# Tunisian Extra Virgin Olive Oil Traceability in the EEC Market: Tunisian/Italian (Coratina) EVOOs Blend as a Case Study

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**Abstract:** In order to check the reliability of an NMR-based metabolomic approach to evaluating blend composition (and declaration), a series of 81 Italian/Tunisian blends samples at different percentage composition (from 10/90 to 90/10% Coratina/Tunisian oil by 10% increase step) were prepared starting from five Coratina (Apulia) and five Tunisian extra virgin olive oil (EVOO) batches. Moreover, a series of nine binary mixtures blend oils were obtained, starting from the two batches' oil sums. The models built showed the linear relationship between the NMR signals and the percentage composition of the blends. In particular, a high correlation with the percentage composition of blends was obtained from the partial least squares (PLS) regression model, when the two batches oil sums were used for the binary mixtures of blend samples. These proposed methods suggest that a multivariate analysis (MVA)-based NMR approach—in particular PLS regression (PLSR)—could be a very useful tool (including for trading purposes) to assess quantitative blend composition. This is important for the sustainability of the goods' free movement, especially in the agrifood sector. This cornerstone policy of current common markets is also clearly linked to the availability of methods for certifying the origin of the foodstuffs and their use in the assembly of final product for the consumer.

**Keywords:** extra virgin olive oil; commercial purpose; $^1$H-NMR spectroscopy; EVOOs origin assessment; multivariate statistical analysis; PLSR; projections to latent structure by means of partial least squares regression

## 1. Introduction

Extra virgin olive oil (EVOO) is one of the most famous symbols of Italian agricultural products. It can be considered a strategic foodstuff for the national economy that leads Italy to an internationally significant position in olive oil commerce. The important commercial value of authentic olive oils led to the risk of adulteration, as recently described in the Report of the Parliamentary Committee Inquiry on Counterfeiting [1]. As reported, frauds and adulterations threatening 250 million plants, 50 million working days, sales of over 2 billion euro, and 43 Italian olive oils with denomination of origin recognized by the European Union. Among fraudulent practices: alterations in the composition of the organoleptic character of the product and of geographical indications (reported as forgeries), adulteration (addition or subtraction of specific components of the product), sophistication (addition of foreign substances), falsifications (substitutions of specific components). All of these conducts represent violations of industrial property rights. Recently, the so-called "Italian sounding" has been added to the list of scams. In particular, it is considered as the "production and marketing of foods containing a false evocation of the Italianness of the product", able to induce the consumer

to presume an Italian origin of the product. To this, a sophisticated fraudulent technique has been considered: deodorized oil, wherein poor-quality olive oil is manipulated and enriched in order to be introduced in the market with competitive prices. Moreover, the faked production of extra virgin olive oil supported by invoicing for unreal product or even by milling yields higher than effective ones lead to a misbranding system, known in Italy as "paper oil", by which foreign olive oils are introduced in the Italian extra virgin olive oil production and labeled as Italian oils [2]. In particular, Italian producers criticized the recent regulation 2016/580 of the European Parliament and of the Council of 13 April 2016 [3], by which an autonomous annual duty free tariff quota of 35,000 tons for 2016 and 2017 for imports of lampante, virgin, and extra virgin olive oils (CN codes 15091010 and 15091090) originating in Tunisia, was opened. Italian producers and farmers' association severely criticized this measure, by which they said Italian producers could be harmed and the risk that consumers will be exposed to "*fake oil*" could be seriously increased. Notwithstanding the assessment of the impact of this Regulation on the Union olive oil market [4], performed by the European Commission, according to which the implementation of Regulation (EU) 2016/580 would have had a marginal impact on the EU olive oil market, Coldiretti Association President Roberto Moncalvo declared that cheaply imported Tunisian oil could be mixed with Italian oil and falsely labeled "*Made in Italy*" for a premium price on the international market [5].

In 2014, The New York times reported that "Much of the extra virgin Italian olive oil flooding the world's market shelves is neither Italian, nor virgin". More recently, the economics and finance journal Forbes reported that "It's reliably reported that 80% of the Italian olive oil on the market is fraudulent . . . it's likely that when you buy olive oil, you're not buying what it says on the label. . . . Italian extra virgin is very probably a fake" [6].

As a consequence, the detection of adulteration in extra virgin olive oil (EVOO) is one of the main aspects in the quality control and authenticity of the product [7–17]. Moreover, the need of a scientific tool to assess EVOOs geographical origin represents a hot topic issue since the European Regulation 182 of 6 March 2009—which declared the compulsory labeling of EVOOs with the geographical origin of the olives in all European countries [18]—still lacks an official validation methodology. We are currently involved in several NMR based metabolomics and chemometric studies to assess cultivar composition and geographical areas origin of extra virgin olive oils [19–25]. In this work we focused on a methodological $^1$H-NMR spectroscopy coupled with a chemometrics approach in order to provide a quantitative blend composition assessment.

In particular, we build a specific $^1$H-NMR spectral database with blends of a typical Apulian oil obtained from the popular cultivar Coratina [20,25,26], and a widely available Tunisian oil (obtained from Chemlali and Chetoui cultivars) at different known Coratina/Tunisian percentage composition. The relation obtained between the $^1$H-NMR based metabolic profiles of the reference blends (accounting for their overall molecular content) and their content could be used as a tool to evaluate the blend composition in analogous possible test samples.

## 2. Materials and Methods

### 2.1. Sampling

EVOO oil batches (from the same single harvesting season 2014/2015) from five monocultivar Italian (from Apulia, Italy) Coratina (indicated as C1, C2, C3, C4, C5) and five Tunisian (from Sfax, Tunisia) Chemlali/Chetoui cultivars (indicated as T1, T2, T3, T4, T5), obtained from local producers, were supplied by *Certified Origins Italia* Srl. All the samples were stored in sealed dark glass bottles at room temperature in the dark prior to analysis.

Nine series of Coratina/Tunisian blend samples were obtained by using several combinations (C1, T1; C2, T2, etc.) of the available original oils following a regular grid sampling (see Scheme 1). Each series consisted of nine blends with different percentage composition (see Table 1) (from 10/90 to 90/10% Coratina/Tunisian oil by 10% increase step) reaching a total of 81 blend samples.

The 112 overall number of analyzed samples also included 31 further samples. These latter were constituted by two technical replicates from each original (C1–C5 and T–T5) batch EVOO sample (for a total of 10 C and 10 T samples), two batches oil sums: Cs = C1 + C2 + C3 + C4 + C5 and Ts = T1 + T2 + T3 + T4 + T5) (Figure 1) and nine further blends (from 10/90 to 90/10% Cs/Ts oil by 10% increase step). The analyses were performed by using $^1$H-NMR spectroscopy and multivariate analysis (MVA), within the maximum optimal shelf life (12–18 months from the date of bottling) [27].

| | T1<br>% Composition<br>10,20,30,40,50,60,70,80,90 | T2<br>% Composition<br>10,20,30,40,50,60,70,80,90 | T3<br>% Composition<br>10,20,30,40,50,60,70,80,90 | T4<br>% Composition<br>10,20,30,40,50,60,70,80,90 | T5<br>% Composition<br>10,20,30,40,50,60,70,80,90 |
|---|---|---|---|---|---|
| **C1**<br>% Composition<br>90,80,70,60,50,40,30,20,10 | C1T1 | | | | C1T5 |
| **C2**<br>% Composition<br>90,80,70,60,50,40,30,20,10 | | C2T2 | | C2T4 | |
| **C3**<br>% Composition<br>90,80,70,60,50,40,30,20,10 | | | C3T3 | | |
| **C4**<br>% Composition<br>90,80,70,60,50,40,30,20,10 | | C4T2 | | C4T4 | |
| **C5**<br>% Composition<br>90,80,70,60,50,40,30,20,10 | C5T1 | | | | C5T5 |

**Scheme 1.** Square matrix describing the Coratina/Tunisian blend samples preparation following a regular grid sampling (red and green background, respectively). Samples were prepared according to the couples of Coratina and Tunisian samples in the two main diagonals (highlighted in yellow). A blend sample at different percentage composition was obtained for each pair of oils (C1T1, C2T2, ... C*n*T*n*).

**Table 1.** Weighted percentage composition (from 90 to 10) for preparation of blends with different percentage composition.

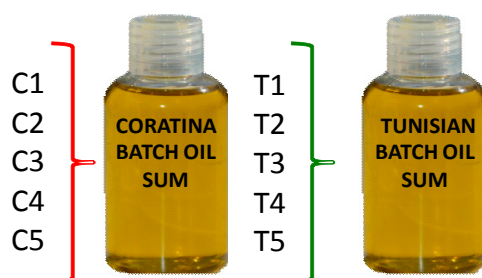| | % | Weight (g) | | % | Weight (g) |
|---|---|---|---|---|---|
| C | 90 | 0.828 | T | 10 | 0.092 |
| C | 80 | 0.736 | T | 20 | 0.184 |
| C | 70 | 0.644 | T | 30 | 0.276 |
| C | 60 | 0.552 | T | 40 | 0.368 |
| C | 50 | 0.46 | T | 50 | 0.46 |
| C | 40 | 0.368 | T | 60 | 0.552 |
| C | 30 | 0.276 | T | 70 | 0.644 |
| C | 20 | 0.184 | T | 80 | 0.736 |
| C | 10 | 0.092 | T | 90 | 0.828 |



**Figure 1.** Schematic representation of Coratina and Tunisian batch oil sums composition. The overall batches oil sums were formed by the same amount of each of the five Coratina and each of the five Tunisian olive oil samples.

## 2.2. Sample Preparation for $^{1}$H-NMR Analysis

NMR samples were prepared dissolving ~140 mg of olive oil in $CDCl_3$ and adjusting the overall batches oil sums ratio of olive oil:$CDCl_3$ to 13.5%:86.5%. Next, 600 µL of the prepared mixture were transferred into a 5-mm NMR tube. This ratio was chosen to give the best tradeoff for sensitivity/solution viscosity in spectral acquisition (Bruker Italia, standardized procedure for olive oil analysis) [21]. $^{1}$H-NMR spectra were recorded on a Bruker Avance spectrometer (Bruker, Karlsruhe, Germany) operating at 400.13 MHz, T = 300 K, equipped with a PABBI 5-mm inverse detection probe incorporating a z axis gradient coil. NMR experiments were performed under full automation for the entire process after loading individual samples on a Bruker Automatic Sample Changer (BACS-60), interfaced with the software IconNMR (Bruker).

Automated tuning and matching, locking and shimming, and calibration of the 90° hard pulse P(90°) were done for each sample using standard Bruker routines ATMA, LOCK, TOPSHIM, and PULSECAL to optimize NMR conditions. For each sample, after a 5-min waiting period for temperature equilibration, a standard one-dimensional ($^{1}$H ZG) NMR experiment was performed. The relaxation delay (RD) and acquisition time (AQ) were set to 4 s and ~3.98 s, respectively, resulting in a total recycle time of ~7.98 s. Free Induction Decays (FIDs) were collected into time domain (TD) = 65,536 (64 k) complex data points by setting: spectral width (SW) = 20.5524 ppm (8223.685 Hz), receiver gain (RG) = 4, number of scans (NS) = 16. An accumulation of 16 scans (or even fewer) are usually used for samples where metabolites are present in high concentrations, as in the case of olive oil [19,28].

## 2.3. $^{1}$H-NMR Spectra Pre-Processing and Multivariate Statistical Analysis

The NMR raw data set was pre-processed using Topspin 2.1 and AMIX 3.9.15 (Bruker BioSpin GmbH, Rheinstetten, Germany). The FIDs were multiplied by an exponential line broadening function (0.3 Hz) before Fourier transformation and automatically phased. Spectra were referenced to the tetramethylsilane (TMS) single signal at 0.00 ppm, used as an internal standard, obtaining good peak alignment. NMR spectra were processed using Topspin 2.1 (Bruker) and visually inspected using Amix 3.9.15 (Bruker, Biospin, GmbH, Germany). Furthermore, spectra were segmented in rectangular buckets of fixed 0.04 ppm width and integrated using the Bruker Amix software. Bucketing was performed within 10.00–0.5 ppm region, excluding the signal of the residual non-deuterated chloroform and its carbon satellites (7.6–6.9 ppm); total sum normalization was applied to minimize small differences due to total olive oil concentration and/or acquisition conditions among samples. The Pareto scaling method (performed by dividing the mean-centered data by the square root of the standard deviation) was then applied to the variables [29]. The data table generated by all aligned buckets row-reduced spectra was used for multivariate data analysis. Each bucket row represents the entire NMR spectrum, and all the molecules present in the sample. Each bucket in a buckets row-reduced spectrum is labeled with the value of the central chemical shift for its specific 0.04 ppm width. The variables used as descriptors for each sample in chemometric analyses are the buckets.

Multivariate analyses (MVAs) and graphics were obtained using Simca-P version 14 (Umetrics, Malmö, Sweden) using different procedures: principal components analysis (PCA), partial least-squares discriminant analysis (PLS-DA), and orthogonal partial least-squares discriminant analysis (OPLS-DA) [30]. PCA is an unsupervised pattern recognition method, and was performed to examine the intrinsic variation in the data set. PLS-DA was applied to maximize the separation between sample classes. PLS-DA is the regression extension of PCA, and gives the maximum covariance between the measured data (X variable, matrix of buckets related to metabolites in NMR spectra), and the response variable (Y variable, matrix of data related to the class membership). In addition to PLS-DA, OPLS-DA was also applied in MVA. As shown in several recent metabolomics studies, OPLS-DA represents the most recently used technique for the discrimination of samples with different characteristics (such as cultivars and/or geographical origin). OPLS-DA is a modification of the usual PLS-DA method which filters out variation that is not directly related to the response.

The further improvements made by the OPLS-DA in MVA resides in the ability to separate the portion of the variance useful for predictive purposes from the not predictive variance (which is made orthogonal). Furthermore, OPLS-DA focuses the predictive information in one component, facilitating the interpretation of spectral data. On the other hand, when a four-category (i.e., the cultivars) model was used for further classification purposes, PLS-DA rather than OPLS-DA was preferred [31]. For both PLS-DA and OPLS-DA, the quality of the models obtained was assessed by $R^2$ and $Q^2$ values. The first ($R^2$) is a cross-validation parameter defined as the portion of data variance explained by the models, and indicates goodness of fit. The second ($Q^2$) represents the portion of variance in the data which is predictable by the model. This latter indicates the model's predictive ability, which is extracted according to the internal seven-fold cross-validation method and further evaluated with permutation test (400 permutations) of SIMCA-P software [32,33]. The minimal number of components required can be easily defined since $R^2$(cum) and $Q^2$(cum) parameters display completely diverging behaviour as the model complexity increases. The addition of further unnecessary components to the model can therefore be easily detected and avoided.

PLS-regression (PLSR) is the PLS (projections to latent structure by means of partial least squares) approach in its simplest and—in chemistry and technology—most-used form (two-block predictive PLS). PLS-regression is a method for relating two data matrices, X and Y, by a linear multivariate model, but goes beyond traditional regression in that it also models the structure of X and Y. Its usefulness arises from its ability to analyze data with many, noisy, collinear, and even incomplete variables in both X and Y. PLSR has the desirable property that the precision of the model parameters improves with the increasing number of relevant variables and observations. In addition, PLSR models the structure of X and of Y, which gives richer results than the traditional multiple regression approach. PLSR is of particular interest because it also simultaneously models several response variables, Y (i.e., *profiles of performance*). The purpose of the PLS-regression is to build a linear model enabling the prediction of a desired characteristic y from a measured spectrum **x** and profitably applies to the task of the present work when analyzing and predicting olive oil blends of different composition by $^1$H-NMR spectra. The predictive power of the PLS model is evaluated by the RMSECV(Y) (root mean square error of cross-validation) [34]. In general, multivariate regression methods are used to make quantitative predictions relative to one or more properties of the system in question. The aim was to find the best relationship between a set of variables describing the objects studied (the oil samples) and a set of measured responses of the same objects. In our case, we created a regression model for interpolation of nuclear magnetic resonance spectroscopy data (matrix of X variables, NMR signals) with the percentages of mixed-composition oil (Italian/Tunisian, blend samples, response variable, Y).

*2.4. Chemicals*

All chemical reagents for analysis were of analytical grade. CDCl$_3$ (99.8 atom % D) and tetramethylsilane, TMS (0.03 *v/v* %) were purchased from Armar Chemicals (Switzerland).

## 3. Results and Discussion

A $^1$H-NMR spectral database with blends of a typical Apulian oil obtained from the popular cultivar, Coratina, and a widely available Tunisian oil (obtained from Chemlali and Chetoui cultivars) at different known Coratina/Tunisian percentage composition was specifically constituted for this study. We chose Italian monocultivar Coratina EVOO for the model because Coratina is the most important cultivar of the Apulia region—the leading olive oil producer in Italy, accounting for almost 40% of the total country's production. Therefore Coratina-based blends represent an essential part of Italian EVOOs. A regression model was obtained by the PLSR procedure described in the Materials and Methods section for 101 Coratina/Tunisian EVOO blend samples (81 C*n*T*n* together with 10 C and 10 T samples obtained from the original C1–C5 and T1–T5 batches EVOO samples) as a function of the percentage of Coratina oil calculated for each blend sample. The existence of a linear relationship can be clearly observed in Figure 2. The estimated regression line is more appropriate to describe the

relationship between the two variables, as the points observed are close to this line, while the observed distance from the line observation may represent potential measurement or response variable Y errors. The linear relationship between the two matrices (X, the NMR data; and Y, the dependent variable—i.e., the percentage of Coratina oil for each blend oil) was expressed by the linear function $y = x + 3.13 * e^{-007}$, and the correlation is described by the regression coefficient ($R^2 = 0.961$), which expresses how much the dependent character increases on an independent character unit on average. The model parameters (three components) indicate both a good descriptive ($R^2X(cum) = 0.837$, $R^2Y(cum) = 0.961$) and predictive ($Q^2(cum) = 0.953$) ability of the system. The overall result could be considered satisfactory since variable Y errors (RMSECV(Y) = 6.7652%) also account for the heterogenic blend composition (blends formed by five Coratina and five Tunisian different oil batches).
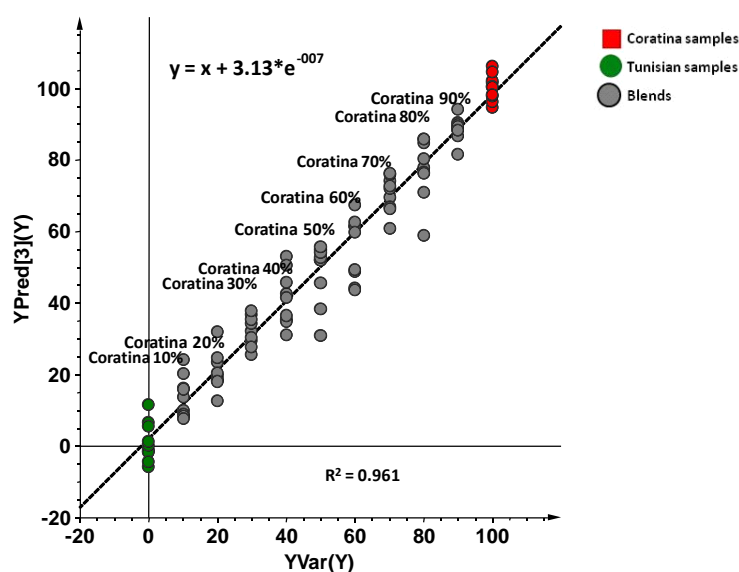


**Figure 2.** The partial least squares regression (PLSR) model for 101 Coratina/Tunisian extra virgin olive oil (EVOO) blend samples (81 C*n*T*n* together with 10 C and 10 T samples obtained from the original C1–C5 and T1–T5 batches EVOO samples) as a function of the percentage of Coratina oil calculated for each blend sample (three components, $R^2X(cum) = 0.837$, $R^2Y(cum) = 0.961$, $Q^2(cum) = 0.953$, goodness of fit $R^2 = 0.961$, root mean square error of cross-validation (RMSECV)(Y) = 6.7652%).

Italian Coratina and Tunisian EVOO oil batches were also used to build a two-group OPLS-DA model (Figure 3a). To search for a better model with higher prediction capability, the original samples of Coratina and Tunisian oils were duplicated (total of 20 samples). The two groups appeared well-separated in the scoreplot, according to the cultivar properties, with the Coratina samples characterized by a higher relative content of monounsaturated fatty acids ($\delta_H$ 1.30 ppm signal corresponding to the acyl group of oleic acid, loadings plot analysis, data not shown). On the other hand, the Tunisian oils showed a considerably higher relative content of polyunsaturated acyl groups ($\delta_H$ 1.38 ppm signal corresponding to the methylene of the unsaturated acyl groups, $\delta_H$ 2.74 and 2.78 ppm, signals of linoleic and linolenic diallilyc groups, signals in the range $\delta_H$ 5.38–5.42 ppm ascribed to linoleic and linolenic olefinic protons). This model was also used to predict all the oil blends prepared in the laboratory. From the score plot of the model which included—as predicted—the 81 C*n*T*n* blends prepared in the laboratory (Figure 3b), the distribution of these latter ones according to the percentage of Coratina over Tunisian oil can be observed. Coratina's highest percentage blends (containing from 90 to 60% of Coratina oil) are evidently placed in the area of the graphic which is clearly closer to the monocultivar Coratina reference class, while the other mixed oils are gradually distributed in the dispersion graph, with the increasing amount of Tunisian percentage positioned towards the area identified by the pure Tunisian samples.
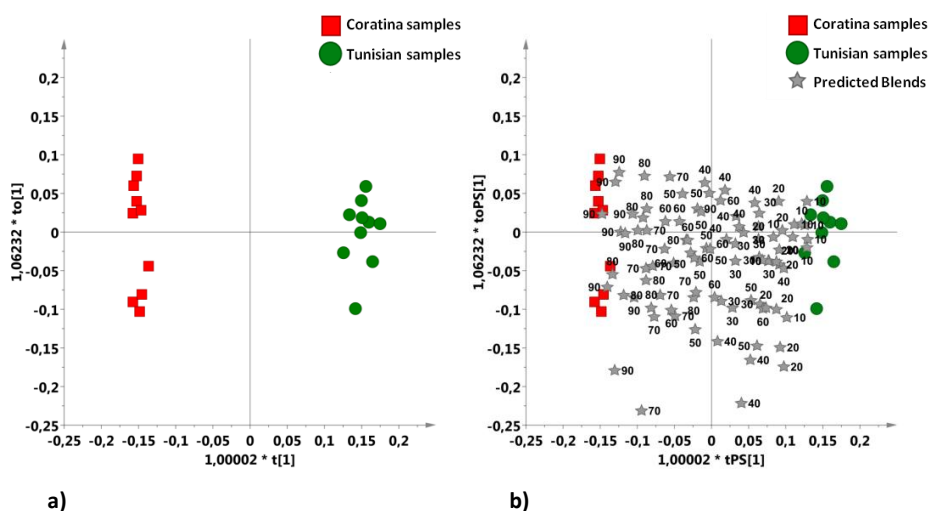
**Figure 3.** (**a**) Scoreplot of the orthogonal partial least-squares discriminant analysis (OPLS-DA) model for Coratina and Tunisian EVOO samples (one predictive and one orthogonal component give $R^2X(cum) = 0.843$ and $Q^2(cum) = 0.993$); (**b**) OPLS-DA prediction scoreplot for known percentage Coratina/Tunisian blends. The predicted test samples are depicted as grey five-pointed stars; label of samples refers to the percentage of Coratina present for each blend oils.

Finally, a series of 11 blend oils, starting from the 2 batches oil sums (Cs = C1 + C2 + C3 + C4 + C5 and Ts = T1 + T2 + T3 + T4 + T5), from 0/100 to 100/0% Cs/Ts oil by 10% increase step, were obtained. From the PLSR analysis a clear improvement with respect to the model originated by the blends formed by five Coratina and five Tunisian different oil batches (Figure 2) could be observed. The obtained linear function $y = 0.9757x + 0.9308$ showed higher goodness of fit ($R^2 = 0.998$) and much lower RMSECV(Y) = 1.6221%. Accordingly, the model parameters were better for both descriptive ($R^2X(cum) = 0.905$, $R^2Y(cum) = 0.998$) and predictive ($Q^2(cum) = 0.997$) ability of the system (Figure 4). This occurs because the two "overall batches oil sums" (Cs and Ts) obtained by mixing the individual Coratina and Tunisian oil batches clearly average the small variations that differentiate the different samples batches within each individual class (Coratina or Tunisian). The blends originated from the overall batches oil sums line up along the regression line, confirming the perfect linear dependence between the NMR data and the percentage composition of each mixed oil sample.
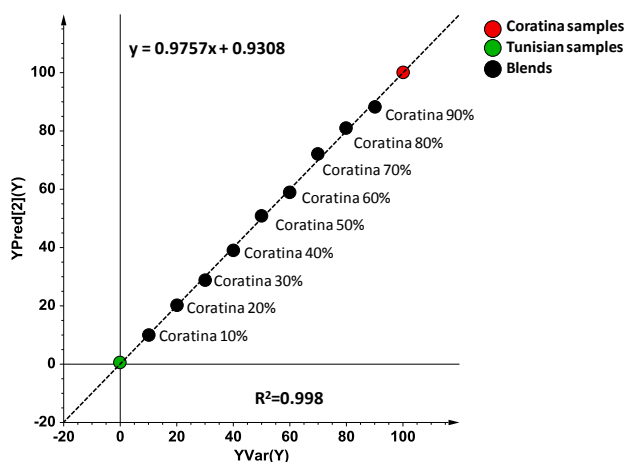


**Figure 4.** PLSR analysis for the 11 blend oils, starting from the 2 batches oil sums, Cs and Ts, from 0/100 to 100/0% Cs/Ts oil by 10% increase step). Two components, $R^2X(cum) = 0.905$, $R^2Y(cum) = 0.998$ and $Q^2(cum) = 0.997$, goodness of fit $R^2 = 0.998$. RMSECV(Y) = 1.6221%.

The eleven samples consisting of the two batches oil sums Cs and Ts and the nine blends (from 0/100 to 100/0% Cs/Ts oil by 10% increase step) used for the PLSR model of Figure 4 were also predicted on the OPLS-DA model (Figure 5), built with the pure Coratina (10 C) and Tunisia (10 T) reference samples. Again, a very good scoreplot was obtained for the predicted samples. A potentially good degree of blend composition assessment was observed, as the samples distribution follows the trend of the Coratina vs. Tunisian percentage present in the blend (from 0/100 to 100/0% Cs/Ts oil by 10% increase step).
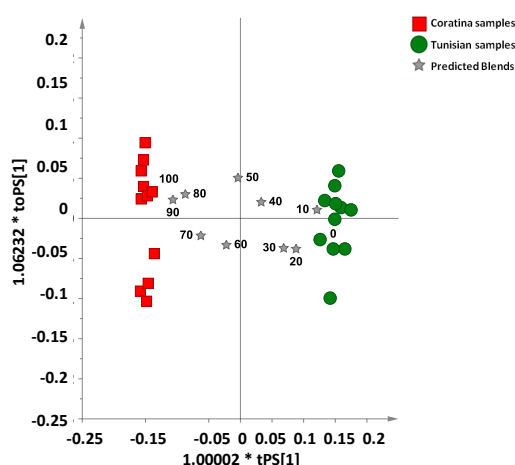


**Figure 5.** OPLS-DA prediction scoreplot for Coratina/Tunisia blend samples at known percentage obtained starting from the overall batches oil sums, Cs and Ts, from 0/100 to 100/0% Cs/Ts oil by 10% increase step (1 predictive and 1 orthogonal component, $R^2X$(cum) = 0.843, $Q^2$(cum) = 0.993). The predicted samples are depicted as grey five-pointed stars; the label of the samples refers to the percentage of Coratina in the blend.

The 11 blends series consisting of known percentages of Coratina and Tunisian overall batches oil sums used for the PLSR model of Figure 4 were also predicted by using the PLSR model of 101 blend samples (81 C$n$T$n$ together with 10 C and 10 T samples obtained from the original C1–C5 and T1–T5 batches EVOOs) (Figure 2). The PLSR prediction plot (Figure 6) showed the observed versus predicted samples in the model. The predicted oil samples fall close to the 45 degree regression line (goodness of fit $R^2$= 0.964), confirming the averaging effect obtained by using overall batches oil sums on the small variations that differentiate the different samples batches within each individual class (Coratina or Tunisian).
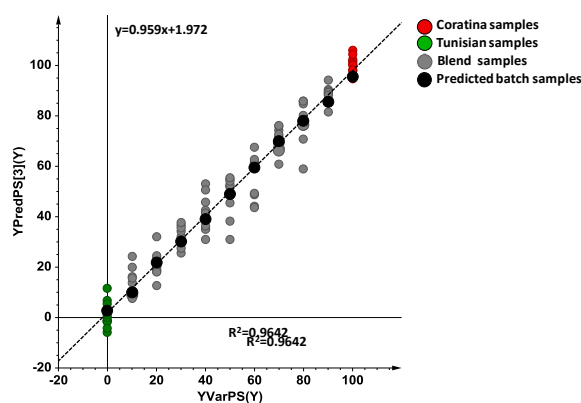


**Figure 6.** PLS prediction plot of 11 blend oil samples obtained from the 2 batches oil sums, Cs and Ts, from 0/100 to 100/0% Cs/Ts oil by 10% increase step) (three components, $R^2X$(cum) = 0.837, $R^2Y$(cum) = 0.961, $Q^2$(cum) = 0.953), goodness of fit $R^2$ = 0.961, RMSECV(Y) = 6.7652%).

## 4. Conclusions

In this work, a chemometric approach was applied on a ^{1}H-NMR spectral database of blends Italian (Apulian) and Tunisian oils (obtained from Chemlali and Chetoui cultivars) at different known Coratina/Tunisian percentage composition. Two PLSR models were built: one for 101 Coratina/Tunisian EVOO blend samples (81C$n$T$n$, 10 C and 10 T obtained from the original C1–C5 and T1–T5 batches) and another for 11 blend samples (9 Cs/Ts blends, Cs and Ts) obtained from the 2 overall batches oil sums (Cs, Ts). The PLSR quality parameters showed that both PLSR models could be profitably used for blend prediction and classification. This was also confirmed by predicting, in the 101 PLSR model, the samples used to build the 11 blend system. The gradual merging of the characteristics of Coratina and Tunisian oils in the blend formation was clearly shown by predicting all the studied blends in an OPLS-DA model built using pure Coratina (10 C) and Tunisian (10 T) samples. A clear improvement in the goodness of fit and the predictive power was observed in the 11 with respect to 101 PLSR model. This occurs because the two "overall batches oil sums" obtained by mixing the individual Coratina and Tunisian oil batches clearly average the small variations that differentiate the different samples batches within each individual class (Coratina or Tunisian). Although further studies should be conducted taking into account commercial olive oils, it can be concluded that the MVA-based NMR approach could be a very useful tool to assess not only cultivar and/or geographical origin, but also quantitative blend composition of EVOOs. In particular, PLSR models built with a statistically significant number of EVOOs could also be used as a tool for identifying products for commercial quality characterization related to blend composition. On the other hand, the sustainability of the goods free movement—especially in the agrifood sector—is clearly also linked to the availability of methods for certifying the origin of the foodstuffs and their use in the final product assembly for the consumer.

**Author Contributions:** C.R.G. and L.D.C. prepared the samples for NMR analysis; performed the NMR experiments; analyzed and interpreted the NMR and statistical data; wrote and reviewed drafts of the manuscript, prepared the final writing; F.P.F. supervised NMR experiments and statistical analysis, wrote and reviewed drafts of the paper and contributed to the final writing. All authors read and approved the final manuscript.

**Conflicts of Interest:** The authors declare no conflict of interest.

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