Crystal Structure of 1 β -Hydroxy- β -homopipitzolone (9-Hydroxy-2,6,9-trimethyltricyclo[6,3,1,0^{1,6}]dodeca-5,10,11,12-tetraone)

Manuel SORIANO-GARCÍA,^{*†} Ezequiel HUIPE-NAVA,^{**} Virgilio Mendoza GONZÁLEZ,^{***} and Esther García GARIBAY^{***}

^{*}*Instituto de Química, UNAM, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México D. F.*

^{**}*Instituto Tecnológico, Av. Tecnológico 1500, C. P. 58120, Morelia, Mich., México*

^{***}*Instituto de Investigaciones Químico-Biológicas, U. M. S. N. H., Morelia Mich., México*

C₁₅H₁₈O₅ is orthorhombic, $P2_12_1$. The unit-cell dimensions at 293 K are $a = 6.526(3)$, $b = 10.247(4)$, $c = 21.008(13)$ Å, $V = 1404.8(12)$ Å³, $D_x = 1.316$ g/cm³, and $Z = 4$. The R value is 0.044 for 1288 observed reflections. The A, B and C rings adopt chair, twist, and half-chair conformations. The absolute configuration is inferred from the C6 stereochemistry of (+)-cedrol. The crystal structure is stabilized by an O-H...O hydrogen bond and van der Waals forces.

(Received February 1, 2002; Accepted June 19, 2002)

1 β -Hydroxy- β -homopipitzolone was prepared as a unique product of the spontaneous photochemical transformation¹ of the β -homopipitzolone² (**1**) (one of two isomers of the intermediate product in the homocedrole synthesis). This transformation results in a breaking of the double bond C9-C10, with the absorption of an oxygen atom, and migration of the hydrogen atom from the hydroxyl group O3 to the O2 atom. The title compound (**2**) was crystallized from ethyl acetate as yellow crystals with a melting point of 172 - 173°C.

Intensity data for the crystals of the title compound were collected by graphite-monochromatized Mo K α radiation at 293 K, and were corrected for Lorentz and polarization effects. No absorption correction was applied. The compound is sufficiently stable, and no change in the crystalline appearance was observed during X-ray exposure. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic temperature factors for the non-hydrogen atoms. The hydrogen atoms bonded to C atoms were assigned based on the expected bonding geometry, and the only one bonded to the O atom was found in a difference-Fourier map. All H atom positions and isotropic displacement parameters were not refined, with the exception of the H atom bonded to O2. The software used to prepare the material for publication was PARST97.³ Table 1 summarizes the crystal and experimental data. The molecular structure of the title compound is shown in Fig. 1.

Scheme 1

The structure of 1 β -hydroxy- β -homopipitzolone has been unequivocally established by an X-ray diffraction study as (1*S*,2*R*,6*R*,8*S*,9*S*)-9-hydroxy-2,6,9-trimethyltricyclo[6,3,1,0^{1,6}]dodeca-5,10,11,12-tetraone. The absolute configuration of (**2**) is inferred from the known C6 stereochemistry of (+)-cedrol deduced from chemical studies⁴ and from X-ray studies on cedryl chromate⁵ and β -pipitzol.⁶ The six-membered ring A and the five-membered ring B adopt

Table 1 Crystal and experimental data

Formula: C ₁₅ H ₁₈ O ₅
Formula weight = 278.30
Crystal system: orthorhombic
Space group: $P2_12_1$ $Z = 4$
$a = 6.526(3)$ Å
$b = 10.247(4)$ Å
$c = 21.008(13)$ Å
$V = 1404.8(12)$ Å ³
$D_x = 1.316$ g/cm ³
$D_c = 1.32$ g/cm ³ (measured by flotation)
$\mu(\text{Mo K}\alpha) = 0.099$ mm ⁻¹
$T = 293$ K
Color: yellow prisms
$F(0\ 0\ 0) = 592$
$0.3 \times 0.2 \times 0.6$ mm
Radiation: Mo K α ($\lambda = 0.7107$ Å)
$2\theta/\theta$ scans with $2\theta_{\text{max}} = 50^\circ$
$R = 0.044$ (on I)
$R_w = 0.088$ (on I)
$(\Delta\sigma)_{\text{max}} = 0.035$
$(\Delta\rho)_{\text{max}} = 0.143$ eÅ ⁻³
$(\Delta\rho)_{\text{min}} = -0.134$ eÅ ⁻³
No. of reflections used = 1288
No. of parameters refined = 185
Goodness-of-fit = 1.072
Measurement: Siemens P4/PC diffractometer
Program system: SHELXTL (PC version)
Structure determination: direct methods (SHELXS-86)
Refinement: full matrix (SHELXL-97)

[†] To whom correspondence should be addressed.

Fig. 1 Molecular structure of the title compound with atom labeling. The thermal ellipsoids are drawn at the 50% probability level.

chair and twist conformations, respectively, while the C ring has a half-chair conformation. The O2 addition at the β -face of the double bond, seems to be influenced by the near methyl group at C15 and the axial methylene hydrogen H8. The O2-H2A hydroxyl group forms an intermolecular hydrogen bond with O5 carbonyl group of a molecule symmetry related by screw axis 2_1 [$O2-H2 = 0.81(4)\text{\AA}$; $H2A\cdots O5 = 1.99(4)\text{\AA}$; $O2\cdots O5 = 2.789(3)\text{\AA}$ and $O2-H2A\cdots O5 = 167(4)^\circ$]. The molecules are held in the crystal by van der Waals forces.

Acknowledgements

Contribution No. 1762 of the Instituto de Quimica, UNAM.

References

1. V. Mendoza, E. García, J. A. Guzmán, L. Chacon, E.

Table 2 Final atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2$)^a

Atom	x	y	z	U_{iso}
O1	0.6266(5)	-0.2116(3)	0.64905(14)	0.0617(9)
O2	0.2417(4)	0.2048(2)	0.48289(12)	0.0450(7)
O3	-0.0823(5)	-0.0291(3)	0.47330(14)	0.0684(10)
O4	-0.1439(4)	0.0269(3)	0.59940(14)	0.0538(8)
O5	0.4670(4)	0.1938(2)	0.60598(11)	0.0403(6)
C1	0.2179(5)	0.0186(3)	0.61997(16)	0.0300(9)
C2	0.1717(6)	0.0562(4)	0.68885(16)	0.0437(10)
C3	0.3550(7)	0.0358(4)	0.73101(18)	0.0553(12)
C4	0.4283(8)	-0.1053(4)	0.72870(19)	0.0622(13)
C5	0.4754(7)	-0.1506(4)	0.66200(18)	0.0431(10)
C6	0.3129(5)	-0.1223(3)	0.61053(16)	0.0328(9)
C7	0.4126(5)	-0.1180(3)	0.54331(16)	0.0345(9)
C8	0.4260(5)	0.0266(3)	0.52457(15)	0.0298(9)
C9	0.2541(6)	0.0659(3)	0.47800(16)	0.0351(9)
C10	0.0544(6)	0.0150(4)	0.50458(18)	0.0362(9)
C11	0.0260(6)	0.0229(3)	0.57781(18)	0.0359(9)
C12	0.3817(5)	0.0978(3)	0.58573(16)	0.0282(8)
C13	0.0883(7)	0.1955(4)	0.69521(18)	0.0595(13)
C14	0.1547(6)	-0.2333(4)	0.6164(2)	0.0487(11)
C15	0.2924(7)	0.0219(4)	0.41027(16)	0.0522(12)

a. $U_{eq} = (1/3)\sum_i\sum_j U_{ij}(a_i^*a_j^*)(a_i\cdot a_j)$.

- Huipé, and S. V. Lindeman. XXVIII Congreso Mexicano de Química Pura y Aplicada, Puerto Vallarta, Jal., México, **1992**, Abstract No. 261.
- V. Mendoza, E. García, M. Reyes, and J. A. Guzmán, XXIV Congreso Mexicano de Química Pura y Aplicada, Querétaro, Qro., México, **1988**, Abstract No. 161.
- M. Nardelli, *J. Appl. Cryst.*, **1995**, 28, 659.
- G. Stork and F. H. Clarke Jr., *J. Am. Chem. Soc.*, **1961**, 83, 3114.
- V. Amirthalingam, D. F. Grant, and A. Senol, *Acta Crystallogr.*, **1972**, B28, 1340.
- M. Soriano-García, F. Walls, and R. A. Toscano, *Acta Crystallogr.*, **1986**, C42, 329.