COMPARISON OF THE SECONDARY-ION AND ELECTRON-IMPACT MASS SPECTRA OF ALKALOIDS

Ya. V. Rashkes, E. G. Mil'grom, and Yu. M. Mil'grom*

An advantage of using secondary-ion spectra for determining the molecular masses of quaternary bases and bases the molecular ions of which are unstable to electron impact is shown. The LSIMS spectra of four groups of diterpene alkaloids include the 100% peaks of the (M + H)⁺ ions and the peaks of the main fragments present in the EI spectra. The B/E = const. spectra of the key ions obtained by the different methods are compared. The closeness of the values of A of analogous transitions calculated from the B/E and MD spectra is confirmed.

Electron-impact (EI) mass spectrometry has hitherto provided the bulk of structural—analytical information in the field of alkaloid chemistry. An exception is formed by nonvolatile bases unstable to heat and to electron impact. Beginning from the 70s the problem of analyzing such substances have been solved with the aid of "mild" methods of ionization, among which one of the leading positions is occupied by secondary-ion mass spectrometry using liquid matrices (LSIMS). By using bombardment with Ar⁺ ions and a solid silver support, Benninghoven et al. obtained secondary-ion spectra of polar and unstable compounds of various groups, including the alkaloids ephedrine and atropine, that contained the stable (M + H)⁺ or M⁺ ions and some fragments [1, 2]. The same group of workers showed the possibility of performing the quantitative and qualitative analysis of a mixture of opium alkaloids present at the nanogram level in urine extracts [3]. Meyer [4] successfully used the LSIMS method to obtain the spectra of quaternary bases. A number of investigations have been devoted to the search for compositions of liquid matrices for improving the quality of the spectra [5, 6]. However, in recent years, in spite of the wide use of the LSIMS method for analyzing various types of polar compounds, there have been practically no publications describing its application to the investigation of alkaloids. Nevertheless, this method can be used not only as a supplement to EI spectra but also completely independently in the analysis of mixtures of alkaloids in order to confirm the composition of quaternary bases and bases unstable to EI.

In the present paper we give the results of an investigation of various groups of alkaloids by the LSIMS method.

*Deceased.

The mass number of the positive ion of the berberine chloride molecule (I) is 336 a.m.u. It is impossible to identify this compound from its EI spectrum (Table 1). In the region of high mass numbers it contains the weak peak of an ion with \( m/z \) 351, ions of medium height with \( m/z \) 337 and 336, and a triplet of peaks of ions with \( m/z \) 322-320. Then a series of homologous peaks with decreasing heights is observed down to the region below 170 m.u., where doubly charged variants of the same ions appear. The maximum peaks in the spectrum are those of the \( \text{CH}_3\text{Cl} \) ions with \( m/z \) 50/52. This compound probably undergoes far-reaching thermal decomposition under the inlet conditions (\( t = 170^\circ\text{C} \)). In the LSIMS spectrum the peak of the ion with \( m/z \) 336 has a height far exceeding those of the other ions that are characteristic for compounds with methoxy and methylenedioxy groups — (\( M - 15 \))\(^+\), (\( M - 30 \))\(^+\), (\( M - 44 \))\(^+\), and (\( M - 58 \))\(^+\). In the high-mass region a cluster ion with \( m/z \) 428 (336 + 92) is observed.

The quaternary base magnoflorine iodide (II) is, in essence, the methiodide of a tertiary base of the aporphine series. Its EI spectrum is characterized by the properties common to this type of compounds [7]. Together with the peak of an ion with \( m/z \) 327 (\( M - \text{CH}_3\text{I} \))\(^+\), the more intense peak of an ion with \( m/z \) 341 (\( M - \text{HI} \))\(^+\) is observed. In the region of low mass numbers there are peaks of ions with \( m/z \) 142 (\( \text{CH}_3\text{I} \))\(^+\), 128 (\( \text{HI} \))\(^+\), and 127 (\( \text{I} \))\(^+\) and the 100% peak of an ion with \( m/z \) 58. The breakdown of the \( m/z \) 327 ion by the alternative elimination of \( \text{CH}_3 \) and \( \text{CH}_2\text{O} \) is recorded.

In the LSIMS spectrum of (II) the ion with \( m/z \) 58 is again the maximum ion. But the main characteristic of this spectrum is the presence of the peak of the quaternary magnoflorine ion with \( m/z \) 342. The breakdown of this ion with the elimination of \( \text{CH}_4 \) and \( \text{CH}_2\text{O} \) takes place to an insignificant degree.

In the molecule of O-methylarmepavine methiodide (III) there is an increment analogous to magnoflorine; however, here the (\( M - \text{CH}_3 \))\(^+\) ion with \( m/z \) 327 is unstable because of the energetically favorable ejection of a \( \text{p-methoxybenzyl} \) radical and the stability of the resulting ion with \( m/z \) 206 (in the EI regime). In addition to this, the quaternary form of the base is confirmed by the presence in the spectrum of the peaks of ions with \( m/z \) 142, 127, and 58. The \( \text{p-methoxybenzyl} \) moiety appears in the spectrum in the form of an ion with \( m/z \) 121.

The LSIMS spectrum of (III) is more complex. In addition to the 100% peak of the cation of this compound with \( m/z \) 342, there is the peak of an ion with \( m/z \) 328 which can be represented in the form of the (\( M + \text{H} \))\(^+\) ion of the tertiary O-methylarmepavine formed in the matrix after the elimination of \( \text{CH}_3\text{I} \). An ion with \( m/z \) 326 may be formed by alternative routes. All three quaternary ions have a tendency to split out the substituent at C-1, but in the form of a neutral \( \text{p-methoxytoluene} \) molecule. This leads to the formation of even-electron fragments with \( m/z \) 220, 206, and 204. The ion with \( m/z \) 58 is second in intensity in this spectrum. The ion with \( m/z \) 342 also breaks down with the elimination of the particles \( \text{CH}_2\text{O} \), \( \text{CH}_2\text{O} + \text{CH}_3 \), and \( \text{CH}_3 + \text{CO} \), which is characteristic for methoxy-substituted aromatics. All the above-mentioned transitions are confirmed by metastable peaks. In the low-mass region, the peak of the methoxytropylium cation with \( m/z \) 121 is also observed. Among the high masses there is the weak peak of the (\( M - \text{H} \))\(^+\) ion with \( m/z \) 468 and that of a cluster ion with \( m/z \) 434 (342 + 92).

The electron-impact spectrum of the tertiary base armepavine (IV) shows a weak \( \text{M}^+ \) peak (\( m/z \) 313, 0.4%), while the maximum peak of an ion with \( m/z \) 206, far exceeding all the others in height, arises after the ejection of a \( \text{p-hydroxybenzyl} \) radical [8]. In the LSIMS spectrum of (IV), the peak of an ion with \( m/z \) 314 (\( M + \text{H} \))\(^+\) stands out by its intensity. Its fragmentation takes place more selectively than that of the methiodide (III), and the height of the peak of the ion with \( m/z \) 206, formed by a mechanism analogous to the process leading to the appearance of the ion with \( m/z \) 220 (III), amounts to 60% of the height of the peak of the \( m/z \) 314 ion. Of ions characterizing the decomposition of the MeO groups it is possible to record only the presence of the peak of the (\( \text{MH} - \text{CH}_2\text{O} \))\(^+\) ion with \( m/z \) 284. The region of low masses has the peak of the hydroxytropylium ion with \( m/z \) 107.

Thus the advantage of LSIMS spectra for determining the molecular masses of quaternary bases and of bases the \( \text{M}^+ \) ions of which are unstable to EI is obvious.