geometrical parameters of selected intermolecular interactions are given in Table 2. A perspective view of the title compound with the atom numbering is given in Fig. 1. The arrangement of the molecules in the crystal, viewed along the *a* axis, is shown in Fig. 2.

Discussion. Bond lengths and valence angles of the pyrimidine-2,4-dione moiety conform to those found for 6-[cinnamoyl(2-morpholinoethyl)amino]-1,3-dimethyluracil (Warin, Lobry, Bernier & Henichart, 1984) and for 1,3-dimethyluracil (Banerjee, Dattagupta, Saenger & Rabczenko, 1977). In the epoxide ring, the C7—O3 and C8—O3 bond lengths of 1·416 (3) and 1·429 (3) Å, respectively, are significantly shorter than the accepted value of 1·446 (14) Å for C_{sp^3}—O bonds in epoxides with any substitution (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The least-squares planes of the rings form a dihedral angle of 63·4 (1)°, showing an antiperiplanar arrangement, the N1—C6—C7—O3 torsion angle being 166·6 (2)°, which is stabilized by intermolecular C—H···O interactions (Taylor & Kennard, 1982) as listed in Table 2. The group of atoms defining the pyrimidine-2,4-dione ring deviate significantly from planarity, $\sum(d/\sigma)^2 = 141{\cdot}3$, and the value of χ^2 at 95% for three degrees of freedom is 7·81. The molecular arrangement, shown in Fig. 2, is governed by van der Waals interactions.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Banerjee, A., Dattagupta, J. K., Saenger, W. & Rabczenko, A. (1977). *Acta Cryst.* B**33**, 90–94.

Botta, M., Nicoletti, R., Saladino, R., La Colla, P., Lamba, D. & Fabrizi, G. (1991). *J. Med. Chem.* In the press.

Botta, M., Saladino, R., Gambacorta, A. & Nicoletti, R. (1990). *Tetrahedron Asymmetry*, **7**, 441–444.

Chu, C. K. & Cutler, S. J. (1986). *J. Heterocycl. Chem.* **23**, 289–319.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Mijasaka, T., Tanaka, H., Baba, M., Hayakawa, H., Walker, R. T., Balzarini, J. & De Clercq, E. J. (1989). *J. Med. Chem.* **32**, 2507–2509.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Rogers, D. (1981). *Acta Cryst.* A**37**, 734–741.

Sheldrick, G. M. (1989). *SHELXTL-Plus.* Release 3.4 for Siemens *R3m/V* crystallographic research system. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Warin, V., Lobry, M., Bernier, J. L. & Henichart, P. (1984). *Acta Cryst.* C**40**, 1428–1429.

Acta Cryst. (1992). C**48**, 83–86

Absolute Configuration of Seiricuprolide, a New Phytotoxin from *Seiridium cupressi*

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Abstract. $C_{14}H_{20}O_5$, $M_r = 268{\cdot}31$, monoclinic, $P2_1$, $a = 5{\cdot}0680\,(5)$, $b = 19{\cdot}519\,(2)$, $c = 7{\cdot}3968\,(8)$ Å, $\beta = 106{\cdot}03\,(1)°$, $V = 703{\cdot}3\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}27$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54184$ Å, $\mu = 7{\cdot}55$ cm^{-1}, $F(000) = 288$, $T = 298$ K, $R = 0{\cdot}029$ for 1286 reflections with $F_o \geq 4\sigma(F_o)$. The absolute configurations of C4, C5, C6, C7 and C13 are *R*, *S*, *R*, *S* and *S* respectively. The C1—C2 and C8—C9 double bonds have *E* and *Z* configurations respectively. The determination of the absolute configuration of the title compound also allows that of its *trans*-bromohydrin derivative to be established.

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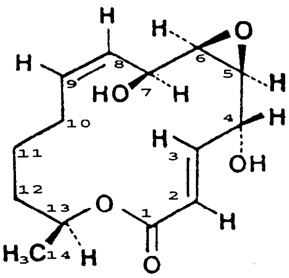
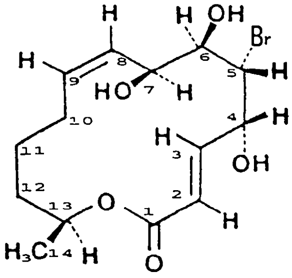
Introduction. A strain of *Seiridium cupressi*, a fungus causing a canker disease of cypress (*Cupressus sempervirens*) in Greece, produces several phytotoxins in culture. Two of them were identified as seiridin and iso-seiridin, the butenolides previously isolated from another cypress pathogen, *Seiridium cardinale* (Sparapano, Evidente, Ballio, Graniti & Randazzo, 1986; Evidente, Randazzo & Ballio, 1986). A third phytotoxin, which is present in small amounts in the culture filtrate of *S. cupressi* and is not produced by *S. cardinale*, was identified as a new macrolide which has been called seiricuprolide (1). Its structure was established by the spectroscopic analysis of the metabolite and of some key derivatives (Ballio, Evidente, Graniti, Randazzo & Sparapano, 1988, 1989). An X-ray crystallographic analysis was undertaken to determine the absolute stereochemistry of the five chiral centers and of the two double bonds present in seiricuprolide (1).



(1)



(2)

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	8602 (3)	−1714 (1)	8703 (2)	48 (1)
O2	4387 (3)	160	2153 (2)	41 (1)
O3	4524 (5)	1202 (1)	4929 (2)	61 (1)
O4	5303 (5)	1047 (1)	9399 (3)	57 (1)
O5	12073 (3)	−1014 (1)	10127 (2)	50 (1)
C1	9675 (4)	−1103 (1)	9322 (3)	38 (1)
C2	7508 (4)	−582 (1)	8793 (3)	37 (1)
C3	8005 (4)	85 (1)	8846 (3)	38 (1)
C4	5785 (5)	592 (1)	8023 (3)	40 (1)
C5	6631 (6)	1033 (1)	6601 (3)	47 (1)
C6	6797 (5)	790 (2)	4758 (3)	45 (1)
C7	6185 (4)	70 (1)	4019 (2)	34 (1)
C8	8790 (5)	−284 (2)	3957 (3)	44 (1)
C9	9310 (5)	−951 (2)	4102 (3)	47 (1)
C10	7488 (5)	−1520 (2)	4395 (3)	50 (1)
C11	8992 (7)	−2208 (2)	4943 (4)	60 (1)
C12	11303 (6)	−2215 (2)	6795 (5)	59 (1)
C13	10466 (5)	−2281 (2)	8609 (4)	51 (1)
C14	8961 (7)	−2922 (2)	8848 (5)	65 (1)

Experimental. Colorless rod-like crystals of (1) were grown by slow evaporation of an ethyl acetate–petrol (b.p. 313–343 K) solution. The crystal used for data collection had approximate dimensions 0·4 × 0·5 × 0·8 mm and was mounted on a glass fiber with epoxy cement. Preliminary cell parameters and space group from photographic methods; Siemens *R*3*m*/*V* automated diffractometer with Cu radiation and graphite monochromator; orientation matrix and lattice parameters from setting angles of 18 reflections with $79 \leq 2\theta \leq 90°$; θ–2θ scan mode, variable speed scans (1·30 to 14·65° min^{-1}), $2\theta_{max} = 140°$; 1868 intensities scanned (h −1/6, k −1/23, l −8/8), 1332 unique after averaging, $R_{int} = 0·097$ on F_o. Decay correction was based on intensities of three check reflections (0$\bar{6}$0, 1$\bar{4}$0, 11$\bar{1}$) measured every 97 reflections. Lorentz and polarization corrections, no correction for absorption. 1286 reflections with $F_o \geq 4\sigma(F_o)$ were used for the structure refinement. The structure was solved by direct methods using the *SHELXTL-Plus* suite of programs (Sheldrick, 1989) and refined on F_o by full-matrix least squares. A difference Fourier synthesis was used to locate the 20 H atoms, whose coordinates were refined and U_{iso} values were fixed equal to the U_{eq} values of their bearing atoms. Hamilton's (1965) R-value test (the ratio of the wR values is 1·012) and the refinement of the chirality η parameter, defined by Rogers (1981) [$\eta = 0·9$ (3)], were used to establish the absolute configuration at a very high level of confidence. The minimized function was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(F_o) + 0·0023F_o^2]^{-1}$. Final $R = 0·029$, $wR = 0·046$, $S = 0·93$, maximum shift/e.s.d. = 0·08 and $-0·12 < \Delta\rho < 0·11$ e Å^{-3}. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV); *PARST* (Nardelli, 1983) was used for the molecular-geometry calculations. Final fractional coordinates and U_{eq} values of the non-H atoms are listed in Table 1,* geometrical parameters are given in Table 2. A perspective view of seiricuprolide (1) is given in Fig. 1; Fig. 2 shows the molecular packing.

Discussion. The absolute configuration of seiricuprolide (1) is illustrated in Fig. 1, the absolute stereochemistry at C4, C5, C6, C7 and C13 being *R*, *S*, *R*, *S* and *S* respectively. The C1—C2 and C8—C9 double bonds have *E* and *Z* configurations respectively. The O2 and O4 hydroxyls, the C14 methyl and the epoxide ring protrude from the same face of the molecule, whereas the O5 carbonyl lies on the opposite face of the macrolide ring. The hydroxyl groups on C4 and C7 are *cis*. The epoxide and the 14-membered ring form a *cis* junction, with the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54372 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *valence angles* (°), *torsion angles* (°) *and geometrical parameters of selected intermolecular interactions* (Å, °)

O1—C1	1·336 (3)	O1—C13	1·470 (4)
O2—C7	1·440 (2)	O3—C5	1·431 (3)
O3—C6	1·439 (4)	O4—C4	1·422 (3)
O5—C1	1·209 (2)	C1—C2	1·470 (3)
C2—C3	1·325 (4)	C3—C4	1·496 (3)
C4—C5	1·510 (4)	C5—C6	1·467 (3)
C6—C7	1·509 (4)	C7—C8	1·502 (3)
C8—C9	1·328 (5)	C9—C10	1·498 (4)
C10—C11	1·543 (4)	C11—C12	1·537 (4)
C12—C13	1·520 (5)	C13—C14	1·502 (5)
C1—O1—C13	118·8 (2)	C5—O3—C6	61·5 (2)
O1—C1—O5	123·8 (2)	O1—C1—C2	108·8 (2)
O5—C1—C2	127·3 (3)	C1—C2—C3	123·4 (2)
C2—C3—C4	121·5 (2)	O4—C4—C3	112·4 (2)
O4—C4—C5	106·3 (2)	C3—C4—C5	109·5 (2)
O3—C5—C4	116·5 (2)	O3—C5—C6	59·5 (2)
C4—C5—C6	124·3 (2)	O3—C6—C5	59·0 (2)
O3—C6—C7	117·6 (2)	C5—C6—C7	125·3 (2)
O2—C7—C6	104·3 (2)	O2—C7—C8	110·8 (2)
C6—C7—C8	110·2 (2)	C7—C8—C9	127·3 (2)
C8—C9—C10	128·5 (2)	C9—C10—C11	113·8 (2)
C10—C11—C12	116·2 (3)	C11—C12—C13	117·3 (3)
O1—C13—C12	108·5 (2)	O1—C13—C14	105·6 (2)
C12—C13—C14	116·7 (3)		
O1—C1—C2—C3	−165·4 (2)	C7—C8—C9—C10	−1·1 (4)
C1—C2—C3—C4	170·6 (2)	C8—C9—C10—C11	−166·8 (2)
C2—C3—C4—C5	−124·3 (2)	C9—C10—C11—C12	61·5 (4)
C3—C4—C5—C6	71·0 (3)	C10—C11—C12—C13	80·4 (4)
C4—C5—C6—C7	−0·7 (4)	C11—C12—C13—O1	−57·7 (3)
C5—C6—C7—C8	−109·3 (3)	C12—C13—O1—C1	−82·2 (2)
C6—C7—C8—C9	152·0 (2)	C13—O1—C1—C2	163·9 (2)

D—H···*A*	*D*···*A*	*D*—H	H···*A*	*D*—H···*A*
O2—H20···O5^{i}	2·811 (2)	0·73 (3)	2·09 (3)	169 (3)
O4—H40···O2^{ii}	2·808 (3)	0·81 (4)	2·02 (4)	164 (4)
C14—H143···O3^{iii}	3·335 (4)	1·11 (3)	2·45 (4)	136 (3)

Symmetry code: (i) $x-1, y, z-1$; (ii) $x, y, z+1$; (iii) $-x+1, y-\frac{1}{2}, -z+1$.

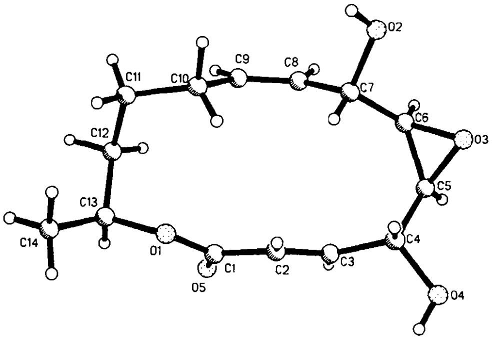

Fig. 1. Structure and conformation of the title compound with the numbering of the atoms.

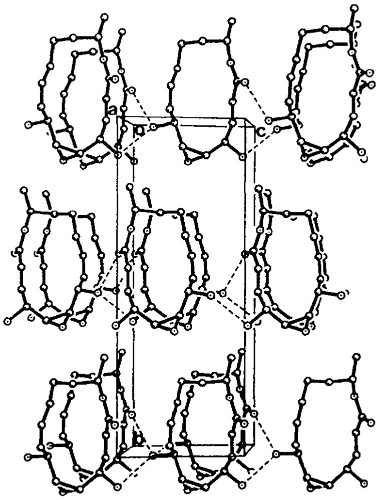

Fig. 2. The crystal packing of the molecules projected along the *a* axis.

torsion angle C4—C5—C6—C7 being −0·7 (4)°, and their mean planes form an angle of 54·2 (1)°. The 14-membered ring contains five synclinal, four antiperiplanar, three anticlinal and two synperiplanar dihedral angles (Table 2), with C1, O1 and C9—C13 being in a boat-like conformation and C2—C9 in a chair-like conformation. The molecular arrangement shown in Fig. 2 is governed by two hydrogen bonds involving the hydroxyl O2 as a donor and acceptor, and the hydroxyl O4 as only a donor, bridging the molecules along planes perpendicular to the *b* axis, while a short intermolecular contact of the C—H···O type (Taylor & Kennard, 1982) between an H atom of C13 and O3 links the molecules along the screw axis. The present assignment of the absolute configuration of seiricuprolide (1) also allows that of its *trans*-bromohydrin derivative (2) to be established (Ballio *et al.*, 1988). This derivative was prepared by treating (1) with a dilithium tetrabromonickelate(II) complex in dry tetrahydrofuran, a procedure recently reported for the regioselective opening of epoxide rings (Dawe, Molinski & Turner, 1984). This highly regioselective reaction involves nucleophilic attack at C5 by the bromine anion to give the *trans*-bromohydrin (2); the absolute stereochemistry at C5 now being *R*.

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References

Ballio, A., Evidente, A., Graniti, A., Randazzo, G. & Sparapano, L. (1988). *Phytochemistry*, **27**, 3117–3121.
Ballio, A., Evidente, A., Graniti, A., Randazzo, G. & Sparapano, L. (1989). *Phytotoxins and Plant Pathogenesis*, NATO ASI series, Vol. H27, edited by A. Graniti, R. D. Durbin & A. Ballio, pp. 373–376. Berlin: Springer-Verlag.
Dawe, R. D., Molinski, T. F. & Turner, J. V. (1984). *Tetrahedron Lett.* **25**, 2061–2064.
Evidente, A., Randazzo, G. & Ballio, A. (1986). *J. Nat. Prod.* **49**, 593–603.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

ROGERS, D. (1981). *Acta Cryst.* A37, 734–741.
SHELDRICK, G. M. (1989). *SHELXTL-Plus*. Release 3.4 for Siemens *R3m/V* crystallographic research system. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
SPARAPANO, L., EVIDENTE, A., BALLIO, A., GRANITI, A. & RANDAZZO, G. (1986). *Experientia*, **42**, 627–628.
TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

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Structure of 2-(2,6-Dimethoxyphenyl)-7-hydroxy-4*H*-1-benzopyran-4-one (7-Hydroxy-2′,6′-dimethoxyflavone)

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Abstract. $C_{17}H_{14}O_5$, $M_r = 298{\cdot}29$, monoclinic, $I2/a$, $a = 15{\cdot}538\,(6)$, $b = 11{\cdot}919\,(4)$, $c = 16{\cdot}083\,(4)$ Å, $\beta = 104{\cdot}72\,(12)^\circ$, $V = 2881\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}375$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}95$ cm^{-1}, $F(000) = 1248$, $T = 294$ K, $R = 0{\cdot}051$ for 1898 observed reflections [$F > 1\sigma(F)$]. The general shape of the molecule can be defined by two different regions: the chromone atoms including the O atom of the hydroxyl group lie in a plane, while the phenyl atoms including the O atoms of the methoxy groups lie in another plane. The angle between these mean planes is 68·2°.

Introduction. Hydrogen bonds are frequently responsible for stabilization of the crystal structures of hydroxyflavonoids. When a hydroxy group is located at C5 an intramolecular hydrogen bond is formed with the neighbouring carbonyl oxygen atom. Other hydroxyl groups in the molecule can form intermolecular hydrogen bonds with either the carbonyl oxygen or hydroxyl groups [centaureidin (Fronczek, Parodi & Fischer, 1989)] and in addition with solvent molecules such as water [quercetin (Rossi, Rickles & Halpin, 1986); penduletin (Parmar, Jain, Simonsen & Boll, 1987)].

The crystallization of fully methoxylated flavonoids is generally governed by stacking and packing forces. However, intermolecular hydrogen bonds are possible with solvent molecules. 5,6-Benzoflavone crystallizes with a water molecule in the asymmetric unit (Rossi, Cantrell, Farber, Dyott, Carrell & Glusker, 1980). 2′,6′-Dimethoxyflavone crystallizes with numerous acids [acetic (Wallet, Gaydou & Baldy, 1989); formic, propionic (Tinant, Declercq, Wallet, Gaydou & Baldy, 1991)].

Hydrogen bonds which involve the carbonyl oxygen atom are thought to influence the twist of the exocyclic phenyl ring. The role of these associations may be important in predicting the way flavonoids bind to biological macromolecules (Cody, 1988).

Experimental. Irregular prismatic crystal of approximate dimensions 0·50 × 0·30 × 0·66 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell constants from least-squares analysis of 25 high-angle reflections, intensity data collected by the ω–2θ zigzag scan technique, no fluctuations in standard reflections (0·8%), $2 \le 2\theta \le 50^\circ$, $-18 \le h \le 18$, $0 \le k \le 14$, $0 \le l \le 19$, 3848 reflections collected, 2537 unique, and 1898 considered to be observed [$F > 1\sigma(F)$] and used in structure analysis; Lp correction, no correction for absorption.

The structure was solved by direct methods with a straightforward run of the *MULTAN*11/84 program (Main, Germain & Woolfson, 1984). Full-matrix refinement on F was carried out with the *SHELX*76 least-squares program (Sheldrick, 1976) using anisotropic thermal parameters for the non-H atoms and two kinds of global isotropic temperature factors for the H atoms. The H atoms were located by difference Fourier syntheses. The refinement process converged at $R = 0{\cdot}0508$, $wR = 0{\cdot}0555$ with $w =$

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