Crystal Structure of Sewarine N^4-Methiodide

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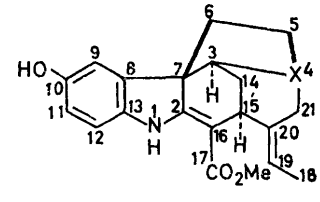
Summary *X*-ray crystallographic analysis of sewarine N^4-methiodide substantiates the structure inferred for sewarine from chemical and spectral data, and establishes the absolute configuration of the molecule.

THE proposed structure for sewarine (I) was based mainly on spectral data.[1]



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We now report an *X*-ray crystal structure analysis of sewarine N^4-methiodide (II) which substantiates the proposed structure and absolute configuration of sewarine and establishes structural parameters for the molecule.

Crystal data: $a = 12{\cdot}007 \pm 0{\cdot}005$ Å, $b = 15{\cdot}047 \pm 0{\cdot}006$ Å and $c = 10{\cdot}974 \pm 0{\cdot}006$Å, space group $P2_12_12_1$, four formula units per unit cell. Intensities of both the *hkl* and $\bar{h}kl$ reflections were collected on a four-circle automatic diffractometer using the θ—2θ scan technique. A total of 2338 reflections was recorded with copper radiation. The structure was solved by locating the I^- ion in an $(E^2 - 1)$ Patterson map and phasing the $F(hkl)$ on the basis of the position of the I^- ion. A least-squares refinement with anisotropic thermal factors and using anomalous dispersion correction for the I^- ion resulted in an *R*-factor of 11·0% for the configuration in Figure 1 and 13·3% for the mirror image. Examination of the differences of individual $F(hkl)$ and $F(\bar{h}kl)$ of the observed values with the calculated values further corroborated the choice of the enantiomorph shown in Figure 1.

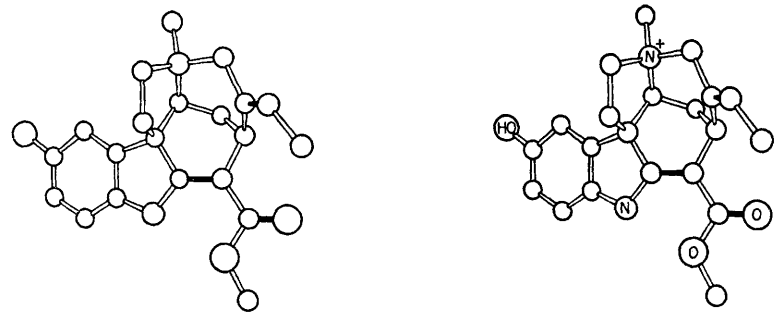

FIGURE 1. *A stereodiagram of the sewarine cation showing the absolute stereoconfiguration.*

Bond lengths and angles are shown in Figure 2. In the indole moiety atoms C(7) and C(2) are twisted respectively by 0·09 Å above and below the plane of ring A. Ring C has a twisted conformation with atom C(14) at 1·18 Å below and atom C(3) at 0·64 Å below the plane of the other four atoms; while ring D is in the boat conformation with atoms C(14) and C(21) 0·75 and 0·53 Å below the average plane of the other four atoms. The five-membered ring E has the envelope conformation characteristic of saturated five-membered rings with atom C(5) 0·56 Å below the plane of the other four. There is a relatively short intramolecular approach between the NH group of the indole moiety to the O atom of the OCH_3 group where N(1)···O (3) distance is only 2·67 Å. In the crystal lattice only one hydrogen bond is formed to the I^- ion with an I^-···HO distance of 3·61 Å.

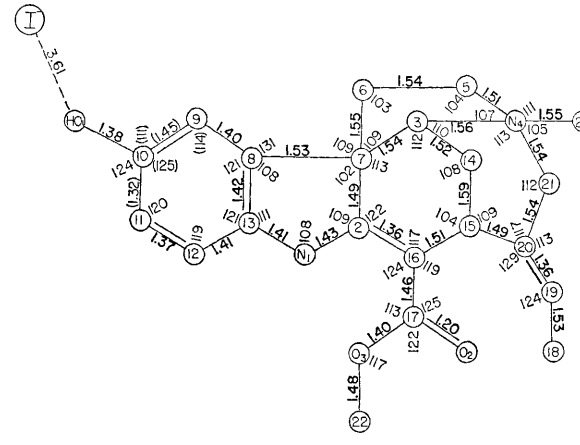

FIGURE 2. *Bond lengths and angles in sewarine methiodide. The standard deviations are of the order of* 0·01 Å *for the bond lengths and* 1° *for the angles except for parameters involving* C(10). *Values for additional angles are:* N(4) C(3) C(7), 103°; C(5) N(4) C(21), 111°; *and* C(3) N(4) C(23), 111°.

This work appears to be the first *X*-ray structure determination of an akuammicine derivative. The results, where the molecules have structural elements in common, are in accord with the investigations of strychnine,[2-4] and with later work on the curare bisindole alkaloids.[5-7] The rather precise data obtained for the sewarine molecule may serve as references for structure comparisons within this large group of diverse physiologically active compounds.

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