

acid. The apparent change in the bond lengths of the ethyl group might be due to the strong thermal vibrations of C(8) and C(9). The ester moiety is *cis* to the C=O about the C–O bond and the phenylhydrazone group is in the *anti* position to the ethyl group about the N(1)–C(2) bond; the C(10)–N(2)–N(1)–C(2) torsion angle is $-178.4(3)^\circ$.

The bond lengths in the propionate group are normal and agree with the standard values associated with C(sp^2)–C(sp^3) single-bond, C(sp^2)–C(sp^2) single-bond and C(sp^2)–O single-bond distances. The geometry of the benzene and furan rings is normal and they are essentially planar. The dihedral angle between the two planes is $82.4(4)^\circ$.

The molecules are held by hydrogen bonding along a between N(2) and O(2) of the molecule at $\frac{1}{2} + x, \bar{y}, z$ [N(2)···O(2) = 2.971 \AA and N(2)–HN(2)···O(2) = 143°]. All other contacts are of van der Waals type.

Table 2. Intermolecular contacts less than 3.6 \AA

Symmetry code: (i) x, y, z ; (ii) $\bar{x}, \bar{y}, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, \bar{y}, z$; (iv) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (v) $x, 1 + y, z$.

C(13)–C(9 ⁱⁱ)	3.569 (6)	C(13)–C(1 ^v)	3.559 (6)
C(12)–C(15 ⁱⁱⁱ)	3.596 (5)	C(13)–O(2 ^v)	3.469 (5)
C(15)–O(2 ⁱⁱⁱ)	3.382 (4)	C(14)–C(2 ^v)	3.593 (5)
C(5)–O(3 ⁱⁱⁱ)	3.573 (4)	C(14)–C(1 ^v)	3.405 (5)
C(3)–O(2 ⁱⁱⁱ)	3.399 (4)	C(14)–O(1 ^v)	3.574 (5)
C(4)–O(2 ⁱⁱⁱ)	3.562 (4)	C(15)–O(1 ^v)	3.578 (5)
N(2)–C(7 ^{iv})	3.513 (5)		

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(1 β ,9 β)-1-Methoxypicras-12-en-16-one

BY R. CURTIS HALTIWANGER

Department of Chemistry, University of Colorado, Boulder, Colorado 80309, USA

AND PAUL A. GRIECO

Department of Chemistry, Indiana University, Bloomington, Indiana 47405, USA

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Abstract. C₂₁H₃₂O₃, $M_r = 332.484$, monoclinic, $P2_1/n$, $a = 8.522(2)$, $b = 22.773(4)$, $c = 10.190(2) \text{ \AA}$, $\beta = 111.32(2)^\circ$, $U = 1842.4(6) \text{ \AA}^3$, $Z = 4$, $d_m = 1.22$ (by flotation), $d_c = 1.20 \text{ Mg m}^{-3}$, $F(000) = 728$. The structure was solved by direct methods. Full-matrix least-squares refinement converged to $R = 0.056$ for 1713 observed reflections. (1 β ,9 β)-1-Methoxypicras-12-en-16-one has the tetracyclic framework of quassinoids (e.g. quassin) and, with the exception of the

The intermolecular contacts less than 3.6 \AA are given in Table 2.

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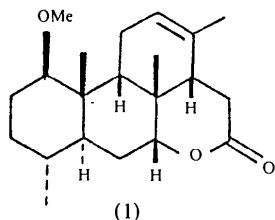
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configuration at C(9), six of the seven chiral centers found in quassin.

Introduction. The synthesis of (1 β ,9 β)-1-hydroxypicras-12-en-16-one and its derivative (1 β ,9 β)-1-methoxypicras-12-en-16-one (1) has been described by Grieco, Vidari, Ferriño & Haltiwanger (1980). Subsequently, Grieco, Ferriño & Vidari (1980) have reported the total synthesis of (\pm)-quassin in which (1)

was a key intermediate. To confirm the stereochemical assignments about the chiral centers, this single-crystal X-ray diffraction study was undertaken.



A single crystal of (1) (approximate dimensions 0.4 × 0.3 × 0.3 mm) was selected and mounted using an epoxy resin. Intensity data were collected at room temperature (~295 K) on a Syntex (now Nicolet) P1 auto diffractometer (Mo K α radiation, graphite monochromator, $2\theta_m = 12.2^\circ$). The cell dimensions were determined on the diffractometer and were refined by least-squares fit of the parameters to 15 centered reflections using programs supplied by Syntex Analytical Instruments (now Nicolet XRD Corporation). Intensity measurements were made using θ - 2θ scanning techniques. The scan speed was varied from 2° min^{-1} to $24^\circ \text{ min}^{-1}$ as a function of intensity (150 to 1500 counts s^{-1}). Backgrounds were measured in a stationary mode at the beginning and end of each measurement cycle for a total time equal to one-half the scan time. The space group was determined by examination of the intensity data for systematic absences. The absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, uniquely conform to $P2_1/n$.

Reflections were surveyed within a single unique quadrant over the range $3.0^\circ \leq 2\theta \leq 50.0^\circ$. Standards monitored every 100 measurement cycles showed no significant variation over the course of the data collection. Data were corrected for Lorentz and polarization effects. Of the 3240 independent reflections surveyed, 1713 were determined to have intensity significantly above background and were used for the solution and refinement of the structure. A reflection was considered significant when $F_o^2 > 3.0\sigma(F_o^2)$ where $\sigma(F_o^2) = (1/Lp)\{TSC + \text{BACK} + [P(TSC - \text{BACK})]^2\}^{1/2}$. TSC is the total counts collected during the measurement cycle and BACK is the number of counts accumulated during the background-counting portion of the measurement cycle. For P , a damping factor to down-weight stronger intensities, a value of 0.04 was used (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967). No correction was made for absorption [$\mu(\text{Mo K}\alpha) = 0.084 \text{ mm}^{-1}$].

The structure was solved by direct methods using the program MULTAN 78 (Main, Woolfson, Hull, Lessinger, Germain & Declercq, 1978). Isotropic full-matrix least-squares refinement on this model with atom types assigned on the basis of peak height,

Table 1. Atomic coordinates for nonhydrogen atoms

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

	x	y	z	B_{eq} (\AA^2)
O(1)	0.1480 (3)	0.3429 (1)	0.2093 (3)	3.9 (1)
O(2)	0.6527 (3)	0.4265 (1)	0.7348 (3)	3.7 (1)
O(3)	0.6609 (4)	0.5056 (1)	0.8629 (3)	5.4 (2)
C(1)	0.3240 (5)	0.3570 (2)	0.2579 (4)	3.2 (2)
C(2)	0.4075 (5)	0.3309 (2)	0.1631 (4)	3.9 (2)
C(3)	0.5957 (5)	0.3434 (2)	0.2208 (4)	4.4 (2)
C(4)	0.6822 (5)	0.3237 (2)	0.3731 (4)	3.7 (2)
C(5)	0.5926 (5)	0.3520 (2)	0.4638 (4)	3.1 (2)
C(6)	0.6803 (5)	0.3376 (2)	0.6200 (4)	3.7 (2)
C(7)	0.6001 (5)	0.3651 (2)	0.7166 (4)	3.3 (2)
C(8)	0.4090 (5)	0.3591 (2)	0.6687 (4)	3.0 (2)
C(9)	0.3220 (4)	0.3707 (2)	0.5063 (4)	2.9 (2)
C(10)	0.4041 (5)	0.3369 (2)	0.4132 (4)	2.9 (2)
C(11)	0.3095 (5)	0.4372 (2)	0.4739 (4)	3.4 (2)
C(12)	0.2311 (5)	0.4708 (2)	0.5600 (4)	4.0 (2)
C(13)	0.2376 (5)	0.4538 (2)	0.6853 (4)	4.0 (2)
C(14)	0.3414 (5)	0.4021 (2)	0.7583 (4)	3.7 (2)
C(15)	0.4924 (5)	0.4244 (2)	0.8851 (4)	3.8 (2)
C(16)	0.6085 (5)	0.4565 (2)	0.8305 (4)	3.4 (2)
C(17)	0.8696 (5)	0.3386 (2)	0.4240 (5)	5.3 (2)
C(18)	0.3745 (5)	0.2967 (2)	0.7131 (4)	4.3 (2)
C(19)	0.3729 (5)	0.2702 (2)	0.4159 (4)	3.9 (2)
C(20)	0.1431 (6)	0.4858 (2)	0.7645 (5)	6.4 (3)
C(21)	0.0465 (6)	0.3773 (2)	0.0945 (5)	5.0 (3)

geometry and chemical considerations converged with $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.14$. Refinement with all atoms treated anisotropically converged with $R = 0.119$. The positions of all 32 H atoms were located in the subsequent three-dimensional difference map. Positions for H atoms were calculated assuming a C—H bond length of 0.95 \AA and, as appropriate, sp^2 or sp^3 hybridization around the C atom. The H atoms were added to the model with isotropic thermal parameters. The entire model excluding H atoms was refined using full-matrix least-squares procedures to convergence; $R = 0.0565$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.0655$. The standard deviation of an observation of unit weight was 1.85. The maximum shift over error for all parameters was 0.06. The ratio of observations to parameters was 8 to 1. A final three-dimensional difference map was featureless. The weighting scheme used for all refinements was based on counting statistics where $w = 1/\sigma^2(F_o) = 4.0F_o^2/\sigma^2(F_o^2)$. The scattering factors used for O, C, and H were taken from *International Tables for X-ray Crystallography* (1974). Table 1 gives the final parameters for the atoms.* All calculations were performed using programs contained in or derived from the MULTAN 78 package, the Northwestern University

* Lists of structure factors, anisotropic thermal parameters, H-atom positions and valence angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36372 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Crystallographic Computing Library of J. A. Ibers, and routines supplied by Syntex (now Nicolet). The function minimized in all least-squares procedures was $\sum w(|F_o| - |F_c|)^2$.

Discussion. A view of (1) is shown in Fig. 1. Rings *A* and *B* of (1) are in chair configurations. Rings *C* and *D* are in envelope-like configurations. Carbon atoms C(2), C(3), C(5), C(7), C(8), and C(10) are approximately planar with C(8) 0.09 Å below the plane defined by all six atoms and C(10) 0.11 Å above. Bond lengths (Table 2) and bond angles are as expected.

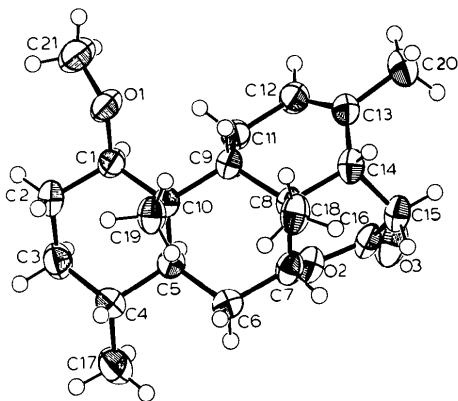


Fig. 1. ORTEP drawing (Johnson, 1965) of (1 β ,9 β)-1-methoxypicras-12-en-16-one showing the numbering scheme adopted. H atoms are included on an arbitrary scale. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Bond distances (Å)

O(1)—C(1)	1.435 (4)	C(7)—C(8)	1.527 (5)
O(1)—C(21)	1.413 (5)	C(8)—C(9)	1.571 (5)
O(2)—C(7)	1.460 (4)	C(8)—C(14)	1.582 (5)
O(2)—C(16)	1.352 (4)	C(8)—C(18)	1.554 (5)
O(3)—C(16)	1.203 (4)	C(9)—C(10)	1.569 (5)
C(1)—C(2)	1.516 (5)	C(9)—C(11)	1.546 (5)
C(1)—C(10)	1.547 (5)	C(10)—C(19)	1.545 (5)
C(2)—C(3)	1.521 (6)	C(11)—C(12)	1.492 (5)
C(3)—C(4)	1.524 (5)	C(12)—C(13)	1.316 (5)
C(4)—C(5)	1.539 (5)	C(13)—C(14)	1.499 (5)
C(4)—C(17)	1.527 (5)	C(13)—C(20)	1.517 (5)
C(5)—C(6)	1.529 (5)	C(14)—C(15)	1.542 (5)
C(5)—C(10)	1.537 (5)	C(15)—C(16)	1.492 (5)
C(6)—C(7)	1.522 (5)		

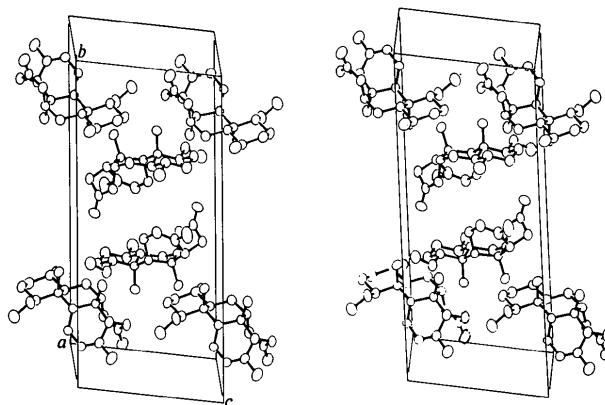


Fig. 2. A stereoview of the unit cell. Molecules which lie only partially in the cell are shown in their entirety for clarity. H atoms are not included.

Fig. 2 is a stereoview of the packing of the molecules. The most striking feature of this drawing is the basket shape of the molecule and the orientation of the molecules about the center of inversion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. They appear to be held in this head-to-tail orientation by a weak interaction between O(3) and C(1) and H(1C1). The O(3)···H(1C1) distance is 2.47 Å and the O(3)···C(1) distance 3.382 Å. The O(3)···H(1C1)—C(1) angle is 154°. Except for this contact, intermolecular contacts appear to be of the van der Waals type.

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