# A NOVEL TRANSFORMATION OF TETRAHYDROBERBERINE METHIODIDE TO ALLOCRYPTOPINE BY PHOTO-OXYGENATION

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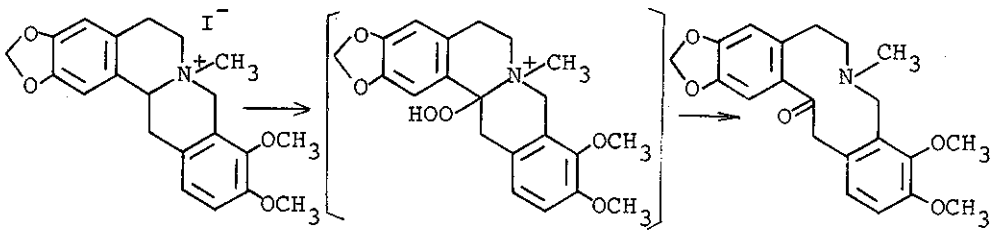
Allocryptopine (II) was synthesized from tetrahydroberberine methiodide (I) in one step by photo-oxygenation.

The protoberberine alkaloids have been shown to be the precursor of the protopine alkaloids[1] and further tetrahydrocoptisine methochloride was proved to be incorporated into protopine.[2] Oxygenation would be one of their possible biogenetic routes. On this assumption the biomimetic one-step synthesis of allocryptopine (II) from tetrahydroberberine methiodide (I) was accomplished by photo-oxygenation.



I II

Irradiation (100W high-pressure Hg lamp, with Pyrex filter) of I in water in a stream of oxygen for 24 hr at room temperature in the presence or absence of rose bengal, followed by purifica-

tion of the resulting product with preparative thin-layer chromatography afforded allocryptopine (II)[mp 159.5-161°, m/e: 369 ($M^+$), $\nu_{max}^{KBr}$ $cm^{-1}$: 1643 (C=O)] in 16% yield. The same product was also obtained using benzophenone instead of rose bengal in aqueous methanol or methanol even though in a lower yield and was not detected when the reaction was carried out without irradiation.

The synthetic allocryptopine was proved to be completely identical with the authentic specimen[3] by mixed mp, infrared and mass spectral comparison, and thin-layer chromatographic behavior.

Though the yield is rather low, the above transformation provides a simple and convenient method for the synthesis of the protopine alkaloids. The reaction would proceed through the peroxidation[4] at C-14 of I as depicted.

REFERENCES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