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Fiano, Greco and Falanghina grape cultivars differentiation by volatiles fingerprinting, a case study

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ABSTRACT

The biomolecular characterization of edible products is gaining an increasing importance in food chemistry. The characteristic aroma or bouquet of a wine is the result of complex interactions of volatile molecules and odor receptors. Its characterization is the subject of many different studies, aimed at the development of new methods to be used for the discovery of frauds and for the typization of Protected Designation of Origin (P.D.O.) or Protected Geographic Indication (P.G.I.) wines.

We previously outlined the proteomic profile of three cultivars of *Vitis vinifera* from South Italy (Campania) used for white wine production (Fiano, Greco and Falanghina) during the ripening. In this work, we present a mass spectrometry based study aimed at obtaining the profile of volatiles on the same samples using solid phase micro extraction coupled to gas chromatography.

We demonstrated that some of the main constituents of aroma (namely terpenes, alcohols, aldehydes, etc.) were characteristic of certain grapes and absent in others.

1. Introduction

The biomolecular characterization of foods and beverages represent nowadays an intriguing task for the scientific community. While nonvolatile compounds of a wine, e.g. polysaccharides, organic acids, mineral salts and polyphenols, have a great impact on the mouthfeel with acidity and salinity perceptions and astringency, the volatile component is the main responsible of wine aroma that contributes to the peculiar recognizability of a vine. Food aroma is the result of the complex interaction of small volatile molecules and odor receptors (Genovese et al., 2007) and, although its perception might be affected by subjectivity, it is considered as the first step in quality assessment. A common practice for the recognition of wines is in fact based on the flavors recognition: this peculiar capacity of tasters needs to be properly trained and developed. The specific combination of odour active compounds clearly perceived by tasters is a crucial parameter for differentiating Protected Designation of Origin (P.D.O.) or Protected Geographic Indication (P.G.I.) wines based on their geographical origin, production technology or variety, which outlines their quality, overall finesse and their harmony (the way all the aromas are tied one to the other). The characteristic smell of wines aroma come from grapes; pedoclimatic conditions and viticultural practices can enormously influence the varietal flavorings (Molina et al., 2007; Styger et al., 2011). Volatile molecules are secondary metabolites of the plant, i.e. they do not participate in the metabolic processes essential for the life of the plant itself but they have a crucial role in the defense mechanisms of the plant against the adversities characterizing the environment in which they live (Ali et al., 2010; Dunlevy et al., 2009). The ecological function of secondary metabolism is expressed in the defense role that these substances have with regard to the biotic environment due to their irritating, toxic and repellent properties. During the evolution, plants have developed systems and strategies for growth and survival (Bennett and Wallsgrove, 1994; Qiu et al., 2015). The stimulation of secondary metabolism takes place at the expense of the growth of the plant, as it hampers part of the nourishment towards defense substances. Secondary metabolites can therefore be considered as available molecules for growth and development, but are indispensable for the survival of the species.

On a total 800 volatile compounds identified in wines (terpenoids, phenols, alcohols, esters, aldehydes, ketones, lactones) only few of them contribute to the wine bouquet (Bosch-Fusté et al., 2007; Francis and

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Newton, 2005; Sagratini et al., 2012; Sánchez-Palomo et al., 2005). For example Sauvignon blanc is recognized by the higher content of thiols, i.e. 4-methyl-4-mercaptopentan-2-one, conferring the peculiar flavor defined from taster as "cat's pee" (Lacey et al., 1991; Marais and Swart, 1999; Swiegers et al., 2009).

The olfactory impact, considered as the threshold of perception of each individual compound, is dependent on chemical nature of molecule as well as its concentration (Francis and Newton, 2005). In fact, some compounds present in trace amounts may have a greater impact than other aromatic compounds present in higher concentrations(Francis and Newton, 2005).

The study of the volatile compounds in grapes has been scarcely examined unlike that of wine (Gürbüz et al., 2006; Razungles et al., 1993) but it is equally important for the characterization of a specific cultivar (Gürbüz et al., 2006; Pozo-Bayón et al., 2001). The main reason for this lack of informations, relies in the fact that within the berries, the majority of volatile molecules are still in their glycosylated form (Dimitriadis and Williams, 1984; Gunata et al., 1985; Nasi et al., 2008; Palomo et al., 2006; Selli et al., 2006). During fermentation oligosaccharides are hydrolyzed thus releasing the free volatile molecules.

Recently, we outlined the proteomic profile (Carpentieri et al., 2019) of three different cultivars of *Vitis vinifera* peculiar of south Italy (Campania) used for white wine production (Fiano, Greco and Falanghina) showing significant changes in protein expression along the ripening process. On the same set of samples, we outlined the molecular profiling of the volatile fraction based on SPME/GC-MS. In a single experiment, we could capture heterogeneous analytes (by SPME) that can be unambiguously identified by GC-MS. The workflow adopted in this paper can be extended to the typization of different foods and beverages thanks to its high sensitivity, reproducibility and accuracy.

2. Materials and methods

2.1. Chemicals

The fibers used for volatile fractions (SPME) analysis were purchase from Supelco (Bellefonte Park, USA).

Acetonitrile, formic acid, chloroform and methanol were purchased from Baker and sodium chloride from Carlo Erba.

2.2. Sampling

Different grape lots of each varieties were purchased by local producers; each analyzed vine is typical of South Italy (Campania region):

- Pool1: Falanghina Del Sannio DOP
- Pool2: Fiano DOP Sannio
- Pool 3: Greco Sannio DOP

The sampling took place in the vineyards with 10-day intervals for each grape variety examined. Samples were then pooled and further analyses were performed on the pools.

Each sample was obtained choosing the same row and pick the grapes from the first cluster-bearing plant. For each sample, about 50 grapes were harvested taking care to remove, from each cluster selected, the grape together with the pedicel in order to obtain the whole grapes that were immediately frozen. Each sampling was repeated in duplicate, the first aliquot of the sample was used for monitoring the state of ripening of its variety and the other aliquot was used for protein analysis (Carpentieri et al., 2019).

2.3. Samples preparation

Grapes were partially thawed to allow to cut the pedicel and to eliminate the grape seeds by cutting in two halves each single berry. The peel and the pulp were frozen with liquid nitrogen and powdered.

Each powder was aliquoted (15g) in a falcon tube and then centrifuged at 5000rpm for 10 min at 4 °C. The liquids (7.5ml) thus obtained were separated from the insoluble fractions and transferred into a 20ml conical flasks.

2.4. Maturation state assessment

Analyses for the assessment of maturation level were performed as reported in our previous paper (Carpentieri et al., 2019) (see Table 1).

2.5. Analysis of volatile compounds (SPME/GC-MS)

Extraction and desorption of molecules were carried out by SPME using a 2 cm 50/30 μm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS), 30 μm polydimethylsiloxane (PDMS), 85 μm Polyacrilate and a 75μm Carboxen/Polydimethylsiloxane (CAR/PDMS) fibers (Supleco). The adsorption was conducted for 30 minutes at 60 °C, and the fibers were then exposed in GC injector at a temperature of 230 °C for 3 minutes (desorption).

All gas chromatography analyses were performed using Agilent GC 6890, coupled with a 5973 MS detector. The column used is an HP-5 capillary (30 m × 0.25mm, 0.25mM, 5% polisilarilene 95% polydimethylsiloxane). Helium was used as carrier gas, at a rate of 1.0 ml/min. The GC injector was maintained at 230 °C, while the analyzer is kept at 250 °C. The collision energy was set to a value of 70eV, fragment ions generated were analyzed mass range 20–450 m/z.

The injection temperature was 250 °C the oven temperature was held at 60 °C for 3 min and then increased to 150 °C at 10 °C/min, increasing to 230 °C at 14 °C/min and finally to 280 °C at 15 °C/min held for 5 min for a total separation time of 23 min.

The identification of each compound was based on combination of retention time and mass spectrum matching using Ms search-Nist 05 library software.

An external standard solution mix containing two analytes for each category of compounds identified (namely: nonanal, eptanal, ethanol, buthanol, ethyl acetate, benzyl acetate, geraniol, linalool, limonene and eucalyptol) was used for GC-MS quantification. Each analysis was performed in triplicate.

Table 1
Analytical parameters used to monitor the maturation process.

Greco	date	Sugars (Brix)	Total Acidity (g/lt)	pH	Berries average weight (g)
1st Sampling	20/07/2014	3.7	27.28	2,69	0,87
2nd Sampling	19/08/2014	9.5	21.37	2.83	1.15
3rd Sampling	8/9/2014	15.8	16.93	3.01	1.29
Falanghina	date	Sugars (Brix)	Total Acidity (g/lt)	pH	Berries average weight (g)
1st Sampling	20/07/2014	3.8	30.18	2.58	0.97
2nd Sampling	19/08/2014	6.5	26.27	2.63	1.19
3rd Sampling	8/9/2014	15.9	17.56	2.91	1.28
Fiano	date	Sugars (Brix)	Total Acidity (g/lt)	pH	Berries average weight (g)
1st Sampling	20/07/2014	3.8	29.81	2.69	0.83
2nd Sampling	19/08/2014	12.7	12.87	3.1	1.3
3rd Sampling	8/9/2014	16.2	8.75	3.31	1.49

2.6. Statistical analysis

Multivariate statistical analysis by using the Principal Component Analysis (PCA) and Heat maps were performed by XLStat 2016.5 version.

Both statistical analyses were carried out on the peaks area of 52 volatile compounds as determined by GC-MS analyses for 9 variables (3 for each cultivar sampling).

The parameters to perform PCA were summarized in Table 2, including minimum, maximum, mean and deviation standard values; no missing data was considerated.

3. Results and discussions

The aroma of a wine is the result of a complex mixture of volatile molecules; some of them are generated during fermentation and some others (a relatively small population) are present on the same grapes used for vinification. The latter are the subject of the present study. To this aim, different lots of each cultivar (Greco, Fiano, and Falanghina) were harvested with a cadence of approximately 30 days for each vine and analyzed according to parameters in Tab 1. For the investigation of volatile compounds, we tested different fibers for the extraction, the best results in terms of number of identified molecules and signal to noise ratio were obtained with DVB/CAR/PDMS. Analytes absorbed on the DVB/CAR/PDMS fiber were eluted by the exposure of the fiber to 230 °C directly in the inlet valve of the GC, as described in the previous section. After elution, each component was analysed by electron impact mass spectrometry and a total ion current (TIC) was recorded for each sample. As an example, the TICs from the third sampling (1A for Falanghina, 1B for Fiano and 1C for Greco) are reported in Fig. 1. The chromatograms were compared revealing a considerable number of peaks with differences in the relative intensity. Each molecule was identified by comparing its fragmentation spectra with the ones in the NIST library. We could identify five classes of compounds for each cultivar: aldehydes, alcohols, esters, terpenes and norisoprenoids (Tab 2a, b and c). We performed a relative quantification of the analytes based on chromatographic peak areas, thus obtaining the trend for each molecule during maturation process for each cultivar.

PCA was performed on the peak area of the 52 volatile compounds identified by GC-MS for each sampling of the three different cultivars. The first two principal components, PC1 and PC2, accounted for 69.35% of total variance (50.84% and 18.52% respectively) (Fig. 2). The values of deviation standard resulted to be about 20 % for each variable (tab 3).

Heat-map (representing volatile profile of three vine cultivars is reported in Fig. 3) was obtained using the chromatographic peaks area of each volatile compound (Table 3).

Such results showed a peculiarity of the biomolecular pattern of Fiano and a good overlap between Greco and Falanghina. The same behavior was registered for proteomic pattern (Carpentieri et al., 2019).

Diagrams in Figs. 4, 5, and 6 showed the general trend of the identified compounds. We divided the analytes into five categories and then plotted the average area of each class of compounds to monitor their trends. For Falanghina (Fig. 4), during the maturation process, we observed a general decrease of aldehydes, alcohols (except for hexanal, 2-hexen-1-ol e 1-hexanol), terpenes (except for eucalyptol) and esters; the same behavior cannot be observed for norisoprenoids. The same trend for the majority of compounds was observed in Greco (Fig. 5); butanol, 3-methyl, pentanal, hexanal, 5-hepten-2-one, 6methyl represent an exception in the general behavior. As for Fiano (Fig. 6), the general trend of molecules is not linear as the ones described before. For this cultivar, we could observe a reduction in esters amount.

Our results are generally consistent with other studies showing a general decrease in the free volatile component during the ripening. These factors were highly influenced by pedoclimatic conditions and farming techniques (Razungles et al., 1993).

Among the identified compounds, we focused on some of the aromatic descriptors, which resulted to be present in the three samplings of each cultivar. These results were then compared with data from the other cultivars.

Actinidol-hepoxy is part of the norisoprenoid family, found only in Greco sampling; little is known about the formation of isomeric actinidols in wines as well as their sensorial contribution to wine aroma. Their odor, though, has been described as camphoraceous or as woody and resinous.

5-caranol is another component of the norisoprenoid family found only in Falanghina samples. Many of the norisoprenoids are powerful odorants with pleasant odors, usually described as flowery and fruity. We could also identify (solely for Falanghina grapes) 2-hexen-1-ol acetate, an odor descriptor responsible of sweet leafy green with a fresh, fruity apple nuance and 2-nonen-1-ol Green, fatty, melon, with an oily tallow nuance.

As for Fiano samples we could identify some unique molecules such as: cyclohexanal, 2-methyl-5- (1-methylethenyl) characterized by a floral woody and sweat spicy flavor, propanoic acid, 2-octyl ester with a fruity, fatty fragrance with a soft and humid undertone reminiscent of parsley and fern root (Burdock, 2016), 1-nonalol with a fresh clean fatty floral rose orange dusty wet oily. and finally terpinolen with a woody, terpy, lemon and lime-like with a slight herbal and floral nuance also known for its repellent activity against insects.

While the majority of volatile compounds are glycosylated within grapes (Gunata et al., 1985; Nasi et al., 2008), molecules identified in this paper represent the non-glycosylated (therefore more volatile) fraction. Glycosylated volatiles pass from the grape to the wine where they undergo chemical and enzymatic hydrolysis, which liberates terpenes and norisoprenoids from the sugar making them volatile (Mateo and Jiménez, 2000). This process explains why the volatile component of the grapes is composed of only few molecules, compared to the complexity of the compounds identified in wine, in which not only the varietal component but also the esters and alcohols produced by the yeast are found.

Data reported in our previous paper (Carpentieri et al., 2019) showed that the bio-molecular signature of a vine is strictly related to intrinsic characteristics of the plant itself and to external factors (such as adverse meteorological conditions and farming habits). Proteins related to stress response in particular, are highly expressed in vines exposed to stress conditions (heavy rains and/or parasite attacks). For Fiano cultivar, as an example, we observed the over expression of peroxidases. This finding can be linked to the general high ketone content in the same cultivar, which suggest a high level of oxidation.

Even if a direct comparison and/or any correlation between

Table 2
Summary of data used to perform PCA of Fiano, Greco and Falanghina volatiles compounds.

Variable	Obs. (VOCs)	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
Fiano 30/07/14	52	0	52	0,1	919890,000	93095,175	182488,748
Fiano 19/08/14	52	0	52	0,1	625788,600	72609,223	134189,033
Fiano 08/09/14	52	0	52	0,1	618334,500	83882,971	150312,212
Greco 20/07/14	52	0	52	0,1	862495,000	56206,019	150342,779
Greco 19/08/14	52	0	52	0,1	757669,000	70581,904	172706,821
Greco 8/9/14	52	0	52	0,1	2305397,000	114765,192	383196,828
Falanghina 20/07/14	52	0	52	0,1	1402747,000	119281,815	239363,730
Falanghina 19/08/14	52	0	52	0,1	1023401,000	116014,644	208252,771
Falanghina 8/9/14	52	0	52	0,1	915858,000	90025,146	202062,919

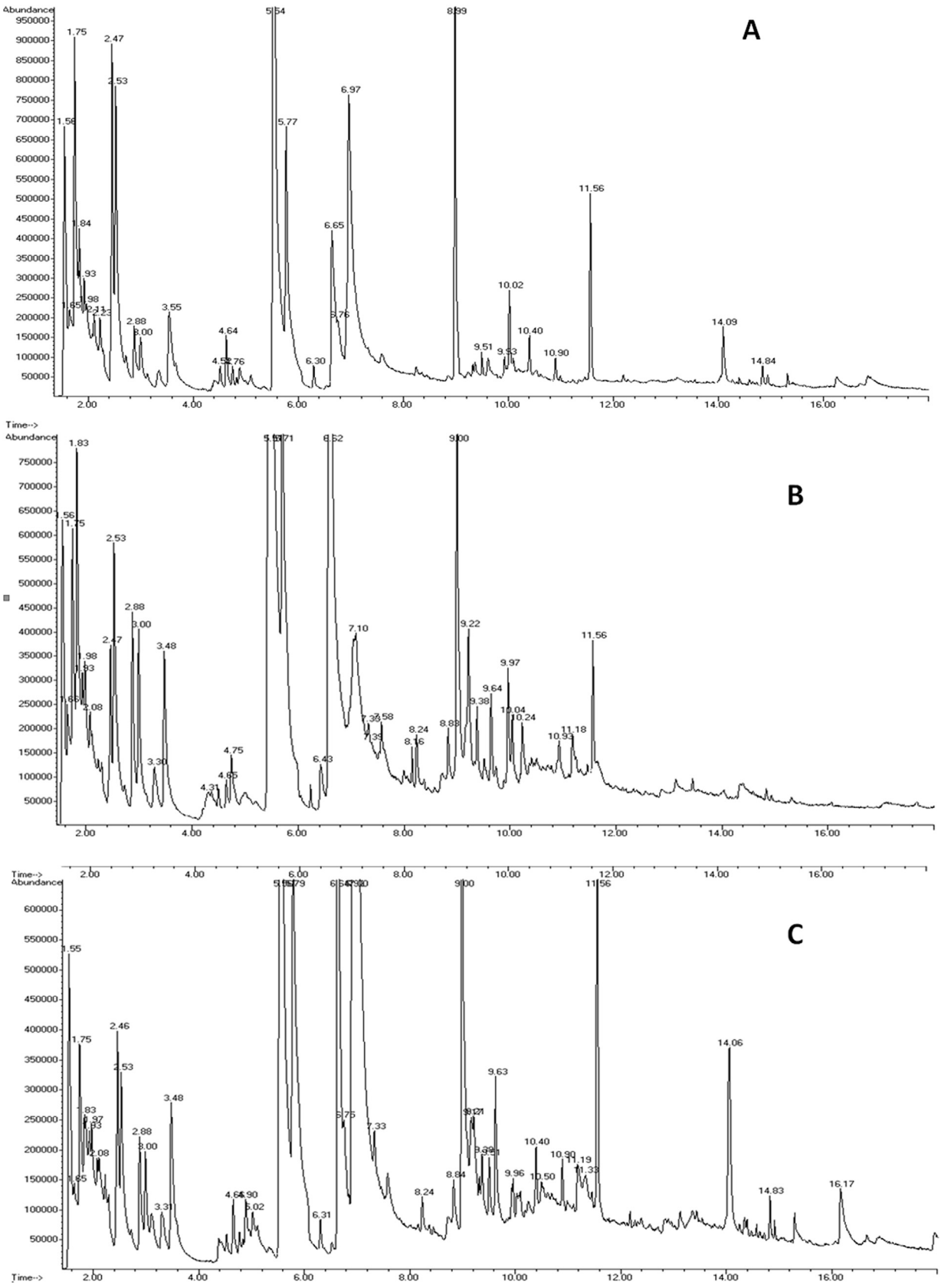

Fig. 1. TICs of the analysis of the third sampling for the three cultivars (1A for Falanghina, 1B for Fiano and 1C for Greco).

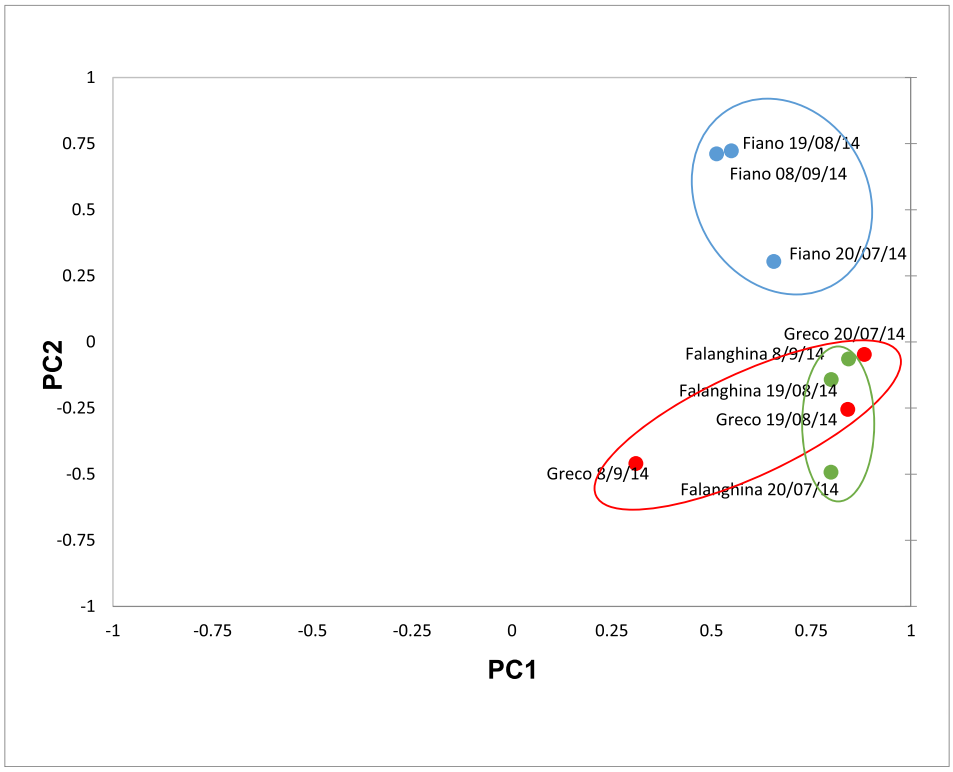

Fig. 2. PCA shows the peculiarity of the general biomolecular pattern of Fiano compared to the other two cultivars.

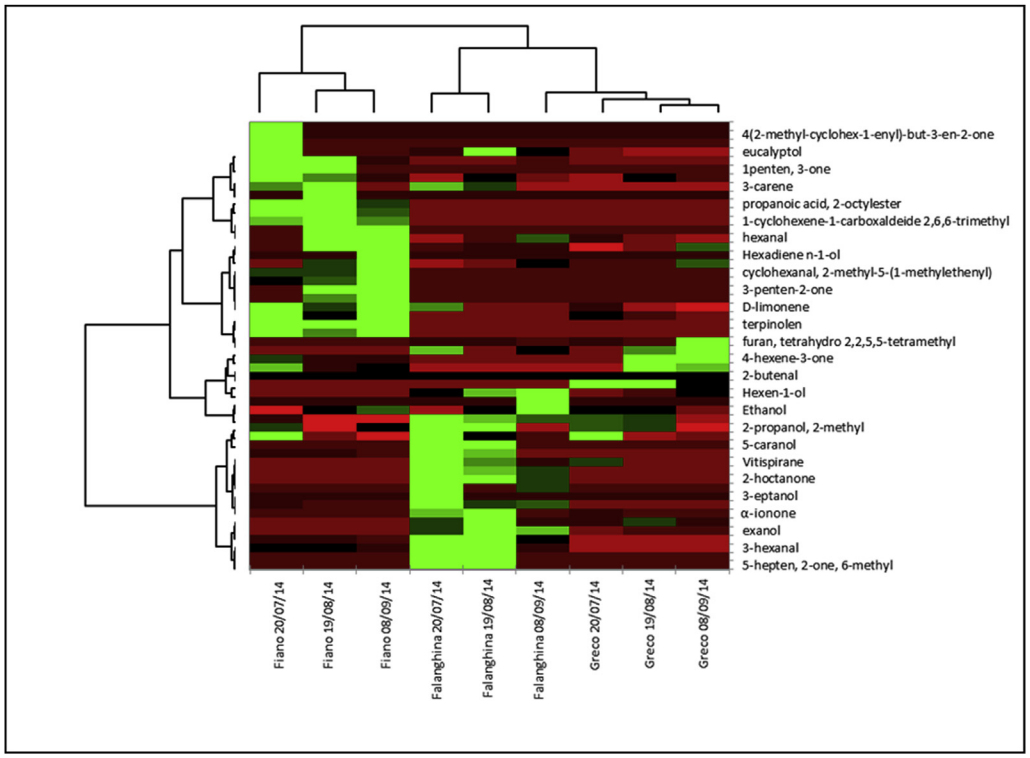

Fig. 3. Heatmap showing the peculiarity of the general biomolecular pattern of Fiano cultivar and the good overlap between identified volatiles for Greco and Falanghina. Red, green and black colors represent higher, medium and lower value of the chromatographic area, respectively. Clusters related to the grouping of volatiles (vertical axis) and samples (horizontal axis) were designated.

proteomes and metabolomes is quite a huge issue, we could find similarities in the general trend of identified biomolecules. This finding seems to be more evident in Fiano with respect to Falanghina and Greco vines. Proteomic and metabolomic data showed in fact a peculiar molecular signature in Fiano cultivar, which resulted to be quite different if compared to the other two.

Table 3
Compounds identified for each cultivar (respectively A. Greco, B. Falanghina and C. Fiano). Retention times and chromatographic peak areas are reported.

A

R.T.	Compound	MW	Greco 20/07/14	Greco 19/08/14	Greco 8/9/14
1.75	Ethanol	46	500559	489566	373795
1.93	2-propanol, 2-methyl	74	387077	327148	45773
2.11	2-butanal	70	210768	39330	61399
2.42	Ethyl acetate	88	862495	736938	333735
2.88	butanol, 3-methyl	86	43993	70199	181341
3.10	3-pentan, 2-one	84	198671	145484	44692
3.32	2-pentanone	86	47366	94631	58609
3.53	pentanal	86	144397	371598	249150
4.72	furan, tetrahydro 2,2,5,5-tetramethyl	128	132590	57639	36212
5.55	hexanal	100	186877	358810	423201
6.95	Hexen-1-ol	100	N.I.	757669	1508892
7.00	exanol	102	N.I.	N.I.	2305397
7.58	heptanal	114	N.I.	59106	47591
9.22	5-hepten-2-one, 6-methyl	126	66124	56596	189129
9.96	D-limonene	136	73029	38115	68278
10.02	eucalyptol	154	27217	20185	40596
14,26	Actinidol-hepoxy	222	54120	41333	26541
13.99	α-ionone	192	19433	24854	N.I.
14.26	Vitispirane	194	22117	22391	N.I.

B

R.T.	Compound	MW	Falanghina 20/07/14	Falanghina 19/08/14	Falanghina 8/9/14
1.75	Ethanol	46	343143	480108	915858
1.93	2-propanol, 2-methyl	74	580402	506471	97924
2.14	2-butanal	70	239463	118682	80272
2.22	1-pentene, 2-methyl	84	258457	77974	95656
2.42	ethyl acetate	88	1402747	1023401	818299
2.73	3-hexanal	102	73071	82908	24023
2.88	butanal, 3-methyl	86	8179	18720	120437
3.34	2-pentanone	86	99242	378277	44658
4.33	3-eptanol	116	92665	N.I.	N.I.
3.55	pentanal	86	127765	378277	179141
4.75	furan, tetrahydro 2,2,5,5-tetramethyl	128	127665	112536	42752
5.55	hexanal	100	11495.4	143560.5	325655.6
6.91	2-hexen-1-ol	100	144716	377082	706738
6.96	1-hexanol	102	189549	667926	332598
7.59	heptanal	114	22812	29656	25705
8.24	2-hoctanone	128	68925	55683	22757
9.15	5-hepten, 2-one, 6-methyl	126	181898	204684	N.I.
9.24	cyclohexane-1-methylene-4-(1-methylethenyl)	136	N.I.	N.I.	10520
9.37	propanoicacid, 2,2-dimethyl, propylester	144	108530	57882	34741
9.49	2-hexen-1-ol, acetate	142	121442	120529	N.I.
9.61	2-nonen-1-ol	142	196901	N.I.	47521
9.96	D-limonene	136	134139	42465	41474
10.02	eucalyptol	154	131240	498145	193519
10.45	3-carene	136	158116	99364	N.I.
12.67	cis-β-terpineol	154	130602	62034	N.I.
12.81	5-caranol	154	53116	32662	N.I.
14.27	vitispirane	194	95644	39895	8952
15.38	β-damascone	190	69158	106371	30878
15.99	α-ionone	192	146846	317469	N.I.

C

R.T.	Compound	MW	Fiano 30/07/14	Fiano 19/08/14	Fiano 08/09/14
1.75	Ethanol	46	233388	511194	591731
1.93	2-propanol, 2-methyl	74	342093	34264	307664
2.14	2-butanal	70	243683	51882	18153
2.22	1-pentene, 2-methyl	84	37434	19973	24835
2.30	2-butanone	72	74104	80451	38198
2.42	ethyl acetate	88	553099	157644	104645
2.73	3-hexanal	102	30492	28780	20097
2.88	butanal, 3-methyl	86	24377	147401	421668
3.10	3-penten, 2-one	84	111091	N.I.	N.I.
3.29	1penten, 3-one	84	140954	100802	N.I.
3.47	pentanal	86	919890	489602	324677
4.20	2-hesanone	100	34312	12540	19429
4.81	4-hexene-3-one	98	156559	70506	98105
5.13	2-hexenal	98	7914	N.I.	N.I.
5.44	hexanal	100	151894.1	625788.6	618334.5
6.31	3,3-dimethyl-6-methylenecyclohexene	122	11178	29553	84320
7.01	Hexadiene n-1-ol	98	N.I.	N.I.	246004
7.05	1-nonalol	144	N.I.	294884	N.I.

(*continued on next page*)

Table 3 (*continued*)

7.57	heptanal	114	24728	65761	60111
8.42	3-penten-2-one	84	N.I.	12817	22579
8.82	propanoic acid, 2-methyl, methylester	102	111449	63487	107312
9.16	5-hepten-2-one, 6-methyl	126	225160	68527	305745
9.72	1-3-cyclohexadiene, 1-methyl-4-(1-methylethyl)	136	153367	104939	22697
9.95	D-limonene	136	163362	95655	206307
10.02	eucalyptol	154	728735	91651	99697
10.44	3-carene	136	143561	249861	19545
10.72	limonene-oxide, cis	152	N.I.	20321	19105
10.93	terpinolen	136	92438	80570	71456
11.14	cyclohexanal, 2-methyl-5-(1-methylethenyl)	154	23001	23262	93439
12.19	propanoic acid, 2-octylester	186	19547	27590	9495
12.34	4 (2-methyl-cyclohex-1-enyl)-but-3-en-2-one	164	5705	N.I.	N.I.
12.60	cis-β-terpineol	154	13602	11855	9541
13.16	1-cyclohexene-1-carboxaldeide 2,6,6-trimethyl	152	13255	26078	11250
14.85	2-pyrazine, 1-buthyl-5-methyl	150	24046	N.I.	N.I.
15.38	β-damascone	190	21268	20093	12632

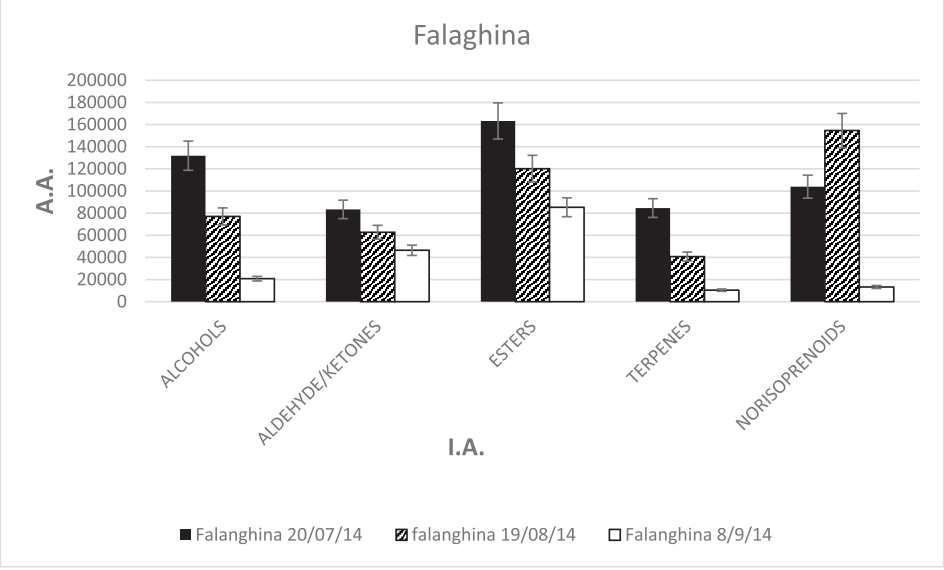

Fig. 4. The general trend of the chemical compounds for Falanghina samples. Analyses were performed in triplicate. Identified analytes (I.A.) were divided into five categories (reported on X-axis) and then plotted against the average area (A.A.) of each class of compounds (Y-axis) ± standard deviation (5%).

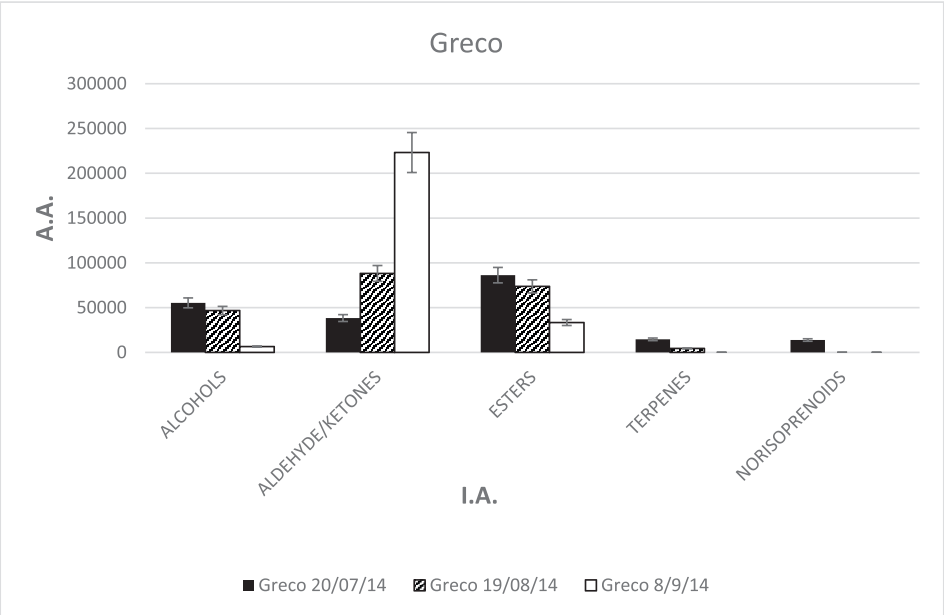

Fig. 5. The general trend of the chemical compounds for Greco samples. The plot was constructed as described for Fig. 4.

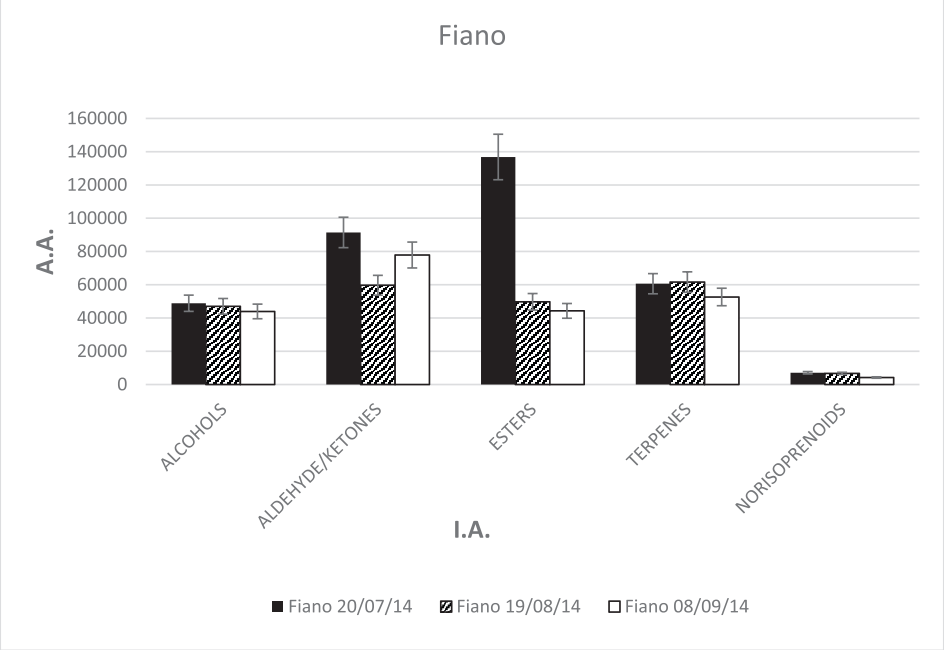

Fig. 6. The general trend of the chemical compounds for Fiano samples. The plot was constructed as described for Fig. 4.

4. Conclusion

The development of fast and simple analytical approaches and their application on real samples has a key role in food quality assessment and product typization. The increasing demand of products in the food market led the producers to introduce new and intensive farming techniques that, in turn, introduced a higher level of complexity among existing cultivars.

Farming conditions as long as the quality of the soil and the water deeply influence the quality of natural products, any variation can greatly change the biomolecular profile of a single cultivar. Our previous study (Carpentieri et al., 2019) show the possibility to depict a wide molecular fingerprinting of grape berries of three varieties specific of South Italy.

In this paper, we identified numerous molecules diversely distributed (in terms of quality and relative quantity) among the Falanghia, Greco and Fiano cultivars. The variation of key molecules belonging to specific categories (such as aldehydes, alcohols and terpenes) was monitored and, at the same time, some unique aromatic descriptors were detected as putative marker of a specific cultivar.

As a whole, our data suggest that the typization of edible products on a molecular level is nowadays possible and of fundamental important not only for the safeguard of DOP/IGP products but also for preserving the local economies.

Declarations

Author contribution statement

Andrea Carpentieri: Conceived and designed the experiments; Wrote the paper.

Angelo Sebastianelli, Vincenzo Lettera: Performed the experiments.

Chiara Melchiorre, Gabriella Pinto: Analyzed and interpreted the data.

Marco Trifuoggi: Contributed reagents, materials, analysis tools or data.

Angela Amoresano: Conceived and designed the experiments.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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