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THE BEHAVIOR OF SOME ALDOSES WITH 2,2-DIALKOXYPROPANE–*N*,*N*-DIMETHYLFORMAMIDE–TOLUENE-*p*-SULPHONIC ACID*†

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ABSTRACT

Various *N*-substituted 2-amino-2-deoxy-D-glucoses react with 2,2-dimethoxypropane (or 2,2-dibenzyloxypropane)–*N*,*N*-dimethylformamide–toluene-*p*-sulphonic acid at room temperature to give 4,6-*O*-isopropylidene derivatives. However, at 80–90° and using 2,2-dibenzyloxypropane, 2-acetamido-2-deoxy-D-glucose afforded benzyl 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside and 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-D-glucose; 2-benzyloxycarbonylamino-2-deoxy-D-glucose gave benzyl 2-benzyloxycarbonylamino-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside and 2-benzyloxycarbonylamino-2-deoxy-4,6-*O*-isopropylidene-D-glucopyranose; but 2-deoxy-2-(2,4-dinitrophenylamino)-D-glucose gave only the 4,6-*O*-isopropylidene derivative.

INTRODUCTION

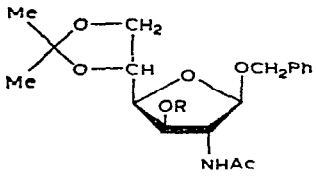
Recent work[1–5] has shown that a mixture of 2,2-dimethoxypropane, *N*,*N*-dimethylformamide, and toluene-*p*-sulphonic acid constitutes a unique acetonating reagent capable, *inter alia*, of protecting vicinal, *trans*-diequatorial, hydroxyl groups and of forming *N*-acetyl-2,2-dimethyloxazolidines from vicinal hydroxyl and acetamido groups. We have shown[6,7] that aldohexoses react with the reagent at 20° to give 4,6-*O*-isopropylidene derivatives, and at 80° to give mainly methyl 5,6-*O*-isopropylidenehexofuranosides in which MeO-1 is *trans* to the function at C-2. We now describe a further exploration of the potential utility of this reagent for syntheses in the amino sugar field.

RESULTS

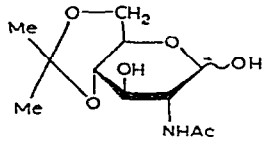
Treatment[7] of 2-acetamido-2-deoxy-D-glucose with the 2,2-dimethoxypropane reagent at 80° gave a mixture from which methyl 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside and methyl 2-acetamido-2-deoxy-4,6-*O*-isopro-

*Dedicated to the memory of Dr. Hewitt G. Fletcher, Jr.
†Part III. For Part II, see Ref. 7.

pylidene-β-D-glucopyranoside were isolated. When 2,2-dimethoxypropane was replaced by 2,2-dibenzyloxypropane[8], then, after 2 h at 85°, 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-D-glucose (**3**, 20–40%) was formed together with a syrupy product *X* (30–56%). The n.m.r. and i.r. spectra of *X* were consistent with a benzyl glycoside containing acetamido and isopropylidene groups. The n.m.r. signal for H-1 was a singlet indicative of a furanoid structure. Benzylation of *X* gave a crystalline di-*O*-benzyl derivative (**2**) without changing the chemical shift or character of the n.m.r. signal for H-1. Hydrolysis of **2** with 50% aqueous acetic acid for 2 h at 50° gave a crystalline diol which consumed 1 mol. of periodate and possessed spectral characteristics compatible with those for benzyl 2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucofuranoside (**4**). Thus, *X* is benzyl 2-acetamido-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (**1**).



1 R = H
2 R = CH_2Ph



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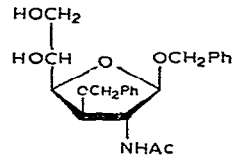

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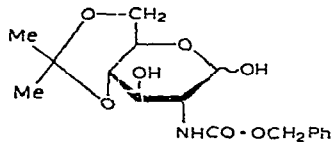

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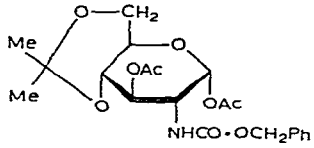

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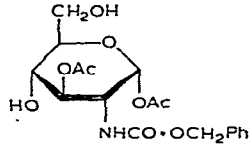

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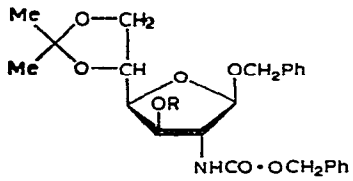
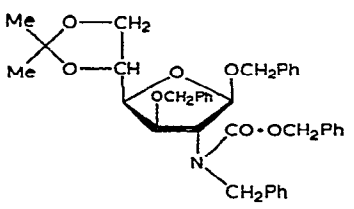
Treatment of 2-benzyloxycarbonylamino-2-deoxy-D-glucose[9] with the 2,2-dimethoxypropane (or 2,2-dibenzyloxypropane) reagent at room temperature gave a crystalline isopropylidene derivative *Y* in good yield which reduced Fehling's solution and therefore had HO-1 unsubstituted. Acetylation of *Y* gave a syrupy product (**6**), the n.m.r. spectrum of which indicated it to be substantially a single anomer. The isopropylidene group was selectively hydrolyzed from **6** to give a syrupy, periodate-stable diol (**7**). Thus, *Y* is 2-benzyloxycarbonylamino-2-deoxy-3,5(or 4,6)-*O*-isopropylidene-D-glucose. Treatment of 4,6-*O*-benzylidene-2-benzyloxycarbonylamino-2-deoxy-D-glucose with pyridine and acetic anhydride at room temperature gave the α- and the known[10] β-diacetate. Removal of the benzylidene group from the α-diacetate by mild, acidic hydrolysis gave the diol **7**. Thus, *Y* is 2-benzyloxycarbonylamino-2-deoxy-4,6-*O*-isopropylidene-D-glucopyranose (**5**).

Treatment of 2-benzyloxycarbonylamino-2-deoxy-D-glucose with the 2,2-dibenzyloxypropane reagent at 85° gave two products. Spectral data indicated that the

first product (40%) contained amide, isopropylidene, and benzyloxy groups; the n.m.r. signal for the anomeric proton was a singlet. The product was therefore benzyl 2-benzyloxycarbonylamino-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (**8**). Benzylation of **8** gave a dibenzyl ether having the composition and properties expected of **9** and a di-*O*-benzyl-*N*-benzyl derivative (**10**). Removal of the isopropylidene group from **9** with 60% aqueous acetic acid at 40° gave, in high yield, a crystalline diol (**11**) that reduced periodate. Compounds **8**–**11** were laevorotatory, and each showed a singlet at τ 4.8–5.0 in the n.m.r. spectra. Thus, **11** is designated as benzyl 2-benzyloxycarbonylamino-3-*O*-benzyl-2-deoxy-β-D-glucofuranoside. The second product (30%) was 2-benzyloxycarbonylamino-2-deoxy-4,6-*O*-isopropylidene-D-glucopyranose.



8 R = H
9 R = OCH_2Ph



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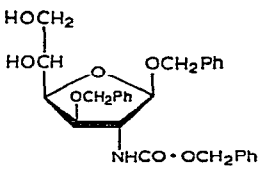

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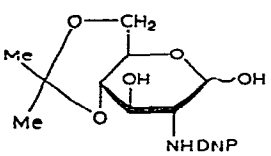
Treatment of 2-deoxy-2-(2,4-dinitrophenylamino)-D-glucose with the 2,2-dimethoxypropane reagent at 20° or 90° gave the same crystalline product (*Z*) in high yield. The elemental composition and n.m.r. spectra of *Z* indicated that a single isopropylidene group had been introduced and that the dinitroanilino group was unaltered. The rapid reduction of Fehling's solution showed that HO-1 was unsubstituted. Acetylation of *Z* gave a crystalline diacetate (**13**) from which the isopropylidene group could be cleaved by mild, acid hydrolysis to give a diol (**14**) which was resistant to sodium metaperiodate. Thus, *Z* is 2-deoxy-2-(2,4-dinitroanilino)-4,6-*O*-isopropylidene-D-glucopyranose (**12**). When 2-deoxy-2-(2,4-dinitrophenylamino)-D-glucose was converted into the 4,6-*O*-benzylidene derivative, followed by acetylation and mild hydrolysis with acid, a crystalline diol was obtained which was identical with **14**. Acetylation of **14** afforded the known 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitrophenylamino)-α-D-glucopyranose[11] (**15**).



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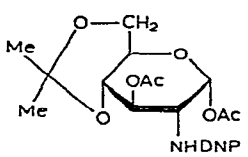

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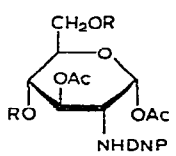
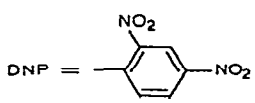


14 R = H
15 R = Ac



DISCUSSION

The foregoing results show that the reagent 2,2-dibenzyloxypropane–*N*,*N*-dimethylformamide–toluene-*p*-sulphonic acid converts 2-acylamino-2-deoxy-D-glucose derivatives into 4,6-*O*-isopropylidene derivatives at room temperature. At 80–90°, benzyl furanosides are formed. Glycosidic products were not formed in the reaction of 2-deoxy-2-(2,4-dinitrophenylamino)-D-glucose with the reagent. Glycoside formation has not been observed[12] when aldopentoses are acetonated with the reagent at elevated temperature. Acetonation under similar conditions of aldoses bearing a substituent at C-2 which could be involved in a neighbouring-group reaction gave glycosides with the glycosidic substituent *trans* to the function at C-2.

Under mild reaction conditions, *N*,*N*-dimethylformamide dialkyl acetal is, presumably, a potential component of the reagent mixture, and this product is known to react with vicinal diols to form labile (dimethylamino)methylene acetals[13,14]. Thus, it is possible that the initial formation of such labile acetals may direct isopropylidenation to abnormal positions. The labile acetal groups would be hydrolysed during the isolation procedure. Glycoside formation may involve an oxazoline intermediate which controls the stereochemistry of the product.

The combination 2,2-dialkoxypropane–*N*,*N*-dimethylformamide–toluene-*p*-sulphonic acid is an acetonating agent that may give abnormal and potentially useful isopropylidene derivatives.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Specific rotations were determined with a Yanagimoto OR-50 polarimeter. I.r. spectra were recorded with a Jasco IRA-1 spectrophotometer. N.m.r. spectra were recorded at 60 MHz for solutions in chloroform-*d* unless otherwise noted. Preparative chromatography was performed on 100-mesh silicic acid (Mallinckrodt) with the solvent systems specified. *N*,*N*-Dimethylformamide was distilled and dried over Drierite (W. A. Hammond Drierite Co.).

Benzyl 2-acetamido-2-deoxy-5,6-O-isopropylidene-β-D-glucofuranoside (**1**) *and 2-acetamido-2-deoxy-4,6-O-isopropylidene-D-glucopyranose* (**3**). — To a stirred solution of 2-acetamido-2-deoxy-D-glucose (15 g) in dry *N*,*N*-dimethylformamide (150 ml) at 85°, 2,2-dibenzyloxypropane[8] (25 ml) and toluene-*p*-sulphonic acid monohydrate (200 mg) were added; stirring was continued for 2 h at 80–85°. The mixture was cooled, deacidified with Amberlite IRA-410 (HO^-) resin, and filtered, and the insoluble material was washed with dry *N*,*N*-dimethylformamide. The combined filtrate and washings were concentrated *in vacuo*, and the syrupy residue was eluted from a column of silicic acid (200 g) with chloroform, and with chloroform–methanol (100:1 and 20:1). The chloroform–methanol (100:1) eluate yielded **1** (7.1 g, 30%), $[\alpha]_D^{20}$ −48° (*c* 0.6, chloroform); ν_{max}^{film} 3500 (OH), 3300 (NH), 1650, 1550 (amide), 840 (Me_2C), and 740 and 690 cm^{-1} (phenyl). N.m.r. data: τ 2.75 (Ph), 5.0 (s, H-1), 8.05 (s, NAc), and 8.60 and 8.63 (2 s, Me_2C).

Anal. Calc. for $C_{18}H_{25}NO_6$: C, 61.52; H, 7.17; N, 3.99. Found: C, 61.22; H, 7.42; N, 3.70.

The chloroform–methanol (20:1) eluate yielded **3** (5.6 g, 30%) as fine needles, m.p. 189–190°, $[\alpha]_D^{20}$ +57.5° (*c* 1, equil., methanol); lit.[6] m.p. 189–190°, $[\alpha]_D^{20}$ +57.5° (*c* 0.99, equil., methanol).

Benzyl 2-acetamido-3-O-benzyl-2-deoxy-5,6-O-isopropylidene-β-D-glucofuranoside (**2**). — To a stirred solution of **1** (7 g) in *N,N*-dimethylformamide (150 ml) at 0°, benzyl bromide (4.2 g), barium oxide (5 g), and barium hydroxide octahydrate (2 g) were added. The mixture was stirred for 18 h at 0 to 5°. Chloroform (200 ml) was added, the mixture was filtered, and insoluble material was washed with chloroform. The combined filtrate and washings were washed with 2M HCl, 10% aqueous Na_2CO_3, and water, dried, and concentrated *in vacuo*. Recrystallization of the residue from ethanol–hexane gave **2** (6.6 g, 75%) as needles, m.p. 141°, $[\alpha]_D^{19}$ −104° (*c* 0.5, chloroform); ν_{max}^{Nujol} 3300 (NH), 1650 and 1550 (amide), 840 (Me_2C), and 750 and 690 cm^{-1} (phenyl). N.m.r. data: τ 2.75 (Ph), 4.98 (s, H-1), 8.04 (s, NAc), 8.60 and 8.64 (2 s, CMe_2).

Anal. Calc. for $C_{25}H_{31}NO_6$: C, 68.00; H, 7.08; N, 3.17. Found: C, 68.11; H, 7.15; N, 3.25.

Benzyl 2-acetamido-3-O-benzyl-2-deoxy-β-D-glucofuranoside (**4**). — A solution of **2** (2.1 g) in 50% aqueous acetic acid (40 ml) was kept for 2 h at 50° and then concentrated *in vacuo* to a syrup which was crystallized from ether–hexane to give **4** (1.6 g, 84%). Recrystallization from ether gave colourless needles, m.p. 99°, $[\alpha]_D^{12}$ −98° (*c* 0.5, methanol); ν_{max}^{Nujol} 3500–3300 (OH, NH), 1640 and 1540 (amide), and 740 and 680 cm^{-1} (phenyl). N.m.r. data: τ 2.75 (Ph), 5.00 (s, H-1), and 8.10 (s, NAc). The product reduced 1.0 mol. of sodium metaperiodate in 24 h.

Anal. Calc. for $C_{22}H_{27}NO_6$: C, 65.82; H, 6.78; N, 3.49. Found: C, 65.70; H, 6.88; N, 3.56.

2-Benzyloxycarbonylamino-2-deoxy-4,6-O-isopropylidene-D-glucose (**5**). — (*a*) To a solution of 2-benzyloxycarbonylamino-2-deoxy-D-glucose (2 g) in *N,N*-dimethylformamide (50 ml), 2,2-dimethoxypropane (6 ml), and toluene-*p*-sulphonic acid monohydrate (50 mg) were added. The mixture was stirred for 2 h at room temperature and then deacidified with Amberlite IRA-410 (HO^-) resin. The solution was concentrated *in vacuo* (70° bath), and the syrupy product was eluted from a column of silicic acid (30 g) with chloroform–methanol (50:1) to give **5** (1.86 g, 82%). Recrystallization from ethanol–ether gave needles, m.p. 105–107°, $[\alpha]_D^{21}$ +29° (*c* 0.4, equil., methanol); ν_{max}^{Nujol} 3500 (OH), 3300 (NH), 1650 and 1510 (amide), 850 (Me_2C), and 730 and 690 cm^{-1} (phenyl).

Anal. Calc. for $C_{17}H_{23}NO_7$: C, 57.78; H, 6.56; N, 3.96. Found: C, 57.99; H, 6.61; N, 3.95.

(*b*) 2-Benzyloxycarbonylamino-2-deoxy-D-glucose (2 g) was isopropylidenated with 2,2-dibenzyloxypropane under conditions similar to those described in (*a*) to give **5** (1.15 g, 51%), m.p. 105–107°, $[\alpha]_D^{20}$ +29° (*c* 0.5, equil., methanol).

1,3-Di-O-acetyl-2-benzyloxycarbonylamino-2-deoxy-4,6-O-isopropylidene-α-D-

glucopyranose (**6**). — A solution of **5** (500 mg) in pyridine (10 ml) and acetic anhydride (3 ml) was heated at 60° for 1 h. The mixture was concentrated *in vacuo* and the residue was eluted from a column of silicic acid (22 g) with chloroform to give **6** as an amorphous solid (490 mg, 79%), $[\alpha]_D^{23}$ +74.5° (*c* 0.4, chloroform); ν_{max}^{film} 3300 (NH), 1740 and 1220 (ester), 1710 and 1520 (amide), 840 (Me_2C), and 750 and 690 cm^{-1} (phenyl). N.m.r. data: τ 2.63 (Ph), 3.74 (d, $J_{1,2}$ 4.5 Hz, H-1), 7.97 (s, 6 H, 2 AcO), 8.67 and 8.71 (2 s, Me_2C).

Anal. Calc. for $C_{21}H_{27}NO_9$: C, 57.66; H, 6.22; N, 3.20. Found: C, 57.48; H, 6.50; N, 3.10.

1,3-Di-O-acetyl-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranose (**7**). — (*a*) A solution of **6** (300 mg) in 60% aqueous acetic acid (40 ml) was kept for 3 h at 40°, and then concentrated *in vacuo* at 40°. The residual syrup was eluted from a column of silicic acid (6 g) with 70:1 chloroform–methanol to afford **7** (220 mg, 81%) as a syrup, $[\alpha]_D^{23}$ +25° (*c* 0.4, methanol); ν_{max}^{film} 3300–3400 (NH, OH), 1750 and 1230 (ester), 1710 and 1530 (amide), and 750 and 690 cm^{-1} (phenyl). When dissolved in 40mM sodium metaperiodate, **7** did not consume any oxidant during 24 h at room temperature.

Anal. Calc. for $C_{18}H_{23}NO_9$: C, 54.40; H, 5.83; N, 3.53. Found: C, 54.30; H, 5.90; N, 3.41.

(*b*) A solution of 1,3-di-*O*-acetyl-4,6-*O*-benzylidene-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranose (200 mg) in methyl cellosolve (10 ml) and 60% aqueous acetic acid (25 ml) was heated for 2.5 h at 60° and then concentrated under diminished pressure. The residual syrup was eluted from a column of silicic acid (5 g) with 70:1 chloroform–methanol to give **7** (120 mg, 73%), the i.r. spectrum and specific rotation of which were identical with those of the compound obtained in (*a*).

1,3-Di-O-acetyl-4,6-O-benzylidene-2-benzyloxycarbonylamino-2-deoxy-α- and β-D-glucopyranoses. — 4,6-*O*-Benzylidene-2-benzyloxycarbonylamino-2-deoxy-D-glucose (1 g) was acetylated at room temperature with acetic anhydride (6 ml) and pyridine (20 ml). Recrystallization of the crude ester (1.17 g, 94%) from ethanol gave the β-diacetate (350 mg, 28%), m.p. 247° (lit.[10] m.p. 247°), and the α-anomer (670 mg, 54%), m.p. 168.5°, $[\alpha]_D^{20}$ +51° (*c* 0.5, chloroform); ν_{max}^{Nujol} 3300 (NH), 1740 and 1230 (ester), and 1700 and 1530 cm^{-1} (amide). N.m.r. data: τ 2.60 and 2.66 (Ph), 3.80 (d, $J_{1,2}$ 3.5 Hz, H-1), 7.93 and 8.07 (2 s, 2 AcO).

Anal. Calc. for $C_{25}H_{27}NO_9$: C, 61.85; H, 5.65; N, 2.89. Found: C, 61.85; H, 5.77; N, 2.95.

Isopropylidenation of 2-benzyloxycarbonylamino-2-deoxy-D-glucose[9] *at 85°.* — A solution of the title compound (4 g) in dry *N,N*-dimethylformamide (140 ml) at 85° was stirred whilst 2,2-dibenzyloxypropane (40 ml) and toluene-*p*-sulphonic acid (200 mg) were added. The mixture was stirred for 1 h at 85°, cooled, and deacidified with Amberlite IRA-410 (HO^-) resin. The mixture was filtered, and concentrated *in vacuo*, and the syrupy residue was eluted from a column of silicic acid (50 g) with benzene, and benzene–methanol (70:1 and 20:1). Benzene–methanol (70:1) eluted benzyl 2-benzyloxycarbonylamino-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside

(**8**; 2.26 g, 40%) as a syrup, $[\alpha]_D^{23}$ −35° (*c* 0.1, chloroform); ν_{max}^{film} 3400–3300 (OH, NH), 1700 and 1520 (amide), 840 (Me_2C), and 730 and 690 cm^{-1} (phenyl). N.m.r. data: τ 2.68 (Ph), 5.0 (s, H-1), and 8.60 and 8.68 (2 s, Me_2C),

Anal. Calc. for $C_{24}H_{29}NO_7$: C, 65.00; H, 6.59; N, 3.16. Found: C, 64.88; H, 6.65; N, 3.15.

Benzene–methanol (20:1) eluted 2-benzyloxycarbonylamino-2-deoxy-4,6-*O*-isopropylidene-D-glucose (**5**; 1.3 g, 29%) which was identical with the compound characterized above.

Benzyl 3-O-benzyl-2-benzyloxycarbonylamino-2-deoxy-5,6-O-isopropylidene-β-D-glucofuranoside (**9**) *and benzyl 3-O-benzyl-2-(N-benzyl-N-benzyloxycarbonylamino)-2-deoxy-5,6-O-isopropylidene-β-D-glucofuranoside* (**10**). — To a stirred solution of **8** (800 mg) in *N,N*-dimethylformamide (15 ml) at 0°, benzyl bromide (0.25 ml), barium oxide (320 mg), and barium hydroxide octahydrate (160 mg) were added. The mixture was stirred for 5 h at 0° and then for 18 h at room temperature. The mixture was filtered and insoluble material was washed with chloroform. The combined filtrate and washings were washed with water, dried, and concentrated *in vacuo*. The syrupy residue was eluted from a column of silicic acid (22 g) with chloroform. Eluted first was **10** (170 mg, 15%). Recrystallization from benzene–hexane gave colourless needles, m.p. 98°, $[\alpha]_D^{20}$ −30° (*c* 0.5, chloroform); ν_{max}^{Nujol} 1700 (carbonyl), 840 (Me_2C), and 730 and 690 cm^{-1} (phenyl). N.m.r. data: τ 2.72, 2.80 (20 H, 4 Ph), 4.80 (s, H-1), and 8.61 and 8.69 (2 s, Me_2C).

Anal. Calc. for $C_{38}H_{41}NO_7$: C, 73.17; H, 6.63; N, 2.25. Found: C, 73.15; H, 6.58; N, 2.19.

Eluted second was **9** (240 mg, 25%) as a syrup, $[\alpha]_D^{20}$ −52° (*c* 0.4, chloroform); ν_{max}^{film} 1710 and 1530 (amide), 840 (Me_2C), and 730 and 690 cm^{-1} (phenyl). N.m.r. data: τ 2.70, 2.73 (15 H, 3 Ph), 5.0 (s, H-1), and 8.61 and 8.71 (2 s, Me_2C).

Anal. Calc. for $C_{31}H_{35}NO_7$: C, 69.77; H, 6.61; N, 2.63. Found: C, 69.58; H, 6.51; N, 2.60.

Benzyl 3-O-benzyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucofuranoside (**11**). — A solution of **9** (120 mg) in 60% aqueous acetic acid (15 ml) was heated for 3 h at 40° and then concentrated *in vacuo* at 40°. The residue crystallized from ethanol–ether, and recrystallization from ethanol gave **11** as needles (100 mg, 90%), m.p. 85°, $[\alpha]_D^{20}$ −82° (*c* 0.4, chloroform); ν_{max}^{Nujol} 3400–3300 (OH, NH), 1700 and 1520 (amide), and 730 and 690 cm^{-1} (phenyl). N.m.r. data: τ 2.64, 2.68 (15 H, 3 Ph), and 5.02 (s, H-1). In 40mM sodium metaperiodate at room temperature, **11** consumed 1.0 mol. of oxidant in 24 h.

Anal. Calc. for $C_{28}H_{31}NO_7$: C, 68.17; H, 6.33; N, 2.84. Found: C, 68.25; H, 6.51; N, 2.88.

2-Deoxy-2-(2,4-dinitrophenylamino)-4,6-O-isopropylidene-D-glucopyranose (**12**). — (*a*) To a solution of 2-deoxy-2-(2,4-dinitrophenylamino)-D-glucose (2 g) in dry *N,N*-dimethylformamide (50 ml), 2,2-dimethoxypropane (6 ml) and toluene-*p*-sulphonic acid monohydrate (50 mg) were added. The mixture was stirred for 2 h at room temperature and then deacidified with Amberlite IRA-410 (HO^-) resin. The

solution was filtered, and concentrated *in vacuo*. The syrupy residue crystallized from benzene, and recrystallization from ethanol gave **12** as yellow plates (1.84 g, 82%), m.p. 125°, $[\alpha]_D^{20}$ −16° (*c* 0.5, equil., acetone); ν_{max}^{Nujol} 3500 (OH), 3320, 1520 (NH), 1610, 1580 (DNP), and 850 cm^{-1} (Me_2C).

Anal. Calc. for $C_{15}H_{19}N_3O_9$: C, 46.75; H, 4.97; N, 10.91. Found: C, 46.51; H, 4.99; N, 10.80.

(*b*) Repetition of the acetonation at 90° gave **12** (1.3 g, 58%), m.p. 125°.

1,3-Di-O-acetyl-2-deoxy-2-(2,4-dinitrophenylamino)-4,6-O-isopropylidene-α-D-glucopyranose (**13**). — Acetylation of **12** (400 ml) overnight at room temperature with pyridine–acetic anhydride gave a crude product (420 mg, 86%), which was recrystallized from benzene to give **13** as yellow needles, m.p. 296°, $[\alpha]_D^{20}$ +48° (*c* 0.5, acetone); ν_{max}^{Nujol} 3300 and 1520 (NH), 1760, 1720 and 1240–1200 (ester), 1610 and 1580 (DNP), and 840 cm^{-1} (Me_2C). N.m.r. data (90 MHz): τ 3.76 (d, $J_{1,2}$ 4.0 Hz, H-1), 7.78 and 8.13 (2 s, 6 H, 2 AcO), and 8.47 and 8.58 (2 s, Me_2C).

Anal. Calc. for $C_{19}H_{23}N_3O_{11}$: C, 48.61; H, 4.94; N, 8.95. Found: C, 48.99; H, 4.89; N, 9.01.

1,3-Di-O-acetyl-2-deoxy-2-(2,4-dinitrophenylamino)-α-D-glucopyranose (**14**). — (*a*) To a solution of **13** (200 mg) in methyl cellosolve (30 ml) at 50°, 60% aqueous acetic acid (50 ml) was added, and the mixture was kept at room temperature for 4 h and then concentrated *in vacuo*. Recrystallization of ther esidue from ethanol gave **14** (160 mg, 87%) as yellow needles, m.p. 211–213°, $[\alpha]_D^{20}$ +75° (*c* 0.4, acetone); ν_{max}^{Nujol} 3500–3400 (OH), 3320 and 1520 (NH), 1750, 1730, 1250–1220 (ester), 1620 and 1590 cm^{-1} (NO_2). When dissolved in 40mM sodium metaperiodate, **14** did not change the concentration of the oxidant during 24 h at room temperature.

Anal. Calc. for $C_{16}H_{19}N_3O_{11}$: C, 44.75; H, 4.46; N, 9.79. Found: C, 44.85; H, 4.56; N, 10.05.

(*b*) To a solution of 1,3-di-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-(2,4-dinitrophenylamino)-α-D-glucopyranose (200 mg) in methyl cellosolve (70 ml) at 80°, 60% aqueous acetic acid (120 ml) was added. The mixture was stirred at 80° for 4 h, and then concentrated *in vacuo*. Recrystallization of the residue from ethanol afforded **14** (86 mg, 52%), m.p. 212–213°, $[\alpha]_D^{20}$ +77° (*c* 0.37, acetone).

4,6-O-Benzylidene-2-deoxy-2-(2,4-dinitrophenylamino)-D-glucose. — A mixture of 2-deoxy-2-(2,4-dinitrophenylamino)-D-glucose (2 g), zinc chloride (4 g), and benzaldehyde (20 ml) was vigorously stirred for 3 h at room temperature. The reaction mixture was then stirred with water (200 ml) for 1 h. The product was collected, and recrystallized from 90% methanol to afford the title compound as yellow needles (1.78 g, 71%), m.p. 188–191°, $[\alpha]_D^{20}$ −55° (*c* 1, equil., acetone); ν_{max}^{Nujol} 3500–3300 (OH, NH), 1520 (NH), 1620 and 1590 cm^{-1} (DNP).

Anal. Calc. for $C_{19}H_{19}N_3O_9$: C, 52.65; H, 4.42; N, 9.70. Found: C, 52.71; H, 4.50; N, 9.81.

1,3-Di-O-acetyl-4,6-O-benzylidene-2-deoxy-2-(2,4-dinitrophenylamino)-α-D-glucopyranose. — Acetylation of the foregoing compound (1 g) with pyridine acetic anhydride at room temperature, with recrystallization of the product from acetone,

gave the title compound as yellow needles (1.1 g, 92%), m.p. >300°, $[\alpha]_D^{20}$ +7° (*c* 0.5, *N,N*-dimethylformamide); ν_{max}^{Nujol} 3320 and 1520 (NH), 1780, 1720, and 1250–1200 (ester), and 1620 and 1590 cm^{-1} (DNP).

Anal. Calc. for $C_{23}H_{23}N_3O_{11}$: C, 53.38; H, 4.48; N, 8.12. Found: C, 53.54; H, 4.69; N, 8.12.

*1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitrophenylamino)-α-*D*-glucopyranose* (**15**). — Acetylation of **14** (20 mg) with pyridine–acetic anhydride at room temperature, with recrystallization of the product from chloroform, afforded **15** as yellow needles (22 mg, 92%), m.p. 217–218°, $[\alpha]_D^{20}$ +9° (*c* 1, chloroform); lit.[11] m.p. 218–219°, $[\alpha]_D^{21}$ +9.1° (chloroform).

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