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β-Homopipitzolone

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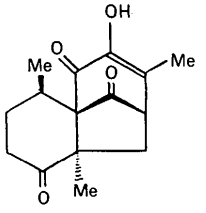
Abstract

The structure of β-homopipitzolone (one of the two isomers of an intermediate product in the homocedrole synthesis) has been unequivocally established as 10-hydroxy-2,6,9-trimethyltricyclo[6.3.1.$0^{1,6}$]dodeca-9-ene-5,11,12-trione with relative 1*R*,2*R*,6*R*,8*S* configuration.

Comment

The thermal (Walls, Padilla, Joseph-Nathan, Giral & Romo, 1965; Joseph-Nathan, Mendoza & Garcia, 1977) and catalytic (Sanchez, Yanez, Enriquez & Joseph-Nathan, 1981) transformations of perezone produce a mixture of α- and β-pipitzols. In continuation of our investigations in this field, we have prepared the new α- and β-homopipitzolone mixture from modified perezone (Mendoza, Garcia, Reyes &

Guzman, 1988). However, the structures of these compounds have not been assigned unambiguously. Thus, the X-ray diffraction study of β-homopipitzolone (1) was undertaken.



(1)

Molecule (1) has a tricyclic framework. The cycle *A* has a distorted chair conformation with the C13- and C14-methyl groups in equatorial and axial orientations, respectively. The five-membered cycle *B*, *cis*-fused to the cycle *A*, has a conformation intermediate between $1\alpha,12\beta$-twist and 12β-envelope. The six-membered cycle *C* has a distorted 12β-sofa conformation. The absolute chirality of molecule (1) could not be established objectively and was arbitrarily assigned as $1R,2R,6R,8S$.

The molecule (1) exists, in the crystal, in the enol form with a C9=C10 double bond [1.337 (3) Å] and an O4-hydroxy group. The latter takes part in intermolecular hydrogen bonding with the O2-oxo group of the molecule related by 2_1 axes [O4···O2′ 2.735 (2), O4—H4 0.86 (2), H4···O2′ 2.18 (2) Å, O4—H4···O2′ 122 (2)°] which results in the formation of infinite chains along the *x* axis. The relative weakness of this hydrogen bond may be explained by the participation of the O4—H4 group in the additional intramolecular interaction O4—H4···O1 [O4···O1 2.712 (3), H4···O1 2.21 (3) Å, O4—H4···O1 117 (2)°].

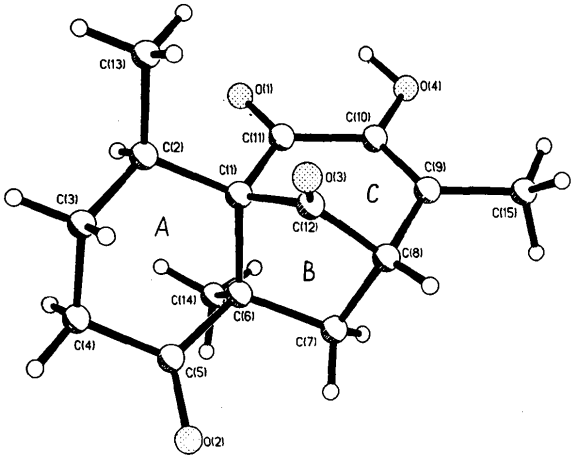


Fig. 1. General view of the molecule (1).

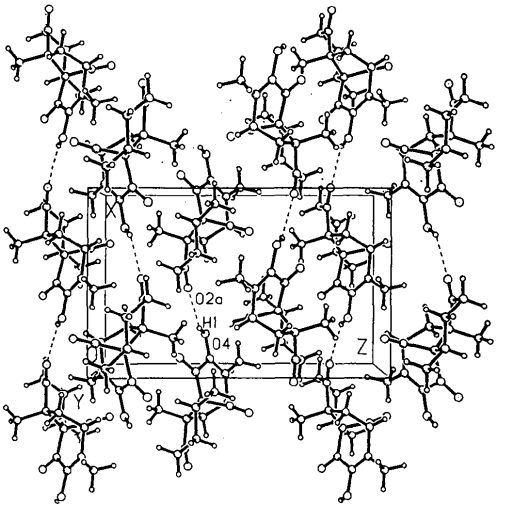


Fig. 2. Crystal structure of (1) with the hydrogen-bonded chains of molecules along the *x* axis.

Experimental

Crystal data

$C_{15}H_{18}O_4$
M_r = 262.3
Orthorhombic
$P2_12_12_1$
a = 9.045 (3) Å
b = 9.670 (3) Å
c = 14.807 (4) Å
V = 1295.1 (7) Å^3
Z = 4
D_x = 1.345 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 24 reflections
θ = 24-26°
μ = 0.097 mm^{-1}
T = 153 K
Needles
0.75 × 0.10 × 0.05 mm
Colourless
Crystal source: from warm ethanol solution

Data collection

Siemens *P3/PC* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1802 measured reflections
1802 independent reflections
1802 observed reflections [$F \geq 6.0\sigma(F)$]

θ_{max} = 50°
h = 0 → 11
k = 0 → 12
l = 0 → 19
2 standard reflections monitored every 98 reflections
intensity variation: ±2.1%

Refinement

Refinement on F
Final R = 0.033
wR = 0.032
S = 0.52
1453 reflections
244 parameters
All H-atom parameters refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.15
$\Delta\rho_{max}$ = 0.158 e Å^{-3}
$\Delta\rho_{min}$ = −0.188 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
O1	0.0825 (2)	0.7040 (2)	0.2957 (1)	0.032 (1)
O2	−0.5281 (2)	0.5810 (2)	0.3200 (2)	0.044 (1)
O3	−0.2181 (2)	0.7018 (2)	0.5323 (1)	0.035 (1)
O4	0.2055 (2)	0.4820 (2)	0.3787 (1)	0.035 (1)
C1	−0.1552 (2)	0.6860 (2)	0.3701 (1)	0.020 (1)
C2	−0.1740 (3)	0.8419 (2)	0.3523 (2)	0.024 (1)
C3	−0.3356 (3)	0.8855 (3)	0.3554 (2)	0.033 (1)
C4	−0.4304 (3)	0.8030 (3)	0.2897 (2)	0.037 (1)
C5	−0.4196 (3)	0.6519 (3)	0.3108 (2)	0.027 (1)
C6	−0.2639 (2)	0.5881 (3)	0.3159 (2)	0.021 (1)
C7	−0.2687 (3)	0.4501 (3)	0.3697 (2)	0.029 (1)
C8	−0.1845 (3)	0.4779 (3)	0.4586 (2)	0.026 (1)
C9	−0.0226 (3)	0.4407 (3)	0.4502 (2)	0.027 (1)
C10	0.0621 (3)	0.5170 (3)	0.3955 (2)	0.027 (1)
C11	0.0051 (2)	0.6411 (2)	0.3487 (1)	0.022 (1)
C12	−0.1888 (3)	0.6350 (3)	0.4666 (2)	0.023 (1)
C13	−0.0814 (3)	0.9316 (3)	0.4163 (2)	0.033 (1)
C14	−0.2144 (3)	0.5653 (3)	0.2173 (2)	0.031 (1)
C15	0.0330 (4)	0.3157 (3)	0.4994 (2)	0.042 (1)

Table 2. *Geometric parameters* (Å, °)

O1—C11	1.215 (3)	C4—C5	1.497 (4)
O2—C5	1.204 (3)	C5—C6	1.540 (3)
O3—C12	1.197 (3)	C6—C7	1.555 (4)
O4—C10	1.363 (3)	C6—C14	1.544 (3)
C1—C2	1.540 (3)	C7—C8	1.544 (4)
C1—C6	1.583 (3)	C8—C9	1.513 (4)
C1—C11	1.546 (3)	C8—C12	1.525 (3)
C1—C12	1.542 (3)	C9—C10	1.337 (3)
C2—C3	1.522 (4)	C9—C15	1.499 (4)
C2—C13	1.534 (4)	C10—C11	1.479 (3)
C3—C4	1.523 (4)		
C2—C1—C6	115.5 (2)	C5—C6—C14	106.0 (2)
C2—C1—C11	110.1 (2)	C7—C6—C14	111.8 (2)
C2—C1—C12	116.7 (2)	C6—C7—C8	105.8 (2)
C6—C1—C11	108.1 (2)	C7—C8—C9	111.5 (2)
C6—C1—C12	99.0 (2)	C7—C8—C12	103.2 (2)
C11—C1—C12	106.5 (2)	C9—C8—C12	105.5 (2)
C1—C2—C3	111.9 (2)	C8—C9—C10	118.3 (2)
C1—C2—C13	112.8 (2)	C8—C9—C15	118.5 (2)
C3—C2—C13	110.4 (2)	C10—C9—C15	123.2 (2)
C2—C3—C4	112.1 (2)	O4—C10—C9	121.3 (2)
C3—C4—C5	110.0 (2)	O4—C10—C11	116.6 (2)
O2—C5—C4	121.8 (2)	C9—C10—C11	122.1 (2)
O2—C5—C6	120.7 (2)	O1—C11—C1	122.1 (2)
C4—C5—C6	117.5 (2)	O1—C11—C10	120.5 (2)
C1—C6—C5	110.7 (2)	C1—C11—C10	117.3 (2)
C1—C6—C7	105.8 (2)	O3—C12—C1	128.6 (2)
C1—C6—C14	112.6 (2)	O3—C12—C8	127.4 (2)
C5—C6—C7	110.1 (2)	C1—C12—C8	103.9 (2)
C1—C2—C3—C4	−55.9 (3)	C8—C12—C1—C6	46.7 (2)
C2—C3—C4—C5	58.5 (3)	C12—C1—C6—C7	−33.0 (2)
C3—C4—C5—C6	−53.7 (3)	C1—C12—C8—C9	74.1 (3)
C4—C5—C6—C1	43.7 (3)	C12—C8—C9—C10	−43.5 (3)
C5—C6—C1—C2	−39.3 (3)	C8—C9—C10—C11	4.4 (4)
C6—C1—C2—C3	46.6 (3)	C9—C10—C11—C1	3.9 (3)
C1—C6—C7—C8	8.2 (3)	C10—C11—C1—C12	27.4 (2)
C6—C7—C8—C12	20.6 (3)	C11—C1—C12—C8	−65.3 (2)
C7—C8—C12—C1	−42.9 (3)		

All calculations were performed by the *SHELXTL-Plus* programs (Sheldrick, 1987) with an IBM-PC/AT computer. Absolute configuration was not determined because of the lack of anomalous scatterers.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55940 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: VS1002]

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Structure of 4-Nitrobenzyl *N*-(4-Nitrobenzyloxy)trifluoroacetimidate

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Abstract

The molecular structure of the title compound is characterized by the *cisoid* geometry of the oximino-ether residue.

Comment

In experiments that were directed to the synthesis of polyamine analogues, a series of condensations were carried out between primary alcohols and *N*-trifluoroacetamidooxyalkyl derivatives by the Mitsunobu reaction (Mitsunobu, 1981). It was hoped that the condensation would lead to *N*-alkyltrifluoroacetamidooxy derivatives. However, the sole

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