7-ISOPENTENYLOXY-γ-FAGARINE FROM Haplophyllum perforatum

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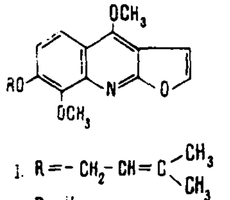
Continuing the separation of the combined alkaloids from the epigeal part of H. perforatum [1], we have chromatographed the neutral fraction on alumina. The substances were eluted with ether. The first fraction yielded an optically inactive base with the composition $C_{18}H_{19}NO_4$ (I), mp 105-106°C (from ethyl acetate), mol. wt. 313 (mass spectrometry), readily soluble in organic solvents and dilute acids but insoluble in water and alkali.

The IR spectrum of the base [λ_{max} 251, 322, 335 nm (log ε 4.99, 3.91, 3.89)] resembles that of the furanoquinoline alkaloids of the skimmianine type [2]. The IR spectrum had maxima at 3120 and 3160 cm^{-1} (furan rings); absorption bands of a hydroxy group were absent. The NMR spectrum (taken in CCl_4) showed the signals of protons with the following values of τ: 2.33 and 3.04 (doublets, 1H each, J = 9 Hz, ortho-aromatic protons); 2.61 and 3.19 (doublets, 1H each, J = 3 Hz, the α- and β-protons of a furan ring); 5.72 and 5.99 (singlets, 3H each, 2 OCH_3); 4.54 (triplet, 1H, J = 6.5 Hz, $=\underline{CH}-CH_2$); 5.38 (doublet, 2H, J = 6.5 Hz, $=CH-CH_2-O-$); 8.26 and 8.30 (singlets, 3H each, $\left(=C\begin{matrix}CH_3\\CH_3\end{matrix}\right)$. Mass spectrum of (I): m/e 313 (M^+4%) 245 (100%), 230 (21%), 227 (97%), 216 (22%).

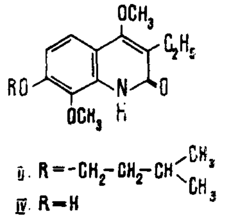
The facts presented permit the assumption that the base is a derivative of dictamnine with ortho-alkoxy substituents in the benzene ring $\left(OCH_3 \text{ and } O-CH_2CH-C\begin{matrix}CH_3\\CH_3\end{matrix}\right)$.

Hydrogenation of the base over a platinum catalyst yielded a hexahydro derivative (II) with mp 235-236°C (from ethanol) [mass spectrum: m/e 219 (M^+ 0.4%) 249 (98%), 234 (100%)] and a substance with mp 163-164°C (from ethanol) shown to be identical with an authentic sample of tetrahydrohaplopine (IV), obtained by the hydrogenation of haplopine (III). Consequently, the alkaloid isolated has the structure (I)



I. $R=-CH_2-CH=C\begin{matrix}CH_3\\CH_3\end{matrix}$

III. R=H



II. $R=-CH_2-CH_2-CH\begin{matrix}CH_3\\CH_3\end{matrix}$

IV. R=H

We have performed a partial synthesis of (I) by the condensation of haplopine with 4-chloro-2-methylbut-2-ene in dry acetone in the presence of anhydrous potassium carbonate. The results of a direct comparison of the compounds synthesized with (I) showed that they were identical.

In the literature is reported the isolation from Ptelea aptera Parry of a substance with mp 101-103°C for which, on the basis of spectroscopic information, the structure of 7-isopentenyloxyfagarine was proposed [3]. Attempts by the authors concerned to check this chemically were unsuccessful. The UV and NMR characteristics that they give correspond to those of the base that we have isolated.

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3. D. L. Dreyer, Phytochemistry, 8, 1013 (1969).