

Scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates for the non-H atoms and the main geometrical parameters are given in Tables 1 and 2,* according to the numbering scheme given in Fig. 1 (*PLUTO*, Motherwell & Clegg, 1978).

Related literature. The synthesis of the title compound is described in Iturrino, Juanes, Mendoza, Rodriguez-Ubis & Serrano (1989). Similar ring conformations around the SO₂ group have been found in four phenylsulfonyl derivatives by searching the Cambridge Structural Database (Allen *et al.*, 1979). In contrast, no 14-membered rings containing N atoms at similar positions could be found.

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* Lists of structure factors, anisotropic thermal parameters, bond distances, bond angles and torsion angles, H-atom parameters and references for the four phenylsulfonyl derivatives mentioned in *Related literature* have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51759 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of the Absolute Configuration of Deoxyprepacifenol, from the Mediterranean Red Alga *Laurencia majuscula*

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Abstract. 3,4'-Dibromo-4-chloro-1',3',3',4-tetramethylspiro(cyclohexane-1,2'-[7]oxabicyclo[4.1.0]hept-4'-ene), C₁₅H₂₁Br₂ClO, *M_r* = 412.6, orthorhombic, *P*2₁2₁2₁, *a* = 11.6520 (14), *b* = 12.079 (2), *c* = 11.606 (3) Å, *V* = 1633.5 (9) Å³, *Z* = 4, *D_x* = 1.678 g cm⁻³, λ(MoKα) = 0.71073 Å, μ = 50.7 cm⁻¹, *F*(000) = 824, *T* = 297 K, *R* = 0.053 for 2288 observations (of 3909 unique data). The original absolute configuration determination has been questioned as based on a small difference in *wR* between enantiomorphous models, 0.085 *vs* 0.088. Our study, on material from a new natural source, confirms the molecular structure and the absolute configuration with

Professor J. Mendoza for suggesting the problem and providing the material.

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correlation to chiroptical data and increases the resolution of the determination.

Experimental. Colorless, tabular crystals of (1) isolated from *Laurencia majuscula*, m.p. 402 K. Crystal size 0.28 × 0.40 × 0.52 mm, space group from systematic

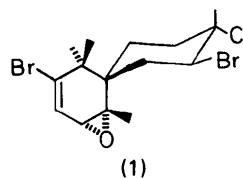


Table 1. Fractional coordinates and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Br(18)	0.26905 (8)	0.54336 (7)	0.10972 (9)	6.28 (2)
Br(19)	0.2469 (1)	-0.12917 (7)	0.19057 (9)	7.43 (2)
Cl(16)	0.0517 (2)	-0.0541 (2)	0.3975 (2)	5.80 (5)
O(17)	0.3080 (5)	0.2861 (4)	0.4448 (4)	5.2 (1)
C(1)	0.2813 (6)	0.2199 (6)	0.2385 (6)	3.6 (2)
C(2)	0.2880 (6)	0.1020 (6)	0.1920 (6)	4.0 (2)
C(3)	0.2293 (7)	0.0160 (5)	0.2652 (6)	4.1 (2)
C(4)	0.1037 (6)	0.0446 (6)	0.2902 (6)	4.2 (2)
C(5)	0.1020 (6)	0.1569 (7)	0.3468 (6)	4.6 (2)
C(6)	0.1578 (6)	0.2442 (6)	0.2709 (6)	3.9 (2)
C(7)	0.3607 (7)	0.2364 (6)	0.3459 (6)	3.9 (2)
C(8)	0.3893 (7)	0.3494 (6)	0.3786 (7)	5.0 (2)
C(9)	0.3465 (7)	0.4396 (6)	0.3072 (7)	4.7 (2)
C(10)	0.3165 (6)	0.4215 (6)	0.2003 (7)	4.3 (2)
C(11)	0.3247 (6)	0.3071 (6)	0.1456 (6)	3.6 (2)
C(12)	0.4531 (7)	0.2894 (7)	0.1141 (7)	5.3 (2)
C(13)	0.2584 (8)	0.3002 (7)	0.0329 (6)	5.4 (2)
C(14)	0.4466 (7)	0.1476 (7)	0.3808 (8)	5.8 (2)
C(15)	0.0228 (7)	0.0348 (8)	0.1884 (7)	5.9 (2)

absences *h*00 with *h* odd, 0*k*0 with *k* odd, 00*l* with *l* odd, cell dimensions from setting angles of 25 reflections having $11 < \theta < 12^\circ$. Data collected on Enraf-Nonius CAD-4 diffractometer, Mo *K*α radiation, graphite monochromator, ω -2θ scans designed for $I = 50\sigma(I)$, subject to max. scan time 120 s, scan rates varied 0.46–4.0° min⁻¹. Data having $1 < \theta < 30^\circ$, $0 \leq h \leq 16$, $0 \leq k \leq 16$, $0 \leq l \leq 16$ measured, also inequivalent *hkl* octant to $\theta = 25^\circ$. Data corrected for background, Lorentz, polarization, absorption by ψ scans, min. relative transmission 74.60, max. 99.77%. Standard reflections 400, 020, 002, decreased 9.7% in intensity, linear correction applied. 3909 unique *hkl* and *hkl* data, 2288 observed with $I > 1\sigma(I)$. Structure solved by heavy-atom methods, refined by full-matrix least squares based on F with weights $w = 4F_o^2 \times [Lp\{S^2(C+R^2B) + (0.02F_o^2)^2\}]^{-1}$, where S = scan rate, C = integrated count, R = scan time/background time, B = background count, using Enraf-Nonius SDP (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), anomalous coefficients of Cromer (1974). Non-H anisotropic, H atoms located from ΔF and included as fixed contributions with $B = 5.0 \text{ \AA}^2$. Final* $R = 0.053$, $wR = 0.053$, $S = 2.653$ for 173 variables. Max. $\Delta/\sigma = 0.01$ in final cycle, max. residual density 0.84 e Å⁻³ [near Br(1)], min. -0.63 e Å⁻³, extinction $g = 1.5(3) \times 10^{-7}$ where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c . Enantiomorph yielded $R = 0.069$, $wR = 0.079$, $S = 3.943$, and had 42 reflections with $10 < \Delta F/\sigma(F) < 27$, while the correct configuration had no such data. The improve-

* Lists of H-atom coordinates, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51762 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å), bond angles (°) and selected torsion angles (°)

Br(18)—C(10)	1.891 (5)	C(4)—C(5)	1.508 (8)
Br(19)—C(3)	1.966 (4)	C(4)—C(15)	1.517 (7)
Cl(16)—C(4)	1.827 (5)	C(5)—C(6)	1.520 (7)
O(17)—C(7)	1.434 (6)	C(7)—C(8)	1.455 (7)
O(17)—C(8)	1.440 (6)	C(7)—C(14)	1.522 (7)
C(1)—C(2)	1.526 (7)	C(8)—C(9)	1.457 (7)
C(1)—C(6)	1.517 (6)	C(9)—C(10)	1.307 (8)
C(1)—C(7)	1.565 (6)	C(10)—C(11)	1.524 (7)
C(1)—C(11)	1.589 (7)	C(11)—C(12)	1.555 (7)
C(2)—C(3)	1.506 (7)	C(11)—C(13)	1.522 (7)
C(3)—C(4)	1.532 (7)		
C(7)—O(17)—C(8)	60.9 (3)	O(17)—C(7)—C(1)	115.9 (4)
C(2)—C(1)—C(6)	108.4 (4)	O(17)—C(7)—C(8)	59.8 (3)
C(2)—C(1)—C(7)	111.7 (4)	O(17)—C(7)—C(14)	111.3 (4)
C(2)—C(1)—C(11)	111.2 (4)	C(1)—C(7)—C(8)	117.5 (4)
C(6)—C(1)—C(7)	109.8 (4)	C(1)—C(7)—C(14)	120.7 (5)
C(6)—C(1)—C(11)	110.0 (4)	C(8)—C(7)—C(14)	116.2 (5)
C(7)—C(1)—C(11)	105.6 (4)	O(17)—C(8)—C(7)	59.4 (3)
C(1)—C(2)—C(3)	114.9 (4)	O(17)—C(8)—C(9)	118.4 (5)
Br(19)—C(3)—C(2)	108.6 (6)	C(7)—C(8)—C(9)	118.3 (5)
Br(19)—C(3)—C(4)	112.6 (4)	C(8)—C(9)—C(10)	120.5 (5)
C(2)—C(3)—C(4)	112.6 (4)	Br(18)—C(10)—C(9)	118.4 (5)
Cl(16)—C(4)—C(3)	107.4 (4)	Br(18)—C(10)—C(11)	119.5 (4)
Cl(16)—C(4)—C(5)	106.6 (4)	C(9)—C(10)—C(11)	122.0 (5)
Cl(16)—C(4)—C(15)	105.9 (4)	C(1)—C(11)—C(10)	107.4 (4)
C(3)—C(4)—C(5)	107.4 (4)	C(1)—C(11)—C(12)	112.0 (4)
C(3)—C(4)—C(15)	115.4 (5)	C(1)—C(11)—C(13)	112.7 (4)
C(5)—C(4)—C(15)	113.7 (5)	C(10)—C(11)—C(12)	106.5 (4)
C(4)—C(5)—C(6)	111.5 (4)	C(10)—C(11)—C(13)	112.1 (4)
C(1)—C(6)—C(5)	114.6 (5)	C(12)—C(11)—C(13)	106.1 (4)
C(6)—C(1)—C(2)—C(3)	-48.5 (8)	Br(19)—C(3)—C(4)—Cl(16)	65.8 (5)
C(2)—C(1)—C(6)—C(5)	50.2 (8)	C(2)—C(3)—C(4)—C(5)	-56.7 (7)
C(2)—C(1)—C(7)—C(14)	9.7 (9)	C(3)—C(4)—C(5)—C(6)	57.9 (7)
C(11)—C(1)—C(7)—C(8)	41.4 (8)	C(4)—C(5)—C(6)—C(1)	-58.2 (8)
C(2)—C(1)—C(11)—C(12)	-62.7 (7)	C(1)—C(7)—C(8)—C(9)	-2.5 (10)
C(2)—C(1)—C(11)—C(13)	56.9 (8)	C(7)—C(8)—C(9)—C(10)	-21.6 (11)
C(7)—C(1)—C(11)—C(10)	-57.8 (7)	C(8)—C(9)—C(10)—Br(18)	-176.8 (6)
C(1)—C(2)—C(3)—Br(19)	179.7 (5)	C(8)—C(9)—C(10)—C(11)	-0.1 (13)
C(1)—C(2)—C(3)—C(4)	54.3 (8)	C(9)—C(10)—C(11)—C(1)	41.5 (9)

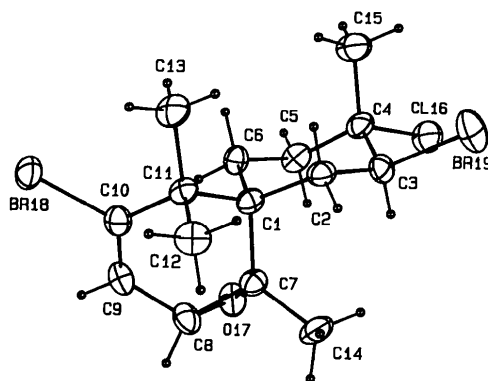


Fig. 1. Structure of (1) with thermal ellipsoids drawn at the 30% probability level.

ment in wR is significant at better than $\alpha = 0.005$ (Hamilton, 1965). The reported configuration has $[\alpha]^{20^\circ\text{C}} (\lambda, \text{nm}) + 50.4^\circ (589)$, $+53.0^\circ (578)$, $+61.1^\circ (546)$, $+112.7^\circ (436)$, ($c = 1.3 \text{ g l}^{-1}$ in CHCl_3).

The atomic parameters are given in Table 1, bond distances, bond angles and torsion angles in Table 2. Fig. 1 shows the structure of the molecule.

Related literature. Isolation from *Laurencia majuscula*: Caccamese & Compagnini (1989). Original determination, as isolated from the sea hare, *Aplysia Californica*, which feeds on *Laurencia* species: Ireland, Stallard, Faulkner, Finer & Clardy (1976). Isolation from *Laurencia okamurai*: Oijka, Shizuri & Yamada (1982). Chemical constituents of *Laurencia* species: Erickson (1983), Faulkner (1984), Caccamese, Toscano, Cerrini & Gavuzzo (1982). Crystal structure of pacifenol, from *Laurencia majuscula*: Fronczek & Caccamese (1986). Crystal structure of dehydrochloroprepacifenol, from *Laurencia majuscula*: Caccamese, Compagnini, Toscano, Nicolo & Chapuis (1987). Criticism of original absolute configuration determination: Selover & Crews (1980).

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Structure of 6-Benzyloxy-2,3-dichloro-4-(2-fluorobenzoyl)phenol

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Abstract. $C_{20}H_{13}Cl_2FO_3$, $M_r = 391.22$, monoclinic, $P2_1/c$, $a = 4.932$ (1), $b = 20.683$ (2), $c = 16.831$ (2) Å, $\beta = 90.14$ (1)°, $V = 1717.0$ (4) Å³, $Z = 4$, $D_x = 1.513$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 3.66$ mm⁻¹, $F(000) = 800$, $T = 295$ K, $R = 0.043$ for 2619 observed reflections [$F_o > 3\sigma(F_o)$]. The molecules are linked by an intermolecular hydrogen bond between O(24)H and O(8) to form an infinite chain extending along the c axis, O(24)H...O(8)($x, \frac{1}{2}+y, \frac{1}{2}+z$) 1.96 (3) Å and O...O 2.792 (3) Å.

Experimental. Prismatic colorless crystals obtained from benzene. Crystal of dimensions 0.2 × 0.2 × 0.2 mm. Rigaku AFC-5 diffractometer, graphite-monochromatized Cu $K\alpha$. Cell dimensions determined from 2θ angles for 25 reflections in the range $30 < 2\theta < 50$ °. Intensities measured up to $2\theta = 140$ ° in $h-5/0, k 0/25$ and $l-20/20, \omega-2\theta$ scans, ω -scan width (1.0 + 0.2 tan θ)°, three standard reflections monitored every 100 measurements showed no significant change. 3193 unique reflections measured, 2619 intensities observed [$F_o \leq 3\sigma(F_o)$ and six very strong reflections rejected], no absorption corrections. Structure solved by

MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located on a difference density map. Positional and thermal parameters refined by block-diagonal least squares, isotropic for H and anisotropic for the others. $\sum(w|\Delta F|^2)$ minimized, $w = 1/[\sigma^2(F_o) + 0.0008|F_o|^2]$, $w = 0$ for 64 reflections with $w^{1/2}|\Delta F| \geq 3$. Final $R = 0.043$, $wR = 0.049$, $S = 1.1116$. Highest peak in final difference map 0.3e Å⁻³. Max. Δ/σ in the final cycle 0.03. Atomic scattering factors calculated by $\sum[a_i \exp(-b_i \lambda^{-2} \sin^2 \theta)] + c$ ($i=1, \dots, 4$) (*International Tables for X-ray Crystallography*, 1974). Calculations performed on a FACOM M340R computer at Shionogi Research Laboratories. The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1. Bond distances and angles are listed in Table 2.* A perspective view of the molecule with the

* Lists of structure factors, anisotropic temperature factors of the non-H atoms and atomic coordinates of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51727 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.