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Structure of 2-(1,5-Dimethyl-4-hexenyl)-3-hydroxy-5-methyl-1,4-benzoquinone (Perezone), a Sesquiterpene*

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Abstract. $C_{15}H_{20}O_3$, $M_r = 248·3$, monoclinic, $P2_1$, $a = 6·662$ (3), $b = 7·343$ (3), $c = 14·537$ (6) Å, $\beta = 98·20$ (4)°, $V = 703·9$ (1) Å^3, $Z = 2$, $D_x = 1·17$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·075$ mm^{-1}, $F(000) = 268$, $T = 293$ K. Final $R = 0·052$ for 796 observed reflections. The structural features determined from chemical and spectroscopic studies are confirmed and extended. The quinone ring is planar and shows normal geometry. The side chain at C(3) adopts an extended form and is oriented out of the plane of the quinone ring. The angle between the plane of the quinone ring and the side chain is 102·6 (6)°. The molecules in the crystal are held together by hydrogen bonds and van der Waals interactions.

Introduction. Perezone (1) is a sesquiterpene compound which was isolated from the roots of a plant, *Perezia adnata*, a member of the Compositae family found in Mexico. This compound exerts very marked physiological action, having purgative properties for which it is much used in Mexico. The chemical and spectroscopic studies led to the proposal of the chemical structure (1) from four different laboratories (Archer & Thomson, 1965; Walls, Salmón, Padilla, Joseph-Nathan & Romo, 1965; Wagner, Moss, Brooker, Heeschen, Potts & Dilling, 1965; Bates, Paknikar & Thalacker, 1965) and this was confirmed by synthesis (Cortés, Salmón & Walls, 1965).

(1)
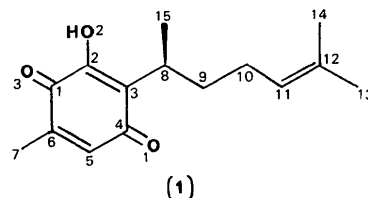
The X-ray crystallographic structural determination of (1) was undertaken in order to establish the crystal structure and the stereochemistry of this compound.

Experimental. Red crystal $0.08 \times 0.31 \times 0.64$ mm. Nicolet $R3$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters from 25 machine-centred reflections with $5.6 < 2\theta < 17.0°$. 1111 reflections with $3 < 2\theta < 45°$ for two octants, 796 independent with $I > 2.5\sigma(I)$, index range $h \pm 7, k\, 0\rightarrow7, l\, 0\rightarrow15$, ω-scan mode, variable scan speed, scan width $1.0°$ (θ), two standard reflections ($0\bar{2}0$, $0\bar{2}1$) monitored every 50 measurements, Lp correction, empirical absorption correction based on reflection intensity measurements at different azimuthal angles, transmission range 0.96–0.98, $R_{int} = 0.023$. Structure solved by combination of direct methods and partial structure expansion by an iterative E–Fourier procedure using $SHELXTL$ (Sheldrick, 1981). Least-squares refinement of all non-H atoms treated anisotropically; H atoms riding on the bonded C with fixed isotropic temperature factor, $U = 0.06$ Å^2; H atom bonded to O refined; $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(F_o) + 0.002(F_o)^2]^{-1}$. In the last cycle $(\Delta/\sigma)_{max} = 0.033$; $\Delta\rho$ from -0.22 to $+0.14$ e Å^{-3}. Isotropic extinction parameter $X = 0.0019$. Final $R = 0.052$, $wR = 0.065$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows the molecular conformation of (1). Final atomic coordinates are in Table 1* and distances, angles and selected torsion angles in Table 2. Calculations of the least-squares plane through the quinone ring and the side chain, the deviations of individual atoms from the planes and interplanar angles have been deposited.*

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42582 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
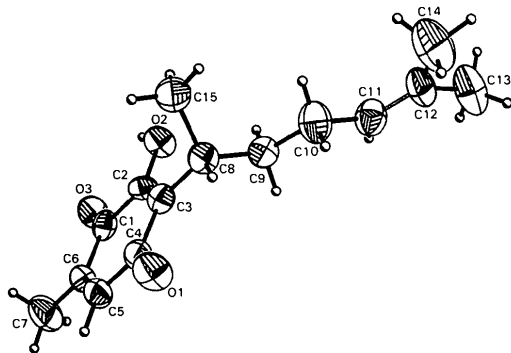
Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

$$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}.$$

	x	y	z	U_{eq}
O(1)	7609 (7)	4898	5875 (3)	65 (2)
O(2)	7738 (7)	11227 (6)	6205 (3)	52 (2)
O(3)	7489 (6)	11418 (7)	4359 (3)	59 (2)
C(1)	7527 (7)	9888 (9)	4688 (4)	42 (2)
C(2)	7664 (8)	9661 (8)	5719 (4)	38 (2)
C(3)	7721 (7)	8044 (8)	6142 (4)	40 (2)
C(4)	7613 (9)	6430 (10)	5540 (4)	47 (2)
C(5)	7474 (8)	6636 (10)	4527 (4)	51 (2)
C(6)	7429 (8)	8246 (8)	4102 (4)	50 (2)
C(7)	7288 (11)	8509 (13)	3067 (4)	77 (3)
C(8)	7835 (8)	7786 (8)	7171 (3)	45 (2)
C(9)	9786 (8)	8579 (9)	7713 (4)	51 (2)
C(10)	10205 (9)	7979 (11)	8714 (4)	66 (2)
C(11)	12129 (9)	8777 (10)	9238 (4)	61 (2)
C(12)	12750 (10)	8683 (9)	10135 (4)	59 (2)
C(13)	14728 (12)	9414 (14)	10569 (5)	97 (3)
C(14)	11533 (13)	7788 (14)	10797 (5)	100 (4)
C(15)	5945 (9)	8532 (11)	7516 (4)	63 (2)

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

O(1)–C(4)	1.226 (7)	O(2)–C(2)	1.347 (7)
O(3)–C(1)	1.220 (8)	C(1)–C(2)	1.498 (8)
C(1)–C(6)	1.472 (9)	C(2)–C(3)	1.334 (8)
C(3)–C(4)	1.469 (9)	C(3)–C(8)	1.499 (7)
C(4)–C(5)	1.469 (8)	C(5)–C(6)	1.332 (9)
C(6)–C(7)	1.507 (8)	C(8)–C(9)	1.535 (7)
C(8)–C(15)	1.523 (8)	C(9)–C(10)	1.509 (8)
C(10)–C(11)	1.512 (9)	C(11)–C(12)	1.312 (8)
C(12)–C(13)	1.478 (10)	C(12)–C(14)	1.495 (11)

O(3)–C(1)–C(2)	119.3 (5)	O(3)–C(1)–C(6)	122.0 (5)
C(2)–C(1)–C(6)	118.6 (5)	O(2)–C(2)–C(1)	115.0 (5)
O(2)–C(2)–C(3)	121.4 (5)	C(1)–C(2)–C(3)	123.6 (5)
C(2)–C(3)–C(4)	116.6 (5)	C(2)–C(3)–C(8)	124.5 (5)
C(4)–C(3)–C(8)	118.9 (5)	O(1)–C(4)–C(3)	120.4 (5)
O(1)–C(4)–C(5)	119.3 (6)	C(3)–C(4)–C(5)	120.3 (6)
C(4)–C(5)–C(6)	123.4 (6)	C(1)–C(6)–C(5)	117.5 (5)
C(1)–C(6)–C(7)	117.6 (6)	C(5)–C(6)–C(7)	124.8 (6)
C(3)–C(8)–C(9)	112.5 (5)	C(3)–C(8)–C(15)	110.9 (4)
C(9)–C(8)–C(15)	111.9 (5)	C(8)–C(9)–C(10)	114.3 (5)
C(9)–C(10)–C(11)	113.6 (6)	C(10)–C(11)–C(12)	127.2 (6)
C(11)–C(12)–C(13)	122.7 (6)	C(11)–C(12)–C(14)	122.6 (6)
C(13)–C(12)–C(14)	114.7 (5)		

O(3)–C(1)–C(2)–O(2)	−0.1 (7)	C(4)–C(3)–C(8)–C(15)	−114.7 (6)
O(3)–C(1)–C(6)–C(7)	0.3 (8)	C(3)–C(8)–C(9)–C(10)	−166.4 (5)
O(2)–C(2)–C(3)–C(8)	1.0 (8)	C(8)–C(9)–C(10)–C(11)	−179.9 (6)
C(8)–C(3)–C(4)–O(1)	0.3 (8)	C(10)–C(11)–C(12)–C(13)	176.0 (7)
C(2)–C(3)–C(8)–C(15)	63.8 (7)	C(10)–C(11)–C(12)–C(14)	−2.5 (12)

Fig. 1. The molecular conformation of (1), showing atom numbering. The thermal ellipsoids are drawn at 50% probability level.
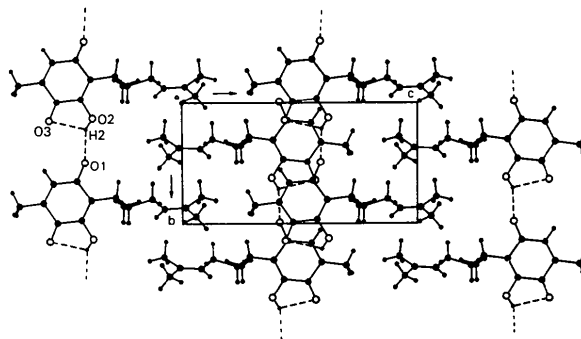

Fig. 2. The packing arrangement as viewed along **a**. Hydrogen bonds are shown by broken lines.

The quinone ring shows normal geometry. The average distances and corresponding angles for the quinone ring are C—C 1·477 (9), C=C 1·333 (9), C=O 1·223 (8) Å; C—C—C 119·5 (6), C=C—C 120·3 (5) and O=C—C 120·2 (5)°, which are in agreement with values determined in other 1,4-benzoquinone compounds (Schmalle, Jarchow, Hausen & Schulz, 1984*a,b,c,d*). The C(9)—C(10) bond distance of 1·509 (8) Å is significantly shorter than the expected value of 1·533 Å for a C—C bond length in *n*-hydrocarbons (Bartell, 1959).

As shown in Fig. 1, the molecular conformation of the side chain at C(3) is the fully extended *trans*-zigzag form and the pertinent torsion angles are given in Table 2.

The crystal structure contains two different types of hydrogen bonds which play an important role in the stabilization. The hydrogen-bonding scheme is shown in Fig. 2. The first type is an intramolecular hydrogen bond between the O(2)—H hydroxyl group and the O(3) carbonyl group. The O(2)···O(3) and H(2)···O(3) distances are 2·669 (6) and 2·34 (7) Å and the O(2)—H(2)···O(3) angle is 107 (5)°. In addition, H(2) participates in a second type of hydrogen bond involving the O(1) carbonyl group of an adjacent molecule (*x*, 1 + *y*, *z*). The O(2)···O(1) and H(2)···O(1) distances are 2·737 (4) and 2·04 (7) Å and the O(2)—H(2)···O(1) angle is 150 (5)°.

An additional intramolecular interaction, C(8)···O(1), 2·826 (7) Å, and the presence of the methyl group C(15) at C(8) appear to define the conformation around the C(3)—C(8) bond which is such that the side chain bonded to C(8) points away from the quinone

ring. The dihedral angle between the side chain and the quinone ring is 102·6 (6)°.

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Structure of (1*S*,3*R*,6*R*,7*S*)-2,2,6,10-Tetramethyl-8,11-dioxotricyclo[5.3.1.0³,⁷]undec-9-en-9-yl Acetate (β-Pipitzol Acetate)*

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Abstract. $C_{17}H_{22}O_4$, $M_r = 290·4$, orthorhombic, $P2_12_12_1$, $a = 9·368$ (4), $b = 11·011$ (3), $c = 15·627$ (5) Å, $V = 1612$ (1) Å³, $Z = 4$, $D_x = 1·20$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 0·079$ mm⁻¹, $F(000) = 624$, $T = 293$ K. Final $R = 0·060$ for 901 observed reflections. The molecular structure is determined from the X-ray data and confirms the structure previously assigned on the basis of chemical and spectroscopic evidence. Both five-membered rings are in a half-chair conformation. The cyclohexene ring adopts a 1,2-diplanar conformation with C(11) 0·85 (1) Å out