SYNTHESIS OF BENZINDENOAZEPINE ALKALOIDS, FUMAROFINE AND FUMARITRINE

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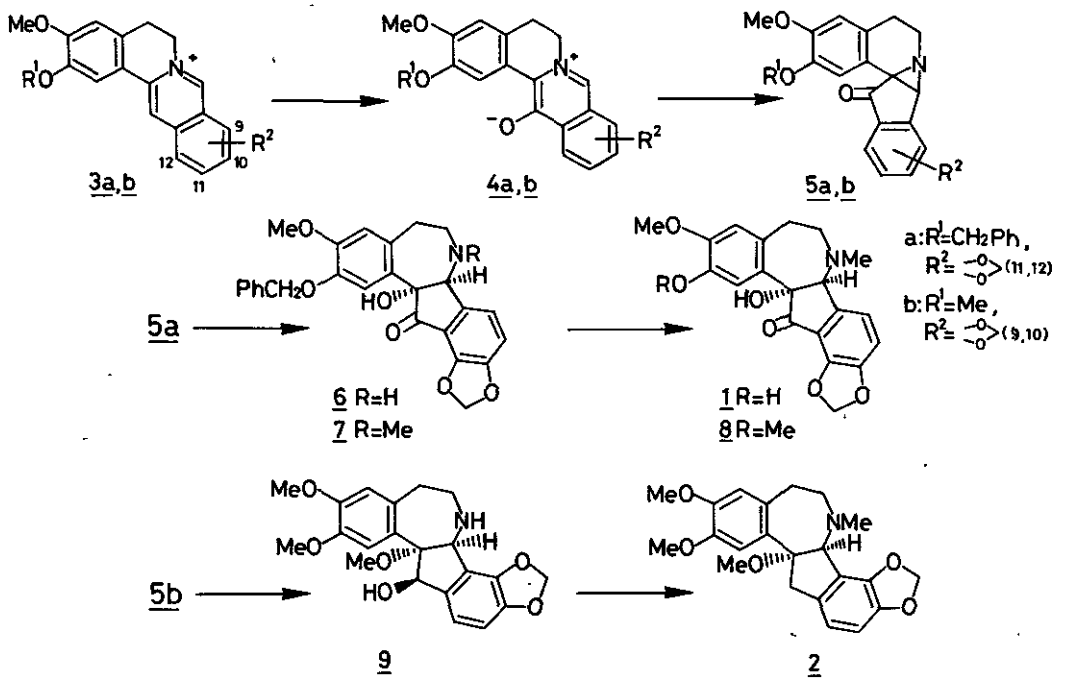
Benzindenoazepine alkaloids, fumarofine (1) and fumaritrine (2), were synthesized from the corresponding protoberberines (3a and 3b) via regioselective C_{14}-N bond cleavage of their 8,14-cycloberbines (5a and 5b), respectively.

The 8,14-cycloberbines (5a and 5b) were obtained[1] by photochemical valence tautomerization of the betaines (4a and 4b) in good yields. Acidic treatment of 5a effected regioselective C_{14}-N bond cleavage to give 6 and its diastereomer. N-Methylation of 6 followed by hydrogenolysis afforded (±)-fumarofine (1), which was methylated to provide O-methylfumarofine (8).

Reduction of 5b with $NaBH_4$ and subsequent treatment with acid gave the benzindenoazepine (9) in high yield, which was transformed into (±)-fumaritrine (2).



1) M. Hanaoka, S. Yasuda, K. Nagami, K. Okajima, and T. Imanishi, Tetrahedron Letters, 1979, 3749.