Food Control 139 (2022) 109055

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Geographical authentication of virgin olive oil by GC-MS sesquiterpene hydrocarbon fingerprint: Scaling down to the verification of PDO compliance

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ARTICLE INFO

Keywords:
Virgin olive oil
Authenticity
Geographical origin
Sesquiterpene hydrocarbons
Fingerprint
SPME-GC-MS
PDO

ABSTRACT

Nowadays, 144 Protected Designations of Origin (PDO) and Protected Geographical Indications (PGI) under the EU quality schemes correspond to extra virgin olive oil (EVOO). As endorsed by the EU Food Fraud Network, PDO/PGI EVOOs are particularly vulnerable to fraudulent practices because of their high economic value. For this reason, the present study aims to develop an instrumental tool to assess the compliance of EVOO with PDO label-declaration using a large sample set (n = 350). As a case study, PDOs from Catalonia were used. Therefore, discriminant analysis based on the sesquiterpene hydrocarbon fingerprint determined by HS-SPME-GC-MS achieved to correctly classify an average of 93.6% of samples among the four Catalan PDOs, leaving unassigned the 6% of the total sampling (external validation results for 3 iterations). On the other hand, the proposed strategy allowed discriminating each Catalan PDO from non-PDO samples produced in different geographical areas with an efficiency between 95% and 99%.

1. Introduction

The current European Union (EU) Regulation on marketing standards for olive oil (Commission Implementing Regulation No 29/2012) specifies labelling rules in order to protect the fair trading of this high-value food product. Apart from the guidelines referred to the commercial category, which are linked to the olive oil quality grade, this regulation states as mandatory the designation of geographical origin for virgin olive oils, both for extra virgin (EVOO) and for virgin (VOO) categories. Even though the declaration of provenance is generally related to the country of origin (single EU member, single third country or blends), EU quality schemes also consider Geographical Indications (GI) such as Protected Designations of Origin (PDO) and Protected Geographical Indications (PGI), which are intended to protect food products that originate from specific regions and present particular qualities linked to the production territory (Regulation (EU) No 1151/2012 of the European Parliament and of the Council). The amount of product's raw materials that must come from the area, or to what extent the production process has to take place within the specific region, make the difference between PDO and PGI products. The new portal to search for GI across the EU and beyond (European Commission, 2021) indicates that a total of 144 GIs for olive oil have been authorized

Abbreviations: BEM, Oli del Baix-Ebre Montsià; CAT, Catalan; COW, Correlation Optimized Warping; E, Oli de l'Empordà; EIC, Extracted Ion Chromatograms; EVOO, Extra Virgin Olive Oil (commercial category); FID, Flame Ionization Detector; GC, Gas Chromatography; GI, Geographical Indications; HPLC-CAD, High Performance Liquid Chromatography-Charged Aerosol Detector; HS-SPME-GC-MS, Headspace-Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry; LG, Les Garrigues; LV, Latent Variables; PDO, Protected Designations of Origin; PGI, Protected Geographical Indications; PLS-DA, Partial Least Squares-Discriminant Analysis; PV, Predicted Value; RSD, Relative Standard Deviation; S, Siurana; SH, Sesquiterpene Hydrocarbons; SIM, Selected Ion Monitoring; TA, Oli de Terra Alta; VOO, Virgin Olive Oil (commercial category).

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https://doi.org/10.1016/j.foodcont.2022.109055
Received 21 February 2022; Received in revised form 11 April 2022; Accepted 22 April 2022
Available online 26 April 2022

so far. A great number of them correspond to PDOs (118), mainly from Italy (50), Spain (40) and Greece (20), matching the top producing countries of olive oil.

In general terms, as reported by the study on economic value of EU quality schemes (European Commission, Directorate-General for Agriculture and Rural Development, 2021), GI-protected products represent a key economic asset for the EU, especially those that are appreciated by their sensory and nutritional properties, such as EVOO. The current control activities for virgin olive oil GI certifications are based on documental review, as described by Cugat & Biel (2016). Since the less efficient the tools available, the higher the risk of counterfeiting, the need for developing a fit-for-purpose authentication tool to support the official geographical verification results evident. Therefore, many studies proposing different geographical markers, analytical methods and data treatment approaches can be found in the literature (Conte et al., 2020; Tahir et al., 2022; Valli et al., 2016). The majority of them focused on verifying the country of origin of virgin olive oils (Cecchi et al., 2020; García-González et al., 2009; Quintanilla-Casas et al., 2020; Winkelmann & Küchler, 2019). Few studies intended the discrimination between virgin olive oils produced within and outside the EU (Bontempo et al., 2019; Palagano et al., 2020), although only one achieved the downscaling from the EU/non-EU discrimination to the single country classification (Quintanilla-Casas et al., 2022) in response to the need for addressing this authentication level as a first priority (Casadei et al., 2021). Other studies have been focused on the assessment of the origin of virgin olive oils produced in different regions from the same country, either considering EU certified GIs or not, for the main producer countries: Spain (Bakhouche et al., 2013; Beltrán et al., 2015; Fort et al., 2021; Ruisánchez et al., 2021), Italy (Araghipour et al., 2008; Bevilacqua et al., 2013; Forina et al., 2015; Woodcock et al., 2008), France (Dupuy et al., 2005; Ollivier et al., 2003), Greece (Karabagias et al., 2013) and Morocco (Bajoub et al., 2016). To a lesser extent, some works intended to verify the belonging to a given PDO against samples coming from a different production country (Alonso-Salces et al., 2015; Cosio et al., 2006; Hennessy et al., 2009; Nescatelli et al., 2014). In spite of the efforts, there is still a need to dispose of an authentication tool that covers different levels of geographical verification, ranging from the discrimination of wide areas (EU vs. non-EU, countries) to the verification of the compliance with PDO schemes.

Sesquiterpene hydrocarbons (SHs) have been previously reported to be suitable virgin olive oil geographical markers given that they are highly dependent on the olive trees' cultivar and growing area, while scarcely influenced by processing and storage conditions (Quintanilla--Casas et al., 2020; Vichi et al., 2018). As reported in Quintanilla-Casas et al. (2022), SH chromatographic fingerprint, combined with Partial Least Squares-Discriminant Analysis (PLS-DA), was used to successfully develop a classification strategy for the geographical authentication of virgin olive oils coming from wide areas (the EU and single country label-declaration). These results led us to hypothesize that the proposed authentication tool could be scaled down for the verification of the PDO compliance.

Catalonia, the north-eastern region of Spain, comprises five PDOs for EVOO. *Les Garrigues* (LG) (Ordre AAM/174/2011) and *Siurana* (S) (Ordre AAR/710/2010) were the first Catalan PDOs recognized for EVOO (Commission Regulation (EC) No 1107/96). Those PDO areas are adjacent regions that share the main olive cultivar *Arbequina*, which results to be the most relevant variety in Catalonia. Despite the geographical closeness and the use of the same cultivar to produce their EVOOs, diverse pedoclimatic conditions (altitude, rainfall, temperature, and soil type) of olive tree crops may influence differently the oils of these two PDOs (Vichi et al., 2019). The third PDO recognized was *Oli de Terra Alta* (TA) (Commission Regulation (EC) No 205/2005; Ordre ARP/136/2017), being *Empeltre* the main olive cultivar. The remaining PDOs, *Oli del Baix-Ebre Montsià* (BEM) (Commission Regulation (EC) No 112/2008; Ordre AAR/374/2010) and *Oli de l'Empordà* (E) (Commission Implementing Regulation (EU) 2015/385; Ordre ARP/110/2019), were recently created. Generally, EVOO produced in BEM are blends of *Morrut*, *Sevillenca* and *Farga* cultivars, while *Argudell* is the main one in E oils. The fact that oils from the same PDO are relatively homogeneous among them, results an advantage for authentication purposes, compared to the verification of wider production areas with high variability. Nevertheless, this purpose becomes challenging when the main olive cultivar is shared between different PDOs, which can even be neighbouring areas. Few authors aimed to discriminate LG and S PDOs, due to the particularities described above, by means of chromatographic fingerprints (high performance liquid chromatography (HPLC)-charged aerosol detector (CAD) and high temperature GC-flame ionization detector (FID)) (Vera et al., 2019) or spectroscopic techniques (fluorescence and fourier transform (FT)-Raman) (Fort et al., 2021). In both cases, the combination of two analytical techniques was necessary to obtain successful results.

Thereby, the present study pursues to move a step forward against false declaration of origin of virgin olive oils by fulfilling two main objectives: i) to discriminate among EVOOs from distinct Catalan PDOs and, ii) to verify the belonging of EVOO samples to a given Catalan PDO against EVOO from different geographical areas and thus not belonging to one of the Catalan PDOs. The authentication strategy proposed is based on the SH chromatographic fingerprint, obtained through an efficient and widespread analytical technique namely headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS).

2. Material and methods

2.1. Sample set

A total of 350 virgin olive oil samples, produced in several crop years (2016/2017, 2017/2018 and 2018/2019) were obtained both in the framework of the project Autenfood (*ACCIÓ- Programa Operatiu FEDER Catalunya 2014–2020*) and by the *Institut de Recerca i Tecnologia Agroalimentària de Catalunya (IRTA)* (Fig. 1). The sample set was composed by 260 traceable commercial EVOOs from the 5 Catalan PDOs (BEM; n = 74; E; n = 35; LG; n = 75; S; n = 65; TA; n = 11) and by 90 EVOO and VOO samples produced outside the above-mentioned PDOs, here for simplicity labelled as "non-CAT PDO". Some of the latter (n = 35) came from other Spanish regions (Andalusia; n = 18; Aragón; n = 1; Valencia; n = 14; Toledo; n = 2) and the rest originate from the top virgin olive oil producing countries according to the Food and Agriculture Organization database (FAO, 2021) (Greece; n = 15; Italy; n = 10; Morocco; n = 10; Tunisia; n = 10; Turkey; n = 10). Several sources of variability, such as crop year, olive cultivar and analytical variability were considered to build the sample set. Additional information about the sample set is available in Table S1 (Supplementary material). Samples were stored under N_2 atmosphere at −20 °C until analysis, which was performed in 3 different analytical batches over 7 months. These batches corresponded mainly to the harvesting season, including samples from different categories that were randomly measured.

2.2. Sample analysis by HS-SPME-GC-MS

According to Torres-Cobos et al. (2021), SHs were extracted from samples (2 g of oil placed into a 10 mL vial fitted with a PTFE/silicone septum) by HS-SPME. After 10 min of sample conditioning at 70 °C under agitation, a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (2 cm length, 50/30 μm film thickness) provided by Supelco (Bellefonte, PA) was exposed to the sample headspace for 60 min. Finally, it was desorbed in the CG injection port at 260 °C for 10 min. The SH chromatographic fingerprinting was determined by an Agilent 6890N Network GC system, coupled to a quadrupolar mass selective analyser Agilent 5975C Inert MSD (Agilent Technologies, Santa Clara, California, USA), using helium as carrier gas, at a flow of 1.5 mL/min. Analytes were separated on a Supelcowax-10 capillary column

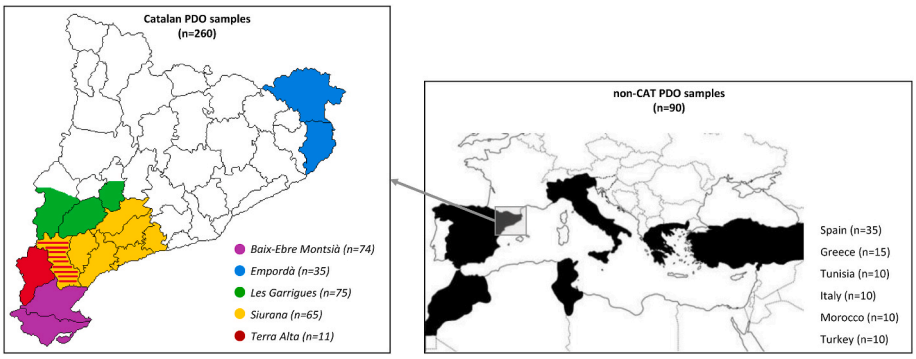

Fig. 1. Virgin olive oil sample set from Catalan PDOs, with the corresponding map of Catalonia, and from other producing regions/countries named as "non-CAT PDO".

(60 m × 0.25 mm i.d., 0.25 μm film thickness) (Supelco, Bellefonte, PA). GC oven temperature program was set as follows: initial temperature at 40 °C for 3 min, first rate 4 °C/min until 100 °C, second rate 5 °C/min until 200 °C and third rate 15 °C/min until 260 °C; holding the final temperature for 5 min. The temperatures of ion source and transfer line were 230 and 280 °C, respectively (Torres-Cobos et al., 2021; Vichi et al., 2006). Mass spectra acquisition was performed in the selected ion monitoring (SIM) mode for *m/z* 93, 119, 157, 159, 161, 189 and 204, which are known to be the main specific ions of SHs (Vichi et al., 2006).

On the other hand, representative virgin olive oils (quality control samples) in terms of SH composition were periodically analysed to evaluate the performances of the analytical system. The relative standard deviation (RSD, in %) was assessed for the analytical signal following part of the protocol stated in Quintanilla-Casas et al. (2020b), in order to detect differences among analytical batches.

2.3. Data extraction and pre-processing

For each of the seven specific ions, a data matrix was built with the 350 samples and the intensities of the extracted ion chromatograms (EIC) from minute 21 to 42 (350 samples × 3197 scans); thus, 7 data matrices were obtained. The raw analytical signal was corrected as follows: first, each of the 7 matrices was aligned to solve retention time shifting among samples by the correlation optimized shifting (coshift) algorithm (Larsen et al., 2006) and the correlation optimized warping (COW) algorithm (Nielsen et al., 1998) in Matlab R2020b®. In view of the differences in the raw signal magnitude among the analytical batches, each matrix was normalized (row wise) to the maximum intensity and baseline corrected (by automated weighted least squares).

Subsequently, an unfolded matrix (350 samples × 22,379 variables) was obtained concatenating the 7 pre-aligned and normalized matrices.

2.4. Classification models

According to the objectives of the study, two types of classification models were built: i) to discriminate between Catalan PDOs (based on a multi-class PLS-DA) in order to verify the PDO to which the oils belong and, ii) to discriminate each Catalan PDO from non-CAT PDO oils (based on binary PLS-DA).

To develop each model, the corresponding sample set was split into a training set (containing 80% of the samples) and a validation set (with the remaining 20% of samples), as detailed below. The training set was used to calibrate the PLS-DA model by cross-validation (leave 10%-out) and it was later externally validated by predicting the geographical origin of the samples in the validation set. For each PLS-DA model, this split was carried out three times (3 iterations), aiming at evaluating the model performance when the samples in the training and validation sets vary. Samples assigned to the corresponding training and validation sets were selected at random, but the balance between cultivars, crop seasons and analytical batches was considered. Unit variance scaling and mean centring (column wise) were selected as data pre-processing techniques.

In all cases, the optimal number of partial least squares (PLS) latent variables (LV) was selected according to the root mean square error of cross validation (RMSEcv), the highest cumulative Q^2 - defined as the estimated total variation of the Y block (discriminant categories) that can be predicted by the model – and classification results. Overfitting of the PLS-DA calibrated models was assessed by the RMSEcv, the Q^2 obtained by the permutation test (Q^2 of 20 models developed after randomly permuting the sample's class) and the ANOVA of cross-validated residuals; even though successful external validation results would be the proof for a non-overfitted model. Hotelling's T^2 and Q-residuals were used to detect outliers. Particularities of discrimination approaches developed in the present study are introduced in the following sub-sections.

2.4.1. Discriminant models between Catalan PDOs: calibration and external validation

To fulfil the first purpose, multi-class PLS-DA was applied to all samples from Catalan PDOs (n = 260), being each PDO a specific class (BEM, n = 74; E, n = 35; LG, n = 75; S, n = 65; TA, n = 11). This PLS-DA model could only be cross-validated since the TA category only contained 11 samples; therefore, sample set splitting into training and validation set was not possible for TA. For this reason, a new multi-class PLS-DA was calibrated and cross-validated with the 80% of the samples from the other 4 PDOs (BEM, n = 59; E, n = 28; LG, n = 60; S, n = 52; Total, n = 199) and externally validated with the remaining 20% (BEM, n = 15; E, n = 7; LG, n = 15; S, n = 13; Total, n = 50). As previously mentioned, sample set splitting as well as model calibration and external validation was carried out three different times (3 iterations).

Multi-class PLS-DA work indeed as multiple binary models. A dummy **Y** matrix holding as many classification vectors as classes is used in the PLS regression, each vector having values of 1 for a given class and 0 for all the remaining classes. Hence, each sample was classified into the class whose vector led to highest predicted value (PV). Samples whose PV did not reach the classification threshold (PV < 0.5) for any vector were left unassigned.

Cross-validation as well as external validation results of each iteration were expressed as: i) % of not assigned samples (those with PV < 0.5), for all samples (eq. (1)) and for each PDO (eq. (2)), and ii) % of correctly classified samples (those with at least one PV > 0.5), also for all samples (eq. (3)) and for each PDO (eq. (4)). Mean and standard deviation were calculated for both cross-validation and external validation results of the three iterations (n = 3).

$$\underset{(all\ samples)}{Not\ assigned\ samples\ (\%)} = \frac{Total\ unassigned\ samples}{Total\ samples} \times 100 \quad (1)$$

$$\text{Not assigned samples (\%) (per PDO)} = \frac{\text{Unassigned samples from a PDO}}{\text{Samples from a PDO}} \times 100 \quad (2)$$

$$\text{Correctly classified samples (\%) (all samples)} = \frac{\text{Total correctly classified samples}}{\text{Total assigned samples}} \times 100 \quad (3)$$

$$\text{Correctly classified samples (\%) (per PDO)} = \frac{\text{Correctly classified samples from a PDO}}{\text{Assigned samples from a PDO}} \times 100 \quad (4)$$

In order to dig into the suitability of the suggested approach to discriminate between border PDOs than even share the main olive cultivar, a binary PLS-DA was carried out for S and LG. This model was also calibrated by cross-validation and externally validated as indicated above, with the corresponding sample split into training (n = 52 for S and n = 60 for LG) and validation set (n = 15 for S and n = 13 for LG). However, as binary model, its results were expressed as explained in the section below (2.4.2).

2.4.2. Discriminant models Catalan PDO vs. non-PDO samples: calibration and external

According to the second purpose of the present study, four binary PLS-DAs were calibrated and externally validated to discriminate four of the five Catalan PDO (BEM, n = 74; E, n = 35; LG, n = 75; S, n = 65) from non PDO samples coming from other countries and Spanish regions (n = 90), which was named "non-CAT PDO" class. In order to do so, four binary models were built and cross-validated with a training set (80% of the samples in each category) (BEM/non- CAT PDO, n = 52/72; E/non-CAT PDO, n = 28/72; LG/non- CAT PDO, n = 60/72; S/non- CAT PDO, n = 52/72) and externally validated with the corresponding validation set (20%) (BEM/non- CAT PDO, 15/18; E/non- CAT PDO, n = 7/18; LG/non- CAT PDO, n = 15/18; S/non- CAT PDO, n = 13/18). As previously mentioned, sample set splitting as well as model calibration and external validation was carried out three different times (3 iterations).

In binary PLS-DA, classes are expressed as PLS dummy variables (being 0 for the PDO class, and 1 for the non- CAT PDO class); hence, samples were classified according to the class that reached the highest PV, provided it was above the classification threshold (here, PV = 0.5). The reliability of each of binary discrimination model in cross-validation and external validation was evaluated by the % of correct classification (for each category and for the total sampling), diagnostic sensitivity (eq. (5)) and diagnostic specificity (eq. (6)) (Magnusson & Örnemark, 2014). For each binary approach, results from the three iterations were averaged and the standard deviation was calculated (n = 3).

$$\text{Diagnostic sensitivity} = \frac{\text{non-CAT PDO samples correctly classified}}{\text{Total non-CAT PDO samples}} \quad (5)$$

$$\text{Diagnostic specificity} = \frac{\text{PDO samples correctly classified}}{\text{Total PDO samples}} \quad (6)$$

In case of the binary PLS-DA developed to discriminate S and LG PDO, diagnostic sensitivity was referred to S and diagnostic specificity to LG category as the values of the dummy variable were 1 for the S class and 0 for the LG class.

Finally, significant PLS-DA coefficients – positive values greater than the corresponding standard error – were extracted from binary models for each of the 4 PDOs, built with training set 1. Their assessment allowed exploring and compare the most relevant variables that influenced the discrimination of each PDO against the same group of samples (non-CAT PDO).

3. Results and discussion

As introduced before, the present study pursues two parallel objectives: i) the discrimination among virgin olive oils belonging to distinct Catalan PDOs and ii) the verification of the belonging of virgin olive oil samples to one of those PDOs, against EVOO produced in different geographical areas and not belonging to one of these Catalan PDO (non-CAT PDO).

3.1. Discrimination among Catalan PDOs

Multi-class PLS-DA was applied to virgin olive oil samples belonging to the five Catalan PDOs (n = 260). As previously commented, the number of samples from TA (n = 11) was not enough to split this category into a training and a validation set to externally validate the model. Thereby, this classification model was only internally validated by leave 10%-out cross-validation with satisfactory results (100% of correct assignment and 2.3% of unassigned samples) (Table S2, Supplementary information), suggesting that the approach could be valid to discriminate among all current PDOs.

Once samples from TA were removed, classification models were developed for the other four Catalan PDOs with the three training sets (3 iterations) (n = 199). Individual contingency tables for each iteration are available at Table S3 (Supplementary material). As shown in Table 1, a full correct classification was achieved in cross-validation for all classes, in addition to a very low % of unassigned samples (less than 2.5%). External validation results of the models with the corresponding validation sets (n = 50) resulted satisfactory as well (93.6% of overall correct classification), although LG and S showed a slight decrease to 88.4% and 88.2% (mean values) of correctly classified samples, respectively. This can be explained by the fact that LG and S are adjacent regions where Arbequina is the main olive cultivar, whereas E and BEM oils are produced with particular olive cultivars. It is known that the SH composition of virgin olive oil is also influenced by genetic factors, therefore their fingerprint carries information regarding the olive cultivar as it has been recently proven by Torres-Cobos et al. (2021). However, when the geographical origin was the variable driving the

Table 1
Internal and external validation results of PLS-DA including virgin olive oil samples from 4 Catalan PDOs: *Oli del Baix-Ebre Montsià* (BEM), *Oli de l'Empordà* (E), *Les Garrigues* (LG) and *Siurana* (S). Mean and standard deviation of three different training sets (80% of sampling) and the corresponding validation sets (20% of sampling) (3 iterations).

	Cross-validation of training sets			External validation		
	n[a]	Not assigned[b] (% of total sampling)	Correctly classified[c,d] (% of assigned samples)	n[e]	Not assigned[b] (% of total sampling)	Correctly classified[c,d] (% of assigned samples)
BEM	59	2.3 ± 1.0	100 ± 0.0	15	2.2 ± 3.9	100 ± 0.0
E	28	1.2 ± 2.1	100 ± 0.0	7	4.8 ± 8.3	100 ± 0.0
LG	60	0.0 ± 0.0	100 ± 0.0	15	4.4 ± 7.7	88.4 ± 8.7
S	52	0.6 ± 1.1	100 ± 0.0	13	12.8 ± 4.4	88.2 ± 8.7
Total	**199**	**1.0 ± 0.00**	**100 ± 0.0**	**50**	**6.0 ± 2.0**	**93.6 ± 1.8**

11-12 Latent variables; $Q^2 > 0.676$; Root mean square error of cross validation (RMSEcv) for BEM <0.199, for E < 0.199, for LG < 0.295, for S < 0.294.

[a] Number of samples in each of the three training sets.

[b] Not assigned samples (%) (predicted value, PV < 0.5) per PDO (unassigned samples from a PDO × 100/samples from a PDO) and for all countries (total unassigned samples × 100/total samples).

[c] Correctly classified samples (%) (PV > 0.5) per country (correctly classified samples from a PDO × 100/assigned samples from a PDO) and for all countries (total correctly classified samples × 100/total assigned samples).

[d] Weighted mean and standard deviation, given that the number of assigned samples was different for each of the three sets.

[e] Number of samples in each of the three validation set.

discrimination, PLS-DA was able to find features in the SH fingerprint related with the geographical origin over the cultivar as observed in Fig. 2. According to the scores scatter plot of the multi-class model, the cultivar effect was very evident in the first LVs (Fig. 2a and b) because a cluster of Arbequina virgin olive oils conformed by both LG and S samples was present; thus, more LVs were needed to discriminate LG from S (Fig. 2c and d).

In view of the results, an independent binary discrimination model was built for LG and S PDOs. As it can be observed in Fig. 3, the first and second LVs of this model already allowed the discrimination of these two geographical areas as this discriminant analysis did not need to model information related to the cultivar, contrarily of what happened in the previous multi-class model (4 PDOs). Although classification results in external validation for the multi-class model were satisfactory (LG: 88.4% of correct classification, 4.4% of not assigned samples; S: 88.2% of correct classification, 12.8% of not assigned samples), the binary strategy performed better for this purpose since the overall correct classification results were similar but no samples were left unassigned (LG: 84.4%; S: 92.3%) (Table S4).

Similar cross-validation results were obtained in a previous work where a PLS-DA model for LG and S PDOs was built with chromatographic fingerprint (high temperature GC-FID), although external validation would be needed (Vera et al., 2019). Besides, it was suggested that classification performance of both PLS-DAs and one-class models could improve by addition of other chromatographic data, such as HPLC-CAD, through data fusion techniques. In this sense, data fusion was proven to be necessary for achieving satisfactory discrimination (PLS-DA) of LG and S EVOOs by means of spectroscopic techniques (Fluorescence and FT-Raman) (Fort et al., 2021).

The results showed in the present section evidence the suitability of the suggested approach to verify the belonging of EVOOs to a given Catalan PDO, even if they are border producing regions that use the same olive cultivar such as LG and S. Nonetheless, in spite of the scientific interest of these successful results, the odds of a high quality EVOO from a specific PDO fraudulently sold as belonging to a different PDO are quite low. Therefore, discrimination models able to detect virgin olive oils with false PDO declaration of origin were developed and explained in the section below (3.2).

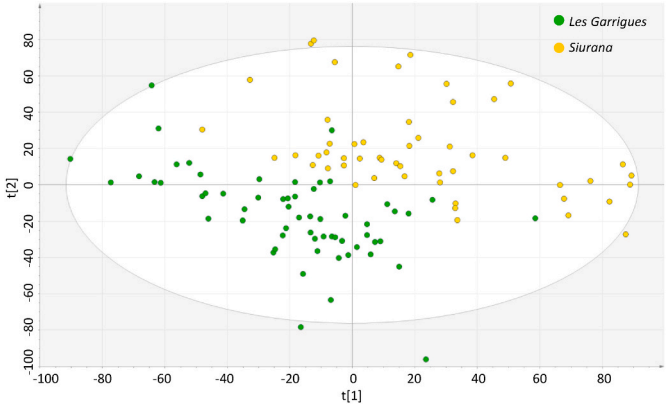

Fig. 3. Score plot of binary PLS-DA built upon the sesquiterpene hydrocarbon fingerprint of virgin olive oils from Siurana and *Les Garrigues* PDOs, for one of the training sets (n = 112, 4 LV).

3.2. Discrimination between PDO vs. non-CAT PDO

A more concerning issue would involve an olive oil that does not belong to any PDO quality scheme and yet it carries a false PDO label-declaration. Binary authentication models for each Catalan PDO (PDO vs. non-CAT PDO) were proposed to face this problem. Hence, PLS-DA models were developed by cross-validation and externally validated for four Catalan PDOs (BEM/non- CAT PDO, E/non- CAT PDO, LG/non-CAT PDO and S/non- CAT PDO), for 3 iterations. While EVOO samples from each Catalan PDO were the same used for the multi-class model presented at the section above (3.1), the non- CAT PDO class included 90 samples (training sets, n = 72; validation sets, n = 18) produced in other Spanish regions and in other main producing countries within and outside the EU.

A correct classification higher than 95% (mean value of iterations) was achieved for all binary models (Table 2). Individual contingency tables for each model are available at Table S5 (Supplementary material). In such type of authentication approaches, breaking down the global outcome results interesting to evaluate the model's performance. In this context, Forina et al. (2008) stated that a discriminant model might be suitable as long as no PDO oil would be classified as non-PDO

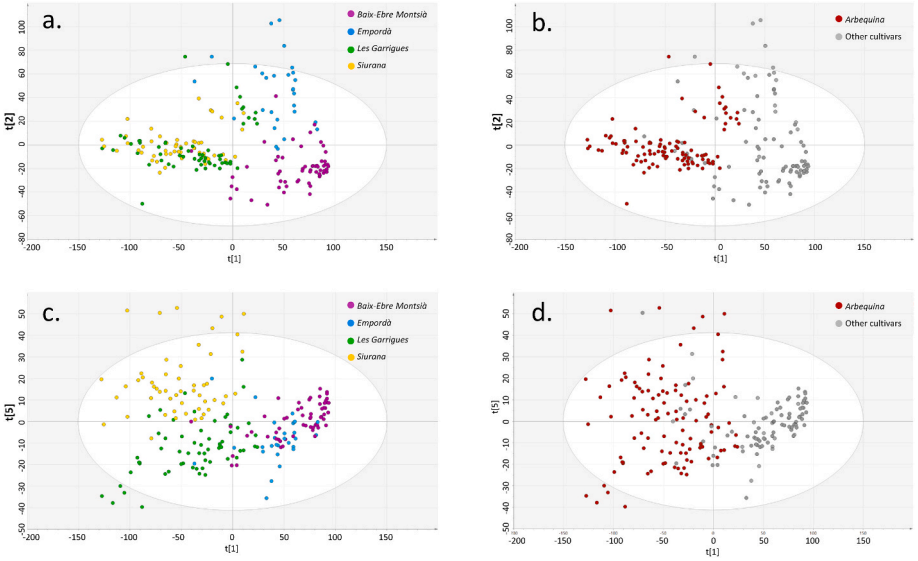

Fig. 2. Score plots of PLS-DA built upon the sesquiterpene hydrocarbon fingerprint of virgin olive oils from four Catalan PDOs, for one of the training sets (n = 199, 11 latent variables (LV)): a) LV1 and LV2, by PDO; b) LV1 and LV2, by olive cultivar (*Arbequina;* Other); c) LV1 and LV5, by PDO; d) LV1 and LV5, by olive cultivar (*Arbequina;* Other).

Table 2
Internal and external validation results of binary PLS-DAs for each virgin olive oil PDO: *Oli del Baix-Ebre Montsià* (BEM), *Oli de l'Empordà* (E), *Les Garrigues* (LG) and *Siurana* (S). For each model, mean and standard deviation were obtained from three different training sets (80% of the sampling) and the corresponding validation sets (20% of the sampling) (3 iterations).

	Cross-validation of training sets							External validation			
	n [a]	LV	Q^2	RMSEcv	Correct classification (%)	Sensitivity[b]	Specificity[c]	n[d]	Correct classification (%)	Sensitivity[b]	Specificity[c]
BEM/non-CAT PDO	59/72	3–4	>0.67	<0.28	98.0 ± 0.4	0.97 ± 0.00	0.99 ± 0.01	15/18	95.0 ± 1.8	0.96 ± 0.06	0.93 ± 0.07
E/non-CAT PDO	28/72	3	>0.65	<0.26	100 ± 0.0	1.00 ± 0.00	1.00 ± 0.00	7/18	98.7 ± 2.3	0.98 ± 0.03	1.00 ± 0.00
LG/non-CAT PDO	60/72	2–3	>0.74	<0.27	99.5 ± 0.9	0.99 ± 0.02	1.00 ± 0.00	15/18	99.0 ± 1.8	0.98 ± 0.03	1.00 ± 0.00
S/non-CAT PDO	52/72	3	>0.77	<0.24	100 ± 0.0	1.00 ± 0.00	1.00 ± 0.00	13/18	98.9 ± 1.9	0.98 ± 0.03	1.00 ± 0.00

[a] Number of samples in each of the three training sets.
[b] Non-CAT PDO samples correctly classified/total non-CAT PDO samples.
[c] PDO samples correctly classified/total PDO samples.
[d] Number of samples in each of the three validation sets.

oil, otherwise the PDO consortium would consider the model unsatisfactory. Considering our definitions of sensitivity (eq. (5)) and specificity (eq. (6)), this would correspond a specificity equal to 1. Indeed, except for BEM PDO, the specificity reached in both internal and external validation was always the maximum value (equal to 1) (Table 2). On the other hand, sensitivity was higher than 0.96 (mean value) for all categories, putting in value the high performance of the developed discrimination models. In any case, at this stage, high specificity and sensitivity values are desired even if they are not equal to 1, since the proposed strategy could serve as a screening tool to guide inspections. By this, oils with a fraudulent declaration of geographical origin would be detected, and inspections could be then addressed targeting these suspicious cases, increasing the efficiency of the inspections and thus protecting consumers and honest producers and traders.

Fig. 4 shows the PLS-DA coefficients for the four Catalan PDOs, extracted from each binary model (PDO vs. non-CAT PDO) for one of the main ions (*m/z* 93). It seems that some variables are relevant for the discrimination of all PDOs, even if they are minor SHs (Fig. 4a), suggesting that they could be related with overall pedoclimatic conditions of Catalonia (see grey column number 2 in Fig. 4). On the other hand, other SHs would carry geographical information regarding a specific area wider than PDO, as observed for BEM (Fig. 4b), LG (Fig. 4d) and S (Fig. 4e) PDOs that are located in the central-south part of Catalonia (see grey column number 1 in Fig. 4). And last, but not least, PLS-DA coefficients revealed that the most significant variables to discriminate LG PDO and S PDO were almost the same. This agrees with the fact that these two PDOs use the same olive cultivar as described above (section 3.1), and to the high influence of the cultivar on the SH fingerprint.

Other studies that intended geographical authentication of EVOOs PDO from EVOOs produced in other different regions or countries, also opted for supervised discrimination tools, such as LDA or PLS-DA (Alonso-Salces et al., 2015; Araghipour et al., 2008; Bajoub et al., 2016; Ollivier et al., 2003). Despite of the promising results, some of them based the proposed authentication strategy on analytical techniques that involved complex analytical methods (Alonso-Salces et al.,

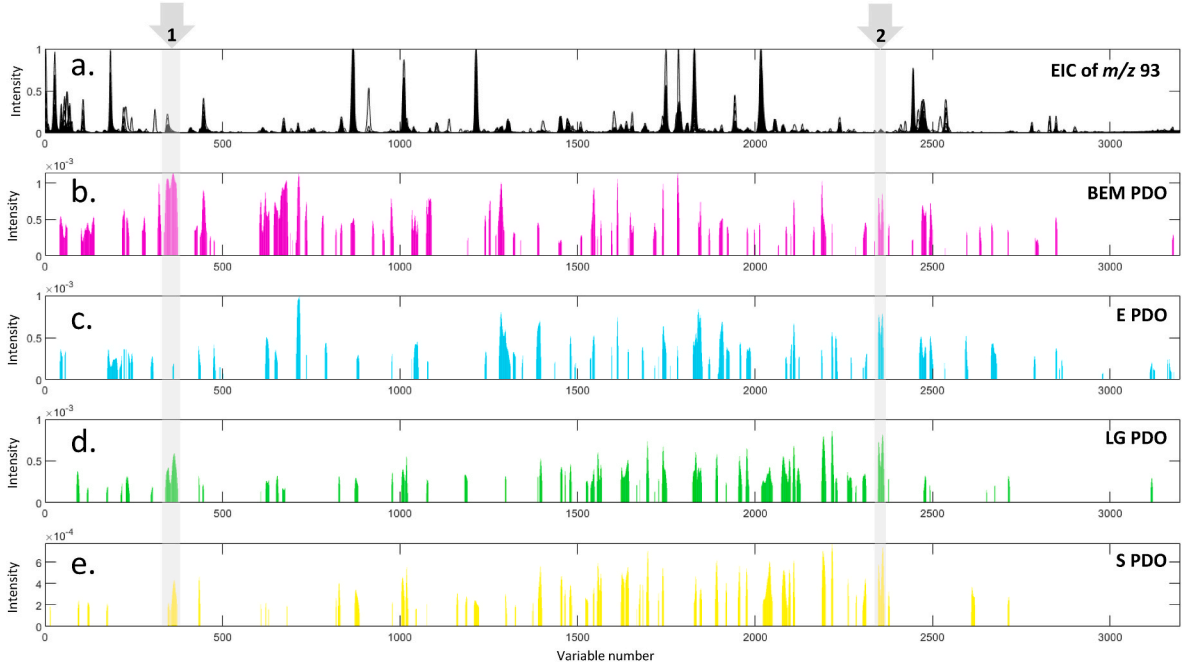

Fig. 4. Exploration of binary discriminant models built upon the sesquiterpene hydrocarbon fingerprint of virgin olive oils from a given Catalan PDO and a pool of non-CAT PDO samples: a) EIC of *m/z* 93; b) Significant PLS-DA coefficients for BEM PDO; c) Significant PLS-DA coefficients for E PDO; d) Significant PLS-DA coefficients for LG PDO; e) Significant PLS-DA coefficients for S PDO. *Oli del Baix-Ebre Montsià* (BEM), *Oli de l'Empordà* (E), *Les Garrigues* (LG) and *Siurana* (S).

2015; Bajoub et al., 2016; Ollivier et al., 2003), or else showed low performances when scaling down from countries to PDO assessment (Araghipour et al., 2008). In this sense, SH fingerprint proved to be successful for PDO verification, while their obtention implies a simple, affordable and solvent-free analytical technique.

4. Conclusions

False declaration of origin is one of the counterfeiting practices affecting virgin olive oil. A reliable instrumental method with the proper chemometric tool should be available for a comprehensive geographical authentication of this valuable food product. As proven in our previous study (Quintanilla-Casas et al., 2022), the proposed tool resulted efficient for the verification of EU label-declaration and country of provenance, and so it has been to verify the compliance with a given PDO scheme. Indeed, it has been tested successful for both purposes set: the discrimination among EVOOs from distinct Catalan PDOs and the verification of the belonging of EVOO samples to a given Catalan PDO, against olive oil samples produced in other regions or countries. Therefore, the SH fingerprint could become the fit-for-purpose screening tool to further guide inspections by the corresponding control bodies.

Funding

This study has been funded by the project AUTENFOOD, from *ACCIÓ-Generalitat de Catalunya* and the European Union through the ERDF programme for Catalonia 2014–2020 [grant number COMRDI-15-1-0035]. B. Quintanilla-Casas and B. Torres-Cobos thank the Spanish Ministry of Universities for the predoctoral fellowships FPU16/01744 and FPU20/01454, respectively. A. Tres acknowledge funding received from the Ramon y Cajal grant [grant number RYC-2017-23601) funded by MCIN/AEI/10.13039/501100011033 and by "ESF Investing in your future". A. Romero acknowledges financial support from the CERCA Program of the Generalitat de Catalunya.

CRediT authorship contribution statement

Beatriz Quintanilla-Casas: Formal analysis, Investigation, Methodology, Validation, Data curation, Visualization, Writing – original draft. **Berta Torres-Cobos:** Formal analysis, Investigation, Data curation. **Francesc Guardiola:** Supervision, Writing – review & editing. **Agustí Romero:** Resources, Writing – review & editing. **Alba Tres:** Methodology, Conceptualization, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing. **Stefania Vichi:** Conceptualization, Methodology, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors thank the Catalan cooperatives that provided traceable virgin olive oil samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodcont.2022.109055.

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