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Promoting calorimetry for olive oil authentication

C. Ferrari, M. Angiuli, E. Tombari, M.C. Righetti, E. Matteoli, G. Salvetti *

Institute for Chemical-Physical Processes (IPCF) of CNR, Via G. Moruzzi 1, I-56127 Pisa, Italy

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Abstract

The aim of this paper is to promote calorimetry for olive oil authentication. It is our belief that the melting and freezing curves by DSC of olive oil and other edible oils could be correlated with quality, origin and storage history of the oil in a simple way, suitable for oil industry and market. Nucleation, crystallization kinetics and transition enthalpies of oil are indeed strongly dependent on molecular interactions, that is any change of oil acidic composition and minor components can be detected, as we have recently demonstrated. In particular, addition of low-cost oils to extra virgin olive oil (EVOO) and thermal and/or mechanical treatments (refinement, deodorization, filtration, etc.) of EVOO can be assessed by a first-sight analysis of the thermograms.

Protocols to obtain reproducible DSC thermograms and experiments to understand the origin of the often-observed non-reproducibility, which prevented until now the use of calorimetry for oil authentication, are here described.

An explanation of the melting curves even limited to the main features is a hard task owing to the polymorphism of the numerous triacylglycerols (TAG), the main component of the oil, the complexity of their mutual interactions and the effects of the minority components. To outline the level of this challenge we report: (i) the evidence that thermodynamic and kinetic processes overlap during heating of solid EVOOs and (ii) the melting curve of one pure TAG with its polymorphic transitions.

Keywords: Isothermal crystallization; Melting; Differential scanning calorimetry; Olive oil authentication; Polymorphism

1. Introduction

Among the numerous experimental techniques currently used for testing nature, quality and geographic origin of edible oils, calorimetry is not present. DSC has been applied mainly to the study of the thermo-oxidative process against temperature, with the purpose of selecting oil type and improving utilization conditions [1–7]. The oxidative stability was also monitored by pressure DSC [8]. The liquid ↔ solid phase transitions of the oil have been particularly studied to this end, as they are affected by molecular composition changes. Therefore freezing and melting are promising also to assess oil nature, quality and origin. Few attempts in this direction can be found in the literature. About 10 years ago, Dyszel and co-worker [9,10] worked to create a data bank with the calorimetric "fingerprints" of the main edible oils. More recently, the effects of heating and cooling rate on the melting and freezing thermograms have been studied with DSC [11,12] and the potentiality of calorimetric methods for oil quality control discussed [13].

The experiments in Refs. [11,12] outlined the strong dependence of the thermograms on the temperature-scanning rate, which was found much larger than that observed for monocomponent molecular liquids [14]. The authors attributed this effect to the complexity of the oil and the polymorphism of the crystalline phase of triacylglycerols (TAG), the main components of the oil [11,12]. They also outlined the difficulty in obtaining experimental reproducible conditions. Our attempts to use calorimetry for edible oil authentication started just from this results with the aim of: (i) understanding the origin of the observed non-reproducibility; (ii) defining a suitable measurement protocol; (iii) studying the physical processes occurring at the oil liquid ↔ solid transitions.

The experiments reported in Refs. [11–14] suggested that the sensitivity of the calorimetric method to oil composition is due, besides to solid TAGs polymorphism, also to the presence of many minor components, generally responsible for the positive or negative organoleptic and healthy features of the oil. The numerous molecular components interfere indeed with

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* Corresponding author. Tel.: +39 050 3152248; fax: +39 050 3512230.
E-mail address: salvetti@ipcf.cnr.it (G. Salvetti).

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crystal nucleation and growth kinetics, so affecting the solidification and melting thermograms in a characteristic way, strictly related to oil identity. Therefore the solidification and melting thermograms can be used for assessing: (i) commercial frauds, if these molecules have been introduced illegally in the genuine oil; (ii) the geographic origin of the oil, inasmuch as it is reflected by typical cultivars and/or production procedures; (iii) the storage history of the oil, clearly depending on ageing and storage conditions [15–17].

We report here in details the foundations of the calorimetric method we have developed and two measuring protocols tested on edible oils, together with preliminary results of a calorimetric study on the physical processes active in the olive oil melting.

Finally, to point out the complexity of the processes occurring during the EVOO heating, the triolein melting is studied and discussed.

2. Experimental

2.1. Materials

A Tuscan extra virgin olive oil (EVOO), crop season 2005–2006, produced at a traditional plant (stone mill and hydraulic press), was used in these experiments without further treatments. The main characteristics of the sample were acidity (oleic acid%) 0.15; peroxides ($\text{mEO}_2\,\text{kg}^{-1}$) 10.85; biophenols (mg/kg gallic acid) 110.00. The sample was sealed in clear glass jar (200 cm^3 in volume) and stored in dark at the laboratory room temperature of $22 \pm 3\,^{\circ}\text{C}$. Triolein was purchased from Fluka (99% purity) and used as received.

2.2. The calorimeter

Calorimetric measurements were performed with a Perkin-Elmer DSC7 equipped with an Intracooler II. Dry nitrogen was used as purge gas at a rate of 30 ml/min. The instrument was calibrated in temperature and energy with high purity standards (indium, naphthalene and cyclohexane) at 10 °C/min, according to the procedure for standard DSC. The temperature was known at $\pm 0.1\,^{\circ}\text{C}$; the samples weighted to ± 0.01 mg. In order to reduce temperature gradients, the sample mass was kept small, approximately equal to 6–8 mg. A blank run with two empty aluminium pans was subtracted from all the experimental curves.

3. Results and discussion

3.1. Preliminary considerations

The applicability of calorimetry to edible oil authentication imposes the fulfilment of two basic conditions: (i) the attainment of a homogeneous liquid state at the high temperature side of the calorimetric cycle and a complete reproducible solidification of the sample at the low temperature side; (ii) a short measuring time, as requested by oil industry and commerce.

Condition (i) is the physical prerequisite to have reproducible thermograms. It can be fulfilled if one takes into account two subtle features of olive oil, which we have experimentally put in evidence:

(a) An oil sample maintains “memory” of its solid phase in the liquid phase. This is supported by measurements of crystallization induction time (IT) performed at 2.9 °C with a TAM isothermal calorimeter and a large sample (about 2.5 cm^3) [15]. In the first isothermal freezing the IT varied in the range of 6–10 h, depending on the oil type and composition. The IT value of the same sample, measured during freezing after melting at room temperature, decreased to less than 1 h and its value was reproduced in successive identical melting–freezing cycles. This behaviour recalls the homogeneous nucleation, which occurs at high undercooling in dynamic conditions or after a long IT in isothermal conditions. On the contrary, the heterogeneous nucleation, due to impurities and/or crystal seeds present in the liquid, occurs at low undercooling or after a short IT. In our case, being crystallization nuclei, if present, fixed, the observed thermal effects suggest that the melting of the oil at room temperature is not complete and structures able to nucleate efficiently the crystalline phases can survive in the liquid.

This “memory effect” was not observed in much smaller samples, as those used for DSC experiments ($\sim 10\,\text{mm}^3$). Indeed an experiment performed with DSC on the same EVOO sample, subjected twice to a temperature cycle from 50 to $-30\,^{\circ}\text{C}$ and successively twice to a cycle from 20 to $-30\,^{\circ}\text{C}$, gave four crystallization and melting thermograms practically coincident.

(b) A liquid oil volume can be heterogeneous at room temperature if it is sufficiently large.

This feature is related to the previous one. Its relevance for DSC reproducibility is related to the high probability to obtain samples substantially different even from the same source oil. This is confirmed by the thermograms depicted in Fig. 1. The panel B of the figure shows the melting thermograms of five samples, prepared from the EVOO stored

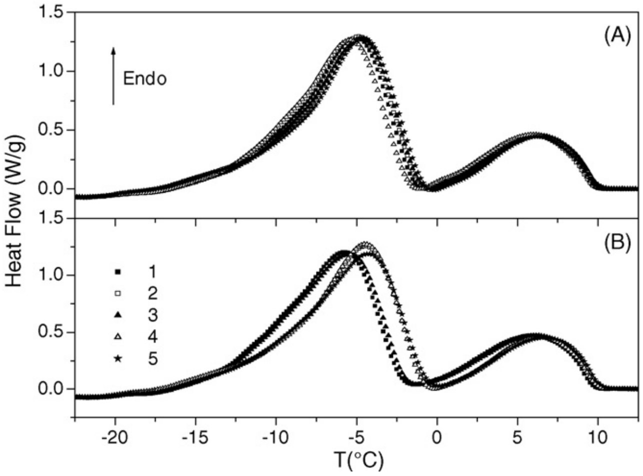

Fig. 1. Melting thermograms of five samples prepared with EVOO from the same container: (A) after thermal treatment of the oil in the container at 50 °C for 3 min and (B) before thermal treatment.