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Structure of 4-Hydroxy-3-(3-hydroxy-1-oxo-3-phenyl-2-propenyl)-6-methyl-2-pyrone

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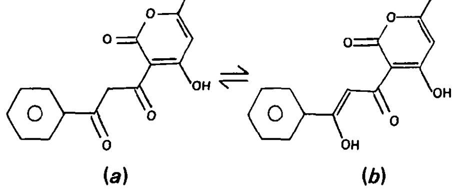
Abstract. $C_{15}H_{12}O_5$, $M_r = 272{\cdot}26$, monoclinic, $P2_1/a$, $a = 13{\cdot}797\,(4)$, $b = 19{\cdot}563\,(3)$, $c = 10{\cdot}075\,(3)$ Å, $\beta = 110{\cdot}97\,(3)°$, $V = 2539\,(1)$ Å^3, $Z = 8$, D_m(flotation) $= 1{\cdot}430\,(1)$, $D_x = 1{\cdot}4243\,(6)$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}7093$ Å, $\mu = 1{\cdot}38$ cm^{-1}, $F(000) = 1136$, $T = 293$ K, $R = 0{\cdot}047$ for 2549 reflections with $I > 2{\cdot}5\sigma(I)$. Resonance between enol and keto form suggested, enolic form confirmed. There are two molecules in the asymmetric unit linked through a hydrogen bond; the torsion angle between the pyran ring and the benzene ring is 137·6 (3) and 19·4 (3)° in molecules (I) and (II), respectively.

Introduction. The title compound (PH-II) is a plant extract isolated from *Pogostemon heynianus* Benth Syn. (Purushothaman, Sarada & Connolly, 1984). The structure of another extract, 3-acetyl-4-hydroxy-6-phenyl-2-pyrone (PH-I), from the same plant, which is more active against fibrosarcoma, has already been reported (Thailambal & Vasantha Pattabhi, 1985). Though both PH-I and PH-II have a phenyl ring and a pyrone group in common, the lack of planarity in PH-II and the substitutional differences may account for the difference in their activities. The present study was undertaken to establish the chemical structure; a resonance between enol and keto form was suggested. Single-crystal X-ray studies confirm that the enolic form (*b*) is preferred in the solid state.



Experimental. Yellow rectangular crystals from ethyl acetate, 0·3 × 0·3 × 0·4 mm; Picker four-circle automatic diffractometer, monochromatic Mo $K\alpha$ radiation; 5796 reflections measured with $2\theta < 50°$, 4496 unique, 1947 unobserved with $I < 2{\cdot}5\sigma(I)$, $R_{\rm int} = 0{\cdot}015$; no absorption correction, correction for direct-beam polarization (Le Page, Gabe & Calvert, 1979) and Lorentz effects; scan range $2\theta = (0{\cdot}6 + 0{\cdot}7\tan\theta + 0{\cdot}6)°$ using profile analysis (Grant & Gabe, 1978); 800, 020 and 030 as standard reflections, intensity variations 1·5%; 48 reflections for lattice-parameter measurement and refinement with $2\theta > 40°$; max. $h = 16$, min. $h = -16$, max. $k = 23$, max. $l = 12$; 2549 reflections with $I > 2{\cdot}5\sigma(I)$; structure solution by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); $\Delta\rho$ map gave the rest of the molecules, full-matrix least-squares refinement in *SHELX76*, $I_{\rm obs}$ (Sheldrick, 1976); H atoms fixed geometrically and checked with $\Delta\rho$ map; except for H(37), which was located from a $\Delta\rho$ map at the final stage and not refined, non-hydrogen atoms were refined anisotropically and H atoms isotropically. At $R = 0{\cdot}07$, to reduce computation time, further refinement of non-hydrogen atoms was carried out using block-diagonal least-squares refinement on $F_{\rm obs}$ (Shiono, 1968) with Cruickshank's weighting scheme (Cruickshank, Bujosa, Lovell & Truter, 1961); $\sigma = [A + B(F_{\rm obs}) + C(F_{\rm obs})^2]^{1/2}$, $A = 20{\cdot}0$, $B = 1{\cdot}0$, $C = 0{\cdot}01$; final $R = 0{\cdot}047$, $wR = 0{\cdot}062$ for 361 parameters, goodness of fit $= 1{\cdot}16$; $-0{\cdot}30 \le \Delta\rho \le 0{\cdot}32$ e Å^{-3}; $(\Delta/\sigma)_{\rm av} = 0{\cdot}06$, $(\Delta/\sigma)_{\rm max} = 0{\cdot}4$; scattering factors for non-hydrogen atoms from *International Tables for X-ray Crystallography* (1968) and for H atoms from Stewart, Davidson & Simpson (1965).

Discussion. Final atomic parameters and temperature coefficients are given in Table 1.† Atom numbering, bond lengths and bond angles are given in Fig. 1. The average e.s.d. in bond lengths is 0·009 Å and in bond angles 0·6°.

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms, H-bonding details and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42820 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The phenyl ring (plane I) in both molecules is planar with $\chi^2 = 3{\cdot}6$ and $7{\cdot}2$, respectively $[\chi^2 = \sum(\Delta/\sigma)^2]$. The phenyl-ring geometry is normal with average bond length 1·381 (12) Å and bond angle 120·0 (6)°. Phenyl-ring atoms C(12), C(13) and C(14) in molecule (I) and C(32), C(33) and C(34) in molecule (II) have higher thermal parameters, and hence the bond lengths involving these atoms have large e.s.d.'s (0·013 and 0·012 Å). In fact, the phenyl group appears to vibrate about the C(9)—C(10) and C(29)—C(30) bonds of molecules (I) and (II). Similar observations have been made in PH-I. Bond lengths and bond angles of similar groups in PH-I and PH-II agree well.

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for non-hydrogen atoms*) *and equivalent isotropic temperature coefficients with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \tfrac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac\cos\beta).$$
$$\sigma(B_{\text{eq}}) = \tfrac{4}{3}\{[a^2\sigma(\beta_{11})]^2 + [b^2\sigma(\beta_{22})]^2 + [c^2\sigma(\beta_{33})]^2 + [ac\cos\beta\sigma(\beta_{13})]^2\}^{1/2}.$$

	x	y	z	B_{eq}(Å^2)
O(1)	1542 (4)	1881 (2)	11471 (5)	4·1 (1)
C(2)	1062 (5)	1831 (3)	9995 (7)	3·6 (2)
C(3)	1028 (5)	2448 (3)	9203 (7)	3·3 (2)
C(4)	1439 (5)	3046 (3)	9954 (7)	3·5 (2)
C(5)	1889 (5)	3049 (3)	11454 (7)	3·7 (2)
C(6)	1942 (5)	2473 (3)	12161 (7)	3·6 (2)
C(7)	615 (5)	2463 (4)	7656 (7)	3·6 (2)
C(8)	223 (6)	1874 (4)	6795 (7)	4·1 (2)
C(9)	−5 (5)	1876 (4)	5364 (7)	3·9 (2)
C(10)	−386 (5)	1274 (4)	4458 (7)	3·9 (2)
C(11)	−982 (6)	776 (4)	4778 (8)	4·8 (2)
C(12)	−1344 (7)	218 (4)	3900 (9)	5·8 (3)
C(13)	−1097 (7)	139 (4)	2702 (9)	5·5 (3)
C(14)	−497 (7)	622 (5)	2383 (8)	5·6 (3)
C(15)	−148 (6)	1189 (4)	3231 (7)	4·8 (3)
O(16)	728 (4)	1274 (2)	9572 (5)	5·2 (2)
O(17)	1445 (4)	3630 (2)	9308 (5)	4·9 (2)
C(18)	2423 (6)	2366 (4)	13719 (7)	4·7 (2)
O(19)	641 (4)	3032 (2)	7049 (5)	4·8 (1)
O(20)	119 (4)	2418 (3)	4649 (5)	5·6 (2)
O(21)	2276 (4)	4213 (2)	6623 (5)	4·0 (1)
C(22)	1556 (5)	4166 (3)	5232 (7)	3·6 (2)
C(23)	1100 (5)	4793 (3)	4550 (7)	3·3 (2)
C(24)	1422 (5)	5404 (3)	5291 (7)	3·7 (2)
C(25)	2183 (6)	5403 (4)	6682 (7)	4·2 (2)
C(26)	2579 (5)	4816 (3)	7303 (7)	3·8 (2)
C(27)	316 (5)	4803 (3)	3116 (7)	3·5 (2)
C(28)	−27 (5)	4202 (3)	2288 (7)	3·9 (2)
C(29)	−743 (5)	4218 (3)	941 (7)	3·9 (2)
C(30)	−1103 (5)	3600 (4)	69 (7)	3·9 (2)
C(31)	−974 (5)	2949 (4)	666 (8)	4·2 (2)
C(32)	−1289 (6)	2380 (4)	−184 (9)	5·3 (2)
C(33)	−1729 (6)	2443 (4)	−1630 (9)	5·6 (3)
C(34)	−1862 (7)	3081 (5)	−2234 (8)	5·7 (3)
C(35)	−1566 (6)	3659 (4)	−1398 (8)	5·0 (3)
O(36)	1410 (4)	3591 (2)	4781 (5)	4·8 (2)
O(37)	1039 (4)	5998 (2)	4743 (5)	5·1 (2)
C(38)	3345 (6)	4724 (4)	8743 (8)	4·8 (2)
O(39)	−64 (4)	5384 (2)	2614 (5)	4·7 (1)
O(40)	−1165 (4)	4794 (3)	301 (5)	5·3 (2)

The least-squares plane through the pyran-group atoms (plane II) in both molecules is nearly planar with $\chi^2 = 26{\cdot}9$ and $23{\cdot}4$ respectively. The angle between plane (I) and plane (II) is 137·6 (3)° in molecule (I) and 19·4 (3)° in molecule (II). The corresponding angle observed in PH-I is 3·5 (2)°. The larger rotation of these groups in molecule (I) of PH-II is a result of packing effects.

Packing of the molecules viewed down the *c* axis is shown in Fig. 2. The pyrone ring of molecule (I) lies nearly perpendicular to the glide plane with the mirror plane running near atoms C(3) and C(6). The longest directions of molecule (I) and (II) make angles of 86 and 73° respectively with the *a* axis.

There are two O—H···O and one C—H···O intramolecular hydrogen bonds in each molecule: O(17)···O(19) 2·444 (6), O(20)···O(19) 2·562 (7), O(37)···O(39) 2·454 (6), O(40)···O(39) 2·557 (6), C(8)···O(16) 2·880 (9) and C(28)···O(36) 2·847 (7) Å. The O—H···O intramolecular bond is comparable with that observed in PH-I. The two molecules in the same asymmetric unit are connected through a hydrogen bond, *viz* O(20)···O(36) [2·879 (7) Å]. There is a weak O(17)···O(39) [2·909 (6) Å] intermolecular hydrogen bond.

C(38)···O(16) [3·487 (9) Å] and C(18)···O(36) [3·147 (10) Å] are two possible intermolecular C—H···O hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984). Hydrogen bonds involving HO(20) and HO(17) are bifurcated.

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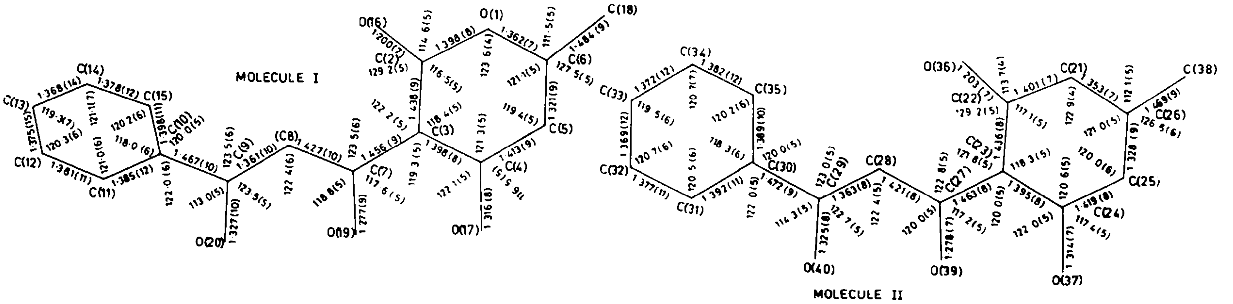

Fig. 1. Atom numbering, bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses.

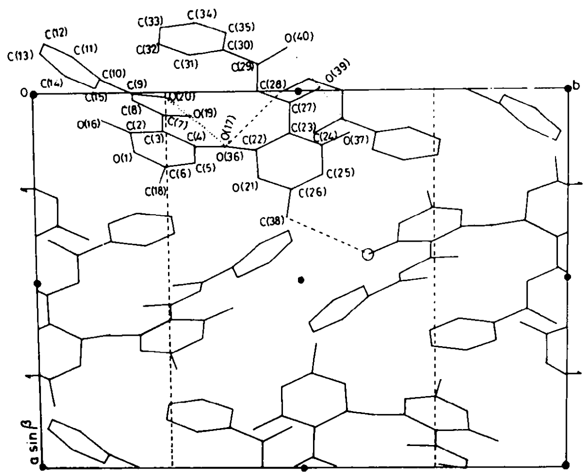

Fig. 2. Packing of the molecule viewed down the *c* axis. Dotted lines indicate intramolecular and dashed lines intermolecular hydrogen bonds. [The large open circle is O(16) twice translated on *z*.]

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Structure of Antischistosome Compounds. II. Benzyltriphenylphosphonium Bromide

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Abstract. $C_{25}H_{22}P^+.Br^-$, $M_r = 433{\cdot}3$, monoclinic, $P2_1/c$, $a = 9{\cdot}761\,(1)$, $b = 20{\cdot}343\,(1)$, $c = 11{\cdot}544\,(1)$ Å, $\beta = 109{\cdot}17\,(1)°$, $V = 2165{\cdot}16$ Å^3, $Z = 4$, $D_m = 1{\cdot}315$, $D_x = 1{\cdot}329$ g cm^{-3}, graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 33{\cdot}4$ cm^{-1}, $F(000) = 888$, $T = 292$ K. Final $R = 0{\cdot}046$ for 2962 observed reflections. The four P—C distances are in the range 1·789 (4)–1·802 (4) Å with a mean of 1·795 (5) Å. The six C—P—C angles vary from 108·2 (2) to 110·4 (2)° with a mean of 109·5 (8)°. The dihedral angle of the phenylmethyl plane and the plane formed by the C atoms of the P—C(phenyl) bonds is 24·2°, which is in sharp contrast to the vertical orientation of the substituted group of the (2-aminoethyl)triphenylphosphonium compound.

Introduction. The crystal and molecular structure of the title compound have been determined as a part of a study of the triphenylphosphonium compounds which exhibit varying effects on the cholinergic nervous system of *Schistosoma mansoni* (McAllister, Dotson, Grim & Hillman, 1980). The biological effects of these compounds cannot be explained solely on the basis of chemical differences in the substituted moiety. The effects may also be due to the differences in the torsion angles in the substituted moieties.

Experimental. Sample provided by Professor G. Hillman, synthesized as described in McAllister *et al.* (1980); colorless crystals (from ethanol), 0·10 × 0·23 × 0·09 mm; Enraf–Nonius CAD-4 diffractometer, cell parameters from 2θ angles for 22 reflections from least-squares refinement with $25 \le \theta \le 35°$; ω–2θ scan, ω width $(0{\cdot}90 + 0{\cdot}14\tan\theta)°$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}6092$ Å^{-1}, $h = -11$ to 11, $k = 0$ to 24 and $l = 0$ to 14; intensities of three standard reflections monitored every 3600 s showed a linear decline in intensity of −9·6%, correction applied; 3679 unique

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