

Stereochemistry and Absolute Configuration of Tecomanine and Alkaloid C, an Oxygenated Skytanthine, Two Monoterpene Alkaloids from *Tecoma stans*

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Summary The stereochemistry and absolute configuration of two alkaloids from *Tecoma stans*, tecomanine and the oxygenated skytanthine 'Alkaloid C', have been determined by single-crystal X-ray diffraction studies.

ONE of us (G.J.) has reported a structure for tecomanine, the principal alkaloid in various samples of *Tecoma stans*; no

assignment of stereochemistry could be made, since deoxygenation yielded an unknown skytanthine.¹ In subsequent work² structures were advanced for a number of less abundant alkaloids. Among these was an oxygenated skytanthine, 'Alkaloid C', for which two possible formulae were advanced; the physical evidence favoured a 5-hydroxy-skytanthine structure. Among the now considerable

number of monoterpene alkaloids³ very little stereochemical information is available; four of the eight possible skytanthines have been synthesized,⁴ and the absolute configurations of some actinidines have recently been obtained by synthesis⁵ or by the use of o.r.d./c.d. determinations.⁶ We report the first crystallographic structure determination on oxygenated skytanthines.

Tecomanine methoperchlorate m.p. 242° was prepared from the methiodide by anionic exchange, and crystallized from methanol. A three-dimensional X-ray analysis of crystals of tecomanine methoperchlorate unambiguously establishes the stereochemistry at the asymmetric centres as shown in (1) and in Figure 1. This is also the absolute stereochemistry as determined by anomalous dispersion methods. Tecomanine therefore has the absolute stereochemistry shown in (2). The six-membered ring in (1) is in a chair conformation while the five-membered ring is in an envelope conformation with C(2) 0.30 Å above the plane C(3)–C(4)–C(5)–C(1). (See Figure 1 for numbering scheme).

The structure and absolute stereochemistry of 'Alkaloid C' methiodide have in addition been established as (3) by three-dimensional X-ray studies. The conformation and

absolute stereochemistry can be seen in Figure 2. Tecomanine and 'Alkaloid C' (4) have identical stereochemistry

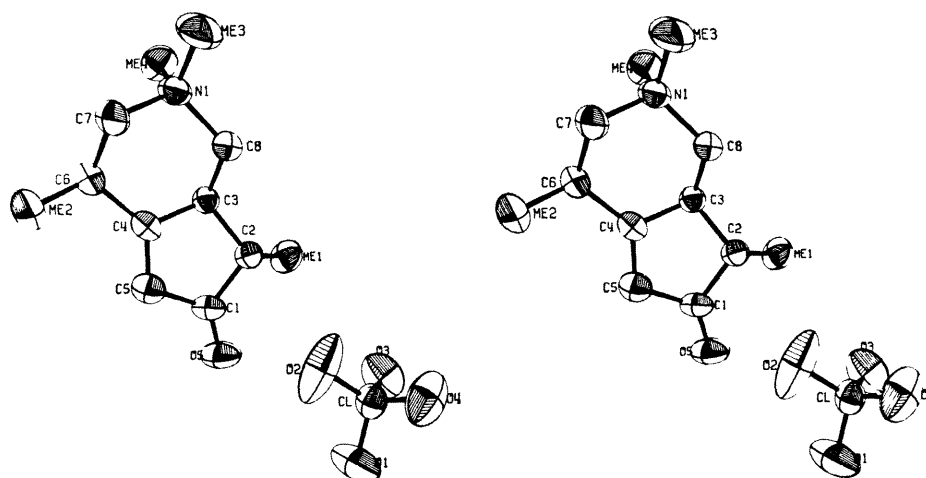
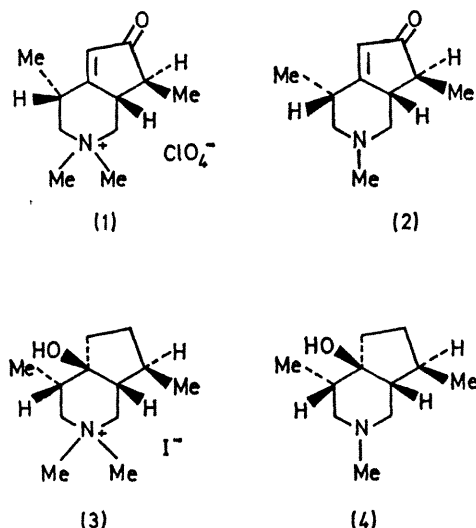


FIGURE 1. Stereoplot of tecomanine methoperchlorate

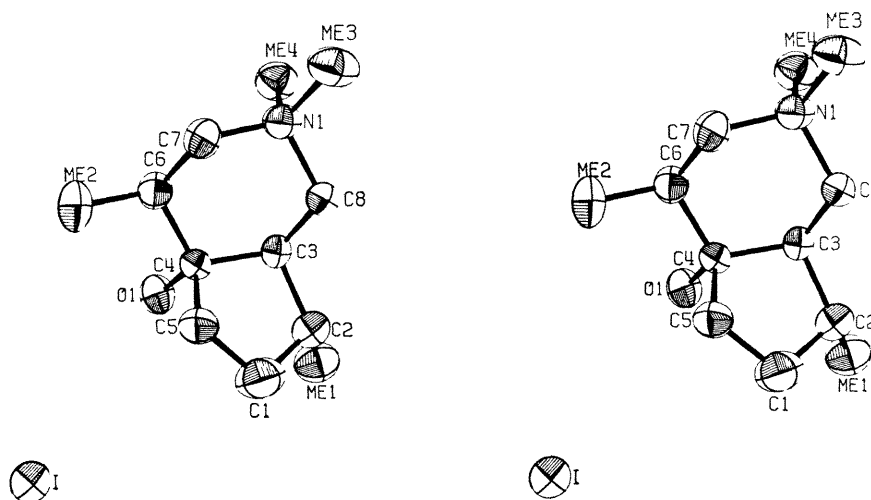


FIGURE 2. Stereoplot of 'Alkaloid C' methiodide

at their common asymmetric centres with the OH group in 'Alkaloid C' equatorial with respect to the six-membered ring which is in a chair conformation. The five-membered ring in (3) and Figure 2 is in a distorted envelope conformation with C(1) and C(5) 0.65 and 0.11 Å respectively above the plane C(2)–C(3)–C(4).

One form of the methoperchlorate of tecomanine, crystallized in the monoclinic system; space group $P2_1$ with two molecules of $C_{12}H_{20}NO_4ClO_4$ in a unit cell; $a = 8.032(1)$, $b = 10.019(1)$, $c = 8.900(2)$ Å, $\beta = 91.44(1)^\circ$; crystals of 'Alkaloid C' methiodide are orthorhombic, space group $P2_12_12_1$ with four molecules of $C_{12}H_{24}NOI$ in a unit cell; $a = 8.874(1)$, $b = 9.361(1)$, $c = 16.861(2)$ Å. Both structures were

determined by the heavy-atom method from data collected with a Hilger computer-controlled four-circle diffractometer and refined by least-squares procedures. For tecomanine methoperchlorate, all hydrogen atoms were located and R at the conclusion of refinement is 4.7% for 1305 observed data. In the case of 'Alkaloid C', 18 of the 24 hydrogen atoms were located from a difference synthesis and at the present stage of the refinement R is 5.1% for 1412 reflexions. In both cases the absolute stereochemistries were determined independently by anomalous dispersion methods utilizing 30 pairs of reflexions for (1) and 20 pairs of reflexions for (3).⁷

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³ See D. Gross, G. Edner, and H. R. Schütte, *Arch. Pharm.*, 1971, 304, 19, and references 1–28 contained therein.

⁴ E. J. Eisenbraun, A. Bright, and H. H. Appel, *Chem. and Ind.*, 1962, 1242; C. G. Casinovi, F. Delle Monache, G. B. Marini-Bettolo, E. Bianchi, and J. A. Garbarino, *Rend. Ist. Super. Sanita*, 1962, 25, 487.

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⁶ L. A. Mitscher, A. B. Ray, and A. Chatterjee, *Experientia*, 1971, 27, 16.

⁷ J. M. Bijvoet, *Proc., k. ned. Akad. Wetenschap*, 1949, 52, 313.