

# Rapid Characterization of Alkaloids using Probe ESI Q-TOF LCMS-9050 in OAD-MS/MS

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## 1. Introduction to OAD-MS/MS

- While low-energy CID-MS/MS is one of the most effective fragmentation techniques for structural analysis, it may not be ideally suited for the analysis of certain isomers.
- Several novel fragmentation techniques have been proposed to complement low-energy CID-MS/MS.

Table 1. Example of proposed novel fragmentation techniques

### Electron-based fragmentation

EIEIO, ECD(Electron Capture Dissociation) by Zubarev et al. (1996)

### Anion-based fragmentation

ETD(Electron Transfer Dissociation) by Syka et al. (2004)

### Photon-based fragmentation

IRMPD (Infrared), UVPD (Ultraviolet), BRID (Blank body infrared)

- We have introduced **neutral radical-based** fragmentation techniques to structural analysis of biomolecules, peptides and lipids, since 2016.

**Neutral radical-based** \*Takahashi et al., *Anal. Chem.* 2018, 90, 12, 7230.

Charge-neutral radical-induced dissociation is available in both positive and negative ion modes!

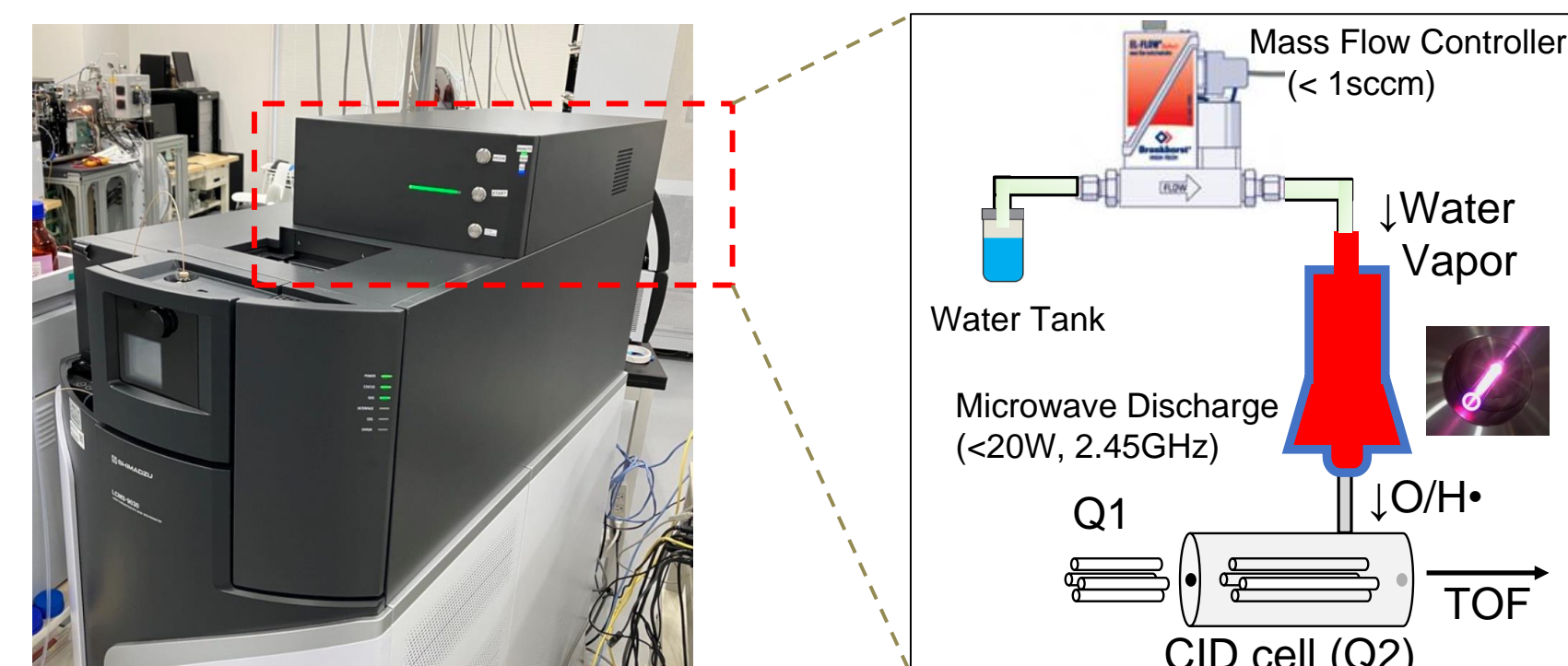
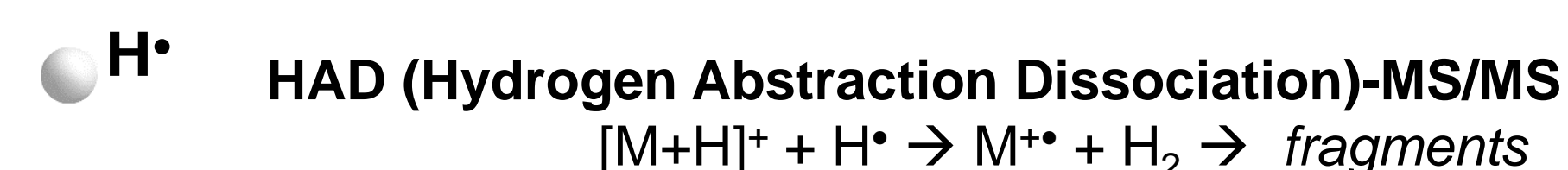
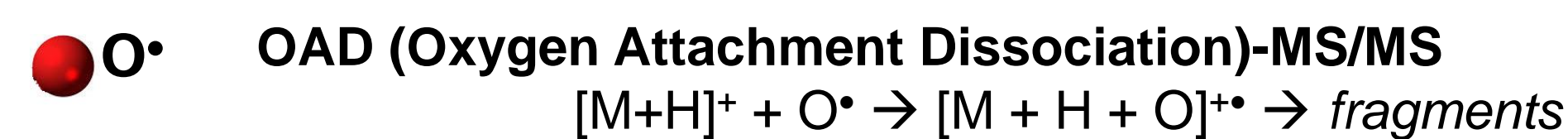


Fig. 1. Shimadzu LCMS-9050 (Q-TOF) with OAD unit.

## 2. Introduction to a direct ionization of PESI

- Probe Electro Spray Ionization (PESI) is one of the direct ionization techniques. Fig. 2 shows the scheme of the PESI system.

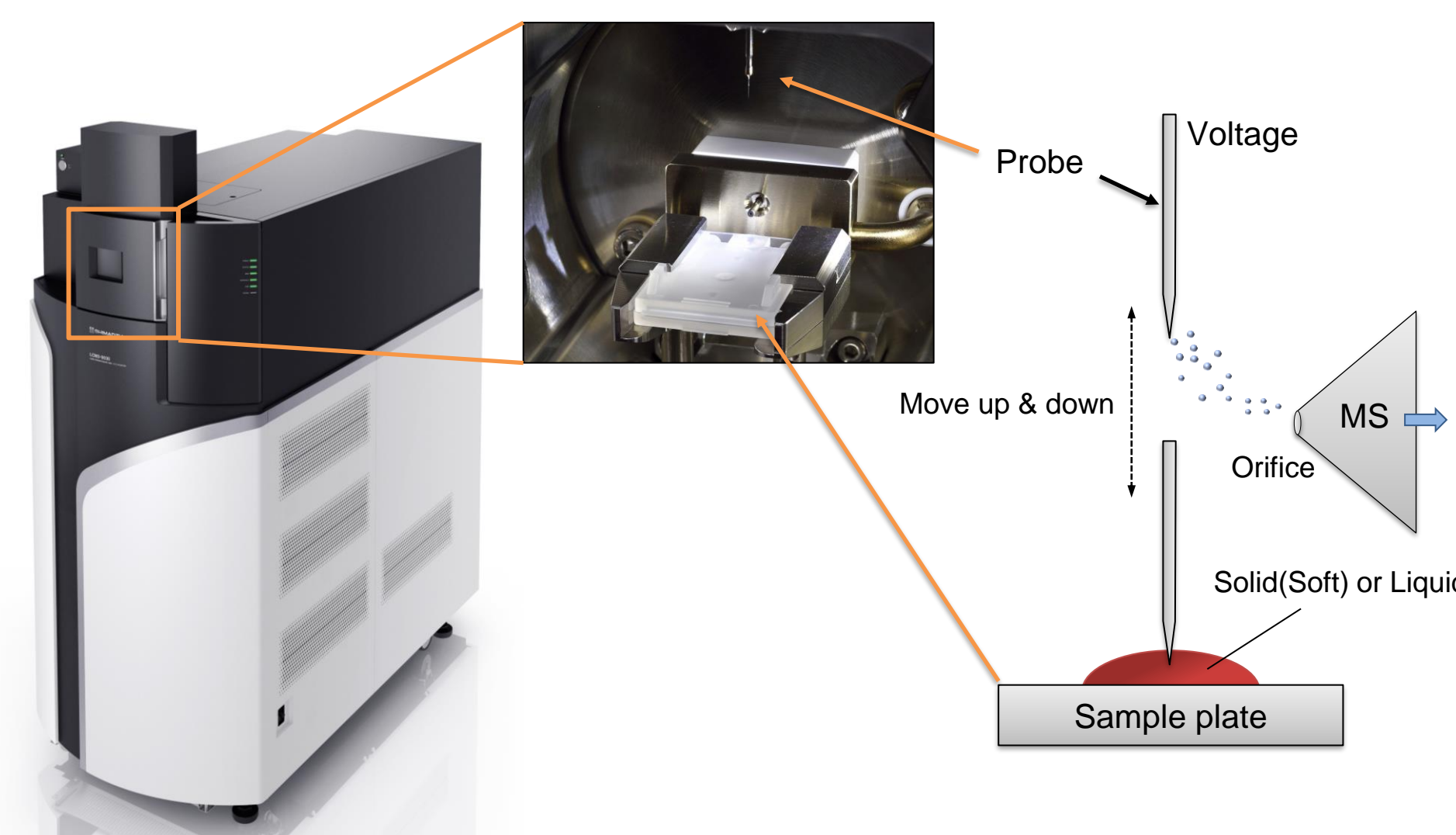


Fig. 2. Schematic diagram of the DPiMS™ QT system.

## 3. PESI-OAD Synergistic Lipid Analysis

Check WP019

- OAD-MS/MS reveals double-bond (C=C) positions not accessible with CID-MS/MS. Atomic oxygen selectively oxidizes and cleaves at C=C.

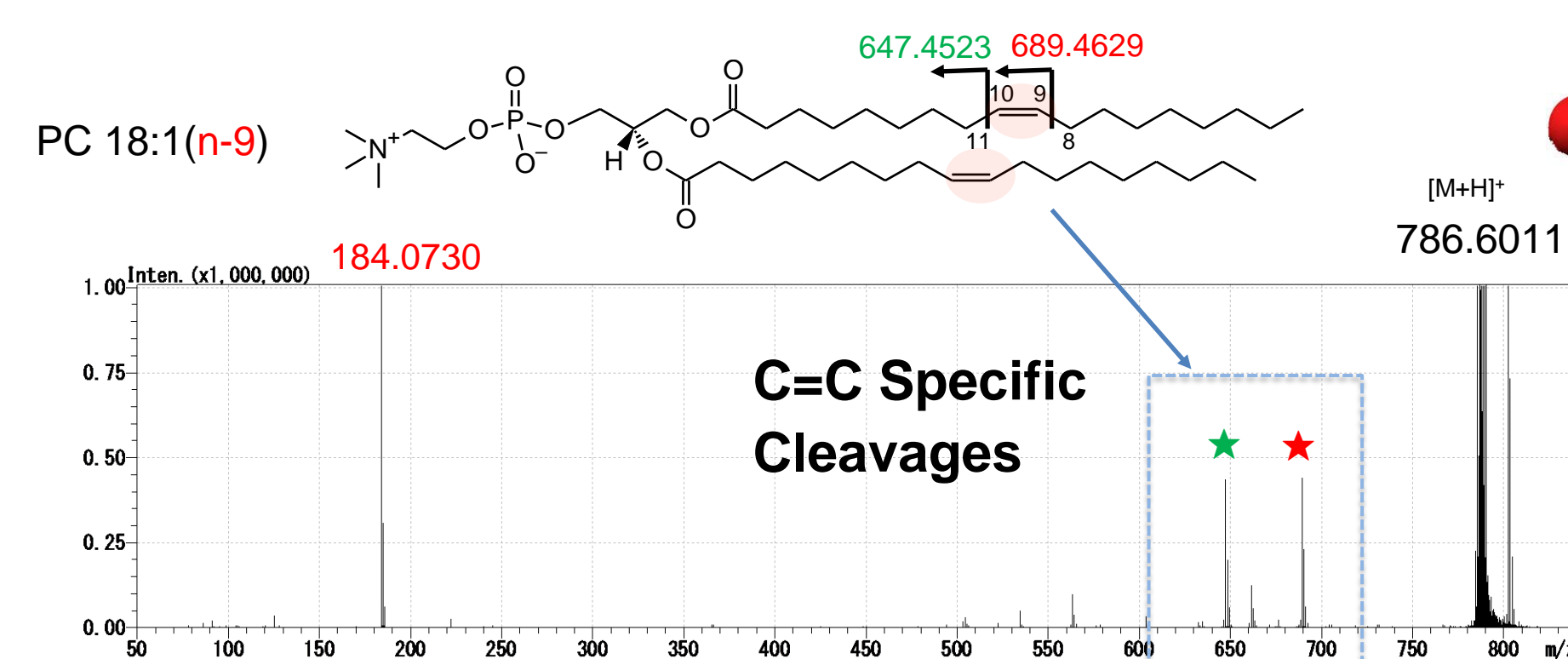
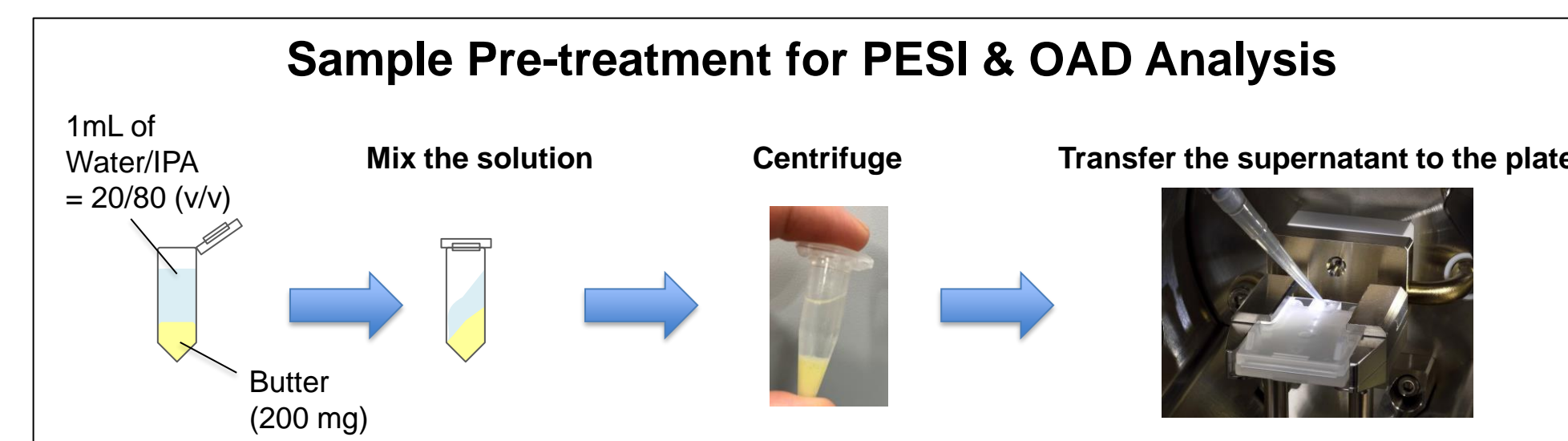


Fig. 3. Typical OAD spectrum of a model lipid of PC (18:1).

## 4. PESI-OAD Synergistic Alkaloids Analysis

- Atomic oxygen selectively oxidizes carbon atoms adjacent to nitrogen in nitrogen-containing heterocycles, leading to OAD-specific fragmentation distinct from CID, as shown in Fig. 4 ( $m/z$  450.2127).

### Scheme 1. Proposed OAD mechanism of nitrogen-containing heterocycles

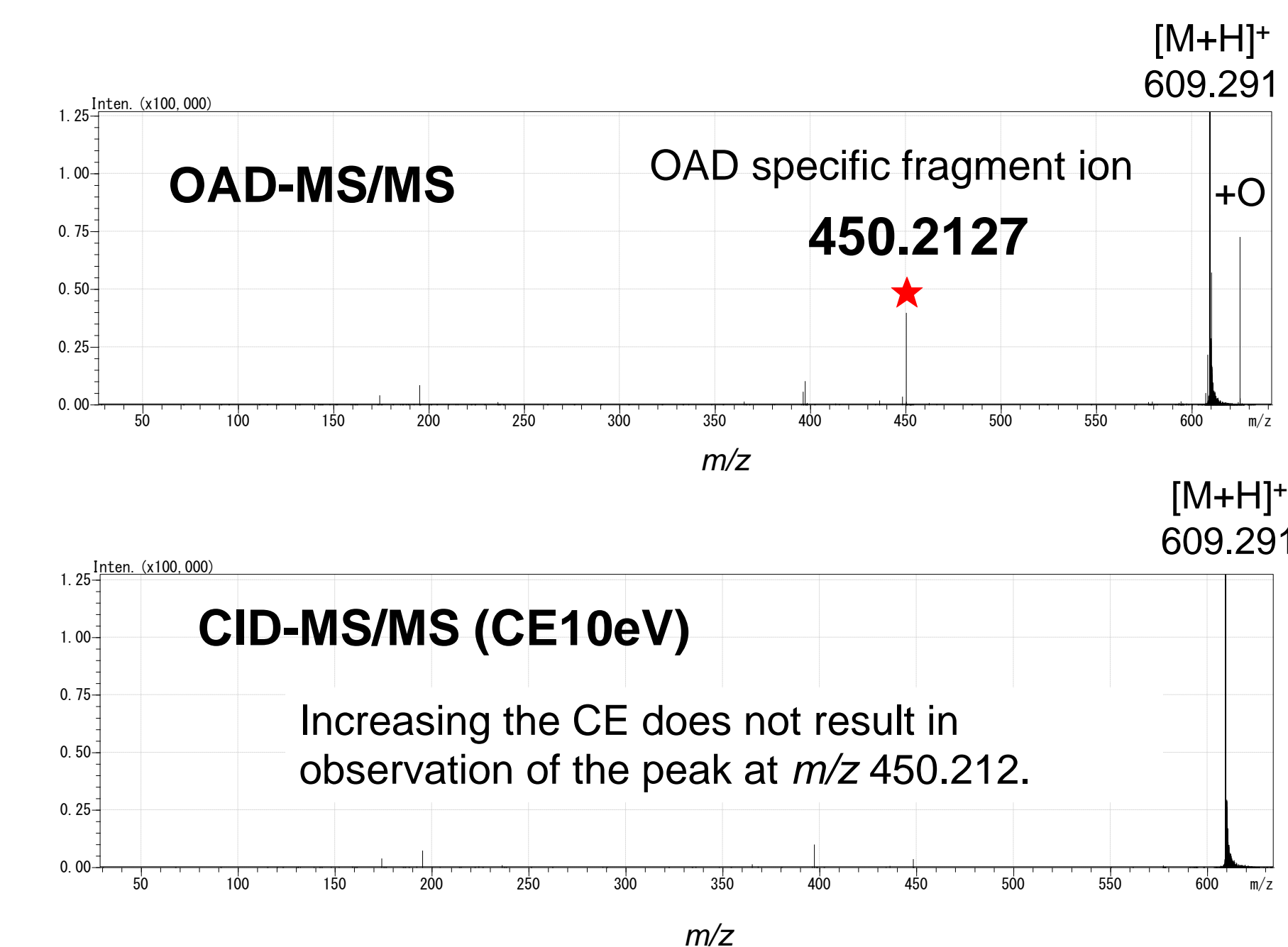
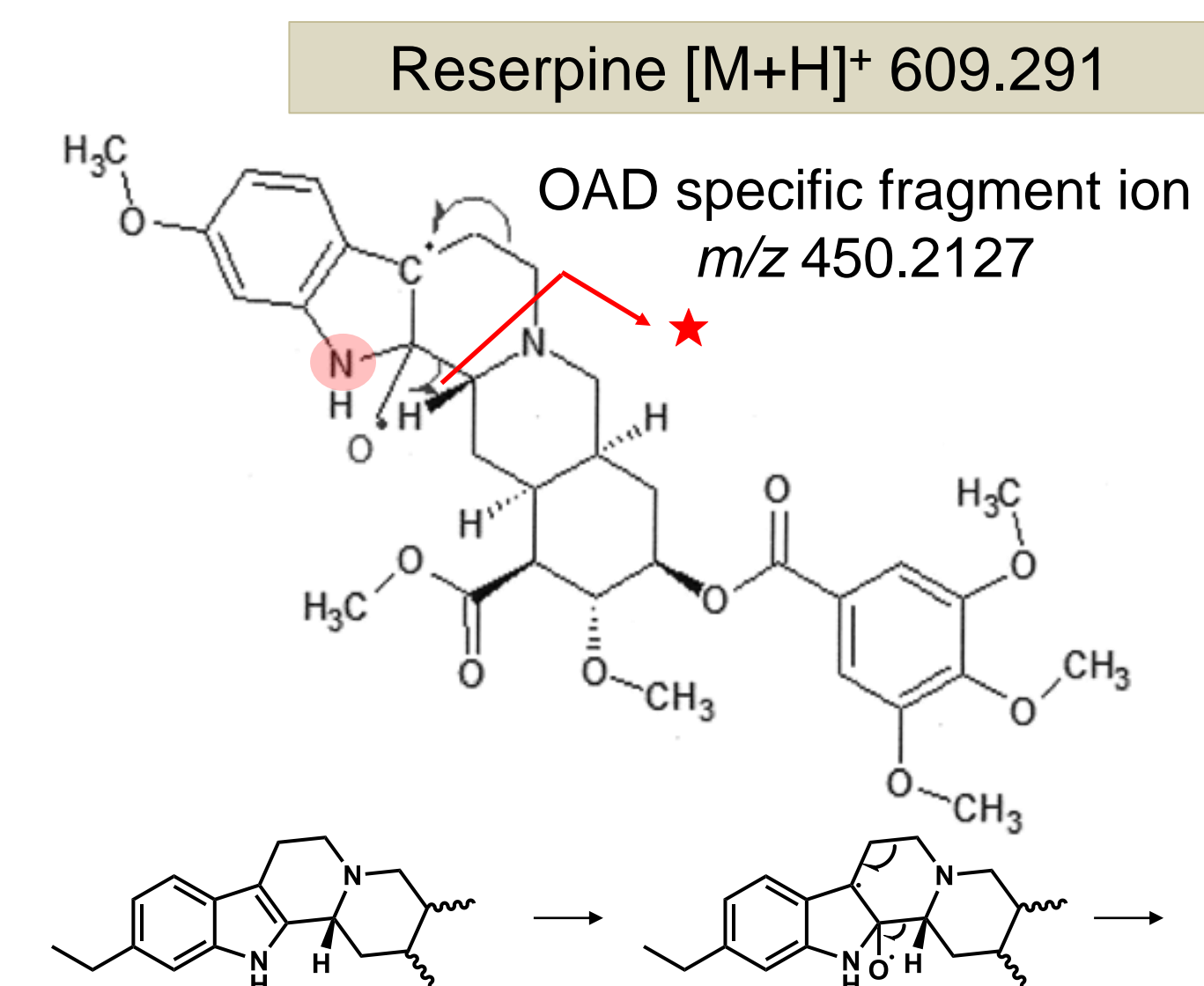
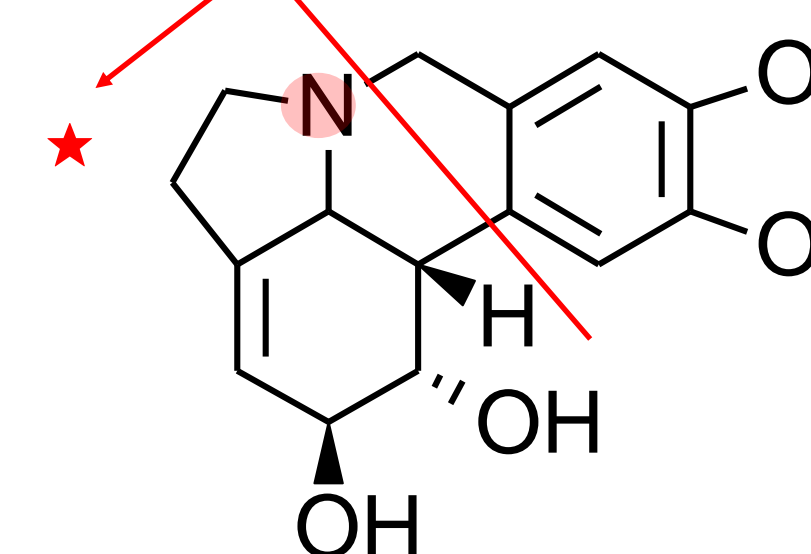


Fig. 4. OAD and CID spectra comparison of reserpine.

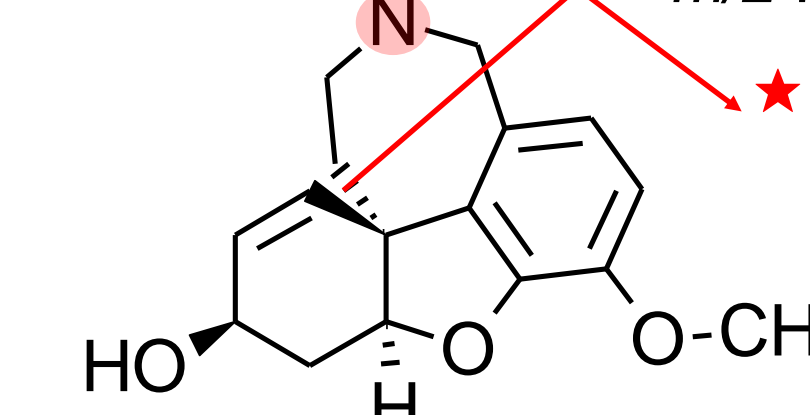
Lycorine  $[M+H]^+$  288.123

OAD specific fragment ion  $m/z$  154.086



Galantamine  $[M+H]^+$  288.159

OAD specific fragment ion  $m/z$  72.081



Solanine  $[M+H]^+$  868.505

OAD specific fragment ion  $m/z$  150.127

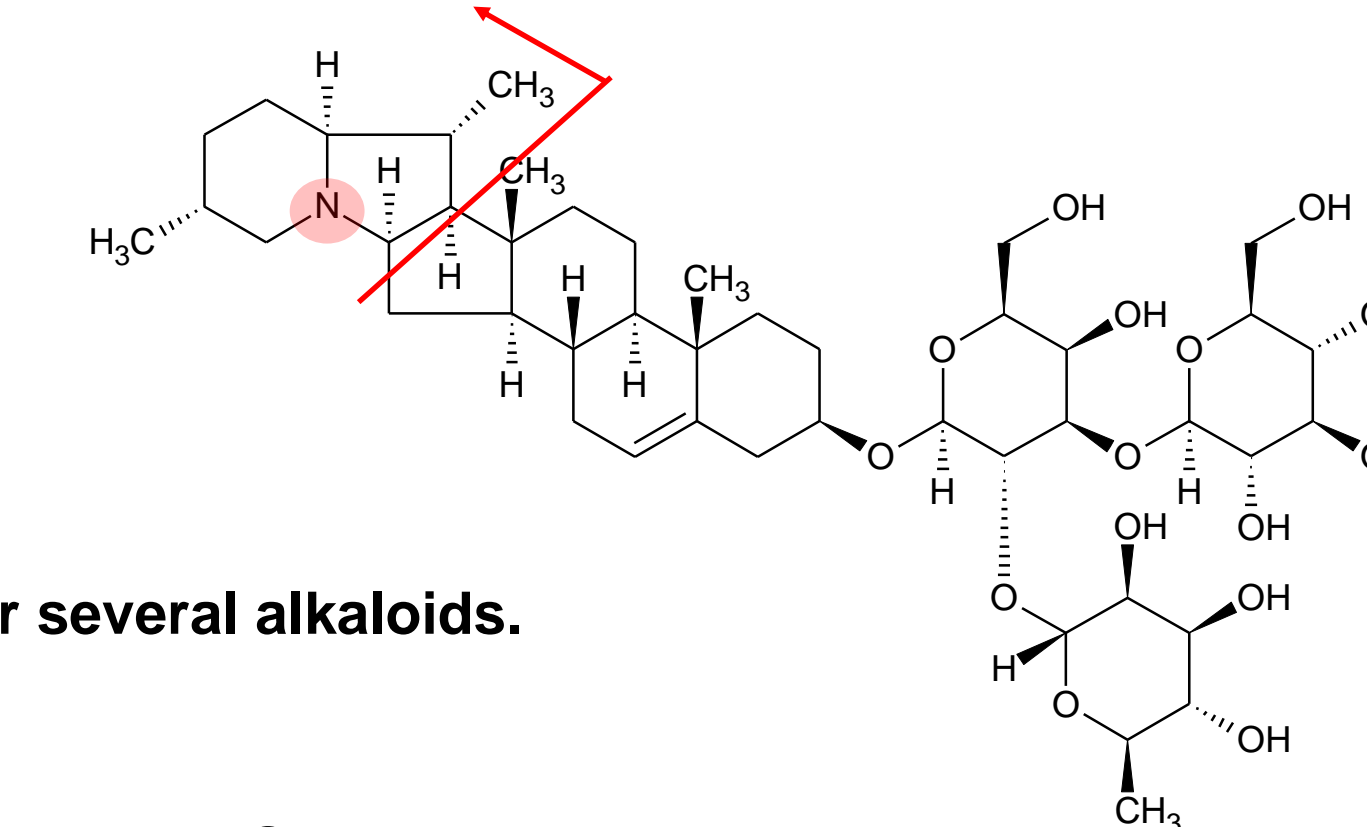


Fig. 5. Example of OAD specific fragmentation for several alkaloids.

## 5. Conclusions

- We have successfully developed the LCMS-9050 system integrating OAD and PESI.
- OAD provides unique structural information on nitrogen-containing heterocycles, which is distinct from CID, particularly observed in alkaloids.
- OAD specific fragment ions observed in alkaloids offer the potential for rapid characterization of alkaloids.

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