

SpiralTOF-TOF

High-Energy CID MS/MS Analysis of Small Organic Molecules

Introduction

The JMS-S3000 SpiralTOF™ is a MALDI-TOF MS that uses an innovative spiral ion optics system to achieve the highest resolution currently available for a MALDI instrument. As a result, small organic molecules can be analyzed on this system with minimal interferences from the matrix peaks. Additionally, the JMS-S3000 is available with a TOF-TOF option that can acquire high-energy collision-induced dissociation (CID) product ion spectra for monoisotopically selected precursor ions. In this work, we analyzed several small organic molecules by using the JMS-S3000 with the TOF-TOF option.

Results and Discussion

The proline sample was measured using positive ion mode which produced an $[M+H]^+$ ion at m/z 116. This ion was monoisotopically selected as the precursor ion for TOF-TOF analysis. The resulting high-energy CID

product ion spectrum is shown in Fig. 2a. The overall MS/MS spectrum was very simple for this sample with the low mass ions m/z 43 and m/z 70 attributed to the fragments shown in Fig. 3.

[Samples]
Compound1 Proline
Compound2 Stearic acid

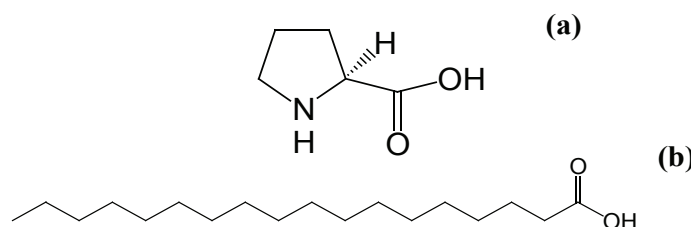


Figure 1. Structural formula of (a) Proline and (b) Stearic acid.

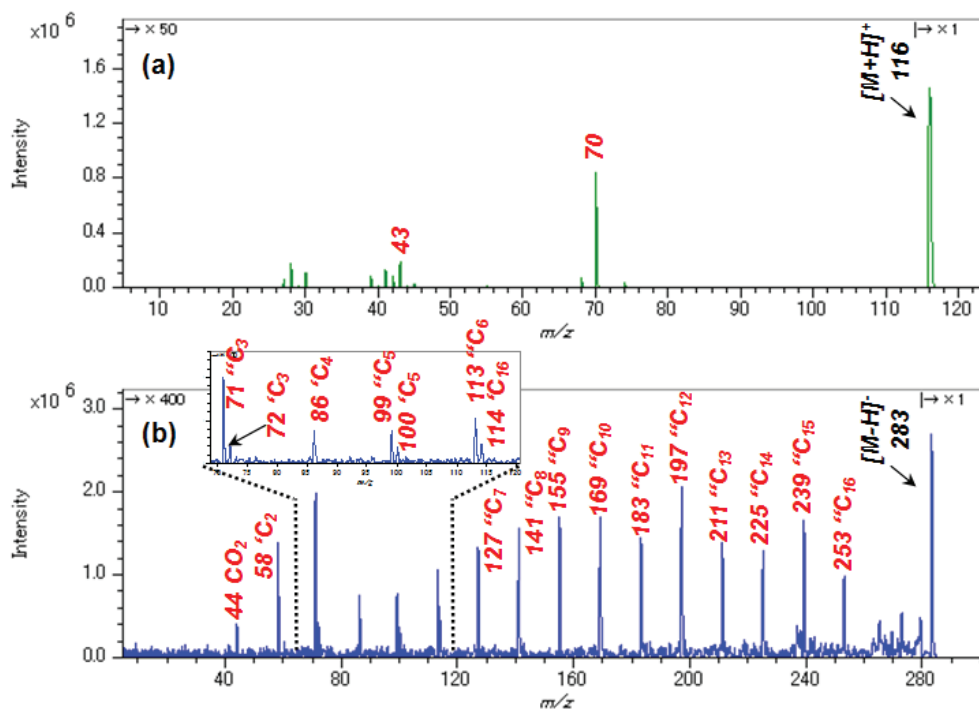


Figure 2. Product ion spectra of (a) Proline (m/z 116 $[M+H]^+$) and (b) Stearic acid (m/z 283 $[M-H]^-$).

The stearic acid sample was then measured using negative ion mode which produced an $[M-H]^-$ ion at m/z 283. This ion was monoisotopically selected as the precursor ion for TOF-TOF analysis. The resulting high-energy CID product ion spectrum is shown in Fig. 2b. This spectrum showed a mass spectral pattern that was attributed to charge remote fragmentation (CRF) by high-energy CID. CRF occurs during CID when the charge is localized to a particular location on the molecule (in this case on the $-COO^-$) and the bonds that are cleaved are located at positions away from this charge.^{1,2} This technique is very useful for structural analysis. Fig. 4 shows the identity of each peak based on the overall structure of stearic acid.

Conclusions

The JMS-S3000 “SpiralTOF” with TOF-TOF option can be used to measure both the $[M+H]^+$ and $[M-H]^-$ precursor ions even for small organic molecules. Furthermore, this technique can be used to acquire high-energy CID product ion spectra that show CRF which involves the systematic cleavage of C-C bonds within the molecular structure.

Reference

- 1) W. J. Griffiths, Y. Yang, J. A. Lindgren, and J. Sjövall, *Rapid Commun. Mass Spectrom.*, 10, 21-28, (1996).
- 2) M. Gross, *Int. J. of Mass Spectrom.*, 200(1-3), 611-624, (2000).

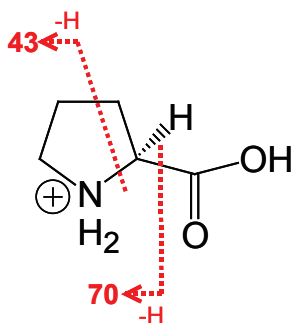


Figure 3. Fragment ions of Proline (m/z 116 $[M+H]^+$).

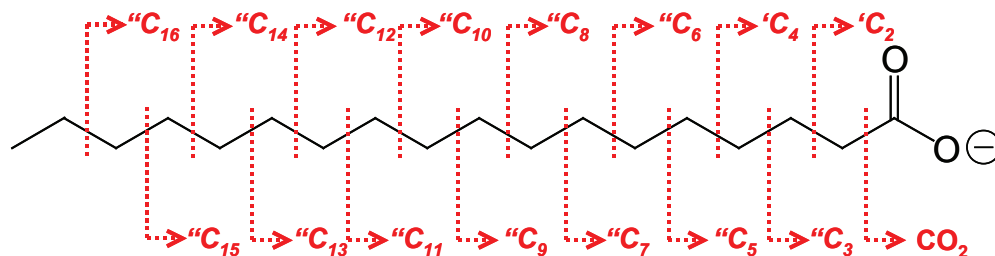


Figure 4. MASCOT MS/MS Ion search result of tBSA by TOF-TOF mode.