

Diterpenoid C-Ring Bromoketones.

I. *ent*-3 β -Acetoxy-11 α -bromoisopimar-8(14)-en-12-one

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Abstract. C₂₂O₃H₃₃Br, *M*=425. Monoclinic *P*2₁, *a*=7.29 (1), *b*=13.88 (1), *c*=11.27 (1) Å, β =106.6 (1)°, *V*=1092 Å³, *D*_c=1.30 g cm⁻³, *Z*=2, μ (Mo *K* α)=20.2 cm⁻¹. *R*=0.058 for 1330 observed data; Br, 8 C and 3 O atoms anisotropic and 15 H atoms included. The Br is pseudo-axial above the mean plane of ring C, *cis* to the H on C(9). The C(12) keto-O(2) is below the mean plane of ring C.

Introduction. From the heartwood of *Cleistanthus schlechteri* var. *schlechteri* were isolated the aromatic diterpene cleistanthol (McGarry, Pegel, Phillips & Waight, 1971) and three related pimarane diterpenes (Candy, Pakshong & Pegel, 1970). Bromination of an 8(14)-en-12-one derivative yielded the 11-bromo compound (Fig. 1) which resisted dehydrobromination across the C(11)–C(9) bond. The conformation of ring C, the nature of the B/C ring junction and the orientation of the Br atom were therefore of great interest and because these could not be obtained from the available chemical evidence, the crystal structure was determined.

Suitable crystals were prepared by Mr C. P. Gorst-Allman. Data were collected from a crystal 0.3 × 0.4 × 0.5 mm on a Philips four-circle diffractometer with graphite-monochromated Mo *K* α radiation (λ =0.7107 Å) for θ between 3 and 23°. The ω -2 θ scan mode was used; the scan width was 1.2°, each peak was scanned for 30 s and the background was counted for 30 s for each peak. Of the 1591 reflexions measured, 1330 were classed as observed, *I* > 1.65 σ (*I*). Three reflexions were used as standards and their intensities were remeasured every hour; no decomposition was detected. The intensities were corrected for Lorentz and polarization effects only. A temperature-sharpened Patterson map gave the coordinates of the Br atom (*y* arbi-

trarily chosen as 0.25). Subsequent Fourier maps yielded the coordinates of the lighter atoms. The structure was refined by block-diagonal least squares with the Br and 11 peripheral atoms (8 C, 3 O) anisotropic; the 15 H atoms bonded directly to the main skeleton were included in the structure factor calculations. The final *R* was 0.058 for 1330 observed data.* Weighting

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31786 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates and thermal parameters*
Fractional atomic coordinates and isotropic thermal parameters. All H atoms were assigned *B*=4.0 Å².

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Br	0.3923 (2)	0.25	1.1284 (1)	
O(1)	0.1297 (10)	0.1520 (6)	0.3987 (5)	
O(2)	0.4281 (13)	0.4810 (7)	1.0366 (8)	
O(3)	−0.0483 (17)	0.0275 (10)	0.4199 (8)	
C(1)	0.2049 (11)	0.2567 (11)	0.7190 (7)	3.18 (16)
C(2)	0.1225 (12)	0.2377 (10)	0.5766 (7)	3.57 (19)
C(3)	0.2099 (15)	0.1600 (8)	0.5308 (9)	3.96 (22)
C(4)	0.4318 (15)	0.1691 (8)	0.5565 (9)	3.99 (23)
C(5)	0.5124 (12)	0.1837 (7)	0.7018 (8)	2.77 (18)
C(6)	0.7359 (14)	0.1894 (8)	0.7440 (9)	3.65 (21)
C(7)	0.8081 (13)	0.1817 (8)	0.8868 (8)	3.26 (20)
C(8)	0.7162 (10)	0.2540 (10)	0.9447 (6)	2.39 (14)
C(9)	0.5017 (10)	0.2487 (10)	0.9031 (6)	2.21 (14)
C(10)	0.4225 (10)	0.2689 (7)	0.7586 (6)	2.19 (16)
C(11)	0.4139 (13)	0.3149 (8)	0.9802 (9)	3.39 (20)
C(12)	0.5169 (15)	0.4075 (9)	1.0302 (9)	4.31 (23)
C(13)	0.7353 (15)	0.4074 (9)	1.0734 (9)	4.15 (22)
C(14)	0.8154 (14)	0.3210 (8)	1.0208 (9)	3.60 (21)
C(15)	0.8013 (17)	0.4070 (11)	1.2179 (10)	
C(16)	1.0130 (20)	0.4173 (12)	1.2739 (13)	
C(17)	0.8061 (21)	0.5018 (10)	1.0220 (14)	
C(18)	0.5067 (19)	0.0692 (11)	0.5236 (11)	
C(19)	0.4850 (14)	0.2493 (19)	0.4780 (7)	
C(20)	0.4742 (15)	0.3711 (8)	0.7289 (9)	
C(21)	0.0044 (18)	0.0803 (11)	0.3575 (10)	
C(22)	−0.0722 (20)	0.0868 (13)	0.2142 (10)	
H(9)	0.462	0.182	0.917	
H(11)	0.291	0.332	0.917	
H(1.1)	0.172	0.201	0.765	
H(1.2)	0.146	0.317	0.740	
H(15.1)	0.761	0.344	1.247	
H(15.2)	0.737	0.462	1.248	
H(7.1)	0.950	0.192	0.914	
H(7.2)	0.777	0.116	0.912	
H(6.1)	0.778	0.252	0.717	
H(6.2)	0.790	0.135	0.706	
H(2.1)	−0.017	0.223	0.559	
H(2.2)	0.141	0.298	0.532	
H(14)	0.958	0.314	1.046	
H(5)	0.469	0.124	0.736	
H(3)	0.184	0.102	0.576	

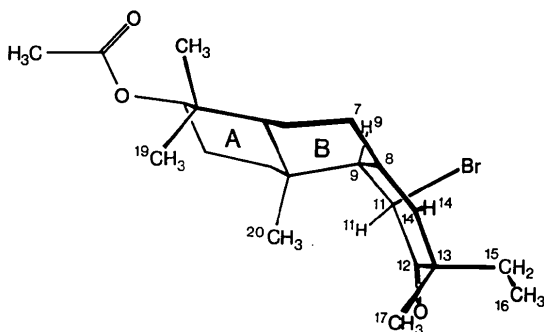


Fig. 1. View of molecule down *x* showing the numbering system.

Table 1 (cont.)

Anisotropic thermal-motion parameters ($\times 10^4$). The expression is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	280 (2)	116 (1)	61 (1)	-59 (5)	139 (2)	-16 (3)
O(1)	208 (18)	101 (7)	46 (6)	-60 (19)	-32 (17)	-4 (11)
O(2)	416 (30)	74 (7)	151 (11)	174 (24)	50 (27)	-61 (15)
O(3)	666 (42)	208 (14)	91 (10)	-495 (42)	-101 (31)	57 (18)
C(15)	293 (34)	84 (10)	99 (13)	19 (33)	-35 (33)	-65 (21)
C(16)	332 (40)	101 (13)	146 (16)	-27 (40)	-105 (40)	-66 (25)
C(17)	418 (45)	37 (8)	189 (19)	-77 (32)	110 (46)	-25 (21)
C(18)	317 (36)	119 (13)	99 (14)	53 (36)	14 (36)	-118 (22)
C(19)	261 (25)	131 (10)	49 (8)	-57 (54)	97 (23)	25 (32)
C(20)	213 (28)	43 (7)	69 (10)	18 (23)	21 (26)	42 (14)
C(21)	327 (36)	106 (12)	58 (10)	-129 (35)	3 (31)	-23 (18)
C(22)	417 (44)	169 (17)	43 (11)	-124 (47)	-98 (34)	-22 (22)

Table 2. Interatomic distances (\AA) and angles ($^\circ$), and least-squares planes

Some intramolecular bond lengths ($\pm 0.01 \text{\AA}$) mainly associated with ring C and the acetate group

C(22)—C(21)	1.55	C(11)—C(12)	1.51
C(21)—O(3)	1.16	C(12)—C(13)	1.52
C(21)—O(1)	1.33	C(13)—C(14)	1.53
O(1)—C(3)	1.44	C(14)—C(8)	1.33
C(18)—C(4)	1.57	C(11)—Br	1.94
C(19)—C(4)	1.54	C(12)—O(2)	1.22
C(10)—C(20)	1.53	C(13)—C(15)	1.56
C(7)—C(8)	1.46	C(13)—C(17)	1.58
C(8)—C(9)	1.50	C(15)—C(16)	1.50
C(9)—C(11)	1.52		

Bond angles associated with ring C ($\pm 1^\circ$)

C(7)—C(8)—C(9)	113	C(9)—C(11)—Br	111
C(10)—C(9)—C(11)	113	C(12)—C(11)—Br	103
C(7)—C(8)—C(14)	122	C(11)—C(12)—O(2)	121
C(9)—C(8)—C(14)	124	C(13)—C(12)—O(2)	120
C(8)—C(9)—C(11)	111	C(12)—C(13)—C(15)	108
C(9)—C(11)—C(12)	119	C(14)—C(13)—C(15)	111
C(11)—C(12)—C(13)	119	C(15)—C(13)—C(17)	111
C(12)—C(13)—C(14)	111	C(12)—C(13)—C(17)	108
C(13)—C(14)—C(8)	127	C(13)—C(15)—C(16)	114

Some intramolecular non-bonded distances

C(20)···C(19)	3.31	Br·····C(1)	4.42
C(20)···O(2)	3.89	O(1)···C(19)	2.83
C(20)···C(17)	3.93	O(1)···C(18)	2.94
C(20)···C(13)	3.84		

Some least-squares planes of the form $Ax + By + Cz = D$, where A , B and C are the direction cosines of the normal to the plane referred to the orthogonal crystallographic axes. The deviations in \AA of the most relevant atoms from the planes are given in square brackets.

Atoms defining the plane

C(7), C(8), C(9), C(13), C(14)

A	B	C
-0.194	-0.580	0.791

[C(7) -0.04, C(8) 0.04, C(9) 0.00, C(13) -0.05, C(14) 0.05, C(10) -1.38, C(11) 0.30, C(12) -0.13, C(15) 1.19, C(16) 1.32, C(17) -1.38, O(2) -0.54, Br 2.21]

Atoms defining the plane

C(8), C(9), C(11), C(12), C(13), C(14)

A	B	C
-0.159	-0.545	0.823

[C(8) -0.02, C(9) -0.12, C(11) 0.20, C(12) -0.15, C(13) 0.01, C(14) 0.07, C(7) -0.12, C(10) -1.54, C(15) 1.29, C(17) -1.27, O(2) -0.54, Br 2.11]

was proportional to $1/\sigma(F)$. Scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, 1962); that of Br was corrected for anomalous dispersion. Final positional and thermal parameters are given in Table 1, with estimated standard deviations in parentheses; bond lengths and angles are in Table 2.

Discussion. The results confirm that the structure deduced from the chemical work is correct. Ring *A* is a near perfect chair; ring *B* is distorted by the double bond at the junction C(8), the five C atoms associated with the double bond being closely coplanar. Ring *C* is approximately planar, bent away from the mean plane of rings *A* and *B*. The torsion angles are Br—C(11)···C(13)—C(15) 12, Br—C(11)—C(12)—O(2) 93, O(2)—C(12)—C(13)—C(17) 44, C(10)—C(9)—C(11)—C(12) 93, C(10)—C(9)—C(11)—Br 148, C(8)—C(9)—C(11)—Br 87, H(9)—C(9)—C(11)—Br 31, H(9)—C(9)—C(11)—H(11) 92°. The Br is pseudo-axial *cis* relative to H(9), consistent with the resistance to dehydrobromination. Br and C(20) are on opposite sides of the molecule. All bond lengths and angles are normal: the non-bonded contacts between the methyl groups are normal. Important non-bonded distances are Br···C(1) 4.42, C(19)···C(20) 3.31, C(17)···C(20) 3.93, C(20)···O(2) 3.89 \AA . The ethyl and acetate groups are ordered and a difference map shows no trace of solvent of crystallization.

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