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β-Isopipitzol

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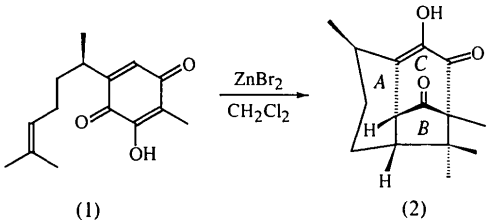
Abstract

The molecular structure of *β*-isopipitzol has been established as (1*R*,3*R*,6*R*,11*R*)-8-hydroxy-1,2,2,6-tetramethyltricyclo[5.2.2.$0^{3,11}$]undec-7-ene-9,10-dione, $C_{15}H_{20}O_3$. The absolute configurations of the asymmetric centers at C3 (*R*) and C11 (*R*) were determined, based on the known configuration of the methyl group at C6, by means of X-ray crystallographic analysis and they confirm the structure previously assigned from chemical and spectroscopic evidence.

Comment

The transformation of perezone, a natural sesquiterpene quinone, into isoperezone, (1), has been described previously (Rodríguez-Hernández *et al.*, 1994). Recently, we described the $ZnBr_2$-catalyzed conversion of isoperezone to *β*-isopipitzol, (2) (Yuste *et al.*, 1994). The formation of the tricyclic compound (2) was postulated to proceed *via* a Lewis acid-promoted *endo*-selective [$\pi4s + \pi2s$] intramolecular cycloaddition reaction. The X-ray crystallographic structure determination of (2) was undertaken in order to establish its conformation and molecular geometry.



(1) (2)

A perspective molecular drawing of compound (2) with the atomic numbering is shown in Fig. 1. The crystal structure, with the hydrogen-bonded chains along **y**, is shown in Fig. 2. The molecule of (2) has a tricyclic framework consisting of two six-membered rings (*A* and *C*) and a five-membered ring (*B*). Ring *A* has a boat conformation with the C12 methyl group oriented equatorially. Rings *A* and *B* are *cis* fused at the C3—C11 junction, with atoms H3 and H11 in a *β-cis* orientation. Rings *B* and *C* are fused along C1—C10—C11. Ring *C* has a distorted 10*β*-sofa conformation, with the C7—C8—C9 and C1—C10—C11 planes forming an angle of 61.3 (6)° with each other. The carbonyl group has a 10*β*-envelope conformation. Ring *A* is fused to ring *C* at the C7—C11 junction. The plane of the O8—C8—C7 enol fragment forms an angle of 105.1 (3)° with the C7—C6—C12 fragment of ring *A*. The C1—C2—C3—C11 fragment of ring *B* deviates slightly from planarity and forms an angle of 131.8 (3)° with the C1—C10—C11

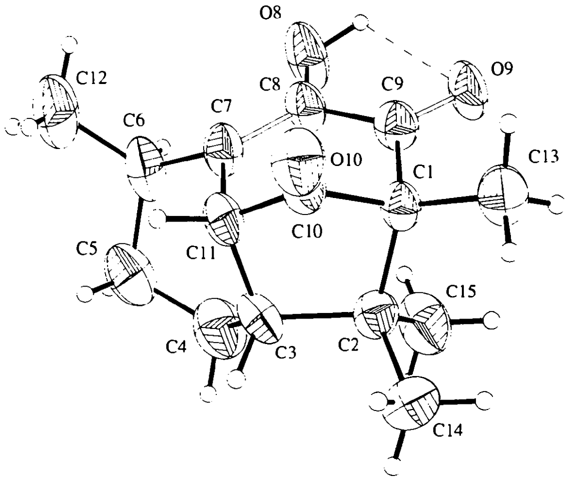


Fig. 1. The molecular structure of (2) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

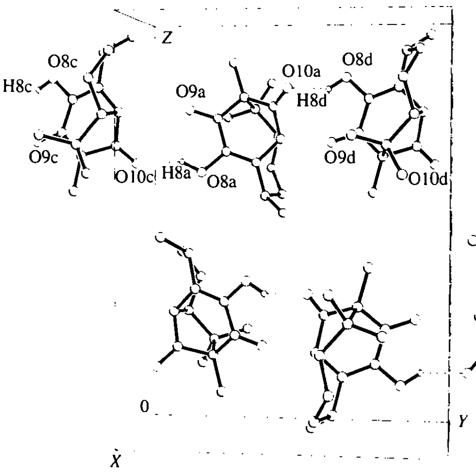


Fig. 2. A packing diagram of (2) showing the hydrogen-bonded chains of molecules along **y**.

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† Contribution No. 1337.

plane, with atom C10 out of the C1—C2—C3—C11 plane by 0.672 (4) Å. This ring has an aproximate half-chair conformation, similar to that in α- and β-pipitzol (Soriano-Garcia, Walls, Toscano & Lopéz-Célis, 1986; Evans, Yee, Garcia-Garibay & Trotter, 1994). These data confirm the structure previously assigned on the basis of chemical and spectroscopic evidence (Yuste *et al.*, 1994).

The absolute configuration of compound (2) was inferred according to the known stereochemistry at C6 of (6*R*)-(−)-perezone deduced from chemical studies (Arigoni & Jeger, 1954) and from a single-crystal X-ray analysis (Soriano-García, Toscano, Flores-Valverde, Montoya-Vega & Lopéz-Célis, 1986).

In the crystal, the molecule of (2) is in the enol form, with a C7═C8 double bond and an O8—H8 hydroxy group. There is an intramolecular O8—H8···O9 hydrogen bond [O8—H8 0.99 (3), H8···O9 2.19 (4), O8···O9 2.695 (5) Å and O8—H8···O9 109 (2)°] and an intermolecular O8—H8···O10^{i} hydrogen bond [O8—H8 0.99 (3), H8···O10^{i} 1.97 (3), O8···O10^{i} 2.789 (5) Å and O8—H8···O10^{i} 136 (2)°; symmetry code: (i) $2-x$, $y+\frac{1}{2}$, $\frac{3}{2}-z$], which result in the formation of chains along **y**. These hydrogen bonds stabilize the crystal structure (Fig. 2).

Experimental

The reaction of compound (1) with 2 equivalents of $ZnBr_2$ in dichloromethane solution at room temperature for 72 h produced three compounds, which were separated by flash chromatography. The least-polar product, (2), was obtained as colorless crystals in 20% yield (m.p. 419–421 K) by slow evaporation from an acetone–hexane solution.

Crystal data

$C_{15}H_{20}O_3$
$M_r = 248.3$
Orthorhombic
$P2_12_12_1$
$a = 6.752\ (1)$ Å
$b = 12.440\ (1)$ Å
$c = 16.251\ (1)$ Å
$V = 1365.1\ (1)$ Å^3
$Z = 4$
$D_x = 1.208$ Mg m^{-3}
D_m not measured

Cu *Kα* radiation
$\lambda = 1.5418$ Å
Cell parameters from 54 reflections
$\theta = 10.88$–$53.02°$
$\mu = 0.666$ mm^{-1}
$T = 293$ K
Hexagonal prism
0.24 × 0.16 × 0.12 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical (Siemens, 1994)
$T_{\min} = 0.879$, $T_{\max} = 0.925$
1079 measured reflections
1079 independent reflections
957 observed reflections [$F > 3\sigma(F)$]

$\theta_{\max} = 56.75°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 97 reflections
intensity decay: <1%

Refinement

Refinement on *F*
$R = 0.057$
$wR = 0.075$
$S = 1.32$
957 reflections
167 parameters
H atoms: see below
$w = 1[\sigma^2(F) + 0.0019F^2]$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Extinction correction: Larson (1970)
Extinction coefficient: 0.011 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.7341 (7)	0.2209 (3)	0.6747 (3)	0.040 (1)
C2	0.5083 (8)	0.2024 (4)	0.7019 (3)	0.047 (2)
C3	0.5201 (8)	0.1170 (4)	0.7745 (3)	0.050 (2)
C4	0.4334 (10)	0.1488 (6)	0.8590 (4)	0.077 (2)
C5	0.5565 (12)	0.0984 (5)	0.9285 (3)	0.079 (3)
C6	0.7724 (12)	0.1454 (4)	0.9306 (3)	0.066 (2)
C7	0.8219 (8)	0.1725 (3)	0.8428 (3)	0.044 (1)
C8	0.8704 (8)	0.2701 (3)	0.8163 (3)	0.047 (2)
O8	0.9315 (9)	0.3483 (3)	0.8687 (2)	0.079 (2)
C9	0.8355 (8)	0.3024 (4)	0.7305 (3)	0.044 (1)
O9	0.8737 (7)	0.3943 (3)	0.7084 (2)	0.064 (1)
C10	0.8194 (7)	0.1136 (3)	0.6980 (3)	0.039 (1)
O10	0.9167 (6)	0.0553 (3)	0.6540 (2)	0.056 (1)
C11	0.7428 (8)	0.0918 (3)	0.7828 (3)	0.041 (1)
C12	0.9107 (15)	0.0693 (6)	0.9728 (4)	0.092 (3)
C13	0.7657 (10)	0.2527 (4)	0.5847 (3)	0.060 (2)
C14	0.3938 (10)	0.1505 (6)	0.6318 (4)	0.079 (2)
C15	0.4091 (10)	0.3081 (5)	0.7235 (5)	0.077 (2)

Table 2. *Selected geometric parameters (Å, °)*

C1—C10	1.502 (6)	C8—C9	1.470 (7)
C6—C7	1.502 (7)	C9—O9	1.227 (6)
C6—C12	1.497 (10)	C10—O10	1.212 (6)
C7—C8	1.329 (6)	C10—C11	1.497 (6)
C8—O8	1.357 (6)		
C2—C1—C10	99.7 (3)	C7—C8—C9	121.1 (4)
C9—C1—C10	105.6 (4)	O8—C8—C9	116.7 (4)
C5—C6—C7	105.6 (5)	C1—C9—C8	117.1 (4)
C5—C6—C12	110.7 (5)	C1—C9—O9	122.7 (4)
C7—C6—C12	116.0 (6)	C8—C9—O9	120.0 (4)
C6—C7—C8	124.6 (4)	C1—C10—O10	126.3 (4)
C6—C7—C11	112.8 (4)	C1—C10—C11	105.1 (4)
C8—C7—C11	119.2 (4)	O10—C10—C11	128.4 (4)
C7—C8—O8	121.7 (4)		

Lorentz and polarization corrections were applied, and an analytical absorption correction was applied based on the face-indexed numerical method. All H atoms were located in a difference Fourier map and refined with a fixed isotropic temperature parameter *U* of 0.06 Å^2 and C—H 0.96 Å, except for H8 which was refined freely.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: direct methods (*SHELXTL/PC*; Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We thank José Luis Lugo Goytia for technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1206). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Nitroacetophenone

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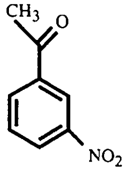
Abstract

Molecules of the title compound, $C_8H_7NO_3$, are connected by a number of C—H···O hydrogen bonds to form planar sheets. Both the nitro and carbonyl O atoms act as hydrogen-bond acceptors.

Comment

Recent reports have demonstrated that many organic reactions can take place in the absence of solvent by simply grinding the crystalline reactants together (Toda, 1993; Etter, Frankenbach & Bernstein, 1989). We are currently investigating the mechanistic aspects of the solvent-free Bayer–Villiger oxidation of ketones to esters by 3-chloroperbenzoic acid. As part of this study we have determined the structure of 3-nitroacetophenone (I), a compound which has been found by us to be particularly inert to such a solid-state oxidation reaction.



(I)

The bond lengths and angles for this molecule are very similar to those found for 4-nitroacetophenone (Kim, Boyko & Carpenter, 1973). Whereas 4-nitroacetophenone is almost planar, the 3-nitroacetophenone molecule is best described by three planar moieties: *A*, the benzene ring (C1–C6) to 0.002 (3) Å; *B*, the nitro group (N1, O1 and O2); *C*, the aceto group (C1, C7, C8 and O7) to 0.008 (4) Å. There is twist of approximately 1.8 (2)° about the C3—N1 bond such that the nitro group lies just out of the plane of the phenyl ring. The dihedral angle *AC* is 9.4 (2)°. This value seems within the typical range of other ring-substituted acetophenones such as 4-hydroxyacetophenone (Vainshtein, Lobanova & Gurskaya, 1974), 4-bromoacetophenone (Lipkowski & Tabaszewska, 1992), 4-aminoacetophenone (Haisa, Kashino, Yuasa & Akigawa, 1976) and also acetophenone (Tanimoto, Kobayashi, Nagakura & Saito, 1973).

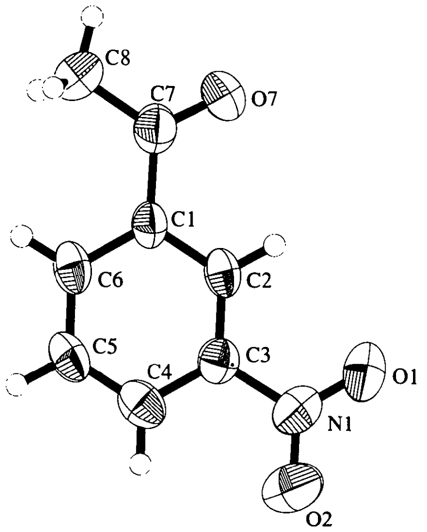


Fig. 1. *ORTEP*II (Johnson, 1976) diagram showing vibration ellipsoids at the 50% probability level.