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PALICOUREA ALKALOIDS: THE STRUCTURE OF PALININE

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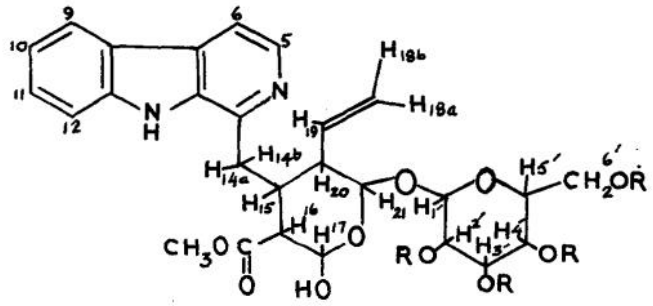
Prompted by reports of the anti-tumor activity of Palicourea species[1] and the isolation of alkaloids of unknown structures[2], Palicourea alpina* (Sw.) DC (Rubiaceae) was extracted for alkaloids. Counter-current separation yielded in addition to harman, a new alkaloid, which we have named palinine, m.p. 166.5 - 168°C, $[\alpha]_D^{28}$ - 252.3° (MeOH) and which analysed for $C_{27}H_{32}N_2O_{10}$. We now report evidence supporting the β-carboline glycosidic structure (1a).

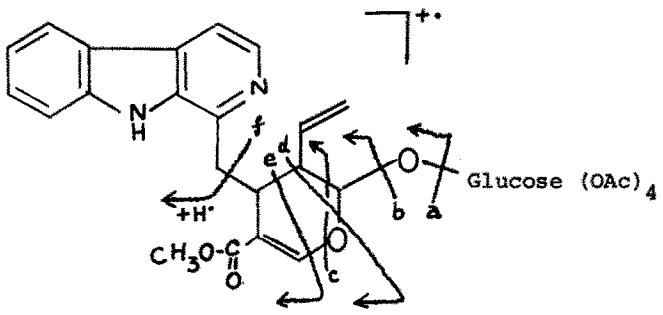


1a: R=H

1b: R=Ac

*Voucher No.31,130 The Herbarium, University of the West Indies, Jamaica.

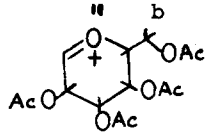
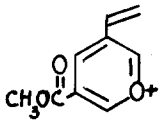
D-Glucose was obtained following hydrolysis by β-glucosidase, while the UV, λ_{max}^{EtOH} (log ε): 236.5(4.62), 290.5(4.20), 349(3.61) nm, which showed a bathochomic shift in acid was supporting evidence for a carbolinium system very similar to that of harman[3]. Acetic anhydride/pyridine acetylation yielded a penta-acetate (NMR evidence), which when purified on silica gave a tetra-acetate, $C_{35}H_{40}N_2O_{14}$ (1b), IR(CCl_4), 3215(NH), 2933(OH), 1748, 1235(OAc), 1686(CO) cm^{-1}*. The NMR of the tetra-acetate in $CDCl_3$ showed exchangeable protons at δ 10.28(NH) and 2.25(OH). The other protons could be assigned as follows: δ 8.30 ($J_{5,6}$ = 5.5 Hz; H-5), 7.83 ($J_{6,5}$ = 5.5 Hz; H-6), 8.15 ($J_{9,10}$ = 7.5 Hz, $J_{9,11}$ ~2 Hz; H-9), 7.45 → 7.70(H-10 + H-12), 7.29 (H-11), 3.2 - 3.7 (H-14a + H-14b), 1.7(H-15) ~3.10(H-16), ~ 5.10(H-17), 4.8 → 5.3(H-18a + H-18b), 5.6 → 6.23 (6 lines, $J_{18a,19}$ = 17.5 Hz, J_{18b-19} = 9.5 Hz; H-19), 2.65(m; H-20), 5.45(d, $J_{20,21}$ = 5.5 Hz, H-21), 4.8 → 5.20(H-1' → H-4'), 3.78(H-5'), 4.20(H-6'), 1.97, 2.01, 2.10(4 Ac groups) and a methoxycarbonyl group at δ 3.85. High resolution MS studies indicated a facile loss of H_2O to yield the ion m/e 694 (2), and some of the fragmentations observed are tabulated on the following page.



2.

*Shift of the carbonyl to 1730 cm^{-1} in a 0.005M(CCl_4) solution indicated intermolecular hydrogen bonding.

TABLE*

	m/e	Found	Formula	Calc.
$M-H_2O$	694	694.2433	$C_{35}H_{38}N_2O_{13}$	694.2369
$M-(H_2O + -COCH_3)$	651	651.2161	$C_{33}H_{35}N_2O_{12}$	651.2186
$M-(H_2O + -COOCH_3)$	635	635.2202	$C_{33}H_{35}N_2O_{11}$	635.2239
Cleavage a	363	363.1340	$C_{21}H_{19}N_2O_4$	363.1343
" b	347	347.1370	$C_{21}H_{19}N_2O_3$	347.1394
 Oxonium ion	331	331.1023	$C_{14}H_{19}O_9$	331.1027
Cleavage c	319	319.1397	$C_{20}H_{19}N_2O_2$	319.1446
" d	294	294.1020	$C_{17}H_{14}N_2O_3$	294.1003
" e	278	278.0994	$C_{17}H_{14}N_2O_2$	278.1054
" f	182	182.0831	$C_{12}H_{10}N_2$	182.0843
	181	181.0760	$C_{12}H_9N_2$	181.0765
Further cleavage of oxonium ion 331...	169	169.0486	$C_8H_9O_4$	169.0500
	127	127.0413	$C_6H_7O_3$	127.0394
	109	109.0300	$C_6H_5O_2$	109.0289
 Pyrylium ion	165	165.0532	$C_9H_9O_3$	165.0551.

*These data were obtained on an AEI MS 902 instrument having a computer attachment, while a preliminary low resolution spectrum was obtained from an ATLAS CH 4-B MS instrument.

A minor alkaloid, palidimine, has also been isolated from P. alpina, and preliminary studies indicate that this dimeric alkaloid contains palinine as one of its units.

Acknowledgement: We thank Professor J.P. Kutney and Dr. Gunter Eigendorf, University of British Columbia for high resolution MS data and some analytical results, Dr. R.T. Brown, The University, Manchester, for copies of NMR spectra of methyldesoxycordifoline tetra-acetate[4] and another 10-desoxycordifoline derivative, and Dr. E.V. Roberts of our Department for drawing our attention to this problem.

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