X-ray Structure Analysis of Obtusallene

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Abstract. $C_{15}H_{17}Br_2ClO_2$, orthorhombic, $P2_12_12_1$, $a = 5.545$ (9), $b = 10.082$ (13), $c = 28.589$ (14) Å and $Z = 4$. The structure was refined to $R = 0.082$ for 1218 reflexions and the molecule may be described as a halogenated bicyclic ether with an allenic side chain.

Introduction. The title compound was isolated from the red form of the alga *Laurencia obtusa* (Cox, Imre, Islimyeli & Thomson, 1982). We undertook a crystal structure analysis of (1) to resolve ambiguous spectroscopic data and to determine its absolute stereochemistry.

(1)
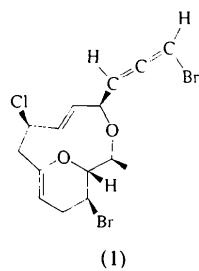
The X-ray intensities were collected on a Nicolet *P*3 automated diffractometer using monochromatized Mo $K\alpha$ radiation. Integrated relative intensities for 1517 independent reflections with $2\theta < 50°$ were measured as θ–2θ scans; 1218 reflexions had $I > 2.5\sigma(I)$. The positions of the bromine atoms were elucidated by direct methods using the program *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The remaining atoms were located in difference electron-density distributions calculated at intermediate stages of structure refinement using the program *SHELX* (Sheldrick, 1976). The coordinates for all atoms, anisotropic thermal parameters for the C, Br, Cl and O atoms and a common isotropic thermal parameter for the H atoms were varied in least-squares calculations. The C–H distances were constrained to be equal to 1.00 Å. The final values of R were 0.082 for the absolute configuration shown in (1) and 0.091 for

the mirror image of (1). Assuming no systematic errors in the data the small change in R provides a reliable demonstration of absolute configuration (Hamilton, 1965). Unit weights were used in all calculations.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent values of the anisotropic temperature factor coefficient* ($\times 10^3$) *with e.s.d.'s*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. $U_{iso} = 0.070$ (19) Å^2 for all H atoms.

	x	y	z	U_{eq}
Br(1)	5198 (7)	4552 (3)	3045 (1)	74 (2)
Br(2)	9908 (7)	0955 (2)	0748 (1)	66 (1)
Cl	6265 (14)	8088 (6)	0646 (3)	68 (4)
C(1)	9069 (59)	6729 (31)	1292 (15)	96 (25)
C(2)	8799 (48)	6968 (20)	0740 (8)	54 (14)
C(3)	8159 (41)	5629 (21)	0515 (8)	50 (13)
C(4)	9886 (51)	4522 (18)	0646 (6)	45 (11)
O(5)	9246 (28)	3984 (13)	1069 (5)	47 (9)
C(6)	11073 (39)	3215 (18)	1298 (7)	39 (12)
C(7)	12753 (33)	4115 (22)	1566 (9)	46 (12)
O(8)	11335 (27)	4760 (12)	1914 (5)	43 (8)
C(9)	11527 (72)	6172 (20)	1944 (7)	82 (19)
C(10)	11047 (83)	6806 (30)	1470 (13)	98 (27)
C(11)	11829 (43)	4160 (23)	0425 (8)	52 (14)
C(12)	13391 (47)	3019 (22)	0573 (7)	53 (14)
C(13)	12298 (39)	2255 (20)	0947 (8)	46 (13)
C(14)	10202 (72)	6600 (20)	2371 (8)	69 (16)
C(15)	9260 (37)	5815 (19)	2692 (7)	40 (12)
C(16)	8277 (53)	5018 (22)	3020 (7)	62 (15)
C(17)	14809 (44)	3428 (19)	1804 (8)	48 (12)
H(1)	7623 (59)	6518 (31)	1488 (15)	
H(2)	10316 (48)	7344 (20)	0605 (8)	
H(3A)	8181 (41)	5737 (21)	0168 (8)	
H(3B)	6500 (41)	5371 (21)	0619 (8)	
H(6)	10345 (39)	2620 (18)	1539 (7)	
H(7)	13507 (33)	4734 (22)	1336 (9)	
H(9)	13189 (72)	6523 (20)	2000 (7)	
H(10)	12371 (83)	7290 (30)	1305 (13)	
H(11)	12308 (43)	4672 (23)	0140 (8)	
H(12A)	14975 (47)	3373 (22)	0684 (7)	
H(12B)	13659 (47)	2425 (22)	0298 (7)	
H(13)	13653 (39)	1741 (20)	1090 (8)	
H(14)	10006 (72)	7576 (20)	2419 (8)	
H(16)	9371 (53)	4664 (22)	3268 (7)	
H(17A)	15825 (44)	2969 (19)	1564 (8)	
H(17B)	14167 (44)	2761 (19)	2030 (8)	
H(17C)	15811 (44)	4095 (19)	1975 (8)	

Table 2. *Bond lengths* (Å) *with e.s.d.'s*

Br(1)—C(16)	1·77 (3)	C(6)—C(7)	1·51 (3)
Br(2)—C(13)	1·95 (2)	C(6)—C(13)	1·55 (3)
Cl—C(2)	1·82 (3)	C(7)—O(8)	1·43 (3)
C(1)—C(2)	1·60 (5)	C(7)—C(17)	1·50 (3)
C(1)—C(10)	1·21 (6)	O(8)—C(9)	1·43 (2)
C(2)—C(3)	1·54 (3)	C(9)—C(10)	1·52 (4)
C(3)—C(4)	1·52 (3)	C(9)—C(14)	1·49 (4)
C(4)—O(5)	1·37 (2)	C(11)—C(12)	1·50 (3)
C(4)—C(11)	1·30 (4)	C(12)—C(13)	1·45 (3)
O(5)—C(6)	1·43 (3)	C(14)—C(15)	1·32 (3)
C(15)—C(16)	1·35 (3)		

Table 3. *Valency angles* (°) *with e.s.d.'s*

C(15)–C(16)–Br(1)	125·1 (19)	C(6)–C(13)–Br(2)	108·1 (14)
C(12)–C(13)–Br(2)	115·2 (16)	C(1)–C(2)–Cl	108·1 (17)
C(3)–C(2)–Cl	107·7 (16)	C(10)–C(1)–C(2)	119·2 (33)
C(3)–C(2)–C(1)	107·5 (18)	C(9)–C(10)–C(1)	120·4 (38)
C(4)–C(3)–C(2)	113·4 (19)	O(5)–C(4)–C(3)	110·2 (19)
C(11)–C(4)–C(3)	127·5 (19)	C(11)–C(4)–O(5)	122·1 (20)
C(6)–O(5)–C(4)	115·7 (17)	C(12)–C(11)–C(4)	123·8 (20)
C(7)–C(6)–O(5)	110·0 (15)	C(13)–C(6)–O(5)	110·6 (16)
C(13)–C(6)–C(7)	115·7 (18)	O(8)–C(7)–C(6)	106·7 (15)
C(17)–C(7)–C(6)	115·0 (18)	C(12)–C(13)–C(6)	109·2 (17)
C(17)–C(7)–O(8)	108·3 (18)	C(9)–O(8)–C(7)	117·1 (18)
C(10)–C(9)–O(8)	110·6 (19)	C(14)–C(9)–O(8)	107·5 (20)
C(14)–C(9)–C(10)	121·5 (27)	C(15)–C(14)–C(9)	126·3 (19)
C(13)–C(12)–C(11)	111·9 (20)	C(16)–C(15)–C(14)	179·5 (26)
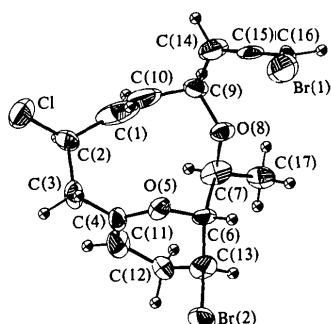
Fig. 1. The atomic arrangement of obtusallene.

Table 4. *Endocyclic torsion angles* (°) *for some ten-membered rings*

(1) Obtusallene; (2) shiromodiol acetate *p*-bromobenzoate; (3) 1,5-cyclodecadiene.

	(1)	(2)	(3)*
$\omega(1-2)$	111	112	89
$\omega(2-3)$	−53	−49	−49
$\omega(3-4)$	83	86	89
$\omega(4-5)$	−163	−151	−168
$\omega(5-6)$	83	79	87
$\omega(6-7)$	62	57	50
$\omega(7-8)$	−130	−129	−111
$\omega(8-9)$	54	53	50
$\omega(9-10)$	66	64	87
$\omega(10-1)$	−160	−166	−168

* Type II conformation; White & Bovill force field.

isolated 1,5-cyclodecadiene (3) (Table 4) as calculated by molecular mechanics (Bovill, Cox, Cradwick, Guy, Sim & White, 1976). Similar conformations have been observed in several germacranolides. The C(1)···O(5) transannular separation is distinctly short [2·84 (3) Å] and again short separations between positions 1 and 5 are common in many germacranolides.

(2)
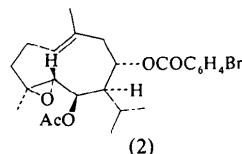
The dihydropyran ring adopts a half-chair conformation $[\Delta C_2(4-11) = 5 (1)°]$ with C(6) and $\overline{C(13)}$ displaced to opposite sides of the mean plane through C(4), O(5), C(11) and C(12). In the bromo-allenic side chain the dihedral angle between the planes C(9)C(14)C(15) and C(15)C(16)Br(1) is 82 (2)°. The only short intermolecular separation is Br(2)···Cl[x,y − 1, z] 3·539 (7) Å.

Discussion. The molecular structure is shown in Fig. 1 and the atomic coordinates, bond lengths and valency angles are listed in Tables 1–3.* Obtusallene has the same bromoallenic side chain as laurallene (Fukuzawa & Kurosawa, 1979) but the oxygen-bridged 12-membered ring is a new structural type in *Laurencia*. The confirmation of the ten-membered dioxecin ring is very similar to that of the cyclodecene ring of shiromodiol acetate *p*-bromobenzoate (2) (McClure, Sim, Coggon & McPhail, 1970). These conformations are also related to a low-energy conformation of

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* Lists of torsion angles, thermal parameters and observed and calculated structure amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36551 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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