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Direct Analysis of Nicotelline from Tobacco by MS with DADI/MIKE Spectrometry

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Abstract □ Nicotelline was directly analyzed from the crude tobacco extract by metastable studies. The metastable transitions of nicotelline were investigated by MS with DADI/MIKE spectrometry.

Keywords □ Nicotelline, DADI/MIKE spectrometry, Metastable transitions

Earlier studies by traditional chromatographic and spectroscopic methods revealed a number of alkaloids in tobacco and alkaloids isolated from a variety of tobacco species are either bicyclic or tricyclic nitrogenous compounds[1,2]. But detection of nicotelline, a tricyclic tobacco alkaloid, is somewhat difficult because of its low volatility and minute content in tobacco.

The object of this research is to detect nicotelline from crude tobacco extract by metastable studies. In the present work, metastable studies were performed by Direct Analysis of Daughter Ions (DADI) or Mass Analyzed Ion Kinetic Energy (MIKE) spectrometry[3].

A very exciting feature of mixture analysis by DADI/MIKE spectrometry is its ability to identify components in very complex mixtures like plant tissue extracts and biological fluids[4]. In this connection the following features of the method are of outstanding interest: sensitivity, minor restrictions of low temperature stability of the samples as compared with combined gas chromatography/mass spectrometry, and the time required for the workup procedure.

The DADI/MIKE spectrometry obtained gives information on the reactions of ions which have little excess energy (between 0 and 20 kcal/mol) above the transition state for unimolecular dissociation, due to the relatively long life time (ca. 10^{-5} s) after the formation of the reacting species[5].

In practical DADI/MIKE spectrometry, one particular ion (m/e 233 for nicotelline) can be selected by tuning the magnetic field and the pure metastable spectrum recorded by automatic variation of the electrostatic analyzer (ESA) voltage from the initial value (E_o) downwards. Each metastable peak arises from unimolecular decompositions in the second drift region between magnetic and electrostatic sector field in a reversed Nier-Johnson geometry MS and occurs at an ESA voltage, E, which allows the assignment of parent (m_M) and daughter (m_D) mass numbers using the relationship $m_D = m_M E/E_0$.

DADI/MIKE spectrum of nicotelline is shown in Fig. 1. The peak at m/e 207 (M^+-26) is formed by the loss of -CN. The metastable peaks at m/e 155 (M^+-78) and m/e 128 (m/e 155-HCN) give important structural information for the identification of tracing nicotelline (Fig. 2). And the identification of nicotelline on the basis of its DADI/MIKE spectrum was confirmed by to compare with the conventional mass spectrum[6] of purified nicotelline.

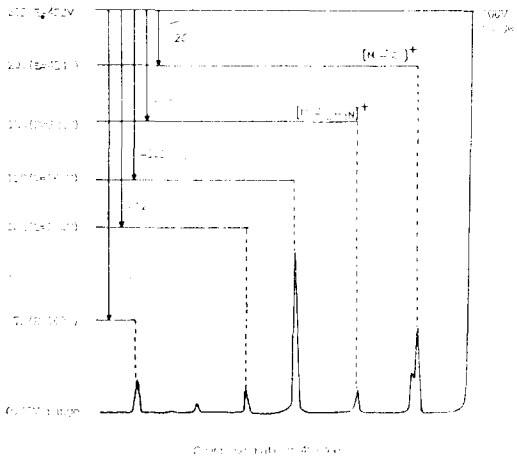

Fig. 1: DADI/MIKE spectrum of nicotelline.

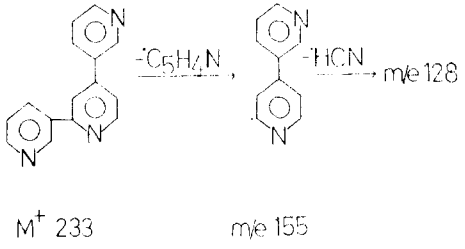

Fig. 2: Fragmentation pathway of nicotelline.

As such an analysis is very simple, it is especially suitable for the systematic search for distinct compounds. And an amount fo the order of 10^{-4} to 10^{-6}g should suffice to produce the highly specific DADI/MIKE spectrum.

EXPERIMENTAL METHODS

Only 1g of dry tobacco leaf powder was used for the analysis. The alkaloids were extracted with hexane-10% NaOH (1 : 1) mixture. After evaporation of the solvent the mixture containing alkaloid was analyzed directly DADI/MIKE spectrometry without further workup.

DADI/MIKE spectrometry was performed on a Varian MAT 212 double focusing MS with reversed Nier-Johnson geometry. Metastable transitions in the second drift region were observed at a nominal 70 eV and 3 kV accelerating voltage, varying the ESA voltage downwards according to the DADI/MIKE spectrometry. The sample was introduced via the direct inlet system with cooled sample probe. The ion source temperature was 250°C. The scanned ESA voltage was continuously checked by a Hewlett-Packard digital voltmeter and the DADI/MIKE spectrum was recorded on a Kipp and Zonen Model BD 40 recorder.

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