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Analytical Methods

Differential scanning calorimeter application to the detection of refined hazelnut oil in extra virgin olive oil

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Abstract

The potential application of differential scanning calorimetry (DSC) to verify adulteration of extra virgin olive oil with refined hazelnut oil was evaluated. Extra virgin olive oil and hazelnut oil were characterised by significantly different cooling and heating DSC thermal profiles. Addition of hazelnut oil significantly enhanced crystallisation enthalpy (at hazelnut oil $\geqslant 20\%$) and shifted the transition towards lower temperatures (at hazelnut oil $\geqslant 5\%$). Lineshape of heating thermograms of extra virgin olive oil was significantly altered by hazelnut oil addition: a characteristic exothermic event originated at -27 °C in extra virgin olive oil and progressively disappeared with increasing hazelnut oil content, while the major endothermic peak at -3.5 °C broadened (at hazelnut oil $\geqslant 40\%$) and the minor endothermic peak at 8 °C shifted toward lower temperatures (at hazelnut oil $\geqslant 5\%$). The preliminary results presented in this study suggest that DSC analysis may be a useful tool for detecting adulteration of extra virgin olive oil with refined hazelnut oil.

Keywords: Extra virgin olive oil; Refined hazelnut oil; Adulteration; DSC; Thermal analysis

1. Introduction

Extra virgin olive oil (EvoO) is a traditional Mediterranean food product, whose market has recently expanded to North Europe, USA, China and Japan, due to its highly appreciated organoleptic attributes and to its health and nutritional properties (Bendini et al., 2007; Harwood & Yaqoob, 2002).

Adulteration of EvoO with cheaper oils from other vegetable sources or seeds (hazelnut oil, in particular), as well as with lower quality olive oils (e.g. olive-pomace olive oil, virgin olive oil and gentle deodorised olive oil), is a serious concern for oil suppliers and consumers. European Commission and international institutions (e.g. International Olive Oil Council, national Customs and Excise Department) are actively involved in the prevention and detection of frauds in the extra virgin olive oil sector.

Hazelnut oil (HaO) is often used in EvoO adulteration, due to the similar chemical compositions of both major (i.e. fatty acid (FA), triacylglycerols (TAG)) and minor components (i.e. total sterols) of the two oils (European Union Research Committee, 2001). This resemblance makes it difficult to evince the presence of HaO in EvoO, especially at concentrations below 20%. In addition, genetic and climatic factors, as well as agricultural practices, largely influence the chemical composition of both oils, making it even more difficult to detect HaO in fraudulent admixtures.

Several methods have been proposed for detecting the presence of HaO in EvoO. Cold pressed HaO could be detected in virgin olive oil by on-line liquid chromatography–gas chromatography (LC–GC) identification of filbertone, (*E*)-5 methylhept-2-en-4-one, which is a typical volatile compound of HaO (Blanch, Caja, Herraiz, & del

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Castillo, 1999; Blanch, Caja, León, & Herraiz, 2000; del Castillo, Caja, Herraiz, & Blanch, 1998), or by reverse-phase high-performance liquid chromatography (RP-HPLC) analysis of the polar components (Gordon, Covell, & Kirsch, 2001; Zabaras & Gordon, 2004). TAG (Vichi, Pizzale, Toffano, Bortolomeazzi, & Conte, 2001), sterols (Mariani, Bellan, Morchio, & Pellegrino, 1999; Vichi et al., 2001) and tocopherols (Azadmard Damirchi, Savage, & Dutta, 2005; Morchio, Pellegrino, Mariani, & Bellan, 1999) composition have been also used as markers of HaO adulteration. Detection of both crude and refined HaO in virgin olive oil was recently achieved by means of direct coupling of headspace-mass spectrometry and multivariate regression techniques (Pena, Cárdenas, Gallego, & Valcárcel, 2005). The addition of refined HaO to olive oil (blend of refined and virgin olive oil) can also be assessed by determining esterified sterols by thin-layer chromatography (TLC-GC) (Cercaci, Rodriguez-Estrada, & Lercker, 2003).

Most of these methods are expensive, time-consuming and have high environmental impact. Nowadays, alternative techniques are requested for evaluating EvoO adulterants, in particular HaO. Spectrofluorimetric methods, often coupled with multivariate statistical models, are emergent. Fluorescence spectroscopy has been recently employed to detect virgin and refined HaO in virgin olive oils (Sayago, Morales, & Aparicio, 2004). Refined HaO can be detected in refined and virgin olive oil by evaluating entire oils and/or the unsaponifiable fraction with Fourier Transformed-Raman (FT-Raman) and FT-Mid-Infrared (FT-MIR) spectroscopy (Baeten et al., 2005). FT-Infrared (FT-IR) has been found to be useful for detecting HaO in EvoO (Ozen & Mauer, 2002), while ^{1}H and ^{13}C nuclear magnetic resonance (NMR) techniques and artificial neural networks have been applied for its identification in both virgin olive oil and olive oil (García-González, Mannina, D'Imperio, Segre, & Aparicio, 2004).

DSC has some advantages over the more classical detection methods, as it is rapid and does not require sample preparation or solvent utilisation. The application of DSC to the analysis and characterisation of oils and fats for the determination of solid fat content, crystallisation and melting profiles, enthalpy of transitions and polymorphic forms, is well known and reviewed (Biliaderis, 1983). DSC application has also been suggested as a valuable tool for characterisation of oils from vegetable sources (Che Man & Tan, 2002; Tan & Che Man, 2002) and thermal parameters have been reported to correlate well with chemical parameters obtained with standard methods (Tan & Che Man, 2000). Thermal properties (measured both in cooling and heating regimes) of monovarietal EvoO samples were found to correlate well with the chemical composition (Chiavaro, Vittadini, Rodriguez-Estrada, Cerretani, & Bendini, 2008; Chiavaro et al., 2007).

Several works have evaluated DSC application to the detection of adulteration of edible oils, fats and fat-based products. In particular, DSC was able to detect the presence of pig and buffalo body fat in cow and buffalo ghees (Lambelet & Ganguli, 1983), tallow and margarine in butter (Aktaş & Kaya, 2001), lard and randomised lard or lipase-catalysed interesterified lard in refined-bleached-deodorised palm oil (Marikkar, Lai, Ghazali, & Che Man, 2001, 2002), and animal fat in butter (Coni, Di Pasquale, Coppolelli, & Bocca, 1994), canola oil (Marikkar, Ghazali, Che Man, & Lai, 2002) and palm olein (Marikkar, Ghazali, Che Man, & Lai, 2003).

Few reports are available in the literature on the application of DSC to assess EvoO adulteration with other vegetable or seed oils of lower quality and/or economic value. Jiménez Márquez (2003) evaluated DSC heating thermograms of admixtures of virgin olive oil with low-quality olive oils (i.e. refined crude olive oil and virgin olive oil obtained by second centrifugation of olives): melting transition enthalpy and peak temperatures discriminated virgin olive oil from other olive oils, as well as from their admixtures (the differences were attributed to the different TAG composition).

The objective of this preliminary work was to evaluate the potential use of DSC to detect adulteration of EvoO with refined HaO, by establishing possible relationships between the thermal properties of cooling and heating thermograms and the TAG and FA composition of the oils and their admixtures.

2. Materials and methods

2.1. Sampling

EvoO was supplied by Coppini Arte Olearia (Parma, Italy) and it was produced by cold pressing two types of olive cultivars (*Nocellara del Belice* and *Ogliarola Messinese*) harvested in 2006. Refined HaO was purchased at a local supermarket. One sample of each oil was analysed. Admixtures of EvoO:HaO were prepared at different ratios (60:40, 70:30, 80:20, 90:10 and 95:5, w/w). Samples were stored in dark bottles without headspace at room temperature before analysis.

2.2. Reagents, solvents and standards

All solvents used were of analytical or HPLC grade (Merck, Darmstadt, Germany). Reagents were purchased from Sigma–Aldrich (St. Louis, MO). The standard mixture of fatty acid methyl esters (GLC 463) was supplied by Nu-Chek (Elysian, MN).

2.3. DSC

Samples of oil (8–10 mg) were weighed into aluminium pans, covers were sealed into place and analysed with a DSC Q100 (TA Instruments, New Castle, DE). Indium (melting temperature 156.6 °C, $\Delta H_f = 28.45$ J/g) and *n*-dodecane (melting temperature −9.65 °C, $\Delta H_f = 216.73$ J/g) were used to calibrate the instrument