THE ALKALOIDS OF GENTIANA OLIVIERI

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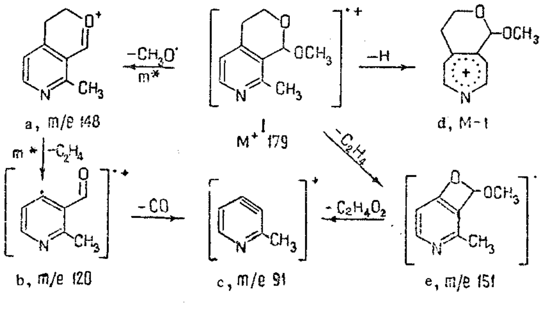
After the removal of the gentianine and gentiananine [1], the combined alkaloids from the epigeal part of G. olivieri were separated according to their solubilities in benzene and acetone and by chromatography on alumina. This gave gentianadine, gentianainine [2], gentioflavine [3], and a base with mp 159–160° C, the constants (mp, UV, IR, NMR, and mass spectra) of which coincided completely with those of an alkaloid from G. tibetica [4]. In addition, two new bases were isolated: oliverine, $C_{20}H_{16}N_2O_4$, mp 206–207° C (methanol), R_f 0.74, and oliveridine, $C_{10}H_{13}NO_2$, with mp 260° C (decomp., acetone), R_f 0.73 [butan-1-ol–acetic acid–water (20 : 1 : 20) system].

The UV spectrum of oliveridine has two absorption maxima at λ_{max} 261 and 268 mμ (log ε 3.42 and 3.41, respectively); it is similar to the UV spectrum of the alkaloid from G. tibetica [4]. The IR spectrum exhibits absorption bands at (cm^{-1}): 1630 (pyridine), 1480 and 1375 ($-CH_3$, $-OCH_3$). The mass spectrum of oliveridine has the molecular peak M^+ 179, which confirms its empirical composition.

These facts, and also the difference in the molecular weights of 14 units made it possible to assume that oliveridine is the O-methyl ether of the base extracted from G. tibetica. To prove this, 50 mg of the base was dissolved in 5 ml of methanol, and the solution was saturated with hydrogen chloride at 0° C. The reaction mixture was left at room temperature for 2 days and was then evaporated; the residue was dissolved in water and the solution was made alkaline with ammonia. Then it was evaporated to dryness in vacuum, the residue was boiled with acetone, and the mixture was concentrated to 50 ml. On cooling, 20 mg of oliveridine deposited. On this basis, structure I may be proposed for oliveridine.

A mass-spectrometric study of oliveridine showed that the main direction of fragmentation begins with the expulsion of the radical $-OCH_3$ from the molecular ion, forming the maximum peak of the ion *a* (100%) with m/e 148. The elimination of a molecule of ethylene from the ion *a* leads to the appearance of ion b with m/e 120. These transitions are confirmed by the presence in the spectrum of the corresponding peaks of the metastable ions with m/e 122 and 97 (calculated: 122.3 and 97.3, respectively). One of the intense ions is M − 1, arising from the molecular ion by the splitting out of an atom of hydrogen. The ion formed in this process has an azotropylium structure (ion d) which is characteristic for alklypyridines [5]. The possible routes of fragmentation of oliveridine in the mass spectrum can be represented by the following scheme:



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