Applications Note

SpiralTOF-TOF

Structural Analysis of Oxidized Triolein

Introduction:
In previous work, we showed that the JEOL SpiralTOF-TOF system's high-energy collision-induced dissociation (HE-CID) is useful for the structural analysis of triglycerides.[1] The resulting HE-CID mass spectra provided detailed information about the fatty acid moieties such as the positions of double bonds, branching, hydroxylation, and oxidation by means of charge-remote fragmentation (CRF).[2]

In this work, we report the structural analysis of oxidized triglycerides by HE-CID using the SpiralTOF-TOF.

Experimental:
Triolein, a triglyceride with 3 oleic acid moieties (Fig.1), was used in this experiment. The triolein sample was kept at 160°C for 60min so that thermal oxidation would occur. The resulting sample was then dissolved in tetrahydrofuran (THF) at a concentration of 10 mg/mL. 2',4',6'-Trihydroxyacetophenone monohydrate (THAP) was used as the matrix and sodium trifluoroacetate (NaTFA) as the cationizing reagent. The THAP and NaTFA were dissolved in THF at a concentration of 10mg/mL and 1mg/mL, respectively. These two solutions and the sample solution were then mixed 1:1:1 by volume. Afterwards, 0.5 µL of this mixture solution was deposited and dried on the MALDI target plate.

Results:
The MALDI mass spectrum of oxidized triolein is shown in Fig. 2. PEG1000 was used as an external calibrant. A series of sodiated peaks were observed for non-oxidized (*m/z* 907), mono-oxidized (*m/z* 923), di-oxidized (*m/z* 939), and tri-oxidized (*m/z* 955) triolein. These results were supported by elemental composition calculations that showed a mass accuracy of < 2 ppm for each ion.

The product-ion spectra for *m/z* 907 and *m/z* 923 are shown in Fig. 3. Many product-ions caused by CRF were observed which simplified the analysis of each structure. The A, B, J2, and G ions in the product-ion spectrum for *m/z* 923 were shifted by 16 Da when compared to the product-ion spectrum for *m/z* 907. An enlarged product-ion spectrum for *m/z* 923 is shown in Fig. 4. The correlating structures for these ions are based on the structural fragmentation assignments shown in

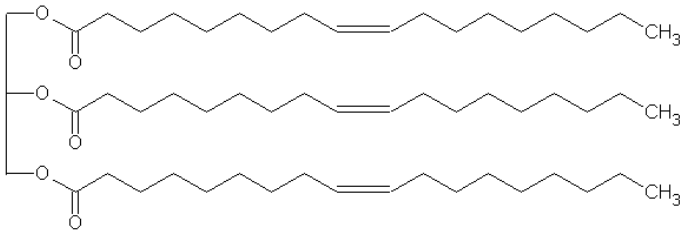

Figure 1. Structure of triolein.

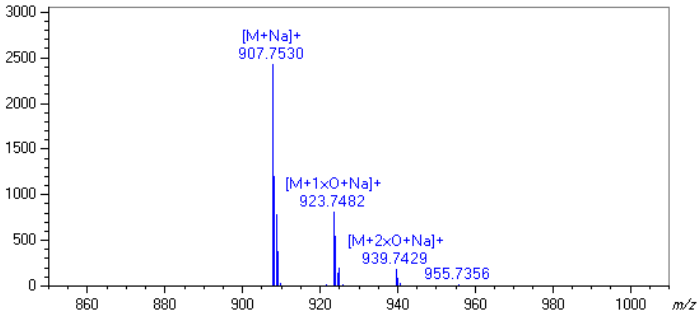

Figure 2. Mass spectrum of triolein after heating at 160°C, 60min.

Fig. 5. These results clearly show that the high-energy CID product ions collected by SpiralTOF-TOF provide a very straightforward pattern for identifying the sample structure and the position of oxidation.

Conclusion:
In this study we demonstrated the structural analysis of an oxidized triglyceride using the high-energy CID available on the MALDI-SpiralTOF-TOF. Additionally, CRF using high-energy CID is a very useful technique for assigning the position of oxidation.

Reference:
1. A.Kubo, et al., Structural analysis of complex lipids using MALDI-TOF-TOF tandem MS with high precursor-ion selectivity. 59th ASMS Conference. 2011, MP240.
2. Cheng, C., Gross, M. L.; Pittenauer, E. Complete structural elucidation of triacylgylcerols by tandem sector mass spectrometry. Anal. Chem. 1998, 70, 4417-4426.

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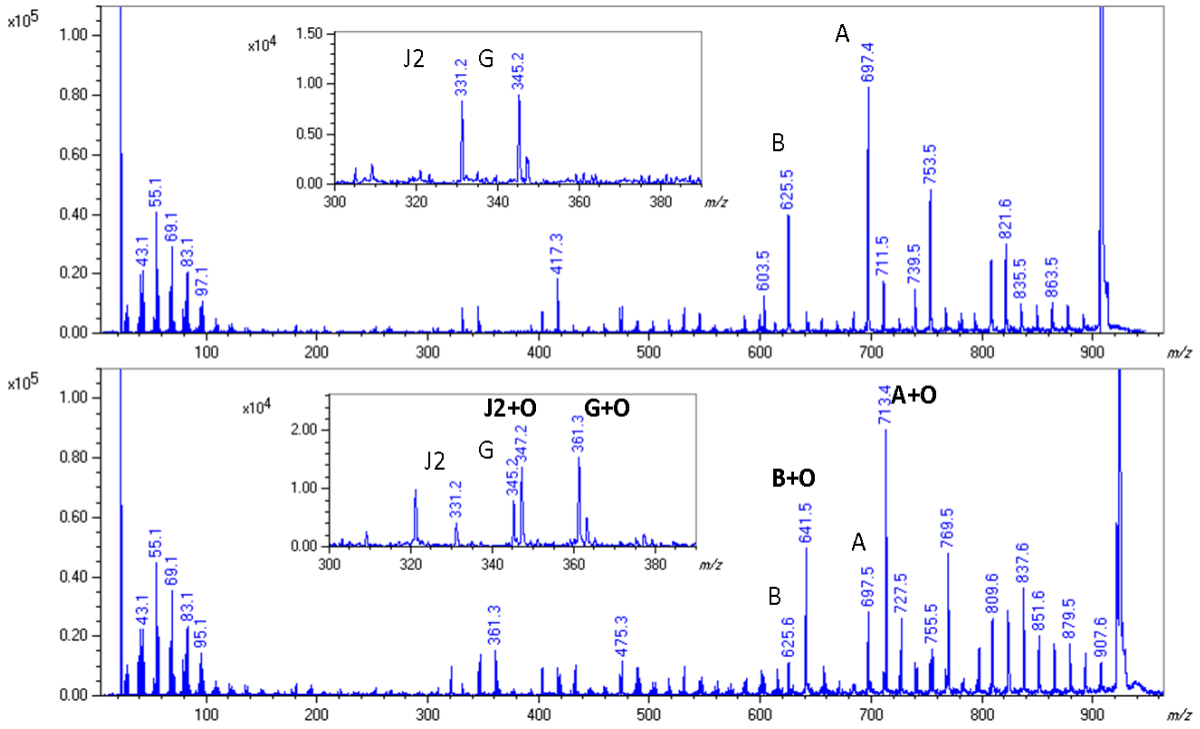

Figure 3. Product ion mass spectrum from *m/z* 907 (top) and *m/z* 923.

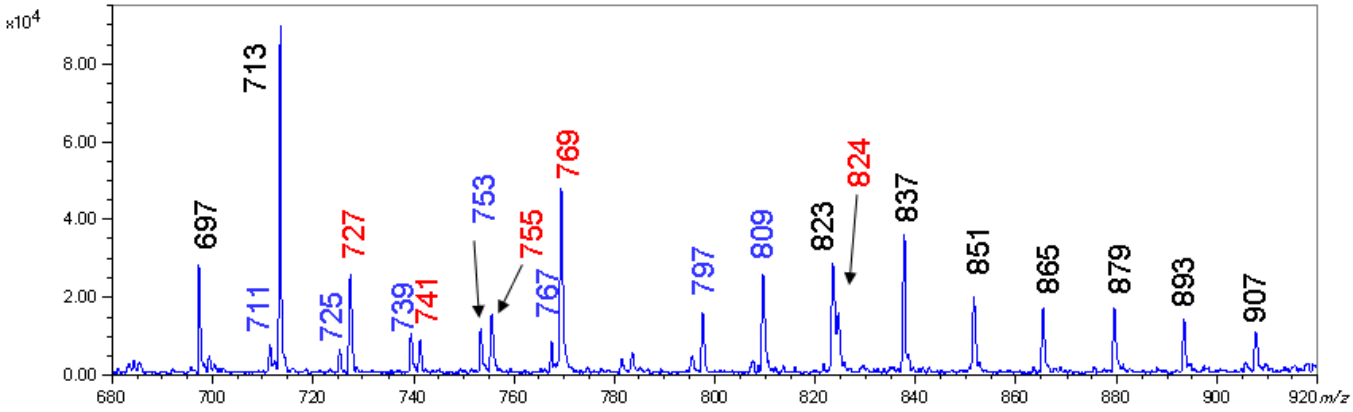

Figure 4. Product ion spectrum from *m/z* 923 (enlarged between *m/z* 680 and *m/z* 920).

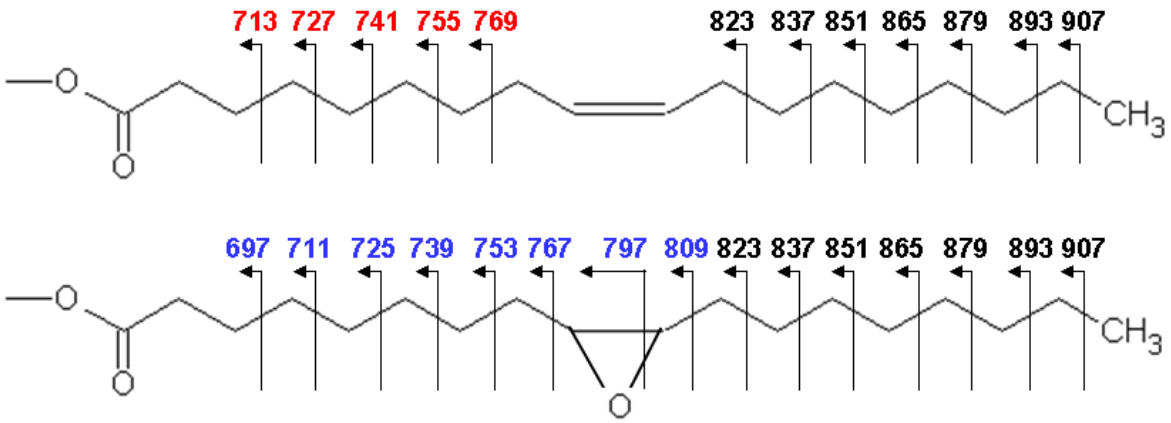

Figure.5. Assignment of product ions from *m/z* 923.

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