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Studies on Amino-hexoses. XVI. Synthesis of Deoxy-analogues of *N*-Acetyl-D-glucosamine

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For deoxy analogues of *N*-acetyl-D-glucosamine and three deoxy-analogues of phenyl *N*-acetyl-β-D-glucosaminide were synthesized by means of chlorination with sulfuryl chloride and reduction of the chlorides with tri-*n*-butyltin hydride. The free sugars thus obtained failed to crystallize except for 6-deoxy and 4,6-dideoxy compounds. Phenyl glycosides were mostly crystalline. The yield of chlorination and reduction was generally high.

As is well-known, many bacteria contain in their cell walls a polysaccharide composed of alternate *N*-acetyl-D-glucosamine and *N*-acetyl-muramic acid residues.[1] It is a substrate for the bacteriolytic enzymes of various origins among which hen egg white lysozyme is known to bind at its active site the substrate, some of the constituent monosaccharide units of which form hydrogen bondings with appropriate portions of the peptide bonds of the enzyme.[2] For a study of the mode of binding between the enzyme and the substrate, it may be interesting to use deoxy-analogues of the substrate as an inhibitor or a model substrate where the definite position of the saccharide is incapable of forming hydrogen bonding. Deoxy-analogues of *N*-acetyl-D-glucosamine are not known except for 6-deoxy-*N*-acetyl-D-glucosamine which was synthesized by Morel[3] and isolated later by Smith[4] from a bacterial polysaccharide. In the following the syntheses of 3-, 4-, 6-deoxy-, and 4,6-dideoxy-*N*-acetyl-D-glucosamine and phenyl glycosides of the former three compounds are described.

Results and Discussion

The routes of the synthesis are shown in Scheme 1 and 2. Partial acetylation of compound II gave compound III in a good yield, and its structure was confirmed by NMR spectrometry. The NMR spectra showed that one OH group (δ 2.87) and three acetyl groups(δ 1.9—2.2) existed. Threatment of II and III with sulfuryl chloride gave the respective chlorodeoxy derivatives. Jennings and Jones reported that 3-chlorodeoxy derivative could not be prepared by the reaction of sulfuryl chloride with alkyl 4,6-*O*-benzylidene-α-glucoside on account of 1,3-diaxial interaction between C–1 axial alkyl group and chloride ion attacking C–3 from an axial direction.[5] The rule held also for the derivatives of *N*-acetyl-glucosaminide, although it had neiboring *trans* acetamide group. Thus, benzyl 2-acetamido-2-deoxy-β-D-glu-

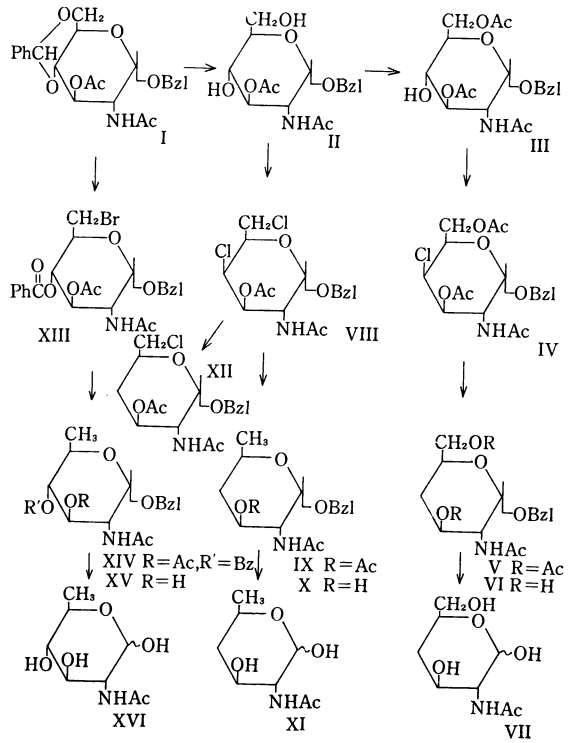
1) M. R. Salton, "The Bacterial Cell Wall," Elsevier Publishing Co., New York, N. Y. (1964).

2) C. C. F. Blake, L. N. Johnson, G. A. Mair, A. C. T. North, D. C. Phillips, and V. R. Sarma, *Proc. Roy. Soc. Ser. B*, **167**, 378 (1967).

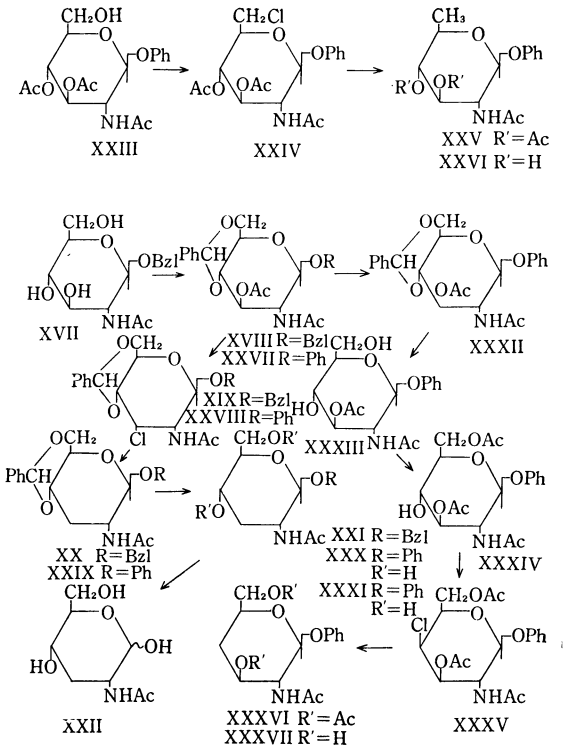
3) C. J. Morel, *Helv. Chim. Acta*, **41**, 1501 (1958).

4) E. J. Smith, *J. Biol. Chem.*, **243**, 5139 (1968).

5) H. J. Jennings and J. K. N. Jones, *Can. J. Chem.*, **43**, 2372 (1965).



Scheme 1.



Scheme 2.

copyranoside(XVII) reacted with sulfuryl chloride to give the chlorodeoxy derivative, but benzyl 2-acetamido-2-deoxy-α-D-glucopyranoside did not give the expected product. Hannesian was successful in obtaining 6-bromo-6-deoxy derivative by the cleavage of 4,6-*O*-benzylidene group with *N*-bromosuccinimide (NBS).[6] This reaction was applied for obtaining XIII from I. Reduction of the deoxyhaloderivatives was successfully performed with tri-*n*-butyltin hydride and α,α'-azobisisobutyronitrile(AIBN). Selectivity between primary and secondary halides of the reduction with tri-*n*-butyltin hydride was observed previously.[7] VIII was then selectively reduced at C-4 under appropriate reaction conditions. NMR spectrometry of XII showed that primary halogen was hardly reduced. The structures of the reduced substances were confirmed by NMR spectrometry (Figs. 1 and 2).

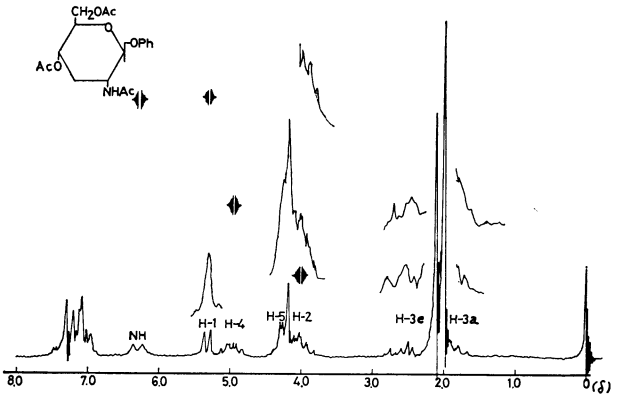


Fig. 1. The NMR spectrum of XXXI in $CDCl_3$.

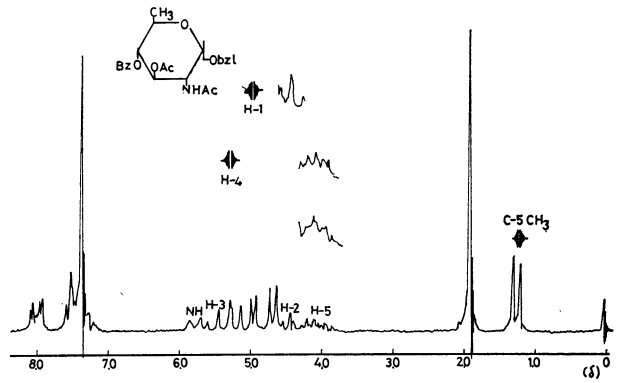


Fig. 2. The NMR spectrum of XIV in $CDCl_3$.

NMR spectra of XIV was assigned as follows. Irradiation at δ 1.20(C-5 CH_3) caused the octet of H-5 at δ 4.10 to collapse to a doublet. Irradiation at δ 5.20(H-4) caused it to collapse to a quartet. Irradiation at δ 4.86(H-1) simplified the region δ 4.35—4.5, which was expected to be H-2 proton signal. NMR spectra of XXXI were assigned as follows. Irradiation at δ 5.0(H-4) simplified the region δ 4.2—4.4 and δ 1.7—2.8. The former was assigned as a H-5 proton signal and the latter as H-3a, H-3e from the irradiation and decoupling data. Irradiation at δ 6.35(NH) and δ 5.35(H-1) simplified the region δ 3.8—4.2, which was expected to be H-2 proton singal. Irradiation at δ 4.10(H-2) caused the doublet of H-1 at δ 5.35 to collapse to a singlet.

6) S. Hannessian, *Carbohyd. Res.*, **2**, 86 (1966).
7) H. Arita, N. Ueda, and Y. Matsushima, This Bulletin, **45**, 567 (1972).

Experimental

General Methods. All the melting points were uncorrected. Nuclear magnetic resonance spectra were recorded with a Varian T-60 spectrometer. The specimens were dissolved in chloroform-d with tetramethylsilane as an internal standard. Thin layer chromatography (tlc) was carried out with Silica gel G(Merck). The spots were detected by spraying with 5% sulfuric acid in methanol and heating. As detection of the 3-deoxy derivatives of *N*-acetyl-D-glucosamine could not be made by this method, they were detected on a plate treated with fluorescein(DC-Fertigplatten Kieselgel F 254). Silica gel column chromatography was carried out with silicic acid (100 mesh, Mallinckrodt) with a solvent system toluene–ethyl acetate(1 : 1) as an eluant. Tri-*n*-butyltin hydride was prepared by the thermal decomposition of tri-*n*-butyltin formate.[8]

Benzyl 2-Acetamido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside(I) Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside(20 g)[9] was dissolved in a mixture of pyridine(150 m*l*) and acetic anhydride(20 m*l*). The solution was kept at room temperature overnight. The solvent was evaporated *in vacuo*, and the residual pyridine was removed by co-distillation with dry toluene. Crystallization took place in ethanol, and recrystallization in the same solvent gave colorless needles(18.5 g), mp 215—216°C. Found: C, 65.35; H, 6.08; N, 3.24%. Calcd for $C_{24}H_{27}O_7N$: C, 65.29; H, 6.16; N, 3.17%.

Benzyl 2-Acetamido-3-O-acetyl-2-deoxy-α-D-glucopyranoside(II). Compound I (16.0 g) was dissolved in 80% aqueous acetic acid (600 m*l*) and the solution was kept at 65—70°C for 2 hr. Evaporation of the solvent *in vacuo* gave a syrup. The residual solvent in the syrup was co-distilled several times with dry toluene. The crystals appeared in toluene (9.0 g), mp 113—116°C. Found: C, 57.79; H, 6.51; N, 3.96%. Calcd for $C_{17}H_{23}O_7N$: C, 57.78; H, 6.56; N, 3.93%.

Benzyl 2-Acetamido-3,6-di-O-acetyl-2-deoxy-α-D-glucopyranoside (III) Compound II (15.0 g) was dissolved in a mixture of pyridine(30 m*l*) and chloroform(50 m*l*). The solution was cooled in a dry ice-acetone bath, and acetic anhydride (2.7 m*l*) was added to the solution. The reaction was continued at −20°C for 48 hr. Evaporation *in vacuo* gave a syrup which was subsequently passed through a column of silica gel. The fractions which contained compound III were collected and dried *in vacuo* to give a syrupy product (9.8 g). $[\alpha]_D^{20}+80°$ (*c* 1.0, chloroform) Found: C, 59.12; H, 6.42; N, 3.43%. Calcd for $C_{19}H_{25}O_8N$: C, 57.71; H, 6.37; N, 3.54%. NMR (in $CDCl_3$) δ2.87(1H, s, OH) 4.92 (1H, d, *J* 3Hz H-1) 5.85 (1H d, *J* 8Hz NH) 2.12 (3H s, NAc) 1.98(3H s, 3–O–Ac) 2.08(3H s, 6–O–Ac)

Benzyl 2-Acetamido-3,6-di-O-acetyl-4-chloro-2,4-dideoxy-α-D-galactopyranoside(IV). Compound III (9.4 g) was dissolved in pyridine (50 m*l*) and the solution was cooled in an ice-water bath. Sulfuryl chloride(2.4 m*l*) was then added to the solution, and the mixture was kept in a refrigerator overnight and then kept at room temperature for 3 hr. Excess solvent was removed by evaporation *in vacuo*, and the residue was extracted with chloroform and the extract was washed with water several times. The chloroform layer was collected and dried *in vacuo* to a syrup which crystallized in toluene. Recrystallization in the same solvent gave colorless crystals(5.5 g); mp 132—133°C, $[\alpha]_D^{20}+159°$ (*c* 1.03, chloroform). Found: C, 55.32; H, 5.85; N, 3.38; Cl, 8.76%. Calcd for $C_{19}H_{24}O_7NCl$: C, 55.14; H, 5.85; N, 3.38; Cl, 8.57%.

Benzyl 2-Acetamido-3,6-di-O-acetyl-2,4-dideoxy-α-D-xylohexopyranoside(V) Compound IV (2.5 g) was dissolved in dry toluene(30 m*l*) under nitrogen atmosphere. To this solution were added tri-*n*-butyltin hydride(3.0 m*l*) and AIBN (*ca.* 30 mg). The reaction was continued for 2 hr at 80—90°C under stirring. The solution was dried *in vacuo* to give a syrup, which was passed through a column of silica gel with a solvent system (toluene–ethyl acetate 1 : 1) as an eluant. The product was crystallized in ethanol. Recrystallization in the same solvent gave needles(1.9 g); mp 105—107°C, $[\alpha]_D^{20}+101°$ (*c* 0.87, chloroform). Found: C, 59.80; H, 6.59; N, 3.63%. Calcd for $C_{15}H_{21}O_5N$: C, 60.14; H, 6.64; N, 3.63%. NMR (in $CDCl_3$) δ4.93 (1H d, *J* 3 Hz H-1) 5.70 (1H d, NH) 1.4—2.1(H-4a,e) 2.05 (3H s, NAc) 1.95 (3H s, 6-OAc) 1.84(3H s, 3-OAc).

Benzyl 2-Acetamido-2,4-dideoxy-α-D-xylohexopyranoside (VI). Compound V(1.23 g) was deacetylated with 0.1 M sodium methoxide in methanol, and the solution was treated with Dowex 50×8 (H^+) to remove sodium ion. Evaporation of methanol *in vacuo* gave crystals, which were recrystallized in ethanol giving 700 mg of a colorless specimen. Mp 170.5—171°C. Found: C, 60.87; H, 7.16; N, 4.68%. Calcd for $C_{15}H_{21}O_5N$: C, 61.00; H, 7.17; N, 4.74%.

2-Acetamido-2,4-dideoxy-D-xylohexopyranose (VII). Compound VI (650 mg) was dissolved in ethanol (50 m*l*) and 10% palladium on charcoal (2.0 g) was added to the solution. Hydrogen was passed through the solution for three days at room temperature. The charcoal was filtered off, and the filtrate was dried *in vacuo* to give 300 mg of a syrup which did not crystallize. $[\alpha]_D^{20}+78°$ (*c* 1.58, water). Found: C, 46.71; H, 7.43; N, 6.57%. Calcd for $C_8H_{15}O_5N$: C, 46.82; H, 7.37; N, 6.83%.

Benzyl 2-Acetamido-3-O-acetyl-4,6-dichloro-2,4,6-trideoxy-α-D-galactopyranoside (VIII). Compound II (4.0 g) was dissolved in pyridine (30 m*l*) and the solution was cooled in an ice-water bath. Sulfuryl chloride(2.3 m*l*) was then added dropwise to the solution. The reaction solution was kept in a refrigerator overnight and then kept at room temperature for 3 hr. Excess pyridine was removed by evaporation. The residue was extracted with chloroform and the extract washed with water several times. The chloroform layer was dried *in vacuo*. The residue was extracted with boiling toluene several times, and the extracts were dried *in vacuo*. Recrystallization in ethanol gave colorless needles(2.8 g); mp 158—160°C, $[\alpha]_D^{20}+128°$ (*c* 1.0, chloroform). Found: C, 52.49; H, 5.44; N, 3.61; Cl, 18.13%. Calcd for $C_{17}H_{21}O_5NCl_2$: C, 52.32; H, 5.42; N, 3.59; Cl, 18.17%. NMR (in $CDCl_3$) δ4.93 (1H, d, *J* 3 Hz H-1)) 5.70 (1H d, NH) 2.05 (3H s, NAc) 1.87 (3H s, 3-O-Ac)

Benzyl 2-Acetamido-3-O-acetyl-2,4,6-trideoxy-α-D-xylohexopyranoside (IX). Compound VIII (1.8 g) was dissolved in dry toluene (30 m*l*) under nitrogen atmosphere. To this solution was added tri-*n*-butyltin hydride (2.0 m*l*) and AIBN (*ca.* 20 mg). The reaction mixture was refluxed for 24 hr. The solution was then dried *in vacuo*. The residual sirup was dissolved in ligroin (10 m*l*) and the solution was kept in a refrigerator overnight. Crystals were obtained and washed with cold ligroin and recrystallized in the same solvent giving 1.5 g of the specimen. Mp 122—123°C, $[\alpha]_D^{20}+106°$ (*c* 1.15, chloroform). Found: C, 62.18; H, 7.06; N, 4.29%. Calcd for $C_{17}H_{23}O_5N$: C, 63.53; H, 7.21; N, 4.36%. NMR (in $CDCl_3$) δ4.93 (1H d, *J* 3 Hz H-1) 1.75—2.2 (1H H-4e) 1.3—1.6 (1H H-4a) 3.7—4.1 (1H m, H-5) 5.83 (1H d, NH) 2.0 (3H s, NAc) 1.9 (3H 3-O-Ac) 1.28 (3H d, *J* 6 Hz CH_3-5).

8) R. Okawara and M. Ohara, *J. Organometal. Chem.*, **3**, 484 (1965).

9) R. Kuhn, H. H. Baer, and A. Seeliger, *Ann.*, **611**, 236 (1958).

Benzyl 2-Acetamido-2,4,6-trideoxy-D-xylohexopyranoside (X). Compound IX (500 mg) was deacetylated with *ca.* 0.1 M sodium methoxide in methanol by the same manner as described for VI. Recrystallization in ethanol gave colorless crystals; mp 183—185°C, $[\alpha]_D^{20}+107°$ (*c* 1.03, methanol). Found: C, 63.96; H, 7.56; N, 4.98%. Calcd for $C_{15}H_{24}O_4N$: C, 64.49; H, 7.58; N, 5.01%.

2-Acetamido-2,4,6-trideoxy-xylohexopyranose (XI). Compound X (300 mg) in 2-propanol (50 ml) was reduced with hydrogen over 10% palladium on charcoal (1.5 g) at room temperature. The reaction was complete within 20 hr and charcoal was filtered off, the filtrate being dried *in vacuo*. Crystallization took place in ethanol–ethyl acetate, and recrystallization in the same solvent gave colorless needles; mp 147—150°C, $[\alpha]_D^{20}+88°$ (*c* 0.43, water). Found: C, 47.17; H, 8.07; N, 6.82%. Calcd for $C_8H_{15}O_4N\cdot H_2O$: C, 46.37; H, 8.27; N, 6.76%.

Benzyl 2-Acetamido-3-O-acetyl-6-chloro-2,4,6-trideoxy-α-D-xylohexopyranoside (XII). Compound VIII (1.3 g) was dissolved in dry toluene (30 ml) under nitrogen atmosphere, and to the solution were added tri-*n*-butyltin hydride (1 ml) and AIBN. The reaction was continued for 1 hr at 80—90°C under stirring. Evaporation *in vacuo* gave a product which was washed with cold ligroin several times. Recrystallization in ethanol gave colorless needles (800 mg); mp 121—126°C, $[\alpha]_D^{20}+136°$ (*c* 1.0, chloroform). Found: C, 58.27; H, 6.32; N, 4.04; Cl, 8.83%. Calcd for $C_{17}H_{22}O_5NCl$: C, 57.55; H, 6.25; N, 3.95; Cl, 9.71%.

Benzyl 2-Acetamido-3-O-acetyl-4-O-benzoyl-6-bromo-2,6-dideoxy-α-D-glucopyranoside (XIII). Compound I (5.0 g) was dissolved in a mixture of carbon tetrachloride (100 ml) and tetrachloroethane (40 ml). To this solution were added NBS (2.25 g) and barium carbonate (10 g). The reaction mixture was refluxed for 1.5 hr. Insoluble substances were filtered off, the brown filtrate was extracted with chloroform and the extract washed with water several times. The solvent was evaporated *in vacuo* to a syrup. The product was found in tlc to be contaminated with the starting material (compound I). The syrup was thus treated with 80% aqueous acetic acid at 70°C for 2 hr to remove benzylidene group from the remaining compound I. Evaporation *in vacuo* gave a syrup, which was subsequently placed on a silica gel column and eluated with a solvent system (ethyl-acetate–toluene 1 : 1). The product (1.4 g) did not crystallize, although it was shown on tlc to be highly pure. $[\alpha]_D^{20}+27°$ (*c* 0.99, chloroform). Found: C, 55.77; H, 5.26; Br, 13.71%. Calcd for $C_{24}H_{26}O_7NBr$: C, 55.41; H, 5.04; Br, 15.36%.

Benzyl 2-Acetamido-3-O-acetyl-4-O-benzoyl-2,6-dideoxy-α-D-glucopyranoside (XIV). Compound XIII (800 mg) was dissolved in dry toluene under nitrogen atmosphere, and to this solution were added tri-*n*-butyltin hydride (1 ml) and AIBN (*ca.* 20 mg). The reaction mixture was refluxed overnight, and the solution was dried in vacuo. The residual syrup was dissolved in ligroin (5 ml) and the solution was kept in a refrigerator overnight. Crystals were obtained and were washed with cold ligroin several times. Purity of the crystals did not improve by recrystallization, and they were subjected to silica gel column chromatography. Colorless crystals were obtained (440 mg); mp 144—146°C, $[\alpha]_D^{20}+57°$ (*c* 0.90, chloroform). Found: C, 65.49; H, 6.23; N, 3.23%. Calcd for $C_{24}H_{27}O_7N$: C, 65.29; H, 6.16; N, 3.17%. NMR (in $CDCl_3$) δ 4.86 (1H d, *J* 3 Hz H-1) 4.3—4.5 (1H unresolved H-2) 5.4 (1H unresolved H-3) 5.3 (H-4) 4.1 (H-5)1.20 (3H d, *J* 6 Hz CH_3-5) 1.88 (3H s, NAc) 1.88 (3H s, 3-OAc) 5.78 (1H d, NH)

2-Acetamido-2,6-dideoxy-glucopyranose (XVI). Compound XIV (400 mg) was treated with *ca.* 0.1 M sodium methoxide in methanol, and the solution was neutralized with acetic acid. Ten percent palladium on charcoal (1.0 g) was added to this solution, and hydrogen was led in for 24 hr at room temperature. The charcoal was filtered off, and the filtrate was passed through a column of Dowex 50X 8 (H^+). The eluant was dried *in vacuo*, and the residue crystallized immediately; mp 207—210°C, $[\alpha]_D^{20}+26.4°$ (*c* 1.0, water). Found: C, 47.01; H, 7.42; N, 6.76%. Calcd for $C_8H_{15}O_5N$: C, 46.82; H, 7.37; N, 6.83%. NMR (in D_2O) δ5.05 (1H d, *J* 3 Hz H-1) 1.25 (3H d, *J* 6 Hz CH_3-5) 2.0 (3H s, NAc)

Benzyl 2-Acetamido-2-Deoxy-β-D-glucopyranoside (XVII).[10] Pentaacetyl glucosamine (20.0 g) was dissolved in glacial acetic acid saturated with HBr (100 ml) and the solution was kept at room temperature overnight under stirring. The solution was extracted with chloroform and the extract was washed with water and aqueous sodium bicarbonate several times.[11] The chloroform layer was dried over sodium sulfate. To this solution was added benzyl alcohol (15 ml), Drierite (20 g) and silver carbonate (15 g), and the mixture was kept at room temperature in the dark under vigorous stirring. The insoluble substances were filtered off, and the filtrate was dried *in vacuo* to a syrup. Crystallization took place in ethanol. Recrystallization in the same solvent gave colorless needles (12.5 g); mp 162—164°C, $[\alpha]_D^{20}-54°$ (*c* 1.23, chloroform). The specimen was subsequently deacetylated with *ca.* 0.1 M sodium methoxide in methanol. Recrystallization in 2-propanol gave colorless needles (6.5 g); mp 191—192°C $[\alpha]_D^{20}-29°$ (*c* 0.93, water). Found: C, 57.83; H, 6.80; N, 4.52%. Calcd for $C_{15}H_{21}O_6N$: C, 57.86; H, 6.80; N, 4.50%.

Benzyl 2-Acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (XVIII). Compound XVII (6.5 g) was mixed with benzaldehyde (50 ml). To this was added zinc chloride (6.5 g), and the mixture was shaken at room temperature overnight. The homogeneous solution thus obtained was poured into ice-water and the precipitates were washed with water and ligroin several times. Recrystallization in ethanol gave a crystalline product (6.7 g) which decomposed over 200°C. Found: C, 63.13; H, 6.64; N, 3.59%. Calcd for $C_{22}H_{25}O_6N$: C, 66.15; H, 6.31; N, 3.51%. Though the specimen was crystalline, its benzylidene residue gradually split for some unknown reason even in the solid state. As a result the analytical value of carbon was far less than the theoretical one.

Benzyl 2-Acetamido-3-chloro-4,6-O-benzylidene-2,3-dideoxy-β-D-allopyranoside (XIX). Compound XVIII (6.0 g) was dissolved in pyridine (150 ml) and the solution was cooled in an ice-water bath. Sulfuryl chloride (1.6 ml) was added to the solution, and the reaction mixture was kept in a refrigerator for 2 hr and then at room temperature overnight. Excess pyridine was removed by evaporation. The residue was extracted with chloroform and the extract was washed with water several times. The chloroform layer was dried *in vacuo* to a syrup, which was immediately crystallized in ethanol. Recrystallization in the same solvent gave colorless crystals (2.0 g); mp 205°C (decomp.), $[\alpha]_D^{20}-87°$ (*c* 0.87, chloroform). Found: C, 63.38; H, 5.85; N, 3.39; Cl, 8.17%. Calcd for $C_{22}H_{24}O_5NCl$: C, 63.23; H, 5.79; N, 3.35; Cl, 8.48%.

Benzyl 2-Acetamido-4,6-O-benzylidene-2,3-dideoxy-β-D-ribo-hexopyranoside (XX). Compound XIX (700 mg) was dissolved in dry toluene under nitrogen atmosphere. To this solution were added tri-*n*-butyltin hydride (1.0 ml) and

10) R. Kuhn and W. Kirschenlohr, *Chem. Ber.*, **86**, 1331 (1953).
11) Y. Inouye, K. Onodera, S. Kitaoka, and H. Ochiai, *J. Amer. Chem. Soc.*, **79**, 4218 (1957).

AIBN (*ca.* 20 mg). The reaction was complete within 15 min, and the product obtained immediately as white needles was collected and washed with ligroin several times. Recrystallization in methanol gave colorless needles (620 mg); mp 246°C (decomp.) Found: C, 68.73; H, 6.59; N, 3.72%. Calcd for $C_{22}H_{25}O_5N$: C, 68.91; H, 6.57; N, 3.65%.

2-Acetamido-2,3-dideoxy-ribohexopyranose (XXII). Compound XX (50 mg) was dissolved in 80% aqueous acetic acid (300 m*l*) and the solution was kept at 65—70°C for 2 hr. The clear solution was evaporated *in vacuo* to a syrup, which was dissolved in cold water (5 m*l*). Insoluble substances were filtered off. To the filtrate was added 10% palladium on charcoal (1.5 g) and hydrogen was passed into the solution at room temperature. The reduction was complete within 24 hr, and charcoal was removed. The filtrate was dried *in vacuo* to a syrup, which did not crystallize. $[\alpha]_D^{20}$ −6.5° (*c* 2.15, H_2O). Found: C, 45.36; H, 7.32; N, 6.73; Calcd for $C_8H_{15}O_5N$: C, 46.82; H, 7.37; N, 6.83.

*Phenyl 2-Acetamido-3,4-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranoside (XXIII).* Compound XXIII was prepared from phenyl 2-acetamido-6-*O*-trityl-3,4-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside according to the method of Mega *et al.*[12] Mp 228—229°C $[\alpha]_D$ −10.8° (*c* 0.5, chloroform).

*Phenyl 2-Acetamido-3,4-di-*O*-acetyl-6-chloro-2,6-dideoxy-β-*D*-glucopyranoside (XXIV).* Compound XXIII (2.0 g) was dissolved in pyridine (20 m*l*) and the solution was cooled in an ice-water bath. To this solution was added sulfuryl chloride (0.56 m*l*) and the reaction mixture was kept in a refrigerator overnight and then at room temperature for 3 hr. Excess pyridine was removed by evaporation *in vacuo*, and the residue was extracted with chloroform and the extract washed with water several times. Chloroform layer was dried *in vacuo* to a syrup. The syrup crystallized in ethanol, and recrystallization in the same solvent gave colorless needles; (800 mg); mp 190°C (decomp.), $[\alpha]_D^{20}$ −15° (*c* 0.93, chloroform). Found: C, 53.55; H, 5.55; N, 3.53; Cl, 8.71%. Calcd for $C_{18}H_{22}O_7NCl$: C, 54.07; H, 5.55; N, 3.50; Cl, 8.87%.

*Phenyl 2-Acetamido-3,4-di-*O*-acetyl-2,6-dideoxy-β-*D*-glucopyranoside (XXV).* Compound XXIV (750 mg) was dissolved in dry toluene (50 m*l*). To this were added tri-*n*-butyltin hydride (0.8 m*l*) and AIBN (*ca.* 20 mg). The reaction was continued overnight at 80—90°C with stirring. The solvent was evaporated *in vacuo* to a syrup, which crystallized immediately. Recrystallization in ethanol gave a colorless product (700 mg); mp 200°C (decomp.), $[\alpha]_D^{20}$+48° (*c* 1.03, chloroform). Found: C, 58.08; H, 6.23; N, 3.68%. Calcd for $C_{18}H_{23}O_7N$: C, 59.18; H, 6.33; N, 3.83%.

*Phenyl 2-Acetamido-2,6-dideoxy-β-*D*-glucopyranoside (XXVI).* Compound XXV (510 mg) was deacetylated with sodium methoxide by the same method as described for VI. Recrystallization in 2-propanol gave colorless needles (1.34 mg); mp 210°C (decomp.), $[\alpha]_D^{20}$ −16° (*c* 0.7, methanol). Found: C, 58.31; H, 6.53; N, 4.96%. Calcd for $C_{14}H_{19}O_5N$: C, 58.77; H, 6.81; N, 4.98%.

*Phenyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-*D*-glucopyranoside (XXVII).*[13] Phenyl 2-acetamido-2-deoxy-β-D-glucopyranoside (5.0 g)[14] was reacted with benzaldehyde (30 m*l*) and zinc chloride (5.0 g) at room temperature overnight. The solution was poured into ice-water and the precipitates were washed with water and ligroin several times. Recrystallization in ethanol gave colorless needles (5.5 g) which decomposed at 250°C. Found: C, 65.32; H, 6.00; N, 3.61%. Calcd for $C_{21}H_{23}O_6N$: C, 65.44; H, 6.02; N, 3.63%.

*Phenyl 2-Acetamido-3-chloro-4,6-*O*-benzylidene-2,3-dideoxy-β-*D*-allopyranoside (XXVIII).* Compound XXVII (4.0 g) was dissolved in pyridine (150 m*l*). To this solution was added sulfuryl chloride (1.0 m*l*) under cooling in an ice-water bath. The reaction solution was kept in a refrigerator overnight and then at room temperature for 10 hr. The solvent was removed by evaporation *in vacuo* and the residue was extracted with chloroform and the extract washed with water several times. The chloroform layer was separated and dried *in vacuo*, and the residue was crystallized in methanol–water (4 : 1). Recrystallization in the same solvent mixture gave colorless needles (1.2 g); mp 184°C (decomp.), $[\alpha]_D^{20}$ −24° (*c* 1.0, chloroform). Found: C, 62.20; H, 5.50; N, 3.49; Cl, 8.85. Calcd for $C_{21}H_{22}O_5NCl$: C, 62.45; H, 5.49; N, 3.47; Cl, 8.87.

*Phenyl 2-Acetamido-4,6-*O*-benzylidene-2,3-dideoxy-β-*D*-ribohexopyranoside (XXIX).* Compound XXVIII (516 mg) was dissolved in dry toluene (100 m*l*). To the solution were added tri-*n*-butyltin hydride (0.5 m*l*) and AIBN (*ca.* 20 mg) at 90°C under stirring. The reaction was complete within 10 min. White precipitates were obtained and were filtered off and washed with ligroin several times. Recrystallization in methanol gave colorless needles (476 mg); mp 250°C. Found: C, 67.46; H, 6.24; N, 3.75%. Calcd for $C_{21}H_{23}O_5N$: C, 68.28; H, 6.28; N, 3.79%.

*Phenyl 2-Acetamido-2,3-dideoxy-β-*D*-ribohexopyranoside (XXX).* Compound XXIX (470 mg) was dissolved in 80% aqueous acetic acid (300 m*l*) and the solution was kept at 65—70°C for 2 hr. The solution was evaporated *in vacuo*, and the residual syrup was dissolved in water (5 m*l*). Insoluble substances were removed by filtration, and the filtrate was dried *in vacuo*. Crystallization took place in 2-propanol. Recrystallization in the same solvent gave colorless needles (170 mg); mp 178—180°C, $[\alpha]_D^{20}$−33° (*c* 0.8, methanol). Found: C, 59.06; H, 6.80; N, 4.91%. Calcd for $C_{14}H_{19}O_5N$: C, 59.77; H, 6.81; N, 4.98%.

*Phenyl 2-Acetamido-4,6-di-*O*-acetyl-2,3-dideoxy-β-*D*-ribohexopyranoside (XXXI).* Compound XXX (50 mg) was dissolved in a mixture of pyridine (5.0 m*l*) and acetic anhydride (2.5 m*l*), and the solution was kept at room temperature overnight. Evaporation *in vacuo* gave a syrup, and the contaminating reagents were co-distilled with toluene. Crystallization took place in ethanol. Recrystallization in the same solvent gave colorless needles (43 mg); mp 138—139°C. Found: C, 58.62; H, 6.33; N, 3.89%. Calcd for $C_{18}H_{23}O_7N$: C, 59.18; H, 6.33; N, 3.83%. NMR (in $CDCl_3$) δ5.32 (1H d, *J* 7 Hz H-1) 4.00 (1H unresolved H-2) 2.50 (1H unresolved H-3e) 1.80 (1H unresolved H-3a) 4.95 (1H octet H-4) 2.15 (3H s, NAc) 2.00 (6H s, OAc) 6.25 (1H d, NH).

*Phenyl 2-Acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-glucopyranoside (XXXII).* Compound XXVII (5.0 g) was acetylated with acetic anhydride (10 m*l*) in pyridine (200 m*l*). Recrystallization in ethanol gave colorless needles (5.0 g). Found: C, 63.91; H, 5.71; N, 3.27%. Calcd for $C_{23}H_{25}O_7N$: C, 64.62; H, 5.90; N, 3.28%.

*Phenyl 2-Acetamido-3-*O*-acetyl-2-deoxy-β-*D*-glucopyranoside (XXXIII).* Compound XXXII (5.0 g) was dissolved in hot glacial acetic acid (500 m*l*). To this solution was added water (100 m*l*) dropwise under shaking in a water bath kept at 65°C. The reaction was continued for 2 hr at 65—70°C. Evaporation of the solvent *in vacuo* gave crystals which were washed with ether several times. Recrystallization in ether gave white powder (3.5 g). Found: C, 56.53; H, 6.21; N, 4.10%. Calcd for $C_{16}H_{21}O_7N$: C,

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13) D. H. Leaback and P. G. Walker, *J. Chem. Soc.*, **1957**, 4754.
14) K. Yamamoto, M. Fujinaga, and Y. Matsushima, This Bulletin, **36**, 1275 (1963).

56.63; H, 6.24; N, 4.13%.

Phenyl 2-Acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranoside (XXXIV). Compound XXXIII (3.0 g) was dissolved in a mixture of pyridine (20 ml) and chloroform (10 ml), and the solution was cooled in a dry ice-acetone bath. Acetic anhydride (0.93 ml) was then added to the solution, and the reaction mixture was kept at −20°C for 48 hr. The solvent was evaporated *in vacuo*, and the residual syrup was crystallized in 2-propanol. Recrystallization in the same solvent gave colorless crystals (2.2 g); mp 180—185°C, $[\alpha]_D^{20}$ −22° (*c* 1.2, chloroform). Found: C, 56.59; H, 6.30; N, 3.62%. Calcd for $C_{18}H_{23}O_8N$: C, 56.68; H, 6.08; N, 3.67%.

Phenyl 2-Acetamido-3,6-di-O-acetyl-4-chloro-2,4-dideoxy-β-D-galactopyranoside (XXXV). Compound XXXIV (1.5 g) was dissolved in pyridine (20 ml). To this solution was added sulfuryl chloride (0.45 ml). The reaction solution was kept in a refrigerator overnight and then at room temperature for 3 hr. Excess pyridine was removed by evaporation *in vacuo*, and the residue was extracted with chloroform and the extract was washed with water several times. Chloroform was evaporated *in vacuo*. Crystals appeared in 2-propanol, and recrystallization in the same solvent gave colorless needles (1.1 g); mp 216°C (decomp.), $[\alpha]_D^{20}$ +21° (*c* 1.25, chloroform). Found: C, 54.05; H, 5.53; N, 3.54; Cl, 9.22. Calcd for $C_{18}H_{22}O_7NCl$: C, 54.07; H, 5.54; N, 3.50; Cl, 8.87.

Phenyl 2-Acetamido-3,6-di-O-acetyl-2,4-dideoxy-β-D-xylohexopyranoside (XXXVI). Compound XXXV (500 mg) was dissolved in toluene (20 ml) and reacted with tri-*n*-butyltin hydride (0.5 ml) in the presence of AIBN (*ca.* 20 mg) at 80—90°C for 2 hr. Crystals were obtained on evaporation of the solvent *in vacuo*. Recrystallization in 2-propanol gave colorless needles (300 mg); mp 168.5—170°C, $[\alpha]_D^{20}$ −47° (*c* 0.57, chloroform). Found: C, 59.07; H, 6.29; N, 3.92%. Calcd for $C_{18}H_{23}O_7N$: C, 59.17; H, 6.34; N, 3.83%.

Phenyl 2-Acetamido-2,4-dideoxy-β-D-xylohexopyranoside (XXXVII). Compound XXXVI (200 mg) was deacetylated with sodium methoxide in methanol. Recrystallization in water gave colorless needles (80 mg); mp 201—203°C, $[\alpha]_D^{18}$ −6.5° (*c* 0.65, water). Found: C, 59.71; H, 6.78; N, 4.92%. Calcd for $C_{14}H_{19}O_5N$: C, 59.77; H, 6.81; N, 4.98%.