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STRUCTURE ELUCIDATION OF PERIFORMYLINE, A NOVEL ALKALOID FROM C. LANCEUS.*

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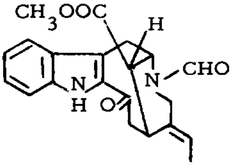
Periformyline (I), $C_{21}H_{22}N_2O_4$, has been isolated recently (1) from the leaves of Catharanthus lanceus (Boj. ex A. DC.) Pich. Data have been accumulated to establish that this new alkaloid is $N_{(b)}$-formyl perivine.*** To our knowledge this is the first report of an $N_{(b)}$-substituted formyl indole alkaloid to be found in nature.



Periformyline (I)

An examination of the ultraviolet spectrum**** of I indicated it to be a 2-acylindole derivative. The infrared spectrum of I in chloroform was very similar to perivine except that the absorption of the 2-acylindole carbonyl

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[*] Studies on Catharanthus Alkaloids VIII.

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[***] For the structure of perivine, see reference (2).

[****] The ultraviolet spectrum in ethanol gave λ max. at 239 and 314 mμ. See reference (1).

was overlapped by the strong amide absorption at 1650 cm^{-1}. (In pervine the absorption of the carbomethoxy carbonyl was stronger than that of the 2-acylindole carbonyl.) Analysis indicated no $N\text{-}CH_3$ to be present in the molecule. The mass spectrum of I gave 366 as the molecular weight. The intense m/e peak at 194 suggested an increase of 14 mass units to the basic ion formed in the spectrum of vobasine (3, 4). This could be explained by the exchange of a formyl group for the $N_{(b)}$-methyl group in vobasine.

The NMR spectrum of I showed the formyl hydrogen as a doublet at 8.2 δ and the indole N-H peak ca. 9.4 δ. After I was shaken with $CDCl_3$ and D_2O the indole N-H peak disappeared, but the doublet due to the formyl hydrogen remained at 8.2 δ. The methyl protons of the carbomethoxy group were present as two peaks at 2.55 δ and 2.65 δ which indicated that the carbomethoxy group is magnetically shielded by the indole ring. The methyl doublet of the ethylidene group at 1.72 δ exhibited a slight splitting of each peak. The overall spectrum was very similar to that of synthetic N-acetyl perivine (5) which also showed two peaks for the methoxy protons of the carbomethoxy group and two peaks for the methyl of the acetyl group.

Finally, perivine was formylated at room temperature using a previously prepared solution of acetic anhydride in excess formic acid. The synthetic product was recrystallized from methanol and melted at 206-209° C. The mixture melting point of synthetic periformyline and I showed no depression. The infrared spectra of synthetic periformyline and I were superimposible and the thin-layer chromatography R_F values for the two compounds were identical following co-chromatography in three different solvent systems.

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