

have been splayed out by 15–20° relative to unbridged structures. These adjustments are all consistent with the need to accommodate the very bulky P(C₆H₁₁)₃ ligand.

The unique Co(2)–Co(3) bond opposite the phosphine ligand is 0.14 (1) Å shorter than the mean of the other two. In CH₃CCO₃(CO)₇, the unique Co–Co bond (in that case bridged by the ffars ligand) is also significantly shortened [by 0.035 (3) Å] but in the non-bridged CH₃CCO₃(CO)₇P(C₆H₅)₃ (Brice, Penfold, Robinson & Taylor, 1970) no such differences are observed.

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3,4,5,6-Tetrahydro-2,9-dimethyl-7-hydroxy-5-isopropyl-2,6-methano-2H-1-benzoxocin

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Abstract. C₁₇H₂₄O₂, *M_r* = 260.38, triclinic, *P* $\bar{1}$, *a* = 10.619 (4), *b* = 10.734 (4), *c* = 15.028 (4) Å, α = 101.11 (2), β = 107.58 (2), γ = 102.90 (2)°, *U* = 1528 Å³, *Z* = 4, *D_m* (floatation) = 1.12, *D_x* = 1.132 g cm⁻³, μ = 4.9 cm⁻¹. There are two independent molecules in the asymmetric unit. The structure was refined to an *R* of 0.057 for 3970 independent reflexions.

Introduction. The title compound (an isocannabinoid) was prepared, as part of the synthesis of a series of terpenophenols with central nervous system activity, by the reaction of α -pinene with orcinol in dry benzene in the presence of POCl₃; large crystals were obtained from petroleum spirit/diethyl ether (R. Mechoulam, private communication). The analogous preparation of the 9-pentyl derivative has been described (Houry, Mechoulam, Fowler, Macko & Loev, 1974; Houry, Mechoulam & Loev, 1975), as has a similar preparation of the title compound (Stevens, Jurd & Manners, 1974). Intensities were measured on an

automated Syntex P2₁ four-circle diffractometer with Cu *K* α radiation and graphite monochromator, with a crystal 0.9 × 0.4 × 0.4 mm. Accurate cell dimensions were obtained by least squares from 15 strong reflexions. The cell used was both the Dirichlet and Delaunay cell; no cell of higher symmetry could be found with the lattice-geometry program XCELL written by Dr R. Taylor. 4443 reflexions were measured in the range 0 < 2 θ < 116°; averaging equivalent reflexions (Lp but no absorption corrections were applied) gave 3970 reflexions with *F* > 4 σ (*F*).

Multiresolution Σ_2 sign expansion with the program SHELX generated *E* maps containing multiple images, which we could not interpret. With the program XCSD, which incorporates a pseudo-tangent refinement to select the starting set (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973), and the negative quartet test NQUEST (De Titta, Edmonds, Langs & Hauptman, 1975) the best *E* map established positions for all 38 heavy atoms in the asymmetric unit: only 7 small peaks in the top 45 were false. Figures of merit were NQUEST –0.685, *R_A* (a point-atom *R* index based on observed

* External Staff, Medical Research Council.

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(2)	4194 (2)	6992 (2)	3650 (1)	
C(3)	3881 (2)	8310 (2)	3792 (2)	
C(4)	2347 (3)	8165 (2)	3445 (2)	
C(5)	1545 (2)	7215 (2)	3869 (1)	
C(6)	1889 (2)	5892 (2)	3678 (1)	
C(7)	151 (2)	4326 (2)	2058 (1)	
C(8)	-205 (2)	3690 (2)	1089 (1)	
C(9)	743 (2)	3932 (2)	635 (1)	
C(10)	2050 (2)	4830 (2)	1166 (1)	
C(11)	2388 (2)	5461 (2)	2135 (1)	
C(12)	1459 (2)	5230 (2)	2613 (1)	
C(13)	3447 (2)	6111 (2)	4126 (1)	
C(14)	5743 (2)	7159 (3)	4000 (2)	
C(15)	1779 (3)	7816 (2)	4947 (2)	
C(16)	1371 (4)	9070 (3)	5109 (2)	
C(17)	1137 (4)	6870 (3)	5392 (2)	
C(18)	378 (2)	3198 (2)	-419 (1)	
O(1)	3711 (1)	6346 (1)	2602 (1)	
O(2)	-735 (1)	4117 (1)	2551 (1)	
C(2')	4468 (2)	7115 (2)	8621 (1)	
C(3')	4539 (2)	6482 (2)	7646 (2)	
C(4')	5005 (2)	7486 (2)	7131 (1)	
C(5')	6328 (2)	8621 (2)	7778 (1)	
C(6')	6144 (2)	9216 (2)	8735 (1)	
C(7')	5117 (2)	11073 (2)	8418 (1)	
C(8')	3989 (2)	11555 (2)	8148 (1)	
C(9')	2668 (2)	10766 (2)	7982 (1)	
C(10')	2496 (2)	9502 (2)	8106 (1)	
C(11')	3628 (2)	9033 (2)	8367 (1)	
C(12')	4959 (2)	9786 (2)	8524 (1)	
C(13')	5832 (2)	8156 (2)	9254 (1)	
C(14')	4049 (2)	6089 (2)	9127 (2)	
C(15')	7649 (2)	8187 (2)	7911 (1)	
C(16')	7939 (2)	7947 (2)	6966 (2)	
C(17')	8923 (2)	9197 (2)	8727 (2)	
C(18')	1441 (2)	11282 (2)	7651 (2)	
O(1')	3354 (1)	7740 (1)	8452 (1)	
O(2')	6426 (1)	11813 (1)	8578 (1)	
H(1)	2762 (20)	5042 (19)	873 (14)	69 (3)
H(2)	-1094 (21)	3071 (20)	796 (15)	69 (3)
H(3)	1353 (19)	5253 (19)	3976 (13)	66 (1)
H(4)	511 (20)	7034 (18)	3553 (14)	66 (1)
H(5)	2220 (19)	9056 (18)	3629 (14)	66 (1)
H(6)	1976 (19)	7788 (18)	2723 (13)	66 (1)
H(7)	4276 (20)	8846 (20)	3475 (14)	66 (1)
H(8)	4266 (20)	8632 (19)	4466 (16)	66 (1)
H(9)	3676 (19)	5185 (18)	4057 (13)	66 (1)
H(10)	3814 (18)	6578 (19)	4798 (13)	66 (1)
H(11)	1215	3526	-637	144 (2)
H(12)	-495	3399	-848	144 (2)
H(13)	156	2169	-505	144 (2)
H(14)	2854 (21)	8101 (19)	5286 (14)	66 (1)
H(15)	57	6588	5039	144 (2)
H(16)	1397	7335	6133	144 (2)
H(17)	1476	6023	5319	144 (2)
H(18)	291	8828	4778	144 (2)
H(19)	1852	9747	4803	144 (2)
H(20)	1670	9504	5858	144 (2)
H(21)	6185	7621	4751	144 (2)
H(22)	6209	7753	3637	144 (2)
H(23)	5904	6222	3853	144 (2)
H(24)	-1435 (28)	3541 (27)	2192 (21)	116 (5)
H(1')	1600 (22)	8922 (20)	7951 (14)	69 (3)
H(2')	4083 (19)	12486 (20)	8026 (14)	69 (3)
H(3')	6969 (20)	9928 (19)	9174 (14)	66 (1)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(4')	6406 (18)	9398 (19)	7433 (14)	66 (1)
H(5')	5164 (19)	7006 (19)	6557 (15)	66 (1)
H(6')	4246 (20)	7832 (19)	6908 (14)	66 (1)
H(7')	3561 (21)	5903 (19)	7142 (14)	66 (1)
H(8')	5248 (20)	5980 (19)	7789 (14)	66 (1)
H(9')	6526 (18)	7763 (18)	9332 (13)	66 (1)
H(10')	5833 (18)	8530 (18)	9894 (13)	66 (1)
H(11')	534	10554	7562	144 (2)
H(12')	1360	11498	6987	144 (2)
H(13')	1575	12150	8177	144 (2)
H(14')	7527 (19)	7352 (20)	8089 (14)	66 (1)
H(15')	9099	10120	8574	144 (2)
H(16')	9788	8856	8777	144 (2)
H(17')	8761	9304	9390	144 (2)
H(18')	8080	8830	6755	144 (2)
H(19')	7095	7198	6420	144 (2)
H(20')	8837	7648	7074	144 (2)
H(21')	4791	5579	9278	144 (2)
H(22')	3082	5408	8674	144 (2)
H(23')	3978	6571	9780	144 (2)
H(24')	6343 (26)	12425 (25)	8237 (19)	116 (5)

peaks) 0.231, R_α (Roberts *et al.*, 1973) 0.033 (*cf.* figures for the second E map, which showed few recognizable structural fragments: NQUEST-0.620, R_α 0.410, R_α 0.062). Anisotropic least-squares refinement (to $R = 0.124$), followed by a difference synthesis, showed all H atom positions except two methyl H. Further refinement including all H atoms reduced R to 0.072; C-H distances were fixed at 1.05 Å and H-C-H angles at 109.5°. In the final stages of refinement all H atoms except methyl H were allowed to refine freely, and chemically similar H were assigned equal isotropic temperature factors. To allow for pronounced extinction, a parameter x was included

Table 2. *Bond lengths* (Å)

C(11)-C(10)	1.380 (3)	C(11')-C(10')	1.383 (4)
C(11)-C(12)	1.392 (4)	C(11')-C(12')	1.386 (3)
C(11)-O(1)	1.386 (3)	C(11')-O(1')	1.391 (3)
C(10)-C(9)	1.389 (3)	C(10')-C(9')	1.385 (4)
C(9)-C(8)	1.382 (4)	C(9')-C(8')	1.387 (4)
C(9)-C(18)	1.513 (4)	C(9')-C(18')	1.513 (5)
C(8)-C(7)	1.379 (3)	C(8')-C(7')	1.390 (4)
C(7)-C(12)	1.398 (3)	C(7')-C(12')	1.400 (4)
C(7)-O(2)	1.369 (4)	C(7')-O(2')	1.361 (3)
C(12)-C(6)	1.500 (4)	C(12')-C(6')	1.495 (4)
C(6)-C(5)	1.540 (5)	C(6')-C(5')	1.545 (5)
C(6)-C(13)	1.529 (5)	C(6')-C(13')	1.531 (5)
C(5)-C(4)	1.537 (5)	C(5')-C(4')	1.536 (4)
C(5)-C(15)	1.543 (5)	C(5')-C(15')	1.544 (5)
C(4)-C(3)	1.514 (6)	C(4')-C(3')	1.522 (5)
C(3)-C(2)	1.515 (5)	C(3')-C(2')	1.523 (5)
C(2)-C(13)	1.517 (5)	C(2')-C(13')	1.512 (4)
C(2)-C(14)	1.525 (5)	C(2')-C(14')	1.516 (5)
C(2)-O(1)	1.469 (3)	C(2')-O(1')	1.467 (3)
C(15)-C(17)	1.474 (6)	C(15')-C(17')	1.529 (4)
C(15)-C(16)	1.502 (7)	C(15')-C(16')	1.529 (5)

in the calculation, where F_c was multiplied by $[1 - xF^2/(\sin \theta)]$; it refined to $24(3) \times 10^{-6}$. The final $R' = \Sigma w^{1/2} \Delta / \Sigma w^{1/2} |F_o|$ was 0.0784, with an R of 0.0572; the weighting scheme was $w = 1/[\sigma^2(F) + 0.001F^2]$, which gave mean values of $w\Delta^2$ varying only slightly with $\sin \theta$ or $|F_o|$. A final difference map had no peaks greater than $0.4 \text{ e } \text{Å}^{-3}$.

Final atomic coordinates are given in Table 1 with derived interatomic distances and angles in Tables 2 and 3.* C—H bond lengths ranged from 0.923 to 1.068

* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32522 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

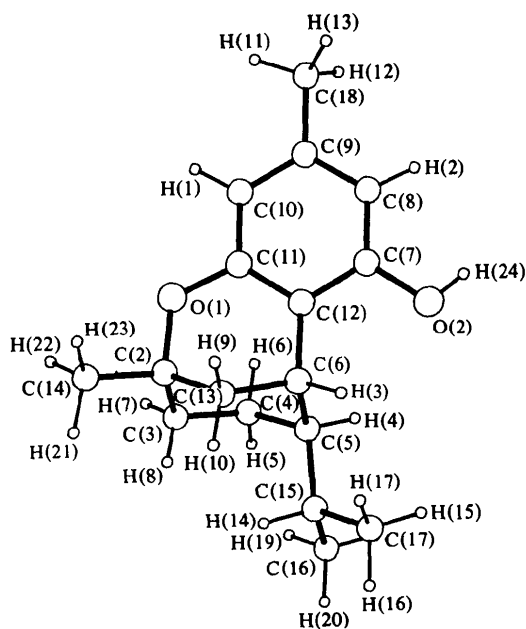


Fig. 1. Perspective view of the first molecule showing the atom numbering scheme. H(18) is obscured by C(17).

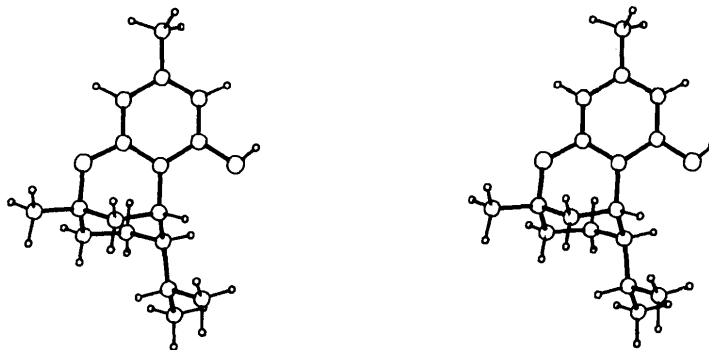


Fig. 2. Stereoview of the first molecule.

Table 3. Bond angles ($^\circ$)

C(10)—C(11)—C(12)	122.3 (2)	C(10')—C(11')—C(12')	122.7 (3)
C(10)—C(11)—O(1)	115.7 (3)	C(10')—C(11')—O(1')	116.0 (2)
C(12)—C(11)—O(1)	122.0 (2)	C(12')—C(11')—O(1')	121.3 (3)
C(11)—C(10)—C(9)	119.9 (3)	C(11')—C(10')—C(9')	119.9 (3)
C(10)—C(9)—C(8)	119.2 (3)	C(10')—C(9')—C(8')	119.0 (3)
C(10)—C(9)—C(18)	120.3 (3)	C(10')—C(9')—C(18')	121.1 (3)
C(8)—C(9)—C(18)	120.5 (2)	C(8')—C(9')—C(18')	119.9 (3)
C(9)—C(8)—C(7)	120.2 (2)	C(9')—C(8')—C(7')	120.4 (3)
C(8)—C(7)—C(12)	122.0 (3)	C(8')—C(7')—C(12')	121.5 (3)
C(8)—C(7)—O(2)	123.0 (2)	C(8')—C(7')—O(2')	122.1 (3)
C(12)—C(7)—O(2)	115.0 (2)	C(12')—C(7')—O(2')	116.5 (3)
C(11)—C(12)—C(7)	116.5 (2)	C(11')—C(12')—C(7')	116.6 (3)
C(11)—C(12)—C(6)	120.5 (2)	C(11')—C(12')—C(6')	121.4 (3)
C(7)—C(12)—C(6)	122.9 (3)	C(7')—C(12')—C(6')	122.0 (3)
C(12)—C(6)—C(5)	112.3 (3)	C(12')—C(6')—C(5')	109.8 (2)
C(12)—C(6)—C(13)	106.6 (3)	C(12')—C(6')—C(13')	107.7 (3)
C(5)—C(6)—C(13)	111.1 (2)	C(5')—C(6')—C(13')	111.5 (2)
C(6)—C(5)—C(4)	108.2 (3)	C(6')—C(5')—C(4')	108.3 (3)
C(6)—C(5)—C(15)	113.4 (3)	C(6')—C(5')—C(15')	114.7 (2)
C(4)—C(5)—C(15)	113.6 (2)	C(4')—C(5')—C(15')	112.5 (3)
C(5)—C(4)—C(3)	113.0 (3)	C(5')—C(4')—C(3')	113.9 (2)
C(4)—C(3)—C(2)	113.5 (2)	C(4')—C(3')—C(2')	113.8 (3)
C(3)—C(2)—C(13)	109.7 (3)	C(3')—C(2')—C(13')	109.9 (3)
C(3)—C(2)—C(14)	112.7 (3)	C(3')—C(2')—C(14')	112.3 (3)
C(13)—C(2)—C(14)	112.3 (3)	C(13')—C(2')—C(14')	111.8 (3)
C(3)—C(2)—O(1)	108.4 (3)	C(3')—C(2')—O(1')	109.0 (2)
C(13)—C(2)—O(1)	109.8 (2)	C(13')—C(2')—O(1')	109.6 (2)
C(14)—C(2)—O(1)	103.7 (3)	C(14')—C(2')—O(1')	104.2 (3)
C(6)—C(13)—C(13)	109.3 (3)	C(6')—C(13')—C(2')	109.3 (2)
C(5)—C(15)—C(17)	114.2 (3)	C(5')—C(15')—C(17')	112.6 (3)
C(5)—C(15)—C(16)	112.5 (3)	C(5')—C(15')—C(16')	111.0 (3)
C(17)—C(15)—C(16)	110.9 (4)	C(17')—C(15')—C(16')	109.4 (3)
C(11)—O(1)—C(2)	119.4 (2)	C(11')—O(1')—C(2')	119.4 (2)

Å (e.s.d. 0.025 Å). Diagrams of the structure are given in Figs. 1–3. Atoms in the second independent molecule are distinguished by the addition of a prime.

Discussion. The investigation confirms the structure deduced by chemical means in the preparative papers. The two independent molecules are structurally very similar. The isopropyl groups have different bond lengths and angles; there are no other bond length

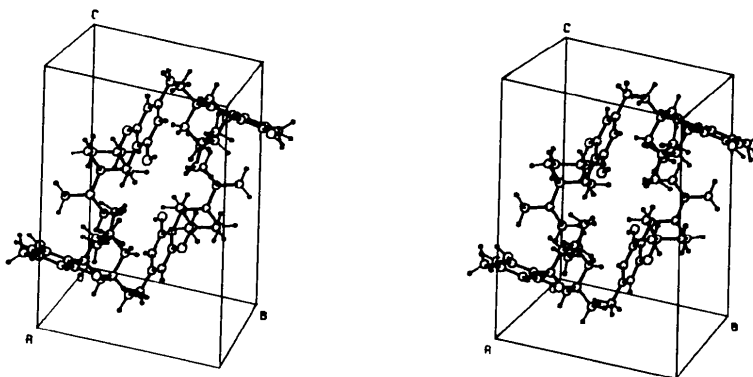


Fig. 3. Stereo packing diagram of the unit-cell contents (four molecules).

Table 4. *Torsion angles for the central ring* ($^{\circ}$)

All errors $\pm 0.5^{\circ}$.

	Molecule 1	Molecule 2
O(1)—C(11)—C(12)—C(6)	-3.0	+3.6
C(11)—C(12)—C(6)—C(13)	-29.3	+29.6
C(12)—C(6)—C(13)—C(2)	+60.1	+57.4
O(1)—C(2)—C(13)—C(6)	-60.3	-60.9
C(13)—C(2)—O(1)—C(11)	+27.3	+34.7
C(12)—C(11)—O(1)—C(2)	+4.6	-5.8

differences greater than 0.011 Å, and the only other substantial ($>1.1^{\circ}$) bond angle difference is for C(12)—C(6)—C(5) (2.5°). The main differences in torsion angles occur in the central ring (Table 4). Both benzene rings are virtually planar [maximum torsion angle 0.5 (5°) in molecule 1 and -1.6 (5°) in molecule 2].

There are intermolecular hydrogen bonds between the hydroxyl H atom and the central ring O atom; non-bonded distances (in Å) are H(24')—O(1) 1.99, O(2')—O(1) 2.90 (second atoms at $1-x$, $2-y$, $1-z$), and O(1')—H(24) 2.01, O(1')—O(2) 2.80

(second atoms at $-x$, $1-y$, $1-z$). There are no other short non-bonded distances.

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