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Evaluating the potential of phenolic profiles as discriminant features among extra virgin olive oils from Moroccan controlled designations of origin

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ABSTRACT

Herewith, the potential of an approach based on the combination of the determination of phenolic compounds and the use of chemometric treatments has been evaluated to establish, for the first time, promising models to authenticate the provenance of Moroccan monovarietal olive oils produced under different geographical origin indication systems. To achieve this purpose, 136 commercial extra virgin olive oil samples from three diverse production areas (Meknès territory; the Protected Geographical Indication Ouazzane; and the Protected Designation of Origin Tyout-Chiadma) were collected over two consecutive crop seasons (2012/2013 and 2013/2014). Their phenolic fraction composition was investigated by using high performance liquid chromatography coupled to mass spectrometry (HPLC-ESI-IT MS). The results showed that geographical provenance and harvest season had a marked influence on the content of identified phenolic compounds. Principal components analysis (PCA) and linear discriminant analysis (LDA) were applied to test the potential of the determined compounds as geographical discriminant features, achieving a noticeable discrimination among the three evaluated regions. The contribution of each analyte to the statistic model has been evaluated in depth.

1. Introduction

Linking foodstuffs and agricultural products to its geographical provenance is an ancient universal practice which allow differentiating them from other conventional products by means of certain characteristics, qualities and/or reputations, attributed to their historic legacy and their distinctive features linked to environmental and human factors, such as soil, climate, production practices, local know-how and traditions (Couillerot, 2000). Geographical Indication Protection systems, in particular, Protected Designations of Origin (PDOs) and Protected Geographical Indications (PGIs) are, nowadays, increasingly considered, in many countries, as great tools giving producers the opportunity to move forward from commodity markets into more lucrative niche markets through differentiation. As such, geographic origin becomes a strategic tool granting high added value to local production systems, since the use of geographical indications allows producers to obtain market recognition and, often, a premium price (Barham, 2003; Verbeke & Roosen, 2009).

Unfortunately, in spite of the importance of these differentiation systems, the general procedure to assess whether the claims of origin are valid remains, till now, mainly limited to the traceability of the production by regional institutions, which act as regulatory councils ensuring rigorous controls of the entire management conditions and giving certification to those products which comply with the quality standards demanded and show typical characteristics of the geographic label. However, because of the economic importance of these labeled products, new and increasingly sophisticated strategies can be used in their adulteration, so it is, sometimes, very difficult to be certain about the geographical authenticity of these products based only on the regulatory council's controls. Therefore, there is a continuous demand for effective, robust and reliable analytical strategies to verify the declared geographical origin, which can constitute a priceless tool for helping regulatory councils to trace foods back to their provenance (Luykx & van Ruth, 2008).

Virgin olive oil (VOO) represents an important example of food for which the establishment of geographic indications is widespread. Indeed, over the past two decades, the olive oil sector has experienced a significant motion towards market differentiation, and consequently, origin-labeled VOOs have proliferated in many producing countries. Indeed, in 2010, there were about 105 origin-labeled extra VOOs all over the world (both PDOs and PGIs); almost all of them (101) are produced in European Union countries, mainly in Italy, Greece and Spain (International Olive Council (IOC), 2010). Additionally, according to Chever, Renault, Renault, and Romieu (2012), the production value of

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marketed European origin-labeled extra VOOs was, on average, 215 M€ per year from 2006 to 2008, and 203 M€ in 2010. Therefore, it is easy to understand that, the characterization of the quality and composition of origin-labeled VOOs, as well as the development of quick and powerful analytical approaches to authenticate their geographical origin are, nowadays, emerging topics within the olive oil sector (Antonini et al., 2015; García-González, Tena, & Aparicio, 2012; López-Feria, Cárdenas, García-Mesa, & Valcárcel, 2008; Pardo, Cuesta, Alvarruiz, Granell, & Álvarez-Ortí, 2011). Certainly, several studies have focused on the quality and compositional profiling of VOO, underlining the relationship between these parameters and geographical origin characteristics. They clearly demonstrated that differences in geographical provenance factors (including intrinsic factors, such as those related to the characteristic of the cultivated olive tree variety, and extrinsic factors such as soil, climate, cultivation and manufacturing methods used for olive oil extraction) and storage conditions actually cause differences in the physicochemical quality, sensorial attributes, and the chemical composition of the produced olive oils (Arslan, Karabekir, & Schreiner, 2013; Ben-Hassine et al., 2013; Issaoui et al., 2009; Noorali, Barzegar, & Sahari, 2014). Furthermore, great effort has been made to investigate the potential of using some chemical component contents combined with the adequate chemometric treatments to trace the geographic origin of this foodstuff (Giacalone, Giuliano, Gulotta, Monfreda, & Presti, 2015; Gurdeniz, Ozen, & Tokatli, 2008; Marini, Magrì, Bucci, Balestrieri, & Marini, 2006; Ollivier, Artaud, Pinatel, Durbec, & Guérère, 2006). Among the various olive oil compounds used with this scope, phenolic compounds have shown a remarkable potential as geographical markers of oils produced in various Mediterranean regions (Lerma-García et al., 2009; Nescatelli et al., 2014; Ouni, Guido, et al., 2011a; Ouni, Taamalli, et al., 2011b; Romero et al., 2016; Servili et al., 2004). The relevance of these compounds is also irrefutable considering, among other reasons, their biological effects (Alesci et al., 2014; Clodoveo et al., 2015).

Morocco is among the leading producing countries of olive oil, and its oils show a wide range of peculiar characteristics which mainly depend on the pedoclimatic conditions and the production process of the predominant olive variety 'Picholine Marocaine' cultivated in this country. Moroccan oils are gaining noteworthy international reputation, but the process for adopting geographic indications systems in this country is still in its earliest stages. Indeed, till October 2013, there was only one recognized PDO for the extra VOO (Tyout-Chiadma, located in the South of Morocco) and one official PGI (Ouazzane, located in the North of this country). Another PDO for the extra VOO produced in Meknès territory is in the process of characterization of its typicality and it is expected that will enlarge the list in the near future (Bajoub et al., 2014).

The present study can be contextualized within a research line devoted to the establishment of efficient analytical approaches combining the comprehensive characterization of the composition of Moroccan monovarietal VOOs and chemometric treatments in order to develop trustworthy and effective geographical origin tracing models. Hence, the main objectives of this work can be formulate as follows: 1) carrying out the characterization of the phenolic fraction of commercial extra VOO samples (coming from Meknès territory, PGI Ouazzane and PDO Tyout-Chiadma over two consecutive crop seasons 2012/2013 and 2013/2014) using LC–MS; 2) investigating the geographical provenance and crop season effects on the phenolic content of the studied samples; and 3) evaluating the potential of combining phenolic data and chemometric treatments (PCA and LDA) for the development of models which will allow the geographical classification of oils under evaluation. To the best of our knowledge, the current work is the first one studying the phenolic fraction from Moroccan origin-labeled VOOs and no geographical discriminant approach for such kind samples has been previously performed and reported in literature.

2. Materials and methods

2.1. Olive oil samples

A total of 136 commercial monovarietal 'Picholine Marocaine' extra virgin olive oil samples, from three different Moroccan geographical locations: Meknès region (57 samples); PGI Ouazzane (42 samples) and PDO Tyout-Chiadma (37 samples), have been collected over two consecutive crop seasons (2012/2013 and 2013/2014). Each sample was a commercial bottle of approximately 250–500 mL, purchased from supermarkets or directly from their own producers ("Coopérative Tyout de Production et de Commercialisation de l'Huile d'Olive" in the case of PDO Tyout-Chiadma samples; and "Groupement d'Intérêt Economique Femmes du Rif (GIE)" for PGI Ouazzane samples), whereas Meknès samples were kindly supplied by "Agro-pôle Olivier Ecole Nationale d'Agriculture de Meknès". About 20 g of each sample were weighed and stored in dark glass bottles (22 mL) at −18 °C, excluding any hade space volume in order to ensure the proper conservation of the olive oils. These aliquots were used when the subsequent analyses had to be carried out. The geo-locations of the three studied zones are given in Fig. 1.

The extra VOOs produced in Tyout-Chiadma were the first receiving the designation PDO in Morocco in 2010, and it has a very limited production (approximately 20 tons of 'Picholine Marocaine' extra VOO per year) because of a cultivated surface of only 100 ha. The olive production is conducted under irrigated system, and oil extraction is made by means of a peculiar production process (a pressing method where olive fruits crushing is carried out in grinder with two cylindrical granite millstones, afterwards the obtained past is mixed by a slow and continuous stirring and, finally, the oil is extracted using a pressing system). This production area is characterized by a sandy limestone soil and a semi-arid climate with a moderate oceanic influence (the rainfall in the area does not exceed 300 mm, the annual mean temperature varies between 20 °C and 21 °C and the temperature fluctuation between the coldest month (January) and the warmest month (August) can reach 17 °C (Chamchati & Bahir, 2011). As far as the PGI Ouazzane is concerned, the production of its oils is made using 'Picholine Marocaine' olive fruits coming from the entire province of Ouazzane (the olive growing area is approximately 40,885 ha), extracted by two or three phases extraction systems. The most remarkable pedoclimatic characteristics of Ouazzane region are: minimum mean temperatures: 17.4 °C, annual mean maximum temperatures: 25.6 °C; annual mean rainfall: 676 mm; soil classes: fluvisols, regosols, lithosols, vertisols, rendzinas, yermosols, xerosols, cambisols, luvisols, acrisols, gleysols and planosols. Finally, regarding Meknès EVOOs, their production comes from 'Picholine Marocaine' olive fruits grown in Meknès region (about 43,000 ha leading to 21,000 tons of olive oil), by various olive oil mills belonging to the association "Union pour le Développement de l'Olivier de Meknès (UDOM)" using two and three phases continuous olive oil extraction systems. The main pedoclimatic characteristics of Meknès region are: annual mean minimum temperatures: 11 °C, annual mean maximum temperatures: 23 °C; annual mean rainfall: 400 to 600 mm; soil classes: fluvisols, regosols, lithosols, rendzinas, yermosols, xerosols, vertisols, kastanozems, chernozems, phaezems, luvisols and acrisols.

2.2. Phenolic compounds analysis

The phenolic compounds from the studied samples were analyzed, in triplicate, following a previously reported procedure (Bajoub et al., 2015). The following sections (Sections from 2.2.1 to 2.2.3) will describe the chemical and reagents, the extraction protocol, and the methodology used for their analysis and quantitative characterization.

2.2.1. Chemicals and reagents

All the solvents were of analytical or high pressure liquid chromatography–mass spectrometry (LC–MS) grade purity (depending on if