0.58 g. (78%) of product, m.p. 218–219°, λ_{max}^{EtOH} 276 mμ (ε 6430), $[\alpha]^{26}D$ +46.5 (*c* 1, chloroform).

Anal. Calcd. for $C_{18}H_{24}N_2O_{10}$: C, 50.54; H, 5.65; N, 6.54. Found: C, 50.77; H, 5.78; N, 6.32.

Acetylation of Xb.—Xb (70 mg., 0.16 mmole) was treated with excess acetic anhydride and pyridine at room temperature for 12 hr. The solution was poured on an ice–potassium carbonate mixture and extracted with chloroform. The chloroform extract was washed with water and dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The solid product, Xc, was recrystallized from 3 ml. of ethanol to yield 65 mg. (86%) of material, m.p. 203.5–204.5°, $[\alpha]^{26}D$ +34.9 (*c* 1, chloroform).

An authentic sample of this material was prepared in 46% yield as described by Hilbert and Jansen.[29] After two recrystallizations from ethanol, a pure product, m.p. 203.5–204.5°, $[\alpha]^{26}D$ +33.9 (*c* 1, chloroform), was obtained (lit.[29] m.p. 206°, $[\alpha]D$ +36.1). Admixture of this materal with the product obtained by the acetylation of Xb did not depress the melting point and the infrared absorption curves of both samples were identical in every respect.

1-[2,3,4-Tri-O-acetyl-6-(2-deoxy-2-benzamido-3,4,6-tri-O-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl]-4-ethoxy-2(1H)-pyrimidone (VIII). A. By the Reaction of VIIc with Diethoxypyrimidine.—A mixture of 0.80 g. (1.1 mmoles) of the chloro sugar VIIc and 2 ml. of 2,4-diethoxypyrimidine was heated at 85° for 40 hr. and then at 130° for 6 hr. The cooled reaction mixture was diluted with 40 ml. of diisopropyl ether; the solid was separated by filtration and crystallized from methanol to yield 80 mg. of product, m.p. 285–287°. The mother liquors were concentrated and two additional crops of product, m.p. 285–286°, were obtained. The total yield was 0.20 g. (21%). Two additional recrystallizations from methanol gave an analytically pure compound, m.p. 287–288°, λ_{max}^{EtOH} 274 mμ (ε 4970), $[\alpha]^{25}D$ −6.0 (*c* 1, chloroform).

Anal. Calcd. for $C_{37}H_{45}N_3O_{18}$: C, 54.21; H, 5.53; N, 5.13. Found: C, 54.23; H, 5.43; N, 5.14.

B. By the Reaction of IXb with 1-(2,3,4-Tri-O-acetyl-β-D-glucopyranosyl)-4-ethoxy-2(1H)-pyrimidone.—A vigorously stirred mixture of 0.47 g. (1.1 mmoles) of the nucleoside Xb, 0.80 g. of silver carbonate, 3 g. of Drierite (predried at 200° for 12 hr.), the bromo sugar IXb (prepared from 1.5 g. of IXa), and 10 ml. of azeotropically dried benzene was refluxed for 3 hr. in the dark, then stirred at room temperature for additional 10 hr. The mixture was then diluted with chloroform and filtered, the residue was washed thoroughly with chloroform, the filtrate and washing were combined, and the solvent was evaporated under reduced pressure. The residual gum, when triturated with ether, solidified. The solid was dissolved in methanol and, after a treatment with charcoal, the solution was concentrated to a small volume. The crystalline product obtained was recrystallized once more from methanol to yield 90 mg. (9% based on Xb) of analytically pure product, m.p 287–288°, $[\alpha]^{26}D$ −6.5 (*c* 1, chloroform). Admixture with the compound obtained by procedure A did not depress the melting point and the infrared absorption curve was identical in every respect with the infrared absorption curve of the nucleoside obtained by procedure A.

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(29) G. E. Hilbert and E. F. Jansen, *J. Am. Chem. Soc.*, **58**, 60 (1936).

Amino Derivatives of Starches. 2,6-Diamino-2,6-dideoxy-D-mannose Dihydrochloride[1]

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2,6-Diamino-2,6-dideoxy-β-D-mannose dihydrochloride (VI), a reference compound required in studies on aminated starch derivatives, was synthesized from 2-acetamido-2-deoxy-D-mannose. Phenyl 2-acetamido-2-deoxy-α-D-mannopyranoside (III), prepared from 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-mannopyranose (I), was *p*-toluenesulfonated at the 6-position, and the 6-*p*-tolylsulfonyloxy group was replaced by the azido group. Reduction of the azido group and removal of the protecting groups gave the diamino sugar VI by a stereochemically unambiguous route.

Our laboratory has been concerned with the preparation of aminated starch and starch derivatives, and with methods for structural characterization of the products. Selective *p*-toluenesulfonation of a slightly derivatized amylose has been shown[2] to yield a product, degree of substitution (D.S.) 1.7, which was considered to be preponderantly the 2,6-di-*p*-toluenesulfonate ester. Hydrazinolysis of this product followed by reduction and selective *N* acetylation, gave an *N*-acetylated, aminated amylose of D.S. 1.4. This derivative is undoubtedly a complex hetero polymer, since several possible reactions between hydrazine and the *p*-toluenesulfonated units of the amylose derivative can be envisaged. We have conducted a series of studies on simple sugar derivatives to provide model systems for the reaction leading to aminated amylose and to provide reference compounds for comparison with possible fragmentation products obtained from aminated amylose in structural studies by degradative methods.

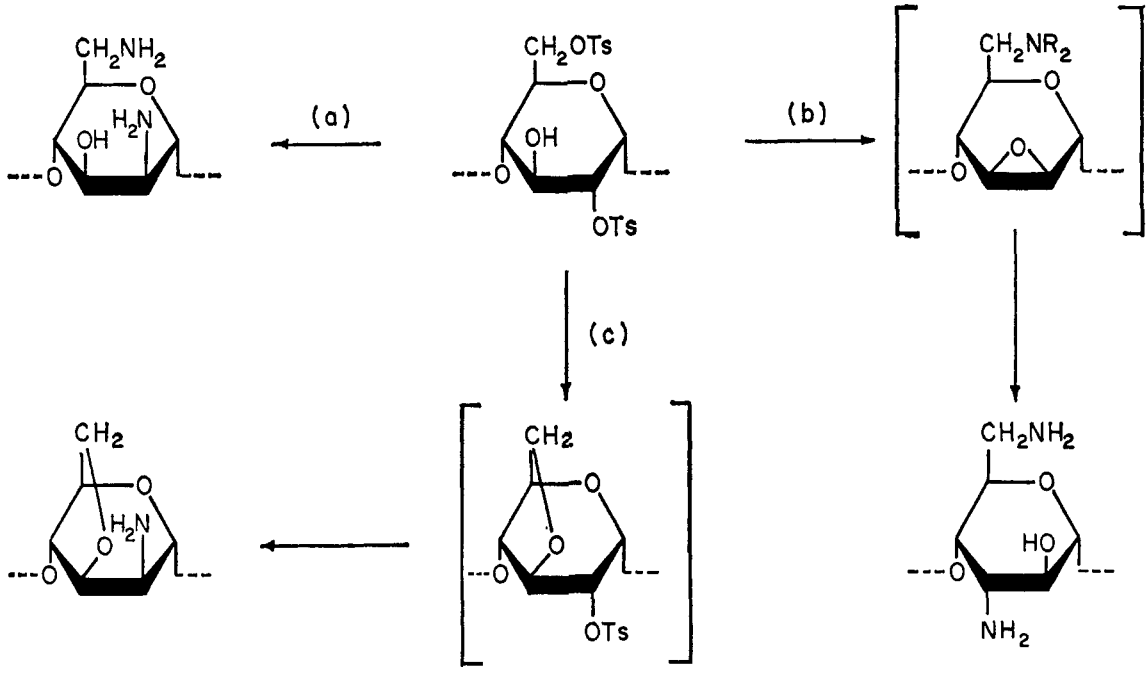
In the amination by a nitrogen nucleophile of a 2,6-di-*O*-*p*-tolylsulfonyl-α-D-glucopyranose monomeric unit in the (1→4)-linked amylose chain, at least three reasonable and possible mechanistic pathways may be postulated, as shown in Scheme I. The products are shown as having been converted into the free amino derivatives. If direct replacement of both *p*-tolylsulfonyloxy groups takes place (pathway a), inversion will occur at C-2, and a 2,6-diamino-2,6-dideoxy-D-mannose residue will be formed. If the reagent functions as a strong base, the initial reaction may involve intramolecular attack by the anion of the C-3 hydroxyl group to displace the 6-*p*-tolylsulfonyloxy group (pathway c) and give a 3,6-anhydro-2-*O*-

(1) This work was supported by the Agricultural Research Service, U. S. Department of Agriculture, Contract No. 12-14-100-5760 (71) (O.S.U. R.F. Project 1301), administered by the Northern Regional Research Laboratory, Peoria, Ill. Preliminary communication: M. L. Wolfrom, P. Chakravarky, and D. Horton, *Chem. Commun.* (London), 143 (1965).

(2) M. L. Wolfrom, M. I. Taha, and D. Horton, *J. Org. Chem.*, **28**, 3553 (1963).

SCHEME I

POSSIBLE ROUTES FOR AMINATION OF A 2,6-DI-*O*-*p*-TOLYLSULFONYL-α-D-GLUCOPYRANOSE RESIDUE IN A (1→4)-LINKED CHAIN



p-tolylsulfonyl-D-glucose residue. Further displacement, intramolecularly, would give a 2-amino-3,6-anhydro-2-deoxy-D-mannose residue. Alternatively (pathway b), amination may first take place by displacement at the unhindered, primary 6-position, and the basicity of the reagent may then facilitate attack at C-2, by the oxygen atom on C-3, to displace the *p*-tolylsulfonyloxy group and give a 2,3-epoxide having the D-*manno* configuration. This epoxide would predictably[3] suffer rapid attack at C-3 by nitrogen, and a 3,6-diamino-3,6-dideoxy-D-altrose residue would be formed.

We have shown[4] that hydrazinolysis followed by reduction, of methyl 2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside (or its di-*O*-*p*-tolylsulfonyl analog), gives methyl 3,6-diamino-3,6-dideoxy-α-D-altropyranoside in high yield. This indicates that pathway b is probably the favored route leading to diamino sugar residues in aminated amylose prepared by hydrazinolysis,[2] whereas pathway c is probably not a major route in this reaction, since it has been observed[5] that methyl 3,6-anhydro-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside is extremely resistant to hydrazinolysis. The extent to which pathway a may be operative is not clear; it could be of major significance, especially if the amination were conducted with a nonbasic nucleophile such as azide ion. The present investigation is concerned with the synthesis of 2,6-diamino-2,6-dideoxy-D-mannose as a reference compound for degradative studies on aminated amylose prepared by hydrazinolysis[2] and related procedures.

2-Acetamido-2-deoxy-D-mannose was prepared from the D-*gluco* epimer by alkaline epimerization[6] and was converted into the known[7,8] 2-acetamido-1,3,4,6-tetra-*O*-acetyl-β-D-mannopyranose (I). Fusion of the latter with phenol and an acid catalyst[9] gave crystalline phenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-mannopyranoside (II) in good yield (Scheme II). The anomeric assignment for II was based on its high specific rotation (+74° in chloroform). *O*-Deacetylation gave crystalline phenyl 2-acetamido-2-deoxy-α-D-mannopyranoside (III). Unimolecular *p*-toluenesulfonation of the latter gave the sirupy, chromatographically homogeneous phenyl 2-acetamido-2-deoxy-6-*O*-*p*-tolylsulfonyl-α-D-mannopyranoside (IV, R = H) in high yield, characterized as the crystalline 3,4-diacetate (IV, R = Ac). Replacement of the *p*-tolylsulfonyloxy group by the azide group in either IV, R = H or Ac, by treatment with sodium azide in aqueous acetone[10] at 100°, gave sirupy phenyl 2-acetamido-6-azido-2,6-dideoxy-α-D-mannopyranoside (V, R = H) or the crystalline 3,4-diacetate (V, R = Ac), respectively, in good yield. Acetylation of the sirupy product (V, R = H) gave crystalline V (R = Ac). Hydrogenolysis of the azido group over palladium–carbon, followed by acetylation with acetic anhydride in pyridine, converted V (R = Ac) into the crystalline phenyl 2,6-diacetamido-2,6-dideoxy-α-D-mannopyranoside in good yield. Hydrolysis of the latter, achieved with 6 *N* hydrochloric acid, gave crystalline 2,6-diamino-2,6-dideoxy-β-D-mannose dihydrochloride (VI), which melted with decomposition at 157° and showed upward mutarotation.

(3) E. Fischer, M. Bergmann, and H. Schotte, *Ber.*, **53**, 509 (1920); P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **55**, 221 (1923); E. W. Bodycote, W. N. Haworth, and E. L. Hirst, *J. Chem. Soc.*, 151 (1934).

(4) M. L. Wolfrom, D. Horton, and Y.-L. Hung, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964 p. 3D; M. L. Wolfrom, Y.-L. Hung, and D. Horton, manuscript submitted for publication.

(5) M. L. Wolfrom, Y.-L. Hung, and D. Horton, unpublished data.

(6) C. T. Spivak and S. Roseman, *J. Am. Chem. Soc.*, **81**, 2403 (1959); R. Kuhn and G. Baschang, *Ann.*, **636**, 164 (1960).

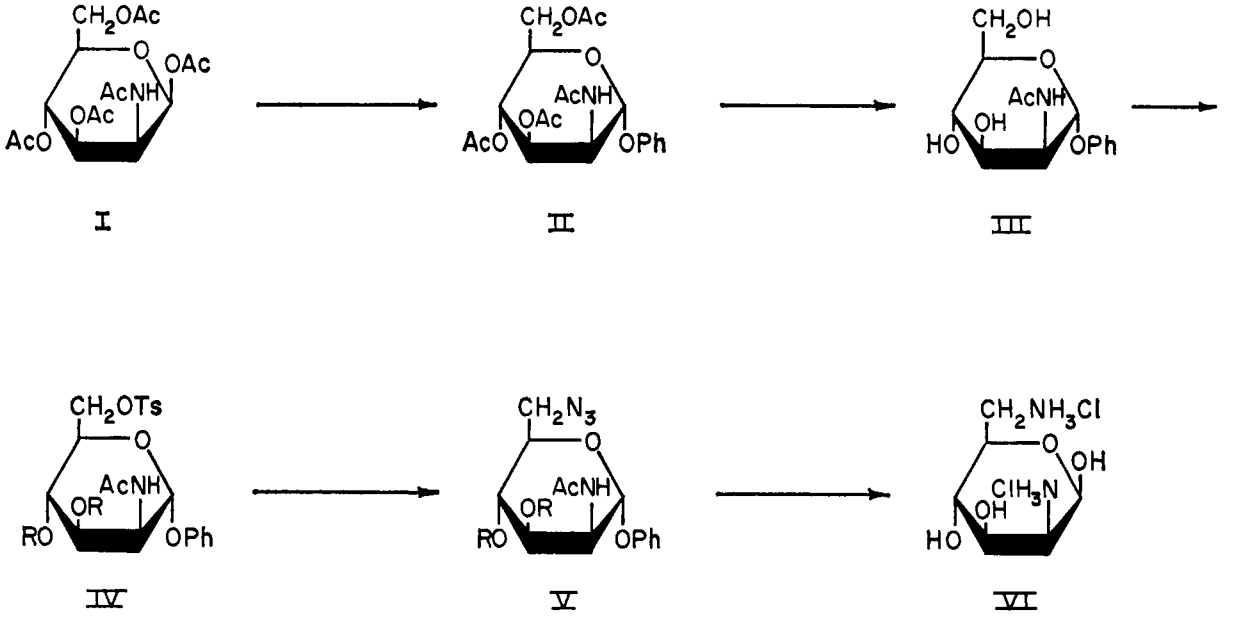
(7) P. A. Levene, "Hexosamines and Mucoproteins," Longmans, Green and Co., London, 1925, p. 16.

(8) A. N. O'Neill, *Can. J. Chem.*, **37**, 1747 (1959).

(9) B. Helferich and E. Schmitz-Hillebrecht, *Ber.*, **66**, 378 (1933); E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson, *J. Am. Chem. Soc.*, **64**, 690 (1942); S. Fujise and K. Yokoyama, *Nippon Kagaku Zasshi*, **72**, 728 (1951); *Chem. Abstr.*, **46**, 11116 (1952).

(10) F. Cramer, *Methods Carbohydrate Chem.*, **1**, 242 (1962).

SCHEME II



While the results of this work were being prepared for publication a paper appeared[11] in which the synthesis of 2,6-diamino-2,6-dideoxy-D-mannose dihydrochloride (VI) was described, by a route which involved configurational inversion at C-3 of a D-*altro* precursor. The reported constants for the diamino sugar are in good agreement with those found in the present work. Although this diamino sugar has not been reported to date as occurring in nature, a number of related diamino sugars have been found as constituents of several antibiotics.[12]

Experimental[13]

Preparation of 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-mannopyranose (I).—Epimerization of 2-acetamido-2-deoxy-D-glucose by the procedure of Kuhn and Baschang[6] gave 2-acetamido-2-deoxy-D-mannose in 12% yield. Most of the unchanged starting material could be recovered and was recycled in the epimerization procedure. The crystalline product (10.0 g.), which was of >95% purity as determined by optical rotation and paper chromatography, was heated with acetic anhydride (100 ml.) and anhydrous sodium acetate (5 g.) for 2 hr. at 100°, the solution was poured onto ice, and the acetylated product was extracted into chloroform. The extract was washed with aqueous sodium bicarbonate, dried (magnesium sulfate), and evaporated. The residue was crystallized from ethanol–ether. Recrystallization from ethanol gave the pure pentaacetate: yield 9.8 g. (56%); m.p. 159°; $[\alpha]^{30}D$ −17° (*c* 1.1, chloroform); λ_{max}^{KBr} 3.03 (NH), 5.74 (OAc), 6.09, 6.49 μ (NHAc); X-ray powder diffraction data,[13] 11.63 vs (2,2), 10.05 vs (2,2), 8.35 w, 7.0 vs (3,3), 6.71 m, 6.07 vw, 5.34 m, 4.77 s, 4.55 m, 4.42 s, 4.25 vs (3,3), 4.06 vs (1,1), 3.88 w, 3.72 vs (1,1), 3.38 s.

The same product was obtained, in approximately the same yield, if the acetylation was performed with acetic anhydride–pyridine by the procedure of O'Neill[8] or Levene,[7] who reported the constants, m.p. 162–163°, $[\alpha]^{24}D$ −17° (chloroform), and m.p. 158–159°, $[\alpha]^{20}D$ −18° (chloroform), respectively.

Phenyl-2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-mannopyranoside (II).—A mixture of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-mannopyranose (I, 1.94 g., 0.005 mole) and phenol (1.88 g., 0.020 mole) was fused, and zinc chloride (0.34 g., 0.0025 mole), dissolved in 19:1 acetic acid–acetic anhydride (2 ml.), was added to the melt. The homogeneous mixture was heated on an oil bath for 75 min. at 120–125°, with continuous evacuation by a water pump to remove acetic acid. The resulting dark sirup was dissolved in chloroform (50 ml.), and the solution was washed with water and with 1 *N* sodium hydroxide, to remove zinc chloride and phenol, respectively. The dried (magnesium sulfate) solution was decolorized and evaporated to a solid, which was recrystallized from 2-propanol as long needles: yield 1.36 g. (65%); m.p. 192–193°; $[\alpha]^{30}D$ +74° (*c* 1, chloroform); λ_{max}^{KBr} 3.06 (NH), 5.77 (OAc), 6.14, 6.50 (NHAc), 6.28, 6.67 (aryl C=C) 14.50 μ (substituted benzene); X-ray powder diffraction data,[13] 11.48 vw, 9.83 s (1), 8.04 vw, 7.31 s (3), 6.11 w, 5.44 m, 5.16 m, 4.93 s (2).

Anal. Calcd. for $C_{20}H_{25}NO_9$: C, 56.73; H, 5.91; N, 3.30. Found: C, 56.56; H, 6.17; N, 3.46.

The same product was obtained, in similar yield, if *p*-toluenesulfonic acid (0.029 g., 0.00015 mole) was used in place of zinc chloride in acetic acid–acetic anhydride in the above preparation.

Phenyl 2-Acetamido-2-deoxy-α-D-mannopyranoside (III).—Phenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-mannopyranoside (II, 1.0 g.) was dissolved in anhydrous methanol (5 ml.) by heating on a steam bath, and to the cooled solution metallic sodium (0.05 g.) was added. After 2 hr. at room temperature, the solution was neutralized with Amberlite IR-120 (H^+) cation-exchange resin, decolorized with activated carbon, and evaporated to a sirup, which was crystallized from ethanol–ether: yield 0.60 g. (85%), m.p. 94–98°. Recrystallization from ethyl acetate gave a pure product: m.p. 98–99°; $[\alpha]^{18}D$ +50° (*c* 1, ethanol); λ_{max}^{KBr} 2.90 (OH), 3.06 (NH), 6.06, 6.45 (NHAc), 6.28, 6.70 (aryl C=C), 14.50 μ (substituted benzene); X-ray powder diffraction data,[13] 16.09 w, 8.42 m, 5.19 m, 5.54 m, 4.59 vs (1), 4.17 s (2), 3.66 s (3), 3.13 s.

Anal. Calcd. for $C_{14}H_{19}NO_6$: C, 56.56; H, 6.44; N, 4.71. Found: C, 56.29; H, 6.90; N, 4.71.

Phenyl 2-Acetamido-2-deoxy-6-*O*-*p*-tolylsulfonyl-α-D-mannopyranoside (IV, R = H).—To a solution of phenyl 2-acetamido-2-deoxy-α-D-mannopyranoside (III, 1.0 g.) in dry pyridine (10 ml.) cooled in a Dry Ice–acetone bath was added a cold solution of *p*-toluenesulfonyl chloride (0.78 g., 1.2 molar equiv.) in dry

(11) W. Meyer zu Reckendorf, *Ber.*, **98**, 93 (1965); *cf.* P. H. Gross, K. Brendel, and H. K. Zimmerman, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April, 1965, p. 6C.

(12) See D. Horton in "The Amino Sugars," R. W. Jeanloz and E. A. Balasz, Ed., Academic Press Inc., New York, N. Y., 1965, in press.

(13) Melting points were determined with a Hershberg type of 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. Microanalytical determinations were made by W. N. Rond. X-Ray powder diffraction data gave interplanar spacings, in Å., for Cu Kα radiation. Relative intensities were estimated visually: s, strong; m, moderate; w, weak; v, very. The strongest lines are numbered (1, strongest); double 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. Unless otherwise stated, the developing solvent was 4:1 ethyl acetate–benzene. All crystalline compounds described in this work were shown by thin layer chromatography to be homogeneous.

pyridine (5 ml.), and the solution was kept for 24 hr. at −10°. The solution was poured into ice and water (200 ml.), the product was extracted into three 50-ml. portions of chloroform, and the extract was washed successively with cold, dilute hydrochloric acid, aqueous sodium bicarbonate, and water, and then dried (sodium sulfate) and evaporated to a glass: yield 1.34 g. (89%); λ_{max}^{KBr} 3.00 (OH, NH), 6.05, 6.50 (NHAc), 6.28, 6.72 (aryl C=C), 8.50 (sulfonate), 13.30, 14.50 μ (substituted benzene). The product was homogeneous by thin layer chromatography[13] with 9:2:1 ethyl acetate–acetic acid–water as the developer.

Anal. Calcd. for $C_{21}H_{25}NO_8S$: S, 7.09. Found: S, 7.04.

Phenyl 2-Acetamido-3,4-di-*O*-acetyl-2-deoxy-6-*O*-*p*-tolylsulfonyl-α-D-mannopyranoside (IV, R = Ac.)—To a solution of phenyl 2-acetamido-2-deoxy-α-D-mannopyranoside (III, 1.0 g.) in dry pyridine (10 ml.), cooled in a Dry Ice–acetone bath, was added a cold solution of *p*-toluenesulfonyl chloride (0.78 g., 1.2 molar equiv.) in dry pyridine (5 ml.). After 24 hr. at −10°, acetic anhydride (15 ml.) was added, and the mixture was kept overnight at room temperature. The reaction was processed as in the preceding experiment, and the product was crystallized from ethanol–petroleum ether (b.p. 60–110°), with recrystallization from 2-propanol: yield 1.4 g. (77%); m.p. 154°; $[\alpha]^{21}D$ + 103° (*c* 2, chloroform); λ_{max}^{KBr} 3.03 (NH), 5.77 (OAc), 6.00, 6.50 (NHAc), 6.24, 6.67 (aryl C=C), 8.50 (sulfonate), 14.50 μ (substituted benzene); X-ray powder diffraction data,[13] 13.81 m, 11.19 s (1), 9.72 w, 8.84 vw, 7.56 m, 6.46 w, 5.87 m, 5.28 vw, 5.04 vw, 4.82 s (3,3), 4.48 s (3,3), 4.21 s (2), 3.92 w.

Anal. Calcd. for $C_{25}H_{29}NO_{10}S$: C, 56.07; H, 5.42; N, 2.61; S, 5.98. Found: C, 56.00; H, 5.59; N, 2.86; S, 5.58.

Phenyl 2-Acetamido-3,4-di-*O*-acetyl-6-azido-2,6-dideoxy-α-D-mannopyranoside (V, R = Ac). A. From Phenyl 2-Acetamido-3,4-di-*O*-acetyl-2-deoxy-6-*O*-*p*-tolylsulfonyl-α-D-mannopyranoside (IV, R = Ac).—Solutions of IV (R = Ac, 500 mg.) in acetone (10 ml.) and of sodium azide (0.5 g.) in water (3 ml.) were mixed and heated in a sealed tube for 24 hr. at 100°. The clear solution was evaporated to dryness, and the product was extracted from the residue with anhydrous acetone. The solution was decolorized with activated carbon and concentrated to a sirup which was crystallized from ethanol–ether–petroleum ether: yield 190 mg. (50%); m.p. 144–145°; $[\alpha]^{18}D$ +22° (*c* 1, ethanol); λ_{max}^{KBr} 3.10 (NH), 4.75 (azide), 5.72 (OAc), 6.10, 6.49 (NHAc), 6.30, 6.75 (aryl C=C), 13.40 μ (substituted benzene); X-ray powder diffraction data,[13] 12.99 m, 11.79 m, 8.76 vs (1), 7.49 m, 6.46 m, 6.18 vw, 5.87 w, 5.34 s (3), 4.98 s, 4.48 m, 4.33 m, 4.11 w, 3.77 s (2), 3.63 m, 3.27 m.

Anal. Calcd. for $C_{18}H_{22}N_4O_7$: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.29; H, 5.74; N, 13.77.

B. From Phenyl 2-Acetamido-2-deoxy-6-*O*-*p*-tolylsulfonyl-α-D-mannopyranoside (IV, R = H).—Solutions of IV (R = H, 1.0 g.) in acetone (21 ml.) and of sodium azide (1 g.) in water (7 ml.) were mixed and heated in a sealed tube for 24 hr. at 100°. The clear solution was evaporated to dryness, and the product was extracted from the residue with anhydrous acetone. The acetone extract was evaporated to give sirupy phenyl 2-acetamido-6-azido-2,6-dideoxy-α-D-mannopyranoside (V, R = H), which was acetylated by treatment with acetic anhydride (10 ml.) and pyridine (10 ml.) for 18 hr. at 20°. The solution was poured into water, the mixture was extracted with chloroform, and the extract was washed with water, dried (magnesium sulfate), and evaporated. Crystallization of the residue from ethanol–ether–petroleum ether gave (V, R = Ac), yield 0.51 g. (57%), with physical constants identical with those of the product described in the preceding paragraph.

Phenyl 2,6-Diacetamido-3,4-di-*O*-acetyl-2,6-dideoxy-α-D-mannopyranoside.—Phenyl 2-acetamido-3,4-di-*O*-acetyl-6-azido-2,6-dideoxy-α-D-mannopyranoside (V, R = Ac, 0.40 g.), dissolved in methanol (10 ml.), was hydrogenated at 3 atm. pressure over 10% palladium–charcoal (0.2 g.) for 1 hr. at room temperature. The suspension was filtered, the filtrate was evaporated, and the residue was acetylated by treatment with acetic anhydride (5 ml.) and pyridine (5 ml.) for 18 hr. at room temperature. The solution was poured into water, the mixture was extracted with chloroform, and the extract was washed with water, dried (magnesium sulfate), and evaporated to a sirup which was crystallized from ethyl acetate–toluene: yield 0.3 g. (72%); m.p. 181°; $[\alpha]^{18}D$ +64.1° (*c* 2, chloroform); λ_{max}^{KBr} 3.10 (NH), 5.76 (OAc), 6.00, 6.48 (NHAc), 6.18, 6.24, 6.70 (aryl C=C), 14.50 μ (substituted benzene); X-ray powder diffraction data,[13] 12.28 m, 10.92 m, 8.67 s (3), 7.31 w, 6.92 m, 6.28 m, 5.50 s (4), 5.09 vw, 4.39 s (2), 4.17 vw, 3.97 s (1).

Anal. Calcd. for $C_{20}H_{26}N_2O_8$: C, 56.86; H, 6.21; N, 6.63. Found: C, 57.13; H, 6.22; N, 6.73.

2,6-Diamino-2,6-dideoxy-β-D-mannose Dihydrochloride (VI).—Phenyl 2,6-diacetamido-3,4-di-*O*-acetyl-2,6-dideoxy-α-D-mannopyranoside (150 mg.) was heated with 6 *N* hydrochloric acid (5 ml.) for 1.5 hr. at 100°. The solution was washed with ether to remove phenol and codistilled several times with 1-propanol to remove acid, and the residue was crystallized from 1-propanol: yield 64 mg. (72%); m.p. 157° dec.; $[\alpha]^{20}D$ − 10.5 (initial, extrapolated) → −1.0 ± 0.5° (*c* 1, water); R_{GN}[14] 0.72; λ_{max}^{KBr} 3.0–3.5 (OH, NH_3^+), 6.20, 6.67 μ (NH_3^+); X-ray powder diffraction data,[13] 6.86 vw, 5.94 s (1), 5.34 vw, 5.09 vw, 4.82 w, 4.29 w, 4.15 m, 3.58 s (2,2), 3.44 s (2,2), 3.28 s (3).

For this compound, prepared by a different route, Meyer zu Reckendorf[11] gave m.p. 155° dec., $[\alpha]^{26}D$ −8.0 → −1.0° (*c* 1, water).

The diamino sugar VI could also be obtained directly from sirupy phenyl 2-acetamido-6-azido-2,6-dideoxy-α-D-mannopyranoside (V, R = H), or its 3,4-diacetate (V, R = Ac), by hydrogenation and subsequent hydrolysis with 6 *N* hydrochloric acid.

(14) Refers to mobility relative to 2-amino-2-deoxy-D-glucose hydrochloride, on Whatman No. 1 paper, with descending chromatography, 5:5:3:1 pyridine–ethyl acetate–water–acetic acid system, according to F. G. Fischer and H. J. Nebel [*Z. Physiol Chem.*, **302**, 10 (1955)] with indication by ninhydrin.