amino-2-deoxy-1-thio-β-D-glucopyranoside (II, 0.5 g.), pyridine (8 ml.), and acetic anhydride (2.5 ml.) was left 18 hr. at room temperature, then poured onto ice (100 g.). A part of the product separated in crystalline form and was filtered, the remainder was extracted from the filtrate with two 100-ml. portions of chloroform, and the extract was washed with sodium bicarbonate solution, dried (magnesium sulfate), evaporated, and crystallized from methanol–ether. The two fractions had identical infrared spectra and were combined, yield 0.35 g. (64%), m.p. 188–189°. Further recrystallization gave pure product: m.p. 190–192°; $[\alpha]^{22}D$ −52 ± 2° (*c* 1, chloroform); λ_{max}^{KBr} 5.72 (OAc), 6.01, 6.45 μ (NHAc); X-ray powder diffraction data,[13] 11.10 (vs, 1), 7.69 (m), 6.81 (m), 5.98 (s), 4.72 (vs, 3,3), 4.40 (s), 4.17 (vs, 2), 3.82 (m), 3.69 (vs, 3,3), 3.56 (s), 3.41 (s), 3.30 (s), 3.05 (m).

Anal. Calcd. for $C_{16}H_{25}NO_8S$: C, 49.07; H, 6.44; N, 3.58; S, 8.19. Found: C, 49.18; H, 6.46; N, 3.71; S, 8.15.

For this compound, Hough and Taha report[9] m.p. 181°, $[\alpha]D$ −35.4° (*c* 1.4, chloroform). A sample prepared essentially by the procedure of Hough and Taha was recrystallized to constant melting point, when it showed m.p. 190–192°, $[\alpha]^{22}D$ −49 ± 2° (*c* 1.2, chloroform), and was identical with the above product by mixture melting point, infrared spectrum, X-ray powder diffraction pattern, and microanalysis.

3,4,6-Tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranosyl Chloride Hydrochloride (III).—A chilled solution of ethyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-1-thio-β-D-glucopyranoside hydrochloride (VI, 0.40 g.) in methylene chloride (25 ml.) was treated with a solution of chlorine (0.1 g.) in chloroform (0.8 ml.). The solution was maintained for 30 min. at 0°; then the solvent was evaporated and the residue was crystallized from methylene chloride as fine needles, yield 0.31 g. (82%), m.p. 155–157°, which on further recrystallization had m.p. 161–163°, $[\alpha]^{22}D$ +158 ± 2° (*c* 1, chloroform). The compound was identical by mixture melting point, infrared spectrum, and X-ray powder diffraction pattern, with a sample prepared by a different route.[10]

Anal. Calcd. for $C_{12}H_{19}Cl_2NO_7$: C, 40.00; H, 5.27; Cl, 19.72; N, 3.88. Found: C, 39.87; H, 5.21; Cl, 19.77; N, 3.96.

3,4,6-Tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl Ethylxanthate Hydrochloride (IV).—A solution of 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranosyl chloride hydrochloride (III, 150 mg.) in dry acetone (5 ml.) was mixed with a solution of potassium ethylxanthate (110 mg.) in ethanol (10 ml.). After 1 hr. the inorganic precipitate was filtered, the filtrate was concentrated to 5 ml., and methanolic hydrogen chloride (2.5%, 2 ml.) was added, followed by ether to incipient crystallization. After 3 hr. at 0° the product was filtered and recrystallized from ethanol–ether. The pure product had m.p. 174–176°, $[\alpha]^{22}D$ +25 ± 3° (*c* 0.3, ethanol). This compound, prepared by a different route, has been reported[11] to have m.p. 177–179° dec., $[\alpha]^{20}D$ +23 ± 1.5° (*c* 0.2, ethanol).

Methyl 3,4,6-Tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside Hydrochloride (VIII).—A solution of 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranosyl chloride hydrochloride (III, 0.50 g.) in dry methanol (5 ml.) was shaken overnight with Drierite (3 g.) and an excess of silver carbonate. The solution was filtered, and 1% methanolic hydrogen chloride was added dropwise until the solution was just acid. The solution was decolorized with activated carbon, then concentrated and treated with ether to give upon refrigeration a crystalline product, yield 0.30 g. (60%), m.p. 225–230° dec., $[\alpha]^{22}D$ +17 ± 2° (*c* 0.7, methanol).

The following constants have been reported[12] for this compound, prepared by a different route: m.p. 233° dec., $[\alpha]D$ +17° (methanol).

Benzylsulfonyl as *N*-Blocking Group in Amino Sugar Nucleoside Synthesis

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3,4,6-Tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-α-D-glucopyranosyl chloride (II), prepared from 1,3,4,6-tetra-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranose (I), was condensed with 6-benzamido-9-chloromercuripurine to give the substituted nucleoside III (amorphous) and this on *N*-debenzoylation yielded 9-(3,4,6-tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)adenine (IV, dimorphous) which was converted to 9-(2-acetamido-2-deoxy-β-D-glucopyranosyl)adenine (VI).

The synthesis of nucleosides of 2-amino-2-deoxy sugars is normally accomplished by the coupling of a properly blocked amino sugar halide with a purine or pyrimidine derivative according to the Fischer–Helferich[2a] method, in the modification of Davoll and Lowy,[2b,3] or the Hilbert–Johnson procedure.[4] *N*-Blocking groups, so far used for the synthesis of nucleosides of 2-amino-2-deoxy-D-glucose, are the acetyl,[5–7] benzyloxycarbonyl,[8] methoxycarbonyl,[8] and, in a recent publication, the 2,4-dinitrophenyl group.[9] The *N*-acetyl group can only be removed from derivatives of 2-amino-2-deoxy-D-glucose by acid hydrolysis, conditions under which the *N*-glucosyl linkages of purine nucleosides are unstable.[10] The benzyloxycarbonyl group could be eliminated by hydrogenolysis to give pyrimidine nucleosides of 2-amino-2-deoxy-D-glucose.[8] The 2,4-dinitrophenyl group serves excellently and gives both anomeric forms of the nucleoside[9] since it shows no tendency to participate at C-1.

In an effort to introduce other *N*-blocking groups into 2-amino-2-deoxy-D-glucose which might stabilize the halide derivative and be removed with reagents not attacking the *N*-glucosyl linkage of the nucleoside, we have used the benzylsulfonyl group in the synthesis of 9-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-adenine.[11] This group was originally used in the amino acid field and is reported to be removed easily by re-

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(3) J. J. Fox, N. Yung, J. Davoll, and G. B. Brown, *ibid.*, **78**, 2117 (1956).

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(8) C. L. Stevens and K. Nagarajan, *J. Med. Pharm. Chem.*, **5**, 1124 (1962).

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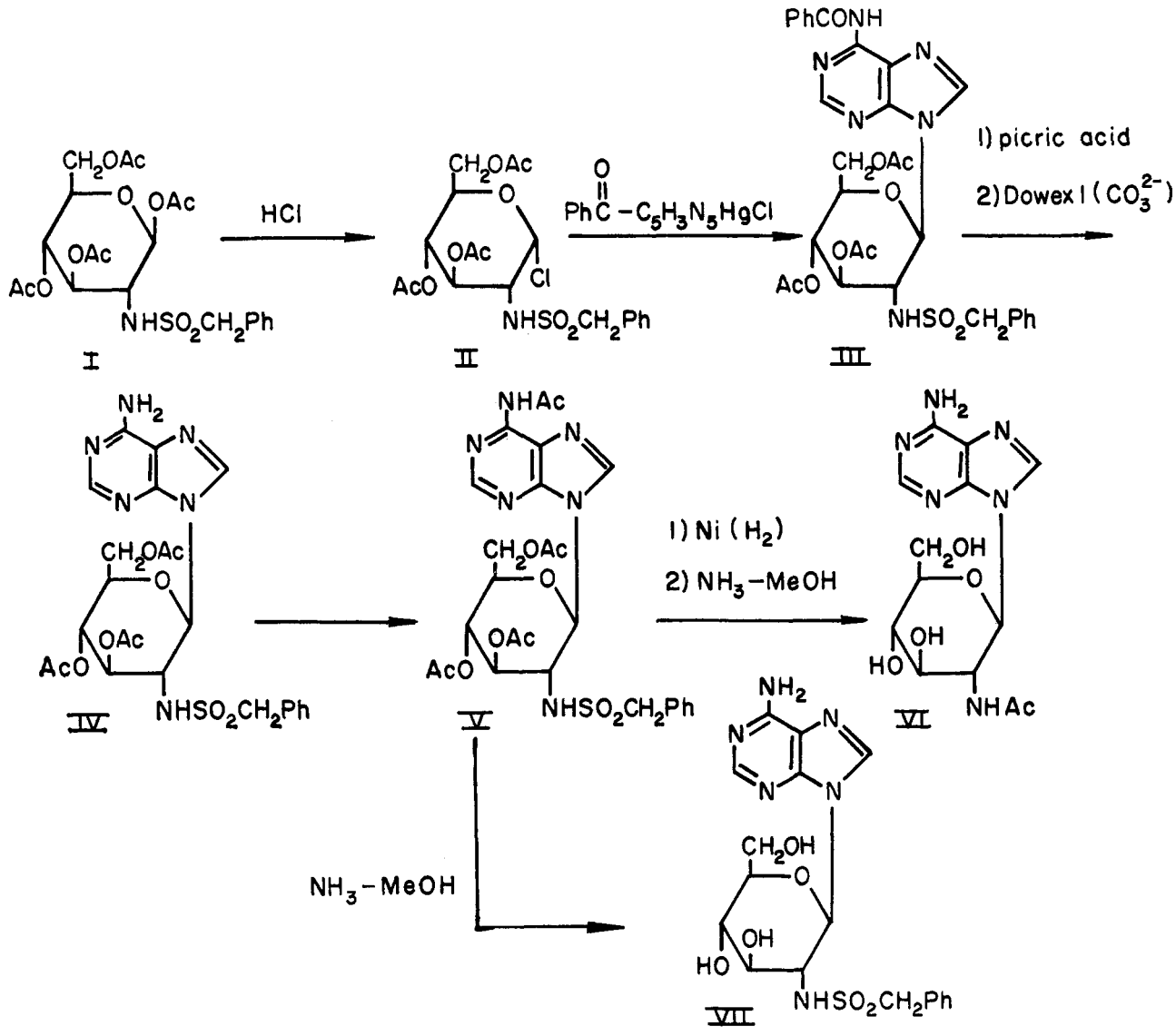
(10) R. S. Tipson, *Advan. Carbohydrate Chem.*, **1**, 193 (1945).

(11) This compound is described in French Patent 1,324,011 (1963).[7] However, no melting point, optical rotation, or analytical values are given for the product.

SCHEME I



duction with Raney nickel.[12] Onodera and co-workers[13] utilized this type of *N*-blocking for the synthesis of glycosides of 2-amino-2-deoxy-D-glucose and removed the protective group by hydrogenation with Raney nickel catalyst.

Treatment of 1,3,4,6-tetra-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranose[13] (I) with hydrogen chloride in an acetic acid–acetic anhydride mixture gave (see Scheme I) the crystalline 3,4,6-tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-α-D-glucopyranosyl chloride (II), which was relatively stable to water and wet solvents and could be stored for an indefinite period in a dry atmosphere. It was converted with sodium methoxide in methanol or with methanol and silver oxide to the known methyl 2-benzylsulfonylamino-2-deoxy-β-D-glucopyranoside or its triacetate, respectively. Coupling of II with 6-benzamido-9-chloromercuripurine in boiling toluene[2b] afforded the crude 6-benzamido-9-(3,4,6-tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)-purine (III) in 84% yield. *N*-Debenzoylation at C-6 with picric acid and removal of the picrate anion with Dowex 1 (CO_3^{2-})[14] yielded 9-(3,4,6-tri-*O*-acetyl-2-benzylsulfonamino-2-deoxy-β-D-glucopyranosyl)adenine (IV) which crystallized in dimorphous forms. However, this product could not be *N*-desulfonylated according to reported procedures,[12,13] and more vigorous conditions were required. Refluxing the reacetylated crystalline nucleoside, 6-acetamido-9-(3,4,6-tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)purine (V), in 70% aqueous ethanol with Raney nickel effected desulfonylation in 56% yield. The product of the *N*-desulfonylation, 6-acetamido-9-(3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl)purine, was not obtained in crystalline form, but was homogeneous by thin layer chromatography. Treatment of this product with ammonia in methanol did not produce the desired 9-(2-amino-2-deoxy-β-D-glucopyranosyl)adenine. Under the deacetylation conditions, *O* → *N* acyl migration took place[15] to give the 9-(2-acetamido-2-deoxy-β-D-glucopyranosyl)adenine (VI) in 88% yield. Structure VI was established by analysis, n.m.r. spectroscopy, and periodate assay. The τ values of VI are given in

(12) H. B. Milne and C.-H. Peng, *J. Am. Chem. Soc.*, **79**, 639 (1957).
(13) K. Onodera, S. Kitaoka, and H. Ochiai, *J. Org. Chem.*, **27**, 156 (1962).
(14) J. R. Parikh, M. E. Wolff, and A. Burger, *J. Am. Chem. Soc.*, **79**, 2778 (1957).
(15) T. White, *J. Chem. Soc.*, 1498 (1938).

TABLE I

N.M.R. ABSORPTION DATA FOR 9-(2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL)PURINE (VI)[a]

τ	Intensity	Multiplicity	Assignment
2.0	2	2 singlets	Purine protons
4.4	1	Doublet, J = 9 c.p.s.	Anomeric proton
5.4–6.4	7	Unresolved masses of lines	C—H protons of the sugar
8.4	3	Singlet	Protons of the N-acetyl group

[a] Measured in deuterium oxide solution, with a tetramethylsilane external standard, on a Varian A-60 spectrometer; τ values, tetramethylsilane = 10.

Table I. The signal at τ 8.4, assigned to the three protons of the N-acetyl function, appears at a somewhat higher field than is normally found for this group. The doublet at τ 4.4 with J = 9 c.p.s. and an area of 1 is assigned to the proton at C-1. The coupling constant shows that the protons at C-1 and C-2 are in axial positions,[16] thus indicating the β-D anomeric configuration for the nucleoside. Attempts to isolate any α-D nucleoside that may have formed were not successful. The β-D form indicates that, with benzylsulfonyl as the N-blocking group in 2-amino-2-deoxy-D-glucose, the nucleoside isolated was the one whose structure would be predicted by the "*trans* rule" discussed by Baker.[17]

O-Deacetylation of V yielded 9-(2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)adenine (VII) in crystalline form. However, treatment of VII with Raney nickel under the same conditions, successful for N-desulfonylation of V, resulted in decomposition with no definitive products isolated.

The benzylsulfonyl group has thus proved to be a suitable N-protecting group in nucleoside synthesis with 2-amino-2-deoxy-D-glucose. Although in this case the nucleoside with the free 2-amino group was not obtained, it might be possible to obtain nucleosides with a free 2-amino group, in the case of 2-amino-2-deoxy sugars in which the relationship between adjacent amino and hydroxyl group is *cis*.[10]

Experimental[18]

Tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-α-D-glucopyranosyl Chloride (II).—Tetra-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranose[13] (I, 17 g.) was dissolved in 45 ml. of acetic acid and 15 ml. of acetic anhydride, nearly saturated at 0° with hydrogen chloride. This solution was maintained at room temperature for 24 hr. in a desiccator over phosphorus pentaoxide and was then poured into 500 ml. of iced water. The resulting solid was filtered with suction, washed with water, and dissolved in 150 ml. of dichloromethane. This solution was washed with aqueous sodium hydrogen carbonate and water and dried over sodium sulfate, and the solvent was removed under reduced pressure. The product crystallized on trituration with dry ether, yield 14 g. For recrystallization, the substance was dissolved in 20 ml. of dichloromethane, the solution was diluted with an equal volume of dry ether, and then petroleum ether (b.p. 30–60°) was added to incipient turbidity: yield 12.6 g. (75%); m.p. 135°; $[\alpha]^{22}D$ +105° (c 0.5, chloroform); λ_{max}^{KBr} 3.05 (NH), 3.40 (C–H), 5.75 (ester CO), 6.70, 6.90 (benzene), 7.35 (sulfonamide), 8.10 (broad C–O–C of acetates), 9.70 (broad C–O–C), 12.75, 14.30 μ (monosubstituted phenyl); X-ray powder diffraction data,[19] 10.65 (vw), 8.86 (s, 1), 7.47 (m), 6.94 (m), 6.15 (s, 3), 5.79 (vw), 5.25 (vw), 4.95 (s), 4.52 (s), 4.19 (m), 3.99 (w), 3.77 (w), 3.56 (s, 2), 3.46 (w), 3.31 (w), 3.26 (w), 3.14 (vw), 3.02 (vw).

Anal. Calcd. for $C_{19}H_{24}ClNO_9S$: C, 47.75; H, 5.01; N, 2.93; S, 6.71. Found: C, 47.59; H, 4.77; N, 3.20; S, 6.64.

9-(3,4,6-Tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)adenine (IV) Hemihydrate.—A mixture of 29.7 g. (62.8 mmoles) of 6-benzamido-9-chloromercuripurine,[2b,20] 5.7 g. (32.0 mmoles) of cadmium carbonate, and 8.0 g. of Celite[21] was azeotropically dried by codistillation with 150 ml. of toluene. The solution was cooled to 40° and 15.0 g. (31.4 mmoles) of tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-α-D-glucopyranosyl chloride (II) was added and the mixture was refluxed for 4.5 hr. with stirring. The hot suspension was filtered, the filter cake was washed several times with hot chloroform, and the combined filtrates were evaporated to dryness under reduced pressure. The slightly yellow solid was dissolved in chloroform and the solution was washed with 30% aqueous potassium iodide and water, dried over sodium sulfate, and evaporated to dryness under reduced pressure. The residue was again dissolved in chloroform. Upon the addition of ether, an amorphous product (III) precipitated, yield 17.9 g. (84%). Thin layer chromatography (ethyl acetate–methanol, 95:5 v./v.) showed one main spot at R_f 0.60 and minor spots at R_f 0.75, 0.85, and 0.95.

This crude product (III), 17.0 g., was dissolved in 185 ml. of hot ethanol. Picric acid, 6.5 g. in 60 ml. of ethanol, was added and the solution was refluxed for 1 hr. After cooling and standing in the refrigerator, an amorphous picrate separated, yield 18.0 g. (89%). This was filtered by suction, washed with ether, and dissolved in 300 ml. of 90% aqueous acetone. Under gentle heating and stirring, a slight excess of Dowex-1 (CO_3^{2-} form)[22] was added. The ion-exchange resin was filtered and washed with acetone. The filtrate was treated with decolorizing carbon and, after solvent removal under reduced pressure, there was obtained an amorphous, slightly yellow product, which was crystallized from acetone as small, white needles (IV), yield 3.4 g., m.p. 276–278° dec., $[\alpha]^{24}D$ −64° (c 1.195, N,N-dimethylformamide). The mother liquor was evaporated to dryness and the residue was crystallized from acetone–ether acetate, total yield 5.5 g., 44.5% from the picrate or 29.4% over-all yield from the chloro sugar II. Occasionally a first crystallization yielded a product of m.p. 198–200°, which changed its melting point to the higher value on standing. The forms showed slightly different X-ray diffraction patterns and were dimorphous. The crystals were a hemihydrate. The water was removed by drying the substance at 0.2 mm. and 56° and was regained on standing in air. Absorption spectra data were $\lambda_{max}^{95\% EtOH}$ 259 mμ; λ_{max}^{KBr} 3.00 (broad NH, NH_2), 5.70 (ester CO), 6.10. 6.30, 6.80 (purine ring and benzene ring), 7.35 (sulfonamide), 8.10 (broad C–O–C of acetates), 9.60 (C–O–C), 12.75, 14.30 (monosubstituted phenyl) μ; X-ray diffraction data[19] for the higher melting form were 15.10 (m, 1), 11.19 (vw), 9.56 (m, 3), 7.83 (vw), 7.14 (w). 5.98 (vw), 5.40 (w), 5.22 (m, 2), 4.76 (vw), 4.36 (vw), 3.94 (m, 3); for the lower melting form, 16.21 (m, 1), 11.19 (vw), 9.07 (w), 7.76 (w), 7.10 (w), 6.03 (vw), 5.38 (vw), 5.08 (m, 2), 4.78 (vw), 4.35 (vw), 3.94 (m, 3), 3.38 (vw), 2.99 (w).

Anal. Calcd. for $2C_{24}H_{28}H_6O_9S \cdot H_2O$: C, 49.23; H, 4.99; N, 14.35; S, 5.23; H_2O, 1.53. Found: C, 49.03; H, 5.27; N, 14.05; S, 5.69; H_2O, 2.17.

Attempts to isolate any α-D nucleoside from the mother liquor of the above crystallization, which showed in thin layer chromatography (ethyl acetate–methanol, 9:1 v./v.) besides the spot of IV, R_f 0.59, minor spots at R_f 0.02, 0.05–0.65, 0.72, and 0.85, were unsuccessful.

6-Acetamido-9-(3,4,6-tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)purine (V).—An amount of 2.0 g. of 9-(3,4,6-tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)adenine (IV) was dissolved in 60 ml. of pyridine and 40 ml. of acetic anhydride were added with ice-cooling and stirring.

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

(17) B. R. Baker in CIBA Foundation Symposium, Chemistry and Biology of Purines, E. W. Wolstenholme and C. M. O'Conner, Ed., J. and A. Churchill Ltd., London, 1957, p. 120.

(18) The infrared spectra data were obtained on a Perkin-Elmer Infracord spectrometer and ultraviolet spectra on a Bausch and Lomb spectrometer.

(19) Interplanar spacing, in Å., Cu Kα radiation. Relative intensity estimated visually: s, strong; m, medium; w, weak; v, very; three strongest lines numbered (1, strongest).

(20) B. R. Baker, K. Hewson, H. J. Thomas, and J. A. Johnson, Jr., *J. Org. Chem.*, **22**, 954 (1957).

(21) A silicous filter aid, Johns-Manville Co., New York, N. Y.

(22) A product of the Dow Chemical Co., Midland, Mich.

After 20 hr. standing at room temperature, the solution was poured into 300 ml. of iced water. The white precipitate was filtered with suction, washed with water, and dried over phosphorus pentaoxide, yield 2.0 g. (93%). The substance crystallized from ethanol: m.p. 210° dec.; $[\alpha]^{18}D$ −10° (*c* 1.16, *N*,*N*-dimethylformamide); $\lambda_{max}^{95\% EtOH}$ 259 mμ; λ_{max}^{KBr} 4.90, 3.00 (NH), 5.70, 5.80 (ester CO, amide I), 6.10 (purine ring), 7.35 (sulfonamide), 8.10 (broad, C–O–C of acetates), 9.50 (C–O–C), 12.75, 14.30 (monosubstituted phenyl) μ; X-ray diffraction data,[19] 11.875 (s, 1), 7.87 (s), 5.36 (s, 3), 3.80 (s, 2), 3.48 (m).

Anal. Calcd. for $C_{20}H_{30}N_6SO_{10}$: C, 50.48; H, 4.88; N, 13.58; S, 5.18. Found: C, 50.67; H, 4.91; N, 13.68; S, 5.08.

9-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)adenine (VI) Dihydrate.—An amount of 970 mg. of 6-acetamido-9-(3,4,6-tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)purine (V) was dissolved in 120 ml. of hot ethanol and 35 ml. of water and 5.0 g. of W2 Raney nickel[23] was added. After 6 hr. of refluxing on a steam bath, 2.0 g. of fresh nickel was added and, after further heating for 3 hr., 2.0 g. of fresh nickel was again added and heating continued for 3 hr. longer. After this time the starting material was no longer present [thin layer chromatography (ethyl acetate–methanol, 8:2 v./v.), R_f 0.80] and only one new substance was present (R_f 0.40). The hot solution was then decanted from the nickel and the catalyst was extracted four times with 50 ml. of boiling ethanol. The combined extracts were filtered through a Celite[21] filter and evaporated under reduced pressure to dryness. On trituration with ether the sirupy material solidified and was collected by filtration, yield 432 mg. (56.5%). This *N*-desulfonylated product was used without further purification in the next step.

The *N*-desulfonylated product (660 mg.) was dissolved in 20 ml. of methanol and the solution was nearly saturated at 0° with ammonia. After 24 hr. standing at 0° the solvent was evaporated under reduced pressure, leaving a partially crystalline material. This material was treated with methanol and stored for 8 hr. in a refrigerator. The methanol was then diluted with chloroform and the crystals were collected by filtration, yield 300 mg. (88%). Recrystallization by dissolving in 3 ml. of water and addition of 20 ml. of acetone gave white needles, m.p. 236–237° dec., $[\alpha]^{22}D$ −11° (*c* 0.99, methanol–water, 7:3), as a dihydrate: $\lambda_{max}^{H_2O}$ 261 mμ; λ_{max}^{KBr} 3.10, 3.20 (OH, NH_2), 6.10, 6.25, 6.40 (purine ring and amide CO) μ; n.m.r. absorption data, see Table I; X-ray diffraction data,[19] 10.78 (m), 7.93 (w), 7.28 (w), 6.65 (w), 6.00 (w), 5.75 (w), 5.37 (m), 4.80 (vs, 1), 4.26 (w), 3.65 (s, 2), 3.29 (s, 3), 3.09 (s), 2.89 (vw). The substance consumed 1.18 moles of sodium metaperiodate.[24]

Anal. Calcd for $C_{13}H_{18}N_6O_5 \cdot 2H_2O$: C, 41.72; H, 5.92; N, 22.46; H_2O, 9.63. Found: C, 41.84; H, 6.19; N, 22.97; H_2O, 9.06.

9-(2-Benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)adenine (VII).—An amount of 1.5 g. of 6-acetamido-9-(3,4,6-tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranosyl)purine (V) was suspended in 100 ml. of dry methanol and the suspension was nearly saturated at 0° with ammonia, whereupon solution occurred. After standing at 0° for 24 hr., the solvent was removed under reduced pressure. The residual crystals were treated with chloroform to remove acetamide, filtered, and washed with chloroform, yield 1.1 g. (94%). The substance was recrystallized from ethanol: m.p. 258–260° dec.; $[\alpha]^{23}D$ −44° (*c* 0.478, *N*,*N*-dimethylformamide); $\lambda_{max}^{95\% EtOH}$ 262 mμ; λ_{max}^{KBr} 4.85, 4.95, 3.05, 3.15 (OH, NH, NH_2), 6.10, 6.20, 6.30 (purine and benzene rings), 7.45 (sulfonamide), 12.75, 14.35 (monosubstituted phenyl) μ; X-ray diffraction data,[19] 11.41 (vw), 9.88 (s, 2), 8.50 (vw), 7.19 (w), 6.71 (vw), 6.26 (m, 3), 5.64 (m), 5.40 (m), 5.02 (s, 1).

Anal. Calcd. for $C_{18}H_{22}N_6O_6S$: C, 47.99; H, 4.92; N, 19.09; S, 7.12. Found: C, 47.99; H, 5.16; N, 18.85; S, 6.90.

Attempts to *N*-desulfonylate this product failed. Treatment of VII with W2 Raney nickel under reflux in 70% aqueous ethanol for 36 hr. led to decomposition. Some starting material was still present in the reaction mixture, as shown by chromatography with cellulose on glass plates[25] (upper layer of the system 1-butanol–ethanol–water, 4:1:5 v./v. used as developer), and reisolating approximately 10% of crystalline starting material from the reaction mixture.

Methyl 3,4,6-Tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-β-D-glucopyranoside.[13]—II (2.0 g.) was dissolved in 30 ml. of dichloromethane and this solution was added dropwise with stirring to a suspension of 5.0 g. of freshly prepared silver oxide, 10.0 g. anhydrous sodium sulfate, 20 ml. of dichloromethane, and 6 ml. of anhydrous methanol. After stirring at room temperature for 24 hr., the mixture was filtered and the filter cake was washed with dichloromethane. The dark solution was treated with hydrogen sulfide, filtered, washed with aqueous sodium bicarbonate and water, dried over sodium sulfate, and evaporated to dryness under reduced pressure. The resulting sirup was dissolved in hot ether. The white crystals which separated upon cooling were recrystallized from methanol: yield 1.3 g. (68%), m.p. 153–154° (lit.[13] m.p. 155–156°).

Methyl 2-Benzylsulfonylamino-2-deoxy-β-D-glucopyranoside.[13]—Tri-*O*-acetyl-2-benzylsulfonylamino-2-deoxy-α-D-glucopyranosyl chloride (II, 500 mg.) was dissolved in 15 ml. of absolute methanol and 0.5 *N* methanolic sodium methoxide solution was added at such a rate that the solution did not become acid. After 1 hr. the solvent was removed under reduced pressure. The crystalline residue was dissolved in hot methanol. Addition of petroleum ether (b.p. 30–60°) gave a crystalline product, yield 110 mg. (28%), m.p. 204–206° (lit.[13] m.p. 202–203°).

Anal. Calcd. for $C_{14}H_{21}NO_7S$: C, 48.41; H, 6.09; N, 4.03; S, 9.23. Found: C, 48.47; H, 6.13; N, 4.03; S, 8.83.

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(23) Freshly prepared according to R. Mozingo, *Org. Syn.*, **21**, 15 (1941).

(24) Periodate oxidation made according to R. D. Guthrie, "Methods in Carbohydrate Chemistry," R. L. Whistler and M. L. Wolfrom, Ed., Academic Press Inc., New York, N. Y., 1962, p. 435.

(25) M. L. Wolfrom, D. Patin, and R. de Lederkremer, *Chem. Ind.* (London), 1065 (1964); *J. Chromatog.*, **17**, 488 (1965).