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ALKALOIDS OF THE GENUS CINNAMOMUM

ISOLATION, STRUCTURE AND SYNTHESIS OF CINNAMOLAURINE

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The occurrence of alkaloids in plants of the genus Cinnamomum (Family Lauraceae) has previously been reported by Tomita and Kozuka[1] who isolated laurolitsine and reticuline from C. camphora. Field tests have also indicated the presence of alkaloids in other members of this genus[2,3,4]. During a survey of the alkaloidal constituents of a number of Cinnamomum species we have isolated, from a yet unnamed New Guinea species (T.G.H. 13,077)[5], a new benzylisoquinoline alkaloid for which we propose the name Cinnamolaurine.

Cinnamolaurine, $C_{18}H_{19}NO_3$ (Found: C, 72.7; H, 6.5; N, 5.0; O, 15.8) was obtained as colourless prisms m.p. 212 - 213°C (dec)*, B.HCl m.p. 230 - 233°C (dec), $[\alpha]_D^{25}$ -100° (EtOH), λ_{max}^{EtOH} 287 mμ (log e 3.72) and gave a positive $FeCl_3$ test. On the basis of spectral evidence the structure (-)-1-(4'-hydroxybenzyl)-6,7-methylenedioxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (I) was assigned to Cinnamolaurine.

Its N.M.R. spectrum in deuterated dimethylsulphoxide showed peaks at 2.30 p.p.m. ($N-CH_3$), 5.85 p.p.m. ($O-CH_2-O$), 6.45 p.p.m. (ArH) and 6.57 p.p.m. (ArH). Four more aromatic protons appeared as the four peaks of an AA'BB' system centred at 6.56 and 6.92 p.p.m. (J = 8.0 c.p.s.) indicating that the phenolic hydroxyl group is attached to the benzyl portion of the molecule. Its mass spectrum showed a weak molecular ion signal at m/e 297 and strong signals at m/e 190 (base peak) and m/e 107 which can be interpreted in terms of the following cleavages:

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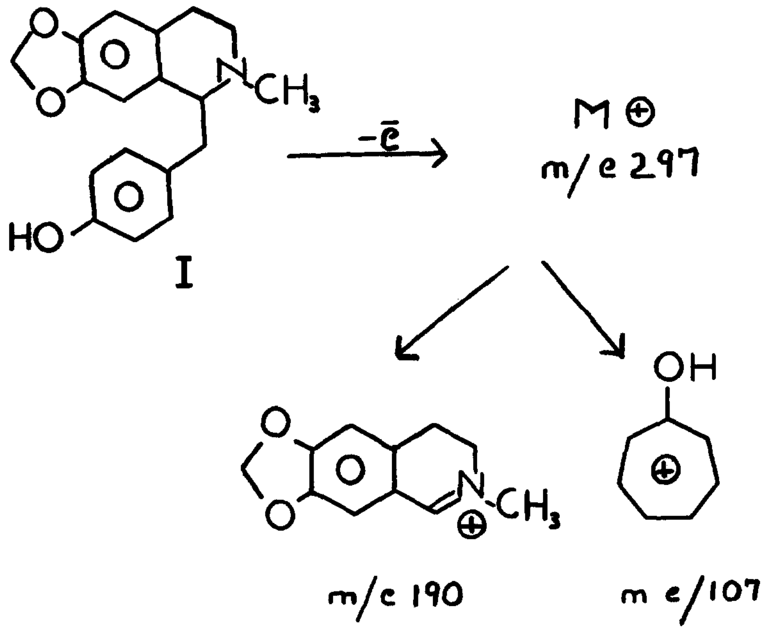
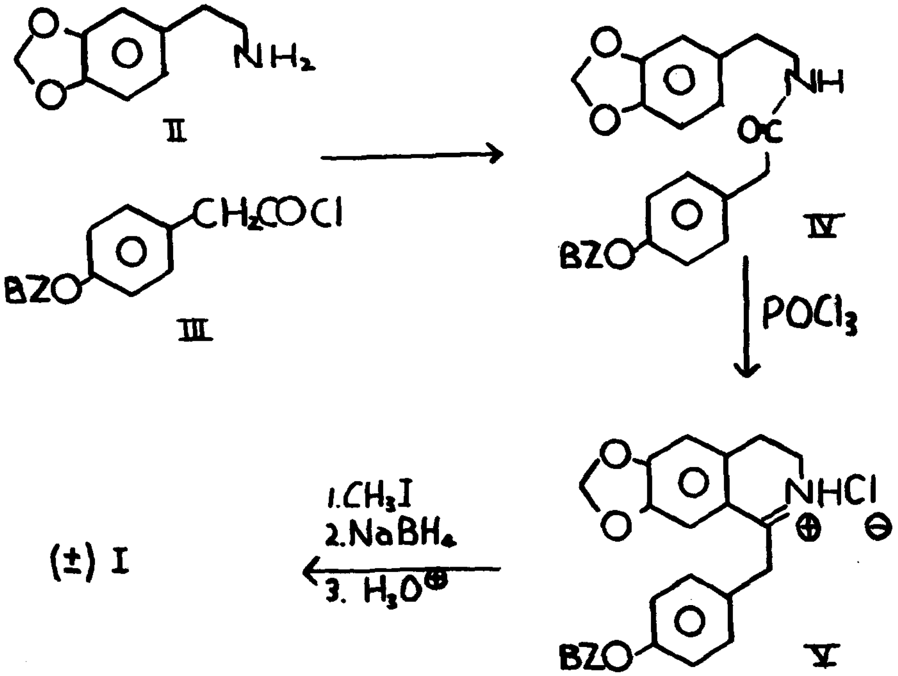
*All melting points uncorrected.



That the structure of the alkaloid is correctly represented by (I) was confirmed by the synthesis of its racemate using the standard Bischler-Napieralski method.

3,4-Methylenedioxyphenylethylamine (II) was condensed with 4-benzyloxyphenylacetylchloride (III) in ether saturated with alkali to yield the known amide (IV) m.p. 132°C (Lit. m.p. 133°C)[6]. (IV) cyclised smoothly in refluxing toluene in the presence of phosphorus oxychloride to give the amine hydrochloride (V) of m.p. 208°C. (V) was converted to the free base and allowed to stand at room temperature under nitrogen with methyliodide for two hours. The resulting methiodide was dissolved in methanol, reduced with sodium borohydride and then refluxed under nitrogen for two hours in a mixture of hydrochloric acid and ethanol (1:1). The product was recrystallised from ethanol to give colourless prisms of the racemate of (I) m.p. 212°C (dec). Found: C, 72.7; H, 6.4; N, 4.9%.



The U.V., I.R., and mass spectra of the alkaloid were indistinguishable from those of the synthetic racemate. The identity of the two compounds was also confirmed by their T.L.C. behaviour and by mixed melting point determinations both on the free bases and their hydrochlorides.

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4. J. J. Willaman and B. G. Schubert, "Alkaloid-Bearing Plants and their Contained Alkaloids", U.S. Dept. of Agriculture Technical Bulletin No. 1234 (1961).

5. The active plant T.G.H. 13,077 was collected in the Morobe district of the Territory of Papua and New Guinea.

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