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Application News

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MALDI-TOF Mass Spectrometry

Simple and Rapid Detection of Thermal Degradation Products of Cooking Oils Using a Benchtop MALDI-TOF Mass Spectrometer

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometers (MALDI-TOF MS) feature simple and rapid detection of low molecular to high molecular weight compounds in a wide range of samples. MALDI-TOF MS is widely used to determine molecular weights of synthesized products and natural substances in R&D laboratories and quality control sectors. In addition, utilizing the feature of MALDI-TOF MS which can detect multiple components in a wide mass range as singly-charged ions (1 component = 1 peak), an attempt is being made to use the instrument for profiling property changes of food and biological specimens.

This article introduces an example of simple and rapid detection of heating-induced degradation products in cooking oils, using a benchtop MALDI-TOF MS.

The MALDI-8020 is a compact-design, small footprint linear mode-only MALDI-TOF mass spectrometer. Its performance in linear mode (positive ion) is comparable to the same mode of a larger conventional MALDI-TOF mass spectrometer. Equipped with a 200 Hz solid-state laser and a load-lock chamber mechanism that enables a target plate change while maintaining the degree of vacuum at the measuring position, the instrument ensures rapid measurements.

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Materials and Methods

A commercially available olive oil was heated at 180 °C for eight hours to prepare model samples of cooking oil degraded by heating. Each heated or unheated olive oil sample (1 mg/mL, 90 % hexane / 10 % diethyl ether solution) was mixed with an equal volume of matrix solution and cationization agent, spotted onto a reusable MALDI target slide (FlexiMass-SR) and dried.

The matrix was prepared by dissolving 2,5-dihydroxybenzoic acid (DHB, 10 mg/mL) in methanol, and the cationization agent was prepared by dissolving sodium iodide (1 mg/mL) in tetrahydrofuran. Samples were analysed using the MALDI-8020 benchtop MALDI-TOF mass spectrometer (Fig. 1).

To increase the number of detected degradation products of cooking oils, heated oil samples were fractionated using silica gel 60 (particle size: 42 to 105 µm) generally used for column chromatography. Non-polar fractions were eluted with 90 % hexane / 10 % diethyl ether solution, and polar fractions were eluted with 100 % diethyl ether solution, both of which were measured by using the MALDI-TOF MS.

Results

The mass spectra of unfractionated cooking oil samples, heated and unheated, are shown in Fig. 2. From both mass spectra, sodium adduct molecules originating from triacylglycerols (TAG) are detected at around *m/z* 900 (*m/z* 881, 905, 907, etc.). In the mass spectrum of the heated cooking oil sample, peaks are detected at *m/z* 923 and 939 (indicated with arrows in Fig. 2), which are derived from oxidized TAG.

Fig. 1 MALDI-8020 Benchtop MALDI-TOF MS

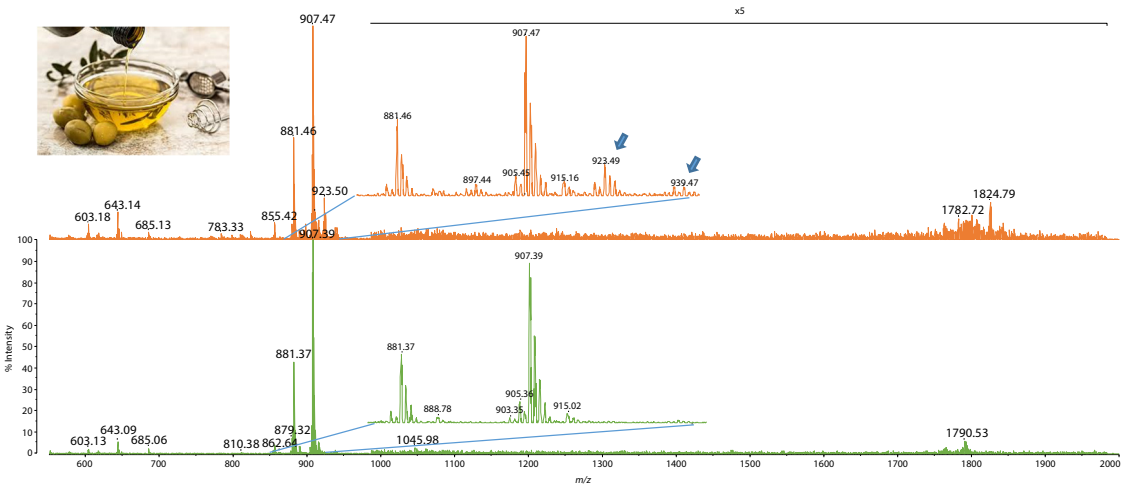

Fig. 2 Mass Spectra of Olive Oil
Upper: Heated, Lower: Unheated

Fig. 3 shows the mass spectrum of polar fractions from the heated olive oil. The compounds of the major peaks detected are inferred from the references as listed in Table 1. With the heated olive oil, in addition to TAG oxides, inference can be made that fractions made by the β-scission of TAG are detected at *m/z* 783, 797 and 823, and that the TAG dimerized by bridging and then oxidized are detected near *m/z* 1800. Fig. 3 also shows estimated structures of major degradation products. As shown, simple fractionation enabled us to detect more heating-induced degradation products of the cooking oil. Among the observed peaks, multiple components of different constituent fatty acids or those oxidized at different positions are also considered to be included in addition to those given in Table 1.

Conclusion

This article demonstrates that simple and rapid detection of degradation products induced by heating cooking oils can be performed simply and rapidly using the MALDI-8020 benchtop MALDI-TOF mass spectrometer. In this analysis, lipids were measured and we assume that similar analyses can be applicable to a variety of samples including proteins, glycans, synthetic products, and biological specimens.

The benchtop MALDI-8020 features compactness and capabilities sufficient for molecular profiling, and its future dissemination in simple and rapid detection of property changes in versatile samples is expected.

Table 1 Compounds Inferred from Major Peaks *m/z* in the Mass Spectrum of Polar Fractions [1), 2)] in Heated Olive Oil

Observation m/z	Inferred Compounds
643.1	Diacylglycerol (OO) *1
783.3	Oxidized β-scission fragment: $C_{54:4} - C_{10}H_{18} + O$
797.2	Oxidized β-scission fragment: $C_{54:4} - C_{9}H_{16} + O$
823.2	Oxidized β-scission fragment: $C_{54:4} - C_{7}H_{14} + O$
881.4	TAG (POO)
905.3	TAG (LOO)
907.4	TAG (OOO)
923.4	Oxidized TAG (OOO)
937.4	2Oxidized TAG (LOO)
939.4	2Oxidized TAG (OOO)
953.3	3Oxidized TAG (LOO)
1796.4	2-oxidized TAG dimer; $C_{54} - C_{52;}$ n*2 = 5 + 2O
1798.4	2-oxidized TAG dimer; $C_{54} - C_{52;}$ n = 4 + 2O
1808.4	Oxidized TAG dimer; $C_{54} - C_{54;}$ n = 5 + O
1822.4	2-oxidized TAG dimer; $C_{54} - C_{54;}$ n = 6 + 2O
1824.4	2-oxidized TAG dimer; $C_{54} - C_{54;}$ n = 5 + 2O

*1 O = oleic acid, L = linoleic acid, P = palmitic acid in parentheses
*2 Number of double bonds in the dimer

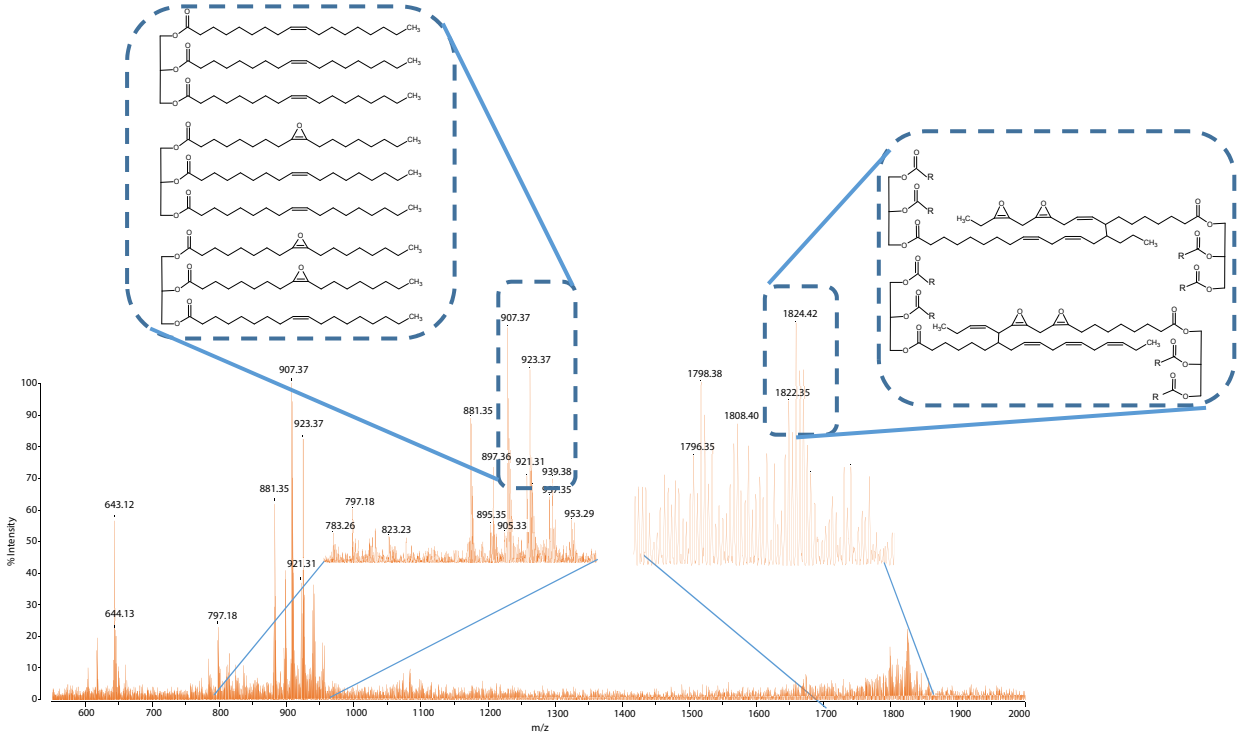

Fig. 3 Mass Spectrum of Polar Fractions in Heated Olive Oil

<References>
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2) Picariello G, Paduano A, Sacchi R, Addeo F, 2009. Maldi-tof mass spectrometry profiling of polar and nonpolar fractions in heated vegetable oils. *J. Agric. Food Chem.*, 57 (12), pp. 5391-5400

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