MASS SPECTROMETRIC STUDY OF APOGALANTHAMINE AND ITS DERIVATIVES

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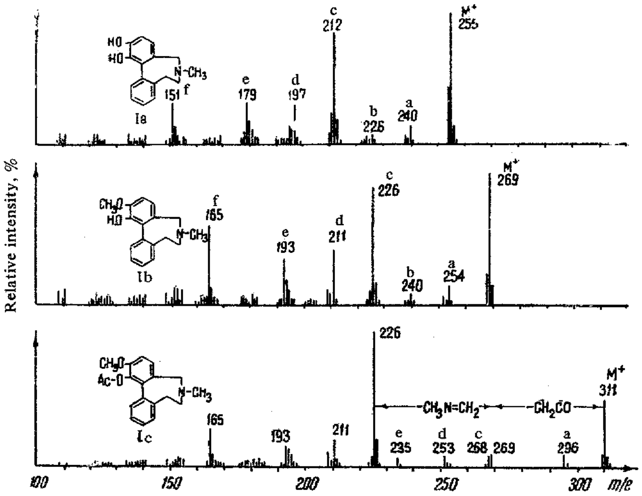
Continuing a mass-spectrometric investigation of alkaloids of the type of galanthamine and their derivatives, we have studied the mass spectra of a product of the chemical transformation of galanthamine—apogalanthamine (Ia, $R_1 = R_2 = H$), its monomethyl ether (Ib, $R_1 = CH_3$, $R_2 = COCH_3$) (figure). It was found that for these compounds the same fragmentation rules are characteristic as for the alkaloids of the galanthamine type: the formation of the $(M - 1)^+$ ion, the contraction of ring C, both with the retention and with the empulsion of the nitrogen atom, and the elimination of ring B (see Scheme). However, the presence of the second aromatic ring and the absence of ring D in compounds Ia–Ic introduces some specific features into the fragmentation of the molecular ions of these compounds. For example, in contrast to the mass spectra of the alkaloids of the galanthamine type, the peak of ion d $(M - 58)^+$ is considerably more intense than the of the ion $(M - 57)^+$ (see figure). This is explained by the high stability of the substituted fluorenyl cation.

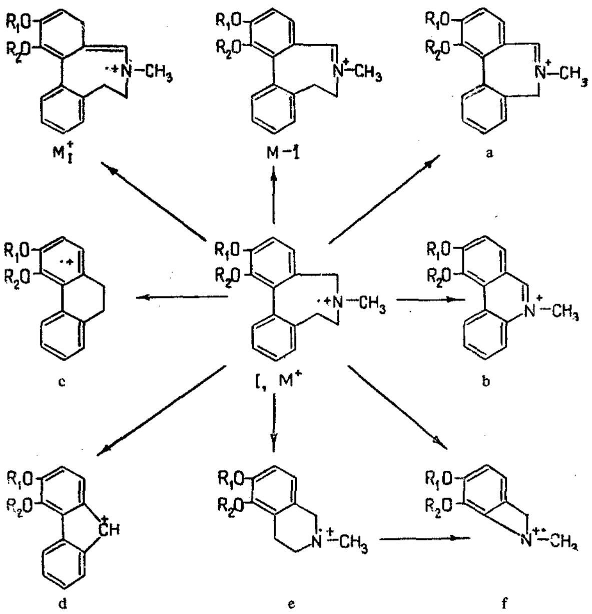


Mass spectra of apogalanthamine (Ia), the monomethyl ether of apogalanthamine (Ib), and the acetate of the monomethyl ether of apogalanthamine (Ic).

The ejection from the molecular ion of the aromatic ring B, leading to the appearance of the ion e $(M - 76)^+$, is due to the energetically favorable formation of the molecular ion of N-methyltetrahydroisoquinoline substituted in the aromatic ring. It is interesting to note that the peak of the ion with m/e 147 arising through the elimination of ring A from the molecular ion has an extremely low intensity (1–2%) in the spectra of compounds Ia–Ic (see figure). This is probably due to the possibility of the production of a stable tautomeric form of the molecular ion M_1^+, in which the unpaired electron of the nitrogen is in conjugation with a system of double bonds (see Scheme).

In the spectra of compounds Ia–Ic, the ion *f* $(M - 104)^+$, formed as a result of the elimination of a molecule of ethylene from ion e also has a high intensity. The structures of the fragmentary ions obtained in the decomposition of compounds Ia–Ic are shown in the scheme.

Under the action of electron impact, the molecular ion Ic readily loses a molecule of ketene (42 mass units), being converted into the molecular ion Ib. This process is characteristic for phenol acetates [1, 2]. Consequently, the peaks with m/e 240 (M – 42 – 29) and 165 (M – 42 – 104) in the spectrum of compound Ic (see figure) correspond to ions b and *f*.



The mass spectra were recorded on a standard MKh-1303 instrument fitted with a system for the introduction of the sample directly into the ion source at 100–140° C and with an energy of the ionizing electron of 30–50 eV.

CONCLUSIONS

1. The mass spectra of apogalanthamine, its monomethyl ether, and the acetate of the monomethyl ether have been studied.
2. The general nature of the fragmentation of these compounds and of alkaloids of the galanthamine type has been shown and specific features of fragmentation due to the presence of the second aromatic ring have been determined.

REFERENCES

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