The factors leading to unfavorable orientation of the carbazate in the enzyme-substrate complex might be eliminated by protonation of the α-nitrogen atom of the carbazate. However, in the conjugate acid of the carbazate the apparent basicity of the carbethoxy carbonyl oxygen atom would be diminished to such a degree that even if the conjugate acid were able to assume those conformations accessible to ethyl acetyl-L-phenylalaninate in its enzyme-substrate complex, it is probable that it would still be unable to function as a substrate.

If the conjugate acid of the carbazate is able to assume those conformations accessible to ethyl acetyl-L-phenylalaninate in its complex with the enzyme, it should also be able to assume those conformations available to ethyl acetyl-D-phenylalaninate in its complex with the enzyme. This situation in itself would not prevent the carbazate from functioning as a substrate. However, the fact that the K_I value of the carbazate is substantially greater than that of ethyl acetyl-D-phenylalaninate does not support the view that the carbazate is present in its complex with the enzyme in the form of the conjugate acid unless one invokes the added hypothesis that protonation is possible only in those conformations that are analogous to those assumed by ethyl acetyl-L-phenylalaninate.

The most direct explanation of the inability of ethyl 1-acetyl-2-benzylcarbazate to function as a substrate of α-chymotrypsin is that it is unable to assume an orientation in the enzyme substrate complex that can lead to reaction products.

Experimental

Attempted Hydrolysis of Ethyl 1-Acetyl-2-benzylcarbazate by α-Chymotrypsin.—A solution of 3.06 g. of ethyl 1-acetyl-2-benzylcarbazate[3] and 0.275 g. of α-chymotrypsin in 230 ml. of carbon dioxide free water was adjusted to *p*H 7.95 with 0.1 *N* aqueous sodium hydroxide, the resulting solution made up to 250 ml., thermostatted at 25° and the *p*H held at 7.95 by the addition of 0.1 *N* aqueous sodium hydroxide. After 70 min. 2.35 ml. of base had been added, after 275 min. a total of 3.50 ml., after 16.5 hr. a total of 4.00 ml., after which time no further addition of base was required to maintain the *p*H at 7.95 for a period of one week. The total amount of base added corresponded to a maximum extent of hydrolysis of 1.3%, a value less than that observed for a comparable system containing only enzyme.

At the end of the reaction period the system was extracted with three 100 ml. portions of carbon tetrachloride and three 100 ml. portions of ethyl ether. The combined extracts were dried over anhydrous sodium sulfate and the solvent removed *in vacuo* at 25°[3] to give 2.88 g. (94%) of a viscous, non-crystallizable oil, $n^{25}D$ 1.5131. The infrared spectrum in carbon tetrachloride was identical with that of ethyl 1-acetyl-2-benzyl carbazate.[3]

Base Catalyzed Hydrolyses of Ethyl 1-Acetyl-2-benzyl Carbazate and Ethyl Acetyl-DL-phenylalaninate.—Stock solutions 0.040 *M* in substrate were prepared from carbon dioxide free water. Aliquots of these solutions were used to prepare reaction systems 0.1 *M* in sodium chloride and with a total volume of 10.0 ml. All hydrolyses were conducted at 25.0 ± 0.1° in an atmosphere of nitrogen at a constant *p*H maintained with a *p*H-stat. Aqueous sodium hydroxide, 0.0107 *N*, was used as the titrant and each hydrolysis was followed for a period of 8 min. The schedule used for each substrate is given in Table III.

TABLE III

SCHEDULE OF EXPERIMENTS FOR DETERMINATION OF k_B

Molarity of substrate *M*	*p*H
0.024	7.50
.024	7.90
.024	8.50
.036	8.50
.004	9.00
.016	9.00
.024	9.00
.028	9.00

The recorder traces of extent of reaction *vs.* time were linear and the velocities were computed from the chart coordinates. The data so obtained were described by the relation $v = k_B[RCO_2R'][OH^-]$ to within ± 10% and the second order constant k_B evaluated by a least squares fit of *v vs.* the product $[RCO_2R'][OH^-]$ using a program written for the Datatron 205 digital computer.

Inhibition Studies.—The inhibition of the α-chymotrypsin catalyzed hydrolysis of chloroacetyl-L-valine methyl ester in aqueous solutions at 25.0 ± 0.1°, *p*H 7.90 ± 0.01 and 0.1 *M* in sodium chloride by ethyl 1-acetyl-2-benzylcarbazate[3] was studied with the aid of a *p*H-stat as described previously.[5] The only departure from the previous procedure was in the use of equal time intervals of one min. from $t = 1$ min. to $t = 9$ min. instead of $t = 0$ to $t = 8$ min. In this particular study some difficulty was experienced in adjusting the *p*H of the enzyme solution so as to minimize "hunting" during the initial minute of reaction. Crystalline α-chymotrypsin, Armour lot No. 283, was used throughout.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, BETHESDA 14, MD.]

Synthetic Kanosamine

BY HANS HELMUT BAER

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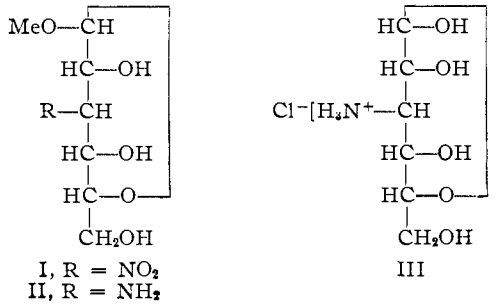
A methyl 3-amino-3-deoxy-β-D-hexopyranoside that has recently become readily available by a new synthesis was proved to belong to the *gluco* series, *i.e.*, to be the methyl β-glycopyranoside of kanosamine. Acid hydrolysis and subsequent N-acetylation afforded kanosamine hydrochloride and N-acetylkanosamine, respectively. The latter was degraded by means of periodate to give 2-acetamido-2-deoxy-4-*O*-formyl-D-arabinose and N-acetyl-D-arabinosamine.

Recently we have described a synthesis that afforded, *via* a nitromethane condensation of periodate-oxidized methyl β-D-glycosides and subsequent hydrogenation, a methyl 3-nitro-3-deoxy-β-D-hexopyranoside (I, m.p. 204–205°, $[\alpha]^{20}D$ −12°) and the corresponding methyl 3-amino-3-deoxy-β-D-hexopyranoside (II, m.p. 207–208° dec., $[\alpha]^{20}D$ −34°).[1] Since the course of the synthesis was non-specific with regard to the stereochemistry at carbon atoms 2, 3 and 4, the configuration of the products remained unsettled. Three of the eight

(1) H. H. Baer, *Ber.*, **93**, 2805 (1960).

possible configurations could be excluded on the basis of data available in the literature, and of the remainder the D-*gluco* configuration seemed to be most likely. The present report offers proof that the products do indeed belong to the D-glucose series.



I, R = NO_2
II, R = NH_2

III

Acid hydrolysis of the aminodeoxy hexoside II furnished a reducing aminodeoxy hexose hydrochloride III ($[\alpha]^{20}D$ +47° → +43°) as a white powder. While it has not yet been obtained in complete chromatographic purity it afforded upon N-acetylation a pure, crystalline acetamidodeoxy hexose (IV) of m.p. 204–205° dec. and $[\alpha]^{24}D$ +17° → +52.7°. The latter proved to be N-acetylkanosamine.

The antibiotic kanamycin discovered by Umezawa and co-workers[2] possesses a sugar component that has been termed kanosamine[3] and demonstrated to be 3-amino-3-deoxy-D-glucose.[4,5] While the isolation of the pure, free aminodeoxy sugar or its hydrochloride has not yet been described, its crystalline N-acetyl derivative[3] is suitable for characterization. We have compared an authentic sample of N-acetylkanosamine with our acetamidodeoxy hexose IV and found them identical according to mixed melting point, X-ray patterns, infrared spectra, R_f-values and mutarotation. In the same manner IV was identified with an authentic sample of 3-acetamido-3-deoxy-β-D-glucose that had been prepared[6] from N-acetyl-D-arabinosamine by the cyanohydrin synthesis but had not yet been compared experimentally with the corresponding derivative of the natural product.

For further confirmation of the structure, IV was degraded by means of one mole of periodate. As a primary oxidation product N-acetyl-4-*O*-formyl-D-arabinosamine (V) was formed and could be isolated in the crystalline state. Removal of the formyl ester group by mild alkaline treatment led to the same pentosamine, N-acetyl-β-D-arabinosamine (VI), that had previously been obtained upon analogous periodate oxidation of 3-acetamido-3-deoxy-D-mannose (VII).[7] Thus the works of Kuhn and Baschang[6] and of ourselves have been correlated as shown in the series of formulas.

Peat and Wiggins[8] were the first to synthesize various derivatives of 3-amino-3-deoxy-D-glucose.[9] Among these was a methyl β-glycoside that apparently was identical with a compound recently obtained in a different way by Lindberg and Theander.[10] The present results demonstrating independently that II is methyl 3-amino-3-deoxy-β-D-glucopyranoside agree well with those authors' findings.

Acknowledgment.—The author is indebted to Dr. N. K. Richtmyer for his interest in the work. Thanks are due to Dr. I. R. Hooper, Bristol Laboratories, Inc., Syracuse, N. Y., Professor R. Kuhn and Dr. G. Baschang, Heidelberg, Germany, for providing samples of comparison of N-acetylkanosamine and other rare aminosugars.

Experimental[11]

3-Amino-3-deoxy-D-glucose Hydrochloride (III).—Two grams of methyl 3-amino-3-deoxy-β-D-glucopyranoside (II) in 100 ml. of 4 *N* hydrochloric acid was heated in a boiling water-bath for 3 hours. The slightly yellow hydrolyzate was evaporated *in vacuo* (bath, 40°) to a small volume. The evaporation was repeated four times with 50-ml. portions of water added each time. The solution was then decolorized with activated charcoal, again evaporated several times with addition of water and finally brought to a colorless sirup that was dried in a desiccator over calcium oxide and phosphorus pentoxide. Constant weight (2.23 g.) of the material was attained only after prolonged drying at 40° in high vacuum; hygroscopic foam, $[\alpha]^{20}D$ +62.5°, +71° (*c* 1 in water; different experiments). Paper chromatographic[1,11] and electrophoretic[1] assays revealed the material not to be homogeneous (ninhydrin spray). The main spot migrated like D-glucosamine hydrochloride and was distinct from that given by 3-amino-3-deoxy-D-mannose hydrochloride.[7] It was accompanied by 2 or 3 streaking products (reversion?) that moved more slowly on chromatograms, faster on electrophoreograms. Repeated fractional precipitation from methanolic solution by careful addition of propyl alcohol afforded a white powder of III that contained only very small amounts of the by-products; the latter accumulated in the forefractions. The product reduced Fehling solution and gave positive ninhydrin and Elson–Morgan color tests; $[\alpha]^{20}D$ +47° (5 min.) → +43° (6 hours, final; *c* 1 in water).

A sample of III which was obtained by hydrolysis of its N-acetate IV (50 mg. of IV, see below, in 5 ml. of *N* HCl for 3 hours at 100°) followed by removal of excess acid with Amberlite CG-45(OH^-) likewise contained traces of by-products, though markedly less than the crude hydrolyzate from II. Without further purification it showed $[\alpha]^{20}D$ +47.4° (5 min.) → +44.5° (final; *c* 0.9 in water). For analysis the moderately hygroscopic powder was dried at 56°.

Anal. Calcd. for $C_6H_{14}NO_5Cl$ (215.6): C, 33.42; H, 6.54; N, 6.50; Cl, 16.44. Found: C, 33.35; H, 6.85; N, 6.24; Cl, 15.98.

3-Acetamido-3-deoxy-β-D-glucose (IV).—Crude hydrochloride III was N-acetylated with acetic anhydride in water and methanol in the presence of either triethylamine

(2) H. Umezawa, *et al.*, *J. Antibiotics*, **A10**, 107, 181, 228 (1957).

(3) M. J. Cron, O. B. Fardig, D. L. Johnson, H. Schmitz, D. F. Whitehead, I. R. Hooper and R. U. Lemieux, *J. Am. Chem. Soc.*, **80**, 2342 (1958).

(4) M. J. Cron, D. L. Evans, F. M. Palermiti, D. F. Whitehead, I. R. Hooper, P. Chu and R. U. Lemieux, *ibid.*, **80**, 4741 (1958).

(5) H. Ogawa, T. Ito, S. Kondo and S. Inoue, *Bull. Agr. Chem. Soc. Japan*, **23**, 289 (1959).

(6) R. Kuhn and G. Baschang, *Ann.*, **628**, 206 (1959).

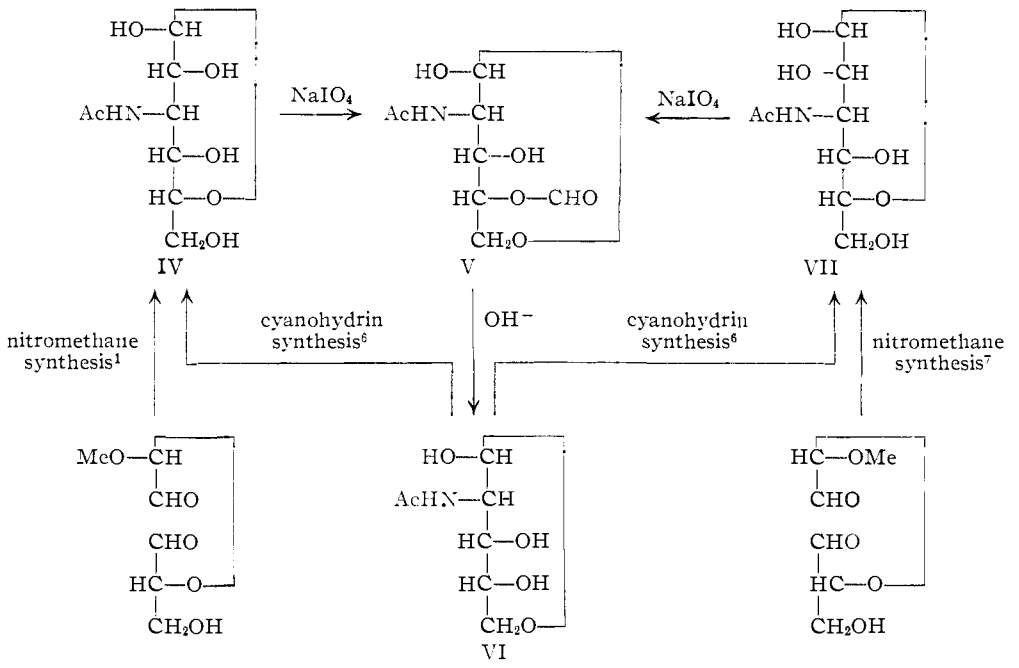
(7) H. H. Baer and H. O. L. Fischer, *J. Am. Chem. Soc.*, **82**, 3709 (1960).

(8) S. Peat and L. F. Wiggins, *J. Chem. Soc.*, 1810 (1938).

(9) Earlier, some compounds had been described, although not without reservations, to be 3-amino-3-deoxy-D-glucose derivatives [K. Freudenberg, O. Burkhart and E. Braun, *Ber.*, **59**, 714 (1926)]. However, they were recently shown to belong to the D-allose series [R. U. Lemieux and P. Chu, *J. Am. Chem. Soc.*, **80**, 4745 (1958); B. Coxon and L. Hough, *Chemistry & Industry*, 1249 (1959)].

(10) B. Lindberg and O. Theander, *Acta Chem. Scand.*, **13**, 1226 (1959).

(11) For paper chromatography Whatman No. 1 paper and the descending technique with pyridine–ethyl acetate–water–acetic acid (5:5:3:1) were used; *cf.* F. G. Fischer and H. Dörfel, *Z. physiol. Chem.*, **301**, 224 (1955). Melting points were taken with short-stem thermometers.



or sodium acetate[12a] or of Dowex-1 (carbonate form)[12b] according to known general procedures. Whereas all the three variants of acetylation afforded the same product, the method of Roseman and Ludowieg[12b] proved most satisfactory. To an ice-cooled, magnetically stirred solution of 167 mg. of crude III in 4.5 ml. of water and 0.6 ml. of methanol were added 5 ml. of Dowex-1 (CO_3^{--}) and 0.1 ml. of acetic anhydride. After 90 minutes the resin was filtered off and washed well with water, and the combined filtrates were stirred briefly with 2 ml. of Amberlite IR-120 (H^+). The colorless sirup of IV obtained upon evaporation was readily crystallized by heating with 0.5—1 ml. of moist ethanol, slow addition of hot ethyl acetate, and careful trituration of the white precipitate. The yield of washed (cold ethanol–ethyl acetate, 1:1) and dried IV that was chromatographically uniform and melted at 202–203° dec. was 129 mg. (75% based upon crude III). Recrystallization from boiling 85% aqueous ethanol gave fine, colorless needles showing $[\alpha]^{20}D$ +18.6° (2 min.) → +52.7° (8 hours, final; *c* 2.5 in water). The melting point of the recrystallized material, 204–205° dec., remained unchanged upon admixture of N-acetylkanosamine[3,13] or of an authentic specimen of synthetic 3-acetamido-3-deoxy-β-D-glucose.[6,14] The identity of IV with the two reference compounds was further established by comparison of the infrared spectra and X-ray diffraction patterns. On paper chromatograms[11] the three samples were indistinguishable from one another but clearly distinct from faster moving 3-acetamido-3-deoxy-D-mannose[7] and 3-acetamido-3-deoxy-D-gulose[15] (aniline hydrogen phthalate spray).

Compound IV reduced Fehling solution and was negative in the ninhydrin and Morgan–Elson color reactions.

2-Acetamido-2-deoxy-4-*O*-formyl-β-D-arabinose (V).—In an aqueous solution (5 ml.) of 50.1 mg. of the acetamidodeoxy glucose IV that had been allowed to attain rotational equilibrium ($\alpha^{20}D$ +0.53°, observed in a 1-dm. tube) was dissolved 48.5 mg. of well-powdered sodium metaperiodate. The solution became levorotatory immediately ($\alpha^{20}D$ −0.16°, −0.20°, −0.32° and −0.44°; after 2, 10, 45 and 120 minutes, respectively) and showed virtually constant readings of −0.49° after 5.5 hours. After 6 hours, 30 ml. of ethanol was added to precipitate most of the iodate; the solution was cooled for a short time at 0° and then filtered. The filtrate was evaporated *in vacuo* leaving a crystalline residue that was taken up in 5 ml. of warm absolute ethanol. After cooling, some remaining insoluble inorganic matter was removed and the solution was evaporated again, finally with the addition of ethyl acetate. The white crystalline residue (V) was recrystallized from 3 ml. of hot ethyl acetate–isopropyl alcohol (1:1); yield 30 mg. (60%) in several chromatographically uniform crops of prismatic needles, m.p. 155–156.5° dec., $[\alpha]^{20}D$ −96° (2 min.) → −64° (1 hour, final; *c* 0.5 in water). The chromatographic mobility of the formyl ester V is very similar to that of N-acetyl-D-ribosamine (!) and about 1.18 times greater than that of N-acetyl-D-arabinosamine.[11,16]

Anal. Calcd. for $C_8H_{13}NO_6$ (219.2): C, 43.83; H, 5.98; N, 6.40; *O*-acyl, 1 equiv. Found: C, 43.70; H, 6.51; N, 6.95; *O*-acyl, 1.12 (alkalimetric).

The compound was Morgan–Elson positive. The presence of a formyl ester group was indicated by a sharp band at 5.75 μ in the infrared spectrum, by the reduction of a warm mercuric chloride solution to yield insoluble mercurous chloride, and also by the following experiment.

A solution of 10 mg. of V in 2 ml. of water was stirred for one hour with 1 ml. of Amberlite CG-45(OH^-). The resin was filtered off and washed well with water. N-Acetylarabinosamine was detected chromatographically[11,16] in the filtrate. Formic acid was eluted from the resin with *N* ammonia; the eluate was strongly acidified with hydrochloric acid and the formic acid detected by means of the magnesium reduction test (formaldehyde formation) according to Finke.[17]

Similarly, a sample of the formyl ester V was treated with a slight excess of sodium bicarbonate in aqueous solution (1 hour at 23° and 15 minutes at 50°), deionized, and chromatographed. The ester had disappeared, and N-acetylarabinosamine was formed.

Upon acid hydrolysis of a sample of V (2 hours in 0.8 *N* HCl at 100°) chromatography revealed the formation of

(12) *Cf.* the N-acetylations of: (a) lactosamine hydrochloride [R. Kuhn and W. Kirschenlohr, *Ann.*, **600**, 135 (1956)] and various pentosamine hydrochlorides [R. Kuhn and G. Baschang, *ibid.*, **628**, 193 (1959)]; (b) glucosamine and galactosamine hydrochlorides [S. Roseman and J. Ludowieg, *J. Am. Chem. Soc.*, **76**, 301 (1954)].

(13) An authentic sample generously supplied by Dr. Hooper, Syracuse, N. Y., showed after one recrystallization m.p. 204–205° dec. and $[\alpha]^{22}D$ +18.1° (3 min.) → +52.5° (final; *c* 1.6 in water).

(14) The slightly lower values for m.p. and $[\alpha]D$ reported (ref. 6) were due to the presence of small amounts of the epimeric 3-acetamido-3-deoxy-D-mannose in the preparation. After further purification Dr. Baschang now finds m.p. 204–206° and $[\alpha]D$ +17.2° (2 min.) → +53.0° (final; in water; personal communication, Sept. 7, 1960).

(15) A. C. Richardson and H. O. L. Fischer, *Proc. Chem. Soc.*, 341 (1960).

(16) For the paper chromatography of aminodeoxy and acetamidodeoxy pentoses, see R. Kuhn and G. Baschang, ref. 12a. In all instances authentic samples were used for comparison.

(17) Quoted in Houben-Weyl, "Methoden der organischen Chemie," Vol. 11, Georg Thieme Verlag, Stuttgart, 1953, p. 944.

arabinosamine hydrochloride that is readily distinguished from the hydrochlorides of ribosamine, xylosamine and lyxosamine.[16]

2-Acetamido-2-deoxy-β-D-arabinose (VI) from IV.—For the preparation of crystalline N-acetyl-β-D-arabinosamine (VI) 80.2 mg. of 3-acetamido-3-deoxy-D-glucose (IV) in 10 ml. of water (equilibrium solution) was oxidized with 77.5 mg. of sodium metaperiodate as described above. However, the formyl ester produced was not isolated but was subjected, instead, to immediate hydrolysis with sodium bicarbonate as described earlier[7] for the periodate degradation of 3-acetamido-3-deoxy-β-D-mannose including the working-up of the resulting pentose. With the alkaline conditions involved being very mild no epimerization of the pentose was observed.[18] The yield of crude VI with m.p. 157–159° was 52.5 mg. (76%). After one recrystallization from 95% ethanol–ethyl acetate (1:1) the m.p. was 161–162° and a mixed m.p. with authentic 2-acetamido-2-deoxy-β-D-arabinose[7,12a] was 160–162°. The identity of VI with N-acetyl-β-D-arabinosamine was further confirmed by the infrared spectra and through chromatography.[16]

(18) *Cf.* B. Coxon and L. Hough, *Chemistry & Industry*, 374 (1960).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF ATHENS, GREECE]

On β-D-Glucosylamides of L-Amino Acids and of Nicotinic Acid

BY CHARALAMBOS COUTSOGEORGOPOULOS[1] AND LEONIDAS ZERVAS[2]

RECEIVED NOVEMBER 17, 1960

4,6-O-Benzylidene-D-glucose (I) is converted by methanolic ammonia into 4,6-O-benzylidene-D-glucosylamine (II). N-Acylation of II with the appropriate derivatives of L-amino acids and of nicotinic acid, followed by removal of the protective groups, yields the N-β-D-glucosylamides of L-phenylalanine (IVc), L-aspartic acid (IVd), L-glutamic acid (IVe) and of nicotinic acid (IVf).

Introduction

The increased interest in glycosylamines and N-acylated glycosylamines[3] has made desirable the development of general methods for their synthesis. These acyl derivatives, especially those derived from the L-amino acids, are of particular significance since it has been shown that N-ribosyl derivatives of glycinamide are intermediates in the biosynthesis of purines.[4]

Direct condensation of amides with sugars has not been accomplished, except in the special case of urea.[5] N-Acylglycosylamines have been isolated, in low yields, as by-products of the deacylation of fully O-acylated sugars with ammonia[6,7] or of the Wohl degradation of fully O-acylated aldonitriles.[7,8] The partial hydrolysis of the fully acylated glycosylamines has been used only in the preparation of N-acetylglycosylamines.[9-12] Similarly, selective N-monoacylation of free 1-amino sugars has been restricted to the N-monoacetyl compounds[9,11,13] and only recently a more general method, involving free glycosylamines as starting material, has been used[14] for the preparation of N-monoacetyl and N-monobenzoyl derivatives.

None of the above methods appears to be applicable to the synthesis of N-α-aminoacylglycosylamines and the only reported procedure[15] is a rather tedious one, involving the conversion of O-acylated glycosyl halides to O-acylated 1-amino sugars which are coupled with N-protected amino acids.

In the present work, 4,6-O-benzylidene-D-glucosylamine (II) is proposed as a new, readily available starting material for the general synthesis of N-acyl-D-glucosylamines and especially of N-(α-aminoacyl)-D-glucosylamines (IV). Compound II is obtained from 4,6-O-benzylidene-α-D-glucopyranose (I),[16] which represents a peculiar case of a sugar with an "acidic" glycosidic hydroxyl group capable of forming quite stable crystalline salts with alkali in aqueous solution.[16] In the same way, I dissolves immediately in ammonium hydroxide to form an ammonium salt, which according to findings of this Laboratory,[17] is slowly converted to the sparingly soluble 1-amino compound II. The yield is not high in this case, but the formation of the 1-amino sugar in aqueous ammonia is interesting, in view of the known sensitivity of the free 1-amino sugars to hydrolysis. The existence of a six-membered *m*-dioxane ring in I ap-

(1) This paper is based in part on the doctoral dissertation of Charalambos Coutsogeorgopoulos, Faculty of the Natural Sciences (Chemistry Section), University of Athens, Greece, 1958. Now at Department of Pharmacology, Yale University, School of Medicine, New Haven, Conn.

(2) This investigation was partly supported by the Royal Hellenic Research Foundation to which I am greatly indebted.

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(4) D. A. Goldthwait, R. A. Peabody and G. R. Greenberg, *J. Am. Chem. Soc.*, **76**, 5258 (1954); *J. Biol. Chem.*, **221**, 555, 1071 (1956); S. C. Hartman, B. Levenberg and J. M. Buchanan, *J. Am. Chem. Soc.*, **77**, 501 (1955); *J. Biol. Chem.*, **221**, 1057 (1956); J. M. Buchanan, in "The Nucleic Acids," ed. by E. Chargaff and J. N. Davidson, Vol. 3, Academic Press, Inc., New York, N. Y., 1960, p. 303.

(5) I. Goodman, *Adv. in Carbohydrate Chem.*, **13**, 215 (1958); B. Herlferich and W. Kosche, *Ber.*, **59**, 69 (1926); A. Hynd, *Biochem. J.*, **20**, 205 (1926); M. H. Benn and A. S. Jones, *J. Chem. Soc.*, 3837 (1960).

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(7) R. C. Hockett and L. B. Chandler, *J. Am. Chem. Soc.*, **66**, 957 (1944).

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