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CRYSTAL AND MOLECULAR STRUCTURES OF 2,3,4,6-TETRA-*O*-ACETYL-1-BROMO-D-GALACTOPYRANOSYL CYANIDE AND 2,3,4,5,7-PENTA-*O*-ACETYL-β-D-*galacto*-2-HEPTULOPYRANOSONONITRILE

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ABSTRACT

2,3,4,6-Tetra-*O*-acetyl-1-bromo-D-galactopyranosyl cyanide (**1**) and 2,3,4,5,7-penta-*O*-acetyl-β-D-*galacto*-2-heptulopyranosononitrile (**2**) crystallise in the orthorhombic system; **1** has space group $P2_12_12_1$, with cell dimensions a = 7.256(1), b = 8.957(2), c = 29.450(3) Å, and **2** has space group $P2_12_12_1$, with a = 7.035(1), b = 15.080(2), c = 19.635(3) Å. The earlier observation, inferred from n.m.r. data, that the reaction of **1** with silver or mercury(II) acetate in acetic acid–acetic anhydride gave **2** with inversion of configuration at the cyanide-bearing carbon is substantiated. The presence of Br in **1** permitted establishment of the absolute configuration.

INTRODUCTION

The X-ray study reported aimed to substantiate the conclusion, inferred from ^{1}H- and ^{13}C-n.m.r. spectra, that the reaction of 1-bromo-D-glycosyl cyanides[1–4] with silver acetate or mercury(II) acetate in acetic acid–acetic anhydride is always accompanied by inversion of configuration at the cyanide-bearing carbon, as exemplified by the conversion of 2,3,4,6-tetra-*O*-acetyl-1-bromo-D-galactopyranosyl cyanide (**1**) into 2,3,4,5,7-penta-*O*-acetyl-β-D-*galacto*-2-heptulopyranosononitrile (**2**).

EXPERIMENTAL

The intensities from colourless crystals of **1** (0.18 × 0.16 × 0.30 mm^3) and **2** (0.08 × 0.10 × 0.40 mm^3) were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated MoKα radiation (λ 0.71073 Å), using an $\omega/2\theta$ scan technique in the range $1.5 > \theta > 25.0°$ with a scan width $0.35 + 0.35\tan\theta$. The

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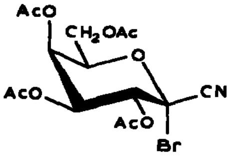
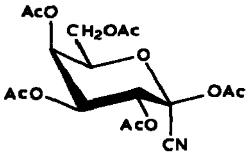


1



2

lattice parameters were determined by least-squares from the setting angles of 25 reflections. Three standard reflections were monitored every hour; these showed 3.5% loss of intensities for **1** and 1.2% for **2**. No absorption corrections were applied.

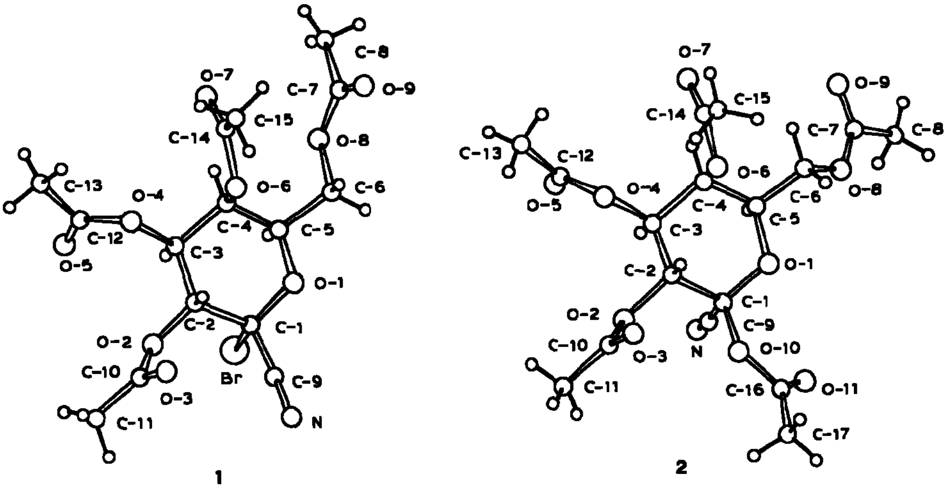
For **1**, 2228 unique reflections were collected, of which 1465 with $F^2 > \sigma(F^2)$ were taken as observed; for **2**, 1963 unique reflections were collected, of which only 1513 with $F^2 > 0.5\sigma(F^2)$ could be used for the structure analysis.

Crystal data: **1** $C_{15}H_{18}BrNO_9$, M_r = 436.22, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 7.256(1)$, $b = 8.957(2)$, $c = 29.450(3)$ Å, $V = 1914.0(9)$ Å^3, $F(000) = 888$, $D_c = 1.514$ Mg.m^{-3}, μ(MoKα) = 21.68 cm^{-1}; **2** $C_{17}H_{21}NO_{11}$, M_r = 415.36, orthorhombic, space groups $P2_12_12_1$, $Z = 4$, $a = 7.035(1)$, $b = 15.080(2)$, $c = 19.635(3)$ Å, $V = 2083.0(9)$ Å^3, $F(000) = 872$, $D_c = 1.324$ Mg.m^{-3}, μ(MoKα) = 1.05 cm^{-1}.

The phase problems were solved by the Patterson method for **1** and by the MULTAN-78 program[5] for **2**.

The refinement of the atomic positional and thermal parameters was performed by the full-matrix, least-squares procedure included in the standard SDP System provided by Enraf–Nonius (1978), using atomic scattering factors implemented therein. At the end of the refinement with isotropic thermal parameters, the hydrogen atoms were entered in calculated positions since they were all bonded to carbon atoms of well-defined geometry. They were only included in the structure factor calculations with a mean isotropic temperature factor ($B_{iH} = B_{iC} + 1$ in Å^2). The refinement of 236 parameters for **1**, minimising $\Sigma w(\Delta F)^2$ with the weighting scheme $w = [\sigma^2(F_o) + 0.25(pF_o)^2]^{-1}$ $(p = 0.01)$, resulted in $R = 0.051$ and $R_w = 0.047$. The other enantiomer furnished $R = 0.065$ and $R_w = 0.071$, underscoring the correct absolute configuration depicted in Fig. 1. Due to the low quality of intensities, the refinement of 267 parameters for **2** was terminated at $R = 0.099$ and $R_w = 0.087$. In order to obtain better resolution of the atomic positions, a new data set was collected from a second crystal with the dimensions of 0.30 × 0.30 × 0.35 mm^3. As indicated by the profile analysis of the reflections, the quality of the crystal, even after numerous recrystallisations, remained rather low. Consequently, even after absorption correction, the refinement for 1770 new observations with $F > \sigma(F)$ gave no better agreement than $R = 0.15$. Careful analysis of $\Delta\rho$ maps computed from both data sets did not permit the assignment of any spurious peak around the terminal atoms affected in particular by intensive thermal motions. All attempts to assign and refine two "disordered" 6-*O*-acetyl groups, which is suggested by the unusually high thermal vibration, were inconclusive. Therefore, the crystal structure of **2** is given by the parameters obtained from the first cycle of refinement.

The final positional parameters for the non-H atoms of **1** and **2** together with B_{eq} values are given in Table I*.



1

2

Fig. 1. Perspective views of the molecular structures of **1** and **2** with atomic numbering. The hydrogen atoms are shown but not labelled.

RESULTS AND DISCUSSION

The established absolute configurations of **1** and the identical enantiomer of **2** are shown in Fig. 1. The relevant torsion angles are listed in Table II. Comparison of these structures confirms the inversion of configuration at C-1. In **1**, the cyanide group is equatorial and in **2** it is axial.

The limited accuracy of the parameters pertaining to **2** does not permit a comparison of the conformations. The sugar ring in **1** assumes a chair conformation, to the mean plane of which those of the four acetyl groups are approximately perpendicular (Table III).

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*Lists of structural factors and other data have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/375 *Carbohydr. Res.*, 168 (1987) 1–5.

TABLE I

FRACTIONAL COORDINATES (× 10^4) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS[a] (Å^2) FOR **1** AND **2**[b]

Atom	**1**				**2**			
	x/a	y/b	z/c	B_{eq}	x/a	y/b	z/c	B_{eq}
Br	2510(1)	8746(1)	3130(1)	5.0(1)	—	—	—	—
O-1	3011(6)	11852(5)	3064(1)	4.2(2)	−86(8)	4241(3)	6625(3)	6.2(3)
O-2	4694(6)	9572(5)	4003(1)	3.9(2)	−2401(8)	4647(3)	4990(2)	5.6(3)
O-3	7478(8)	10700(5)	4092(2)	6.4(3)	−5178(7)	5064(4)	5363(3)	8.0(3)
O-4	2202(6)	11606(4)	4445(1)	3.9(2)	−457(8)	6290(4)	5217(3)	6.6(3)
O-5	1056(8)	9470(6)	4703(2)	6.0(3)	1813(11)	6194(6)	4413(4)	14.2(5)
O-6	2224(6)	13782(4)	3826(1)	3.7(2)	−341(8)	6146(4)	6621(3)	6.6(3)
O-7	−207(9)	14762(7)	4184(2)	10.2(4)	1276(13)	7354(4)	6584(6)	16.4(6)
O-8	−1186(7)	13858(5)	3055(1)	4.5(2)	3634(10)	4442(5)	7481(3)	10.4(4)
O-9	−753(10)	16269(6)	3017(3)	9.8(4)	5585(15)	5383(8)	7700(11)	25.9(10)
O-10	—	—	—	—	−2685(9)	3586(3)	6134(3)	6.3(3)
O-11	—	—	—	—	−1090(12)	2358(4)	6504(4)	9.6(4)
N	7122(10)	10260(8)	2928(2)	7.1(4)	1428(11)	3142(5)	5231(4)	8.0(4)
C-1	3839(10)	10615(8)	3273(2)	4.1(3)	−925(11)	4036(5)	5997(4)	5.0(4)
C-2	4013(9)	10855(7)	3795(2)	3.2(3)	−1465(10)	4886(5)	5634(4)	4.8(3)
C-3	2035(7)	11171(7)	3975(2)	3.1(3)	159(10)	5448(5)	5522(4)	4.8(4)
C-4	1205(9)	12454(7)	3722(2)	3.1(3)	1084(12)	5648(5)	6207(5)	6.1(4)
C-5	1197(8)	12157(7)	3214(2)	3.3(3)	1591(12)	4826(6)	6581(4)	6.6(4)
C-6	619(10)	13520(8)	2939(2)	4.2(3)	2126(18)	5037(8)	7295(5)	10.9(6)
C-7	−1656(12)	15308(9)	3092(2)	5.4(4)	5128(15)	4683(7)	7689(6)	9.3(6)
C-8	−3731(14)	15390(13)	3192(3)	8.7(6)	6349(17)	4045(15)	7933(7)	17.5(10)
C-9	5685(10)	10451(9)	3074(2)	4.8(4)	322(12)	3489(5)	5567(4)	5.8(4)
C-10	6502(10)	9607(8)	4148(3)	4.7(4)	−4275(9)	4774(5)	4914(4)	4.9(4)
C-11	7016(10)	8229(9)	4355(3)	6.7(5)	−4859(14)	4503(7)	4239(5)	8.3(5)
C-12	1540(9)	10698(9)	4766(2)	4.0(3)	554(16)	6616(7)	4675(5)	9.4(6)
C-13	1553(11)	11457(10)	5215(3)	5.8(4)	−180(17)	7518(7)	4526(6)	10.2(7)
C-14	1327(12)	14893(8)	4073(2)	4.9(4)	−55(14)	7000(5)	6743(5)	7.4(5)
C-15	2459(13)	16114(8)	4178(3)	6.5(4)	−1584(18)	7388(7)	7113(5)	10.4(7)
C-16	—	—	—	—	−2605(20)	2733(5)	6383(4)	8.6(5)
C-17	—	—	—	—	−4508(19)	2421(6)	6450(6)	10.1(6)

[a]B_{eq} = 4/3∗trace(B∗*G*), where *G* is the direct metric tensor. [b]Estimated standard deviations in parentheses.

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TABLE II

RELEVANT TORSION ANGLES (DEGREES) FOR **1** AND **2**

Angle	**1**	**2**
C-1–C-2–C-3–C-4	−55.0(9)	−57.4(11)
C-2–C-3–C-4–C-5	56.4(9)	55.6(12)
C-3–C-4–C-5–O-1	−56.3(8)	−52.3(11)
C-4–C-5–O-1–C-1	59.6(9)	54.9(11)
C-5–O-1–C-1–C-2	−61.4(9)	−56.6(11)
O-1–C-1–C-2–C-3	56.6(8)	58.8(10)
Br–C-1–C-2–C-3	−68.4(7)	—
C-9–C-1–C-2–C-3	174.7(12)	−65.4(11)
O-10–C-1–C-2–C-3	—	174.5(12)
O-2–C-2–C-3–C-4	−174.3(9)	−178.6(13)
O-4–C-3–C-4–C-5	173.1(10)	174.7(12)
O-6–C-4–C-5–O-1	64.8(8)	56.4(10)
C-6–C-5–O-1–C-1	−179.7(11)	174.1(15)
O-8–C-6–C-5–O-1	177.8(10)	97.6(14)
C-10–O-2–C-2–C-3	−137.3(10)	−128.0(12)
C-12–O-4–C-3–C-4	129.3(10)	107.0(14)
C-14–O-6–C-4–C-3	−112.9(10)	−109.2(13)
C-7–O-8–C-6–C-5	141.4(11)	124.8(18)
C-16–O-10–C-1–C-2	—	171.6(14)
C-16–O-10–C-1–O-1	—	71.6(12)

TABLE III

THE DIHEDRAL ANGLES OF THE BEST PLANES OF THE ACETYL MOIETIES WITH THAT OF THE PYRANOSE RING OF **1**

Plane	
1	C-1, C-2, C-3, C-4, C-5, O-1; $-0.5392x - 0.8194y - 0.1948z = -11.4926$
2	O-2, C-10, O-3, C-11; $0.2925x - 0.3554y - 0.8878z = -12.5175$
3	O-4, C-12, O-5, C-13; $-0.9263x + 0.3344y - 0.1736z = -0.2750$
4	O-6, C-14, O-7, C-15; $-0.2855x + 0.4437y - 0.8495z = -4.5553$
5	O-8, C-7, O-9, C-8; $-0.2275x - 0.0121y - 0.9737z = -8.7193$
Dihedral angles (degrees)	
P1/P2	72.2(2)
P1/P3	75.0(3)
P1/P4	87.5(2)
P1/P5	71.2(3)