

Diterpenoid C-Ring Bromoketones.

III. *ent*-3 β -Acetoxy-11 α -bromobeyer-2,12-dione

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Abstract. C₂₂O₄H₃₁Br, *M*=439. Orthorhombic *P*2₁2₁2₁, *a*=8.06 (1), *b*=10.69 (1), *c*=24.50 (2) Å, *V*=2111 Å³, *D*_c=1.39 g cm⁻³, *Z*=4, $\mu(\text{Mo } K\alpha)=21.0$ cm⁻¹. *R*=0.068 for 1163 observed data; Br, 6 C and 4 O atoms anisotropic and 16 H atoms included. The Br is above the mean plane of ring C; the C(12) keto-O(2) is nearly in the plane.

Introduction. The compound (Fig. 1) is an 11-bromo derivative of *ent*-3 β -hydroxybeyer-15-en-2,12-dione.

The conformation of the *B/C* ring junction was of interest because of the extreme rigidity forced on the C ring by the ethano bridge. The environments of the Br atom in this and in the related 11-bromo 8(14)-en-12-one (Sommerville & Laing, 1976*a*) and the 11-bromo 12-one (Sommerville & Laing, 1976*b*) derivatives were also of interest because it was hoped to find some correlation between these conformations and the known chemical reactivity (Candy, Pakshong & Pegel, 1970; McGarry, Pegel, Phillips & Waight, 1971). Suitable crystals were prepared by Mr C. P. Gorst-Allman. Data were collected from a crystal 0.4 × 0.4 × 0.4 mm on a Philips four-circle diffractometer with graphite-monochromated Mo *K* α radiation ($\lambda=0.7107$ Å) for θ between 3 and 20°. The ω -2 θ scan mode was used; the scan width was 1°, each peak was scanned for 33 s and the background was counted for 33 s for each peak. Of the 1180 reflexions, 1163 were classed as observed, $I > 1.65\sigma(I)$. Three reflexions were used as standards and their intensities 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. Subsequent Fourier maps yielded the coordinates of the lighter atoms. The structure was refined by block-diagonal least squares with the Br and 10 peripheral atoms (6 C, 4 O)

anisotropic; the 16 H atoms bonded directly to the main skeleton were included in the structure factor calculations. The final *R* was 0.068 for 1163 observed data.* Weighting was proportional to $1/\sigma(F)$. Scatter-

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31817 (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	0.0937 (2)	-0.6522 (2)	-0.3873 (1)	
O(1)	0.0577 (9)	-0.6023 (8)	-0.1001 (3)	
O(2)	-0.1363 (14)	-0.4775 (15)	-0.4571 (5)	
O(3)	0.2907 (11)	-0.7076 (9)	-0.1193 (4)	
O(4)	0.1746 (12)	-0.4548 (8)	-0.1816 (4)	
C(1)	0.0415 (13)	-0.5630 (11)	-0.2534 (5)	3.01 (27)
C(2)	0.0856 (17)	-0.5400 (11)	-0.1956 (4)	3.75 (27)
C(3)	-0.0008 (14)	-0.6260 (12)	-0.1553 (4)	3.30 (25)
C(4)	-0.1935 (14)	-0.6210 (11)	-0.1576 (4)	3.35 (26)
C(5)	-0.2371 (13)	-0.6397 (11)	-0.2190 (4)	2.79 (23)
C(6)	-0.4243 (15)	-0.6446 (12)	-0.2286 (4)	3.60 (24)
C(7)	-0.4625 (15)	-0.7012 (11)	-0.2853 (5)	3.74 (29)
C(8)	-0.3806 (14)	-0.6286 (11)	-0.3312 (4)	2.90 (24)
C(9)	-0.1935 (14)	-0.6145 (10)	-0.3192 (4)	2.70 (24)
C(10)	-0.1511 (14)	-0.5570 (11)	-0.2623 (4)	2.80 (25)
C(11)	-0.1046 (16)	-0.5540 (11)	-0.3667 (4)	3.60 (26)
C(12)	-0.1940 (18)	-0.5431 (13)	-0.4208 (6)	5.31 (35)
C(13)	-0.3646 (15)	-0.5992 (11)	-0.4298 (5)	3.74 (29)
C(14)	-0.3933 (16)	-0.6987 (11)	-0.3861 (5)	4.19 (27)
C(15)	-0.4722 (15)	-0.5038 (12)	-0.3449 (5)	4.06 (30)
C(16)	-0.4836 (15)	-0.4979 (12)	-0.4079 (5)	4.16 (30)
C(17)	-0.3955 (22)	-0.6405 (16)	-0.4880 (5)	
C(18)	-0.2544 (16)	-0.7339 (12)	-0.1236 (5)	
C(19)	-0.2557 (19)	-0.4963 (14)	-0.1325 (5)	
C(20)	-0.1951 (16)	-0.4149 (10)	-0.2562 (6)	
C(21)	0.2099 (15)	-0.6488 (15)	-0.0875 (5)	
C(22)	0.2624 (20)	-0.6068 (20)	-0.0302 (6)	
H(6.1)	-0.475	-0.700	-0.199	
H(6.2)	-0.471	-0.559	-0.225	
H(7.1)	-0.426	-0.791	-0.287	
H(7.2)	-0.588	-0.699	-0.291	
H(14.1)	-0.305	-0.767	-0.390	
H(14.2)	-0.505	-0.741	-0.392	
H(15.1)	-0.585	-0.500	-0.327	
H(15.2)	-0.406	-0.428	-0.330	
H(16.1)	-0.603	-0.519	-0.420	
H(16.2)	-0.455	-0.414	-0.422	
H(9)	-0.144	-0.702	-0.316	
H(11)	-0.087	-0.466	-0.352	
H(5)	-0.186	-0.725	-0.229	
H(3)	0.037	-0.714	-0.165	
H(1.1)	0.096	-0.496	-0.277	
H(1.2)	0.083	-0.647	-0.265	

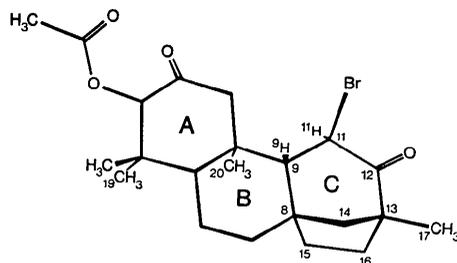


Fig. 1. View of molecule down *x* showing the numbering system.

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	155 (2)	219 (2)	24 (0)	85 (5)	41 (2)	0 (2)
O(1)	119 (15)	117 (10)	17 (2)	17 (22)	-10 (9)	-28 (7)
O(2)	250 (26)	375 (25)	35 (3)	-61 (47)	8 (15)	141 (15)
O(3)	174 (18)	184 (14)	22 (2)	122 (28)	1 (11)	-9 (10)
O(4)	226 (21)	95 (11)	29 (2)	-143 (27)	-9 (12)	-8 (9)
C(17)	322 (35)	186 (22)	11 (2)	71 (67)	-23 (18)	3 (14)
C(18)	174 (26)	101 (15)	16 (3)	-101 (37)	-11 (16)	27 (12)
C(19)	183 (24)	101 (15)	18 (3)	134 (36)	-15 (14)	-38 (11)
C(20)	202 (29)	2 (11)	28 (3)	0 (33)	20 (18)	3 (10)
C(21)	137 (23)	162 (20)	22 (3)	41 (47)	25 (14)	26 (15)
C(22)	236 (35)	350 (36)	14 (3)	157 (67)	-50 (18)	-52 (17)

Table 2. Interatomic distances (Å), bond angles (°), and least-squares planes

Some intramolecular bond lengths (± 0.01 Å)

C(22)—C(21)	1.53	C(11)—C(12)	1.51
O(3)—C(21)	1.19	C(12)—C(13)	1.52
C(21)—O(1)	1.36	C(13)—C(14)	1.53
O(1)—C(3)	1.45	C(14)—C(8)	1.54
C(4)—C(18)	1.55	C(8)—C(15)	1.56
C(4)—C(19)	1.55	C(15)—C(16)	1.55
C(7)—C(8)	1.52	C(16)—C(13)	1.54
C(8)—C(9)	1.54	C(13)—C(17)	1.51
C(10)—C(20)	1.57	C(11)—Br	1.98
C(9)—C(11)	1.51	C(12)—O(2)	1.22

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

C(7)—C(8)—C(9)	110	C(9)—C(8)—C(15)	115
C(10)—C(9)—C(11)	115	C(8)—C(15)—C(16)	106
C(11)—C(9)—C(8)	111	C(15)—C(16)—C(13)	106
C(9)—C(11)—C(12)	119	C(16)—C(13)—C(12)	104
C(11)—C(12)—C(13)	122	C(16)—C(13)—C(14)	99
C(12)—C(13)—C(14)	108	C(16)—C(13)—C(17)	115
C(13)—C(14)—C(8)	105	C(17)—C(13)—C(14)	116
C(14)—C(8)—C(9)	106	C(17)—C(13)—C(12)	114
C(14)—C(8)—C(7)	112	O(2)—C(12)—C(13)	118
C(7)—C(8)—C(15)	113	O(2)—C(12)—C(11)	120
C(14)—C(8)—C(15)	101	Br—C(11)—C(9)	111
		Br—C(11)—C(12)	102

Some intramolecular non-bonded distances (Å)

C(20)···C(19)	3.19	O(1)···C(19)	2.88
C(20)···C(16)	4.47	O(1)···C(18)	2.94
C(20)···C(13)	4.88	Br·····C(1)	3.44
C(20)···C(15)	3.26		

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 real crystallographic axes. The deviations in Å of the most relevant atoms from the planes are given in square brackets.

Atoms defining the plane

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

A	B	C
-0.465	0.865	0.189

[C(8) 0.41, C(9) -0.11, C(11) -0.10, C(12) 0.08, C(13) 0.16, C(14) -0.45, C(7) 0.26, C(10) 0.53, C(15) 1.84, C(16) 1.65, C(17) -0.37, Br -1.85, O(2) 0.30]

Atoms defining the plane

C(8), C(13), C(15), C(16)

A	B	C
0.819	0.569	0.076

[C(8) -0.05, C(13) 0.05, C(15) 0.08, C(16) -0.08, C(14) -0.66]

ing 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. Ring *A* is a near perfect chair while ring *B* is distorted due to the bridging of the *C* ring at the junction C(8). Ring *C* is a distorted chair with the ethano bridge and the Br atom on opposite sides of the mean plane of the ring. C(8), C(16), C(15), C(13) of the bridge ring are nearly coplanar (± 0.08 Å). The torsion angles are Br—C(11)—C(12)—O(2) 70, O(2)—C(12)—C(13)—C(17) 38, C(10)—C(9)—C(11)—C(12) 145, C(10)—C(9)—C(11)—Br 98, H(9)—C(9)—C(11)—H(11) 139, H(9)—C(9)—C(11)—Br 14°. The Br is *cis* to and nearly eclipses H(9). Important non-bonded distances are Br···C(1) 3.44, C(19)···C(20) 3.19, C(15)···C(20) 3.26 Å. The acetate group is ordered and a difference map shows no solvent of crystallization.*

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* *Note added in proof:* The correlation between the conformation of ring *C* and the UV-visible spectrum in this series of compounds will be described in a forthcoming publication by Dr K. H. Pegel and co-workers.

References

- CANDY, H. A., PAKSHONG, J. M. & PEGEL, K. H. (1970). *J. Chem. Soc. (C)*, pp. 2536–2538.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 203, 206, 216. Birmingham: Kynoch Press.
 MCGARRY, E. J., PEGEL, K. H., PHILLIPS, L. & WRIGHT, E. S. (1971). *J. Chem. Soc. (C)*, pp. 904–909.
 SOMMERVILLE, P. & LAING, M. (1976a). *Acta Cryst.* B32, 2683–2684.
 SOMMERVILLE, P. & LAING, M. (1976b). *Acta Cryst.* B32, 2685–2686.