

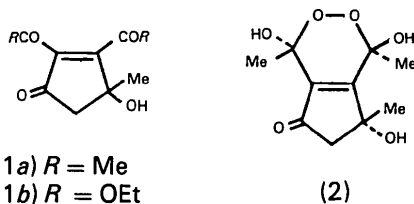
Structure of (1*RS*,4*RS*,7*RS*)-1,4,7-Trihydroxy-1,4,7-trimethyl-6,7-dihydrocyclopenta- [*d*][1,2]dioxin-5-one

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Abstract. C₁₀H₁₈O₈, $M_r = 266.25$, monoclinic, $P2_1/a$, $a = 11.129(4)$, $b = 14.272(4)$, $c = 8.297(3)$ Å, $\beta = 104.64(4)^\circ$, $V = 1275(1)$ Å³, $Z = 4$, $D_x = 1.39$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.79$ cm⁻¹, $F(000) = 568.00$, $T = 293$ K, final conventional R is 0.056 for 1798 unique observed reflections. The molecular structure allows the definition of the relative configuration at the three asymmetric centres. Each molecule is hydrogen bonded to molecules of water through the two OH groups of the dioxin ring. A complex pattern of hydrogen bonds connects every molecule with five other molecules, either directly or through the water molecules.

Introduction. In the course of our studies on ethylenic systems bearing electron-withdrawing groups (Celli, Lampariello, Chimichi, Nesi & Scotton, 1982, 1983; Adembri, Donati, Lampariello & Scotton, 1982; Adembri, Anselmi, Camparini, Celli & Scotton, 1983), we became interested in the oxidation of cyclopentenones of type (1). Thus 2,3-diacetyl-4-hydroxy-4-methylcyclopent-2-en-1-one, (1*a*), reacted easily at room temperature with 30% hydrogen peroxide to give a product (m.p. 369–371 K dec.) in quantitative yield. On the basis of analytical and spectral data and keeping in mind the behaviour of ketones with hydrogen peroxide we formulated this product as 1,4,7-trihydroxy-1,4,7-trimethylcyclopenta-2,3-dioxin-5-one, (2). The determination of the molecular structure of (2) was carried out not only to confirm our proposal, but, above all, to assign the relative configuration at the three asymmetric centres; once known, the stereochemistry would allow speculation on the mechanism of the reaction.



Experimental. Colourless prismatic crystals obtained by slow crystallization from ethyl acetate/cyclohexane.

Philips PW 1100 diffractometer, lattice parameters determined using 25 reflections (θ range: 10–13°); 2515 unique measured reflections, $2\theta < 51^\circ$, θ - 2θ scan technique, $-13 \leq h \leq 12$, $0 \leq k \leq 16$, $0 \leq l \leq 9$; 1798 observed reflections with $I \geq 3\sigma(I)$; three standard reflections ($5\bar{4}1$, $4\bar{3}\bar{3}$, $\bar{4}33$), no significant variation of their intensity; L_p correction, no absorption correction; parallelepipedal crystal, $0.3 \times 0.2 \times 0.2$ mm, delimited by (100), (010) and (001), and their centrosymmetric faces; scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974) and for H atoms from Stewart, Davidson & Simpson (1965), anomalous-dispersion corrections according to *International Tables for X-ray Crystallography* (1974). Direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and Fourier methods; full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic thermal parameters for all non-H atoms; H atoms (determined by ΔF Fourier) refined isotropically; H atoms of water molecules with fixed overall U of 0.08 Å², 219 refined parameters; max. $\Delta/\sigma = 0.92$, final $R = 0.056$, $wR = 0.061$, $S = 2.42$, $w = 1/\sigma^2$, $\Delta\rho$ excursions 0.09 and 0.49 e Å⁻³; Gould-SEL32/70 computer, *SHELX76* program (Sheldrick, 1976).

Discussion. Final atomic coordinates are given in Table 1,* and bond lengths and angles in Table 2. An *ORTEPII* plot (Johnson, 1976) (Fig. 1) shows the asymmetric unit with two molecules of water bound to the O(1)H and O(4)H groups and clearly demonstrates the stereochemistry of the three methyl groups; thus the relative configuration is (1*RS*,4*RS*,7*RS*)-1,4,7-trihydroxy-1,4,7-trimethyl-6,7-dihydrocyclopenta[*d*][1,2]-dioxin-5-one.

The C(1), C(4), C(4a), C(5), C(6), C(7), C(7a) and O(5) atoms lie on the same plane [the maximum deviation from the best plane is 0.035 (4) Å]. In the six-membered ring, torsion angles C(4a)–C(4)–O(3)–

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43251 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) of non-H atoms

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

	x	y	z	U_{eq}
O(1)	-562 (2)	2202 (2)	3821 (3)	44 (1)
O(2)	190 (2)	3379 (1)	2386 (3)	43 (1)
O(3)	-641 (2)	3094 (1)	795 (3)	42 (1)
O(4)	885 (2)	3334 (2)	-659 (3)	46 (1)
O(5)	1471 (2)	987 (2)	-1267 (3)	59 (2)
O(6)	2940 (2)	1286 (2)	4448 (3)	41 (1)
O(7)	-6991 (2)	3995 (2)	1675 (4)	83 (2)
O(8)	4606 (3)	420 (2)	7142 (4)	77 (2)
C(1)	501 (3)	2558 (2)	3425 (4)	35 (2)
C(4)	93 (3)	2677 (2)	-208 (4)	36 (2)
C(4a)	892 (3)	1929 (2)	818 (4)	32 (2)
C(5)	1506 (3)	1149 (2)	193 (4)	38 (2)
C(6)	2164 (3)	575 (3)	1667 (4)	43 (2)
C(7)	1853 (3)	1011 (2)	3205 (4)	33 (2)
C(7a)	1073 (2)	1861 (2)	2473 (4)	36 (2)
C(8)	1164 (4)	344 (3)	4083 (5)	48 (2)
C(9)	1358 (4)	2947 (3)	4993 (5)	47 (2)
C(10)	-880 (4)	2310 (3)	-1698 (5)	47 (3)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

O(2)—O(3)	1.466 (2)	C(4)—C(4a)	1.508 (3)
O(1)—C(1)	1.400 (3)	C(4)—C(10)	1.517 (3)
O(2)—C(1)	1.445 (3)	C(4a)—C(5)	1.467 (3)
O(3)—C(4)	1.435 (3)	C(4a)—C(7a)	1.340 (3)
O(4)—C(4)	1.400 (3)	C(5)—C(6)	1.501 (3)
O(5)—C(5)	1.224 (3)	C(6)—C(7)	1.536 (3)
O(6)—C(7)	1.433 (2)	C(7)—C(7a)	1.526 (3)
C(1)—C(7a)	1.506 (3)	C(7)—C(8)	1.518 (3)
C(1)—C(9)	1.511 (3)		
C(1)—O(2)—O(3)	108.3 (1)	C(4)—C(4a)—C(7a)	123.0 (2)
C(4)—O(3)—O(2)	108.4 (1)	C(5)—C(4a)—C(7a)	110.2 (2)
O(1)—C(1)—O(2)	110.1 (2)	C(4a)—C(5)—O(5)	126.2 (2)
C(7a)—C(1)—O(1)	112.1 (2)	C(4a)—C(5)—C(6)	107.5 (2)
C(7a)—C(1)—O(2)	107.0 (2)	C(6)—C(5)—O(5)	126.2 (2)
C(9)—C(1)—O(1)	108.6 (2)	C(5)—C(6)—C(7)	106.9 (2)
C(9)—C(1)—O(2)	102.6 (2)	C(6)—C(7)—O(6)	112.6 (2)
C(7a)—C(1)—C(9)	115.9 (2)	C(6)—C(7)—C(7a)	102.5 (2)
O(3)—C(4)—O(4)	111.5 (2)	C(6)—C(7)—C(8)	113.0 (2)
C(4a)—C(4)—O(3)	107.9 (2)	C(7a)—C(7)—O(6)	111.2 (2)
C(4a)—C(4)—O(4)	107.7 (2)	C(7a)—C(7)—C(8)	112.5 (2)
C(4a)—C(4)—C(10)	114.4 (2)	C(8)—C(7)—O(6)	105.3 (2)
C(10)—C(4)—O(3)	102.8 (2)	C(1)—C(7a)—C(7)	126.1 (2)
C(10)—C(4)—O(4)	112.5 (2)	C(1)—C(7a)—C(4a)	121.0 (2)
C(4)—C(4a)—C(5)	126.7 (2)	C(4a)—C(7a)—C(7)	112.9 (2)

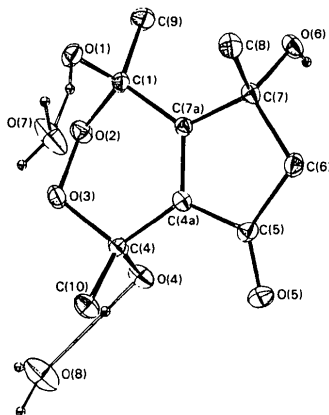


Fig. 1. ORTEP (Johnson, 1976) view of compound (2) with the atomic labelling scheme.

O(2), C(1)—O(2)—O(3)—C(4) and C(7a)—C(1)—O(2)—O(3) are 51.9 (3), -78.7 (3) and 57.0 (3) $^\circ$ respectively. These angles involve a distorted boat conformation for the dioxin ring with O(2) and O(3) at a symmetrical distance (0.44 and -0.41 \AA respectively) from the plane already cited.

The molecular packing (see Fig. 2 and Table 3) shows the complex H-bond system: one molecule is linked to five other molecules, either directly [O(6)—H(6)···O(1)] or through water molecules.

Comparison with analogous systems was not possible since, to our knowledge, only one crystal structure of a 1,2-dioxin ring has been reported in the literature (Yamada, Nakayama, Takayama, Itai & Itaka, 1979), but this ring is in too different a system.

The most interesting feature of the reaction is the complete stereospecificity: since the attack of hydrogen peroxide can occur on both faces of either acetyl groups at the 2- and 3-positions of (1a), only intermediates with a suitable conformation can evolve into the final product (2). The great influence of the methyl group at the 4-position on the stereochemical course of reaction has

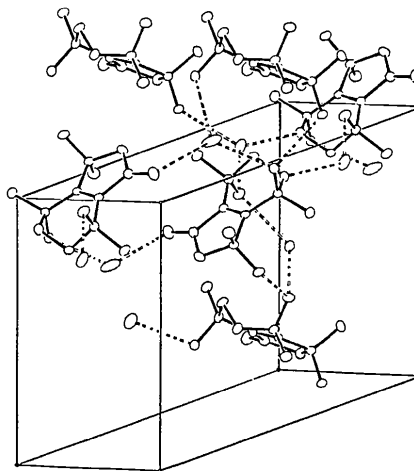


Fig. 2. Molecular packing of (2) with the complex H-bond system.

Table 3. Inter- and intramolecular hydrogen-bond lengths (\AA) and angles ($^\circ$)

O—H···O	O···O	H···O	H—O	\angle O—H···O
O(1)—H(1)···O(7 ⁱ)	2.682 (4)	1.87 (6)	0.83 (6)	164 (2)
O(4)—H(4)···O(8 ⁱⁱ)	2.685 (4)	1.78 (4)	0.90 (4)	177 (1)
O(6)—H(6)···O(1 ⁱⁱⁱ)	2.853 (4)	2.04 (5)	0.82 (5)	170 (1)
O(7)—H(7 ^A)···O(5 ⁱⁱⁱ)	2.938 (4)	2.50 (4)	1.15 (4)	100 (1)
O(7)—H(7 ^B)···O(4 ^{iv})	2.812 (3)	2.09 (4)	0.73 (4)	170 (1)
O(8)—H(8 ^A)···O(6 ^v)	2.805 (3)	1.94 (4)	0.89 (4)	161 (1)
O(8)—H(8 ^B)···O(2 ^{vi})	2.939 (3)	2.08 (4)	0.87 (4)	170 (1)

Symmetry code: (i) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - 1$; (iii) $\bar{x} - \frac{1}{2}, y - \frac{1}{2}, \bar{z}$; (iv) $x - 1, y, z$; (v) x, y, z ; (vi) $\bar{x} + \frac{1}{2}, y - \frac{1}{2}, \bar{z} + 1$.

already been observed in the additions to the C(2)=C(3) double bonds of compounds (1a) and (1b) (Adembri, Donati, Lampariello & Scotton, 1982; Adembri, Anselmi, Camparini, Celli & Scotton, 1983).

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Structure du Diméthylamino-2 Phényl-2 (Phénylséléno-2 oxo-3 cyclohexyl-1)acétonitrile

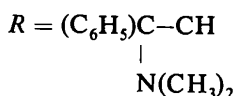
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(Reçu le 26 mars 1986, accepté le 10 juillet 1986)

Abstract. $C_{22}H_{24}N_2OSe$, $M_r = 411.41$, triclinic, $P\bar{1}$, $a = 7.9659$ (7), $b = 10.208$ (2), $c = 14.607$ (2) Å, $\alpha = 69.65$ (1), $\beta = 78.77$ (1), $\gamma = 64.27^\circ$ (1), $V = 1001.88$ Å³, $Z = 2$, $D_x = 1.364$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu(Mo K\alpha) = 18.646$ cm⁻¹, $F(000) = 424$, $T = 295$ K, $R = 0.037$ for 1773 independent reflexions [$I > 2\sigma(I)$]. The cyclohexanone ring adopts a twist-boat conformation; the phenylseleno substituent lies in an axial position and the length of the Se–C bond is 1.996 (6) Å.

Introduction. Une étude par RMN de différents complexes *cis* et *trans* de phénylséléno-2 *R*-3 cyclohexanone montre que le groupe 2-SePh se trouve en position axiale, le cycle cyclohexanone adoptant en général une conformation type 'chaise'. Il n'en est pas de même pour le composé *trans* où



La conformation du cycle cyclohexanone serait type 'bateau déformé' (Zervos, Wartski, Goasdoue & Platzer, 1986).

La structure cristallographique de ce dernier composé a été déterminée en vue d'affiner cette dernière hypothèse.

Partie expérimentale. Les cristaux sont obtenus après addition conjuguée du dérivé lithié du diméthylamino-phénylacétonitrile sur la cyclohexénone-2 dans le THF et piégeage de l'énolate intermédiaire par PhSeBr (Zervos, Wartski, Goasdoue & Platzer, 1986).

Cristal incolore, de forme prismatique (0,25 × 0,20 × 0,65 mm). Groupe centrosymétrique $P\bar{1}$ imposé par les tests statistiques. Intensités mesurées à l'aide d'un diffractomètre automatique Enraf-Nonius CAD-4 équipé d'un monochromateur graphite. Paramètres cristallins obtenus à partir de 25 réflexions indépendantes ($8 < \theta < 12^\circ$); corrections de Lorentz-polarisation, facteur de diffusion des atomes neutres des *International Tables for X-ray Crystallography* (1974) corrigés de f' et f'' (respectivement $-0,178$ et $2,223$ pour le sélénium); facteurs de température des atomes de sélénium, d'azote et d'oxygène rendus anisotropes; atomes d'hydrogène affinés; programmes *SDP-plus* (Frenz, 1983); mesures effectuées entre 1 et $22^\circ\theta$; scan $\omega-2\theta$, ($\Delta\omega = 0,8 + 0,35\text{tg}\theta$); $10^\circ \text{min}^{-1} \geq$ vitesse de