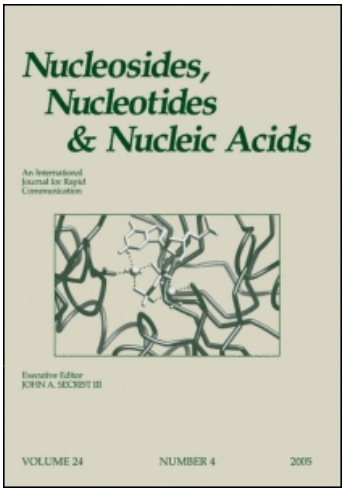

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X-Ray Crystal Structure of Luminarine - Aglycone of Highly Fluorescent Luminarosine

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X-RAY CRYSTAL STRUCTURE OF LUMINARINE - AGLYCONE OF HIGHLY FLUORESCENT LUMINAROSINE

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Abstract: The X-ray structure of luminarine (7-amino-pyrido [2,1-h] pteridin -11 ium -5-olate) is reported.
The structure of heterocycle confirms previously obtained NMR data.

Highly fluorescent nucleoside 7-(β-D-ribofuranosylamino)-pyrido [2,1-h]pteridin-11-ium-5-olate, termed luminarosine /1,2/, bear tricyclic betaine as an aglycone. Its structure was established by NMR and MS /1/. In order to confirm these data and to facilitate molecular modeling studies of DNA duplexes composing of luminarine as nucleobase analogue, we have searched for a long time for a suitable nucleoside crystals to perform X-ray analysis. However this attempts were unsuccessful. Here we would like to report on an aglycone structure luminarine crystallized from acidic medium.

Deep-red crystals have been obtained from a mixture: isopropanol/dioxane/HCl, temp.4°C. Crystals were stable but unfortunately twinned. Luminarine: $(C_{10}H_8ON_6)^{2+} \cdot 2CL^- \cdot 2H_2O$ crystallizes in the monocline form, space group $P2_1/n$, with a=6.510(1), b=11.309(2) and c=18.352(3) Å, β=97.99(2)°, Z=4. 1357 X-ray reflections were recorded with Syntex $P2_1$ diffractometer (CuKα radiation, θ/2θ scan) and corrected for geometric factors. The structure was solved by Direct Methods using SHELX86 /3/ . Nonhydrogen atoms refined anisotropically by full-matrix least-squares method SHELX76/4/. The structure is refined to R=0.13 The results of X-ray analysis fully confirm proton and C-13 NMR data/1/, see figures and table. Figures were drawn using PLUTO /5/.

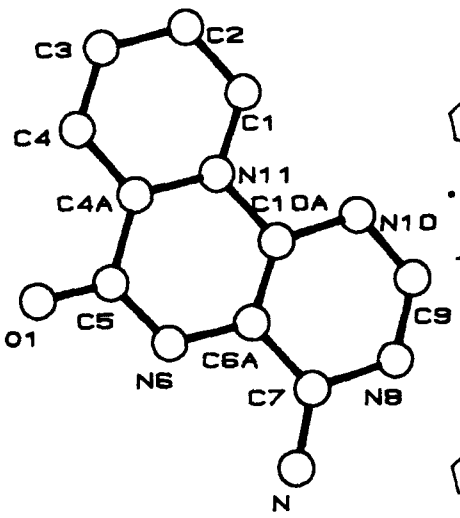

FIG 1. Molecular structure and numbering scheme of the luminarine

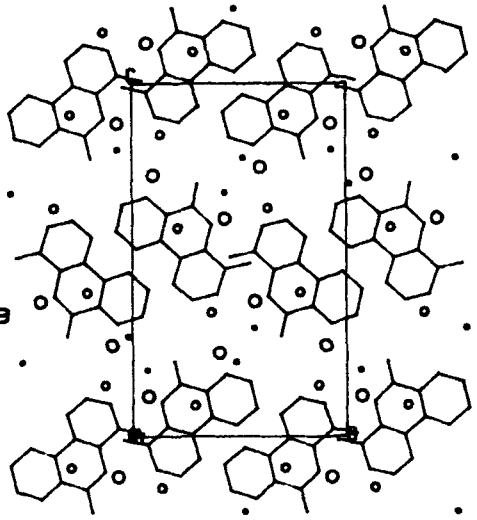

FIG 2. Projection of the structure down a crystallographic a axis.

TABLE 1. Final fractional coordinates and equivalent isotropic thermal parameters ($Å^2$)

$$Ueq = 1/3 \sum_i \sum_j Uij\ ai^*\ aj^*\ aiaj$$

	x	y	z	Ueq
CL(1)	0.2033(8)	0.7889(4)	0.4101(2)	0.048(2)
CL(2)	1.3390(9)	0.6321(4)	0.6465(3)	0.062(2)
N(10)	0.794(3)	0.809(1)	0.5649(7)	0.050(6)
N(11)	0.721(2)	0.869(1)	0.4443(7)	0.036(5)
N(6)	0.690(3)	0.631(1)	0.3994(7)	0.048(6)
O(1)	0.607(2)	0.695(1)	0.2853(6)	0.065(6)
C(1)	0.735(3)	0.982(1)	0.4673(9)	0.040(6)
C(3)	0.680(3)	1.049(2)	0.344(1)	0.050(7)
N	0.759(2)	0.455(1)	0.5094(8)	0.045(6)
C(4A)	0.680(3)	0.841(1)	0.3720(9)	0.038(6)
N(8)	0.820(3)	0.607(1)	0.5951(8)	0.051(6)
C(7)	0.767(3)	0.567(2)	0.5232(8)	0.043(7)
C(4)	0.666(3)	0.933(2)	0.3228(9)	0.049(7)
C(2)	0.713(3)	1.075(2)	0.419(1)	0.054(8)
C(5)	0.659(3)	0.719(2)	0.350(1)	0.052(7)
C(6A)	0.739(3)	0.661(2)	0.4721(9)	0.040(7)
C(10A)	0.748(2)	0.774(2)	0.4940(9)	0.035(6)
C(9)	0.829(3)	0.720(2)	0.6115(9)	0.053(7)
O(5)	0.153(3)	-0.026(2)	0.284(1)	0.16(1)
O(6)	0.379(2)	1.068(1)	0.1905(6)	0.061(5)

Moreover, structure obtained from the crystals grown in an acidic medium reflects one of the possible prototropic forms of the heterocycle/2/. Two features :C(5)-N(6)-C(6A) angle =121.5(9) and the N(6)...Cl(2) distance equal 3.13(5)Å clearly indicate that nitrogen N(6) is protonated. The presence of the other short contacts namely:Cl(1)...N =3.08Å, Cl(2)...O(5) =3.35Å, N(8)...O(6) =2.66Å and O(5)...O(6) =2.71Å also confirms the conclusion. In this respect observed molecular structure might be correlated to one of the prototropic forms of this heterocycles suggested from its photophysical properties in solution/2/.

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