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Structure of a Potential Steroid Intermediate – $C_{15}H_{20}O_2$

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Abstract. 3-(2-Ethynyl-2-hydroxy-1-methylcyclohexyl)cyclohex-2-en-1-one, $C_{15}H_{20}O_2$, $M_r = 232{\cdot}29$, monoclinic, $C2/c$, $a = 30{\cdot}206\ (4)$, $b = 6{\cdot}686\ (1)$, $c = 13{\cdot}412\ (1)$ Å, $\beta = 107{\cdot}87\ (1)°$, $V = 2578{\cdot}1\ (6)$ Å^3, $Z = 8$, $T = 295$ K, $D_m = 1{\cdot}201$, $D_x = 1{\cdot}197$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 6{\cdot}2$ cm^{-1}, $F(000) = 1008$, $R(F) = 0{\cdot}056$, $wR = 0{\cdot}079$ for 1870 observations with $I_{net} > 3{\cdot}0\sigma(I)$. The hydroxyl and methyl groups attached to ring *A* are in axial orientations, while ring *B* is in an equatorial position. Ring *A* is in the most favoured chair conformation. The packing of the molecule is stabilized by O—H···O hydrogen bonds.

Introduction. Oxy-Cope moieties like hexa-1,5-diene (Fig. 1*a*) are capable of undergoing a Cope rearrangement. An anionic oxy-Cope rearrangement is a 3,3-sigmatropic shift in which an oxygen (as an alkoxide) attached to either of the carbon atoms numbered 1 in Fig. 1(*b*) undergoes rearrangement. However, when the vinyl groups are attached to the ring, the product will be a ring-enlarged carbonyl compound (Fig. 1*d*).

The title compound (I) and its reduction product (II) contain an oxy-Cope moiety. Compound (II) easily undergoes the oxy-Cope rearrangement to give the tricyclic compound (III) – a potential steroid intermediate (Satyamoorthi, Thangaraj, Srinivasan & Swaminathan, 1989). It is presumed that a *cis* orientation of the two double bonds (Fig. 2) in cyclic compounds will be highly conducive to a concerted rearrangement (Gadwood & Lett, 1982). In the present investigation it has been established that an anionic oxy-Cope rearrangement can occur even when the two vinyl moieties are in a 1,2-diequatorial orientation (*i.e. trans*).

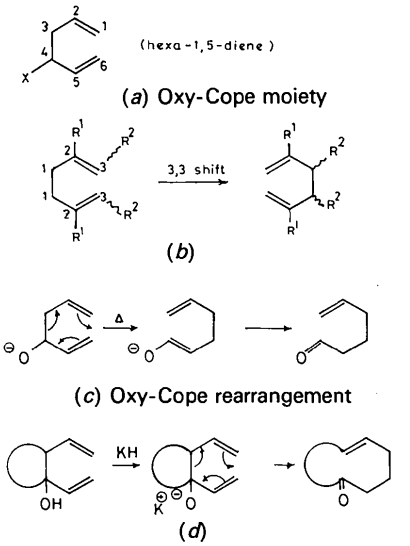

Fig. 1. Schematic representation of a molecule undergoing oxy-Cope rearrangement: (*a*) oxy-Cope moiety; (*b*), (*c*) oxy-Cope rearrangement; (*d*) oxy-Cope rearrangement involving a vinyl group attached to a ring.

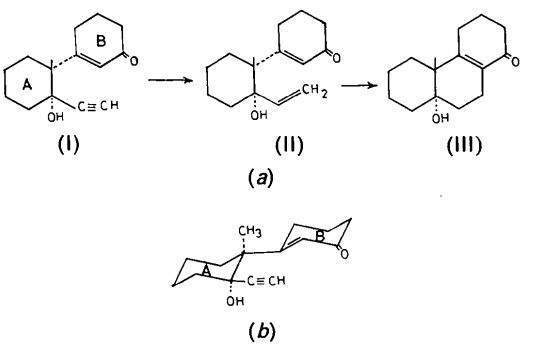

Fig. 2. Schematic diagram of the molecule and its reduction products: (*a*) proposed stereochemistry; (*b*) observed stereochemistry.

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Table 1. *Positional parameters with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}/B_{iso}(Å^2)
O1	0·13027 (4)	0·4216 (3)	0·6621 (1)	4·03 (3)
O2	0·27370 (4)	−0·0089 (3)	0·8198 (1)	4·46 (4)
C1	0·11436 (6)	0·0751 (3)	0·5979 (1)	3·25 (4)
C2	0·10330 (6)	0·3039 (3)	0·5753 (1)	3·19 (4)
C3	0·05205 (6)	0·3480 (4)	0·5649 (2)	4·30 (5)
C4	0·03808 (7)	0·2806 (5)	0·6590 (2)	5·38 (6)
C5	0·04923 (7)	0·0639 (5)	0·6848 (2)	5·57 (6)
C6	0·10034 (7)	0·0176 (4)	0·6956 (2)	4·51 (5)
C7	0·08627 (8)	−0·0533 (4)	0·5045 (2)	4·65 (5)
C8	0·11178 (7)	0·3725 (4)	0·4782 (2)	3·79 (4)
C9	0·11705 (8)	0·4334 (4)	0·3996 (2)	5·13 (6)
C10	0·16622 (6)	0·0381 (3)	0·6157 (1)	3·10 (4)
C11	0·19685 (6)	0·0202 (3)	0·7110 (1)	3·34 (4)
C12	0·24703 (6)	−0·0015 (4)	0·7300 (1)	3·49 (4)
C13	0·26470 (7)	−0·0090 (4)	0·6373 (2)	4·63 (5)
C15	0·18430 (8)	0·0260 (6)	0·5226 (2)	6·53 (8)
C14	0·2311 (2)	0·0762 (8)	0·5377 (4)	4·47 (9)
C14*P*	0·2272 (1)	−0·0641 (7)	0·5369 (3)	3·84 (8)

C14 and C14*P* were refined isotropically as they are disordered.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O1—C2	1·434 (2)	C5—C6	1·537 (3)
O2—C12	1·227 (2)	C8—C9	1·185 (4)
C1—C2	1·576 (3)	C10—C11	1·333 (2)
C1—C6	1·544 (3)	C10—C15	1·511 (3)
C1—C7	1·540 (3)	C11—C12	1·465 (3)
C1—C10	1·531 (3)	C12—C13	1·497 (3)
C2—C3	1·539 (3)	C13—C14	1·519 (5)
C2—C8	1·476 (3)	C13—C14*P*	1·516 (4)
C3—C4	1·517 (4)	C15—C14	1·406 (5)
C4—C5	1·504 (5)	C15—C14*P*	1·387 (5)
C2—C1—C6	107·9 (2)	C2—C8—C9	177·1 (2)
C2—C1—C7	110·7 (1)	C1—C10—C11	122·7 (2)
C2—C1—C10	109·5 (2)	C1—C10—C15	119·5 (1)
C6—C1—C7	109·0 (2)	C11—C10—C15	117·8 (2)
C6—C1—C10	111·2 (1)	C10—C11—C12	123·5 (2)
C7—C1—C10	108·6 (2)	O2—C12—C11	120·5 (2)
O1—C2—C1	110·0 (1)	O2—C12—C13	121·3 (2)
O1—C2—C3	105·9 (2)	C11—C12—C13	118·2 (1)
O1—C2—C8	109·7 (2)	C12—C13—C14	114·0 (3)
C1—C2—C3	110·6 (2)	C12—C13—C14*P*	112·7 (2)
C1—C2—C8	112·8 (2)	C14—C13—C14*P*	36·3 (3)
C3—C2—C8	107·6 (2)	C10—C15—C14	118·1 (3)
C2—C3—C4	113·3 (2)	C10—C15—C14*P*	117·9 (2)
C3—C4—C5	112·2 (2)	C14—C15—C14*P*	39·6 (3)
C4—C5—C6	111·3 (2)	C13—C14—C15	114·0 (4)
C1—C6—C5	113·5 (2)	C13—C14*P*—C15	115·4 (3)

Experimental. Colourless parallelepiped-shaped crystals 0·15 × 0·20 × 0·25 mm were obtained from a mixture of benzene, acetone and methanol. Cell constants were refined using 25 reflections in the range $30 < 2\theta < 70°$, $\theta/2\theta$ scan, Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated Cu $K\alpha$ radiation used for data collection; empirical absorption correction with minimum and maximum correction factors 0·8994 and 0·9984, respectively, applied; data were corrected for polarization and Lorentz effects, but no extinction corrections were applied. 2809 reflections with $2\theta_{max} = 140°$, $-28 \le h \le 36$, $0 \le k \le 8$, $-15 \le l \le 15$ were measured, of which 2646 were unique. 1870 were observed with $I \ge 3{\cdot}0\sigma(I)$; $R_{int} = 0{\cdot}026$. Three standard reflections (monitored) did not show any significant variation. Structure solution was by direct methods. The H atoms (except that attached to C15) were obtained from $\Delta\rho$ maps. Full-matrix least-squares refinement was carried out on F_o with non-H atoms anisotropic and H atoms isotropic. The individual weighting scheme was $w = 4(F_o)^2/[\sigma^2(F_o^2)]$, where $\sigma(F_o^2) = [\sigma^2(I) + q^2I^2]^{1/2}/\text{Lp}$ and $q = 0{\cdot}05$ is the ignorance factor, based on counting statistics. Final $R(F) = 0{\cdot}056$ for all reflections, and $wR = 0{\cdot}079$. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). $(\Delta/\sigma)_{max} = 0{\cdot}26$, $S = 0{\cdot}42$ for 229 parameters. Final map had $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 0{\cdot}34/-0{\cdot}34$ e Å^{-3}. All calculations were on a VAX 11/730 computing system using the *SDP* package (Frenz, 1978).

Discussion. Positional and thermal parameters are given in Table 1.* The bond lengths and bond angles are listed in Table 2. Fig. 3 gives a stereoview of the molecule.

Bond lengths and angles agree with values reported for 5-(3-oxocyclohexenyl)-5-ethylbarbituric acid (Chentli-Benchikha, Declercq, Germain, Van Meerssche, Bouché & Draguet-Brughmans, 1977) and other related structures (Holbrook & van der Helm, 1975; Roe, McPhail & Porter, 1983). They are normal within experimental error except C1—C2 which is 1·576 (3) Å. Elongation of this bond may be necessary to avoid steric interactions between the bulky substituents. Atom C14 is disordered. The

* Lists of structure factors, anisotropic thermal parameters. H-atom parameters, torsion angles and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53262 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

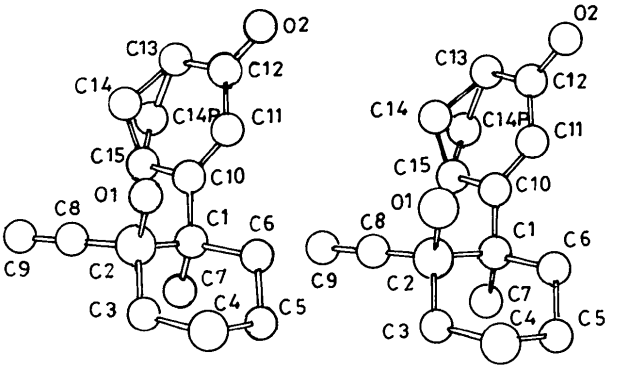

Fig. 3. Stereoview of the molecule with atom numbering.

lowest R value was obtained when the two positions for C14 had half ocupancy.

Ring A is in chair form with C1 and C4 deviating from best plane through C2, C3, C5 and C6 by 0·70 and 0·62 Å, respectively. Ring B is in a twisted conformation with C10, C11 and C12 approximately in a plane, and C13 and C15 above and C14 below this plane. The hydroxyl and the methyl groups are attached to ring A in an axial orientation while ring B is attached in an equitorial position. The packing is stabilized by an O1—H···O2 hydrogen bond. The O1—H···O2 and H—O1···O2 angles are 163·4 (5) and 11·2 (5)°, respectively, and the O···H distance is 1·96 (2) Å. The two rings are almost perpendicular to each other as found in the case of 5-(3-oxocyclohexenyl)-5-ethylbarbituric acid (Chentli-Benchikha *et al.*, 1977). The best plane through the atoms in rings A and B makes an angle of 51·2 (1)° with C14 and 121·7 (1)° with C14P in the ring.

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Structure of 7-Methyl-6,8-dithioxo-7,8-dihydroguanosine Monohydrate

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Abstract. 2-Amino-7-methyl-9-β-D-ribofuranosyl-1*H*,9*H*-purine-6,8-dithione monohydrate (1), $C_{11}H_{15}N_5O_4S_2.H_2O$, $M_r = 363{\cdot}41$, monoclinic, $P2_1$, $a = 5{\cdot}9889\ (12)$, $b = 20{\cdot}772\ (4)$, $c = 6{\cdot}7374\ (15)$ Å, $\beta = 113{\cdot}843\ (16)°$, $V = 766{\cdot}6\ (3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}574$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 34{\cdot}141$ cm^{-1}, $F(000) = 380$, $T = 295$ K, $R = 0{\cdot}0253$ for 3105 reflections ($F \geq 4\sigma_F$). The sugar conformation and puckering parameters are $^2T_1$ ($C_{2'}$-*endo*/$C_{1'}$-*exo*), $P = 149{\cdot}1°$ and $\tau_m = 34{\cdot}8°$. The C5′–O5′ side chain is *gauche–gauche*. The glycosidic torsion angle is 61·0 (2)° corresponding to the *syn* conformation which is stabilized by the O5′—H···N3 intramolecular hydrogen bond [d(O5′···N3) = 2·900 (3) Å]. The purine ring is nearly planar [r.m.s. deviation: 0·020 (2) Å]; the dihedral angle between the pyrimidine and imidazole rings is 0·31 (8)°. Purine rings are parallel to the (101) planes but do not overlap. The only interbase interaction is a weak head-to-tail (N10···S13) hydrogen bond [3·329 (2) Å].

Introduction. The title compound (1) is a 6-thioxo derivative of 7-methyl-8-oxo- (2) and 7-methyl-8-thioxoguanosine (3) both of which have exhibited immunostimulatory activity. For example, (2) has been studied as an intracellular mitogen of murine splenic B lymphocytes (Goodman & Weigle, 1984) and as a promoter of proliferation and differentiation of murine T cells in the presence of other stimulating signals (Ahmad & Mond, 1986; Feldbush & Ballas, 1985). 7-Methyl-8-thioxoguanosine (3) has immunomodulating properties similar to (2) (Henry, Kini, Larson, Robins, Alaghamandan & Smee, 1990). On the other hand, (1) is also a derivative of 6-thioguanosine (4) which is currently utilized in the clinic as an anticancer agent (Fox, Wempen, Hampton & Doerr, 1958). The potential of (1) as both an immunomodulator and an antitumor drug was envisioned. However, 7-methyl-6,8-thioxoguano-

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