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Quality control of olive oil by UV/VIS spectroscopy and DSC

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Olive oil is associated with healthy food due to its high content of Vitamin E, antioxidants, and mono-unsaturated fatty acids. Olive oils are available in different qualities such as extra virgin, virgin, olive oil, and others. In this article, we compare two olive oils of different quality by UV/VIS spectroscopy and DSC.

Introduction

Mediterranean cooking is difficult to imagine without olive oil. Because of its high content of mono-unsaturated fatty acids, vitamin E and antioxidants, olive oil is looked on as a "healthy" oil. Cold-pressed extra virgin olive oil is the highest quality. Olive oils that do not have a precise quality declaration are usually blends of refined olive oil and extra virgin or virgin olive oil.

Olive oils of lower quality contain conjugated dienes and trienes (see Figure 1). These and other compounds are formed as a result of oxidative degradation processes in the oil. The conjugated carbon-carbon double bonds of the dienes and trienes absorb UV light in the wavelength range 200 to 300 nm.

Criterion	Condition for extra virgin quality
K_{232}	≤2.7
K_{270}	≤0.4
ΔK	≤0.01

Table 1. Spectrophotometric criteria defined by the International Olive Council that must be fulfilled by an extra virgin olive.

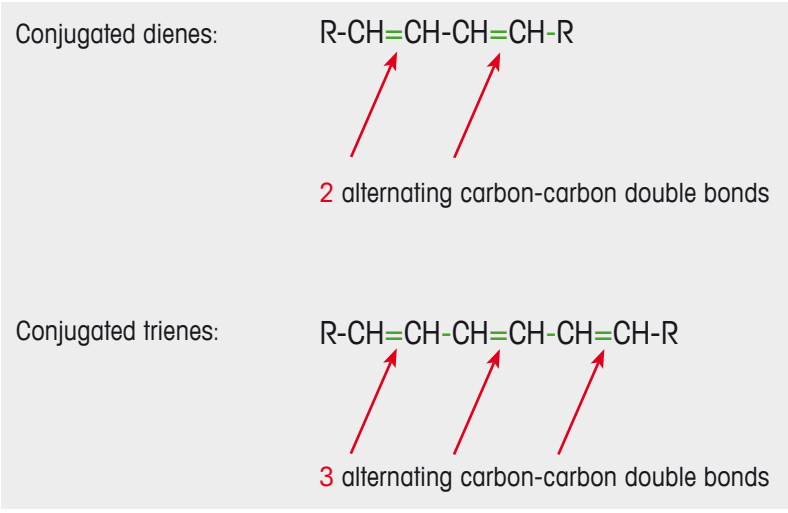

Figure 1. Conjugated carbon-carbon double bonds are formed in olive oil as a result of oxidation processes.

In contrast, substances with non-conjugated double bonds that are also present in extra virgin oil (e.g. unsaturated fatty acids) do not absorb light in this spectral range.

This provides the basis for a simple method to check the quality of olive oil:

- low absorption in the spectral range 200 to 300 nm points to high quality extra virgin oil, and
- high absorption to an olive oil of lower quality.

The International Olive Council has defined three criteria that must be fulfilled for an olive oil to be given the extra virgin label when using UV/VIS spectroscopy for the quality control of olive oils.

The criteria are based on the extinction coefficient K_λ at four different wavelengths, λ (232 nm, 266 nm, 270 nm and 274 nm). Specifically, extra virgin olive oils must fulfill the criteria given in Table 1 [1, 2].

Whereby:

$$K_\lambda = A_\lambda/(c \cdot L) \quad (1)$$

and

$$\Delta K = K_{232} - ((K_{266} + K_{274})/2) \quad (2)$$

where A_λ is the absorbance at the wavelength λ, c is the concentration of the sample in the solvent, and L is the path length of the cuvette.

According to the standard described here, the olive oil must be diluted to a one percent solution in cyclohexane (c = 0.01).

Experimental details

The UV/VIS spectra, crystallization and melting behavior, and oxidative stability of two olive oils obtained from a supermarket were compared. One olive oil was labeled extra virgin and the other olive oil had no precise quality declaration.

The UV/VIS spectra were recorded using a METTLER TOLEDO UV5 Excellence spectrometer and the data evaluated with the LabX software. The crystallization and melting behavior and oxidative stability was investigated by DSC using a METTLER TOLEDO DSC3+ instrument equipped with an Intracooler.

Results

The UV/VIS spectra of the two oils are displayed in Figure 2. The absorption of the extra virgin oil in the range 200 to 300 nm (see the red arrow in the diagram) is noticeably weaker than that of the olive oil with no quality declaration.

Evaluation of the spectra of the two oils according to equations 1 and 2 yield the values summarized in Table 2.

The values in Table 2 show that the olive oils are clearly different – the unlabeled olive oil does not fulfill any of the three quality criteria for extra virgin oil. In contrast, the extra virgin olive oil is correctly declared as such.

DSC is not mentioned in the different regulations [1, 2] as a method for the characterization of olive oils. Differences in the quality of olive oils can however be detected with DSC measurements. The olives for extra virgin olive oil must be cold pressed in an oxygen-free atmosphere within a few hours of picking.

This conserves the antioxidants in the oil and protects it from oxidative degradation. Olive oils with no clear quality declaration are usually blends of refined oil and extra virgin or virgin olive oils. Refined olive oils are heated strongly during their production.

This largely destroys the antioxidants in the olives. The so-called oxidation induction time, OIT is correspondingly shorter in olive oils of lower quality.

The OIT is usually determined by first measuring the oxidation onset temperature (OOT). This is done by heating a sample in oxygen and determining the temperature at which exothermic oxidation begins. The OOT curves of the two oils measured at a heating rate of 20 K/min are displayed in the lower part of Figure 3.

The curves show that the olive oil sample begins to oxidize at about 170 °C and the extra virgin olive at a somewhat higher temperature. The shapes of the curves are also different. The OOT measurements allow a suitable temperature, T_{OIT}, to be chosen for the OIT measurements.

In an OIT measurement, the sample is first heated in nitrogen to T_{OIT}. After this, it is held isothermally at T_{OIT} in an oxygen atmosphere. The time at which exothermic decomposition begins at this temperature is known as the OIT. In this example, T_{OIT} was 145 °C.

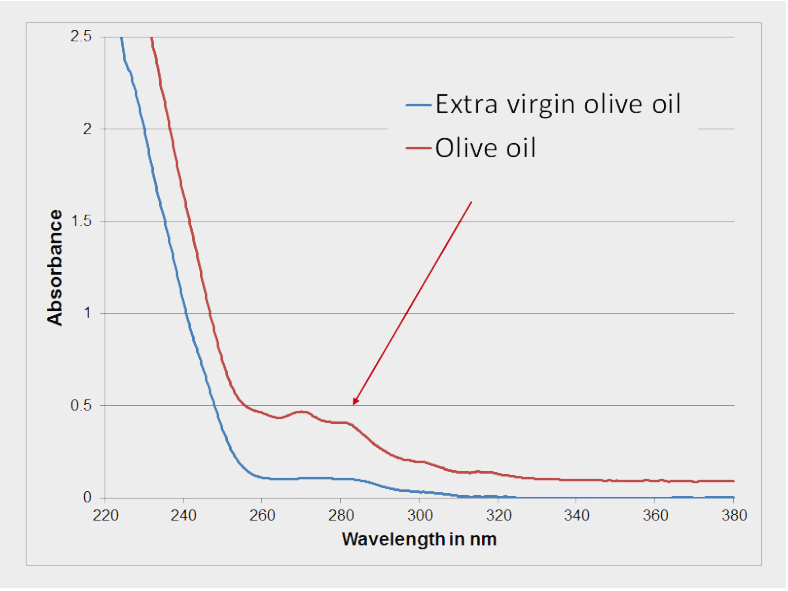

Figure 2.
UV spectra of the two olive oil samples.

	K_{232}	K_{270}	ΔK
Extra virgin criteria	≤2.40	≤0.20	≤0.01
Olive oil	2.66	0.43	0.04
Extra virgin olive oil	1.85	0.12	0.00

Table 2.
Regulatory requirements for an extra virgin olive oil and values for the olive oil with no quality declaration and the extra virgin olive oil.

The measurement curves are displayed in the diagram in upper left part of Figure 3 (only the isothermal segments are shown).

It can be seen that the OITs of the two oils are clearly different. As expected, the OIT of the extra virgin oil is longer than that of the olive oil of lower quality.

Extra virgin oils differ from olive oils of lower quality in their chemical composition. This leads to differences in their crystallization and melting behavior.

Figure 4 displays cooling and heating curves of the two olive oils investigated. It can be seen that the DSC curves of the extra virgin oil exhibit a second peak at higher temperature, both on cooling and heating.

These peaks are due to the crystallization or melting of long chain molecules that are no longer or hardly present in the olive oil of lower quality. Crystallization or melting curves of this type are specific fingerprints for oils and can be used to characterize the oils.

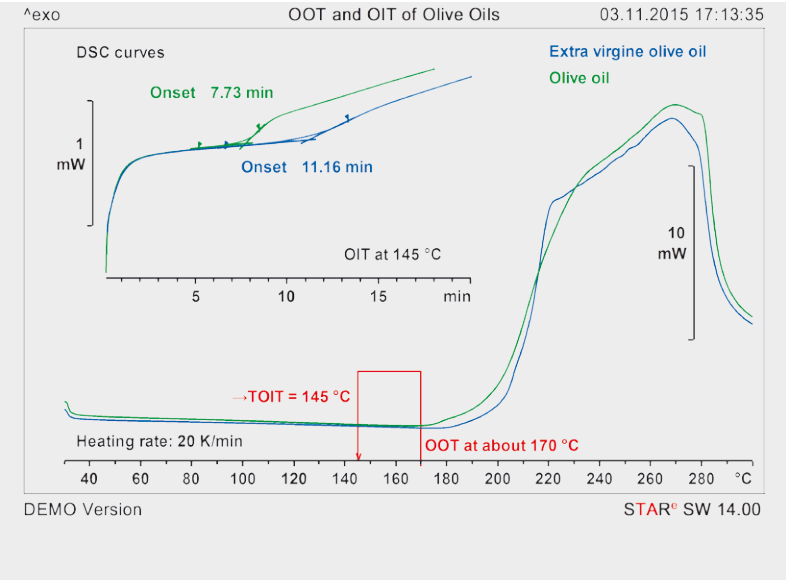

Figure 3.
OIT and OOT of olive oils of different quality.

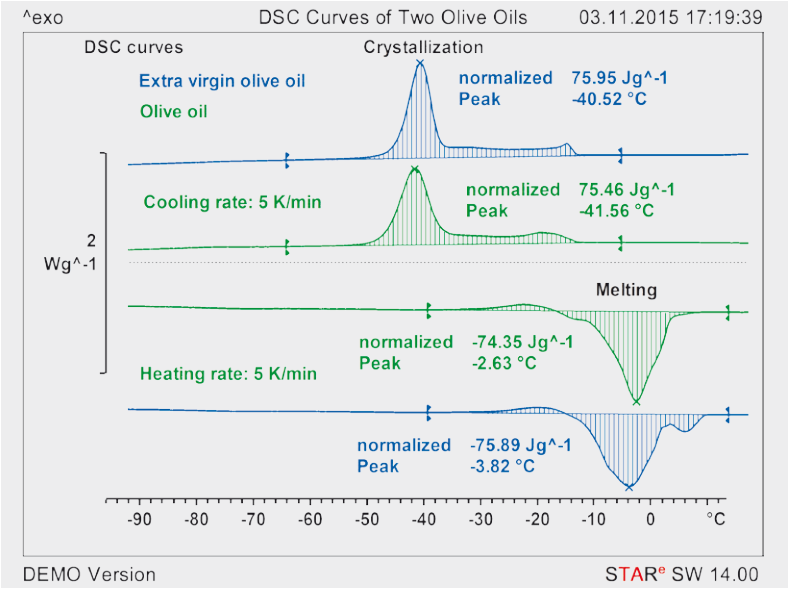

Figure 4. DSC crystallization and melting curves of two olive oils of different quality.

Conclusions

Two olive oils of different quality were analyzed by UV/VIS spectroscopy and by DSC.

Whether or not an olive oil fulfills the criteria for extra virgin quality can be quickly and easily determined by UV/VIS spectroscopy using the criteria laid down by the International Olive Council.
At present, there are no quantitative criteria for DSC. Differences between an extra virgin olive oil and an olive oil with no precise quality declaration can however also be determined by DSC.

References

[1] EEC Regulation 2568/91 Annex IX (http://eur-lex.europa.eu/).
[2] International Olive Council, IOC COI/T20/Doc.no.19/Rev.3 2010 (www.internationaloliveoil.org).