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Single-cultivar extra virgin olive oil classification using a potentiometric electronic tongue

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ABSTRACT

Label authentication of monovarietal extra virgin olive oils is of great importance. A novel approach based on a potentiometric electronic tongue is proposed to classify oils obtained from single olive cultivars (Portuguese cvs. Cobrançosa, Madural, Verdeal Transmontana; Spanish cvs. Arbequina, Hojiblanca, Picual). A meta-heuristic simulated annealing algorithm was applied to select the most informative sets of sensors to establish predictive linear discriminant models. Olive oils were correctly classified according to olive cultivar (sensitivities greater than 97%) and each Spanish olive oil was satisfactorily discriminated from the Portuguese ones with the exception of cv. Arbequina (sensitivities from 61% to 98%). Also, the discriminant ability was related to the polar compounds contents of olive oils and so, indirectly, with organoleptic properties like bitterness, astringency or pungency. Therefore the proposed E-tongue can be foreseen as a useful auxiliary tool for trained sensory panels for the classification of monovarietal extra virgin olive oils.

1. Introduction

Olive oils may be classified according to their quality, in a decreasing order of both quality and price, as extra virgin olive oils (EVOO), virgin olive oils (VOO) or lampante olive oils (LOO) (Cano et al., 2011; Dais, & Hatzakis, 2013; Garcia, Martins, & Cabrita, 2013; García-González, & Aparicio, 2004). Some high quality and expensive olive oils (EVOO and VOO) are certified as Protected Denomination of Origin (PDO), which among other features are related to olive oil production and processing made in a specific geographical origin (Casale, Casolino, Oliveri, & Forina, 2010; Cosio, Ballabio, Benedetti, & Gigliotti, 2006; Haddi et al., 2011; Haddi et al., 2013; Karabagias, Michos, Badeka, Kontakos, & Kontominas, 2013; Montealegre, Alegre, & Garcia-Ruíz, 2010; Pizarro, Rodríguez-Tecedor, Pérez-del-Notario, Esteban-Díez, & González-Sáiz, 2013). Recently, extra emphasis has been given to the botanical origin of olive oils, due to the marketing of high-quality and high-price monovarietal hallmark EVOO (Cimato et al., 2006; Cosio et al., 2006; Garcia et al., 2013; Matos et al., 2007; Montealegre et al., 2010; Ruiz-Samblás et al., 2012). Label information regarding region of origin affects product acceptability, while information about cultivar significantly affects the expectation of bitterness and pungency for olive oils (Delgado, Gómez-Rico, & Guinard, 2013). Indeed, consumers' preference is changing towards food products with certified genuineness and geographical origin (Cosio et al., 2006). EVOO are high-price food products, highly appreciated and an important component of the Mediterranean diet (Ruiz-Samblás et al., 2012). Their quality and uniqueness is attributed to several factors like cultivar or varietal olive origin, environment, crop season, degree of maturation and cultural practises (Bakhouche et al., 2013; Cosio et al., 2006; Longobardi et al., 2012). Therefore, EVOO are one of the food products most prone to frauds that mainly involve mislabelling, adulteration or mixing with cheaper oils (Moore, Spink, & Lipp, 2012; Nunes, 2013; Pizarro et al., 2013).

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Several official methods and recommended practises have been established by the American Oil Chemists' Society to assess oil quality (Nunes, 2013). However, some of these methods are quite expensive, non-green techniques, and require fulfilment of straight standardised procedures to ensure accuracy. Therefore, other approaches have been reported trying to overcome some of these drawbacks, namely gas-, liquid-chromatography and, more recently, mass-spectrometry based-methodologies (Bakhouche et al., 2013; Garcia et al., 2013; Garrido-Delgado et al., 2011; Karabagias et al., 2013; Lauri et al., 2013; Longobardi et al., 2012; López-Feria, Cárdenas, García-Mesa, & Valcárcel, 2008; Matos et al., 2007; Montealegre et al., 2010; Romero, & Brenes, 2012; Ruiz-Samblás et al., 2012). These are based on the identification and quantification of several chemical olive oil components that allow assessment of the quality, authenticity or adulteration of olive oils. Also, DNA-based methods have been proposed to authenticate the varietal origin of olive oils (Bazakos et al., 2012), and non-destructive spectroscopy-based methods have been used to evaluate olive oils quality, authenticity and possible adulterations (Dais, & Hatzakis, 2013; Nunes, 2013; Pizarro et al., 2013). Nevertheless, these approaches require highly-skilled technicians and usually are not suitable for *in situ* applications, being far beyond the economic possibilities of small producers or retailers.

Therefore, low-cost, portable, fast, accurate, reliable and robust analytical methodologies are still needed for authentication purposes and routine analysis. The potential use of electrochemical sensors to evaluate olive oil quality and their application in authentication or adulteration assays can be seen as a possible alternative tool. Indeed, electronic noses (E-noses) and electronic tongues (E-tongues), individually or combined, have been proposed in the last decade for olive oil characterisation (Ruiz-Samblás et al., 2012) using different multivariate statistical techniques. E-noses have been successfully used to classify and discriminate EVOO, VOO and LOO (Escuderos, Sánchez, & Jiménez, 2010; Escuderos, Sánchez, & Jiménez, 2011; García-González, & Aparicio, 2004); to classify VOO according to their geographical origin (Haddi et al., 2011), and to differentiate single-cultivar or multi-cultivar EVOO according to Protected Designation of Origin (Cimato et al., 2006). Voltammetric E-tongues have been applied with success to separate EVOO, VOO, LOO and refined olive oils (Apetrei, & Apetrei, 2013; Apetrei, Rodríguez-Méndez, & de Saja, 2005; Oliveri, Baldo, Daniele, & Forina, 2009) and to distinguish EVOO from maize oils, different EVOO from the same geographical region or EVOO from different countries (Oliveri et al., 2009). Hybrid systems, combining E-noses and voltammetric E-tongues, were proposed and effectively applied to discriminate monovarietal or multivarietal EVOO or VOO according to their geographical origin (Apetrei et al., 2010; Cosio et al., 2006; Haddi et al., 2013). Among these works on the application of electrochemical methodologies for olive oils analysis, only one deals with the possibility of differentiating monovarietal EVOO according to the olive cultivar: Cimato et al. (2006) applied an E-nose to classify samples of 12 Italian single-cultivar EVOO but the results showed that it was only possible to separate among clusters of different monovarietal EVOO. These electrochemical devices have also been applied to evaluate olive oil chemical composition changes during storage under different conditions, namely temperature, light and storage time, showing that those conditions clear influence olive oil organoleptic characteristics, namely the polyphenols composition of VOO due to lipid-radical reactions or to enzymatic activity (Clodoveo, Hbaieb, Kotti, Mugnozza, & Gargouri, 2014; Cosio, Ballabio, Benedetti, & Gigliotti, 2007; Lerma-García, Simó-Alfonso, Bendini, & Cerretan, 2009).

These satisfactory results for olive oil analysis using electrochemical sensors have stimulated the present work. In this study, and to the authors' best knowledge, a potentiometric E-tongue with cross-sensitivity non-specific lipidic sensor membranes is proposed for the first time to discriminate Portuguese (PT) and Spanish (ES) monovarietal EVOO according to the olive cultivar (cv. Cobrançosa (COB), cv. Madural (MAD) or cv. Verdeal Transmontana (VER); and cv. Arbequina (ARB), cv. Hojiblanca (HOJ) or cv. Picual (PIC), respectively). Furthermore, for the first time ever an electrochemical approach is applied to the analysis of PT monovarietal EVOO. To establish linear discriminant models with the best cross-validation predictive performance, the most informative potentiometric sensor signal profiles obtained during EVOO analysis were selected using a simulated annealing (SA) algorithm, which is a meta-heuristic variable selection algorithm. Due to the difficulty of carrying out electrochemical assays in non-conductive liquids with high viscosity (Apetrei et al., 2010) in the present work, hydro-ethanolic extracts of EVOO were used. Previously, the use of hydro-methanolic mixtures was already reported to overcome this issue (Rodríguez-Méndez, Apetrei, & de Saja, 2008). These alcoholic extracts are expected to be rich in polar compounds, such as sterols, polyphenols and tocopherols, which differ considerably among olive oils cultivars and are the main contributors to olive oil bitterness, astringency and pungency (Apetrei et al., 2010; Carrasco-Pancorbo et al., 2006; García, Brenes, Garcí, Romero, & Garrido, 2003; García, Brenes, Romero, García, & Garrido, 2002; Matos et al., 2007; Morelló, Romero, & Motilva, 2004; Romero, & Brenes, 2012). Therefore their use as suitable discriminating descriptors was investigated, since it is expected that those compounds (e.g., sterols, polyphenols and tocopherols) are the major constituents of the hydro-ethanolic extracts. The three PT cultivars were chosen due to their economic importance since they account for more than 90% of the olive cultivation area in Trás-os-Montes region (northeast of Portugal) and can be used to produce PDO "Trás-os-Montes olive oil" (Matos et al., 2007). The three ES cultivars were selected since they are the most common varieties cultivated in Spain (Ruíz-Samblás et al., 2012) and recently they have been introduced in northeast PT olive groves due to their high productivity and easy adaptation to the edapho-climatic conditions.

2. Materials and methods

2.1. Extra-virgin olive oil samples

The PT and ES EVOO of different olive cultivars (cvs. Cobrançosa, Madural, Verdeal Transmontana; and Arbequina, Hojiblanca, Picual, respectively), produced in the northeast of Portugal (Mirandela and Valpaços in the Trás-os-Montes region) and the north of Spain (Valladolid region), were studied. Eighteen samples of monovarietal EVOO were obtained directly from certified olive oil producers. Details regarding olive oil variety, geographical origin and year of production are given in Table 1. All olive oil samples analysed were packed and stored in the dark at −20 °C in a 24-h period after their production in olive mills with a two-phase extraction process (in 2011 and 2012), and kept under those conditions until further analysis. All samples were electrochemically analysed on the same day, equivalent to storage times of one year or less.

2.2. Extra-virgin olive oil extraction procedure

Polar compounds from each monovarietal EVOO were extracted using a hydroethanolic solution (H_2O:EtOH, 80:20 v/v), using deionised water (type II) and ethanol p.a. (from Panreac, Barcelona). The alcohol used in the extraction solution and its relative proportion were set to minimise sensor degradation as well as to allow obtain stable potentiometric signals in a minimum time period, avoiding known interferences from other organic solvents,