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JACULARINE, A NEW REDUCED PROAPORPHINE FROM CROTON LINEARIS JACQ.

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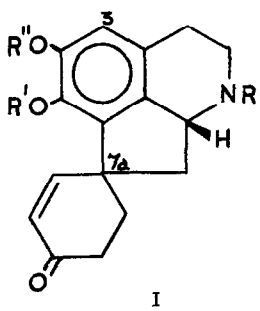
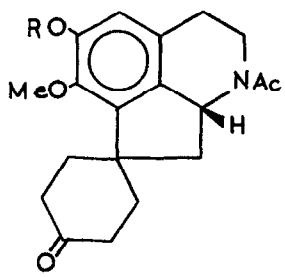
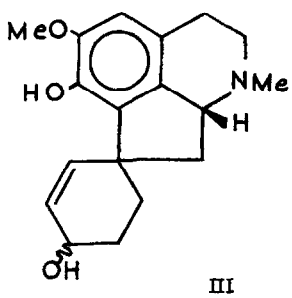
Proaporphine and reduced proaporphine alkaloids are a rapidly expanding group of natural products (1) and we wish to report the isolation and structural characterisation of a new member of the latter group. Jacularine (I; R = R' = H, R'' = CH_3), was isolated as the NO-diacetyl derivative (I; R = R' = Ac, R'' = CH_3), $C_{21}H_{23}NO_5$, by using countercurrent, column chromatographic and acetylation techniques on the alkaloidal fractions from C. linearis which were recently shown to also contain two new reduced morphinandienone alkaloids (2).



I



II



III

NO-Diacetyljacularine had physical data consistent with the structure (I; R = R' = Ac, R'' = CH_3) ; [uv, $\lambda_{max.}^{EtOH}$ 205 nm (logε 4.54), sh. 230 (4.15), 280 (3.33); ir, $\nu_{max.}^{CHCl_3}$ 1767 (Ph-OAc), 1669 (α, β -unsaturated -C=O), 1637 (N-Ac) cm^{-1}; nmr, δ^{CDCl_3} 2.17 (N-Ac), 2.20 (Ph-OAc), 3.82 (OMe), an AB system (-CH = CH-) with doublets centered at δ 6.03, 6.71 (J = 9 cps) and 6.79 (C3-H)] .

Hydrogenation of NO-diacetyljacularine over 5% palladium - carbon in ethanol gave a

dihydro derivative, m.p. 173-174°, $[\alpha]_D$ -122° (MeOH), $\nu_{max.}^{CHCl_3}$ 1757 (Ph-OAc), 1704 (C=O), 1631 (N-Ac) cm^{-1}. Its molecular formula, $C_{21}H_{25}NO_5$, was established by accurate mass spectural measurements; M^+ = 371.172114; Calculated: $C_{21}H_{25}NO_5$, 371.173261. [The spectrum shows M^+ - 42 (CH_2=C=O) → m/e 329 $\xrightarrow{-H.}$ m/e 328]. This dihydro product was not identical to the isomeric compound NO-diacetyltetrahydrocrotonosine (II; R = Ac) m.p. 107-108°, $[\alpha]_D$ -127.3° (MeOH) (3). Base hydrolysis of the latter compound yielded N-acetyltetrahydrocrotonosine (II; R = H), $C_{19}H_{23}NO_4$, m.p. 272° (decomp.) and treatment of this with diazomethane gave N-acetyl-O-methyltetrahydrocrotonosine (II; R = CH_3), $[\alpha]_D$ -136° ($CHCl_3$), nmr, δ^{CDCl_3} 2.20 (N-Ac), 3.87 (2 OMe), 6.68 (C3-H). When NO-diacetyltetrahydrojacularine was similarly treated, a compound indistinguishable from N-acetyl-O-methyltetrahydrocrotonosine was obtained.

The above conversions therefore establish the structure of NO-diacetyljacularine as (I; R = R' = Ac, R'' = CH_3), except for the configuration at C-7a.

The occurrence of jacularine in C. linearis is of bio-genetic interest in view of the known biosynthesis of crotonosine from (+) - coclaurine in this plant (4). Base E (III) which also occurs in C. linearis (5) could be formed from jacularine by enzymatic N-methylation and reduction of the carbonyl group.

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