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

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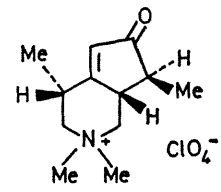
Summary The stereochemistry and absolute configuration of two alkaloids from *Tecoma stans*, tecomanine and the oxygenated skytanthine 'Alkaloid C', have been determined by single-crystal *X*-ray diffraction studies.

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 work[2] 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-hydroxyskytanthine structure. Among the now considerable

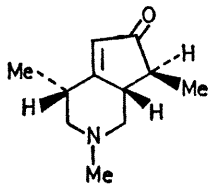
number of monoterpene alkaloids[3] very little stereochemical information is available; four of the eight possible skytanthines have been synthesized,[4] and the absolute configurations of some actinidines have recently been obtained by synthesis[5] or by the use of o.r.d./c.d. determinations.[6] We 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 wihle 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).

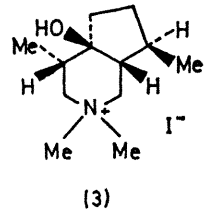
The structure and absolute stereochemistry of 'Alkaloid C' methiodide have in addition been established as (**3**) by three-dimensional *X*-ray studies. The conformation and absolute stereochemistry can be seen in Figure 2. Tecomanine and 'Alkaloid C' (**4**) have identical stereochemistry



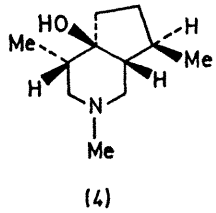
(1)



(2)



(3)



(4)

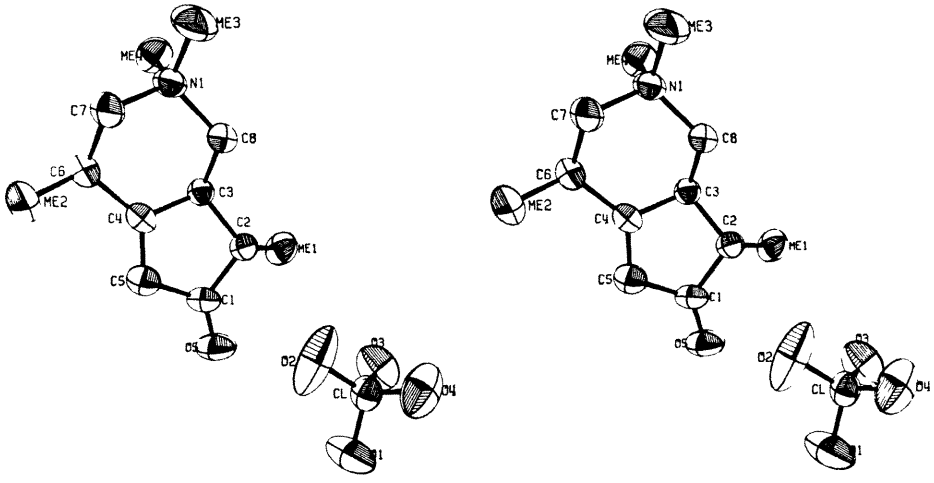


FIGURE 1. *Stereoplot of tecomanine methoperchlorate*

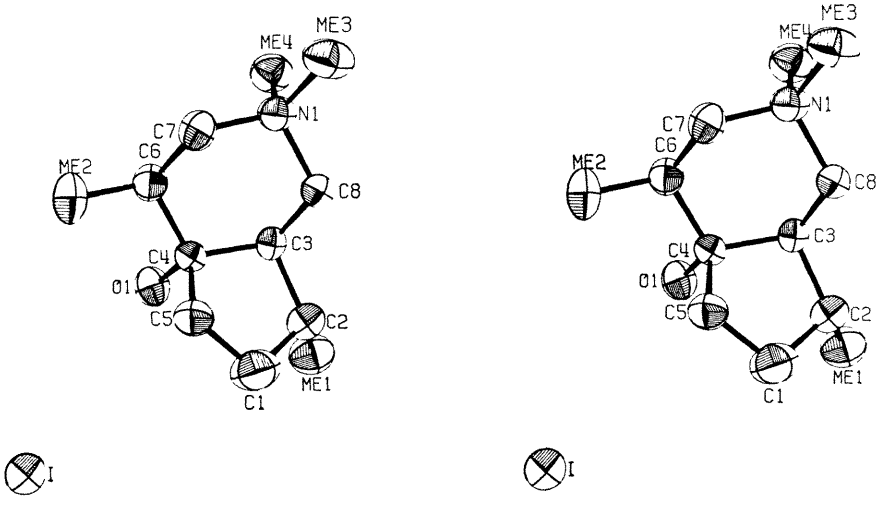


FIGURE 2. *Stereoplot of 'Alkaloid C' methiodide*

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 $C_{12}H_{20}NO,ClO_4$ in a unit cell; $a = 8{\cdot}032(1)$, $b = 10{\cdot}019(1)$, $c = 8{\cdot}900(2)$ Å, $\beta = 91{\cdot}44(1)°$; 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; $a = 8{\cdot}874(1)$, $b = 9{\cdot}361(1)$, $c = 16{\cdot}861(2)$ 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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[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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