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Elloramycin, $C_{32}H_{36}O_{15}$

BY PETER G. JONES AND GEORGE M. SHELDRICK

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen, Federal Republic of Germany*

AND JÜRGEN ROHR AND AXEL ZEECK

Institut für Organische Chemie der Universität, Tammannstrasse 2, *D*-3400 *Göttingen, Federal Republic of Germany*

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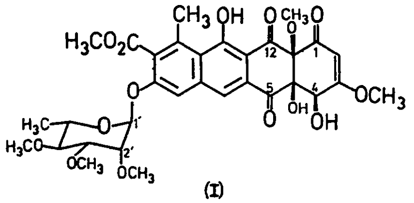
Abstract. $C_{32}H_{36}O_{15}.xH_2O$ (x *ca* 0·5), M_r(for $x =$ 0·5) = 669·64, monoclinic, $P2_1$, $a =$ 10·801 (2), $b =$ 9·277 (2), $c =$ 16·660 (3) Å, $\beta =$ 105·71 (2)°, $V =$ 1607·0 (6) Å^3, $Z = 2$, $D_x =$ 1·38 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu =$ 1·0 cm^{-1}, $F(000) = 706$, $T = 293$ K. R = 0·041 for 3566 observed reflections. The structural features determined from chemical and spectroscopic studies are confirmed and extended. The molecule is an anthracycline analogue containing a permethylated α-L-rhamnose moiety. All ring systems show the expected conformations, the non-aromatic fused rings both being half-chairs. The extended structure, including the partly occupied water, is linked by hydrogen bonds.

Introduction. Elloramycin (I), a new antibiotic produced by *Streptomyces olivaceus* (strain Tü 2353), was detected by chemical screening and characterized by chemical and spectroscopic methods (Drautz, Reuschenbach, Zähner, Rohr & Zeeck, 1984). Elloramycin is an anthracycline-like antibiotic with weak antibacterial and antitumour activities; the aglycone resembles tetracenomycin C (Weber, Zähner, Siebers, Schröder & Zeeck, 1979), and the sugar moiety consists of permethylated α-L-rhamnose. We describe below the crystal-structure analysis of elloramycin by which the total structure of the antibiotic, including the relative stereochemistry, is proved.



(I)

Large, air-stable yellow blocks and plates were obtained by diffusion of n-pentane into an acetone solution at room temperature.

Experimental. Crystal 0·6 × 0·55 × 0·4 mm. 5109 profile-fitted intensities (Clegg, 1981) recorded on a Stoe–Siemens four-circle diffractometer. Monochromated Mo $K\alpha$ radiation, $2\theta_{max}$ 55°, h $-14\rightarrow13$, k $0\rightarrow12$, l $0\rightarrow21$ and some Friedel opposites with negative k. Three check reflections, no intensity change. R_{int} 0·023 for 3913 unique reflections (Friedel opposites merged), 3566 with $F > 4\sigma(F)$ used for all calculations (program systems *SHELXTL* and *SHELX*84, written by GMS). Cell constants refined from 2θ values of 40 reflections in range 20–24°. No correction for absorption.

Structure solution by random-start multisolution direct methods. Refinement on $|F|$ to R 0·041, wR 0·043 [all non-H atoms anisotropic; H atoms (except OH) included using a riding model with C—H 0·96 Å,

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H—C—H 109·5°, $U(\mathrm{H}) = 1{\cdot}2U_{\mathrm{eq}}(\mathrm{C})$; hydroxyl H refined with O—H constrained to 0·96 ±0·02 Å, $U(\mathrm{H}) = 1{\cdot}2\ U_{\mathrm{eq}}(\mathrm{O})$; half-occupied O atom, presumably water, refined isotropically but water H not located; 460 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00045\ F^2$, $S = 1{\cdot}71$, slope of normal probability plot 1·47]. Max. Δ/σ 0·06. Max. and min. heights in final $\Delta\rho$ map +0·2 and −0·3 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). An absolute configuration consistent with the presence of L-rhamnose was chosen.

Discussion. Final atomic coordinates for non-H atoms are given in Table 1,* bond lengths in Table 2.

The X-ray structure (Fig. 1) confirms the structure as determined by chemical and spectroscopic methods and resolves the one remaining ambiguity, namely the position of a methyl group on either O(12a) or O(4a).

The ring conformations are as expected: the sugar ring adopts the chair form (mean absolute torsion angle 57·1°), the aromatic rings are planar [but with some minor deviations from 0° torsion angles, maximum −6·3° for C(6)—C(6a)—C(10a)—C(11)], the third fused ring is a somewhat distorted half-chair (mean absolute deviation from ideal values 4·2°) and the fourth fused ring an almost ideal half-chair (mean deviation 1·6°) (Bucourt & Hainaut, 1965).

An internal hydrogen bond O(11)—H(11)···O(12) is observed (H···O 1·64 Å). The water molecule also participates in hydrogen bonding, with O*w*···O(5′) 2·87 Å, O(91)···O*w*($-x$, $\frac{1}{2}+y$, $1-z$) 3·02 Å. One intermolecular hydrogen bond of 2·77 Å exists between O(3′) and O(4), with O···H 1·93 Å (second atoms at

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 ×10^3)

	x	*y*	*z*	*U*
O*w*	−981 (8)	1367 (13)	3954 (6)	153 (3)
C(1)	3746 (2)	5479 (3)	415 (1)	32 (1)*
O(1)	4491 (2)	4986 (2)	60 (1)	46 (1)*
C(2)	3229 (2)	6919 (3)	290 (1)	35 (1)*
C(3)	2208 (2)	7327 (2)	559 (1)	31 (1)*
O(3)	1711 (1)	8648 (2)	501 (1)	41 (1)*
C(31)	2305 (3)	9757 (3)	135 (2)	53 (1)*
C(4)	1521 (2)	6337 (2)	1018 (1)	29 (1)*
O(4)	179 (1)	6525 (2)	714 (1)	40 (1)*
C(4a)	1857 (2)	4736 (2)	915 (1)	27 (1)*
O(4a)	1274 (1)	4256 (2)	106 (1)	35 (1)*
C(5)	1450 (2)	3830 (2)	1571 (1)	30 (1)*
O(5)	519 (2)	3050 (2)	1371 (1)	46 (1)*
C(5a)	2221 (2)	4030 (2)	2452 (1)	27 (1)*
C(6)	1746 (2)	3576 (2)	3084 (1)	30 (1)*
C(6a)	2411 (2)	3866 (2)	3934 (1)	27 (1)*
C(7)	1894 (2)	3347 (3)	4573 (1)	35 (1)*
C(8)	2529 (2)	3645 (3)	5386 (1)	33 (1)*
C(9)	3620 (2)	4544 (2)	5585 (1)	31 (1)*
C(91)	4196 (2)	4898 (3)	6492 (1)	37 (1)*
C(92)	5919 (4)	4394 (5)	7664 (2)	77 (1)*
O(91)	3780 (2)	5749 (3)	6875 (1)	72 (1)*
O(92)	5250 (2)	4117 (2)	6798 (1)	56 (1)*
C(10)	4151 (2)	5088 (2)	4982 (1)	29 (1)*
C(101)	5262 (2)	6111 (3)	5243 (1)	45 (1)*
C(10a)	3560 (2)	4691 (2)	4130 (1)	27 (1)*
C(11)	4082 (2)	5082 (2)	3454 (1)	30 (1)*
O(11)	5219 (1)	5754 (2)	3634 (1)	43 (1)*
C(11a)	3426 (2)	4761 (2)	2630 (1)	27 (1)*
C(12)	4000 (2)	5150 (2)	1962 (1)	29 (1)*
O(12)	4996 (1)	5854 (2)	2079 (1)	42 (1)*
C(12a)	3327 (2)	4589 (2)	1082 (1)	28 (1)*
O(12a)	3582 (1)	3096 (2)	1051 (1)	37 (1)*
C(121)	4908 (2)	2679 (3)	1346 (2)	47 (1)*
C(1′)	1393 (2)	1906 (3)	6010 (1)	42 (1)*
O(1′)	2187 (2)	3157 (2)	6067 (1)	48 (1)*
C(2′)	1690 (2)	1356 (3)	6908 (1)	39 (1)*
O(2′)	1096 (2)	0	6893 (1)	49 (1)*
C(21′)	1854 (4)	−1107 (6)	7270 (5)	164 (4)*
C(3′)	1172 (2)	2445 (3)	7424 (1)	37 (1)*
O(3′)	1414 (2)	2025 (2)	8266 (1)	46 (1)*
C(31′)	2643 (3)	2474 (4)	8765 (2)	55 (1)*
C(4′)	−278 (2)	2576 (3)	7036 (1)	41 (1)*
O(4′)	−913 (2)	3403 (2)	7520 (1)	58 (1)*
C(41′)	−386 (4)	4790 (4)	7801 (2)	78 (2)*
C(5′)	−496 (2)	3157 (3)	6137 (2)	48 (1)*
O(5′)	91 (2)	2201 (2)	5661 (1)	49 (1)*
C(51′)	−1896 (3)	3244 (5)	5675 (2)	78 (1)*

* Equivalent isotropic *U* calculated from anisotropic *U*.

Table 2. *Bond lengths* (Å) *between non-*H *atoms*

C(1)–O(1)	1·210 (4)	C(1)–C(2)	1·442 (4)
C(1)–C(12a)	1·547 (4)	C(2)–C(3)	1·352 (4)
C(3)–O(3)	1·331 (4)	C(3)–C(4)	1·512 (4)
C(31)–O(3)	1·432 (5)	C(4)–O(4)	1·411 (3)
C(4)–C(4a)	1·549 (4)	C(4a)–C(5)	1·535 (4)
C(4a)–O(4a)	1·397 (3)	C(5)–O(5)	1·210 (4)
C(5)–C(5a)	1·489 (4)	C(5a)–C(6)	1·358 (4)
C(6)–C(6a)	1·429 (4)	C(6a)–C(7)	1·413 (4)
C(7)–C(8)	1·372 (4)	C(8)–C(9)	1·408 (4)
C(8)–O(1′)	1·362 (4)	C(9)–C(91)	1·507 (4)
C(91)–O(91)	1·179 (5)	C(91)–O(92)	1·329 (4)
C(92)–O(92)	1·451 (4)	C(10)–C(9)	1·379 (4)
C(10)–C(101)	1·500 (4)	C(10)–C(10a)	1·438 (4)
C(10a)–C(6a)	1·419 (4)	C(10a)–C(11)	1·437 (4)
C(11)–O(11)	1·337 (4)	C(11)–C(11a)	1·396 (4)
C(11a)–C(12)	1·458 (4)	C(11a)–C(5a)	1·425 (4)
C(12)–C(12a)	1·540 (4)	C(12)–O(12)	1·228 (4)
C(12a)–O(12a)	1·415 (4)	C(12a)–C(4a)	1·542 (4)
C(1′)–O(1′)	1·431 (5)	C(121)–O(12a)	1·436 (4)
C(1′)–O(5′)	1·396 (4)	C(1′)–C(2′)	1·530 (4)
C(2′)–C(3′)	1·528 (5)	C(2′)–O(2′)	1·409 (4)
C(3′)–C(4′)	1·529 (4)	C(21′)–O(2′)	1·358 (6)
C(4′)–O(4′)	1·418 (5)	C(3′)–O(3′)	1·410 (4)
C(41′)–O(4′)	1·434 (5)	C(31′)–O(3′)	1·425 (4)
C(5′)–C(51′)	1·502 (5)	C(4′)–C(5′)	1·549 (5)
		C(5′)–O(5′)	1·446 (5)

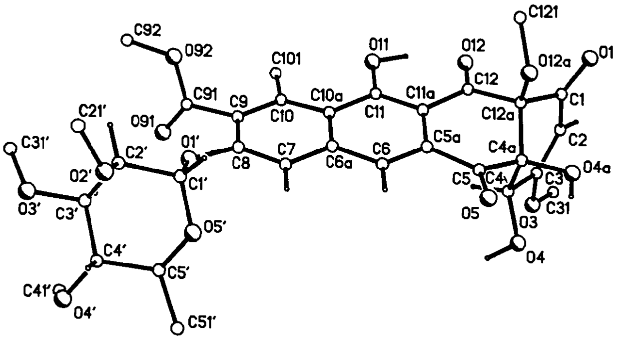

Fig. 1. Perspective view of the elloramycin molecule (methyl H omitted for clarity) showing the atom-numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond lengths involving H atoms and valence and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39803 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$-x, -\frac{1}{2}+y, 1-z$). A less clear-cut, apparently bifurcated, hydrogen-bonding system is seen in the contacts O(4a)–H(4a)···O(4) and O(4a)–H(4a)···O(3), with O···O 3·10, 3·16 Å, H···O 2·36, 2·42 Å respectively, receptor atoms at $-x, -\frac{1}{2}+y, -z$.

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Di(3,3′,4,4′-tetramethyl-2,2′,5,5′-tetraselenafulvalenium) Difluorophosphate,[*] $(C_{10}H_{12}Se_4)_2PO_2F_2$, at 293 and 125 K

BY K. ERIKS,[†] H. H. WANG, P. E. REED,[‡] M. A. BENO, E. H. APPELMAN AND J. M. WILLIAMS[§]

Chemistry and Materials Science and Technology Divisions, Argonne National Laboratory, Argonne, Illinois 60439, USA

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Abstract. $(TMTSF)_2PO_2F_2$: $M_r = 997·07$, triclinic, $P\bar{1}$, $Z = 1$, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 112·8$ cm^{-1}, $F(000) = 465$. At 293 K: $a = 7·271$ (1), $b = 7·704$ (1), $c = 13·361$ (2) Å, $\alpha = 84·28$ (1), $\beta = 86·70$ (1), $\gamma = 70·50$ (1)°, $V = 701·8$ (2) Å^3, $D_x = 2·359$ g cm^{-3}, $R(F) = 0·046$, $R_w = 0·029$%, $S = 1·46$ for 1962 reflections. At 125 K: $a = 7·128$ (2), $b = 7·694$ (2), $c = 13·201$ (5) Å, $\alpha = 85·35$ (3), $\beta = 87·23$ (3), $\gamma = 69·76$ (2)°, $V = 676·9$ (4) Å^3, $D_x = 2·446$ g cm^{-3}, $R(F) = 0·038$, $R_w = 0·029$%, $S = 1·68$ for 2005 reflections. $(TMTSF)_2PO_2F_2$ exhibits a metal–insulator (M–I) phase transition at 137 K. The structures both above and below the transition temperature are isomorphous with other 2:1 TMTSF:X (X = monovalent anion) salts. In the room-temperature structure the $PO_2F_2^-$ ion is positioned with its phosphorus atom at the origin ($\bar{1}$ at 0,0,0). At 125 K (*i.e.* below the transition temperature) the phosphorus atom is shifted away from the origin by 0·38 Å with a total P—P separation of 0·76 Å. There is no indication of doubling of any of the three crystallographic axes, therefore the anion is disordered at both temperatures. This behavior has not been previously observed for a TMTSF salt containing any anion. Although the $PO_2F_2^-$ anion possesses a dipole moment, this has little or no effect on the electrical properties. Rather, these properties are dominated almost entirely by the random potentials induced by the anion disorder that persists even below the 137 K phase transition. Therefore, contrary to other $(TMTSF)_2X$ systems such as $X = PF_6^-$ and AsF_6^-, it is unlikely that $(TMTSF)_2PO_2F_2$ will exhibit superconductivity even under an applied pressure.

Introduction. Structures of electrically conducting and superconducting salts of stoichiometry $(TMTSF)_2{}^+MX_4^-$, where TMTSF is $C_{10}H_{12}Se_4$ and MX_4^- is an anion of tetrahedral geometry, have been determined for $MX_4^- = BF_4^-$, ClO_4^-, BrO_4^-, ReO_4^- and FSO_3^- (for a summary see Thorup, Rindorf, Soling, Johannsen, Mortensen & Bechgaard, 1983). Of these only FSO_3^- is an asymmetric dipolar ion. It has a M–I phase transition at 86 K, but that temperature lies below the lowest temperature (125 K) at which the crystal structure has been studied (Williams, Beno, Appelman, Capriotti, Wudl, Aharon-Shalom & Nalewajek, 1982). The difluorophosphate, $PO_2F_2^-$, anion almost certainly has a higher dipole moment than FSO_3^-, and the $(TMTSF)_2PO_2F_2$ salt has a M–I transition at 137 K (Cox, Boysel, Moses, Wudl, Chen, Ochsenbein, Heeger, Walsh & Rupp, 1984), which lies above the temperature of 125 K that can be reached conveniently for X-ray crystallographic studies. The difluoprophosphate salt therefore provides an opportunity of determining the structure above and below the phase transition. The results of the study are described

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[*] Alternative nomenclature: di(4,4′,5,5′-tetramethyl-2,2′-bi-1,3-diselenolyliden)ium difluorophosphate.

[†] Participant in 1983–84 Faculty Research Leave Program coordinated by the Argonne Division of Educational Programs. On leave from Boston University, Boston, MA.

[‡] Participant in the Student Research Participation Program coordinated by the Argonne Division of Educational Programs, from the University of Wisconsin–Eau Claire.

[§] Author to whom correspondence is to be addressed.

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