ent-(1a*R*)-1-α-(1a-Hydroxy-1a-phenyl)-3β-hydroxy-11α-bromo-12-oxo-2-norbeyeran-3β-carboxylic Acid 2,1a-Lactone*

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Abstract. $C_{27}H_{33}BrO_4$, $M_r = 501$, orthorhombic, $P2_12_12_1$, $a = 21 \cdot 20$ (2), $b = 11 \cdot 42$ (1), $c = 9 \cdot 84$ (1) Å, $V = 2382$ Å^3, $D_c = 1 \cdot 40$ g cm^{-3}, $Z = 4$, μ(Mo $K\alpha$) = $18 \cdot 7$ cm^{-1}. $R = 0 \cdot 07$ for 1230 observed data: Br only anisotropic and 20 H atoms included. The phenyl on the nor-ring *A*/lactone system crowds the Br atom on ring *C* and the strain is relieved by angular distortions. The Br atom almost eclipses the C(12) keto O atom.

Introduction. When a mixture of the ketol (I*a*) and benzaldehyde in aqueous ethanol is treated with dilute NaOH in the presence of O_2, a lactone is obtained. Because chemical and spectroscopic methods could not determine unequivocally the configuration of the nor-ring *A*/lactone system the crystal structure of the 11-bromo derivative (I*b*) was determined (Laing, Pegel, Piacenza, Phillips & Waight, 1973).

(I*a*)   (I*b*)
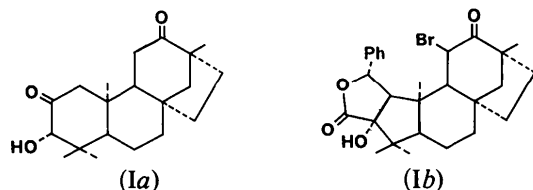
Suitable crystals were prepared by Dr L. P. L. Piacenza. Data were collected from a crystal $0 \cdot 3 \times 0 \cdot 4 \times 0 \cdot 4$ mm on a Philips four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0 \cdot 7107$ Å) for θ between 3 and 20°. The ω–2θ scan mode was used; the scan width was $1 \cdot 0°$, each peak being scanned for 50 s and the background for 50 s for each peak. Of the 1310 reflexions measured, 1230 were classed as observed, $I > 1 \cdot 65\sigma(I)$. There 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 only anisotropic; 20 H atoms

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were included in the structure factor calculations. The final R was $0 \cdot 07$ for 1230 observed data.‡ A Hughes weighting scheme was used, with $4F_{min} = 60 \cdot 0$. Weights were proportional to $1/F$ for $F > 4F_{min}$ and to F for $F < 4F_{min}$, with a proportionality factor such that the weight $= 1$ for $F = 4F_{min}$. Scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, 1962); that of Br was corrected

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‡ Lists of structure factors, anisotropic thermal parameters for Br and the fractional atomic coordinates of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33308 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters*

	x	y	z	B(Å^2)
Br	1161 (1)	1154 (1)	909 (1)	
O(1)	1307 (5)	4189 (9)	4797 (10)	4·67 (25)
O(2)	498 (6)	5154 (10)	5627 (13)	6·32 (29)
O(3)	−229 (4)	3406 (8)	4496 (10)	3·63 (22)
O(12)	2037 (5)	−853 (10)	737 (12)	5·51 (27)
C(1a)	1424 (6)	3107 (11)	3983 (14)	2·99 (28)
C(1)	782 (6)	2488 (11)	3874 (14)	2·35 (28)
C(2)	729 (7)	4195 (14)	5188 (17)	4·28 (37)
C(3)	384 (6)	3122 (12)	4955 (14)	2·79 (30)
C(4)	400 (7)	2306 (13)	6296 (15)	3·68 (33)
C(5)	836 (6)	1326 (12)	5841 (15)	2·86 (28)
C(6)	822 (7)	155 (12)	6625 (15)	3·33 (32)
C(7)	1398 (7)	−507 (13)	6184 (15)	3·88 (33)
C(8)	1414 (6)	−777 (11)	4623 (13)	2·52 (28)
C(9)	1299 (6)	350 (11)	3737 (12)	2·15 (26)
C(10)	778 (6)	1136 (12)	4284 (14)	2·59 (27)
C(11)	1236 (8)	−96 (12)	2294 (14)	3·75 (31)
C(12)	1769 (7)	−909 (13)	1860 (16)	3·45 (34)
C(13)	1928 (7)	−1890 (13)	2821 (15)	3·47 (32)
C(14)	2047 (6)	−1307 (12)	4202 (15)	3·36 (30)
C(15)	959 (7)	−1826 (13)	4258 (17)	3·90 (36)
C(16)	1270 (7)	−2554 (13)	3179 (15)	4·33 (34)
C(17)	2446 (8)	−2665 (14)	2345 (17)	5·02 (37)
C(18)	731 (8)	2939 (16)	7556 (19)	6·20 (43)
C(19)	−282 (8)	1941 (16)	6742 (20)	6·02 (42)
C(20)	86 (7)	693 (13)	3793 (16)	3·74 (34)
C(1′)	1767 (7)	3509 (12)	2732 (15)	3·34 (33)
C(2′)	1406 (7)	4116 (14)	1743 (17)	4·38 (37)
C(3′)	1761 (8)	4602 (15)	599 (18)	5·31 (42)
C(4′)	2371 (8)	4468 (15)	565 (18)	5·38 (40)
C(5′)	2726 (8)	3842 (17)	1464 (18)	5·32 (40)
C(6′)	2393 (8)	3367 (14)	2629 (18)	4·79 (39)

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

Intramolecular bond lengths (±0·02 Å)

Br—C(11)	1·98	C(1)—C(3)	1·54
O(12)—C(12)	1·24	C(3)—C(4)	1·62
C(11)—C(12)	1·52	C(4)—C(5)	1·52
C(12)—C(13)	1·50	C(4)—C(18)	1·60
C(13)—C(17)	1·49	C(4)—C(19)	1·57
C(13)—C(14)	1·53	C(1)—C(1a)	1·54
C(13)—C(16)	1·63	C(1a)—O(1)	1·49
C(16)—C(15)	1·50	O(1)—C(2)	1·28
C(14)—C(8)	1·53	C(2)—C(3)	1·45
C(8)—C(15)	1·58	C(2)—O(2)	1·28
C(8)—C(9)	1·57	C(3)—O(3)	1·41
C(9)—C(11)	1·51	C(1a)—C(1')	1·50
C(9)—C(10)	1·52	C(1')—C(2')	1·42
C(10)—C(5)	1·55	C(2')—C(3')	1·46
C(5)—C(6)	1·54	C(3')—C(4')	1·30
C(6)—C(7)	1·50	C(4')—C(5')	1·36
C(7)—C(8)	1·57	C(5')—C(6')	1·45
C(10)—C(20)	1·63	C(6')—C(1')	1·34
C(10)—C(1)	1·60		

Bond angles (±2°)

Br—C(11)—C(9)	114	C(10)—C(1)—C(3)	106
Br—C(11)—C(12)	108	C(10)—C(1)—C(1a)	116
O(12)—C(12)—C(11)	124	C(1)—C(3)—C(4)	106
O(12)—C(12)—C(13)	120	C(3)—C(4)—C(5)	101
C(9)—C(11)—C(12)	114	C(4)—C(5)—C(6)	119
C(11)—C(12)—C(13)	116	C(4)—C(5)—C(10)	110
C(12)—C(13)—C(14)	106	C(4)—C(3)—O(3)	114
C(12)—C(13)—C(17)	114	C(1)—C(3)—O(3)	113
C(12)—C(13)—C(16)	107	O(3)—C(3)—C(2)	109
C(17)—C(13)—C(16)	115	C(2)—C(3)—C(4)	110
C(13)—C(16)—C(15)	106	C(3)—C(4)—C(18)	112
C(13)—C(14)—C(8)	106	C(3)—C(4)—C(19)	111
C(14)—C(8)—C(9)	108	C(18)—C(4)—C(19)	108
C(14)—C(8)—C(15)	100	C(5)—C(4)—C(18)	107
C(14)—C(13)—C(16)	99	C(5)—C(4)—C(19)	117
C(14)—C(13)—C(17)	115	C(1)—C(3)—C(2)	103
C(8)—C(15)—C(16)	108	C(3)—C(2)—O(1)	116
C(15)—C(8)—C(9)	114	C(3)—C(2)—O(2)	126
C(8)—C(9)—C(11)	105	O(2)—C(2)—O(1)	118
C(8)—C(9)—C(10)	114	C(2)—O(1)—C(1a)	109
C(9)—C(10)—C(5)	112	O(1)—C(1a)—C(1)	106
C(10)—C(9)—C(11)	118	C(1a)—C(1)—C(3)	103
C(9)—C(10)—C(20)	112	O(1)—C(1a)—C(1')	106
C(9)—C(10)—C(1)	118	C(1)—C(1a)—C(1')	121
C(20)—C(10)—C(1)	103	C(1')—C(2')—C(3')	116
C(20)—C(10)—C(5)	114	C(2')—C(3')—C(4')	119
C(10)—C(5)—C(6)	112	C(3')—C(4')—C(5')	126
C(5)—C(6)—C(7)	106	C(4')—C(5')—C(6')	116
C(6)—C(7)—C(8)	114	C(5')—C(6')—C(1')	120
C(7)—C(8)—C(9)	112	C(6')—C(1')—C(2')	123
C(7)—C(8)—C(14)	111	C(1a)—C(1')—C(2')	117
C(7)—C(8)—C(15)	111	C(1a)—C(1')—C(6')	120
C(5)—C(10)—C(1)	96		

Some intramolecular non-bonded distances

Br···C(1')	3·48	C(20)···C(19)	3·33
Br···C(2')	3·52	C(20)···C(15)	3·45
Br···C(1)	3·39	C(20)···O(3)	3·24
Br···C(1a)	3·80	C(18)···O(3)	3·67
Br···C(10)	3·42	C(18)···O(2)	3·20
Br···C(20)	3·68	C(19)···O(3)	2·77
Br···O(12)	2·95	O(2)···O(3)	2·76
O(12)···C(17)	2·75	C(2)···C(18)	2·74

Table 2 (cont.)

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 and D is the perpendicular distance from the origin. The deviations in Å of the most relevant atoms from the planes are given in square brackets.

Atoms defining the plane: C(1), C(3), C(4), C(5), C(10)

A	B	C	D
−0·908	−0·361	−0·212	3·13

[C(1) 0·21, C(3) −0·07, C(4) −0·10, C(5) 0·24, C(10) −0·27, C(6) −0·10, C(9) 0·29, C(18) 1·06, C(19) −1·47, C(20) −1·89, C(1a) 1·72, C(3) −0·07, O(3) −1·23]

Atoms defining the plane: C(1), C(3), C(4), C(5)

A	B	C	D
−0·800	−0·510	−0·314	3·99

[C(1) −0·01, C(3) 0·02, C(4) −0·02, C(5) 0·01, C(10) −0·68]

Atoms defining the plane: C(5), C(6), C(7), C(8), C(9), C(10)

A	B	C	D
−0·834	−0·522	−0·179	3·02

[C(5) 0·28, C(6) −0·30, C(7) 0·24, C(8) −0·16, C(9) 0·15, C(10) −0·21, C(11) −0·48, Br −0·12, C(14) 0·56, C(15) −1·66, C(18) 1·36, C(19) −1·17, C(20) −1·78, C(1a) 2·06, C(1) 0·53, C(4) 0·18]

Atoms defining the plane: C(8), C(9), C(11), C(12), C(13), C(14)

A	B	C	D
−0·795	−0·607	0·005	2·17

[C(8) −0·35, C(9) 0·24, C(11) −0·17, C(12) 0·17, C(13) −0·25, C(14) 0·35, Br 0·58, O(12) 0·67, C(17) 0·09, C(15) −1·84, C(16) −1·82, C(7) −0·20, C(10) −0·09, C(20) −1·57]

Atoms defining the plane: C(8), C(13), C(15), C(16)

A	B	C	D
−0·460	0·556	−0·692	5·01

[C(8) 0·01, C(13) −0·01, C(15) −0·02, C(16) 0·02, C(14) 0·68, C(7) 0·89, C(9) −1·42, C(12) −1·44, Br −3·99, O(12) −1·98]

Atoms defining the plane: O(1), C(1), C(1a), C(2)

A	B	C	D
−0·227	0·520	−0·823	2·05

[O(1) −0·02, C(1) −0·01, C(1a) 0·02, C(2) 0·01, C(3) 0·30, O(2) −0·31, O(3) −0·54, C(4) 1·88, C(10) 1·12, C(1') −1·07]

Some torsion angles (°)

Br—C(11)—C(12)—O(12)	9
O(12)—C(12)—C(13)—C(17)	5
Br—C(11)—C(9)—C(10)	58
C(11)—C(9)—C(10)—C(1)	80
C(9)—C(10)—C(1)—C(1a)	46
Br—C(11)—C(9)—H(9)	54
O(3)—C(3)—C(4)—C(19)	4
C(2)—C(3)—C(4)—C(18)	5
C(19)—C(4)—C(5)—H(5)	151
C(20)—C(10)—C(5)—H(5)	177
C(20)—C(10)—C(9)—H(9)	155
H(9)—C(9)—C(11)—H(11)	174

for anomalous dispersion. The absolute configuration was determined, and it confirmed previous assignments for this family of compounds (Laing, Pegel & Piacenza, 1973; Laing, Pegel, Piacenza, Waight & Phillips, 1974; Laing, Sommerville, Hanouskova, Pegel, Piacenza, Phillips & Waight, 1972; Laing & Sommerville, 1975; Sommerville & Laing, 1976a,b,c). Final positional and
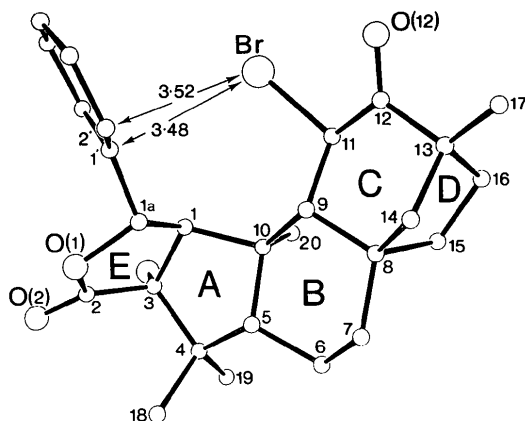
Fig. 1. View of the molecule showing the numbering system. O(3) is bonded to C(3).

thermal parameters are given in Table 1, with e.s.d.'s in parentheses; bond lengths and angles are in Table 2. Fig. 1 shows the molecular geometry.

Discussion. The results show that the structure deduced from the chemical work is correct. Nor-ring A and the lactone ring E have envelope conformations and are *cis* fused at C(1) and C(3). Ring E stands above the molecule relative to the mean plane of ring A while ring D lies below the plane; dihedral angles are A/E 74, A/D 80°; ring E is twisted clockwise relative to ring C. The phenyl ring at C(1a) is perpendicular to ring E, dihedral angle 88°, and is in close contact with the Br atom at C(11): Br$\cdots$C(1') 3·48, Br$\cdots$C(2') 3·52 Å. These close contacts cause torsional and angular strain throughout the molecule, especially along the chain of atoms from C(1a) to Br; the largest effects are seen in the bond angles C(9)—C(11)—Br 114, C(12)—C(11)—Br 108, C(1')—C(1a)—C(1) 121 and C(1')—C(1a)—O(1) 106°.

Rings B and C are distorted chairs and most of the angles within ring B have opened, mean value 112°. Rings C and D are distorted, *e.g.* C(14)—C(13)—C(16) 99°, so that C(15) below ring C is now 3·45 Å from C(20) compared with 3·17–3·26 Å in related compounds (Laing, Pegel & Piacenza, 1973; Laing *et al.*, 1974; Sommerville & Laing, 1976c). The dihedral

angles are B/C 12, C/D 80°. Br and C(17) eclipse O(12) and are almost in the mean plane of ring C; Br$\cdots$O(12), 2·95, and O(12)$\cdots$C(17), 2·75 Å, are shorter than in the related molecules (Sommerville & Laing, 1976a,b,c). H(9) is no longer perfectly *trans* to C(20), H(9)—C(9)—C(10)—C(20) 155°, emphasizing the large distortion in the molecule, but H(9) is *trans* to H(11), H(9)—C(9)—C(11)—H(11) 174°, consistent with the observed coupling constant of 12·4 Hz.

The eclipsed pentano conformation of ring A allows C(19) and C(20) to move apart [3·33 Å, similar to 3·37 Å in a closely related molecule also with a five-membered A ring (Laing *et al.*, 1974)]. C(5)—C(10)—C(9) has opened to 112° while C(5)—C(10)—C(1) has closed to 96°. O(3) and methyl C(19) are almost eclipsed and in very close contact (2·77 Å) as are C(2) and methyl C(18), 2·74 Å.

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