

for a Grant-in-Aid and the Science and Engineering Research Council for partial funding towards the purchase of the diffractometer.

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Structure of 5-Hydroxymethyl-7,7-dimethyl-6-oxabicyclo[3.2.1]octane-1-carboxylic Acid

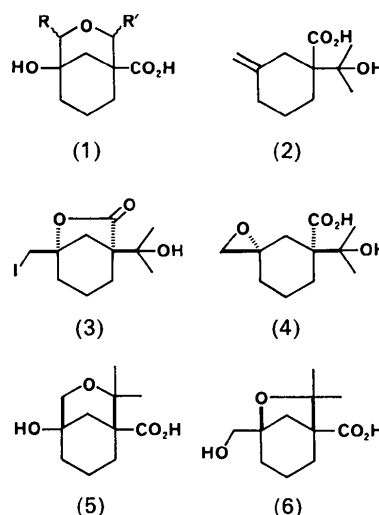
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Abstract. $C_{11}H_{18}O_4$, $M_r = 214.26$, monoclinic, $P2_1/c$, $a = 6.832$ (1), $b = 14.933$ (2), $c = 11.315$ (1) Å, $\beta = 106.74$ (1)°, $V = 1105.5$ (2) Å³, $Z = 4$, $D_x = 1.287$ g cm⁻³, Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å, $\mu = 7.633$ cm⁻¹, $F(000) = 464$, room temperature, $R = 0.069$ for 1359 unique observed reflections with $|F_o| > 3\sigma(|F_o|)$. The five-membered ring has a twist conformation with the twofold axis of symmetry bisecting the bond between the two out-of-plane atoms (C5—C6). The six-membered ring is in a distorted chair conformation flattened at C3. Each molecule is involved in four hydrogen bonds of the type O—H...O.

Introduction. Our interest in the asymmetric synthesis of medium-sized cyclic ethers with specific stereochemistry on the α, α' -dialkyl substituents (Alvarez, Manta, Martín, Rodríguez & Ruiz-Pérez, 1988) has led us to consider the synthesis of 2,4-dialkylated-1-hydroxy-2-oxabicyclo[3.3.1]nonane-5-carboxylic acids, such as (1), as suitable intermediates, which can afford substituted oxocane systems by decarboxylation and further Grob fragmentation. The success of the synthetic plan depends upon the cyclization of an epoxy alcohol such as (4) to give the required (5) or the 6-oxabicyclo[3.2.1]octane system

(6). In this paper we report that the acid-catalyzed cyclization of (4) affords exclusively the crystalline heterocycle (6), whose structure is established by X-ray analysis.



Experimental. The synthesis was initiated from the racemic β -hydroxy acid (2), available on a large scale by condensing the dilithium salt of 3-methylenecyclo-

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) of the non-H atoms with e.s.d.'s in parentheses

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	3031 (3)	2323 (1)	1268 (1)	320 (6)
O2	-2 (3)	3683 (1)	1135 (2)	365 (7)
O3	291 (4)	824 (1)	3822 (2)	460 (9)
O4	2292 (4)	-118 (1)	3205 (2)	492 (9)
C1	3095 (4)	2899 (2)	2313 (2)	275 (8)
C2	5328 (4)	3043 (2)	3052 (3)	409 (10)
C3	6410 (4)	2139 (2)	3354 (3)	465 (10)
C4	5121 (4)	1412 (2)	3727 (2)	398 (10)
C5	2830 (4)	1432 (1)	2946 (2)	264 (8)
C6	2012 (4)	2367 (1)	3077 (2)	271 (8)
C7	2537 (4)	1409 (1)	1522 (2)	291 (9)
C8	299 (5)	1233 (2)	797 (2)	454 (10)
C9	3906 (6)	769 (2)	1084 (3)	510 (13)
C10	1689 (5)	700 (2)	3367 (2)	287 (9)
C11	2105 (5)	3784 (2)	1822 (2)	370 (9)

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) involving the non-H atoms with e.s.d.'s in parentheses

O1—C1	1.452 (3)	C2—C3	1.531 (4)
O1—C7	1.453 (3)	C3—C4	1.531 (4)
O2—C11	1.433 (3)	C4—C5	1.561 (3)
O3—C10	1.222 (4)	C5—C6	1.526 (3)
O4—C10	1.319 (3)	C5—C7	1.566 (3)
C1—C2	1.529 (4)	C5—C10	1.497 (4)
C1—C6	1.515 (4)	C7—C8	1.535 (4)
C1—C11	1.514 (3)	C7—C9	1.517 (5)
C1—O1—C7	110.5 (2)	C7—C5—C10	112.8 (2)
O1—C1—C2	108.7 (2)	C6—C5—C7	100.3 (2)
O1—C1—C6	104.4 (2)	C1—C6—C5	99.9 (2)
O1—C1—C11	108.2 (2)	O1—C7—C5	102.4 (2)
C2—C1—C6	109.6 (2)	C5—C7—C8	111.5 (2)
C2—C1—C11	110.3 (2)	C5—C7—C9	116.2 (2)
C6—C1—C11	115.3 (2)	O1—C7—C8	107.9 (2)
C1—C2—C3	109.8 (2)	O1—C7—C9	109.1 (2)
C2—C3—C4	114.1 (2)	C8—C7—C9	109.2 (2)
C3—C4—C5	113.1 (2)	O3—C10—O4	120.7 (3)
C4—C5—C6	107.3 (2)	O3—C10—C5	124.4 (2)
C4—C5—C7	113.1 (2)	O4—C10—C5	114.8 (2)
C4—C5—C10	109.5 (2)	O2—C11—C1	112.4 (2)
C6—C5—C10	113.4 (2)		
C1—O1—C7—C5	-13.4 (2)	C2—C3—C4—C5	39.8 (3)
C7—O1—C1—C6	-16.2 (2)	C3—C4—C5—C6	-56.6 (3)
O1—C1—C6—C5	39.4 (2)	C4—C5—C6—C1	71.8 (2)
C2—C1—C6—C5	-76.9 (2)	C6—C5—C7—O1	37.3 (2)
C6—C1—C2—C3	61.7 (3)	C7—C5—C6—C1	-46.4 (2)
C1—C2—C3—C4	-40.9 (3)		

hexanecarboxylic acid with acetone (92% yield). Reaction of the diisopropylamine salt of (2) with iodine in dichloromethane produced the iodolactone (3) (96% yield). Treatment of (3) with 1.5 equivalents of aqueous potassium hydroxide, in tetrahydrofuran at 273 K for 60 min, provided, after isolation of the acidic fraction, the unstable epoxy acid (4) (97% yield), which without further purification was treated with a catalytic amount of *p*-toluenesulfonic acid in methylene chloride to produce quantitatively the crystalline heterocycle (6).

Single crystals of (6), suitable for X-ray crystallography, were grown at room temperature from dichloromethane–hexane. Colourless crystal, $0.16 \times 0.26 \times 0.30$ mm. Diffraction maxima were collected on a computer-controlled four-circle Siemens AED diffractometer, using graphite-monochromated Cu $K\alpha$ radiation and ω - θ scan mode. Two standard reflections ($\bar{1}22$, 013) monitored every hour showed no significant intensity decay. Cell parameters were established by least-squares adjustment of 21 reflections in the range $18 < 2\theta < 40^\circ$. Of 1600 measured independent reflections in the range $3 < 2\theta < 128^\circ$, 1359 with $|F_o| > 3\sigma(|F_o|)$ were judged as observed and corrected for Lorentz and polarization factors, index range $h -9,9$; $k 0,18$; $l 0,14$; no absorption correction was performed. Space group $P2_1/c$ uniquely determined from systematic absences $0k0$, $k = 2n$, $00l$, $l = 2n$, $h0l$, $l = 2n$. The structure was solved by direct methods using the *TREF* procedure of program *SHELXS86* (Sheldrick, 1986). Structure refinement of least squares based on F values, using anisotropic thermal parameters for non-H atoms and unit weights (*XRAY80*; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1980). Most of the H atoms (H atoms of the hydroxyl groups included) were

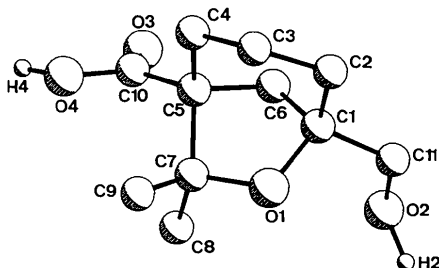


Fig. 1. Perspective view of the molecule showing the atomic numbering scheme (only H atoms of the hydroxyl groups included).

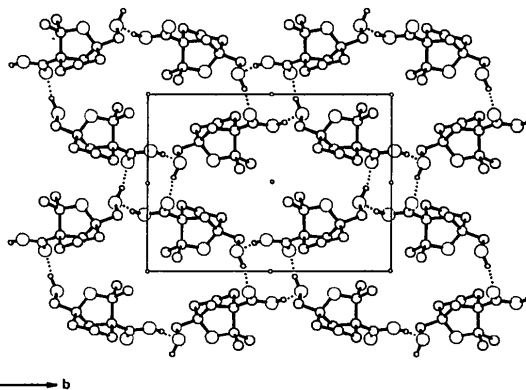


Fig. 2. Projection of the crystal structure viewed along *a*. The H atoms attached to the C atoms are omitted. Hydrogen bonds are shown by broken lines.

located on a difference electron-density map and the remainder placed in calculated positions (Fayos & Martínez-Ripoll, 1980). A convenient weighting scheme of type $w = w_1 \times w_2$ with $w_1 = k/(a + b|F_o|)^2$ and $w_2 = 1/\{c + d[(\sin\theta)/\lambda] + e[(\sin\theta)/\lambda]^2\}$, was used in order to obtain flat dependence in $\langle w \times \Delta^2 F \rangle$ vs $\langle F_o \rangle$ and vs $\langle (\sin\theta)/\lambda \rangle$ (Martínez-Ripoll & Cano, 1980). A final weighted anisotropic full-matrix refinement (fixed isotropic contribution for H atoms) gave the discrepancy indices: $R = 0.069$ and $wR = 0.077$. 136 parameters, $S = 1.3$, maximum electron density in final difference map $0.20 \text{ e } \text{Å}^{-3}$, maximum $\Delta/\sigma = 0.003$. Scattering factors from *International Tables for X-ray Crystallography* (1974); geometrical calculations using *PARST* (Nardelli, 1983).

Discussion. Final positional parameters are reported in Table 1.* The molecular structure of the title compound including the atom-numbering scheme is illustrated in Fig. 1. Bond distances, bond angles and relevant torsion angles are shown in Table 2.

The six-membered ring C1, C2, C3, C4, C5, C6 is in a distorted chair conformation flattened at C3. Atoms C3 and C6 are displaced by -0.440 (3) and 0.889 (3) Å on opposite sides of the plane containing C2, C3, C4, C5. The ring flattening is also evidenced by the values of torsion angles C1—C2—C3—C4 (-40.9°) and C2—C3—C4—C5 (39.8°) compared with C2—C1—C6—C5 (-76.9°) and C5—C6—C1—C2 (71.8°). The five-membered ring has a twist conformation with the twofold axis of symmetry

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles, least-squares planes and intermolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52729 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Sila Analogues of Cyclic Nucleotides

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Abstract. (I) $\text{C}_{18}\text{H}_{29}\text{N}_5\text{O}_4\text{Si}$, 3',5'-*O*-(di-*tert*-butylsilylanediyl)adenosine, $M_r = 407.6$, monoclinic, $P2_1$, $a = 9.750$ (2), $b = 8.373$ (2), $c = 13.157$ (3) Å, $\beta = 104.93$ (2)°, $V = 1037.8$ (3) Å³, $Z = 2$, $D_x = 1.30 \text{ Mg m}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ Å}$, $\mu(\text{Cu } K\alpha) =$

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Table 3. *Geometry of the hydrogen bonds*

X—H...Y	X—H (Å)	X...Y (Å)	H...Y (Å)	X—H...Y (°)
O2—H2...O3 ⁱ	1.004 (2)	2.781 (3)	1.975 (3)	135.5 (1)
O4—H4...O2 ⁱⁱ	0.940 (2)	2.624 (3)	1.697 (2)	168.0 (2)

Symmetry-equivalent positions of the acceptor atoms: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

bisecting the bond between the two out-of-plane atoms (C5—C6) (see Table 2).

Fig. 2 gives a representation of the hydrogen-bonding scheme around the $\bar{1}$ along the a axis; donor-acceptor distances are listed in Table 3. Each molecule is involved in four H bonds of the type O—H...O. The strongest interaction is O4—H4...O2 ($-x, y - 1/2, -z + 1/2$) with O...O donor-acceptor distance of 2.624 (3) Å.

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1.188 mm^{-1} , $F(000) = 436$, $T = 295 \text{ K}$, $R = 0.049$ for 1685 independent reflections [$I_o > 2\sigma(I_o)$]. The furanose ring is in the twist form, the six-membered silyl ring is in a flattened chair conformation and the glycosidic bond conformation is *anti*. (II)

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