin was removed by filtration and washed well with hot methanol. The solvent was removed by evaporation under diminished pressure from the filtrate and washings, and the residue was triturated with

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(14) Melting points were determined with a Thomas–Hoover apparatus. 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. Nmr spectra were recorded by J. D. Wander with a Varian A-60 nmr spectrometer and were taken in deuterium oxide (freshly prepared solutions) with internal standards of sodium 4,4-dimethyl-4-silapentane 1-sulfonate. Microanalytical determinations were made by W. N. Rond. X-Ray powder diffraction data given interplanar spacings in angstroms, for Cu Kα radiation. Relative intensities were estimated visually: s, strong; m, medium; w, weak; v, very. The strongest lines are numbered (1, strongest); multiple numbers indicate approximately equal intensities. Thin layer chromatography was performed with Desaga equipment using silica gel G (E. Merck, Darmstadt, Germany) activated at 110° with indication by sulfuric acid. Indicated amounts of developers are by volume. Paper chromatography was performed on Whatman No. 1 paper using the descending technique. Unless otherwise noted, evaporations were performed under diminished pressure.

methanol–dichloromethane until there was obtained a filterable solid in a yield of 1.54 g. This material was dissolved in aqueous methanol and treated with decolorizing carbon. The residue obtained on solvent removal was crystallized from methanol–ethanol to yield 1.28 g (72%): mp 195–197°; $[\alpha]^{22}D$ +17 ± 3° (*c* 0.62, methanol); λ_{max}^{KBr} 2.90–3.10 (OH, NH), 6.01, 6.20, 6.40, and 6.80 μ (NH, purine); $\lambda_{max}^{H_2O}$ 262 mμ (ε 14,800); nmr spectrum (deuterium oxide), δ 3.94–5.4 (sugar ring protons and solvent), 6.05 (0.5 proton, distinct doublet, $J_{1,2}$ = 7.9 cps, H-1′), 6.51 (0.5 proton, distinct doublet, $J_{1,2}$ = 6.6 cps, H-1′), 8.22, 8.26, 8.45, and 8.50 (two protons, H-2 and H-8) at 98°, 3.85–4.67 (sugar ring protons and solvent), 6.07 (0.5 proton, distinct doublet, $J_{1,2}$ = 8.0 cps, H-1′), 6.52 (0.5 proton, $J_{1,2}$ = 6.6 cps, H-1′), 8.35, 8.38, 8.46, and 8.54 (two protons, H-2 and H-8); X-ray powder diffraction data 10.65 s (2), 9.50 vw, 7.37 w, 6.19 m, 5.30 s (1), 4.95 m, 4.71 m, 4.13 vw, 3.86 vw, 3.59 s, 3.26 s (3), and 2.90 w.

Anal. Calcd for $C_{10}H_{14}N_6O_3$: C, 45.09; H, 5.30; N, 31.56. Found: C, 45.29; H, 5.55; N, 31.23.

When a solution of the above crystals was examined by thin layer chromatography, with ethyl acetate–methanol (1:1) as developer, there was revealed an elongated spot of R_f 0.30 which gave a positive coloration with ninhydrin. This was later shown (see below) to be two coalescent spots with R_f values of 0.28 and 0.31. Paper chromatography, with 1-butanol–ethanol–water (40:11:19) as developer, revealed a single spot, $R_{adenine}$ 0.62, which was ultraviolet absorbing and gave a positive ninhydrin test.

Separation of the Anomeric Nucleosides.—Following the general technique of Dekker,[7] the above anomeric mixture (700 mg) in methanol–water (1:9) was siphoned onto a 50 × 3.2 cm column of Bio Rad AG 1-X2 (OH^-, 200–400 mesh). Elution was effected with the same solvent and was monitored by an ultraviolet fraction analyzer with 10-ml fractions being collected. At tube 115 an ultraviolet-absorbing component issued from the column. At tube 189 this component was almost completely eluted and a second component appeared. The second component was completely eluted at tube 310. Tubes 115–179 (fraction 1) and 195–310 (fraction 2) were combined separately and evaporated to dryness. The residue from the first fraction was crystallized from water–ethanol to give **9-(2-amino-2-deoxy-α-D-ribofuranosyl)adenine** (**6**) in a yield of 230 mg (33%): mp 149–151°; $[\alpha]^{23}D$ +90 ± 2° (*c* 0.653, methanol); λ_{max}^{KBr} 2.90–3.10 (OH, NH), 6.07, 6.27, 6.42, and 6.82 μ (NH, purine); $\lambda_{max}^{H_2O}$ 262 mμ (ε 14,500); nmr spectrum (deuterium oxide at 98°), δ 3.84–4.60 (sugar ring and solvent), 6.52 (one proton, distinct doublet, $J_{1,2}$ = 6.6 cps, H-1′), 8.38 and 8.54 (two protons, H-2 and H-8); X-ray powder diffraction data 8.84 s (3), 6.60 w, 5.79 vw, 5.48 m, 5.06 s (1), 4.79 w, 4.46 s (3), 4.09 w, 3.73 w, 3.47 m, 3.38 m, 3.23 s (2), 3.01 s, 2.89 w, and 2.86 w.

Anal. Calcd for $C_{10}H_{14}N_6O_3$: C, 45.09; H, 5.30; N, 31.56. Found: C, 45.03; H, 5.15; N, 32.05.

The residue from fraction 2 was crystallized from methanol–ethanol to give **9-(2-amino-2-deoxy-β-D-ribofuranosyl)adenine** (**7**) in a yield of 215 mg (31%): mp 194–196°; $[\alpha]^{22}D$ −66 ± 2° (*c* 0.98, methanol); λ_{max}^{KBr} 2.90–3.10 (OH, NH), 5.88, 6.18, 6.38, and 6.80 μ (NH, purine); $\lambda_{max}^{H_2O}$ 262 mμ (ε 14,400); nmr spectrum (deuterium oxide), δ 3.87–5.14 (sugar ring and solvent), 6.05 (one proton, distinct doublet, $J_{1,2}$ = 7.9 cps, H-1′), 8.22 and 8.45 (two protons, H-2 and H-8); X-ray powder diffraction data 7.97 vw, 7.13 m, 6.65 s (3), 6.02 s (2), 4.90 w, 4.69 m, 4.37 m, 4.21 w, 4.04 w, 3.83 w, 3.63 s (2), 3.40 s (1), 3.18 w, 3.09 vw, 3.01 vw, 2.94 w, 2.85 vw, and 2.77 w.

Anal. Calcd for $C_{10}H_{14}N_6O_3$: C, 45.09; H, 5.30; N, 31.56. Found: C, 45.09; H, 5.11; N, 31.48.

Thin layer chromatography, with ethyl acetate–methanol (1:1) as developer, of the two separate anomers showed two distinct spots with R_f 0.28 (α-D) and 0.31 (β-D). The infrared spectra of the anomers were very similar at all wavelengths except in the region 10.5–12.5 μ. The α-D anomer was less soluble in water than the β-D form.

Registry No.—**4**, 10407-61-1; picrate of **4**, 10407-62-2; **5**, 10407-63-3; **6**, 10407-64-4; **7**, 10414-81-0.

Acknowledgment.—This work was supported by Grants No. CA-03232-09 and CA-03232-10 from the Department of Health, Education, and Welfare, U. S. Public Health Service, National Institutes of Health, Bethesda, Md. (The Ohio State University Research Foundation Projects 759 H and 759 I).

Synthesis of Guanosine and Its Derivatives from 5-Amino-1-β-D-ribofuranosyl-4-imidazolecarboxamide. I. Ring Closure with Benzoyl Isothiocyanate[1]

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Received December 12, 1966

Guanine (VIIa) was synthesized by condensation of 5-amino-4-imidazolecarboxamide (Ia) with benzoyl isothiocyanate followed by methylation and ring closure. This method has also been applied to the synthesis of 2′,3′-O-isopropylideneguanosine (VIIb) from 5-amino-1-(2′,3′-O-isopropylidene-β-D-ribofuranosyl)-4-imidazolecarboxamide (Ib).

5-Amino-1-β-D-ribofuranosyl-4-imidazolecarboxamide (AICA-riboside) is a constituent of 5-amino-1-β-D-ribofuranosyl-4-imidazolecarboxamide 5′-phosphate (AICAR) which has been found to be an important intermediate in the biosynthesis of purine nucleotides.[2,3] Inosine could easily be obtained by treating AICA-riboside with formic acid and acetic anhydride,[4,5] but the synthesis of guanosine has not yet been reported. Since disodium guanosine 5′-phosphate is known to be a useful seasoning agent, development of a new procedure for synthesizing guanosine from AICA-riboside was desirable.

AICA-riboside, the starting material for the present investigation, has been prepared enzymatically[6] or synthetically.[7–9] We used material which was isolated from the culture broth of the mutant of *Bacillus subtilis*[10] and purified by ion-exchange chromatography.

As a preliminary, we investigated the synthesis of guanine (VIIa) from 5-amino-4-imidazolecarboxamide

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