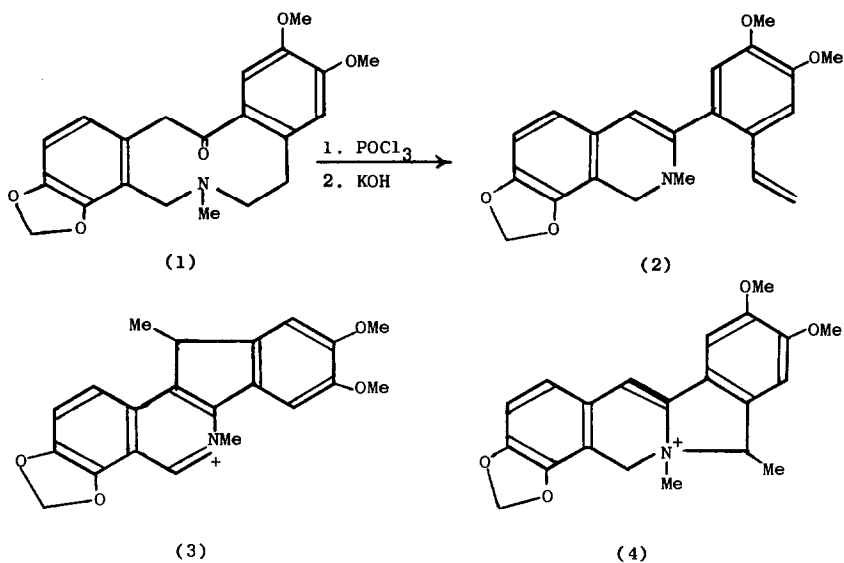


Ψ -Cryptopine Chloride

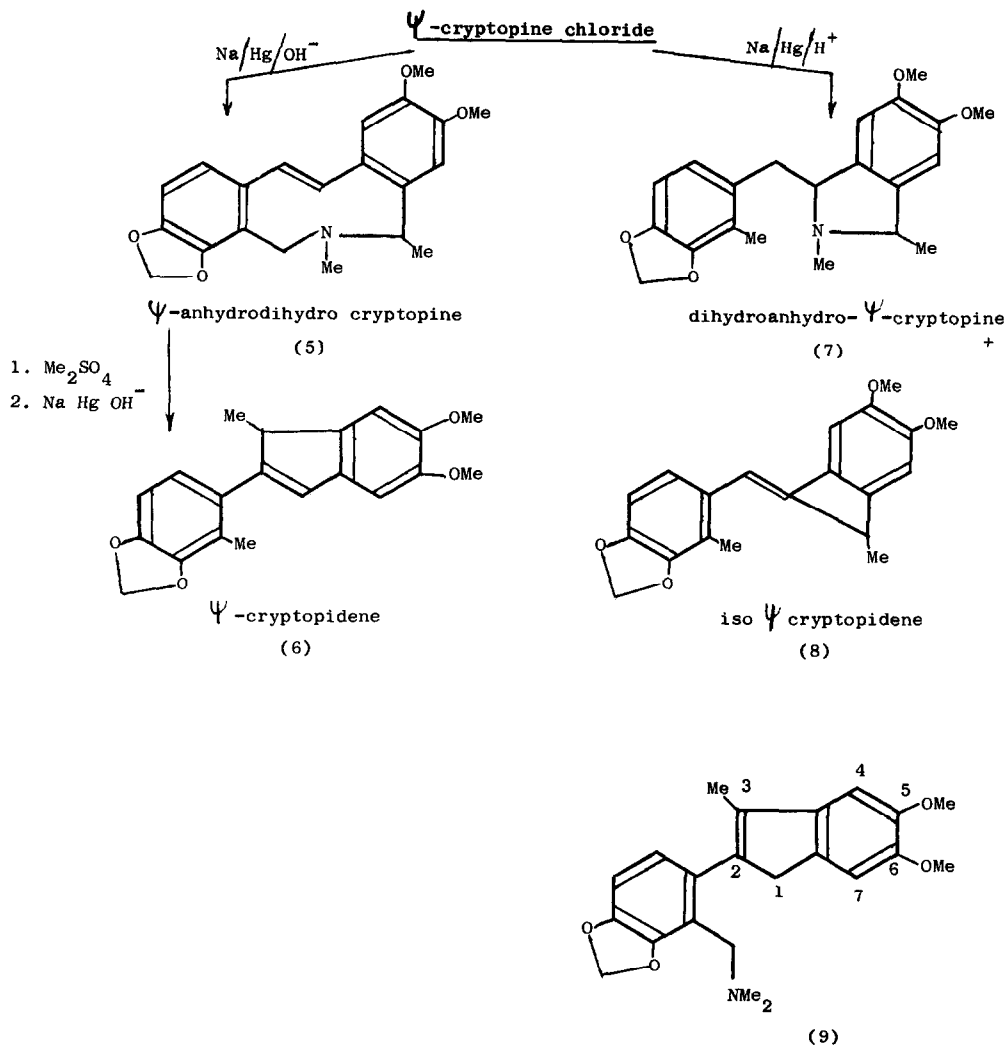
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When the opium alkaloid cryptopine (1) is treated successively with POCl_3 and KOH , the product¹ is anhydrocryptopine (2), which, when reacted with conc. HCl is transformed into epicryptopyrubin chloride and the epicryptopines A, B and C. We have recently^{2,3} shown that the structure of epicryptopyrubin chloride is (3) and we have also corrected the structures of the epicryptopines.

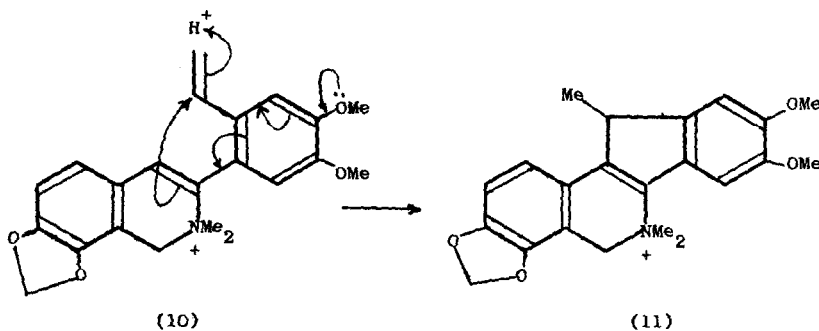


Now, when the methosulphate of anhydrocryptopine is treated¹ with conc. HCl a new quaternary salt, pseudocryptopine chloride is formed and Perkin assigned to it structure (4) on the basis of some degradation reactions that are summarised in Scheme I.

Scheme I

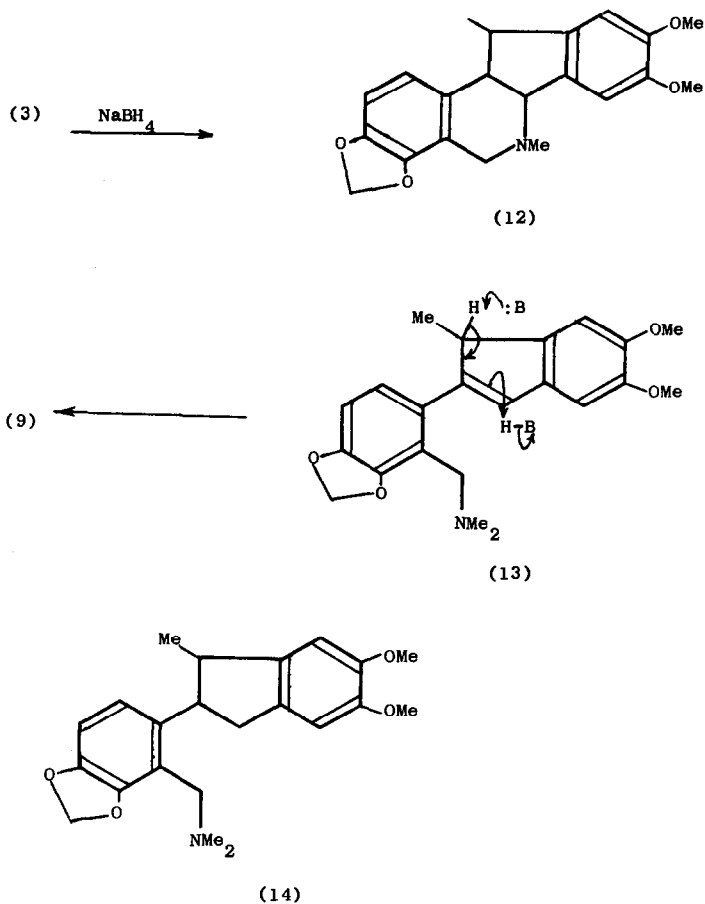


We have repeated these reactions and find that the NMR spectrum of Ψ -anhydrodihydro-cryptopine (taken at 60 Mc/s in CDCl_3 with internal TMS as standard) is completely consistent with structure (9); in particular it exhibits resonances characteristic of ONE $\text{CH}_3\text{-C}=\text{C}$ -group, TWO N-methyl groups, TWO O-methyl groups and ONE methylenedioxy group and the $\text{C}_1\text{-H-C}_3\text{-Me}$ coupling constant of 2c/s and the $\text{C}_1\text{-H-C}_7\text{H}$ coupling constant of Ca 0.5c/s are in agreement with the published data⁴ for 3-methylindene itself. Pseudocryptopine chloride is then better regarded as (11), formed from anhydrocryptopine methosulphate (10) as shown.



It is seen at once that the formation of Ψ -cryptopine chloride from (10) does not involve the N-demethylation reaction originally postulated by Perkin.

The structure (9) for Ψ -anhydrodihydrocryptopine is strongly supported by its alternative preparation from epicryptopirubin chloride (3) by reduction to the tetrahydro base (12) followed by Hofmann degradation via (13).



Catalytic hydrogenation of (9) occurs with the uptake of 1 mole of gas to yield (14) which is identical with dihydroanhydro- Ψ -cryptopine, formed by the treatment of Ψ -cryptopine chloride with sodium amalgam in acid solution. Thus it seems that degradation of Ψ -cryptopine chloride in alkaline solution may involve the initial formation of (13), which can then isomerise to (9) whereas in acid solution the same intermediate (13) is further reduced to (12).

References

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- 4 J.A. Elvidge and R.G. Foster, J.Chem.Soc., 1964, 981; Bergson and Wordler, Acta Chem. Scand., 1963, 17, 862.