Crystal Structure of the Thallium Salt of the Antibiotic Grisorixin

By Marc Alleaume* and Daniel Hickel

(Laboratoire de Cristallographie et de Physique Cristalline associé au CNRS, Université de Bordeaux I-33 Talence, France)

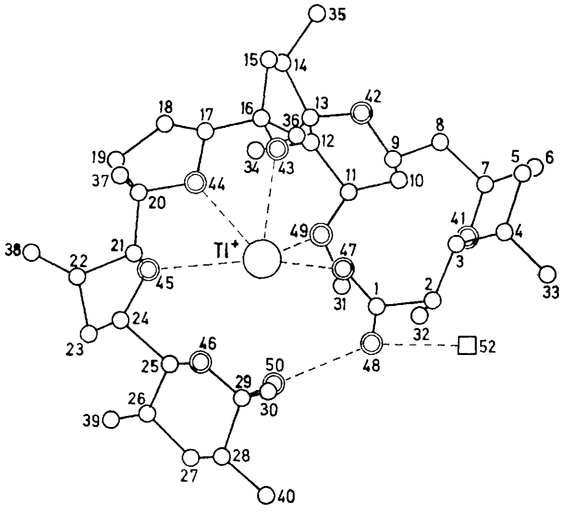
Summary The structure of the thallium salt of the antibiotic grisorixin ($C_{40}O_{10}H_{68}$) has been solved; it confirms the conformation obtained with the silver salt.

A new antibiotic, extracted from *Streptomyces griseus*, and named grisorixin, has been recently isolated and purified.[1] The chemical structure and conformation of the grisorixin silver salt has been determined by *X*-ray crystallography.[2] This compound was found to be very similar to nigericin,[3] monensin,[4] and X-573 A,[5] three natural antibiotics also obtained from *Streptomyces*. The molecule is wrapped around the cation, and forms co-ordination bonds with it.

Several grisorixin salts have been prepared. Since the thallium salt gives good crystals which are non-isomorphous with the silver salt, a structure determination was carried out to learn if the difference in space group was related to a completely new conformation or to a different molecular packing.

Thallium grisorixin was crystallised from an aqueous ethanol solution, with one molecule of water of crystallisation. *Crystal data:* Monoclinic, $a = 11{\cdot}626$, $b = 16{\cdot}766$, $c = 11{\cdot}779$ Å, $\beta = 109° 36'$, $D_m = 1{\cdot}4$, $D_c = 1{\cdot}43$ g cm^{-3}, $Z = 2$, space group $P2_1$. 4256 independent reflections were collected on a Siemens computer-controlled automatic diffractometer. The crystal slowly decomposed in the *X*-ray beam, so the intensities were corrected by comparison with a check-reflection. Only 2750 non-zero reflections with $\theta < 56°$ were introduced in the last steps of the calculations.

The structure (see Figure) was determined by the heavy-atom method although in such a space group, a pseudo-mirror through the heavy atom makes the problem more difficult than usual. The positional and anisotropic thermal parameters were refined by block-diagonal least-squares methods. The hydrogen atoms have not been located. The final *R* value is 0·058. We obtained the absolute configuration from the anomalous dispersion of the thallium atom. It confirms the results given by the silver salt structure.



Figure†

The conformation is very similar to that observed in the silver salt. The hydrogen bond distance O(50)–H · · ·O(48) is 2·73 Å; the size of the "pocket" containing the cation is slightly modified by the size of the cation; the thallium atom is co-ordinated to the same five oxygen atoms that

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† In our previous communication on grisorixin silver salt,[2] the Figure shows not the true conformation, but its mirror image. We apologize for this error.

the silver was, but the distances range between 2·6 Å and 3·0 Å instead of 2·4—2·7 Å. This dilation of the cage induces rotations of the rings around bonds C(16)–C(17), C(20)–C(21), and C(24)–C(25) of about 10°.

This conformation forces out the O(48) of the carboxylic acid. This oxygen can then be hydrogen bonded with a water molecule [O(48) ··· O(52) 2·87 Å]. Each molecule has 12 intermolecular distances of less than 4·0 Å with its neighbours.

(*Received*, *October* 14*th*, 1971; *Com.* 1782.)

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