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Structure of Calycanthidine

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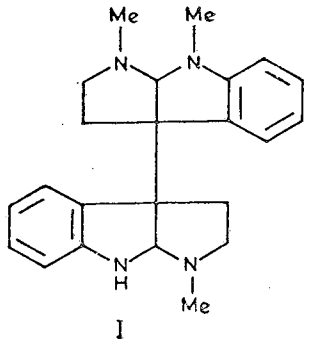
Calycanthidine, the minor alkaloid isolated from the seeds of *Calycanthus floridus*, has been shown, through ultraviolet, infrared and NMR spectral data, to have the dimer structure like folicanthine, chimonathine and calycanthine. This conclusion is in agreement with the structure assigned to calycanthidine through X-ray crystallographic data by J. E. Saxton, W. G. Bardsley and G. F. Smith [*Proc. chem. Soc.*, (1962), 148].

RECENT communications[1,2] on the structure (I) of calycanthidine[2], the minor alkaloid of *Calycanthus floridus*, prompt us to publish our independent observations. These had made it clear that the earlier formula[3], $C_{13}H_{16}N_2$, and structure assigned to the alkaloid[4] were untenable and that calycanthidine was more likely to be a dimer as folicanthine[5,6], chimonathine[7] and calycanthine[8,9].

Calycanthidine isolated from the seeds of *Calycanthus floridus* was crystallized from benzene-ligroin mixture.

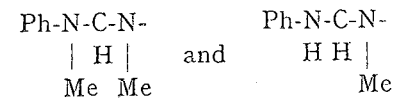
Analytical results were in agreement with the formula $C_{13}H_{16}N_2$, but also fitted $C_{23}H_{28}N_4.0{\cdot}5C_6H_6$. The mass spectrum, besides indicating the presence of benzene, showed peaks of mass higher than required for the older formula [highest 296 (!)]. The molecular ion peak itself was not seen because of extensive fragmentation (of particular interest was that pairs of peaks differing by a mass of 14 were seen in several regions).

The infrared spectrum of calycanthidine had bands at 2·9 μ (NH or OH) and 6·23 μ (indoline). In alcohol solution, the ultraviolet spectrum had λ_{max} at 250 mμ (log ϵ 4·09) and 305 mμ (log ϵ 3·70), shifted by hydrochloric acid to 242·5 mμ (log ϵ 4·13) and 295 mμ (log ϵ 3·70). The slight shift to lower wavelengths was indicative of a Ph-N-C-N system[10].



I

The NMR spectrum of calycanthidine (in $CDCl_3$; at 60 MC; chemical shifts are in τ units; TMS as internal standard) was particularly revealing. Sharp singlets were seen at τ 7·63, 7·58 and 7·00. Distribution of the total integral on the basis of 16 protons in the molecule (earlier formula) required these singlets to correspond to approximately 1·5 hydrogens each, which was considered unlikely. A rational interpretation could be achieved by assuming a dimeric formula for the alkaloid. Using the well-isolated singlet at τ 7·00 as a reference standard of 3 protons, the alkaloid was found to have 28-30 protons. The singlets at τ 7·63 and 7·58 were each for 3 protons and ascribed to two N_b-Me groups while the reference peak at τ 7·00 was from one N_a-Me group. A sharp singlet for 1 proton at τ 5·58 and a somewhat broadish singlet again for 1 proton at τ 5·52 corresponded to



respectively. A very broad peak for 1 hydrogen centred at around τ 5·75 probably arose from a single NH. The aromatic proton signals were spread from τ 3·80 to τ 2·7. The general characteristics of the NMR spectrum were thus seen to be consistent with the 'unsymmetrical' dimeric structure (I) now established for calycanthidine.

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