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Cuauhtemone

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Abstract. Orthorhombic, $P2_12_12_1$, $a=8.869$ (8), $b=26.82$ (6), $c=6.009$ (9) Å, $C_{15}H_{24}O_3$, M.W. 252.17, $Z=4$, $V=1432$ Å³, $\mu(\text{Cu } K\alpha)=5.51$ cm⁻¹, $D_m=1.18$ (by flotation), $D_c=1.168$ g cm⁻³, $\lambda(\text{Cu } K\alpha)=1.54178$ Å. *trans*-fused cyclohexane rings with an α,β -unsaturated ketone moiety imparting biological activity.

Introduction. Cuauhtemone is a sesquiterpene isolated in 0.03% yield from the nonsaponifiable matter of the aerial part of *Pluchea odorata* (*Compositae*): m.p. 140°; $[\alpha]_D^{25} 59.2^\circ$; ultraviolet (MeOH) 254 nm (ϵ 7700); infrared (3640, 3560, 1675, 1585 cm⁻¹). The plant is a Mexican medicinal shrub known as cuauhtematl, and the purified cuauhtemone is a growth inhibitor of corn and bean seeds (Grarciduenar, 1972).

A crystal of dimensions 0.15 × 0.45 × 0.80 mm was selected for X-ray data collection and was mounted with the c axis coincident with the rotation axis. Systematic absences consistent with space group $P2_12_12_1$ were observed on precession and Weissenberg photo-

graphs and on all counter-collected data. Three-dimensional intensity data for $hk0$ to $hk5$ were collected with a Philips PAILRED diffractometer using equi-inclination geometry and the continuous ω -scan technique. A scan speed of 2.5° min⁻¹ was used and background counts of 10 s were taken at the extremes of the scan range. The scan widths ranged from 2.0 to 7.8° depending upon the value of 2θ and the intensity. This variation was imposed by the long unit-cell dimension and the idiosyncracies of the instrument. Several reflections were monitored during the data collection and only statistical fluctuations in intensities were observed. 2519 measured intensities yielded 1375 independent reflections of which 1166 had intensities greater than $2\sigma(I)$. Equivalent reflections were averaged, and 33 reflections exhibiting large differences in intensities were omitted. No absorption correction was made.

MULTAN was used to calculate phases for the 440 $|E|$'s > 1.00, and the set of phases with the highest figure

Table 1. *Positional and thermal parameters for cuaehtemone*

Thermal parameters are of the form $\exp[-\frac{1}{2}(\sum_i \sum_j B_{ij} a_i^* a_j^* h_i h_j)]$. Non-hydrogen parameters $\times 10^4$; hydrogen parameters $\times 10^3$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C(1)	257 (10)	3899 (2)	2537 (16)	3.7 (4)	3.3 (3)	4.7 (5)	0.5 (3)	1.0 (4)	-0.2 (3)
C(2)	-269 (10)	3382 (3)	3212 (17)	4.3 (5)	4.1 (4)	4.9 (5)	-0.2 (3)	1.6 (4)	0.2 (3)
C(3)	509 (10)	2974 (3)	1890 (15)	5.1 (5)	3.3 (3)	3.0 (5)	-0.7 (4)	0.7 (3)	0.6 (3)
C(4)	2210 (9)	3007 (3)	2076 (14)	3.5 (3)	2.6 (3)	3.1 (4)	0.3 (2)	-0.4 (3)	0.2 (3)
C(5)	2775 (8)	3531 (3)	1525 (13)	3.0 (3)	2.8 (3)	2.5 (3)	0.3 (2)	0.0 (3)	0.2 (2)
C(6)	4481 (9)	3583 (3)	1559 (16)	3.1 (4)	3.8 (4)	4.8 (5)	0.3 (2)	-0.6 (3)	0.4 (3)
C(7)	4980 (10)	4093 (3)	163 (17)	3.3 (4)	4.0 (4)	4.9 (5)	-0.6 (3)	-0.7 (4)	0.2 (3)
C(8)	4137 (11)	4523 (3)	1546 (17)	4.6 (5)	3.4 (4)	4.6 (5)	-0.6 (3)	-0.3 (4)	-0.4 (3)
C(9)	2439 (9)	4454 (2)	1674 (15)	3.7 (4)	2.7 (3)	3.9 (4)	0.5 (2)	0.3 (3)	-0.3 (2)
C(10)	1958 (9)	3965 (3)	2800 (13)	3.5 (3)	3.4 (3)	2.0 (4)	-0.2 (2)	0.4 (2)	-0.2 (2)
C(11)	6045 (11)	4146 (3)	1017 (16)	3.8 (4)	5.3 (4)	4.4 (5)	0.6 (3)	0.6 (3)	0.2 (3)
C(12)	6399 (14)	4645 (4)	2038 (24)	5.9 (6)	6.0 (5)	8.9 (8)	1.3 (5)	-1.7 (6)	1.4 (6)
C(13)	6833 (12)	3704 (4)	2071 (22)	4.0 (5)	7.2 (6)	7.6 (7)	-1.3 (5)	-0.2 (5)	-1.5 (6)
C(14)	2769 (13)	2795 (4)	4353 (19)	7.9 (6)	4.6 (4)	4.5 (5)	0.4 (4)	-1.6 (5)	2.3 (4)
C(15)	2390 (14)	4007 (3)	5274 (16)	9.2 (7)	5.3 (5)	2.3 (5)	-0.8 (5)	0.3 (5)	-0.8 (3)
O(16)	121 (7)	3001 (2)	-422 (10)	4.0 (3)	3.9 (2)	4.3 (3)	-0.3 (2)	-0.4 (2)	0.2 (2)
O(17)	2819 (7)	2669 (2)	400 (10)	4.3 (2)	3.5 (2)	4.3 (3)	0.5 (2)	0.8 (2)	-0.6 (2)
O(18)	4705 (8)	4910 (2)	2103 (15)	5.0 (3)	4.6 (3)	10.0 (6)	-1.5 (2)	-0.4 (4)	-2.2 (3)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1A)	-005	397	080	1.7
H(1B)	-033	418	349	1.7
H(2A)	-005	333	497	1.7
H(2B)	-147	335	300	1.7
H(3)	014	262	249	1.7
H(5)	236	358	-013	1.7
H(6A)	499	329	056	1.7
H(6B)	490	354	323	1.7
H(9A)	196	447	002	1.7
H(9B)	194	476	255	1.7

of merit yielded an *E* map in which 17 peaks formed a reasonable molecular framework. The additional atom was found in subsequent electron density calculations. Full-matrix anisotropic least-squares refinement using 1133 reflections produced a final *R* of 0.079 and *R*_w of 0.103, where $R = \sum |\Delta F| / \sum |F_o|$ and $R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$. The function minimized was $w(F_o - F_c)^2$ where $w = 1/[\sigma(F_o)]^2$. Initially, $\sigma(F_o)$ was calculated from counting statistics; however, for the final refinement an empirical weighting scheme was derived in which $w = 1$ for $|F_o| < 4|F_{\min}|$ and $w = 1/[a|F_o| + b]^2$ for all other values. A least-squares fit of ΔF vs. F_o was used to find the values of *a* and *b*. All ring hydrogen atoms were located on a difference Fourier map, but no definite positions could be assigned to the methyl or hydroxyl hydrogen atoms.

A final difference Fourier map showed no additional areas of significant electron density. Atomic scattering factors of Cromer & Waber (1965) were used for carbon and oxygen atoms while those of Stewart, Davidson & Simpson (1965) were used for the hydrogen atoms. The contributions of the ring hydrogen atoms to the structure factors were calculated but the positions were not refined. The estimated standard deviations were calculated from the inverse of the nor-

mal equations matrix of the last least-squares cycle, and all shifts in parameters during the final cycle were less than one-tenth of the estimated standard devia-

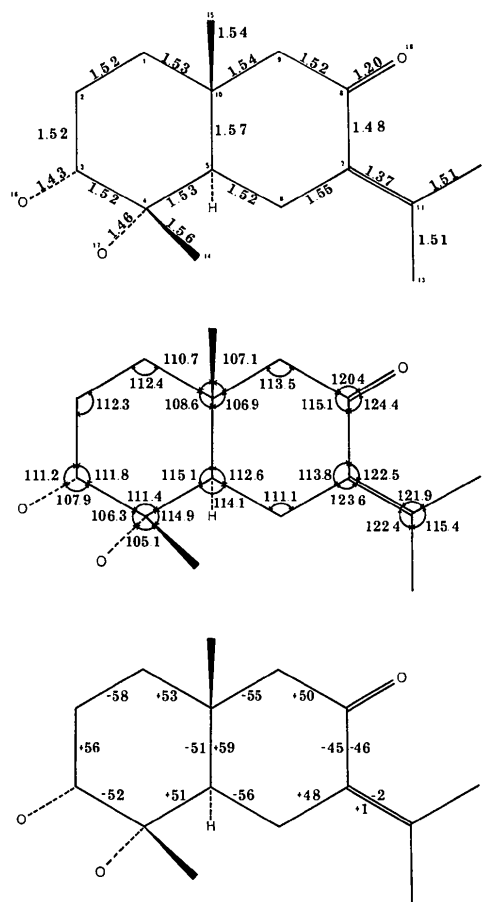


Fig. 1. Bond lengths, bond angles and torsion angles for cuaehtemone.

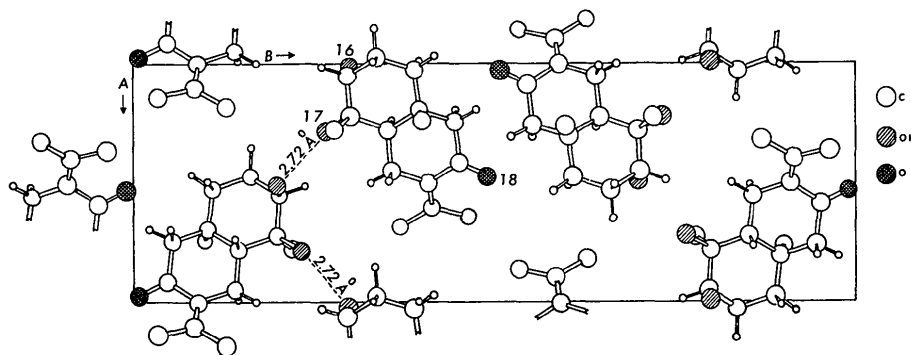


Fig. 2. Projection of the unit-cell contents onto the ab plane for cuaehtemone.

tions.* The atomic and thermal parameters along with their estimated standard deviations are given in Table 1.

Discussion. Bond lengths, bond angles and internal torsion angles are given in Fig. 1. Fig. 2 shows a projection of the unit cell contents onto the xy plane. The two cyclohexane rings are *trans* fused with the C(5)–C(10) bond elongated to 1.57 (1) Å. The C(7)–C(8) single bond between the two sp^2 hybridized carbon atoms is shortened to 1.48 (1) Å. The remaining carbon–carbon distances average 1.53 Å. The two methyl groups attached to C(11) exhibit lengths of 1.51 (1) Å while the two other methyl–carbon distances are 1.54 (1) and 1.56 (1) Å. The methyl groups attached to C(4) and C(10) are *syn* with respect to the ring. A large anisotropic thermal component along the x axis for C(14) and C(15) is consistent with some steric interference between the groups. The carbon–carbon and carbon–oxygen double-bond distances of 1.37 (1) and 1.20 (1) Å are within the normal range as are the two hydroxyl distances of 1.43 (1) and 1.46 (1) Å.

The cyclohexane rings are in the chair conformation. The conjugated system C(11)C(7)C(8)O(18) is not planar, as indicated by the torsion angle of -46° . Torsion angles C(8)C(7)C(11)C(12) and C(6)C(7)–C(11)C(13) indicate planarity in this portion of the molecule. The intermolecular hydroxyl oxygen distance of 2.72 (1) Å is consistent with hydrogen bonding, and the molecules form hydrogen-bonded chains parallel to the a axis. The chains are bound together by van der Waals interactions.

Although there are relatively few protons in the mol-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30603 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ecule, the p.m.r. spectrum could not be interpreted. The technique of Partially Relaxed Fourier Transform ^{13}C nuclear magnetic resonance was applied, and the structure of cuaehtemone was partially elucidated (Nakanishi, Crouch, Miura, Dominguez, Zamudio & Villarreal, 1974). The entire spectrum was interpreted when the X-ray structure became available, and the absolute configuration was confirmed to be that shown in the figures.

The observed growth inhibition of corn and bean seeds is probably associated with the α,β -unsaturated ketone moiety, since this group has been found to be the source of activity in many cytotoxic agents (Lee, Huang, Piantadosi, Pagano & Geissman, 1971; Lee, Furakawa & Huang, 1972; Lee, Meek, Piantadosi & Huang, 1973).

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