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CRYSTAL AND MOLECULAR STRUCTURES OF THE SESQUITERPENE LACTONE PYRETHROIDININ

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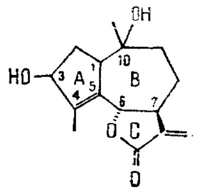
The crystal structure of the sesquiterpene lactone pyrethroidinin, in the independent part of the elementary cell of which there are two molecules, has been determined by x-ray structural analysis. A stereochemical analysis is given of the results, and the structure 3α,10α-dihydroxy-1α,6β,7α(H)-guaia-4(5),11(13)-dien-6,12-olide is proposed for pyrethroidinin.

The sesquiterpene lactone pyrethroidinin $C_{15}H_{20}O_4$ (I), isolated from Pyrethrum pyrethroides was subjected to a preliminary study by spectral methods and for it was proposed a guaianolide structure with the translinkage of rings B/C [1]:



I

In order to ascertain the other stereochemical aspects of the structure of pyrethroidin — the configuration of the three asymmetric centers C1, C3, and C10, and the conformations of the rings — we have performed an x-ray structural investigation.

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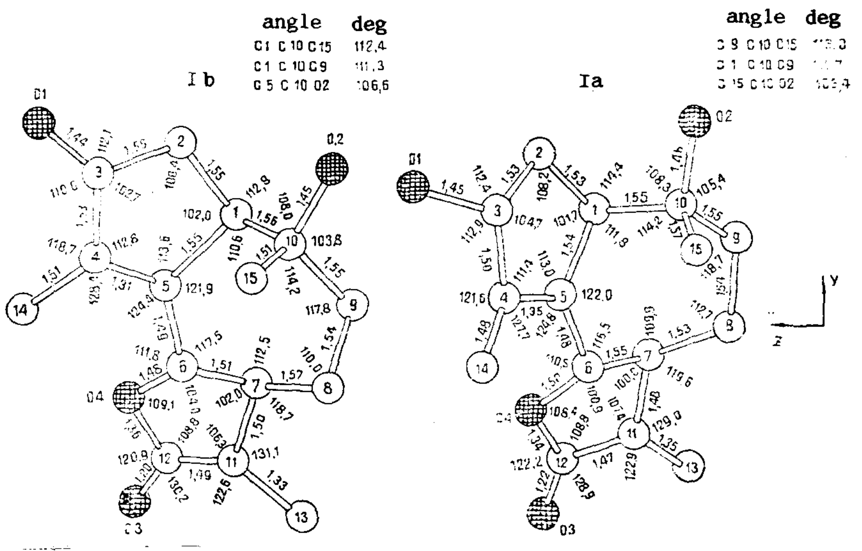

Fig. 1. Structures of molecules Ia and Ib.

TABLE 1. Endocyclic Torsional Angles of the Structure of (I) (φ, deg) in Comparison with the Theoretical Figures for Unsubstituted Cyclopentane and Cycloheptane

Ring	Fragment	φ_{Ia}	φ_{Ib}	φ_{theor}
A Cyclopentene	C1—C2—C3—C4	—14	—6	—46
	C2—C3—C4—C5	10	4	29
	C3—C4—C5—C1	2	1	0
	C4—C5—C1—C2	— 7	—5	—29
	C5—C1—C2—C3	13	7	46
B Cycloheptane	C8—C9—C10—C1	—70	—70	—62
	C9—C10—C1—C5	85	83	99
	C10—C1—C5—C6	—64	—60	—82
	C1—C5—C6—C7	—13	—10	0
	C5—C6—C7—C8	79	75	82
	C6—C7—C8—C9	—84	—82	—99
	C7—C8—C9—C10	67	65	62
C Lactone	O4—C12—C11—C7	16	10	15
	C12—C11—C7—C6	—35	—27	—39
	C11—C7—C6—O4	38	32	48
	C7—C6—O4—C12	—31	—27	—39
	C6—O4—C12—C11	11	12	15

TABLE 2. Coordinates (× 10^4) of the Nonhydrogen Atoms in the Structure of Pyrethroidinin

Atom	Molecule Ia			Molecule Ib		
	x	*y*	*z*	*x*	*y*	*z*
C1	2038(12)	1248(4)	4704(2)	— 794(14)	1410(5)	6819(2)
C2	3312(12)	1898(4)	4995(2)	— 118(18)	2317(5)	7069(2)
C3	4659(14)	1272(5)	5280(2)	268(18)	2050(5)	7572(3)
C4	3805(14)	290(5)	5241(2)	— 447(14)	1017(5)	7596(2)
C5	2379(13)	272(4)	4925(2)	—1013(13)	684(5)	7207(2)
C6	1353(14)	— 596(4)	4770(2)	—1660(13)	— 314(5)	7127(2)
C7	—398(13)	— 447(5)	4443(2)	—2452(15)	— 554(5)	6658(2)
C8	376(16)	— 237(5)	3969(3)	— 775(17)	— 648(5)	6307(2)
C9	952(17)	820(5)	3905(2)	— 194(14)	344(6)	6130(2)
C10	2611(14)	1241(4)	4200(2)	741(12)	1053(4)	6468(2)
C11	—1510(14)	—1335(5)	4527(2)	—3710(15)	—1405(5)	6761(3)
C12	—1108(14)	—1625(4)	4993(3)	—4349(17)	—1297(7)	7238(3)
C13	—2715(16)	—1826(6)	4253(3)	—4195(22)	—2157(6)	6512(4)
C14	4632(14)	—527(5)	5494(3)	— 324(18)	503(6)	8040(2)
C15	4680(17)	787(5)	4100(3)	2601(15)	694(6)	6587(3)
O1	4789(9)	1599(3)	5740(2)	—829(12)	2645(4)	7876(2)
O2	2836(9)	2227(3)	4051(1)	1289(9)	1860(4)	6192(2)
O3	—1980(10)	—2202(3)	5224(2)	—5568(16)	—1730(7)	7448(3)
O4	335(8)	—1079(3)	5157(1)	—3280(10)	— 590(4)	7432(2)

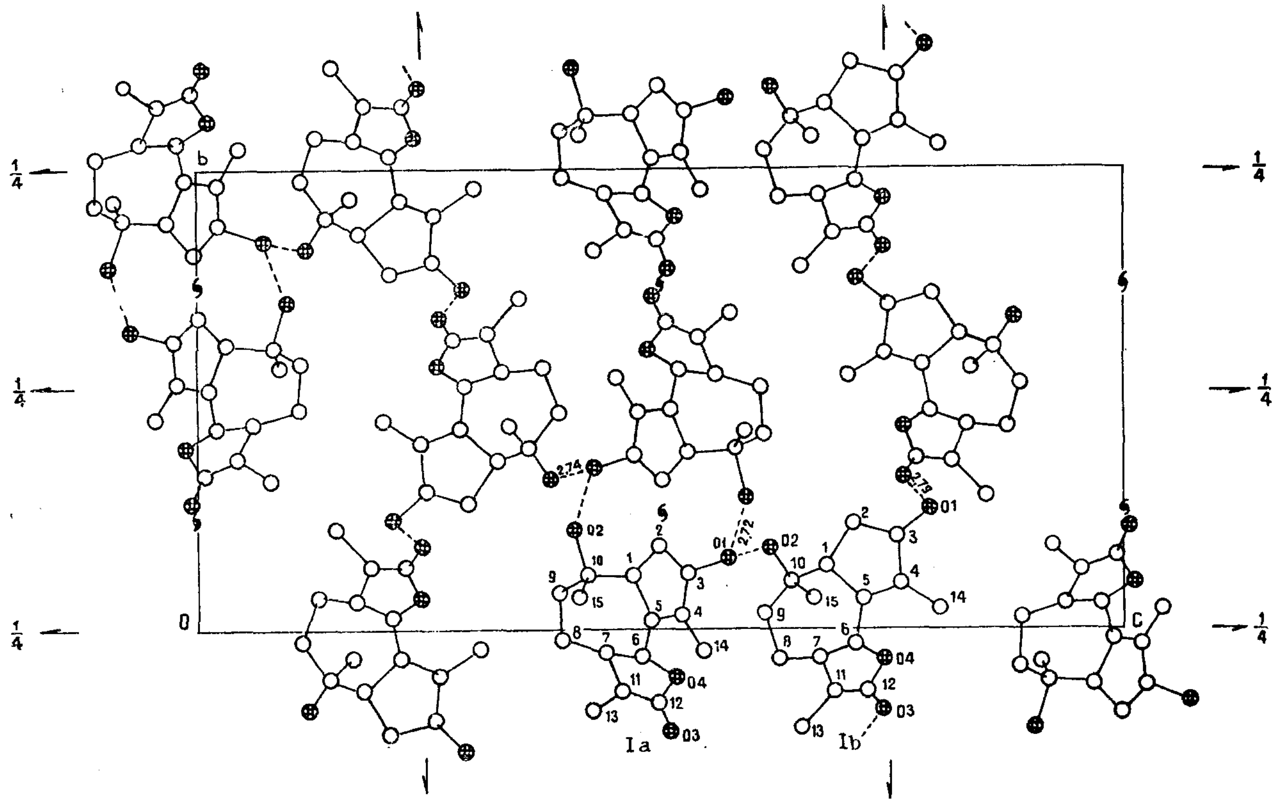

Fig. 2. Packing of the molecules in the structure of (I).

Pyrethroidinin crystallizes with two molecules (Ia and Ib) in the independent part of the elementary cell. Figure 1 shows in a projection on the bc plane, the spatial structures of molecules Ia and Ib, from which it can be seen that the crystallographically independent (but chemically equivalent) pyrethroidinin molecules Ia and Ib have the same conformations of the rings and orientations of the substituents. The orientation of the substituents in the C6 and C7 asymmetric centers (linkage of rings B/C) agrees with that proposed previously. The orientations of the other substituents are as follows: α-orientations of the H atom in position 1 and of the hydroxy groups in positions 3 and 10; β-orientation of the methyl group at C10. Consequently, pyrethroidinin has the structure of 3α,10α-dihydroxy-1α,6β,7α(H)-guaia-4(5),11(13)-dien-6,12-olide.

The conformations of rings A, B, and C of guaianolides are usually described in two ways: a) the characteristic planes through certain atoms are given and then the deviations of other atoms from the given planes are considered [2-5]; and b) the intracyclic torsional angles are calculated and are compared with the values calculated for the unsubstituted cycloalkanes [6, 7]. It is generally assumed that the latter variant better characterizes the stereochemistry of the rings, particularly when they adopt intermediate conformations [7], and we shall use it in our analysis of the conformations of the rings of pyrethroidinin.

In the molecule of (I), the cyclopentadiene ring A assumes a flattened envelope conformation with C_s symmetry (in Ib, the ring is greatly flattened and has a practically planar conformation; Table 1). The cycloheptene ring has a slightly distorted chair conformation, since the difference $\varphi_{exp} - \varphi_{theor}$ (deviation from the ideal chair) in some fragments reaches 22°, but on the whole the symbatic and antisymmetric natures of these magnitudes are retained. The values of the intracyclic torsional angles of the lactone ring agree better from the values calculated for cyclopentane with the half-chair conformation and C_2 symmetry. However, because of the presence of two sp^2-hybridized carbon atoms and the O heteroatom, the lactone ring C is appreciably flattened.

The geometry (lengths of the bonds and the valence angles) of the structure of (I) is given in Fig. 1. A comparative analysis of the chemically identical interatomic distances and valence angles of molecules Ia and Ib reveals no anomalous deviations and shows good agreement of them (averaged values) with those observed in known sesquiterpene lactones [3, 4]. The errors of the determination of the bond lengths and valence angles were not more than 0.011 Å and 0.7°, respectively.

The packing of the molecules is shown in Fig. 2 in a projection on the bc plane. Intermolecular H-bonds of the O—H···O type exist in the crystals. The nominally identical molecules Ia (with the $O1_{Ia}\cdots O2_{Ia}$ intermolecular distance 2.72 Å) and Ib ($O1_{Ib}\cdots O3_{Ib}$ distance 2.79 Å), connected with one another by alternating H-bonds, form infinite helices along the a and b axes. These helices are linked by other $O1_{Ia}\cdots O2_{Ib}$ H-bonds (2.74 Å) forming an infinite three-dimensional system in the crystal.

EXPERIMENTAL

Single crystals of (I) were grown from a mixture of the solvents ethyl acetate and hexane. The space group and the parameters of the elementary cell were determined from precession photographs and were refined on a Syntex $P2_1$ diffractometer using Cu K_α radiation: a = 6.798(4), b = 14.026(7), c = 29.78(1) Å, d_{calc} = 1.242 g/cm³; space group $P2_12_12_1$; z = 8. A three-dimensional set of intensities was obtained on the diffractometer mentioned, and 1616 structural factors exceeding 2σ were used in the calculations. The search for a model of the structure was begun by the direct method using the Rentgen-75 program [8]. However, numerous variations — a change in the number of $E_{hk\ell}$ products in the TPSR, the "manual" choice of coordinate and reference reflections, and the combination of these parameters with the use of the Σ_1 criteria — did not lead to the solution of the problem. The search was therefore continued with the aid of the MULTAN program included in the XTLSM group [9]. It was possible to reveal a model of the structure by this program with an extension of the number of $E_{hk\ell}$ products in the TPSR. The further refinement of the structure was performed by the method of least squares according to the Rentgen-75 program, first in the isotropic and then in the anisotropic approximation. The final value of the divergence factor taking the H atoms found experimentally into account was 0.091. The coordinates of the nonhydrogen atoms of the molecules Ia and Ib are given in Table 2.

CONCLUSIONS

The spatial structure of the sesquiterpene lactone pyrethroidinin has been determined by the x-ray structural method; it corresponds to 3α,10α-dihydroxy-1α,6β,7α(H)-guaia-4(5),-11(13)-dien-6,12-olide.

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