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THE STRUCTURE OF RAUCAFFRICINE

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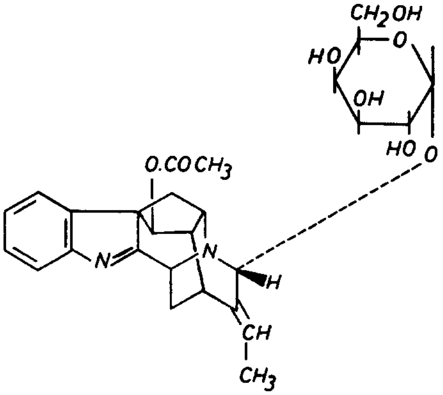
For raucaffricine, an alkaloid isolated from *Rauwolfia caffra* Sonder by one of the present authors, M.A.K., and co-workers[1], they proposed the molecular formula $C_{26}H_{32}O_8N_2$, ½ H_2O, for its tetra-acetate $C_{34}H_{40}O_{12}N_2$, for its tetrabenzoate $C_{54}H_{48}O_{12}N_2$ and for the methiodide $C_{26}H_{32}O_8N_2$, CH_3I. In accordance with the structure (I) we now propose, the proof of which is in the sequel, the molecular formula for the base is modified to $C_{27}H_{32}O_8N_2$, ½ H_2O and thus the tetra-acetate becomes $C_{35}H_{40}O_{12}N_2$, the tetra-benzoate $C_{55}H_{48}O_{12}N_2$ and the methiodide $C_{27}H_{32}O_8N_2$, CH_3I, which is in agreement with the analytical data of the above compounds.



(I)

The uv spectrum of raucaffricine exhibits absorption in the regions known for indolenine alkaloids, λ max 219.8, 258 mμ; λ min 236 mμ[1]. Its easy conversion to indole bases, under mild alkaline conditions similar to that of perakine[2] also suggests that it is an indolenine derivative[3]. Thus we recorded the nmr spectrum (60 MHz) of raucaffricine in pyridine and observed a close similarity to that of vomilenine[4].

Attention is specially drawn to the peaks for the ethylidine group (1.56 δ, 3H, d, J=6.7 Hz; 5.98 δ, 2H, q, J=7 Hz), the single hydrogens at C-15 (2.80 δ, 1H, m), C-5 (3.33 δ, 1H, q) and at C-3 (4.31δ, 1H). The peak centred at 5.00δ corresponds to that in the vomilenine spectrum[4] at exactly the same position. A noteworthy difference in the two spectra is for the anomeric hydrogen atom which appears as a broad doublet at 5.42δ[5].

Hydrolysis of raucaffricine with 1N hydrochloric acid yielded two components, one of which was identified as D-(+)-galactose through paper chromatography[6] and the preparation of the osazone. The aglycone (as hydrochloride and free base) was identical (ir, uv and tlc) with the product of a parallel experiment with vomilenine run under identical conditions. In both cases uv reveals a complete change from indolenine to indole type bases, as is to be expected[4].

Enzymatic studies suggested that the linkage at the anomeric C atom is α. Sweet almond emulsin does not affect raucaffricine, while an attempted partial synthesis from its constituents in presence of brewer's yeast shows its formation on tlc (silica gel) (butanol: acetic acid: water: 4:1:1).

Molecular models of raucaffricine also indicate that the preferred glycosidic linkage is α, that the C-21 oxygen of the vomilenine moiety is axial and the geometry of the C-18 methyl is possibly that of the sarpagine alkaloids[7](I).

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