

**COMPREHENSIVE REVIEW**

# Nuclear magnetic resonance spectroscopy in extra virgin olive oil authentication

Valentina Maestrello<sup>1,2</sup>  | Pavel Solovyev<sup>1</sup>  | Luana Bontempo<sup>1</sup>  |  
Luisa Mannina<sup>3</sup>  | Federica Camin<sup>1,2,4</sup> 

<sup>1</sup>Fondazione Edmund Mach (FEM), San Michele all'Adige, Italy

<sup>2</sup>Center Agriculture Food Environment (C3A), University of Trento, San Michele all'Adige, Italy

<sup>3</sup>Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, Piazzale Aldo Moro, Roma

<sup>4</sup>International Atomic Energy Agency, Vienna International Centre, Vienna, Austria

## Correspondence

Federica Camin, International Atomic Energy Agency, Vienna International Centre, PO Box 100, A-1400 Vienna, Austria.

Email: [federica.camin@unitn.it](mailto:federica.camin@unitn.it)

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## Abstract

Extra virgin olive oil (EVOO) is a high-quality product that has become one of the stars in the food fraud context in recent years. EVOO can encounter different types of fraud, from adulteration with cheaper oils to mislabeling, and for this reason, the assessment of its authenticity and traceability can be challenging. There are several officially recognized analytical methods for its authentication, but they are not able to unambiguously trace the geographical and botanical origin of EVOOs. The application of nuclear magnetic resonance (NMR) spectroscopy to EVOO is reviewed here as a reliable and rapid tool to verify different aspects of its adulteration, such as undeclared blends with cheaper oils and cultivar and geographical origin mislabeling. This technique makes it possible to use both targeted and untargeted approaches and to determine the olive oil metabolomic profile and the quantification of its constituents.

## KEYWORDS

EVOO, NMR Spectroscopy, Metabolomics, Traceability

## 1 | INTRODUCTION

Olive oil is the product obtained from the fruit of the olive tree (*Olea europaea*) through extraction by mechanical procedures (Morin et al., 2018). It is a fundamental component of the Mediterranean diet, and according to several studies (Gaforio et al., 2019; Owen et al., 2000) and a specific health claim (European Commission, 2012), the intake of a proper amount of olive oil improves health thanks to its nutritional values and antioxidant properties, attributable to its content of polyphenols, which contribute

to the protection of blood lipids from oxidative stress (Gorzynik-Debicka et al., 2018). Due to its excellent health and organoleptic characteristics (del Caño-Ochoa et al., 2018), the demand for olive oil has significantly increased in recent decades.

The economic relevance of olive oil is highlighted by the trade number statistics: olive oil production has tripled in the last 60 years, reaching maximum production in 2017/18 of 3,379,000 tons. The 2020/2021 global production was 3,034,000 tons of olive oil (IOC, 2022), 93.4% of which is produced by European International Olive

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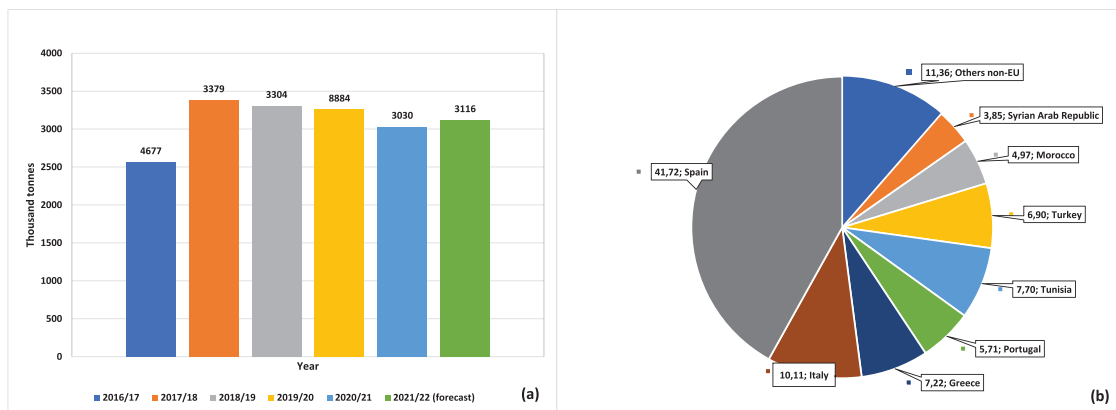


FIGURE 1 (a) World olive oil production in the last 5 years; (b) production for EU and non-EU countries for 2021/2022 (forecasts) (European Commission, 2022)

Council (IOC) member countries. The forecast of oil production for 2021/2022 is expected to be in line with the past 5 years (Figure 1) (European Commission, 2022).

From a chemical point of view, olive oil is composed of a saponifiable fraction (~98% by weight: triacylglycerols, mono- and di-glycerides) and an unsaponifiable fraction (~2% by weight: hydrocarbons, sterols, aliphatic alcohols, tocopherols, pigments, and phenolic and volatile compounds), both contributing to the distinctive character of olive oils of different cultivars or geographical origins (Blekas et al., 2006).

From a regulatory perspective, different organizations regulate olive oil classification: the European Commission (EU), the IOC, and the Codex Alimentarius (Conte et al., 2020). The European Union Commission recognizes eight classes of olive oil (European Commission, 1991): extra virgin olive oil (EVOO), virgin olive oil (VOO), lampante olive oil (LOO), refined olive oil, olive oil as a blend, and different categories of pomace oil. These categories have different quality standards, based on different physicochemical and organoleptic characteristics, defined by regulation (Contreras et al., 2019).

Protected designation of origin (PDO) and protected geographical identification (PGI) denominations were introduced to label products of particular quality in 1992 (European Commission, 1992 followed by European Commission, 2006). Moreover, the EU Member States agreed to compulsory origin labeling for virgin and EVOO (European Commission, 2009).

“High quality” often means higher prices, which makes olive oils prone to adulteration (Contreras et al., 2019; Rabiei & Enferadi, 2012); malpractices have increased by 87.5% in the last 10 years, as reported by Unaprol (Consorzio Olivicolo Italiano, 2019). The adulteration of an extra virgin olive oil with cheaper oils, as well as the mislabeling of the geographical or botanical origin, are both frauds. The identification of the geographical and botani-

cal origin of an olive oil is a very important aspect because the peculiar characteristics of a given olive oil depend on genetics, environment, agronomic practices, and harvesting time (Longobardi et al., 2012; Nikou et al., 2020; Perri et al., 2012; Portarena et al., 2012.; Rabiei & Enferadi, 2012). Tools able to trace the geographical and botanical origins of olive oils are thus becoming extremely important for olive oil authentication.

## 2 | STATE OF THE ART

### 2.1 | Official methods to assess the authenticity of EVOOs

Olive oils are complex mixtures of different compounds that can vary depending on different factors, and it is difficult to define reliable and absolute parameters and methods for authentication and traceability (Nikou et al., 2020). International regulation bodies (especially the European Union and IOC) have already approved different methods to identify and quantify different compounds in olive oil. These standard methods are “targeted” methods for specific compounds. They are mainly based on spectroscopic (e.g., ultraviolet absorption) and chromatographic techniques, namely, gas chromatography (GC) and liquid chromatography (LC) combined with various detectors. Triacylglycerols are analyzed through high-performance liquid chromatography (HPLC) coupled with refractive index detectors, whereas waxes, partial glycerides, fatty acids, sterols, aliphatic alcohols, and aliphatic hydrocarbons are analyzed through GC coupled to a flame ionization detector (FID) (Aparicio et al., 2013; Conte et al., 2020).

An efficient method recognized by the IOC to define the quality of a virgin olive oil is based on a sensory evaluation of the organoleptic characteristics of the sample

(Kalogiouri et al., 2016) through a panel test (European Commission, 2013). The panel test is performed by 8–10 people as trained tasters, who have to verify about 19 different attributes that can take some time because panelists need to be trained before the test.

These standards are efficient for detecting adulterations such as additions with refined oils or with other botanical origins, soft deodorization, or synthetic mixtures, but they are not capable of detecting authenticity in terms of geographical and botanical origin in a complete and unambiguous way (Aparicio et al., 2013). Therefore, as reported by different studies (Contreras et al., 2019; Kalogiouri et al., 2016), there is increasing interest in new, robust, rapid, and cost-efficient analytical methods to investigate different compounds in olive oils for authentication and traceability purposes.

## 2.2 | Alternatives to official methods for authenticity detection

Many analytical procedures proposed for olive oil authentication are extensions of existing official methods, relying on liquid and gas chromatography coupled with different detectors, sometimes followed by chemometric analysis, which can be useful support for analytical methods (Gomez-Caravaca et al., 2016).

A recent review (Kalogiouri et al., 2020) gives an overview of the applications of mass spectrometry (MS) coupled with different statistical approaches for authenticity issues, showing the possibilities of analyzing both specific compounds or obtaining a fingerprint of the sample. The method proposed by Quintanilla-Casas, Bustamante, et al. (2020) adopted headspace GC in combination with MS and chemometric analysis of volatile compounds of olive oils to verify sensory quality, while in another work (Quintanilla-Casas, Bertin, et al., 2020), the sesquiterpene hydrocarbons were analyzed. Volatile compounds have also been successfully investigated using GC coupled with ion mobility spectrometry (IMS) to verify the geographical origins of EVOO (Gerhardt et al., 2017). This method was also used for oil mapping and sample classification (Contreras et al., 2019). A complex method based on two-dimensional GC coupled with MS has been recently proposed to perform studies that could last years (e.g., involving different harvest years) (Stilo et al., 2019), whereas a simpler GC-FID method was used to discriminate different cultivars of the Peloponnese region (Valli et al., 2016). Liquid chromatography was coupled with diode array (DAD) and fluorescence (FLD) detectors for the analysis of phenolic fractions (Bajoub et al., 2017). The phenolic fraction has also been studied in combination with the sterolic profile by Ghisoni et al. (2019)

through untargeted metabolomics using UHPLC and time-of-flight to discriminate olive oils with different cultivars and geographical origins. LC in combination with MS and supervised statistical analysis was able to investigate the authenticity of EVOOs with both a targeted and an untargeted approach for screening strategies (Kalogiouri et al., 2016; Nikou et al., 2020). LC was also combined with orbitrap to verify the efficiency of a method based on flow-injection analysis-magnetic resonance mass spectrometry to classify Greek olive oils (Nikou et al., 2020). Different cultivars of EVOOs were discriminated using HPLC-MS with positive APCI detection without derivatization (Nagy et al., 2005). Da Ros et al. (2019) analyzed the volatile compounds of oils combining a targeted and an untargeted method (GC-MS) and phenols with a targeted approach using high-liquid chromatography (HPLC-DAD-ESI/MS), showing that the two methods can be complementary and powerful for this purpose. For industrial application, Thermo Fisher Scientific has developed a platform based on UHPLC coupled with a charged-aerosol detector and principal component analysis (PCA) to detect adulterations, studying changes in triacylglycerol patterns (Plante et al., 2013).

Spectroscopic techniques are also employed for authenticity purposes, including Raman spectroscopy (Aykas et al., 2020), UV-absorption (Milanez et al., 2017), and front-face fluorescence spectroscopy (Merás et al., 2018). Synchronous fluorescence spectroscopy was found to be a useful tool coupled with multivariate statistical analysis to detect and quantitatively assess EVOO adulteration (Nigri & Oumeddour, 2016; Poulli et al., 2007). A development of this technique is 3D-excitation-emission matrix fluorescence spectroscopy, which is widely used in food areas because of its rapidity and simplicity, coupled with chemometrics, mostly parallel factor analysis (Lia, Formosa, et al., 2020; Xu et al., 2015). Fourier transform infrared spectroscopy (Aykas et al., 2020; Christy & Egeberg, 2006; Karunathilaka et al., 2016; Rohman & Man, 2010) coupled with attenuated total reflection (Poiana et al., 2015) has been adopted not only for research purposes but also by industries. Bruker GmbH developed a Fourier transform near-infrared spectroscopy (FT-NIR) protocol for routine analysis of olive oils, making quality control and the production process easy (Behmer, 2018). Violino et al. (2020) instead have recently developed a method based on an open source visible-near infrared spectrophotometer coupled with a specific app relying on artificial intelligence neural networks for traceability purposes. Through this advanced approach, a correct classification of 94.6% of the samples was obtained, and specific wavelengths for origin authentication were found. A deeper explanation of the abovementioned approaches is reported in the review of Meenu et al. (2019). Another review (Rifna

et al., 2022) summarizes the spectroscopic techniques coupled with chemometric analysis as Process Analytical Technology tools for the verification of edible oils, having the advantages of being used for on-line and nondestructive measurements. Finally, Rabiei and Enferadi (2012) reported a good overview regarding the use of DNA-based markers, pointing out the drawbacks and challenges of the methodology.

A method giving good results is based on isotopic analysis. Stable isotope ratios are strictly correlated to the geo-climatic characteristics of the production site and the agricultural practices (Paolini et al., 2017); thus, by analyzing their composition in the samples, the geographical provenance can be revealed. For these reasons, the isotopic fingerprint has been a useful tool for authentication (Perri et al., 2012). The stable isotope ratios studied in olive oils are mainly  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ , and  $^{18}\text{O}/^{16}\text{O}$ , but Janin et al. (2014) also proposed measuring the ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  as a geographical traceability marker. The stable isotope ratios of C, H, and O are measured with isotopic ratio mass spectrometry in the bulk of EVOOs (Lukić et al., 2019) or in the fatty acid fraction (Paolini et al., 2017). A better discrimination of the samples is obtained by combining isotopic analysis with elemental composition analysis, which is related to geological and pedoclimatic characteristics (Camin et al., 2010). Despite the high potential of stable isotope ratios and elemental composition, it is important to mention that these analytical approaches are based on a database in which the number of analyzed samples must be sufficient to truly reflect commercial samples. Furthermore, the database must be updated year by year, as these parameters reflect the yearly climatic situation of the place of growth of olive plants. Therefore, the combination of these techniques with rapid profiling techniques (e.g.,  $^1\text{H}$  NMR) and classical parameters (e.g., concentration of specific organic compounds) should not be overlooked, as they often provide invaluable additional information useful for the traceability of EVOOs.

### 3 | NUCLEAR MAGNETIC RESONANCE FOR EVOO AUTHENTICATION

Nuclear magnetic resonance (NMR) methodology is not yet recognized by regulation bodies as a tool for authentication and traceability assessment, but it is a reliable tool that should be adopted in an official way. In this review, different NMR methods will be presented, divided into targeted and untargeted approaches, to accomplish authentication of EVOOs (Table 1).

NMR spectroscopy, well known for structure elucidation, is also a powerful tool for food quality control, geographical characterization, and product authentication

(Mannina et al., 2012; Piccinonna et al., 2016), and it is a very promising technique, especially if followed by a chemometric approach (Beteinakis et al., 2020). The NMR methodology has numerous advantages, such as no need for time-consuming sample preparation steps plus high reproducibility and automation (Calò et al., 2022). The major drawback of NMR is its intrinsic sensitivity, which is lower than the sensitivity of other chromatographic and mass-spectrometry methodologies, even if it can be improved through the application of more elaborate equipment, such as cryoprobes (Pan & Raftery, 2007).

Two approaches can be followed for NMR analysis: the targeted and the untargeted approaches. The targeted approach is based on the identification and quantification of specific compounds, whereas the untargeted approach studies the entire set of molecules present in the sample (the sample metabolome), allowing a comprehensive characterization (Girelli et al., 2016), which can be useful for the discrimination of different categories of samples.

The NMR-based metabolome is becoming a central topic in food analysis because changes are seen as the response of an organism to a disease, genetic modification, or environmental conditions (Lioupi et al., 2020). Because of the large amount of collected data in metabolomics, chemometric analysis helps to pull out the most relevant information according to the purpose of the study, such as adulteration and the identification of cultivar and geographical origin (Rezzi et al., 2005).

#### 3.1 | NMR targeted and untargeted approaches for adulteration

Because of its higher nutritional and commercial values, EVOO is often subjected to the undeclared addition of less valuable botanical oils (Fauhl et al., 2000). These vegetable oils generally have a different chemical composition in terms of the amount of triacylglycerols. To show the intrinsic and easily recognizable difference among oils, several edible oils (canola, corn, peanut, olive, sesame, and sunflower oils) have been distinguished by a simple  $^1\text{H}$  NMR analysis and PCA, as demonstrated by Anderson et al. (2017). By collecting the NMR spectra of oils of different botanical origins (four samples for each origin) and simple PCA, it was easy to recognize the botanical origin of an unknown oil sample. Nevertheless, numerous studies based on this evidence have been reported for the authentication of olive oils. Regarding targeted approaches, Castejón et al. (2014) optimized the  $^1\text{H}$  NMR method for the analysis of total FA by reducing the analysis time without losing quality in the results. Other authors (Guillén & Ruiz, 2003) focused only on some FAs, such as linoleic, oleic, linolenic acid, and saturated acyl

TABLE 1 Summary of the NMR methods discussed in this review

	Nucleus/frequency	Aim	Statistics	References
<i>Adulteration</i>				
Untargeted	<sup>1</sup> H NMR/400 MHz	Adulteration detection	PCA	Anderson et al. (2017)
Targeted	<sup>1</sup> H NMR/500 MHz	Discrimination of different botanical origins	Quantification and comparison of FAs	Castejón et al. (2014)
Targeted	<sup>1</sup> H NMR/400 MHz	Discrimination of 14 different botanical origins	Quantification and comparison of saturated FAs, linoleic acid, linolenic acid, oleic acid	Guillen and Ruiz (2003)
Targeted	<sup>1</sup> H NMR/600 MHz	Adulteration with hazelnut oil	Five selected signals coupled with LDA and a stepwise regression model	Mannina et al. (2009)
Targeted	<sup>1</sup> H NMR/500 MHz	Adulteration with hazelnut and sunflower oil	Three selected signals and two signal height ratios with discriminant analysis	Fauhl et al. (2000)
Targeted	<sup>1</sup> H NMR/60 MHz benchtop spectrometer	Adulteration with hazelnut oil	Comparison of the peak area ratio (olefinic to glyceride) and PLS regression	Parker et al. (2014)
Targeted	<sup>1</sup> H NMR/22.5 MHz	Adulteration with soybean and corn oil	Determination of relaxation times coupled with ANOVA and PCA and PLS	S. Wang et al. (2021)
Targeted	<sup>1</sup> H NMR/19.91 MHz	Adulteration with three types of edible oils	Determination of relaxation times coupled with PCA and SVM	X. Wang et al. (2020)
Targeted	<sup>1</sup> H NMR/19.91 MHz	Adulteration with hazelnut and high-oleic sunflower oil	Determination of relaxation times coupled with several machine learning algorithms	Hou et al. (2021)
Targeted	<sup>13</sup> C NMR/500 MHz ( <sup>1</sup> H frequency)	Adulteration with hazelnut oil	Quantification of triacylglycerides and squalene coupled with PCA and LDA	Vlahov (2009)
Targeted	<sup>1</sup> H and <sup>13</sup> C NMR/400 MHz and 100.6 MHz, respectively	Discrimination of different botanical origins	Quantification of selected signals coupled with descriptive statistical analysis and PCA	Popescu et al. (2015)
Targeted	<sup>1</sup> H and <sup>31</sup> P NMR/500 MHz and 202.2 MHz, respectively	Discrimination of different botanical origins	Quantification of FAs and iodine value coupled with one-way ANOVA and PCA	Vigli et al. (2003)
Targeted	<sup>1</sup> H and <sup>31</sup> P NMR/500 MHz and 202.2 MHz, respectively	Adulteration with refined hazelnut oil	Determination of iodine number, FAs and minor compounds coupled with stepwise forward CDA	Agiomyrgianaki et al. (2010)
Targeted	<sup>31</sup> P NMR/202.2 MHz	Adulteration with lampante and refined olive oil	Quantification of five signals with one-way ANOVA coupled with HCA and DA	Fragaki et al. (2005)
Targeted	<sup>1</sup> H and <sup>19</sup> F NMR/500 MHz and 470 MHz, respectively	Adulteration with refined olive oil and soybean oil	Determination of FAs and squalene coupled with classical statistical analysis	Jiang et al. (2018)
Targeted	<sup>1</sup> H NMR/300 MHz (diffusion experiment)	Discrimination of different botanical origins	Measurement of diffusion coefficient coupled with DA	Šmejkalová and Piccolo (2010)
Targeted	<sup>1</sup> H NMR/43.62 MHz	Discrimination of different botanical origins	Quantification of selected signals coupled with PLS	Gouilleux et al. (2018)

(Continues)



TABLE 1 (Continued)

	Nucleus/frequency	Aim	Statistics	References
Untargeted	$^1\text{H}$ NMR/400 MHz	Classification of commercial 100% Italian blends of olive oil	Fingerprint (0.04 ppm buckets width) coupled with PCA and PLS-DA	Girelli et al. (2020)
Untargeted	$^1\text{H}$ NMR/400 MHz	Determination of the origin of Italian/Tunisian blends	Fingerprint (0.04 ppm buckets width) coupled with PCA and PLS-DA and PLSR	Girelli et al. (2017)
Untargeted	$^1\text{H}$ NMR/500 MHz	Discrimination of different botanical origins	Fingerprint (542 buckets) coupled with PCA and PLS-DA and PLSR	Alonso-Salces et al. (2022)
Untargeted	$^1\text{H}$ NMR/400 MHz	Adulteration of other edible oils	Fingerprint (0.05 ppm buckets width) coupled with PCA	Ray et al. (2022)
<i>Cultivar discrimination</i>				
Targeted	$^1\text{H}$ NMR/400 MHz	Discrimination of different botanical origins	Quantification and comparison of FAs	Barison et al. (2010)
Targeted	$^1\text{H}$ NMR/400 MHz	Discrimination of different botanical origins	Quantification and comparison of FAs	Knothe and Kenar (2004)
Targeted	$^1\text{H}$ NMR/600 MHz	Discrimination among different cultivars	Quantification of oleocanthal and oleacein	Karkoula et al. (2012)
Targeted	$^1\text{H}$ NMR/500 MHz	Discrimination of varietal traceability	Determination of the unsaponifiable fraction coupled with ANOVA and various supervised methods	Sayago et al. (2019)
Targeted	$^1\text{H}$ and $^{13}\text{C}$ NMR/400 MHz	Discrimination among different cultivars	Quantification of nine selected signals coupled with ANOVA and LDA	Cabrita et al. (2021)
Targeted	$^1\text{H}$ and $^{31}\text{P}$ NMR/500 MHz and 202.2 MHz, respectively	Discrimination among different cultivars	Determination of 23 selected signals coupled with forward stepwise CDA	Agiomyrgianaki et al. (2012)
Targeted	$^{13}\text{C}$ NMR/500 MHz	Discrimination among different cultivars	Determination of 44 selected variables coupled with ANOVA, PCA, HCA, and DA	Brescia et al. (2003)
Targeted	$^{13}\text{C}$ NMR/150.9 MHz	Discrimination among different cultivars cultivated in Sicily	Determination of 77 selected signals coupled with ANOVA, PCA, TCA, and MDS	Mannina et al. (2003)
Targeted	$^1\text{H}$ NMR/700 MHz (experimental configuration of MAS)	Discrimination of different Spanish cultivars	Quantification of linolenic, linoleic, oleic acid and saturated FAs coupled with PCA	Corsaro et al. (2015)
Untargeted	$^1\text{H}$ NMR/400 MHz	Discrimination of Coratina or Coratina-based blends	Fingerprint (0.04 ppm buckets width) coupled with PCA and PLS-DA	Girelli et al. (2016)
Untargeted	$^1\text{H}$ NMR/400 MHz	Discrimination of Coratina-based blends	Fingerprint (0.04 ppm buckets width) coupled with PCA	Del Coco et al. (2014)
Untargeted	$^1\text{H}$ NMR/600 MHz	Discrimination among Slovenian and Turkish varieties	Fingerprint (0.04 ppm buckets width) coupled with ANOVA, PCA and PLS-DA	Özdemir et al. (2018)
Targeted	$^1\text{H}$ NMR/700 MHz	Cultivar classification	Determination of the FA profile coupled with ANOVA, PCA, PLS, and RF	Tang et al. (2022)

(Continues)

TABLE 1 (Continued)

	Nucleus/frequency	Aim	Statistics	References
Untargeted	$^1\text{H}$ NMR/700 MHz	Differentiating cultivars of processed olives	Fingerprint (0.05 ppm buckets width) coupled with PCA and OPLS-DA	Crawford et al. (2020)
<i>Geographical origin</i>				
Targeted	$^1\text{H}$ NMR/600 MHz	Discrimination of PDO samples from Veneto region	Quantification of 19 signals coupled with ANOVA and PCA	Mannina et al. (2005)
Targeted	$^1\text{H}$ NMR/400 MHz	Discrimination of samples from different regions of Lebanon	Quantification of FAs and minor components coupled with ANOVA, PCA, CDA, and LDA	Merchak et al. (2017)
Targeted	$^1\text{H}$ NMR/400 MHz and 600 MHz	Discrimination of samples from different areas of Tunisia	Quantification of the phenolic profile coupled with ANOVA	Ben Mansour et al. (2016)
Targeted	$^1\text{H}$ NMR/600 MHz	Discrimination of samples from different areas of Italy	Quantification of 15 signals coupled with LDA	Ingallina et al. (2019)
Targeted	$^1\text{H}$ NMR/600 MHz	Discrimination of samples from Liguria region	Quantification of seven selected signals coupled with PLS-DA and SIMCA	Mannina et al. (2010)
Targeted	$^1\text{H}$ NMR/600 MHz	Discrimination of samples from Lazio region	Quantification of 13 selected signals coupled with ANOVA and PCA	Circi et al. (2018)
Targeted	$^1\text{H}$ and $^{13}\text{C}$ NMR/600 MHz and 250 MHz ( $^1\text{H}$ frequency), respectively	Discrimination of samples from different areas of Lazio region	Quantification of 27 selected signals coupled with ANOVA, PCA, and LDA	D'Imperio et al. (2007)
Untargeted	$^1\text{H}$ NMR/600 MHz	Discrimination of VOO samples from different countries at a national, regional, or PDO levels	Fingerprint (0.02 ppm buckets width) coupled with ANOVA, PCA, LDA, and PLS-DA	Alonso-Salces, Moreno-Rojas, et al. (2010)
Targeted	$^1\text{H}$ NMR/600 MHz	Discriminate olive oils from Italy to Tunisia	Quantification of 17 selected signals coupled with PCA and RF (adding isotopic results)	Camin et al. (2016)
Targeted	$^1\text{H}$ NMR/400 MHz	Discriminate PDO olive oils from family farms to commercial-blends	Quantification of lipids coupled with ANOVA, PCA, HCA, and PLS-DA	Lukić et al. (2019)
Untargeted	$^1\text{H}$ NMR/500 MHz	Discriminate of samples from the Mediterranean basin from "Italian olive oil" available in the United States	Fingerprint (0.04 ppm buckets width) coupled with PCA	Coco et al. (2012)
Untargeted	$^1\text{H}$ NMR/500 MHz	Discriminate samples from different countries	Fingerprint (0.04 ppm buckets width) coupled with univariate procedures and PCA, LDA, PLS-DA, CART, and SIMCA	Alonso-Salces, Héberger, et al. (2010)
Untargeted	$^1\text{H}$ NMR/700 MHz	Discriminate samples from Bejaia region (Algeria)	Fingerprint (0.002 ppm buckets width) coupled with PCA	Laincer et al. (2016)
Untargeted	$^1\text{H}$ NMR/400 MHz	Discriminate samples from different countries	Fingerprint (0.002 ppm buckets width) coupled with PCA-CA-KNN	Winkelmann and Küchler (2019)

(Continues)

TABLE 1 (Continued)

	Nucleus/frequency	Aim	Statistics	References
Untargeted	$^1\text{H}$ NMR/500 MHz	Discriminate the geographical origin of commercial EVOOs	Fingerprint (0.04 ppm buckets width) coupled with PCA and PLS-DA	Rongai et al. (2017)
Untargeted	$^1\text{H}$ NMR/400 MHz	Discriminate samples from different countries	Fingerprint (0.04 ppm buckets width) coupled with PCA and PLS-DA	Calò et al. (2021)
Untargeted	$^1\text{H}$ NMR/400 MHz	Discriminate samples from different areas of Bari district	Fingerprint (0.04 ppm buckets width) coupled with PCA and PLS-DA	Del Coco et al. (2016)
Untargeted	$^1\text{H}$ NMR/400 MHz	Discriminate PGI Tuscan olive oils	Fingerprint (0.04 ppm buckets width) coupled with PCA and PLS-DA	Girelli et al. (2018)
Untargeted	$^1\text{H}$ NMR/600 MHz	Discriminate samples from Sardinian region (Bosana)	Fingerprint (0.02 ppm buckets width) coupled with PCA and PLS-DA	Culeddu et al. (2017)
Untargeted	$^1\text{H}$ NMR/600 MHz	Discriminate oils from Gemlik olives	Fingerprint (0.04 ppm buckets width) coupled with univariate analysis and PLS-DA	Özdemir and Bekiroğlu (2019)
Untargeted	$^1\text{H}$ and $^{13}\text{C}$ NMR/500 MHz	Discriminate Maltese olive oils	Fingerprint (32,768 buckets) coupled with PCA, PLS-DA, and ANN	Lia, Vella, et al. (2020)
Untargeted	$^1\text{H}$ NMR/400 MHz	Discriminate olive oils produced with different methods	Fingerprint (0.04 ppm buckets width) coupled with PCA and PLS-DA	Del Coco et al. (2020)

Abbreviations: ANN, artificial neural network; CDA, Canonical discriminant analysis; CART, classification and regression trees; CA-KNN, Canonical analysis k-nearest neighbors; DA, discriminant analysis; FA, fatty acid; HCA, hierarchical discriminant analysis; LDA, linear discriminant analysis; NMR, nuclear magnetic resonance; MDS, multidimensional scaling; PCA, principal component analysis; PLS(R), partial least square (regression); RF, random forest; SIMCA, soft independent modelling of class analogy; SVM, support vector machine; TCA, tree clustering analysis.

groups, for the discrimination of oils with different botanical origins. NMR spectra of oils from 14 different botanical origins (such as EVOO, mixtures of pomace olive oils, hazelnut oils, sesame oils, sunflower oils) were acquired, and through the calculation of the different proportions of the acyl groups, it was possible to see differences among the various samples.

Adulteration with refined hazelnut oil up to 10% was detected through the quantification of specific  $^1\text{H}$  NMR signals selected through analysis of variance (ANOVA) (only five signals with the most discriminant power were considered) in combination with linear discriminant analysis (LDA) and a multiple regression model (Mannina et al., 2009). Fauthl et al. (2000) analyzed fraudulent mixtures of hazelnut or sunflower oils with EVOO considering five selected peaks from the  $^1\text{H}$  NMR spectrum and discriminant analysis.

A promising, quick alternative for binary blends, such as EVOO and hazelnut oil, is the adoption of a 60 MHz benchtop NMR spectrometer. Parker et al. (2014) identified an adulteration at the 13% w/w level based on selected internal peak ratios (olefinic/glyceride peaks) and an adulteration at the 11.2% w/w level through a chemometric approach

on the whole spectrum, making this technique a valuable and rapid screening tool. This technique also has some minor drawbacks that Gunning et al. (2022) attempted to partially overcome. S. Wang et al. (2021) adopted low-field NMR with pattern recognition for the verification of adulterated EVOOs with soybean and corn oils. Through the study of the relaxation times and the aid of multivariate statistical analysis, it was possible to discriminate adulterated olive oils with an adulteration ratio no less than 30%. By using a low-field NMR spectrometer (19.91 MHz magnetic field) and support vector machine (a statistical tool based on machine learning, SVM), 84.92% accuracy in the identification of fraud was achieved when the adulteration with three seed oils was above 10% for EVOO blends (X. Wang et al., 2020).

A similar study (Hou et al., 2021) discriminated adulterated EVOO with hazelnut and high-oleic sunflower oil with high accuracy (approximately 89%) even at low percentages of adulteration (volumetric ratio range 10%–100% of adulteration) with a spectrometer working at a proton resonance frequency of 19.91 MHz.

Other authors used  $^{13}\text{C}$  NMR, as Vlahov (2009), who detected the adulteration of olive oil with 5%, 10%, and



20% of hazelnut oil through the quantification of triacylglycerides and squalene on the  $^{13}\text{C}$  NMR spectra and chemometrics. Good predictability was achieved, especially regarding the samples adulterated with 5% and 20%, obtaining a total result of 86.2% correctly classified samples. Popescu et al. (2015) used both  $^1\text{H}$  and  $^{13}\text{C}$  spectroscopy and chemometrics to discriminate olive oils of different botanical origins with low levels of adulteration (under 5%). It was possible to calculate the saturated FAs, oleic acid, linolenic acid, linoleic acid, and iodine values and to delineate samples on the basis of their botanical origin with PCA, showing that this technique can be used for fast screening of oils.

Another helpful approach is the combination of  $^1\text{H}$  and  $^{31}\text{P}$  NMR (Agiomyrgianaki et al., 2010; Vigli et al., 2003) to determine the addition of different vegetable oils and refined hazelnut oil with a lower adulteration limit of 5% w/w through the quantification of various compounds. Additions of LOO and ROO (Lampante and Refined Olive Oil) were detected with high-field  $^{31}\text{P}$  NMR through the selection of the most discriminant signals and multivariate statistical analysis (MVA) in different Greek olive oils with an adulteration ratio of 5% w/w (Fragaki et al., 2005). Jiang et al. (2018) combined  $^1\text{H}$  and  $^{19}\text{F}$  NMR to assess the adulteration of EVOO with seed oil and ROO, respectively, through the quantification of FA and squalene, achieving a detection limit of 4.5% of adulteration. Šmejkalová and Piccolo (2010) adopted a diffusion experiment to calculate the diffusion NMR coefficient to discriminate peanut, soybean, hazelnut, and sunflower oils in EVOO, in combination with discriminant analysis, allowing a rapid recognition of adulterations with the lowest adulteration levels of 10% for sunflower and soybean oils and 30% for hazelnut and peanut oils. A promising technique is represented by low-field (LF) NMR spectroscopy. Gouilleux et al. (2018) evaluated the performances of a low-field NMR spectrometer working at 43.62 MHz for the discrimination of different edible oils using a 2D UltraFast experiment: EVOO, hazelnut oil, sunflower oil, corn oil, sesame oil, and rapeseed oil. By considering 13 signals of the 2D spectra, it was possible to show the enormous potential of this instrument in quality control.

As an untargeted method, recently Girelli et al. (2020) proposed  $^1\text{H}$  NMR and chemometric analysis of the entire spectra to classify over 200 samples of commercial 100% Italian blends of olive oil by comparison to a database of 126 monocultivar oils from specific geographical origins, making this a useful tool for the fight against adulterated blends. Another untargeted study (Girelli et al., 2017) determined the origin of Italian/Tunisian blends in the range 10%–90% w/w by building an ad hoc NMR database and multivariate statistical analysis. The database was built using selected blends of Apulian Coratina olive oils

and a common Tunisian oil. With multivariate statistical analysis, in particular partial least square (PLS) regression, it was possible to quantitatively assess the composition of blends. Recently, Alonso-Salces et al. (2022) adopted  $^1\text{H}$  NMR fingerprinting and regression models based on decision trees to determine the botanical origin and the compositional percentages of blends. This methodology proved good robustness and predictability, which was also confirmed by a validation step. Ray et al. (2022) recently developed a new NMR-based method with new processing parameters for the discrimination of olive oils adulterated with other edible oils in different percentages with just a simple PCA. This study can be a valuable step toward the use of NMR in the industry for quality control because it is a fast and simple method, and the results are easy to interpret.

### 3.2 | NMR targeted and untargeted approaches for cultivar

The olive cultivar is an important issue to correctly assign the label of authenticity since botanical origin is one of the requirements for PDO assignment.

Regarding targeted approaches, Barison et al. (2010) focused on the determination of the FA composition of oils of different botanical origins (soybean, canola, sunflower, corn, rice, and olive oil). Each edible oil has a specific FA composition; thus, it is possible to authenticate an oil by determining its characteristic composition directly in the NMR spectrum, without the use of any mathematical manipulation, but simply through the relationships between areas of different signals. Other studies focus on the determination of FAs by working with the areas in the NMR spectrum and some mathematical formulas (e.g., Knothe & Kenar, 2004).

Karkoula et al. (2012) found that oleocanthal and oleacein could be quantified with NMR spectroscopy, and the different amounts can be used to discriminate between cultivars and, regarding small areas, even differentiating samples from the geographical area.

By combining the characterization of the unsaponifiable fraction and  $^1\text{H}$  NMR fingerprint with data mining tools, tocopherols, squalene, sterols, and aliphatic alcohols were found to be the most significant compounds for varietal and geographical traceability (Sayago et al., 2019). The combination of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR DEPT 45 was used to discriminate samples from nine different cultivars. Through the signal areas of triacylglycerols determined on both proton and carbon NMR spectra and linear discriminant analysis (LDA), Cabrita et al. (2021) developed a fast methodology for varietal discrimination, achieving good results in terms of predictivity, especially for  $^{13}\text{C}$

NMR spectroscopy.  $^{13}\text{C}$  NMR allowed the determination of the FA composition and the positional distribution on glycerol moieties, which, in combination with chemometrics, allowed varietal discrimination (Mannina et al., 2003; Perri et al., 2012), even though GC was considered preferable for its better separation. For example, Brescia et al. (2003) adopted 44 selected variables on the  $^{13}\text{C}$  spectrum (assigned to FAs, sterols, and triacylglycerols) and showed a good delineation between Apulian virgin olive oils of four different cultivars: Coratina, Leccino, Peranzana, and Ogliarola.  $^1\text{H}$  and  $^{31}\text{P}$  NMR and biometric analyses were employed to study the influence of cultivar, geographical origin, and harvest period on Greek EVOOs. Nine phenolic compounds and linoleic and linolenic acids were the most discriminant compounds (Agiomyrgianaki et al., 2012). A new approach was the adoption of high-resolution magic angle spinning NMR spectroscopy to characterize Sicilian EVOOs (Corsaro et al., 2015). MAS NMR proved to be a useful technique for quality assessment and to give similar results to GC. By quantifying linolenic acid, linoleic acid, oleic acid, and saturated acids with two different NMR methods based on peak areas, Corsaro et al. (2015) were able to discriminate samples of different Spanish cultivars (Arbosana and Arbequina) with PCA, even though the discrimination of the different Sicilian provinces of origin of the samples was not well achieved.

The untargeted approach has also been used for distinguishing olive cultivars (Crawford et al., 2020; Mannina et al., 2003), and an interlaboratory study has confirmed the robustness of NMR-based metabolomics for cultivar discrimination (Piccinonna et al., 2016). With this approach, monocultivar and commercial Coratina or Coratina-based blend olive oils were discriminated on the basis of a reference model built with 100 original samples and different multivariate analyses (namely, PCA and partial-least square discriminant analysis [PLS-DA]) of 40 Italian EVOOs (Girelli et al., 2016). It was found that the Carolea cultivar had higher saturated amounts of FA, whereas Coratina and Picholine had higher levels of unsaturated acyl groups. Coratina-based blends were also found to be characterized by the highest number of polyphenols responsible for bitterness among samples of other cultivars through simple proton and 2D J-resolved experiments (Del Coco et al., 2014). Özdemir et al. (2018) discriminated olive oils from major Turkish and Slovenian olive varieties on the basis of their  $^1\text{H}$  NMR profiling performed with a multisignal suppression, finding that the most important compounds are phenolic compounds, terpenes, and diacylglycerols.

Performances of  $^1\text{H}$  NMR spectroscopy have been compared to GC-FID and UHPLC-CAD for cultivar classification when coupled with chemometrics by Tang et al. (2022), finding the metabolites that most characterize the

different cultivars. Despite the best sensitivity and separation achieved by GC-FID, NMR spectroscopy showed good results and agreement with data obtained from GC-FID, whereas UHPLC-CAD had the lowest performance.

A recent study proposed the comparison of DNA analysis, targeted analysis, and NMR fingerprinting for processed olives to discriminate cultivars (Crawford et al., 2020). The results showed that DNA analysis correctly classified three out of four cultivars. FA profiling through GC-FID can well differentiate the four classes, phenolic profiling through LC-DAD is not reliable because of the high variability found, and NMR fingerprinting can distinguish well genetically related cultivars and the growing region.

### 3.3 | NMR targeted and untargeted approaches for geographical origin

The assessment of the geographical origin of EVOOs is one of the most important issues that need to be addressed by authorities because it is the most popular fraud in this field. In fact, different reviews focused on this particular topic. One of the latest is the work from Tahir et al. (2022), which reports recent studies on olive oil geographical traceability using different analytical techniques coupled with chemometric analysis.

$^1\text{H}$ -NMR spectroscopy has been shown to be a promising method to assess the geographical origin of olive oils (D'Imperio et al., 2007) on a Mediterranean, national, regional, and PDO scale (Mannina & Sobolev, 2011), also by analyzing both  $^1\text{H}$  and  $^{13}\text{C}$  NMR fingerprinting (Lia, Vella, et al., 2020) or through the measurement of selected signals combined with chemometrics. Preliminary results were obtained to discriminate different PDO olive oils of distinct microareas from the Veneto region with PCA using 19 signals selected through ANOVA (Mannina et al., 2005). Eight signals out of 19 belonged to volatile compounds, indicating the influence of these components on the geographical classification. The influence of geographical, temporal, and morphological factors on olive oils from different regions of Lebanon has been investigated by selecting the resonances in  $^1\text{H}$  spectra of monounsaturated and saturated FAs, linoleic acid, linolenic acid, and minor compounds with different statistical tools (Merchak et al., 2017). The results showed an increase in the concentration of monounsaturated fatty acids and a decrease in saturated fatty acids from south to north. Another study (Ben Mansour et al., 2016) performed different analyses on Tunisian olive oils, such as free acidity, peroxide value, FA composition, Rancimat assay, pigment content and phenolic compounds by NMR, to study the influence of the production area on the phenolic

profile. Through NMR, the concentrations of oleocanthal, oleacein, oleuropein aglycone, and ligstroside aglycone have been determined, revealing that the profile changes according to the geographical origin. Additionally, Italian olive oils were studied (Ingallina et al., 2019) by taking samples from nine Italian regions, selecting the intensity of 15 NMR signals, and applying different LDA models, allowing a discrimination of the samples first among northern, central, and southern Italy and then in the respective microareas. Mannina et al. (2010) studied Ligurian olive oils and found that these oils are marked by terpenes and a low number of saturated FAs compared to oils from the Mediterranean basin. These authors considered seven signals and treated them with partial least-square discriminant analysis and soft independent modelling by class analogy analysis. A recent study (Circi et al., 2018) considered geographical discrimination of samples from a small area of Lazio. Thirteen selected NMR signals treated with ANOVA and PCA were able to well characterize oils of that particular region.

The combination of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR is a promising approach to address geographical traceability (Lia, Vella, et al., 2020), and there are already studies on this topic. For example, 27 signals from both  $^1\text{H}$  and  $^{13}\text{C}$  NMR were considered to investigate the role of irrigation and altitude on olive oil composition, and the minor volatile compounds, such as aldehydes, squalene, terpenes, and b-sitosterol, were found to be influenced by pedoclimatic conditions and thus by geographical origin (D'Imperio et al., 2007). The combination of NMR with isotopic analysis has also shown promising results for geographical classification (Alonso-Salces, Moreno-Rojas, et al., 2010; Camin et al., 2016). A recent study by Lukić et al. (2019) combined different techniques to assess the differentiation of EVOOs according to their origin. The analysis of the lipid profile through HPLC with MS detection and through  $^1\text{H}$  NMR allowed the identification of new markers, uvaol, and oleanolic acid, the most significant, which distinguish PDO EVOO from family farms to commercially blended EVOO. Calò et al. (2022) deeply discussed the use of NMR and MS spectroscopies combined with chemometrics for geographical assessment, highlighting the good performances and usefulness of these two techniques. A development of NMR fingerprint methods in combination with statistical analysis to address the geographical origin issue of EVOOs was reported by Coco et al. (2012), who studied 12 authentic olive oils from Italy, Greece, Tunisia, and Spain and 25 commercially available "Italian olive oils" in the US market with NMR and PCA. The majority of the products studied were found to be more similar to Greek and Spanish olive oils than Italian ones (as declared), and the discriminant factor for the classification was the composition in FAs. At a national level,

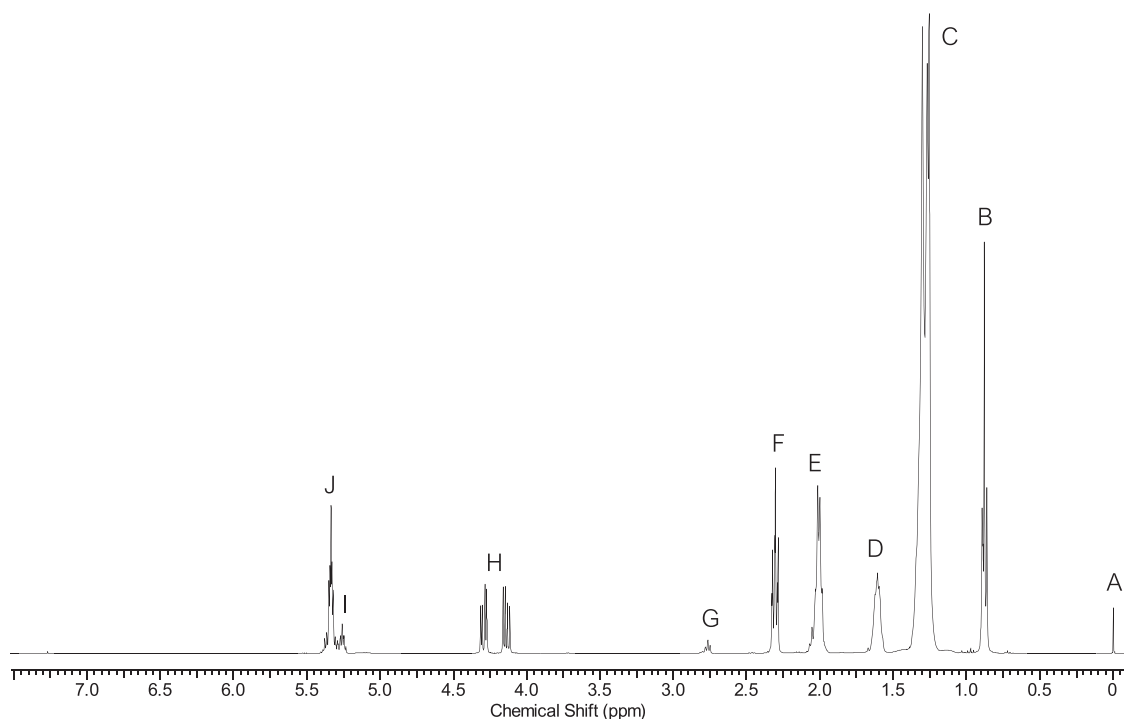
samples from six different countries (Italy, Spain, Syria, Turkey, Tunisia, and Greece) were discriminated on the basis of their unsaponifiable fraction, in which it is possible to recognize some trends, and multivariate statistical analysis (Alonso-Salces, Héberger, et al., 2010). In another study on Bejaia (Algeria) olive oils, in addition to traditional analyses, such as the determination of tocopherols, pigment content and phenolic compounds,  $^1\text{H}$  NMR profiling of the bulk oil and phenolic fraction supported the characterization of the samples, showing that phenolic analysis can be very informative for traceability purposes (Laincer et al., 2016). By studying the polar fraction of olive oils, increasing the amount of minor compounds through a liquid-liquid extraction with acetonitrile, and using a complex classification model based on PCA-CA-KNN (k-nearest neighbor), it was possible to discriminate samples from the main producer countries, namely, Italy, Spain, and Greece (Winkelmann & Kuchler, 2019).

Rongai et al. (2017) tried to characterize commercial EVOO samples, adding a possible correlation with climate through NMR, PCA, and OPLS-DA; however, further studies are needed to confirm these preliminary results. Recently, Calò et al. (2021) studied the NMR metabolic profiles of blends of Italian EVOOs with EVOOs coming from different countries (Portugal, Spain, Tunisia, and Greece). An unsupervised PCA showed good differentiation among samples with increasing percentages of Italian oil until a maximum amount of 20%, making it possible in the future to discriminate if the reported geographical origin on the label is correct. Moreover, it was pointed out that Italian EVOOs are characterized by the amounts of oleic acid and polyphenols.

At a regional level, PDO "Terra di Bari" samples could be distinguished from others of the Bari district (Del Coco et al., 2016). This study described the characterization of PDO samples with a proper dataset of genetically classified monocultivar samples and a multivariate statistical analysis, finding that the most discriminant compounds were oleic acid, linoleic acid, and linolenic acid.

The Tuscan PGI olive oils were discriminated with multivariate analysis, and the authors pointed out the need for a database of monocultivar samples (Girelli et al., 2018), whereas the Bosana Sardinian olive oils were discriminated according to the different amounts of FAs, acylglycerols, and volatile compounds (Culeddu et al., 2017). Alonso-Salces et al. (2012) conducted a study at the PDO level through NMR fingerprinting and PLS-DA. This approach allowed the assessment of the quality of olive oils at the country, regional, and PDO levels.

With NMR fingerprinting, Gemlik olives cultivated in PDO regions were also distinguished from olives of non-PDO regions because of the different amounts of terpenes (Özdemir & Bekiroğlu, 2019). By combining  $^1\text{H}$  with  $^{13}\text{C}$



**FIGURE 2**  $^1\text{H}$  NMR spectrum at 400 MHz of the lipidic fraction of extra virgin olive oil (EVOO) obtained with a simple proton experiment

**TABLE 2** Peak assignments of the monodimensional lipid spectrum reported in Figure 2 (Cabrita et al., 2021)

Peak (ppm)	Assignment	
A	0.00 ppm	Tetramethylsilane
B	0.83–0.93	Methylic protons ( $-\text{CH}_3$ )
C	1.20–1.40	Methylene protons ( $-\text{CH}_2-$ )
D	1.53–1.70	H-3 protons of acyl moiety ( $-\text{CH}_2-\text{CH}_2-\text{CO}-$ )
E	1.90–2.10	Allylic methylene protons ( $-\text{CH}_2-\text{CH}=\text{CH}-$ )
F	2.25–2.35	H-2 protons of acyl moiety ( $-\text{CH}_2-\text{CO}-$ )
G	2.75–2.80	Bis-allylic methylene protons ( $=\text{CH}-\text{CH}_2-\text{CH}=\text{}$ )
H	4.10–4.35	Methylene protons ( $\alpha$ and $\alpha'$ ) of the glycerol unit of TAGs ( $-\text{CH}_2-\text{OCOR}$ )
I	5.30	Methine proton of the glycerol unit of TAGs ( $-\text{CH}-\text{OCOR}$ )
J	5.35	Olefinic protons ( $-\text{CH}=\text{CH}-$ )

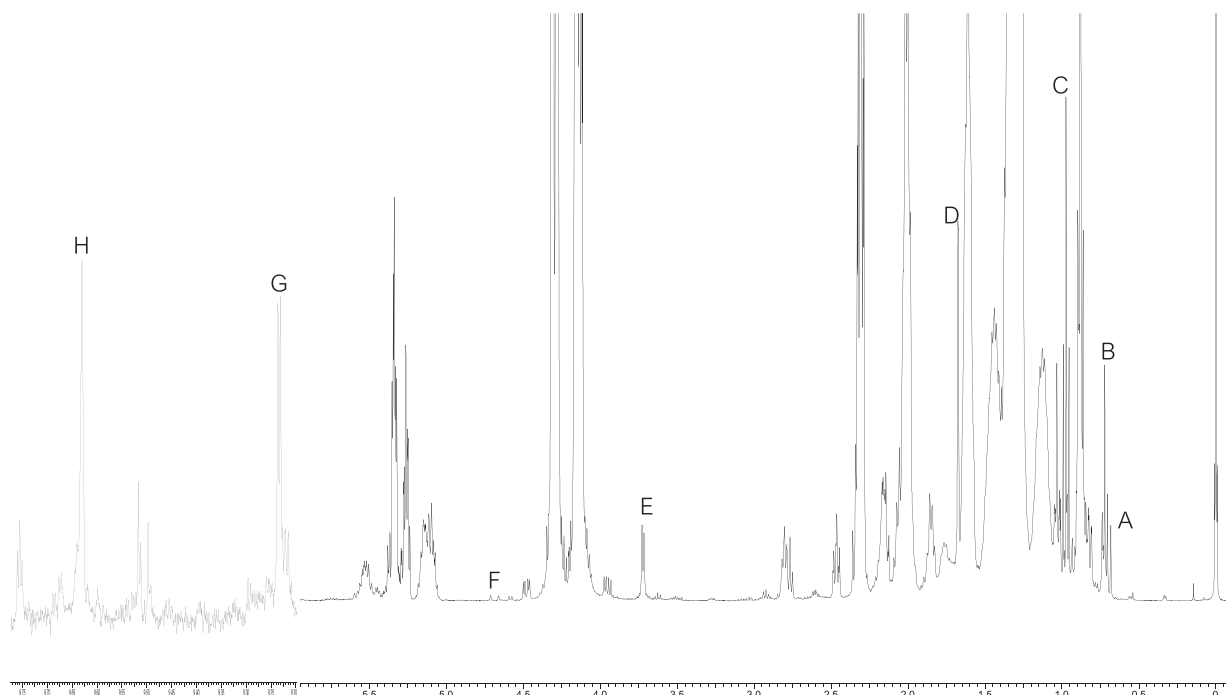
NMR and supervised statistical analysis, PLS-DA and an artificial neural network, Maltese olive oils were characterized (Lia, Vella, et al., 2020). Following preliminary visualization of the samples through PCA score plots, subsequent application of PLS-DA and artificial neural network to the data allowed the discrimination of oils. The discrimination from  $^{13}\text{C}$  NMR data proved to provide better results; however,  $^1\text{H}$  NMR analysis is preferred as the acquisition time is faster.

NMR and MVA can also provide useful information to optimize production processes. Del Coco et al. (2020) studied Apulian olive oils extracted with two different methods, the traditional method and the newest ultra-

sound with thermal exchanger extraction. The results revealed that the oils extracted with the new method are richer in biophenols, known as bioactive compounds.

### 3.4 | NMR: Preparation and analytical steps

NMR has the advantage of requiring very simple preparation steps. Different nuclei in oil can be analyzed:  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , and  $^{19}\text{F}$  (Lioupi et al., 2020; Mannina & Sobolev, 2011). In this review, we focus only on sample preparation for  $^1\text{H}$  NMR, the most common technique. Olive



**FIGURE 3**  $^1\text{H}$  NMR spectrum at 400 MHz of the lipidic fraction of extra virgin olive oil (EVOO) obtained with a multisuppression experiment

**TABLE 3** Peak assignments of the minor components of the lipid spectrum reported in Figure 3 (Ingallina et al., 2019)

	Peak (ppm)	Assignment
A	0.68	Sitosterol (18- $\text{CH}_3$ )
B	0.69	Stigmasterol (- $\text{CH}_3$ )
C	0.97	Linolenic acid (acyl- $\text{CH}_3$ )
D	1.66	Squalene (- $\text{CH}_3$ )
E	3.69–3.73	sn 1,2 diglycerides (- $\text{CH}_2$ -OH)
F	4.56–4.90	Terpenes (- $\text{CH}_2=\text{CH}_2$ )
G	9.23	Trans-2-hexenaldehyde (- $\text{CH}=\text{O}$ )
H	9.70	Hexanaldehyde (- $\text{CH}=\text{O}$ )

oil samples are usually diluted with nonpolar deuterated solvent, with no need for any other pretreatments or extractions, except targeted studies that need to extract specific compounds (e.g., Karkoula et al., 2012). In this case, an extraction is performed with different methods, but the most common solvents used are methanol and acetonitrile (Agiomyrgianaki et al., 2012; Lainer et al., 2016). EVOO is usually diluted with deuterated chloroform,  $\text{CDCl}_3$ , which is added in excess, typically 100–200 mg of olive oil in a ratio of 13.5% oil/86.5% solvent, w/w (Girelli et al., 2020; Piccinonna et al., 2016; Poiana et al., 2015). DMSO- $d_6$  (deuterated dimethyl sulfoxide) can be added to facilitate the dissolution of polar compounds (Castejón et al., 2014; Fauhl et al., 2000; Ingallina et al., 2019; Mannina et al.,

2005, 2010), and tetramethylsilane can be used as an internal chemical shift reference (Guillén & Ruiz, 2003; Jiang et al., 2018). After dilution, the sample can be shaken, manually or by vortexing, for 20 s, and then 600  $\mu\text{l}$  of this mixture is transferred to a 5-mm NMR tube. pH adjustment is not necessary for untargeted analysis because many tools exist for pH alignment after acquisition (Solovyev et al., 2021). Regarding the spectrometer, olive oil has been analyzed mostly with instruments ranging from 400 to 600 MHz at 300 K. The most commonly used measurements are simple  $^1\text{H}$  and NOESY with multiple signal suppression to suppress the strong peaks of solvent and lipids (Longobardi et al., 2012) to better visualize the signals of minor components. Both targeted and untargeted approaches can be adopted. The chemometric analysis of spectra can be *supervised* or *unsupervised*, depending on the purpose of the study.

After a simple proton experiment and the phase and baseline correction, a spectrum as reported in Figure 2 is obtained. The main signals are those of triacylglycerols and glycerol, as reported in the table of assignments (Table 2). Minor constituents (Figure 3 and Table 3) can be better shown with a multisuppression experiment of those main signals, and thus, a more detailed picture of the sample is obtained. Once all the signals have been assigned, it is possible to quantify specific compounds or proceed with an untargeted approach. Various results from targeted analysis have been reported to identify polyphenols



(Olmo-Cunillera et al., 2020), minor constituents (Ok, 2014), and even quantify different types of FAs (Barison et al., 2010; Castejón et al., 2014, 2016; Knothe & Kenar, 2004). The untargeted approach, instead, is based on the entire profile of the oil, its fingerprint, which contains much information on the sample. Due to the high amount of information, the best approach is bucketing, or binning, of the spectra (0.04 ppm is the usual width of the bins), which means “segmenting” the spectra to obtain data reduction. Usually, performing a PCA allows more “compact” information and identifies outliers in the entire spectrum, or it is possible to add more preprocessing steps after binning. After the bucketing step, to further reduce the data dimension, in some works (e.g., Alonso-Salces et al., 2015; Mannina et al., 2005), the most discriminant buckets are selected using different statistical tools, and a matrix with only those extracted signals is built. Then, the obtained matrix was used to perform different statistical analyses. After these various possible paths, different statistical tests, supervised or unsupervised, can be run to classify samples, depending on the aim of the intended study.

#### 4 | CONCLUSION

As reported in this review, NMR spectroscopy is a helpful technique for the analysis of oils, and in particular, it is suitable for traceability and authenticity purposes of EVOOs. Different methods for traceability of olive oils have already been approved by regulatory bodies, but NMR has some advantages. For example, it is highly reproducible, it has easy preparative steps, and with just a single analysis, the fingerprint of the sample and the quantification of the characteristic compounds can be obtained. We reported many different studies for EVOO authenticity based on NMR using both targeted and untargeted approaches, achieving different goals: the detection of adulterations with cheaper oils or from different botanical origins and the varietal and geographical traceability of the samples, showing the potentialities of this technique. In most of the cases, these studies did not consider a representative number of samples; thus, their results should be confirmed with a larger dataset to use this approach for detecting the authenticity of olive oil in real-life cases.

Recently, the NMR approach for the assessment of EVOOs was exploited by Bruker, GmbH. Bruker is developing a completely automated solution for targeted and untargeted analysis to test origin authenticity and mislabeling of olive oils, the FoodScreener (FoodScreener, 2021). Moreover, Bruker is also developing a method based on an 80 MHz benchtop system that could be appealing for the industry and giving the right boost to a greater use of

NMR spectroscopy not only for research purposes but also in industry and quality control laboratories.

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#### AUTHOR CONTRIBUTIONS

Federica Camin and Luana Bontempo made substantial contributions to the conception and design of the work. Valentina Maestrello and Pavel Solovyev acquired, analyzed, and interpreted the data for the work. Valentina Maestrello aided in drafting the work, while Federica Camin, Luana Bontempo, Pavel Solovyev, and Luisa Mannina aided in revising it critically for important intellectual content. Federica Camin and Luana Bontempo gave final approval of the version to be published. Federica Camin, Luana Bontempo, Valentina Maestrello, and Pavel Solovyev agreed to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

#### CONFLICTS OF INTEREST

The authors declare no conflict of interest.

#### ORCID

Valentina Maestrello  <https://orcid.org/0000-0001-5563-8915>

Pavel Solovyev  <https://orcid.org/0000-0001-7152-3157>

Luana Bontempo  <https://orcid.org/0000-0001-7583-1501>

Luisa Mannina  <https://orcid.org/0000-0001-8659-5890>

Federica Camin  <https://orcid.org/0000-0003-0509-6745>

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