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DETECTION OF MOLECULAR IONS OF THERMALLY UNSTABLE COMPOUNDS BY IN BEAM ELECTRON IMPACT

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Some remarkable characteristics of "in beam" electron impact spectra of several thermally unstable compounds have been reported. The spectra almost always exhibited the M+1 peak in place of M. Intensities of M+1 peaks of several thermally unstable compounds, of which molecular ion peaks are not observed with conventional direct inlet systems, are reported.

In the course of an investigation of echinomycin structure Williams and his co-workers obtained its complete spectrum which showed the molecular ion peak at m/e 1100, using a modified electron impact technique called "in beam" electron impact.[1] Though the technique seems to be highly competent for obtaining mass spectral information of least volatile or thermally unstable compounds, no information on the characteristics of "in beam" EI spectra has been reported.[2] In order to reveal the general characteristics of the in beam EI spectrometry we devised an in beam inlet system using a conventional direct inlet probe of Hitachi RMU-6M single focusing mass spectrometer and examined several in beam EI spectra of thermally unstable compounds, of which molecular ion peaks were hardly identified by means of an ordinary direct inlet probe.

To obtain in beam EI spectra a method similar to Williams' was employed, i.e., a sample was loaded on a top of the quartz tip of a modified direct inlet probe and inserted gently until the electron beam was interrupted. Spectra were then recorded immediately. In the case of D-glucose, measuring conditions such as source temperature, ionization voltage, sample position and time factor of the fragmentation pattern were examined. All these factors affected the relative intensity of each peak to some extent but its position was unchanged. Useful spectra were obtained with the use of the ionization voltage at 10-20 eV and the source temperature at 130-200°C. As an example Fig. 1 represents the 10 eV spectrum at the source temperature of 180°C. Peaks at m/e M+1, M+1-18, M+1-32, M+1-18-18, 73 and 60 were observed. The in beam EI spectrum changed gradually as time passed after the insertion was completed and consequently a spectrum similar to that taken by the use of a conventional direct inlet source was obtained.

In beam EI spectra so far studied almost always exhibited the M+1 peak in place of M. The complete spectrum was apparently a combination of a conventional EI spectrum and some conspicuous peaks from the high mass region. The spectral features were somewhat similar to those obtained from closed source instruments.[3]

Although the relative abundance of each peak was sensitive to electron bombardment conditions, peak positions in the molecular ion region were clearly ascertained. Intensities of M+1 peaks of several thermally unstable compounds, of which molecular ion peaks are difficult to be identified by the use of a conventional direct inlet probe, are listed in the Table. This technique is, however, inferior to FD[4] in the detection of M+1 ions of extremly unstable compounds such as creatine of which in beam spectrum exhibited no M+1 but M-18 peak.[5] Even though the in beam EI is not so powerful as FD to detect M+1 ions, the technique is easily achieved by a simple modification of an ordinary direct inlet probe and obviously adds very important mass spectrometric information of relatively involatile or thermally unstable compounds.

Table. Intensities of M+1 peaks examined by in beam EI

Compound	Ionization voltage(eV)	Source temp(°C)	Base peak	M+1 peak (rel. int.%)	signal/ noise
D-Xylose	10	180	73	151(1.4)	~20
L-Fucose	10	180	143	165(1.6)	~10
Saccharose	10	240	163	343(0.6)	~10
Adenosine	10	250	164	268(40)	>100
Guanosine	10	240	151	283(M, 5.9)	~60
Inosine	10	240	136	269(2.0)	>100
Ephedrin-HCl	10	180	58	166(16)	>100
N-Methylephedrine	20	180	72	180(14)	>100
Quinine	20	230	136	325(11)	>100
L-Glutamic acid	20	180	83	148(3.8)	>100
Glucosamic acid	10	250	99	196(4.0)	~20

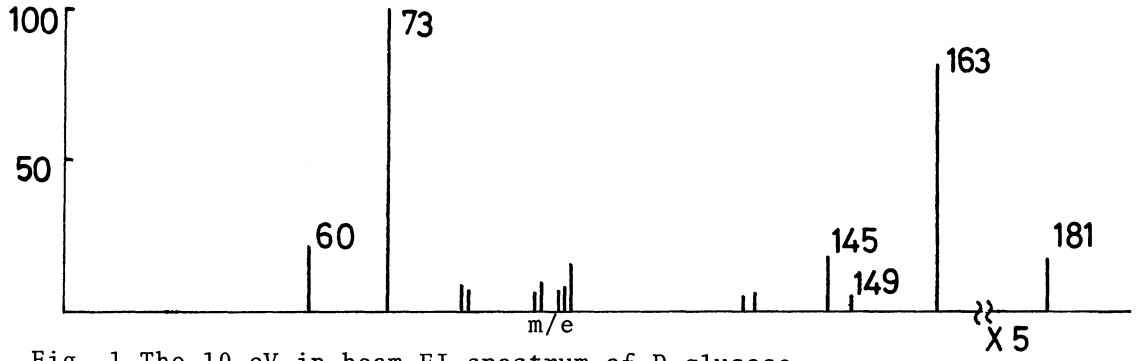

Fig. 1. The 10 eV in beam EI spectrum of D-glucose, source temperature 180°C.

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