Anal. Calcd. for $C_{15}H_{23}O_7N$: C, 51.14; H, 7.59. Found: C, 51.16; H, 7.60.

3,6-Di-O-methyl-α-D-galactosamine hydrochloride (2-amino-2-deoxy-3,6-di-O-methyl-α-D-galactose) (IX). A solution of 95 mg. of VI in 3 ml. of 2*N* hydrochloric acid was heated in a sealed tube on a steam bath for 3 hr. After cooling, the reaction mixture was evaporated to dryness with additions of absolute ethanol and toluene to remove the last traces of acids and water. The quantitative yield of sirup was decolorized through a double layer of Darco G-60 and Celite and crystallized on standing (49 mg., 56%). Recrystallization from a mixture of methanol, acetone, and ether afforded clusters of small prisms, which darken at 157° and decompose above 170°; $[\alpha]_D^{24}$ + 132 (after 15 min.) to $[\alpha]_D^{25}$ + 121 ± 2° after 3 and 22 hr. (in water, *c* 0.5).

Anal. Calcd. for $C_8H_{18}O_5NCl$: C, 39.43; H, 7.44; Cl, 14.55. Found: C, 39.46; H, 7.58; Cl, 14.61.

2-Acetamido-2-deoxy-3,6-di-O-methyl-α-D-galactose (X). Acetylation of 98 mg. of 3,6-di-*O*-methyl-α-D-galactosamine hydrochloride (IX) was done at room temperature for 19 hr. in the presence of 1 ml. of methanol, 0.1 ml. of acetic anhydride, and 95 mg. of silver acetate. After the reaction mixture was filtered through a layer of Celite and the residue washed with 2 ml. of hot water, the filtrate and washings were treated with 2 drops of 2*N* hydrochloric acid. Filtration after 2 hr. and evaporation to dryness gave a quantitative yield of sirup. The sirup was chromatographed on silicic acid, and a fraction of 82 mg. of sirup was eluted with acetone. This was re-chromatographed and from a mixture of ethyl acetate and acetone 1:1 and pure acetone partially crystalline fractions were obtained (75 mg.). From 42 mg. of the above product, 7 mg. of 2-acetamido-2-deoxy-3,6-di-*O*-methyl-α-D-galactose was obtained as needles; m.p. 162–164°; $[\alpha]_D^{24}$ + 120 ± 2° (after 15 min.) to $[\alpha]_D^{24}$ + 97 ± 2° (after 21 hr., in water, *c* 0.39).

Anal. Calcd. for $C_{10}H_{19}O_6N$: C, 48.18; H, 7.68. Found: C, 48.12; H, 7.75.

2-Deoxy-2-(2'-hydroxynaphthylidenamino)-3,6-di-O-methyl-β-D-galactose (XI). A solution of 62 mg. of IX and 84 mg. of sodium acetate trihydrate in 1 ml. of water was treated as previously described[11,12] with 125 mg. of 2-hydroxynaphthaldehyde in 8 ml. of methanol. Purification was effected by silicic acid chromatography; the substance (66 mg., 72%) was eluted by ethyl acetate and a mixture of ethyl acetate and acetone. Crystallization from Methyl Cellosolve and ether yielded 40 mg. of prisms, m.p. 191–194°. A slow mutarotation was observed from $[\alpha]_{5461}^{25}$ + 96 ± 2° (after 1 hr.) to $[\alpha]_{5461}^{25}$ + 243 ± 3° after 140 and 145 hr. (in Methyl Cellosolve, *c* 0.19).

Anal. Calcd. for $C_{19}H_{23}O_6N$: C, 63.15; H, 6.41. Found: C, 63.07; H, 6.46.

Acknowledgment. The authors are indebted to Hoffmann-La Roche, Basel, for a generous gift of D-galactosamine hydrochloride.

BOSTON 14, MASS.

(12) R. W. Jeanloz, *J. Am. Chem. Soc.*, **74**, 4597 (1952)

[CONTRIBUTION FROM THE DEPARTMENT OF MEDICINE, HARVARD MEDICAL SCHOOL, AND THE MASSACHUSETTS GENERAL HOSPITAL]

3,6-Di-*O*-methyl-D-glucosamine Hydrochloride (2-Amino-2-deoxy-3,6-di-*O*-methyl-D-glucose Hydrochloride)[1]

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3,6-Di-*O*-methyl-D-glucosamine hydrochloride (2-amino-2-deoxy-3,6-di-*O*-methyl-D-glucose hydrochloride) has been synthesized from the known methyl 2-acetamido-2-deoxy-3-*O*-methyl-α-D-glucopyranoside and its free base was characterized by the crystalline *N*-acetyl and *N*-(2'-hydroxynaphthylidene) derivatives.

The synthesis of 3,6-di-*O*-methyl-D-glucosamine hydrochloride (XV) was undertaken in order to complete the series of the *O*-methyl ethers of 2-amino-2-deoxy-D-glucopyranose used as reference compounds in the determination of the structure of D-glucosamine containing natural products.[3–8]

Although this synthesis was completed seven years ago,[1] publication has been delayed until the final identification of side products was made. In addition, a derivative of 3,6-di-*O*-methyl-D-glucosamine has been recently isolated from the hydrolyzate of methylated α_1-acid glycoprotein of human serum.[9]

The route followed began with the previously described methyl 2-acetamido-2-deoxy-3-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (I)[6] by blocking position 4 with a benzoyl group to give II. The removal of the trityl group afforded III and subsequent methylation of the liberated primary

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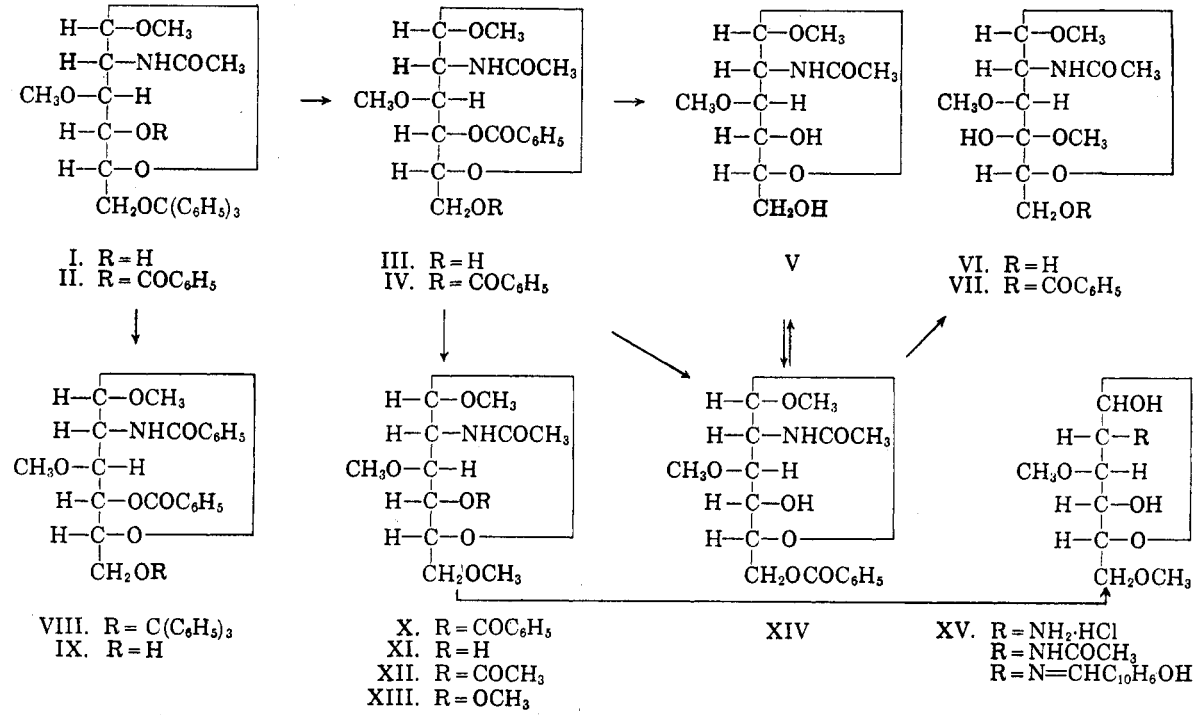

hydroxyl group gave X. Alkaline hydrolysis of the protective benzoyl group at C_4 gave methyl 2-acetamido-2-deoxy-3,6-di-*O*-methyl-α-D-glucopyranoside (XI), in an over-all yield of 44% from I to XI.

Side reactions occurred in two of the preceding steps. During benzoylation of the hydroxyl group at C_4, displacement of the acetyl group linked to the amino group by a benzoyl group occurred in a proportion of about 20%. The separation of the *N*-benzamido-4-*O*-benzoyl derivative VIII from the *N*-acetyl-4-*O*-benzoyl derivative II could not be effected easily by crystallization or chromatography, but the latter procedure was effective after the trityl groups had been removed from both compounds. The location of the second benzoyl group of IX on the amino group was shown by its resistance to alkaline hydrolysis and by the non-identity of IX with methyl 2-acetamido-4,6-di-*O*-benzoyl-3-*O*-methyl-α-D-glucopyranoside (IV). During the methylation of methyl 2-acetamido-2-deoxy-4-*O*-benzoyl-3-*O*-methyl-α-D-glucopyranoside (III), a secondary product was isolated, in addition to the expected X which was in a 65% yield. In an identical manner as shown first in the galactosamine series,[10] but to a smaller extent, the benzoyl group at position 4 migrates to the primary hydroxyl group. The product, a result of incomplete methylation, was shown to be methyl 2-acetamido-6-*O*-benzoyl-2-deoxy-3-*O*-methyl-α-D-glucopyranoside (XIV), since alkaline hydrolysis of it gave the known methyl 2-acetamido-2-deoxy-3-*O*-methyl-α-D-glucopyranoside (V),[3] and monobenzoylation of the latter compound gave back XIV. No 3,4-di-*O*-methyl-6-*O*-benzoyl derivative VII, which could have resulted from a further methylation of XIV, could be detected.

Methylation of XI afforded the known methyl 2-acetamido-2-deoxy-3,4,6-tri-*O*-methyl-α-D-glucopyranoside (XIII),[8] showing that no shift of the ring had occurred during the various transformations. Acid hydrolysis of XI produced the hydrochloride XV, which failed to crystallize. However, its free base was characterized by a crystalline *N*-acetyl derivative XVI and a crystalline Schiff's base with 2-hydroxynaphthaldehyde XVII.[11]

EXPERIMENTAL

Melting points were taken on a hot stage, equipped with a microscope, and correspond to "corrected melting point." Rotations were determined in semimicro or micro (for amounts smaller than 3 mg.) tubes with lengths of 100 or 200 mm., using a Rudolph Photoelectric Polarimeter Attachment, Model 200; the chloroform used was A.R. grade and contained approximately 0.75% of ethanol. Chromatograms were made with the flowing method using either silicic acid or alumina. The latter, "Alcoa Activated Alumina," Grade F-20, 80–200 mesh, a product of the Aluminum Ore Co. of America, East St. Louis, Ill., was washed with acetic acid, then with distilled water to a *p*H above 5.5, dried, and activated at 200° *in vacuo* for 24 hr. The silicic acid used for chromatograms was "Silica Gel Davison," from the Davison Co., Baltimore 3, Md. (grade 950; 60–200 mesh) without pretreatment. When deactivation by contact with moist air occurred, reactivation was obtained by heating to 170–200° (manufacturer's instructions). The sequence of eluants was hexane, benzene, ether, and methanol individually or in binary mixtures for alumina,

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and hexane, benzene or chloroform, ether, ethyl acetate, acetone, and methanol for silicic acid. The proportion of weight of substance to be adsorbed to weight of adsorbent was 1 to 20–30 for alumina, and 1 to 50–100 for silicic acid. The proportion of weight of substance in g. to volume of fraction of eluant in ml. was 1 to 100. The ratio of diameter to length of the column was 1 to 5 for alumina and 1 to 20 for silicic acid. Evaporations were carried out *in vacuo*, with an outside bath temperature kept below 45°. Amounts of volatile solvent smaller than 20 ml. were evaporated by blowing dry nitrogen. The microanalyses were done by Dr. K. Ritter, Basel, Switzerland.

Methyl 2-acetamido-4-O-benzoyl-2-deoxy-3-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (II). To a solution precooled at −20° of 1.18 g. of methyl 2-acetamido-2-deoxy-3-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (I)[6] in 10 ml. of anhydrous pyridine was added 1.0 ml. of benzoyl chloride. After standing 2 days at 0° the solution was poured into 100 ml. of chloroform and washed four times with a 5% cold solution of sodium bisulfate, three times with a saturated solution of sodium bicarbonate, then three times with water, dried over sodium sulfate, and evaporated. The remaining traces of pyridine were removed by codistillation with toluene. Crystallization from a mixture of acetone, ether, and pentane gave 1.35 g. (95%) of prismatic needles, m.p. 190–193°. After two recrystallizations, the m.p. was increased to 192–194°, $[\alpha]_D^{21}$ +111 ± 2° (in chloroform, *c* 0.87).

Anal. Calcd. for $C_{36}H_{37}O_7N$: C, 72.58; H, 6.26. Found: C, 72.02; H, 5.79.

The material melting at 190–193° contained a certain amount of methyl 2-benzamido-4-O-benzoyl-2-deoxy-3-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (VIII), as shown in the following experiment.

Methyl 2-acetamido-4-O-benzoyl-2-deoxy-3-O-methyl-α-D-glucopyranoside (III). To a hot solution of 500 mg. of crude II (m.p. 190–193°) in 16 ml. of glacial acetic acid was added dropwise 8 ml. of water. After heating for 1 hr. on the water bath, the solution was evaporated to dryness, the last traces of acetic acid being removed by codistillation with toluene. The dry residue was dissolved in benzene and chromatographed on silicic acid. Benzene and a mixture of benzene and ether 2:1 eluted 217 mg. of crude triphenylcarbinol. Ether and a mixture of ether and ethyl acetate 9:1 eluted 96 mg. (20%) of crystalline fractions. After recrystallization from a mixture of acetone, ether, and pentane, 86 mg. of crystalline needles were obtained, m.p. 167–168°, $[\alpha]_D^{23}$ +46 ± 2° (in chloroform, *c* 1.17). Based on the elementary analysis, the formula of *methyl 2-benzamido-4-O-benzoyl-2-deoxy-3-O-methyl-α-D-glucopyranoside* (IX) was attributed to this compound.

Anal. Calcd. for $C_{22}H_{25}O_7N$: C, 63.60; N, 6.07; N, 3.37. Found: C, 63.52; H, 5.96; N, 3.71.

Elution with pure ethyl acetate gave 220 mg. (75%) of crystalline fractions. The product III was recrystallized with difficulties from pure acetone, easily forming a gel. A m.p. of 143–147° was obtained with traces of material up to 155°; $[\alpha]_D^{23}$ +20 ± 1° (in chloroform, *c* 0.63).

Anal. Calcd. for $C_{17}H_{23}O_7N$: C, 57.78; H, 6.56. Found: C, 57.77; H, 6.66.

The product was probably contaminated by a trace of methyl 2-acetamido-6-O-benzoyl-2-deoxy-3-O-methyl-α-D-glucopyranoside (XIV) (see below).

Alkaline hydrolysis of 32 mg. of IX with barium methylate in the usual manner gave, after recrystallization from a mixture of methanol and ether, 22 mg. (90%) of *methyl 2-benzamido-2-deoxy-3-O-methyl-α-D-glucopyranoside* as short prisms, m.p. 189–190°, $[\alpha]_D^{24}$ +124 ± 3° (in methanol, *c* 1.05).

Anal. Calcd. for $C_{15}H_{21}O_6N$: C, 57.86; H, 6.80; N, 4.50. Found: C, 57.93; H, 6.96; N, 4.35.

Alkaline hydrolysis of 24 mg. of III with barium methylate in the usual manner gave, after recrystallization from a mixture of methanol and ether, 11 mg. (65%) of methyl 2-acetamido-2-deoxy-3-O-methyl-α-D-glucopyranoside (V), m.p. 209–212°. In admixture with authentic material,[3] it showed no depression of the melting point.

Methyl 2-acetamido-4-O-benzoyl-2-deoxy-3,6-di-O-methyl-α-D-glucopyranoside (X). A mixture of 210 mg. of III, 10 ml. of methyl iodide, and 500 mg. of silver oxide was shaken overnight. After filtration and washing the residue with acetone, the combined filtrates were evaporated to dryness and the residue treated in a similar manner with silver oxide and methyl iodide. The solution was filtered over Celite and Darco G-60 and gave, after evaporation, 240 mg. of sirup. It was crystallized from a mixture of acetone, ether, and pentane, affording 132 mg. (60%) of elongated prisms, m.p. 139–140°, $[\alpha]_D^{25}$ +48 ± 1° (in chloroform, *c* 1.13).

Anal. Calcd. for $C_{18}H_{25}O_7N$: C, 58.84; H, 6.86; OCH_3, 25.34. Found: C, 58.71; H, 6.70; OCH_3, 25.22.

The mother liquors were methylated again in a similar manner and gave an additional crop of 12 mg. of X (total yield 65%).

In one experiment where 1.33 g. of II was detritylated and the resulting sirup methylated without further purification, 97 mg. (11%) of crystalline material, insoluble in hot benzene, was obtained. Recrystallized from a mixture of chloroform and ether, it gave needles, m.p. 191–194°, $[\alpha]_D^{22}$ +85 ± 2° (in chloroform *c* 0.69). From its elementary analysis, the product was assumed to be *methyl 2-acetamido-6-O-benzoyl-2-deoxy-3-O-methyl-α-D-glucopyranoside* (XIV).

Anal. Calcd. for $C_{17}H_{23}O_7N$: C, 57.78; H, 6.56; OCH_3, 17.57. Found: C, 57.77; H, 6.51; OCH_3, 17.61.

In admixture with the product XIV described below, it showed no depression of the melting point.

Alkaline hydrolysis of 60 mg. of XIV with barium methylate in the usual manner gave 31 mg. (74%) of methyl 2-acetamido-2-deoxy-3-O-methyl-α-D-glucopyranoside (V), m.p. 218–220°, $[\alpha]_D^{27}$ +137 ± 2° (in methanol, *c* 0.89).

Anal. Calcd. for $C_{10}H_{19}O_6N$: C, 48.18; H, 7.68; OCH_3, 24.90. Found: C, 47.37; H, 7.89; OCH_3, 25.02. In admixture with authentic material,[3] the melting point was not depressed.

Methyl 2-acetamido-2-deoxy-3,6-di-O-methyl-α-D-glucopyranoside (XI). To a solution of 145 mg. of X in 2 ml. of methanol, cooled at 0°, was added 0.5 ml. of 1*N* barium methoxide. After standing overnight at 0°, the solution was deionized by passing through a column of Dowex 50 in the acid form and then evaporated to dryness. The crystalline residue was recrystallized from a mixture of methanol, ether, and pentane, to give 99 mg. (95%) of prismatic needles, m.p. 161–162°, $[\alpha]_D^{26}$ +129 ± 2° (in methanol *c* 0.80).

Anal. Calcd. for $C_{11}H_{21}O_6N$: C, 50.18; H, 8.04; OCH_3, 35.36. Found: C, 50.31; H, 8.12; OCH_3, 35.53.

Acetylation of 34 mg. of XI with pyridine and acetic anhydride in the usual manner gave the *4-O-acetyl* (XII) derivative. After recrystallization from a mixture of acetone, ether, and pentane, 38 mg. (97%) of fine needles were obtained, m.p. 163–164°, $[\alpha]_D^{24}$ +116 ± 2° (in chloroform, *c* 1.23).

Anal. Calcd. for $C_{13}H_{23}O_7N$: C, 51.14; H, 7.59. Found: C, 51.08; H, 7.72.

Twenty-eight milligrams of XI was refluxed for 1 day with 5 ml. of methyl iodide and 100 mg. of silver oxide. After filtration and evaporation, the residue was refluxed overnight with 5 ml. of methyl iodide and 200 mg. of silver oxide. After filtration and evaporation, the residue was dissolved in benzene and chromatographed on alumina. Elution with a mixture of benzene and ether 1:1, ether, and a mixture of ether and methanol 4:1 gave crystalline fractions. Recrystallization from a mixture of chloroform, ether, and pentane gave 22.5 mg. (76%) of methyl 2-acetamido-2-deoxy-3,4,6-tri-O-methyl-α-D-glucopyranoside (XIII), m.p. 155–156°, $[\alpha]_D^{25}$ +127 ± 3° (in chloroform, *c* 0.91). In admixture with authentic material (m.p. 153–154°; 167–168°)[6,8] the melting point was not depressed.

3,6-Di-O-methyl-D-glucosamine hydrochloride (*2-amino-2-deoxy-3,6-di-O-methyl-D-glucose hydrochloride*) (XV). A solu-

tion of 100 mg. of XI in 5 ml. of 3*N* hydrochloric acid was heated on the steam bath for 3 hr. After evaporation to dryness the residue was left in a desiccator over soda lime; then it was dissolved in methanol and filtered through Celite and Darco G-60 to give a quantitative yield of a colorless sirup; $[\alpha]_D^{26}$ +84 ± 1° (in water, *c* 1.09).

Anal. Calcd. for $C_8H_{15}O_5NCl$: C, 39.43; H, 7.44; Cl, 14.55; OCH_3, 25.47. Found: C, 39.34; H, 7.54; Cl, 14.52; OCH_3, 25.34.

2-Acetamido-2-deoxy-3,6-di-O-methyl-α-D-glucopyranose (XVI)[12]. The *N*-acetylation of XV was carried out with acetic anhydride in methanol in presence of silver acetate as previously described.[6] After recrystallization from a mixture of ethanol, ether, and pentane, the reaction of 11.7 mg. of XV gave 10 mg. (83%) of needles, m.p. 232–233°. The product showed mutarotation, from $[\alpha]_D^{25}$ +90° (after 15 min.) to $[\alpha]_D^{25}$ +35 ± 5° (after 24 hr., in water, *c* 0.29).

Anal. Calcd. for $C_{10}H_{19}O_6N$: C, 48.18; H, 7.68. Found: C, 48.35; H, 7.86.

2-Deoxy-2-(2'-hydroxynaphthylidenamino)-3,6-di-O-methyl-D-glycopyranose (XVII). A solution of 47 mg. of XV in 1 ml. of water was treated as previously described[6] with 90 mg. of 2-hydroxynaphthaldehyde and 25 mg. of sodium acetate trihydrate. Purification was obtained by chromatography on silicic acid. Elution with acetone and a mixture of acetone and methanol 4:1 gave crystalline fractions. The product being sparingly soluble in methanol was recrystallized from a mixture of pyridine and pentane to give 35 mg. (51%) of yellow prisms, m.p. 215–218° dec $[\alpha]_{5461}^{25}$ +305 ± 5° (at equilibrium, in methanol, *c* 0.15).

Anal. Calcd. for $C_{19}H_{23}O_6N$: C, 63.14; H, 6.41. Found: C, 63.16; H, 6.42.

Methyl 2-acetamido-4,6-di-O-benzoyl-2-deoxy-3-O-methyl-α-D-glucopyranoside (IV). To a solution precooled at −20° of 17 mg. of methyl 2-acetamido-2-deoxy-3-*O*-methyl-α-D-glucopyranoside (V)[3] in 1 ml. of anhydrous pyridine, was added 0.025 ml. of benzoyl chloride. After standing one day at 0°, the solution was diluted with chloroform, washed a few times each with 2*N* sulfuric acid, saturated sodium bicarbonate, then water, and dried over sodium sulfate. After evaporation, the residue was dissolved in benzene and chromatographed on silicic acid. Elution with a mixture of benzene and ether 2:1 and pure ether gave crystalline fractions. Recrystallization from a mixture of acetone, ether, and pentane gave 12 mg. (39%) of needles, m.p. 123–125°, $[\alpha]_D^{24}$ +85 ± 2° (in chloroform, *c* 0.74).

Anal. Calcd. for $C_{24}H_{27}O_8N$: C, 63.01; H, 5.95. Found: C, 62.56; H, 5.98.

Methyl 2-acetamido-6-O-benzoyl-2-deoxy-3-O-methyl-α-D-glucopyranoside (XIV)[13]. Twenty milligrams of V was cooled to −20° before addition of 0.20 ml. of pyridine and 0.01 ml. of benzoyl chloride previously cooled to −20°. After 1 day at 0°, 10 ml. of chloroform was added and the solution washed once with cold water, and twice each with cold 2*N* sulfuric acid, saturated sodium bicarbonate, and water. Concentration of the solution after drying over anhydrous sodium sulfate yielded 14 mg. (50%) that was crystallized from a mixture of chloroform and ether, m.p. 195–197°; $[\alpha]_D^{30}$ +84 ± 2° (in chloroform, *c* 0.39). In admixture with the product described above, the m.p. was not depressed.

Methyl 2-acetamido-6-O-benzoyl-2-deoxy-3,4-di-O-methyl-α-D-glucopyranoside (VII)[13]. To a cold solution of 10 mg. of methyl 2-acetamido-2-deoxy-3,4-di-*O*-methyl-α-D-glucopyranoside (VI)[6] in 0.1 ml. of pyridine was added 0.1 ml. of benzoyl chloride previously cooled to −20°. After standing overnight at 0° and at room temperature for an additional 24 hr., 10 ml. of chloroform was added and VII was isolated as outlined above for XIV. Crystallization from a mixture of chloroform and ether yielded 7 mg. (50%) of needles, m.p. 192–194°, $[\alpha]_D^{27}$ +110 ± 2° (in chloroform, *c* 0.25).

Anal. Calcd. for $C_{15}H_{25}O_7N$: C, 58.84; H, 6.86. Found: C, 58.79, H, 6.95.

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(12) This product was prepared by Dr. M. Cleland-Trémège and was described in thesis No. 1282 of the University of Geneva, Switzerland.

(13) This product was prepared by Dr. D. K. Stearns.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

The Anomers of Tetra-*O*-acetyl-2-deoxy-D-glucose

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The optically pure α- and β-anomers of tetra-*O*-acetyl-2-deoxy-D-glucose have been prepared for the first time by acetylation of 2-deoxy-D-glucose with acetic anhydride in pyridine, followed by fractional crystallization of the crude acetylation product. The β-anomer has been subjected to sulfuric acid catalyzed anomerization in 1:1 acetic anhydride–acetic acid solvent and found to yield a 91:9/α:β-anomer mixture. The anomerization using $10^{-3}M$ catalyst proceeded at a rate comparable to that of penta-*O*-acetyl-β-D-glucose using 0.5*M* catalyst, indicating an abnormally high rate of anomerization for the acetylated 2-deoxy-D-glucoses.

Although the 2-deoxyladoses constitute a chemically interesting and biologically important class of compounds[1] and although the first 2-deoxyhexose, 2-deoxy-D-glucose, was first described by Fischer in 1920,[2] the anomeric tetra-*O*-acetates of the latter substance appear to have been prepared only once. In 1949 Overend, Stacy and Staněk[3] reported the preparation of tetra-*O*-acetyl-2-deoxy-α-D-glucose, m.p. 91°, $[\alpha]_D^{20}$ +12.3° (C_2H_5OH) by acetylation of 2-deoxy-D-glucose with acetic anhydride in pyridine at 0°, and tetra-*O*-acetyl-2-deoxy-β-D-glucose, m.p. 75–78°, $[\alpha]_D^{20}$ +30° (C_2H_5OH) by acetylation with hot acetic anhy-

(1) *Cf.* W. G. Overend and M. Stacey, *Advances in Carbohydrate Chem.*, **8**, 45–105 (1953).

(2) E. Fischer, M. Bergmann, and H. Schotte, *Ber.*, **53**, 509 (1920); *cf.* also M. Bergmann, H. Schotte, and W. Lechinsky, *Ber.*, **55**, 158 (1922); **56**, 1052 (1923).

(3) W. G. Overend, M. Stacey, and J. Staněk, *J. Chem. Soc.*, 2841 (1949).