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The Crystal and Molecular Structure of Axivalin Hydrate

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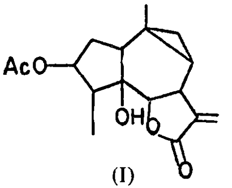
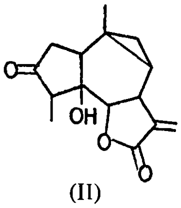
The crystal structure at 25 °C of the hydrate of the cyclopropanoid guaianolide axivalin, $C_{17}O_5H_{22}.H_2O$, has been determined from three-dimensional X-ray diffractometer data with the tangent refinement formula. The crystal is orthorhombic, space group $P2_12_12_1$ with four molecules per unit-cell and the cell dimensions are $a=8{\cdot}601$ (3); $b=10{\cdot}555$ (4); $c=18{\cdot}734$ (9) Å. All hydrogen atoms have been located and the structure refined by least-squares calculations to an R of 0·077. The absolute stereochemistry has been determined from the CD curves of axivalin and its pyrazoline.

Introduction

Axivalin (I) is one of a group of novel cyclopropanoid guaianolides isolated from *Iva axillaris* Pursh. ssp *robustior* (Hook.) Bassett (Herz, Sundarsanam & Schmid, 1966). It has been chemically correlated with the other two compounds in this group, ivaxillarin (II) and anhydroivaxillarin (III). Since it was desirable to establish whether the structures of these novel compounds fitted the proposed biogenetic scheme for sesquiterpene lactones and whether the stereochemistry of these compounds was in accord with that of other lactones isolated from the tribe Heliantheae, an X-ray structure analysis was undertaken.



(I)



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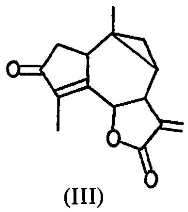


(III)

Several efforts to prepare heavy-atom derivatives of axivalin were unsuccessful. These included attempted hydrolysis of the acetate so as to allow preparation of a bromoacetate or bromobenzoate, attempted esterification of the tertiary alcohol group with bromoacetyl bromide, and attempted 1,3 dipolar addition of *o*-bromobenzonitrile oxide to the *exo*-methylene group to form an *o*-bromophenylisoxazole. Hence we decided to attempt the use of direct methods, in particular the tangent refinement formula, for the solution of the crystal structure of axivalin.

Experimental

Crystallization of axivalin from methanol–water at room temperature yielded crystals of the monohydrate which were colorless, transparent, thin, hexagonal plates elongated in the **b** direction. One such crystal was cleaved with a razor blade to give a rectangular fragment measuring 0·8 by 0·36 by 0·04 mm. The cleavage planes were parallel to the (100) and the (010) planes.

Weissenberg photographs for the $h0l$, $h1l$, and $h2l$ layers and precession photographs for the $0kl$ and $hk0$ layers showed the crystal to be orthorhombic. Systematic absences in the $h00$ ($h=2n+1$), $0k0$ ($k=2n+1$), and $00l$ ($l=2n+1$) reflections uniquely determined the space group as $P2_12_12_1$.

The crystal was mounted on a Hilger–Watts four-circle automatic diffractometer with the b axis approximately parallel to the axis of rotation of the φ circle. A least-squares fit of the observed angles (θ/ω, φ, and χ) for twelve reflections gave a refined alignment matrix and the unit-cell dimensions of:

a = 8·601 (3) b = 10·555 (4) c = 18·734 (9) Å .

For four formula units of axivalin hydrate, $C_{17}O_5H_{22}.H_2O$, per unit cell, the calculated density was 1·267 g cm^{-3} in good agreement with the value of 1·26 g cm^{-3} obtained by flotation in heptane–carbon tetrachloride.

Intensity data were collected to a 2θ value of 40° using the $2\theta/\omega$ scan technique, Zr-filtered molybdenum $K\alpha$ radiation, scintillation counter and pulse-height discrimination. There was no visible sign of deterioration of the crystal during the time period necessary for the data collection. Three reflections which were remeasured periodically during the data collection suffered less than a 15% change in intensity.

The X-RAY 70 System of programs (Stewart, Kundell & Baldwin, 1970) was used throughout the analysis for computation. The *DATCO5* link was used to correct for minor changes in the intensities of the standard reflections and to average the equivalent reflections. From a total of 2911 measurements, 1285 were independent and had a positive intensity. Of these, 161 were considered unobserved since their intensities (I) were less than three times the standard deviations of the measurements [$\sigma(I)$]. Standard corrections only were applied since absorption was negligible.

Phase determintion

The structure was solved by means of the tangent refinement formula (Karle & Hauptman, 1956). Normalized structure factors were obtained through the use of the *NORMSF* link with a linear isotropic fit of the data to the Wilson plot. The *SIGMA* link found 37038 triplets for phase determination from the 501 reflections having $E \geq 1·00$. Initial attempts at phasing starting with four suitable two-dimensional reflections as origin definers (OD) and enantiomer definers (ED) were unsuccessful with these E values. Observed reflections were then redefined as any reflection having a positive intensity rather than greater than $3\sigma(I)$ and E values recalculated. In this new set, 285 E's $\geq 1·2$ produced 7970 triplets. Assignment of origin defining and enantiomer defining phases as follows:

h	k	l	E	φ	
0	3	2	4·33	90°	OD
2	0	7	2·61	90	OD
0	2	1	2·54	180	OD
3	0	1	1·88	90	ED

in the *TANGEN* link led to the determination of 271 phases having an agreement factor of 0·24.

The use of these phases allowed the preparation of a new E map in which 22 of the 24 strongest unique peaks were readily recognizable as the molecular structure of axivalin. A structure-factor calculation carried out with the *FC* link with all atoms considered to have

Table 1. *Final atomic coordinates* (× 10^4) *and thermal parameters* (× 10^2) *for carbon and oxygen atoms in axivalin hydrate*

Estimated errors in the last two significant digits are shown in parentheses. The temperature factor expression used was

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2778 (10)	6793 (09)	3473 (04)	4·11 (44)	5·16 (50)	4·71 (43)	−0·59 (41)	−0·73 (39)	0·07 (39)
C(2)	2463 (13)	7507 (10)	2778 (05)	6·70 (61)	5·50 (54)	5·27 (47)	−0·64 (52)	−0·74 (49)	0·68 (45)
C(3)	3070 (10)	6684 (10)	2179 (04)	5·31 (53)	7·38 (61)	4·33 (43)	−2·23 (47)	−0·15 (39)	0·69 (45)
C(4)	3362 (11)	5357 (10)	2509 (05)	4·36 (46)	7·55 (65)	4·86 (47)	0·54 (48)	0·28 (38)	0·19 (44)
C(5)	2622 (09)	5385 (08)	3253 (04)	3·52 (40)	5·29 (53)	4·56 (42)	−0·27 (40)	−0·20 (33)	0·09 (36)
C(6)	964 (09)	4885 (08)	3307 (04)	3·39 (40)	5·55 (51)	4·68 (44)	0·92 (37)	−1·03 (34)	−0·18 (40)
C(7)	126 (09)	5138 (09)	4015 (04)	3·06 (37)	6·24 (57)	4·30 (41)	−0·08 (39)	−0·45 (35)	0·43 (40)
C(8)	512 (11)	6408 (10)	4365 (05)	5·47 (53)	6·47 (63)	4·17 (45)	−0·29 (48)	−1·15 (40)	−0·31 (41)
C(9)	1968 (11)	6545 (10)	4786 (04)	5·66 (54)	6·12 (59)	5·42 (49)	−1·75 (48)	−1·62 (44)	0·54 (44)
C(10)	1825 (11)	7239 (08)	4100 (05)	5·66 (52)	4·16 (51)	5·20 (47)	−0·50 (42)	−1·30 (42)	−0·28 (39)
C(11)	−1544 (09)	5116 (08)	3753 (04)	3·97 (45)	5·38 (53)	6·04 (52)	0·08 (41)	−0·50 (40)	−1·53 (44)
C(12)	−2811 (11)	4814 (11)	4100 (06)	3·71 (48)	7·85 (73)	8·64 (69)	−0·48 (50)	1·07 (50)	−2·46 (61)
C(13)	−1500 (10)	5555 (08)	3002 (04)	4·62 (47)	4·10 (44)	5·93 (48)	1·65 (42)	−1·22 (40)	−0·09 (39)
C(14)	2972 (15)	4223 (11)	2043 (06)	8·86 (81)	6·47 (68)	5·65 (59)	1·14 (63)	0·95 (58)	−1·20 (49)
C(15)	1550 (16)	8666 (10)	4152 (06)	11·84 (96)	5·37 (64)	7·54 (68)	0·66 (69)	−2·04 (70)	−2·29 (54)
C(16)	2420 (14)	6574 (10)	932 (05)	8·34 (74)	6·43 (66)	4·73 (49)	−0·46 (62)	−0·70 (54)	0·23 (48)
C(17)	1060 (16)	6632 (11)	434 (05)	11·21 (89)	7·38 (71)	4·36 (50)	0·73 (75)	−0·80 (58)	−1·06 (50)
O(1)	−19 0(6)	5499 (06)	2760 (03)	4·26 (28)	5·58 (35)	5·03 (31)	0·03 (29)	−0·84 (28)	−0·04 (29)
O(2)	3476 (06)	4628 (06)	3752 (03)	3·98 (32)	6·21 (39)	5·37 (36)	0·83 (30)	−0·96 (26)	0·03 (30)
O(3)	−2556 (08)	5874 (07)	2629 (03)	5·10 (35)	8·22 (48)	7·48 (41)	0·68 (35)	−2·13 (36)	0·97 (37)
O(4)	1917 (07)	6676 (07)	1615 (03)	6·07 (38)	8·05 (45)	4·42 (32)	−0·57 (36)	−0·27 (29)	0·89 (32)
O(5)	3747 (10)	6496 (08)	770 (04)	7·30 (48)	9·83 (62)	6·43 (43)	−0·55 (46)	0·88 (40)	−0·12 (41)
O(6)	−3077 (09)	6998 (07)	1257 (04)	8·24 (51)	8·18 (52)	7·50 (45)	0·08 (46)	0·29 (40)	1·10 (40)

an atomic number of six gave a conventional R index of 0·337.

A Fourier map based on the observed structure factor amplitudes and the calculated phases for all reflections showed the 22 unique peaks for axivalin as well as one additional peak corresponding to the strongest of those not assigned in the original E map. This peak was accepted as the location of the oxygen atom of the water molecule.

Refinement

With all 23 heavy atoms located, three cycles of full-matrix least-squares refinement using the *CRYLSQ* link with individual isotropic temperature factors and unit weights led to a value of 0·234 for the conventional R index. After appropriate assignment of atoms as carbon or oxygen in the now clearly recognizable structure, four cycles of full-matrix least-squares refinement with individual anisotropic temperature factors and unit weights further reduced the R index to 0·116.

At this point 'unobserved' reflections were again defined as those reflections with an intensity less than three times the estimated standard deviation (3σ) and not considered in further refinement. Hydrogen atoms were located on difference maps. Application of a new weighting scheme [$w=1/(6{\cdot}5+F_o+0{\cdot}005F_o^2)$], and further full-matrix least-squares refinement with individual anisotropic temperature factors for carbon and oxygen atoms and an overall isotropic temperature factor for the hydrogen atoms gave a final R index of 0·077 excluding the 161 'less-thans'.

Table 2. *Final atomic coordinates* ($\times 10^3$) *for hydrogen atoms in axivalin hydrate*

Estimated errors in the last two significant figures are shown in parentheses.

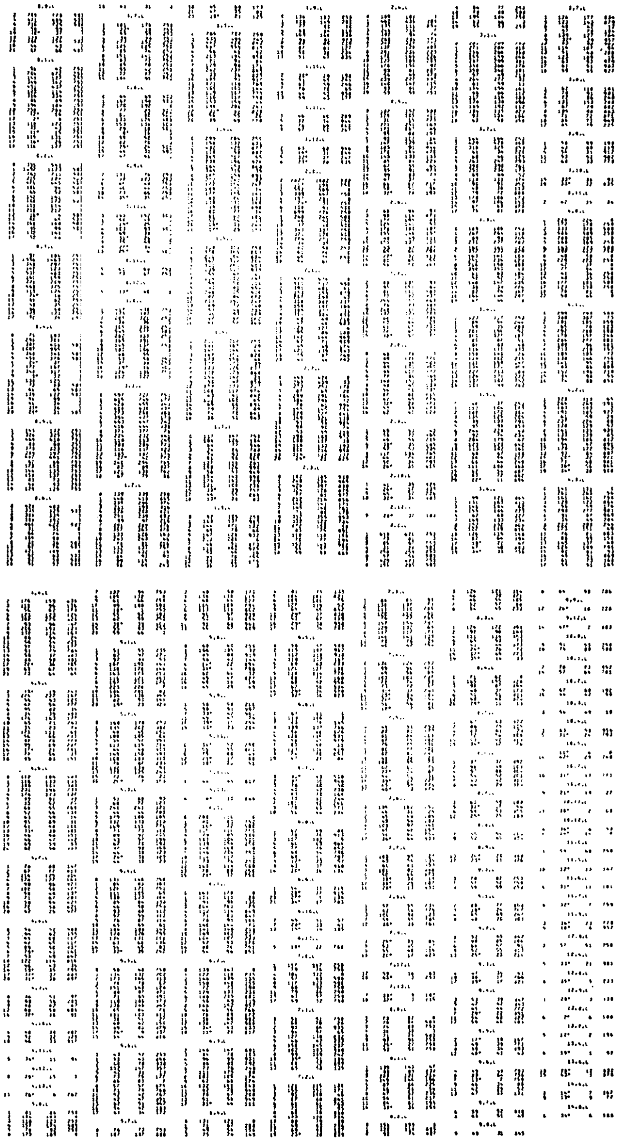
	x	y	z
H(1)	389 (14)	713 (10)	371 (05)
H(2*A*)	286 (13)	854 (12)	273 (06)
H(2*B*)	139 (15)	773 (11)	271 (06)
H(3)	404 (14)	706 (11)	194 (05)
H(4)	455 (14)	541 (11)	266 (06)
H(6)	103 (13)	400 (11)	313 (05)
H(7)	36 (13)	442 (11)	443 (06)
H(8)	−56 (14)	694 (11)	452 (06)
H(9*A*)	197 (14)	716 (11)	522 (05)
H(9*B*)	278 (13)	611 (11)	481 (05)
H(12*A*)	−387 (14)	482 (11)	388 (06)
H(12*B*)	−290 (14)	421 (10)	462 (05)
H(14*A*)	318 (13)	316 (12)	234 (06)
H(14*B*)	183 (15)	404 (12)	187 (06)
H(14*C*)	354 (14)	398 (12)	168 (06)
H(15*A*)	108 (13)	904 (11)	374 (05)
H(15*B*)	271 (13)	899 (11)	426 (05)
H(15*C*)	111 (14)	881 (11)	473 (05)
H(17*A*)	142 (15)	740 (12)	12 (06)
H(17*B*)	117 (14)	632 (12)	15 (06)
H(17*C*)	30 (12)	703 (11)	66 (05)
H(*W*1)	−284 (13)	649 (11)	170 (06)
H(*W*2)	−395 (14)	714 (11)	129 (06)
H(OH)	392 (14)	435 (12)	345 (06)

A final difference map showed no feature greater than 0·4 eÅ^{-3}. The features in the difference map were unrelated to any part of the structure.

The form factors for carbon, oxygen and hydrogen were from *International Tables for X-ray Crystallography* (1968).

The final coordinates and thermal parameters of the carbon and oxygen atoms are shown in Table 1. The final coordinates for the hydrogen atoms are shown in Table 2. The final values of the overall temperature factor for the hydrogen atoms was $U=0{\cdot}0739$ (80). The final calculated structure factors and phases are shown in Table 3 together with the observed structure factor amplitudes.

Table 3. *Structure factors*



Geometry of the molecule

The axivalin molecule is highly folded with two puckered five-membered rings mutually perpendicular and approximately normal to the plane of five of the six atoms in the cyclohexane ring.

Bond lengths and angles involving the heavy atoms are shown in Tables 4 and 5 respectively. All bond lengths and angles are as expected. A few of the bonds involving hydrogen atoms are slightly shorter than expected but the average length of these bonds is 1·0 ± 0·1 Å which, within the limits of estimated error, is as expected.

Table 4. *Bond lengths for axivalin hydrate*

Estimated errors in the last significant digit are given in parentheses.

C(1)-C(2)	1·53 (1) Å	C(7)—C(11)	1·52 (1) Å
C(1)-C(5)	1·55 (1)	C(8)—C(9)	1·49 (1)
C(1)-C(10)	1·51 (1)	C(8)—C(10)	1·51 (1)
C(2)-C(3)	1·51 (1)	C(9)—C(10)	1·48 (1)
C(3)-C(4)	1·55 (1)	C(10)-C(15)	1·53 (1)
C(3)-O(4)	1·45 (1)	C(11)-C(12)	1·31 (1)
C(4)-C(5)	1·53 (1)	C(11)-C(13)	1·48 (1)
C(4)-C(14)	1·52 (2)	C(13)-O(1)	1·35 (1)
C(5)-C(6)	1·52 (1)	C(13)-O(3)	1·19 (1)
C(5)-O(2)	1·43 (1)	C(16)-C(17)	1·50 (2)
C(6)-C(7)	1·53 (1)	C(16)-O(4)	1·36 (1)
C(6)-O(1)	1·48 (1)	C(16)-O(5)	1·18 (2)
C(7)-C(8)	1·53 (1)		

There is considerable hydrogen bonding between the water molecule and the polar groups of the axivalin molecule. Each axivalin molecule is hydrogen bonded to three water molecules and each water molecule is hydrogen bonded to three axivalin molecules. These hydrogen bonds are shown as dashed lines in the pack-

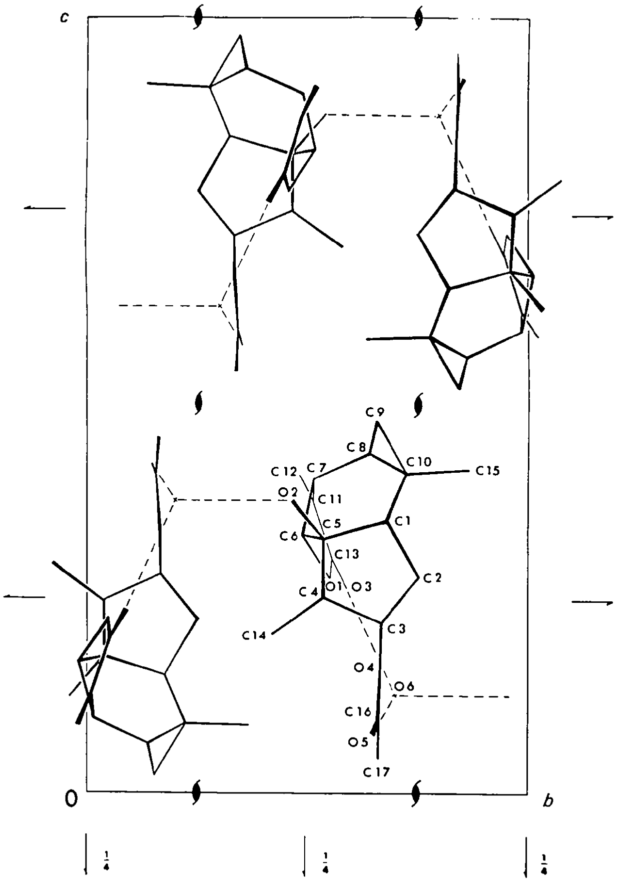


Fig. 1. Packing diagram of one unit cell of axivalin hydrate; projection down the *a* axis. The oxygen atom of the water molecule is shown as a cross and hydrogen bonds by dashed lines.

Table 5. *Bond angles for axivalin hydrate*

Estimated errors in the last significant digit are shown in parentheses.

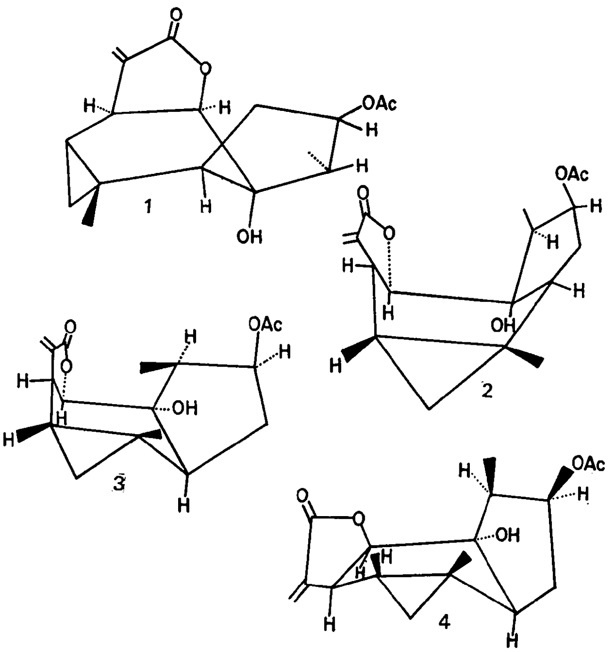
C(2)-C(1)-C(5)	103·3 (7)	C(7)—C(8)—C(9)	119·7 (8)
C(2)-C(1)-C(10)	114·4 (8)	C(7)—C(8)—C(10)	121·9 (7)
C(5)-C(1)-C(10)	117·4 (7)	C(9)—C(8)—C(10)	59·3 (6)
C(1)-C(2)-C(3)	106·7 (8)	C(8)—C(9)—C(10)	61·3 (6)
C(2)-C(3)-C(4)	106·2 (7)	C(1)—C(10)-C(8)	118·8 (8)
C(2)-C(3)-O(4)	107·9 (8)	C(1)—C(10)-C(9)	118·4 (8)
C(4)-C(3)-O(4)	113·3 (8)	C(1)—C(10)-C(15)	116·2 (8)
C(3)-C(4)-C(5)	106·1 (7)	C(8)—C(10)-C(9)	59·5 (6)
C(3)-C(4)-C(14)	116·5 (8)	C(8)—C(10)-C(15)	115·8 (8)
C(5)-C(4)-C(14)	116·5 (8)	C(9)—C(10)-C(15)	116·4 (8)
C(4)-C(5)-C(6)	116·2 (7)	C(7)—C(11)-C(12)	129·2 (8)
C(4)-C(5)-C(1)	103·0 (7)	C(7)—C(11)-C(13)	106·1 (7)
C(4)-C(5)-O(2)	111·7 (7)	C(12)-C(11)-C(13)	124·7 (8)
C(1)-C(5)-C(6)	113·3 (7)	C(11)-C(13)-O(1)	109·2 (7)
C(1)-C(5)-O(2)	108·5 (6)	C(11)-C(13)-O(3)	128·6 (8)
C(6)-C(5)-O(2)	104·1 (6)	O(1)—C(13) O(3)	122·2 (8)
C(5)-C(6)-C(7)	115·9 (6)	C(17)-C(16)-O(4)	109·6 (9)
C(5)-C(6)-O(1)	109·7 (6)	C(17)-C(16)-O(5)	126·6 (9)
C(7)-C(6)-O(1)	104·7 (6)	O(4)—C(16)-O(5)	123·7 (10)
C(6)-C(7)-C(8)	115·0 (7)	C(6)—O(1)—C(13)	109·0 (6)
C(6)-C(7)-C(11)	99·4 (6)	C(3)—O(4)—C(16)	118·1 (8)
C(8)-C(7)-C(11)	111·0 (7)		

ing diagram (Fig. 1) and their lengths are given in Table 6. There are no abnormally short intermolecular contact distances.

Table 6. *Hydrogen-bonding distances for axivalin hydrate*

Donor	Acceptor	O···O	O···H	Symmetry operation for acceptor
O (6)	O (3)	2·87 Å	1·87 Å	x, y, z
O (6)	O (5)	2·93	2·31	$x-1, y, z$
O (2)	O (6)	2·80	2·80	$-x, y-\frac{1}{2}, \frac{1}{2}-z$

Examination of a model shows that axivalin could exist in solution as one of four major conformers (1–4) with a fair amount of flexibility in the cyclopentane ring in each case. One of these (2) is highly unlikely because of the extreme interactions between the lactone ring and the cyclopentane ring. An examination of the other three shows significant differences in the H(6)–H(7) and H(7)–H(8) dihedral angles.



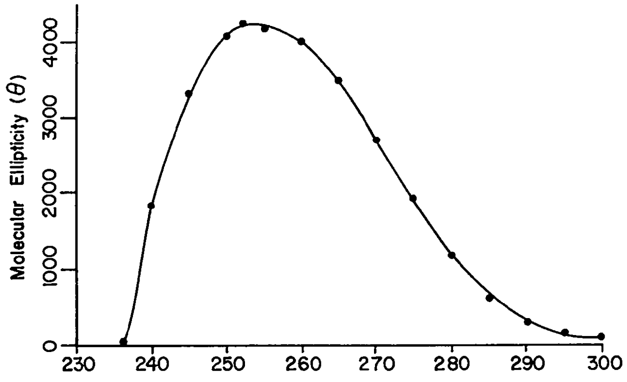
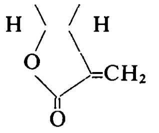


Fig. 2. CD curve of axivalin.

Table 7 shows the H(6)–H(7)–H(8) dihedral angles for the crystalline state and for conformers 1–4 along with the coupling constants calculated from the Karplus (1963) equation for these dihedral angles and compares these calculated coupling constants with the ones obtained experimentally. It can be seen from the table that conformer 1 is obviously the preferred conformation in the crystalline state.

Since the conditions of the X-ray experiment did not allow the determination of absolute stereochemistry, other techniques were examined to see if they could be used for this purpose. An empirical rule (Stöcklin, Waddell & Geissman, 1970) relates the sign of the lactone Cotton effect in sesquiterpene lactone containing partial structure



to the stereochemistry of the lactone ring fusion. The generalization has been made that, regardless of structural type, *cis*-fused lactones closed to C(8) exhibit negative Cotton effects, and that in *trans*-fused lactones closed to C(8) the Cotton effect is positive. The reverse situation prevails in lactones closed to C(6). *cis*-fused lactones display positive Cotton effects; *trans*-fused lactones show negative values.

This empirical rule frequently fails when the lactone oxygen is in an allylic position and is sometimes ambiguous when the C(5) position is oxygenated as in axivalin. However, if the rule does hold for axivalin which is now known to be a *cis* lactone fused to C(6), a positive Cotton effect would indicate a β orientation for the C(7) side chain. When the CD curve of axivalin

Table 7. *Comparison of calculated and observed n.m.r. coupling constants for axivalin*

	Conformer 1		Conformer 2		Conformer 3		Conformer 4		
Protons involved	J_{calc}	Dihedral* angle	J_{calc}	Dihedral* angle	J_{calc}	Dihedral* angle	J_{calc}	Dihedral* angle	J_{obs}
H(6), H(7)	6·0	30	6·0	30	4·6	40	4·6	40	6
H(7), H(8)	0·4	60	1·7	60	−0·3	90	5·4	140	<·1

* Dihedral angles were obtained by measurements on Dreiding models. For comparison the dihedral angles calculated from the absolute atomic positions in the crystalline state are: H(6), H(7) 40° and H(7), H(8) 104° which predicts coupling constants of 4·6 and 0·4 respectively.

(Fig. 2) is examined, it does have a positive Cotton effect ($\theta = 4430$) at 252 nm thus indicating a β orientation for the C(7) side chain and the same absolute stereochemistry as that obtained through the original phase assignment.

Also, Snatzke (1969) has shown by examining the CD curves of a number of acyl pyrazolines that the Cotton effect in the CD of an acyl pyrazoline is related to the stereochemistry of the pyrazoline ring. Model considerations indicate that steric factors would require diazomethane to attack axivalin in such a way as to give the pyrazoline (IV) or its mirror image. The very strong negative Cotton effect ($\theta = -42940$) in the CD curve of the pyrazoline (Fig. 3) at 326 nm requires the former which has the same absolute stereochemistry as that deduced from the CD of axivalin.

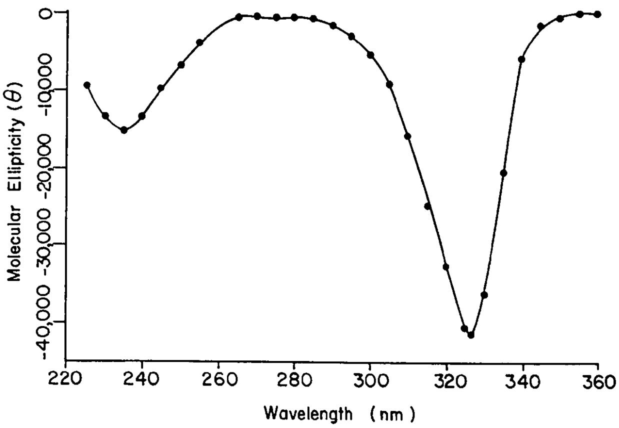


Fig. 3. CD curve of axivalin pyrazoline.

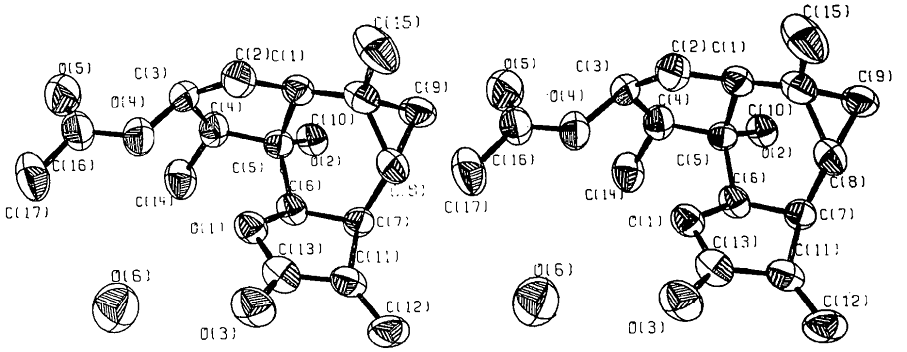
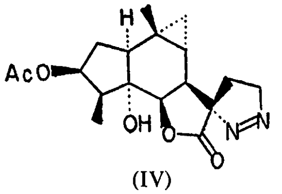


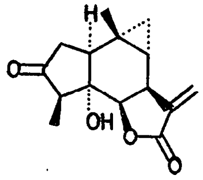
Fig. 4. Three-dimensional view of axivalin showing ellipsoids of thermal motion at 50% probability.



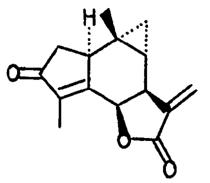
(IV)

The absolute configuration of axivalin is shown in Fig. 4 as that enantiomer deduced from the optical data.

Since axivalin had been previously correlated with ivaxillarin and anhydroivaxillarin, the stereochemistry of the latter compounds must be as shown in (V) and (VI) respectively.



(V)



(VI)

That the stereochemistry of axivalin and its congeners does indeed fit the proposed biogenesis (Parker, Roberts & Ramage, 1967) of guaianolides from *trans*-farnesol through the germacrane ring system is shown in Fig. 5. Step *b* is the electrophilic cyclization of the germacradiene to the guaiane and proceeds in such a manner that all new bonds are parallel. Step *c* is the

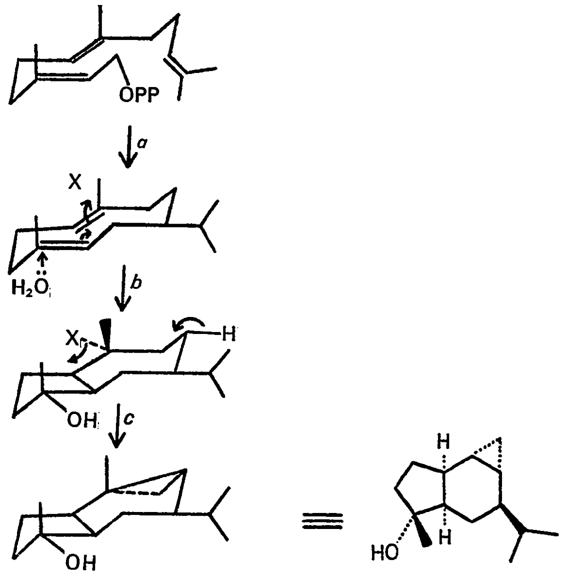


Fig. 5. Possible biogenesis of the axivalin carbon skeleton.

intramolecular nucleophilic displacement of some group (likely pyrophosphate) in the α orientation at C(10). This would invert the configuration at C(10) and would normally place the methyl group in the α configuration. However, if one examines this system carefully, it is seen that although inversion occurs, the formation of the highly strained cyclopropane ring causes a pseudo-inversion such that the methyl group is still in the β orientation. The α orientation of the C(5) hydroxyl group of axivalin is in accord with other evidence (Battersby, 1972) that biological hydroxylations occur with retention of configuration.

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The Crystal Structure of Tsumcorite, a New Mineral from the Tsumeb Mine, S.W. Africa

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Tsumcorite, $Pb(Zn,Fe^{3+},Fe^{2+})_2(OH,OH_2)_2(AsO_4)_2$, crystallizes in the monoclinic space group $C2/m$ with $a=9{\cdot}124$ (3), $b=6{\cdot}329$ (2), $c=7{\cdot}577$ (2) Å, $\beta=115°17$ (2)′, $Z=2$. The crystal structure has been determined from X-ray diffractometer data by Patterson and Fourier methods and refined to $R=0{\cdot}03$ for 594 observed F_{hkl}. It consists of layers of composition $[(Zn,Fe)(OH,OH_2)AsO_4]^-$ parallel to the a, b plane which are formed by the coordination octahedra around (Zn,Fe) and the AsO_4 tetrahedra *via* shared edges and corners. The Pb atoms occupy special positions with site symmetry $\bar{1}$ between these layers. There are six short Pb–O bonds of 2·591 Å (2 ×) and 2·597 Å (4 ×) and two weaker bonds of 2·955 Å. Iron and zinc atoms replace each other in one crystallographic site with a mean (Zn,Fe)–O distance in the $(Zn,Fe)(OH,OH_2)_2O_4$ coordination octahedron of 2·065 Å. Crystal chemical and analytical evidence strongly suggests that the iron in tsumcorite is mostly Fe^{3+}.

Introduction

The mineral tsumcorite from the Tsumeb mine, S.W. Africa, was first described by Geier, Kautz & Müller (1971) who proposed the chemical formula $PbZnFe(AsO_4)_2.H_2O$ based on several chemical analyses. Crystal data for tsumcorite are reported by Geier, Kautz & Müller (1971) as $a=9{\cdot}131$, $b=6{\cdot}326$, $c=7{\cdot}583$ Å, $\beta=115{\cdot}3°$, $Z=2$, space group $C2/m$. Tsumcorite occurs in crusts several mm thick in the second (deep) oxidation zone of the Tsumeb mine, with other Pb–Fe-arsenate and sulphate minerals such as beudantite, $PbFe_3[(OH)_6/SO_4/AsO_4]$, anglesite, $PbSO_4$, mimetite, $Pb_5(AsO_4)_3Cl$ and carminite, $PbFe_2[(OH)AsO_4]_2$. After registration of the mineral with the Commission on New Minerals and Mineral Names, IMA, other so-far unidentified or wrongly classified specimens in the British Museum, London, were identified as tsumcorite. One of these (specimen Nr. MB 1929,93) which comes from the first oxidation zone of the Tsumeb mine has been used for this investigation.

It is surprising that all the iron in tsumcorite is reported to be in the divalent state, while nearly all other minerals found together with tsumcorite in the oxidation zones of the Tsumeb mine contain only trivalent iron. In addition, the cell content of two formula units per cell requires that the two water molecules occupy one of the twofold positions in space group $C2/m$ which all have the site symmetry $\bar{1}$. This site symmetry however does not correspond to the geometry of the water molecule unless the hydrogen atoms are disordered. The crystal structure was determined in order to obtain definite information about the chemical formula and crystal chemistry of tsumcorite.

As has been pointed out by Geier, Kautz & Müller (1971) the lattice constants of tsumcorite are very similar to those of brackebuschite, $Pb_2(Mn,Fe)(VO_4)_2.H_2O$, which crystallizes in space group $P2_1/m$