Oxidation of Aldose Oximes. Formation and Structure of Hydroxydiazene Oxide Acetals and Preparation of Hydroximolactones. *X*-Ray Crystal Structure of 2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl-*ONN*-azoxy 2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranoside

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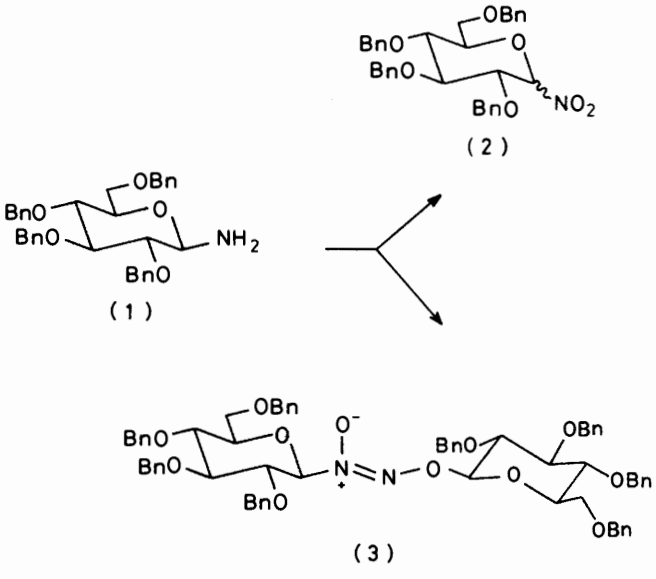
Oxidation of the glucopyranosylamine (1) with peracid gave, in low yield, either the stable 1-deoxy-1-nitro-compound (2) or the dimer (3), depending on the reaction conditions. Oxidation of the oximes (4), (9), (13), and (17) with periodate at low pH gave the hydroxiolactones (5), (10), (14), and (18), respectively, and, in the case of the oxime (17), the dimer (20) also [at higher pH]. The structure of compound (20) was determined by *X*-ray analysis. The structures of the hydroximolactones were deduced from spectroscopic data and chemical transformations; they were obtained in high yield from the aforementioned oximes by oxidation with periodate at higher pH.

ALTHOUGH nitro-sugars have been extensively studied from the point of view of their reactivity and stereochemical properties,[1] 1-deoxy-1-nitro-sugars do not seem to have been described and no useful method for their synthesis is known. We expect them to be stable compounds [2] and useful intermediates with reversed polarity at the anomeric centre, allowing chain extension without concurrent β-elimination from the intermediate nitronate salts. Owing to its position at the anomeric centre, the nitro-group might also serve as a leaving group which could thus be replaced by other substituents.

We felt that nucleophilic substitution of glycosyl halides with nitrite ions (in spite of recent improvement in the general method of nitro-sugar preparation [3]) would lead to large amounts of nitrite esters or olefins.[4] Therefore, and in connection with our interest in the reactions of sugar derivatives possessing a C(1)–N bond,[5] we first examined the oxidation of glycosylamines.

The crystalline tetrabenzylglucosylamine (1) [6] is easily available from an improved synthesis *via* the corresponding 1-*O*-methylsulphonate. Its oxidation (Scheme 1) with *m*-chloroperbenzoic acid (*m*-CPBA) [7] in boiling 1,2-dichloroethane gave the expected 1-deoxy-1-nitro-derivative (2) as an amorphous mixture of the anomers in 20% yield. Under milder conditions (*m*-CPBA in refluxing dichloromethane) a crystalline, dimeric product was formed which analysed correctly for a 1-deoxy-1-nitroso-derivative. Its ^{13}C- and ^{1}H-n.m.r. spectra were incompatible with an (*E*)- or (*Z*)-azodioxy-structure, showing a separate set of signals for both glycosyl moieties. These signals did not coalesce (^{13}C n.m.r. [$C_2{}^2H_2Cl_4$]) at temperatures <107 °C, but rather became sharper, thus excluding conformational isomerism as a source of the diastereotopic relationship between the glycosyl moieties, and casting doubt on the presence of an azodioxy-compound in equilibrium with *C*-nitroso-monomers.[8] Moreover, the u.v. spectrum displayed a maximum at much lower wavelength [$\lambda_{max.}$ (MeOH) 232 nm (ε 11 800)] than expected for an azodioxy-compound.[9a] The i.r. spectrum was devoid of bands typical for *C*-nitroso-compounds,[9b] but showed an absorption of medium intensity at 1 505 cm^{-1}, similar to that in the i.r. spectrum of compound (21).[10] The structure (3) for the dimer was finally indicated by its close analogy with that of the glycoside (20) (*vide infra*).



Bn = CH_2Ph

SCHEME 1

The low yield of the nitro-compound (2) obtained on oxidation of the glycosylamine (1) prompted us to examine the oxidation of the glycosylhydroxylamines, known to be formed reversibly from the corresponding γ- or δ-hydroxy-oximes.[5a,5b,11]

Both the crystalline (*E* or *Z*)-tetrabenzylglucose oxime (4) and the amorphous (*E*,*Z*)-tetrabenzylmannose

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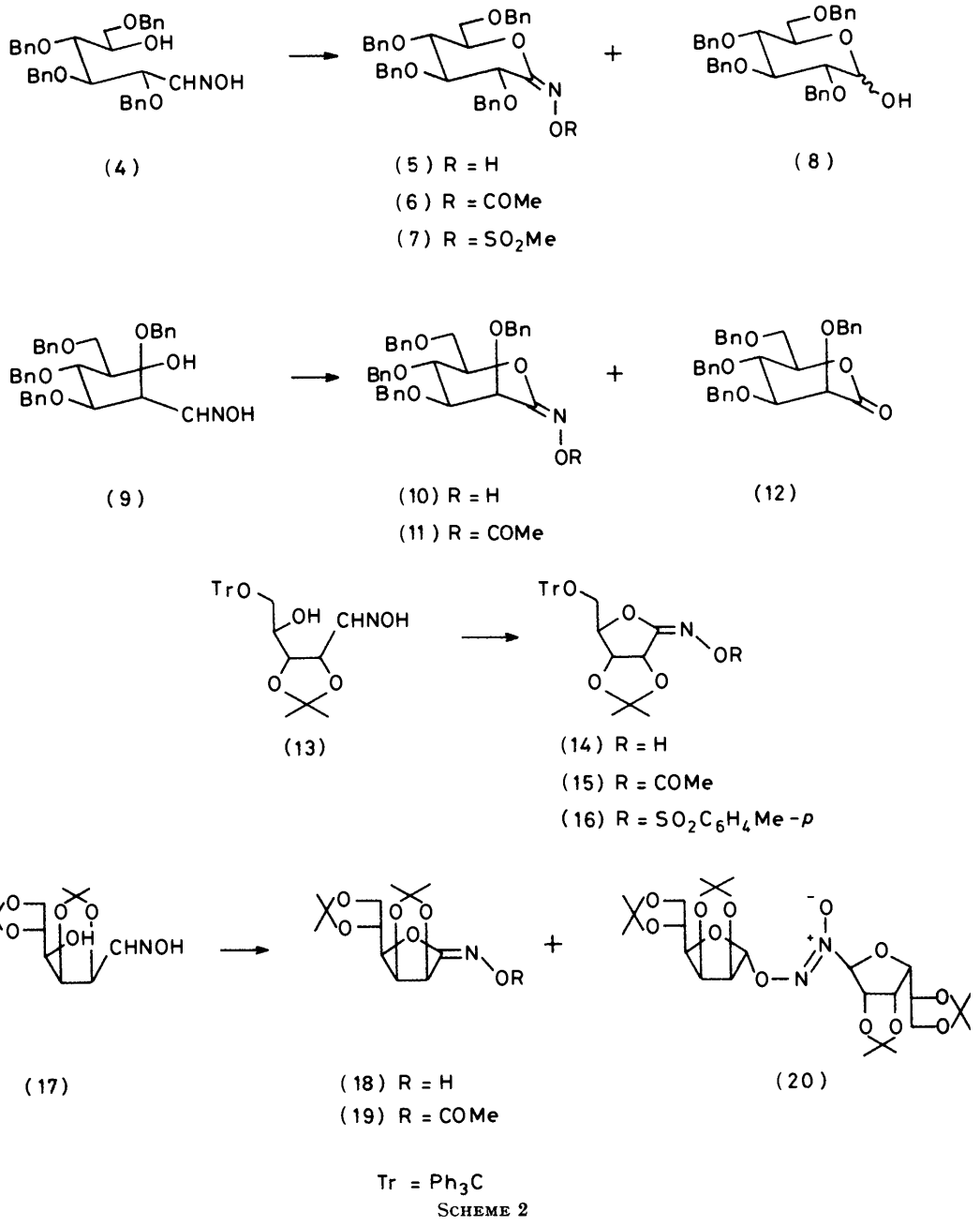


SCHEME 2

oxime (9) (Scheme 2) are readily available from the corresponding aldoses. Oxidation of the protected glucose oxime (4) under a variety of conditions failed to give the desired nitro-compound, but treatment with sodium metaperiodate[12] at 50—60 °C gave the crystalline hydroximolactone (5). The structure of this compound is in accord with its combustion analysis and spectroscopic data. Especially diagnostic is the absence of a signal for the 1-H in the ^{1}H n.m.r. spectrum and the appearance of a singlet at δ 151.43 p.p.m. in the ^{13}C n.m.r. spectrum.

Acetylation of compound (5) gave a monoacetate (6) showing no OH bands in its i.r. spectrum. It was converted back into the hydroximolactone (5) by treatment with methanolic sodium methoxide. The fact that a single, thermally stable isomer is formed suggests that compounds (5) and (6) have the (*E*)-configuration, since it is known that (*E*)-hydroximolactones are the thermodynamically more stable diastereoisomers, and that thermal (*E*/*Z*) interconversion occurs readily.[13] Finally, compound (5) proved to be stable to typical Beckmann rearrangement conditions.[14] Moreover, Beckmann rearrangement could not be achieved by treating the methanesulphonate (7) with triethylamine, pyridine, or potassium acetate in aqueous ethanol.

In a similar way the mannose oxime (9) gave, on oxidation in the absence of sodium acetate, the oily

hydroximolactone (10) as a single isomer in 72% yield, and the lactone (12) in 10% yield. The (*E*)-configuration of compound (10) was assigned by analogy with compound (5) since it is consistent with the chemical-shift values of the 2-H in the ^{1}H n.m.r. spectra of compound (10) (δ 4.22), the corresponding acetate (11) (δ 4.40), and the lactone (12) (δ 4.37).

In the furan series, oxidation of the protected ribose oxime (13) [5a] in the absence of sodium acetate gave the hydroximolactone (14) as a single isomer in a yield of 82%. The corresponding tosylate (16) was stable under Beckmann rearrangement conditions. In contrast to the oxidation of the ribose oxime (13), oxidation of the diisopropylidenemannose oxime (17) [5b] in the absence of sodium acetate afforded only 11% of the hydroximolactone (18). The main product (20), formed in *ca.* 54% yield, was a readily crystallisable dimeric compound, whose i.r. spectrum showed a new band at 1 500 cm^{-1}. The u.v. spectrum of the dimer (20) was very similar to that of the dimer (3). The dimer (20) also showed two sets of partially overlapping signals for both furanosyl moieties in the ^{1}H- and ^{13}C-n.m.r. spectra. The signals of the anomeric hydrogens appeared at δ_H 5.76 as a broad singlet, indicating the α-D-configuration for both anomeric centres.

X-Ray Analysis of Compound (20).—Compound (20) crystallizes from methanol in the monoclinic space group $I2/c$, $a = 19.144$, $b = 5.547$, $c = 25.888$ Å, $\beta = 88.4°$, $Z = 4$. Out of 2 991 independent reflections with $\theta \leqslant 26°$ (Mo-K_α, graphite monochromator) measured on a CAD-4 diffractometer, 1 755 had $I > 3\sigma(I)$ and were used for the structure refinement. Standard runs of the direct-method programs MULTAN 78 and SHELX failed to solve the structure. The positions of 14 heavy atoms were found by selecting manually, from a SIGMA 2 listing, the origin-fixing reflections and 8 reflections for phase permutation. The remaining heavy atoms were located from a Fourier difference-synthesis. All atoms were refined by least-squares analysis using experimental weights.[15,16] At an intermediate stage, all hydrogen atoms were located from a difference synthesis and were refined with isotropic temperature factors; the other atoms were refined anisotropically. The final R was 0.037, $R_w = 0.040$. A stereoscopic view of the molecule (20) is shown in the Figure. Positional parameters are given in Table 1. Bond lengths are shown in Table 2.†

The close analogy between the u.v., i.r., and n.m.r.

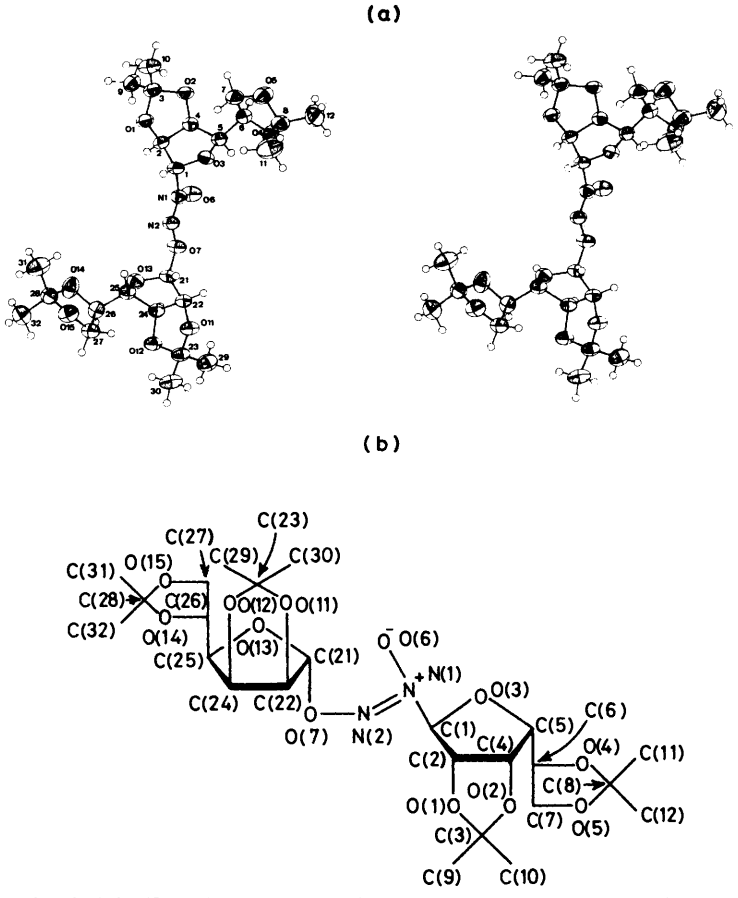


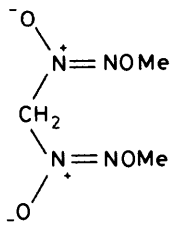
FIGURE (a) Stereoview of molecule (20). [17] Vibration ellipsoids for non-hydrogen atoms are drawn at the 50% probability level. (b) Crystal-structure numbering scheme

† Vibrational parameters are given in Supplementary Publication No. SUP 23327 (3 pp.). For details, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

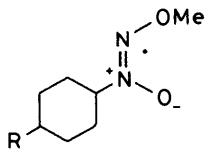
TABLE 1

Final atomic co-ordinates ($\times 10^4$) for compound (20). Standard deviations in parentheses

	x/a	*y/b*	*z/c*
C(1)	3 957(2)	751(9)	7 921(1)
C(2)	3 471(2)	1 771(9)	7 519(1)
C(3)	3 263(2)	759(9)	6 680(1)
C(4)	3 967(2)	3 236(8)	7 157(1)
C(5)	4 700(2)	2 785(9)	7 356(1)
C(6)	5 264(2)	2 267(10)	6 955(2)
C(7)	5 238(2)	−126(11)	6 677(2)
C(8)	6 310(2)	208(10)	7 028(1)
C(9)	2 630(2)	2 314(11)	6 581(2)
C(10)	3 345(3)	−1 332(10)	6 316(2)
C(11)	6 294(3)	−1 655(13)	7 473(2)
C(12)	7 020(3)	962(16)	6 840(2)
C(21)	3 856(2)	2 239(9)	9 692(1)
C(22)	4 063(2)	4 243(9)	10 050(1)
C(23)	4 074(2)	4 611(9)	10 927(1)
C(24)	3 367(2)	5 319(8)	10 240(1)
C(25)	2 817(2)	3 693(9)	10 000(1)
C(26)	2 207(2)	3 023(9)	10 344(2)
C(27)	2 322(2)	930(10)	10 720(1)
C(28)	1 390(2)	1(10)	10 225(2)
C(29)	4 477(3)	6 935(11)	10 996(2)
C(30)	4 061(3)	3 076(11)	11 402(2)
C(31)	1 235(3)	−1 622(12)	9 775(2)
C(32)	770(3)	378(16)	10 581(2)
O(1)	3 234(2)	−146(6)	7 202(1)
O(2)	3 884(1)	2 161(6)	6 660(1)
O(3)	4 624(1)	747(6)	7 704(1)
O(4)	5 919(1)	2 234(7)	7 200(1)
O(5)	5 954(2)	−761(7)	6 607(1)
O(6)	3 985(2)	−5 328(7)	8 285(1)
O(7)	3 892(1)	3 292(6)	9 179(1)
O(11)	4 360(1)	3 269(6)	10 498(1)
O(12)	3 375(1)	5 068(6)	10 790(1)
O(13)	3 190(1)	1 552(6)	9 830(1)
O(14)	1 649(2)	2 199(7)	10 031(1)
O(15)	1 958(2)	−1 021(6)	10 493(1)
N(1)	3 923(2)	2 455(7)	8 376(1)
N(2)	3 889(2)	1 468(7)	8 824(1)
H(01)	3 817(15)	−691(64)	8 061(10)
H(02)	3 083(16)	2 691(69)	7 666(11)
H(04)	3 823(15)	4 954(64)	7 186(10)
H(05)	4 871(14)	4 259(60)	7 556(10)
H(06)	5 270(17)	3 534(76)	6 697(13)
H(071)	4 978(17)	−4(75)	6 331(12)
H(072)	5 004(16)	−1 402(72)	6 908(12)
H(091)	2 225(27)	1 215(**)	6 604(18)
H(092)	2 645(22)	3 112(96)	6 218(16)
H(093)	2 549(20)	3 640(91)	6 859(15)
H(101)	2 932(21)	−2 273(91)	6 344(15)
H(102)	3 789(21)	−2 128(90)	6 397(15)
H(103)	3 391(16)	−700(70)	5 953(12)
H(111)	6 713(34)	−2 814(**)	7 208(25)
H(112)	5 719(29)	−1 453(**)	7 568(20)
H(113)	6 607(23)	−933(**)	7 629(17)
H(121)	7 307(19)	−514(87)	6 704(14)
H(122)	7 256(27)	1 469(**)	7 074(20)
H(123)	6 832(20)	2 001(85)	6 556(14)
H(21)	4 165(15)	919(71)	9 671(10)
H(22)	4 411(15)	5 372(64)	9 880(10)
H(24)	3 282(16)	7 048(71)	10 141(11)
H(25)	2 652(15)	4 463(64)	9 734(11)
H(26)	2 054(17)	4 385(74)	10 535(12)
H(271)	2 110(15)	1 330(66)	11 099(11)
H(272)	2 867(19)	509(83)	10 735(12)
H(291)	4 234(22)	7 797(98)	11 285(16)
H(292)	4 437(22)	7 886(99)	10 665(15)
H(293)	4 937(20)	6 714(79)	11 055(13)
H(301)	4 487(22)	2 898(93)	11 469(15)
H(302)	3 703(19)	1 720(79)	11 389(13)
H(303)	3 817(24)	3 879(**)	11 741(16)
H(311)	941(23)	−2 955(98)	9 943(16)
H(312)	1 670(23)	−1 944(**)	9 552(16)
H(313)	923(21)	−777(92)	9 523(14)
H(321)	456(23)	1 474(**)	10 374(16)
H(322)	909(29)	1 193(**)	10 890(21)
H(323)	541(31)	−471(**)	10 689(23)

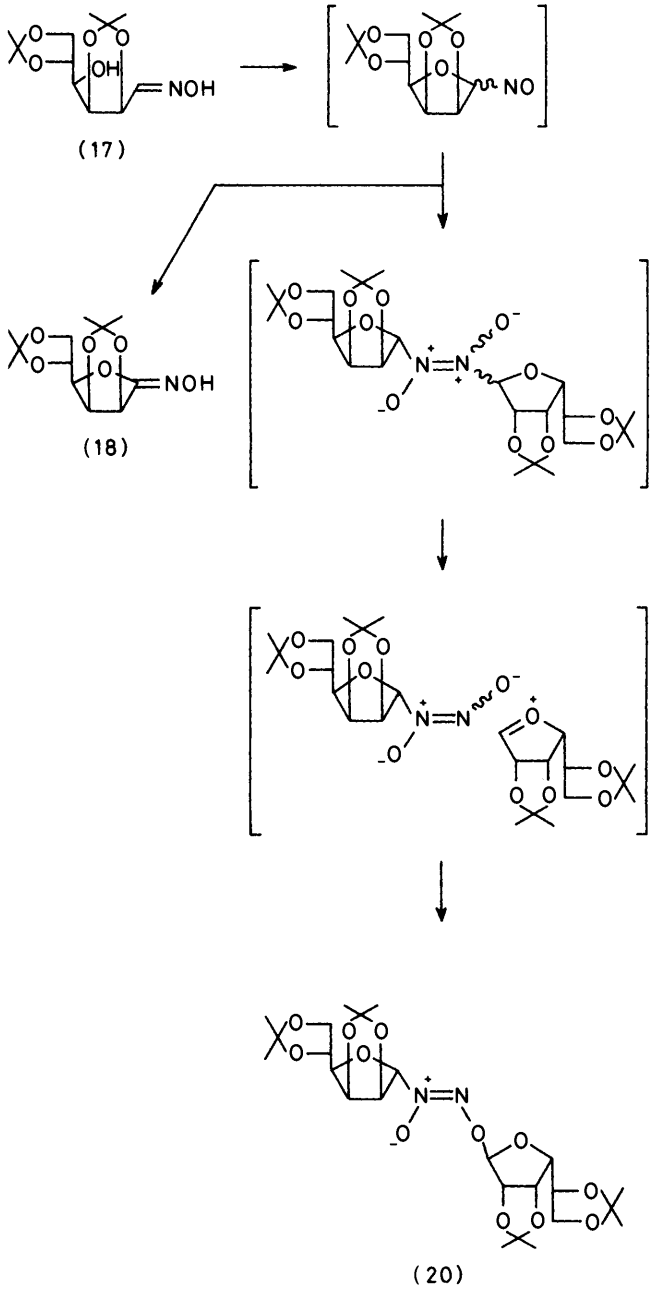


(21)



(22) R = H

(23) R = Me



SCHEME 3

TABLE 2

Bond lengths (Å) for compound (20). Standard deviations in parentheses

C(1)	–C(2)	1.524(6)	C(1)	–N(1)	1.510(5)	C(1)	–O(3)	1.380(5)	C(10)	–C(3)	1.501(7)
C(11)	–C(8)	1.547(8)	C(12)	–C(8)	1.491(7)	C(2)	–C(4)	1.545(6)	C(2)	–O(1)	1.426(5)
C(21)	–C(22)	1.508(6)	C(21)	–O(13)	1.369(5)	C(21)	–O(7)	1.451(5)	C(22)	–C(24)	1.529(6)
C(22)	–O(11)	1.414(5)	C(23)	–C(29)	1.516(7)	C(23)	–C(30)	1.494(6)	C(23)	–O(11)	1.432(5)
C(23)	–O(12)	1.417(5)	C(24)	–C(25)	1.531(6)	C(24)	–O(12)	1.432(4)	C(25)	–C(26)	1.496(6)
C(25)	–O(13)	1.448(5)	C(26)	–C(27)	1.534(7)	C(26)	–O(14)	1.435(5)	C(27)	–O(15)	1.424(6)
C(28)	–C(31)	1.509(7)	C(28)	–C(32)	1.497(7)	C(28)	–O(14)	1.404(6)	C(28)	–O(15)	1.424(6)
C(3)	–C(9)	1.515(7)	C(3)	–O(1)	1.441(5)	C(3)	–O(2)	1.420(5)	C(4)	–C(5)	1.528(6)
C(4)	–O(2)	1.432(4)	C(5)	–C(6)	1.505(6)	C(5)	–O(3)	1.451(5)	C(6)	–C(7)	1.512(8)
C(6)	–O(4)	1.421(5)	C(7)	–O(5)	1.422(6)	C(8)	–O(4)	1.416(6)	C(8)	–O(5)	1.408(5)
N(1)	–N(2)	1.283(5)	N(1)	–O(6)	1.257(5)	N(2)	–O(7)	1.366(5)			

spectra of compounds (3) and (20) clearly indicates a [presumably (*Z*)] oxy-*NNO*-azoxy-acetal structure for compound (3). The u.v. spectra of compounds (3) and (20) are also very similar to those of the azoxy-ethers (22) and (23),[18] in particular with regard to the absorption coefficient and the absence of n–π* absorption bands. This fact is further evidence that compounds (22) and (23) are methoxy-diazene oxides rather than *N*-nitroso-hydroxylamine *O*-methyl ethers and also corroborates the hydroxydiazene oxide structure of *aci*-nitramines in solution.[18] The formation of the dimers (3) and (20) is interpreted as indicated in Scheme 3 for the formation of compound (20). Thus, oxidation of the oxime (17) proceeds from the tautomeric, ring-closed hydroxylamine form to give an intermediate 1-nitroso-compound which can either tautomerise to the hydroximolactone (18), or else dimerise to an unstable nitroso-dimer which undergoes rapid solvolysis. The ease with which solvolysis occurs is not surprising in view of the strong inductive effect of the alkoxy-diazene oxide group [10] and the stable oxonium ion produced. Solvolysis of the dimeric nitroso-compound produces an (intimate?) ion pair which collapses to give the observed product. This interpretation suggests that formation of the hydroximolactone (18) may be promoted by high dilution or by favouring the tautomerisation of the 1-deoxy-1-nitro-intermediate. In accord with this, oxidation of the hydroxy-oximes (4), (9), (13), and (17) with sodium metaperiodate in the presence of sodium acetate, *i.e.* at a higher pH value, gave the corresponding hydroximolactones (5), (10), (14), and (18) in excellent yield and without formation of the alkoxy-*NNO*-azoxy-acetals. Thus, the hydroximolactones such as (5) *etc.* have become readily accessible, new carbohydrate derivatives which are potential intermediates for the preparation of 1-deoxy-1-nitroaldoses.

EXPERIMENTAL

All solvents were distilled before use. Anhydrous dichloromethane was distilled from P_2O_5, anhydrous pyridine from CaH_2, and anhydrous triethylamine from sodium. *m*-Chloroperbenzoic acid (Fluka Pract.) was purified by washing with a phosphate buffer of pH 7.5.[19] Hydroxylamine hydrochloride, sodium metaperiodate, ceric ammonium nitrate, methanesulphonyl chloride, toluene-*p*-sulphonyl chloride (all *Purum*) were obtained from Fluka; acetic anhydride and sodium acetate were (pro analysi) Merck reagents. Processing of solutions was as previously described; [5a] solutions were evaporated at or below 50 °C on a Büchi rotary evaporator. Thin-layer chromatography (t.l.c.) was performed with Merck precoated silica gel 60 F-254 plates and compounds were detected by spraying with a 0.025M iodine solution in 10% aqueous H_2SO_4, followed by heating at about 200 °C. Column chromatography was carried out on silica gel Merck 60 (70—230 mesh) with redistilled solvents. M.p.s (uncorrected) were determined with a Büchi 510 apparatus. Optical rotations were measured on a Perkin-Elmer 141 MC polarimeter at 25 °C in a 1 dm cell at 365, 436, 546, 578, and 589 nm; the specific rotation at 589 nm was determined using a regression curve, unless an o.r.d. effect was noted in which case the value obtained at 589 nm was considered. Unless otherwise stated, ^1H n.m.r. spectra were recorded at 90 MHz on a Varian EM 390 spectrometer and ^{13}C n.m.r. spectra at 25.18 MHz on a Varian XL 100 spectrometer; chemical shifts refer to solutions in $CDCl_3$ with tetramethylsilane as internal standard. Unless otherwise stated, i.r. spectra refer to 3% $CHCl_3$ solutions and were recorded with a Perkin-Elmer 599 spectrometer. U.v. spectra were measured on a Beckman 25 spectrometer in a 1 cm cell. Mass spectra were determined using a Du Pont-21-491 apparatus. Microanalyses were performed using a Perkin-Elmer 240 CHN analyser. Molecular weights were determined using the thermoelectrical method.

1-*Amino*-2,3,4,6-*tetra*-O-*benzyl*-1-*deoxy*-β-D-*glucopyranose* (1). A solution of methanesulphonyl chloride (4 g, 35 mmol) in anhydrous dichloromethane (20 ml) was added to 2,3,4,6-tetra-*O*-benzyl-D-glucose [20] (10.8 g, 20 mmol) and triethylamine (4 g, 40 mmol) in dichloromethane (150 ml) at −20 °C and the resulting solution was saturated with ammonia. After 20 h at room temperature, the mixture was filtered and the filtrate was washed with water and dried ($MgSO_4$). Concentration produced a solid (10.5 g) which was recrystallised from diethyl ether–hexane to give the glucopyranosylamine (1) (8.0 g, 74%), m.p. 109—109.5 °C (lit.,[6] 106.5—107.5 °C); $[\alpha]_D$ +17.3—+21.8° (*c* 1.06, $CHCl_3$) (lit.,[6] +22.6°, *c* 1.24, $CHCl_3$); δ_H 7.47—6.97 (20 H, m, 4 × Ph), 5.08—4.44 (8 H, m, 4 × CH_2Ph), 4.12 (1 H, d, $J_{1,2}$ 9 Hz, 1-H), 3.81—3.11 (total 6 H, m, 2-, 3-, 4-, 5-, 6-, and 6-H), and 1.94 (2 H, s, NH_2); δ_C ([$^2H_6$]acetone) 140.13 (s), 139.54 (s), 128.73 (d), 128.30 (d), 127.85 (d), 87.27 (d), 86.48 (d), 84.59 (d), 79.14 (d), 76.36 (t), 75.72 (t), 75.07 (t), 74.88 (d), 73.67 (t), and 70.31 p.p.m. (t).

Oxidation of the Glucopyranosylamine (1) *with* m-*Chloroperbenzoic Acid.*—(a) *In dichloromethane.* A solution of the amine (1) (3 g, 5.6 mmol) in anhydrous dichloromethane (100 ml) was added dropwise (90 min) to a boiling solution of *m*-CPBA (6.55 g, 38 mmol) in anhydrous dichloromethane (120 ml). The mixture was refluxed and stirred for 1 h, then cooled, and washed successively with aqueous solutions

of $NaHSO_3$, $NaHCO_3$, and NaCl. Concentration of the dried ($MgSO_4$) organic phase gave a yellow oil which partially dissolved in boiling methanol (40 ml). The residue obtained upon filtration was recrystallised from methanol and the original mother liquors were chromatographed [diethyl ether–hexane as eluant (1 : 1)] to afford a solid (1.0 g, 32%), m.p. 132—134 °C that was recrystallised from diethyl ether–hexane to afford 2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*-ONN-*azoxy*-2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranoside* (3), m.p. 140—140.5 °C (Found: C, 73.65; H, 6.35; N, 2.5%; M^+, 1 121.31. $C_{68}H_{70}N_2O_{12}$ requires C, 73.76; H, 6.37; N, 2.53%; *M*, 1 107.32); $[\alpha]_D$ +9.7° (*c* 1.1, $CHCl_3$); $\nu_{max.}$ 1 505m, 1 495m, 1 450m, 1 360m, 1 305m, 1 150s, 1 075s, 1 030s, and 1 005s cm^{-1}; δ_H 7.44—7.05 (40 H, m, 8 × Ph), 5.33—5.17 (total 2 H, m, 1- and 1′-H), 5.08—4.13 (total 17 H, m), and 3.88—3.50 (total 11 H, m); δ_H (360 MHz) 5.25 (1 H, d, $J_{1',2'}$ 8 Hz, 1′-H), and 5.23 (1 H, d, $J_{1',2'}$ 8.9 Hz, 1-H); δ_C 138.20 (s), 137.87 (s), 137.65 (s), 137.45 (s), 137.17 (s), 128.18 (d), 127.83 (d), 127.68 (d), 127.50 (d), 104.33 (d), 96.94 (d), 84.59 (d), 84.30 (d), 80.05 (d), 78.28 (d and t), 77.04 (d), 76.88 (t), 75.61 (2 × t), 75.11 (t), 75.01 (t), 73.48 (t), 73.34 (t), 68.49 (t), and 68.26 p.p.m. (t); $\lambda_{max.}$ (MeOH) 208 (ε 53 000), 232 (11 800), 257sh, 263sh, and 268sh nm.

(b) *In* 1,2-*dichloroethane*. In an analogous way the amine (1) (2.16 g, 4 mmol) was oxidized with *m*-CPBA (6.9 g, 40 mmol) in boiling 1,2-dichloroethane. After chromatography [silica gel (250 g); ethyl acetate–toluene [1 : 30 v/v as eluant] of the residue from the organic phase, a mixture (R_F 0.34; 736 mg) was obtained which was rechromatographed on silica gel (60 g) with 1,2-dichloroethane–toluene (1 : 1 v/v) as eluant to provide an anomeric mixture (α : β = 85 : 15) of 2,3,4,6-*tetra*-O-*benzyl*-1-*deoxy*-1-*nitro*-D-*glucopyranose* (2) (450 mg, 20%) (Found: C, 71.9; H, 6.2; N, 2.5. $C_{34}H_{35}NO_7$ requires C, 71.69; H, 6.19; N, 2.46%); $[\alpha]_D$ +64.8° (*c* 0.8, $CHCl_3$); $\nu_{max.}$ 1 570sh, 1 562s, 1 500m, 1 458m, 1 369m, 1 109s, 1 089s, 1 074s, and 1 031s cm^{-1}; δ_H 7.30—7.07 (20 H, m, 4 × Ph), 5.77 (0.85 H, d, *J* 5.3 Hz, 1-H), 5.28 (0.15 H, d, *J* 7.5 Hz, 1-H), and 4.82—3.64 (total 14 H, m); δ_C (α-D-anomer) 137.68 (s), 137.43 (s), 136.41 (s), 128.18 (d), 127.61 (d), 104.26 (d), 79.07 (d), 75.92 (d), 75.68 (2 × d), 74.89 (t), 74.41 (t), 74.81 (t), 73.30 (t), and 67.68 p.p.m. (t).

(E)- and (Z)-2,3,4,6-*Tetra*-O-*benzyl*-D-*glucose Oxime* (4).—Hydroxylamine hydrochloride (22.2 g, 320 mmol) was added to a stirred solution of sodium (3.67 g, 160 mg-atom) in 96% aqueous ethanol (800 ml) at 60 °C. Stirring was continued for 5 min, after which 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (8) [20] (21.62 g, 40 mmol) was added. The reaction was followed by t.l.c. [(ethyl acetate–chloroform (5 : 95 v/v)]. When the starting material had disappeared (5—6 h) the mixture was filtered, the salts were washed with ethyl acetate, and the combined filtrate and washings were concentrated. The residue was taken up in ethyl acetate, washed (H_2O), dried ($MgSO_4$), and concentrated to give a residue which crystallised when dried *in vacuo* to yield the crude oxime (21.8 g, 98%), m.p. 73—75 °C. Recrystallisation (diethyl ether–hexane) gave an analytical sample of the *oxime* (4), m.p. 76—76.5 °C (Found: C, 73.5; H, 6.8; N, 2.45. $C_{34}H_{37}NO_6$ requires C, 73.49; H, 6.71; N, 2.52%); $[\alpha]_D$ +28.6° (*c* 1.4, $CHCl_3$); $\nu_{max.}$ 3 570m, 3 350br,w, 1 500m, 1 460s, 1 095s, 1 070s, and 1 030s cm^{-1}; δ_H 7.50 [0.7 H, d, *J* 8.4 Hz, 1-H (*E*)], 7.40—7.14 (20 H, m, 4 × Ph), 6.95 [0.3 H, d, *J* 7.2 Hz, 1-H (*Z*)], and 4.93—3.43 (total 14 H, m); δ_C ([$^2H_6$]acetone) 148.93 (d), 139.70 (s), 139.57 (s), 139.33 (s), 139.04 (s), 128.83 (d), 128.70 (d), 128.43 (d), 128.00 (d), 127.90 (d), 80.81 (d), 79.55 (d), 78.55 (d), 75.20 (t), 74.00 (t), 73.59 (t), 72.41 (t), 71.44 (t), and 70.80 p.p.m. (d). A second form was isolated, m.p. 110—111 °C; δ_C ([$^2H_6$]-acetone) 139.84 (s), 139.41 (s), 128.76 (d), 128.42 (d), 128.03 (d), 127.86 (d), 93.30 (d), 86.66 (d), 79.32 (d), 78.93 (d), 76.84 (d), 75.75 (t), 75.14 (t), 74.78 (t), 73.76 (t), and 70.00 p.p.m. (t).

(E)- *and* (Z)-2,3,4,6-*Tetra*-O-*benzyl*-D-*mannose Oxime* (9).—Similarly, the mixture from hydroxylamine hydrochloride (2.95 g, 42 mmol), sodium (0.49 g, 21.3 mg-atom) in 96% aqueous ethanol (150 ml), and a solution of 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose [18] (4.60 g, 8.5 mmol) in ethanol (30 ml) at 50 °C (5 h) as indicated for the preparation of the oxime (4) gave, after work-up and evaporation, a residue which was extracted five times with diethyl ether. The dried ($MgSO_4$) extracts were evaporated and the remaining oil was chromatographed on silica gel (60 g) with chloroform as eluant to afford the *oxime* (9) as a syrup (4.31 g, 91% after drying for 48 h at 10^{-3} mmHg) (Found: C, 73.55; H, 6.8; N, 2.45. $C_{34}H_{37}NO_6$ requires C, 73.49; H, 6.71; N, 2.52%); $[\alpha]_D$ +8.8° (*c* 1.1, $CHCl_3$); $\nu_{max.}$ 3 570m 3 370br, 1 450s, 1 395m, 1 360m, 1 330m, 1 310m, 1 090br.s, 1 070s, and 1 030s cm^{-1}; δ_H 8.50—7.78br (0.8 H, NOH), 7.47 [0.8 H, d, *J* 8.4 Hz, 1-H (*E*)], 7.39—7.08 (20 H, m, 4 × Ph), 6.92 [0.2 H, d, *J* 7.0 Hz, 1-H (*Z*)], 4.78—4.18 (total 9 H, m, 4 × CH_2Ph and 1 × H), and 4.18—3.42 (5 × H, m, chain); δ_C (CCl_4) 148.78 (d), 138.08 (s), 137.89 (s), 137.43 (s), 127.64 (d), 127.26 (d), 126.90 (d), 79.97 (d), 78.86 (d), 76.51 (d), 74.20 (t), 73.70 (t), 72.88 (t), 70.80 (t), 70.11 (t), and 69.63 p.p.m. (d).

Typical Procedure for the Oxidation of the Oximes with Sodium Metaperiodate in the Presence of Sodium Acetate.—N-*Hydroxy*-2,3:5,6-*di*-O-*isopropylidene*-D-*mannonimido*-1,4-*lactone* (18). A solution of sodium metaperiodate (12.8 g, 60 mmol) in water (250 ml) was added during 1 h to a solution of the oxime (17) [5b] (13.8 g, 50 mmol) and sodium acetate (4.1 g, 50 mmol) in ethanol (750 ml) at a bath temperature of 75 °C. The mixture was stirred at that temperature until the starting oxime had disappeared (2 h) as indicated by t.l.c. [ethyl acetate–hexane (1 : 1 v/v)]. The mixture was filtered and the residue was washed with ethyl acetate. The combined filtrate and washings were concentrated and the residue was extracted with ethyl acetate. The extract was washed successively with aqueous sodium sulphite and brine, dried ($MgSO_4$), and concentrated to afford a solid (13.68 g, quantitative), m.p. 166—168 °C, which was recrystallised from dichloromethane–hexane to yield the *hydroximolactone* (18), m.p. 174—174.5 °C (12.32 g, 90%). Chromatography [silica gel (60 g); ethyl acetate–hexane (1 : 1 v/v) as eluant] of the material remaining in the mother liquors, followed by crystallisation, provided a second crop of compound (18) (0.4 g, 3%), m.p. 174—174.5 °C (raised to 175.5—176 °C after sublimation) (Found: C, 52.8; H, 7.05; N, 5.25. $C_{12}H_{19}NO_6$ requires C, 52.74; H, 7.01; N, 5.13%); $[\alpha]_D$ +98.6° (*c* 1.1, $CHCl_3$); $\nu_{max.}$ 3 575m, 3 340br., 1 693s, 1 385s, 1 375s, 1 152s, 1 120s, 1 067s, 971s, and 950d cm^{-1}; δ_H 5.15 (1 H, d, $J_{2,3}$ 5.6 Hz, 2-H), 4.85 (1 H, dd, $J_{3,4}$ 3.5 Hz, 3-H), 4.51 (1 H, ddd, *J* 8.0, 5.4, and 4.2 Hz, 5-H), 4.29 (1 H, dd, *J* 8.0 and 3.5 Hz, 4-H), 4.18br. (2 H, d, *J ca.* 4.8 Hz, 6-H_2), 1.47 and 1.45 (both 3 H, s, Me), and 1.39 (6 H, s, 2 × Me); δ_C 156.68 (s), 114.14 (s), 109.67 (s), 82.48 (d), 77.44 (2 × d), 72.66 (d), 66.61 (t), 26.85 (q), 25.84 (q), and 25.14 p.p.m. (2 × q).

In a similar way, oxidation of the oxime (4) obtained from (8) (25.65 g, 47.5 mmol) at 50—60 °C, followed by crystallisation (diethyl ether–hexane) of the product, gave 2,3,4,6-*tetra*-O-*benzyl*-N-*hydroxy*-D-*gluconimido*-1,5-*lactone* (5) (22.63 g, 86%), m.p. 88.8—89 °C (Found: C, 73.8; H, 6.4; N, 2.5. $C_{34}H_{35}NO_6$ requires C, 73.76; H, 6.37; N, 2.53%); $[\alpha]_D$ +46.2° (*c* 1.1, $CHCl_3$); $\nu_{max.}$ 3 580m, 3 440w, 3 350br, 1 670m, 1 650w, 1 635w, 1 495m, 1 450s, 1 070s, and 1 030s cm^{-1}; δ_H 7.45—7.03 (20 H, m, 4 × Ph), 4.85—4.27 (total 9 H, m, 4 × CH_2Ph and 2-H), 4.11 (1 H, d, *J* 2 Hz, 3-H), 3.99—3.63 (4 H, m, 4-, 5-, 6-, and 6-H); δ_C 151.43 (s), 138.07 (s), 137.81 (s), 137.30 (s), 137.22 (s), 128.56 (d), 128.48 (d), 128.27 (d), 128.00 (d), 127.78 (d), 81.43 (d), 77.56 (d), 76.12 (d), 73.53 (t), 73.21 (d), 72.99 (t), 71.64 (t), 70.59 (t), and 68.18 p.p.m. (t). This compound was treated with the following reagents: (a) thionyl chloride (1 equiv.), dry dioxan, room temperature to 60 °C; (b) neat thionyl chloride, room temperature; (c) thionyl chloride (10% solution in pyridine); (d) methanolic HCl, room temperature to 60 °C, (e) PCl_5 (2 equiv.), dioxan, room temperature to 40 °C, and (f) trifluoroacetic anhydride (1 equiv.), 1,2-dimethoxyethane). In every case the only identifiable products were the starting material and some 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone.

Similarly, oxidation of the oxime (9) (1.515 g, 2.73 mmol) gave 2,3,4,6-*tetra*-O-*benzyl*-N-*hydroxy*-D-*mannonimido*-1,5-*lactone* (10) (1.34 g, 89%) as an oil (Found: C, 73.6; H, 6.4; N, 2.5. $C_{34}H_{35}NO_6$ requires C, 73.76; H, 6.37; N, 2.53%); $[\alpha]_D$ −10.2° (*c* 1.1, $CHCl_3$); $\nu_{max.}$ 3 570w, 3 430w, 3 330br, 1 660m, 1 650m, 1 635m, 1 495m, 1 455s, 1 105s, 1 070s, and 1 035s cm^{-1}; δ_H 7.52—7.13 (20 H, m, 4 × Ph), 4.90 and 4.53 (both 1 H, d, *J* 11.0 Hz, CH_2Ph), 4.73 and 4.45 (both 1 H, d, *J* 12.0 Hz, CH_2Ph), 4.67 and 4.51 (total 2 H, 2 × d, both *J* 12.0 Hz, CH_2Ph), 4.52 (2 H, s, CH_2Ph), 4.37 (1 H, t, *J* 8.4 Hz, 4-H), 4.22 (1 H, d, *J* 3 Hz, 2-H), 4.03 (1 H, dt, *J* 8.4 and 3.5 Hz, 5-H), 3. 80 (2 H, d, *J* 3.5 Hz, 6-H_2), and 3.83 (1 H, dd, *J* 8.5 and 3 Hz, 3-H); δ_C 151.50 (s), 137.79 (s), 137.44 (s), 137.12 (s), 128.17 (d), 127.79 (d), 127.56 (d), 80.61 (d), 79.57 (d), 74.72 (t), 73.33 (d and t), 71.44 (t), 70.85 (d), 70.25 (t), and 68.76 p.p.m. (t).

In identical manner, oxidation of the oxime (13) [5a] (21.43 g, 40 mmol) co-crystallised with 1 equiv. of ethyl acetate, followed by crystallisation of the product from diethyl ether–hexane, gave N-*hydroxy*-2,3-O-*isopropylidene*-5-O-*trityl*-D-*ribonimido*-1,4-*lactone* (14) (17.05 g, 88.3%), containing 0.5 mol equiv. of diethyl ether of crystallisation. The product had m.p. 151—152 °C. Chromatography of the mother liquors and crystallisation of the product gave a second crop of compound (14) (1.58 g, 7.7%), containing 0.9 mol equiv. of diethyl ether, m.p. 151—152 °C. An analytically pure sample was prepared by drying at 60 °C *in vacuo*, and had m.p. 152—153 °C (Found: C, 72.65; H, 6.3; N, 3.2. $C_{27}H_{27}NO_5$ requires C, 72.79; H, 6.11; N, 3.14%); $[\alpha]_D$ −42.8° (*c* 1.0 $CHCl_3$); $\nu_{max.}$ 3 580m, 3 320br, 1 495m, 1 455s, 1 390s, 1 380s, 1 350m, 1 160s, 1 100s, and 1 010s cm^{-1}; δ_H 7.47—7.10 (total 16 H, m, 3 × Ph and OH), 5.29 (1 H, d, *J* 6 Hz, 2-H), 4.68 (1 H, dd, *J* 2.8 and 2 Hz, 4-H), 4.58 (1 H, d, *J* 6 Hz, 3-H), 3.65 (1 H, dd, *J* 10.4 and 2.8 Hz, 5-H), 3.00 (1 H, dd, *J* 10.4 and 2 Hz, 5-H), 1.47 (3 H, s, Me), and 1.32 (3 H, s, Me); δ_C 158.36 (s), 142.91 (s), 128.96 (d), 128.30 (d), 127.84 (d), 127.01 (d), 113.17 (s), 87.42 (s), 85.95 (d), 80.04 (d), 77.72 (d), 63.78 (t), 26.78 (q), and 25.68 p.p.m. (q).

Typical Procedure for the Oxidation of the Oximes with Sodium Metaperiodate in the Absence of Sodium Acetate.—*Oxidation of the oxime* (17). A solution of sodium metaperiodate (10.27 g, 48 mmol) in 75% aqueous ethanol (320 ml) was added during 45 min to a solution of the oxime (17) (11 g, 40 mmol) in the same solvent (240 ml). The reaction, monitored by t.l.c. [ethyl acetate–hexane (1:1, v/v)], was allowed to proceed until the starting material had disappeared (75 min). The mixture was allowed to cool to room temperature and was then filtered, and the filtrate was concentrated. The residue was taken up in diethyl ether, and the solution was dried ($MgSO_4$) and concentrated to give another residue which was crystallised three times from dichloromethane–hexane to give (Z)-2,3:5,6-*di*-O-*isopropylidene*-α-D-*mannofuranosyl*-ONN-*azoxy* 2,3:5,6-*di*-O-*isopropylidene*-α-D-*mannofuranoside* (20) (4.79 g, 44%), m.p. 145—147 °C. Recrystallisation from methanol gave an analytical sample, m.p. 147—147.5 °C (Found: C, 52.8; H, 7.1; N, 5.2%; M^+, 550.25. $C_{24}H_{38}N_2O_{12}$ requires C, 52.74; H, 7.01; N, 5.13%; *M*, 546.58 $[\alpha]_D$ +42.6° (*c* 0.9, $CHCl_3$); $\nu_{max.}$ 2 980s, 2 930m, 1 500m, 1 455m, 1 380s, 1 370s, 1 305w, 1 160s, 1 150sh, 1 120s, 1 080br sh, 1 065s, 990s, 960s, 930s, 890m, 860s, and 840s cm^{-1}; δ_H 5.76 (total 2 H, s, 1- and 1′-H), 5.27—3.93 (total 12 H, m, carbohydrate-H), 1.53, 1.50, and 1.37 (each 3 H, s, Me), 1.47 (6 H, s, 2 × Me), and 1.40 (9 H, s, 3 × Me); δ_C 113.55 (s), 113.17 (s), 109.28 (2 × s), 108.84 (d), 102.61 (d), 85.97 (d), 83.94 (d), 83.79 (d), 82.20 (d), 80.09 (d), 79.23 (d), 72.79 (d), 66.63 (t), 66.48 (t), 26.89 (q), 26.77 (q), 25.91 (2 × q), 25.15 (2 × q), 24.55 (q), and 24.46 p.p.m. (q); $\lambda_{max.}$ (MeOH) 232 nm (ε 10 700); *m/z* 531 [(*M* − 15)$^+$, 4.5], 516 (2.8), 487 (3.4), 245 (7.3), 243 (10.2), 213 (6.1), 187 (6.1), 186 (10.2), and 185 (100). Chromatography [ethyl acetate–chloroform (1 : 9 v/v) as eluant] of the mother liquors gave a second crop of the glycoside (20) (1.01 g, 9%) and also some of the hydroximolactone (18) (1.48 g, 14%).

In a similar way, oxidation of the oxime (13) (6.0 g, 11.2 mmol) co-crystallised with 1 equiv. of ethyl acetate gave, after chromatography [silica gel (250 g); ethyl acetate–hexane (1 : 2) as eluant] of an aliquot (4.6 g) prepared from the crude product (5.35 g), the hydroximolactone (14) (3.5 g, 82%).

Similarly, the oxime (9) (2.21 g, 4 mmol) gave, after chromatography [silica gel (100 g); ethyl acetate–hexane (1 : 2)], the hydroximolactone (10) (1.59 g, 72%) and 2,3,4,6-*tetra*-O-*benzyl*-D-*mannono*-1,5-*lactone* (12) (207 mg, 10%), which was recrystallised from diethyl ether–hexane, m.p. 83—83.5 °C (Found: C, 75.7; H, 6.45. $C_{34}H_{34}O_6$ requires C, 75.81; H, 6.36%); $[\alpha]_D$ −0.5° (*c* 10.5, $CHCl_3$); $\nu_{max.}$ 1 765s cm^{-1}; δ_H 7.46—7.00 (20 H, m, 4 × Ph), 5.07 and 4.57 (total 2 H, 2 × d, both *J* 11.7 Hz, CH_2Ph), 4.85 and 4.62 (total 2 H, 2 × d, both *J* 12.3 Hz, CH_2Ph), 4.55 (2 H, s, CH_2Ph), 4.40 and 4.23 (total 2 H, 2 × d, both *J* 11.7 Hz, CH_2Ph), 4.37 (1 H, d, *J* 2.7 Hz, 2-H), 4.25 (1 H, dt, *J* 6.7 and 4.8 Hz, 5-H), 4.05 (1 H, dd, *J* 2.7 and 1.8 Hz, 3-H), 3.80 (1 H, dd, *J* 6.7 and 1.8 Hz, 4-H), and 3.63 (2 H, d, *J* 4.8 Hz, 6-H_2); δ_C 169.05 (s), 137.50 (s), 137.04 (s), 136.61 (s), 128.21 (d), 127.98 (d), 127.67 (d), 78.47 (d), 76.59 (d), 75.91 (t), 75.40 (d), 73.32 (d and t), 72.82 (t), 71.73 (t), and 69.05 p.p.m. (t).

In identical manner, the oxime (4) (3.15 g, 5.67 mmol) gave an intimate mixture of the crude hydroximolactone (5) (2.04 g, 65%), and the tetrabenzyl-D-glucopyranose (8). Separation was only possible after acetylation.

Typical Acetylation of the Hydroximolactones.—To a cold (0 °C) solution of the hydroximolactone (5) (277 mg, 0.5 mmol) in pyridine (3 ml) was added a solution of acetic

anhydride (255 mg, 2.5 mmol) in pyridine (2 ml) and the mixture was warmed to 50 °C during 3 h. The solvent was evaporated off under reduced pressure and the residue was purified by preparative t.l.c. [ethyl acetate–hexane (1 : 2)] to give N-*acetoxy*-2,3,4,6-*tetra*-O-*benzyl*-D-*gluconimido*-1,5-*lactone* (6) (290 mg, 97%) (Found: C, 72.45; H, 6.35; N, 2.25. $C_{36}H_{37}NO_7$ requires C, 72.59; H, 6.26; N, 2.35%); $[\alpha]_D$ +25.5° (*c* 1.7, $CHCl_3$); $\nu_{max.}$ 1 763s and 1 651s cm^{-1}; δ_H 7.48—7.07 (20 H, m, 4 × Ph), 4.89—4.26 (total 10 H, m, 4 × C*H*$_2$Ph and 2 × carbohydrate-H), 4.07—3.72 (4 H, m), and 2.17 (3 H, s, COMe); δ_C 167.66 (s), 155.96 (s), 137.81 (s), 137.31 (s), 136.65 (s), 128.24 (d), 127.88 (d), 127.69 (d), 127.49 (d), 80.36 (d), 77.18 (d), 76.69 (d), 73.22 (t), 72.86 (d), 72.62 (t), 71.43 (t), 70.84 (t), 67.67 (t), and 19.44 p.p.m. (q). This acetate (980 mg, 1.65 mmol) was converted back into the starting material (5) (850 mg, 93%) upon treatment with a solution of sodium (10 mg, 0.43 mg-atom) in methanol (20 ml) during 40 min.

In a similar way, the hydroximolactone (10) (390 mg, 0.7 mmol) was acetylated to give N-*acetoxy*-2,3,4,6-*tetra*-O-*benzyl*-D-*mannonimido*-1,5-*lactone* (11) (357 mg, 85%) (Found: C, 72.3; H, 6.35; N, 2.3. $C_{36}H_{37}NO_7$ requires C, 72.59; H, 6.26; N, 2.35%); $[\alpha]_D$ −24.2° (*c* 1.6, $CHCl_3$); $\nu_{max.}$ 1 760s, and 1 645s cm^{-1}; δ_H 7.53—7.12 (20 H, m, 4 × Ph), 4.88 and 4.55 (total 2 H, 2 × d, both *J* 11.1 Hz, C*H*$_2$Ph), 4.82 and 4.54 (total 2H, 2 × d, both *J* 12 Hz, C*H*$_2$Ph) 4.65 and 4.49 (total 2 H, 2 × d, both *J* 12 Hz, C*H*$_2$Ph), 4.55 (2 H, s, C*H*$_2$Ph), 4.40 (1 H, d, *J* 3 Hz, 2-H), 4.33 (1 H, dd, *J* 8.3 and 7.9 Hz, 4-H), 4.13 (1 H, dt, *J* 7.9 and 3.6 Hz, 5-H), 3.78 (1 H, dd, *J* 8.3 and 3.0 Hz, 3-H), 3.77 (2 H, d, *J* 3.6 Hz, 6-H$_2$), and 2.14 (3 H, s, COMe); δ_C 167.81 (s), 156.65 (s), 137.65 (s), 137.30 (s), 136.86 (s), 128.17 (d), 127.81 (d), 127.64 (d), 127.53 (d), 81.65 (d), 79.02 (d), 74.61 (t), 73.24 (t and d), 71.59 (t), 71.02 (d), 70.88 (t), 68.70 (t), and 19.44 p.p.m. (q).

Similarly, the hydroximolactone (18) (547 mg, 2 mmol) gave N-*acetoxy*-2,3:5,6-*di*-O-*isopropylidene*-D-*mannonimido*-1,4-*lactone* (19) (625 mg, 99%) (Found: C, 53.3; H, 6.8; N, 4.4. $C_{14}H_{21}NO_7$ requires C, 53.33; H, 6.71; N, 4.44%); $[\alpha]_D$ +90.5° (*c* 1.0, $CHCl_3$); $\nu_{max.}$ 1 770s and 1 680s cm^{-1}; δ_H 5.33 (1 H, d, *J* 5.6 Hz, 2-H), 4.91 (1 H, dd, *J* 5.6 and 3.3 Hz, 3-H), 4.63—4.30 (total 2 H, m, 4- and 5-H), 4.30—4.00 (2 H, m, 6-H$_2$), 2.13 (3 H, s, COMe), 1.51 and 1.47 (both 3 H, s, Me), and 1.40 (6 H, s, 2 × Me); δ_C 167.56 (s), 162.60 (s), 114.30 (s), 109.39 (s), 83.55 (d), 78.02 (d), 77.24 (d), 72.69 (d), 65.97 (t), 26.71 (2 q), 25.70 (q), 25.24 (q), and 19.20 p.p.m. (q); *m/z* 316 [$(M + 1)^+$, 5], 315 (M^+, 3), and 300 [$(M - 15)^+$, 100].

In identical manner the hydroximolactone (14) (223 mg, 0.5 mmol) gave N-*acetoxy*-2,3-O-*isopropylidene*-5-O-*trityl*-D-*ribonimido*-1,4-*lactone* (15) (237 mg, 97%), (Found: C, 71.2; H, 6.0; N, 2.85. $C_{29}H_{29}NO_6$ requires C, 71.44; H, 6.00; N, 2.87%); $[\alpha]_D$ −56.4° (*c* 1.1, $CHCl_3$); $\nu_{max.}$ 1 769s and 1 677s cm^{-1}; δ_H 7.47—7.12 (15 H, m, 3 × Ph), 5.42 (1 H, d, *J* 6 Hz, 2-H), 4.74 (1 H, dd, *J* 2.8 and 2.1 Hz, 4-H), 4.63 (1 H, d, *J* 6 Hz, 3-H), 3.66 (1 H, dd, *J* 10.5 and 2.8 Hz, 5-H), 3.06 (1 H, dd, *J* 10.5 and 2.1 Hz, 5-H), 2.23 (3 H, s, COMe), 1.47 (3 H, s, Me), and 1.34 (3 H, s, Me); δ_C 167.60 (s), 163.21 (s), 142.77 (s), 128.28 (d), 127.92 (d), 127.19 (d), 113.55 (s), 87.64 (s), 87.51 (d), 79.62 (d), 78.23 (d), 63.50 (t), 26.79 (q), 25.56 (q), and 19.37 p.p.m. (q); *m/z* 487 (M^+, 1.5), 428 [$(M - 59)^+$, 3.5] and 43 (100).

1-*Deoxy*-1-(2,3:5,6-*di*-O-*isopropylidene*-α-D-*mannofuranosyl*-ONN-*azoxy*)-2,3:5,6-*di*-O-*isopropylidene*-α-D-*mannofuranose*.—Ceric ammonium nitrate (13.2 g, 24 mmol) was added in portions to a well stirred mixture of the oxime (17) (2.20 g, 8 mmol) and sodium carbonate (2.54 g, 24 mmol) in acetonitrile (80 ml) and water (50 ml). After 20 min at room temperature the mixture was filtered and the filtrate was concentrated to *ca.* 10 ml and then extracted with ethyl acetate. Concentration of the dried ($MgSO_4$) extract followed by chromatography [silica gel (250 g); ethyl acetate–hexane (1 : 2) as eluant; impure fractions were re-chromatographed with ethyl acetate–chloroform (1 : 9)] gave the title *azoxy-compound* (681 mg, 32%) (Found: C, 54.3; H, 7.3; N, 5.25. $C_{24}H_{38}N_2O_{11}$ requires C, 54.33; H, 7.22; N, 5.28%); $[\alpha]_D$ +3.5° (*c* 0.9, $CHCl_3$); $\nu_{max.}$ 3 000s, 2 940m, 2 895m, 1 505s, 1 455m, 1 385s, 1 375s, 1 355w, 1 330w, 1 300m, 1 165s, 1 150s, 1 125s, 1 105s, 1 070s, 1 020m, 970m, 950m, 890m, and 860m cm^{-1}; δ_H 5.67 (1 H, s, 1′-H), 5.54 (1 H, s, 1-H), 5.11—4.00 (total 12 H, m, carbohydrate-H), 1.52 and 1.47 (both 6 H, s, 2 × Me), 1.38 (9 H, s, 3 × Me), and 1.36 (3 H, s, Me); δ_C 113.69 (s), 113.35 (s), 109.28 (s), 109.09 (s), 106.54 (d), 95.99 (d), 85.70 (d), 85.12 (d), 83.75 (d), 82.35 (d), 79.95 (d), 79.36 (d), 72.81 (d), 72.73 (d), 66.77 (t), 66.57 (t), 28.81 (q), 25.99 (q), 25.20 (q), 24.79 (q), and 24.52 p.p.m. (q); $\lambda_{max.}$ (MeOH) 222 nm (ε 7 600); *m/z* 515 [$(M - 15)^+$, 9.5] and 101 (100).

2,3-O-*Isopropylidene*-N-p-*tolylsulphonyloxy*-5-O-*trityl*-D-*ribonimido*-1,4-*lactone* (16).—A solution of toluene-*p*-sulphonyl chloride (286 mg, 1.5 mmol) in anhydrous pyridine (1 ml) was added to a solution of the hydroximolactone (14) (446 mg, 1 mmol) in pyridine (10 ml). After 10 h at 80 °C, the mixture was concentrated under reduced pressure and the residue was worked up in the usual way with ethyl acetate. Chromatography [silica gel (70 g); ethyl acetate–hexane (1 : 3) as eluant] of the crude product gave the starting material (41 mg, 9.2% recovery) and the *tosylate* (16) (534 mg, 89%) (Found: C, 68.15; H, 5.6; N, 2.2. $C_{34}H_{33}NO_7S$ requires C, 68.10; H, 5.55; N, 2.34%); $[\alpha]_D$ −75.7° (*c* 1.0, $CHCl_3$); $\nu_{max.}$ 1 675m, 1 600m, 1 450s, 1 375s, 1 175s, 1 155s, 1 000s, 990s, and 870s cm^{-1}; δ_H 7.87 and 7.13 (total 4 H, 2 × d, both *J* 8.3 Hz, C_6H_4), 7.27 (15 H, s, 3 × Ph), 5.27 (1 H, d, *J* 6 Hz, 2-H), 4.79—4.67 (1 H, m, 4-H), 4.49 (1 H, d, *J* 6 Hz, 3-H), 3.69 (1 H, dd, *J* 10.7 and 3 Hz, 5-H), 2.95 (1 H, dd, *J* 10.7 and 1.6 Hz, 5-H), 2.27 (3 H, s, C_6H_4*Me*), and 1.30 (6 H, s, 2 × Me); δ_C 163.91 (s), 144.42 (s), 142.61 (s), 132.20 (s), 129.24 (d), 128.97 (d), 128.71 (d), 128.14 (d), 127.90 (d), 127.10 (d), 113.60 (s), 87.70 (s and d), 79.92 (d), 78.23 (d), 63.11 (t), 26.56 (q), 25.60 (q), and 21.49 p.p.m. (q); *m/z* 599 (M^+, 0.1) and 243 (100).

2,3,4,6-*Tetra*-O-*benzyl*-N-*methylsulphonyloxy*-D-*gluconimido*-1,5-*lactone* (7).—Triethylamine (0.2 ml, 1.5 mmol) and methanesulphonyl chloride (0.1 ml, 1.2 mmol) were added in turn to a solution of the hydroximolactone (5) (553 mg, 1 mmol) in dichloromethane (10 ml). After 45 min the mixture was worked up as usual with dichloromethane. Preparative t.l.c. [ethyl acetate–hexane (3 : 1)] of the crude product gave the *mesylate* (7) (448 mg, 71%) (Found: C, 66.75; H, 6.1; N, 1.95. $C_{35}H_{37}NO_8S$ requires C, 66.54; H, 5.90; N, 2.22%); $[\alpha]_D$ +37.6° (*c* 1.3, $CHCl_3$); $\nu_{max.}$ 1 655m, 1 455s, 1 370s, 1 185s, 1 100s, 1 075s, 970s, and 845s cm^{-1}; δ_H 7.40—7.10 (20 H, m, 4 × Ph), 4.83—4.20 (9 H, m), 4.20—4.10 (1 H, m), 4.03—3.57 (4 H, m), and 3.08 (3 H, s, Me); δ_C 157.11 (s), 137.55 (s), 137.13 (s), 136.56 (s), 136.11 (s), 128.14 (d), 127.88 (d), 127.73 (d), 127.49 (d), 80.24 (d), 77.29 (d), 76.74 (d), 73.18 (t), 72.84 (t), 72.22 (d), 71.49 (t), 70.95 (t), 67.22 (t), and 35.97 p.p.m. (q).

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