CRYSTAL AND MOLECULAR STRUCTURE OF RETAMINE BROMIDE, $C_{15}H_{26}N_2O \cdot Br$

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INTRODUCTION

Retamine, an alkaloid contained in *Genista Sagitaris,* was isolated and chemical studied by I. Ribas Marqués and collaborators.[1] A morphological, optical and preliminary X-rays study of retamine and its bromide and chloride was carried out by M. Font-Altaba[2] and by J. M. Bosch-Figueroa, L. Miravitlles-Millé and M. Font-Altaba.[3,4]

Retamine molecule is transformed into sparteine by hydrogenation, being the difference between them the presence of a hydroxyl group in retamine. Our interest is to find its absolute molecular configuration to confirm that is the oxoderivate (trans-cis) of the C_{15} lupin alkaloids family as was predicted by L. Marton and J. Leonard.[5]

MORPHOLOGY

Retamine bromide appears as nice colourless enantiomorphic crystals of tabular habit (100), with a very simple combination of forms (010), (111), (101) and (001), belonging to monoclinic system, point group 2 (fig. 1).
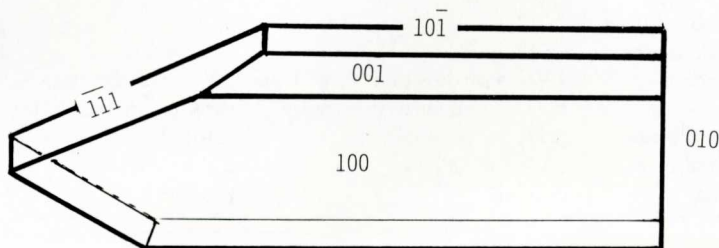

Fig. 1. Crystal of retamine bromide.

Crystals of retamine are very varied in size and thickness, lieing fre-
quently on the face (101), with a very simple combination of forms (001),
(011) and (100), belonging to the same monoclinic system, point group 2.

Table I. Morphological data of retamine and retamine bromide.

	Retamine			Retamine bromide	
HKL	φ	ρ	HKL	φ	ρ
001	90° 00'	15° 07'	100	90° 00'	90° 00'
101	270° 00'	28° 48'	010	0° 00°	90° 00'
011	11° 15'	54° 08'	001	90° 00'	10° 38'
100	270° 00'	90' 00'	101	270° 00'	31° 27'
			111	223° 33'	41° 35'

A:B:C = 1.7137:1:1.3565   A:B:C = 0.81704:1:0.6440
   β = 105° 07'   β = 100° 38'

OPTICAL PROPERTIES

The orientation of the optical ellipsoid was determined by means of
the polarizing microscope and the universal stage. Refractive indices were
measured by the immersion method using Cargille liquids.

Table II. Optical properties for sodium light of retamine and retamine bromide.

	Retamine	Retamine bromide
	no pleochroism	no pleochroism
α	1.594_6	1.602
β	1.600	1.614
γ	1.614	1.636
¼ (α + 2 β + γ)	1.602	1.6165
Maximum birefringence	0.019_4	0.034
Medium birefringence	0.012_9	0.023
Acute bisectric	2 V = γ (in direction 56° 12' from the C axis in the obtuse angle)	2 V = γ (in direction 60° 30' from the C axis in the obtuse angle)
Optical axial plane	(010)	(010)
Optical axial angle	2 V = 66° 48'	2 V = 77° 00'
Optical sign	positive	positive

X-Rays powder data

X-ray powder photograph of retamine and its bromide have been taken by the asymmetric focalization technique of Guinier, as modified by De Wolff, in a Nonius quadruple camera which corresponds to a camera of diameter 229.2 mm. Relative peak intensities and indices of the low-orders lines are given in the following table.

Table III. X-rays powder data of retamine and retamine bromide.

	Retamine			Retamine bromide	
d_{hkl}	I	HKL	d_{hkl}	I	HKL
8.908	45	100	9.135	30	100
8.028	60	101	7.131	45	110
6.281	30	101	6.237	30	101
5.813	60	110	6.069	30	011
5.731	30	200	5.684	15	020
5.378	100	011	5.443	100	111
5.192	30	111	4.830	10	120
4.607	60	111	4.740	15	111
4.550	25	102	4.584	15	200
4.460	45	002	4.459	30	021
4.331	45	210	4.200	30	201, 121
4.300	20	211	3.962	15	211
4.015	45	202	3.836	60	121
3.820	15	112	3.575	45	002, 102
3.749	10	012	3.490	30	130
3.623	30	211	3.425	25	211
3.451	5	212	3.412	15	012
3.387	45	020	3.343	30	031
	etc.			etc.	

Structural data

A retamine bromide crystal of $0.21 \times 0.32 \times 0.48$ mm was selected for measurements on a Philips PW 1100 four-circle diffractometer, using graphite monochromatized MoKα radiation ($\lambda MoK\alpha = 0.71069$ Å). The unit cell measured by centering 25 independent reflections and refining the orientation matrix and unit-cell parameters by least squares calculations, is the indicated on the table IV by B, which have a good agreement with the ones obtained by J. M. Bosch-Figueroa and others,[3,4] indicated on the table IV by A.

Table IV. Structural data on retamine and retamine bromide.

	Retamine (A)	Retamine · Br (A)	Retamine · Br (B)
A_0	11.873 Å	9.319 Å	9.327 (3) Å
B_0	6.774 Å	11.298 Å	11.355 (5) Å
C_0	9.227 Å	7.298 Å	7.307 (3) Å
β	105° 08'	100° 20'	100, 55° (5)
Space group	$P 2_1$	$P 2_1$	$P 2_1$

Crystals are monoclinic, space group $P2_1$, V = 760.79 Å^3, Dc = 1.43 Mgm^{-3}; 2432 independent reflections were measured within the rang $2\theta \leq$ 60°, with scan-technique (scan width 1°); 32 reflections were rejected because of the imposed criterion, I $\geq$ 2.5 σ(I), where σ(I) is the standard deviation based on counting statistics, only Lorentz-polarisation corrections were made.

The structure was solved with Multan82 system computer program, an E map computed from a set of phases with the highest combined figure-of-merit revealed peaks for 15 non-hydrogen atoms. By means of a difference Fourier synthesis were located the four last C atoms. Full-matrix least square refinements were carried out with the Shelx76 program. All hydrogen atoms, located with a difference Fourier synthesis, were refined with an overall isotropic temperature factor and the rest of the atoms were refined anisotropically. Refinement converged with an R index of 0.0602, and Rw of 0.0583.

Dscussion

X-ray structural analysis of retamine bromide, confirmed the all-chair conformation of the retamine moiety, being a chair-chair-trans-quinolizidine A/B system and a chair-chair-cis-quinolizidine C/D system, equal that sparteine molecule (6), with an OH group in C_{12} position. The projection of the molecule is show in figure 2. Retamine is the sparteine C_{12}-hydroxy or one C_{15} lupin trans-cis C_{12} hydroxy alkaloid.

The bond distances between non-hydrogen atoms are shown in the figure 3. Medium value for C–C bonds is 1.529 Å (minimum distance 1.513 Å for C_2–C_3, and maximum of 1.549 Å for C_{12}–C_{11}), which agrees with the mean values reported in the literature (1.528 Å for sparteine N_{16}–oxide monoperchlorate, 1.527 Å for 2-phenyl-sparteine N_{16}–oxide monoperchlorate, etc.).

The values for N–C bonds obtained by us are slightly smaller than the ones reported by Kaluski and Maluszynska[6] (table V (A)), Maluszynska
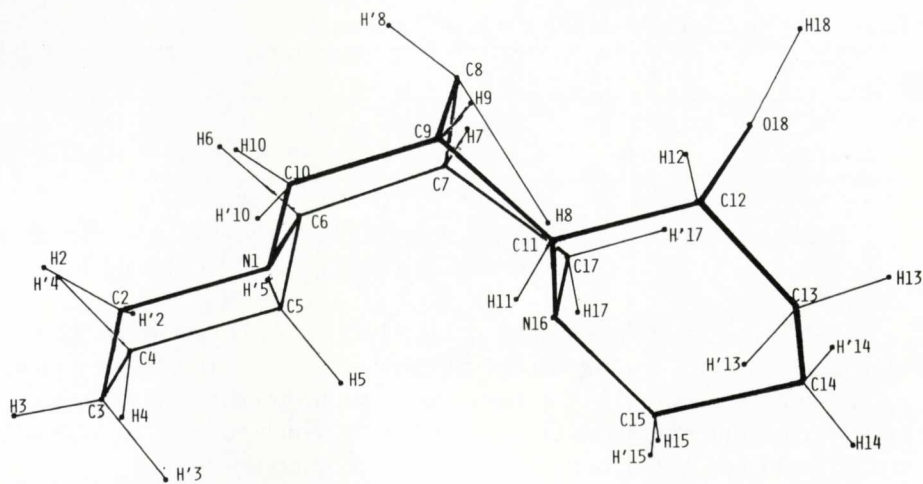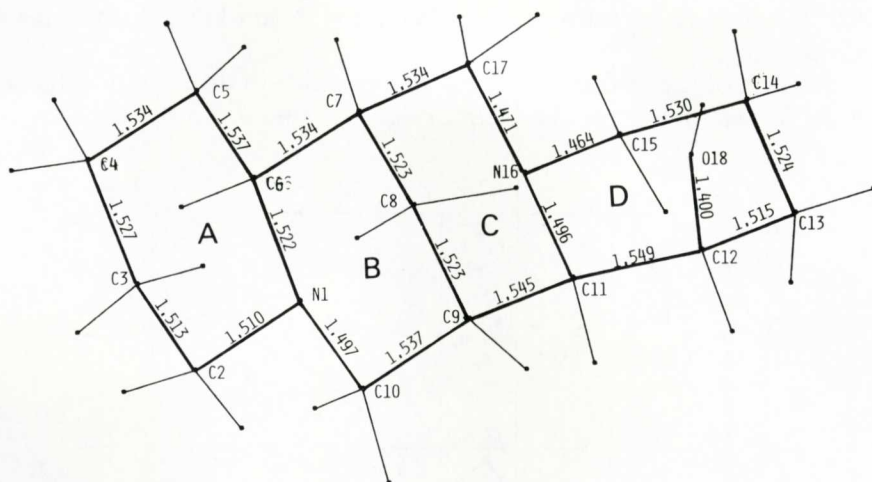
Fig. 2. Retamine molecule projection.

Fig. 3. Interatomic bond distances in retamine molecule.

and Okaya[7] (table V (B)) or Birnbaum[8] (table V (C)). Also we find the N–C bonds in A/B system longer than in C/D system which is in disagreement with the reported by Kaluski and others,[6,7,8] and agrees with the difference in sign between torsion angles find by us and the ones reported by Kaluski and others.[6,7,8]

Table V. N–C bonds from Kaluski and others[6,7,8] and us.

	(A)	(B)	(C)	
$C - N_{16}$	1.525 Å	1.527 Å		1.477 Å
$C - N_1$	1.483 Å	1.502 Å	1.499 Å	1.510 Å

The mean value of C–C–C angle is 110.7° ($C-_7C-_{17}C-_{15}$ minimum angle is 108.0°, $C_{13}–C_{14}–C_{15}$ maximum of 114.5°), 109.9° from Kaluski and others.[6,7,8]

C–N–C angle in A/B system is 111.4° and in C/D system is 112.9°, which do not mean any significant difference. The value of O–C distance agrees with the reported in the literature for single bond, being a non active oxygen, opposite to the O in N_{16} position which stablish an internal strong hydrogen bridge with N_1 (Kaluski and others).[6,7,8]

The mean value for H–C bond is 0.96 Å (1.18 to 0.72) and the mean angle is 108°.

The retamine molecule has a quite regular distribution of their atoms in 10 different planes, with similar dihedral angles. Their mean value is 126.9° for all chairs in trans position, being 134.0° and 128.9° for the chair in cis position.

Packing of the molecules of retamine bromide in the crystal is due to van der Waals forces, no hydrogen bridge was found, no any other type
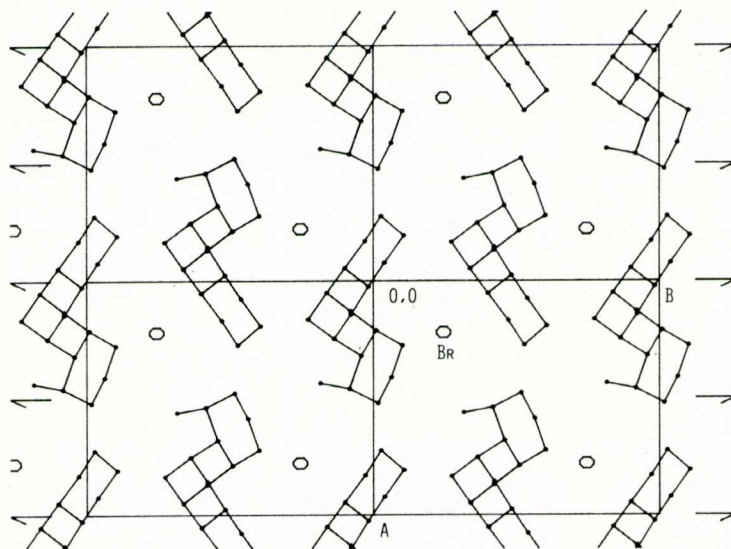

Fig. 4. Projection of the retamine bromide structure on (001).

of possible bonding. Br atoms are located in holes between molecules, being the shortest distance 3.02 Å to H of OH group; distance Br–O is 3.357 Å and Br–N is 3.461 Å (fig. 4 and 5).
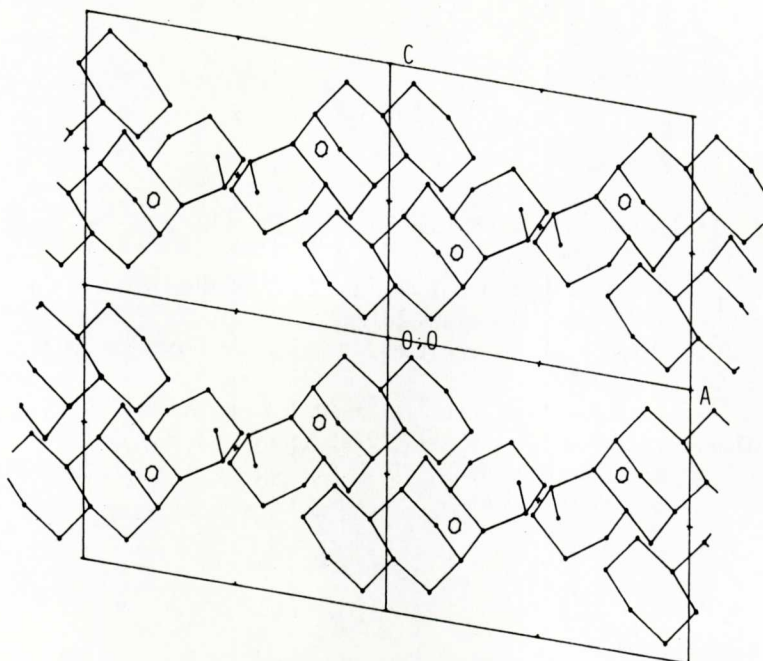

Fig. 5. Projection of the retamine bromide structure on (010).

ABSTRACT

Retamine is an alkaloid contained in *Genista Sagitaris*, which is transformed into sparteine by hydrogenation, being the difference between them the presence of a hydroxil group in retamine. Crystals appears as nice colourless enantiomorphic monoclinic of tabular habit, point group 2. Optical properties are $\alpha = 1.602$, $\beta = 1.614$, $\gamma = 1.636$, $2V = 77°\ 00'$, optical axial plane (010), positive. Space group $P2_1$, cell parameters a = 9.327(3) Å, b = 11.355(5) Å, c = 7.307(3) Å, $\beta = 100,55°$, V = 760.79 Å^3, Dc = 1.43 Mgm^{-3}; 2432 independent reflections were measured within the rang $2\theta \leq 60°$, scan width 1°; 32 were rejected, only Lorentz-polarisation corrections were made. The structure was solved with Multan 82 system computer program, an E map computed from a set of phases with the highest combined figure-of-merit revealed peaks for 15 non-hydrogen atoms. Applying a difference Fourier synthesis to located the last four C atoms and a full-matrix least square refinements were carried out with the ShelX 76 program. All hydrogen atoms were located with a difference Fourier synthesis. Refinement converged with an R index of 0.0602, and Rw of 0.0583.

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B. NON-STOICHIOMETRY AND PHASES IN FLUORIDES, AND CRYSTAL PROPERTIES OF SUPERIONIC CONDUCTORS

Lecture

B. P. Sobolev. "Non-stoichiometry in inorganic fluorides and phases with fluorite structure".

Research papers

V. B. Alexandrov. "X. ray and neutron diffraction studies of non-stoichiometric fluorite phases $M_{1-x}R_xF_{2+x}$ (M=Ca, Sr, Ba; R=Ln, Y)".

P. P. Fedorov. "Association of point defects in non-stoichiometric $M_{1-x}R_xF_{2+x}$ fluorite-type solid solutions".

L. P. Otroshchenko, V. B. Alexandrov, L. A. Muradyan, B. A. Sarin and B. P. Sobolev. "Neutron diffraction study of the features of fluorine ions incorporation into $Ba_{1-x}R_xF_{2+x}$ solid solutions".

E. A. Krivandina. "Preparation of single crystals of multicomponent fluoride materials with the fluorite type structure".

A. K. Ivanov-Shitz and S. Kh. Aityan. "Molecular dinamics simulation of superionic conductors $BaFe_2$".

T. S. Chernaya, L. A. Muradyan and V. I. Simonov. "Structural features that cause different ionic conductivity in RbNbWO and TiNbWO".

A. K. Ivanov-Shitz. "Superionic conductors with intrinsic and impurity-induced structure disorders".