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Application News

Probe Electrospray Ionization Kit
Quadrupole Time-of-Flight Liquid Chromatograph Mass Spectrometer

Evaluation of Tissue-Specific Plant Metabolites Using Probe Electrospray Ionization Kit and LC-MS

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User Benefits

- Intuitive operation allows for the simple detection of metabolites from complex and minute parts of plant tissue.
- Enables high-throughput analysis since metabolites adhering to the probe are ionized directly, and column separation is unnecessary.
- Applicable to various functional components.

■ Introduction

Plants contain numerous components related to color, taste, and functionality, which exhibit their functionality by being localized in specific parts of the plant. Detecting each component from the complex and minute parts of plants with high sensitivity requires many samples and time. Thus, there is a demand for simple and rapid analytical systems for micro-regions. So far, a detection system for anthocyanins in plants using probe electrospray ionization[1)] (PESI) and triple quadrupole LC-MS has been developed, demonstrating the utility of PESI in plant analysis[2)]. In PESI, the probe moves up and down while voltage is applied to the tip, ionizing the sample adhered to the probe surface and directly introducing it into the mass spectrometer. This article introduces an analytical method focused on localizing plant metabolites using PESI and quadrupole time-of-flight (QTOF) mass spectrometer. This method allows for intuitive and rapid sampling with the probe while enabling accurate mass spectrometry with TOF.

■ Sampling and Analytical Conditions

Strawberry fruits were obtained from a grocery store. Sansho (Japanese pepper) fruits were harvested at the production site and stored frozen. For the strawberries, a dedicated probe was inserted for about one second into areas with different coloration in the surface achenes (seed-like fruits) and in the receptacle (flesh) (Fig. 1A). For the sansho, the probe was inserted into the surface secretory cavities (organs that accumulate aromatic components) and the nearby pericarp (Fig. 1B). A total of 10 µL of solvent (50% isopropanol aqueous solution) was added to a dedicated plate well, and the probe with the sampled material was placed into the PESI unit.

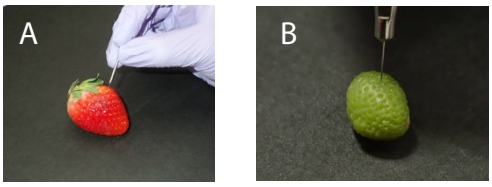

Fig. 1 Sampling of Metabolites in Fruit Parts Using a Probe
(A: Strawberry, B: Sansho)

The probe electrospray ionization kit DPiMS™ QT and the QTOF mass spectrometer LCMS-9030 were used for the analysis. The analytical conditions are shown in Table 1. MS was performed in positive mode, and Data Dependent Acquisition (DDA) for MS/MS was performed. The obtained data were analyzed using LabSolutions Insight Explore™, with composition estimation and online searches based on the ChemSpider database.

Table 1 Analytical Conditions

System	DPiMS QT + LCMS-9030
Polarity	Positive
DL temp	250 °C
Heat block temp	50 °C
Interface voltage	3.5 kV
Mode	Data Dependent Acquisition (DDA)
TOF-MS (Strawberry)	MS *m/z* 50-1000, MS/MS *m/z* 10-1000
TOF-MS (Japanese pepper)	MS *m/z* 50-300, MS/MS *m/z* 10-300
Measurement Time	0.1 min (Strawberry), 1.0 min (Sansho)

■ Metabolite Profiles of Strawberry Fruit Parts

The mass spectra obtained from the analysis of strawberry fruits are shown in Fig. 2. Peaks corresponding to hexoses (Hex) and disaccharides (Hex_2), which are representative sugar components of strawberry fruits, as well as citric acid, a typical organic acid, were detected in the receptacle, regardless of coloration. In the colored receptacle, the anthocyanin pelargonidin-3-hexoside (Pel-3-Hex) was specifically detected. In contrast, peaks for hexoses and organic acids were almost undetectable from the red achenes, while anthocyanins cyanidin-3-glucoside (Cya-3-Hex) and Pel-3-Hex were detected. The mass errors in composition estimation were all within 0.32 mDa, indicating high mass accuracy. The anthocyanin profile was consistent with previous reports[2)], demonstrating that specific molecular species are localized in each part.

■ Metabolite Profiles of Sansho Fruit Parts

The mass spectra obtained from the analysis of sansho fruit are shown in Fig. 3. Peaks estimated to be sanshool and hydroxy-sanshool, the pungent components of sansho[3)], were detected in the secretory cavities. On the other hand, a slight peak of hydroxy-sanshool was detected in the pericarp near the secretory cavities. The mass errors for the sanshool components in the composition estimation were all within 0.59 mDa, indicating high mass accuracy. The results suggest that sanshool components are mainly localized in the secretory cavities.

■ Conclusion

In this article, we conveniently sampled metabolites from micro-regions of fruits using the provided probe and rapidly detected them with a system combining DPiMS QT and LCMS-9030. The sampling time was approximately 1 second, and the measurement time was up to 1 minute, allowing for structural estimation with high mass accuracy. Furthermore, even when sampling from the same area, the mass spectra profiles may vary depending on the solvent added to the plate (data not shown). By optimizing the sampling and analytical conditions according to the plant species, its parts, and the target metabolites, the system is expected to find use in a variety of applications.

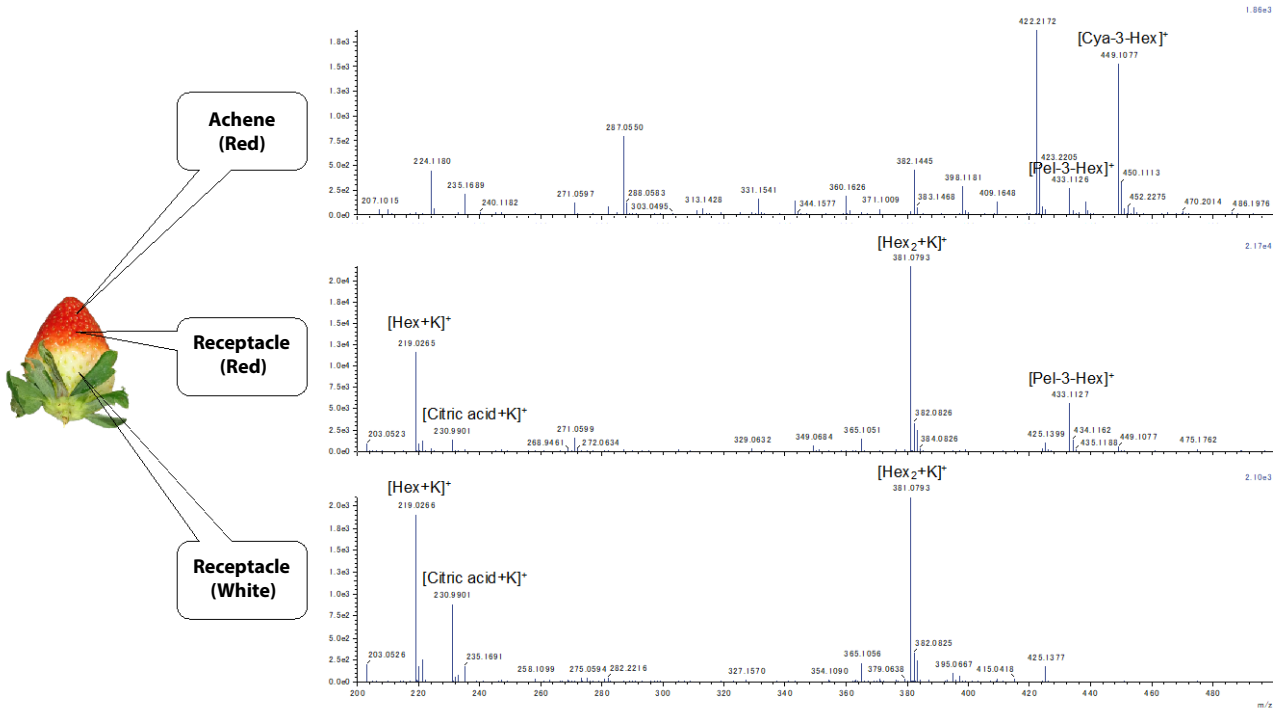

Fig. 2 Mass Spectra of Strawberry Fruit Parts
From top to bottom, the colored part of the achene, the colored part of the receptacle, and the non-colored part of the receptacle are shown.
The range of *m/z* 200-500 is displayed.

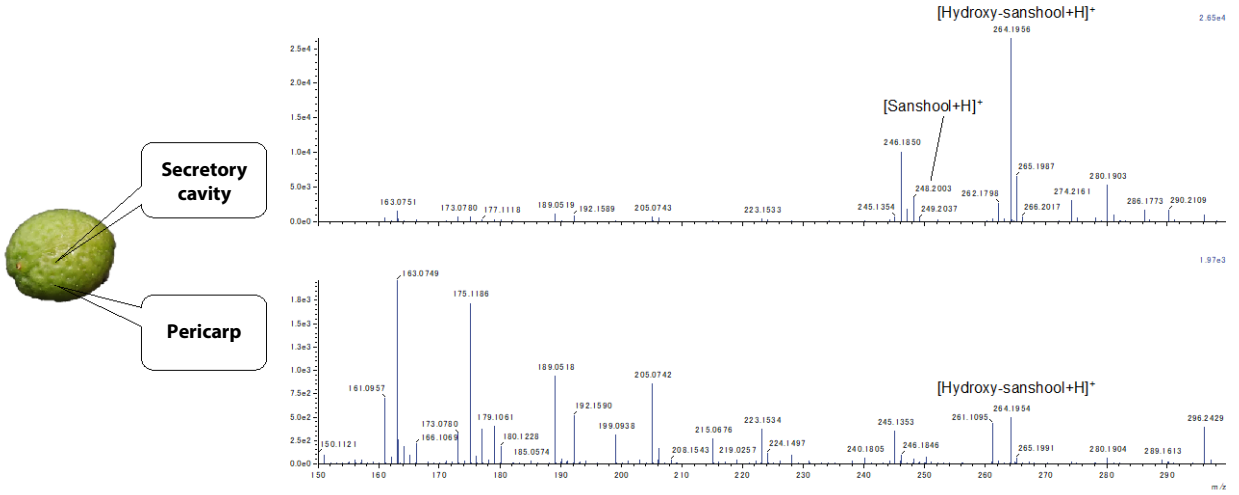

Fig. 3 Mass Spectra of Sansho Fruit Parts
From top to bottom, the secretory cavity and the pericarp near the secretory cavity are shown. The range of *m/z* 150-300 is displayed.

<References>

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2) Ishibashi, M., Zaitsu, K., Yoshikawa, I., Otagaki, S., Matsumoto, S., Oikawa, A. & Shiratake, K., Hort. Res. 10 (2023), uhad039.
3) Luo, J., Hou, X., Li, S., Luo, Q., Wu, H., Shen, G., Gu, X., Mo, X. & Zhang, Z., Food Chem. X 14 (2022), 100342.

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