THE STRUCTURE OF THE ALKALOID DELAVAYINE

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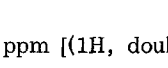
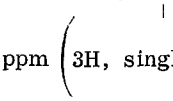
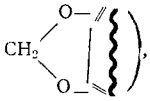
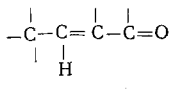
From the herb Stephania Delavayi Diels (Menispermaceae) growing in Transcaucasia, by chromatography of the total alkaloids on alumina [eluent: ethyl ether–methanol (99 : 1)] we have isolated a base with mp 149–150° C (ethanol), $[\alpha]_D$ −240° (c 1; chloroform), with the composition $C_{20}H_{23}O_5N$, mol. wt. 364 (Rast); hydrochloride with mp 203–203.5° C (ethanol). The alkaloid contains two OCH_3, one CH_2O_2, and one $N \cdot CH_3$ groups. The IR spectrum has absorption bands at, cm^{-1}: 1670 (conjugated carbonyl) and 1608 (C=C). UV spectrum: λ_{max} 238, 268 mμ (log ε 3.59, 3.97). The alkaloid proved to be new, and we have called it "delavayine."

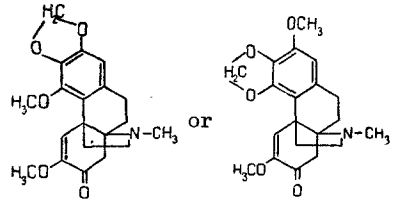
The Hofmann degradation of delavayine was carried out with subsequent acetolysis of the methine base (methiodide, mp 190–192° C; des-base mp 118–120° C). A nitrogen-free product was obtained the composition and UV spectrum of which showed it to be a substituted phenanthrene. Consequently, delavayine may be assigned to phenanthrene derivatives of the type of morphinan or hasubanonine.

The saponification of the CH_2O_2 group gave a substance with mp 212–213° C. Its IR spectrum had absorption bands at 3300 and 3500 cm^{-1} (OH). Methylation of the substance with diazomethane led to the precipitation of an amorphous base giving a crystalline hydrochloride with mp 173–175° C. The base was not identified with any known alkaloid.

The NMR spectrum of delavayine had signals at 2.49 ppm (3H, singlet; $N \cdot CH_3$ group), 2.46 ppm (1H, doublet, J = 16 Hz), and 3.00 ppm [(1H, doublet, J = 16 Hz, ) the assignment of the signals was confirmed by the spectra taken at 60 and 100 MHz], 3.60 ppm (3H, singlet, ), 4.06 ppm (3H, singlet, CH_3O—Ar), 5.84 ppm (2H, singlet, ), 6.41 (1H, singlet, proton attached to an aromatic ring), and 6.64 ppm (1H, singlet, ).

The signal with δ 6.41 ppm is somewhat broadened because of long-range spin-spin coupling with a constant not greater than 0.5 Hz. This signal is ascribed to a proton in position 1, in view of the fact that only for this is there the possibility of a homoallyl interaction with the protons in position 10. The olefinic proton must be present in position 5. The corresponding signals in the spectra of isosinomenine, norsinoacutine, and salutaridine are located in the range from 6.75 to 7.62 ppm [1, 2]. Position 8 is excluded for this proton, since in this case the signal should appear at 5.5–5.7 ppm (cepharamine, sinomenine) [2, 3].

On the basis of the above information, delavayine must be assigned to the derivatives of hasubanan and one of the following two possible structures must be assumed for it:



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2. K. Z. Stuart and C. Chaunbes, Tetrah. Let., 30, 2879, 1967.
3. M. Tomita and M. Kozuka, Tetrah. Let., 50, 6229, 1966.

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