

Conformation and Absolute Configuration of Shiromodiol 6-*O*-Acetate 8-*O*-*p*-Bromobenzoate*

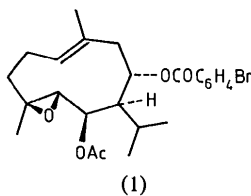
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Abstract. $C_{24}H_{31}BrO_5$, $M_r = 479.46$, orthorhombic, $P2_12_12_1$, $a = 17.139$ (3), $b = 13.925$ (2), $c = 10.028$ (2) Å, $V = 2393$ (1) Å³, $Z = 4$, $D_x = 1.33$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 1.85$ mm⁻¹, $F(000) = 1000$, $T = 293$ K, $R = 0.036$ for 1429 reflections. The absolute configuration was defined by Rogers' η -method. The ten-membered ring adopts the boat-chair conformation with the C(14) and C(15) methyl groups *syn* and on the α face of the ring.

Introduction. The absolute stereochemistry and conformation of the title compound (1) were reported briefly some years ago (McClure, Sim, Coggon & McPhail, 1970). Since then a number of other sesquiterpenoids have been found to have similar conformations (e.g. Cox & Sim, 1974; Calleri, Chiari & Viterbo, 1983; Appendino, Calleri & Chiari, 1986). A new X-ray analysis of the shiromodiol derivative was undertaken to confirm the assignment of absolute configuration and to provide details of the molecular geometry.



Experimental. Colourless crystal, dimensions $0.15 \times 0.20 \times 0.30$ mm. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation. Cell dimensions from setting angles of 25 independent reflections with θ 12–13°; 3266 reflections surveyed in the range θ 1.5–28°; h 0→20, k 0→18, l 0→12; 1429 independent reflections with $I > 2.5\sigma(I)$. Two reference reflections monitored periodically showed no significant variation in intensity. No absorption correction. H atoms located in difference Fourier syntheses. Full-matrix least-squares calculations on F with anisotropic thermal

parameters for Br, C and O atoms and isotropic for H atoms. Convergence at $R = 0.036$, $wR = 0.038$, $S = 1.83$ for 396 parameters, $\Delta/\sigma < 0.5$, $w = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max. 0.31, min. -0.32 e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974). Absolute configuration established by refinement of the η parameter (Rogers, 1981); at convergence $\eta = 0.984$ (39). Calculations on a SEL 32/27 computer with the *GX* system of programs (Mallinson & Muir, 1985).

Discussion. Atomic coordinates are listed in Table 1 and the molecular dimensions in Table 2.† The torsion angles for the ten-membered ring are shown in Table 3. Fig. 1, drawn with *ORTEP* (Johnson, 1965), illustrates the molecular structure. The atomic parameters obtained in the analysis are in good agreement with the earlier (unpublished) results but are of improved precision. The assignment of absolute stereochemistry is confirmed.

The C(1)=C(10) double-bond system is subject to some strain, with the C(2)–C(1)–C(10)–C(9) torsion angle of -165 (1)° appreciably different from the ideal value of 180°. The *trans* double bonds in other germacranes sesquiterpenoids also deviate from ideal geometry (Cox & Sim, 1974; Calleri, Chiari & Viterbo, 1983). The distortions can be partitioned between out-of-plane bending at the carbon atoms (χ) and twisting around the double bond (τ) (Winkler & Dunitz, 1971). The values of these parameters in the shiromodiol derivative (1) are $\chi[C(1)] = 8$, $\chi[C(10)] = -4$ °, $\tau = -171$ ° (i.e. a twist of 9°). There is a marked asymmetry in the ring C–C–C angles at the C=C bond [C(2)–C(1)–C(10) is 130.8° whereas C(1)–C(10)–C(9) is 121.3°] and a similar asymmetry occurs at the epoxide where C(4)–C(5)–C(6) is 124.4° and C(3)–C(4)–C(5) is 118.8°. In both cases the smaller angle is at the C atom carrying the methyl substituent, consistent with a steric effect.

* 6,10-Dimethyl-3-(1-methylethyl)-11-oxabicyclo[8.1.0]undec-6-ene-2,4-diol 2-acetate 4-*p*-bromobenzoate (*Chemical Abstracts* name).

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and additional torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43828 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)*

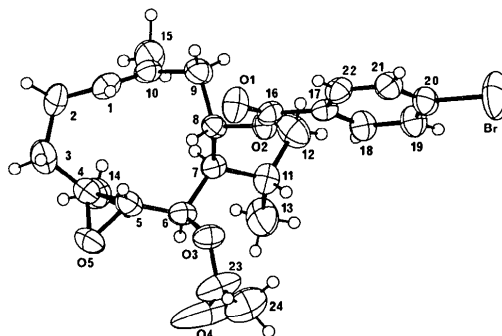
	$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}$.			
	x	y	z	U_{eq}
C(1)	0.5715 (4)	0.7422 (4)	1.1980 (7)	0.050
C(2)	0.6010 (5)	0.7722 (6)	1.3300 (6)	0.059
C(3)	0.5395 (5)	0.8266 (6)	1.4102 (6)	0.068
C(4)	0.5015 (4)	0.9056 (5)	1.3312 (6)	0.056
C(5)	0.4331 (3)	0.8822 (5)	1.2475 (6)	0.052
C(6)	0.4125 (4)	0.9328 (5)	1.1215 (6)	0.047
C(7)	0.4612 (4)	0.9054 (4)	1.0008 (6)	0.043
C(8)	0.4586 (4)	0.7956 (4)	0.9746 (6)	0.044
C(9)	0.5397 (4)	0.7477 (6)	0.9608 (7)	0.057
C(10)	0.5903 (3)	0.7702 (4)	1.0792 (6)	0.049
C(11)	0.4467 (5)	0.9690 (5)	0.8767 (6)	0.059
C(12)	0.5028 (5)	0.9481 (7)	0.7641 (8)	0.075
C(13)	0.4512 (7)	1.0755 (6)	0.9116 (10)	0.092
C(14)	0.5510 (4)	0.9905 (5)	1.3001 (7)	0.074
C(15)	0.6610 (4)	0.8316 (6)	1.0494 (6)	0.072
C(16)	0.3753 (3)	0.6956 (4)	0.8414 (6)	0.045
C(17)	0.3391 (3)	0.6886 (4)	0.7075 (5)	0.042
C(18)	0.3369 (4)	0.7652 (4)	0.6208 (6)	0.053
C(19)	0.3044 (4)	0.7565 (5)	0.4962 (6)	0.058
C(20)	0.2737 (4)	0.6698 (5)	0.4597 (5)	0.055
C(21)	0.2739 (4)	0.5926 (4)	0.5434 (6)	0.055
C(22)	0.3070 (4)	0.6033 (4)	0.6667 (6)	0.051
C(23)	0.2744 (5)	0.9690 (6)	1.1081 (9)	0.088
C(24)	0.1973 (4)	0.9345 (6)	1.0667 (10)	0.094
O(1)	0.3722 (3)	0.6355 (3)	0.9254 (4)	0.067
O(2)	0.4146 (2)	0.7793 (3)	0.8543 (3)	0.047
O(3)	0.3316 (2)	0.9061 (3)	1.0881 (4)	0.054
O(4)	0.2867 (3)	1.0455 (5)	1.1543 (10)	0.183
O(5)	0.4232 (3)	0.9311 (4)	1.3727 (4)	0.073
Br	0.22934 (7)	0.65974 (6)	0.28734 (8)	0.113

Table 2. *Interatomic distances (\AA) and angles ($^\circ$)*

C(1)–C(2)	1.477 (10)	C(1)–C(10)	1.294 (10)
C(2)–C(3)	1.528 (11)	C(3)–C(4)	1.504 (11)
C(4)–C(5)	1.478 (9)	C(4)–C(14)	1.489 (10)
C(4)–O(5)	1.450 (9)	C(5)–C(6)	1.489 (9)
C(5)–O(5)	1.438 (8)	C(6)–C(7)	1.519 (9)
C(6)–O(3)	1.475 (8)	C(7)–C(8)	1.552 (8)
C(7)–C(11)	1.547 (9)	C(8)–C(9)	1.547 (10)
C(8)–O(2)	1.440 (7)	C(9)–C(10)	1.504 (10)
C(10)–C(15)	1.512 (10)	C(11)–C(12)	1.511 (12)
C(11)–C(13)	1.526 (11)	C(16)–C(17)	1.483 (9)
C(16)–O(1)	1.189 (8)	C(16)–O(2)	1.352 (8)
C(17)–C(18)	1.376 (8)	C(17)–C(22)	1.371 (8)
C(18)–C(19)	1.374 (9)	C(19)–C(20)	1.366 (9)
C(20)–C(21)	1.364 (9)	C(20)–Br	1.893 (6)
C(21)–C(22)	1.369 (9)	C(23)–C(24)	1.466 (11)
C(23)–O(3)	1.329 (9)	C(23)–O(4)	1.181 (11)
C(2)–C(1)–C(10)	130.8 (7)	C(1)–C(2)–C(3)	112.1 (7)
C(2)–C(3)–C(4)	112.6 (6)	C(3)–C(4)–C(5)	118.8 (6)
C(3)–C(4)–C(14)	116.4 (6)	C(3)–C(4)–O(5)	115.4 (6)
C(5)–C(4)–C(14)	120.6 (6)	C(5)–C(4)–O(5)	58.8 (4)
C(14)–C(4)–O(5)	113.1 (6)	C(4)–C(5)–C(6)	124.4 (6)
C(4)–C(5)–O(5)	59.6 (4)	C(6)–C(5)–O(5)	119.2 (6)
C(5)–C(6)–C(7)	115.3 (6)	C(5)–C(6)–O(3)	107.2 (5)
C(7)–C(6)–O(3)	105.8 (5)	C(6)–C(7)–C(8)	111.5 (5)
C(6)–C(7)–C(11)	114.2 (6)	C(8)–C(7)–C(11)	115.0 (5)
C(7)–C(8)–C(9)	114.5 (6)	C(7)–C(8)–O(2)	108.2 (5)
C(9)–C(8)–O(2)	109.1 (5)	C(8)–C(9)–C(10)	111.0 (6)
C(1)–C(10)–C(9)	121.3 (6)	C(1)–C(10)–C(15)	123.5 (6)
C(9)–C(10)–C(15)	115.1 (6)	C(7)–C(11)–C(12)	112.9 (7)
C(7)–C(11)–C(13)	111.3 (6)	C(12)–C(11)–C(13)	109.1 (7)
C(17)–C(16)–O(1)	125.2 (6)	C(17)–C(16)–O(2)	110.6 (5)
O(1)–C(16)–O(2)	124.2 (6)	C(16)–C(17)–C(18)	122.2 (5)
C(16)–C(17)–C(22)	119.7 (6)	C(18)–C(17)–C(22)	118.1 (6)
C(17)–C(18)–C(19)	121.2 (6)	C(18)–C(19)–C(20)	118.5 (6)
C(19)–C(20)–C(21)	122.0 (6)	C(19)–C(20)–Br	117.7 (5)
C(21)–C(20)–Br	120.3 (5)	C(20)–C(21)–C(22)	118.1 (6)
C(17)–C(22)–C(21)	122.0 (6)	C(24)–C(23)–O(3)	113.9 (7)
C(24)–C(23)–O(4)	124.5 (8)	O(3)–C(23)–O(4)	121.6 (8)
C(8)–O(2)–C(16)	118.5 (5)	C(6)–O(3)–C(23)	119.5 (6)
C(4)–O(5)–C(5)	61.6 (4)		

Table 3. *Torsion angles in the ten-membered ring ($^\circ$)*

C(10)–C(1)–C(2)–C(3)	111.9 (10)	C(5)–C(6)–C(7)–C(8)	55.8 (6)
C(1)–C(2)–C(3)–C(4)	–49.3 (7)	C(6)–C(7)–C(8)–C(9)	–128.0 (7)
C(2)–C(3)–C(4)–C(5)	86.8 (8)	C(7)–C(8)–C(9)–C(10)	53.7 (6)
C(3)–C(4)–C(5)–C(6)	–149.6 (10)	C(8)–C(9)–C(10)–C(1)	63.0 (7)
C(4)–C(5)–C(6)–C(7)	76.8 (7)	C(9)–C(10)–C(1)–C(2)	–164.9 (12)

Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids of the C, O and Br atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1 \AA .

In each pair of $C(a)–C(b)–C$ and $C(a)–C(b)–O$ angles of the epoxide group the former angle is larger than the latter, e.g. $C(6)–C(5)–C(4)$ is 124.4° and $C(6)–C(5)–O(5)$ is 119.2° . This distinction has been noted in other epoxides (Cox & Sim, 1974). The $C–C(sp^3)–C$ angles in the ten-membered ring at C(2), C(3), C(6), C(7), C(8), C(9) are greater than tetrahedral, 111.0 – 115.3° , mean 112.8° . In cyclodecane-1,6-diol, where there are additional $H\cdots H$ repulsions, the $C–C–C$ angles are larger, 113.4 – 120.1° (Ermer, Dunitz & Bernal, 1973).

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