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USE OF MIKE SPECTRUM OR CID/MIKE SPECTRUM OF A QUASI-MOLECULAR OR CATIONIZED ION OBTAINED BY THE MBSA-FAB METHOD IN ORDER TO CHARACTERIZE A POLAR COMPOUND

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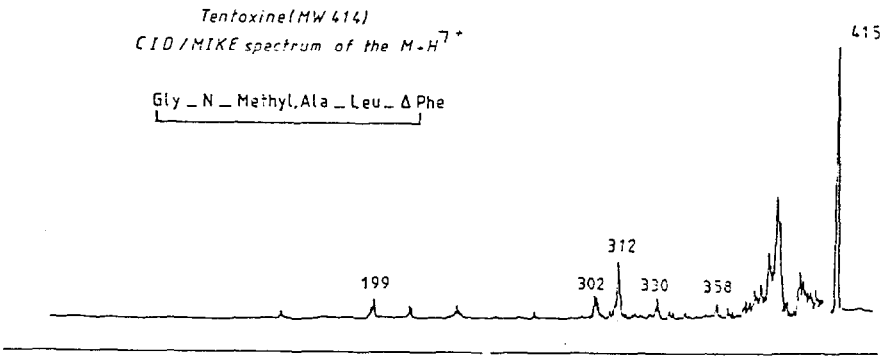
SUMMARY : CID/MIKE (or MIKE) spectrum of the quasi-molecular (or cationized) ion obtained by the MBSA-FAB method characterizes a polar compound.

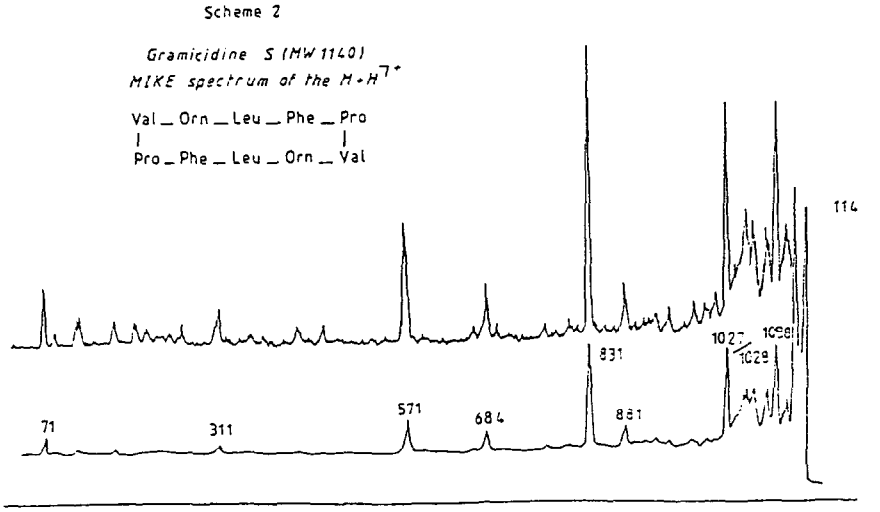
The possibilities of the mass spectrometer that we have constructed in order to characterize the polar compounds such as peptides, oligosaccharides and nucleotides by the use of the MBSA-FAB method have been established in previous works (1, 2, 3). We pointed out at the time having the intention of adding to our mass spectrometer a conventional geometry EB a third analyser in the form of an electric sector preceded by a collision chamber in order to be able to put to work the MS/MS technique permitting the identification of a compound in a complex mixture (4, 5, 6). We carried out this transformation : the length of the collision chamber is 35 mm and the gas used is argon. The characteristics of the electric sector are as follows : rotational angle : 90° and radius curvature : 200 mm. The other characteristics of our mass spectrometer have already been presented (2). Before presenting our results, we have to mention that the resolution obtained in the CID/MIKE spectra is necessarily limited by the liberation of the kinetic energy intervening during the fragmentations. However, the resolution of our mass spectrometer is more than the value 100, considered as a medium resolution observed in the CID/MIKE spectra obtained by means of a reversed geometry mass spectrometer (6).

The spectra of metastable ions and spectra of ions formed by collision (MIKE spectra, CID/MIKE spectra and spectra obtained by linked scan) were already used in the characterization of peptides (7, 8, 9, 10, 11, 12, 13, 14). One problem raised during these works : the peptides, polar compounds, are slightly volatile. It was overcame by three ways : the studied peptides having a reducced size can be ionized by the conventional methods (electron impact and chemical ionization) (7, 8, 9), the peptides are previously derived (8, 10) or a soft method of ionization was used : field desorption (11,12,13) and secondary ion mass spectrometry (14). We describe in this work the high possibilities which procure for the characterization of underived peptides and oligosaccharides the simultaneous use of the ionization method MBSA-FAB and the MIKE and CID/MIKE spectra (MS/MS technique). The studied polar compound is identified with

Scheme 1



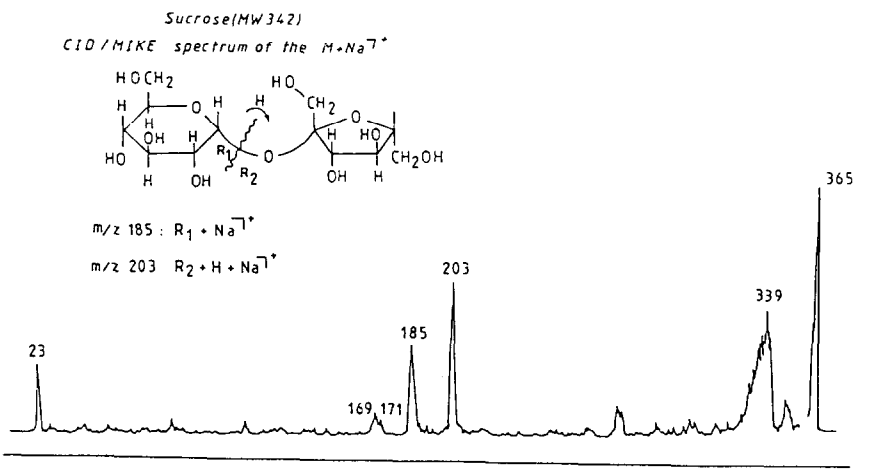
Scheme 2



the spectrum of a characteristic ion of the structure. The MBSA-FAB ionization method supplied us with a ions beam having a noticeable abondance during a long time (more than 30 minutes) : this is not the case when field desorption is used. We used for each compound 1 mg of substance. Compared with SIMS method, the MBSA FAB method shows two advantages : bombardment of sample with fast neutral atoms does not induce surface charging and acceleration voltage is limited. It is not necessary with MBSA-FAB method to prepare previous derivatives ; on the other hand, this is necessary when electron impact and chemical ionization are used. The use of MIKE and CID/MIKE spectra (MS/MS technique) allows us to obtain a spectrum in which the observed fragment ions are characteristic only of the studied structure. A consequence of the two dimensional aspect of the MS/MS technique is the following : when the studied compound is in a complex mixture, there is elimination of characteristic ions of other compounds.

Schemes 1, 2 and 3 represent the CID/MIKE (or MIKE) spectra of ions obtained by the MBSA-FAB method : $M + H^{+}$ from tentoxine (MW 414) and gramicidine S (MW 1140) and $M + Na^{+}$ from the mixture of sucrose (MW 342)- sodium chloride. Regarding tentoxine (scheme 1), one would notice by comparision with the already published MBSA-FAB spectrum (1), the presence in the two spectra of ions $\frac{m}{z}$ 358 ; $\frac{m}{z}$ 330 ; $\frac{m}{z}$ 312 ; $\frac{m}{z}$ 302 and $\frac{m}{z}$ 199. On the other hand, one cannot get much information from the CID/MIKE spectrum about the ions $\frac{m}{z}$ 273 ; $\frac{m}{z}$ 256 ; $\frac{m}{z}$ 217 and $\frac{m}{z}$ 143. If in the previous work, the whole observed ions had permitted the determination of structure of the tentoxine, the ions found in the CID/MIKE spectrum would enable one only to identify the four aminoacids : Gly ($\frac{m}{z}$ 358 : 415-57); N-Methyl Ala ($\frac{m}{z}$ 330 : 415-85); Leu ($\frac{m}{z}$ 302 : 415-113); Δ-Phe ($\frac{m}{z}$ 199 : 415-159-57) and to show the chaining Δ-Phe-Gly. Hence two structures are possible for this cyclic tetrapeptide according to the CID/MIKE spectrum following the availiability of Leu and N-Methyl Ala respectively.

Scheme 3



In the spectrum of the $M + H^{+}$ ion of gramicide S (scheme 2), one can notice with differing abundances the ions $\frac{m}{z}$ 831 ; $\frac{m}{z}$ 684 ; $\frac{m}{z}$ 571 and $\frac{m}{z}$ 311 which hald already occur in the MBSA-FAB spectrum (1). These ions permit the establishement of chaining Pro-Val-Orn

and the presence of two Leu and of two Phe. On the other hand, one can notice in the MIKE spectrum two ions which did not appear in the MBSA-FAB spectrum (1) : $\frac{m}{z}$ 1027 and $\frac{m}{z}$ 881. These high mass ions are very significant in the structure and allowing to demonstrate Orn ($\frac{m}{z}$ 1027 : 1141-114) or Leu ($\frac{m}{z}$ 1028 : 1141-113) and the chaining Leu-Phe ($\frac{m}{z}$ 881 : 1141-113-147).

The CID/MIKE spectrum of the M + Na^{+} ion $\frac{m}{z}$ 365 obtained from the mixture of sucrose-sodium chloride presents as well as the sodium ion : $\frac{m}{z}$ 23 two ions available : $\frac{m}{z}$ 203 and $\frac{m}{z}$ 185 ; the formation of which is explained in scheme 3. These two ions caractérize two complementary parts of the sucrose molecule ; the migration of hydrogen was already considered in order to interpret the spectrum obtained by chemical ionization of a similar compound (15).

Now, it is possible for us to characterize a polar compound by the spectrum of a characteristic ion of the structure with the mass spectrometer which we built. We are going to analyse complex mixtures of peptides, oligosaccharides, oligonucleotides and more generally polar compounds.

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