1360, 1172 (sulfonate), 1105 (C–O–C), 760, 720, 700 (C_6H_5), no C=O near 1765 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{24}O_5S$: C, 57.8; H, 5.54; S, 7.34. Found: C, 57.7; H, 5.54; S, 7.30.

Similarly, reduction of 105 mg. (0.29 mmole) of XXX gave, after recrystallization from absolute ethanol–petroleum ether, 97 mg. (92%) of **methyl 4-6-O-benzylidene-2-O-mesyl-α,D-allopyranoside (XXXIIIb)** as white needles: m.p. 143–145°; $[\alpha]^{25}D$ +58.0 ± 1.5°; ν_{max} 3540 (OH), 1360, 1180 (sulfonate), 1130, 1110 (C–O–C), 755, 700 (C_6H_5), no C=O near 1760 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{20}O_8S$: C, 50.0; H, 5.59; S, 8.90. Found: C, 50.1; H, 5.66; S, 8.77.

Methyl 4,6-O-Benzylidene-α-D-allopyranoside (XXXIV). **A.**—A mixture of 200 mg. of lithium aluminum hydride (5.3 mmoles), 427 mg. of XXXIIIa (0.98 mmole), and 30 ml. of dry tetrahydrofuran was refluxed with stirring; after 18 hr. an additional 200 mg. of lithium aluminum hydride was added, and the reaction was refluxed for an additional 25 hr. The excess hydride was decomposed by dropwise addition of ethanol; then water was added until the inorganics formed an insoluble cake. The mixture was filtered and the solids were washed with hot ethanol, then hot acetone. The combined filtrate and washings were spin evaporated *in vacuo*. Crystallization from ethanol–petroleum ether gave 199 mg. (72%) of thick needles, m.p. 174–178°. Recrystallization from the same solvent pair afforded white crystals: m.p. 175–177°; $[\alpha]^{25}D$ +117 ± 2°; ν_{max} 3500, 3450 (OH), 1120, 1095 (C–O–C), 745, 705 (C_6H_5), no sulfonate absorption near 1360 or 1180 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.7; H, 6.44. Found: C, 59.7; H, 6.60.

Hydrolysis of 137 mg. of XXXIV with hot 1 *N* sulfuric acid gave, after work-up and recrystallization from 1 drop of water by addition of methanol and ethanol, white crystals of D-allose, m.p. 122–126°, that was identical with an authentic sample[28] by mixture melting point and by comparative infrared spectra.

B.—A solution of 63 mg. of XXXIIIa and 9.5 mg. of sodium methoxide in 0.75 ml. of methanol was refluxed for 5 hr., then diluted with several volumes of water. Unchanged XXXIII (18 mg., 29%) was removed by filtration. The combined filtrate and washings were extracted with three 10-ml. portions of chloroform. The combined extracts, after being washed with water, were spin evaporated *in vacuo;* yield 23 mg. (80%), m.p. 165–172°. The residue was dissolved in methanol and diluted with water. The trace of unchanged starting material was removed by filtration and the filtrate was evaporated *in vacuo*. Crystallization from absolute ethanol–petroleum ether gave pure XXXIV, m.p. 175–177°, that was identical with preparation A.

Neither methyl 2,3-anhydro-α-D-mannopyranoside nor methyl 2,3-anhydro-α-D-allopyranoside[13] could be detected by thin layer chromatography of the mother liquors. Although this reaction was run only once, it is probable that increasing the reaction time and quantities would give near quantitative yields.

C.—Lithium aluminum hydride cleavage of 37 mg. (0.10 mmole) of XXXIIIb, as described in preparation A, gave 16 mg. (55%) of product, m.p. 176–178°, that was identical with preparation A; in this case the oil remaining on spin evaporation was partitioned between water and chloroform prior to crystallization. The water-washed chloroform solution was then spin evaporated *in vacuo*, and the residue was recrystallized.

(28) This sample was kindly provided by Professor I. J. Goldstein of this university who, in turn, had obtained it from Dr. N. K. Richtmyer, National Institutes of Health, Bethesda, Md.

Synthetic Nucleosides. LXIV.[1,2] Synthesis and Stereospecific Reduction of Some 2(3)-Acylamino-3(2)-oxopyranosides

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Oxidation of methyl 3-benzamido-4,6-O-benzylidene-3-deoxy-α-D-altropyranoside (Ia) and methyl 3-benzamido-4,6-O-benzylidene-3-deoxy-α-D-glucopyranoside (IVa) with phosphoric acid and dicyclohexylcarbodiimide in dimethyl sulfoxide—the Pfitzner–Moffatt reagent—gave the identical ketone, methyl 3-benzamido-4,6-O-benzylidene-3-deoxy-α-D-*arabino*-hexopyranosid-2-ulose (IIa) in 86 and 96% yields, respectively; the axial benzamido group of Ia, after oxidation of the hydroxyl to a ketone, was isomerized to the more stable equatorial configuration of IIa. Much lower yields, but similar results, were obtained with the corresponding 3-acetamido derivatives, Ib and IVb. Reduction of the two ketones with sodium borohydride proceeded virtually stereospecifically by axial attack to regenerate IVa and IVb. Oxidation of methyl 2-benzamido-4,6-O-benzylidene-2-deoxy-α-D-altropyranoside (Va) and methyl 2-benzamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (XIa) gave the same ketone, methyl 2-benzamido-4,6-O-benzylidene-2-deoxy-α-D-*ribo*-hexopyranosid-3-ulose (VIa), in 83 and 95% yields, respectively; the benzamido group adjacent to the ketone again was equatorial, showing an isomerization of the benzamido group during oxidation of Va. Reduction of the ketone VIa with sodium borohydride proceeded virtually stereospecifically by equatorial attack to give methyl 2-benzamido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside with an axial hydroxyl at C-3. Similar results, but lower yields, were obtained with the corresponding acetamido sugars.

Oxidation of either primary or secondary sugar hydroxyl groups to ketones with phosphoric acid–dicyclohexylcarbodiimide–dimethyl sulfoxide, the Pfitzner–Moffatt reagent,[3] bears promise to take its place among the most useful in the carbohydrate area.[2,3] Its use for oxidizing sugar alcohols bearing an adjacent sulfonyloxy function has been described in the previous paper in this series.[2] In this paper are presented studies on the oxidation of some pyranosidic alcohols bearing an adjacent acylamido group with the Pfitzner–Moffatt reagent and the stereospecific reduction of the resultant ketones by sodium borohydride.

When either methyl 3-benzamido-4,6-O-benzylidene-3-deoxy-α-D-glucopyranoside (IVa)[4,5] or the corresponding altroside (Ia)[5,6] was oxidized with the Pfitzner–Moffatt reagent, the identical ketone was obtained in 96 and 86% yields, respectively; since it was more

(1) This work was generously supported by Grant CA-05845 from the National Cancer Institute, U. S. Public Health Service.

(2) Paper LXIII: B. R. Baker and D. H. Buss, *J. Org. Chem.*, **30**, 2304 (1965).

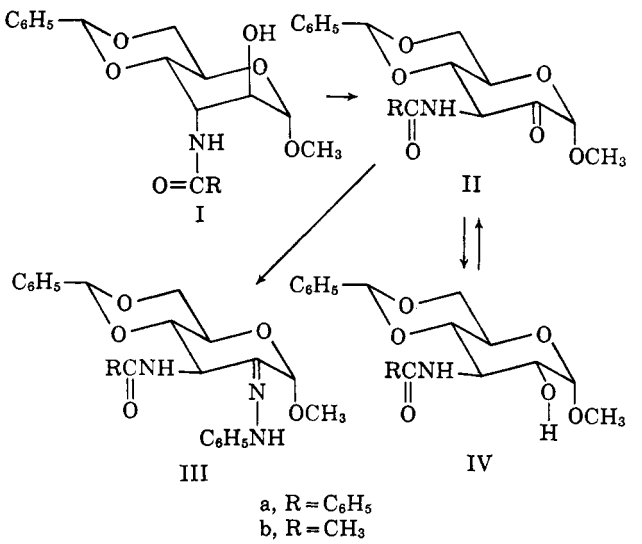
(3) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963).

(4) R. D. Guthrie and G. P. B. Mutter, *J. Chem. Soc.*, 1614 (1964).

(5) Methyl 3-amino-4,6-O-benzylidene-3-deoxy-α-D-altropyranoside and methyl 2-amino-4,6-O-benzylidene-2-deoxy-α-D-altropyranoside were prepared by the method of W. H. Myers and G. J. Robertson [*J. Am. Chem. Soc.*, **65**, 8 (1943)]; from the mother liquors of the latter, methyl 3-acetamido- or 3-benzamido-4,6-O-benzylidene-3-deoxy-α-D-glucopyranoside were obtained by selective N acylation.[6]

(6) D. H. Buss, L. Hough, and A. C. Richardson, *J. Chem. Soc.*, 5295 (1963).

likely that the benzamido group adjacent to the ketone could epimerize from axial to the more stable equatorial conformation than *vice versa*, the ketone probably had the D-*arabino* configuration depicted in IIa. That the structural assignment for IIa was correct was shown by reduction with sodium borohydride to the glucoside (IVa) in 95% yield. It is clear that the borohydride attacked the carbonyl group from the axial side to give the equatorial hydroxyl of IVa. The possibility for equatorial attack is considerably hindered by the axial C-1 α-methoxyl group; as can be expected with the equatorial C-1 β-methoxyl group, reduction of methyl β-D-*arabino*-hexopyranosid-2-ulose with borohydride proceeds less stereospecifically by 65% equatorial and 35% axial attack.[7] It is interesting to note that the C-1 methoxyl groups of IIa did not epimerize

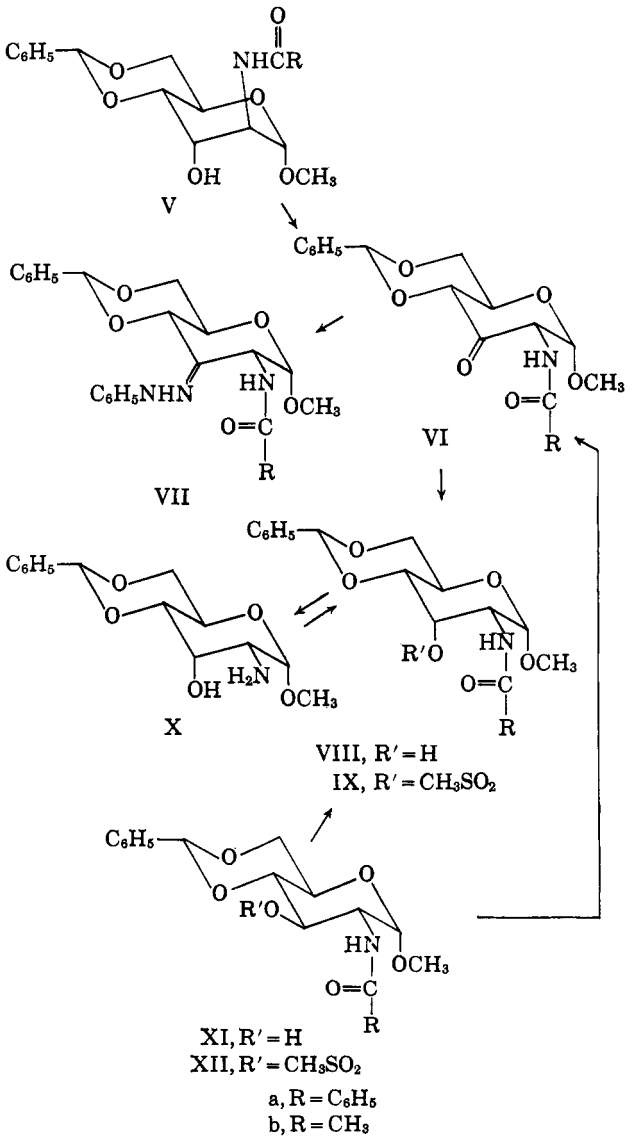


to the more stable equatorial conformation under the oxidation conditions.

The ketone IIa formed a crystalline phenylhydrazone (IIIa); whether catalytic reduction of IIIa will form a 2,3-diamino sugar derivative with *trans* diequatorial groups of D-*gluco* configuration, as might be anticipated,[8a] remains to be determined.[8b]

Oxidation of the corresponding acetamido sugars Ib and IVb to the crystalline ketone IIb proceeded in 3 and 29% yields, respectively—considerably poorer than with the corresponding benzamido sugars (86 and 96%). Nevertheless, sodium borohydride was still virtually stereospecific in its reduction of IIb, the D-*gluco* configuration (IVb) being obtained in better than 77% yield.

Attention was then directed to the oxidation of 2-acylamidopyranosides by the Pfitzner–Moffatt reagent. Both methyl 2-benzamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (XIa) and the corresponding altroside (Va)[5,6] gave the same ketone in 95 and 83% yields, respectively; presumably the ketone had an equatorial benzamido group (VIa); VIa was further characterized by formation of the phenylhydrazone VIIa.[8b] It had previously been shown that oxidation of methyl 4,6-O-benzylidene-2-O-(*p*-tolylsulfonyl)-α-D-glucopyranoside with the Pfitzner–Moffatt reagent gave methyl 4,6-O-benzylidene-2-O-(*p*-tolylsulfonyl)-α-D-*ribo*-hexopyranosid-3-ulose with an equatorial sulfonyloxy group[2]; since reduction of this D-*ribo*-hexosid-3-ulose gave a D-*allo* derivative with an axial 3-hydroxyl group, it was anticipated that VIa should also reduce to the D-*allo* configuration. Sodium borohydride reduction of VIa was virtually stereospecific giving an



88% yield of an unknown 2-benzamido pyranoside that was isomeric to Va and XIa, but which was proven below to have the expected D-*allo* configuration (VIIIa).

(7) O. Theander, *Advan. Carbohydrate Chem.*, **17**, 223 (1962).

(8) (a) Reduction of the sterically hindered oxo group of DL-*epi*-inosose-2 has been shown to proceed by equatorial attack to give an axial hydroxyl with either sodium borohydride or platinum and hydrogen: see D. Reymond, *Helv. Chim. Acta*, **40**, 492 (1957); N. Z. Stanacev and M. Kates, *J. Org. Chem.*, **26**, 912 (1961). Thus reduction of the phenylhydrazone IIIa with platinum catalyst could be expected to give an equatorial 2-amino group. (b) Whether the phenylhydrazone is a true phenylhydrazone or an isomeric phenylazo derivative is not yet known with certainty; if a reduction proceeds through a phenylazo derivative, the stereochemistry will probably be controlled by the equatorial phenylazo group to give an equatorial amine, whereas, if the reduction would proceed through a true phenylhydrazone, the stereochemistry of reduction will be dependent upon which side of the C=N group is least hindered (equatorial attack at C-3, axial attack at C-2). The colorless nature of the phenylhydrazone and the sharp, strong band in the infrared at 1605 cm.$^{-1}$ would indicate that this is a true phenylhydrazone, since the N=N group would impart a yellow color and would be unlikely to have a strong sharp band near 1605 cm.$^{-1}$: see R. D. Guthrie and L. F. Johnson, *J. Chem. Soc.*, 4166 (1961); G. J. F. Chittenden and R. D. Guthrie, *Proc. Chem. Soc.*, 289 (1964); L. L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 272. It is possible that a phenylazo peroxide, obtained by air oxidation of the phenylhydrazone, may also have to be considered: see A. J. Bellamy and R. D. Guthrie, *Chem. Ind.* (London), 1575 (1964).

Oxidation of the 2-acetamidopyranosides Vb and XIb also gave the identical ketone, which was presumed to have an equatorial 2-acetamido group (VIb), in 74 and 90% yields, respectively. Sodium borohydride reduction of VIb gave the 2-acetamido-D-allopyranoside VIIIb that was identical with a sample of VIIIb prepared by neighboring-group inversion[9] of the 3-O-mesyl-D-glucosaminide (XIIb) as described by Jeanloz[10]; the properties of the O-acetyl derivative IXb agreed with those reported.[10]

An attempt to convert the 2-benzamido-3-O-mesylglucoside (XIIa) to VIIIa by a neighboring group reaction was only partially successful, since the intermediate 2′-phenyloxazoline was quite stable to hydrolytic conditions. An authentic sample of the benzamido-D-alloside VIIIa was finally synthesized by basic hydrolysis of the acetamido-D-alloside VIIIb to X followed by selective N-benzoylation with benzoic anhydride in ethanol.

Thus, methyl 3-benzamido-4,6-O-benzylidene-3-deoxy-α-D-*arabino*-hexopyranosid-2-ulose (IIa) is now readily available from methyl 4,6-O-benzylidene-α-D-glucopyranoside either *via* Ia[5,6] or *via* IVa[4]; methyl 2-benzamido-4,6-O-benzylidene-2-deoxy-α-D-*ribo*-hexopyranosid-3-ulose (VIa) is also readily available from methyl 4,6-O-benzylidene-α-D-glucopyranoside *via* Va[5,6] or from D-glucosamine *via* XIa. These two ketones should be able to serve as intermediates for synthesis of a wide variety of unusual amino sugar derivatives.

Experimental[11]

Methyl-3-Benzamido-4,6-O-benzylidene-3-deoxy-α-D-*arabino*-hexopyranosid-2-ulose (IIa). A.—To a stirred solution of 7.10 g. (18.4 mmoles) of Ia[5,6] in 200 ml. of dimethyl sulfoxide was added 14.7 g. (71.3 mmoles) of dicyclohexylcarbodiimide; then 4.65 ml. (88.8 mmoles) of anhydrous orthophosphoric acid was added portionwise with cooling so that the temperature was 25–30°. After being stirred in a stoppered flask 21 hr., the mixture was filtered and the insoluble dicyclohexylurea was washed with a little dimethyl sulfoxide and acetone. The combined filtrate and washings were diluted with several volumes of chloroform, then water was added, and finally 2.4 *M* potassium carbonate solution was added to about pH 8. The aqueous layer was thoroughly extracted with chloroform and the combined extracts were washed with water until neutral. Spin evaporation of the chloroform solution *in vacuo* and dilution of the residue with ether gave 6.10 g. (86%) of white needles,[12] m.p. 248–249° dec. Recrystallization from acetone–petroleum ether gave the analytical sample: m.p. 247–248° dec.; $[\alpha]^{25}D$ −18 ± 2°; ν_{max} 3300 (NH), 1750 (ketone C=O), 1650, 1530 (amide I and II), 1120, 1100, 1070 (C—O—C), 743, 695 (C_6H_5), and 725 cm.$^{-1}$ (CH of benzoyl).

Anal. Calcd. for $C_{21}H_{21}NO_6$: C, 65.8; H, 5.52; N, 3.65. Found: C, 65.9; H, 5.70; N, 3.67.

B.—Treatment of 602 mg. (1.56 mmoles) of IVa[4,5] in 25 ml. of dimethyl sulfoxide with 1.2 g. (5.82 mmoles) of dicyclohexylcarbodiimide and 0.41 ml. (7.82 mmole) of anhydrous orthophosphoric acid as described in procedure A gave, after recrystallization from acetone, 575 mg. (96%) of nearly pure white needles,[12] m.p. 240–243° dec., that were identical with preparation A.

Phenylhydrazone[8b] of Methyl 3-Benzamido-4,6-O-benzylidene-3-deoxy-α-D-*arabino*-hexopyranosid-2-ulose (IIIa).—A suspension of 437 mg. (1.14 mmoles) of IIa in 80 ml. of ethanol containing 0.25 ml. (2.54 mmoles) of phenylhydrazine was refluxed for 30 min. The solution was spin evaporated *in vacuo* and the residue was recrystallized from absolute ethanol–petroleum ether: yield, 468 mg. (87%) of white needles; m.p. 217–221° dec.; $[\alpha]^{25}D$ +90 ± 3°; ν_{max} 3325 (NH), 1655, 1530 (amide I and II), 1605 (C=N), 1095 (C—O—C), 745, 695 (C_6H_5), and 740 cm.$^{-1}$ (CH of benzoyl), no ketone C=O near 1750 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{27}N_3O_5$: C, 68.5; H, 5.75; N, 8.87. Found: C, 68.7; H, 5.93; N, 9.01.

Sodium Borohydride Reduction of Methyl 3-Benzamido-4,6-O-benzylidene-3-deoxy-α-D-*arabino*-hexopyranosid-2-ulose (IIa).—To a stirred solution of 124 mg. of IIa in 1.3 ml. of N,N-dimethylformamide was added 20 ml. of methanol; then about 100 mg. of sodium borohydride was added portionwise. After 2 hr., during which time crystals separated, the mixture was filtered and the product was washed with methanol; yield, 97 mg. (78%), m.p. 329–331° (identical with authentic IVa[4]).

The combined filtrate and washings were diluted with water and extracted with chloroform. From the chloroform solution could be isolated an additional 21 mg. of IVa (total 95%).

Methyl 3-Acetamido-4,6-O-benzylidene-3-deoxy-α-D-*arabino*-hexopyranosid-2-ulose (IIb). A.—Oxidation of 104 mg. (0.32 mmoles) of IVb[4,5] as described for the preparation of IIa gave an oil on evaporation of the chloroform solution. The oil was dissolved in hot ethanol and decanted from some insoluble gum. Evaporation of the ethanol *in vacuo* gave a solid which was a mixture of several compounds, as shown by thin layer chromatography, and which could not be purified further by recrystallization. The material was purified by preparative thin layer chromatography with chloroform–methanol (9:1). The ketone-containing fraction (R_f about 0.6) was scraped from the plates and eluted with hot chloroform and ethanol. Spin evaporation of the extract *in vacuo* gave 29.5 mg. (29%) of product, m.p. 252–254° dec. Recrystallization from ethanol–ether afforded white crystals: m.p. 254–255° dec.; $[\alpha]^{25}D$ +44 ± 4°; ν_{max} 3320 (NH), 1755 (ketone C=O), 1665, 1555 (amide I and II), 1100 (C—O—C), 750, and 697 cm.$^{-1}$ (C_6H_5).

Anal. Calcd. for $C_{16}H_{19}NO_6$: N, 4.36. Found: N, 4.17.

B.—Oxidation of 98.5 mg. (0.30 mmoles) of Ib[9,13] as described in preparation A gave 3 mg. (3%) of white crystals, m.p. 247–250° dec., that were identical with those of preparation A.

Sodium Borohydride Reduction of Methyl 3-Acetamido-4,6-O-benzylidene-3-deoxy-α-D-*arabino*-hexopyranosid-2-ulose (IIb).—Sodium borohydride reduction of 13 mg. of IIb, as described later for the reduction of VIa, gave, on recrystallization from absolute ethanol–petroleum ether, 10 mg. (77%) of methyl 3-acetamido-4,6-O-benzylidene-3-deoxy-α-D-glucopyranoside (IVb), m.p. 311–313° dec., that was identical with an authentic sample of IVb.[4,5] No attempt was made to isolate a second crop, although thin layer chromatography showed that additional IVb was present.

Methyl 2-Benzamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (XIa).—To a solution of the crude 2-benzamido-2-deoxy-D-glucose[14] from 16.6 g. (77.4 mmoles) of D-glucosamine hydrochloride in 350 ml. of methanol was added 18 g. of Dowex 50W-X8 [H^+ form, dried at 80° (1 mm.) over P_2O_5]. The mixture was refluxed with stirring for 11 hr. and then filtered and the resin was washed with hot methanol. Concentration of the solution to a smaller volume gave 8.7 g. (71% based on D-glucosamine hydrochloride) of crude methyl 2-benzamido-2-deoxy-α-D-glucopyranoside[15]: m.p. 226–228° dec., $[\alpha]^{25}D$ +100° (1.25% in H_2O). Neuberger[16] has recorded a melting point of

(9) B. R. Baker and R. E. Schaub, *J. Org. Chem.*, **19**, 646 (1954).

(10) R. W. Jeanloz, *J. Am. Chem. Soc.*, **79**, 2591 (1957).

(11) Melting points were determined in capillary tubes with a Mel-Temp block and those below 230° are corrected. Infrared spectra were determined in Nujol mulls with a Perkin-Elmer Model 137B spectrophotometer. Thin layer chromatograms (t.l.c.) were run with Brinkmann silica gel G and spots were detected by iodine vapor. Optical rotations were determined in N,N-dimethylformamide in a 1-dm. microtube. Petroleum ether was a fraction boiling at 40–60°.

(12) (a) Thin layer chromatography with chloroform–acetone (2:1, 3:1, or 4:1) or chloroform–methanol (4:1 or 9:1), depending upon the mobility of the product, was employed to show the absence of dicyclohexylurea. (b) The presence of larger amounts of dicyclohexylurea could be detected by the broadening of the carbonyl band near 1650 cm.$^{-1}$ in the infrared as well as by an auxiliary band in the urea at 895 cm.$^{-1}$.

(13) B. R. Baker and T. Neilson, *J. Org. Chem.*, **29**, 1057 (1964).

(14) Y. Inouye, K. Onodera, S. Kitaoka, and S. Hirano, *J. Am. Chem. Soc.*, **78**, 4722 (1956).

(15) The stereospecific conversion of 2-acetamido-2-deoxy-D-glucose to its α-methylpyranoside with a dry cationic exchange resin in the H^+ form has been reported by S. A. Barker, M. Stacey, and D. J. Tipper [*Nature*, **184**, 1718 (1959)]. This method has also been used on 2-benzamido-2-deoxy-D-glucose [L. Hough and J. Tjebbes, private communication to D. H. B.].

(16) A. Neuberger, *J. Chem. Soc.*, 47 (1941).

225–226° and $[\alpha]_D$ +114° (H_2O). The corresponding β anomer[17] had α^{22}_D −24° (1.49% in H_2O).

The above crude methyl 2-benzamido-2-deoxy-α-D-glucopyranoside (7.7 g. containing some inorganic material) was dissolved as quickly as possible in 38 ml. of 98% formic acid, then 38 ml. of benzaldehyde was immediately added. After being shaken at ambient temperature for exactly 5 min., the mixture was poured into a stirred mixture of 450 ml. of 2.4 *M* aqueous potassium carbonate and 400 ml. of petroleum ether. The solid was collected on a filter and washed with petroleum ether until free of the odor of benzaldehyde. Recrystallization from ethanol–water gave 6.35 g. (64%) of white needles: m.p. 253–256°; $[\alpha]^{25}_D$ +72 ± 2°; ν_{max} 3450 (OH), 3330 (NH), 1640, 1550 (amide I and II), 1115, 1100, 1080 (C—O—C), 755, 700 (C_6H_5), and 735 cm.$^{-1}$ (CH of benzoyl).

Anal. Calcd. for $C_{21}H_{23}NO_6$: C, 65.4; H, 6.02; N, 3.63. Found: C, 65.0; H, 6.18; N, 3.40.

This new method for formation of other O-benzylidene derivatives has been developed by Schwarz.[18]

Methyl 2-Benzamido-4,6-O-benzylidene-2-deoxy-α-D-*ribo*-hexopyranosid-3-ulose (VIa). **A.**—Oxidation of 2.25 g. (5.84 mmoles) of Va,[6] as described for the preparation of IIa, gave, after recrystallization from acetone–petroleum ether, 1.87 g. (83%) of product, m.p. 202–206°. Recrystallization from same solvent pair afforded 1.57 g. (70%) of white needles,[12] m.p. 204–206° dec., which showed one spot on t.l.c.: $[\alpha]^{25}_D$ +114 ± 1°; ν_{max} 3340 (NH), 1745 (ketone C=O), 1640, 1530 (amide I and II), 1135, 1120, 1080 (C—O—C), 752, 700 (C_6H_5), and 725 cm.$^{-1}$ (CH of benzoyl).

Anal. Calcd. for $C_{21}H_{21}NO_6$: C, 65.8; H, 5.52; N, 3.65. Found: C, 66.0; H, 5.73; N, 3.83.

When further recrystallized from chloroform–methanol an apparently different crystal form, m.p. 212–215° dec., was obtained, although the infrared spectra were the same.

B.—Oxidation of 1.06 g. (2.75 mmoles) of XIa, as described for the preparation of IIa, gave, after recrystallization from chloroform–methanol, 0.99 g. (95%) of long needles,[12] m.p. 213–215° dec., identical with those of preparation A.

The **phenylhydrazone VIIa**[8b] was prepared from 112 mg. (0.29 mmoles) of VIa as described for the preparation of IIIa with a reflux time of 1 hr. After evaporation of the ethanol *in vacuo*, the residue was triturated with ether; the insoluble, unchanged VIa (14 mg., 12%) was removed by filtration. Evaporation of the ether and recrystallization of the residue from absolute ethanol–petroleum ether gave 67 mg. (55% based on unrecovered VIa) of phenylhydrazone. Recrystallization from the same solvent pair gave white needles: m.p. 240–242° dec; $[\alpha]^{25}_D$ +140 ± 3°; ν_{max} 3320 (NH), 1630,1535 (amide I and II), 1605 (C=N), 1130, 1090 (C—O—C), 745, 690 (C_6H_5), and 725 cm.$^{-1}$ (CH of benzoyl), no C=O near 1745 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{27}N_3O_5$: C, 68.5; H, 5.75; N, 8.87. Found: C, 68.5; H, 5.93; N, 8.81.

Methyl 2-Acetamido-4,6-O-benzylidene-2-deoxy-α-D-*ribo*-hexopyranosid-3-ulose (VIb). **A.**—Oxidation of 1.92 g. (5.94 mmoles) of Vb,[5,19] as described for the preparation of IIa, gave a crude product that was difficult to separate from dicyclohexylurea by crystallization.[12b] The product was purified by column chromatography on silica gel (grade 950, 60–200 mesh, Will Scientific, Inc., Buffalo), being eluted by chloroform–acetone (2:1); VIb was obtained initially as an amorphous solid that was analytically pure; yield, 1.41 g. (74%). Ultimately it was crystallized by prolonged heating with acetone under reflux as white crystals: m.p. 227–228° dec.; $[\alpha]^{25}_D$ +110 ± 4°; ν_{max} 3320 (NH), 1740 (C=O), 1650, 1545 (amide I and II), 1115, 1080 (C—O—C), 757, and 700 cm.$^{-1}$ (C_6H_5).

Anal. Calcd. for $C_{16}H_{19}NO_6$: C, 59.8; H, 5.96; N, 4.36. Found: C, 60.1; H, 5.95; N, 4.37.

B.—Oxidation of 590 mg. (1.83 mmoles) of XIb[20] was performed as described for IIa; from acetone, 527 mg. (90%) of amorphous solid[12] was obtained. Crystallization from N,N-dimethylformamide by addition of water gave white crystals, m.p. 223–225° dec., identical with those of preparation A.

Methyl 2-Acetamido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside (VIIIb).—Reduction of 64.5 mg. (0.20 mmoles) of VIb with sodium borohydride, as described for the reduction of VIa, gave, after recrystallization from ethanol, 49 mg. (74%) of white needles: m.p. 215–216°; ν_{max} 3500, 3375 (NH, OH), 1635, and 1520 cm.$^{-1}$ (amide I and II), no C=O near 1740 cm.$^{-1}$. This compound was identical with an authentic sample prepared from XIIb by the method of Jeanloz.[10]

Acetylation of a small portion of VIIIb gave the O-acetyl derivative IXb, m.p. 216–218°, that showed ester absorption at 1730 cm.$^{-1}$; Jeanloz[10] has recorded m.p. 213–214° (uncor.).

Methyl 2-Benzamido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside (VIIIa). **A.**—To a stirred solution of 140 mg. (0.365 mmole) of VIa in 1.5 ml. of N,N-dimethylformamide diluted with 20 ml. of methanol was added about 100 mg. of sodium borohydride. After 35 min. at ambient temperature, the mixture was heated to boiling, then concentrated to about 1–2 ml. by spin-evaporation *in vacuo*. Diluted with several volumes of water, the mixture was thoroughly extracted with chloroform. The combined extracts were washed with water, then spin evaporated *in vacuo*. Crystallization from absolute ethanol–petroleum ether gave 124 mg. (88%) of product, m.p. 170–175°. Recrystallization from the same solvents gave white needles: m.p. 176–178°; $[\alpha]^{25}_D$ +81 ± 4°; ν_{max} 3450, 3380 (OH, NH), 1630, 1530 (amide I and II), 1125, 1100 (C—O—C), 750, 696 (C_6H_5), and 715 cm.$^{-1}$ (CH of benzoyl), no C=O near 1745 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{23}NO_6$: C, 65.4; H, 6.01; N, 3.63. Found: C, 65.6; H, 6.01; N, 3.69.

B.—A solution of 34 mg. (0.105 mmoles) of VIIIb in 4 ml. of 1 *N* aqueous sodium hydroxide was refluxed for 19 hr., cooled, and extracted with chloroform (five 3-ml. portions). The combined extracts were washed with a small amount of water, then spin evaporated *in vacuo*. The residual X crystallized on addition of ether: yield, 18 mg. (61%); m.p. 166° (turbid); ν_{max} 3450, 3350 (OH, NH), and 1570 cm.$^{-1}$ (NH), no amide I or II near 1630 and 1520 cm.$^{-1}$. No attempt was made to purify this compound (X) further, but the N-acetyl of VIIIb was clearly removed.

To a solution of 11 mg. of m in 2 Xl. of ethanol was added 12 mg. of benzoic anhydride. After 20 min., the solvent was removed *in vacuo* and the residue was recrystallized from absolute ethanol–petroleum ether yielding 9.5 mg. (63%) of VIIIa as white crystals, m.p. 177–179°, that were identical with those of preparation A.

Methyl 2-Benzamido-4,6-O-benzylidene-2-deoxy-3-O-mesyl-α-D-glucopyranoside (XIIa).—To a solution of 438 mg. (1.14 mmoles) of XIa in 6 ml. of reagent pyridine was added 0.22 ml. (2.88 mmoles) of methanesulfonyl chloride. After 26 hr. at room temperature in a stoppered flask, the solution was diluted with water and the product was collected on a filter. Recrystallization from ethanol containing a little acetone gave 453 mg. (86%) of white needles, m.p. 193–197° dec. One more recrystallization gave the analytical sample: m.p. 195–197°; $[\alpha]^{25}_D$ +77.8 ± 1.6°; ν_{max} 3250 (NH), 1640, 1540 (amide I and II), 1370, 1170 (sulfonate), 1125, 1100, 1090 (C—O—C), 750, 695 (C_6H_5), and 725 cm.$^{-1}$ (CH of benzoyl).

Anal. Calcd. for $C_{22}H_{25}NO_8S$: C, 57.0; H, 5.44; N, 3.02; S, 6.92. Found: C, 56.8; H, 5.21; N, 3.06; S, 6.67.

An attempt to convert XIIa to VIIIa with sodium acetate in boiling 95% 2-methoxyethanol gave as the major product the intermediate 2-phenyloxazoline,[9,10] m.p. 195–202° dec., which showed C=N absorption at 1640 cm.$^{-1}$, but no amide I and II near 1640 and 1540 cm.$^{-1}$; the compound was not further characterized. When the supposed oxazoline was refluxed with 0.5 *N* sodium hydroxide in 50% aqueous 2-methoxyethanol for 20 hr., the material was recovered unchanged.

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(20) W. Roth and W. Pigman, *J. Am. Chem. Soc.*, **82**, 4608 (1960). XIb was prepared in our work from methyl 2-acetamido-2-deoxy-α-D-glucopyranoside in 38% yield by the method used for XIa.