"No-prep" Analysis of Lipids in Cooking Oils and Detection of Adulterated Olive Oil

Introduction

Dietary fats are categorized according to the level of unsaturation. Oils are a mixture of triglycerides and free fatty acids. Olive oil contains a high concentration of monounsaturated fatty acids, while other oils such as Canola and safflower oil contain larger amounts of polyunsaturated fatty acids. Characterizing the type of lipids present is important for quality control and for detecting adulteration of more expensive oils (e.g. olive oil) with cheaper products. Analysis by HPLC is time-consuming and requires solvents and consumables. DART provides a convenient alternative: no solvents are required and the analysis can be completed in seconds.

Experimental

Analysis was carried out by using a JEOL AccuTOF-DART™ mass spectrometer operated in positive-ion mode at a resolving power of >6000 (FWHM). The DART source was operated with helium and the gas heater was set to 375°C. Melting point tubes were dipped in oil samples and placed in front of the DART ion source for a few seconds. A cotton swab dipped in dilute ammonium hydroxide was placed nearby to enhance formation of $[M+NH_4]^+$ from triglycerides. A spectrum of PEG 600 was measured between samples to permit exact mass measurements.

Results

Figure 1 shows the DART mass spectrum of a grocery-store olive oil and Figure 2 shows a comparison of mass spectra for different cooking oils. Free fatty acids (Figure 3), squalene and di- and triglycerides (Figure 4) are detected as $[M+NH_4]^+$. The relatively high abundance of free fatty acids in Figure 1 (bottom) is a result of thermal decomposition and is only observed at higher gas temperatures for large amounts of (neat) oil. However, the abundant peaks for the free

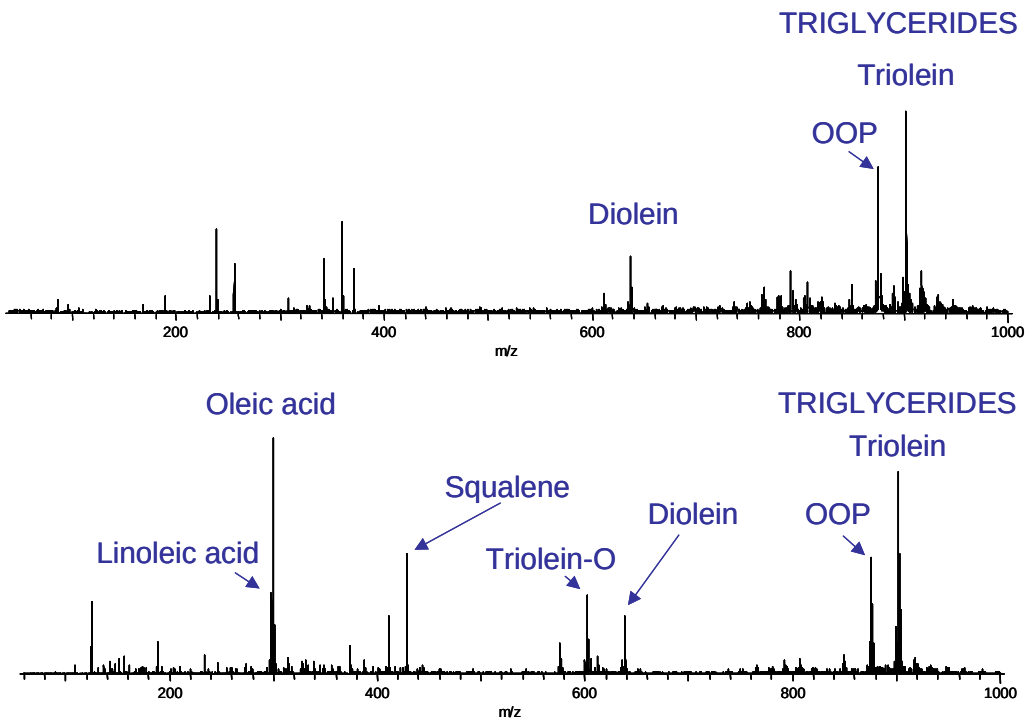

Figure 1. Medium-quality grocery store olive oil. Top: dilute solution of olive oil in hexane, bottom: neat oil (DART at 375°C).

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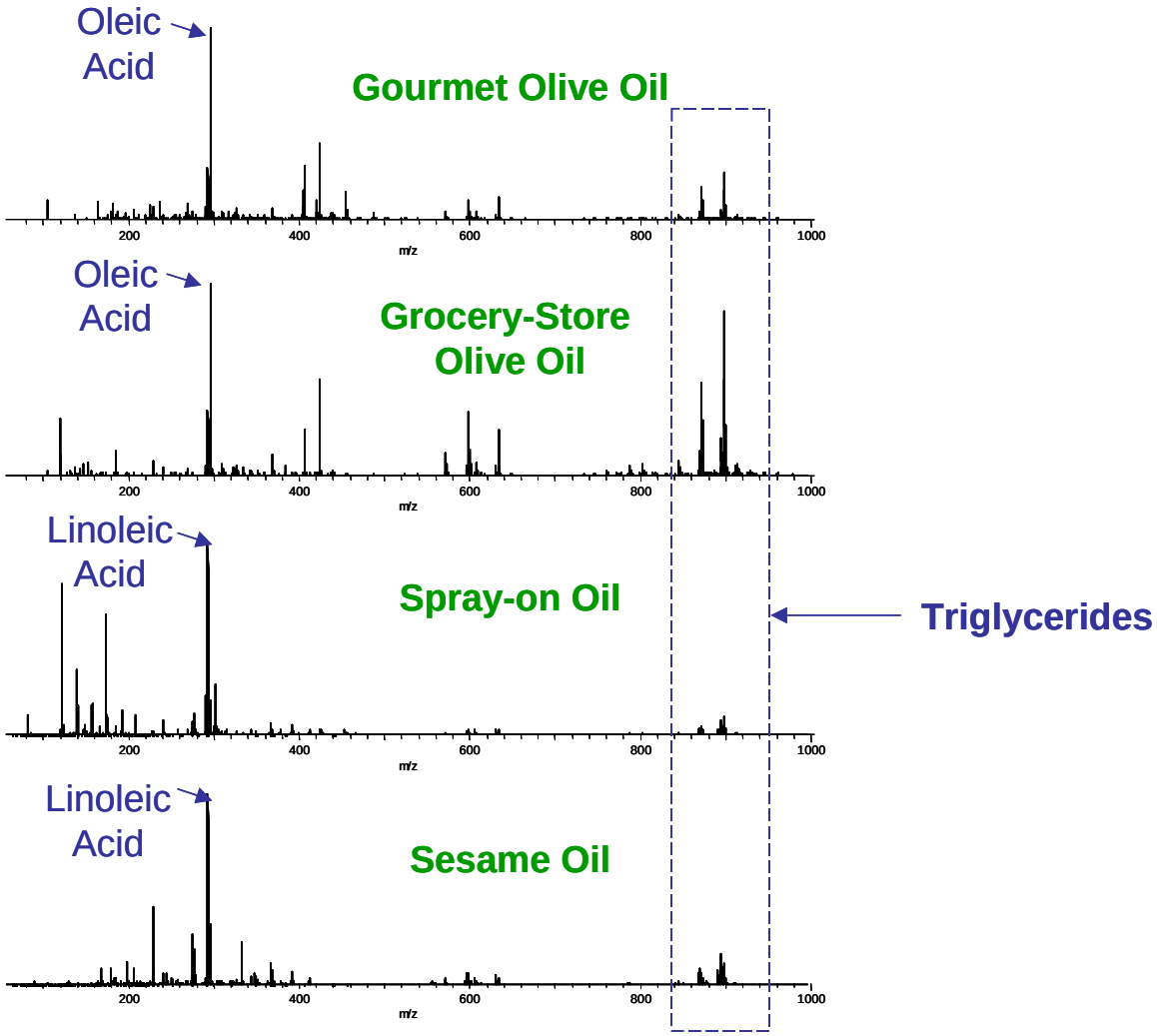

Figure 2. Comparison of cooking oils

fatty acids under these conditions make it easy to see differences in the overall fatty acid content of the oil.

Of the C_{18} fatty acids, oleic acid (O) comprises 55-85% of olive oil[1], while the Omega-6 fattty acid linoleic acid (L) is present at about 9% and the Omega-3 fatty acid linolenic acid (Ln) is present at less than 1.5%. Other fatty acids including the C_{16} palmitic acid (P) are also detected.

The triglyerides are readily detected (Figure 4) and their elemental compositions confirmed by exact mass measurements (Table 1) and isotope pattern matching. Triolein (OOO) is the major component in olive oil, while increasing unsaturation is observed for the Canola/safflower oil blend and the sesame oil.

Elemental compositions were confirmed for the triglyceride $[M+NH_4]^+$ peaks by exact mass measurements and isotope pattern matching. Examples for triolein (OOO) and OOP are shown in Table 1. Figure 5 shows the DART mass spectrum of an olive oil sample to which 50% of the Canola/safflower oil blend has been added. In comparison with the unadulterated olive oil (Figures 3 and 4), the adulterated oil is easily recognized by the higher degree of unsaturation and the relatively higher abundance of linoleic and linolenic acids.

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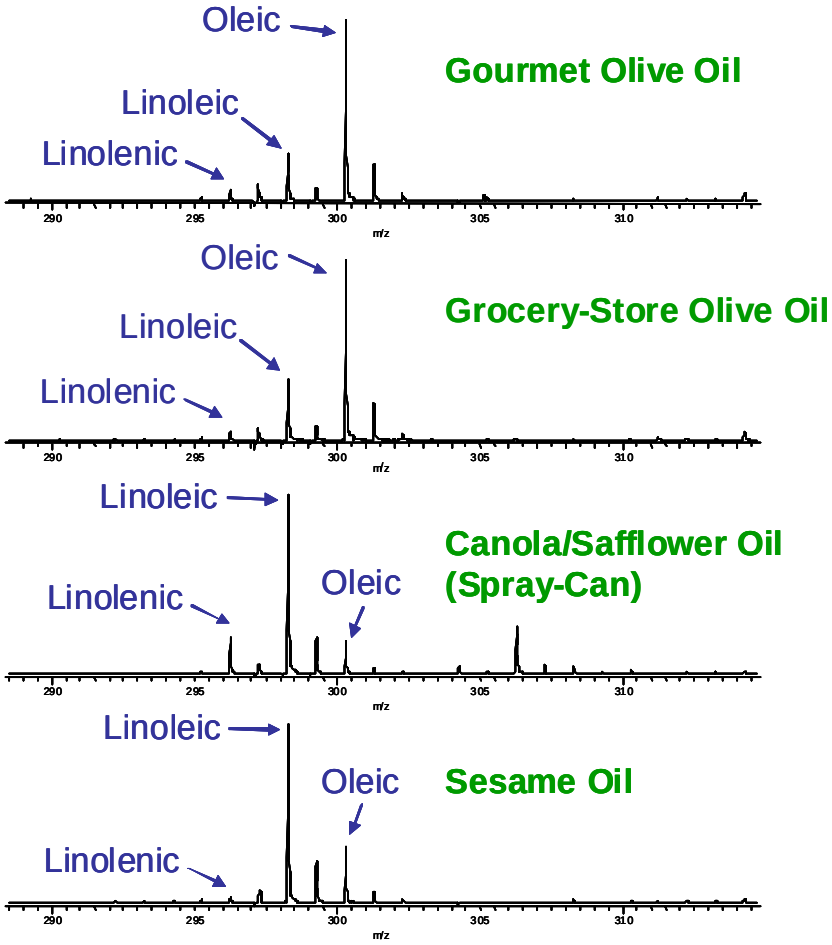

Figure 3. Enlarged view of free fatty acid region

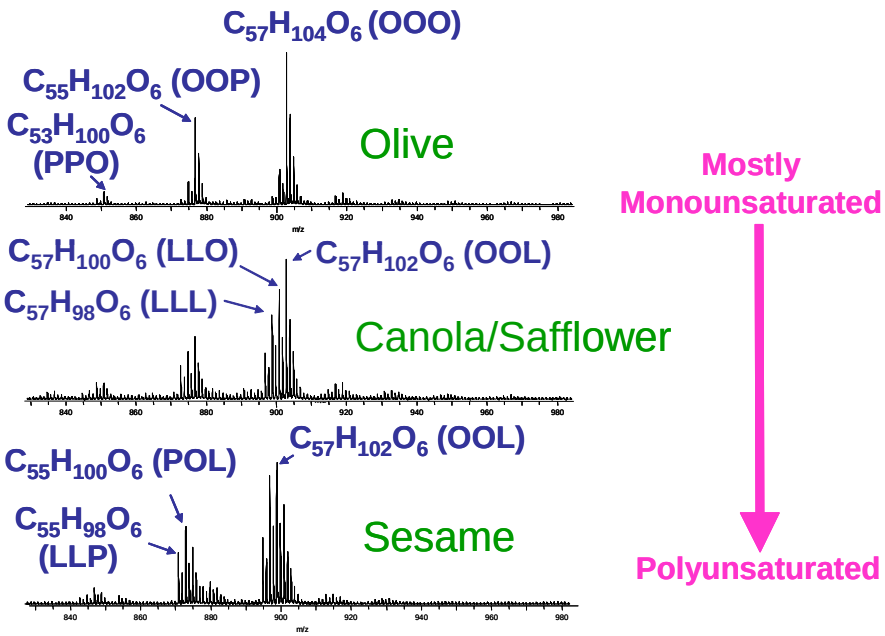

Figure 4. Enlarged view of triglycerides in cooking oils

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Meas. mass (um)	Abund. (%)	Difference (mmu)	Unsaturation	Compositions
876.801270	25.14	-0.75	3.5	C55 H106 O6 N1 (OOP)
902.816040	35.62	-1.61	4.5	C57 H108 O6 N1 (OOO)

Table 1. Elemental compositions from exact mass measurements

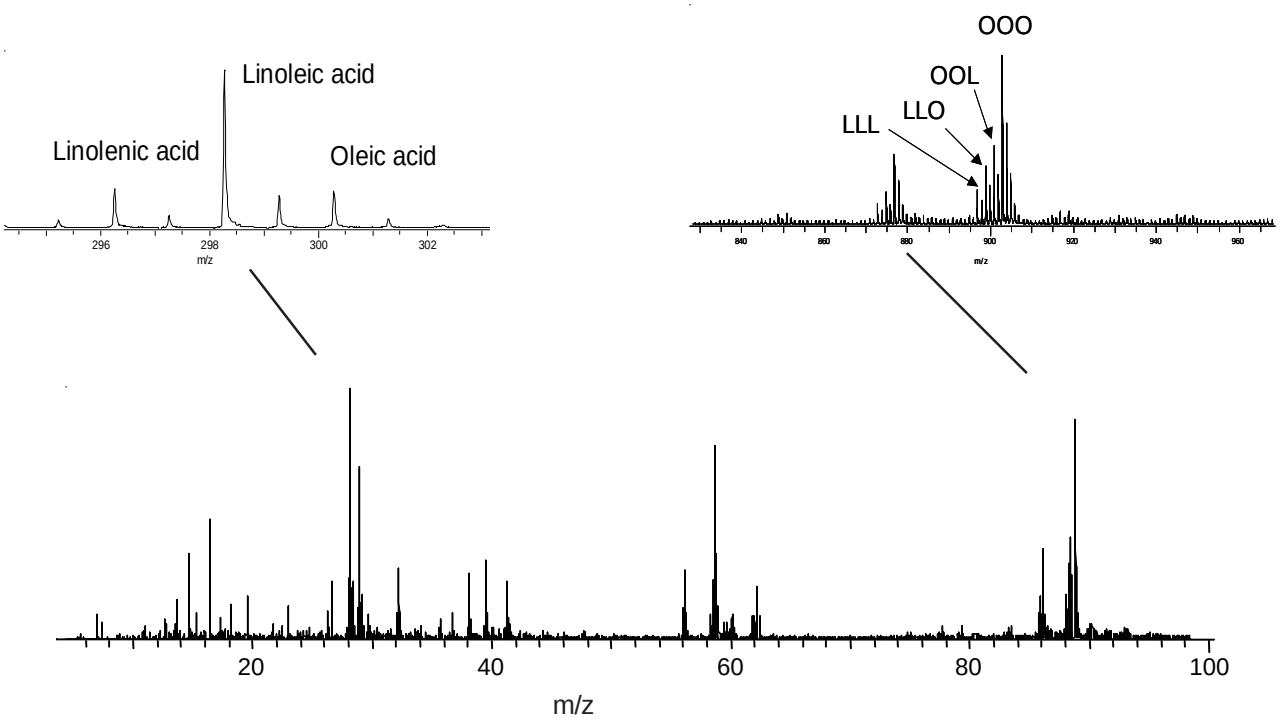

Figure 5. DART mass spectrum of adulterated olive oil

Conclusion

DART can characterize lipids such as fatty acids and mono-, di-, and triglycerides in cooking oils and detect adulterated olive oil within seconds and with no sample preparation.

Reference

1.http://www.oliveoilsource.com/olivechemistry.htm

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