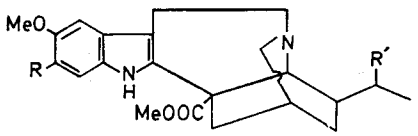
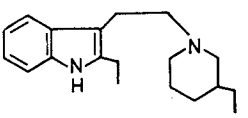
The isolation and identification of jollyanine from *Tabernamontana cumminsii*

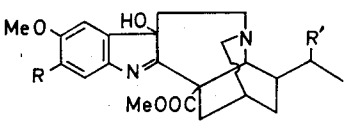
As well as conopharyngine (I,R=OCH_3, R′=H), the major alkaloidal component (Thomas & Starmer, 1963; see also Renner, Prins & Stoll, 1959), 2-ethyl-3-[2-(3-ethylpiperidino)ethyl]indole (II), an alkaloid of particular biogenetic significance, has also been isolated in very small amounts (Crooks, Robinson & Smith, 1968) from the ether-soluble bases obtained from the leaves of *T. cumminsii*. We now report the isolation and identification of a third alkaloid from this source.



I



II



III

The total ether-soluble basic extract (14·2 g) was subjected to column chromatography on alumina (grade H) using ether as eluant. The initial eluates afforded a base which, after further purification by rechromatography under the conditions already described, gave an oil (1·9 mg) which was identified as (II) (Crooks, Robinson & Smith, 1968). The subsequent eluates from the initial column consisted mainly of conopharyngine together with two minor basic components. Recrystallization of this mixture from ethanol-ether gave conopharyngine (9·74 g), and further smaller amounts of slightly impure conopharygine were obtained by three further successive crystallizations from the mother liquors. The final mother liquor was subjected to preparative thin-layer chromatography on alumina using ether-light petroleum (b.p. 30–40°) (5:1 v/v) as solvent and iodine vapour followed by exposure to ultraviolet light as developer. The zone with Rf=0·80 was extracted with ether and, on crystallization from ether, afforded light-tan coloured prisms (6·8 mg), m.p. 184–191° which upon vacuum sublimation (200°/0·04 mm) afforded white prisms, m.p. 188–191° (with sublimation to needles at 145°), which are presently being investigated. The zone with Rf = 0·65 was similarly extracted to give a white crystalline solid, which after recrystallization from ether afforded white prisms (11·7 mg), m.p. 154–156°. Elemental analysis gave an empirical formula $C_{23}H_{30}N_2O_5$ which was confirmed and shown to be the molecular formula by mass spectrometry. The ultraviolet spectrum in absolute ethanol had λ_{max} 239·5 nm (log ϵ = 4·23), λ_{max} 312 nm (log ϵ = 3·54), λ_{infl} 302–305 nm (log ϵ = 3·50) and λ_{min} 276–277 nm (log ϵ = 3·21) and in ethanolic hydrochloric acid had λ_{max} 244 nm (log ϵ = 4·23), λ_{max} 332·5 nm (log ϵ = 3·56), λ_{infl} 303–305 nm (log ϵ = 3·40) and λ_{min} 272–274 nm (log ϵ = 3·10), data which suggest the presence of an indolenine-type chromophore in the alkaloid. The infrared spectrum in chloroform showed bands at 3585 ± 10 and 3480 ± 10 cm^{-1} (O–H stretchings), but no other absorption bands between this and 3100 cm^{-1}, showing N–H groups to be absent, and also had strong absorption bands at 1740 and 1692

cm^{-1}, characteristic of the free and hydrogen-bonded stretchings respectively of an ester carbonyl group intramolecularly hydrogen bonded to the hydroxyl function [cf. voacangine hydroxyindolenine (III, R=R′=H) (Thomas & Biemann, 1968)]. The proton magnetic resonance spectrum showed 3-proton singlets at 6·14, 6·15 τ (2 aromatic O–CH_3) and 6·34 τ ($COOCH_3$), 1-proton singlets at 2·95 and 3·14 τ (2 aromatic protons in a 1 : 4 substitution relation), a 3-proton triplet centred at 9·16 τ (J = 6Hz) (methyl group protons of an ethyl group) and a singlet at 6·53 τ which disappeared upon addition of D_2O (O–H). The mass spectrum indicated a molecular ion at m/e = 414, which was also the base peak, and other significant peaks at m/e = 399 (M–CH_3), 397 (M–OH), 385 (M–C_2H_5), 367 [M-(C_2H_5 + HO)], 355 (M–$COOCH_3$) 290, 248, 231, 220 and 122.

The above data are in good agreement with those reported for the alkaloid jollyanine (conopharyngine hydroxyindolenine) (III, R = OCH_3, R′ = H) whose isolation from *Conopharyngia jollyana* and structural elucidation has been reported (Hootele, Levy & others, 1967). The structure of the alkaloid at present under investigation was further confirmed as III (R = OCH_3, R′ = H) by its synthesis by continuous oxygenation for 7 h of a solution of conopharyngine (I, R = OCH_3, R′ = H) in benzene in the presence of ultraviolet light under the conditions already described for the conversion of voacristine (I, R = H, R′ = OH) into its hydroxyindolenine (III, R=H, R′=OH) (Schnoes, Thomas & others, 1968).

Three hydroxyindolenines, III (R=R′=H) (Thomas & Biemann, 1968), III (R=H, R′=OH) (Schnoes, Thomas & others, 1968) and jollyanine III (R=OCH_3, R′=H) have been isolated from plant sources. Owing to the facile preparation of these compounds by oxidation of the corresponding indoles (I, R=R′=H; R=H, R′=OH and R=OCH_3, R′=H, respectively) it is possible that they are artifacts formed by similar oxidations of their corresponding indoles during extract "work-up" (Hootele, Levy & others, 1967; Thomas & Biemann, 1968).

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