Norsinoacutine and Salutaridine isolated from *Croton balsamifera* Jacq.

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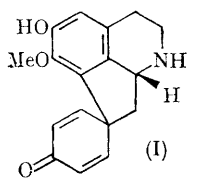
THE *Croton* species has previously yielded dienone alkaloids of biogenetic importance. The isolation of the proaporphine alkaloids crotonosine (I) and L(−)-*N*-methylcrotonosine (II) from *C. linearis* Jacq.[1] and the morphine precursor salutaridine (III) from *C. salutaris* Casar,[2] exemplify this. We now report the occurrence of salutaridine (III) and a new alkaloid norsinoacutine (IV; R=H) in *C. balsamifera* Jacq. (collected in Barbados by Dr. R. C. Russell whom we thank).

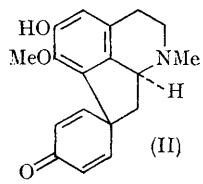
A 60 tube countercurrent distribution of the crude alkaloid mixture extracted from *C. balsamifera* in a chloroform–buffer (pH 1·99) system afforded an alkaloid in tubes 20—43 which was identical in all respects with authentic salutaridine.[3] Tubes 40—60 yielded an amorphous base which gave a deep blue colour with ethanolic ferric chloride.

N-Methylation of the latter base with formic acid–formaldehyde produced a crystalline compound, m.p. 194—196° which was identical in t.l.c. behaviour and infrared spectrum to salutaridine (III), $C_{19}H_{21}NO_4$, m.p. 197—198°, but which had the opposite sign of rotation, $[\alpha]_D^{16}-112°$ (EtOH). This derivative is therefore the alkaloid sinoacutine (IV; R=Me), m.p. 198°, recently isolated from *Sinomenium acutum*.[4]

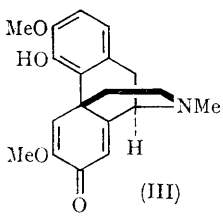
Norsinoacutine has resisted all attempts at crystallisation although it is homogeneous on t.l.c. The n.m.r. ($CDCl_3$) showed two aryl protons (δ 6·70 and 6·68), two *O*-methyl groups (δ 3·75 and 3·88), a singlet at δ 7·62 (1H, C-5 olefinic proton) and a singlet at δ 6·28 (1H, C-8 olefinic proton). The ultraviolet (λ_{max} 240, sh. 280 mμ) and infrared [(Nujol) ν_{max} 3400 (OH), 3150 (NH), 1672, 1643, 1623 (dienone) cm.$^{-1}$] spectra are also in full accord with structure (IV; R=H) for norsinoacutine.



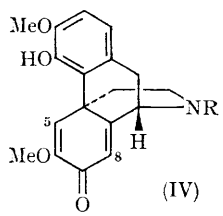
(I)



(II)



(III)



(IV)

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[1] L. J. Haynes and K. L. Stuart, *J. Chem. Soc.*, 1963, 1784; L. J. Haynes, K. L. Stuart, D. H. R. Barton, and G. W. Kirby, *Proc. Chem. Soc.*, 1964, 261.

[2] R. A. Barnes, unpublished work quoted by D. H. R. Barton, G. W. Kirby, W. Steglich, G. M. Thomas, A. R. Battersby, T. A. Dobson, and H. Ramuz, *J. Chem. Soc.*, 1965, 2423; See also K. Heydenreich and S. Pfeifer, *Pharmazie*, 1966, **21**, 121; A. R. Battersby and T. H. Brown, *Chem. Comm.*, 1966, 170.

[3] We thank Professor Barton for a sample of salutaridine.

[4] J. H. Chu, S.-Y. Lo, and Y. L. Chou, *Acta Chim. Sinica*, 1964, **30**, 265; (*Chem. Abs.*, 1964, **61**, 12047h).