

Derivatized volatile organic compound characterization of Friulano wine from Collio (Italy–Slovenia) by HS-SPME-GC-MS and discrimination from other varieties by chemometrics

Sabina Licen^{ID}

Department of Chemical and Pharmaceutical Science, University of Trieste, Trieste, Italy

Elija Muzic^{ID}

Azienda Agricola MUZIC di Muzic Giovanni, Gorizia, Italy

Sara Briguglio^{ID}, Arianna Tolloi^{ID} and Pierluigi Barbieri^{ID}

Department of Chemical and Pharmaceutical Science, University of Trieste, Trieste, Italy, and

Pasquale Giungato^{ID}

Department of Chemistry, University of Bari Aldo Moro, Bari, Italy

Abstract

Purpose – Methods to assess the authenticity and traceability of wines have been extensively studied as enhancers of food quality, allowing producers to obtain market recognition and premium prices. Among analytical techniques, the volatilome profile attained by gas chromatography coupled with mass spectrometry is acquiring more and more attention by the scientific community, together with the use of chemometrics

Design/methodology/approach – The volatilome profile of three varieties of blanc wines from the Collio area (namely Ribolla Gialla, Malvasia and Friulano) between Italy and Slovenia, was determined by head space-solid phase micro extraction-gas chromatography-mass spectrometry, enhancing the carbonyl compounds identification with O-(2, 3, 4, 5, 6-pentafluorobenzyl)-hydroxylamine with the aim of identifying the autochthonous Friulano variety.

Findings – A two-step chemometric approach based on an unsupervised technique (PCA) followed by a supervised one (PLS-DA) allowed to identify possible markers for discriminating the Friulano Collio variety from the others, in particular two chemical classes were identified by PCA (ketones and long chain esters). PLS-DA showed 87% accuracy in classification. A correct classification (i.e. non-Friulano Collio) of a group of wines obtained from the same grape variety but produced in an extra-Collio area was obtained as well. The results confirmed the benefits of using a derivatization step prior to volatile organic compounds analysis.

Research limitations/implications – Among methods to assess the authenticity and traceability of wines, volatilome profile of wines determined by head space-solid phase micro extraction-gas chromatography-mass spectrometry, enhanced by the carbonyl compound identifications with O-(2, 3, 4, 5, 6-pentafluorobenzyl)-hydroxylamine, may have a key role in conjunction with chemometrics and, in particular with principal component analysis and partial least square discriminant analysis.



Practical implications – Among methods to assess the authenticity and traceability of Friulano wine, volatilome profile of wines determined by head space-solid phase micro extraction-gas chromatography-mass spectrometry, enhanced by the carbonyl compound identifications with O-(2, 3, 4, 5, 6-Pentafluorobenzyl) Hydroxylamine hydrochloride, may have a key role in conjunction with chemometrics.

Originality/value – Few works investigated both wine traceability with a volatilome enhancer and chemometrics of the Friulano wine variety obtaining such an improvement in this wine variety discrimination.

Keywords Blanc wine, Friulano, Volatilome, Collio, Authentication, Partial least square discriminant analysis, Derivatization with PFBHA

Paper type Research paper

1. Introduction

Methods to assess the authenticity of wines have been extensively studied as using geographical indications allows producers to obtain market recognition and premium prices (Berna *et al.*, 2009). Authenticity allows consumers to be aware of the importance of diet to ensure a healthy living, to make correct choices. Sustainability among Italian wine consumers seems not to be the main criterion of the consumer's choices, although it is increasing, Italian consumers are mainly attracted by organoleptic properties and terroir characteristics (Mastroberardino *et al.*, 2019). Moreover, consumers are aware that regular and moderate intake of wine reduces the incidence of heart disease, diabetes mellitus and hormonal issues, increasing longevity, with a recently improvement of the aspects of personal hedonistic well-being and social relations (Fiore *et al.*, 2019). For these reasons, the development of new selective techniques for determining the geographical origin of agricultural products is of ongoing concern. Among classification techniques, molecular spectroscopy (Chandra *et al.*, 2017; Giannetti *et al.*, 2016; Guzmán *et al.*, 2015) and chemical characterization of wine's aroma (Francis and Newton, 2005) are of increasing interest. Wine aroma is determined by a broad pool of volatile organic compounds (VOCs), basically ethyl esters, acetates, cinnamic esters, acids, alcohols, phenols, lactones, norisoprenoids and sulfur compounds (Styger *et al.*, 2011). VOCs are present in wine in a very low concentration, nevertheless they significantly influence the olfactory peculiarities. The aroma of wines is influenced by a variety of factors: grapes employed, production area, climate, fermentation conditions, yeast strain, winemaking production steps and storage conditions (Cordente *et al.*, 2012; Ebeler, 2001; Styger *et al.*, 2011). A technique currently and widely used to analyze the volatiles in wine is HS-SPME-GC-MS (head space-solid phase micro extraction-gas chromatography-mass spectrometry). It limits the manipulation of the sample and avoids the use of solvent and its parameters can be tailored to detect a wide variety of analytes in wine (Azzi-Achkouty *et al.*, 2017; Perestrelo *et al.*, 2014). Moreover, the use of derivatizing agents has proved to enhance the detection of specific compounds such as carbonyls (Panighel and Flamini, 2014; Zapata *et al.*, 2010), phenols (Pizarro *et al.*, 2007) and thiols (Coetzee and du Toit, 2012; Rodríguez-Bencomo *et al.*, 2009). Progress in authentication and traceability of grapes and wines by using data mining and analysis with chemometric approaches has been the subject of a recent review (Versari *et al.*, 2014). Liu *et al.*, used PCA (principal component analysis) to disclose realtions between different volatile compounds detected in Danish Solaris white wines (Liu *et al.*, 2015). South African wines were classified analyzing the volatilome by using FA (Factor Analysis), PCA and LDA (linear discriminant analysis) (Weldegergis *et al.*, 2011). Markers of typical red wine varieties from the Valley of Tulum (San Juan–Argentina) were identified analyzing the volatilome by HS-SPME-GC-MS using PCA and S-LDA (stepwise linear discriminant analysis) (Fabani *et al.*, 2013). HS-SPME-GC-MS analysis of VOCs of samples of Montepulciano monovarietal red wines from two different regions (Marche and Abruzzo, Italy) combined with CA (cluster analysis) and PCA was used to identify markers of Montepulciano wines (Sagratiini *et al.*, 2012). Springer *et al.* (2014) proposed a discrimination

model for German white wine varietal authentication based on exploratory data analysis by PCA of the VOCs data set obtained by an untargeted analytical approach followed by a classification performed by PLS-DA (partial least square discriminant analysis) (Springer *et al.*, 2014). Ríos-Reina *et al.* (2019) used PLS-DA approach to obtain a high performance in the classification volatile profiles of three Spanish wine vinegar PDOs (Ríos-Reina *et al.*, 2019). The aim of this study was to make a first survey of the volatile organic compound profiles (volatilome) of three varieties of blanc wines from the *Collio* area (Italy and Slovenia), namely *Ribolla Gialla*, *Malvasia* and *Friulano* by using a derivatizing agent (PFBHA) on samples before performing HS-SPME-GC-MS analysis to foster the carbonyl compound identification. Our main goal was to verify if these different wine varieties, produced in a relatively small territory, could be differentiated from their VOCs profiles, particularly focusing on the very little studied *Friulano* VOCs profiles.

Only two studies concerning these wine varieties have been published before, but they were not focused on *Collio* area wines. One reported few data on *Friulano* (formerly named *Tocai*) VOCs from extra-*Collio* areas (*Tocai di Lison*–Veneto region and *Tocai Grave*–Friuli Venezia Giulia region) (Moret *et al.*, 1994) and one reported on VOCs of *Malvasia* and *Ribolla Gialla* wines produced in laboratory for research purposes on the influence on final wine aroma of grape skin contact during the fermentation process (Bavčar *et al.*, 2011). Both studies lacked in the carbonyl compounds information. A two step chemometric approach based on an unsupervised technique (PCA) followed by a supervised one (PLS-DA) allowed to identify possible markers for discriminating the *Friulano Collio* variety from the others. We also compared the *Friulano* wines with a group of wines obtained from the same grape variety but produced in an extra-*Collio* area.

2. Materials and methods

2.1 Wine samples

The *Collio* wine-producing area (Figure 1) is a hilly area of Friuli Venezia Giulia region–northeast of Italy, which extended between *Isonzo* river and *Iudrio* stream, divided in an Italian side and in a Slovenian one. The Italian side is included in the *Gorizia* province (Figure 1a) and divided in the municipalities of *San Floriano del Collio*, *Gorizia*, *Cormons*, *Dolegna del Collio*, *Farra d'Isonzo* and *Capriva d'Isonzo* (Figure 1b). The whole area where grapes were cultivated has obtained the Italian quality assurance *Denominazione di Origine Controllata* (designation of origin) and it is well-known world-wide to produce excellent local white wines. Among these wines, we chose three varieties (*Friulano*, *Ribolla Gialla* and *Malvasia*) which are the older autochthonous and most present ones in the *Collio* area, thus representing the best indicators of local flavor characteristics.

According to the designation of origin protocol the grape varieties permitted were (all *Vitis Vinifera*): *Friulano* (100%), *Ribolla Gialla* (100%) and *Malvasia* (100%), respectively. The *Collio* wine samples ($n = 15$, five for each variety, vintage 2014) used in this study were with certified origin and directly collected at the wineries of local producers. Three additional *Friulano* samples produced in extra-*Collio* areas (Friuli Annia, Colli Orientali del Friuli, Friuli Grave, vintage 2014) were further analyzed for comparison. All the samples were collected in wineries, which operated as similar as possible winemaking processes in terms of maceration, pressing, must draining, fermentation conditions, refinement and bottling.

2.2 Volatile organic compounds analysis

2.2.1 Sample preparation and derivatization. Samples were transported to the laboratory in the commercial 750 mL glass bottles which had been opened right before analysis. A sample of diluted wine (10 mL, 1:5 sample dilution with deionized water) with addition of 2 mg of O-(2, 3, 4, 5, 6-Pentafluorobenzyl) Hydroxylamine hydrochloride (PFBHA, CAS 57981-



Figure 1.
The wine-producing
Collio area (Italy–
Slovenia)

02-9, Sigma–Aldrich S.r.l., Milan, Italy) as derivatizing agent (Figure 2a) and 2 g of anhydrous NaCl (JT Baker, Phillipsburg, NJ, USA) was directly prepared in a 20 mL vial successively crimp sealed with a PTFE septum cap. The derivatization process was carried out at 50 °C for 15 min at 500 rpm using the automatic sampling system Gerstel MPS2-Twister (Gerstel GmbH and Co., Mülheim, Germany).

2.2.2 Sample analysis. The analysis was conducted by a GC–MS system (Agilent 6890/5973 Inert, Agilent, Santa Clara, CA, United States) equipped with the abovementioned autosampler (Gerstel MPS2-Twister) with helium as carrier gas (1.5 ml min^{−1}). A coated Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber (Sigma–Aldrich

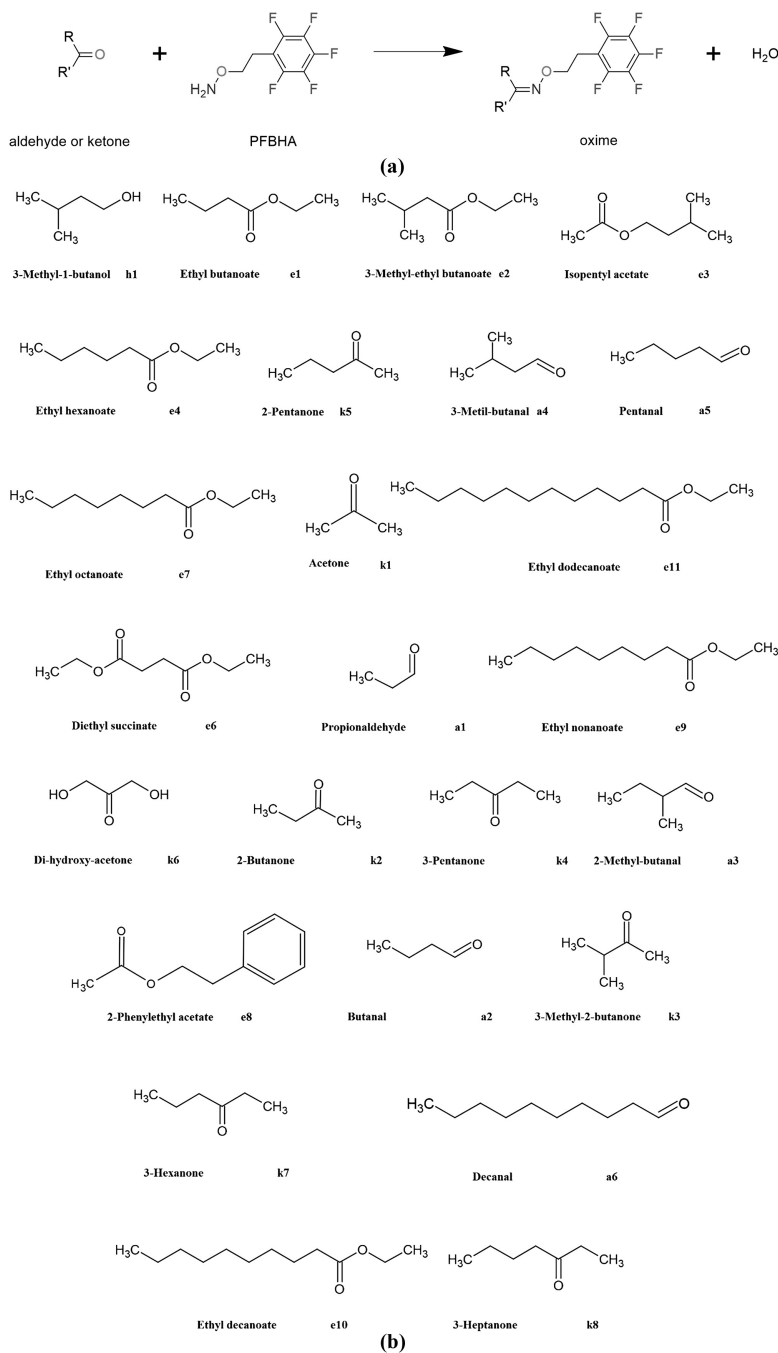


Figure 2.
(a) Derivatization reaction scheme of carbonyl compounds with PFBHA. (b) Chemical structure and abbreviations used in PCA and PLS-DA, of the 25 selected VOCs

S.r.l., Milan, Italy) was exposed to the headspace of the derivatized sample for 15.00 min at 50 °C and 500 rpm. The fiber was desorbed for 4.00 min at 250 °C in the injection unit. The separation was carried out in an Agilent DB 5ms UI capillary column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness). The GC oven temperature program started at 45 °C for 5 min and then was ramped to 100 °C at 2 °C/min and to 270 °C at 15 °C/min with a final isothermal stage held for 4 min. The mass spectrometer operated with ion source at 230 °C, quadrupole temperature of 170 °C, 70 eV electron energy, acquiring in SIM (m/z 161, 181, 195, 239) and TIC mode from m/z 35–400 amu. The SPME fiber was thermally cleaned prior to each analysis at 265 °C for 15.00 min. Analysis were conducted on three replicates. All chemicals were analytical reagent grade unless otherwise stated, and water was obtained from a Milli-Q purification system (Merck-Millipore, Darmstadt, Germany).

2.3 Chemometric data analysis

The VOCs selected are reported in [Figure 2b](#), and their chromatogram areas were organized in a dataset according to variety (*Ribolla*, *Friulano* and *Malvasia*) of wines. The calculations have been performed in R software environment ([R Foundation for Statistical Computing, Vienna, 2016](#)).

The data set has been normalized to have zero mean and unit variance (z-score normalization) to give to all the variables the same importance independently from their absolute value ranges. Then the dataset has been mined by a two steps chemometric analysis. First the variables have been grouped according to their chemical class as in ([Giungato *et al.*, 2019](#)) and elaborated by PCA using *pcaMethods* package ([Stacklies *et al.*, 2007](#)). Then the supervised method PLS-DA has been applied to a subset of variables according to the findings obtained by PCA. For performing PLS-DA the *mdatools* package ([Kucheryavskiy, 2020](#)) has been used.

2.4 VOCs composition of wines and dataset selection for classification purposes

In total, 40 VOCs were detected in the sample chromatograms and, among these, 25 compounds were selected for their higher peak area variability across the samples ([Figure 2b](#)). The selected compounds (aldehydes, esters, ketones and one alcohol) were identified ([Table 1](#)) by comparison of their mass spectra with the NIST 09 MS library. Among the selected compounds ethyl decanoate, 2-butanone, ethyl octanoate and acetone, showed the highest variations in peak area ([Figure 3](#)).

For every sample, the chromatographic peak areas averaged on three replicates of the 25 selected VOCs were used for chemometric analysis. We obtained a matrix of 15 $\times$ 25 elements to be analyzed for the classification among *Collio* wine varieties. Before chemometric analysis, the data sets were subjected to an in-depth analysis following the best practices in statistical analysis applied in food science ([Granato *et al.*, 2014](#)).

3. Results and discussion

3.1 Principal component analysis

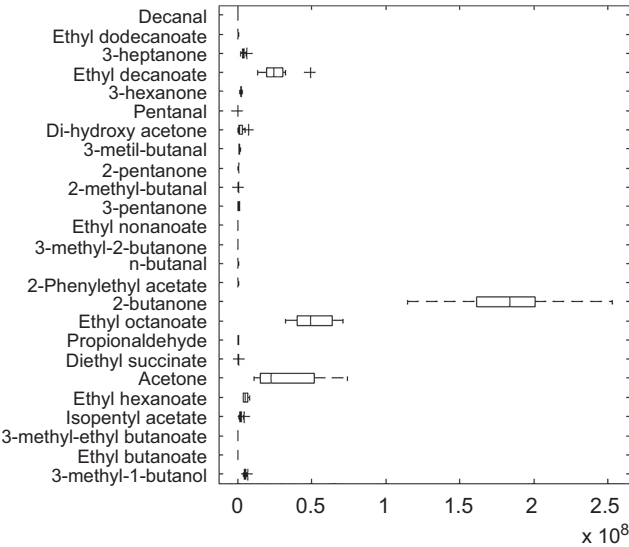
The data set has been z-score normalized and the variables have been grouped according to their chemical class as follows: alcohols (h1), aldehydes (from a1 to a5), long chain aldehydes (a6), diesters (e6), esters (from e1 to e4), aromatic esters (e8), long chain esters (e7, e9, e10, e11), ketones (from k1 to k5, k7, k8), saccharides (k6). Then PCA has been performed on a 15 $\times$ 9 data set.

PC1, PC2 and PC3 accounted for 74.27 % of the total variance (36.28 %, 23.61 % and 14.38 %, respectively.) Bi-plots of PC1 vs PC2 and PC2 vs PC3 are reported in [Figure 4](#).

Table 1.
Volatile organic
compounds identified
by analysis of the wine
samples with HS-
SPME-GC/MS

Code	Name
h1	3-methyl-1-butanol
e1	Ethyl butanoate
e2	3-methyl-ethyl butanoate
e3	Isopentyl acetate
e4	Ethyl hexanoate
k1	Acetone
e6	Diethyl succinate
a1	Propionaldehyde
e7	Ethyl octanoate
k2	2-butanone
e8	2-phenylethyl acetate
a2	n-Butanal
k3	3-methyl-2-butanone
e9	Ethyl nonanoate
k4	3-pentanone
a3	2-methyl-butanal
k5	2-pentanone
a4	3-metil-butanal
k6	Di-hydroxy-acetone
a5	Pentanal
k7	3-hexanone
e10	Ethyl decanoate
k8	3-heptanone
e11	Ethyl dodecanoate
a6	Decanal

Figure 3.
Boxplot of the peak
areas of the 25 selected
VOCs in the volatilome
of blanc wines from the
Collio area. Horizontal
line within box, box
and error bars
represent median,
interquartile range and
range, respectively



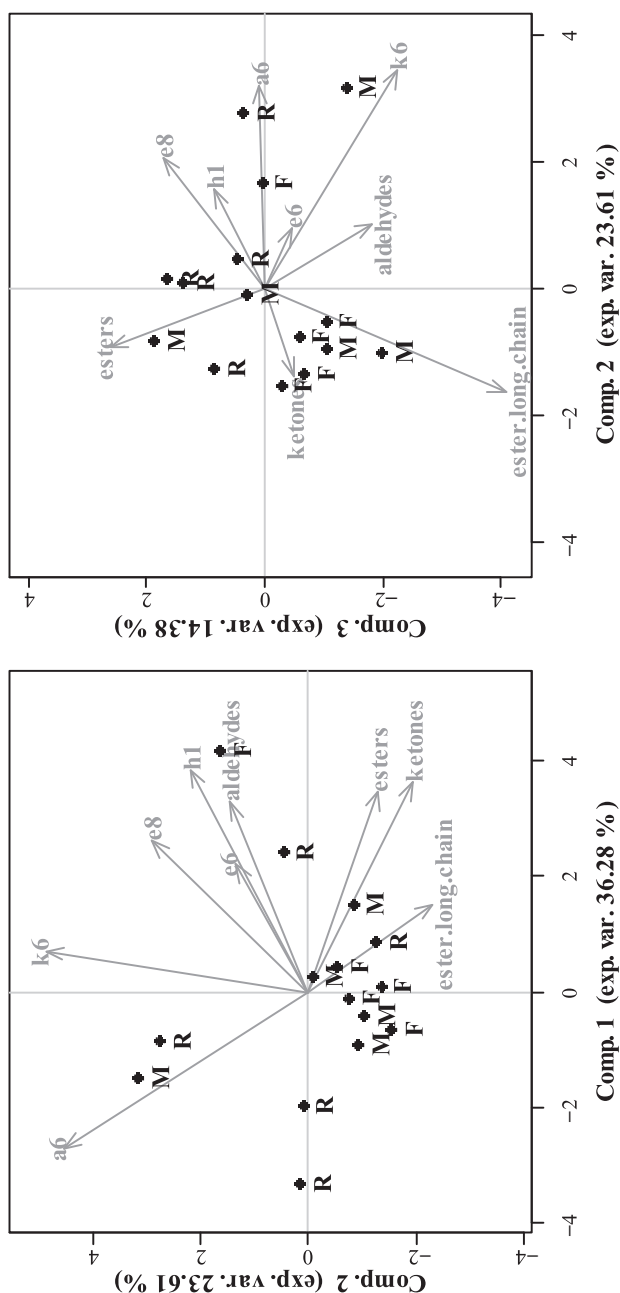


Figure 4. Biplots of the PC1, PC2 and PC3 for the three blanc wine varieties from the Collio area (five samples per variety – F=Friulano, R = Ribolla, M = Malvasia)

As it can be observed in Figure 4, in PC1 all the loadings are positive except for a6 compound. Therefore, we can say that the samples that showed the higher values for this component are those which contained higher relative total VOC concentrations.

Friulano samples showed negative values both for PC2 and PC3 except for one of the samples that showed a positive value for PC2 and a nearly zero value for PC3. Only one non *Friulano* wine (*Malvasia*) had similar values. Considering the graph representing PC2 vs PC3 it appears that all the *Friulano* samples are pulled in the both components negative quadrant by ketones and long chain esters classes, except for the *Friulano* sample pulled in the both components positive quadrant by a6 compound.

The *Friulano* extra-*Collio* samples data set, not used for building the PCA model, has been normalized by variable with the same parameters as the previous data set and with the same class grouping. The resulting data set has been projected into the PCA model obtaining the following component values for the scores: Friuli Annia (14.66, 7.46, -11.95), Colli Orientali del Friuli (-3.28, 1.17, 0.15), Friuli Grave (-1.03, 1.72, 1.52). It can be observed that no one of them lies in the both PC2 and PC3 negative quadrant, with Friuli Annia vary far apart from all the other samples. The graphs are presented in the Supplementary Materials. Therefore we considered that the compounds present in the ketones and long chain esters classes could be good candidates to discriminate *Friulano Collio* wines from the other *Collio* wines and *Friulano* extra-*Collio* wines.

3.2 Partial least square discriminant analysis

Considering the outcomes obtained by PCA exploratory analysis we decided to perform PLS-DA on a new 15 × 10 data set containing the following variables: e7, e9, e10, e11, from k1 to k5, k7, k8. A one class model (*Friulano* vs. non *Friulano*) and a leave-one-out cross-validation method have been used. One component was selected based on the minimum cross-validation error. The results of calibration and cross-validation are presented in Table 2.

Both in classification and cross-validation one of the *Friulano* samples was misclassified, namely the outlier shown in the PCA model. Additionally, both in classification and cross-validation one of the non *Friulano* wines was misclassified (*Malvasia*). Nevertheless the model showed a high sensitivity and accuracy in cross-validation and, moreover, the *Friulano* extra-*Collio* samples, not used for building the model, were correctly classified as non *Friulano Collio* wines (Table 2).

4. Conclusions

This study provides a first survey of the volatile organic compound profiles of three varieties of blanc wine from the *Collio* area (Italy and Slovenia), namely *Ribolla Gialla*, *Malvasia* and *Friulano* and tested the effectiveness of the chemometrics in fostering the identification of *Friulano* samples by using a variable selection method. The carbonyl compound identification has been fostered using a derivatizing agent (PFBHA) before performing HS-SPME-GC-MS analysis. Chemometric analysis has been applied to the obtained data set to identify possible markers of discrimination between varieties. PCA data set reduced by grouping VOCs belonging to the same chemical family, revealed good classification capabilities for the *Friulano*

Table 2.
Specificity, sensitivity and accuracy of PLS-DA of the *Collio* and extra-*Collio* wine samples

	TP	FP	TN	FN	Specificity	Sensitivity	Accuracy
<i>Collio</i> wines (calib.)	4	1	9	1	0.9	0.8	0.867
<i>Collio</i> wines (cross val.)	4	1	9	1	0.9	0.8	0.867
Extra <i>Collio</i> wines	0	0	3	0	1	–	1

Note(s): TP = true positive; FP = false positive; TN = true negative; FN = false negative

wine samples. PCA showed that compounds belonging to the ketones and long chain esters fostered the separation of Friulano samples. Therefore, a PLS-DA model based on these predictors was built. It showed a very good discrimination (87 % accuracy) between *Friulano* and other *Collio* varieties as well as between the former and other Friulano extra-*Collio* wines (100% accuracy).

Most of the useful predictors were carbonyl compounds, confirming the benefit in the use of the derivatizing agent. Improvements in the applicability of the authentication/discrimination model we presented could be achieved analyzing *Collio* wines with diverse wine-making processes and of different vintages.

ORCID iDs

Sabina Licen  <http://orcid.org/0000-0002-8895-396X>

Elija Muzic  <http://orcid.org/0000-0002-1616-2288>

Sara Briguglio  <http://orcid.org/0000-0003-4315-9049>

Arianna Tolloi  <http://orcid.org/0000-0001-5203-2715>

Pierluigi Barbieri  <http://orcid.org/0000-0001-8847-6916>

Pasquale Giungato  <http://orcid.org/0000-0002-2214-9362>

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Authors' contribution: Pasquale Giungato and Pierluigi Barbieri participated in study conception, supervision and coordination. Pasquale Giungato and Sabina Licen participated in data analysis, bibliographic research and drafted the manuscript. Sara Carmela Briguglio, Arianna Tolloi and Elija Muzic participated in collecting samples and setting-up the analytical method. All authors carefully read and approved the final manuscript.

Conflict-of-interest statement: All authors disclose any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

Abbreviations

VOC	Volatile organic compound
DVB/CAR/PDMS	Divinylbenzene/carboxen/polydimethylsiloxane
FVG	Friuli-Venezia Giulia
HS-SPME-GC-MS	Head space-Solid phase micro extraction-gas chromatography-mass spectrometry
PFBHA	O-(2, 3, 4, 5, 6-pentafluorobenzyl) -Hydroxylamine hydrochloride
FA	Factor analysis
CA	Cluster analysis
LDA	Linear discriminant analysis
PCA	Principal component analysis
PLS-DA	Partial least square discriminant analysis

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Corresponding author

Pasquale Giungato can be contacted at: pasquale.giungato@uniba.it

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