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Application News

MALDI Time-of-Flight Mass Spectrometer

Determination of Authenticity of Manuka Honey Using the MALDI-8030 Benchtop Linear MALDI-TOF Mass Spectrometer

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User Benefits

- Simple and rapid method to detect the key polyphenol markers in Manuka honey.
- Minimal sample preparation and fast analysis on an affordable, easy-to-use benchtop MALDI-TOF system.
- The proposed workflow can be used to rapidly screen the authenticity of Manuka honey products.

■ Introduction

Manuka honey is produced by bees using nectar from the Manuka tree *Leptospermum scoparium* (Figure 1). There are reported health benefits and qualities associated with Manuka honey including antimicrobial activity, antioxidant and anti-inflammatory properties. Given the criteria that must be met in order for a honey product to qualify as 'Manuka honey', the number of producers and yield of Manuka honey is lower than that of regular non-Manuka honey. As a result, Manuka-certified honey products attract a price-premium making them obvious targets for adulteration and misrepresentation. MALDI-TOF mass spectrometry has several advantages for high-throughput screening applications. Here, we evaluate for the first time the use of MALDI-TOF MS to detect and characterise key Manuka honey markers allowing the differentiation of Manuka/non-Manuka products.

■ Measurement Conditions and Samples

Honey products labelled as 'Manuka' were purchased from local supermarkets. In order to detect the polyphenols, including the unique Manuka honey markers, the samples were subjected to SPE extraction to remove the abundant sugar component. Using Strata-X polymeric reversed phase (RP) SPE cartridges (Phenomenex), the extraction procedure was optimised allowing efficient enrichment of the non-polar components which were subsequently analysed using 2,4,6-trihydroxy-acetophenone (THAP) MALDI matrix containing 10 mM sodium trifluoroacetate (NaTFA) in positive ion mode on a benchtop linear MALDI-TOF mass spectrometer (MALDI-8030, Shimadzu; Figure 2). The MS-based assignments from the MALDI-MS analysis were confirmed by MALDI-MS/MS (data not shown).

Figure 1. *Leptospermum scoparium* flower

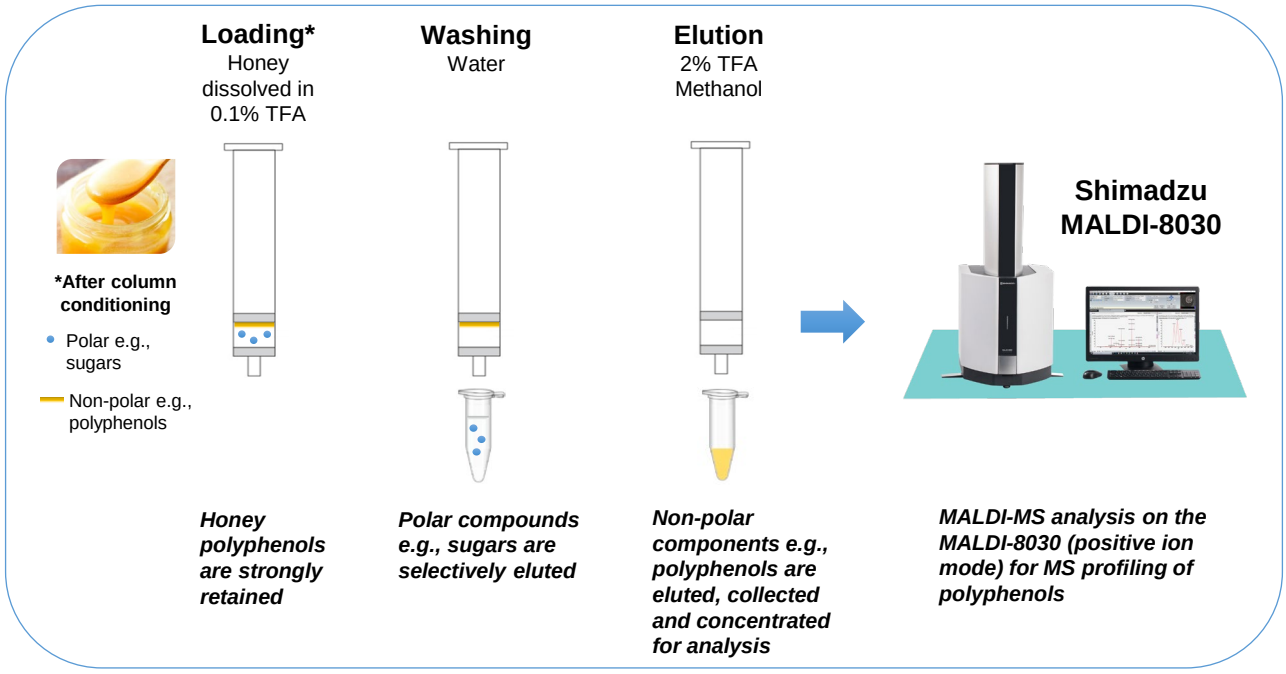

Figure 2. Sample preparation and analysis workflow for the profiling of honey polyphenols.

■ Results

Preliminary tests on direct analysis of honey solutions without any pre-treatment resulted in the detection of intense signals corresponding to the abundant sugar components present in the honey which mask/suppress the lower abundance target peaks of interest. Using the polymeric RP Strata-X SPE cartridges, the washing and elution steps were optimised, resulting in significantly cleaner MALDI spectra allowing the detection of several key polyphenols. Figure 3 shows the MALDI-MS profiles of the polyphenols after SPE enrichment of a blossom (non-Manuka) and Manuka 100+ MGO honey (Figure 3; blue and red traces, respectively).

As it can be seen from the Manuka honey profile, the leptosperin (a known Manuka honey marker for authenticity [1]) was clearly detected at *m/z* 559 ($[M+Na]^+$), along with other known markers such as 4-hydroxyphenyllactic acid (*m/z* 205; $[M+Na]^+$), 3-phenyllactic acid (*m/z* 189; $[M+Na]^+$), and 2-methoxybenzoic acid (*m/z* 175; $[M+Na]^+$), providing a means for the classification of Manuka/non-Manuka honey products. In the blossom honey profile, none of the Manuka honey markers are detected, as expected. Other minor flavonoid components were also detected among which were chrysin (*m/z* 277; 1), pinocembrin (*m/z* 279; 2), apigenin (*m/z* 293; 3), pinobanksin (*m/z* 295; 4), luteolin (*m/z* 309; 5) and 8-methoxykaempferol (*m/z* 339; 6) (Figure 4).

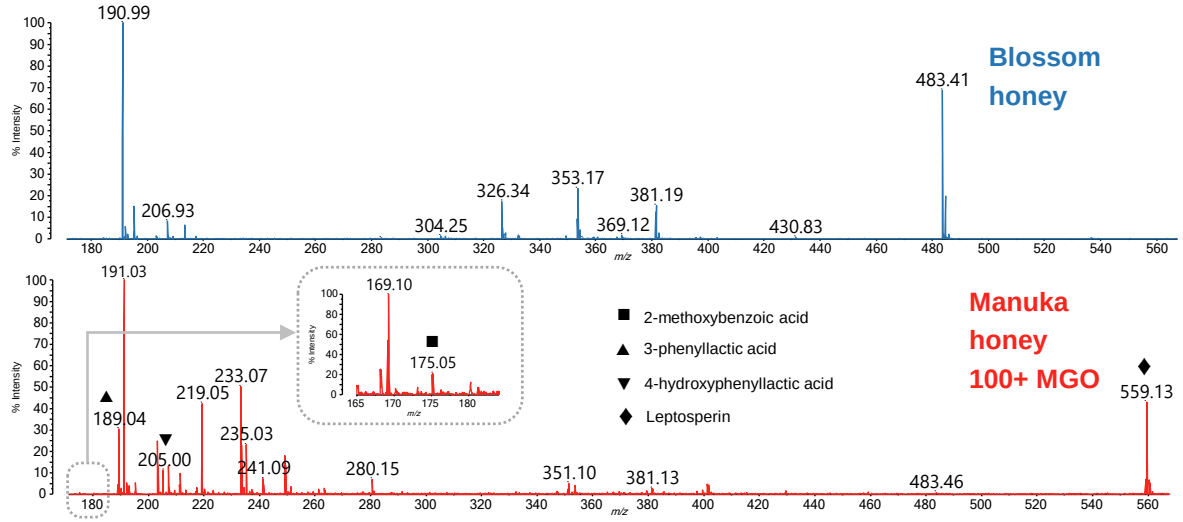

Figure 3. MALDI-MS profiles of the polyphenols after SPE enrichment of a blossom (non-Manuka) honey (blue trace) and a Manuka 100+ MGO honey (red trace). Key markers of Manuka honey, including the leptosperin (a marker for authenticity [2]) are detected in the Manuka honey sample.

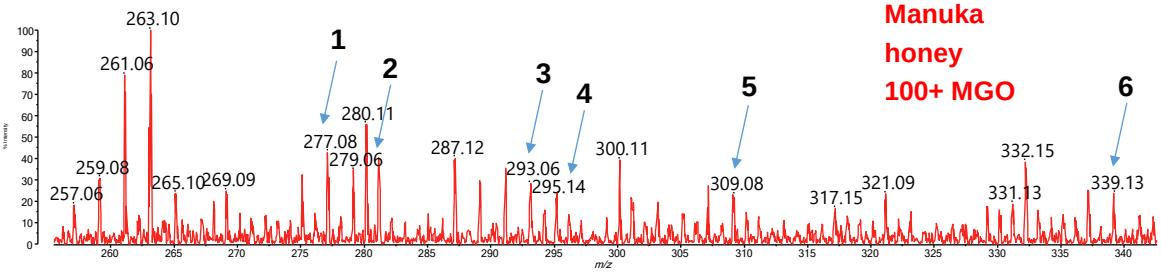

Figure 4. Expansion of the MALDI-MS spectrum of the Manuka 100+ MGO honey in the flavonoid region. 1: chrysin. 2: pinocembrin. 3: apigenin. 4: pinobanksin. 5: luteolin. 6: 8-methoxykaempferol.

■ Conclusion

This work demonstrates the usefulness of MALDI-TOF mass spectrometry to determine the authenticity of Manuka honey through detection of key markers. We hope the proposed new workflow can be used to rapidly screen the authenticity of Manuka honey products.

<References>

1) "The Golden Standard in Mānuka Honey" Unique Mānuka Factor Honey Association, https://www.umf.org.nz/unique-manuka-factor/

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