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Note

The crystal structure of methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-*β*-DL-arabinopyranoside*

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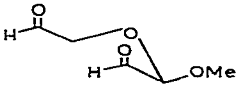
We have shown[2] that base-catalysed cyclisation of the "dialdehyde" **1** (obtained on periodate oxidation of methyl *β*-D-xylopyranoside) with nitroethane gives, after acetylation, a mixture containing five of the eight possible methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitropentopyranosides. Chemical and ^{1}H-n.m.r. spectroscopic evidence established[2] that four of the stereoisomers possess *α*-L-*lyxo*, *α*-L-*xylo*, *β*-D-*xylo*, and *α*-L-*arabino* configurations, *i.e.*, **2**, **3**, **4**, and **5**, respectively, each having the 3-nitro group equatorially disposed in the preferred, chair conformation. Because only a small quantity of the fifth stereoisomer {m.p. 132–133°, $[\alpha]_D$ −199° (*c* 1, chloroform)} was isolated, its structure was not determined, although ^{1}H-n.m.r. spectroscopy indicated that the *β*-D-*lyxo* configuration was unlikely if, as in the stereoisomers **2–5**, the 3-nitro group prefers an equatorial orientation.



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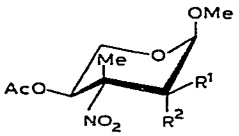
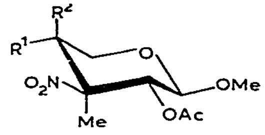
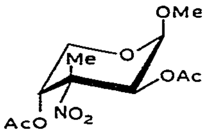


2 R¹ = H, R² = OAc
3 R¹ = OAc, R² = H



4 R¹ = OAc, R² = H
5 R¹ = H, R² = OAc



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In seeking to obtain more of the unidentified stereoisomer, we repeated the nitroethane cyclisation on **1** and isolated a small amount of material which, although its ^{1}H-n.m.r. spectrum was indistinguishable from that of the unidentified stereoisomer, had m.p. 160–162.5°, $[\alpha]_D$ ~0° (*c* 0.6, chloroform). Because it displayed no optical rotation, this material was considered, and was shown subsequently by single-crystal X-ray analysis, to be the racemic form. Its origin is uncertain, but it could have arisen either *via* racemisation of **1** under the basic conditions of the

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*Branched-chain Sugars, Part XII. For Part XI, see ref. 1.

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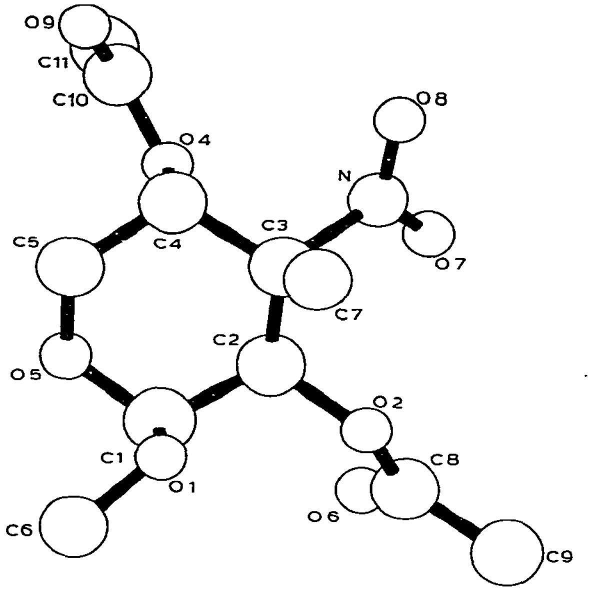

Fig. 1. Stereoview of methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-DL-arabinopyranoside, and the numbering scheme for the atoms.

reaction, or from contamination of methyl β-D-xylopyranoside, from which **1** was prepared, with the corresponding α-D-glycoside.

The racemate proved to be more amenable to single-crystal X-ray analysis (see Experimental section) than the pure optical isomer. The stereoview of one of the components shown in Fig. 1 identifies the racemic form as methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-DL-arabinopyranoside. The interatomic distances and bond angles (see Table II) are unexceptional and require no comment. Like the stereoisomers **2**–**5**, the molecule assumes the chair conformation that places the 3-nitro group in an equatorial orientation. The ^{1}H-n.m.r. spectrum of the racemate in deuteriochloroform is also consistent with the molecule's adopting the conformation shown in Fig. 1, or its antipode, since the ring-proton couplings, all of which are small, preclude alternative chair-conformations. The pure optical isomer isolated in our original work[2] is undoubtedly methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-D-arabinopyranoside (**6**), a legitimate product of nitroethane cyclisation of the "dialdehyde" **1**.

EXPERIMENTAL AND RESULTS

*Methyl 2,4-di-O-acetyl-3-deoxy-3-C-methyl-3-nitro-β-*DL*-arabinopyranoside.* — (*a*) *Crystal data.* $C_{11}H_{17}NO_8$; $M = 291.3$, monoclinic, space group $P2_1/c$, $a = 8.920(6)$, $b = 11.509(11)$, $c = 13.784(17)$ Å, $\beta = 99.39(9)°$, volume = 1396.1 Å^3, $D_c = 1.386$ g.cm^{-3}, $Z = 4$, $F(000) = 616$, $\lambda(\text{CuK}\alpha) = 1.5418$ Å, μ_λ (for CuKα) = 9.3 cm^{-1}.

(*b*) *Data collection.* Data were collected from crystals which grew as colourless laths extended in the *b* direction and with prominent {001} faces. The systematic absences unambiguously indicated the centrosymmetric space-group $P2_1/c$, which implies the presence of both enantiomers in the crystal. Equi-inclination, multi-film Weissenberg photographs (levels 0-6*kl* and *h*0-1*l*) were scanned by using a microdensitometer (S.R.C. Microdensitometer Service, Daresbury Laboratory), and 1235 reflections were classified as statistically significant.

(*c*) *Structure analysis.* The structure was solved without difficulty by direct methods. The *E*-map of lowest parachor, calculated from 207 reflections with $|E| \geqslant 1.2$, showed nineteen of the twenty non-hydrogen atoms. Two cycles of Fourier refinement located the remaining atom and permitted the assignment of carbon, nitrogen, and oxygen atoms in the structure. During full-matrix, least-squares refinement, with isotropic thermal parameters for all atoms, *R* fell progressively to 0.149, and this value was reduced to 0.087 when anisotropic thermal parameters were included. A difference Fourier synthesis then showed peaks of comparable intensity to the stronger "noise" peaks near the positions expected for the seventeen hydrogen atoms. These atoms were included with fixed co-ordinates and U_H set at 0.07 in subsequent cycles of refinement (1235 reflections, 181 parameters, and unit weights for all reflections), which converged at *R* 0.066. The anisotropic thermal parameters

TABLE I

FRACTIONAL ATOMIC CO-ORDINATES ($\times$ 10^4) FOR DL-6, WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
O-1	−2171(4)	4825(3)	1693(3)
O-2	−1709(4)	3645(3)	3464(2)
O-4	2175(4)	2770(3)	2135(3)
O-5	−688(4)	3475(3)	1008(2)
O-6	−2608(5)	1822(3)	3344(3)
O-7	1215(6)	2655(5)	4259(4)
O-8	2912(6)	3962(5)	4176(3)
O-9	4260(6)	3379(4)	1624(6)
N	1697(6)	3504(5)	3881(3)
C-1	−1639(6)	3673(5)	1716(4)
C-2	−775(6)	3395(4)	2734(4)
C-3	703(6)	4069(4)	2980(4)
C-4	1622(6)	3971(4)	2133(4)
C-5	636(7)	4210(5)	1157(4)
C-6	−3246(7)	5091(6)	836(4)
C-7	513(7)	5335(5)	3265(4)
C-8	−2594(6)	2765(5)	3706(4)
C-9	−3489(7)	3157(5)	4472(5)
C-10	3531(7)	2600(5)	1831(5)
C-11	3925(7)	1363(6)	1759(5)

TABLE II

MOLECULAR DIMENSIONS[a] FOR DL-6, WITH STANDARD DEVIATIONS IN PARENTHESES

Bond lengths (Å)

C-1–C-2	1.521(7)	O-2–C-2	1.437(5)
C-2–C-3	1.520(7)	O-2–C-8	1.358(6)
C-3–C-4	1.537(7)	O-4–C-4	1.468(6)
C-3–C-7	1.526(7)	O-4–C-10	1.357(7)
C-3–N	1.547(7)	O-5–C-1	1.412(6)
C-4–C-5	1.507(8)	O-5–C-5	1.440(7)
C-8–C-9	1.493(8)	O-6–C-8	1.195(6)
C-10–C-11	1.474(8)	O-7–N	1.218(6)
O-1–C-1	1.407(6)	O-8–N	1.214(6)
O-1–C-6	1.428(6)	O-9–C-10	1.170(7)

Bond angles (degrees)

C-1–O-1–C-6	113.5(4)	N–C-3–C-7	105.6(4)
C-2–O-2–C-8	116.7(4)	C-2–C-3–C-4	110.1(4)
C-4–O-4–C-10	116.8(4)	C-2–C-3–C-7	114.7(5)
C-1–O-5–C-5	112.2(4)	C-4–C-3–C-7	111.2(4)
O-7–N–O-8	124.3(5)	O-4–C-4–C-3	106.8(4)
O-7–N–C-3	118.9(5)	O-4–C-4–C-5	108.7(4)
O-8–N–C-3	116.7(5)	C-3–C-4–C-5	111.1(5)
O-1–C-1–O-5	112.0(4)	O-5–C-5–C-4	111.5(4)
O-1–C-1–C-2	109.7(4)	O-2–C-8–O-6	122.8(5)
O-5–C-1–C-2	109.4(4)	O-2–C-8–C-9	110.4(5)
O-2–C-2–C-1	109.8(4)	O-6–C-8–C-9	126.8(5)
O-2–C-2–C-3	108.8(4)	O-4–C-10–O-9	121.6(6)
C-1–C-2–C-3	112.9(4)	O-4–C-10–C-11	113.2(5)
N–C-3–C-2	109.1(4)	O-9–C-10–C-11	125.1(6)
N–C-3–C-4	105.8(4)		

[a] Sum of bond-angles at sp^2-hybridised atoms: C-8, 360°; C-10, 359.9°; N, 359.9°. Excluding contacts involving hydrogen atoms, the shortest intermolecular contact is C-11 . . . O-1 $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z) = 3.35(2)$ Å.

(submitted as supplementary data) for one of the acetyl groups (atoms C-10, C-11, and O-9) suggested that this group might be slightly disordered. However, the final difference-synthesis (maximum amplitude <0.25 e.Å^{-3}) did not suggest an alternative model for refinement. All calculations were carried out on the Dundee University DEC 10 computer using the SHEL-X 76 program[3].

The numbering system used (see Fig. 1) is such that the carbon and oxygen atoms of the parent pentose are numbered in the normal carbohydrate convention and the remaining atoms are numbered arbitrarily.

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