Acta Cryst. (1986). C**42**, 1184–1185

Structure of Isororidin E

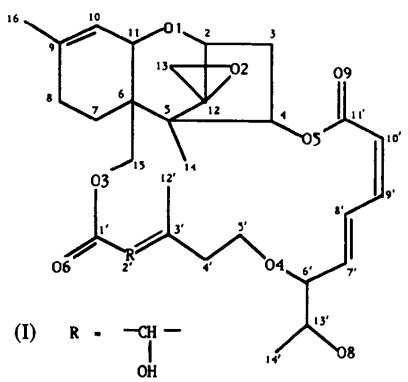
BY JUDITH L. FLIPPEN-ANDERSON AND RICHARD GILARDI

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375–5000, *USA*

(*Received* 14 *October* 1985; *accepted* 24 *March* 1986)

Abstract. $C_{29}H_{38}O_8$, $M_r = 514{\cdot}62$, monoclinic, $P2_1$, $a = 10{\cdot}278$ (2), $b = 9{\cdot}169$ (2), $c = 14{\cdot}197$ (4) Å, $\beta = 91{\cdot}93$ (2)°, $V = 1337{\cdot}2$ (6) Å^3, $Z = 2$, $D_x = 1{\cdot}28$ Mg m^{-3}, D_m not measured, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}78$ mm^{-1}, $F(000) = 552$, $T = 295$ K, $R = 0{\cdot}037$ for all 1880 unique data. Isororidin E (II) is structurally very similar to roridin A (I); however, in (I) the configuration of both C(6′) and C(13′) is '*R*' while in (II) both are '*S*'.

Introduction. Mycotoxins exhibit potent biological activity. Macrocyclic trichothecenes, which include the roridins as well as the verrucarins and baccharinoids, form the largest subclass of the mycotoxins. The X-ray study on isororidin E (ISOE) (II) was undertaken to compare it with the structurally similar roridin A (RORA) (I) (Jarvis, Midiwo, Flippen-Anderson & Mazzolo, 1982).



(I) R = —CH(OH)—

(II) R = —CH=

Experimental. Crystals were provided by Dr B. Jarvis of the University of Maryland. Unit-cell parameters from 25 reflections (20–63°), $P2_1$ derived from systematic absences, 1880 independent reflections with $2\theta_{max} = 112°$, *hkl* limits ±11,9,14), three standard reflections (600, 040, 007) indicated crystal remained stable during data collection. Nicolet P3F diffractometer, graphite monochromator on incident beam. θ–2θ scan technique with variable scan speed between 4 and 30° min^{-1}. Structure solved by direct methods (Karle & Karle, 1966; Karle, 1968). Refined by restrained least-squares methods (Flippen-Anderson, Gilardi & Konnert, 1983; Flippen-Anderson, Konnert & Gilardi, 1982), anisotropic for non-H, H atoms coordinates refined, thermal parameters riding on covalently bonded atoms (226 total parameters), weights according to Gilardi (1973). No absorption or extinction corrections. The molecule was not explicitly restrained to fix the y location of the $P2_1$ cell origin since we have found that the sparse-matrix program *RESLSQ* does not shift the origin in such cases. (This may be due to the neglect of most atom–atom correlation terms; the only off-diagonal elements of the

Table 1. *Fractional coordinates and* B_{eq} *values for isororidin E*

Standard deviations are based solely on least-squares results. The B_{eq} values are calculated according to the equation:

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$$

where the β_{ij} values are the final refined anisotropic thermal parameters.

	x	y	z	B_{eq}(Å^2)
O(1)	0·4745 (2)	0·2882 (2)	0·0178 (1)	3·77 (6)
O(2)	0·1763 (2)	0·2168 (3)	0·1429 (2)	5·52 (7)
O(3)	0·4929 (2)	0·6489 (2)	0·2748 (1)	3·32 (5)
O(4)	0·1725 (2)	1·0172 (2)	0·4487 (1)	3·50 (5)
O(5)	0·1454 (2)	0·5752 (2)	0·1007 (1)	3·96 (5)
O(6)	0·5826 (3)	0·8652 (3)	0·2479 (2)	7·02 (8)
O(8)	−0·1162 (2)	1·2495 (3)	0·4536 (2)	5·60 (7)
O(9)	0·2258 (2)	0·7755 (3)	0·1724 (1)	4·56 (6)
C(2)	0·3344 (3)	0·2885 (4)	0·0221 (2)	4·16 (9)
C(3)	0·2713 (3)	0·4308 (5)	−0·0068 (2)	4·66 (10)
C(4)	0·2774 (3)	0·5273 (4)	0·0822 (2)	3·54 (8)
C(5)	0·3343 (3)	0·4284 (4)	0·1623 (2)	3·15 (8)
C(6)	0·4888 (3)	0·4448 (3)	0·1623 (2)	2·84 (7)
C(7)	0·5539 (3)	0·3356 (4)	0·2305 (2)	3·64 (8)
C(8)	0·7027 (3)	0·3446 (5)	0·2303 (2)	4·85 (10)
C(9)	0·7548 (3)	0·3502 (4)	0·1336 (2)	4·41 (10)
C(10)	0·6795 (3)	0·3838 (4)	0·0595 (2)	3·93 (9)
C(11)	0·5353 (3)	0·4136 (4)	0·0614 (2)	3·35 (8)
C(12)	0·3027 (3)	0·2767 (4)	0·1241 (2)	3·73 (8)
C(13)	0·2924 (3)	0·1408 (4)	0·1763 (3)	5·07 (11)
C(14)	0·2742 (3)	0·4521 (4)	0·2584 (2)	3·76 (8)
C(15)	0·5336 (3)	0·6006 (4)	0·1835 (2)	3·40 (8)
C(16)	0·8972 (3)	0·3170 (6)	0·1246 (4)	7·01 (15)
C(1′)	0·5147 (3)	0·7886 (4)	0·2952 (2)	3·75 (8)
C(2′)	0·4460 (3)	0·8321 (4)	0·3802 (2)	3·53 (8)
C(3′)	0·4648 (3)	0·9503 (3)	0·4305 (2)	3·25 (8)
C(4′)	0·3864 (3)	0·9832 (4)	0·5158 (2)	3·59 (9)
C(5′)	0·2763 (3)	1·0906 (4)	0·4978 (2)	4·20 (9)
C(6′)	0·0665 (3)	1·1073 (4)	0·4153 (2)	3·72 (8)
C(7′)	−0·0130 (3)	1·0186 (4)	0·3467 (2)	4·01 (0)
C(8′)	0·0328 (3)	0·9154 (4)	0·2916 (2)	3·70 (9)
C(9′)	−0·0448 (3)	0·8323 (4)	0·2248 (2)	4·36 (8)
C(10′)	−0·0049 (3)	0·7349 (4)	0·1626 (2)	4·26 (9)
C(11′)	0·1336 (3)	0·7019 (4)	0·1469 (2)	3·66 (9)
C(12′)	0·5676 (4)	1·0613 (5)	0·4113 (3)	6·14 (12)
C(13′)	−0·0126 (4)	1·1678 (4)	0·4967 (2)	4·49 (0)
C(14′)	−0·0645 (4)	1·0552 (5)	0·5612 (3)	6·53 (1)

0108-2701/86/091184-02$01.50

refinement matrix kept by *RESLSQ* are those relating bonded and next-nearest neighbors.) Final $R(F)$ and $wR = 0.037$ and 0.039 for all data, max. shift in final least-squares cycle 0.019 Å for a hydrogen atom, $S = 1.72$, final difference Fourier excursions 0.30 and -0.18 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 lists the coordinates and B_{eq} values for the non-H atoms of ISOE.* Fig. 1 shows the conformation of ISOE. The chirality shown in Fig. 1 was chosen to conform to the absolute configuration of verrucarin A (McPhail & Sim, 1966). As in RORA the C(5)–C(6) bond is somewhat long [1.579 (6) Å in RORA and 1.595 (4) Å in ISOE] and the external CCC angles of the epoxide ring [C(2)–C(12)–C(13) = 125.2 (4) and C(5)–C(12)–C(13) = 128.2 (3)°] are significantly larger than the external CCO angles [C(5)–C(12)–O(2) = 117.6 (3) and C(2)–C(12)–O(2) = 115.6 (3)°]. In RORA these values were 125.6 (4), 126.0 (4), 117.1 (4) and 115.2 (4)° respectively. The conformation of the trichothecene ring system is also similar to that found for RORA. In RORA the configuration at both C(6′) and C(13′) was '*R*' while in ISOE the configuration at both these atoms is '*S*'. In ISOE there is only one intermolecular hydrogen bond. The hydrogen on O(8) is the donor to the ether oxygen O(4) with an O–H distance of 1.89 Å and an O···O distance of 2.89 Å and an O–H···O angle of 172.4°. The only other intermolecular approaches less than van der Waals separations are an O(2)···C(16) approach of 3.01 Å and C(14)···C(14′) approach of 3.53 Å.

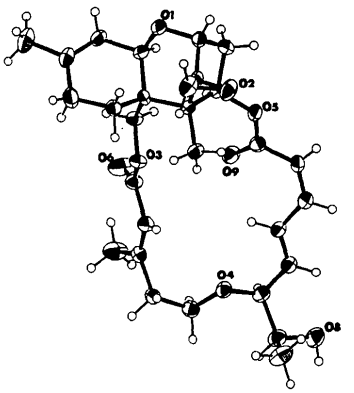


Fig. 1. *ORTEP* (Johnson, 1965) drawing of ISOE. The thermal parameters are drawn at the 50% probability level.

* Lists of structure factors, bond lengths and angles, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42938 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

FLIPPEN-ANDERSON, J. L., GILARDI, R. & KONNERT, J. (1983). NRL Memorandum Rep. No. 5042. Washington, DC: Naval Research Laboratory.

FLIPPEN-ANDERSON, J. L., KONNERT, J. H. & GILARDI, R. D. (1982). *Acta Cryst.* B**38**, 2865–2869.

GILARDI, R. D. (1973). *Acta Cryst.* B**29**, 2089–2095.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JARVIS, B. B., MIDIWO, J. O., FLIPPEN-ANDERSON, J. L. & MAZZOLO, E. P. (1982). *J. Natural Prod.* **45**, 440–448.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KARLE, J. (1968). *Acta Cryst.* B**24**, 182–186.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

MCPHAIL, A. T. & SIM, G. A. (1966). *J. Chem. Soc. C*, pp. 1394–1396.

Acta Cryst. (1986). C**42**, 1185–1189

Neurotoxins Producing Parkinson's Syndrome

BY JUDITH L. FLIPPEN-ANDERSON, RICHARD GILARDI AND CLIFFORD GEORGE

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375–5000, *USA*

(*Received* 14 *October* 1985; *accepted* 26 *March* 1986)

Abstract. 1-Methyl-4-phenyl-1,2,5,6-tetrahydropyridinium chloride (I), $C_{12}H_{16}N^+.Cl^-$, $M_r = 209.72$, monoclinic, $P2_1$, $a = 7.014$ (2), $b = 6.634$ (1), $c = 12.248$ (3) Å, $\beta = 96.78$ (2)°, $V = 565.9$ (2) Å^3, $Z = 2$, $D_x = 1.23$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 2.69$ mm^{-1}, $F(000) = 224$, $T = 295$ K, $R = 0.041$ for 1512 observed reflections. 1,3-Dimethyl-4-phenyl-1,2,5,6-tetrahydropyridine–borane complex (II), $C_{13}H_{20}BN$, $M_r = 201.12$, monoclinic, $P2_1/c$, $a = 11.480$ (3), $b = 22.809$ (5), $c = 10.226$ (2) Å, $\beta = 107.76$ (2)°, $V = 2549.7$ (10) Å^3, $Z = 8$, $D_x = 1.05$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 0.412$ mm^{-1}, $F(000) = 880$, $T = 295$ K, final $R = 0.052$ for 2718 observed reflections. 4-(3-Methoxy-4-hydroxyphenyl)-1,2,5,6-tetrahydro-1-pyridinecarbaldehyde (III), $C_{13}H_{15}NO_3$, $M_r = 233.27$, orthorhombic, *Pbca*, $a = 6.563$ (2), $b = 21.964$ (9), $c = 16.016$ (6) Å, $V = 2308$ (1) Å^3, $Z = 8$, $D_x = 1.34$ Mg m^{-3},

0108-2701/86/091185-05$01.50