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Stereochemical Investigations of the Methyl α-D-*threo*- and Ethyl α-D-*erythro* Anomers of 4,6-Di-*O*-acetyl-2,3-dideoxyhex-2-enopyranoside by X-ray Diffraction Methods

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Abstract

The stereochemistries of methyl 4,5-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (THREO) and ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (ERYTHRO) in the crystalline state have been determined by X-ray diffraction studies. THREO: $C_{11}H_{16}O_6$, $M_r = 244.24$, monoclinic, space group $P2_1$ (*c* unique axis), $Z = 2$, $\mu(Cu\ K\alpha) = 0.92$ mm^{-1}, $d_m = 1.29$, $d_c = 1.30$ Mg m^{-3}, $a = 5.160$ (1), $b = 8.971$ (2), $c = 13.903$ (2) Å, $\gamma = 103.62$ (1)°, $V = 622.4$ Å^3. ERYTHRO: $C_{12}H_{18}O_6$, $M_r = 258.26$, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $\mu(Cu\ K\alpha) = 0.872$ mm^{-1}, $d_m = 1.27$, $d_c = 1.29$ Mg m^{-3}, $a = 5.377$ (1), $b = 14.839$ (2), $c = 16.641$ (2) Å, $V = 1327.8$ Å^3. The six-membered unsaturated hetero rings appear to have the half-chair $^0H_5$ conformation in both cases. The 2-enopyranosides differ from each other in their 4-*O*-acetyl configurations: pseudo-axial in THREO and pseudo-equatorial in ERYTHRO.

Introduction

Recently, Grynkiewicz, Priebe & Zamojski (1979) published a series of syntheses leading to various alkyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*(and -*erythro*)-hex-2-enopyranosides. Two of these, the methyl α-D-*threo*- (THREO, m.p. 332 K) and ethyl α-D-*erythro*-(ERYTHRO, m.p. 352 K) anomers, have been chosen for comparative X-ray diffraction investigations from the point of view of their conformational and geometrical relations.

Experimental

Colourless crystals of THREO and ERYTHRO were obtained by slow evaporation of their solutions in aqueous ethanol. The crystals appear to be unstable in air. Selected crystals were sealed in capillary tubes and used for intensity-collecting procedures. The measurement details and results are presented in Table 1.

Both structures were solved by a direct multi-solution method using the program *SHELX* (Sheldrick, 1976). The refinements of the atomic coordinates were carried out using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). A common computing scheme was applied to both cases: the first refinement step involved individual isotropic thermal parameters and unit weights; in the second step anisotropic thermal parameters and statistical weights ($w = 1/\sigma_F^2$) were used. The last refinement procedure was performed with geometrically calculated (program *XANADU*, Roberts & Sheldrick, 1975) positions for the H atoms, all their parameters being held invariant. The final reliability factor values were: for THREO: $R = 0.10$, $R_w = 0.097$, average shift/error $= 0.03$; for ERYTHRO: $R = 0.079$, $R_w = 0.076$, average shift/error $= 0.04$. The refined atomic coordinates for both α-anomers are presented in Table 2.*

Table 1. *Crystal data*

	THREO	ERYTHRO*
Molecular formula	$C_{11}H_{16}O_6$	$C_{12}H_{18}O_6$
Molecular weight	244.24	258.26
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$ (c unique axis)	$P2_12_12_1$
Z	2	4
a (Å)	5.160 (1)	5.377 (1)
b (Å)	8.971 (2)	14.839 (2)
c (Å)	13.903 (2)	16.641 (2)
γ (°)	103.62 (1)	
V (Å³)	622.4	1327.8
d_c (Mg m⁻³)	1.30	1.29
Diffractometer	Syntex $P2_1$†	CAD-4‡
Radiation	Cu $K\alpha$	Cu $K\alpha$
Scan technique	$\theta/2\theta$	$\theta/2\theta$
Scan range ($2\theta_{max}$) (°)	150	120
Number of reflections	1092 (995 with $I > 2\sigma_I$)§	1209 (879 with with $I > 2\sigma_I$)

* *cf.* Cesario, Guilhem & Martin (1977).
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‡ SLAF & BS, Kraków, Poland.
§ 899 reflections with $I > 3\sigma_I$ were used in the last refinement step.

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary publication No. SUP 34642 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

The calculated bond lengths and bond angles for the THREO and ERYTHRO molecules are listed in Tables 3 and 4. The steric structure of the compounds may be seen from the *ORTEP* diagrams (Johnson, 1965) (Fig. 1).

The unsaturated pyranoside rings in both anomeric molecules of THREO and ERYTHRO are found to have similar geometries. The respective interatomic distances are: for $C(sp^2)-C(sp^2)$ 1.37 (3) and 1.33 (2) Å; for $C(sp^2)-C(sp^3)$ 1.47 (2) and 1.52 (2) Å

Table 2. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å²) *for THREO and ERYTHRO*

E.s.d.'s are in parentheses.

	THREO				ERYTHRO			
	x	y	z	$B_{eq.}$*	x	y	z	$B_{eq.}$*
C(1)	−2567 (34)	1884 (18)	549 (11)	6.0 (8)	1173 (21)	875 (7)	4152 (6)	4.0 (5)
C(2)	−2836 (41)	3183 (23)	−99 (12)	7.3 (10)	2323 (19)	1555 (7)	4717 (7)	4.0 (5)
C(3)	−1431 (33)	4658 (21)	70 (12)	6.0 (9)	1880 (19)	1526 (8)	5503 (7)	4.2 (5)
C(4)	435 (34)	5017 (18)	884 (12)	6.2 (8)	107 (19)	838 (8)	5856 (6)	3.7 (5)
C(5)	1064 (34)	3538 (17)	1294 (11)	5.0 (7)	−1527 (18)	417 (6)	5200 (6)	3.3 (5)
C(6)	2500 (32)	3821 (17)	2235 (12)	6.6 (9)	−2869 (22)	−366 (7)	5524 (6)	4.2 (5)
C(7)	469 (26)	7019 (16)	2039 (13)	3.8 (8)	−944 (25)	1236 (8)	7210 (7)	4.3 (6)
C(8)	−1300 (37)	7438 (20)	2829 (13)	7.5 (9)	−2957 (23)	1717 (8)	7694 (6)	5.2 (6)
C(9)	4951 (36)	2463 (20)	3199 (14)	6.4 (9)	−6235 (21)	−1312 (7)	5076 (8)	4.1 (5)
C(10)	5690 (34)	956 (19)	3349 (13)	7.4 (10)	−7363 (24)	−1751 (7)	4355 (6)	4.6 (6)
C(11)	−1150 (41)	−436 (17)	496 (15)	7.3 (10)	−1671 (27)	826 (8)	3043 (6)	5.2 (6)
C(12)	−	−	−	−	−3471 (26)	1416 (8)	2591 (6)	5.3 (6)
O(1)	−1259 (19)	2392 (11)	1417 (−)	4.8 (5)	62 (12)	150 (4)	4559 (4)	3.2 (3)
O(2)	−1137 (25)	975 (12)	25 (8)	6.3 (6)	−559 (13)	1370 (5)	3676 (4)	3.9 (3)
O(3)	−1015 (19)	5704 (11)	1644 (9)	5.6 (5)	−1560 (13)	1284 (5)	6417 (4)	4.4 (4)
O(4)	2738 (20)	7528 (12)	1935 (12)	6.7 (7)	926 (25)	892 (7)	7443 (5)	5.8 (5)
O(5)	3220 (25)	2377 (12)	2464 (9)	7.0 (6)	−4304 (13)	−747 (5)	4869 (4)	4.0 (3)
O(6)	5786 (27)	3596 (14)	3665 (11)	8.7 (8)	−6819 (21)	−1433 (5)	5762 (5)	5.0 (4)

* Calculated from the refined anisotropic thermal parameters (deposited).

Table 3. *Bond distances* (Å) *with e.s.d.'s in parentheses*

	THREO	ERYTHRO
Ring		
C(1)–C(2)	1·51 (3)	1·51 (2)
C(2)–C(3)	1·37 (3)	1·33 (2)
C(3)–C(4)	1·47 (2)	1·52 (2)
C(4)–C(5)	1·55 (2)	1·54 (1)
C(5)–O(1)	1·39 (2)	1·42 (1)
O(1)–C(1)	1·41 (2)	1·41 (1)
O(3)–acetyl		
C(4)–O(3)	1·51 (2)	1·45 (1)
O(3)–C(7)	1·36 (2)	1·36 (1)
C(7)–C(8)	1·53 (3)	1·53 (2)
C(7)–O(4)	1·16 (2)	1·19 (2)
Acetoxy–methylene		
C(5)–C(6)	1·50 (2)	1·47 (1)
C(6)–O(5)	1·46 (2)	1·45 (1)
O(5)–C(9)	1·35 (2)	1·38 (1)
C(9)–C(10)	1·50 (3)	1·49 (2)
C(9)–O(6)	1·20 (2)	1·20 (2)
	Methoxy	Ethoxy
C(1)–O(2)	1·42 (2)	1·43 (1)
O(2)–C(11)	1·42 (2)	1·46 (1)
C(11)–C(12)	–	1·51 (2)

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

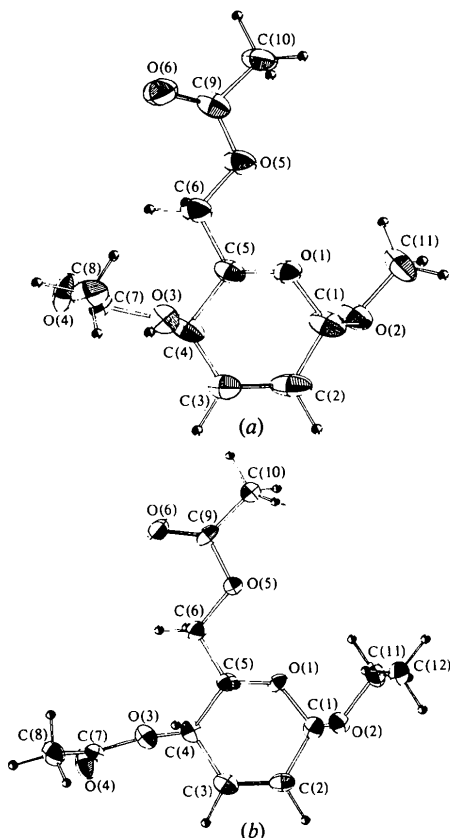|	THREO	ERYTHRO
Ring		
O(1)–C(1)–C(2)	113 (1)	112·6 (9)
C(1)–C(2)–C(3)	121 (2)	121 (1)
C(2)–C(3)–C(4)	121 (2)	121 (1)
C(3)–C(4)–C(5)	111 (1)	109·4 (9)
C(4)–C(5)–O(1)	111 (1)	107·6 (8)
C(5)–O(1)–C(1)	113 (1)	113·8 (7)
O(3)–acetyl		
C(3)–C(4)–O(3)	105 (1)	109·4 (9)
C(5)–C(4)–O(3)	108 (2)	106·8 (8)
C(4)–O(3)–C(7)	114 (1)	116·6 (8)
O(3)–C(7)–C(8)	105 (1)	108 (1)
O(3)–C(7)–O(4)	127 (2)	123 (1)
O(4)–C(7)–C(8)	127 (2)	129 (1)
Acetoxy–methylene		
C(4)–C(5)–C(6)	112 (1)	110·0 (8)
O(1)–C(5)–C(6)	109 (1)	110·4 (8)
C(5)–C(6)–O(5)	105 (1)	107·1 (8)
C(6)–O(5)–C(9)	115 (1)	116·7 (8)
O(5)–C(9)–C(10)	111 (1)	112 (1)
O(5)–C(9)–O(6)	124 (2)	122 (1)
O(6)–C(9)–C(10)	125 (2)	126 (1)
	Methoxy	Ethoxy
O(1)–C(1)–O(2)	111 (1)	112·6 (9)
C(2)–C(1)–O(2)	107 (1)	115·6 (8)
C(1)–O(2)–C(11)	112 (1)	112·7 (8)
O(2)–C(11)–C(12)	–	107·7 (9)

Fig. 1. *ORTEP* diagrams of the molecules of (*a*) THREO and (*b*) ERYTHRO. The projections are normal to the C(1)–C(2)–C(3)–C(4) least-squares planes, and the thermal ellipsoids are set to the 40% probability level. H atoms are shown as spheres of conventional size.

(average). The bond angles C(4)–C(5)–O(1) for THREO and ERYTHRO differ slightly: 111 (1) and 107·6 (8)° respectively.

Some literature geometrical data on alkyl 2,3-unsaturated pyranoside rings are: for the C(sp^2)–C(sp^2) and both C(sp^2)–C(sp^3) bond lengths and for the C(4)–C(5)–O(1) angle: 1·318 (7), 1·477 (7), 1·491 (7) Å, 111·7 (4)° (López de Lerma, Martínez-Carrera & Garcia-Blanco, 1973); 1·323 (4), 1·503 (4), 1·511 (4) Å, 111·5 (2)° (Kojić-Prodić, Rogić & Ruzić-Toroš, 1976); 1·31, 1·44, 1·52 Å, 106·8° (last value calculated from reported data) (Stockhuyzen & Chung Chieh, 1976).

Similarly, the geometry of the endocyclic C–O bonds was found to be very close in both α-anomers: the bond lengths C(5)–O(1) and O(1)–C(1) are 1·39 (2) and 1·41 (2) Å for THREO, and 1·42 (1) and 1·41 (1) Å for ERYTHRO. The angle at O(1) is 113 (1) and 113·8 (7)° for THREO and ERYTHRO respectively. Kojić-Prodić *et al.* (1976) reported for the same geometry elements: 1·440 (3), 1·394 (3) Å and 112·5 (2)°. Much more dissymmetrized endocyclic C–O bonds were found recently for a 3,4,6-tri-*O*-acetyl-D-1,2-dideoxypyranoside derivative (GLUCAL) (Krajewski, Urbańczyk-Lipkowska, Gluziński, Bleidelis & Kemme, 1978, 1979; Vangehr, Luger & Paulsen, 1979): the bond lengths C(5)–O(1) and

O(1)—C(1) found were 1·433 (6) and 1·364 (6) Å, respectively, but the O(1) angle value was very close to those reported above: 113·8 (4)°. Such dissymmetry in the case of the GLUCAL molecule may be explained partly by different hybridization of both bonded C atoms [C(5)=C(sp^3) and C(1)=C(sp^2)]. Only a small difference in the endocyclic C—O bond lengths was found in a 3,4-unsaturated pyranoside (Krajewski, Urbańczyk-Lipkowska & Gluziński, 1978, 1979): 1·43 (1) and 1·41 (1) Å, respectively, with the O(1) angle 114·0 (3)°.

The methoxy or ethoxy substituents attached to the anomeric C(1) in both presently investigated eno-pyranosides differ in their C—O bond lengths. In THREO the values found for the methoxy group are both nearly equal [1·42 (2) Å], whereas in ERYTHRO they vary significantly [C(1)—O(2) 1·43 (1), O(2)—C(11) 1·46 (1) Å]. The O(2) angles are 112 (1) and 112·7 (8)° respectively. These differences may be partly due to the elongated carbon chain in the ethoxy substituent.

The geometry of C(4) attached to the O-acetyl group differs in both compounds investigated, mostly in respect of the bond angles. The respective values differ by 2–4·5° (Table 4). Similarly, the C(4)—O(3) bond length also varies strongly: 1·51 (2) Å for the THREO and 1·45 (1) Å for the ERYTHRO anomer. However, the O(3)—C(7) bond lengths are equal within the mean e.s.d. value: 1·36 (2) and 1·36 (1) Å respectively. For O-acetyl groups attached to ring C atoms, Kojić-Prodić et al. (1976) and Krajewski, Urbańczyk-Lipkowska, Gluziński, Bleidelis & Kemme (1979) reported for the C_{ring}—O bonds the values 1·435–1·448 Å, and for O—$C_{carbonyl}$ bonds the value 1·357 Å (average). Thus, the C(4)—O(3) bond length in THREO may be regarded as unusually long.

C(1), C(2), C(3) and C(4) in both molecules form an approximate plane. O(1) and C(5) deviate from this plane (calculated as a least-squares plane) in opposite directions. The deviations of the O atoms are approximately equal in the THREO and ERYTHRO anomers (+0·31 Å), unlike the C(5) deviations (−0·39 and −0·45 Å respectively). The values found for ERYTHRO are in full agreement with those reported by Cesario, Guilhem & Martin (1977). The

Table 6. *Intermolecular distances less than* 3·5 Å *with e.s.d.'s in parentheses*

THREO		ERYTHRO	
O(1)—C(9)[i]	3·17 (2)	O(1)—C(9)[i]	3·07 (1)
O(1)—C(10)[i]	3·23 (2)	O(1)—C(10)[i]	3·16 (1)
O(1)—C(5)[i]	3·20 (2)	O(1)—O(5)[i]	3·35 (1)
O(3)—C(6)[i]	3·47 (2)		
O(4)—C(8)[i]	3·34 (2)		
C(11)—C(7)[ii]	3·38 (3)		
O(2)—C(8)[v]	3·48 (2)		
O(2)—C(10)[vi]	3·47 (2)		

Symmetry code

(i)	$1 + x, y, z$	(v)	$-x, 1 - y, \frac{1}{2} + z$
(ii)	$x, 1 + y, z$	(vi)	$-x, -y, \frac{1}{2} + z$

conformation of both enopyranoside rings may then be defined as a half-chair, $^0H_5$ (for nomenclature see Schwartz, 1973), in agreement with the results of other physicochemical observations.

Table 5 presents the torsion angles for the six-membered hetero-rings of both anomers compared with their equivalent values in the half-chair cyclohexene molecule (Chiang & Bauer, 1969). The differences (deviation from C_2 symmetry) due to the presence of the O hetero-atom in the pyranoside rings are not greater than 2–3° (taking into account the e.s.d. values). The pyranoside ring in ERYTHRO appears to be slightly more distorted than that in THREO.

The O-acetyl chain configuration at C(4) may be established from the following:

– the deviations of O(3) from the least-squares plane formed by C(1), C(2), C(3) and C(4) are in opposite directions (+1·42 and −0·98 Å, for THREO and ERYTHRO respectively).

– the C(4)—O(3) bonds form with their projections on the above plane the angles 109 and 138°, for THREO and ERYTHRO respectively.

Thus, the C(4)—O—acetyl chain configurations may be defined as pseudo-axial in THREO and pseudo-equatorial in ERYTHRO.

The acetoxymethylene and alkoxy substituents are similarly situated with respect to the rings in both compounds. They are pseudo-equatorial and pseudo-axial, respectively, and lie below the rings.

Table 6 gives the intermolecular distances less than 3·5 Å. It can be seen that besides the much more numerous relatively strong intermolecular interactions observed for the THREO anomer, the most remarkable similarity in the cell packing involves the van der Waals interactions between O(1) and C(9), and between C(10) and O(5) of the neighbouring molecule generated by an a translation.

Table 5. *Comparison of ring torsion angles* (°)

	ERYTHRO	THREO	Equivalent angle in cyclohexene*
C(1)—C(2)—C(3)—C(4)	−3·0 (1·6)	−1·1 (2·7)	0
C(4)—C(5)—O(1)—C(1)	−67·5 (1·0)	−64·9 (1·7)	−60·2
O(1)—C(1)—C(2)—C(3)	−11·5 (1·4)	−13·2 (2·6)	−15·2
C(2)—C(3)—C(4)—C(5)	−15·9 (1·4)	−14·8 (2·4)	−15·2
C(3)—C(4)—C(5)—O(1)	48·5 (1·0)	46·6 (1·7)	44·9
C(5)—O(1)—C(1)—C(2)	48·3 (1·0)	46·8 (1·9)	44·9

* Chiang & Bauer (1969).

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The Crystal and Molecular Structure of 1,5-Diphenylcarbazone

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Abstract

Crystals of 1,5-diphenylcarbazone, $C_{13}H_{12}N_4O$, are triclinic, space group $P\bar{1}$, $a = 9.639$ (1), $b = 11.250$ (1), $c = 12.840$ (1) Å, $\alpha = 74.82$ (1), $\beta = 86.33$ (1), $\gamma = 67.37$ (1)°, $V = 1239$ Å³, $Z = 4$. The structure was determined from three-dimensional diffractometer data by the multi-solution technique (*MULTAN*) from 2010 independent reflections and refined by a least-squares block-diagonal approximation to a final R value of 0.075. The asymmetric unit contains two molecules of different conformation having nearly identical bond distances and bond angles. The diphenylcarbazone molecule differs from its sulphur analogue, dithizone. It is not planar and there is only π-electron delocalization in the hydrazo chain of the molecule. The molecules in the cell are held together by N—H···O hydrogen bonds while two other N—H···O hydrogen bonds join the molecules of successive cells in chains parallel to [100].

Introduction

1,5-Diphenylcarbazone (hereinafter DPCO) forms highly coloured metal complexes that provide the basis for its use as a sensitive reagent for the detection and colorimetric determination of metal ions. In particular, those reactions with Cr^{VI}, Cr^{III} and Cr^{II} have been studied in this laboratory (Willems, Blaton, Peeters & De Ranter, 1977).

The IR spectrum of pure DPCO in $CHCl_3$ or CCl_4 shows two absorption bands in the 3000–4000 cm⁻¹ region at 3410 and 3350 cm⁻¹. As the DPCO concentration increases the intensity of the two bands decreases and three new bands appear at 3275, 3195 and 3075 cm⁻¹. Kemula & Janowski (1966) ascribe: (i) the 3410 cm⁻¹ band to free N—H stretching vibration of