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# The Crystal and Molecular Structure of Latumcidin Selenate

BY YOSHIKI KONO, SETSUO TAKEUCHI AND HIROSHI YONEHARA Institute of Applied Microbiology, University of Tokyo, Bunkvo-ku, Tokyo 113. Japan

ie of Applieu Microbiology, Oniversity of Tokyo, Dunkyo-ku, Tokyo 115, Jup

and Fumiyuki Marumo and Yoshihiko Saito

Institute for Solid State Physics, University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

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The crystal structure and absolute configuration of latumcidin selenate  $(C_{10}H_{11}NO.H_2SeO_4)$ , an antiviral antibiotic produced by a *Streptomyces sp.* has been determined by three-dimensional X-ray analysis. Crystals are monoclinic, space group C2, with four molecules in the unit cell of dimensions: a =26.07, b = 4.87, c = 9.66 Å and  $\beta = 95.1^{\circ}$ . Refinement was carried out with 1200 observed reflexions by the block-diagonal least-squares method to the final *R* value of 0.095. The absolute configuration was determined by the use of an anomalous dispersion effect of the selenium atom for Cr K $\alpha$  radiation. The structure of latumcidin conforms to the formula (4R,4aS)-5-ethylidene-2,3-dihydro-1,5-pyrindine 4,4aoxide.

### Introduction

Latumcidin is an antiviral antibiotic isolated from the cultured broth of *Streptomyces reticuli var. latumcidicus* by Sakagami, Yamaguchi, Yonehara, Okimoto, Yamanouchi, Takiguchi & Sakai (1958). Latumcidin is identical with abikoviromycin produced by *Streptomyces abikoensis* (Umezawa, Tazaki & Fukuyama, 1951). Structural studies of this antibiotic were carried out by chemical methods by Gurevich, Kolosov, Korobko & Onoprienko (1968). They reported that the substance is (4S, 4aR)-5-ethylide: -2,3-dihydro-1,5-pyrindine 4,4a-oxide (I). The structure determination of latumcidin selenate was undertaken to establish the molecular structure as well as the absolute configuration of the antibiotic.



### Experimental

Latumcidin selenate was prepared by treating latumcidin with selenic acid in ether-acetone at -10 °C. It crystallizes from the solution as colourless needles. The density was measured by the flotation method in ethercarbon tetrachloride mixture. Cell dimensions and the space group were determined from Weissenberg photographs taken with Cu K $\alpha$  radiation (1.5418 Å). Crystal data are:  $C_{10}H_{11}NO.H_2SeO_4$ , m.p. 121 °C dec., M.W. = 306; Monoclinic, space group C2,  $a = 26.07 \pm 0.05$ ,  $b = 4.87 \pm 0.02$ ,  $c = 9.66 \pm 0.02$  Å,  $\beta = 95.1 \pm 0.2$ °, U =1221.5 Å<sup>3</sup>,  $D_m = 1.61$  g.cm<sup>-3</sup>, Z = 4,  $D_x = 1.67$  g.cm<sup>-3</sup>, F(000) = 920,  $\mu$ (Cu K $\alpha$ ) = 47.9 cm<sup>-1</sup>. The needle axis is parallel to **b**.

Intensities of 1392 independent reflexions were obtained by visual estimation from equi-inclination Weissenberg photographs, taken around the *b* axis (*h*0*l* to *h*4*l*) and the *c* axis (*h*k0) with Cu K $\alpha$  radiation, employing the multiple-film technique. The data were corrected for Lorentz and polarization factors, and then brought to the same arbitrary scale. Since the crystals were fragile and easily destroyed by mechanical force, it was impossible to prepare a crystal with isometric shape for the X-ray work. The data collected from the (*h*k0) photographs were rather inaccurate due to crystal elongation along the *b* axis; therefore, these data were used only for interlayer scaling at the initial stage. The remaining 1200 reflexions collected around the *b* axis were used for the structure determination.

# Determination and refinement of the structure

The two-dimensional Patterson projection along the b axis was calculated. The position of the selenium atom was easily found from the map, which gave only one salient peak in an asymmetric unit besides the origin peak. The y coordinate can be taken to be zero in the present case. The first electron density maps were synthesized with phases based on the contribution of the selenium atom only, utilizing 883 reflexions for which calculated structure factors showed relatively good coincidence with observed ones. Positions of three lighter atoms were revealed from the maps. The R value was 0.37 for the 883 reflexions. With successive three-dimensional Fourier and difference Fourier syntheses, the 14 atoms including the above four were

located. Isotropic least-squares refinement of the parameters of these atoms and of individual-layer scale factors, carried out by five cycles with block-diagonal least-squares program HBLS IV (Ashida, 1967), lowered the R value to 0.20. With all 1200 reflexions, five further cycles of least-squares refinement were carried out by assigning anisotropic thermal parameters to the selenium atom. All atoms, except hydrogen atoms. were found in the electron density maps synthesized at this stage. Further refinements of the structure were carried out with anisotropic thermal parameters for all atoms using least-squares program HBLS IV. The final R value is 0.095 for all 1200 reflexions. The weighting scheme employed was: w = 1 when  $F_a \ge 5.0$ , w = 0.8 when  $F_o < 5.0$ . Scattering factors used were taken from International Tables for X-ray Crystallography (1962). Final positional parameters together with estimated standard deviations are given in Table 1. Thermal parameters are listed in Table 2. Observed and calculated structure factors are compared in Table 3.

Table 1. Fractional atomic coordinates  $(\times 10^4)$  with e.s.d.'s in parentheses

	x	У	z
Se	1050 (1)	0 (16)	2210 (2)
O(1)	4025 (5)	5377 (59)	2506 (11)
O(2)	0577 (5)	1300 (44)	1065 (13)
O(3)	1590 (5)	0285 (77)	1626 (14)
O(4)	0828 (7)	-2817 (61)	2744 (19)
O(5)	1028 (8)	2448 (45)	3494 (15)
N(1)	4191 (5)	0267 (78)	0867 (11)
C(1)	4689 (7)	1216 (80)	1639 (19)
C(2)	4619 (7)	1247 (60)	3218 (18)
C(3)	4146 (7)	2999 (71)	3440 (17)
C(4)	3679 (6)	2906 (62)	2435 (15)
C(5)	3116 (7)	3169 (61)	2569 (18)
C(6)	2882 (7)	1275 (57)	1535 (19)
<b>C</b> (7)	3233 (7)	0050 (108)	0732 (17)
C(8)	3761 (6)	1112 (61)	1281 (17)
C(9)	2914 (7)	5032 (115)	3446 (19)
<b>C</b> (10)	2355 (7)	5285 (106)	3561 (24)

The absolute configuration was determined by the use of the anomalous dispersion effect of the selenium atoms for Cr K $\alpha$  radiation ( $\lambda$ =2·2909 Å:  $\Delta f'_{se}$ = -0·7,  $\Delta f''_{se}$ =2·4,  $\Delta f'_{o}$ =0·1,  $\Delta f''_{o}$ =0·2,  $\Delta f''_{n}$ =0,  $\Delta f''_{n}$ =0·1,  $\Delta f''_{c}$ =0,  $\Delta f''_{c}$ =0·1). Structure factors for the Friedel pairs of reflexions were evaluated by assuming that the coordinates of the atoms were derived from a right-handed set of axes. Some calculated intensities and observed relations are listed in Table 4. Since the crystal has a twofold axis of rotation along the *b* axis intensities of  $h\bar{k}l$  reflexions on oscillation photographs taken around the *b* axis. From the good accordance in Table



Fig. 1. Molecular structure of latumcidin viewed along the b axis.

Table 2. Thermal parameters (×10<sup>4</sup>) in the form exp  $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ Standard deviations (×10<sup>4</sup>) are in parentheses.

	B <sub>11</sub>	B <sub>22</sub>	B33	<b>B</b> <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Se	13 (0)	588 (10)	68 (1)	56 (4)	0(1)	41 (12)
O(1)	20 (2)	656 (138)	81 (12)	-89(34)	16 (8)	- 103 (79)
O(2)	26 (3)	1102 (159)	73 (14)	84 (36)	-43(11)	184 (76)
O(3)	19 (2)	1486 (201)	141 (18)	-190 (53)	-23(11)	293 (154)
O(4)	25 (3)	1340 (195)	185 (26)	-71(47)	-4(15)	356 (128)
O(5)	46 (5)	738 (127)	112 (19)	-47 (45)	43 (16)	-414(89)
N(1)	15 (2)	799 (138)	53 (119)	-62(45)	0 (8)	-6(110)
C(1)	13 (3)	1623 (352)	77 (20)	31 (50)	-2 (12)	-170(129)
C(2)	15 (3)	954 (195)	71 (19)	26 (40)	-24 (12)	-166 (99)
C(3)	15 (3)	1225 (222)	50 (17)	-62(46)	-6(11)	14 (109)
C(4)	12 (3)	1064 (186)	39 (15)	-123(39)	-2(10)	-11(91)
C(5)	14 (3)	859 (173)	76 (19)	-6 (39)	-1(12)	13 (103)
C(6)	14 (3)	750 (153)	87 ( <b>2</b> 0)	-12(36)	-17 (12)	34 (94)
C(7)	15 (3)	859 (154)	109 (20)	-108(62)	-8 (12)	-115(184)
C(8)	10 (2)	1097 (235)	73 (18)	-10 (36)	-11 (11)	156 (99)
C(9)	14 (3)	1047 (179)	128 (23)	91 (74)	23 (13)	159 (223)
C(10)	13 (3)	765 (192)	209 (32)	28 (58)	35 (15)	85 (204)

4, it can be concluded that the atomic coordinates given in Table 1 correctly represent the absolute configuration of the molecule referred to the right-handed set of axes. A perspective drawing of the molecular structure viewed along the b axis is shown in Fig. 1.

### Description of the structure and discussion

The molecular structure of latumcidin that was revealed in the present investigation together with the number-

Table 3	Observed	and	calculated	structure	factors
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Fig. 2. Bond lengths (Å) in latumcidin selenate.

ing scheme of atoms, is shown in Fig. 1. The structure conforms to the formula 5-ethylidine-2,3-dihydro-1,5pyrindine 4,4a-oxide, and confirms the relative configuration obtained by Gurevich *et al.* (1968). It is bicyclic, consisting of a six- and a five-membered ring, ethylidene group side chain, and an epoxide group. Two rings are fused to form a pyrindine skeleton. The methyl group of the ethylidene group is in the *trans* position relative to the six-membered ring. The plane of the epoxide group is nearly perpendicular to the average plane of the six-membered ring.

Table 4	4.	Determination	of	the	absolute	configurati	on
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Indices	$F_{c^{2}}(hkl)$	Observed	Fc²(hkl)
11 1 1	2097	>	1678
11 1 1	5117	>	4779
911	1771	<	2217
<u>1</u> 1 2	2516	<	3206
513	4705	>	4254
9 1 3	1896	<	2110
313	486	<	803
3 1 3	3652	<	4842
515	4720	>	4320

Intramolecular bond lengths and angles are given in Figs. 2 and 3 respectively. Mean standard deviations are 0.03 Å and 1.9° in the latumcidin molecule, and 0.02 Å and 1.0° in the selenic-acid molecule. Distances C(5)-C(9) (1.38 Å) and C(6)-C(7) (1.39 Å) are normal for the C-C conjugated double bonds. The C(5)-C(6)bond (1.45 Å) is shortened by conjugation of the double bonds. Distance C(4)-C(8) (1.45 Å) is also a little short for the C-C single bond. This might suggest the existence of an interaction between the C-N double bond and the epoxide group. The remaining six C-C single bond lengths are normal, having the mean value of 1.51 Å. The C(8)–N(1) and C(1)–N(1) distances correspond to the C-N double-bond lengths and singlebond lengths within the experimental errors, respectively. The epoxide group has an equilateral triangular form. C-O distances of 1.49 and 1.50 Å are in good

accordance with the value (1.47 Å) reported for the group in 1,2-epoxycylopentane (Erlandsson, 1955).

The shape of the SeO<sub>4</sub> group is fairly different from shapes observed in ordinary orthoselenates. In the present substance, there are two kinds of Se–O distances, while the SeO<sub>4</sub><sup>2-</sup> anion is an almost regular tetrahedron (*e.g.*, in K<sub>2</sub>SeO<sub>4</sub>; Kálmán, Stephens & Cruickshank, 1970). The two longer distances are in good agreement with the length between Se and bridging O atoms in selenium trioxide (Mijlhoff, 1965), indicating that these are of Se–OH. The remaining Se–O distances, as well as all the bond angles, are also in excellent agreement with corresponding distances and angles in SeO<sub>3</sub>.

# Table 5. Least-squares plane and distances (Å) of atoms from the plane

Equations of plane: lX+mY+nZ+P=0 with  $X=ax+cz\cos\beta$ , Y=by,  $Z=cz\sin\beta$ .

Plane		1	m	n	Р
	-0	0.033	0.761	-0.648	0.720
Distance	s				
C(1) −0·25	C(4) −0·03	C(5) 0·03	C(6) -0·01	C(7) 0·00	C(8) C(9) 0·01 0·19
C(10) 0·27	N(1) −0·08				

The five-membered ring is planar. The equation of the least-squares plane and deviations of atoms from the plane are given in Table 5. Atoms C(1), C(9), C(10) and N are also nearly coplanar with the five-membered ring. The six-membered ring has a half-chair conformation with C(1) displaced largely from the least-squares plane defined by the other five constituent atoms.

The latumcidin molecule has two asymmetric carbon atoms. Absolute configurations of these atoms are:



Fig. 3. Bond angles (°) in latumcidin selenate.



● ○ ◎ • Se O N C

Fig. 4. Projection of the crystal structure of latumcidin selenate along the b axis. The short contact between molecules is shown by broken lines (Å).

C(3)R and C(4)S respectively. They are opposite to the previously reported configurations C(3)S and C(4)R, which were assigned on the basis of the benzoate rule (Gurevich *et al.*, 1968). The contradiction may be due to the limitation of the benzoate rule or to the inversion of the hydroxy group of latumcidin during reduction.

### Table 6. Intermolecular contacts less than 3.50 Å

	$i \qquad \frac{1}{2} - x$ $ii \qquad \frac{1}{2} + x$ $iii \qquad \frac{1}{2} + x$ $iv \qquad x$ $v \qquad \frac{1}{2} - x$	$\frac{1}{2} + y - z$ $\frac{1}{2} + y z$ $-\frac{1}{2} + y z$ $1 + y z$ $-\frac{1}{2} + y - z$	
O(2)-N(1 <sup>i</sup> )	2·790 Å	O(3)-C(7 <sup>i</sup> )	3∙309 Å
$C(7) - O(3^{i})$	3.473	$C(2) - O(4^{ii})$	3.257
$C(1) - O(4^{ii})$	3.104	$C(1) - O(2^{111})$	3.410
$O(5) - O(4^{iv})$	2.459	$O(2) - O(4^{iv})$	3.329
$O(1) - C(2^{iv})$	3.295	$O(1) - C(7^{iv})$	3.428
$O(1) - C(8^{iv})$	3.087	$O(1) - N(1^{iv})$	2.912
$O(3) - C(7^{v})$	3.473	$C(7) - O(3^{v})$	3.309
$N(1) - O(2^{v})$	2.790	- ( )	

A projection of the crystal structure viewed along the b axis, with designations of short intermolecular atomic distances, is shown in Fig. 4. Also, molecular contacts less than 3.50 Å are given in Table 6. Strong hydrogen bonds (2.46 Å) are observed between atoms O(5) and O(4'); chains of selenic acid molecules are formed parallel to the b axis. Here, the prime means that the atom belongs to the adjacent molecule displaced by a unit translation along the b axis. Hydrogen bonds are also observed between O(2) and N(1) atoms (2.79 Å). Distances O(1)...N(1') (2.91 Å) and O(1)...C(8') (3.09 Å) are fairly short. These distances may indicate some

interaction between O(1) and N(1'), and/or between O(1) and C(8'). The former interaction may be due to charge-transfer from O(1) to N(1'). Thus, the structure is made up of chains of selenic acid and columns of latumcidin molecules parallel to the *b* axis. Each chain of selenic acid is connected to a column of latumcidin with the hydrogen bonds. These structural units are laterally combined by the van der Waals force. Thus, the needle-like form of the crystal is well explained by the existence of the rather strong intermolecular forces along the *b* axis.

Calculations were carried out on the HITAC 5020E computer at the computer centre of this university. The authors acknowledge Dr Yasuaki Ogawa for his kind collaboration on this work.

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# Sur Quelques Fluométallates Alcalino-Terreux. I. Structure Cristalline de BaFeF5 et SrAlF5

PAR RÉGNAULT VON DER MÜHLL, STEN ANDERSSON\* ET JEAN GALY

Service de Chimie Minérale Structurale de la Faculté des Sciences de Bordeaux associé au C.N.R.S., 351, cours de la Libération, 33-Talence, France

### (Reçu le 11 décembre 1970, revu le 12 mars 1971)

The crystal structure of the tetragonal  $A^{II}B^{III}F_s$  phases has been determined by single-crystal analysis of BaFeF<sub>5</sub> and SrAlF<sub>5</sub>. In the BaFeF<sub>5</sub> lattice iron and fluorine atoms are grouped in two different kinds of chains, both having the formula  $(FeF_5)_n^{2n-}$ : the first is linear, the second ramified. To a first approximation the space group is *I*4, but a small distortion along the *c* axis in fact doubles the *c* parameter, the space group becoming *P*4.

Lors de l'étude des systèmes  $AF_2$ - $FeF_2$ - $FeF_3$  dans lesquels A était un élément alcalino-terreux, Ravez, Viollet, de Pape & Hagenmuller (1967) ont mis en évidence un grand nombre de composés inédits parmi lesquels la phase quadratique BaFeF<sub>5</sub> semblait jouer le rôle de pivot (Ravez & Hagenmuller, 1967; Ravez *et al.*, 1967; Ravez, 1968). D'après ces auteurs cette phase donne des solutions solides avec un autre fluoferrite  $Sr_3(FeF_6)_2$  et avec une phase  $Sr_2Fe_2F_9$  dans laquelle le fer se trouve simultanément aux degrés d'oxydation

<sup>\*</sup> Adresse actuelle: Institute of Technology, Chemical Centre Department of Inorganic Chemistry, Box 740, S-22007 Lund 7, Suède.