Conformation of (±)-19,20-Cyclopodocarpa-8,11,13-trien-19-one

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The conformation of (±)-19,20-cyclopodocarpa-8,11,13-trien-19-one (1b) has been determined by *X*-ray diffraction. Ring A assumes a distorted chair conformation while ring B, adjacent to the aromatic ring, takes up a distorted boat conformation. Crystals are monoclinic, space group $P2_1/c$, with a = 8.41(2), b = 7.40(2), c = 21.04(6) Å, β = 94.0(4)°, and Z = 4. The structure has been solved by direct methods from visually estimated photographic data, and refined by least-squares calculations to R 0.109 for 985 observed reflections.

Two novel methods of stereocontrolled syntheses of (±)-13-methoxy-19,20-cyclopodocarpa-8,11,13-trien-19-one (1a) and the corresponding demethoxy-compound (1b) have recently been reported,[1] and have established synthetic intermediates for diterpenoid alkaloids and C-20 gibberellins. These bridged ketones may exist in two possible extreme conformations, *e.g.* (A) or (B). The exact conformation of the ring B, adjacent to the aromatic ring, in these two compounds could not however be ascertained from the 220 MHz n.m.r. data. In order to obtain complete conformational data for (1b) (±)-19,20-cyclopodocarpa-8,11,13-trien-19-one we have carried out a crystal-structure determination. A re-

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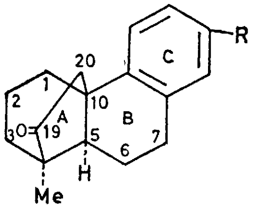
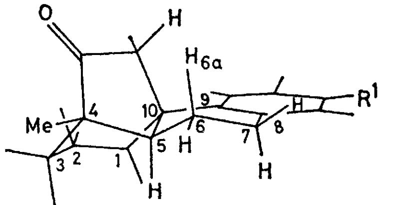
[1] U. R. Ghatak, B. Sanyal, and S. Ghosh, *J. Amer. Chem. Soc.*, 1976, **98**, 3721; U. R. Ghatak and S. Chakraborty, *J. Org. Chem.*, 1976, **41**, 1089, and refs. therein.

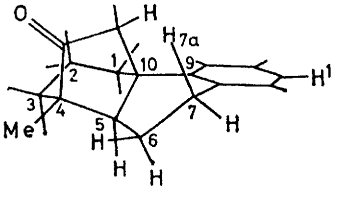
markable lack of co-relation between the various spectroscopic data of these types of compounds had led to the complete X-ray analysis of three bromine-substituted derivatives of podocarpic acid.[2,3] In these, the conformation of the B-ring has varied from almost pure boat to half boat. However, it is known that bromine substitution may change the conformation of this ring drastically. The present determination therefore also gives a model for the conformation in such compounds when they are not substituted by heavy atoms.



(1) a; R = OMe
b; R = H



(A)



(B)

EXPERIMENTAL

Colourless crystals of (1b), elongated along the b axis, were obtained by slow evaporation of an alcoholic solution at room temperature.

Crystal Data.—$C_{17}H_{20}O$, $M = 240.16$. Monoclinic, $a = 8.41(2)$, $b = 7.40(2)$, $c = 21.04(6)$ Å, $\beta = 94.0(4)°$, $U = 1\,306.2$ Å^3, $D_m = 1.21$, $Z = 4$, $D_c = 1.22$ g cm^{-3}. Space group $P2_1/c$. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 5.69 cm^{-1}.

Three-dimensional intensity data were collected (hkl, $k = 0$ to 6) for the layers $h0$—$6l$ by the multiple-film equi-inclination Weissenberg technique with Cu-K_α radiation. The crystal used had an approximate cross-section of 0.30 × 0.30 mm. Intensity values were visually estimated using a calibrated strip and were corrected for Lorentz, polarization, and spot-size effects.[4] No absorption correction was applied. Each layer of data was then individually brought to the absolute scale applying Wilson's statistics.

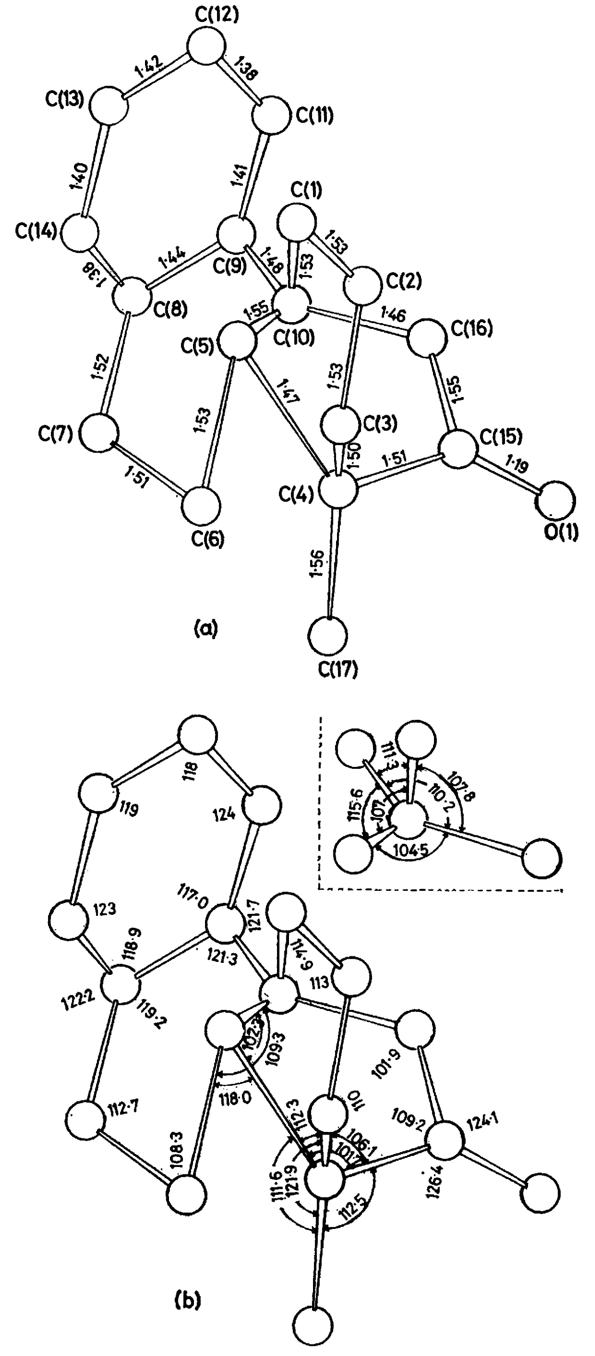


FIGURE 1 Projection of the molecule showing (a) bond lengths (Å) and crystallographic atom numbering, and (b) angles (°)

The solution of the structure was attempted by direct methods using 253 reflections with normalized structure factors $E \geqslant 1.35$ by use of the MULTAN program.[5] Of the total sixteen sets of signs obtained by this procedure, that

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[2] G. R. Clark and T. N. Waters, *J. Chem. Soc.* (*C*), 1970, 887.

[3] J. F. Cutfield, T. N. Waters, and G. R. Clark, *J.C.S., Perkin II*, 1974, 150.

[4] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746; 1956, **9**, 819.

[5] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

having the best figures-of-merit produced an E map which revealed most of the atom positions. A subsequent Fourier synthesis established the positions of all non-hydrogen atoms.

The structure was refined by full-matrix least-squares methods using a modified version of ORFLS.[6] The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$ is the weighting function, and σ, the standard deviation of each reflection was taken as 0.15 $|F_o|$ for $|F_o| \leqslant 8.0$, 0.10 $|F_o|$ for $8.0 < |F_o| \leqslant 20.0$, 0.12 $|F_o|$ for $20.0 < |F_o| \leqslant 45.0$, and 0.20 $|F_o|$ for $|F_o| > 45.0$.

After two cycles of isotropic and one cycle of anisotropic refinements the R value was reduced to 0.193. At this stage the positions of all the seventeen trigonal and tetrahedral hydrogen atoms were calculated. These hydrogens were then assigned the temperature factors of the atoms to which they were attached, and included in all subsequent structure factor calculations without refinement. After four more cycles of anisotropic refinement R converged to 0.109 for 985 observed reflections. Scattering factors were taken from ref. 7. Final values of observed and calculated structure factors and thermal parameters, are listed in Supplementary Publication No. SUP 22274 (11 pp., 1 microfiche).*

TABLE 1

Positional parameters of the atoms, with standard deviations in parentheses; H atom positions were fixed during refinement

Atom	*x*	*y*	*z*
C(1)	0.0992(6)	0.2150(17)	0.1094(6)
C(2)	0.1691(17)	0.0558(18)	0.0743(7)
C(3)	0.3488(16)	0.0346(16)	0.0882(6)
C(4)	0.4274(13)	0.2173(11)	0.0904(4)
C(5)	0.3681(13)	0.3342(12)	0.1402(4)
C(6)	0.4619(15)	0.5055(15)	0.1582(6)
C(7)	0.3802(13)	0.6004(14)	0.2107(5)
C(8)	0.2075(13)	0.6439(10)	0.1919(4)
C(9)	0.1209(13)	0.5358(12)	0.1440(5)
C(10)	0.2002(13)	0.3867(13)	0.1113(4)
C(11)	−0.0391(14)	0.5835(17)	0.1276(6)
C(12)	−0.1183(15)	0.7214(17)	0.1562(6)
C(13)	−0.0318)14)	0.3245(15)	0.2038(5)
C(14)	0.1286(12)	0.7814(16)	0.2195(5)
C(15)	0.3660(13)	0.3141(13)	0.0304(4)
C(16)	0.2248(14)	0.4376(15)	0.0457(5)
C(17)	0.6131(16)	0.2028(17)	0.0965(6)
O(1)	0.4238(10)	0.3110(9)	−0.0197(3)
H(1)1	0.079	0.179	0.156
H(1)2	−0.015	0.248	0.091
H(2)1	0.114	−0.059	0.086
H(2)2	0.147	0.077	0.027
H(3)1	0.372	−0.026	0.131
H(3)2	0.397	−0.042	0.056
H(5)	0.413	0.207	0.147
H(6)1	0.474	0.584	0.122
H(6)2	0.575	0.472	0.178
H(7)1	0.436	0.722	0.219
H(7)2	0.386	0.530	0.250
H(11)	−0.097	0.526	0.092
H(12)	−0.235	0.734	0.143
H(13)	−0.081	0.935	0.225
H(14)	0.195	0.849	0.255
H(16)1	0.251	0.566	0.040
H(16)2	0.127	0.408	0.016

DISCUSSION

Final positional and vibrational parameters are shown in Table 1 and bond lengths and angles in Figure 1.

TABLE 2

Torsion angles (°) for (Ib)

(*a*) Aromatic ring	
C(9)–C(11)–C(12)–C(13)	1.8
C(11)–C(12)–C(13)–C(14)	−0.2
C(12)–C(13)–C(14)–C(8)	−0.7
C(13)–C(14)–C(8)–C(9)	−0.04
C(14)–C(8)–C(9)–C(11)	1.5
C(8)–C(9)–C(11)–C(12)	−2.5
(*b*) Ring A	
C(1)–C(10)–C(5)–C(4)	67.7
C(10)–C(5)–C(4)–C(3)	−73.7
C(5)–C(4)–C(3)–C(2)	60.1
C(4)–C(3)–C(2)–C(1)	−40.3
C(3)–C(2)–C(1)–C(10)	41.1
C(2)–C(1)–C(10)–C(5)	−55.0
(*c*) Ring B	
C(10)–C(9)–C(8)–C(7)	−1.9
C(9)–C(8)–C(7)–C(6)	25.5
C(8)–C(7)–C(6)–C(5)	−56.8
C(7)–C(6)–C(5)–C(10)	64.8
C(6)–C(5)–C(10)–C(9)	−41.8
C(5)–C(10)–C(9)–C(8)	10.5
(*d*) Five-membered ring	
C(10)–C(16)–C(16)–C(4)	−7.1
C(16)–C(15)–C(4)–C(5)	21.0
C(15)–C(4)–C(5)–C(10)	−39.3
C(4)–C(5)–C(10)–C(16)	−46.4
C(5)–C(10)–C(16)–C(15)	31.3
(*e*) Between rings	
C(11)–C(9)–C(10)–C(1)	−50.1
C(9)–C(10)–C(1)–C(2)	177.8
C(9)–C(10)–C(5)–C(4)	−167.7
C(9)–C(10)–C(16)–C(15)	156.1
C(8)–C(9)–C(10)–C(1)	132.9
C(11)–C(9)–C(10)–C(5)	−172.4
C(11)–C(9)–C(10)–C(16)	69.4
C(11)–C(9)–C(8)–C(7)	−179.0
C(12)–C(11)–C(9)–C(10)	−179.6
C(13)–C(14)–C(8)–C(7)	−179.4
C(14)–C(8)–C(9)–C(10)	178.7
C(14)–C(8)–C(7)–C(6)	−155.1
C(7)–C(6)–C(5)–C(4)	−179.0
C(6)–C(5)–C(4)–C(3)	166.4
C(6)–C(5)–C(4)–C(15)	−80.6
C(6)–C(5)–C(10)–C(16)	79.4
C(6)–C(5)–C(10)–C(1)	−166.4
C(2)–C(1)–C(10)–C(16)	56.9
C(1)–C(10)–C(16)–C(15)	−82.2
C(16)–C(15)–C(4)–C(3)	96.6
C(15)–C(4)–C(3)–C(2)	−50.2
C(16)–C(10)–C(9)–C(8)	107.6
(*f*) Side groups	
C(17)–C(4)–C(3)–C(2)	−173.3
C(17)–C(4)–C(15)–O(1)	33.1
C(17)–C(4)–C(5)–C(10)	−159.5
C(17)–C(4)–C(5)–C(6)	−39.6
O(1)–C(15)–C(16)–C(10)	179.1
O(1)–C(15)–C(4)–C(3)	−89.8
O(1)–C(15)–C(4)–C(5)	152.6
C(17)–C(4)–C(15)–C(16)	−140.6

Estimated standard deviations for bond lengths vary between 0.01 to 0.02 Å, while those for angles are of the

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[6] W. R. Busing, K. O. Martin, and H. A. Levy, Fortran Crystallographic Least Squares Program, 1962, Oak Ridge National Laboratory.

[7] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

order of 1.0°. Torsion angles are given in Table 2.

There are three six-membered and one five-membered rings in the molecule. Of these the aromatic ring is substantially planar. The equation of the least-squares plane passing through the ring is $0.333\,5\ X' + 0.629\,4\ Y' - 0.701\,8\ Z' - 0.654\,2 = 0$ where X', Y', Z' are co-ordinates in Å referred to an orthogonal set defined by $X' = X + Z \cos \beta$, $Y' = Y$, and $Z' = Z \sin \beta$. The deviations of the atoms from this plane are: C(8) 0.003, C(9) −0.011, C(11) 0.012, C(12) −0.003, C(13) −0.005, C(14) 0.005, C(7) 0.014, and C(10) 0.002 Å, respectively.

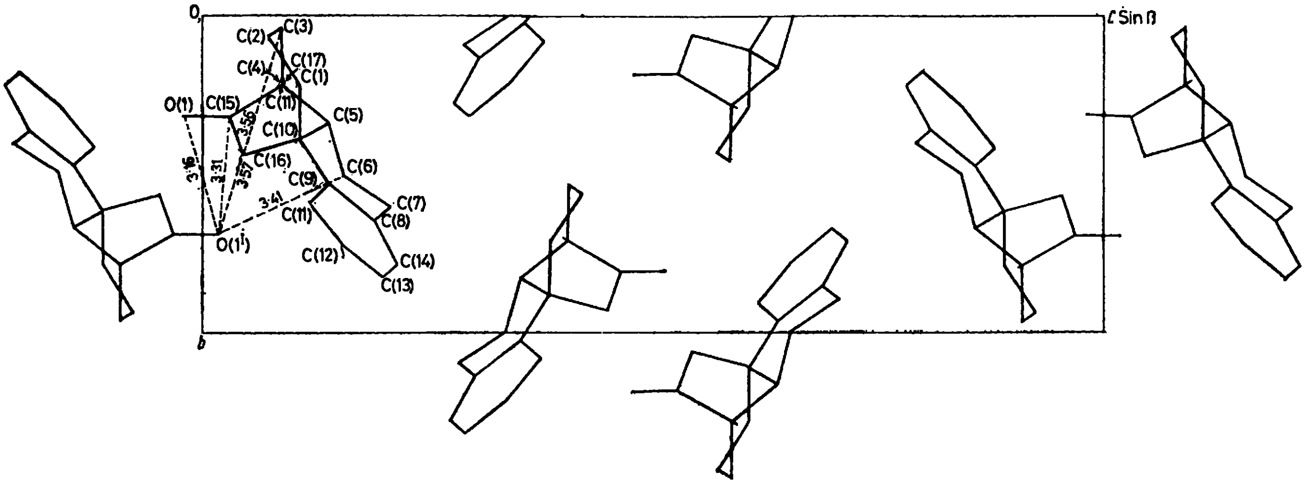

FIGURE 2 The packing of the molecules down the *a* axis; dashed lines show intermolecular contacts <3.6 Å

Ring A [C(1)—(5), C(10)] assumes a distorted chair configuration. The amount of distortion can be discerned from the deviation of the observed torsion angles from the ideal alternating values of 60 and −60°. As a result some of the valence angles also show considerable deviation from the tetrahedral value. Ring B is very much distorted but assumes a configuration much nearer to a boat than chair. The conformation of the molecule as a whole is therefore more akin to the structure (B).

The deviations of the atoms C(7) and C(10) from the mean plane of the benzene ring are very small. The four atoms C(7)—(10) of ring B are therefore substantially planar. This is due to the delocalization arising out of the adjacent aromatic ring which in turn gives rise to considerable distortion of ring B from the boat configuration.

The packing of the molecules viewed down the *a* axis is shown in Figure 2. All five intermolecular contacts <3.6 Å involve atom O(1$^{\text{I}}$) at $1 - x$, $1 - y$, $-z$.

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