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ACETONATION OF 2-(ACYLAMINO)-2-DEOXY-D-GLUCOSES*

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ABSTRACT

2-Acetamido-2-deoxy-D-glucose and 2-(benzyloxycarbonylamino)-2-deoxy-D-glucose were each treated with 2,2-dimethoxypropane in *N,N*-dimethylformamide containing a trace of *p*-toluenesulfonic acid. The new 5,6-*O*-isopropylidene derivatives 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-D-glucofuranose, 2-acetamido-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol, 2-acetamido-2-deoxy-3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose-dimethyl acetal, and 2-(benzyloxycarbonylamino)-2-deoxy-5,6-*O*-isopropylidene-D-glucofuranose were isolated. The formation of these furanoid acetals may be important in ascertaining the mechanism of this unique acetonation accompanied by glycosidation.

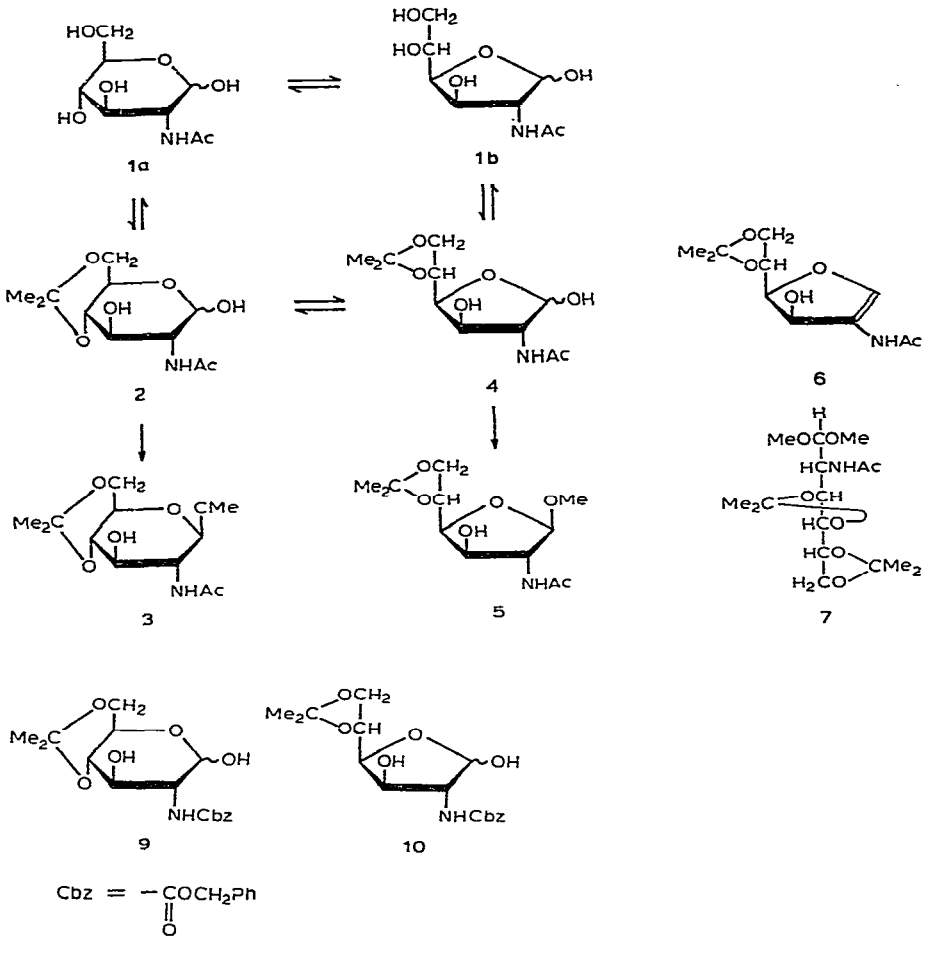
INTRODUCTION

The acetonation of various *N*-substituted 2-amino-2-deoxy-D-aldohexoses with 2,2-dimethoxypropane, *N,N*-dimethylformamide, and *p*-toluenesulfonic acid has been studied[1–3], and it has found potential utility in our recent studies[4–6]. In the preceding two papers[7,8], we have shown that, using D-glucose and some pentoses, this reaction is kinetically controlled, with favored attack by the reagent at the primary hydroxyl group. However, the reaction with 2-(acylamino)-2-deoxy-D-aldohexoses accompanied by glycosidation as well as acetonation is very complicated. We now report the acetonation of 2-(acylamino)-2-deoxy-D-glucoses with the 2,2-dimethoxypropane reagent, and discuss the reaction mechanism.

RESULTS AND DISCUSSION

Treatment of 2-acetamido-2-deoxy-D-glucose (**1**) with 3.8 mole-equivalents of 2,2-dimethoxypropane in dry *N,N*-dimethylformamide in the presence of a trace of *p*-toluenesulfonic acid for 15 min at 80–85° (reaction *A*) gave 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-D-glucopyranose[1] (**2**, 68%), 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-D-glucofuranose (**4**, 5%), and 2-acetamido-1,4-anhydro-2-deoxy-5,6-*O*-

*The Behavior of Some Aldoses with 2,2-Dialkoxypropane–*N,N*-Dimethylformamide–*p*-Toluenesulfonic Acid, Part VI. For Part V, see ref. 8.



isopropylidene-D-*arabino*-hex-1-enitol (**6**, 14%). Subsequent addition of 1.6 mole-equivalents of 2,2-dimethoxypropane to the reaction mixture of reaction *A*, and continuation of the reaction for a further 45 min at 80–85°, gave methyl 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-*β*-D-glucofuranoside[2] (**5**, 46%) as the main product and compound **6** (12%) as a second product. Small proportions of methyl 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranoside[2] (**3**, 9%) and 2-acetamido-2-deoxy-3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (**7**, 7%) were also isolated. When this reaction was performed at room temperature, **2** was obtained in almost quantitative yield (90%), as reported[1], and a trace (1.2%) of **4** was also isolated from the final filtrate. A similar result was obtained by the reaction of 2-(benzyloxycarbonylamino)-2-deoxy-D-glucose with the 2,2-dimethoxypropane reagent at room temperature; 2-(benzyloxycarbonylamino)-2-deoxy-4,6-*O*-isopropylidene-D-glucopyranose (**9**, 85%) and 2-(benzyloxycarbonylamino)-2-deoxy-5,6-*O*-isopropylidene-D-glucofuranose (**10**, 2%) were isolated.

In column chromatography on silicic acid, product **4** was eluted slightly faster than **2**; **4** had an elemental composition corresponding to that calculated for a mono-*O*-isopropylidene derivative, $C_{11}H_{19}NO_6$, of **1**, but the i.r. spectrum of **4** was clearly different from that of **2**. In the n.m.r. spectrum of **4** in methanol-d_4, a narrow doublet at δ 5.47 (H-1α, $J_{1,2}$ 4.3 Hz) and a singlet at δ 5.18 (H-1β) indicated an anomeric mixture of furanoid structures. The mass spectrum showed the parent peak at *m/e* 246, which was assigned to the $M^+ - CH_3$ ion. Especially, the highest peak at *m/e* 101 is strongly indicative of the presence of a 5,6-*O*-isopropylidene group[7,9–12]. Acetylation of **4** gave a syrupy di-*O*-acetyl derivative (**4a**); for this, the n.m.r. signal of H-1 was shifted to δ 6.26 (H-1α, $J_{1,2}$ 4.5 Hz), and that of H-3 was at δ 5.52 ($J_{2,3}$ 7.4, $J_{3,4}$ 6.4 Hz). The value of $J_{2,3}$ seems much larger than that for a furanoid structure having a *trans* disposition of adjacent groups. However,

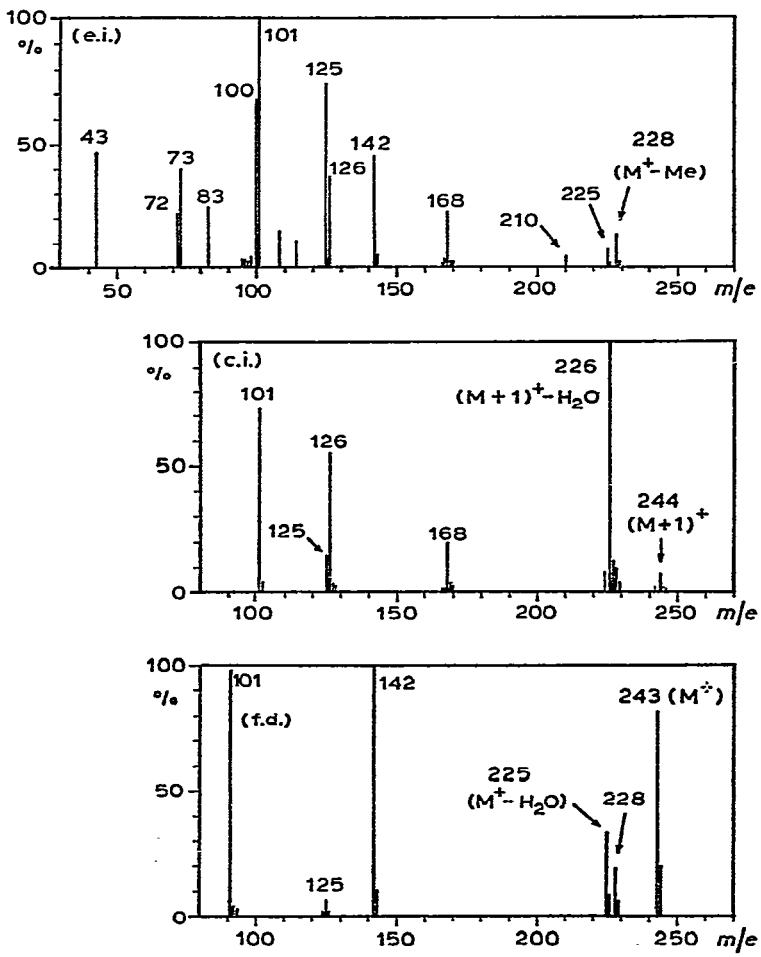
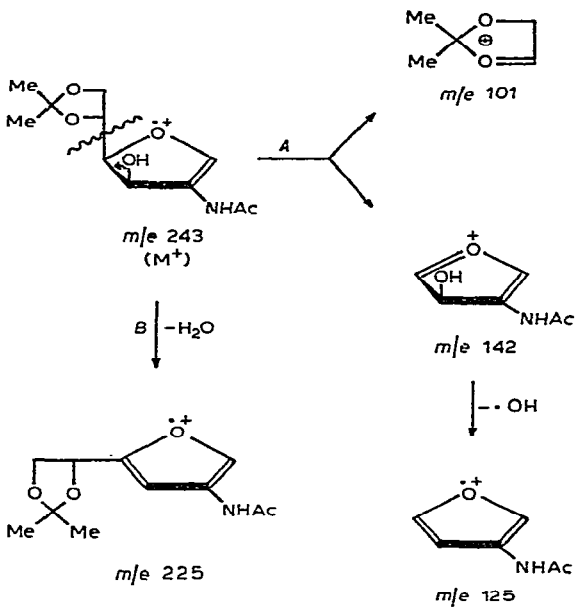


Fig. 1. Electron-impact, c.i., and f.d. mass spectra of 2-acetamido-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**6**).

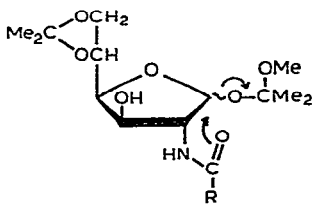


it has been observed that the $J_{2,3}$ value of furanose derivatives having an α-1-*O*-acetyl group, such as 1,2,3-tri-*O*-acetyl-5,6-*O*-isopropylidene-α-D-glucofuranose (4.5 Hz)[7], 1,3-di-*O*-acetyl-2-(benzyloxycarbonylamino)-2-deoxy-5,6-*O*-isopropylidene-α-D-glucofuranose (5.4 Hz), and 2,5-bis(acetamido)-1,3-di-*O*-acetyl-2,5-dideoxy-α-D-xylofuranose[13] (6.8 Hz), is quite large.

Product **6** had an elemental composition agreeing with that calculated for $C_{11}H_{17}NO_5$, and did not reduce Fehling solution. The i.r. spectrum showed the presence of an acetamido group and a double bond, and the n.m.r. data suggested the structure of 2-acetamido-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol. The structure was further analyzed by mass spectrometry (see Fig. 1). In the electron impact (e.i.) mass spectrum of **6**, the parent peak at *m/e* 228 represents the loss of a methyl group, as generally observed for *O*-isopropylidene compounds, whereas *m/e* 225 is due to the loss of H_2O. The highest peak, at *m/e* 101, is strongly indicative of the presence of a 5,6-*O*-isopropylidene group, and the second-highest peak, at *m/e* 125, represents the stable fragment ion of 3-acetamidofuran. The c.i. and f.d. mass spectra show the existence of two main pathways of fragmentation (see Scheme 2); one is pathway *A*, containing the first cleavage of the 5,6-*O*-isopropylidene group, and the other is pathway *B*, with a loss of H_2O.

The structure of **7** was determined by i.r. and n.m.r. spectroscopy and mass spectrometry; the presence of an acetamido, two *O*-isopropylidene, and two *O*-methyl groups was shown by the i.r. and n.m.r. spectra, and the major peaks in the mass spectrum (*m/e* 332, 101, 85, and 75) well support structure **7**. The structures of **9** and **10** were determined on the basis of the chemical and physical evidence reported in ref. 3.

Formula **11** illustrates the mechanism proposed for the acetonation of 2-acetamido-2-deoxy-D-glucose (**1**) with the 2,2-dimethoxypropane reagent. The existence of the pyranose–furanose equilibrium (**1a** ⇌ **1b**) in the reaction solution is considered to be responsible for the variation of final products with temperature, as for D-glucose[7] and some pentoses[8]. However, when the reaction was performed for 15 min at 80–85°, the accumulation of 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-D-glucofuranose (**4**) was not so remarkable as that of 5,6-*O*-isopropylidene-D-glucofuranose in the case of D-glucose[7], whereas 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-D-glucopyranose (**2**) was formed in high yield. This result shows that the reaction does not operate by such a simple kinetic control as that reported for non-nitrogenous aldoses[7,8]. In addition, it was found that the subsequent addition of 2,2-dimethoxypropane and continuation of the reaction for a further 45 min (total, 1 h) at 80–85° gave the methyl furanoside (**5**) and substituted glycal (**6**) as major products, strongly suggesting rapid isomerization of **2** to **4**. It is, therefore, compound **4** that is the unstable intermediate in this reaction, and the transformation of **4** into **5** is faster than that of **2** into **3**. The mechanism for the formation of the glycal **6** is not yet clear, but it is certain that the presence of **6** in the reaction solution is not observable by t.l.c., and



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R = Me or OCH_2Ph

that compound **6** is formed during the isolation procedure[14]. It is interesting that acetonation and glycosidation occur simultaneously in the same reaction solution. The main route of glycoside formation may involve the attack of a methoxyl group on an acetal intermediate[14] (**11**) formed by the addition of an excess of 2,2-dimethoxypropane in the course of the reaction, and such an intermediate may control the stereochemistry of the glycoside by neighboring-group participation of the *N*-acyl group on C-2. Such glycoside formation did not, in fact, occur by addition of methanol under the same acidic conditions in solution in *N*,*N*-dimethylformamide.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Specific rotations were determined with a Yanagimoto OR-50 polarimeter, and i.r. spectra were recorded with a Jasco IRA-spectrophotometer. N.m.r. spectra were recorded at 60 and 90 MHz with Hitachi R-24 and R-22 spectrometers for solutions in chloroform-*d*, unless otherwise noted. Mass spectra were recorded with a Jeol D-300 spectrometer. *N*,*N*-Dimethyl-

formamide was distilled, and dried with Drierite (W. A. Hammond Drierite Co.). Evaporations were conducted *in vacuo*.

*Acetonation of 2-acetamido-2-deoxy-*D*-glucose* (**1**). — (*A*) *At 80–85°* (*15 min*). A stirred solution of 2-acetamido-2-deoxy-D-glucose (**1**; 9.5 g, 43 mmol) and *p*-toluenesulfonic acid monohydrate (100 mg) in *N*,*N*-dimethylformamide (130 mL) was heated to 80–85°, and then 2,2-dimethoxypropane (20 mL, 3.8 mol/mol of **1**) was added; stirring was continued for 15 min at 80–85° (the starting material was then no longer detectable by t.l.c.). The mixture was cooled, and treated with Amberlite IRA-410 (OH^-) ion-exchange resin to remove the acid. After filtration, the filtrate was evaporated at 60° (bath). Crystallization was spontaneous, and when evaporation was complete, the mass was cooled, stirred with chloroform, and the product removed by filtration. The crystalline product (6 g, 54%) was identical with 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-D-glucopyranose[1] (**2**). The filtrate was concentrated, and chromatographed on a column of silicic acid with chloroform and then with 70:1 chloroform–methanol. The chloroform–methanol eluate afforded 2-acetamido-1,4-anhydro-2-deoxy-5,6-isopropylidene-D-*arabino*-hex-1-enitol (**6**) (1.5 g, 14%) and 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-D-glucofuranose (**4**) (0.56 g, 5%).

(*B*) *At 80–85°* (*1 h*). To the stirred mixture obtained by reaction *A* was further added 2,2-dimethoxypropane (8.4 mL; total amount, 5.4 mol/mol of **1**), and stirring was continued for 45 min at 80–85°. The mixture was cooled, and treated with Amberlite IRA-410 (OH^-) ion-exchange resin to remove the acid; the suspension was filtered, and the filtrate was evaporated at 60° (bath) to a syrup which was chromatographed on a column of silicic acid (100 g) with chloroform and then with 30:1 chloroform–methanol. The chloroform eluate yielded 2-acetamido-2-deoxy-3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (**7**) (1.0 g, 7%). The chloroform–methanol eluate afforded compounds **5** (5.4 g, 46%), **6** (1.3 g, 12%), **3** (1.1 g, 9%), and **2** (430 mg, 4%), respectively.

(*C*) *At room temperature* (*2 h*). This reaction was conducted with 9.5 g of **1** by the same method and procedure reported in ref. 1. After crystallization of **2** (10.0 g, 90%), the final filtrate was chromatographed on a column of silicic acid (30 g) with 30:1 chloroform–methanol. Compound **4** (130 mg, 1.2%) was obtained as crystals.

The new products are characterized in the sections immediately following.

*2-Acetamido-2-deoxy-5,6-*O*-isopropylidene-*D*-glucofuranose* (**4**). — The crude needles of **4** were recrystallized from methanol–ether, to give colorless needles, m.p. 145–147°, $[\alpha]_D^{21}$ +9° (*c* 0.85, methanol; equil.); ν_{max}^{Nujol} 3360 (OH), 3300 (NH), 1620 and 1560 (amide), and 860 and 840 cm^{-1} (Me_2C); n.m.r. data at 60 MHz (in methanol-d_6): δ 1.34 and 1.40 (6 H, 2 s, Me_2C), 1.97 and 2.0 (3 H, 2s, AcNα,β), 3.5–4.7 (6 H, m, H-2–H-6), 5.18 (s, H-1β), and 5.47 (d, $J_{1,2}$ 4.3 Hz, H-1α); the anomeric ratio (α:β) was estimated as 17:10 on the basis of the intensity of H-1α, and H-1β; mass-spectral data (e.i., 40 eV): *m/e* 246 (6.7, M^+ −Me), 228 (11, M^+ −Me −H_2O), 168 (9.8, *m/e* 228 −AcOH), 149 (36), 145 (24), 143 (27), 126 (18), 125 (8.0), 114

(8.0), 102 (8.9), 101 (100, $Me_2C_3H_3O_2^+$), 100 (7.6), 85 (8.4), 83 (6.7), 73 (28), 72 (24), 61 (9.8), 60 (10), 59 (28, Me_2C^+OH), 58 (7.6), 57 (12), 55 (7.1), and 43 (77, MeC^+O).

Anal. Calc. for $C_{11}H_{19}NO_6$: C, 50.57; H, 7.33; N, 5.36. Found: C, 50.30; H, 7.48; N, 5.19.

*2-Acetamido-1,3-di-*O*-acetyl-2-deoxy-5,6-*O*-isopropylidene-α-*D*-glucofuranose* (**4a**). — Compound **4** (100 mg) was acetylated overnight at room temperature with acetic anhydride–pyridine. The product was purified by column chromatography on silicic acid, to give the di-*O*-acetyl derivative (**4a**) as a syrup: wt. 110 mg (83%); n.m.r. data at 90 MHz (in chloroform-*d*): δ 1.29 and 1.34 (6 H, 2 s, Me_2C), 1.48 (3 H, s, AcN), 2.06 and 2.07 (6 H, 2 s, AcO), 4.70 (1 H, m, $J_{1,2}$ 4.5, $J_{2,3}$ 7.4, $J_{2,NH}$ 8.4 Hz, H-2), 5.52 (1 H, near t, $J_{2,3}$ 7.4, $J_{3,4}$ 6.4 Hz, H-3), 6.26 (1 H, d, $J_{1,2}$ 4.5 Hz, H-1), and 6.93 (1 H, d, NH).

Anal. Calc. for $C_{15}H_{23}NO_8$: C, 52.17; H, 6.71; N, 4.06. Found: C, 51.90; H, 6.49; N, 3.79.

*2-Acetamido-1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-*D*-*arabino*-hex-1-enitol* (**6**). — Recrystallization of the crude crystals of **6** from methanol–ether gave plates, m.p. 152°, $[\alpha]_D^{24}$ −1° (*c* 0.5, methanol); ν_{max}^{Nujol} 3200 (OH), 3140 (NH), 1670 (C=C), 1650 and 1530 (amide), and 850 cm^{-1} (Me_2C); n.m.r. data at 90 MHz (in dimethyl sulfoxide-d_6): δ 1.12 and 1.28 (6 H, 2 s, Me_2C), 1.93 (3 H, s, AcN), 3.55–4.05 (3 H, m, H-5,6,6'), 4.65 (1 H, near t, H-4), 5.68 (1 H, d of d, $J_{3,OH}$ 8.0, $J_{3,4}$ 4.0 Hz, H-3), 6.03 (1 H, s, H-1), 6.48 (1 H, d, $J_{3,OH}$ 8.0 Hz, OH-3), and 9.78 (1 H, s, NH); mass-spectral data (e.i., 20 eV): *m/e* 228 (13, $M^+ - Me$), 225 (7.4, $M^+ - H_2O$), 210 (4.4, $M^+ - Me - H_2O$), 163 (23), 142 (45), 126 (37), 125 (74, $C_6H_7O_2N$, $M^+ - 101 - OH$), 114 (11), 108 (15), 101 (100, $Me_2C_3H_3O_2^+$), 100 (68), 83 (25), 73 (40), 72 (22), and 43 (47, MeC^+O); (e.i., 75 eV): 228 (4.2), 225 (3.5), 210 (1.5), 168 (6.9), 142 (11), 126 (14), 125 (26), 101 (35), 100 (29), 96 (6.2), 83 (14), 73 (11), 72 (14), 59 (5.5, Me_2C^+OH), and 43 (100); c.i. (20 eV, *iso*-C_4H_{10}): *m/e* 244 [7, $(M + 1)^+$], 226 [100, $(M + 1)^+ - H_2O$], 168 (20), 126 (55), 125 (15), 101 (73); f.d. (emitter current 14 mA): *m/e* 244 [20, $(M + 1)^+$], 243 (82, M^+), 228 (19, $M^+ - Me$), 225 (33, $M^+ - H_2O$), 143 (11), 142 (100), and 101 (98).

Anal. Calc. for $C_{11}H_{17}NO_5$: C, 54.31; H, 7.04; N, 5.76. Found: C, 54.14; H, 7.07; N, 5.46.

*2-Acetamido-2-deoxy-3,4:5,6-di-*O*-isopropylidene-*aldehydo*-*D*-glucose dimethyl acetal* (**7**). — After recrystallization of crude **7** from ether, the compound was obtained as needles, m.p. 55–57°, $[\alpha]_D^{21}$ +5.0° (*c* 0.5, methanol); ν_{max}^{Nujol} 3280 (NH), 1650 and 1530 (amide), 1080 (ether), 870 and 840 cm^{-1} (Me_2C); n.m.r. data at 60 MHz (in chloroform-*d*): δ 1.35, 1.37, 1.47 (12 H, 3 s, 2 Me_2C), 2.02 (3 H, s, AcN), 3.36 and 3.40 (6 H, 2 s, 2 MeO), 3.5–4.7 (7 H, m), and 5.9 (1 H, d, NH); mass-spectral data (e.i., 75 eV): *m/e* 332 (18, $M^+ - Me$), 317 (11, $M^+ - 2$ Me), 288 (18), 246 (7.2, $M^+ - 101$), 182 (10), 143 (14), 142 (12), 140 (10), 101 (12, $Me_2C_3H_3O_2^+$), 96 (11), 85 (14, $MeC^+C_2O_2H_2$), 82 (12), 75 [100, $(MeO)_2C^+H$], 73 (21), 72 (13), 59 (26, Me_2C^+OH), 57 (19), 47 (21), and 43 (80, MeC^+O).

Anal. Calc. for $C_{16}H_{29}NO_7$: C, 55.31; H, 8.41. Found: C, 55.25; H, 8.66.

Acetonation of 2-(benzyloxycarbonylamino)-2-deoxy-D-glucose (**8**). — To a stirred solution of **8** (8 g) in *N,N*-dimethylformamide (200 mL) were added 2,2-dimethoxypropane (24 mL) and *p*-toluenesulfonic acid monohydrate (100 mg). The mixture was stirred for 2 h at room temperature and then deacidified with Amberlite IRA-410 (OH^-) resin. The solution was evaporated at 60° (bath), and the product was crystallized from ethanol–ether, to give **9** (7.7 g, 85%). Recrystallization from ethanol–ether gave colorless needles, m.p. 165–167°, $[\alpha]_D^{25}$ +23° (*c* 0.5, methanol; equil.); ν_{max}^{Nujol} 3480 and 3300 (OH), 3280 (NH), 1680 and 1530 (amide), 840 (Me_2C), and 740–680 cm^{-1} (phenyl); mass-spectral data (e.i., 40 eV): *m/e* 338 (2.2, $M^+ - Me$), 145 (14), 111 (18), 108 (19), 107 (18), 101 (22), 92 (41), 91 (79, $C_7H_7^+$), 90 (15), 89 (16), 79 (29), 77 (27), 73 (16), 65 (55, $C_5H_5^+$), 59 (100, Me_2C^+OH), 51 (17), and 43 (94, MeC^+O).

Anal. Calc. for $C_{17}H_{23}NO_7$: C, 57.78; H, 6.56; N, 3.96. Found: C, 57.95; H, 6.33; N, 3.94.

The final filtrate (after crystallization of **9**) gave **10** (180 mg, 2.0%). Recrystallization from ethanol–ether gave colorless needles, m.p. 105–107°, $[\alpha]_D^{25}$ +30° (*c* 0.5, methanol; equil.); ν_{max}^{Nujol} 3480 (OH), 3300 (NH), 1660 and 1500 (amide), 850 and 840 (Me_2C), and 730–680 (phenyl); n.m.r. data at 90 MHz (in dimethyl sulfoxide-d_6): δ 1.22 and 1.27 (6 H, 2 s, Me_2C), 3.4–4.5 (7 H, m), 4.7–5.6 (3 H, m), 5.0 (2 H, s, benzyl methylene), 6.17 and 6.43 (1 H, 2 d, *J* 6.2 and *J* 4.5 Hz, OH −1α,β), 6.9–7.6 (2 H, 2 d, NHα,β), and 7.31 (5 H, s, Ph); (after D_2O treatment): δ 1.22 and 1.27 (6 H, 2 s, Me_2C), 3.4–4.4 (6 H, m), 4.94 (d, $J_{1\beta,2}$ 2.0 Hz, H-1β), 4.98 (2 H, s, benzyl methylene), 5.22 (d, $J_{1\alpha,2}$ 4.5 Hz, H-1α), and 7.31 (5 H, s, Ph); mass-spectral data (e.i., 40 eV): *m/e* 338 (1.7, $M^+ - Me$), 320 (1.8, $M^+ - Me - H_2O$), 145 (16), 108 (16), 107 (15), 101 (81, $Me_2C_3H_3O_2^+$), 92 (26), 91 (100, $C_7H_7^+$), 79 (16), 77 (14), 73 (19), 65 (25, $C_5H_5^+$), 59 (31, Me_2C^+OH), 57 (16), 55 (12), and 43 (70, Me_2C^+O).

Anal. Calc. for $C_{17}H_{23}NO_7$: C, 57.78; H, 6.56; N, 3.96. Found: C, 57.90; H, 6.28; N, 3.88.

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