Crystal Structures of Analogues of D-Galactose.
I. 2,3-Di-*O*-acetyl-1,6-anhydro-β-D-galactopyranose (DAG)

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The structure of DAG has been determined from three-dimensional diffractometer data by direct methods with the tangent formula. The space group is $P2_1$ with $a = 11\cdot3328$ (17), $b = 6\cdot1197$ (4), $c = 8\cdot2568$ (11) Å, $\beta = 103\cdot44$ (1)°. The molecule has an anhydro bridge across the galactose moiety forming a five-membered ring which has an envelope conformation while the pyranose ring has a strained chair conformation. An intermolecular hydrogen bond (2·864 Å) occurs between the hydroxyl group and the O atom of the bridge.

Introduction

The compound, hereinafter DAG, was obtained by partial acetylation of 1,6-anhydro-β-D-galactopyranose (Chacon-Fuertes & Martín-Lomas, 1975) as part of a research programme recently started in the Instituto Química Orgánica General, CSIC, in order to synthesize oligosaccharides. In one such synthesis two compounds were obtained, one crystalline, the other amorphous. Both were used for the synthesis of disaccharides exhibiting α and β-1,3 and 1,4 glycosidic bonds and will be the subject of further crystallographic studies. This work was carried out in order to establish the structure which has been proposed by n.m.r. spectra for the crystalline compound and to obtain structural information on the factors which control the selective esterification of carbohydrates.

Experimental

A preliminary study showed that the crystal is monoclinic. The only systematic absences were 0*k*0, *k* odd.

The space group was uniquely determined as $P2_1$, since the sample was obtained from a D compound, its optical rotations having been determined with a Perkin–Elmer 141 polarimeter. Accurate unit-cell dimensions were determined by the least-squares fit of the Bragg angles (θ) of 32 reflexions ranging between 2·5° and 20° as measured on a single-crystal diffractometer.

Crystal data

$C_{10}H_{14}O_7$, monoclinic, $a = 11\cdot3328$ (17), $b = 6\cdot1197$ (4), $c = 8\cdot2568$ (11) Å, $\beta = 103\cdot44$ (1)°. Space group $P2_1$, $Z = 2$, $V = 557$ Å^3, $D_o = 1\cdot49$, $D_c = 1\cdot47$ g cm^{-3}, λ(for Mo $K\alpha = 0\cdot7107$ Å).

The density was determined by flotation in a mixture of benzene and methylene iodide solution. A crystal of dimensions $0\cdot6 \times 0\cdot4 \times 0\cdot2$ mm was used for collecting the intensities on a Philips PW 1100 four-circle diffractometer operating in the $\omega/2\theta$ scan mode (scan width $= 1\cdot60°$, scan speed $= 0\cdot03$ s^{-1}). Mo $K\alpha$ radiation, monochromatized by graphite, was used for measurement of the 1783 independent reflexions up to $\theta = 30°$.

Table 1. *Final positional and thermal parameters and their standard deviations for the heavy atoms*

Anisotropic temperature factors are expressed as exp $(-2\pi^2\sum U_{ij}a_i^*a_j^*h_ih_j)$ and are multiplied by 10^4.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·1316 (2)	0·2368 (0)	0·4849 (3)	299 (12)	319 (13)	330 (12)	−3 (11)	86 (9)	−31 (11)
C(2)	0·1095 (2)	0·1731 (6)	0·3017 (3)	284 (11)	281 (13)	271 (10)	−32 (10)	57 (9)	39 (10)
C(3)	0·1984 (2)	−0·0033 (7)	0·2722 (3)	258 (11)	311 (13)	341 (12)	−31 (10)	96 (9)	−45 (11)
C(4)	0·2240 (3)	−0·1681 (7)	0·4142 (4)	344 (13)	245 (12)	482 (15)	−21 (11)	146 (11)	25 (12)
C(5)	0·2373 (3)	−0·0577 (7)	0·5843 (4)	373 (14)	382 (15)	355 (13)	23 (12)	99 (11)	130 (12)
C(6)	0·3260 (3)	0·1316 (7)	0·6173 (3)	373 (13)	414 (15)	316 (12)	20 (13)	32 (10)	33 (12)
C(7)	−0·0695 (2)	0·0765 (6)	0·0986 (3)	290 (11)	259 (11)	354 (11)	39 (10)	53 (9)	−1 (10)
C(8)	−0·1893 (3)	−0·0328 (9)	0·0770 (4)	298 (12)	455 (18)	404 (14)	−34 (13)	75 (11)	−15 (14)
C(9)	0·3648 (2)	0·0535 (7)	0·1425 (3)	308 (12)	441 (16)	393 (13)	26 (12)	146 (10)	68 (13)
C(10)	0·4827 (3)	0·1700 (11)	0·1653 (6)	396 (17)	885 (37)	652 (24)	−208 (21)	229 (17)	−33 (24)
O(1)	0·2530 (2)	0·3160 (6)	0·5404 (2)	346 (9)	342 (10)	368 (10)	−29 (9)	42 (7)	−24 (8)
O(2)	−0·0118 (2)	0·0839 (6)	0·2621 (2)	266 (8)	411 (11)	323 (8)	−45 (8)	65 (6)	12 (8)
O(3)	0·3099 (1)	0·1078 (6)	0·2657 (2)	278 (8)	372 (11)	340 (8)	−59 (8)	111 (6)	−11 (8)
O(4)	0·3285 (2)	−0·2908 (7)	0·4057 (4)	457 (13)	329 (12)	761 (17)	91 (10)	230 (12)	94 (12)
O(5)	0·1244 (2)	0·0514 (6)	0·5824 (2)	372 (10)	443 (12)	367 (9)	−22 (9)	149 (7)	41 (9)
O(6)	−0·0269 (2)	0·1472 (6)	−0·0102 (3)	434 (11)	462 (12)	353 (9)	−16 (10)	65 (8)	100 (9)
O(7)	0·3230 (2)	−0·0669 (7)	0·0304 (3)	577 (14)	745 (19)	544 (13)	−103 (14)	283 (12)	−223 (14)

259 reflexions had intensities $< 2\sigma(I)$ and were treated as unobserved. The data were corrected for Lorentz and polarization effects but not for absorption.

Structure determination

The data were placed on an absolute scale by Wilson's method and normalized structure factors were computed. The E statistics confirmed that the structure is non-centrosymmetric and in all subsequent computations space group $P2_1$ was used. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The phases of one enantiomorph and three origin-defining reflexions, together with the fourfold phases for two reflexions, were used to calculate phases for all 100 reflexions with $|E| \geq 1\cdot67$. The E map calculated for the best solution gave the positions of all the non-hydrogen atoms except four. A Fourier map phased on these atoms yielded the remaining non-hydrogen atom positions. The atomic coordinates and temperature factors, firstly isotropic and then anisotropic, were refined by the full-matrix least-squares method, and R was reduced to 0·071. The resulting structure factors were used to compute a difference map and this showed peaks at all the positions where H atoms were expected. H atoms were introduced into

the refinement with isotropic temperature factors equivalent to the anisotropic temperature factors of the bonded atoms (Hamilton, 1959).

The weighting scheme was $w = K/[f(F_o)]^2$ where $K = 0\cdot013$ and $f(F_o) = 0\cdot52 - 0\cdot11|F_o|$ when $|F_o| < 2\cdot6$, $f(F_o) = 0\cdot38 - 0\cdot04|F_o|$ when $2\cdot6 \leq |F_o| < 4\cdot85$ and $f(F_o) = 0\cdot12 + 0\cdot02|F_o|$ when $4\cdot85 \leq |F_o|$. After several further cycles of refinement under these conditions R and R_w [$R_w = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$] for the observed reflexions converged to 0·043 and 0·050 respectively. This weighting scheme

Table 2. *Fractional coordinates and thermal parameters* ($\times 10^2$) *for the hydrogen atoms*

|	x	y	z	U (Å^2)
H(1)	0·076 (3)	0·332 (6)	0·512 (4)	2·8 (7)
H(2)	0·114 (3)	0·322 (6)	0·233 (4)	2·5 (7)
H(3)	0·166 (3)	−0·074 (6)	0·169 (4)	2·8 (8)
H(4)	0·150 (3)	−0·262 (6)	0·395 (4)	3·6 (9)
H(O4)	0·322 (4)	−0·391 (10)	0·443 (5)	5·3 (13)
H(5)	0·256 (3)	−0·155 (7)	0·671 (4)	3·4 (8)
H(6a)	0·353 (3)	0·159 (7)	0·732 (4)	3·8 (9)
H(6b)	0·400 (3)	0·114 (7)	0·568 (4)	3·4 (8)
H(8a)	−0·238 (3)	0·002 (8)	−0·027 (5)	4·3 (9)
H(8b)	−0·179 (4)	−0·182 (10)	0·090 (6)	7·0 (13)
H(8c)	−0·225 (4)	−0·027 (9)	0·159 (5)	6·1 (12)
H(10a)	0·529 (5)	0·177 (11)	0·271 (7)	8·9 (18)
H(10b)	0·510 (6)	0·184 (13)	0·074 (7)	10·9 (22)
H(10c)	0·479 (5)	0·326 (13)	0·195 (7)	8·3 (18)
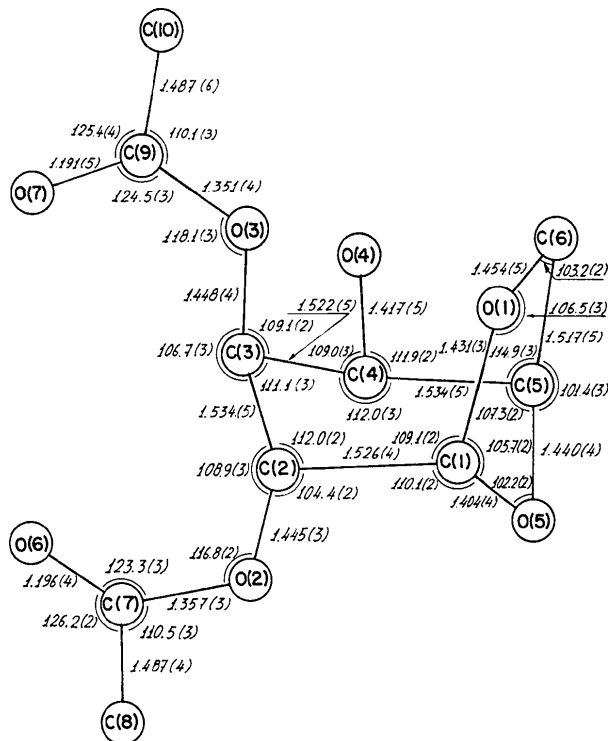
Fig. 1. Bond lengths (Å) and valence angles (°) with their estimated standard deviations referred to the last significant digits.

Table 3. *Bond distances and angles involving hydrogen atoms with e.s.d.'s from least squares in parentheses*

C(1)–H(1)	0·92 (4) Å	C(2)–C(1)–H(1)	116 (2)°	C(6)—H(6b)	1·02 (4) Å	C(5)——C(6)—H(6b)	115 (2)°
		O(1)–C(1)–H(1)	112 (2)			O(1)——C(6)—H(6b)	110 (2)
		O(5)–C(1)–H(1)	104 (2)			H(6a)–C(6)—H(6b)	108 (3)
C(2)–H(2)	0·98 (4)	C(1)–C(2)–H(2)	111 (2)	C(4)—H(O4)	0·70 (6)	C(4)——O(4)—H(O4)	106 (4)
		C(3)–C(2)–H(2)	111 (2)	C(8)—H(8a)	0·93 (4)	C(7)——C(8)—H(8a)	110 (3)
		O(2)–C(2)–H(2)	110 (2)	C(8)—H(8b)	0·93 (6)	C(7)——C(8)—H(8b)	110 (3)
C(3)–H(3)	0·95 (3)	C(2)–C(3)–H(3)	109 (2)	C(8)—H(8c)	0·87 (5)	C(7)——C(8)—H(8c)	118 (3)
		O(3)–C(3)–H(3)	110 (2)			H(8a)–C(8)—H(8b)	112 (4)
		C(4)–C(3)–H(3)	111 (2)			H(8a)–C(8)—H(8c)	115 (4)
C(4)–H(4)	1·00 (4)	C(3)–C(4)–H(4)	105 (2)			H(8b)–C(8)—H(8c)	91 (5)
		O(4)–C(4)–H(4)	112 (2)	C(10)–H(10a)	0·91 (5)	C(9)——C(10)–H(10a)	116 (4)
		C(5)–C(4)–H(4)	107 (2)	C(10)–H(10b)	0·89 (6)	C(9)——C(10)–H(10b)	115 (4)
C(5)–H(5)	0·92 (4)	C(4)–C(5)–H(5)	113 (3)			H(10a)–C(10)–H(10b)	125 (5)
		O(5)–C(5)–H(5)	111 (2)	C(10)–H(10c)	0·99 (8)	C(9)——C(10)–H(10c)	114 (3)
		C(6)–C(5)–H(5)	109 (2)			H(10a)–C(10)–H(10c)	77 (5)
C(6)–H(6a)	0·94 (3)	C(5)–C(6)–H(6a)	111 (2)			H(10b)–C(10)–H(10c)	99 (6)
		O(1)–C(6)–H(6a)	109 (2)				

produced $\langle w(F_o - F_c)^2 \rangle$ values independent of sin θ and magnitudes of F_o.

In the last cycle of refinement the average ratio of parameter shift to standard deviation was 0·06. The atomic parameters are given in Tables 1 and 2. In the final difference synthesis no anomalous peak was observed, the residual electron density being between ± 0·23 e Å⁻³. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962) for all atoms except H (Stewart, Davidson & Simpson, 1965).*

Description of the structure and discussion

The numbering of the heavy atoms in the molecule and bond distances and angles are shown in Fig. 1, while those involving hydrogen atoms are listed in Table 3. Some least-squares planes in the molecule are shown in Table 6.

The molecule has an anhydro bridge across the galactose moiety forming five-membered and seven-membered rings with the pyranose ring.

The five-membered ring has an envelope confor-

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mation at O(5) (Table 4 and plane 2 in Table 6). This conformation has been studied in terms of the torsion angles following Altona, Geise & Romers's (1968) convention. The Δ phase angle found for this ring is 167°, which is closer to the 180° value for an envelope conformation than to the 144° value for a half-chair conformation.

The mean C–C and C–O distances in the pyranose ring are 1·529 and 1·422 Å respectively, which are in good agreement with the mean hypothetical values given by Kim & Jeffrey (1967). This ring has a strained chair conformation as can be seen from the torsion angles (Klyne & Prelog, 1960) given in Table 4 and from plane 1 in Table 6. There are differences in the torsion angles between this compound and 1,6-hydro-β-D-glucopyranose (Park, Kim & Jeffrey, 1971) involving atoms O(3) and O(4). For O(3) this could be due to the different flattening of the ring and for O(4) to its equatorial position in the present compound in contrast to its axial position in 1,6-anhydro-β-D-glucopyranose. The dihedral angles between plane 1 (Table 6) and the planes through C(1), C(2), O(2) and C(5), C(4), H(4) are 81·9 and 87·7° respectively. Moreover O(3)–C (6) and O(2)–H (4) are 2·870 (3) and 2·85 (4) Å respectively, which are greater than the 2·5 Å value for non-bonding axial distances. These results can be mainly attributed to the repulsion between the five-membered ring and the axial group at C(3) which brings about a flattening of the pyranose

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Table 4. *Main torsion angles around the bond defined by the central atoms*

Five-membered ring		Pyranose ring	
C(6)–O(1)–C(1)–O(5)	22·9°	O(5)–C(1)–C(2)–C(3)	−56·6°
C(5)–C(6)–O(1)–C(1)	5·3	C(1)–C(2)–C(3)–C(4)	37·4
O(5)–C(5)–C(6)–O(1)	−30·4	C(2)–C(3)–C(4)–C(5)	−40·2
C(1)–O(5)–C(5)–C(6)	44·8	C(3)–C(4)–C(5)–O(5)	60·5
O(1)–C(1)–O(5)–C(5)	−42·9	C(4)–C(5)–O(5)–C(1)	−76·0
		C(5)–O(5)–C(1)–C(2)	74·8
Other lateral angles			
C(1)–C(2)–O(2)–C(7)	19·9°	C(3)–C(4)–C(5)–C(6)	−51·4°
C(3)–C(2)–O(2)–C(7)	−80·2	H(4)–C(4)–C(5)–O(5)	−54·1
C(2)–O(2)–C(7)–C(8)	−3·9	C(4)–C(3)–C(2)–O(2)	−77·5
C(4)–C(3)–O(3)–C(9)	−74·5	C(1)–C(2)–C(3)–O(3)	−81·4
C(2)–C(3)–O(3)–C(9)	45·5	C(5)–C(4)–C(3)–O(3)	77·1
C(3)–O(3)–C(9)–C(10)	5·0	C(2)–C(3)–C(4)–H(4)	75·8
O(1)–C(1)–C(2)–C(3)	58·9	H(5)–C(5)–C(6)–H(6b)	87·4
O(2)–C(2)–C(1)–O(5)	61·0	H(5)–C(5)–C(6)–H(6a)	−30·9

Table 5. *Short X–H · · · Y van der Waals contacts involving hydrogen atoms*

Distances in Å and angles in degrees with the e.s.d.'s from least squares in parentheses. The more likely hydrogen bond is shown with an asterisk.

X	H	Y	X · · · Y	H · · · Y	X–H · · · Y	H–X · · · Y
C(1) (A)	H(1) (A)	O(2) (B)	3·469 (4)	2·65 (4)	148 (2)	23 (2)
C(1) (A)	H(1) (A)	O(5) (B)	3·417 (3)	2·60 (3)	149 (2)	23 (2)
C(2) (A)	H(2) (A)	O(6) (A)	2·682 (3)	2·44 (3)	93 (2)	65 (2)
C(3) (A)	H(3) (A)	O(7) (A)	2·728 (4)	2·33 (3)	105 (2)	56 (2)
O(4) (A)	H(O4) (A)*	O(1) (C)	2·864 (5)	2·18 (6)	166 (5)	11 (4)
C(6) (A)	H(6b) (A)	O(3) (A)	2·870 (3)	2·47 (3)	103 (2)	57 (2)

Symmetry code
(A) x,y,z; (B) $-x,\frac{1}{2}+y,-z+1$; (C) $x,y-1,z$.

Table 6. *Deviations* (Å) *of the atoms from some least-squares planes in the molecule with their dihedral angles*

The equations of the planes are in the form $PX + QY + RZ = S$ in orthogonal space with i parallel to a, k perpendicular to a in the plane of a and c and j perpendicular to the plane of a and c. An asterisk denotes the atoms not used in the plane calculations.

Plane 1		Plane 2		Plane 3		Plane 4	
C(1)	−0·018	C(1)	0·020	C(2)	−0·025	C(3)	−0·034
C(2)	0·016	O(1)	−0·031	O(2)	0·031	O(3)	0·046
C(3)	0·505*	C(5)	−0·019	O(6)	0·004	O(7)	0·010
C(4)	−0·016	O(5)	0·625*	C(7)	0·011	C(9)	0·001
C(5)	0·018	C(6)	0·029	C(8)	−0·021	C(10)	−0·024
O(5)	−0·823*						

Plane 1: $0.8927X + 0.4437Y − 0.0791Z = 0.8533$
Plane 2: $−0.4210X + 0.1801Y + 0.8890Z = 3.4665$
Plane 3: $−0.4421X + 0.8915Y + 0.0992Z = 0.9170$
Plane 4: $−0.3666X + 0.7650Y − 0.5295Z = −1.7724$

Dihedral angles

(Plane 1) (Plane 2)	68·5°
(Plane 1) (Plane 3)	89·6
(Plane 1) (Plane 4)	86·9

ring, referred to by Sandris & Ourissan (1958) as the 'reflex effect'.

Both acetyl groups are planar (planes 3 and 4 in Table 6). However, the C(10) methyl group has the highest U values, as can be seen from Table 2, and the acetyl group which includes the C(10) methyl has fewer contacts than the C(2) acetyl group. The short contacts involving heavy atoms for these groups are in the 3·1 to 3·7 Å range.

The mean value for C–H bonds is 0·94 Å and the O–H distance is 0·70 Å which, although rather short, is similar to the values in other carbohydrates (Hackert & Jacobsen, 1971; Kim, Jeffrey & Rosenstein, 1971; Jeffrey & Park, 1972; Brown, Rohrer, Berking, Beevers, Gould & Simpson, 1972).

The packing of the molecules in the crystal is due to van der Waals forces, weak hydrogen interactions and a hydrogen bond (Table 5). The more likely weak hydrogen interactions are those involving H(1), H(3) and H(6b), the atom geometry of the first being rather symmetric. The hydrogen bond operates between the hydroxyl group and the oxygen atom of the bridge.

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