CHEMISTRY LETTERS, pp. 617-620, 1983.

CRYSTAL AND MOLECULAR STRUCTURE OF PIQUEROL A
A POTENT GROWTH-INHIBITING FACTOR+

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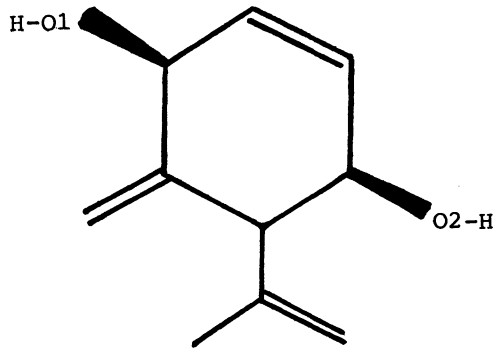
Crystal and molecular structure of piquerol A isolated from Piqueria trinervia Cav was determined. The X-ray study confirms that in the solid-state the structure of piquerol A is similar to that inferred from NMR spectra. The isopropenyl group is planar and makes approximately 38.4° with the mean plane for the six-membered ring. The two hydroxyl groups are above the plane through the six-membered ring, while the C4 and H5 are below this plane.

Piquerol A is a terpene component of the plant Piqueria trinervia Cav, first isolated and characterized by Romo et al.,[1]. Based on nuclear magnetic resonance study, these investigators assigned to piquerol A the following structure:



Piquerol A is an effective inhibitor of seed germination and plant growth and it also has insecticidal properties[2]. This paper presents the results of the three-dimensional structure analysis of piquerol A.

Crystals of piquerol A, $C_{10}H_{14}O_2$ were grown by slow evaporation from chloroform solution. These crystals are orthorhombic, space group $P\,2_12_12_1$ with unit cell constants: a= 6.859(2), b= 9.232(3), c= 14.851(6) Å, F(000)= 360, ρ_{obsd}= 1.16, ρ_{calcd}= 1.17 g cm^{-3}, μ=7.5 cm^{-1} and Z= 4.

Lattice parameters were derived from the setting angles of 15 machine-centred reflections (Nicolet R3m system, monochromatic Mo K_α radiation). Data collection (θ-2θ scans, background-peak-background, $2\theta < 50°$) yielded 764 observed independent reflections with $I > 2.5\,\sigma(I)$. The structure

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+Contribution No. 610 from the Instituto de Química UNAM.

was solved by direct methods and refined by a cascade-matrix procedure with anisotropic temperature factors for the non-H atoms and with a fixed isotropic temperature factor, U = 0.06 $Å^2$, for the H atoms, to converge with a weighted R = 0.045 (unweighted R = 0.048). The weighting scheme was $W = 1/\sigma^2(F)$. Calculations were carried out on a Nova 4 computer, and plots were drawn on a Tektronix plotter. The program package was SHELXTL[3]. The final atomic coordinates and U_{eq} values are presented in Table 1.

Figure 1 shows the conformation of piquerol A.

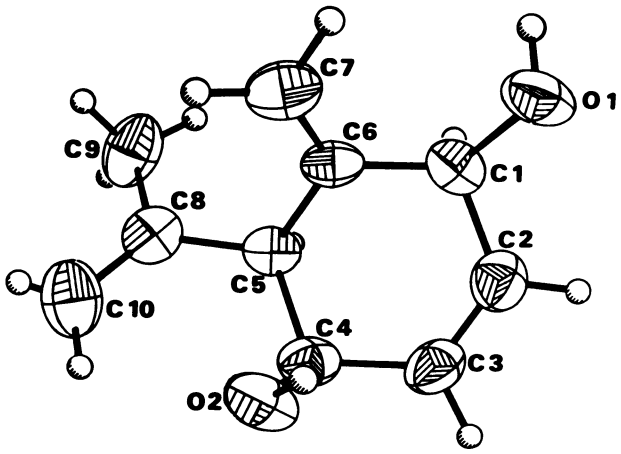

Fig. 1. Molecular structure of piquerol A. Thermal ellipsoids at 50% probability level.

Table 1. Final atomic coordinates and isotropic thermal parameters ($\times 10^4$) for piquerol A.

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

Atom	x	y	z	$U_{eq}/Å^2$	Atom	x	y	z	$U/Å^2$
O1	5403(5)	11385(3)	10273(2)	598(12)	H1	4837(6)	9322(4)	10248(3)	600
O2	-1092(4)	10903(3)	9500(2)	555(10)	H2	3071(7)	10621(5)	11511(3)	600
C1	4102(6)	10201(4)	10189(3)	446(14)	H3	-94(7)	10281(5)	11310(3)	600
C2	2621(7)	10352(5)	10922(3)	540(16)	H4	-1106(7)	8993(6)	10018(3)	600
C3	757(7)	10150(5)	10803(3)	563(16)	H5	1869(5)	8131(4)	9596(3)	600
C4	-114(7)	9709(6)	9918(3)	487(18)	H7A	4744(56)	11442(41)	8581(27)	600
C5	1439(5)	9019(4)	9325(3)	407(12)	H7B	2898(59)	10849(43)	8018(25)	600
C6	3131(6)	10062(5)	9285(3)	407(16)	H9A	3332(9)	7327(5)	8376(3)	600
C7	3621(9)	10825(5)	8584(4)	581(17)	H9B	2516(9)	7694(5)	7417(3)	600
C8	769(7)	8390(4)	8432(3)	495(15)	H9C	1611(9)	6417(5)	7973(3)	600
C9	2180(9)	7366(5)	8010(3)	750(21)	H10A	-1939(70)	9200(52)	8335(29)	600
C10	-933(11)	8645(5)	8066(4)	740(23)	H10B	-1088(84)	8303(58)	7642(30)	600
					HO1	-3541(82)	11220(53)	10008(28)	600
					HO2	-474(66)	11806(52)	9540(29)	600

Bond lengths and angles involving non-hydrogen atoms are listed in Table 2.

Table 2. Bond lengths and bond angles in piquerol A.

Bond length / Å				Bond angle /°			
C1-O1	1.417(5)	C6-C7	1.303(7)	O1-C1-C2	107.0(3)	C4-C5-C8	117.0(4)
C1-C2	1.496(6)	C8-C9	1.492(7)	O1-C1-C6	115.1(4)	C6-C5-C8	116.3(4)
C1-C6	1.504(6)	C8-C10	1.310(9)	C2-C1-C6	110.9(4)	C5-C6-C1	111.1(4)
C2-C3	1.305(7)			C1-C2-C3	123.7(4)	C5-C6-C7	125.1(5)
C3-C4	1.500(7)			C2-C3-C4	123.2(4)	C1-C6-C7	123.6(4)
C4-O2	1.433(6)			O2-C4-C3	111.0(4)	C5-C8-C9	114.4(4)
C4-C5	1.523(6)			O2-C4-C5	113.5(4)	C5-C8-C10	124.3(4)
C5-C6	1.509(6)			C3-C4-C5	110.0(4)	C9-C8-C10	121.2(4)
C5-C8	1.519(6)			C4-C5-C6	107.1(4)		

The mean observed value for the sp^2-sp^3 carbon-carbon single bonds in piquerol A is 1.509(6) Å, in agreement with the accepted value (1.501(3) Å, Sutton[4]).

The least-squares plane for the six-membered ring and the isopropenyl group are given in Table 3.

Table 3. Least-squares planes and deviations of atoms from these planes in piquerol A.

Plane	Atoms determining the plane	ℓ	m	n	d / Å	rms/ Å
1	C1,C2,C3,C4,C5,C6	-.195	.934	-.299	3.811	.218
2	C5,C8,C9,C10	.406	.768	-.495	-.050	.010

Atom	Plane 1	Plane 2	Atom	Plane 1	Plane 2
C1	-.087 **	.940	C8	-.423	.018 **
C2	-.084 **	.096	C9	-1.308	-.005 **
C3	.043 **	-.480	C10	.187	-.007 **
C4	.172 **	-.385	O1	.722	2.080
C5	-.367 **	-.005**	O2	1.519	.497
C6	.324 **	1.234	H4	-.357	-1.242
C7	1.228	2.428	H5	-1.311	-.715

The equation of the plane is $\ell X + m Y + n Z = d$; X, Y and Z are cartesian coordinates in Å units along the a, b and c^* axes and the coefficients of X, Y, Z are the direction cosines with respect to these axes. Atoms used to define the plane are marked by **.

The dihedral angle between planes is approximately 38.4°. The isopropenyl group is planar to the precesion of our analysis and the torsion angle C4-C5-C8-C10 is ± 13.9°. The cyclohexene ring adopts

a distorted half-chair conformation. The C4, C5 and C6 atoms show a deviations (0.172,-0.367 and 0.324 Å) from the mean plane. The O1 and O2 lying above, while C9 and H5 below this plane. Similar distortions have been observed in other cyclohexene derivatives[5]

Details of the hydrogen-bonding scheme are given in Table 4. The molecules are connected by hydrogen bonds between hydroxyl groups, forming a continous parallel ribbons along the a-axis direction. The hydroxyl substituent at C1 is hydrogen-bonded to O2 of an adjacent molecule, an almost linear hydrogen bond, while the hydroxyl substituent at C4 is hydrogen-bonded to O1 of an adjacent molecule related by the two fold screw axis along (100) direction with coordinates (x, 1/4, 0).

Table 4. Hydrogen-bond distances Å and angles ° in piquerol A.

D - H ... A	D - H	H ... A	D ... A	D - H ... A
O1-HO1 ... $O(2^{i})$	0.84(5)	1.86(5)	2.701(4)	176(4)
O2-HO2 ... $O(1^{ii})$	0.94(5)	1.80(5)	2.727(4)	171(4)

D is the donor and A is an acceptor atom. Superscripts refer to the following symmetry-related positions: (i) 1 + x, y, z and (ii) $-\frac{1}{2}$ + x, $2\frac{1}{2}$ - y, 2 - z.

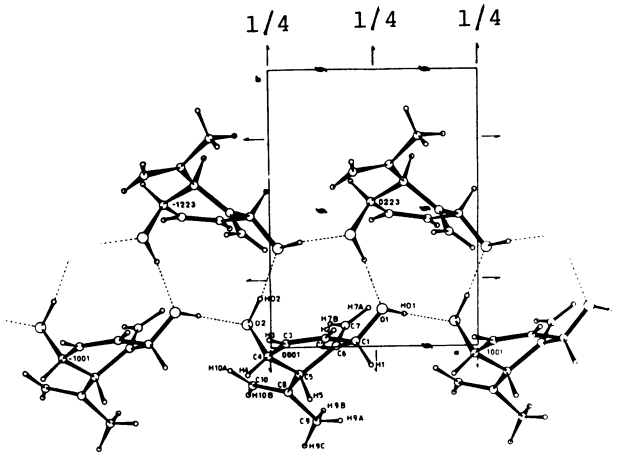

Fig. 2. Crystal structure of piquerol A. Molecules generated by 2_1 axes along b and c are omitted for clarity.

We thank Mr. Abelardo Cuéllar for excellent technical assistance.

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(Received August 23, 1982)