other except for those in the —CH_2NO_2 moiety which, as mentioned earlier, is disordered in (2a) but not in (2b).

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Structure of Wigandol*
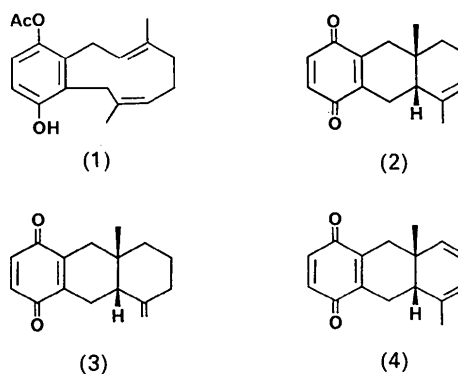
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Abstract. (Z,E)-5,8,9,12-Tetrahydro-4-hydroxy-6,10-dimethylbenzocyclodecen-1-yl acetate, $C_{18}H_{22}O_3$, M_r = 286.4, monoclinic, $C2/c$, $a = 20.828$ (5), $b =$ 8.364 (2), $c = 21.508$ (4) Å, $\beta = 122.39$ (2)°, $V =$ 3164 (1) Å^3, $Z = 8$, $D_x = 1.20$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 6.09$ cm^{-1}, $F(000) = 1232$, $T =$ 292 K, final $R = 0.049$ for 1697 unique observed reflections [$F_o > 3\sigma(F_o)$]. Wigandol is characterized by a cis,trans-cyclodeca-1,5-diene with the methyl groups anti-related. The cyclodecadiene ring adopts a chair–half-chair conformation. The acetate group lies nearly perpendicular to the planar phenyl ring. In the crystal the molecules are held together by hydrogen bonds involving the phenolic group and the carbonyl O atom in the acetate group of a symmetry-related molecule, forming endless zigzag chains along the b axis.

Introduction. Wigandol (1), isolated from *Wigandia kunthii Choysi* (Gómez, Quijano, Calderón & Ríos, 1980), is the monoacetate derivative of the hypothetical precursor in the biogenetic route to the cordiachromes (Manners & Jurd, 1977; Manners, 1983). The putative precursor was proposed as a *trans,trans*-cyclodeca-1,5-diene, which in a boat conformation could undergo acid-catalyzed cyclization to cordiachromes A and B (2 and 3) with *cis* ring junction, while Cope rearrangement would give

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cordiachrome C (4), a *cis*-1,2-divinylcyclohexane derivative (Moir & Thompson, 1973).

Although, in a few cases, Cope rearrangement has already been observed proceeding *via* a boat conformation (Wiberg, Matturro & Adams, 1981; Shea & Phillips, 1980), it is also true that the structures had been 1,5-diene systems with a high degree of rigidity. On the other hand, although it is well known (Takeda & Horibe, 1975) that *trans,trans*-cyclodeca-1,5-dienes undergo Cope rearrangement to give *trans*-1,2-divinylcyclohexane derivatives (contrary to cordiachrome C) whereas the *cis,trans*-cyclodeca-1,5-diene system gives a *cis*-1,2-divinyl derivative, two compounds (neolinderolactone and sericenine: *cis,trans*- and *trans,cis*-cyclodeca-1,5-dienes) with structures closely related to wigandol, failed to follow this path (Takeda, Horibe & Minato, 1970).

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

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
C(1)	1716 (1)	8536 (3)	1171 (1)	49 (1)
C(2)	1857 (2)	9729 (3)	1658 (1)	59 (1)
C(3)	2585 (2)	9940 (3)	2252 (1)	64 (1)
C(4)	3152 (1)	8943 (3)	2339 (1)	55 (1)
C(4a)	3018 (1)	7714 (3)	1845 (1)	47 (1)
C(5)	3698 (1)	6699 (3)	2016 (1)	53 (1)
C(6)	4074 (1)	7152 (4)	1600 (1)	57 (1)
C(7)	4356 (2)	6083 (4)	1355 (2)	69 (1)
C(8)	4313 (2)	4315 (4)	1367 (2)	80 (2)
C(9)	3577 (2)	3667 (4)	682 (2)	73 (2)
C(10)	2912 (2)	4044 (3)	743 (1)	59 (1)
C(11)	2575 (1)	5451 (3)	525 (1)	54 (1)
C(12)	2010 (1)	6150 (3)	671 (1)	56 (1)
C(12a)	2275 (1)	7493 (3)	1236 (1)	46 (1)
C(13)	4129 (2)	8904 (4)	1500 (2)	75 (2)
C(14)	2763 (2)	2859 (4)	1169 (2)	80 (2)
O(1)	963 (1)	8423 (2)	542 (1)	53 (1)
C(15)	488 (1)	7379 (3)	562 (2)	57 (1)
O(2)	675 (1)	6524 (3)	1074 (1)	86 (1)
C(16)	−276 (1)	7407 (4)	−125 (2)	70 (2)
O(3)	3884 (1)	9111 (3)	2931 (1)	80 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for wigandol*

C(1)—C(2)	1.359 (4)	C(1)—C(12a)	1.400 (4)
C(1)—O(1)	1.424 (2)	C(2)—C(3)	1.373 (3)
C(3)—C(4)	1.374 (4)	C(4)—C(4a)	1.395 (4)
C(4)—O(3)	1.374 (3)	C(4a)—C(5)	1.517 (4)
C(4a)—C(12a)	1.406 (3)	C(5)—C(6)	1.520 (5)
C(6)—C(7)	1.324 (5)	C(6)—C(13)	1.494 (4)
C(7)—C(8)	1.483 (5)	C(8)—C(9)	1.548 (3)
C(9)—C(10)	1.494 (5)	C(10)—C(11)	1.321 (4)
C(10)—C(14)	1.492 (5)	C(11)—C(12)	1.492 (5)
C(12)—C(12a)	1.525 (4)	O(1)—C(15)	1.337 (4)
C(15)—O(2)	1.191 (4)	C(15)—C(16)	1.482 (5)

C(2)—C(1)—C(12a)	123.7 (2)	C(2)—C(1)—O(1)	117.1 (2)
C(12a)—C(1)—O(1)	119.1 (2)	C(1)—C(2)—C(3)	119.2 (3)
C(2)—C(3)—C(4)	119.2 (3)	C(3)—C(4)—C(4a)	122.5 (2)
C(3)—C(4)—O(3)	120.7 (2)	C(4a)—C(4)—O(3)	116.8 (2)
C(4)—C(4a)—C(5)	116.7 (2)	C(4)—C(4a)—C(12a)	118.5 (2)
C(5)—C(4a)—C(12a)	124.8 (2)	C(4a)—C(5)—C(6)	115.2 (2)
C(5)—C(6)—C(7)	123.0 (3)	C(5)—C(6)—C(13)	115.6 (3)
C(7)—C(6)—C(13)	121.4 (3)	C(6)—C(7)—C(8)	128.5 (3)
C(7)—C(8)—C(9)	111.7 (2)	C(8)—C(9)—C(10)	109.5 (3)
C(9)—C(10)—C(11)	119.8 (3)	C(9)—C(10)—C(14)	115.0 (3)
C(11)—C(10)—C(14)	124.4 (3)	C(10)—C(11)—C(12)	127.1 (3)
C(11)—C(12)—C(12a)	117.9 (2)	C(1)—C(12a)—C(4a)	116.9 (2)
C(1)—C(12a)—C(12)	117.0 (2)	C(4a)—C(12a)—C(12)	125.9 (2)
C(1)—O(1)—C(15)	118.0 (2)	O(1)—C(15)—O(2)	122.8 (2)
O(1)—C(15)—C(16)	112.0 (3)	O(2)—C(15)—C(16)	125.2 (3)

Table 3. *Selected torsion angles* (°) *for wigandol*

C(12a)—C(4a)—C(5)—C(6)	82.5 (2)	C(7)—C(8)—C(9)—C(10)	−72.2 (2)
C(5)—C(4a)—C(12a)—C(12)	3.8 (1)	C(8)—C(9)—C(10)—C(11)	84.9 (2)
C(4a)—C(5)—C(6)—C(7)	−143.0 (3)	C(9)—C(10)—C(11)—C(12)	−167.6 (3)
C(5)—C(6)—C(7)—C(8)	5.7 (1)	C(10)—C(11)—C(12)—C(12a)	106.0 (2)
C(6)—C(7)—C(8)—C(9)	86.8 (2)	C(11)—C(12)—C(12a)—C(4a)	−28.7 (1)

In order to establish unambiguously the geometry of the double bonds and relative position of the acetate group we have undertaken the crystal structure analysis of wigandol.

Experimental. Wigandol was obtained as colorless crystals by slow evaporation from a dichloromethane solution. A crystal of dimensions 0.16 × 0.24 × 0.36 mm was selected for study. The space group was

determined from Laue symmetry and systematic absences: *hkl* for *h* + *k* odd, *h0l* for *h*, *l* odd, *0k0* for *k* odd; *Cc* or *C2/c*. Successful structure solution and refinement on *C2/c* proved it to be the correct space group. Data were collected on a Nicolet *P3/F* diffractometer with Ni-filtered Cu $K\alpha$ radiation. Unit-cell parameters were determined from least-squares fitting of 25 reflections ($10.07 < 2\theta < 28.73°$). Intensities were measured by $\theta/2\theta$ scans ($h = 0$ to 22, $k = 0$ to 8, $l = \pm 22$, $3 \le 2\theta \le 110°$) with variable scan speed (minimum 4.0, maximum 29.3° min^{-1}). Two standards (5$\bar{1}$6, 3$\bar{1}$2), measured every 50 reflections, showed no significant fluctuation. Of 2236 reflections collected, 1993 were unique and 296 were unobserved [$F_o < 3\sigma(F_o)$]. Lp corrections were applied but absorption was ignored. The structure was solved by direct methods and refined by block-matrix least squares. Refinement of 194 parameters included positional and anisotropic thermal parameters for non-H atoms, a scale factor and an isotropic extinction parameter $x = 0.0012$ (4) [$F_c^* = F_c(1.0 + 0.002xF_c^2/\sin 2\theta)^{-0.25}$]. H atoms attached to C atoms
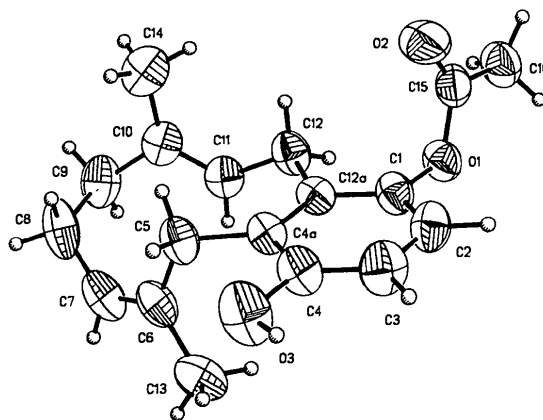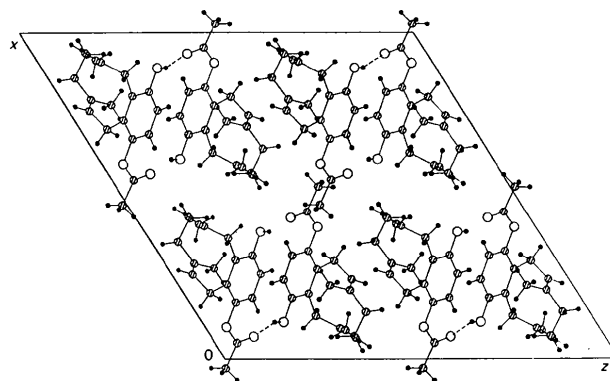

Fig. 1. Drawing of wigandol with thermal ellipsoids at the 50% probability level.

Fig. 2. Crystal packing viewed along the *b* axis.

were placed in idealized positions and that bonded to O(3) located on a difference Fourier map and its coordinates refined; all H atoms had fixed thermal parameters $U = 0.06$ Å^2. In the final cycle, $R = 0.049$, $wR = 0.064$ for 1697 observed reflections, $S = 1.30$. The function minimized was $\sum w(\Delta F)^2$, where $w = [\sigma(F_o)^2 + 0.0028(F_o)^2]^{-1}$. Maximum $\Delta/\sigma = 0.291$. Minimum and maximum residuals in the final $\Delta\rho$ synthesis were -0.20 and 0.19 e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a NOVA 4S computer using *SHELXTL* (Sheldrick, 1983).

Discussion. Final atomic coordinates are given in Table 1.* Fig. 1 shows a view of the molecule and the atom-numbering scheme. Bond lengths and angles are listed in Table 2. The structure of wigandol determined by X-ray analysis is characterized by the *cis,trans* geometry of the cyclodeca-1,5-diene system, the *anti* arrangement of methyl groups at C(6) and C(10), and by the crossed orientation [angle between planes $29.5(1)°$] of the C(6)=C(7) and C(10)=C(11) double bonds. The conformation of the ten-membered ring can be described as a chair–half-chair and closely resembles that found in NMR studies of neolinderolactone (Tori, Horibe, Kuriyama & Takeda, 1970). Comparison of the inner torsion angles of the ten-membered ring in wigandol (Table 3) with those of the schkuriolid (Rychlewska, 1982) shows that they differ mainly by

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55287 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0594]

distortions at the ring fusion. Significant departures form the ideal torsion angles of the *cis* (6°) and *trans* ($-168°$) double bonds reflect strain from trans-annular non-bonded interactions [C(7)···C(10) 3.075 (5) and C(6)···C(11) 3.064 (5) Å]. The dihydrobenzoquinone moiety is essentially planar and the acetate group lies nearly perpendicular [angle between planes 81.2 (2)°] to the phenyl ring. In the crystal the molecules are held together by hydrogen bonds [D—H 0.855 (31), H···A 1.928 (27), D···A 2.719 (3) Å; D—H···A 153 (3)°] involving the phenolic group O(3)—H(3a) and the carbonyl atom O(2) in the acetate group of a symmetry-related molecule $(0.5 - x, 0.5 + y, 0.5 - z)$, forming endless zigzag chains along the b axis. Fig. 2 shows the crystal packing.

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Triphenylphosphine Oxide Hydrogen Bromide

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Abstract. $C_{18}H_{16}OP^+.Br^-$, $M_r = 359.20$, monoclinic, $P2_1/n$, $a = 9.540(3)$, $b = 17.763(5)$, $c = 10.390(6)$ Å, $\beta = 106.91(4)°$, $V = 1685(1)$ Å^3, $Z = 4$, $D_x = 1.416$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.504$ mm^{-1}, $F(000) = 728$, $T = 298$ K, $R = 0.042$ for 1122 observed reflections [$I > 2\sigma(I)$]. The structure

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