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# Structure of 2-(1,5-Dimethyl-4-hexenyl)-3,6-dihydroxy-5-methyl-1,4-benzoquinone (Hydroxyperezone), a Sesquiterpene*

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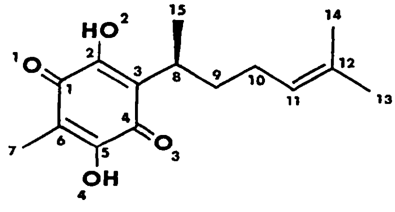
**Abstract.** $C_{15}H_{20}O_4$, $M_r = 264{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}449\,(2)$, $b = 7{\cdot}361\,(1)$, $c = 31{\cdot}089\,(9)$ Å, $V = 1476\,(1)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}19$ Mg m$^{-3}$, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}663$ mm$^{-1}$, $F(000) = 568$, $T = 300$ K, $R = 0{\cdot}060$ for 1031 observed reflections. The structural features determined from chemical and spectroscopic studies are confirmed and extended. The atoms of the quinone ring form a planar system. The quinone ring shows normal geometry. The angle between the quinone ring and the 1,5-dimethyl-4-hexenyl side chain is 32·1 (7)°. The molecules in the crystal are connected by intermolecular O—H···O hydrogen bonds forming continuous parallel ribbons along **b** and intramolecular O—H···O and C—H···O hydrogen bonds lend conformational stability to the molecules.

**Introduction.** Hydroxyperezone (1) is a sesquiterpene which was isolated from the dried and ground roots of *Perezia adnata* Gr., a member of the Compositae family found in Mexico. Chemical and spectroscopic studies led to the chemical structure (1) (Joseph-Nathan, González & Rodriguez, 1972; Joseph-Nathan, González, García, Barrios & Walls, 1974). The X-ray crystallographic structural determination of (1) was undertaken in order to understand the detailed geometry of this molecule as well as its intra- and intermolecular interactions.



(1)

**Experimental.** Red crystal 0·04 × 0·34 × 0·58 mm. Nicolet *R*3 four-circle diffractometer, Ni-filtered Cu *Kα* radiation. Lattice parameters from 25 machine-centred reflections with $5{\cdot}7 < 2\theta < 51{\cdot}0°$. 1140 reflections with $3 < 2\theta < 110°$ for one octant, 1031 independent with $I > 2{\cdot}5\sigma(I)$, index range $h$ 0→6, $k$ 0→7, $l$ 0→32, ω-scan mode, variable scan speed, scan width 1·0°(θ), two standard reflections ($00\bar{2}$; 102) monitored every 50 measurements, Lp correction, absorption ignored, $R_{\text{int}} = 0{\cdot}020$. 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; C(12), C(13) and C(14) show

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some disorder (see thermal parameters in Table 1); H atoms riding on the bonded C with fixed isotropic temperature factor, $U = 0{\cdot}06$ Å$^2$; H atoms bonded to O refined; $\sum w(\Delta F^2)$ minimized, $w = [\sigma^2(F_o) + 0{\cdot}005\,(F_o)^2]^{-1}$. In the last cycle $(\Delta/\sigma)_{\max} = 0{\cdot}160$; $\Delta\rho$ from $-0{\cdot}24$ to $+0{\cdot}23$ e Å$^{-3}$, $S = 1{\cdot}286$. Isotropic extinction parameter $X = 0{\cdot}0049$. Final $R = 0{\cdot}060$, $wR = 0{\cdot}095$. 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 bond distances and angles in Table 2.

In the quinone ring the average lengths of the bonds C(1)–C(6) and C(3)–C(4) are shorter by 0·057 Å than those of C(1)–C(2) and C(4)–C(5). This difference may be due to electron delocalization between O(4) and O(1), and O(2) and O(3) involving the groupings HO—C=C—C=O. The overall average distances and corresponding angles for the quinone ring are C—C 1·470 (5), C=C 1·352 (5), C=O 1·239 (4) Å; C—C—C 119·6 (3), C=C—C 120·8 (3) and O=C—C 119·6 (4)°, which are in agreement with the values determined in perezone (Soriano-García, Toscano, Flores-Valverde, Montoya-Vega & López-Celis, 1986) and in other 1,4-benzoquinone compounds (Schmalle, Jarchow, Hausen & Schulz, 1984 *a,b,c,d*).

The maximum deviation from the mean plane through the atoms C(1)–C(6) of the quinone ring is 0·008 (7) Å for C(1); maximum deviations from the mean plane of the side chain [C(3), C(8)–C(14)] are much larger, 0·612 (7), 0·759 (7) and −1·359 (7) Å for C(11), C(14) and C(13), respectively. The dihedral angle between these two planes is 32·1 (7)°. This conformation is different from that of perezone (Soriano-García *et al.*, 1986) in which the side chain at C(3) is inclined at 102·6 (6)° with respect to the quinone ring.

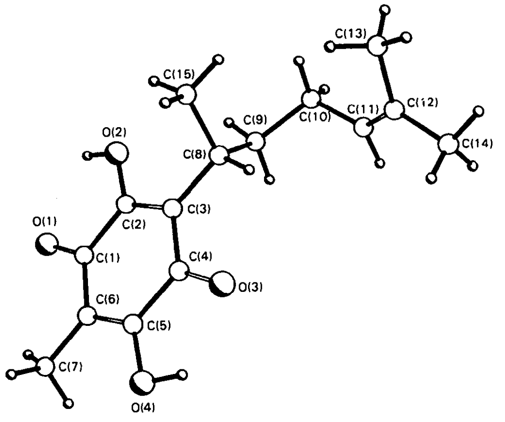

Fig. 1. A molecule of hydroxyperezone showing the atom labelling.

Table 1. *Atomic coordinates* (× 10$^4$) *and equivalent isotropic temperature factors* (Å$^2$ × 10$^3$)

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| O(1) | 1531 (6) | 1854 (3) | 152 (1) | 54 (1) |
| O(2) | 1535 (6) | 2177 (4) | −687 (1) | 53 (1) |
| O(3) | 1544 (5) | 8505 (3) | −481 (1) | 51 (1) |
| O(4) | 1563 (5) | 8138 (3) | 362 (1) | 51 (1) |
| C(1) | 1551 (7) | 3446 (5) | 21 (1) | 41 (1) |
| C(2) | 1535 (7) | 3718 (5) | −454 (1) | 41 (1) |
| C(3) | 1546 (7) | 5373 (5) | −643 (1) | 42 (1) |
| C(4) | 1564 (7) | 6912 (5) | −354 (1) | 41 (1) |
| C(5) | 1546 (7) | 6623 (5) | 126 (1) | 41 (1) |
| C(6) | 1536 (7) | 4965 (5) | 311 (1) | 43 (1) |
| C(7) | 1534 (9) | 4703 (6) | 784 (1) | 54 (1) |
| C(8) | 1551 (8) | 5706 (6) | −1124 (1) | 50 (1) |
| C(9) | 3553 (8) | 4981 (7) | −1326 (1) | 65 (2) |
| C(10) | 3892 (10) | 5584 (7) | −1791 (2) | 70 (2) |
| C(11) | 4329 (13) | 7498 (10) | −1833 (2) | 99 (3) |
| C(12) | 3250 (18) | 8816 (9) | −2031 (2) | 128 (4) |
| C(13) | 1430 (27) | 8343 (13) | −2288 (3) | 211 (7) |
| C(14) | 3671 (29) | 10706 (10) | −2040 (3) | 292 (11) |
| C(15) | −360 (9) | 4953 (10) | −1337 (2) | 86 (2) |

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

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1·241 (4) | O(2)–C(2) | 1·346 (4) |
| O(3)–C(4) | 1·237 (4) | O(4)–C(5) | 1·334 (4) |
| C(1)–C(2) | 1·491 (6) | C(1)–C(6) | 1·436 (5) |
| C(2)–C(3) | 1·353 (5) | C(3)–C(4) | 1·447 (5) |
| C(3)–C(8) | 1·513 (5) | C(4)–C(5) | 1·507 (5) |
| C(5)–C(6) | 1·350 (5) | C(6)–C(7) | 1·484 (5) |
| C(8)–C(9) | 1·532 (7) | C(8)–C(15) | 1·506 (8) |
| C(9)–C(10) | 1·526 (6) | C(10)–C(11) | 1·443 (9) |
| C(11)–C(12) | 1·343 (11) | C(12)–C(13) | 1·461 (18) |
| C(12)–C(14) | 1·418 (11) | | |

| | | | |
|---|---|---|---|
| O(1)–C(1)–C(2) | 116·8 (3) | O(1)–C(1)–C(6) | 122·0 (4) |
| C(2)–C(1)–C(6) | 121·2 (3) | O(2)–C(2)–C(1) | 114·9 (3) |
| O(2)–C(2)–C(3) | 121·7 (3) | C(1)–C(2)–C(3) | 123·5 (3) |
| C(2)–C(3)–C(4) | 115·8 (4) | C(2)–C(3)–C(8) | 125·1 (4) |
| C(4)–C(3)–C(8) | 119·1 (3) | O(3)–C(4)–C(3) | 123·0 (4) |
| O(3)–C(4)–C(5) | 116·7 (3) | C(3)–C(4)–C(5) | 120·3 (3) |
| O(4)–C(5)–C(4) | 115·2 (3) | O(4)–C(5)–C(6) | 121·4 (3) |
| C(4)–C(5)–C(6) | 123·4 (3) | C(1)–C(6)–C(5) | 115·8 (4) |
| C(1)–C(6)–C(7) | 121·4 (3) | C(5)–C(6)–C(7) | 122·7 (3) |
| C(3)–C(8)–C(9) | 110·6 (4) | C(3)–C(8)–C(15) | 111·9 (4) |
| C(9)–C(8)–C(15) | 112·3 (4) | C(8)–C(9)–C(10) | 114·1 (4) |
| C(9)–C(10)–C(11) | 113·5 (4) | C(10)–C(11)–C(12) | 130·2 (7) |
| C(11)–C(12)–C(13) | 119·6 (7) | C(11)–C(12)–C(14) | 128·2 (11) |
| C(13)–C(12)–C(14) | 112·2 (9) | | |

| | | | |
|---|---|---|---|
| O(1)–C(1)–C(2)–C(3) | 179·8 (4) | C(8)–C(3)–C(4)–O(3) | 1·3 (7) |
| O(1)–C(1)–C(6)–C(7) | 1·1 (7) | C(2)–C(3)–C(8)–C(15) | 61·8 (6) |
| O(1)–C(1)–C(2)–O(2) | −1·0 (6) | C(4)–C(3)–C(8)–C(15) | −118·5 (5) |
| O(2)–C(2)–C(3)–C(8) | 0·2 (7) | C(3)–C(8)–C(9)–C(10) | −168·5 (4) |
| O(2)–C(2)–C(3)–C(4) | −179·5 (4) | C(8)–C(9)–C(10)–C(11) | 68·9 (7) |
| O(4)–C(5)–C(6)–C(7) | 0·3 (7) | C(10)–C(11)–C(12)–C(13) | −6·9 (13) |
| O(3)–C(4)–C(5)–O(4) | −1·6 (6) | C(10)–C(11)–C(12)–C(14) | 175·3 (9) |

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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 Document Supply Centre as Supplementary Publication No. SUP 43121 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

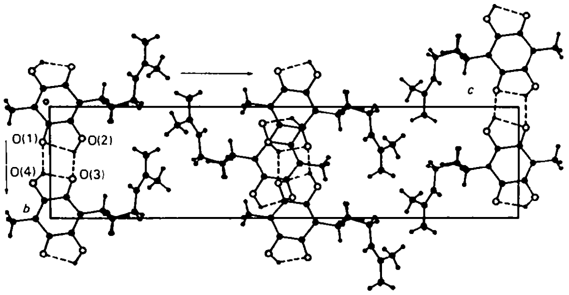

Fig. 2. Packing arrangement of the hydroxyperezone molecules as viewed along **a**. Broken lines indicate hydrogen bonds.

Fig. 2 shows the crystal structure projected along **a** showing the hydrogen-bonding scheme. The crystal structure contains both intra- and intermolecular hydrogen bonds* which play an important role in the stabilization; intramolecular hydrogen bonds occur between the O(2)–H(2) and O(4)–H(4) hydroxyl groups and the O(1) and O(3) carbonyl groups. H(2) and H(4) each form another hydrogen bond, intermolecularly with the O(3) and O(1) carbonyl groups of adjacent molecules at ($x$, $y-1$, $z$) and ($x$, $y+1$, $z$) forming continuous parallel ribbons along **b**. An additional C(8)···O(3), 2·870 (5) Å, intramolecular contact can be considered as a possible C—H···O hydrogen bond (Berkovitch-Yellin & Leiserowitz, 1984). A similar hydrogen-bonding scheme occurs in perezone (Soriano-García *et al.*, 1986).

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* A table of hydrogen-bond distances and angles has been deposited. See deposition footnote.

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# Structure of a Mixed Crystal of Sesquiterpene Stereoisomers of 2,2,6,10-Tetramethyl-8,11-dioxotricyclo[5.3.1.$0^{3,7}$]undec-9-en-9-yl Acetate (α- and β-Pipitzol Acetates)*

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**Abstract.** $C_{17}H_{22}O_4.C_{17}H_{22}O_4$, $M_r = 580·7$, orthorhombic, $P2_12_12_1$, $a = 11·271$ (6), $b = 15·334$ (6), $c = 18·206$ (7) Å, $V = 3147$ (1) Å$^3$, $Z = 4$, $D_x = 1·23$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·081$ mm$^{-1}$, $F(000) = 1248$, $T = 293$ K, final $R = 0·07$ for 1527 observed reflections. The molecular structure of the two stereoisomers is determined from the X-ray data and agrees with earlier chemical work. In both molecules the five-membered rings are *cis*-fused. In the α-isomer

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