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SYNTHESES OF HIGHER SUGARS BY A NEW CHAIN-ELONGATION REACTION*†

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ABSTRACT

The reaction of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside and 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-1-deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol with carbon disulfide, methyl iodide, and sodium hydride gave methyl 2,3,4-di-*O*-acetyl-6,7-dideoxy-7,7-bis(methylthio)-6-nitro-α-D-*gluco*-hept-6-enopyranoside (**3**) and 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-2-deoxy-2-nitro-D-*glycero*-L-*manno*-oct-1-enose dimethyl dithioacetal, respectively. Substitution reactions of **3** were investigated.

INTRODUCTION

Freund[2] recorded that the reaction of nitromethane with carbon disulfide in the presence of potassium hydroxide yielded potassium nitroethenedithiolate, which gave the corresponding ketene dithioacetals[3] with alkylating reagents. We have reported on the reactions of nitroketene dimethyl dithioacetal[4,5].

It was postulated[3,6] that the reaction of nitroalkanes with carbon disulfide is limited to nitromethane. However, as a part of a programme on the syntheses of *C*-nucleoside analogues, we have shown that methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside[7] (**1**) and 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-1-deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol[8,9] (**5**) react with carbon disulfide and methyl iodide in an alkaline medium to give so-called push-pull alkenes[10,11] with a sugar moiety.

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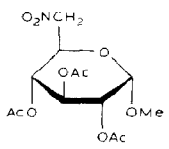
RESULTS AND DISCUSSION

Treatment of **1** with 2 mol of sodium hydride in tetrahydrofuran gave the sodium salt which reacted with carbon disulfide and methyl iodide to yield 50% of methyl 2,3,4-tri-*O*-acetyl-6,7-dideoxy-7,7-bis(methylthio)-6-nitro-α-D-*gluco*-hept-6-enopyranoside (**3**) presumably via the dithiolate **2**. Attempted monomethylation of the intermediate **2** with 1 mol of methyl iodide and subsequent acidification failed to give the dithiouronate **4**.

Likewise, reaction of **5** with 2 mol of sodium hydride and then an excess of carbon disulfide and methyl iodide yielded 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-2-deoxy-2-nitro-D-*glycero*-L-*manno*-oct-1-enose dimethyl dithioacetal (**6**).

The structures of **3** and **6** were established on the basis of elemental analysis and spectral data (see Experimental). The small difference between the chemical shifts of the resonances of C-6 (145.4 p.p.m.) and C-7 (149.5 p.p.m.) in **3** compared with the typical push-pull alkene **7** reflects decreased polarization of the C=C bond by twisting of the substituents out of its plane owing to steric hindrance by the sugar moiety (*cf.* ref. 12). The signal for the nitro-substituted C-2 in **7** was at higher field (125.1 p.p.m.), whereas that for C-1 appeared at lower field (164.7 p.p.m.) (*cf.* ref. 13). Similarly, resonances at 148.2 and 145.5 p.p.m. for C-1 and C-2, respectively, of **6** indicated the steric influence of the sugar moiety.

Treatment of **3** with aniline in boiling ethanol gave 79% of **8**, presumably by addition at C-7 followed by elimination of methanethiol. Comparable reactions occurred with toluidine and *p*-anisidine, to give high yields of **9** and **10**, respectively. The ketene-N,S-acetal **8** is more stable than **3** and displacement of the second methylthio group cannot be effected. Indeed, compared with **3**, the resonance of C-6 of **8** was shifted upfield (124.0 and 124.6 p.p.m.) and, for C-7, the signals were at 147.9 and 148.5 p.p.m., respectively. The expected downfield shift could not be observed, probably because of the steric hindrance by the sugar moiety. Accordingly, the upfield and downfield signals of C-2 and C-1 of the (*E*)-ketene-N,S-acetal **11** appeared at 107.5 and 164.5 p.p.m., respectively.



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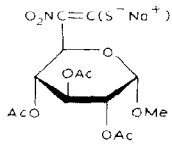

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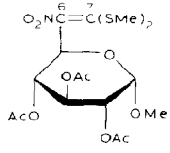

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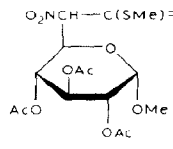

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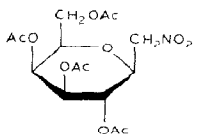

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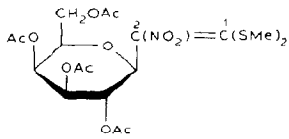

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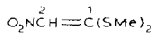

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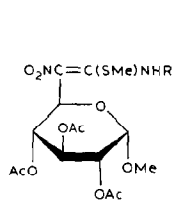
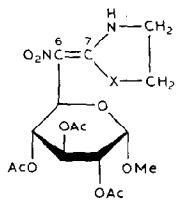
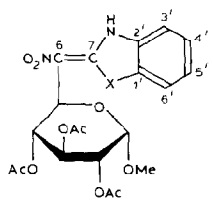


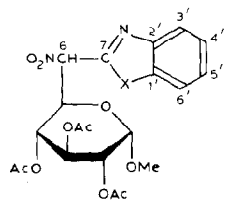
8 R = Ph
9 R = *p*-MeC_6H_4
10 R = *p*-$MeOC_6H_4$
12 R = PhNH
13 R = PhCONH
14 R = *p*-$MeOC_6H_4CONH$



15 X = NH
16 X = O



17 X = NH
18 X = O



19 X = NH
20 X = O

$O_2NCH=C(SMe)NHC_6H_4OMe$-*p*

11

Compounds **8–10** were isolated as *EZ*-mixtures. The *EZ*-ratios (~1:3 and ~1:2, respectively) for **8** and **10** were determined from the intensities of the signals for C-6 and C-7 in the ^{13}C-n.m.r. spectra. The preference of the *E*-isomer is probably due to an intramolecular hydrogen bond between the NH and NO_2 groups (*cf.* refs. 14 and 15).

Attempts to prepare **8** by reaction of **1** with phenyl isothiocyanate in alkaline medium with subsequent methylation were unsuccessful.

The reactions of **3** with phenylhydrazine, benzoylhydrazine, and 4-methoxybenzoylhydrazine afforded good yields of the respective (*EZ*)-nitroketene-N,S-acetals **12–14**, the structures of which were determined mainly by ^1H-n.m.r. parameters (see Experimental). The sharp m.p. and chromatographic behaviour of **12** indicated the existence of only one isomer (probably *E*), because of intramolecular hydrogen-bonding.

Treatment of **3** with ethylenediamine and ethanolamine in boiling ethanol replaced both methylthio groups to give the expected imidazolidine (**15**) and oxazolidine (**16**) derivatives, respectively. Compared with **3** and **8–10**, the resonances for C-6 at 103.8 (**15**) and 106.6 (**16**) and for C-7 at 159.3 (**15**) and 167.3 p.p.m. (**16**) indicated higher push-pull stabilization, probably reflecting the effect of NH- and O-, and the absence of steric strain. As for **12**, only the *E*-isomer of the derivative **16** was isolated.

An S-free product was obtained when **3** was treated with *o*-phenylenediamine in boiling ethanol, which was identified, on the basis of ^1H- and ^{13}C-n.m.r. data, as the dihydrobenzimidazole derivative **17**. In the ^{13}C-n.m.r. spectrum, the upfield and downfield signals given by C-6 and C-7 were at 104.8 and 147.3 p.p.m., respectively, corresponding to a C=C bond. Thus, the tautomeric form **19** can be excluded. However, treatment of **3** with *o*-aminophenol in ethanol gave **20** as a mixture of diastereomers. The tautomeric form **18** could not be observed. The ^1H-n.m.r. spectrum of **20** contained no resonance for NH, and the resonances at 82.6 and 84.7 p.p.m. for C-6 in the ^{13}C-n.m.r. spectrum indicated the presence of a saturated carbon. The assignments were established by an off-resonance spectrum

of **20**. The 1:2 ratio of the diastereomers was based on the intensities of the ^1H signals for OMe and OAc and that for C-6.

EXPERIMENTAL

General. — Melting points were determined with a Boetius apparatus and are corrected. N.m.r. spectra (internal Me_4Si) were recorded with Tesla BS 487 C (^1H, 80 MHz) and BP 497 (^{13}C, 25.2 MHz) spectrometers. Optical rotations were measured mainly on solutions in chloroform (*c* 1) with a Carl Zeiss Jena Polamat polarimeter. Column chromatography was performed on Silica Gel 60 (Merck).

*Methyl 2,3,4-tri-O-acetyl-6,7-dideoxy-7,7-bis(methylthio)-6-nitro-α-*D-gluco*-hept-6-enopyranoside* (**3**). — To a well-stirred suspension of sodium hydride (0.48 g, 20 mmol) in tetrahydrofuran (50 mL), under argon, was added methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside[7] (**1**; 3.5 g, 10 mmol). The mixture was stirred for 2 h, and a mixture of carbon disulfide (1.2 mL, 20 mmol) and methyl iodide (3 mL, 48 mmol) was added dropwise with stirring. The mixture was boiled under reflux for 1 h, poured onto crushed ice (500 g), and extracted with chloroform (3 × 100 mL). The combined extracts were washed with water (3 × 100 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue was crystallized and recrystallized from ethanol to give yellow crystals of **3** (2.26 g, 50%), m.p. 140–141°, $[\alpha]_D^{18}$ −29°. N.m.r. data ($CDCl_3$): ^1H, δ 1.95, 2.00, 2.05 (3 s, 3, 3, and 3 H, 3 Ac), 2.38 (s, 3 H, MeS), 2.46 (s, 3 H, MeS), 3.46 (s, 3 H, MeO), 4.78–5.90 (m, 5 H, H-1,2,3,4,5); ^{13}C, δ 17.8, 18.0 (CH_3S), 20.6 (CH_3CO), 55.9 (CH_3O), 67.5, 69.9, 69.9, 70.4 (C-2,3,4,5), 97.1 (C-1), 145.4 (C-6), 149.5 (C-7), 168.9, 169.8, 169.9 (CO).

Anal. Calc. for $C_{16}H_{23}NO_{10}S_2$: C, 42.4; H, 5.1; N, 3.1; S, 14.1. Found: C, 42.7; H, 5.3; N, 3.3; S, 14.4.

*4,5,6,8-Tetra-O-acetyl-3,7-anhydro-2-deoxy-2-nitro-*D-glycero-L-manno*-oct-1-enose dimethyl dithioacetal* (**6**). — Treatment of 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-1-deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol[8,9] (**5**, 3.9 g, 10 mmol) as described above, with recrystallization of the product from ethanol, gave yellow crystals of **6** (2.3 g, 45%), m.p. 165–167°, $[\alpha]_D^{19}$ +24°. N.m.r. data ($CDCl_3$): ^1H, δ 1.99, 2.00, 2.03, 2.16 (4 s, 3, 3, 3, and 3 H, 4 Ac), 2.38 (s, 3 H, MeS), 2.47 (s, 3 H, MeS), 4.09 (m, 2 H, CH_2), 5.00–6.09 (m, 5 H, H-3,4,5,6,7); ^{13}C, δ 17.8, 18.0 (SCH_3), 20.6 (CH_3CO), 61.3 (C-8), 67.2, 67.2, 72.1, 74.5, 75.5 (C-3,4,5,6,7), 145.5 (C-2), 148.2 (C-1), 168.8, 170.1, 170.3, 170.4 (CO).

Anal. Calc. for $C_{18}H_{25}NO_{11}S_2$: C, 43.6; H, 5.1; N, 2.8; S, 12.9. Found: C, 44.0; H, 5.3; N, 2.6; S, 12.8.

*Methyl 2,3,4-tri-O-acetyl-7-anilino-6,7-dideoxy-7-methylthio-6-nitro-α-*D-gluco*-hept-6-enopyranoside* (**8**). — A solution of **3** (4.5 g, 10 mmol) and aniline (0.9 g, 10 mmol) in 95% ethanol (20 mL) was boiled under reflux for 4 h and cooled to 15°, and the precipitated **8** was collected and washed with ethanol. More **8** was obtained on concentration of the mother liquor. Recrystallization from methanol gave yellow crystals of **8** (3.9 g, 79%), m.p. 140–161°, $[\alpha]_D^{18}$ −33°. N.m.r. data

($CDCl_3$): ^1H, δ 1.99, 2.01, 2.01 (3 s, 3, 3, and 3 H, 3 Ac), 2.06 (s, 3 H, MeS), 3.48 (s, 3 H, MeO), 4.82–6.15 (m, 5 H, H-1,2,3,4,5), 7.36 (m, 5 H, Ph), 11.65 (s, NH); ^{13}C, δ 14.6 (*Z*, CH_3S), 16.8 (*E*, CH_3S), 20.6 (CH_3CO), 55.7, 56.5 (CH_3O), 67.3, 67.5, 69.6, 69.9, 70.2, 70.4, 70.6, 70.8 (C-2,3,4,5), 97.0 (C-1), 119.2, 119.7 (C-2′ of Ph), 126.8 (C-4′), 129.4, 129.6 (C-3′), 138.3 (C-1′), 124.0 (*Z*, C-6), 124.6 (*E*, C-6), 147.9 (*E*, C-7), 148.5 (*Z*, C-7), 169.4, 170.2, 170.9 (CO).

Anal. Calc. for $C_{21}H_{26}N_2O_{10}S$: C, 50.6; H, 5.3; N, 5.6; S, 6.4. Found: C, 50.7; H, 5.3; N, 5.3; S, 6.7.

*Methyl 2,3,4-tri-*O*-acetyl-6,7-dideoxy-7-methylthio-6-nitro-7-*(p-*toluidino)-α-*D-gluco-*hept-6-enopyranoside* (**9**). — Similar reaction of **3** (4.5 g, 10 mmol) with *p*-toluidine (1.1 g, 10 mmol) gave yellow crystals of **9** (4.5 g, 88%), m.p. 165–177°, $[\alpha]_D^{18}$ −31°. ^1H-N.m.r. data ($CDCl_3$): δ 1.99, 2.01, 2.02 (3 s, 3, 3, and 3 H, 3 Ac), 2.08 (s, 3 H, MeS), 2.35 (s, 3 H, MeC_6H_4), 3.48 (s, 3 H, MeO), 4.81–6.25 (m, 5 H, H-1,2,3,4,5), 7.19 (m, 4 H, C_6H_4), 11.8 (s, NH).

Anal. Calc. for $C_{22}H_{28}N_2O_{10}S$: C, 51.6; H, 5.5; N, 5.5; S, 6.2. Found: C, 51.3; H, 5.6; N, 5.2; S, 6.0.

*Methyl 2,3,4-tri-*O*-acetyl-7-*(p-*anisidino)-6,7-dideoxy-7-methylthio-6-nitro-α-*D-gluco-*hept-6-enopyranoside* (**10**). — Reaction of **3** (4.5 g, 10 mmol) and *p*-anisidine (1.2 g, 10 mmol) as described above, with recrystallization of the product from methanol, gave yellow needles of **10** (5.0 g, 94%), m.p. 165–180°, $[\alpha]_D^{18}$ −277°. N.m.r. data ($CDCl_3$): ^1H, δ 2.00, 2.01, 2.01 (3 s, 3, 3, and 3 H, 3 Ac), 2.11 (s, 3 H, MeS), 3.51 (s, 3 H, MeO), 3.84 (s, 3 H, $MeOC_6H_4$), 4.89–6.15 (m, 5 H, H-1,2,3,4,5), 7.13 (m, AA′BB′, 4 H, C_6H_4), 11.93 (s, NH): ^{13}C [$(CD_3)_2SO$], δ 14.4 (*Z*, CH_3S), 16.4 (*E*, CH_3S), 20.3 (CH_3CO), 55.1 (CH_3O), 55.7 ($CH_3OC_6H_4$), 67.4, 68.7, 69.3, 69.3, 69.6, 69.8 (C-2,3,4,5), 96.4 (C-1), 114.3 (C-3′ of C_6H_4), 123.9 (C-2′), 132.3 (C-1′), 156.6, 156.7 (C-4′), 120.4 (*Z*, C-6), 121.1 (*E*, C-6), 140.4 (*E*, C-7), 141.1 (*Z*, C-7), 168.9, 169.1, 169.5, 169.7 (CO).

Anal. Calc. for $C_{22}H_{28}N_2O_{11}S$: C, 50.0; H, 5.3; N, 5.3; S, 6.1. Found: C, 49.8; H, 5.3; N, 5.0; S, 6.4.

*Methyl 2,3,4-tri-*O*-acetyl-6,7-dideoxy-7-methylthio-6-nitro-7-(2-phenylhydrazino)-α-*D-gluco-*hept-6-enopyranoside* (**12**). — A solution of **3** (1 g, 2.2 mmol) and phenylhydrazine (0.5 g, 4.4 mmol) in aqueous 95% ethanol (10 mL) was boiled under reflux for 45 min, then concentrated under reduced pressure. Column chromatography (chloroform) of the syrupy residue gave **12** as a yellow powder (0.9 g, 79%), m.p. 70–71°, $[\alpha]_D^{19}$ +113°. ^1H-N.m.r. data ($CDCl_3$): δ 1.98, 2.00, 2.05 (3 s, 3, 3, and 3 H, 3 Ac), 2.26 (s, 3 H, MeS), 3.45 (s, 3 H, MeO), 4.75–5.88 (m, 5 H, H-1,2,3,4,5), 7.12 (m, 5 H, Ph), 8.95 (s, 1 H, NH), 12.0 (s, 1 H, NH).

Anal. Calc. for $C_{21}H_{27}N_3O_{10}S$: C, 49.1; H, 5.3; N, 8.2; S, 6.2. Found: C, 49.2; H, 5.1; N, 8.2; S, 6.0.

*Methyl 2,3,4-tri-*O*-acetyl-7-(2-benzoylhydrazino)-6,7-dideoxy-7-methylthio-6-nitro-α-*D-gluco-*hept-6-enopyranoside* (**13**). — A solution of **3** (1 g, 2.2 mmol) and benzoylhydrazine (0.3 g, 2.2 mmol) in aqueous 95% ethanol (10 mL) was heated under reflux for 4 h, then filtered and concentrated under reduced pressure.

Column chromatography (chloroform) of the residue gave **13** as an orange powder (0.62 g, 52%), m.p. 82–90°, $[\alpha]_D^{19}$ −10°. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.94 (s, 9 H, 3 Ac), 2.38 (s, 3 H, MeS), 3.35 (s, 3 H, MeO), 4.62–5.75 (m, 5 H, H-1,2,3,4,5), 7.50 (m, 5 H, Ph), 9.25 (s, 1 H, NH), 9.78 (s, 1 H, NH).

Anal. Calc. for $C_{22}H_{27}N_3O_{11}S$: C, 48.8; H, 5.0; N, 7.8; S, 5.9. Found: C, 48.6; H, 5.0; N, 7.6; S, 5.9.

*Methyl 2,3,4-tri-*O*-acetyl-6,7-dideoxy-7-[2-(*p*-methoxybenzoyl)hydrazino]-7-methylthio-6-nitro-α-*D*-gluco-hept-6-enopyranoside* (**14**). — Reaction of **3** (1 g, 2.2 mmol) with *p*-methoxybenzoylhydrazine (0.4 g, 2.2 mmol), as described above, gave **14** as a yellow powder (0.73 g, 58%), m.p. 75–80°, $[\alpha]_D^{19}$ +48°. ^{1}H-N.m.r. data ($CDCl_3$): δ 2.01 (s, 9 H, 3 Ac), 2.35 (s, 3 H, MeS), 3.38 (s, 3 H, MeO), 3.80 (s, 3 H, *Me*OC_6H_4), 4.68–5.80 (m, 5 H, H-1,2,3,4,5), 7.38 (m, AA'BB', 4 H, C_6H_4), 8.90 (s, 1 H, NH), 9.82 (s, 1 H, NH).

Anal. Calc. for $C_{23}H_{29}N_3O_{12}S$: C, 48.3; H, 5.1; N, 7.4; S, 5.6. Found: C, 48.0; H, 5.3; N, 7.2; S, 5.9.

*Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-(imidazolidin-2-ylidene)-6-nitro-α-*D*-glucopyranoside* (**15**). — A solution of **3** (1 g, 2.2 mmol) and ethylenediamine (0.13 g, 2.2 mmol) in aqueous 95% ethanol (10 mL) was heated under reflux for 2 h, then filtered, and concentrated under reduced pressure. The residual syrup was treated with water and the resulting solid was recrystallized from ethanol to afford **15** as slightly yellow crystals (0.44 g, 48%), m.p. 230–232°, $[\alpha]_D^{19}$ +200° (methyl sulfoxide). N.m.r. data: ^{1}H [$(CD_3)_2SO$], δ 1.80, 1.91, 1.99 (3 s, 3, 3, and 3 H, 3 Ac), 3.30 (m, 4 H, CH_2CH_2), 3.60 (s, 3 H, MeO), 4.72–5.78 (m, 5 H, H-1,2,3,4,5), 8.28 (s, 2 H, NH); ^{13}C ($CDCl_3$), δ 20.1, 20.3, 20.4 (CH_3CO), 43.1 (CH_2CH_2), 54.8 (CH_3O), 65.6, 68.5, 69.8, 69.9 (C-2,3,4,5), 96.4 (C-1), 103.8 (C-6), 159.3 (C-7), 169.0, 169.4, 169.7 (CO).

Anal. Calc. for $C_{16}H_{23}N_3O_{10}$: C, 46.0; H, 5.6; N, 10.1. Found: C, 46.0; H, 5.8; N, 9.8.

*Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro-6-(oxazolidin-2-ylidene)-α-*D*-gluco-pyranoside* (**16**). — A solution of **3** (1 g, 2.2 mmol) and ethanolamine (0.13 g, 2.2 mmol) in aqueous 95% ethanol (10 mL) was boiled under reflux for 1 h, then cooled to 20°, treated with cold (0°) water (200 mL), and extracted with chloroform. The extract was dried ($MgSO_4$) and concentrated under reduced pressure. Column chromatography (chloroform) of the residual syrup afforded **16** as light-yellow needles (0.42 g, 46%), m.p. 96–98°, $[\alpha]_D^{19}$ +139° N.m.r. data ($CDCl_3$): ^{1}H, δ 1.92, 2.00, 2.05 (3 s, 3, 3, and 3 H, 3 Ac), 3.45 (s, 3 H, MeO), 3.97 (t, 2 H, CH_2N), 4.82 (t, 2 H, CH_2O), 4.93–5.82 (m, 5 H, H-1,2,3,4,5), 9.42 (s, 1 H, NH); ^{13}C, δ (CH_3CO), 43.1 (CH_2N), 55.4 (CH_3O), 65.6 (CH_2O), 69.4, 70.3, 70.3, 71.0 (C-2,3,4,5), 96.7 (C-1), 106.6 (C-6), 167.3 (C-7), 169.7, 170.3, 170.3 (CO).

Anal. Calc. for $C_{16}H_{22}N_2O_{11}$: C, 45.9; H, 5.3; N, 6.7. Found: C, 45.7; H, 5.4; N, 6.5.

*Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-(2,3-dihydrobenzimidazol-2-ylidene)-6-nitro-α-*D*-glucopyranoside* (**17**). — A solution of **3** (1 g, 2.2 mmol) and *o*-

phenylenediamine (0.48 g, 4.4 mmol) in aqueous 95% ethanol (10 mL) was heated under reflux for 3 h, then worked-up as described above to give **17** as a light-yellow powder (0.3 g, 29%), m.p. 164–168°, $[\alpha]_D^{19}$ +174°. N.m.r. data ($CDCl_3$): ^1H, δ 1.89, 1.95, 2.05 (3 s, 3, 3, and 3 H, 3 Ac), 3.48 (s, 3 H, MeO), 4.81–6.12 (m, 5 H, H-1,2,3,4,5), 7.31 (m, 4 H, C_6H_4), 7.48 (s, 2 H, NH); ^{13}C, δ 20.4, 20.7, 20.7, (CH_3CO), 55.8 (CH_3O), 66.4, 70.1, 70.1, 71.2 (C-2,3,4,5), 97.3 (C-1), 104.8 (C-6), 112.6 (C-3′,6′ of C_6H_4), 124.7 (C-4′,5′), 130.2 (C-1′,2′), 147.3 (C-7), 169.8, 170.4, 170.7 (CO).

Anal. Calc. for $C_{20}H_{23}N_3O_{10}$: N, 9.0. Found: N, 9.0.

*Methyl 2,3,4-tri-*O*-acetyl-6-(benzoxazol-2-yl)-6-deoxy-6-nitro-α-*D*-glucopyranoside* (**20**). — Reaction of **3** (1 g, 2.2 mmol) with *o*-aminophenol (0.48 g, 4.4 mmol), as described above, gave **20** as a light-red powder (0.2 g, 20%), m.p. 68–70°, $[\alpha]_D^{19}$ −15°. N.m.r. data ($CDCl_3$): ^1H, δ 1.81, 1.95 (2 s, 3 H, Ac), 2.00, 2.05 (2 s, 3 and 3 H, 2 Ac), 3.60, 3.61 (2 s, 3 H, MeO), 4.78–5.98 (m, 6 H, H-1,2,3,4,5,6), 7.25–7.98 (m, 4 H, C_6H_4); ^{13}C, δ 19.4, 20.6 (CH_3CO), 56.3, 56.6 (CH_3O), 67.5, 67.9, 69.8, 69.9, 70.3 (C-2,3,4,5), 97.0, 97.2 (C-1), 82.6, 84.7 (C-6), 111.3 (C-6′), 121.2 (C-3′), 125.2, 125.5, 126.7, 127.1 (C-4′,5′), 140.2, 140.4 (C-1′), 150.9, 151.2 (C-2′), 154.4, 154.8 (C-7), 168.8, 169.1, 169.6, 169.9 (CO).

Anal. Calc. for $C_{20}H_{22}N_2O_{11}$: C, 51.5; H, 4.8; N, 6.0. Found: C, 51.0; H, 4.8; N, 5.8.

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