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Structure of 1-Hydroxy-5,11,15-trimethylpentacyclo[9.5.1.0^{2,9}.0^{4,8}.0^{12,16}]heptadec-2(9)-en-3-one, C₂₀H₂₈O₂*

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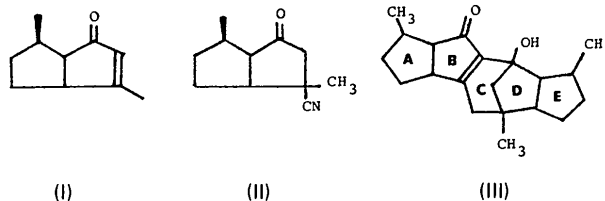
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Abstract. $M_r = 300.4$, orthorhombic, $P2_12_12_1$, $a = 10.677$ (4), $b = 7.205$ (2), $c = 22.749$ (4) Å, $V = 1750$ Å³, $D_x = 1.13$ Mg m⁻³, $Z = 4$, $F(000) = 656$, $\text{Cu K}\alpha$, $\lambda = 1.54178$ Å, $\mu = 0.522$ mm⁻¹, $T = 300$ K, $R = 0.050$ for 1095 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. The molecule is stabilized by the formation of an intramolecular hydrogen bond between the hydroxyl and carbonyl groups [H(O1)⋯O(2) 2.047 (4) Å, O(1)–H(O1)⋯O(2) 152.8 (2)°].

Introduction. In the course of synthetic studies directed towards α -piztol (Walls, Padilla, Joseph-Nathan, Giral, Escobar & Romo, 1966) we obtained an intermediate (III) whose structure required elucidation.

The ketonitrile (II) was obtained from the enone (I) (Achmad & Cavill, 1965; Setzer, Ortiz & Walls, 1980) by conjugated addition of HCN when treated with KCN in aqueous ethanol in the presence of ammonium chloride (Rodig & Johnston, 1969). Treatment of ketonitrile (II) with sodium hydride in refluxing benzene afforded (I) and the pentacyclic (III).



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

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Experimental. Colourless crystal 0.20 × 0.22 × 0.40 mm. Nicolet R3m automated diffractometer, graphite-monochromated Cu K α radiation. Unit-cell dimensions by least squares from the 2 θ values of 45 high-angle reflections. Reflections in a single octant of reciprocal space measured with a maximum h, k, l 12, 8, 25. θ -2 θ scans up to 2 θ = 115°. 1222 reflections measured, 1095 observed [$I > 2.5\sigma(I)$]. Two reference reflections checked every 100 measurements: constant within 3.0% of their initial intensities. Intensities corrected for Lorentz-polarization factor but not for absorption. Data adjusted to an approximately absolute scale and an overall U value of 0.057 Å². Structure solved by direct methods and refined by least-squares using a cascade-matrix procedure; coordinates and anisotropic temperature factors refined for the non-H atoms; hydroxylic H refined, other H atoms in calculated positions with fixed isotropic $U = 0.06$ Å². Final $R = 0.050$, $R_w = 0.063$. $\sum w|\Delta F|^2$ minimized; $w^{-1} = [\sigma^2(F_o) + 0.00486(F_o)^2]$, where σ is the standard deviation of the observed amplitudes, based on counting statistics. In last cycle $(\Delta/\sigma)_{\max} = 0.2$. Residual electron density in final difference map within ± 0.2 e Å⁻³. Atomic scattering factors with anomalous-dispersion corrections for C and O from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction. All computations performed on a Nova 4 computer and plots drawn on a Tektronix plotter with the *SHELXTL* system of programs (Sheldrick, 1981).

Table 1. Final fractional positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for non-hydrogen atoms

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

	x	y	z	$U_{\text{eq}}(\text{Å}^2)$
C(1)	3135 (4)	2779 (5)	707 (2)	60 (1)
C(2)	4440 (4)	2476 (5)	923 (2)	53 (1)
C(3)	5151 (5)	3665 (6)	1314 (2)	67 (1)
C(4)	6338 (4)	2673 (7)	1482 (2)	65 (1)
C(5)	6394 (4)	2146 (8)	2142 (2)	76 (2)
C(6)	6988 (5)	221 (8)	2138 (2)	82 (2)
C(7)	6392 (5)	-735 (7)	1607 (2)	72 (2)
C(8)	6293 (4)	841 (5)	1145 (2)	53 (1)
C(9)	5068 (3)	917 (5)	822 (1)	48 (1)
C(10)	4561 (4)	-548 (5)	433 (2)	55 (1)
C(11)	3180 (4)	-175 (6)	252 (2)	55 (1)
C(12)	2315 (4)	-357 (5)	800 (2)	51 (1)
C(13)	933 (4)	-882 (7)	677 (2)	73 (2)
C(14)	209 (4)	281 (7)	1109 (2)	78 (2)
C(15)	874 (4)	2148 (7)	1091 (2)	76 (2)
C(16)	2256 (4)	1590 (5)	1088 (2)	54 (1)
C(17)	3025 (4)	1859 (6)	102 (2)	65 (1)
C(18)	7062 (7)	3515 (11)	2515 (2)	124 (3)
C(19)	2868 (5)	-1469 (7)	-257 (2)	76 (2)
C(20)	543 (6)	3484 (10)	1577 (3)	120 (3)
O(1)	2807 (3)	4707 (4)	679 (2)	86 (1)
O(2)	4815 (4)	5203 (4)	1497 (2)	98 (1)

Discussion. Table 1 gives the final atomic parameters.* The molecular structure with the numbering scheme is illustrated in Fig. 1. Bond lengths, bond angles and selected torsion angles are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters, atomic coordinates of H atoms and interatomic distances involving H atoms, and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38974 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(1)-C(2)	1.493 (6)	C(1)-C(16)	1.537 (6)
C(1)-C(17)	1.533 (6)	C(1)-O(1)	1.435 (5)
C(2)-C(3)	1.450 (6)	C(2)-C(9)	1.328 (5)
C(3)-C(4)	1.505 (7)	C(3)-O(2)	1.237 (5)
C(4)-C(5)	1.549 (6)	C(4)-C(8)	1.527 (6)
C(5)-C(6)	1.526 (8)	C(5)-C(18)	1.484 (8)
C(6)-C(7)	1.529 (6)	C(7)-C(8)	1.551 (6)
C(8)-C(9)	1.503 (5)	C(9)-C(10)	1.479 (5)
C(10)-C(11)	1.554 (6)	C(11)-C(12)	1.557 (5)
C(11)-C(17)	1.515 (6)	C(11)-C(19)	1.524 (6)
C(12)-C(13)	1.549 (6)	C(12)-C(16)	1.549 (5)
C(13)-C(14)	1.504 (7)	C(14)-C(15)	1.521 (7)
C(15)-C(16)	1.530 (6)	C(15)-C(20)	1.509 (8)
C(2)-C(1)-C(16)	107.6 (3)	C(2)-C(1)-C(17)	107.6 (3)
C(16)-C(1)-C(17)	102.6 (3)	C(2)-C(1)-O(1)	112.6 (3)
C(16)-C(1)-O(1)	114.6 (3)	C(17)-C(1)-O(1)	111.1 (4)
C(1)-C(2)-C(3)	127.1 (4)	C(1)-C(2)-C(9)	122.5 (3)
C(3)-C(2)-C(9)	110.0 (3)	C(2)-C(3)-C(4)	108.4 (4)
C(2)-C(3)-O(2)	125.7 (4)	C(4)-C(3)-O(2)	125.8 (4)
C(3)-C(4)-C(5)	113.3 (4)	C(3)-C(4)-C(8)	104.9 (3)
C(5)-C(4)-C(8)	106.0 (4)	C(4)-C(5)-C(6)	103.5 (4)
C(4)-C(5)-C(18)	114.2 (5)	C(6)-C(5)-C(18)	114.1 (4)
C(5)-C(6)-C(7)	104.0 (4)	C(6)-C(7)-C(8)	103.5 (4)
C(4)-C(8)-C(7)	106.9 (3)	C(4)-C(8)-C(9)	104.0 (3)
C(7)-C(8)-C(9)	114.7 (3)	C(2)-C(8)-C(8)	112.7 (3)
C(2)-C(9)-C(10)	121.5 (3)	C(8)-C(9)-C(10)	125.8 (3)
C(9)-C(10)-C(11)	112.5 (3)	C(10)-C(11)-C(12)	109.6 (3)
C(10)-C(11)-C(17)	109.3 (3)	C(12)-C(11)-C(17)	101.4 (3)
C(10)-C(11)-C(19)	107.7 (3)	C(12)-C(11)-C(19)	115.3 (3)
C(17)-C(11)-C(19)	113.4 (3)	C(11)-C(12)-C(13)	116.2 (3)
C(11)-C(12)-C(16)	106.6 (3)	C(13)-C(12)-C(16)	105.0 (3)
C(12)-C(13)-C(14)	103.6 (4)	C(13)-C(14)-C(15)	103.6 (4)
C(14)-C(15)-C(16)	102.6 (4)	C(14)-C(15)-C(20)	115.8 (4)
C(16)-C(15)-C(20)	113.4 (4)	C(1)-C(16)-C(12)	104.0 (3)
C(1)-C(16)-C(15)	116.4 (3)	C(12)-C(16)-C(15)	106.2 (3)
C(1)-C(17)-C(11)	102.0 (3)		
Ring A (cyclopentane)		Ring D (cyclopentane)	
C(8)-C(4)-C(5)-C(6)	26.0 (5)	C(17)-C(11)-C(12)-C(16)	-26.3 (4)
C(4)-C(5)-C(6)-C(7)	-39.6 (5)	C(11)-C(12)-C(16)-C(11)	-2.3 (4)
C(5)-C(6)-C(7)-C(8)	37.7 (4)	C(17)-C(1)-C(16)-C(12)	29.9 (4)
C(6)-C(7)-C(8)-C(4)	-21.3 (4)	C(16)-C(1)-C(17)-C(11)	-47.5 (4)
C(5)-C(4)-C(8)-C(7)	-2.9 (4)	C(12)-C(11)-C(17)-C(1)	44.9 (4)
Ring B (cyclopentane)		Ring E (cyclopentane)	
C(9)-C(2)-C(3)-C(4)	-1.7 (5)	C(16)-C(12)-C(13)-C(14)	-23.3 (4)
C(2)-C(3)-C(4)-C(8)	1.8 (4)	C(12)-C(13)-C(14)-C(15)	41.2 (4)
C(3)-C(4)-C(8)-C(9)	-1.2 (4)	C(13)-C(14)-C(15)-C(16)	-42.8 (4)
C(4)-C(8)-C(9)-C(2)	0.2 (4)	C(14)-C(15)-C(16)-C(12)	27.5 (4)
C(3)-C(2)-C(9)-C(8)	0.9 (4)	C(13)-C(12)-C(16)-C(15)	-2.8 (4)
Ring C (cyclohexene)			
C(17)-C(1)-C(2)-C(9)	-36.6 (5)		
C(1)-C(2)-C(9)-C(10)	6.6 (6)		
C(2)-C(9)-C(10)-C(11)	-8.9 (5)		
C(9)-C(10)-C(11)-C(17)	42.6 (4)		
C(10)-C(11)-C(17)-C(1)	-70.7 (4)		
C(2)-C(1)-C(17)-C(11)	65.9 (4)		

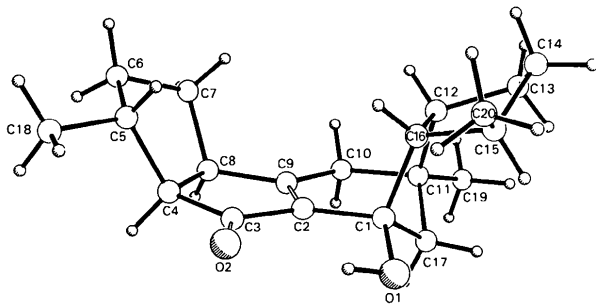


Fig. 1. The molecular structure of the title compound (III) showing the atom labelling.

The carbon skeleton of the molecule comprises a system of five *cis*-fused rings which all have tetrahedral atoms with the exception of C(2), C(3) and C(9).

Three of the five-membered rings have non-planar 'envelope' conformations (see Table 3),* but in the case of ring *B* the presence of a double bond between C(2) and C(9) and the carbonyl substituent on C(3) cause this ring to be planar.

In the six-membered ring, four neighbouring atoms lie approximately in a plane resulting in a half-chair conformation. The substituents at C(1) and C(11) are in equatorial positions with torsion angles C(19)–C(11)–C(17)–C(1) = 169.2 (4) and O(1)–C(1)–C(17)–C(11) = –170.4 (3)°.

Bond lengths and angles generally appear to be normal and, considering the complex framework involved, are not significantly different from the expected values. The C=O bond C(3)–O(2) [1.237 (5) Å] agrees well with the accepted value of 1.215 (5) Å (Sutton, 1965).

The bond length C(2)–C(3) [1.450 (6) Å] shows the influence of conjugation between the keto group and the double bond C(2)–C(9). The torsion angle C(9)–C(2)–C(3)–O(2) is –179.1 (4)°. The considerable double-bond character in the C(2)–C(3) bond is indicated by the shortening of this bond by 0.055 Å, compared to the C(3)–C(4) bond length.

The molecule is stabilized by the formation of an intramolecular hydrogen bond between the 1-hydroxyl group and the carbonyl oxygen, O(2). The H(O1)···O(2) distance is 2.047 (4) Å and the O(1)–H(O1)···O(2) angle is 152.8 (2)°.

* Table 3 which summarizes the geometries of the rings and lists their asymmetry parameters has been deposited. See deposition footnote.

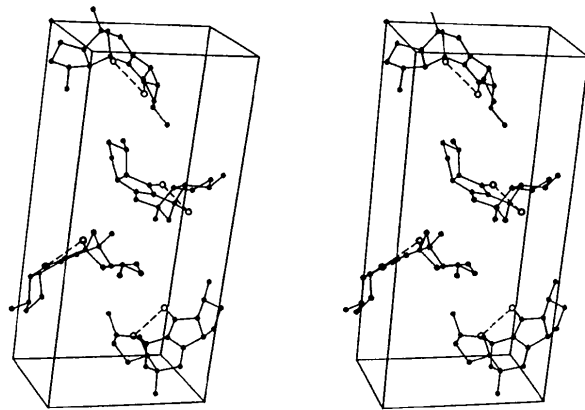


Fig. 2. Stereoscopic view of the unit cell showing the intramolecular hydrogen bonding.

The intramolecular hydrogen bonding is shown by broken lines in the stereoscopic drawing of the unit cell in Fig. 2. There is only one intermolecular approach <3.4 Å, O(2)···C(7) ($x, 1 + y, z$) 3.386 (5) Å. The molecules are held in the crystal by van der Waals forces.

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