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Structure of Isopropylidene Sedoheptulosan

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Abstract

The title compound, 2,7-anhydro-4,5-*O*-isopropylidene- β -D-*altro*-2-heptulopyranose, $C_{10}H_{16}O_6$, has a pyranoid conformation which is a distorted E_0 conformation with $Q = 0.609$ (1) Å, $\theta = 147.4$ (1)° and $\Phi = 188.1$ (3)° [Cremer & Pople (1975). *J. Am. Chem. Soc.* **97**, 1354–1358].

The structure is stabilized by hydrogen bonds. The absolute structure, determined through the Flack parameter, $x = -0.08$ (14) [Flack (1983). *Acta Cryst.* **A39**, 876–881], corresponds to the known chirality of the title compound (Friedel opposites collected and not merged).

Comment

The title compound was synthesized according to known procedures (Haskins, Hann & Hudson, 1952) and crystals melting at 500 K were obtained from methanol by slow evaporation. The positions of all H atoms were refined with no distance restraints. Both hydroxyl groups O1—H10 and O3—H20 form intermolecular hydrogen bonds. Details of the hydrogen-bonding scheme are given in Table 3. Of the above hydrogen bonds, the latter results in an infinite one-dimensional chain along [0 0 1]. Other distances and angles are generally as expected.

It should be mentioned that this structure is of the 1,6-anhydro- β -D-glycopyranose type and therefore the puckering parameters, $Q = 0.609$ (1) Å, $\theta = 147.4$ (1)° and $\Phi = 188.1$ (3)° (Cremer & Pople, 1975), can be compared with these compounds. A similar conformation of the pyranoid ring, as found in the title compound, is reported for 1,6-anhydro-3,4-*O*-isopropylidene- β -D-talopyranose (Panagiotopoulos, 1974) and 1,6-anhydro-3,4-*O*-isopropylidene- β -D-galactopyranose (Cano, Foces-Foces, Jimenez-Barbero & Martin-Lomas, 1984), and some selected benzylidene derivatives (Cano, Foces-Foces, Jimenez-Barbero, Bernabe & Martin-Lomas, 1986).

The conformation of the 2,7-anhydro five-membered ring is $Q = 0.396$ (1) Å and $\Phi = 263.3$ (2)°. For the other

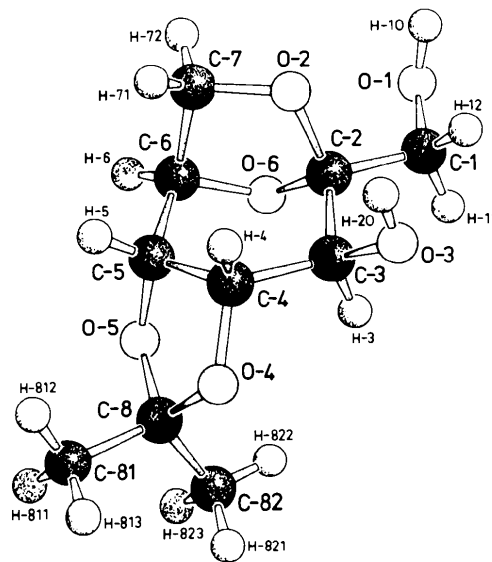


Fig. 1. *SCHAKAL88* drawing (Keller, 1986) of the molecular conformation and atomic numbering scheme.

five-membered 4,5-*O*-isopropylidene ring the conformation is $Q = 0.301(2) \text{ \AA}$ and $\Phi = 255.0(3)^\circ$ (Cremer & Pople, 1975). The program used to calculate these special details of molecular geometry was *PLATON92* (Spek, 1990).

Experimental

Crystal data

C₁₀H₁₆O₆
 $M_r = 232.23$
 Tetragonal
 $P4_3$
 $a = 12.400(1) \text{ \AA}$
 $c = 7.102(1) \text{ \AA}$
 $V = 1092.0(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.413 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 39.76\text{--}52.18^\circ$
 $\mu = 1.001 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Transparent blocks
 $0.8 \times 0.4 \times 0.4 \text{ mm}$
 Colourless

Data collection

Enraf-Nonius CAD-4 four-circle diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 5079 measured reflections
 2268 independent reflections (Friedel pairs not merged)
 2116 observed reflections [$I > 2\sigma(I)$]

$R_{\text{int}} = 0.0254$
 $\theta_{\text{max}} = 76.5^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 8$
 3 standard reflections
 frequency: 120 min
 intensity variation: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0277$
 $wR(F^2) = 0.0711$
 $S = 1.010$
 2268 reflections
 210 parameters
 Calculated weights
 $w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.0480P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.510$
 $\Delta\rho_{\text{max}} = 0.187 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.137 \text{ e \AA}^{-3}$

Extinction correction:
 $F_c^* = kF_c[1 + 0.001F_c^2 \times \lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient:
 0.0084 (8)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8, 6.1.1.4)
 Absolute configuration:
 Flack (1983); $x = -0.08(14)$

Friedel opposites were collected for the range: $h = -15\text{--}0$, $k = -15\text{--}0$ and $l = -8\text{--}0$. These Friedel pairs were regarded as symmetry independent and were not merged. Data collection: Enraf-Nonius CAD-4 software. Cell refinement: Enraf-Nonius CAD-4 software. Data reduction: *CADSHL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1993). Molecular graphics: *SCHAKAL88* (Keller, 1986). Software used to prepare material for publication: *CIF2TEX* (Kopf, 1992); *FCF2FOC* (Kopf, 1992).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
O1	1.0378 (1)	0.3011 (1)	-0.2780 (2)	0.044 (1)
O2	1.0716 (1)	0.2830 (1)	0.1240 (2)	0.036 (1)
O3	0.9278 (1)	0.0997 (1)	0.1746 (1)	0.035 (1)
O4	0.7747 (1)	0.2429 (1)	0.4335 (2)	0.052 (1)
O5	0.7848 (1)	0.4196 (1)	0.3491 (2)	0.043 (1)
O6	0.9270 (1)	0.3833 (1)	0.0329 (1)	0.034 (1)
C1	0.9771 (1)	0.2327 (1)	-0.1603 (2)	0.039 (1)
C2	0.9675 (1)	0.2765 (1)	0.0379 (2)	0.031 (1)
C3	0.8918 (1)	0.2087 (1)	0.1617 (2)	0.030 (1)
C4	0.8802 (1)	0.2586 (1)	0.3571 (2)	0.035 (1)
C5	0.8927 (1)	0.3817 (1)	0.3669 (2)	0.035 (1)
C6	0.9617 (1)	0.4266 (1)	0.2103 (2)	0.035 (1)
C7	1.0764 (1)	0.3836 (1)	0.2243 (2)	0.042 (1)
C8	0.7153 (1)	0.3428 (1)	0.4325 (3)	0.047 (1)
C81	0.6890 (2)	0.3709 (2)	0.6345 (3)	0.070 (2)
C82	0.6162 (2)	0.3321 (2)	0.3093 (5)	0.072 (1)

Table 2. Geometric parameters (\AA , $^\circ$)

O1—C1	1.409 (2)	O6—C6	1.435 (2)
O2—C2	1.431 (2)	C1—C2	1.514 (2)
O2—C7	1.438 (2)	C2—C3	1.536 (2)
O3—C3	1.426 (2)	C3—C4	1.527 (2)
O4—C4	1.429 (2)	C4—C5	1.535 (2)
O4—C8	1.441 (2)	C5—C6	1.510 (2)
O5—C8	1.415 (2)	C6—C7	1.522 (2)
O5—C5	1.423 (2)	C8—C82	1.514 (3)
O6—C2	1.416 (2)	C8—C81	1.512 (3)
C2—O2—C7	107.4 (1)	O4—C4—C5	102.2 (1)
C4—O4—C8	110.4 (1)	C3—C4—C5	115.8 (1)
C8—O5—C5	108.2 (1)	O5—C5—C6	110.2 (1)
C2—O6—C6	102.8 (1)	O5—C5—C4	103.3 (1)
O1—C1—C2	112.2 (1)	C6—C5—C4	113.0 (1)
O6—C2—O2	106.1 (1)	O6—C6—C5	109.7 (1)
O6—C2—C1	109.9 (1)	O6—C6—C7	101.9 (1)
O2—C2—C1	110.2 (1)	C5—C6—C7	110.6 (1)
O6—C2—C3	108.1 (1)	O2—C7—C6	103.4 (1)
O2—C2—C3	109.7 (1)	O5—C8—O4	105.6 (1)
C1—C2—C3	112.6 (1)	O5—C8—C82	108.2 (2)
O3—C3—C4	110.8 (1)	O4—C8—C82	110.1 (2)
O3—C3—C2	111.4 (1)	O5—C8—C81	111.9 (2)
C4—C3—C2	110.8 (1)	O4—C8—C81	107.7 (2)
O4—C4—C3	112.1 (1)	C82—C8—C81	113.2 (2)
O6—C2—C3—C4	-55.7 (1)	C4—C5—C6—O6	48.5 (2)
C2—C3—C4—C5	29.2 (2)	C5—C6—O6—C2	-75.0 (1)
C3—C4—C5—C6	-26.3 (2)	C6—O6—C2—C3	78.6 (1)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D	H	A	D—H	H...A	D...A	D—H...A
O1	H10	O4 ⁱ	0.93 (2)	1.80 (2)	2.725 (2)	169 (2)
O3	H20	O3 ⁱⁱ	0.90 (2)	1.92 (3)	2.795 (1)	164 (2)

Symmetry codes: (i) $1 + y, 1 - x, z - \frac{1}{2}$; (ii) $1 + y, 1 - x, z + \frac{1}{2}$.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71477 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1033]

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Structures of the Diels–Alder Reaction Products of Thymoquinone and 1-Vinylcyclohexene. II. 7-Isopropyl-4-methyltricyclo[8.4.0.0^{2,7}]tetradeca-4,9-diene-3,6-dione, C₁₈H₂₄O₂

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Abstract

The title molecule has an all-*cis* ring-fusion tricyclic structure, with the angular isopropyl group opposite to the two cyclohexene ring substituents. The cyclohexenedione and the cyclohexene rings are both in a slightly distorted sofa conformation, whereas the cyclohexane ring adopts an almost ideal chair conformation.

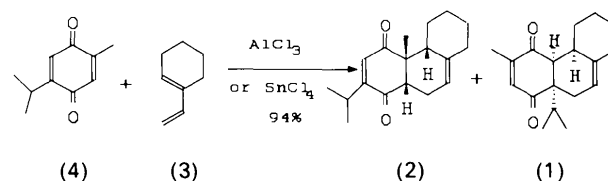
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formation. The molecule has an overall distorted hemispherical conformation.

Comment

The Diels–Alder reactions of thymoquinone (4) and 1-vinylcyclohexene (3) lead to several different products, depending mainly upon the reaction conditions used; the thermal reaction products have been analyzed in part I (Iulek, Zuckerman-Schpector, Brocksom & Silva, 1993). Lewis acid-catalyzed reaction conditions (AlCl₃ or SnCl₄) produce, in excellent yield, a 1:1 ratio of two principal products. Product (1) has been isolated, purified and crystallized thus allowing the definition of the relative stereochemistry of the three contiguous stereogenic centres by a single-crystal X-ray diffraction study. Compounds (1) and (2) are precursors in the reaction pathway aiming at the synthesis of naturally occurring cembrane diterpenes which possess interesting biological activities (Tius, 1988); therefore, the knowledge of the molecular conformation helps in the prediction of the steric course of subsequent reactions.



The cyclohexenedione ring conformation is close to that of a sofa with C(7) 0.617 (5) Å out of the plane defined by C(2)–C(6); O(1) is 0.223 (3) Å in the same direction as C(7) and O(2) is 0.239 (5) Å out of the plane in the opposite direction. The cyclohexene ring is in a slightly distorted sofa conformation with C(7) 0.569 (5) Å out of the plane defined by C(2)—C(1)—C(10)—C(9)—C(8). The cyclohexane ring is in an almost ideal chair conformation, with C(1) 0.690 (4) Å above and C(12) 0.646 (6) Å below the plane defined by the other four atoms. The Cremer & Pople (1975) ring-puckering parameters are: cyclohexenedione, $q_2 = 0.362$ (5), $q_3 = -0.274$ (5), $Q =$

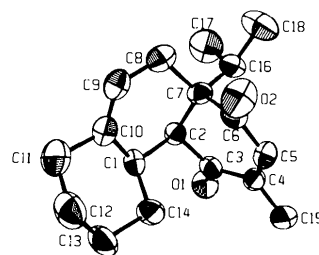


Fig. 1. The molecular structure of (1) with the atom labelling; 50% probability thermal ellipsoids are shown.