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Doctoral Thesis

Chemical characteristics of wine made by disease tolerant varieties

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To the best gift that life gave us:

to you Nonna Rosa

CONTENTS

Abstract

Vitis vinifera L. is the most widely cultivated *Vitis* species around the world which includes a great number of cultivars. Owing to the superior quality of their grapes, these cultivars were long considered the only suitable for the production of high quality wines. However, the lack of resistance genes to fungal diseases like powdery and downy mildew (*Uncinula necator* and *Plasmopara viticola*) makes it necessary the application of huge amounts of chemical products in vineyard. Thus, the search for alternative and more sustainable methods to control the major grapevine pathogens have increased the interest in new disease tolerant varieties. Chemical characterisation of these varieties is an important prerequisite to evaluate and promote their use on the global wine market.

The aim of this project was to produce a comprehensive study of some promising new disease tolerant varieties recently introduced to the cultivation by identifying the peculiar aspects of their composition and measuring their positive and negative quality traits. A multi-targeted approach using different analytical techniques (GC-MS, UPLC-MS, NMR and FTIR analysis) was adopted to investigate the main classes of volatile and non-volatile compounds which play a key role in the organoleptic and sensory properties of wine. The findings of this study provide a clear picture of the chemical profile of wine made from a selection of mildew tolerant varieties. Knowledge gained would serve to evaluate their use for quality wine production as well as to suggest the most appropriate winemaking style, allowing the improvement of the wine quality and valorisation of the characteristics of each grapevine variety. Considering that grape quality is crucial for wine quality, the chemical composition of the grapes from mildew tolerant varieties was also investigated.

Additionally, bearing in mind the role of wild *Vitis* genotypes as a source of genetic resistance to biotic and abiotic stresses, the metabolomic profile of red grapes from non-*V. vinifera* genotypes was explored. By evaluating these wild genotypes, it was possible to assess the value of this grape germplasm and the information acquired could provide wider choices to the breeders. To the best of our knowledge this survey is the most extended metabolomic profiling study on non-*V. vinifera* genotypes.

Aim of the PhD project

Recently, the continuous use of plant protection products and the growing awareness of their negative consequences on environment and human health have led to search for alternative and low impact strategies to control the major grapevine pathogens. Disease tolerant varieties of *Vitis vinifera*, which combine high wine quality and resistance to pathogens, have the potential to reduce the application of chemical products significantly as well as to reduce the production costs. Therefore, they represent one of the most promising tools for a more sustainable viticulture. To promote their use and diffusion for wine production, it is necessary to gain more information about their qualitative traits.

The main aim of the project was to characterise the chemical composition of wine produced by some promising disease tolerant grape varieties grown in Italy and Germany in different vintages. To identify and quantify the main classes of compounds involved in determining the organoleptic and sensory properties of wine, the targeted analysis was taken into account. Both volatile and non-volatile profile of the wines under study was investigated. Since grape quality is a crucial prerequisite for wine quality, the chemical composition of the grapes from mildew tolerant varieties was also determined. Considering the role of wild *Vitis* genotypes as a source of genetic resistance to biotic and also abiotic stresses, it was very interesting to explore the composition of their grapes.

This thesis focuses on the three following topics:

- study of the grape metabolomic composition, in terms of polyphenols and lipids, of seven non-*V. vinifera* genotypes in different vintages (chapter 2);
- analysis of the composition of grape from a selection of some promising disease tolerant varieties cultivated in Italy and Germany (chapter 3);
- analysis of the volatile and non-volatile profile of wine produced by disease tolerant varieties grown in Italy and Germany in three different vintages (chapter 4).

CHAPTER 1

Introduction

General introduction

Grapevine is one of the most widespread and cultivated fruit crops worldwide since ancient times. Today the world's total area under vines accounts for about 7.5 million hectares, of which over 3.3 million hectares of vineyards are distributed in Europe (from 'OIV Statistical Report on World Vitiviniculture' – 2017 release). The high versatility of grapes deriving from their use in production of wine, grape juice, jam, vinegar and other products has also made grapevine one of the most economically important plant species in the world.

1.1 The Genus *Vitis*

The grape is a member of the family Vitaceae, within the genus *Vitis* which involves about 60 species in total classified in two *sub-genera, Euvitis and Muscadinia* (Table 1). The species of these two subgenera differ in anatomic, taxonomist and cytological traits. *Euvitis* species possess 38 chromosomes (2n=2x=38), shredding bark, non-prominent lenticels, pyriform seeds and nodal diaphragms; *Muscadinia* species contain 40 chromosomes (2n=2x=40), non-shredding bark, prominent lenticels, naviform seeds and no diaphragm interrupting the pith at nodes (Reisch, Owens, & Cousins, 2012). Subgenus *Euvitis* comprises the vast majority of the species which are the most important in viticulture while only three species, mainly distributed in the southern United States and eastern Mexico, are included in the subgenus *Muscadinia.* Crosses between two subgenera are feasible even if the resulting progeny is often characterised by poor fertility probably because of an imprecise separation of chromosomes during meiosis. Within the same subgenus, species can be crossed producing a fertile progeny (Mullins, Bouquet, & Williams, 1992). Among all the species of the genus *Vitis*, the most renewed is the European grape *Vitis vinifera* which is native of the Mediterranean basin, southern and central Europe, northern Africa, and southwest and central Asia. The domestication of *V. vinifera* subsp. *vinifera* (or *sativa)* from its wild ancestor (*V. vinifera* ssp. *sylvestris*) probably occurred approximately 5000 years ago somewhere in Asia Minor or Armenia (Alleweldt & Pissingham, 1988). During this process grapes underwent several dramatic changes in order to increase the sugar content for better fermentation and yield, and also to have a more regular production. In particular, the modifications occurred in berry and bunch size, in seed morphology and in its reproductive structure changing from dioecious wild plants to hermaphrodite ones (This, Lacombe, & Thomas, 2006).

Table 1. Classification and geographical distribution of *Vitis* species.

Order Rhamnales

Family Vitaceae

Genus Vitis

Subgenus *Euvitis*			**Subgenus *Euvitis***		
Series	Species	Origin	Series	Species	Origin
I. Candicansae	*V. candicans*	North Am. (East)	VIII. Flexuosae	*V. flexuosa*	Asia
	V. doaniana	North Am. (East)		*V. thunbergii*	Asia
	V. longii	North Am. (East)		*V. betulifolia*	Asia
	V. coriacea	North Am. (East)		*V. reticulata*	Asia
	V. simpsonii	North Am. (East)		*V. amurensis*	Asia
	V. champinii	North Am. (East)		*V. piasekii*	Asia
II. Labruscae	*V. labrusca*	North Am. (East)		*V. embergeri*	Asia
	V. coignetiae	Asia		*V. pentagona*	Asia
III. Caribaeae	*V. caribaea*	North Am. (South)		*V. chunganensis*	Asia
	V. blancoii	North Am. (East)		*V.chingii*	Asia
	V. lanata	Asia		*V. piloso-nerva*	Asia
IV. Arizonae	*V. arizonica*	North Am. (West)		*V. balsalsaeana*	Asia
	V. californica	North Am. (West)		*V. hancockii*	Asia
	V. girdiana	North Am. (West)		*V. hexamera*	Asia
	V. treleasei	North Am. (West)		*V. pedicellata*	Asia
V. Cinereae	*V. cinerea*	North Am. (East)		*V. retordii*	Asia
	V. berlandieri	North Am. (East)		*V. seguinii*	Asia
	V. baileyana	North Am. (East)		*V. silvestrii*	Asia
	V. bourgeana	North Am. (South)		*V. tsoii*	Asia
VI. Aestivalae	*V. aestivalis*	North Am. (East)		*V. byroniifolia*	Asia
	V. lincecumii	North Am. (East)	IX. Spinosae	*V. armata*	Asia
	V. bicolor	North Am. (East)		*V. davidii*	Asia
	V. gigas	North Am. (East)		*V. romanetii*	Asia
	V. rufotomentosa	North Am. (East)	X. Ripariae	*V. riparia*	North Am. (East)
	V. bourquina	North Am. (East)		*V. rupestris*	North Am. (East)
VII. Cordifoliae	*V. cordifolia*	North Am. (East)	XI. Viniferae	*V. vinifera*	Eurasia
	V. rubra	North Am. (East)	**Subgenus *Muscadinia***		
	V. monticola	North Am. (East)		*V. rotundifolia*	North Am. (East)
	V. ilex	North Am. (East)		*V. munsoniana*	North Am. (East)
	V. helleri	North Am. (East)		*V. popenoei*	North Am. (East)

Characteristic attributes of grapevine, such as the ability to climb and to grow well in shallow soils, the minimal requirement for minerals and water, and the remarkable propagative aptitude are the key factors contributing to its success as a domesticated plant (Jackson, 2008). From the primo-domestication sites, grapevine was initially spread to adjacent regions such as Egypt and Lower Mesopotamia and then through the Mediterranean area under the influence of different civilisations, such as Assyrians, Phoenicians, Greeks, Romans, Etruscans and Carthaginians (Mcgovern, 2003). During the Middle Ages, the Catholic Church continued the diffusion of *V. vinifera* grape cultivation through Europe which was successively introduced to America by the missionaries during Renaissance. From the 19th century onwards, *V. vinifera* was also introduced to North and South Africa, Australia and New Zealand (This et al., 2006). Due to the superior quality of the grapes, *V. vinifera* has acquired significant economic interest over time. Nowadays, thousands of *V. vinifera* cultivars exist and are cultivated around the world for fruit, juice and mainly for wine production.

The genus *Vitis* also includes a large number of uncultivated wild species, such as American and Asian indigenous ones, which are distributed worldwide (North and Central America, South Europe, Asia Minor and East Asia). The wild American species are characterised by small berries with an excessive content of seeds and strong pungent flavours (Vivier & Pretorius, 2000). On the other hand, they are highly resistant to many diseases and pests of grapevine, are able to grown in adverse weather and soils conditions, and to ripe extremely early (Acevedo de la Cruz et al., 2013). The wild genotypes native of East Asian countries possess unique characteristics in terms of resistance to diseases and undesirable environmental conditions as well (Koyama, Kamigakiuchi, Iwashita, & Mochioka, 2016). Due to the high resistance to both biotic and abiotic stresses, wild species represent an important and valuable germplasm resource for genetic improvement of *V. vinifera*.

1.2 Genetic improvement of grapevine

As the opening of new trades around the world, North American wild species were transported from new lands towards the Old world in the mid-19th century. However, this importation caused the accidental introduction to Europe of serious grapevine diseases, such as phylloxera (*Daktulosphaira vitifoliae*), powdery mildew (*Uncinula necator*), downy mildew (*Plasmopara viticola*) and black rot (*Guignardia bidwellii*) to which *V. vinifera* varieties were very susceptible. Indeed, when in 1863 the pathogens invaded France, they destroyed thousands of acres of European vineyards in fewer than 30 years (Reynier, 2000). In particular, the phylloxera aphid was the most damaging pest due to its ability to feed on and attack the high susceptible root system of *V. vinifera* vines changing forever the manner in which vines were grown. The spread of this insect was very rapid and led to a general condition of great rural poverty and distress (Mullins et al., 1992).

Upon the spreading of such epidemic throughout Europe, resistant wild American varieties aroused the interest of breeders. In fact, these *Vitis* species co-developed with pathogens in their natural habitats and gaining different degrees of resistance. Thus, in the latter half of the 19th century in an effort to save European vineyards from "phylloxera crisis", American species or their interspecific hybrids were used as rootstocks for *Vitis vinifera* (Alleweldt & Pissingham, 1988). The first crosses for phylloxera resistance occurred in North America and involved native American *Vitis* species, especially *V. labrusca*, *V. aestivalis* and *V. rupestris* and imported *V. vinifera* cultivars. These varieties are generally known as American hybrids to distinguish them from the French hybrids, or also called direct producers, which were developed by crosses of American species with French varieties (Antcliff, 1992; Vivier & Pretorius, 2000). Grafting susceptible *V. vinifera* varieties on resistant rootstocks was a successful strategy that saved European grapevine from the extinction. This method represented the foundation of viticulture which is still adopted. Additionally, it is the first and best example of biological control of a disease with an economic relevance.

In 1878, French scientist Alexis Millardet formulated a remarkable idea proposing that it could be possible to combine the positive characteristics (resistance to cold and fungal diseases) of wild American *Vitis* species with the qualitative traits (high wine quality) of European *V. vinifera* varieties. This postulate paved the way to breeding programs of grapevine in order to introgress genes of interest from wild *Vitis* species to European varieties (Fig. 1) (Pavloušek, 2010). In the first quarter of the 20th century, cultivars of interspecific hybrids called French first-generation hybrids (FFGH) were developed in France. Unfortunately, these varieties carried a significant percentage (more than 50%) of non-*V. vinifera* species in their genome resulting in offspring that produced wines of low quality. The second generation of hybrids (FSGH) contained 55-68% of the genome of *V. vinifera* with a little improvement of the quality of wines (Raddova, Stefkova, Sotolar, & Baranek, 2016). Nevertheless, the enological value of interspecific hybrids was still low and as a consequence, this led to the unpopularity of them which were perceived as a threat and therefore their cultivation was banned in France and similar restrictions were also applied in other European countries (Jackson, 2008). However, if these legislations stopped the breeding works in some European countries, such as Italy and France, they were continued in East Europe. After the Second World War, the investigation and development of hybrids was performed intensively. In fact, at the end of the sixties of past century breeding programs were performed in many countries, such as Germany, Austria, Switzerland, Hungary, Romania, Bulgaria, Greece and Serbia. Repeated back crosses with *V. vinifera* varieties were performed resulting in hybrids with a reduced percentage of the genetic heritage of wild species. The objective was to eliminate negative traits, such as wild flavours, but preserving resistance and tolerance to diseases (Sivčev, Sivčev, & Rankovič-Vasič, 2010).

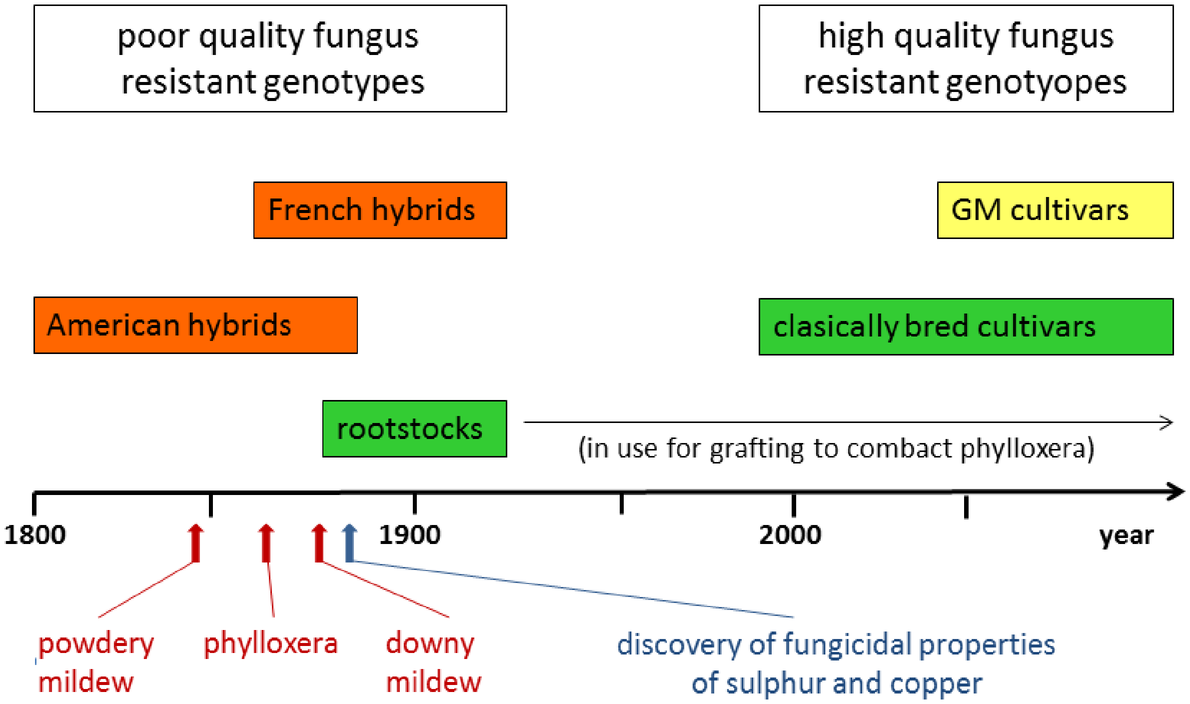

Figure 1. Schematic representation of milestones in grapevine resistance breeding on a time scale (image from Töpfer et al., 2011). In yellow, genetically modified varieties will be available for the market in about two decades.

1.3 New disease tolerant varieties for wine production

1.3.1 PIWI varieties

Nowadays, viticulturists have access to a wide range of plant protection products (PPT) to protect grapevine and the grape harvest from pests and diseases, but it is obvious that this cannot be a long-term control strategy. Based on the last report on pesticide use in Europe (Eurostat 2007), viticulture is the agricultural activity with the most intensive use of these chemical products with strong discrepancies among European countries in the average employment of chemicals (Tables 2 and 3). In particular, the systematic and massive use of pesticides is associated with serious risks in particular for the environment but also for the health of vineyard workers. It also adds heavy costs to grapevine production and creates problems related to the possibility of development of secondary pest outbreaks or strains resistant to fungicides.

Table 2. Dosage of plant protection applied in 2003 on different crops in the 25 countries of the European Union (expressed in kg active substance/ha). Source: Eurostat 2007.

	fungicides			**herbicides**	**insecticides**
	synthetic	inorganic S	Cu compounds		
viticulture	4.10	14.85	0.56	1.28	0.30
fruit trees	2.26	1.44	0.35	0.74	0.78
arable crops	0.31	0.03	0.00	1.01	0.04

*cereals, maize, oilseed, potato, sugar beet

Table 3. Dosage of plant protection applied in viticulture in 2003 in the main wine European countries (expressed in kg active substance/ha). Source: Eurostat 2007.

	total PPP	*%*
Austria	12.2	66
France	32.6	61
Germany	31.3	61
Greece	20.3	84
Hungary	9.2	54
Italy	17.8	56
Portugal	49.6	85
Spain	11.7	82
EU - 25	21.4	69

[1] including molluscicides and plant growth regulators

Consequently, sustainable viticulture represents one of the main current challenges and a more reduced use of pesticides in the wine-making sector has also come to represent an essential social demand. The European Community Directive 2009/128 established a common legal framework for achieving a sustainable use of pesticides by precautionary and preventive approaches. The guidelines focus on the use of resistant/tolerant cultivars, integrated agronomic practices and the choice for sustainable biological, physical and other non-chemical methods rather than chemical ones to control pests.

In recent years, the development of new techniques to study the genome such as marker-assisted selection (MAS) was helpful to introgress specifically the genetic traits of resistance against different pathogens into cultivated *V. vinifera* varieties. This technique also provided the opportunity to combine and monitor resistance loci during the breeding steps as well as to strongly reduce the timing and the cost of selection (Collard & Mackill, 2008; Dalbó, Ye, Weeden, Wilcox, & Reisch, 2001). As a result, marker-assisted selection combined with multiple back-crossing with *V. vinifera* varieties has allowed the development and selection of newer varieties carrying both disease-resistance genes and a significant percentage (more than 85%) of *V. vinifera* in their pedigree (Pedneault & Provost, 2016). Thus, the failure of early breeding programs can be explained by the complex polygenic base which governs the qualitative and resistant traits of the grapes, by the not-use of back crosses necessary to remove the undesired wild characteristics and also by the insufficient knowledge and tools available (Töpfer, Hausmann, & Eibach, 2011). Today, the new disease tolerant varieties are no longer regarded as “interspecific varieties” but belong to *Vitis vinifera*. They are also known as PIWI varieties (from the German word “pilzwiderstandsfähig”) and face as one of the most promising and interesting approach for a more sustainable pest management. The first convincing disease tolerant varieties were introduced into the market in Germany in 1995. Since then, more than 30 cultivars have been developed by the work of breeders. In particular, the promising market of mildew tolerant varieties has been established in Germany with the cultivation of the variety Regent released in 1996 (Reisch et al., 2012).

1.3.2 State of play in Europe and in not-European countries

European Community (CE) Regulation no. 479/2008 establishes that *Vitis vinifera* varieties must be employed to produce quality wines covered by a Protected Denomination of Origin (PDO) whilst wines covered by a Protected Geographical Indication (PGI) can be obtained from vine varieties belonging to *V. vinifera* or a cross between the *Vitis* species and other species of the genus *Vitis*. Additionally, European legislation stipulates that Member States shall classify which wine grape varieties, including new tolerant ones, may be planted for the purpose of wine production. For instance, the Italian legislation (Law decree No. 91/2014) provides the possibility to use these varieties for the production of wines covered by a Typical Geographical Indication (IGT) based on the EU definition of a Protected Denomination of Origin (PDO). Furthermore, it establishes that the varieties eligible as well as those under trial must be included to the National Grape Registry. At the moment, France is aligned with Italy and comparatively, new disease tolerant varieties have been recently added to the French catalogue of vine varieties.

On the other hand, Austria and Germany are the countries more innovative with regards to the use and the regulation of mildew tolerant varieties. In Germany, ampelographic traits are used to evaluate the employment of a PIWI variety for the production of quality wines. For instance, resistant varieties Regent, Hibernal and Solaris comply with the requirements of "quality wines" because it's not possible to clearly distinguish their wines from those obtained by traditional varieties. Equally, disease tolerant varieties Malverina, Savilon and Laurot are widespread in the Czech Republic (Raddova et al., 2016). Several PIWI varieties such as Bianca, Medina and Zalagyöngye are cultivated in Hungary (Hadju, 2015). Poland is not a typically wine country but in recent years there has been a rapid expansion in the cultivation of grapevines and in particular of disease tolerant varieties of *Vitis vinifera*. Rondo and Regent are the principal red grape varieties which produce more than 80% of all red wines. Moreover, due to the good adaptability to cold climatic conditions and to pathogens, these two disease tolerant varieties are also very popular in Sweden, Netherlands and Ireland (Wojdyło, Samoticha, Nowicka, & Chmielewska, 2018).

In not-European countries, PIWI varieties are commonly used for both research purposes and wine production. For instance, these varieties are widely grown in southern Brazil where the climatic conditions are unfavorable for *V. vinifera* ones since grape ripening and harvest mainly occur during the rainy season. Indeed, the wine production from resistant varieties has mostly overcome that made using *V. vinifera* cultivars. The resulting wines are characterised by typical aromas and flavours which meet a growing demand by Brazilian wine market. Furthermore, since consumers are constantly interested in improvements and new products, it is also emerging a great interest for the production of sparkling wines based on *Vitis labrusca* and disease tolerant varieties (Caliari, Burin, Rosier, & BordignonLuiz, 2014). Mildew tolerant varieties are also economically important in northern America areas where they are extensively used for wine production. The most successfully varieties are: Conquistador, Stover and Orlando Seedless in Florida; Traminette, Cayuga White and Chardonel in New York; La Crescent, Frontenac and Marquette in Minnesota; and L'Acadie and Ventura in Ontario (Reisch et al., 2012). In Canada, the province of Quebec in the third largest wine region where wine industry is 100% nearly based on disease tolerant varieties (Pollefeys & Bousquet, 2003).

1.3.3 Assessment of the impact related to the use of PIWI varieties in viticulture

PIWI varieties have high resistance to pests and diseases in comparison to traditional *V. vinifera* varieties and as a consequence, small amounts of pesticides and fungicides are required to protect vines. In this way, the cultivation of disease tolerant varieties may make it possible to reduce significantly the number of chemical treatments in viticulture in the future. For instance, it would allow a significant reduction in the use of copper-based fungicide contributing to decrease copper accumulation in vineyard soils, especially in areas under high disease pressure (Pedneault & Provost, 2016). Furthermore, the use of PIWI varieties would have a direct impact on the production costs with a total decreasing by about 15.4 % for winegrowers. Therefore, it is also possible that this situation could even make these winegrowers more competitive in comparison to the others. Recently, mildew tolerant varieties have been recommended as the most suitable choice in organic viticulture and varieties with high wine quality can definitely have a market potential.

In addition to it, the development and the diffusion of these varieties on the market may lead an expansion of viticulture and wine production in challenging environments such as cold and humid regions. Indeed, since traditional *Vitis vinifera* cultivars require for their growth long growing season, relatively high summer temperatures, low humidity, a rain-free harvest period and mild winter temperatures, their cultivation has been limited to areas showing suitable environmental conditions. However, new disease tolerant varieties showing high tolerance or resistance to cold temperatures as well as high resistance to fungal diseases allow overcoming this problem. For instance, wines with good quality have been produced by varieties cultivated in area showing challenging growing conditions such as Eastern Canada, Norther Europe and Northern Asia (Slegers, Angers, & Pedneault, 2017).

1.3.4 Common concerns about PIWI varieties

Wine has always been made mostly by traditional *Vitis vinifera* cultivars which were long considered the only suitable for wine production due to the superiority quality of their grape berries. Moreover, the disappointing organoleptic characteristics of the first hybrids which didn't meet the expectations of winegrowers and consumers have contributed to the assumption, founded or not, that also the new disease tolerant varieties produce low-quality wines. In particular, undesirable flavour compounds, such as foxy and straw-berry aromas, represent the main concern as regards PIWI varieties. Studies have reported that some of these compounds are mainly attributable to *Vitis labrusca* and show fewer occurrences in other American *Vitis* species (Sun, Gates, Lavin, Acree, & Sacks, 2011). As a result, there are no evidences that all wild American species and the resulting hybrids contain foxy aroma compounds. It is worth noting that some undesirable compounds can be detected also in wines from traditional *V. vinifera* varieties in the case of troubles in fermentation.

The second issue with disease tolerant varieties regards the anthocyanin profile of red grapevine varieties. Unlike *V. vinifera* varieties, PIWI varieties are generally characterised by the presence of diglucoside anthocyanins which are characteristic of wild *Vitis* species. In fact, these compounds are as a marker for the classification of grapes and wines. What is more, the acceptable limit of diglucosides in wine is 15 mg/L according to the International Organisation of Vine and Wine (OIV). Another problem concerns the sugar and acid contents of the grape berries from disease tolerant varieties. It is supposed that these varieties give wines relatively poor in alcohol and not well balanced for acid. Finally, it has also been reported that wines from PIWI varieties generally have contain low amounts of tannins which are responsible for astringency and bitterness of wine.

1.3.5 Research performed on disease tolerant varieties

In the history of disease tolerant varieties, the German variety Regent has an important part being this considered the "pioneer disease tolerant variety". Because of its traits close to those of traditional varieties, Regent has been registered as a *Vitis vinifera* variety in German in 1995. The wine made from this variety, which can be compared to Merlot, enjoy a good reputation in Germany. In particular, the research performed by Antoce et. al., 2008 by studying the physico-chemical and sensory parameters of wines produced from Regent and Dornfelder, showed that these two varieties behave well under the specific conditions of Romania and that are able to produce red wines with superior characteristics.

Therefore, it has also been suggested that the wines produced from these varieties could become an interesting addition to the national assortment of red wines as well as they might even be able to compete with some varieties of much longer tradition in Romania. In another study, the mildew tolerant grape varieties Regent, Rondo and Johanniter, based on the analysis of oenochemical properties, were found to show a better wine quality than Pinot noir and Silvaner (Schwab, Knott, & Schottdorf, 2000). Additionally, the characterisation of the aromatic profile of Brazilian sparkling wines produced from disease tolerant varieties showed a particular and differentiated aroma which could offer a valuable alternative for the production of Brazilian sparkling wines (Caliari et al., 2014).

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Preface to chapter 2

Wild American species represent an important source of genetic diversity within the *Vitis* genus. Due to the long coevolution with grapevine pathogens, they gained varying degrees of resistance or tolerance to pests and diseases. This remarkable characteristic caused close attention by grape breeders in the last decades of the 19th century. As a result, these wild genotypes were first used as rootstocks with the aim to provide protection against phylloxera and they were successively crossed with *V. vinifera* varieties in order to obtain new varieties having the positive traits of both species. Despite non-*V. vinifera* genotypes were long used in grapevine breeding programs, their composition has not been extensively studied. Characterisation of wild genetic resources is of great importance in order to increase knowledge and provide useful information for the varietal improvement of cultivated grape cultivars.

Thus, this work aimed to investigate the grape metabolomic profile, in terms of phenolic, proanthocyanidin, anthocyanin and lipid compounds in two hybrids and five American genotypes in different vintages. With regards to lipids, they were described for the first time in these wild genotypes. The following non-*V. vinifera* genotypes were considered:

V. californica is a Californian grape species which is not very resistant to phylloxera but shows good resistance to Pierce’s disease. It is also susceptible when it is grown on calcareous soils.

V. cinerea extends in South-east of United States and it is very resistant to attacks by phylloxera and also to damages by fungal pathogens, such as *Plasmopara viticola*. However, it shows chlorosis susceptibility.

***V. arizonica* Texas** is a variety of North American wild *Vitis arizonica* with very small grapes also known as the Canyon grape. This species shows good resistance to chlorosis while it is susceptible to phylloxera and active lime present in the soils.

V. champinii is considered to be a natural hybrid between *V. candicans* and *Vitis rupestris* and it is mainly found throughout Central Texas. This species has resistance to phylloxera, very good resistance to nematodes and good tolerance to lime and saline soils.

V. andersonii is a hybrid between *V. riparia* and *V. coignetiae*.

41B is a hybrid obtained by crossing *V. vinifera* Chasselas with *V. berlandieri* and it can be considered one of the first French-American hybrids which was used as rootstock. It tolerates up to 40% active lime in the soil and it is very resistant to phylloxera, chlorosis.

Kober 5BB is a hybrid produced by crossing *Vitis berlandieri* with *Vitis ripari*a. It has good resistance to phylloxera, nematodes and to active lime in the soil (up to 20%). It is also well suited to humid, compact and calcareous clay soils. Kober 5BB is commonly used as rootstock and it has become the most widely cultivated rootstock in Italy and France.

Two high quality *V. vinifera* varieties, Pinot noir and Cabernet Sauvignon, were considered as references. A targeted strategy, based on a combination of LC-MS and LC-DAD methods, was adopted for the analysis of the different classes of compounds under study. The results showed that not all wild genotypes contained both mono- and di-glucoside derivatives. Wild genotype 41B and *V. vinifera* references contained only monoglucoside anthocyanins. Proanthocyanidins of non-*V. vinifera* genotypes were mainly rich in oligomers and short-chain polymers. A certain diversity in the lipid composition in wild *Vitis* genotypes and a strong influence of the environmental conditions on the general lipid pattern, were observed. This work demonstrates the existence of a significant genotypic diversity between the grape composition of *V. vinifera* and other *Vitis* species. The information gained can be useful for further grapevine breeding programs.

My personal contribution to this work mainly concerned the experimental part. I was involved in sample preparation and analysis. I was responsible for writing the manuscript and managing the comments and improvements to the text by other authors.

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CHAPTER 2

The metabolomic profile of red non-*V.vinifera* genotypes

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The metabolomic profile of red non-*V. vinifera* genotypes

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ABSTRACT

Wild American genotypes represent an important part of the *Vitis* germplasm in relation to grape improvement. Today, these genotypes are currently involved in breeding programmes in order to introgress traits resistant to pests and diseases in *V. vinifera* cultivars. Nevertheless, the metabolic composition of their grapes has not been widely investigated. This study aimed to explore in detail the metabolomic profile in terms of simple phenolic, proanthocyanidin, anthocyanin and lipid compounds in two hybrids and five American genotypes. The results were compared with those of two *V. vinifera* cultivars. A multi-targeted metabolomics approach using a combination of LC-MS and LC-DAD methods was used to identify and quantify 124 selected metabolites. The genotypes studied showed considerable variability in the metabolomic profile according to the grape composition of *V. vinifera* and other *Vitis* genotypes. As regards the composition of anthocyanins, not all wild genotypes contained both mono- and di-glucoside derivatives. Wild genotype 41B and *V. vinifera* cultivars contained only monoglucoside anthocyanins. The proanthocyanidins of non-*V. vinifera* genotypes were mainly rich in oligomers and short-chain polymers. The analysis of lipids in wild *Vitis* genotypes, here reported for the first time, showed the existence of a certain diversity in their composition suggesting a strong influence of the environmental conditions on the general lipid pattern.

1. Introduction

Grape is one of the most widely distributed fruits in the world which is mainly used for the production of wine, juice and raisins. Given the chemical diversity of different grape metabolomes, considerable effort and research should be dedicated to studying the grape composition of wild *Vitis* genotypes, which represent an important part of the *Vitis* germplasm. Indeed, the *Vitis* genus accounts for many uncultivated species, widely distributed in southern Europe, Asia Minor, eastern Asia and North and Central America (Arnold, Schnitzler, Douard, & Peter, 2007). Among these, wild American genotypes include a large number of species characterized by small berries with abundant seeds and strong pungent flavours such as the foxy flavour (Vivier & Pretorius, 2000). In particular, foxy compounds have been described in *V. labrusca* and *V. rotundifolia* but not in other American *Vitis* species (Sun, Gates, Lavin, Acree, & Sacks, 2011). Furthermore, non-*V. vinifera* genotypes were also shown to have high resistance to major grapevine diseases such as powdery and downy mildew. This characteristic captured the attention of grape breeders, because it was considered to offer an important solution to the environmental problems caused by intense and systematic use of chemical products to protect *V. vinifera* crops. Indeed, since the 19th century wild American *Vitis* species have been used in breeding programmes in order to combine the resistant traits of American species with the grape quality of *V. vinifera* cultivars, resulting in the development of interspecific hybrids.

Although today wild American genotypes represent an important source of variability in the *Vitis* genus and have considerable agricultural importance, little research has been conducted on their grape composition. A few studies have investigated the phenolic pattern of non-*V. vinifera* genotypes (Acevedo De la Cruz et al., 2012; Hilbert et al., 2015; Liang, Yang, Cheng, & Zhong, 2012; Narduzzi, Stanstrup, & Mattivi, 2015; Zhao, Duan, & Wang, 2010). Recent advances in metabolomics offer the chance to obtain a comprehensive view of the metabolites present in samples using combined targeted analytical techniques. The objective of this work was to characterise the metabolic composition of seven non-*V. vinifera* grape berries from different vintages in terms of quantity and pattern of polyphenols and lipids. To our knowledge, for the first time, the lipid composition of wild American genotypes has been investigated.

Polyphenols represent one of the largest classes of secondary metabolites in the grape, known to contribute to wine quality and to play a significant role in human nutrition and health (Xia et al., 2010). Anthocyanins, mainly present in the skin, are the pigments responsible for the colour of red grapes. Flavan-3-ols, the basic building blocks of grape tannins, represent the most abundant class of polyphenols in

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Table 1
List of genotypes included in this study.

Genotype name	Original pedigree	Species	Vintage
41B	*V. vinifera Chasselas* × *V. berlandieri*	American hybrid	2008, 2009, 2010
Kober 5BB	*V. berlandieri* × *V. riparia*	American hybrid	2007, 2008, 2009, 2010, 2014
V. andersonii	*V. andersonii*	*V. andersonii*	2007, 2008, 2009, 2010
V. champinii	*V. champinii*	*V. champinii*	2007, 2008, 2009, 2010, 2013
V. cinerea	*V. cinerea Engelmann*	*V. cinerea*	2008, 2010, 2013, 2014
V. californica	*V. californica*	*V. californica*	2007, 2008, 2010, 2013, 2014
V. arizonica Texas	*V. arizonica Engelmann*	*V. arizonica Texas*	2007, 2008, 2009, 2014
Pinot Noir		*V. vinifera*	2007, 2008, 2009, 2010
Cabernet Sauvignon		*V. vinifera*	2007, 2008, 2009, 2010

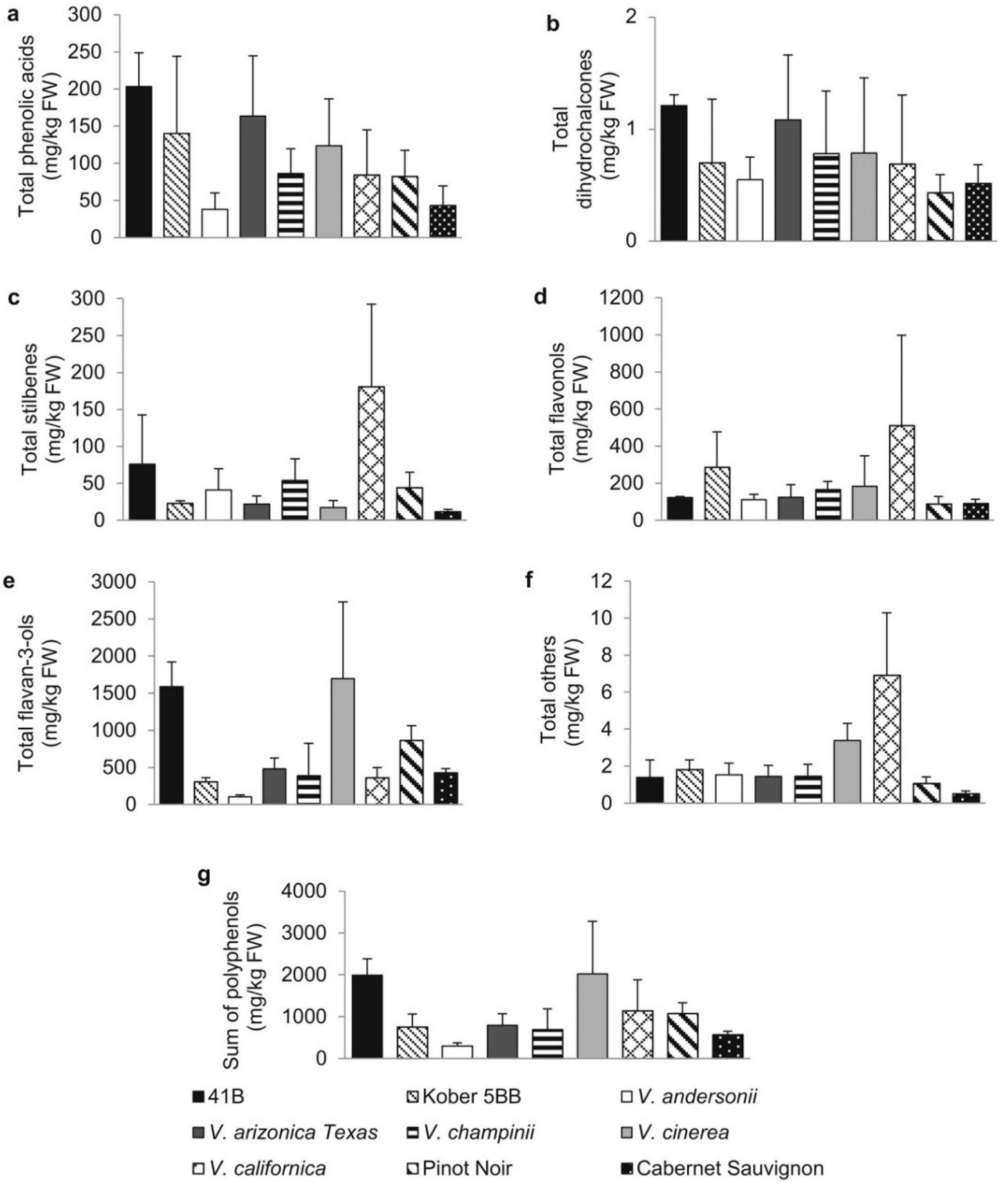

Fig. 1. Distribution of the content of total phenolic acids (a), dihydrochalcones (b), stilbenes (c), flavonols (d), flavan-3-ols (e), others (luteolin, arbutin and naringenin) (f) and sum of all the polyphenols (g).

grape berries. These metabolites are primarily located in the seeds and skins and their content is very important since they are responsible for the astringency and bitterness of red wines (Teixeira, Eiras-Dias, Castellarin, & Gerós, 2013). Stilbenes are phytoalexins produced in response to biotic stress, such as the grape pathogens *Plasmopara viticola* and *Botrytis cinerea*, or abiotic stress (Pezet, Gindro, Viret, & Spring, 2004a).

Another important class of metabolites is made up of lipids, which represent a diverse and ubiquitous group of compounds with many key biological functions, including acting as structural components of cell membranes, providing energy for metabolic activities and participating in signalling events (Fahy, Cotter, Sud, & Subramaniam, 2011). In particular, grape lipids are important factors in oenology since they are capable of modulating the yeast metabolism during the winemaking process (Delfini & Cervetti, 1991).

2. Materials and methods

2.1. Chemicals

Methanol (LC-MS and HPLC grade), acetonitrile (LC-MS grade), 2-propanol, chloroform and phloroglucinol were purchased from Sigma-Aldrich (Milan, Italy). Formic acid and ammonium formate additives for LC-MS were from Fluka Sigma-Aldrich (Milan, Italy). Water was of Milli-Q grade obtained from a Millipore system (Millipore, Billerica, MA, USA). Chemical standards were purchased or isolated as reported by the corresponding method used for the analysis of each class of metabolites.

2.2. Grapes

In the present work, grape samples of two hybrid varieties, five American *Vitis* species and two *V. vinifera* cultivars were studied (Table 1). Grape berries were harvested at technical maturity in the Fondazione Edmund Mach vineyards (San Michele all'Adige, Trento, Italy) in 6 different vintages. The samples were immediately frozen and stored at −80 °C. Then, grape berries were ground under liquid nitrogen using an analytical mill (IKA, Germany) to obtain a frozen powder.

2.3. Extraction procedures

2.3.1. Phenolic compounds

The phenolic compounds were extracted according to Vrhovsek et al. (2012). Two grams of grape powder were extracted twice with a solvent mixture of water, methanol and chloroform (20:40:40 v/v). The supernatants from two extractions were combined and filtered into an LC-MS vial.

2.3.2. Anthocyanins

The anthocyanins were extracted according to Mattivi, Guzzon, Vrhovsek, Stefanini, and Velasco (2006). The skin of 20 frozen berries were subjected two times to extractions with methanol and analysed by LC-MS instrument (Mattivi et al., 2006).

2.3.3. Proanthocyanidins

The samples were prepared by a slightly modified version of the method described in Gris et al., 2011 and Narduzzi et al., 2015. Briefly, 1 g of grape powder was extracted twice with 4 mL of methanol for 15 min, dried in a rotavapor and reconstituted with 20 mL of water. The water extract was loaded onto a C18 Sep-pak, washed with 30 mL of water, eluted with 15 mL of methanol, evaporated and then reconstituted with 2 mL of methanol. One hundred microlitres of the elute was added to 900 μL of methanol and water (50/50 v/v), filtered, and injected into the LC-MS system. A further one hundred microlitres of concentrated sample were added to 100 μL of phloroglucinol reagent at 50 °C for 30 min and then combined with 1 mL of sodium acetate to stop the reaction. The samples were filtered and immediately analysed.

2.3.4. Lipids

The samples were prepared according to Della Corte et al. (2015) by extraction with chloroform. Each sample was injected two times, non diluted and diluted 1:100 with acetonitrile, isopropanol and water (65:30:5 v/v/v), in order to allow quantification of the most abundant lipids (Della Corte et al., 2015).

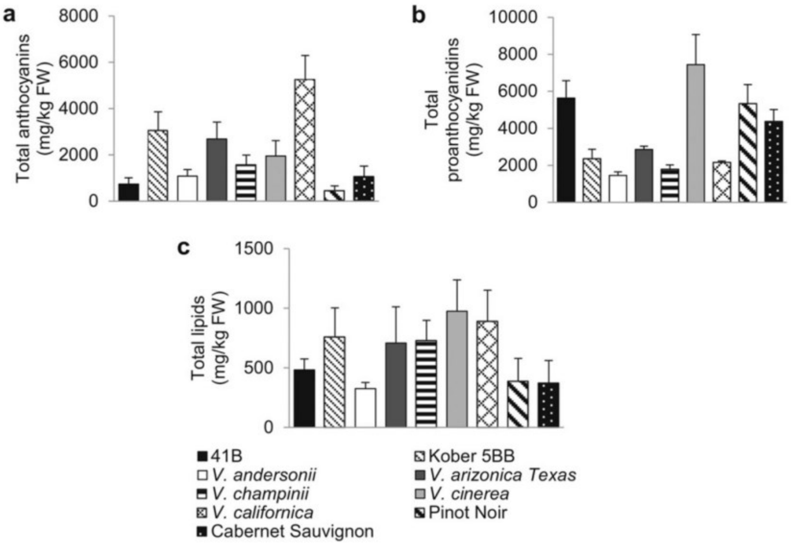

Fig. 2. Distribution of the content of total anthocyanins (a), proanthocyanidins (b) and lipids (c).

2.4. Analysis of compounds

2.4.1. Analysis of phenolic compounds

Analysis of phenolic compounds was performed as previously described (Vrhovsek et al., 2012). A Waters Acquity UPLC system® (Milford, MA, USA) was used. Phenolic compounds were separated on a Waters Acquity HSS T3 column (1.8 μm, 100 × 2.1 mm; Milford, MA, USA), thermostated at 40 °C. The mobile phase was composed of component A (0.1% formic acid in water) and component B (0.1% formic acid in acetonitrile).

Mass spectrometry detection was performed on a Waters Xevo TQMS® (Milford, MA, USA) instrument equipped with an electrospray (ESI) source. Further MS parameters are reported in Vrhovsek et al. (2012). Polyphenol concentrations were calculated in milligrams per kilogram (mg/kg) of fresh weight (FW) by means of calibration curves and using gentisic and rosmarinic acids as internal standards.

2.4.2. Analysis of anthocyanins

HPLC separation and quantification of anthocyanins was carried out on a Waters 2695 separation module equipped with Waters 996 DAD detector (Milford, MA, USA). Anthocyanins were quantified at 520 nm using a calibration curve with malvidin 3-glucoside and expressed as mg/kg FW (Mattivi et al., 2006).

2.4.3. Analysis of proanthocyanidins

Analysis of condensed tannins was performed with Waters Acquity UPLC® system, coupled with Waters Xevo TQMS® (Milford, MA, USA). Chromatographic, separation and detection conditions were the same as reported above (Vrhovsek et al., 2012). Catechin, epicatechin, procyanidins B1 and B2, gallocatechin, epigallocatechin and epicatechin gallate were quantified using a linear regression curve built on the injection of pure chemical standards. Quantification of phloroglucinol-bound flavanols was done as for epicatechin, epigallocatechin, and epicatechin gallate equivalents, respectively. The results were expressed as mg/kg FW (Gris et al., 2011).

2.4.4. Analyisis of lipids

Analysis was carried out on a UHPLC Dionex 3000 (Thermo Fisher Scientific, Germany) connected to an API 5500 triple-quadrupole mass spectrometer (Applied Biosystems/MDS Sciex, Toronto, Canada) equipped with an electrospray source. For the separation of compounds a reversed phase column Ascentis Express C18 (15 cm × 2.1 mm, 2.7 μm; Sigma, Italy) was used. The solvents were: solvent A

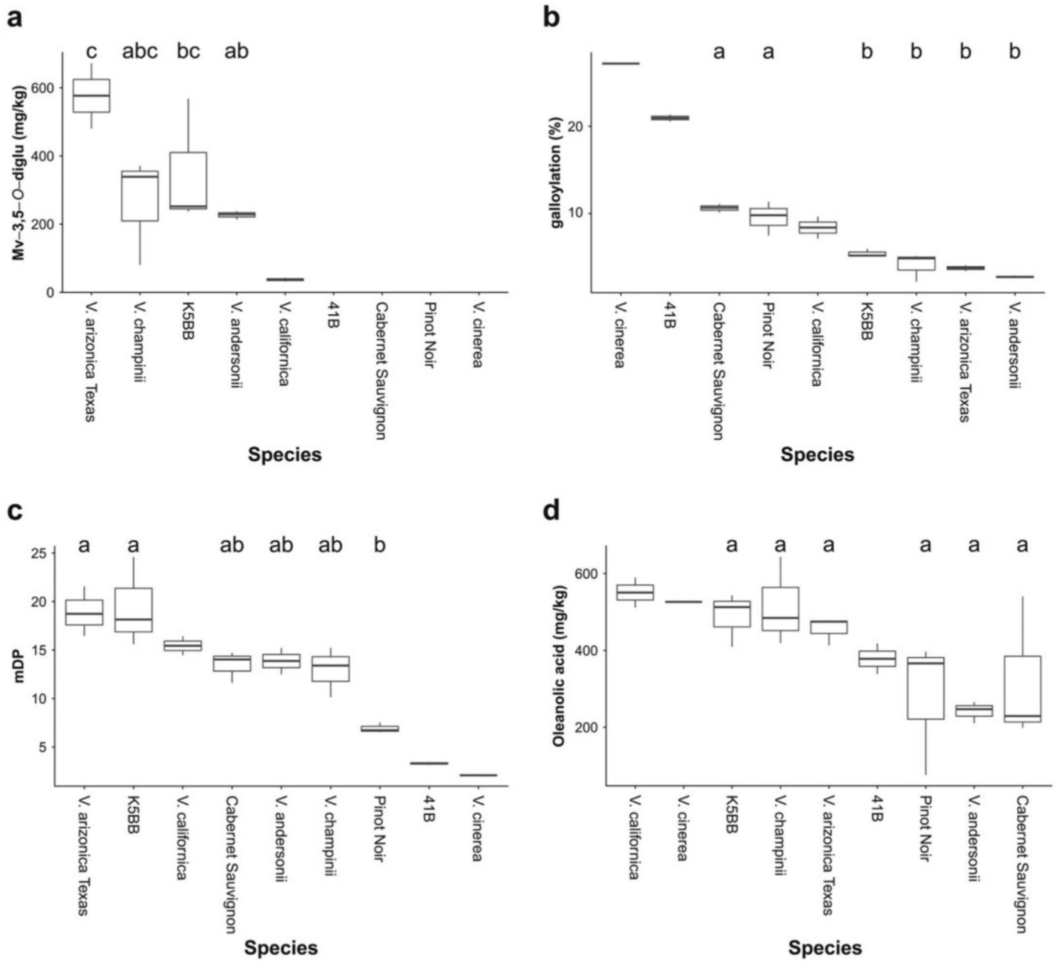

Fig. 3. Box plots illustrating the distribution of the content of malvidin-3,5-O-diglucoside (a), percentage of galloylation (b), mean degree of polymerization (c) and oleanolic acid (d) measured for the vintages 2007, 2008 and 2009; different letters indicate significant different groups in analysis of variance (ANOVA).

(acetonitrile 40% in water, ammonium formate 10 mM and formic acid 0.1%) and solvent B (isopropanol 90%, acetonitrile 10%, ammonium formate 10 mM and formic acid 0.1%).

The target lipids were detected under multiple reaction monitoring (MRM) mode and identified on the basis of their reference standard, retention time and qualifier and quantifier ion. Quantification was carried out using calibration curves for each analyte and data were expressed as mg/kg FW after normalization on the basis of the internal standard docosahexaenoic acid (Della Corte et al., 2015).

2.5. Statistical analysis

All data analysis was performed using R v3.3.1 (R Development Core Team, 2014). The quantitative data recorded was analysed using a fixed effects linear model with species as the fixed effect. The years were thus considered replicates. Prior to modelling zero intensity values (below the limit of quantification) were replaced compound-wise by a random number between the lowest detected intensity and zero. A model was fitted for each compound and these models used for pairwise comparisons between all species without correction for multiple testing. Subsequently, the collection of p-values for all comparisons were corrected for multiple testing by controlling the local false discovery rate (FDR) and q-values calculated (Strimmer, 2008a, 2008b). Unit variance scaling was used for each compound for both PCAs and heatmaps. For heatmaps the Pearson correlation coefficient and Ward's minimum variance methods were used for hierarchical clustering (Murtagh & Legendre, 2014). Missing values were replaced as above for the dendrogram calculations and marked in grey in these figures. Values outside the range of 3 standard deviations were reassigned to 3. For PCA, compounds with more than 50% missing values were excluded and PCA was performed using the NIPALS method (Stacklies, Redestig, Scholz, Walther, & Selbig, 2007; Wold, 1966). The sample of *V. champinii* in 2007 was a clear outlier in the lipid analysis. The sample has therefore been removed in the reported PCA plots. The complete data analysis is available at: https://github.com/stanstrup/vinifera_ruocco.

3. Results

3.1. Phenolic profiles

In total, 57 phenolic compounds were analysed (Table S1) and the corresponding box plots are shown in the Supplementary material 1. The total content of the main chemical classes of phenolic compounds (phenolic acids, dihydrochalcones, stilbenes, flavonols, flavan-3-ols and others) determined in grape berries is shown in Fig. 1. In wild genotypes the phenolic acid content ranged from 20 to 265 mg/kg FW (Fig. 1a). In contrast, phenolic acids varied from 18 to 133 mg/kg FW in *V. vinifera* cultivars. The dihydrochalcones phloridzin and phloretin were found in small amounts in all genotypes (Fig. 1b). *V. californica* was the genotype with the highest mean level of total stilbenes (180 mg/kg FW) compared to all other genotypes (Fig. 1c). The total flavonol content ranged from 14 to 1032 mg/kg FW, showing considerable variation in different genotypes and vintages (Fig. 1d). As regards the total content of flavan-3-ols, it ranged from 335 to 1148 mg/kg FW in *V. vinifera* cultivars, and from 61 to 3120 mg/kg FW in wild genotypes (Fig. 1e). Other phenolic compounds, such as luteolin, arbutin and naringenin, were found in small amounts (Fig. 1f). The sum of all analysed phenols in *V. vinifera* cultivars ranged from 445 to 1426 mg/kg FW, while it varied from 182 to 3695 mg/kg FW in wild genotypes, with differences between genotypes and vintages. *V. cinerea* and *V. andersonii* had the highest and lowest average values over

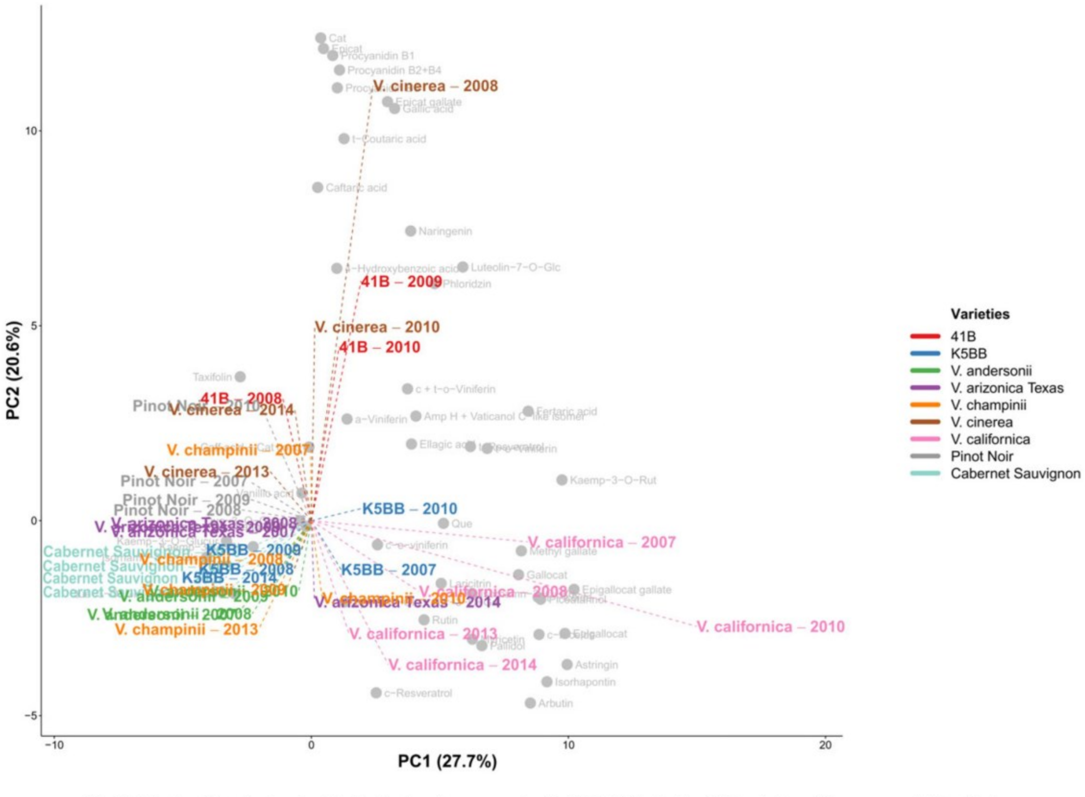

Fig. 4. PCA plot of simple phenols with distribution of grape samples. See Table S1 for the list of abbreviations of the compounds identified.

different vintages for total phenols (2025 and 296 mg/kg FW respectively) (Fig. 1g).

3.2. Anthocyanin profiles

Total anthocyanins varied significantly with the genotype (Fig. 2a). *V. californica* and 41B had the highest and lowest mean anthocyanin content within wild genotypes (5244 and 735 mg/kg FW respectively). In contrast, *V. vinifera* cultivars such as Cabernet Sauvignon and Pinot Noir had a lower mean amount of anthocyanins (1045 and 437 mg/kg FW respectively). The results and the box plots of the 20 anthocyanins detected in the samples are shown in Table S1 and Supplementary material 1, respectively. Malvidin derivatives were the most abundant components of total anthocyanins in Cabernet Sauvignon, Pinot Noir, *V. cinerea* and 41B. Conversely, delphinidin derivatives were the most abundant components in Kober 5BB, *V. andersonii*, V. californica, V. arizonica Texas and V. champinii. In V. vinifera cultivars all the anthocyanins detected were monoglucoside derivatives. In contrast, in wild *Vitis* genotypes diglucoside anthocyanins were found in different amounts: 41B did not contain diglucosides, *V. cinerea* and *V. californica* contained less than 5% of the total amount of anthocyanins (from 5 to 136 mg/kg FW) while Kober 5BB, *V. andersonii*, *V. arizonica Texas* and *V. champinii* contained more than 40% of the total (from 522 to 2658 mg/kg FW). In Fig. 3a the distribution of the malvidin 3,5-diglucoside content determined in the samples is presented as a box plot.

Non-acylated anthocyanins were the most abundant compounds in all the samples. In wild genotypes they ranged from about 93% in *V. californica* to 98% in *V. arizonica Texas*; while in *V. vinifera* cultivars non-acylated anthocyanins accounted for about 80% in Cabernet Sauvignon and 100% in Pinot Noir. Acetyl derivatives were the most abundant compounds in Cabernet Sauvignon (16%) and Kober 5BB (2%) as compared to coumaroyl derivatives in all the other genotypes. In Pinot Noir neither acetyl nor coumaroyl derivatives were detected (Table S1).

3.3. Proanthocyanidin profiles

The highest mean amount of proanthocyanidins was found in *V. cinerea* (7446 mg/kg FW) for wild genotypes and in Pinot Noir (5300 mg/kg FW) for *V. vinifera* cultivars (Fig. 2b). The proanthocyanidin composition of the genotypes analysed is presented in Table S1. Catechin was the most abundant flavan-3-ol terminal unit in Pinot Noir, Cabernet Sauvignon, 41B, Kober 5BB 2014, *V. arizonica Texas* 2007 and 2008, *V. cinerea* and *V. californica* 2008 and 2010. Epigallocatechin was the second most abundant flavan-3-ol terminal unit in all the other wild genotypes with the exception of *V. californica* 2013 and 2014 which contained a high percentage of epicatechins as terminal units. The highest proportion of epicatechin and gallocatechin terminal units were found in *V. cinerea* and Cabernet Sauvignon, with 30% and 6% respectively. Epicatechin gallate was the only gallate-derivative found as an upper unit in all samples.

The flavan-3-ol extension units mainly comprised catechin and epigallocatechin, with the predominance of catechin in *V. vinifera* cultivars and in 41B, Kober 5BB 2007 and 2014, *V. arizonica Texas*, *V. andersonii* 2007, *V. champinii* 2007 and 2008, *V. cinerea*, *V. californica* 2008. On the other hand, only in the 2010, 2013 and 2014 vintages of *V. californica*, epicatechin was found to be the most abundant flavan-3-ol extension unit. Gallocatechin was the extension unit present in the lowest concentration in all samples. The percentage of galloylation (%G) revealed that *V. cinerea* and 41B had a larger percentage of galloylated forms, which accounted for 23% and 22% respectively, in comparison

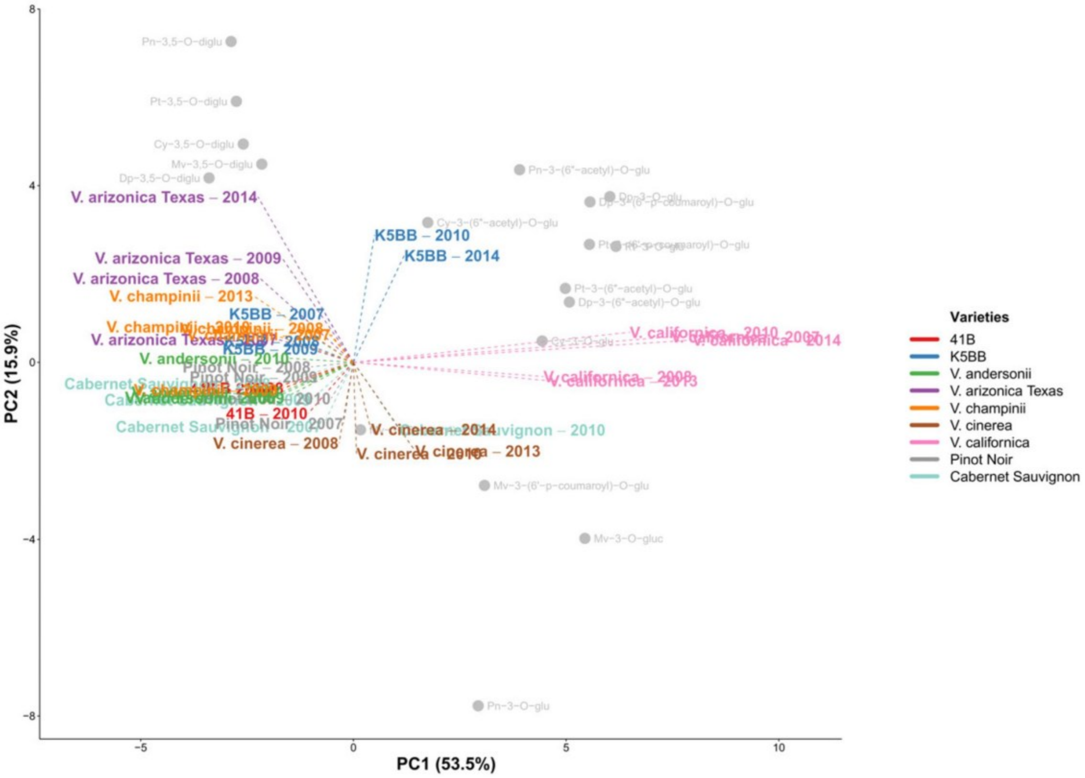

Fig. 5. PCA plot of anthocyanins with distribution of grape samples. See Table S1 for the list of abbreviations of the compounds identified.

to all other samples (Fig. 3b). The values observed for the mean degree of polymerization (mDP) in the genotypes studied ranged from 2 to 26 units (Fig. 3c). *V. cinerea* and 41B had the lowest mean degree of mDP polymerization, while *V. arizonica Texas* and Kober 5BB had the highest as compared to all other genotypes. Of the *V. vinifera* cultivars, Cabernet Sauvignon had the highest values of mDP, which ranged from 12 to 16, similar to the values found for *V. andersonii*, *V. californica* and *V. champinii*. In Supplementary material 1 the box plots of the proanthocyanidins are reported.

3.4. Lipid profiles

In this work different classes of grape lipids were studied: fatty acids, sterols, glycerolipids, glycerophospholipids and sphingolipids (Table S1). The total lipid content of wild genotypes ranged from 330 to 1294 mg/kg FW, while it varied from 114 to 564 mg/kg FW in *V. vinifera* cultivars (Fig. 2c). *V. cinerea* and *V. andersonii* had the highest and lowest mean content of total lipids, 974 and 326 mg/kg FW respectively. Oleanolic acid was the most abundant compound found in all genotypes, and the distribution can be observed in the box plot (Fig. 3d). *V. cinerea* and *V. californica* contained the highest mean content of oleanolic acid (734 and 718 mg/kg FW respectively) while the lowest mean value was found in *V. andersonii* (237 mg/kg FW). The main fatty acids were palmitic, linolenic, linoleic and stearic acids. In wild genotypes, palmitic acid ranged from 1 to 56 mg/kg FW, linolenic acid from 0.2 to 41 mg/kg FW, linoleic from 0.7 to 26 mg/kg FW and stearic acid from 3 to 23 mg/kg FW. In contrast, in *V. vinifera* genotypes these fatty acids were found in smaller amounts. Wild genotypes from the 2013 and 2014 vintages showed a larger amount of some lipids, such as 1,2-dilinoleoyl-sn-glycero-3-phosphocholine, 1,2-dioleoyl-sn-glycero-3-phospho-rac-(1-glycerol) salt, uvaol, 1-linoleoyl-rac-glycerol, glyceril tripalmitoleate, ergosterol, behenic acid, linolenic acid, stearic acid, lignoceric acid, erucic acid, arachidic acid, oleanolic acid, 1,2,3-tripentadecanoylglycerol, and *cis*-11-eicosenoic acid. The box plots of the lipids analysed are shown in Supplementary material 1.

3.5. Multivariate analysis

The data obtained were analysed using multivariate methods in order to evaluate similarities and differences in the metabolomic composition in the genotypes studied. The PCA scores plot of the samples shows that there was good grouping of the genotypes for the different vintages based on the phenolic profile (Fig. 4). This can also be seen in Fig. S1, where cluster analysis shows the existence of year-to-year variations for some genotypes, such as *V. cinerea*, *V. champinii*, 41B and *V. californica*.

In Fig. 5 the first PC distinguished anthocyanin monoglucosides and the rest of the anthocyanins; indeed the grapes of *V. arizonica Texas*, *V. champinii*, *V. andersonii* and Kober 5BB were located in the left part of PC2, explained by their high diglucoside derivative content. Cluster analysis showed that the anthocyanin profiles for each genotype were relatively stable (Fig. S2).

Examination of the PCA scores plot (Fig. 6) shows that *V. cinerea*, 41B and Pinot Noir samples grouped together in the most right-hand part of the score plot, as a consequence of their higher levels of proanthocyanidins (with the sole exception of epigallocatechin, situated slightly to the left) while the remaining wild genotypes grouped together in the left-hand part of the scatter plot, due to the low proanthocyanidin content. These results can also be seen in the heatmap (Fig. S3), since clustering analysis grouped *V. cinerea*, 41B, Pinot Noir and Cabernet Sauvignon together, indicating that the proanthocyanidin patterns were similar.

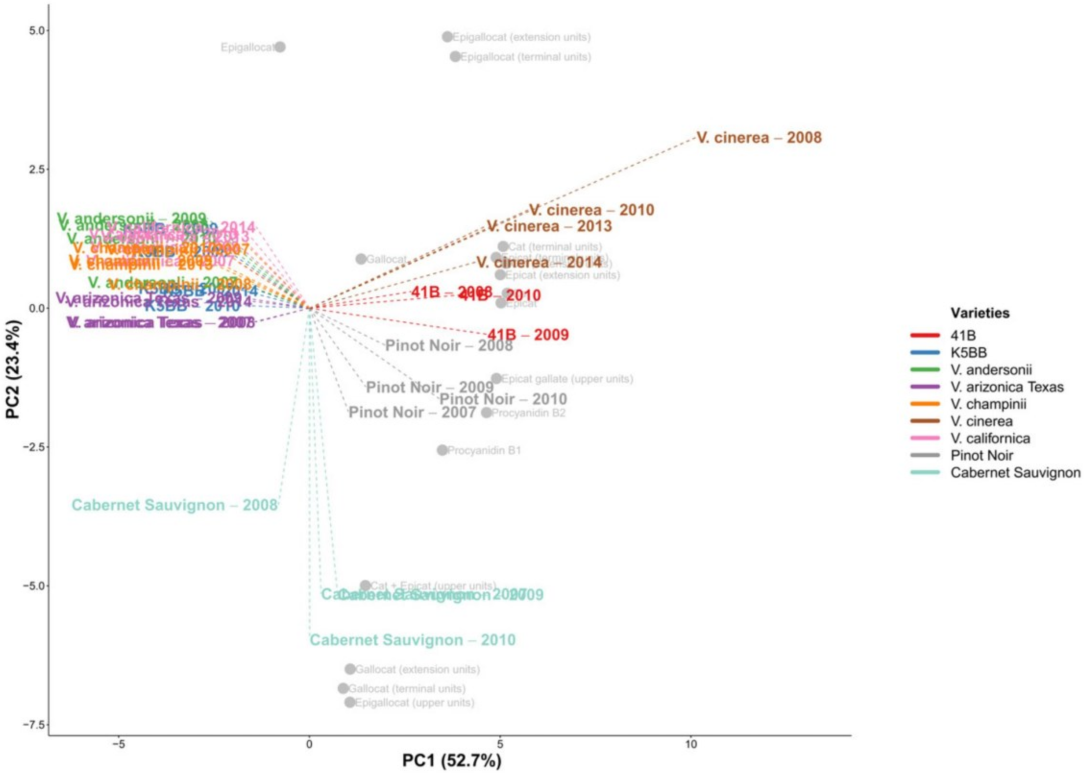

Fig. 6. PCA plot of proanthocyanidins with distribution of grape samples. See Table S1 for the list of abbreviations of the compounds identified.

The PCA analysis results of lipids reveal that most of genotypes did not group together over the years (Fig. 7). In particular, hierarchical clustering showed that only Pinot Noir and Cabernet Sauvignon grouped together over the years (Fig. S4). Furthermore, it can be observed that wild genotypes of the 2013 and 2014 vintages were closely grouped together.

4. Discussion

The grape metabolome is very complex and involves several different classes of compounds. Knowledge about the grape metabolites of non-*V. vinifera* genotypes is still incomplete, since these genotypes have received less attention than *V. vinifera* cultivars. In this context, the present work contributes to bridging this gap in knowledge by analysing the phenolic, anthocyanin, tannin and lipidic profiles of seven non-*V. vinifera* genotypes and two *V. vinifera* cultivars using a targeted metabolomics approach.

The novelty of this study lies in its exhaustive and accurate investigation of a multitude of compounds, in total 124, from different chemical classes. The genotypes included in this study can be directly compared because the impact of soil and climate in the same year was not influential since all genotypes were grown in the same experimental vineyard. Furthermore, the comparison of different years allows to evaluate the influence of climatic conditions among different vintages on the metabolic composition of grape.

4.1. Phenolic composition

In this study, the polyphenolic content varied significantly in the genotypes in agreement with Liang et al. (2012) (Figs. 1, 2). The accumulation of phenolic compounds in grape berries is significantly affected by genetic and also by non-genetic factors such as environmental conditions (Teixeira et al., 2013), pathogen invasion (Zhu, Zhang, & Lu, 2012) and generally in response to biotic and abiotic stresses (Jeandet et al., 2010). Resveratrol, an important phytochemical with many well-known benefits for human health, was not found in all the vintages of the genotypes considered, with the exception of Pinot Noir. Pezet, Gindro, Viret, and Richter (2004b) reported that resistant genotypes transform resveratrol into viniferins which are involved in the resistance mechanism of the grapevine to *Plasmopara viticola*. Later, Malacarne et al. (2011), have observed the existence of a strong negative correlation between the concentrations of stilbenoid viniferins in the leaves and the progress of infection. In our study, the mean amount of viniferins was higher in wild genotypes than in *V. vinifera* cultivars, with the exception of *V. cinerea*. In particular, that found in *V. cinerea* was comparable to that of Pinot Noir suggesting that a different resistance mechanism, which does not include the presence of viniferins, could be involved.

The mean total flavonol content of wild genotypes from the different vintages was higher than in *V. vinifera* cultivars, in accordance with other authors (Liang, Owens, Zhong, & Cheng, 2011; Liang et al., 2012). Quercetin derivatives were the main flavonols found in *V. vinifera* cultivars as previously described (Hilbert et al., 2015; Liang et al., 2012; Mattivi et al., 2006). The main flavonols found in non-*V. vinifera* genotypes were kaempferol, isorhamnetin and quercetin derivatives in contrast to Hilbert et al. (2015) and Liang et al. (2012) who observed that myricetin and quercetin derivatives were the main flavonols. Caftaric acid was the most abundant of all the hydroxycinnamic derivatives in both *V. vinifera* cultivars and wild genotypes as reported by Liang et al. (2011, 2012). Furthermore, they also observed that in the hydroxybenzoic acid group, vanillic acid content was higher than that of gallic acid.

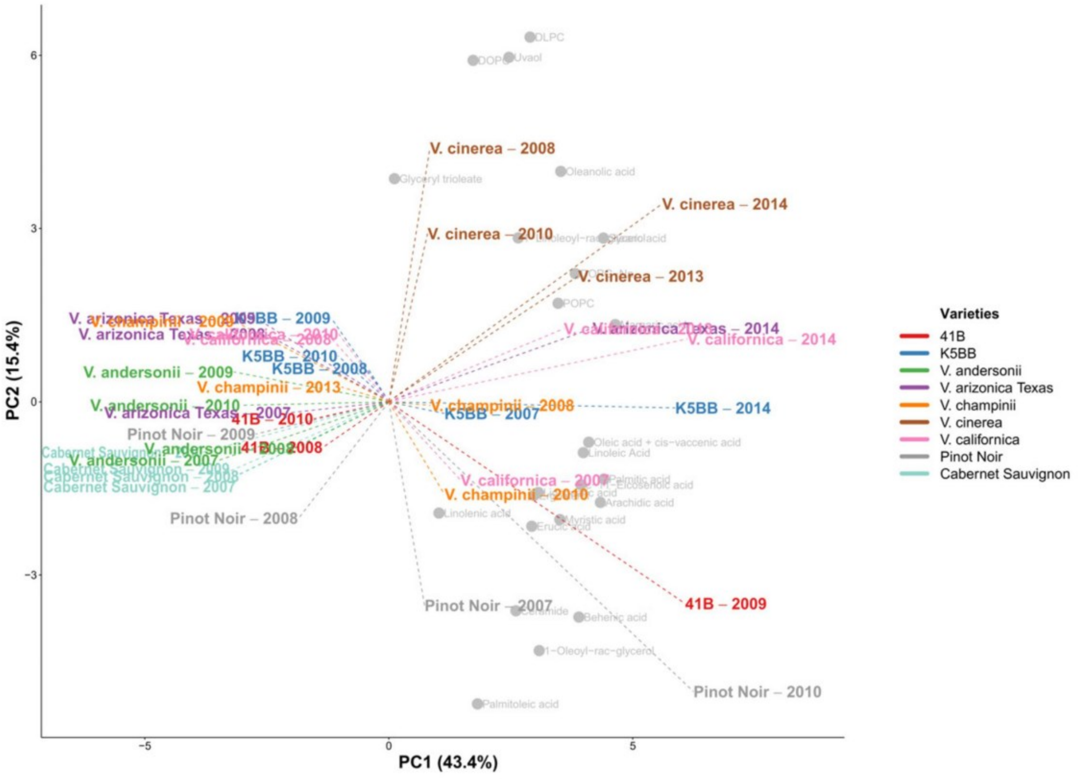

Fig. 7. PCA plot of lipids with distribution of grape samples. See Table S1 for the list of abbreviations of the compounds identified.

Conversely, we found that gallic acid content was highest in all the samples studied.

Of the dihydrochacones, phloridzin was found in all genotypes, even if it has been demonstrated to be a typical component of apples (Vrhovsek, Rigo, Tonon, & Mattivi, 2004). Naringenin, known to be one of the main compounds in oranges, mandarins and grapefruits, was also found in small amounts in the genotypes studied (Erlund, 2004). Differences in the relative amount of variation between years were observed for almost all classes of polyphenols, particularly phenolic acids, flavonols and flavan-3-ols and were more significant in wild genotypes than in *V. vinifera* cultivars in agreement with literature (Liang et al., 2012).

4.2. Anthocyanin composition

Anthocyanin analysis of the skins showed that the mean content of anthocyanins was higher in non-*V. vinifera* genotypes as compared to *V. vinifera* cultivars, with the exception of the genotype 41B, in agreement with previous studies (Liang et al., 2011, 2012). The relative abundance of anthocyanin derivatives varied from one genotype to another as previously reported (Liang et al., 2012). Furthermore, if the anthocyanin profiles for each genotype were relatively stable, the absolute amounts varied in different vintages due to environmental factors. Diglucosides were not found in 41B while, as expected, the other genotypes had both monoglucoside and diglucoside derivatives since it is known that in wild *Vitis* species glycosylation occurs at both the 3- and 5-positions (Acevedo De la Cruz et al., 2012; Mazzuca, Ferranti, Picariello, Chianese, & Addeo, 2005). Acevedo De la Cruz et al. (2012) reported that in *V. cinerea* all anthocyanins were monoglucoside derivatives and the anthocyanin levels were similar to those in *V. vinifera*. In our study, the diglucoside content in *V. cinerea* accounted for 1% of total anthocyanins, while the total anthocyanin amount was higher than in *V. vinifera* cultivars.

4.3. The influence of proanthocyanidins

In terms of proanthocyanidins, differences in composition were found in the genotypes analysed. Previously, Narduzzi et al. (2015) and Springer, Sherwood, and Sacks (2016) reported that the total proanthocyanidin content in the skin and seeds of wild American genotypes analysed was lower than in *V. vinifera* cultivars. In our study, *V. cinerea* and 41B accumulated a higher mean content of total proanthocyanidins as compared to both *V. vinifera* cultivars and wild genotypes.

Del Rio and Kennedy (2006) and Mattivi, Vrhovsek, Masuero, and Trainotti (2009) reported that catechin was the most abundant flavan-3-ol terminal unit in Pinot Noir, however in our study it was also found in wild genotypes. Narduzzi et al. (2015) observed a higher mean degree of polymerization in the skin and seeds of *V. vinifera* than in wild American grapes. Anyway the direct comparison between the two studies cannot be done, since in the study of Narduzzi et al. (2015) different *V. vinifera* varieties were analysed and furthermore the grape flesh was not included in the study. According to our results, the proanthocyanidins which have been extracted from whole berries of non-*V. vinifera* genotypes were rich in oligomers and short-chain polymers, with the exception of *V. cinerea* and 41B. Regarding the percentage of galloylation (%G), as 41B and *V. cinerea* have a lower mDP they showed a proportionally higher abundance of galloylated derivatives in comparison to all other samples. It is known that the bitterness and astringency of wines are affected by the extent of galloylation (Lesschaeve & Noble, 2005). This work demonstrated that the accumulation of proanthocyanidins varied in wild genotypes and was not significantly influenced by environmental factors.

4.4. The diversity of lipid profile

To the best of our knowledge, it is the first time that the class of lipids was analysed in wild American genotypes. Our study showed that non-*V. vinifera* genotypes, with the exception of *V. andersonii*, had a higher total lipid content as compared to *V. vinifera* cultivars. In particular, high variability in lipid content of wild genotypes observed in different vintages suggests the strong influence of environmental factors. Stearic, palmitic and linoleic acids were the main fatty acids detected in all genotypes, in general agreement with previous studies (Bauman, Gallander, & Peng, 1977; Gallander & Peng, 1980; Tumanov et al., 2015). The presence of oleanolic acid, known to act as "survival factor" for yeasts (Lafon-Lafourcade, Larue, & Ribéreau-Gayon, 1979), was noted in all genotypes.

5. Conclusions

In conclusion, this work provides a comprehensive and systematic survey of the content of all the main classes of metabolites in non-*V. vinifera* genotypes. The results obtained provide clear evidence of (i) differences in anthocyanin composition, since not all wild genotypes are characterized by the presence of diglucosides, (ii) genotypic influence on proanthocyanidin profiles, (iii) the existence of a certain diversity in lipid composition according to the genotype and also with reference to the vintage. To our knowledge, this study is the first detailed and extended survey of non-*V. vinifera* grape metabolites. The information gained could potentially be useful, providing important information for future grapevine breeding.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.foodres.2017.01.024.

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Figure S1: Heatmap of simple phenol patterns. The variables have been mean-centered and scaled to unit variance prior to the analysis. Blue and sky blue cells indicate high and low concentrations, respectively. The dendrogram on the side represents the hierarchical clustering of the samples. For abbreviations see Table S1.

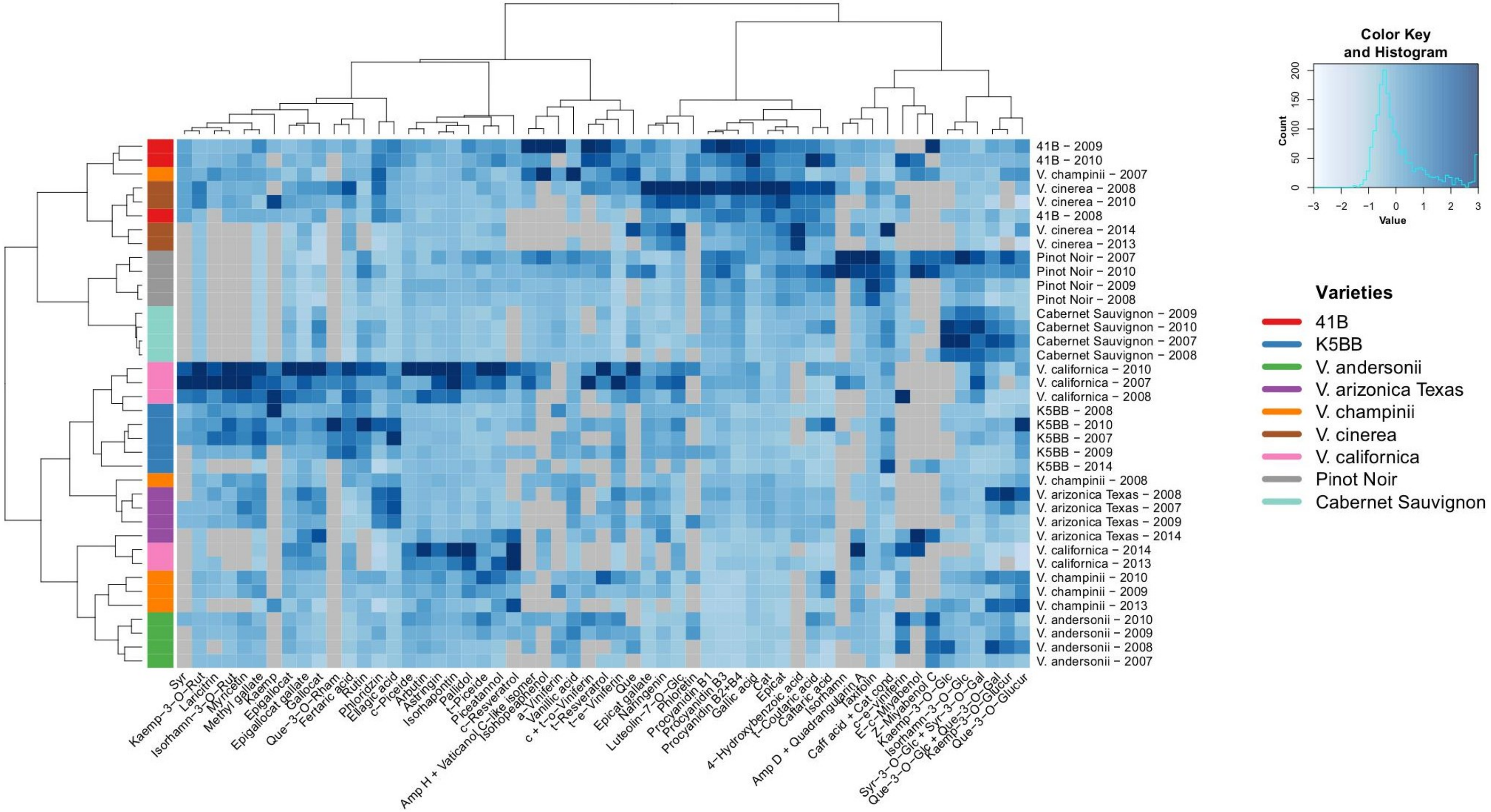


Figure S2. Heatmap of anthocyanin patterns. The variables have been mean-centered and scaled to unit variance prior to the analysis. Blue and sky blue cells indicate high and low concentrations, respectively. The dendrogram on the side represents the hierarchical clustering of the samples. For abbreviations see Table S1.

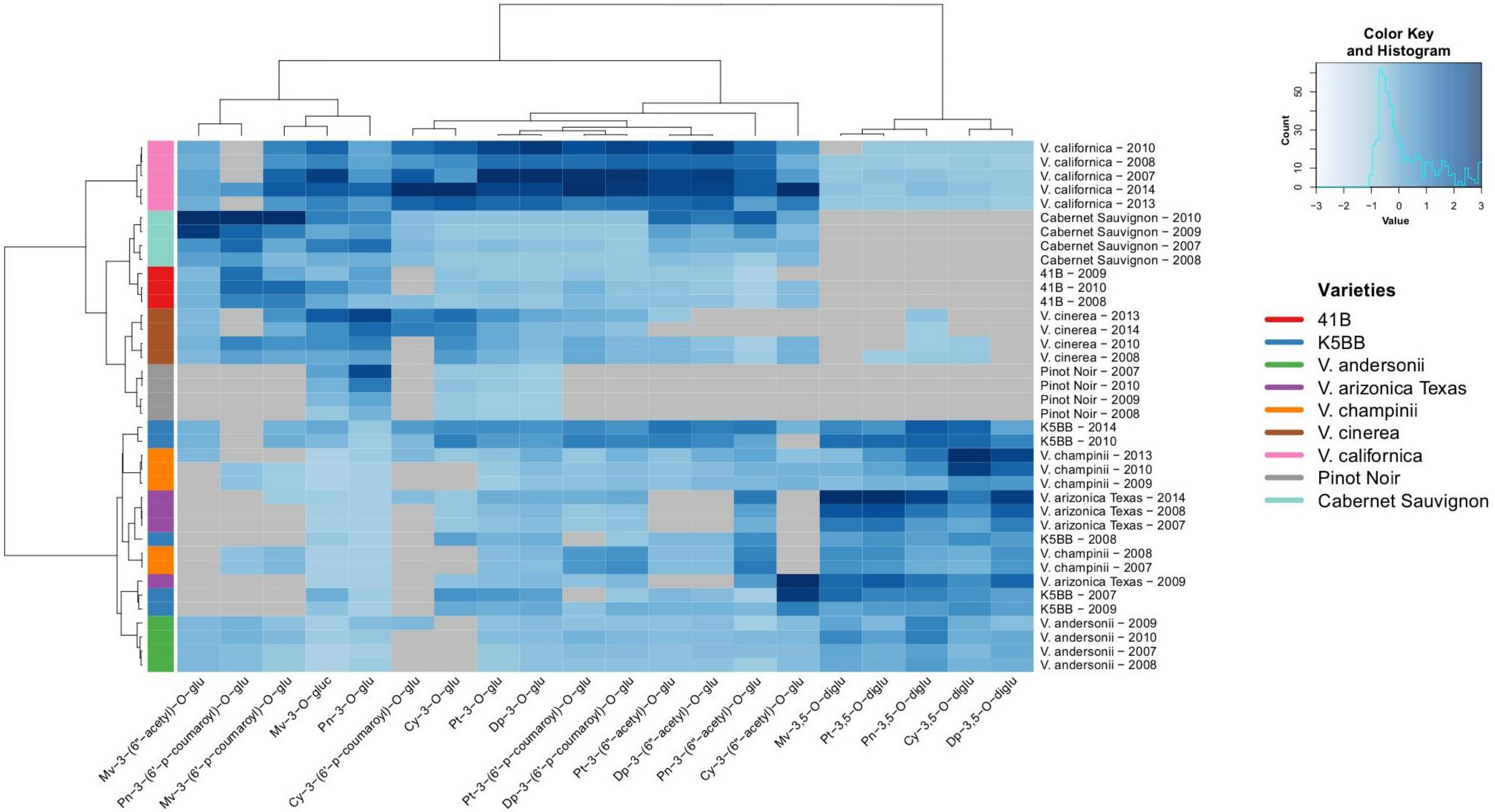


Figure S3. Heatmap of proanthocyanidin patterns. The variables have been mean-centered and scaled to unit variance prior to the analysis. Blue and sky blue cells indicate high and low concentrations, respectively. The dendrogram on the side represents the hierarchical clustering of the samples. For abbreviations see Table S1.

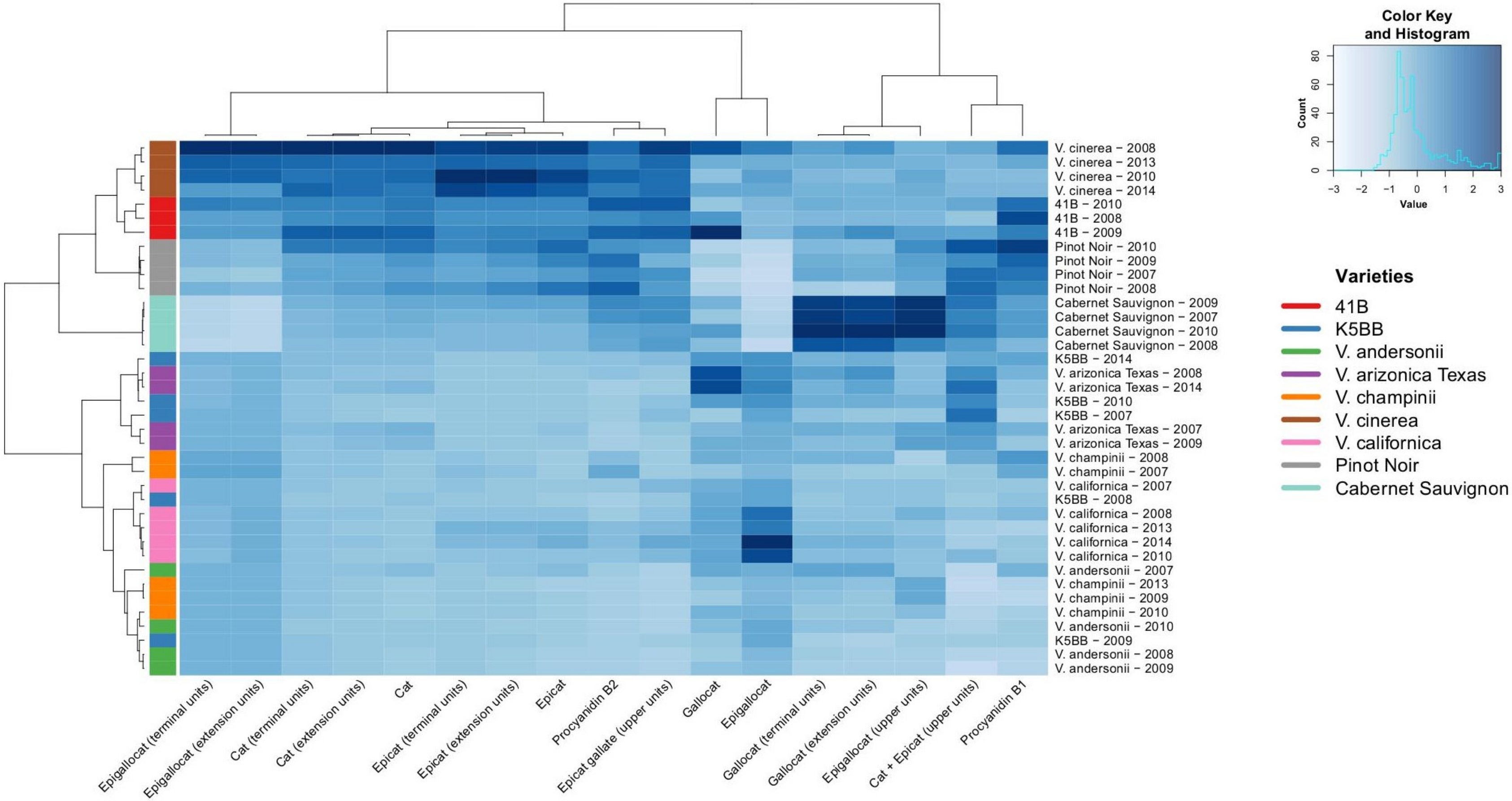
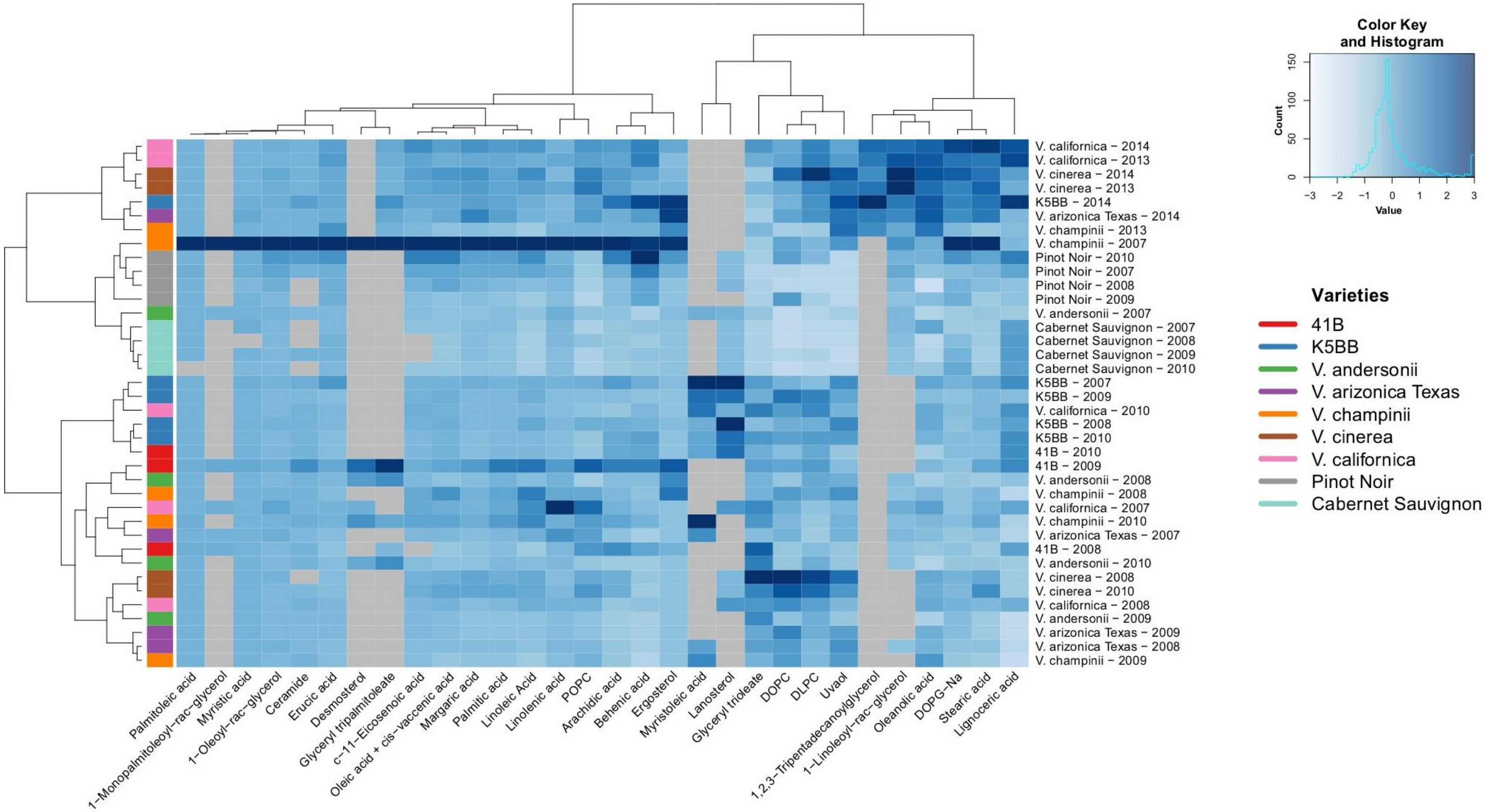
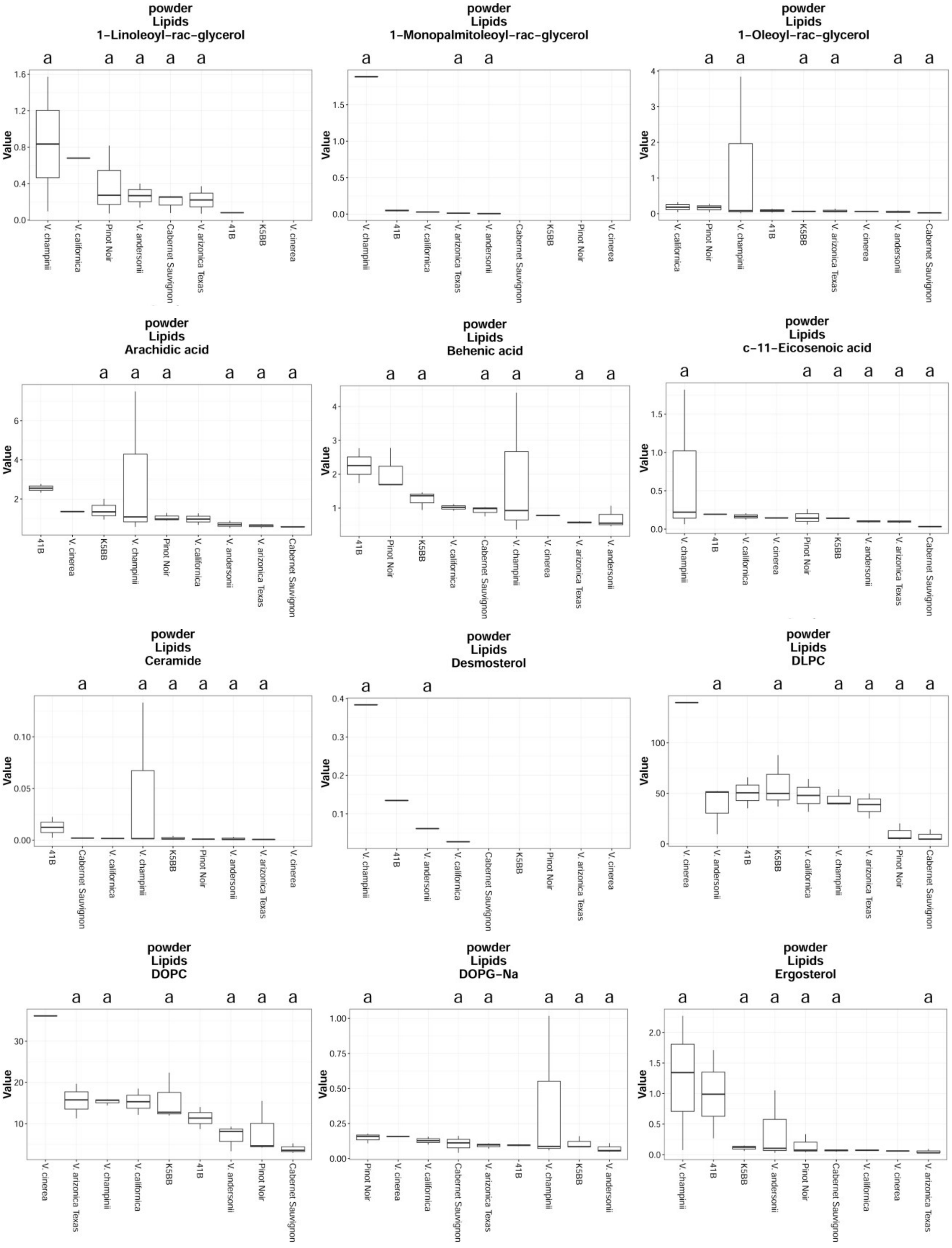
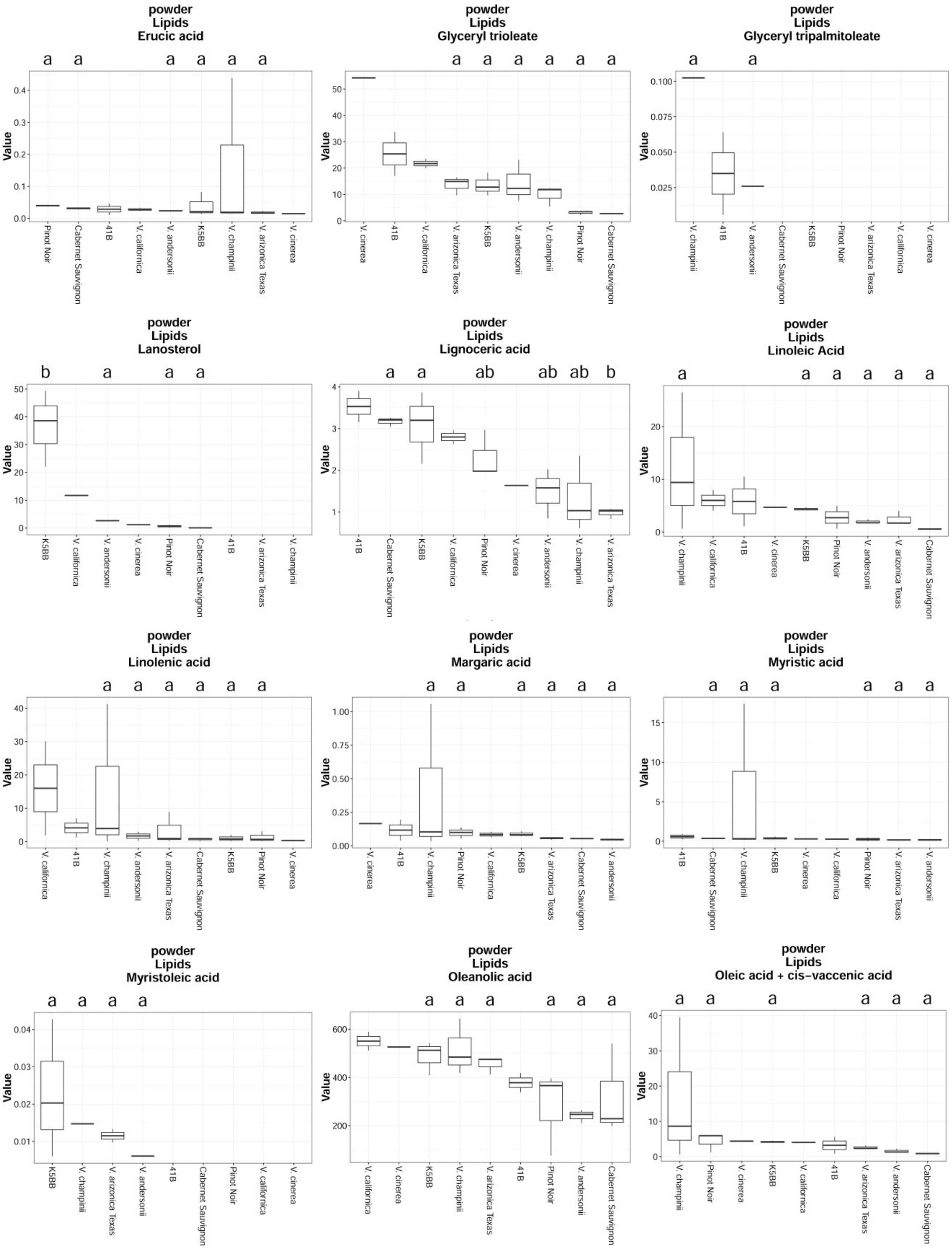


Figure S4. Heatmap of lipid patterns. The variables have been mean-centered and scaled to unit variance prior to the analysis. Blue and sky blue cells indicate high and low concentrations, respectively. The dendrogram on the side represents the hierarchical clustering of the samples. For abbreviations see Table S1.



Supplementary Material 1. Boxplots of all the compounds identified and quantified in the varieties under study.The results are expressed as mg/kg.

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V. andersonii
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V. cinerea
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V. champinii
V. arizonica Texas
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Cabernet Sauvignon
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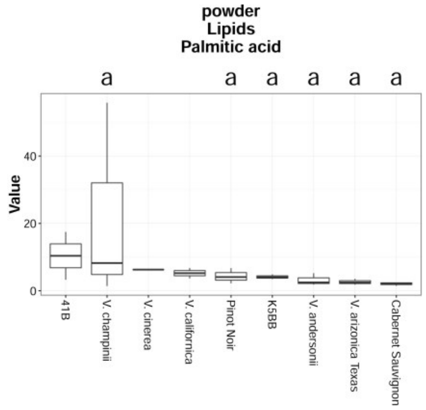
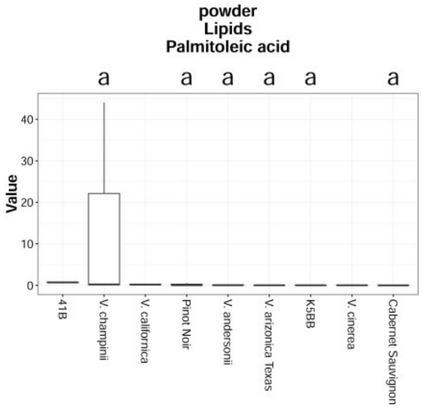
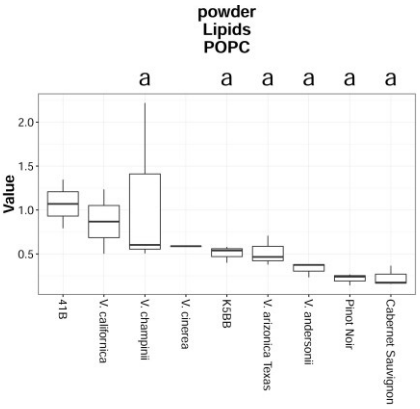
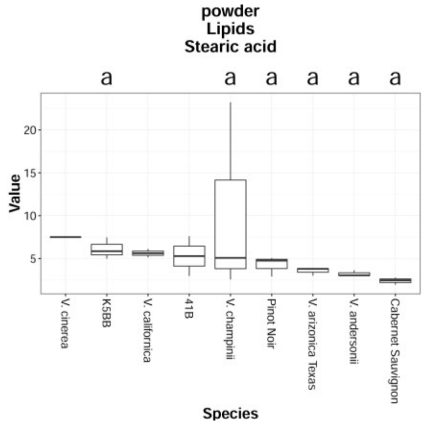
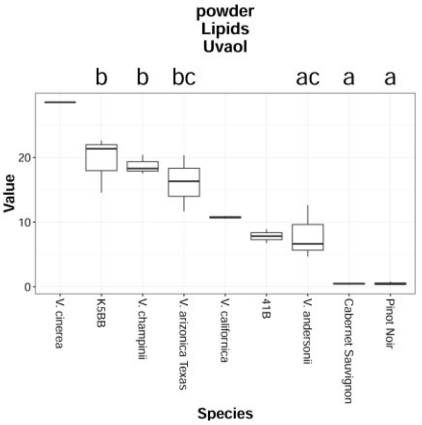
40
V. champinii
Pinot Noir
V. cinerea
K5BB
V. californica
41B
V. arizonica Texas
V. andersonii
Cabernet Sauvignon

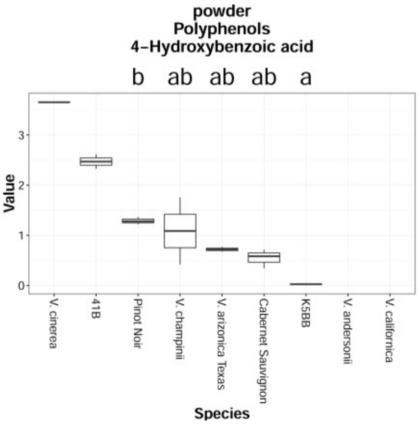

powder
Lipids
Palmitic acid
a
a
a
a
a
a
Value
40
20
0
41B
V. champinii
V. cinerea
V. californica
Pinot Noir
K5BB
V. andersonii
V. arizonica Texas
Cabernet Sauvignon

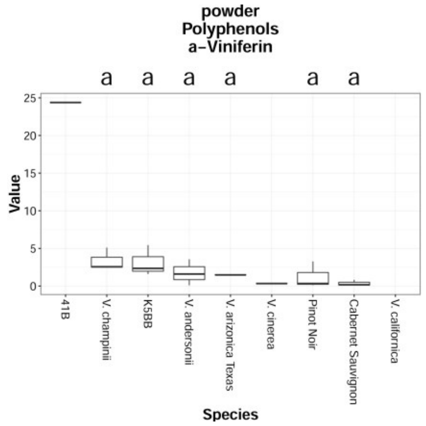

powder
Lipids
Palmitoleic acid
a
a
a
a
a
a
Value
40
30
20
10
0
41B
V. champinii
V. californica
Pinot Noir
V. andersonii
V. arizonica Texas
K5BB
V. cinerea
Cabernet Sauvignon

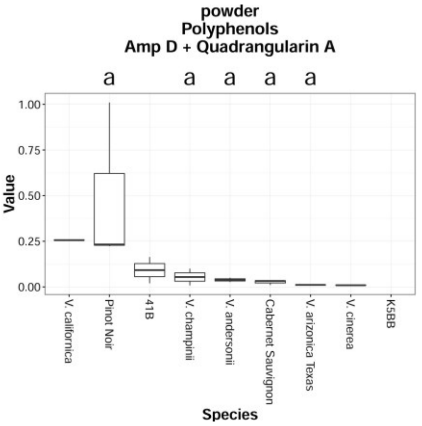

powder
Lipids
POPC
a
a
a
a
a
a
Value
2.0
1.5
1.0
0.5
41B
V. californica
V. champinii
V. cinerea
K5BB
V. arizonica Texas
V. andersonii
Pinot Noir
Cabernet Sauvignon

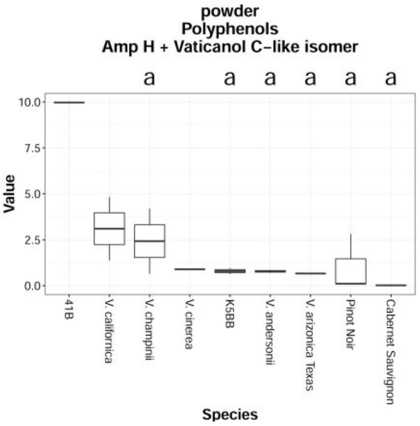

powder
Lipids
Stearic acid
a
a
a
a
a
a
Value
20
15
10
5
V. cinerea
K5BB
V. californica
41B
V. champinii
Pinot Noir
V. arizonica Texas
V. andersonii
Cabernet Sauvignon
Species

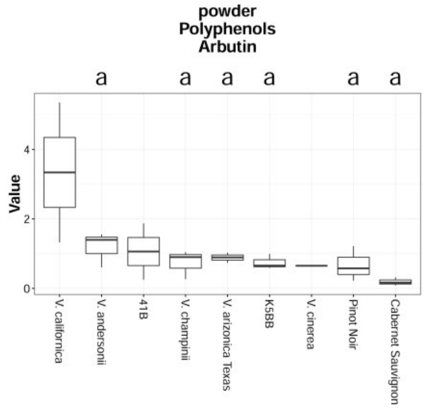

powder
Lipids
Uvaol
b
b
bc
ac
a
a
Value
20
10
0
V. cinerea
K5BB
V. champinii
V. arizonica Texas
V. californica
41B
V. andersonii
Cabernet Sauvignon
Pinot Noir
Species

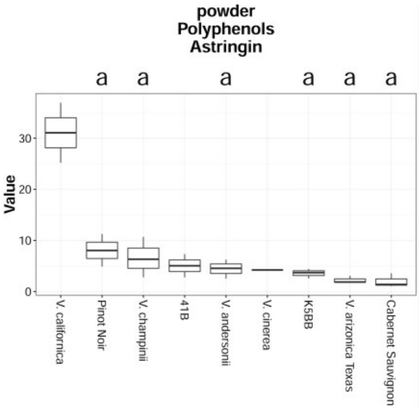

powder
Polyphenols
4-Hydroxybenzoic acid
b
ab
ab
ab
a
Value
3
2
1
0
V. cinerea
41B
Pinot Noir
V. champinii
V. arizonica Texas
Cabernet Sauvignon
K5BB
V. andersonii
V. californica
Species

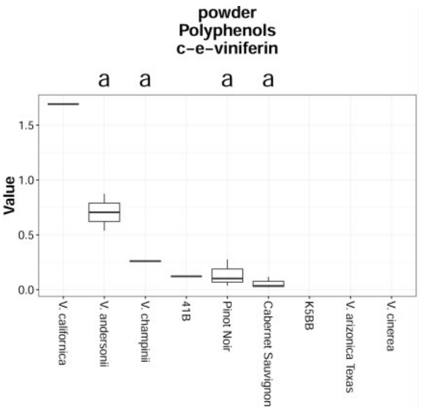

powder
Polyphenols
a-Viniferin
a
a
a
a
a
a
Value
25
20
15
10
5
0
41B
V. champinii
K5BB
V. andersonii
V. arizonica Texas
V. cinerea
Pinot Noir
Cabernet Sauvignon
V. californica
Species

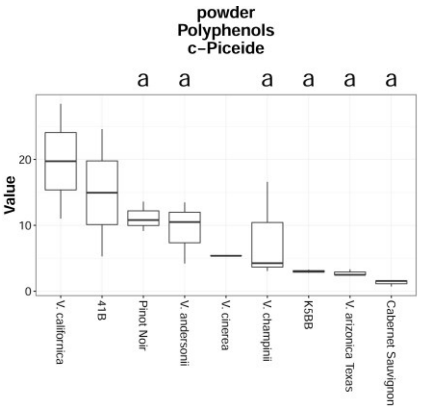

powder
Polyphenols
Amp D + Quadrangularin A
a
a
a
a
a
Value
1.00
0.75
0.50
0.25
0.00
V. californica
Pinot Noir
41B
V. champinii
V. andersonii
Cabernet Sauvignon
V. arizonica Texas
V. cinerea
K5BB
Species

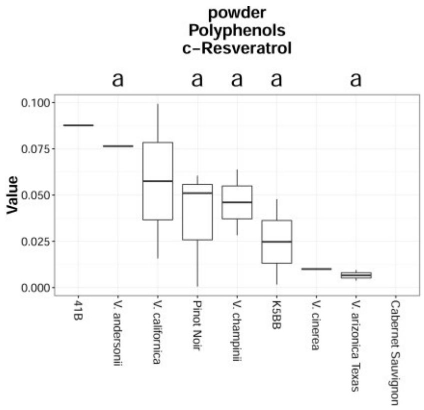

powder
Polyphenols
Amp H + Vaticanol C-like isomer
a
a
a
a
a
a
Value
10.0
7.5
5.0
2.5
0.0
41B
V. californica
V. champinii
V. cinerea
K5BB
V. andersonii
V. arizonica Texas
Pinot Noir
Cabernet Sauvignon
Species

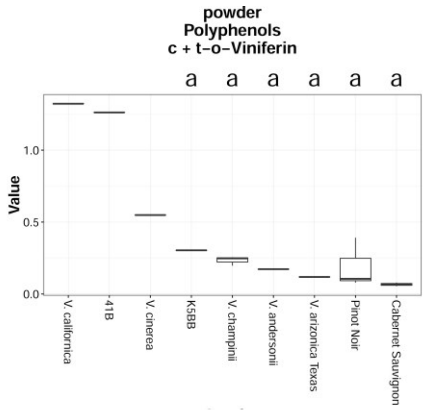

powder
Polyphenols
Arbutin
a
a
a
a
a
a
Value
4
2
0
V. californica
V. andersonii
41B
V. champinii
V. arizonica Texas
K5BB
V. cinerea
Pinot Noir
Cabernet Sauvignon

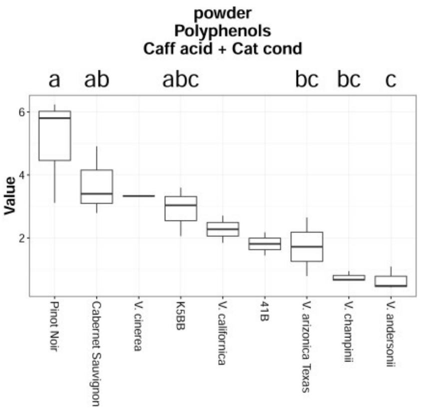

powder
Polyphenols
Astringin
a
a
a
a
a
a
Value
30
20
10
0
V. californica
Pinot Noir
V. champinii
41B
V. andersonii
V. cinerea
K5BB
V. arizonica Texas
Cabernet Sauvignon

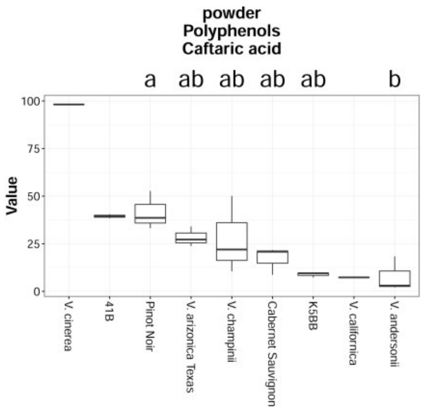

powder
Polyphenols
c-e-viniferin
a
a
a
a
Value
1.5
1.0
0.5
0.0
V. californica
V. andersonii
V. champinii
41B
Pinot Noir
Cabernet Sauvignon
K5BB
V. arizonica Texas
V. cinerea

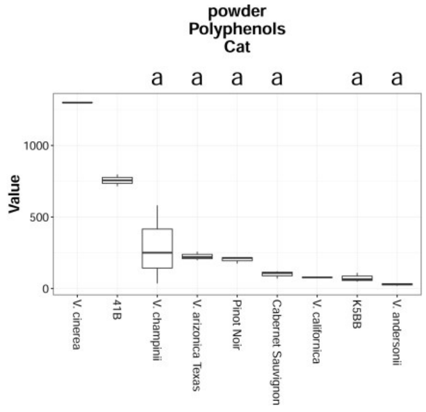

powder
Polyphenols
c–Piceide
a a a a a a
Value
0
10
20
V. californica
41B
Pinot Noir
V. andersonii
V. cinerea
V. champinii
K5BB
V. arizonica Texas
Cabernet Sauvignon

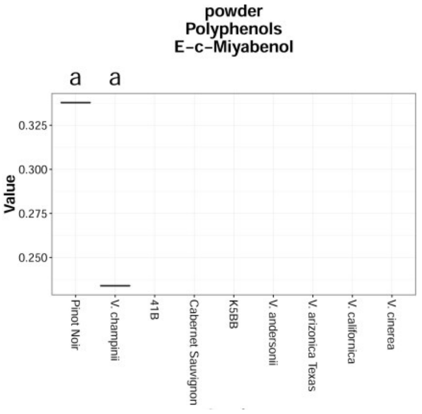

powder
Polyphenols
c–Resveratrol
a a a a a
Value
0.000
0.025
0.050
0.075
0.100
41B
V. andersonii
V. californica
Pinot Noir
V. champinii
K5BB
V. cinerea
V. arizonica Texas
Cabernet Sauvignon

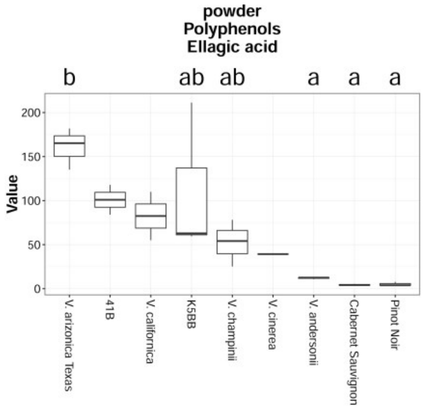

powder
Polyphenols
c + t–o–Viniferin
a a a a a a
Value
0.0
0.5
1.0
V. californica
41B
V. cinerea
K5BB
V. champinii
V. andersonii
V. arizonica Texas
Pinot Noir
Cabernet Sauvignon

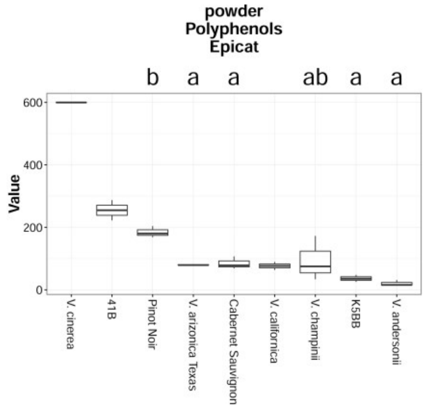

powder
Polyphenols
Caff acid + Cat cond
a ab abc bc bc c
Value
2
4
6
Pinot Noir
Cabernet Sauvignon
V. cinerea
K5BB
V. californica
41B
V. arizonica Texas
V. champinii
V. andersonii

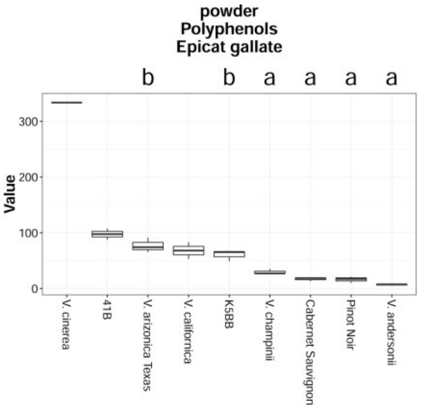

powder
Polyphenols
Caftaric acid
a ab ab ab ab b
Value
0
25
50
75
100
V. cinerea
41B
Pinot Noir
V. arizonica Texas
V. champinii
Cabernet Sauvignon
K5BB
V. californica
V. andersonii

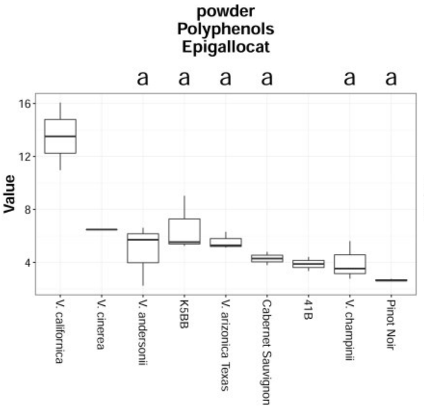

powder
Polyphenols
Cat
a a a a a a
Value
0
500
1000
V. cinerea
41B
V. champinii
V. arizonica Texas
Pinot Noir
Cabernet Sauvignon
V. californica
K5BB
V. andersonii

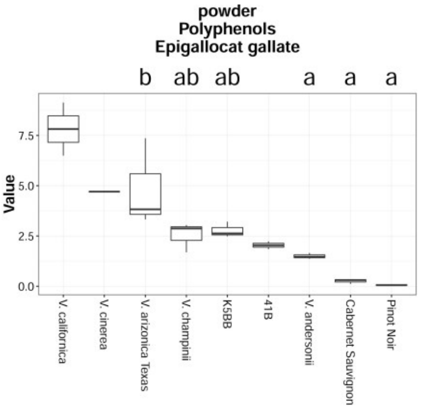

powder
Polyphenols
E–c–Miyabenol
a a
Value
0.250
0.275
0.300
0.325
Pinot Noir
V. champinii
41B
Cabernet Sauvignon
K5BB
V. andersonii
V. arizonica Texas
V. californica
V. cinerea

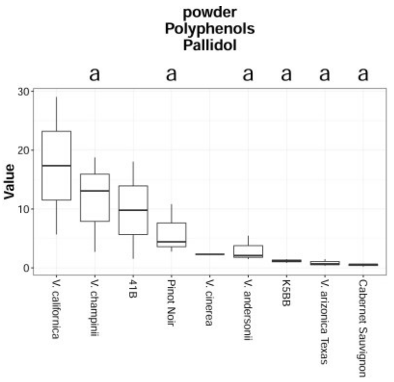

powder
Polyphenols
Ellagic acid
b ab ab a a a
Value
0
50
100
150
200
V. arizonica Texas
41B
V. californica
K5BB
V. champinii
V. cinerea
V. andersonii
Cabernet Sauvignon
Pinot Noir


powder
Polyphenols
Epicat
b a a ab a a
Value
0
200
400
600
V. cinerea
41B
Pinot Noir
V. arizonica Texas
Cabernet Sauvignon
V. californica
V. champinii
K5BB
V. andersonii

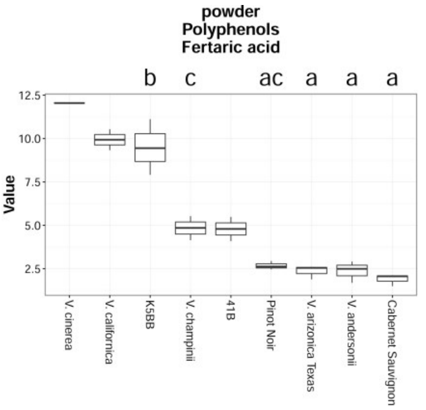

powder
Polyphenols
Epicat gallate
b b a a a a
Value
0
100
200
300
V. cinerea
41B
V. arizonica Texas
V. californica
K5BB
V. champinii
Cabernet Sauvignon
Pinot Noir
V. andersonii


powder
Polyphenols
Epigallocat
a a a a a a
Value
4
8
12
16
V. californica
V. cinerea
V. andersonii
K5BB
V. arizonica Texas
Cabernet Sauvignon
41B
V. champinii
Pinot Noir

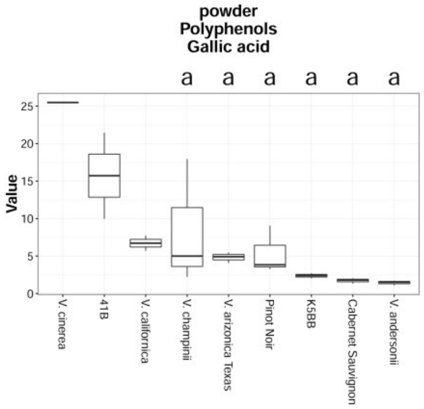

powder
Polyphenols
Epigallocat gallate
b ab ab a a a
Value
0.0
2.5
5.0
7.5
V. californica
V. cinerea
V. arizonica Texas
V. champinii
K5BB
41B
V. andersonii
Cabernet Sauvignon
Pinot Noir



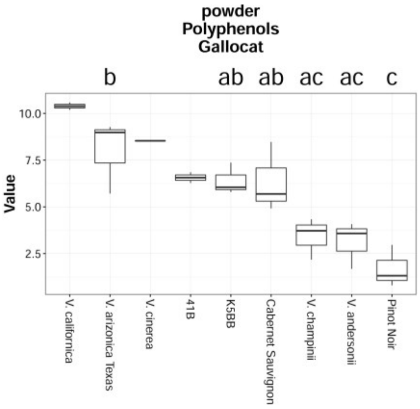
powder
Polyphenols
Pallidol



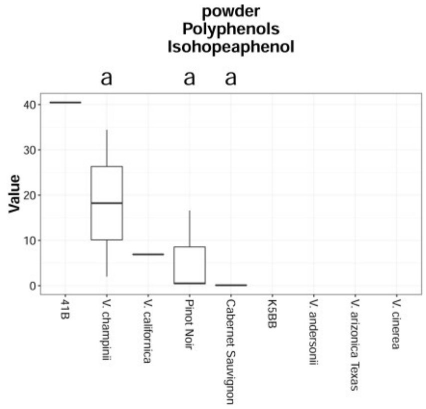
powder
Polyphenols
Fertaric acid



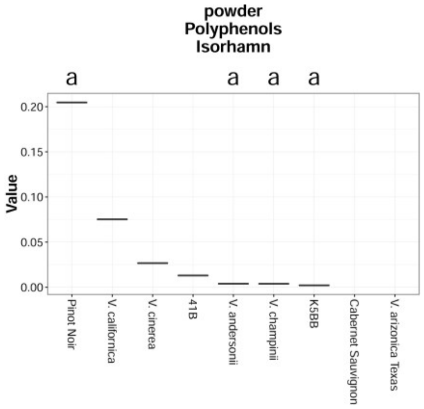
powder
Polyphenols
Gallic acid



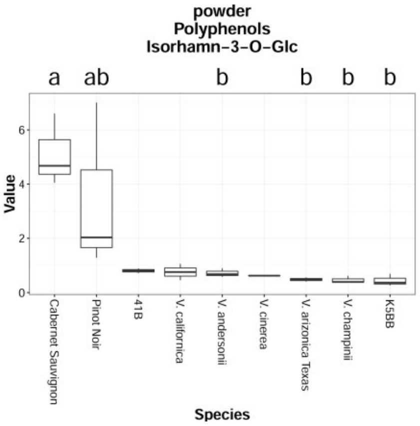
powder
Polyphenols
Gallocat



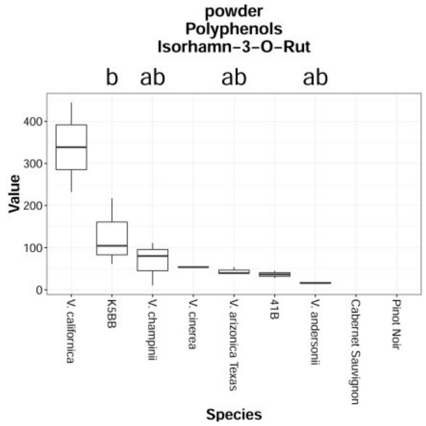
powder
Polyphenols
Isohopeaphenol



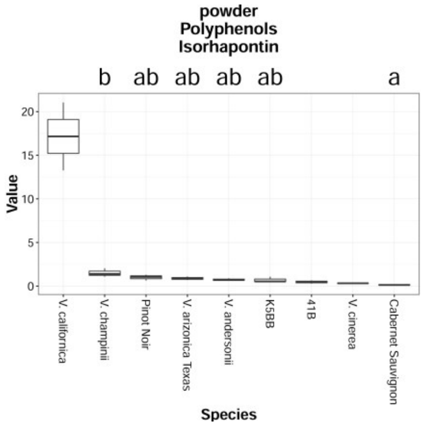
powder
Polyphenols
Isorhamn



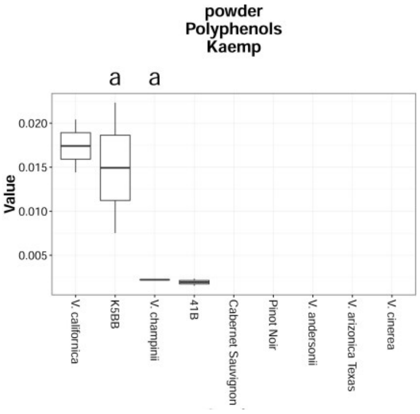
powder
Polyphenols
Isorhamn−3−O−Glc



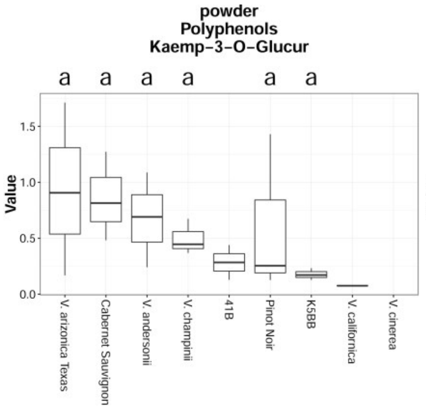
powder
Polyphenols
Isorhamn−3−O−Rut



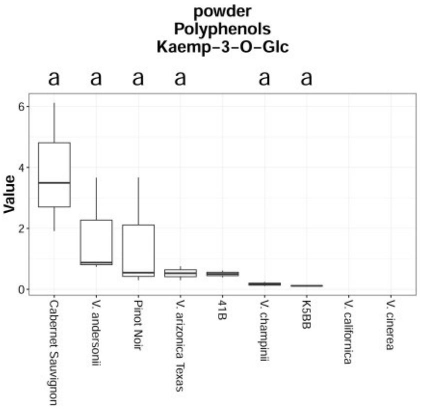
powder
Polyphenols
Isorhapontin



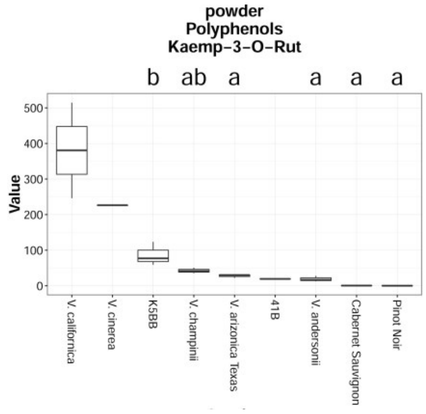
powder
Polyphenols
Kaemp

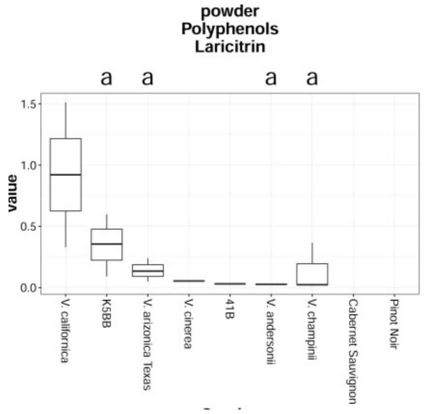


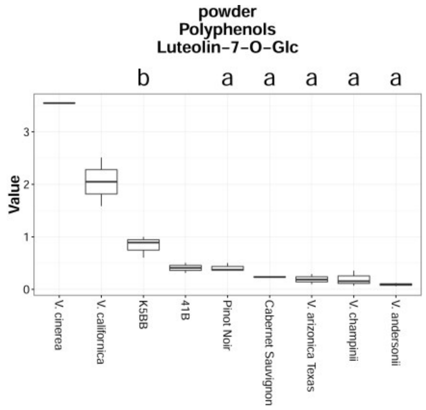
powder
Polyphenols
Kaemp−3−O−Glucur

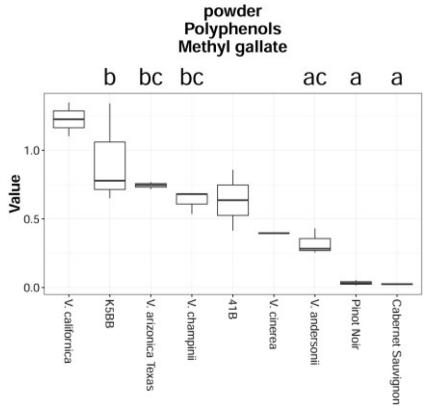


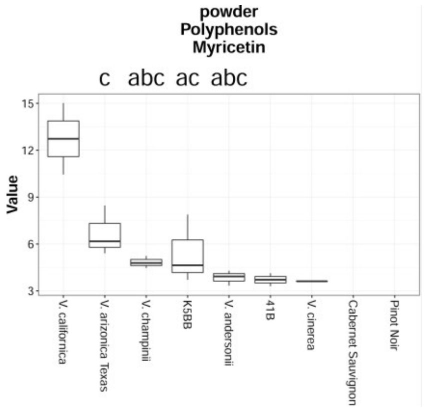
powder
Polyphenols
Kaemp−3−O−Glc

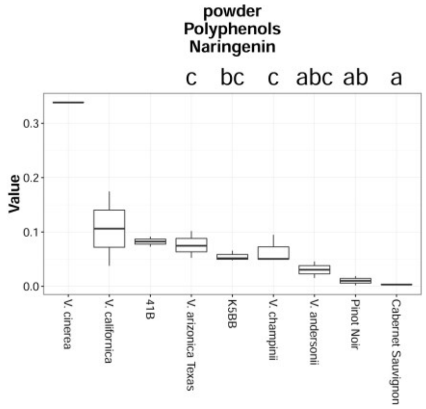

powder
Polyphenols
Kaemp-3-O-Rut
b ab a a a a
Value
0
100
200
300
400
500
V. californica
V. cinerea
K5BB
V. champinii
V. arizonica Texas
41B
V. andersonii
Cabernet Sauvignon
Pinot Noir

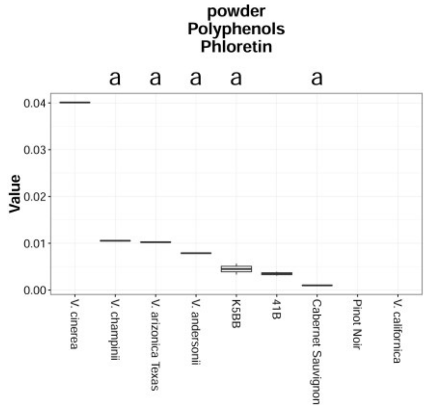

powder
Polyphenols
Laricitrin
a a a a
Value
0.0
0.5
1.0
1.5
V. californica
K5BB
V. arizonica Texas
V. cinerea
41B
V. andersonii
V. champinii
Cabernet Sauvignon
Pinot Noir

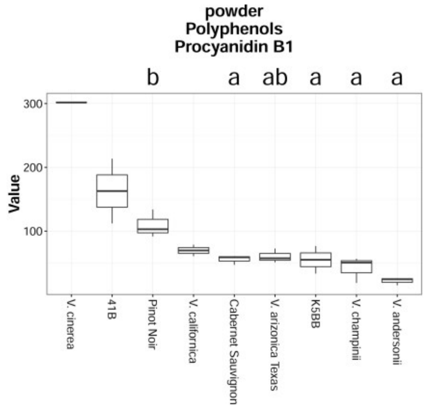

powder
Polyphenols
Luteolin-7-O-Glc
b a a a a a
Value
0
1
2
3
V. cinerea
V. californica
K5BB
41B
Pinot Noir
Cabernet Sauvignon
V. arizonica Texas
V. champinii
V. andersonii

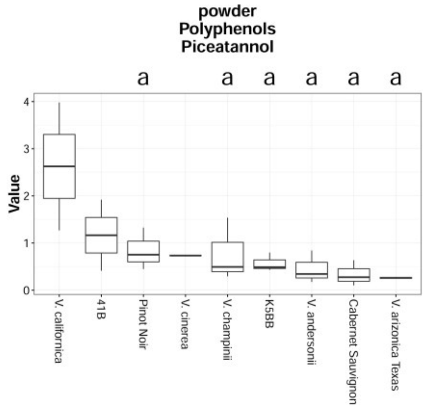

powder
Polyphenols
Methyl gallate
b bc bc ac a a
Value
0.0
0.5
1.0
V. californica
K5BB
V. arizonica Texas
V. champinii
41B
V. cinerea
V. andersonii
Pinot Noir
Cabernet Sauvignon

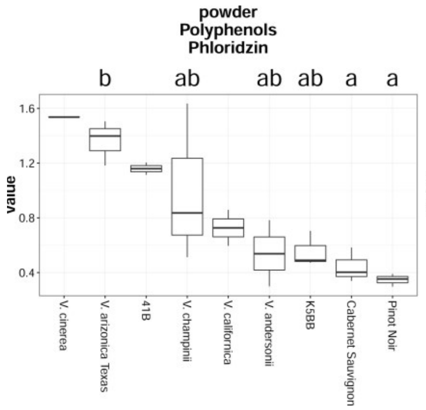

powder
Polyphenols
Myricetin
c abc ac abc
Value
3
6
9
12
15
V. californica
V. arizonica Texas
V. champinii
K5BB
V. andersonii
41B
V. cinerea
Cabernet Sauvignon
Pinot Noir

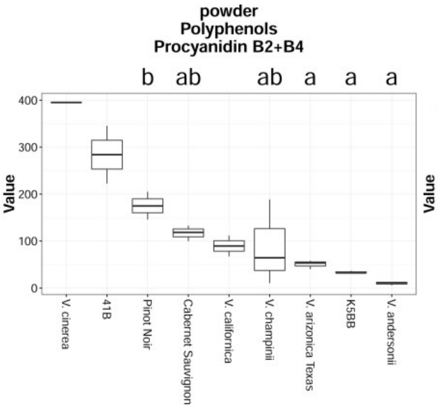

powder
Polyphenols
Naringenin
c bc c abc ab a
Value
0.0
0.1
0.2
0.3
V. cinerea
V. californica
41B
V. arizonica Texas
K5BB
V. champinii
V. andersonii
Pinot Noir
Cabernet Sauvignon

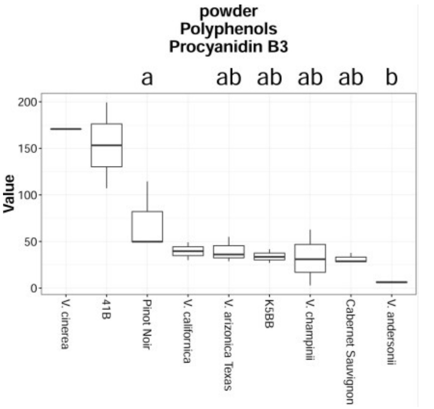

powder
Polyphenols
Phloretin
a a a a a
Value
0.00
0.01
0.02
0.03
0.04
V. cinerea
V. champinii
V. arizonica Texas
V. andersonii
K5BB
41B
Cabernet Sauvignon
Pinot Noir
V. californica

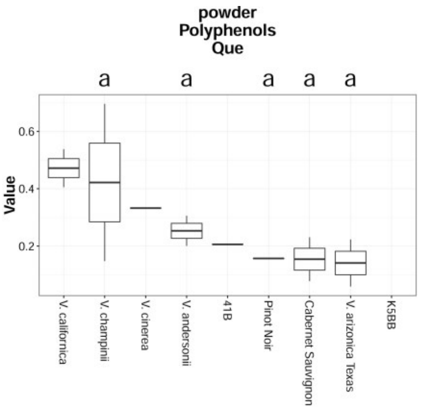

powder
Polyphenols
Procyanidin B1
b a ab a a a
Value
100
200
300
V. cinerea
41B
Pinot Noir
V. californica
Cabernet Sauvignon
V. arizonica Texas
K5BB
V. champinii
V. andersonii

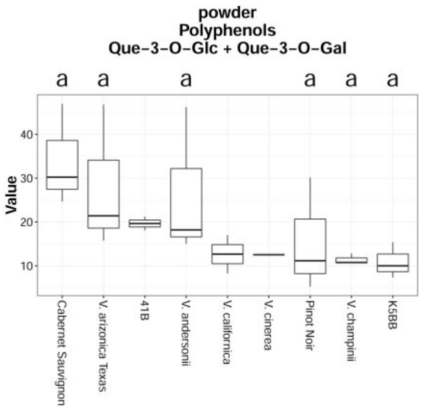

powder
Polyphenols
Piceatannol
a a a a a a
Value
0
1
2
3
4
V. californica
41B
Pinot Noir
V. cinerea
V. champinii
K5BB
V. andersonii
Cabernet Sauvignon
V. arizonica Texas

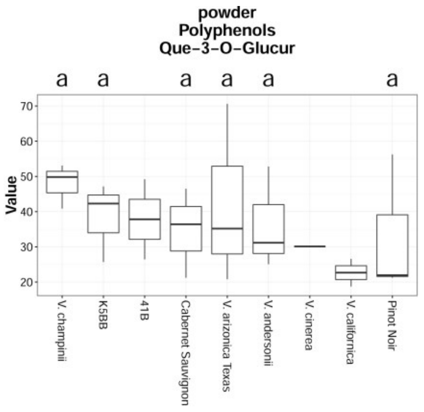

powder
Polyphenols
Phloridzin
b ab ab ab a a
value
0.4
0.8
1.2
1.6
V. cinerea
V. arizonica Texas
41B
V. champinii
V. californica
V. andersonii
K5BB
Cabernet Sauvignon
Pinot Noir

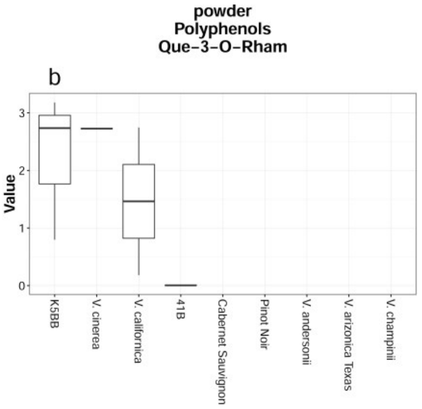

powder
Polyphenols
Procyanidin B2+B4
b ab ab a a a
Value
0
100
200
300
400
V. cinerea
41B
Pinot Noir
Cabernet Sauvignon
V. californica
V. champinii
V. arizonica Texas
K5BB
V. andersonii

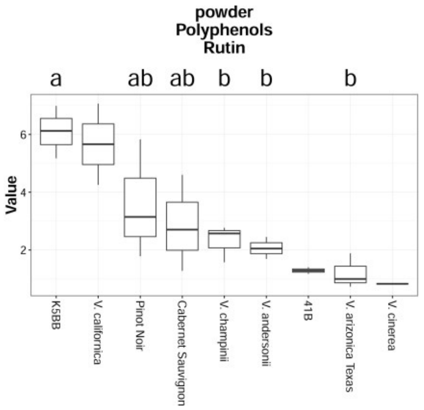

powder
Polyphenols
Procyanidin B3
a ab ab ab ab b
Value
0
50
100
150
200
V. cinerea
41B
Pinot Noir
V. californica
V. arizonica Texas
K5BB
V. champinii
Cabernet Sauvignon
V. andersonii

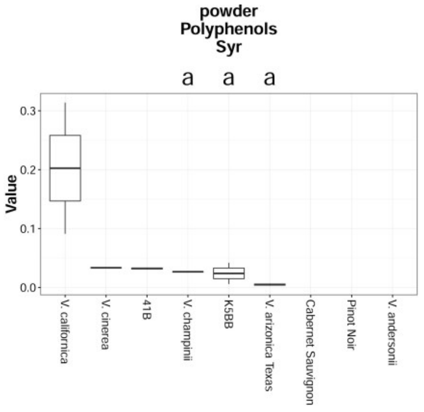

powder
Polyphenols
Que
a
a
a
a
a
Value
0.2
0.4
0.6
V. californica
V. champinii
V. cinerea
V. andersonii
41B
Pinot Noir
Cabernet Sauvignon
V. arizonica Texas
K5BB

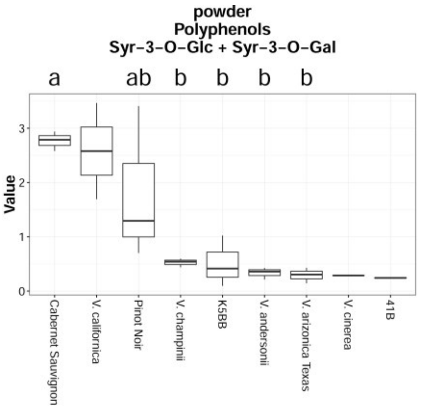

powder
Polyphenols
Que–3–O–Glc + Que–3–O–Gal
a
a
a
a
a
a
Value
10
20
30
40
Cabernet Sauvignon
V. arizonica Texas
41B
V. andersonii
V. californica
V. cinerea
Pinot Noir
V. champinii
K5BB

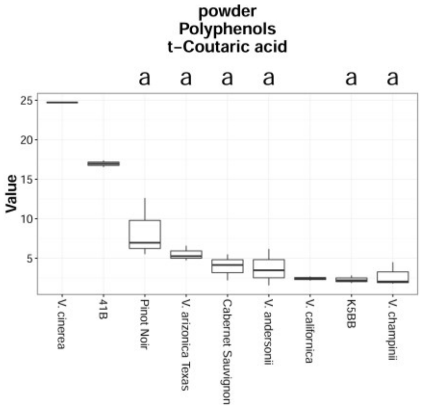

powder
Polyphenols
Que–3–O–Glucur
a
a
a
a
a
a
Value
20
30
40
50
60
70
V. champinii
K5BB
41B
Cabernet Sauvignon
V. arizonica Texas
V. andersonii
V. cinerea
V. californica
Pinot Noir

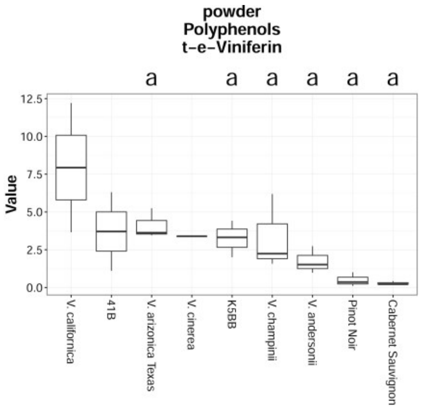

powder
Polyphenols
Que–3–O–Rham
b
Value
0
1
2
3
K5BB
V. cinerea
V. californica
41B
Cabernet Sauvignon
Pinot Noir
V. andersonii
V. arizonica Texas
V. champinii

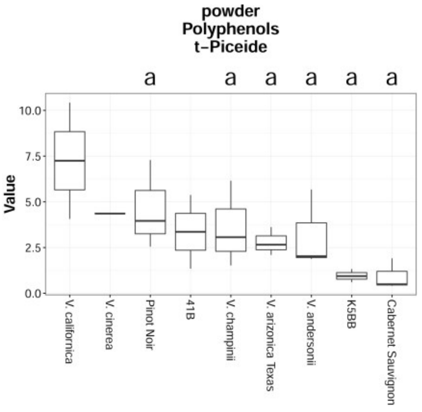

powder
Polyphenols
Rutin
a
ab
ab
b
b
b
Value
2
4
6
K5BB
V. californica
Pinot Noir
Cabernet Sauvignon
V. champinii
V. andersonii
41B
V. arizonica Texas
V. cinerea

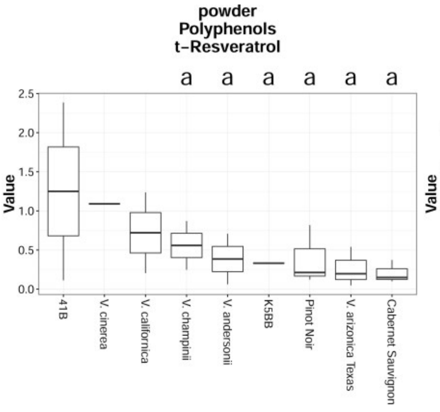

powder
Polyphenols
Syr
a
a
a
Value
0.0
0.1
0.2
0.3
V. californica
V. cinerea
41B
V. champinii
K5BB
V. arizonica Texas
Cabernet Sauvignon
Pinot Noir
V. andersonii

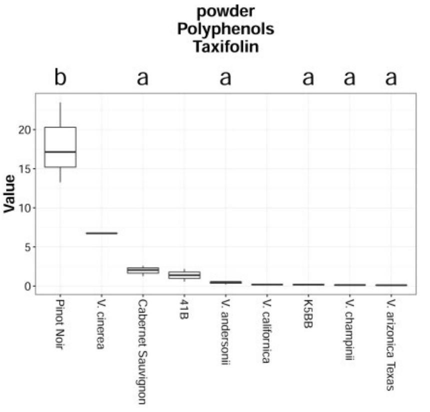

powder
Polyphenols
Syr–3–O–Glc + Syr–3–O–Gal
a
ab
b
b
b
b
Value
0
1
2
3
Cabernet Sauvignon
V. californica
Pinot Noir
V. champinii
K5BB
V. andersonii
V. arizonica Texas
V. cinerea
41B


powder
Polyphenols
t–Coutaric acid
a
a
a
a
a
a
Value
5
10
15
20
25
V. cinerea
41B
Pinot Noir
V. arizonica Texas
Cabernet Sauvignon
V. andersonii
V. californica
K5BB
V. champinii

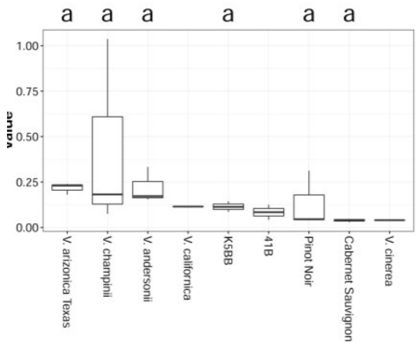

powder
Polyphenols
t–e–Viniferin
a
a
a
a
a
a
Value
0.0
2.5
5.0
7.5
10.0
12.5
V. californica
41B
V. arizonica Texas
V. cinerea
K5BB
V. champinii
V. andersonii
Pinot Noir
Cabernet Sauvignon


powder
Polyphenols
t–Piceide
a
a
a
a
a
a
Value
0.0
2.5
5.0
7.5
10.0
V. californica
V. cinerea
Pinot Noir
41B
V. champinii
V. arizonica Texas
V. andersonii
K5BB
Cabernet Sauvignon

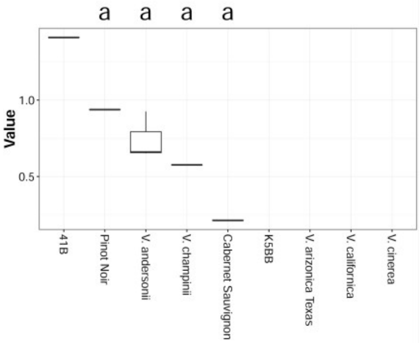

powder
Polyphenols
t–Resveratrol
a
a
a
a
a
a
Value
0.0
0.5
1.0
1.5
2.0
2.5
41B
V. cinerea
V. californica
V. champinii
V. andersonii
K5BB
Pinot Noir
V. arizonica Texas
Cabernet Sauvignon


powder
Polyphenols
Taxifolin
b
a
a
a
a
a
Value
0
5
10
15
20
Pinot Noir
V. cinerea
Cabernet Sauvignon
41B
V. andersonii
V. californica
K5BB
V. champinii
V. arizonica Texas

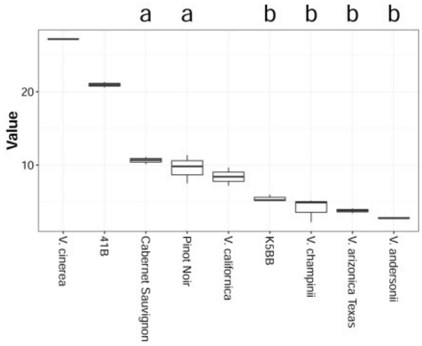
powder
Polyphenols
Vanillic acid



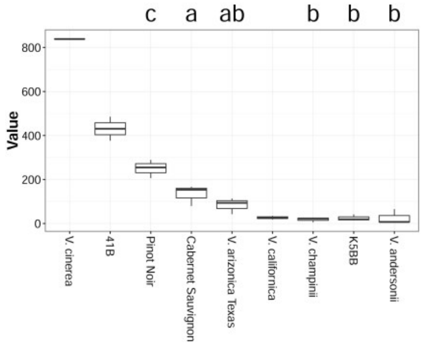
powder
Polyphenols
Z–Miyabenol C



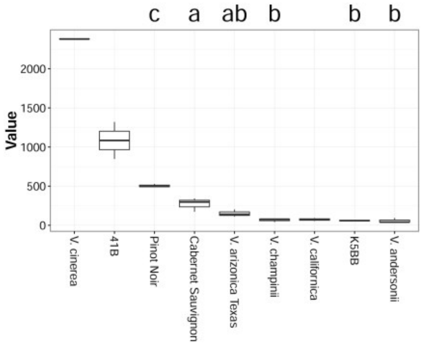
powder
Tannins
% galloylation



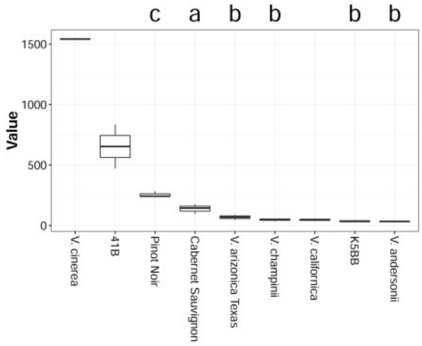
powder
Tannins
Cat



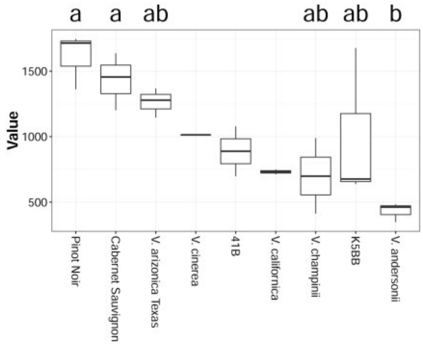
powder
Tannins
Cat (extension units)



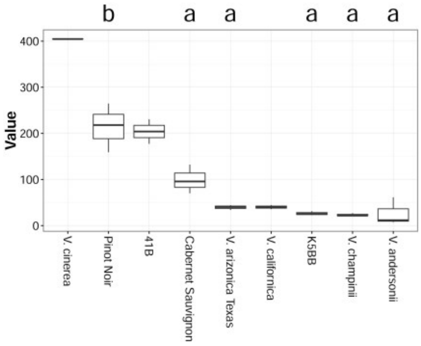
powder
Tannins
Cat (terminal units)



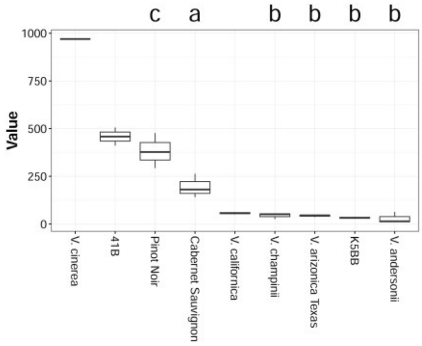
powder
Tannins
Cat + Epicat (upper units)



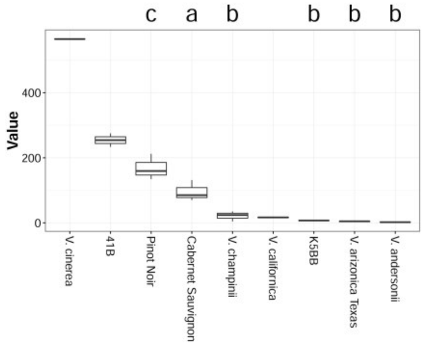
powder
Tannins
Epicat



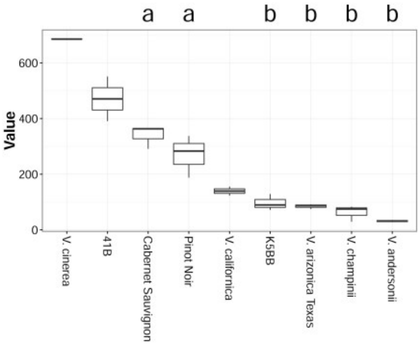
powder
Tannins
Epicat (extension units)



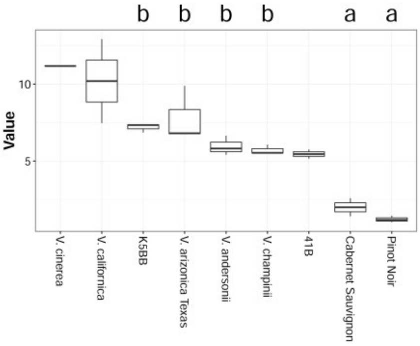
powder
Tannins
Epicat (terminal units)

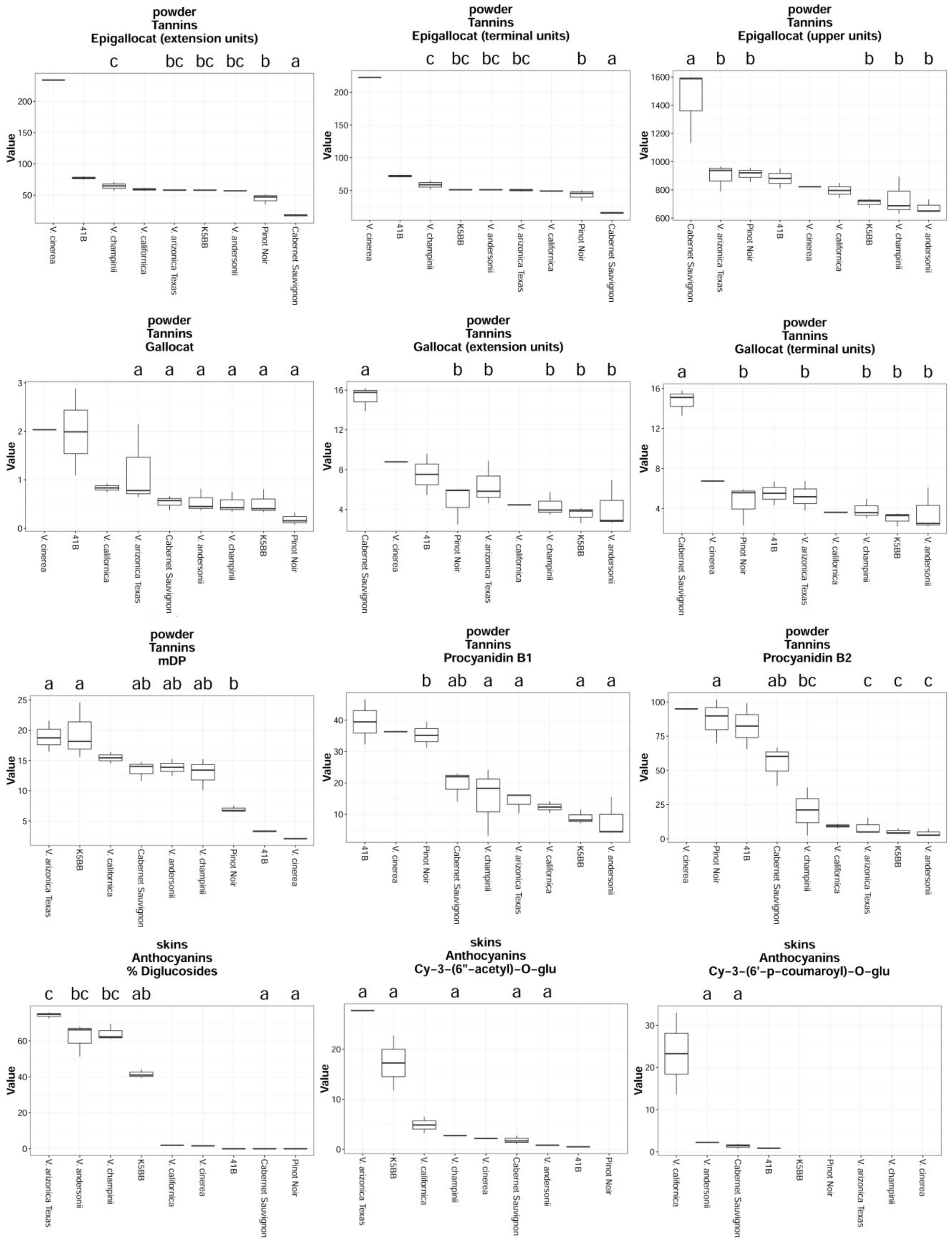


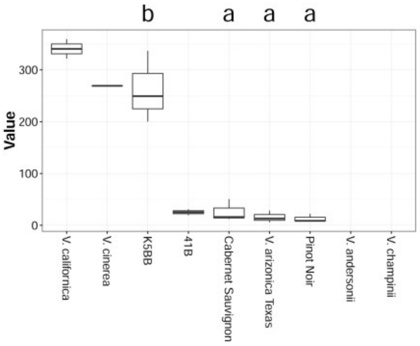
powder
Tannins
Epicat gallate (upper units)



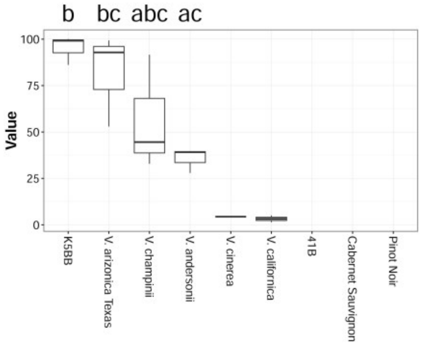
powder
Tannins
Epigallocat



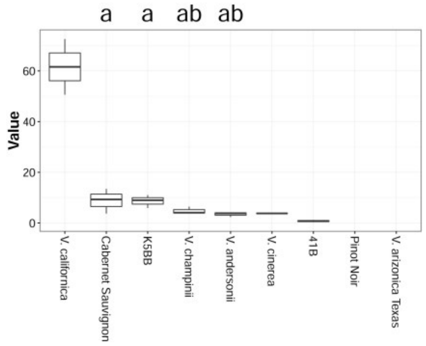

powder
Tannins
Epigallocat (extension units)
c bc bc bc b a
Value
50
100
150
200
V. cinerea
41B
V. champinii
V. californica
V. arizonica Texas
K5BB
V. andersonii
Pinot Noir
Cabernet Sauvignon
powder
Tannins
Epigallocat (terminal units)
c bc bc bc b a
Value
50
100
150
200
V. cinerea
41B
V. champinii
K5BB
V. andersonii
V. arizonica Texas
V. californica
Pinot Noir
Cabernet Sauvignon
powder
Tannins
Epigallocat (upper units)
a b b b b b
Value
600
800
1000
1200
1400
1600
Cabernet Sauvignon
V. arizonica Texas
Pinot Noir
41B
V. cinerea
V. californica
K5BB
V. champinii
V. andersonii
powder
Tannins
Gallocat
a a a a a a
Value
0
1
2
3
V. cinerea
41B
V. californica
V. arizonica Texas
Cabernet Sauvignon
V. andersonii
V. champinii
K5BB
Pinot Noir
powder
Tannins
Gallocat (extension units)
a b b b b b
Value
4
8
12
16
Cabernet Sauvignon
V. cinerea
41B
Pinot Noir
V. arizonica Texas
V. californica
V. champinii
K5BB
V. andersonii
powder
Tannins
Gallocat (terminal units)
a b b b b b
Value
4
8
12
16
Cabernet Sauvignon
V. cinerea
Pinot Noir
41B
V. arizonica Texas
V. californica
V. champinii
K5BB
V. andersonii
powder
Tannins
mDP
a a ab ab ab b
Value
5
10
15
20
25
V. arizonica Texas
K5BB
V. californica
Cabernet Sauvignon
V. andersonii
V. champinii
Pinot Noir
41B
V. cinerea
powder
Tannins
Procyanidin B1
b ab a a a a
Value
10
20
30
40
41B
V. cinerea
Pinot Noir
Cabernet Sauvignon
V. champinii
V. arizonica Texas
V. californica
K5BB
V. andersonii
powder
Tannins
Procyanidin B2
a ab bc c c c
Value
0
25
50
75
100
V. cinerea
Pinot Noir
41B
Cabernet Sauvignon
V. champinii
V. californica
V. arizonica Texas
K5BB
V. andersonii
skins
Anthocyanins
% Diglucosides
c bc bc ab a a
Value
0
20
40
60
V. arizonica Texas
V. andersonii
V. champinii
K5BB
V. californica
V. cinerea
41B
Cabernet Sauvignon
Pinot Noir
skins
Anthocyanins
Cy-3-(6"-acetyl)-O-glu
a a a a a
Value
0
10
20
V. arizonica Texas
K5BB
V. californica
V. champinii
V. cinerea
Cabernet Sauvignon
V. andersonii
41B
Pinot Noir
skins
Anthocyanins
Cy-3-(6'-p-coumaroyl)-O-glu
a a
Value
0
10
20
30
V. californica
V. andersonii
Cabernet Sauvignon
41B
K5BB
Pinot Noir
V. arizonica Texas
V. champinii
V. cinerea



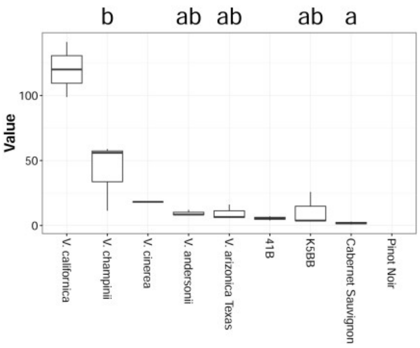
skins
Anthocyanins
Cy-3-O-glu



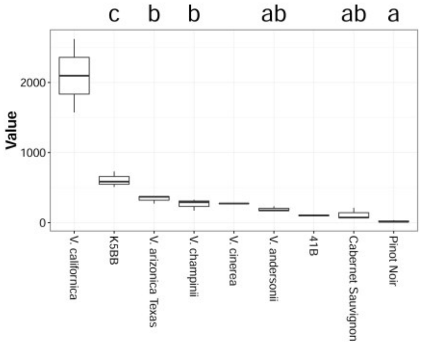
skins
Anthocyanins
Cy-3,5-O-diglu



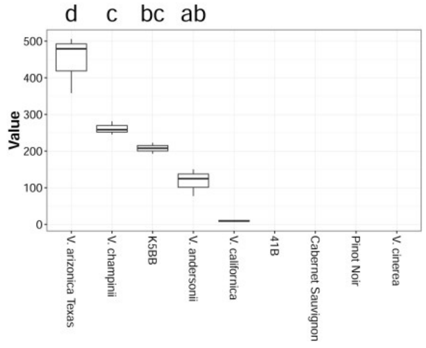
skins
Anthocyanins
Dp-3-(6"-acetyl)-O-glu



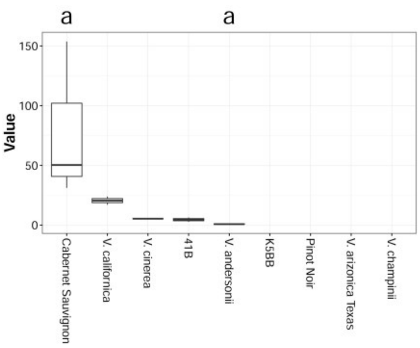
skins
Anthocyanins
Dp-3-(6'-p-coumaroyl)-O-glu



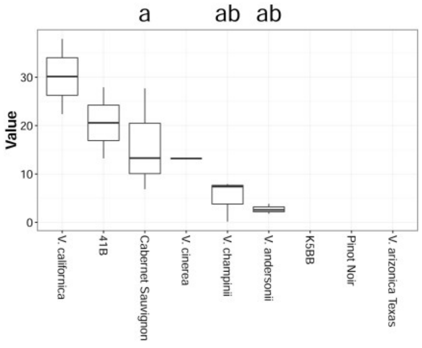
skins
Anthocyanins
Dp-3-O-glu



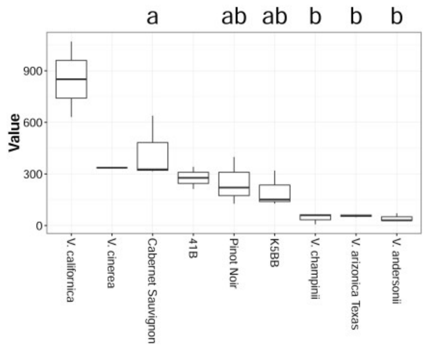
skins
Anthocyanins
Dp-3,5-O-diglu



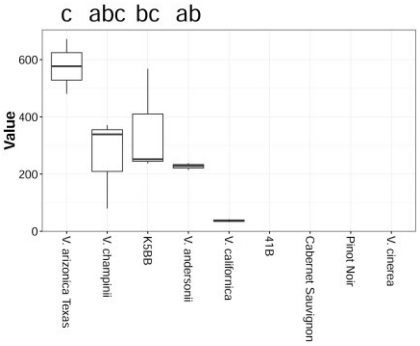
skins
Anthocyanins
Mv-3-(6"-acetyl)-O-glu



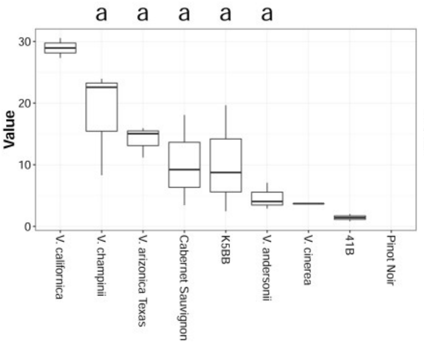
skins
Anthocyanins
Mv-3-(6'-p-coumaroyl)-O-glu



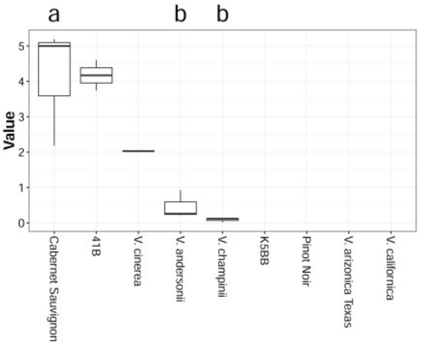
skins
Anthocyanins
Mv-3-O-gluc



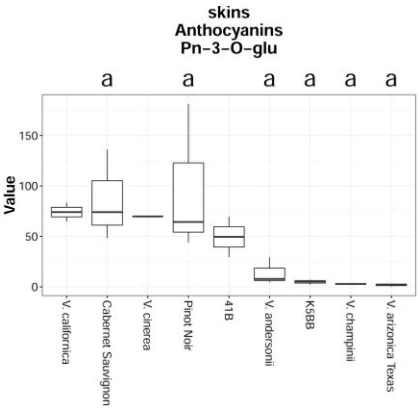
skins
Anthocyanins
Mv-3,5-O-diglu

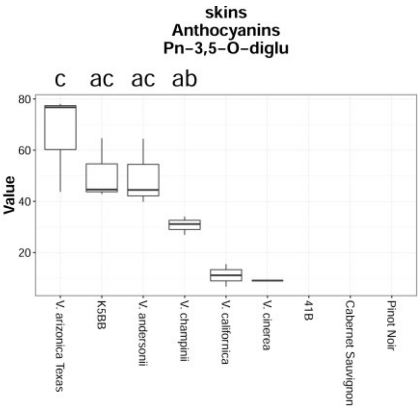


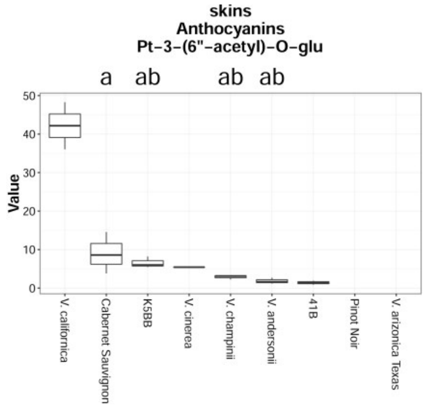
skins
Anthocyanins
Pn-3-(6"-acetyl)-O-glu

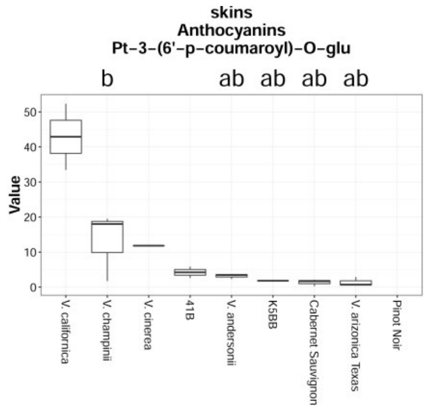


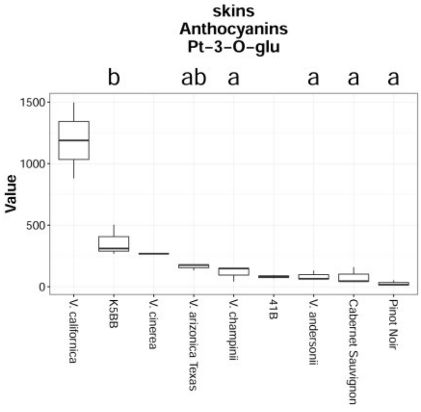
skins
Anthocyanins
Pn-3-(6'-p-coumaroyl)-O-glu


skins
Anthocyanins
Pn−3−O−glu
a a a a a a
Value
0
50
100
150
V. californica
Cabernet Sauvignon
V. cinerea
Pinot Noir
41B
V. andersonii
K5BB
V. champinii
V. arizonica Texas


skins
Anthocyanins
Pn−3,5−O−diglu
c ac ac ab
Value
20
40
60
80
V. arizonica Texas
K5BB
V. andersonii
V. champinii
V. californica
V. cinerea
41B
Cabernet Sauvignon
Pinot Noir


skins
Anthocyanins
Pt−3−(6"−acetyl)−O−glu
a ab ab ab
Value
0
10
20
30
40
50
V. californica
Cabernet Sauvignon
K5BB
V. cinerea
V. champinii
V. andersonii
41B
Pinot Noir
V. arizonica Texas


skins
Anthocyanins
Pt−3−(6'−p−coumaroyl)−O−glu
b ab ab ab ab
Value
0
10
20
30
40
50
V. californica
V. champinii
V. cinerea
41B
V. andersonii
K5BB
Cabernet Sauvignon
V. arizonica Texas
Pinot Noir


skins
Anthocyanins
Pt−3−O−glu
b ab a a a a
Value
0
500
1000
1500
V. californica
K5BB
V. cinerea
V. arizonica Texas
V. champinii
41B
V. andersonii
Cabernet Sauvignon
Pinot Noir

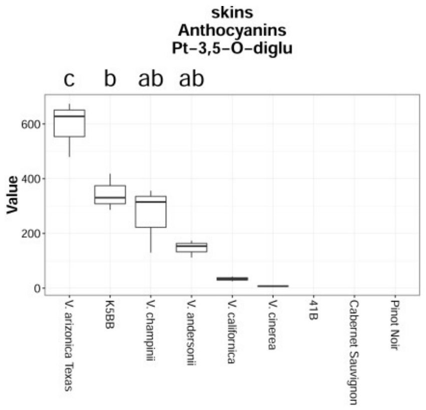

skins
Anthocyanins
Pt−3,5−O−diglu
c b ab ab
Value
0
200
400
600
V. arizonica Texas
K5BB
V. champinii
V. andersonii
V. californica
V. cinerea
41B
Cabernet Sauvignon
Pinot Noir

Table S1. Concentrations of phenolic compounds in the grape berries. The results are expressed as mg/kg FW.

Genoytpe	Year	*p*-hydroxybenzoic acid	vanillic acid	gallic acid	caftaric acid	Fertaric acid	*trans*-coutaric acid	phloridzin	luteolin-7-*O*-glu	naringenin	cat	epicat	epigallocat	gallocat	epigallocat gallate	epicat gallate	procyanidin B1	procyanidin B2+B4	procyanidin B3	kaemp	que	que-3-*O*-rham	kaemp-3-*O*-glu	que-3-*O*-glu + que-3-*O*-gal	sorhamn-3-*O*-glu	kaemp-3-*O*-rut	isorhamn-3-*O*-rut	que-3-*O*-glucur	kaemp-3-*O*-glucur
41B	2008	2.61	0.04	9.98	38.41	4.10	17.38	1.20	0.31	0.09	714.56	222.38	4.42	6.85	1.84	87.53	112.14	222.58	107.16	n.d.	n.d.	n.d.	0.39	18.07	0.72	19.70	45.05	26.45	0.13
41B	2009	2.33	0.13	21.46	40.49	5.49	16.54	1.11	0.51	0.07	796.95	287.22	3.35	6.28	2.23	107.73	213.57	345.41	199.28	n.d.	0.21	n.d.	0.62	21.21	0.89	18.92	27.78	49.20	0.44
41B	2010	1.86	0.09	29.30	83.02	4.27	34.72	1.30	0.37	0.07	557.39	229.60	5.13	6.06	1.64	63.48	104.75	252.83	97.29	n.d.	0.44	n.d.	0.41	15.23	0.85	20.66	44.41	32.55	0.30
K5BB	2007	n.d.	0.14	2.71	9.50	9.45	1.86	0.70	0.89	0.05	48.49	25.39	9.03	7.37	3.21	65.41	33.48	36.49	27.05	0.01	n.d.	2.74	n.d.	15.37	0.69	123.39	217.46	47.15	0.23
K5BB	2008	0.02	0.09	2.01	9.73	7.91	2.20	0.49	0.60	0.05	65.08	35.69	5.54	5.80	2.63	48.64	55.08	31.97	33.44	0.02	n.d.	0.80	0.11	7.33	0.26	77.01	104.44	25.68	0.13
K5BB	2009	0.04	0.11	2.40	7.25	11.12	2.81	0.47	1.00	0.07	109.63	48.00	5.25	6.05	2.48	67.51	76.68	32.26	41.64	n.d.	n.d.	3.18	n.d.	9.99	0.37	59.03	61.41	42.29	0.17
K5BB	2010	n.d.	0.11	3.44	81.28	9.74	13.26	1.66	1.67	0.07	60.80	51.10	10.92	10.03	3.87	75.84	37.93	45.91	39.39	n.d.	n.d.	11.11	0.23	18.34	0.38	132.72	253.36	89.22	0.37
K5BB	2014	0.36	0.05	1.61	10.35	5.43	1.55	0.14	0.75	n.d.	59.64	40.70	2.91	3.54	3.03	50.87	28.32	25.94	32.99	n.d.	n.d.	n.d.	0.22	9.21	0.43	2.96	n.d.	30.79	0.14
V. andersonii	2007	n.d.	0.15	1.72	2.12	1.69	1.57	0.30	0.06	0.02	19.95	14.44	2.24	1.68	1.37	5.21	15.02	5.63	6.16	n.d.	n.d.	n.d.	0.87	15.00	0.58	12.48	16.20	25.07	0.24
V. andersonii	2008	n.d.	0.17	1.52	3.00	2.91	3.47	0.54	0.12	0.03	30.91	15.76	5.71	4.07	1.66	7.55	26.28	11.32	7.35	n.d.	0.31	n.d.	3.67	46.19	0.90	16.75	13.62	52.82	1.09
V. andersonii	2009	n.d.	0.33	1.09	18.37	2.50	6.17	0.78	0.09	0.05	36.38	31.55	6.62	3.58	1.47	8.29	24.50	12.61	5.67	n.d.	0.20	n.d.	0.74	18.19	0.67	27.90	17.99	31.16	0.69
V. andersonii	2010	n.d.	0.24	2.45	35.00	2.42	13.94	0.57	0.14	0.02	28.53	14.28	5.15	3.11	1.72	4.15	18.70	15.99	9.36	n.d.	n.d.	n.d.	0.74	16.40	0.66	30.20	40.77	22.87	0.57
V. arizonica Texas	2007	0.77	0.23	4.91	23.78	1.89	4.73	1.40	0.19	0.05	257.65	82.28	5.29	9.27	3.83	65.31	51.24	53.26	36.05	n.d.	n.d.	n.d.	0.30	21.39	0.40	30.99	53.80	35.18	0.91
V. arizonica Texas	2008	0.68	0.24	5.50	27.20	2.55	5.26	1.51	0.29	0.07	198.09	79.25	6.31	8.98	7.36	91.43	72.63	57.78	54.93	n.d.	0.22	n.d.	0.76	46.82	0.48	30.13	38.65	70.62	1.71
V. arizonica Texas	2009	0.72	0.18	4.06	34.07	2.61	6.58	1.18	0.10	0.10	219.81	78.52	5.12	5.71	3.33	74.24	57.45	40.07	28.80	n.d.	0.06	n.d.	n.d.	15.79	0.56	22.12	39.60	20.79	0.17
V. arizonica Texas	2014	0.84	0.06	1.79	14.34	2.62	5.54	0.24	0.17	0.12	103.37	33.59	3.84	15.37	5.96	26.63	26.66	28.24	21.88	n.d.	n.d.	n.d.	0.15	14.17	0.20	0.64	n.d.	21.24	0.20
V. champinii	2007	1.75	1.04	17.93	21.96	4.85	2.04	1.64	0.36	0.09	581.37	172.66	2.77	2.18	3.04	35.20	56.69	188.46	62.73	n.d.	0.70	n.d.	0.11	10.76	0.39	41.23	80.10	49.83	0.67
V. champinii	2008	0.42	0.18	4.99	10.55	5.53	1.78	0.84	0.16	0.05	250.53	74.96	3.54	3.72	2.87	27.22	50.62	64.32	30.95	n.d.	n.d.	n.d.	0.24	12.83	0.37	50.78	111.16	40.86	0.37
V. champinii	2009	n.d.	0.08	2.23	50.13	4.15	4.50	0.51	0.07	0.05	35.90	33.80	5.61	4.34	1.69	27.10	18.83	10.33	2.88	n.d.	0.15	n.d.	0.17	10.57	0.62	35.32	10.44	53.09	0.45
V. champinii	2010	n.d.	0.12	2.53	73.85	4.46	5.49	0.77	0.05	0.07	24.09	21.69	5.34	4.42	2.05	12.85	19.07	7.54	4.44	n.d.	0.20	n.d.	0.68	32.38	1.28	48.67	10.93	56.25	0.81
V. champinii	2013	n.d.	0.09	2.87	10.39	3.50	2.50	0.11	0.04	n.d.	12.62	9.58	2.72	1.68	2.52	10.63	8.83	8.32	3.91	0.01	n.d.	n.d.	1.63	38.94	1.43	0.72	n.d.	73.78	1.13
V. cinerea	2008	3.65	0.04	25.48	98.15	12.05	24.72	1.54	3.55	0.34	1299.14	599.89	6.48	8.53	4.71	333.59	301.71	395.09	170.76	n.d.	0.33	2.73	n.d.	12.52	0.62	226.31	53.89	30.11	n.d.
V. cinerea	2010	2.34	0.07	14.98	55.71	7.18	16.05	1.09	2.60	0.22	762.22	436.37	7.58	5.78	3.25	134.98	132.84	241.63	59.50	0.02	0.10	0.22	n.d.	5.86	0.21	206.91	80.98	7.32	n.d.
V. cinerea	2013	4.24	0.06	9.04	26.15	5.28	6.50	0.17	2.00	0.12	354.64	231.65	1.66	0.99	2.18	59.39	53.66	95.77	35.35	n.d.	n.d.	n.d.	n.d.	5.40	0.34	0.81	n.d.	9.59	n.d.
V. cinerea	2014	4.39	n.d.	9.45	54.98	5.45	13.55	0.30	2.84	0.16	398.28	297.41	1.03	1.39	2.72	97.45	83.41	128.17	40.76	n.d.	0.73	n.d.	n.d.	13.85	0.27	3.54	n.d.	45.86	0.02
V. californica	2007	n.d.	0.11	7.74	7.15	9.33	2.17	0.86	2.51	0.17	76.05	89.26	10.97	10.19	9.14	83.33	78.71	111.82	49.09	0.01	0.54	2.75	n.d.	17.01	0.45	514.79	444.78	26.60	n.d.
V. californica	2008	n.d.	0.12	5.69	7.49	10.54	2.68	0.60	1.59	0.04	79.88	63.80	16.07	10.59	6.50	52.88	60.68	67.21	30.01	0.02	0.41	0.18	n.d.	8.29	1.06	246.21	232.14	18.73	0.08
V. californica	2010	n.d.	0.10	9.37	35.57	13.69	11.28	1.65	1.93	0.10	51.41	83.71	34.06	22.12	15.75	57.41	47.47	106.67	36.87	0.01	0.99	3.86	n.d.	15.85	0.39	496.11	367.86	42.07	0.10
V. californica	2013	0.27	0.02	2.62	6.47	5.82	1.90	0.16	0.79	n.d.	35.46	79.32	8.15	7.89	4.61	34.06	13.06	44.65	22.75	n.d.	n.d.	n.d.	0.09	5.07	0.12	1.05	n.d.	8.24	n.d.
V. californica	2014	n.d.	0.02	1.96	5.70	5.47	1.58	0.15	0.99	n.d.	18.03	42.85	11.33	6.46	6.19	23.64	15.55	38.75	9.91	n.d.	n.d.	n.d.	n.d.	5.11	n.d.	0.88	n.d.	7.92	0.01
Pinot noir	2007	1.37	0.31	9.06	38.59	2.95	5.52	0.35	0.50	n.d.	213.98	168.38	2.76	0.80	0.10	10.05	134.03	205.05	114.51	n.d.	0.16	n.d.	3.67	30.14	7.01	0.42	n.d.	56.25	1.43
Pinot noir	2008	1.28	0.04	3.26	33.18	2.47	6.96	0.30	0.37	0.02	218.81	204.13	2.58	1.32	0.03	21.24	91.72	145.75	49.75	n.d.	n.d.	n.d.	0.30	5.27	1.28	0.08	n.d.	21.23	0.13
Pinot noir	2009	1.22	0.05	3.83	52.71	2.63	12.62	0.39	0.35	0.01	175.04	180.41	2.63	2.96	0.05	17.25	102.96	174.69	49.57	n.d.	n.d.	n.d.	0.55	11.16	2.03	0.15	n.d.	21.95	0.25
Pinot noir	2010	2.11	0.17	1.27	101.53	3.53	18.80	0.67	0.53	0.03	326.05	264.08	3.60	3.64	0.19	135.68	131.49	150.00	133.08	n.d.	0.38	n.d.	2.26	25.85	2.29	0.43	n.d.	53.53	0.78
Cabernet Sauvignon	2007	0.71	0.05	2.02	20.82	2.06	4.14	0.58	0.23	n.d.	120.40	78.18	4.80	8.47	0.31	18.75	60.80	118.46	37.76	n.d.	0.23	n.d.	6.12	46.95	6.60	0.89	n.d.	46.51	1.27
Cabernet Sauvignon	2008	0.34	0.04	1.32	8.72	1.50	2.20	0.34	0.25	n.d.	69.98	68.42	3.80	4.92	0.35	13.05	47.21	99.52	27.95	n.d.	n.d.	n.d.	3.49	30.22	4.68	0.51	n.d.	36.41	0.81
Cabernet Sauvignon	2009	0.58	0.03	1.80	21.63	2.12	5.49	0.40	0.23	n.d.	108.41	107.02	4.29	5.69	0.12	19.10	58.97	133.04	28.73	n.d.	0.08	n.d.	1.91	24.67	4.05	0.38	n.d.	21.23	0.48
Cabernet Sauvignon	2010	0.57	0.05	0.99	61.35	2.78	10.52	0.72	0.21	0.03	107.55	76.37	5.78	10.67	0.32	17.80	67.71	120.22	39.97	n.d.	0.15	n.d.	5.01	34.65	5.54	0.75	n.d.	37.31	0.78

Abbreviations: glu, glucoside; cat, catechin; epicat, epicatechin; epigallocat, epigallocatechin; gallocat, gallocatechin; kaemp, kaempferol; que, quercetin; rhamn, rhamnoside; gal, galactoside; isorhamn, isorhamnetin; rut, rutinoside; glucur, glucuronide; n.d., not detected.

Genoytpe	Year	arbutin	*trans*-resveratrol	*cis*-resveratrol	piceatannol	*trans*-piceide	*cis*-piceide	astringin	isorhapontin	*cis*-ε-viniferin	*trans*-ε-viniferin	*cis* + *trans*-ω-viniferin	caff acid + cat cond	pallidol	amp D + quadrangularin A	rutin	taxifolin	myricetin
41B	2008	0.25	0.11	n.d.	0.41	1.35	5.29	2.76	0.28	0.12	1.11	n.d.	1.44	1.54	0.02	1.18	0.57	4.13
41B	2009	1.87	2.39	0.09	1.92	5.37	24.61	7.31	0.65	n.d.	6.31	1.26	2.18	18.06	0.16	1.40	2.19	3.30
41B	2010	0.62	1.90	0.12	2.72	5.73	24.21	6.07	1.54	1.06	4.38	0.92	1.44	7.12	0.11	2.24	0.88	5.59
K5BB	2007	0.66	n.d.	n.d.	0.43	1.32	2.98	4.42	1.08	n.d.	3.32	n.d.	3.04	0.85	n.d.	6.99	0.18	7.88
K5BB	2008	0.59	n.d.	n.d.	0.49	0.60	2.79	2.55	0.47	n.d.	2.00	n.d.	2.06	1.20	n.d.	5.17	0.11	4.64
K5BB	2009	0.99	0.33	0.05	0.80	0.94	3.27	3.69	0.53	n.d.	4.42	0.30	3.60	1.47	n.d.	6.12	0.17	3.71
K5BB	2010	0.85	0.47	0.05	0.53	3.18	5.90	3.01	0.39	n.d.	3.15	0.34	5.65	0.76	0.01	17.93	0.10	7.35
K5BB	2014	0.80	n.d.	n.d.	0.74	1.80	1.88	3.12	0.42	n.d.	3.17	n.d.	8.30	4.92	n.d.	4.55	0.14	n.d.
V. andersonii	2007	0.61	0.06	n.d.	0.17	2.03	4.21	2.51	0.62	n.d.	0.98	n.d.	0.43	1.48	n.d.	2.05	0.21	3.33
V. andersonii	2008	1.55	n.d.	n.d.	0.34	1.88	10.50	6.24	0.70	0.87	1.52	n.d.	1.09	2.09	0.03	2.45	0.51	3.92
V. andersonii	2009	1.40	0.71	0.08	0.84	5.68	13.48	4.53	0.89	0.54	2.74	0.17	0.48	5.47	0.05	1.69	0.54	4.29
V. andersonii	2010	2.04	0.85	0.02	1.27	10.00	33.50	8.49	1.57	1.07	4.86	0.59	0.45	10.90	0.06	2.27	0.30	5.49
V. arizonica Texas	2007	0.74	0.54	n.d.	0.26	3.62	3.33	1.73	1.10	n.d.	3.45	n.d.	1.72	1.49	n.d.	1.00	0.12	8.46
V. arizonica Texas	2008	0.89	0.05	n.d.	0.28	2.10	2.49	3.08	0.85	n.d.	5.24	n.d.	2.65	0.68	0.01	1.88	0.10	6.17
V. arizonica Texas	2009	1.03	0.20	0.01	0.24	2.66	2.49	1.86	0.70	n.d.	3.62	0.12	0.79	0.36	n.d.	0.73	0.08	5.41
V. arizonica Texas	2014	2.02	n.d.	0.37	2.76	4.26	3.86	3.92	1.46	0.28	3.37	0.22	1.07	9.00	0.21	n.d.	0.05	n.d.
V. champinii	2007	0.26	0.87	0.03	0.29	3.07	4.26	2.78	1.39	0.26	6.19	0.26	0.94	13.08	n.d.	2.57	0.12	5.24
V. champinii	2008	0.90	n.d.	n.d.	0.49	1.52	3.07	6.31	1.07	n.d.	2.24	0.20	0.67	2.73	0.01	2.77	0.14	4.47
V. champinii	2009	1.04	0.25	0.06	1.54	6.15	16.61	10.69	2.04	0.26	1.58	0.25	0.65	18.77	0.10	1.57	n.d.	4.78
V. champinii	2010	1.81	1.90	0.15	3.25	13.36	25.28	17.19	2.29	0.38	4.34	0.16	0.45	14.53	0.05	3.67	0.21	6.14
V. champinii	2013	2.27	n.d.	0.46	1.84	1.24	3.03	7.06	0.45	n.d.	0.78	n.d.	1.75	2.70	0.19	2.32	0.04	n.d.
V. cinerea	2008	0.65	1.09	0.01	0.73	4.36	5.38	4.21	0.32	n.d.	3.39	0.55	3.33	2.31	0.01	0.83	6.74	3.62
V. cinerea	2010	0.33	0.09	0.01	0.98	1.77	1.41	2.40	0.22	0.41	2.50	n.d.	1.61	1.26	n.d.	1.51	2.60	4.06
V. cinerea	2013	0.17	n.d.	n.d.	0.52	1.09	0.41	1.23	0.08	n.d.	0.45	n.d.	1.40	0.62	n.d.	n.d.	0.95	n.d.
V. cinerea	2014	0.52	n.d.	n.d.	1.23	2.33	3.69	3.14	0.50	n.d.	0.81	n.d.	9.67	0.95	0.21	n.d.	1.09	n.d.
V. californica	2007	1.32	1.24	0.10	3.98	10.43	11.02	36.95	21.05	n.d.	12.21	1.32	2.71	29.05	0.26	4.25	0.23	15.02
V. californica	2008	5.35	0.20	0.02	1.27	4.06	28.44	25.19	13.27	1.69	3.66	n.d.	1.84	5.68	n.d.	7.07	0.14	10.45
V. californica	2010	9.97	2.89	0.38	7.40	26.50	192.94	66.25	22.81	n.d.	5.03	0.40	4.07	29.86	0.05	10.92	0.08	13.77
V. californica	2013	2.87	n.d.	0.56	4.22	4.68	48.86	15.84	10.81	0.02	0.45	n.d.	3.03	34.50	0.22	n.d.	0.02	n.d.
V. californica	2014	6.89	n.d.	0.54	1.22	6.43	56.91	28.28	22.21	1.10	0.39	n.d.	3.62	51.83	0.77	n.d.	0.07	n.d.
Pinot noir	2007	0.22	0.82	0.06	1.33	7.29	9.15	11.26	1.30	0.28	1.01	0.39	5.80	10.83	1.01	5.83	23.47	n.d.
Pinot noir	2008	0.58	0.12	n.d.	0.45	2.55	10.80	4.89	0.63	0.10	0.36	0.11	3.12	2.77	0.22	1.78	13.27	n.d.
Pinot noir	2009	1.22	0.21	0.05	0.75	3.96	13.60	8.03	1.05	0.04	0.11	0.08	6.24	4.43	0.23	3.14	17.14	n.d.
Pinot noir	2010	0.38	0.88	0.04	0.96	1.79	4.51	1.85	0.24	0.37	0.85	0.25	7.31	6.39	0.67	7.43	14.90	n.d.
Cabernet Sauvignon	2007	0.17	0.15	n.d.	0.10	1.91	1.56	3.56	0.18	0.02	0.22	0.08	4.91	0.21	0.01	4.60	2.58	n.d.
Cabernet Sauvignon	2008	0.09	0.10	n.d.	0.28	0.49	0.72	1.38	0.13	0.12	0.42	0.05	2.79	0.64	0.03	2.71	1.25	n.d.
Cabernet Sauvignon	2009	0.32	0.37	n.d.	0.64	0.41	1.62	1.07	0.08	0.03	0.21	n.d.	3.40	0.59	0.03	1.28	2.05	n.d.
Cabernet Sauvignon	2010	0.46	0.08	n.d.	0.11	1.55	2.07	2.89	0.22	0.02	0.16	n.d.	5.14	0.30	0.03	3.92	2.21	n.d.

Abbreviations: caff acid, caffeic acid; cat cond, catechin condensation product; amp D, ampelosin D; n.d., not detected.

Table S2. Concentrations of anthocyanins in the grape berries (mg/kg FW).

Genotype	Year	dp-3-*O*-glu	cy-3-*O*-glu	pt-3-*O*-glu	pn-3-*O*-glu	mv-3-*O*-glu	dp-3-(6”-acetyl)-*O*-glu	cy-3-(6”-acetyl)-*O*-glu	pt-3-(6”-acetyl)-*O*-glu	pn-3-(6”-acetyl)-*O*-glu	mv-3-(6”-acetyl)-*O*-glu	dp-3-(6”-p-coumaroyl)-*O*-glu	cy-3-(6”-p-coumaroyl)-*O*-glu	pt-3-(6”-p-coumaroyl)-*O*-glu	pn-3-(6”-p-coumaroyl)-*O*-glu	mv-3-(6”-p-coumaroyl)-*O*-glu	dp-3.5-*O*-diglu	cy-3.5-*O*-diglu	pt-3.5-*O*-diglu	pn-3.5-*O*-diglu	mv-3.5-*O*-diglu
41B	2008	116.50	19.42	95.82	29.52	341.90	1.19	0.50	1.89	2.00	6.37	7.04	0.85	5.86	3.74	27.91	n.d.	n.d.	n.d.	n.d.	n.d.
41B	2009	89.39	30.95	67.35	69.66	212.90	0.32	n.d.	0.88	0.84	2.73	3.97	n.d.	2.60	4.60	13.24	n.d.	n.d.	n.d.	n.d.	n.d.
41B	2010	174.45	31.11	153.90	64.36	551.24	0.95	0.77	1.57	2.30	6.30	7.68	n.d.	7.78	5.06	36.16	n.d.	n.d.	n.d.	n.d.	n.d.
K5BB	2007	730.52	336.83	503.60	7.08	319.70	5.92	22.73	5.45	2.45	n.d.	3.80	n.d.	n.d.	n.d.	n.d.	207.83	86.15	418.37	64.69	568.32
K5BB	2008	509.81	249.30	267.98	2.27	127.79	8.98	n.d.	6.00	19.65	n.d.	3.52	n.d.	n.d.	n.d.	n.d.	222.59	100.07	330.70	42.87	251.96
K5BB	2009	585.61	200.26	310.17	5.34	151.83	11.00	11.78	8.20	8.73	n.d.	25.86	n.d.	1.83	n.d.	n.d.	192.76	99.17	286.29	44.63	237.34
K5BB	2010	827.51	469.70	474.88	10.34	241.51	35.00	n.d.	27.95	13.77	6.36	72.49	2.97	28.54	n.d.	11.08	330.41	152.95	557.71	89.64	531.63
K5BB	2014	972.16	365.91	629.74	16.28	338.91	41.09	2.51	32.09	24.17	10.85	57.22	11.12	24.04	n.d.	10.08	175.56	155.17	324.85	96.49	394.38
V. andersonii	2007	166.15	n.d	64.71	4.73	30.30	4.21	0.89	1.62	7.08	0.83	12.03	n.d.	3.74	0.22	2.58	150.10	27.91	173.73	39.82	238.37
V. andersonii	2008	175.01	n.d	61.78	7.92	27.92	2.34	0.77	1.17	4.03	0.65	8.39	n.d.	2.32	0.26	1.78	124.82	39.12	153.58	44.46	214.03
V. andersonii	2009	233.26	n.d	131.27	29.35	71.60	3.80	0.82	2.68	2.89	1.51	8.14	2.23	3.47	0.93	3.83	77.48	39.71	112.10	64.45	228.40
V. andersonii	2010	279.10	n.d	147.88	13.74	90.72	5.51	1.58	4.00	8.34	3.23	17.39	n.d.	7.71	0.90	8.35	161.45	41.99	233.52	70.19	402.32
V. arizona Texas	2007	272.73	5.95	132.40	0.39	48.57	n.d.	n.d.	n.d.	11.17	n.d.	5.83	n.d.	0.43	n.d.	n.d.	358.33	52.94	479.46	43.75	480.35
V. arizona Texas	2008	368.92	13.10	179.11	2.34	64.12	n.d.	n.d.	n.d.	15.04	n.d.	6.55	n.d.	0.72	n.d.	n.d.	505.88	92.87	674.04	78.11	672.05
V. arizona Texas	2009	377.26	28.41	176.18	2.57	57.99	n.d.	27.74	n.d.	15.92	n.d.	16.11	n.d.	2.92	n.d.	n.d.	479.13	99.34	628.02	76.75	576.89
V. arizona Texas	2014	530.30	5.48	273.08	5.83	98.22	n.d.	n.d.	n.d.	23.96	n.d.	30.89	0.73	9.11	n.d.	1.58	629.08	129.02	869.85	110.83	918.80
V. champinii	2007	291.28	n.d	148.11	2.89	59.77	4.06	n.d.	3.13	23.94	n.d.	58.76	n.d.	19.51	0.12	7.92	258.33	32.87	314.95	31.13	338.98
V. champinii	2008	326.24	n.d	152.91	3.57	65.65	3.85	n.d.	3.29	22.57	n.d.	55.90	n.d.	18.02	0.12	7.40	281.09	44.56	356.09	34.08	371.13
V. champinii	2009	171.27	n.d	41.02	2.27	7.20	6.48	2.74	2.22	8.31	n.d.	11.40	n.d.	1.74	0.02	0.17	245.30	91.63	130.14	26.90	79.75
V. champinii	2010	295.98	n.d	62.83	4.96	9.01	5.83	2.23	1.63	9.18	n.d.	13.91	n.d.	1.78	0.10	0.22	470.49	211.94	222.15	58.74	155.43
V. champinii	2013	516.39	18.93	102.42	7.41	13.96	12.59	0.14	2.04	13.51	n.d.	23.15	2.84	1.41	n.d.	n.d.	604.43	244.77	311.50	75.82	86.45
V. cinerea	2008	273.17	269.13	268.24	69.83	336.13	3.78	2.17	5.42	3.69	5.35	18.17	n.d.	11.83	2.03	13.20	n.d.	4.39	7.44	9.04	n.d.
V. cinerea	2010	326.87	354.04	339.55	118.14	537.41	2.83	2.46	5.77	2.75	8.34	16.02	n.d.	11.87	3.57	21.11	n.d.	2.83	n.d.	8.80	n.d.
V. cinerea	2013	603.25	543.54	565.36	186.21	904.55	n.d.	n.d.	0.32	n.d.	2.53	21.46	20.04	10.55	n.d.	21.86	n.d.	n.d.	n.d.	12.94	n.d.
V. cinerea	2014	327.23	442.26	333.73	140.58	539.05	n.d.	n.d.	n.d.	n.d.	0.42	8.39	20.74	5.84	n.d.	10.74	n.d.	n.d.	n.d.	5.27	n.d.
V. californica	2007	2620.86	321.50	1496.71	83.56	1070.26	72.58	6.51	48.29	30.54	23.95	141.28	33.00	52.33	n.d.	37.93	11.90	5.03	42.37	15.51	42.21
V. californica	2008	1572.75	359.50	879.89	64.62	630.77	50.62	3.21	36.07	27.33	17.05	98.86	13.54	33.46	n.d.	22.39	6.81	1.40	25.40	6.72	31.81
V. californica	2010	2371.63	646.71	1254.41	63.69	826.58	70.71	7.61	44.99	28.12	17.85	128.52	25.66	44.59	n.d.	27.56	13.45	5.27	39.76	10.15	n.d.
V. californica	2013	1728.27	661.80	926.29	77.54	624.53	55.68	12.76	35.79	15.20	17.31	85.09	29.15	30.55	n.d.	19.77	6.28	4.72	21.87	9.73	27.16
V. californica	2014	2189.90	1047.68	1239.75	149.05	903.41	68.98	24.06	48.26	30.93	24.95	139.78	64.82	55.88	2.46	41.16	10.51	10.70	27.79	19.64	67.34
Pinot noir	2007	35.56	22.32	52.35	181.30	398.63	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pinot noir	2008	10.98	8.57	11.01	44.15	127.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pinot noir	2009	12.23	7.96	16.51	64.30	220.86	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pinot noir	2010	62.44	25.56	52.56	124.47	267.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cabernet Sauvignon	2007	211.96	50.55	159.46	136.23	638.48	9.29	2.73	8.59	9.20	50.31	3.00	1.88	2.12	5.00	13.29	n.d.	n.d.	n.d.	n.d.	n.d.
Cabernet Sauvignon	2008	69.68	15.92	44.61	48.31	316.10	3.70	1.67	3.79	3.44	31.18	1.76	1.45	1.68	2.18	6.86	n.d.	n.d.	n.d.	n.d.	n.d.
Cabernet Sauvignon	2009	72.71	12.16	45.03	74.08	326.28	13.45	1.09	14.56	18.07	153.74	0.79	0.73	0.29	5.20	27.71	n.d.	n.d.	n.d.	n.d.	n.d.
Cabernet Sauvignon	2010	199.66	33.57	109.22	102.50	648.81	41.56	4.61	35.01	30.04	273.68	5.93	0.89	2.89	10.77	59.59	n.d.	n.d.	n.d.	n.d.	n.d.

Abbreviations: dp, delphinidin; cy, cyanidin; pt, petunidin; pn, peonidin; malvidin, malvinidin; glu, glucoside; diglu, diglucoside; n.d., not detected.

Table S3. Proanthocyanidin subunit composition of the grape samples. The values are expressed as mg/kg FW.

Genotype	Year	procyanidin B1	Procyanidin B2	cat	cat (extension units)	cat (terminal units)	epicat	epicat (extension units)	epicat (terminal units)	gallocat	gallocat (extension units)	gallocat (terminal units)	epigallocat	epigallocat (extension units)	epigallocat (terminal units)	cat + epicat (upper units)	epigallocat (upper units)	epicat gallate (upper units)	%G	mDP
41B	2008	46.61	65.67	376.16	847.40	471.24	177.31	410.79	233.47	1.09	5.45	4.35	5.15	74.82	69.67	697.98	810.52	390.53	20.56	3.44
41B	2009	32.31	99.14	485.41	1320.52	835.10	230.73	505.97	275.24	2.89	9.61	6.72	5.75	79.96	74.21	1078.89	951.71	550.91	21.34	3.17
41B	2010	36.98	106.30	388.41	939.82	551.41	213.48	496.57	283.09	0.43	5.76	5.33	5.62	101.83	96.21	1039.50	843.33	576.70	23.45	3.63
K5BB	2007	7.16	7.85	14.14	59.09	44.95	31.26	38.40	7.14	0.34	3.85	3.52	7.39	58.87	51.49	1676.08	720.77	128.83	5.10	24.58
K5BB	2008	11.50	4.31	41.40	68.38	26.97	25.19	32.08	6.89	0.81	4.11	3.31	7.34	57.65	50.32	676.31	734.41	89.58	5.97	18.15
K5BB	2009	8.17	3.46	18.78	52.94	34.16	22.74	29.95	7.20	0.41	2.61	2.20	6.85	57.91	51.06	637.32	671.59	71.78	5.20	15.59
K5BB	2010	10.73	7.42	24.51	57.34	32.83	33.30	41.01	7.71	1.02	6.23	5.20	9.63	58.47	48.84	1420.50	835.56	122.33	5.14	26.15
K5BB	2014	20.04	15.56	77.19	159.12	81.93	46.28	52.85	6.57	1.14	6.22	5.08	9.55	59.61	50.06	1025.36	787.89	149.83	7.63	14.67
V. andersonii	2007	15.48	7.32	65.24	92.76	27.52	61.36	63.36	2.00	0.82	6.94	6.12	6.65	57.50	50.85	461.92	732.25	35.60	2.89	15.22
V. andersonii	2008	4.50	2.40	7.10	40.93	33.83	11.69	14.17	2.48	0.37	2.89	2.53	5.81	56.85	51.04	482.08	643.15	31.67	2.74	13.87
V. andersonii	2009	4.15	2.65	6.05	39.59	33.54	7.53	9.47	1.94	0.45	2.68	2.23	5.41	56.87	51.46	346.80	650.37	27.55	2.69	12.49
V. andersonii	2010	8.91	3.54	35.08	52.86	17.79	16.39	18.19	1.80	0.52	4.08	3.56	7.27	57.80	50.53	538.94	653.26	35.24	2.87	17.66
V. arizonica Texas	2007	16.22	4.55	113.65	201.83	88.17	44.24	49.11	4.87	0.65	5.83	5.19	6.74	57.53	50.79	1278.37	937.48	87.16	3.78	16.45
V. arizonica Texas	2008	16.09	15.49	42.34	111.82	69.48	33.97	36.46	2.49	2.15	8.90	6.75	9.88	57.96	48.08	1367.91	788.76	91.57	4.07	18.73
V. arizonica Texas	2009	10.29	5.01	93.86	139.20	45.34	40.45	45.20	4.76	0.78	4.61	3.83	6.80	59.16	52.36	1145.47	965.24	74.75	3.42	21.56
V. arizonica Texas	2014	11.51	5.03	93.30	136.81	43.51	36.02	41.69	5.67	2.17	7.16	4.98	10.83	59.03	48.20	1693.86	775.78	80.98	3.17	25.92
V. champinii	2007	18.29	37.52	22.47	79.05	56.57	21.40	56.35	34.96	0.43	3.50	3.07	5.52	70.82	65.31	698.28	687.37	74.94	5.13	10.13
V. champinii	2008	24.18	21.13	26.99	76.79	49.79	27.08	51.13	24.05	0.75	5.73	4.98	6.07	64.74	58.67	989.00	632.74	83.18	4.88	13.40
V. champinii	2009	3.25	2.44	5.96	40.50	34.53	21.68	26.08	4.40	0.35	3.95	3.60	5.53	56.90	51.37	411.91	893.83	29.29	2.19	15.22
V. champinii	2010	7.41	2.83	13.17	42.19	29.02	18.59	25.65	7.06	0.67	3.89	3.23	6.27	57.02	50.74	477.98	780.23	34.50	2.67	15.36
V. champinii	2013	4.60	2.76	8.52	44.45	35.92	7.79	9.91	2.11	0.51	4.39	3.89	5.72	56.84	51.12	375.82	902.49	39.24	2.98	15.16
V. cinerea	2008	36.34	94.96	838.46	2380.39	1541.93	404.56	969.69	565.13	2.03	8.79	6.75	11.17	233.97	222.80	1013.66	822.10	685.45	27.19	2.08
V. cinerea	2010	12.75	97.62	464.18	1162.01	697.83	381.32	1068.55	687.23	0.46	4.85	4.39	8.00	128.68	120.68	844.12	889.45	489.57	22.02	2.47
V. cinerea	2013	19.02	76.28	435.41	1183.50	748.09	271.67	691.00	419.33	0.79	6.04	5.25	6.81	130.48	123.67	859.22	823.00	502.90	23.01	2.69
V. cinerea	2014	13.75	75.80	390.86	1175.31	784.45	317.77	873.94	556.16	0.82	5.71	4.89	7.11	80.31	73.20	886.80	856.19	477.00	21.49	2.56
V. californica	2007	10.55	10.99	18.46	54.65	36.19	35.72	50.99	15.27	0.74	4.44	3.70	7.47	56.82	49.35	712.76	742.30	155.50	9.65	16.41
V. californica	2008	14.08	7.79	34.31	91.64	57.32	44.47	62.70	18.23	0.92	4.49	3.57	12.92	61.64	48.72	749.53	849.31	123.02	7.14	14.47
V. californica	2010	10.22	16.45	19.93	62.16	42.23	54.12	71.58	17.45	0.91	4.97	4.06	16.10	60.55	44.45	847.23	731.64	151.31	8.75	16.99
V. californica	2013	5.64	20.08	32.87	67.53	34.66	91.31	169.08	77.78	0.88	4.92	4.04	11.89	60.46	48.57	617.75	735.48	153.30	10.18	10.13
V. californica	2014	9.31	21.63	34.48	82.38	47.90	99.48	153.76	54.28	0.82	5.90	5.08	18.69	64.39	45.70	589.65	764.89	234.84	14.78	11.39
Pinot noir	2007	35.14	69.78	206.48	488.06	281.58	158.99	293.51	134.52	0.08	6.01	5.93	1.03	34.91	33.88	1714.92	920.58	337.39	11.35	7.52
Pinot noir	2008	31.18	101.88	288.93	528.27	239.35	264.69	476.91	212.22	0.16	2.49	2.34	1.17	51.30	50.12	1745.76	856.26	283.22	9.82	6.72
Pinot noir	2009	39.49	89.81	254.92	497.21	242.29	217.95	377.32	159.37	0.33	5.92	5.59	1.44	47.02	45.58	1362.07	955.66	187.51	7.48	6.53
Pinot noir	2010	49.24	60.83	417.65	1058.44	640.79	294.92	569.28	274.36	0.14	4.54	4.40	1.72	48.60	46.88	1987.75	1077.33	316.47	9.36	4.50
Cabernet Sauvignon	2007	22.92	60.21	153.42	297.44	144.02	95.75	180.89	85.14	0.38	16.17	15.79	2.59	19.93	17.34	1455.53	1597.29	364.72	10.67	14.03
Cabernet Sauvignon	2008	13.96	38.70	79.61	173.12	93.51	70.14	140.21	70.07	0.57	13.87	13.30	1.40	16.19	14.79	1201.92	1131.16	291.25	11.10	14.69
Cabernet Sauvignon	2009	22.00	66.83	166.92	342.52	175.61	132.32	263.86	131.55	0.66	15.77	15.11	1.99	17.49	15.50	1637.61	1587.94	363.25	10.12	11.63
Cabernet Sauvignon	2010	22.74	41.06	124.37	258.41	134.04	75.83	147.92	72.09	1.02	19.57	18.55	2.73	19.57	16.84	1562.40	1723.87	258.96	7.30	15.68

Abbreviations: cat, catechin; epicat, epicatechin; gallocat=gallocatechin; epigallocat, epigallocatechin; %G, percentage of galloylation; mDP, mean degree of polymerisation, n.d., not detected.

Table S4. Concentrations of lipids in the grape berries. The results are expressed as mg/kg FW.

Genotype	Year	DLPC	DOPC	DOPG-Na	uvaol	ceramide	POPC	1-linoleoyl-rac-glycerol	1-oleoyl-rac-glycerol	glyceryl trioleate	glyceryl tripalmitoleate	1-monopalmitoleoyl-rac-glycerol	ergosterol	lanosterol	linoleic acid	behenic acid	linolenic acid	stearic acid	palmitoleic acid	lignoceric acid	erucic acid	arachidic acid	oleic acid + *cis*-vaccenic acid	myristic acid	palmitic acid	myristoleic acid	margaric acid	oleanolic acid	desmosterol	*cis*-11-eicosenoic acid	1.2.3-tripentadecanoylglycerol
41B	2008	35.28	8.71	0.09	6.74	n.d.	0.79	0.08	0.03	33.75	0.01	0.04	0.27	n.d.	1.11	1.74	1.27	2.96	0.49	3.16	0.01	2.32	0.81	0.24	3.29	n.d.	0.04	338.58	n.d.	n.d.	n.d.
41B	2009	65.95	14.06	0.10	8.92	0.02	1.35	n.d.	0.13	17.03	0.06	0.06	1.71	n.d.	10.51	2.77	6.98	7.61	0.96	3.90	0.05	2.77	5.63	0.92	17.49	n.d.	0.19	417.89	0.13	0.19	n.d.
41B	2010	53.60	9.74	0.11	6.59	n.d.	0.34	n.d.	0.03	13.53	n.d.	n.d.	0.06	21.77	3.06	1.80	0.27	4.70	0.03	3.70	0.01	1.45	3.36	0.28	3.75	0.01	0.05	293.12	n.d.	0.10	n.d.
K5BB	2007	37.05	12.00	0.16	21.35	n.d.	0.58	n.d.	0.08	18.21	n.d.	n.d.	0.15	49.30	4.11	1.46	2.05	7.47	0.08	3.86	0.08	2.01	3.91	0.58	4.88	0.04	0.11	542.90	n.d.	0.14	n.d.
K5BB	2008	49.95	12.79	0.08	22.62	n.d.	0.54	n.d.	0.06	9.66	n.d.	n.d.	0.12	38.59	4.71	1.37	0.81	5.86	0.03	3.20	0.02	1.34	4.51	0.31	4.01	0.01	0.08	512.72	n.d.	0.15	n.d.
K5BB	2009	87.88	22.37	0.08	14.58	n.d.	0.40	n.d.	0.04	12.78	n.d.	n.d.	0.06	22.12	4.24	0.95	0.20	5.00	0.03	2.16	0.01	0.95	4.13	0.32	3.48	0.02	0.07	409.43	n.d.	0.14	n.d.
K5BB	2010	67.62	15.05	0.11	17.01	n.d.	0.34	n.d.	0.03	18.98	n.d.	n.d.	0.06	22.03	3.10	1.82	0.27	4.76	0.03	3.75	0.01	1.47	3.40	0.29	3.79	0.01	0.05	457.49	n.d.	0.10	n.d.
K5BB	2014	77.34	12.02	0.41	34.84	0.01	0.69	2.36	0.14	7.48	0.02	n.d.	2.25	n.d.	3.98	4.05	1.01	14.33	0.04	6.38	0.05	3.15	4.84	0.62	7.93	n.d.	0.18	1003.53	n.d.	0.21	0.07
V. andersonii	2007	9.67	3.36	0.05	4.68	n.d.	0.37	0.40	0.09	7.54	n.d.	0.01	0.10	2.67	1.75	0.46	2.93	3.64	0.04	1.58	0.02	0.69	1.21	0.16	2.48	0.01	0.04	210.57	n.d.	0.08	n.d.
V. andersonii	2008	52.40	8.12	0.06	12.63	n.d.	0.23	0.13	0.04	12.31	0.03	n.d.	1.05	n.d.	2.43	1.07	1.71	2.99	0.27	2.02	0.03	0.88	1.31	0.29	5.23	n.d.	0.05	265.12	0.06	0.11	n.d.
V. andersonii	2009	51.22	9.31	0.11	6.64	n.d.	0.38	n.d.	0.04	23.13	n.d.	n.d.	0.03	n.d.	1.69	0.56	0.28	3.05	0.01	0.84	0.02	0.51	2.23	0.15	1.86	n.d.	0.05	247.13	n.d.	0.10	n.d.
V. andersonii	2010	48.85	8.64	0.07	6.46	n.d.	0.31	0.08	0.03	25.47	0.03	n.d.	0.06	n.d.	2.46	0.76	0.89	3.20	0.21	1.57	0.02	0.48	1.61	0.23	3.97	n.d.	0.04	224.70	0.03	0.08	n.d.
V. arizonica Texas	2007	25.22	11.33	0.07	11.65	n.d.	0.71	0.37	0.14	9.72	n.d.	0.01	0.09	n.d.	4.01	0.57	8.92	3.80	0.10	1.07	0.02	0.71	3.21	0.17	3.56	0.01	0.06	413.00	n.d.	0.11	n.d.
V. arizonica Texas	2008	38.96	15.79	0.10	20.34	n.d.	0.47	0.07	0.06	16.48	n.d.	n.d.	0.03	n.d.	1.69	0.61	0.95	3.85	0.03	1.03	0.02	0.65	2.33	0.23	2.47	0.01	0.06	474.86	n.d.	0.08	n.d.
V. arizonica Texas	2009	50.07	19.72	0.11	16.32	n.d.	0.38	n.d.	0.04	14.93	n.d.	n.d.	0.03	n.d.	1.67	0.55	0.28	3.01	0.01	0.83	0.02	0.51	2.21	0.15	1.84	n.d.	0.05	477.85	n.d.	0.10	n.d.
V. arizonica Texas	2014	77.25	14.56	0.35	26.92	n.d.	0.75	1.87	0.11	4.70	0.01	n.d.	2.17	n.d.	3.66	1.95	1.09	13.78	0.03	2.36	0.04	1.39	5.36	0.87	8.80	n.d.	0.31	992.43	n.d.	0.16	0.04
V. champinii	2007	40.12	14.44	1.02	18.30	0.13	2.22	1.57	3.84	5.43	0.10	1.89	2.27	n.d.	26.49	4.41	41.23	23.23	44.04	2.35	0.44	7.50	39.54	17.35	55.85	n.d.	1.06	484.46	0.38	1.82	n.d.
V. champinii	2008	54.13	15.70	0.09	20.41	n.d.	0.60	0.09	0.09	12.29	n.d.	n.d.	1.34	n.d.	9.41	0.93	3.93	5.08	0.23	1.03	0.01	1.08	8.63	0.32	8.24	n.d.	0.10	418.98	n.d.	0.22	n.d.
V. champinii	2009	38.97	15.92	0.06	17.51	n.d.	0.51	n.d.	0.01	11.80	n.d.	n.d.	0.07	n.d.	0.65	0.37	0.18	2.56	0.02	0.62	0.02	0.57	0.63	0.17	1.42	0.01	0.04	643.78	n.d.	0.06	n.d.
V. champinii	2010	28.80	10.72	0.10	11.08	0.01	0.75	0.14	0.11	19.76	0.01	n.d.	0.08	n.d.	8.40	1.35	3.08	7.46	0.76	1.35	0.03	1.61	5.66	0.31	9.98	0.03	0.11	439.51	0.07	0.23	n.d.
V. champinii	2013	22.70	6.70	0.14	28.05	n.d.	0.50	0.75	0.05	10.35	0.01	n.d.	1.06	n.d.	0.67	1.40	1.93	3.17	n.d.	2.13	0.09	1.24	1.01	0.18	1.25	n.d.	0.06	858.64	n.d.	0.10	0.03
V. cinerea	2008	139.86	36.14	0.16	28.54	n.d.	0.59	n.d.	0.06	54.23	n.d.	n.d.	0.06	1.21	4.68	0.78	0.36	7.50	0.03	1.64	0.01	1.35	4.39	0.29	6.29	n.d.	0.17	526.33	n.d.	0.14	n.d.
V. cinerea	2010	111.69	27.13	0.15	18.48	n.d.	0.80	n.d.	0.02	24.36	n.d.	n.d.	0.03	1.77	4.91	0.77	0.67	10.72	0.03	1.68	0.02	1.29	5.64	0.25	7.82	n.d.	0.16	494.19	n.d.	0.17	n.d.
V. cinerea	2013	83.97	13.14	0.41	25.57	n.d.	1.09	4.86	0.13	10.69	0.01	n.d.	0.33	n.d.	5.94	1.39	3.57	16.07	0.03	2.63	0.05	1.80	6.53	0.27	8.35	n.d.	0.20	888.73	n.d.	0.24	0.04
V. cinerea	2014	152.23	23.94	0.57	33.39	n.d.	0.99	4.66	0.19	5.17	0.01	n.d.	0.24	n.d.	7.71	1.80	1.17	14.09	0.03	3.18	0.05	1.89	8.36	0.34	8.10	n.d.	0.24	1025.12	n.d.	0.29	0.03
V. californica	2007	31.88	12.18	0.10	10.96	n.d.	1.23	0.68	0.32	23.45	n.d.	0.03	0.06	11.79	7.96	1.12	30.06	6.11	0.36	2.97	0.03	1.27	4.26	0.26	6.79	n.d.	0.10	589.52	0.03	0.21	n.d.
V. californica	2008	64.16	18.52	0.16	10.52	n.d.	0.50	n.d.	0.04	19.98	n.d.	n.d.	0.09	11.69	4.02	0.92	1.94	5.14	0.03	2.63	0.02	0.67	3.83	0.28	3.68	n.d.	0.06	511.57	n.d.	0.12	n.d.
V. californica	2010	82.24	15.91	0.13	11.47	n.d.	0.36	n.d.	0.03	25.48	n.d.	n.d.	0.03	4.93	2.90	1.23	0.29	5.13	0.04	3.64	0.02	0.63	3.32	0.27	3.96	0.02	0.08	527.56	n.d.	0.19	n.d.
V. californica	2013	94.52	14.40	0.47	17.17	n.d.	0.69	3.29	0.07	12.92	0.01	n.d.	0.18	n.d.	4.39	2.80	3.53	13.48	0.10	5.95	0.07	1.59	4.62	0.32	6.64	n.d.	0.14	1009.50	n.d.	0.26	0.04
V. californica	2014	90.42	13.13	0.69	15.03	n.d.	0.80	2.61	0.15	19.24	0.01	n.d.	0.46	n.d.	7.13	2.62	2.31	21.18	0.15	5.65	0.07	1.93	6.54	0.41	10.13	n.d.	0.24	950.24	n.d.	0.41	0.04
Pinot noir	2007	5.83	4.66	0.11	0.39	n.d.	0.27	0.82	0.27	2.24	n.d.	n.d.	0.34	0.20	4.99	2.78	3.11	5.06	0.54	2.97	0.04	1.28	5.94	0.47	6.73	n.d.	0.14	366.23	n.d.	0.26	n.d.
Pinot noir	2008	4.58	4.24	0.16	0.78	n.d.	0.24	0.27	0.18	3.43	n.d.	n.d.	0.08	1.12	2.71	1.69	0.69	4.76	0.05	1.96	0.04	0.90	6.02	0.03	4.07	n.d.	0.10	75.94	n.d.	0.14	n.d.
Pinot noir	2009	20.33	15.54	0.18	0.41	n.d.	0.14	0.07	0.04	3.67	n.d.	n.d.	0.04	n.d.	0.63	1.69	0.20	2.91	n.d.	1.98	0.04	0.97	1.21	0.25	2.21	n.d.	0.05	396.32	n.d.	0.06	n.d.
Pinot noir	2010	38.83	14.61	0.34	0.46	0.01	0.31	0.42	0.55	4.33	n.d.	n.d.	0.82	0.23	7.80	4.82	1.98	7.97	0.44	4.32	0.09	2.84	11.87	0.59	8.87	n.d.	0.19	448.14	n.d.	0.51	n.d.
Cabernet Sauvignon	2007	4.41	2.97	0.04	0.49	n.d.	0.17	0.26	0.03	2.73	n.d.	n.d.	0.07	0.05	0.68	1.03	0.90	2.46	0.03	3.05	0.03	0.57	0.97	0.45	2.44	n.d.	0.06	540.36	n.d.	0.03	n.d.
Cabernet Sauvignon	2008	4.80	3.59	0.11	0.63	n.d.	0.37	0.25	0.02	2.86	n.d.	n.d.	0.08	0.20	0.56	0.76	0.98	2.79	0.01	3.26	0.03	0.57	0.88	n.d.	2.24	n.d.	0.05	198.51	n.d.	n.d.	n.d.
Cabernet Sauvignon	2009	14.42	5.25	0.16	0.32	n.d.	0.16	0.08	0.01	2.58	n.d.	n.d.	0.05	0.08	0.48	0.99	0.20	1.95	n.d.	3.21	0.03	0.60	0.63	0.27	1.47	n.d.	0.05	229.08	n.d.	n.d.	n.d.
Cabernet Sauvignon	2010	7.98	3.64	0.20	0.58	n.d.	0.15	0.09	0.01	2.78	n.d.	n.d.	0.08	0.15	0.29	0.80	0.19	2.78	n.d.	3.04	0.03	0.53	0.55	0.04	1.86	n.d.	0.04	329.03	n.d.	0.01	n.d.

Abbreviations: DLPC, 1,2-dilinoleoyl-sn-glycero-3-phosphocholine; DOPC, 1,2-dioleoyl-sn-glycero-3-phosphocholine; DOPG-NA, 1,2-Dioleoyl-sn-glycero-3-phospho-rac-(1-glycerol)sodium salt; POPC, 1-Palmitoyl-sn-glycero-3-phosphocholine.

Preface to Chapter 3 and 4

All traditional European grape varieties are susceptible to pests and diseases (downy and powdery mildew), which were introduced to Europe from North America at the end of the 19th century. Consequently, plant protection measures are required to protect grapevine. Nowadays, the continuous use of chemical products in viticulture is a very significant issue in the general attempt to reduce their impact in the environment. Disease tolerant varieties of *V. vinifera*, which combine the resistant traits to fungal diseases and the wine quality of European grapevines (*V. vinifera* L.) represent an interesting and promising choice for a more sustainable viticulture. Today, a huge number of disease tolerant varieties also known as PIWI varieties are available. Some studies regarding the chemical characterisation of these varieties have been previously reported in the literature although they mainly focused on the study of a limited number of varieties grown in a selected area and on the analysis of one data set of compounds.

In this study, a wide selection of some promising mildew tolerant varieties in terms of quality grown at two experimental fields, in Italy and Germany, were taken into account. The main characteristics of the disease tolerant varieties studied are discussed as follows and summarised in Table 1.

Regent is a cross of Diana and Chambourcin, originated in 1967. It was registered as *Vitis vinifera* variety in Germany in 1999 representing the pioneer variety among the PIWIs. This variety is characterised by medium-high resistance against fungal diseases. The deep red colour of this wine is very intensive and the smell resembles dried plums and sour cherries. This wine can be compared to Merlot.

Rondo is a variety produced by crossing Zarya Severa and Saint Laurent. It is an early ripening variety which presents high resistance to frost and downy mildew but low resistance towards powdery mildew. This variety produces a wine with an intense and deep ruby colour. Its taste is full-bodied while the aroma resembles tones of forest and red fruits (dark cherries, blackberries and raspberries).

Prior derives from the crossing of (Joannes Seyve 234-16 x Pinot noir) with [Merzling x (Zarya Severa x St. Laurent)], developed in 1987. Since the high resistance to main fungal diseases (downy mildew, powdery mildew and grey mould), this variety can be considered as a highly resistant one. It produces wines with fruitiness notes and strong colour. The variety is known to have good yield, producing red juice with deep colour.

Bolero is the result of crossing Geisenheim 6427-5 with Chancellor and shows good resistance to fungal diseases, high yield potential and early ripening. This variety produces a wine of deep Garnet-red colour with a soft tannin structure and ripe red woody fruit notes.

Nero is a crossing between Eger (Médoc Noir x Perle von Csaba) and (S.V. 12375 X Gárdonyi Geza), developed in Hungary. This is an early-ripening variety with good resistance to diseases and winter frost. The resulting wine is soft with a not deep red colour.

Accent is a cross between Kolor and Chancellor with a good tolerance against botrytis. The wine produced from this variety is characterised by deep red colour, high tannin content and vanilla notes.

Cabernet Carbon is a disease tolerant variety produced from the crossing between Cabernet Sauvignon and [Merzling x (Zarya Severa x St. Laurent)], originated in 1983. It presents high and low resistance to downy and powdery mildew. This variety also is very resistant to grey mould (*Botrytis cinerea*). The wine is a kind of intense and spicy Cabernet with a strong colour that requires maturation in durmast barrels.

Cabernet Cortis derives from a cross between Cabernet Sauvignon and [Merzling x (Zarya Severa x Muscat Ottonel)], developed in 1982. It is highly resistance to both downy and powdery mildew. This variety produces wines with a spicy intense Cabernet-type flavour.

Bianca is a variety obtained by crossing Seyve Villard 12375 Eger 2 with Bouvier. It is characterised by high resistance to winter frost and also good resistance to both downy and powdery mildew. Bianca is slowly susceptible to grey mould but it is sensitive to drought and flower set. This variety produces light and neutral wine similar to Gudetel. The ripe wine is full-bodied and harmonious which resembles Pinot Blanc.

Bronner is a cross between Merzling and (Zarya Severa x Saint Laurent), developed in 1975. This variety shows high and good resistance to downy mildew and powdery mildew, respectively. Furthermore, the susceptibility to grey mould is very low. This variety produces a wine with a complex aroma reminiscent the fragrance of apples, honey, grapefruit, pears and pineapple. The wine has a good structure which resembles a mix of characteristics between Pinot Blanc and Pinot Gris.

Muscaris derives from a cross between [Merzling x (Zarya Severa x Muscat Ottonel)] and Moscato Giallo. This variety produces a wine with a strong aroma, taste reminiscent of Muscat table grapes and intense acidity.

Phoenix is a cross of Bacchus and Seyve Villard 12-375, generated in 1964. The wine presents a fruity bouquet reminiscent of Muscat, which it combines with a fresh acid trait.

Helios is a variety generated from the crossing between Merzling and (Seyve Villard 12-481 x Müller Thurgau). It is very resistant to grey mould, downy and powdery mildew. This variety produces a wine with a characteristic aroma which is reminiscent of a fruity honey and nuts. The ripe wine presents a soft and elegant structure.

Johanniter is the result of crossing Weisser Riesling and (Seyve Villard 12-481 x (Pinot Gris x Gutedel). This variety is characterised by high resistance to both downy and powdery mildew. The wine presents a light and fruity aroma reminiscent of Riesling aroma bouquet.

Solaris is the result of crossing Merzling and (Zarya Severa x Muscat Ottonel), obtained in 1975. This variety shows high resistance towards fungal infections and also to frost. This variety produces sweet wines due to its naturally high levels of sugar. The aroma bouquet is fruity and elegant which is reminiscent of pineapple and hazelnut.

Souvignier Gris is a variety generated from the crossing between Cabernet Sauvignon and [Merzling x (Zarya Severa x Saint Laurent)], originated in 1983.It shows high resistance to downy mildew and good resistance to powdery mildew. The wine aroma is light fruity which presents small amounts of tannins reminiscent of Cabernet Sauvignon.

Jasmine derives from a cross between Bianca and SK 77-4/5.

Table 1 Names, pedigrees and origin of the disease tolerant varieties considered.

Variety	Colour of berry	Pedigree	Origin
Accent	black	Kolor x Chancellor[a]	Germany (Geisenheim)
Bolero	black	Geisenheim 6427-5 x Chancellor[a]	Germany (Geisenheim)
Cabernet Cortis	black	Cabernet Sauvignon x [Merzling[b] x (Zarya Severa[c] x Muscat Ottonel)]	Germany (Freiburg)
Cabernet Carbon	black	Cabernet Sauvignon [Merzling[b] x (Zarya Severa[c] x Saint Laurent)]	Germany (Freiburg)
Nero	black	Eger 2 x Gardonyi Geza	Hungary (Kölyuktetö)
Prior	black	(Joannes Seyve 234-16 x Pinot noir) x [Merzling[b] x (Zarya Severa[c] x Saint	Germany (Freiburg)
Regent	black	Diana[d] x Chambourcin[e]	Germany (Geilweilerhof)
Rondo	black	Zarya Severa[c] x Saint Laurent	Germany (Geisenheim)
Bianca	white	Seyve Villard 12375 Eger 2 x Bouvier	Hungary (Eger)
Bronner	white	Merzling[b] x (Zarya Severa[c] x Saint Laurent)	Germany (Freiburg)
Helios	white	Merzlingb x (Seyve Villard 12-481 x Müller Thurgau)	Germany (Freiburg)
Jasmine	white	Bianca x SK 77-4/5	Japan
Johanniter	white	Weisser Riesling x (Seyve Villard 12-481 x (Pinot gris x Gutedel)	Germany (Freiburg)
Muscaris	white	[Merzling[b] x (Zarya Severa[d] x Muscat Ottonel)] x Moscato Giallo	Germany (Freiburg)
Phoenix	white	Bacchus x Seyve Villard 12-375	Germany (Geilweilerhof)
Solaris	white	Merzling[b] x (Zarya Severa[c] x Muscat Ottonel)	Germany (Freiburg)
Souvignier Gris	pink	Cabernet Sauvignon x [Merzling[b] x (Zarya Severa[c] x Saint Laurent)]	Germany (Freiburg)

[a] Chancellor= Seibel 5163 x Seibel 880

[b] Merzling= Seyve Villard 5276 x (Riesling x Pinot Gris)

[c] Zarya Severa= Seyanets Malengra x *Vitis amurensis*

[d] Diana= Silvaner x Müller-Thurgau

[e] Chambourcin= Seyve Villard 12-417 x Seibel 7053

Grape reference varieties, chosen among *V. vinifera* cultivars of recognized high quality, were considered as well. The red varieties selected were Pinot Noir, Cabernet Sauvignon and Teroldego, while the white ones included Chardonnay, Riesling and Moscato Giallo. Both grapes and wines made from disease tolerant varieties were analysed in order to provide a detailed survey of the main chemical compounds influencing their quality traits.

In chapter 3 the composition of grapes from disease tolerant varieties grown in Italy and Germany in 2013 vintage in terms of phenols and lipids was studied. A targeted strategy by means of LC-MS was used for the investigation of these compounds. The results obtained showed a clear difference among the varieties in the total amount of anthocyanins and phenolic compounds as well as a certain diversity as regards the lipid profile.

In chapter 4, the non-volatile and volatile composition of 92 wines obtained from the same disease tolerant varieties for 2013, 2015 and 2016 vintages were investigated. The profile of non-volatile compounds was studied using different techniques: UHPLC-MS/MS methods to study the phenolic composition (including phenols, anthocyanins and tannins), AAS method to analyse the mineral profile and, NMR and FTIR analyses to investigate different parameters (sugars, acids, alcohols, fermentation products, total acidity, volatile acidity, etc.). The volatile profile was analysed by combining GC-MS and HS-GC-PFPD methods. The findings of this study contribute to characterise the chemical composition of wine made by different PIWI varieties identifying their most peculiar aspects. Finally, the results showed the strong influence of the vintage on the chemical composition of wine and the stability of the metabolomic profile of wines produced from grape varieties grown in different vineyard locations.

Information and images were retrieved from the following resources:

Morandell, W. (2014). *Vitigni resistenti - Lieselehof.*

Vitis International Variety Catalogue. (2017). http://www.vivc.de/ Accessed 30 September 2017.

PIWI International. (2017). http://www.piwi-international.de/it/ Accessed 10 October 2017.

CHAPTER 3

Study of the composition of grape from disease tolerant varieties

This chapter is part of a manuscript in preparation.

3.1 Introduction

Grapes are consumed as both fresh and processed products, such as wine, jam, juice, jelly, dried grapes and vinegar. The quality of grape berry is given by its metabolic composition which includes a wide range of compounds. Polyphenols are quantitatively and qualitatively the most abundant grape compounds (Fig. 1). It has been demonstrated that they play important roles in plant metabolism and have interesting beneficial health properties directly connected to the so-called "French paradox". This concept, first explained in 1992, relies on epidemiological studies performed in France which showed a relatively low incidence of coronary heart disease (CHD) despite a diet rich in saturated fats. The regular consumption of red wine by the Mediterranean population was considered one of the main factors responsible for this phenomenon (Renaud & De Lorgeril, 1992).

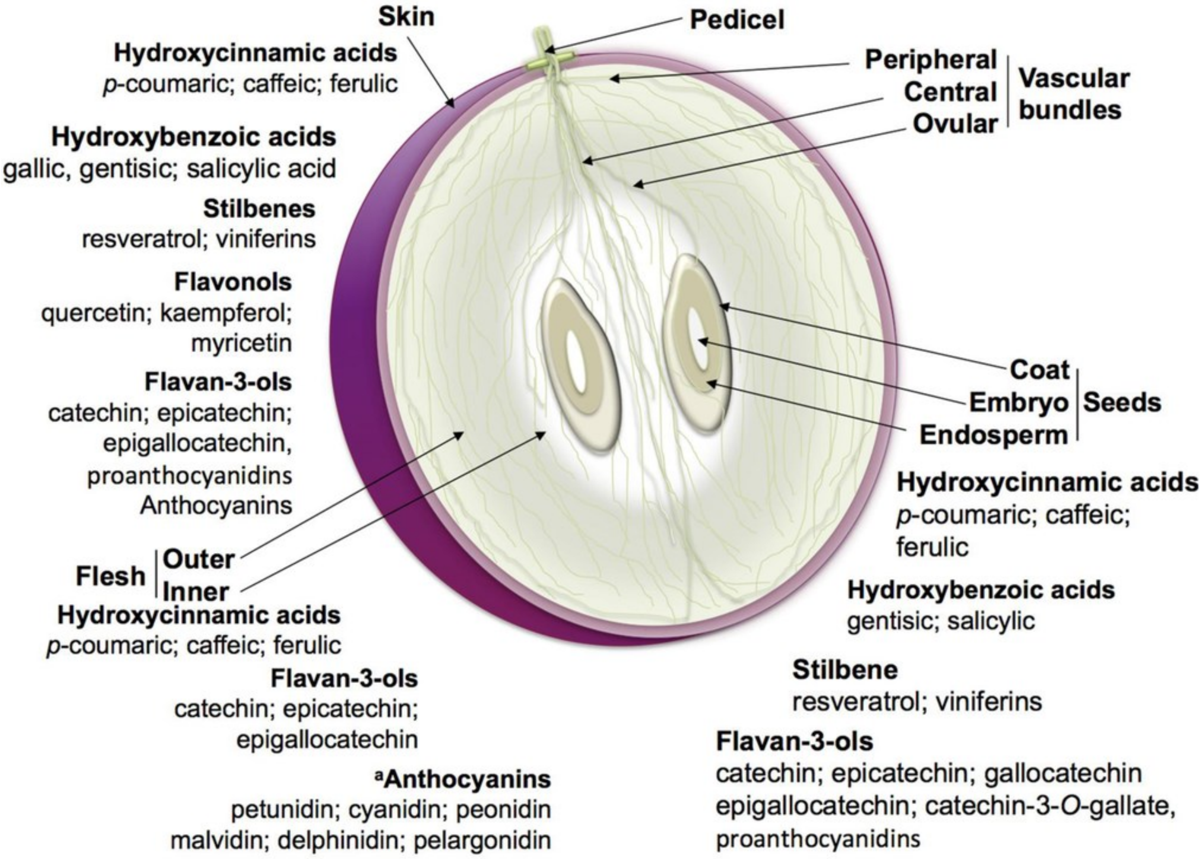


Figure 1. Schematic structure of a ripe grape berry and pattern phenolics biosynthesis distribution between several organs and tissues (image from Teixeira, Eiras-Dias, Castellarin, & Gerós, 2013).

All polyphenols are synthesised from the amino acid phenylalanine through the phenylpropanoid pathway and their composition is highly influenced by the grape variety, environmental factors and cultural practices (Sparvoli et al., 1994). According to their chemical structure, they can be classified in flavonoid and non-flavonoid compounds (Adams, 2006). Flavonoids represent the largest group of phenolic compounds which mainly include anthocyanins, flavonols and flavan-3-ols. Anthocyanins are the pigments responsible for the colour of red grapes which are mainly present in the skin but can also be accumulated in the pulp of "teinturier" varieties. They exert a multitude of biological functions including antioxidant, anti-inflammatory, antidiabetic and antiobesity activities as well as protection against both heart disease and cancer (Pojer, Mattivi, Johnson, & Stockley, 2013). Anthocyanins can also be utilised as natural colourants in order to replace synthetic ones in food, nutraceutical and pharmaceutical industries (Flamini, Mattivi, De Rosso, Arapitsas, & Bavaresco, 2013). The anthocyanin profile is relatively stable for each cultivar and this is of great importance for chemotaxonomic purposes (Mattivi, Guzzon, Vrhovsek, Stefanini, & Velasco, 2006). In general, *V. vinifera* varieties contain only anthocyanins 3-*O*-monoglucosides whereas wild genotypes and disease tolerant varieties also include 3,5-*O*-diglucoside anthocyanins. This difference is attributed to two disruptive mutations that yield inactive the enzyme 5-*O*-glucosyltransferase (5GT) which, as a consequence, is not able to perform 5-glycosylation (Jánváry et al., 2009). Hence, diglucosides are used as markers to distinguish *V. vinifera* varieties from non-*V. vinifera* varieties and their hybrids.

Flavonols are the second most abundant flavonoids in grapes which are primarily present as glycosides in grape skins but they can also occur as aglycones in wines. They are involved in UV screening and their biosynthesis is light-dependent. White and red grape varieties accumulate kaempferol, quercetin and isorhamnetin derivatives while red grapes also contain myricetin, laricitrin and syringetin (Castillo-Muñoz, Goméz-Alonso, García-Romero, & Hermosín-Gutiérrez, 2010). The flavonol profile strongly depends on grape cultivars but quercetin-3-*O*-glucoside and quercetin-3-*O*-glucuronide are the main compounds found in grape berries (Zhu, Zhang, & Lu, 2012). They are also important bioactive compounds since they have been identified as the best phenolics with antioxidant activity in wine, especially in white one (Montoro, Braca, Pizza, & De Tommasi, 2005).

Flavan-3-ols comprise the major constitutive units of proanthocyanidins or also known as condensed tannins. Catechin, epicatechin, gallocatechin and epigallocatechin are the main flavan-3-ols found in grapes (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006). Proanthocyanidins are mainly located in the grape seeds, then in the skins and very little in the pulp. These compounds are responsible for the grape skin organoleptic properties such as astringency and bitterness in grape skin or wine (Teixeira, Eiras-Dias, Castellarin, & Gerós, 2013). It has also been reported that flavan-3-ols exhibit health beneficial effects by acting as anticarcinogenic, cardioprotective, antimicrobial, antiviral, and neuro-protective agents (Aron & Kennedy, 2008). The non-flavonoid group consists of hydroxybenzoic and hydroxycinnamic acids, and stilbenes which are generally present in low concentrations in grape berries (Kennedy, Saucier, & Glories, 2006). Among non-flavonoids, stilbenes have received more attention since they are considered to be promising molecules with positive effects on human health and the main responsible for the benefits of drinking wine. Recent studies showed that these compounds, and in particular resveratrol, are characterised by antioxidant, anti-inflammatory and anticarcinogenic properties (Flamini et al., 2013; Jeandet et al., 2010). Furthermore, stilbenes are vine phytoalexins produced in response to biotic stresses, such as the grape pathogens *Plasmopara viticola* and *Botrytis cinerea,* or abiotic stresses (Pedras, Yaya, Glawischnig, & Links, 2011; Pezet, Gindro, Viret, & Spring, 2004).

Another important group of compounds is represented by lipids, which are essential metabolites of all plants. Lipids are actively involved in many important cellular functions: they are the major structural components of cell membranes, constitute a source of high energy value and participate in signalling events (Fahy, Cotter, Sud, & Subramaniam, 2011). Besides, they are important biomolecules contributing to the nutritional value of foods. In grape berry, lipids make up a portion of the volatile compounds and therefore they are implicated in determining the characteristic aroma of grapes as well as influencing the aromatic composition of wines by either binding some odour-active compounds or being active-compounds themselves (Higgins & Peng, 1976; Serot, Prost, Visan, & Burcea, 2001). Previous studies have shown that lipids are also important factors in oenology since they can limit the production of excessive amounts of acetic acid and their availability can affect yeast metabolism (Delfini, & Cervetti, 1991; Ribéreau-Gayon et al., 2006).

In recent years, there has been an increasing interest into disease tolerant varieties of *V. vinifera* due to their high resistance to fungal diseases as well as good ability to grow in many adverse climates and soils. Although these varieties could have a beneficial impact on the environment by reducing the application of plant protection products, the bad reputation of the first hybrids which showed good resistance but low wine quality, prevent their spreading and use for the production of high quality wines. Thus, the characterisation of the chemical composition of grapes from new disease tolerant varieties is important also considering that grape quality is a an essential prerequisite for wine quality. Some research into the phenolic composition of grapes from PIWI varieties with regards to the anthocyanin profile has been reported in the literature (Ehrhardt, Arapitsas, Stefanini, Flick, & Mattivi, 2014; Kapusta, Cebulak, & Oszmiański, 2017; Samoticha, Wojdyło, & Golis, 2017). On the contrary, to the best of our knowledge the lipid composition of grapes from disease tolerant varieties has not been yet investigated.

The present study aimed to investigate the phenolic and lipid composition of both red and white grapes of some promising new disease tolerant varieties cultivated at two experimental vineyards, in Italy and Germany, during the 2013 vintage. Research results would promote their use for the production of high quality wines and provide for future grapevine breeding programs.

3.2 Materials and Methods

3.2.1 Reagents

Methanol (LC-MS and HPLC grade), acetonitrile (LC-MS grade), 2-propanol and chloroform were obtained from Sigma-Aldrich (Milan, Italy). Formic acid and ammonium formate additives for LC-MS were purchased from Fluka Sigma-Aldrich (Milan, Italy). Water was purified in a Milli-Q water purification system (Millipore, Billerica, MA, USA). Chemical standards were purchased or isolated as reported by the corresponding method used for the analysis of each class of metabolites.

3.2.2 Grape samples

In this work, fourteen disease tolerant varieties were evaluated and compared with six high quality *V. vinifera* varieties (Table 1). Grape berries were harvested at technological maturity from grapevines cultivated at the experimental vineyards in San Michele all'Adige (Trento, Italy) and Geisenheim (Rheingau, Germany) during the season 2013. The grape samples collected in Italy were directly frozen and stored at -20 °C, whereas those from Germany were transported to Italy within 24 h and then stored at -20 °C. Then, grape berries were ground under liquid nitrogen using an analytical mill (IKA, Germany) to obtain a frozen powder.

Table 1. Grape variety, country of cultivation of the samples investigated in this study.

Variety	Acronym	Colour	Type	Country of cultivation
Regent	Re	red	PIWI	Germany
Cabernet Cortis	CCo	red	PIWI	Italy, Germany
Cabernet Carbon	CCa	red	PIWI	Italy
Prior	Pr	red	PIWI	Italy, Germany
Accent	Ac	red	PIWI	Germany
Rondo	Rn	red	PIWI	Germany
Nero	Ne	red	PIWI	Italy, Germany
Pinot noir	PN	red	reference	Italy
Cabernet Sauvignon	CS	red	reference	Italy
Teroldego	Te	red	reference	Italy
Johanniter	Jo	white	PIWI	Italy, Germany
Helios	He	white	PIWI	Italy
Muscaris	Mu	white	PIWI	Italy
Bronner	Br	white	PIWI	Italy, Germany
Solaris	So	white	PIWI	Germany
Phoenix	Ph	white	PIWI	Italy, Germany
Bianca	Bi	white	PIWI	Italy
Chardonnay	Ch	white	reference	Italy, Germany
Riesling	Ri	white	reference	Italy
Moscato Giallo	MG	white	reference	Italy, Germany

3.2.3 Extraction procedures

3.2.3.1 Phenolic compounds

Two grams of grape powder from each sample were weighed into 20 mL sealed glass vials. Then, 4 mL of a solvent mixture of water, methanol and chloroform (20:40:40 v/v) and 40 µL of internal standard (gentisic and rosmarinic acids 500 mg/L) were added. Samples were shaken for 15 min at room temperature using an orbital shaker and then centrifuged at 3000 rpm at 4 °C for 10 min. The upper aqueous phase was collected and transferred into a 10 mL flask. Extraction was repeated, adding 2.4 mL of a solvent mixture of water and chloroform (1:2 v/v) with shaking and centrifugation as before. The two supernatants from the two extractions were combined in the same flask, brought up to 10 mL and filtered through a 0.22 μm filter into an LC-MS vial (Vrhovsek et al., 2012).

3.2.3.2 Anthocyanins

20 frozen berries from each sample were weighed and peeled with forceps. Successively, both skins and pulps were separately subjected to extraction in a 250 mL round-bottom flask for 12 h in 100 mL of methanol. After the first extraction, the extract was collected and a second extraction was carried out, adding 50 mL of methanol for 2 h. Both methanolic extracts were combined in the same flask. The samples were evaporated using a rotavapor, brought to a final volume of 50 mL, filtered through a 0.22 μm filter into an LC-MS vial and analysed (Mattivi et al., 2006).

3.2.3.3 Lipids

A precise amount of 0.555 g of grape powder from each sample was weighed into 20 mL sealed glass vials and 1.5 mL of chloroform was added. Samples were vortexed for 30 s, then 3 mL of chloroform containing butylated hydroxytoluene (BHT 50 mg/L) and 10 μL of internal standard (IS) (docosahexaenoic acid 100 μg/mL) were added. The extraction mixture was shaken for 60 min at room temperature using an orbital shaker and 1.25 mL of Milli-Q water was added. After 10 min, the samples were centrifuged at 3600 rpm at 4 °C for 10 min. The total lower phase was collected in LC-MS vials and the samples were then subjected to a second extraction by adding 2 mL of a mixture of chloroform, methanol and water (86:14:1 v/v/v) and centrifuged as before. The two fractions were collected in the same vial, evaporated to dryness under N_2 and 300 μL of acetonitrile, isopropanol and water (65:30:5 v/v/v) containing the IS (cholesterol 1 μg/mL) were added before analysis. Each sample was diluted 1:100 with acetonitrile, isopropanol and water (65:30:5 v/v/v) containing cholesterol and reinjected, in order to allow quantification of the most abundant lipids (Della Corte et al., 2015).

3.2.4 Metabolite analysis by UHPLC-MS/MS

3.2.4.1 Analysis of phenolic compounds

Analysis of phenolic compounds was performed with a Waters Acquity UPLC system (Milford, MA, USA) coupled to a Xevo TQ MS System (Waters, UK), based on a method previously described by Vrhovsek et al. (2012). Samples were kept at 6 °C and injected (2 μL) on a Waters Acquity HSS T3 column (1.8 μm, 100 × 2.1 mm; Milford, MA), thermostated at 40 °C. The flow rate was 0.4 mL/min. The solvents were as follows: solvent A (0.1% formic acid in water), solvent B (0.1% formic acid in acetonitrile). The gradient profile was set as follows: 0 min, 5% B; from 0 to 3 min, linear to 20% B; from 3 to 4.3 min, isocratic 20% B; from 4.3 to 9 min, linear to 45% B; from 9 to 11 min, linear to 100% B; from 11 to 13 min, wash at 100% B and from 13.01 to 15 min, back to the initial conditions of 5% B.

The column eluent was directed to the mass spectrometer and analyte detection was performed using multiple reaction monitoring (MRM). Electrospray negative or positive ionisation mode (ESI) was applied with the parameters in the source set as follows: capillary voltage at −2.5 kV or 3.5 kV. Block and desolvation temperatures were set at 150 °C and 500 °C respectively. Cone gas flow was 50 L/h and desolvation gas flow was 800 L/h. Unit resolution was applied to each quadrupole. The two most abundant fragments to use as quantifier and qualifier were identified for each compound. Phenols concentrations were calculated in milligrams per kilogram (mg/kg) of fresh weight (FW) by means of calibration curves and using gentisic and rosmarinic acids as internal standards.

3.2.4.2 Analysis of anthocyanins

Anthocyanins were identified and quantified as described by Arapitsas et al. (2012). Ultraperformance liquid chromatography was carried out on a Waters Acquity UPLC system (Milford, MA, USA). All samples were analysed on a reverse phase (RP) Acquity UPLC BEH C18, 1.7 μm, 2.1 × 150 mm column (Waters), protected with an Acquity UPLC BEH C18, 1.7 μm, 2.1 × 5 mm precolumn (Waters). Flow rate was 0.3 mL/min and temperature of column was set at 40 ºC. Eluent A was 5% formic acid in water and eluent B was 5% formic acid in methanol. The multistep linear gradient was applied as follows: from 95 to 60% of A for the first 4 min, from 60 to 45% A from 4 to 9 min, from 45 to 5% A from 9 to 11 min, and an isocratic hold for 3 min to clean the column. The equilibration time was 4 min, and the injection volume was 2 µL. Samples were kept at 6 °C during the analysis.

Mass spectrometry detection was performed on a Xevo TQ MS System (Waters, UK) equipped with an electrospray (ESI) source. MS conditions were the same as reported above (Vrhovsek et al., 2012). LM resolutions were 2.55 and 2.80 for analysers 1 and 2, respectively, whereas HM resolutions were 14.90 and 15.00 LM for analysers 1 and 2, respectively. Ion energy for analyser 2 was 1.0. Anthocyanins were expressed as mg/kg FW.

3.2.4.3 Analysis of lipids

Quantitative analysis of lipids was carried out on a UHPLC Dionex 3000 (Thermo Fisher Scientific, Germany) connected to an API 5500 triple-quadrupole mass spectrometer (Applied Biosystems/MDS Sciex, Toronto, Canada) equipped with an electrospray source. Separation was performed with a reverse phase column Ascentis Express C18 (15 cm x 2.1 mm, 2.7 µm; Sigma, Italy. Column temperature was set at 55 °C using a Peltier effect column oven (Dionex Thermo Fisher Scientific, Germany). The solvents were: solvent A (acetonitrile 40% in water, ammonium formate 10 mM and formic acid 0.1%) and solvent B (isopropanol 90%, acetonitrile 10%, ammonium formate 10 mM and formic acid 0.1%). The multistep linear gradient profile was as follows: from 0 to 1.5 min isocratic elution with 32% B; from 1.5 to 4 min increase to 45% B, then to 52% B in 1 min, to 58% B in 3 min, to 66% B in 3 min, to 70% B in 3 min, to 75% B in 4 min, to 97% B in 3 min, then 97% B was maintained for 4 min. From 25.0 to 25.1 min solvent B was decreased to 32% and then maintained for another 4.9 min for column re-equilibration. The flow rate was 0.26 mL/min and the samples were maintained at 10 °C throughout the analysis.

The electrospray ionisation was set at 5.5 kV for positive mode and -4.5 kV for negative mode. The source temperature was set at 250 °C; the nebulizer gas (Gas 1) and heater gas (Gas 2) were set at 40 and 20 psi respectively. The target lipids were detected under multiple reaction monitoring (MRM) mode and identified on the basis of their reference standard, retention time and, qualifier and quantifier ion. Quantification was carried out using calibration curves for each analyte and data were expressed as mg/kg FW after normalisation on the basis of the internal standard docosahexaenoic acid (Della Corte et al., 2015).

3.3 Results and Discussion

3.3.1 Phenolic compounds

The phenolic compounds identified and detected are presented in Table S1. The sum of all the detected individual phenols varied among the varieties under study (Fig. 2). Within the red grape samples, Pinot noir and Cabernet Carbon had the highest mean total phenolic levels (950.01 mg/kg FW and 852.59 mg/kg FW, respectively) (Fig. 2a). On the other hand, Bianca (955.10 mg/kg FW) was the white variety with the highest amount of total phenols (Fig. 2b). Considering the varieties cultivated both in Italy and Germany, the grape samples from Germany were generally richer in phenols than those from Italy as also observed in a previous study (Ehrhardt et al., 2014). As compared to this study, we found that the amount of phenolic compounds was lower for the majority of the varieties investigated.

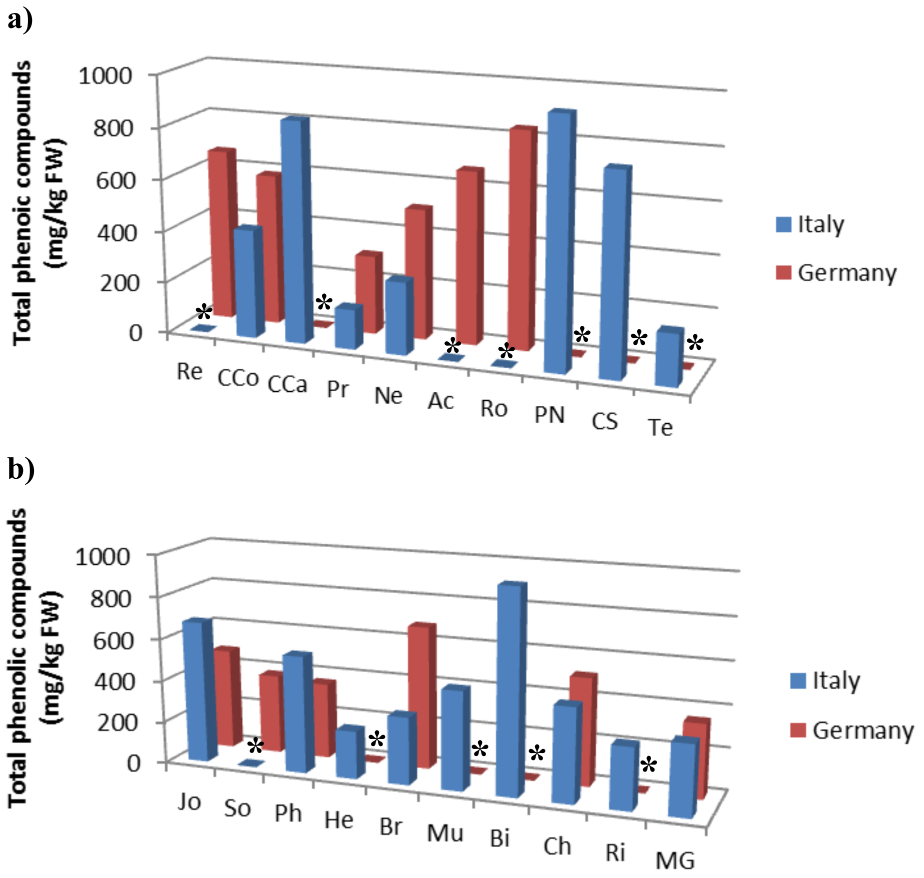


Figure 2. Total phenols in red (a) and white (b) grape varieties. Asterisk marks the grape samples not analysed in this study (See Table 1 for details and for variety acronyms).

The phenolic compounds detected included 6 groups: phenolic acids, dihydrochalcones, flavones, flavonols, flavan-3-ols and stilbenes. Eight compounds belonging to phenolic acids were identified. Total phenolic acids ranged from 6.21 to 24.95 mg/kg FW and from 7.34 to 41.12 mg/kg FW in red and white varieties, respectively. Caftaric acid and gallic acids were the most common compounds in the varieties studied. The other phenolic acids such as *p*-hydroxybenzoic, fertaric and *trans*-coutaric were detected in all the samples. On the other hand, vanillic and ellagic acid, and methyl gallate were not detected in all the varieties and occurred in small amounts. Average amount of phenolic acids was found to be higher in white varieties than in red ones in accordance to Samoticha, Wojdylo, & Golis (2017). Among the phenolic compounds investigated, flavan-3-ols represented the most dominant fraction as previously reported (Samoticha et al., 2017). Nine compounds including procyanidin B1, B2 + B4, B3, catechin, epicatechin, epigallocatechin, epigallocatechin gallate and epicatechin gallate were identified and detected. Total flavan-3-ols ranged from 104.45 to 891.61 mg/kg FW and from 153.41 to 850.78 mg/kg FW in red and white varieties, respectively. Catechin and epicatechin were the most abundant flavan-3-ols in all the grape samples. Rondo (325.80 mg/kg FW) and Cabernet Carbon (261.74 mg/kg) were the red varieties with the highest average amount of catechin and epicatechin, respectively. Among the white varieties studied, Bianca contained the highest amount of both catechin and epicatechin which accounted for 408.32 and 206.82 mg/kg FW, respectively. Epigallocatechin gallate was found in the lowest amount than the other flavan-3-ols.

As regards the group of flavonols, Cabernet Sauvignon and Bianca were found to be the varieties with the highest mean total concentrations which accounted for 186.73 and 83.14 mg/kg FW, respectively. Quercetin derivatives (quercetin 3-*O*-glucoside + quercetin 3-*O*-galactoside, quercetin 3-*O*-glucuronide) were the most abundant metabolites in both PIWI and *V. vinifera* varieties. These results are in agreement with those reported by Wojdylo et al. (2018) since in the two disease tolerant varieties considered (Rondo and Regent), flavonols were mainly quercetin derivatives with the exception of quercetin-3-*O*-glucoside which was not quantified. The other flavonols were present in small amounts and were found only in some varieties. Rutin was detected in all the grape samples but in although in minor amounts. Syringetin-3-*O*-glucoside and syringetin-3-*O*-galactoside were detected in all red grape samples and in one white sample (Moscato Giallo from Italy). These results are in agreement with Castillo-Muñoz et al. (2010). Stilbenes are important compounds synthesised in response to stress, such as a pathogen attack. The highest level of total stilbenes was observed in Pinot noir from Italy (16.78 mg/kg FW) and Johanniter from Germany (4.57 mg/kg FW) among red and white varieties, respectively. *Trans*-resveratrol and its glucoside are the main stilbenes reported in berries of French PIWI varieties grown in Canada (Pedneault et al., 2016). Resveratrol isomers (*cis*- and *trans*-) were not quantified in the grape samples under study rather resveratrol was found in the form of its glucosides (*cis*- and *trans*-piceid). These glycosylated forms of resveratrol were found in higher amount in the mildew tolerant varieties in comparison to reference ones and among PIWI varieties, Rondo and Regent contained the highest amounts of these compounds (1.33 and 1.18 mg/kg, respectively). Furthermore, high levels of pallidol and astringin were also observed in the varieties studied. These results are in accordance with Ehrhardt et al. (2014).

3.3.2 Anthocyanins

A total of 20 anthocyanins were identified and quantified from the skins of the varieties under study. These anthocyanins included glucosides, diglucosides, coumaroyl-glucosides and acetyl-glucosides of five anthocyanidins: delphinidin, cyanidin, petunidin, peonidin and malvidin (Table S2). As it is shown in Fig. 3, there were differences in the total anthocyanin amounts detected in grape skins among the varieties studied. Accent contained the highest level of anthocyanins (2667.96 mg/kg) while the smallest amount was found in Cabernet Carbon (602.53 mg/kg). In particular, Accent, Rondo and Regent were found to contain significantly higher amounts of anthocyanins in comparison to reference and other PIWI varieties.

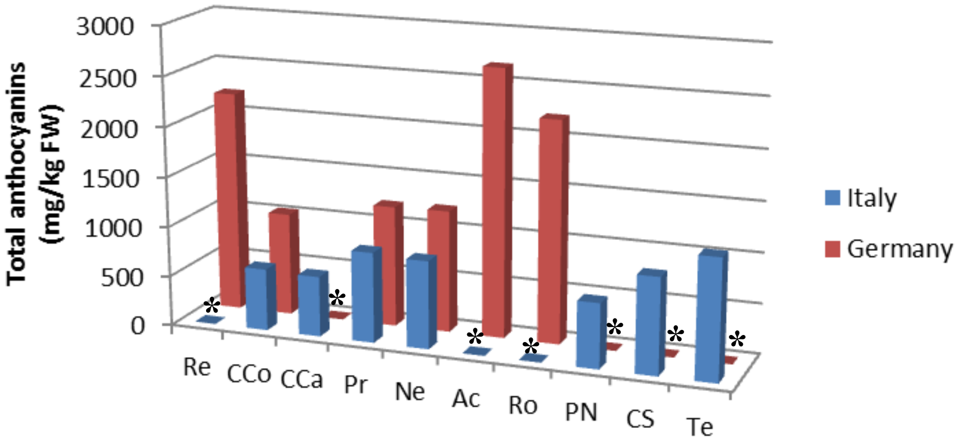


Figure 3. Total anthocyanins in grape skins of red varieties. Asterisk marks the grape samples not analysed in this study (See Table 1 for details and for variety acronyms).

The levels of anthocyanins found in Pinot noir and Regent were comparable to those reported by Balík, Kumšta, & Rop (2013). Our results are also in accordance with those reported by Kontić et al. (2016) who observed that Regent had a higher total anthocyanin amount than other disease tolerant varieties studied, including the variety Cabernet Cortis. Malvidin derivatives were the most abundant anthocyanin type in the grape skins of both PIWI and reference varieties with the exception of the variety Accent where delphinidin derivatives were found in higher amounts. In Cabernet Cortis, Cabernet Carbon, Prior, Nero, Pinot noir and Cabernet Sauvignon, malvidin derivatives accounted for more than 50% of total anthocyanins. Cyanidin derivatives were detected in lower amount than other anthocyanins in the majority of the varieties with the exception of Accent, Teroldego and Cabernet Cortis (from Italy). As previously described, cyanidin derivatives are generally found in low concentrations in red grape varieties because their role as precursor of all the other anthocyanin compounds (Núñez, Monagas, & Bartolomé, 2004).

Coumaroyl derivatives were the most abundant forms in Regent, Cabernet Carbon, Prior, Nero, Rondo and Teroldego. Conversely, the acetylated anthocyanins were found in higher amounts in Cabernet Cortis, Accent and Cabernet Sauvignon while neither coumaroyl nor acetyl derivatives were detected in Pinot noir. In particular, the observations regarding Rondo, Regent and Cabernet Sauvignon are in agreement with the findings previously reported in the literature (Wojdyło et al., 2018; Figueiredo-González et al., 2012). Additionally, Balík et al. (2013) reported that the grapes of *V. vinifera* and disease tolerant varieties mainly exhibited a preponderance of the coumaroylated forms than the acetyl ones.

Generally, *V. vinifera* varieties synthesise only monoglucoside anthocyanins whereas wild genotypes and disease tolerant varieties also contain diglucosides. In our study, diglucoside derivatives were not found in Pinot Noir, Cabernet Sauvignon and the PIWI variety Nero; traces of diglucoside anthocyanins were found in the reference Teroldego. The occurrence of diglucoside anthocyanins also in some *V. vinifera* varieties has been previously reported (Liang, Owens, Zhong, & Cheng, 2011). Among the mildew tolerant varieties studied, the percentage of diglucosides ranged from 16.7 (Cabernet Cortis from Germany) to 58.1 (Prior from Italy). Wojdyło et al. (2018) reported that diglucoside anthocyanins made up 91% and 83% of total anthcyanins in disease tolerant varieties Rondo and Regent. In our study, a lower percentage of diglucosides was observed for these two varieties (17.2% and 20.2% in Regent and Rondo, respectively).

3.3.3 Lipids

In this study, different classes of grape lipids were investigated: glycerophospholipids, glycerolipids, sphingolipids, sterols, prenols and fatty acids (Table S3). Total lipids of red varieties ranged from 357.07 to 639.43 mg/kg FW, while it varied from 307.26 to 602.28 mg/kg FW in white varieties. Cabernet Carbon (639.43 mg/kg FW) and Bronner (560.03 mg/kg FW) were the varieties with the highest mean total amount of lipids in red and white grape samples, respectively (Fig. 4). In particular, it was observed that the range of variation of lipids in PIWI varieties was similar to *V. vinifera* references whereas non-*V. vinifera* genotypes showed a higher content of total lipids as previously reported in chapter 2 (Ruocco et al. 2017).

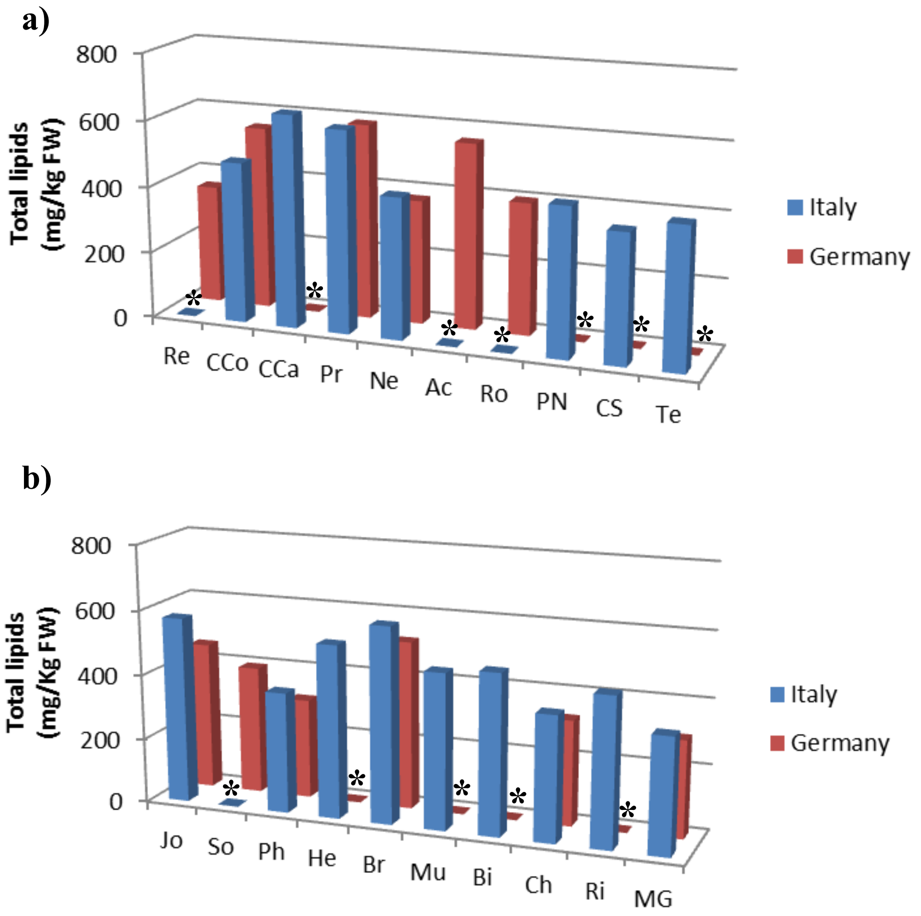


Figure 4. Total lipids of red (a) and white (b) varieties. Asterisk marks the grape samples not analysed in this study (See Table 1 for details and for variety acronyms).

Some lipids, such as sterols and oleanolic acids have been described as "survival factors" for yeasts since they can act in some conditions by increasing the viability of the resting cells and prolonging the fermentation activity (Lafon-Lafourcade, Larue, & Ribereau-Gayon, 1979). Oleanolic acid was the most abundant compound in all the grape samples studied as previously observed in *V. vinifera* and wild genotypes (Ruocco et al., 2017). It was in the range 290.89-550.81 mg/kg FW and 244.84-518.53 mg/kg FW in red and white PIWI varieties, respectively. In reference varieties, the oleanolic concentration ranged from 321.06 to 377.83 mg/kg FW in red varieties and from 212.54 to 377.18 mg/kg FW in white ones. However, the total amount of oleanolic acid found in disease tolerant varieties was lower than that observed in non-*V. vinifera* genotypes (Ruocco et al., 2017).

As regards the sterols, uvaol and ergosterol were detected. The former was present in higher amounts in all the grape samples under study. Among the glycerophospholipids, 1,2-dilinoleoyl-sn-glycero-3-phosphocholine was found in high levels in all the varieties studied. Within the group of glycerolipids, glyceryl tripalmitoleate and 1-linoleoyl-rac-glycerol were the most abundant metabolites. Palmitic, linolenic, linoleic and stearic acids were found to be the most abundant fatty acids in all the varieties in general agreement with Bauman, Gallender & Peng (1977) and Ruocco et al. (2017).

3.4 Conclusions

Phenols, anthocyanins and lipids in grapes of 14 disease tolerant varieties and 6 common grapevine (*V. vinifera* L.) varieties grown at two experimental vineyards (in Italy and Germany) during 2013 vintage were identified and quantified. The phenolic composition for some mildew tolerant varieties has not been previously investigated. To the best of our knowledge, this is the first time that the lipid profiles of PIWI varieties have been described. Chemical characterisation of these compounds provide useful information because of their important role in oenology: polyphenols are the main contributors to some important sensory properties of wines (colour, stability, bitterness, and astringency) and lipids are key factors in oenology capable to affect the properties of the resulting wines.

Present results reveal a clear difference among the varieties in the total amounts of anthocyanins and phenolic compounds as well as a general higher level of these compounds for the varieties cultivated in Germany. A certain diversity among the genotypes studied was also observed as regards the lipid profile. The information gained from this work may be useful to change the bad reputation of disease tolerant varieties in the wine industry and for future grapevine breeding programs as well as to adapt oenological practices to new disease tolerant varieties.

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Table S1. Quantitative results of the phenolic compounds detected in the grape samples studied. The results are expressed as mg/kg.

Variety	Country	Vintage	*p*-hydroxybenzoic acid	vanillic acid	gallic acid	caftaric acid	fertaric acid	t-coutaric acid	ellagic acid	methyl gallate	phloridzin	luteolin-7-*O*-glu	naringenin	cat	epicat	epigallocat	gallocat	epigallocat gallate	epicat gallate	procyanidin B1	procyanidin B2+B4	procyanidin B3	kaemp	que
Regent	Germany	2013	1.65	0.07	2.75	3.23	1.87	1.58	n.d.	0.01	0.06	0.12	n.d.	251.27	151.10	0.44	0.44	1.92	11.63	34.74	101.01	23.05	n.d.	0.68
Cabernet Cortis	Italy	2013	1.01	0.02	2.74	3.08	0.48	0.61	0.16	n.d.	0.01	0.15	n.d.	91.46	106.54	0.29	0.04	n.d.	18.02	49.29	109.71	20.01	n.d.	n.d.
Cabernet Cortis	Germany	2013	1.81	0.02	5.69	5.38	1.23	1.30	0.26	0.01	0.03	0.11	n.d.	174.78	177.99	0.30	0.08	n.d.	20.07	30.68	121.62	17.49	n.d.	0.68
Cabernet Carbon	Italy	2013	1.68	0.08	19.23	2.25	1.22	0.48	n.d.	0.01	n.d.	0.38	n.d.	212.85	261.74	0.35	0.05	n.d.	29.68	71.03	148.40	37.55	0.01	n.d.
Prior	Italy	2013	n.d.	0.06	1.21	5.34	1.07	0.85	n.d.	0.01	0.07	0.04	n.d.	30.57	28.67	n.d.	n.d.	n.d.	4.10	12.61	21.66	6.84	n.d.	n.d.
Prior	Germany	2013	0.45	n.d.	1.47	6.87	1.57	1.37	0.05	0.01	0.14	0.17	n.d.	67.02	79.04	0.34	0.20	1.78	15.59	20.88	70.62	14.33	n.d.	n.d.
Nero	Italy	2013	0.76	0.18	2.24	1.79	0.56	0.67	n.d.	0.01	0.02	0.13	n.d.	72.69	72.26	n.d.	0.04	n.d.	7.28	26.53	46.53	9.99	n.d.	0.75
Nero	Germany	2013	4.11	0.04	1.31	2.23	0.57	0.35	0.15	0.02	0.03	0.10	n.d.	337.78	47.54	0.05	0.36	n.d.	12.32	20.09	37.18	16.53	n.d.	n.d.
Accent	Germany	2013	2.01	0.29	4.55	2.56	1.27	0.05	0.22	0.01	0.10	0.16	0.11	204.31	157.17	n.d.	0.11	1.85	19.68	47.87	140.31	59.34	n.d.	n.d.
Rondo	Germany	2013	4.38	0.10	3.27	10.02	1.43	1.93	0.56	0.03	0.05	0.39	n.d.	325.80	147.23	n.d.	0.07	1.79	67.45	77.78	67.46	43.04	n.d.	n.d.
Pinot noir	Italy	2013	3.50	0.32	4.79	2.61	0.99	0.33	0.03	0.01	0.05	0.26	n.d.	316.12	167.37	n.d.	0.03	n.d.	8.46	99.65	211.15	88.84	n.d.	n.d.
Cabernet Sauvignon	Italy	2013	1.42	0.15	4.94	7.12	1.98	1.23	0.46	0.01	0.10	0.37	n.d.	158.47	85.99	0.60	0.45	1.94	34.99	53.50	149.91	70.38	0.01	0.94
Teroldego	Italy	2013	0.54	0.11	7.62	1.22	0.97	0.10	1.36	0.06	0.01	0.05	n.d.	32.41	46.56	n.d.	0.03	n.d.	8.41	10.87	63.57	8.48	n.d.	n.d.
Johanniter	Italy	2013	2.69	0.05	12.24	2.64	2.80	0.42	n.d.	0.01	0.01	0.17	n.d.	246.16	137.86	0.23	0.40	n.d.	7.99	60.98	117.83	55.95	0.01	0.67
Johanniter	Germany	2013	1.71	0.02	2.02	23.08	2.88	3.07	n.d.	0.03	0.02	0.20	n.d.	186.48	76.61	0.63	0.89	2.53	14.50	40.35	53.86	38.67	n.d.	0.65
Solaris	Germany	2013	1.00	0.02	5.32	5.34	0.76	1.39	n.d.	0.01	n.d.	0.07	n.d.	96.33	116.88	0.18	0.17	1.79	5.69	18.68	86.06	17.31	0.02	0.60
Phoenix	Italy	2013	1.77	0.05	5.75	1.88	2.33	0.43	0.15	n.d.	0.02	0.11	n.d.	181.10	126.21	0.05	n.d.	n.d.	72.07	35.08	43.01	18.83	n.d.	0.68
Phoenix	Germany	2013	1.76	0.01	6.46	1.32	1.06	0.41	n.d.	n.d.	0.03	0.09	n.d.	154.95	104.33	n.d.	n.d.	1.95	6.64	15.01	23.88	18.80	n.d.	n.d.
Helios	Italy	2013	0.52	0.01	0.92	4.55	1.33	2.16	n.d.	n.d.	0.05	0.09	n.d.	57.85	37.62	n.d.	n.d.	1.77	3.88	20.55	24.01	7.73	0.01	0.63
Bronner	Italy	2013	1.11	0.03	1.34	6.43	1.52	2.38	n.d.	0.01	0.01	0.05	n.d.	106.11	72.21	0.18	0.02	1.83	13.71	26.23	43.30	13.87	n.d.	0.65
Bronner	Germany	2013	2.76	n.d.	1.04	3.67	1.23	2.11	n.d.	0.03	0.03	0.15	0.12	305.76	130.02	0.06	0.20	n.d.	16.13	34.17	102.28	36.11	0.06	0.77
Muscaris	Italy	2013	0.73	0.02	5.52	10.34	1.74	1.32	n.d.	n.d.	0.04	0.13	n.d.	76.97	110.96	0.35	0.02	n.d.	4.32	18.80	165.78	19.49	n.d.	n.d.
Bianca	Italy	2013	4.39	0.02	10.81	2.64	1.09	1.07	0.04	0.01	0.07	0.20	0.11	408.32	206.82	0.20	0.08	1.86	50.34	63.34	91.79	28.03	0.01	0.73
Chardonnay	Italy	2013	0.97	0.04	3.11	3.92	0.65	0.62	n.d.	n.d.	n.d.	0.18	n.d.	99.81	84.47	n.d.	n.d.	n.d.	7.89	22.73	53.32	19.32	n.d.	0.69
Chardonnay	Germany	2013	1.17	0.01	1.25	5.42	0.75	1.28	n.d.	n.d.	0.04	0.20	n.d.	131.64	216.01	n.d.	n.d.	n.d.	17.99	24.84	83.08	10.37	n.d.	0.64
Riesling	Italy	2013	0.42	0.03	0.80	3.71	3.98	0.43	0.03	n.d.	n.d.	0.14	n.d.	68.13	34.10	0.18	0.02	2.06	6.82	31.81	68.56	30.33	n.d.	0.64
Moscato Giallo	Italy	2013	1.01	0.02	2.56	2.78	0.58	0.11	0.26	0.02	0.01	0.15	n.d.	116.64	27.52	0.03	0.02	1.83	11.57	20.07	58.77	33.19	n.d.	n.d.
Moscato Giallo	Germany	2013	1.43	0.01	1.65	31.51	1.24	5.24	0.05	n.d.	0.03	0.14	n.d.	105.45	92.07	0.21	n.d.	1.86	15.62	13.52	33.36	18.21	n.d.	n.d.

Abbreviations:lu, glucoside; cat, catechin; epicat, epicatechin; epigallocat, epigallocatechin; gallocat, gallocatechin; kaemp, kaempferol; que, quercetin; n.d., not detected.

Variety	Country	Vintage	taxifolin	kaemp-3-*O*-glu	que-3-*O*-glu + que-3-*O*-gal	isorhamn-3-*O*-glu	kaemp-3-*O*-rut	rutin	que-3-*O*-glucur	kaemp-3-*O*-glucur	arbutin	syr-3-*O*-glu + syr-3-*O*-gal	piceatannol	*trans*-piceide	*cis*-piceide	astringin	isorhapontin	*trans*-ε-viniferin	caff acid + cat cond	pallidol	*E*-*cis*-miyabenol	isohopeaphenol
Regent	Germany	2013	2.93	2.03	17.11	1.10	0.38	2.09	37.73	0.20	n.d.	0.36	0.05	0.86	0.32	1.01	0.66	n.d.	n.d.	8.98	n.d.	n.d.
Cabernet Cortis	Italy	2013	0.12	0.10	4.41	0.26	0.45	0.17	8.29	n.d.	n.d.	0.17	0.07	0.58	0.29	0.49	n.d.	n.d.	n.d.	1.42	n.d.	n.d.
Cabernet Cortis	Germany	2013	0.09	0.34	3.80	0.09	0.60	0.91	15.88	0.13	0.17	0.41	n.d.	0.52	0.15	0.29	n.d.	n.d.	0.41	0.45	n.d.	n.d.
Cabernet Carbon	Italy	2013	13.20	2.99	20.62	6.00	0.25	0.61	18.64	0.57	0.34	1.45	n.d.	0.51	0.14	0.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Prior	Italy	2013	0.12	0.75	19.28	0.57	1.63	0.42	13.67	0.02	0.44	0.27	n.d.	0.60	0.15	0.30	0.57	n.d.	1.64	0.16	n.d.	n.d.
Prior	Germany	2013	0.11	0.30	5.41	0.07	2.04	0.11	10.88	n.d.	0.27	0.23	n.d.	0.61	n.d.	0.82	0.14	n.d.	n.d.	1.34	n.d.	n.d.
Nero	Italy	2013	0.14	2.71	18.78	1.19	1.40	0.21	8.09	0.04	0.16	0.49	0.54	0.73	0.21	1.20	0.82	n.d.	0.15	1.41	n.d.	n.d.
Nero	Germany	2013	0.16	0.32	3.64	0.15	n.d.	0.40	10.12	0.05	0.18	0.33	0.10	0.82	0.25	1.25	1.28	n.d.	1.71	3.08	n.d.	n.d.
Accent	Germany	2013	5.96	n.d.	8.65	0.97	0.40	0.28	7.21	0.04	0.20	0.17	0.06	0.60	0.15	0.48	0.06	n.d.	n.d.	n.d.	n.d.	n.d.
Rondo	Germany	2013	5.80	2.55	23.10	0.99	2.39	4.69	35.89	0.32	0.28	0.26	0.01	1.07	0.26	1.76	0.69	n.d.	n.d.	0.33	0.12	3.47
Pinot noir	Italy	2013	8.70	0.26	4.78	1.69	0.04	0.57	11.45	0.10	0.18	0.61	0.98	0.74	0.31	2.07	1.20	n.d.	1.25	9.12	n.d.	1.11
Cabernet Sauvignon	Italy	2013	0.87	12.76	75.33	13.86	1.74	7.89	70.69	1.62	0.17	0.86	n.d.	0.73	0.16	0.66	n.d.	n.d.	5.59	n.d.	n.d.	n.d.
Teroldego	Italy	2013	0.25	n.d.	0.36	0.10	n.d.	0.06	2.50	n.d.	0.28	0.47	0.07	0.50	0.15	0.47	0.31	0.20	n.d.	8.40	n.d.	0.95
Johanniter	Italy	2013	0.22	1.26	19.25	0.90	0.01	0.63	4.95	0.07	0.17	0.02	n.d.	n.d.	0.15	0.14	n.d.	n.d.	0.30	n.d.	n.d.	n.d.
Johanniter	Germany	2013	0.43	2.06	12.13	0.15	0.22	1.94	11.04	0.15	0.20	n.d.	n.d.	0.52	n.d.	0.20	n.d.	n.d.	3.63	n.d.	n.d.	0.22
Solaris	Germany	2013	0.15	0.47	7.09	0.05	n.d.	0.75	10.79	0.05	n.d.	n.d.	n.d.	0.50	n.d.	0.25	n.d.	n.d.	n.d.	0.31	n.d.	n.d.
Phoenix	Italy	2013	0.07	9.33	40.78	1.74	n.d.	0.06	14.89	0.67	0.23	n.d.	n.d.	n.d.	0.15	0.10	n.d.	n.d.	n.d.	0.11	n.d.	n.d.
Phoenix	Germany	2013	0.08	1.06	9.08	0.54	n.d.	0.06	12.11	0.11	n.d.	n.d.	n.d.	0.50	0.14	0.30	n.d.	n.d.	n.d.	0.25	0.03	0.16
Helios	Italy	2013	10.15	4.80	27.01	0.56	n.d.	0.24	17.23	0.65	0.30	n.d.	n.d.	0.50	0.15	n.d.	n.d.	n.d.	0.90	n.d.	n.d.	n.d.
Bronner	Italy	2013	0.95	1.50	12.39	0.26	n.d.	0.33	8.87	0.15	0.31	n.d.	n.d.	0.53	0.30	0.39	n.d.	n.d.	n.d.	1.26	0.29	n.d.
Bronner	Germany	2013	2.91	3.41	18.03	0.08	0.38	1.48	15.02	1.23	0.18	n.d.	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	0.56	n.d.	n.d.	n.d.
Muscaris	Italy	2013	0.26	5.22	18.82	0.21	n.d.	1.93	21.88	0.28	n.d.	n.d.	n.d.	0.51	n.d.	n.d.	n.d.	n.d.	1.64	n.d.	n.d.	n.d.
Bianca	Italy	2013	0.15	4.03	28.79	1.33	n.d.	0.54	45.71	1.69	0.17	n.d.	n.d.	0.59	0.14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chardonnay	Italy	2013	7.81	27.98	70.57	0.74	n.d.	1.07	32.18	1.42	n.d.	n.d.	n.d.	0.52	n.d.	0.25	n.d.	n.d.	3.77	n.d.	n.d.	n.d.
Chardonnay	Germany	2013	3.19	0.47	2.33	0.02	n.d.	0.11	4.92	0.02	n.d.	n.d.	n.d.	0.51	0.16	0.16	n.d.	n.d.	2.69	0.26	n.d.	n.d.
Riesling	Italy	2013	0.18	5.77	18.00	0.53	0.01	0.81	13.06	0.20	0.29	n.d.	0.05	0.51	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	n.d.
Moscato Giallo	Italy	2013	2.64	10.03	22.99	0.22	0.13	1.37	16.57	0.88	0.21	0.01	n.d.	0.50	0.16	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Moscato Giallo	Germany	2013	0.24	0.81	3.32	n.d.	0.19	1.52	21.03	0.70	0.22	n.d.	n.d.	0.54	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Abbreviations: kaemp, kaempferol; que, quercetin; glu, glucoside; gal, galactoside; rut, rutinoside; glucur, glucuroside; syr, syringetin; caff acid, caffeic acid; cat cond, catechin condensation product, n.d., not detected.

Table S2. Quantitative results of the anthocyanins detected in the grape samples studied. The results are expressed as mg/kg.

	Regent Germany 2013	Cabernet Cortis Italy 2013	Cabernet Cortis Germany 2013	Cabernet Carbon Italy 2013	Prior Italy 2013	Prior Germany 2013	Nero Italy 2013	Nero Germany 2013	Accent Germany 2013	Rondo Germany 2013	Pinot noir Italy 2013	Cabernet Sauvignon. Italy 2013	Teroldego Italy 2013
dp-3-*O*-glu	444.13	53.09	131.15	27.29	85.62	211.35	43.77	166.05	767.79	338.22	19.45	107.10	110.29
cy-3-*O*-glu	122.09	37.48	55.91	21.87	5.92	48.65	8.89	48.70	254.27	137.12	7.71	21.26	n.d.
pt-3-*O*-glu	343.33	30.12	106.13	24.22	51.72	150.90	67.93	192.58	364.27	230.09	28.98	80.98	103.89
pn-3-*O*-glu	111.96	1.90	59.33	10.53	10.01	29.45	34.61	69.46	94.20	111.08	140.66	103.47	65.03
mv-3-*O*-glu	484.95	57.88	327.13	110.17	101.58	279.35	439.48	523.99	203.10	481.68	449.93	349.64	525.67
dp-3-(6”-acetyl)-*O*-glu	9.87	9.34	18.36	2.75	2.44	5.67	3.36	10.52	147.73	48.61	n.d.	19.69	n.d.
cy-3-(6”-acetyl)-*O*-glu	0.49	2.21	4.40	0.62	0.79	n.d.	0.70	2.40	28.14	7.57	n.d.	3.45	31.56
pt-3-(6”-acetyl)-*O*-glu	10.07	7.76	18.92	3.54	1.76	4.83	8.49	16.38	66.33	39.73	n.d.	20.00	2.94
pn-3-(6”-acetyl)-*O*-glu	13.11	12.81	6.54	1.09	8.80	4.25	5.56	4.02	17.95	17.61	n.d.	33.55	n.d.
mv-3-(6”-acetyl)-*O*-glu	12.29	14.53	52.14	17.61	2.93	6.93	70.35	45.29	24.89	65.60	n.d.	108.96	36.92
dp-3-(6”-p-coumaroyl)-*O*-glu	80.96	15.13	12.22	8.92	25.86	29.40	11.53	18.28	82.49	67.18	n.d.	8.97	22.90
cy-3-(6'-p-coumaroyl)-*O*-glu	17.04	0.18	6.20	1.40	2.64	5.66	8.70	9.43	21.84	17.01	n.d.	2.80	243.15
pt-3-(6'-p-coumaroyl)-*O*-glu	55.78	8.70	9.40	4.43	18.01	21.49	16.80	21.09	27.42	39.53	n.d.	6.94	18.69
pn-3-(6'-p-coumaroyl)-*O*-glu	14.96	n.d.	6.56	3.61	2.80	4.59	16.98	11.38	9.85	19.97	n.d.	29.11	7.80
mv-3-(6'-p-coumaroyl)-*O*-glu	108.01	19.73	41.81	40.81	56.86	56.40	139.05	79.15	18.56	91.16	n.d.	61.99	18.62
dp-3,5-*O*-diglu	31.20	28.17	7.59	3.58	25.34	29.12	n.d.	n.d.	95.66	30.32	n.d.	n.d.	n.d.
cy-3,5-*O*-diglu	8.97	0.68	5.10	n.d.	2.47	4.30	n.d.	n.d.	51.00	n.d.	n.d.	n.d.	n.d.
pt-3,5-*O*-diglu	65.49	48.33	16.42	11.06	48.73	51.58	n.d.	n.d.	131.76	52.43	n.d.	n.d.	n.d.
pn-3,5-*O*-diglu	63.12	10.85	43.77	44.39	34.48	32.08	n.d.	n.d.	125.44	116.60	n.d.	n.d.	n.d.
mv-3,5-*O*-diglu	210.37	260.89	98.78	264.65	413.16	232.50	n.d.	n.d.	135.27	300.45	n.d.	n.d.	13.41

Abbreviations: dp, delphinidin; cy, cyanidin; pt, petunidin; pn, peonidin; malvidin, malvinidin; glu, glucoside, diglu, diglucoside, n.d., not detected.

Table S3. Quantitative results of the lipids detected in the grape samples studied. The results are expressed as mg/kg.

Variety	Country	Vintage	DLPC	DOPC	DOPG-Na	POPC	1-linoleoyl-rac-glycerol	1-oleoyl-rac-glycerol	glyceryl trioleate	glyceryl tripalmitoleate	1,2,3-tripentadecanoyl-glycerol	uvaol	ergosterol	oleanolic acid	linoleic acid	behenic acid	linolenic acid	stearic acid	gondoic acid	palmitoleic acid	lignoceric acid	erucic acid	arachidic acid	oleic acid + *cis*-vaccenic acid	myristic acid	palmitic acid	margaric acid
Regent	Germany	2013	5.06	1.75	0.09	0.57	0.99	0.18	8.06	0.02	0.03	9.44	0.17	290.89	8.17	3.06	5.14	6.19	0.15	0.14	4.28	0.02	1.20	2.64	0.29	8.38	0.15
Cabernet Cortis	Italy	2013	5.43	2.21	0.12	1.14	3.13	0.43	18.95	0.02	0.04	3.87	0.11	410.02	4.51	1.55	6.83	6.65	0.11	0.22	4.90	0.02	1.23	3.02	0.27	9.03	0.14
Cabernet Cortis	Germany	2013	10.72	2.51	0.23	1.77	2.66	0.30	20.69	0.03	0.04	4.09	0.20	453.06	7.93	2.49	12.22	7.43	0.19	0.34	6.54	0.03	1.54	3.24	0.31	13.22	0.17
Cabernet Carbon	Italy	2013	6.16	3.51	0.15	1.23	3.67	1.32	3.65	0.02	0.04	8.27	0.16	545.01	7.18	1.96	10.24	7.24	0.20	0.58	7.11	0.02	1.23	16.19	0.49	13.62	0.16
Prior	Italy	2013	5.71	2.14	0.09	1.30	2.71	0.26	3.83	0.01	0.03	4.02	0.11	550.81	5.27	2.04	8.60	4.18	0.16	0.18	3.06	0.03	1.02	2.73	0.25	9.52	0.14
Prior	Germany	2013	7.21	2.06	0.09	1.36	2.04	0.18	8.24	0.01	0.03	3.60	0.16	522.59	6.29	2.86	8.80	4.03	0.23	0.14	4.27	0.03	1.01	2.54	0.26	10.13	0.12
Nero	Italy	2013	4.10	1.77	0.08	0.63	8.19	0.21	20.11	0.02	0.04	4.93	0.12	325.91	11.37	3.11	12.79	4.82	0.25	0.51	2.80	0.05	1.77	6.56	0.31	15.17	0.18
Nero	Germany	2013	5.81	1.65	0.09	0.72	3.00	0.13	8.64	0.02	0.04	3.08	0.18	316.84	5.62	2.13	6.50	4.06	0.19	0.26	2.00	0.03	1.11	2.62	0.24	9.13	0.11
Accent	Germany	2013	10.66	3.06	0.23	1.03	2.87	0.25	n.d.	0.01	0.03	8.11	0.30	472.88	8.59	2.23	12.48	9.60	0.44	0.30	8.53	0.05	1.49	3.44	0.32	11.79	0.17
Rondo	Germany	2013	14.98	2.53	0.13	1.51	1.23	0.20	1.78	0.02	0.03	4.40	0.25	318.49	6.98	2.54	13.27	8.12	0.41	0.31	4.35	0.06	1.71	3.61	0.33	10.58	0.21
Pinot noir	Italy	2013	4.40	2.64	0.11	0.58	3.56	0.49	2.43	0.02	0.03	6.37	0.14	377.83	5.65	2.84	5.28	11.31	0.21	0.29	3.66	0.05	0.86	6.03	0.48	11.47	0.17
Cabernet Sauvignon	Italy	2013	5.29	2.22	0.21	1.23	2.11	0.59	0.98	0.03	0.07	7.18	0.15	321.06	4.94	2.76	4.87	8.12	0.12	0.20	8.14	0.04	1.00	4.67	0.63	11.32	0.24
Teroldego	Italy	2013	4.47	2.69	0.07	0.70	2.86	0.30	11.90	0.02	0.04	3.32	0.13	344.21	6.90	1.75	9.77	13.98	0.39	0.26	2.26	0.03	0.95	4.93	0.43	11.84	0.27
Johanniter	Italy	2013	3.11	1.83	0.11	0.65	7.24	0.48	28.99	0.02	0.04	5.94	0.30	471.68	5.76	2.33	7.37	11.19	0.35	0.14	7.24	0.04	1.22	3.79	0.43	13.16	0.19
Johanniter	Germany	2013	5.84	1.80	0.10	0.74	1.99	0.20	15.66	0.14	4.44	5.95	0.08	385.34	4.26	2.53	6.23	2.38	0.20	0.06	7.33	0.03	1.40	1.81	0.19	6.35	0.09
Solaris	Germany	2013	6.37	1.79	0.16	1.04	1.71	0.33	30.11	0.01	0.03	2.91	0.08	314.96	4.82	1.95	7.42	4.29	0.11	0.15	2.95	0.03	0.89	2.41	0.28	9.49	0.12
Phoenix	Italy	2013	2.84	1.65	0.09	0.77	6.44	0.12	19.00	0.01	0.04	5.36	0.08	305.98	4.80	2.20	5.46	3.67	0.12	0.20	2.65	0.02	0.90	1.60	0.28	7.34	0.11
Phoenix	Germany	2013	4.96	1.49	0.16	1.11	2.77	0.11	11.54	0.01	0.09	3.90	0.20	244.84	4.33	3.99	5.71	4.42	0.23	0.12	5.15	0.05	1.54	1.99	0.26	8.25	0.13
Helios	Italy	2013	3.06	1.53	0.11	0.81	1.38	0.19	24.58	0.02	0.02	4.92	0.06	444.57	12.28	3.02	3.12	5.39	0.26	0.07	8.72	0.02	1.62	8.91	0.16	7.71	0.12
Bronner	Italy	2013	7.51	2.91	0.11	1.49	1.81	0.54	18.90	0.02	0.03	7.17	0.18	518.53	3.73	2.44	8.74	7.91	0.14	0.15	4.23	0.02	2.19	3.59	0.29	9.46	0.15
Bronner	Germany	2013	10.91	2.48	0.29	2.13	1.94	0.42	n.d.	0.01	0.05	5.33	0.05	446.78	7.22	1.77	12.03	6.61	0.29	0.13	1.53	0.03	1.20	5.65	0.22	10.58	0.13
Muscaris	Italy	2013	8.66	2.55	0.10	2.61	3.65	0.35	1.64	0.05	0.04	3.34	0.07	385.97	10.66	2.53	16.94	9.62	0.26	0.37	4.55	0.06	1.53	4.94	0.43	16.78	0.22
Bianca	Italy	2013	6.22	1.99	0.11	1.03	3.14	0.15	2.22	0.01	0.03	2.99	0.11	411.81	7.62	2.50	10.97	16.05	0.28	0.19	2.97	0.04	1.94	2.91	0.68	16.57	0.27
Chardonnay	Italy	2013	3.69	2.24	0.13	0.63	2.21	0.24	11.84	0.02	0.05	7.87	0.07	318.14	3.35	5.16	3.18	6.46	0.27	0.13	7.10	0.02	1.41	3.48	0.33	6.58	0.13
Chardonnay	Germany	2013	9.32	2.63	0.14	1.09	0.93	0.23	7.66	0.03	0.03	4.00	0.06	264.31	6.04	1.71	4.10	5.68	0.23	0.12	4.08	0.02	0.66	3.39	0.22	7.77	0.14
Riesling	Italy	2013	5.11	2.21	0.15	1.21	2.28	0.29	20.84	0.03	0.05	8.10	0.08	377.18	4.40	2.59	5.23	5.95	0.27	0.12	8.06	0.03	0.81	2.75	0.33	8.94	0.15
Moscato Giallo	Italy	2013	3.83	1.75	0.08	0.74	2.39	0.24	13.64	0.02	0.03	4.19	0.11	287.89	5.48	4.32	5.02	7.27	0.23	0.10	3.91	0.03	2.40	2.75	0.39	8.55	0.13
Moscato Giallo	Germany	2013	17.00	11.02	0.10	1.35	0.49	0.42	15.05	0.02	0.04	2.61	0.08	212.54	5.11	2.14	4.32	7.64	0.15	0.13	2.98	0.03	1.71	1.88	0.29	10.94	0.15

Abbreviations: DLPC, 1,2-dilinoleoyl-sn-glycero-3-phosphocholine; DOPC, 1,2-dioleoyl-sn-glycero-3-phosphocholine; DOPG-Na, 1,2-dioleoyl-sn-glycero-3-phospho-rac-(1-glycerol)sodium salt; POPC, 1-palmitoyl-sn-glycero-3-phosphocholine.

CHAPTER 4

Investigation of volatile and non-volatile compounds of wine produced by disease tolerant varieties

This chapter is part of a manuscript in preparation.

4.1 Introduction

Wine is a widely consumed beverage in the world and represents the most important use of grapes by both tonnage and production area. Grape production and winemaking are linked with a long history and tradition since time immemorial. Indeed, ancient civilisations considered wine as divine, a gift from Gods and over the centuries, writers have glorified and commented about its characteristics and uses (Mcgovern, 2003). Therefore, it has evolved as part of life, culture and diet showing today a remarkable commercial value as well as a social importance.

Chemically, wine is an extremely complex matrix made up of compounds of different nature and structure, such as amino acids, carbohydrates, phenols, organic acids, sugars, inorganic compounds, volatile components and proteins. All of these components have a strong influence on the quality and character of the wine contributing to its characterisation and differentiation (Cuadros-Inostroza et al., 2010). Among the non-volatile compounds, polyphenols represent the largest group including different classes of components involved in some of the major organoleptic properties of wine: anthocyanins are natural pigments directly responsible for colour of red wines (Mattivi, Guzzon, Vrhovsek, Stefanini, & Velasco, 2006); flavonols act in the stabilisation of anthocyanins in young red wines through the phenomenon of copigmentation (Boulton, 2001); flavan-3-ols and their polymers, also called proanthocyanidins or condensed tannins, impart astringency to wines, form covalent adducts with anthocyanins retaining some of the original colour of them and contribute to the ability of red wines to age (Peleg, Gacon, Schlich, & Noble, 1999; Remy et al. 2000; Corder et al. 2006; Kennedy, Saucier, & Glories, 2006).

Sugars, organic acids and mineral substances are responsible for taste sensations such as sweetness, sourness and saltiness. In particular, minerals play an important role in the stability of wine and its health impact but they are also associated to toxicological risks which explains the fact that the concentration of some of them are regulated by law (Frías, Conde, Rodríguez, Dohnal, & Pérez-Trujillo, 2002). Low-molecular-weight (LMW) thiols are a class of highly reactive compounds involved in the maintenance of cellular redox homeostasis with effective antioxidants properties (Pivato, Fabrega-Prats, & Masi, 2014). The tripeptide glutathione (γ-glu-cys-gly, GSH) is the principal and important thiol in both plants and animals and its presence has already been reported in both grapes and wines (Lavigne, Pons, & Dubourdieu, 2007; Adams & Liyanage, 1993). It is involved in preventing the oxidation of phenolic compounds in wine as well as it plays a major role in the development of aroma during the aging of bottled white wines (Ribéreau-Gayon et al., 2006). Another group of wine constituents with remarkable importance is represented by volatile compounds. Wine is made up by hundreds of different volatiles which contribute to define its characteristic bouquet. In general, it is possible to classify wine aroma in four groups: primary aroma which originates from grapes; secondary aroma compounds formed due to modifications caused during grape processing; fermentation bouquet produced by alcoholic fermentation and maturation aroma resulting from the transformations that occur during aging. The concentration of wine aroma compounds can be influenced by grape variety, environmental factors, fermentation conditions, wine production and aging of the wine (Rapp, 1998). From a chemical point of view, the main part of wine aroma comprises compounds produced during fermentation by yeasts, such as alcohols, fatty acids, and their acetate and ethyl esters. Esters are the main components present in young wines and in particular, ethyl esters of fatty acids make a positive contribution to the general quality of wine being responsible for “fruity” and “floral” sensory properties (Perestrelo, Fernandes, Albuquerque, Marques, & Câmara, 2006).

Additionally, volatile sulfur compounds (VSC) constitute another interesting group which has a significant influence on the perceived aroma of wine. These compounds have extremely low perception thresholds and their formation is closely linked with yeast metabolism. Some of these VSCs have been identified to impart positive characters to wine such as box tree, citrus zest and passion fruit which are the terms used to describe their aromatic quality. Nevertheless, it is widely acknowledged that other volatile sulfur compounds can sometimes produce off-flavours like boiled or rotten egg, cabbage, garlic, onion and rubber with negative effects on wine aroma (Mestres, Busto, & Guasch, 2000; Smith, Bekker, Smith, & Wilkes, 2015).

Therefore, it is evident how the composition and concentration of volatile and non-volatile compounds can influence the properties of a given wine. However, wine quality is not fully described by the summation of individual chemical traits (Roullier-Gall, Boutegrabet, Gougeon, & Schmitt-Kopplin, 2014). Rather, there are many variables involved in affecting the chemical complexity of wine: the grape variety, environmental conditions (soil, climate) and viticultural practices (Atanassov, Hvarleva, Rusanov, Tsvetkov, & Atanassov, 2009). Nowadays, the global wine industry mainly relies on ancient and traditional cultivars of *V. vinifera* which meet the quality requirements by consumers but require for their cultivation numerous chemical treatments. Disease tolerant varieties of *V.*

vinifera can lead a significant reduction of plant protection products but they still suffer from the negative opinion, related to the first varieties developed at the beginning of the 20th century, to produce low quality wines. The main issue with mildew tolerant varieties is the assumption that they produce wines characterised by undesirable off-flavours, such "foxy" aroma deriving from wild American species. However, the investigation of some wild American species has shown that these compounds are mainly attributable to *V. labrusca* rather than other American *Vitis* species (Sun et al., 2011). Besides, unlike traditional *V. vinifera* varieties, PIWIs are known to produce both monoglucoside and diglucoside anthocyanins. Although no negative evidence of the influence of these compounds on the wine quality exist, the maximum acceptable limit of malvidin 3,5-*O*-diglucoside content in wine is 15 mg/L according to the OIV recommendations. In general, the wines from disease tolerant varieties contain high amounts of diglucosides. Other problems related to the composition of wine produced from these varieties are: low sugar content, high acid content and low levels of condensed tannins (Manns, Lenerz, & Mansfield, 2013).

To date, some studies have investigated the composition of wine made by disease tolerant varieties however they have mainly focused on the analysis of one subset of chemical compounds (Caliari, Burin, Rosier, & BordignonLuiz, 2014; Wojdyło, Samoticha, Nowicka, & Chmielewska, 2018; Slegers, Angers, Ouellet, Truchon, & Pedneault, 2015; Socha, Gałkowska, Robak, & Fortuna, 2015; Pedastsaar et al., 2014). No comparative studies of the overall chemical composition of wine produced by a wide selection of both red and white disease tolerant varieties have not yet been reported in the literature.

The aim of this study was to investigate the volatile and non-volatile composition of wine obtained by a selection of some promising disease tolerant varieties recently introduced to the cultivation. The grapes were grown in Italy and Germany, and the composition of the varietal wines produced at pilot scale (92 wines) over different vintages was compared. A targeted strategy was used to analyse the main classes of compounds involved in determining the quality properties of these wines. A total of 140 parameters were investigated in wines including: anthocyanins (20), phenols (30), flavan-3-ols and proanthocyanidins (20), minerals (7), low-molecular-weight thiols (7), oenochemical parameters (19), volatile compounds (29) and other compounds (8). Knowledge gained would serve to evaluate the use of disease tolerant varieties for quality wine production as well as serve for further studies on the most appropriate winemaking methods.

4.2 Materials and Methods

4.2.1 Reagents

Methanol (LC-MS and HPLC grade), acetonitrile (LC-MS grade), 2-propanol, chloroform and phloroglucinol were obtained from Sigma-Aldrich (Milan, Italy). Formic acid and ammonium formate additives for LC-MS were purchased from Fluka Sigma-Aldrich (Milan, Italy). Water was Milli-Q grade. Helium was purchased from Linde Gas (Bingen, Germany). Standards were purchased or isolated as reported by the corresponding method used for the analysis of each class of compounds.

4.2.2 Wine samples

Red and white wines obtained from seventeen disease tolerant varieties cultivated in Italy (San Michele all'Adige, Trento) and in Germany (Geisenheim, Rheingau) for the 2013, 2015 and 2016 vintages were considered in this study. For reference, six high quality *V. vinifera* varieties were investigated as well. The wine samples studied are listed and reported in Tables 1 and 2. The grapes were harvested at technological maturity in the two experimental fields and they were all vinified at the pilot scale in the experimental winery of Fondazione Edmund Mach (San Michele all'Adige, Trento, Italy).

4.2.2.1 Winemaking procedures

Experimental wines were produced by applying standard winemaking protocols. After destemming, white grapes were crushed and a solution of potassium bisulfite was added in order to adjust the total sulfur dioxide content of the must to 50 mg/L. The must was kept at 12 °C during 36 h. Then, residual solid parts were separated and the must was inoculated with the commercial yeast strain FR95. Alcoholic fermentation was carried out at an average temperature of 22.0 °C for 14 days. After that, wines were stored for the stabilisation process at 4 °C. Finally, the wines were bottled.

Red grapes were destemmed, crushed and the total sulfur dioxide content was adjusted to 50 mg/L by addition of potassium bisulfite. Then, grapes were inoculated with the commercial yeast strain La Claire SP665. Alcoholic fermentation was carried out at 25 °C and manual punching was done two times a day. After 7 days of maceration, the wine was separated from the pomace. Successively, malolactic fermentation was induced by inoculation of Lactobacillus spp. Lalvin 31. Finally, wines were filtered, bottled and stored at 4 °C. Some adjustments were taken into account with regards to red wines of 2016 vintage which were not subjected to filtration process.

Table 1. List and details of wines investigated in this study.

Acronym	Variety	Type	Country of cultivation	Vintage
Re	Regent	rP	Italy	2015, 2016
			Germany	2013, 2015, 2016
CCo	Cabernet Cortis	rP	Italy	2013, 2015, 2016
			Germany	2013, 2015, 2016
CCa	Cabernet Carbon	rP	Italy	2013, 2015
Pr	Prior	rP	Italy	2013, 2015, 2016
			Germany	2013, 2016
Ne	Nero	rP	Italy	2013, 2015, 2016
			Germany	2013
Ac	Accent	rP	Germany	2013, 2015, 2016
Rn	Rondo	rP	Germany	2013, 2015, 2016
Bo	Bolero	rP	Germany	2015, 2016
PN	Pinot noir	rR	Italy	2013, 2015, 2016
CS	Cabernet Sauvignon	rR	Italy	2013, 2015
			Germany	2015, 2016
Te	Teroldego	rR	Italy	2013, 2016
Jo	Johanniter	wP	Italy	2013, 2015, 2016
			Germany	2013, 2015, 2016
Mu	Muscaris	wP	Italy	2013, 2015, 2016
			Germany	2015, 2016
Br	Bronner	wP	Italy	2013, 2015, 2016
			Germany	2013, 2015, 2016
So	Solaris	wP	Italy	2015, 2016
			Germany	2013, 2015, 2016
Ph	Phoenix	wP	Italy	2013, 2015, 2016
			Germany	2013, 2015, 2016
He	Helios	wP	Italy	2013, 2015, 2016
Bi	Bianca	wP	Italy	2013, 2015, 2016
Ja	Jasmine	wP	Italy	2015, 2016
SG	Souvignier Gris	wP	Italy	2015, 2016
Ch	Chardonnay	wR	Italy	2013, 2015, 2016
			Germany	2013, 2015, 2016
Ri	Riesling	wR	Italy	2013, 2015, 2016
			Germany	2015, 2016
MG	Moscato Giallo	wR	Italy	2013, 2015, 2016
			Germany	2013

Abbreviations: rP, red PIWI variety; rR, red reference variety, wP, white PIWI variety; wR, white reference variety.

Table 2. Schematic representation of the wines investigated in this study. Blue colour indicates the samples taken into account, grey colour the samples not analysed.

	Italy			Germany		
	2013	2015	2016	2013	2015	2016
Cabernet Cortis	🟦	🟦	🟦	🟦	🟦	🟦
Regent	⬜	🟦	🟦	🟦	🟦	🟦
Prior	🟦	🟦	🟦	🟦	⬜	🟦
Nero	🟦	🟦	🟦	🟦	⬜	⬜
Cabernet Carbon	🟦	🟦	⬜	⬜	⬜	⬜
Accent	⬜	⬜	⬜	🟦	🟦	🟦
Rondo	⬜	⬜	⬜	🟦	🟦	🟦
Bolero	⬜	⬜	⬜	⬜	🟦	🟦
Pinot noir	🟦	🟦	🟦	⬜	⬜	⬜
Cabernet Sauvignon	🟦	🟦	⬜	⬜	🟦	🟦
Teroldego	🟦	⬜	🟦	⬜	⬜	⬜
Johanniter	🟦	🟦	🟦	🟦	🟦	🟦
Phoenix	🟦	🟦	🟦	🟦	🟦	🟦
Bronner	🟦	🟦	🟦	🟦	🟦	🟦
Solaris	⬜	🟦	🟦	🟦	🟦	🟦
Muscaris	🟦	🟦	🟦	⬜	🟦	🟦
Helios	🟦	🟦	🟦	⬜	⬜	⬜
Bianca	🟦	🟦	🟦	⬜	⬜	⬜
Jasmine	⬜	🟦	🟦	⬜	⬜	⬜
Souvignier Gris	⬜	🟦	🟦	⬜	⬜	⬜
Chardonnay	🟦	🟦	🟦	🟦	🟦	🟦
Riesling	🟦	🟦	🟦	⬜	🟦	🟦
Moscato Giallo	🟦	🟦	🟦	🟦	⬜	⬜

4.2.3 Chemical analysis of non-volatile compounds

The list of non-volatile compounds and oenochemical parameters investigated is presented in Table S1. The oenochemical parameters and the mineral composition of the wines of 2013 vintage were investigated together with those of 2015 vintage.

4.2.3.1 Measurement of oenochemical parameters and other compounds

The antioxidant capacity (AA) was determined using the Trolox equivalent antioxidative capacity (TEAC) assay as described by Re et al. (1999). The AA was expressed as Trolox equivalents in mM of Trolox per liter (mmol TEAC/L wine). Total phenol content was estimated using the Folin-Ciocalteu method and the results were calculated as (+)-

catechin. Nuclear Magnetic Resonance analysis (NMR) was used to evaluate different wine components such as organic acids, alcohol, glycerol, amino acids and fermentation products (Godelmann, Kost, Patz, Ristow, & Wachter, 2016). Other important wine compounds and parameters were estimated by means of liquid Fourier transform-middle infrared spectrometry (FT-MIR) as described by Patz, Blieke, Ristow, & Dietrich (2004). Sugars were analysed with enzymatic kits while organic acids (tartaric, malic and lactic acid) were determined by HPLC with a UV detector at 230 nm.

4.2.3.2 Determination of phenols and anthocyanins

Quantitative analysis of phenolic and anthocyanin compounds was performed by UPLC-MS/MS as reported in chapter 3 and described by Vrhovsek et al. (2012). Results were expressed as milligrams per liter (mg/L).

4.2.3.3 Determination of tannins

Flavan-3-ol monomers and proanthocyanidins were analysed by means of ultraperformance liquid chromatography coupled to mass spectrometry (UPLC-MS/MS). Sample preparation was performed using a slightly modified version of the method described by Gris et al. (2011). Briefly, 10 mL of wine diluted 5 times with water was applied to a C18-SPE cartridge (1 g, Waters, Milford, MA) previously preconditioned with 4 mL of methanol and 10 mL of water. The cartridge was washed with 20 mL of water, eluted with 20 mL of methanol and evaporated to dryness. Then, red and white samples were reconstituted in 2 mL and 1 mL of methanol, respectively. Three hundred microliters of elute of white samples was added to 300 μL of methanol and water (50/50 v/v), filtered, and immediately injected into the LC-MS system. Instead, 200 μL of elute of red samples was added to 800 μL of methanol and water (50/50 v/v), filtered and immediately analysed. A further one hundred microlitres of concentrated white and red wines was added to 100 μL of phloroglucinol reagent at 50 °C for 30 min and then combined with 1 mL of sodium acetate to stop the reaction. The samples were filtered and immediately injected for targeted condensed tannin analysis which was performed using a Waters Acquity UPLC system, coupled with Waters Xevo TQMS (Milford, MA, USA). Chromatographic, separation and detection conditions were the same used for the analysis of phenols and anthocyanins described by Vrhovsek et al. (2012).

Catechin, epicatechin, procyanidins B1 and B2, gallocatechin, epigallocatechin and epicatechin gallate were quantified using a linear regression curve built on the injection of pure chemical standards. Quantification of phloroglucinol-bound flavanols was done as for epicatechin, epigallocatechin, and epicatechin gallate equivalents, respectively(Gris et al., 2011). Results were expressed as mg/L.

4.2.3.4 Determination of minerals

The mineral composition was determined by Atomic Absorption Spectroscopy (AAS) method. The content in potassium, sodium, calcium, magnesium, iron, copper and zinc was analysed using an Analytik Jena ContrAA 300 Atomic Absorption Spectrometer (Jena, Germany).

4.2.3.5 Determination of low-molecular-weight thiols

The sample preparation method was adapted by Fabrega-Prats 2016 (manuscript in preparation) from the methods developed by Oe et al. (1998) and Masi et al. (2002). Wine samples were homogenized in a mixture of components keeping the antioxidant conditions in order to avoid the oxidations of the LMW thiols. Then, the samples were centrifuged at 30.000 rpm for 5 min at 4 °C. Derivatisation of thiol compounds with SBD-F (ammonium 7-fluoro 2,1,3-benzooxadiazole-4-sulfonate) was performed as follows: 50 µL of supernatant were added to a mixture composed of 117 µL of potassium borate buffer (1mol/L pH 10.5), 33 µL of TBP (tributylphosphine) (1% in water) and 33 µL SBD-F (0.3% in water); then, the mixture was incubated for 60 min at 60 °C. After the reaction, the mixture was put into an ice bath and derivatisation was terminated by adding 17 µL of 4M HCl.

Chromatographic separation and quantification was carried out on a HPLC Agilent 1200 series equipped with a fluorescence detector (HPLC-FLD). The column was a Phenomenex Luna RP C18 (150 mm x 3.0 mm, 3 µm). The injection volume was 20 µL, the oven temperature was 35 °C and the samples were kept at 5 °C throughout the analysis. Mobile phase flow rate was 0.3 mL/min, using 75 mM ammonium formate buffer (pH 2.9) containing 3% methanol. Thiols were detected fluorometrically (excitation wavelength: 386 nm; emission wavelength: 516 nm) and identified by comparison with the retention times of standard compounds.

4.2.4 Chemical analysis of volatile compounds

The volatile composition of wine samples of 2013 was analysed together with those of 2015 vintage. The volatile compounds investigated are listed in Table S2.

4.2.4.1 Analysis of fermentation derived aroma compounds

Fermentation derived aroma compounds including alcohols, fatty acids, and their acetate and ethyl esters were analysed by means of gas chromatography coupled to mass spectrometry (GC-MS). Extraction procedure was performed as reported by Rapp et al. (1994) and modified by Fischer and Rauhut (2005) (not published): 2 g of sodium chloride (NaCl), 10 µL of the internal standard solution (2,6-dimethylhept-5-en-2-ol and cumene; c= 1188 µg/L and c= 107 µg/L, respectively), 100 µL of 1,1,2-trichloro-1,2,2-trifluoroethane were added to 10 mL of wine. Samples were agitated for 20 min and centrifuged at 3000 rpm for 8 min. The organic phase was removed and dried over sodium sulfate.

GC-MS analysis was carried out on a GC Hewlett Packard (HP) 5890 Series II (Agilent, Santa Clara, USA) equipped with a 5972 Hewlett Packard (HP) Mass Selective Detector (Agilent) and a 5% phenylmethyl siloxane capillary column (VF-5MS, 60m×0.32mm ID×1 µm) (Varian, Palo Alto, USA). Injection of 2 µL of sample was performed at an injector starting temperature of 30 °C in splitless mode which then was increased to 230 °C at 12 °C/min and held for 4 min. The oven temperature was programmed as follows: 40 °C for 5 min, then increased to 125 °C at a rate of 3 °C/min, and finally increased to 200 °C at a rate of 6 °C/min, and held for 14.2 min. Helium was used as carrier gas with a constant column flow rate of 1 mL/min. Temperature of MS interface was set to 210 °C; ion source temperature was 230 °C. Mass spectral data was acquired in scan mode, covering a mass-to-charge ratio range from m/z 35–250 in Electron Impact mode at 70 eV.

4.2.4.2 Analysis of low volatile sulfur compounds

Volatile sulfur compounds were separated and quantified by headspace gas chromatography with pulsed flame-photometric detection (HS-GC–PFPD) according to Rauhut et al. (2005). The wine samples (5 mL) were cooled down at 4 °C and transferred into argon flushed 5 mL GC vials containing 4 mg/L 2,6-di-tert-butyl-4-methyl-phenol, 0.27 g/mL

NaCl, 0.2 g/L EDTA (ethylenediamine tetra acetic acid) and 500 mg/L propanal to bind SO_2. An ethanolic internal standard solution of methyl-iso-propylsulfide (6 µg/L) and butylmethylsulfide (6 µg/L) was added. Thereafter, the samples were preheated for 45 min at 60 °C and 1 mL of the headspace was injected into the cool injection system.

Chromatography was performed with a GC Hewlett Packard (HP) 6890 Series II (Agilent) equipped with cooled injection system CIS-4 (Gerstel), a headspace sampler HSS, Multi-Purpose-Sampler (MPS2, Gerstel), and coupled to a PFPD Model 5380 (Ol Analytical, College Station, TX, USA). Compounds were separated on a SBP-1 Sulfur column 30 m × 0.32 mm ID × 4 µm (Supelco, Bellefonte, PA, USA). Helium was used as carrier gas with a linear velocity of 21 cm/s at 60 °C. The temperature was held at −60 °C and then increased to 180 °C at a rate of 12 °C/s and then held for 8 min. The oven temperature was held at 35 °C for 5 min and then increased to 180 °C at a rate of 10 °C/min and then was held for 10 min. The detector temperature was set to 250 °C and compressed air and hydrogen flow were controlled by pressure (420 kPa for both).

4.2.5 Statistical analysis

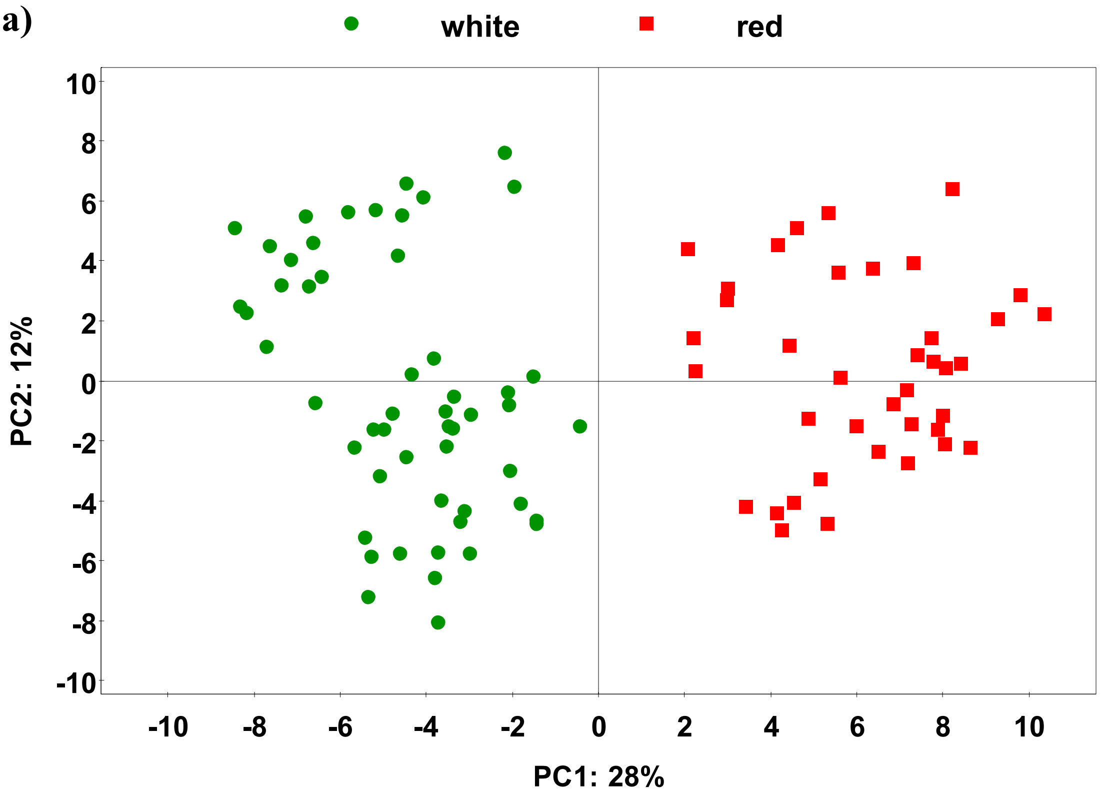
A total of 123 variables found in the majority of the wine samples were taken into account in multivariate statistical data analysis. Principal component analysis (PCA) and orthogonal partial least squares discriminant analysis (OPLS-DA) were carried out using SIMCA-P version 12.0 (Umetrics, Sweden). Univariate analysis was performed using Statistica 13 software (Statsoft,Tulsa, USA).

4.3 Results and Discussion

4.3.1 Multivariate analysis

In order to obtain preliminary and exploratory information, the data set (92 samples and 123 variables) was subjected to multivariate statistical analysis. First step of the analysis was Principal Component Analysis (PCA) which showed, as expected, grouping of the samples based on the wine colour. In Fig. 1a, the score plot shows the distinct separation of wines into two groups in the first component: white wines are located in the left part of the plot while red wines are grouped on the right side. The first two principal components (PC1 and PC2) explained 28% and 12% of the variance, respectively.

Considering the vintage of grape harvest, the PCA analysis also permitted to clearly separate the wine samples. As it shown in Fig. 1b, both red and white wine samples were divided into three groups corresponding to the vintages considered. Indeed, the wines of 2013, 2015 and 2016 vintages were located on the bottom, middle part and top of the plot, respectively. Nevertheless, such a distinct differentiation of the wines also according to where the grape varieties were grown was not found (Fig. 1c). Rather it was possible to note that wines of the same variety, for the same vintage of both countries were located close. Therefore, vintage had a strong influence on the composition of wines produced from a given grape variety and it was found to be a major factor for wine sample discrimination in accordance to previous studies (Pereira et al., 2006; Roullier-Gall et al., 2014). Furthermore, it was observed that the environmental factors at the site of cultivation were not so discriminant to mask the influence of the genotype.



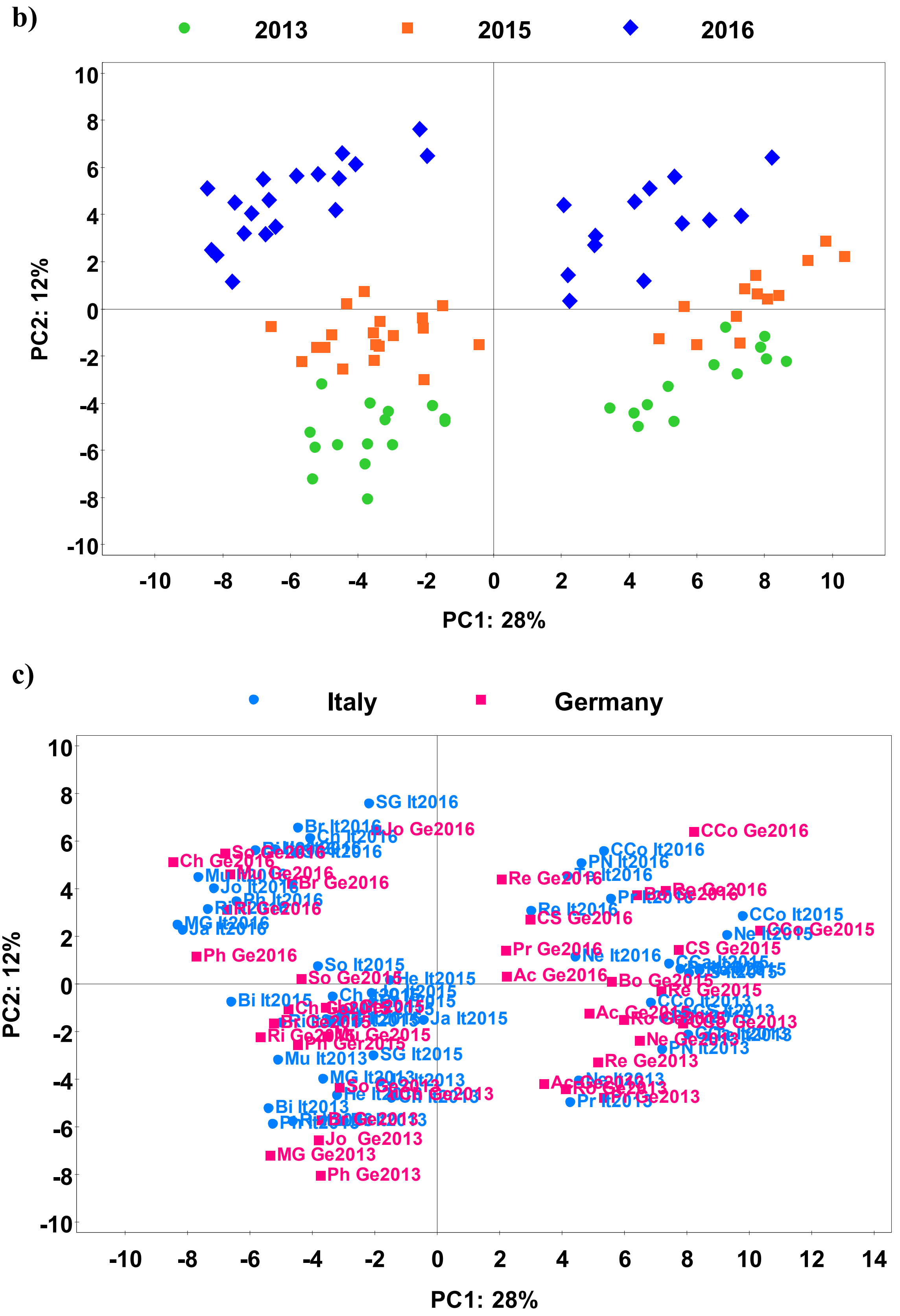


Figure 1. PCA plot of all the wines investigated according to colour (a), vintage (b) and country of cultivation (c) of the grape varieties. For acronyms, see Table 1.

In the second step to tease out the possible differences between wine samples according to the country of origin of the grape varieties, OPLS-DA analysis was applied to the dataset. The OPLS-DA score plot showed a clear separation of wines in relation to place of vineyards (Fig. 2). Then, OPLS-DA loading plot (Fig. 3) was generated to identify and extract the most discriminative metabolites responsible for the variation in the score plots. In this regard, there were considered variables showing PLS weights bigger than 0.1.

Wines produced from grapevines grown in Italy resulted in higher relative amounts of magnesium, phenyl acetate, homocysteine, linalool, γ-glutamylcysteine, isorhamnetin-3-*O*-glucoside, 2-phenylethanol, α-terpineol and fructose than those from Germany. On the other hand, wine samples made from grapes harvested in Germany appear to be richer in tartaric acid, hexanol-1-ol, sodium, calcium, ethyl lactate, cyanidin-3,5-diglucoside, iron, lactic acid, peonidin-3,5-diglucoside and lactic acid. This suggested that the metabolites contributed most to the discrimination between wine samples produced from grapes harvested in Italy and Germany were mainly minerals, fermentation derived aroma compounds, low-molecular-weight thiols and diglucoside anthocyanins (the latter related to red wines only).

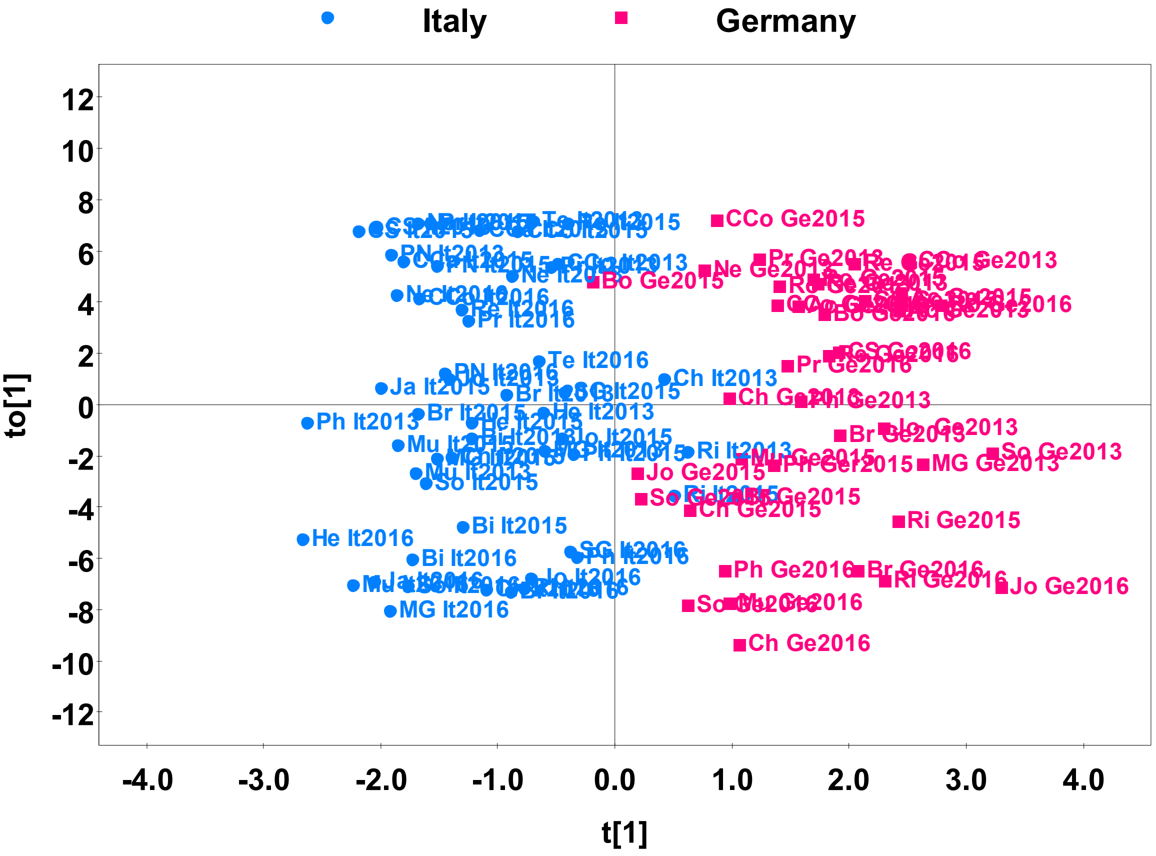


Figure 2. PLS-DA score plot of all the wines studied depending on the country of cultivation of the grape varieties.

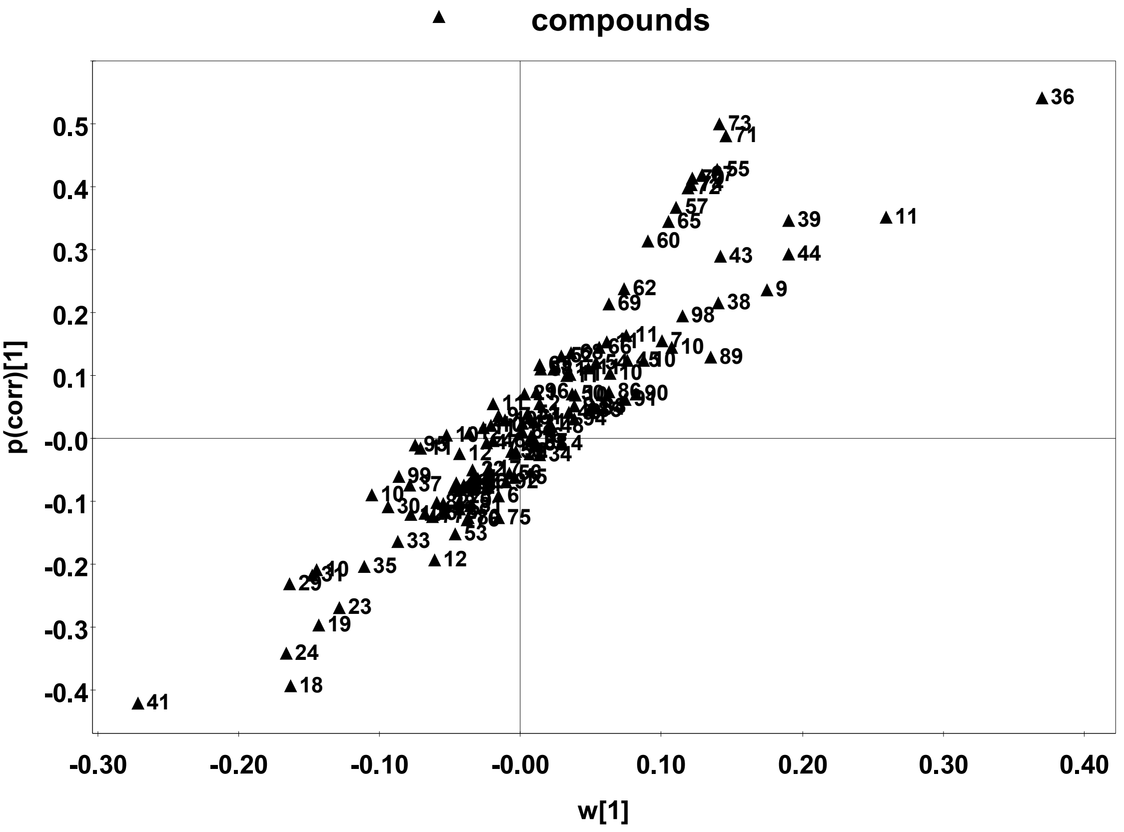


Figure 3. PLS-DA loading plot of composition variables for all the wine samples studied depending on the country of cultivation of the grape varieties. Compounds are represented by numbers for visualisation purposes and the list is as follows: 1, H_2S; 2, DMS; 3, CS_2; 4, MeSAc; 5, ethyl acetate; 6, 3-methyl butanol + 2-methyl butanol; 7, ethyl isobutanoate; 8, ethyl butanoate; 9, ethyl lactate; 10, iso-valerate; 11, hexan-1-ol; 12, 3-methylbutyl acetate + 2-methylbutyl acetate; 13, hexanoic acid; 14, ethyl hexanoate; 15, hexyl acetate; 16, *trans*-linalool oxide; 17, *cis*-linalool oxide; 18, linalool; 19, 2-phenylethanol; 20, octanoic acid; 21, diethyl succinate; 22, ethyl octanoate; 23, α-terpineol ; 24, phenylethyl acetate; 25, decanoic acid; 26, ethyl decanoate; 27, Cys; 28, CysT; 29, HCys; 30, Cys-Gly; 31, g-Glu-Cys; 32, GSH; 33, NAC; 34, glucose; 35, fructose; 36, tartaric acid; 37, malic acid; 38, lactic acid; 39, Ca; 40, K; 41, Mg; 42, Cu; 43, Fe; 44, Na; 45, Zn; 46, 2,3-butanediol; 47, acetic acid; 48, ethanol; 49, glycerol; 50, methanol; 51, proline; 52, shikimic acid; 53, succinic acid; 54, trigonelline; 55, delphinidin-3-*O*-glucoside; 56, cyanidin-3-*O*-glucoside; 57 petunidin-3-*O*-glucoside; 58, peonidin-3-*O*-glucoside; 59, malvidin-3-*O*-glucoside; 60, delphinidin-3-*O*-(6"-acetyl)-glucoside; 61, cyanidin-3-*O*-(6"-acetyl)-glucoside; 62, petunidin-3-*O*-(6"-acetyl)-glucoside; 63, peonidin-3-*O*-(6"-acetyl)-glucoside; 64, malvidin-3-*O*-(6"-acetyl)-glucoside; 65, delphinidin-3-*O*-(6"-*p*-coumaroyl)-glucoside; 66, cyanidin-3-*O*-(6"-*p*-coumaroyl)-glucoside; 67, petunidin-3-*O*-(6"-*p*-coumaroyl)-glucoside; 68, peonidin-3-*O*-(6"-*p*-coumaroyl)-glucoside; 69, malvidin-3-*O*-(6"-*p*-coumaroyl)-glucoside; 70, delphinidin-3,5-*O*-diglucoside; 71, cyanidin-3,5-*O*-diglucoside; 72, petunidin-3,5-*O*-diglucoside; 73, peonidin-3,5-*O*-diglucoside; 74, malvidin-3,5-*O*-diglucoside; 75, procyanidin B1; 76, procyanidin B2; 77, catechin; 78, cat (extension units); 79, cat (terminal units); 80, epicatechin; 81, epicat (extension units); 82, epicat (terminal units); 83, gallocatechin; 84, gallocat (extension units); 85, gallocat (terminal units); 86, epigallocatechin; 87, epigallocat (extension units); 88, epigallocat (terminal units); 89, cat gallate + epicat gallate; 90, cat gallate + epicat gallate (extension units); 91, cat gallate + epicat gallate (terminal units); 92, cat + epicat (upper units); 93, epigallocat (upper units); 94, epicat gallate (upper units); 95, p-hydroxybenzoic acid; 96, vanillic acid; 97, gallic acid; 98, caftaric acid; 99, fertaric acid; 100, *trans*-coutaric acid; 101, phloridzin; 102, luteolin-7-*O*-glucoside; 103, quercetin; 104, taxifolin; 105, kaemp-3-*O*-glu; 106, que-3-*O*-glu + que-3-*O*-gal; 107, isorhamn-3-*O*-glu; 108, que-3-*O*-glucur; 109, kaemp-3-*O*-glucur; 110, arbutin; 111, *trans*-resveratrol; 112, *cis*-resveratrol; 113, *trans*-piceide; 114, *cis*-piceide; 115, astringin; 116, isorhapontin; 117, caff acid + cat cond; 118, pallidol; 119, amp D + quadrangularin A; 120, isohopeaphenol; 121, methyl gallate; 122, ellagic acid; 123, syr-3-*O*-glu + syr-3-*O*-gal. For abbreviations see Supplemenary Tables S3-S10.

Mineral elements present in the soil are known to contribute to the chemical differentiation and identification of the geographical origin of wines (Burin et al., 2010). In fact, it follows that soil, together with vine, climate and "cultural practices constitute an interactive ecosystem defined by the concept of "terroir" in viticulture (Van Leeuwen & Seguin, 2006). In particular, Roullier-Gall et al. 2014 revealed that the terroir definitely impacts the initial chemical composition of a wine but that this effect becomes remarkable and clear with bottle ageing.

Next, PCA analysis was applied separately to white and red wines in order to better compare, within each group, the composition of wines produced from PIWI and *V. vinifera* varieties. The PCA of red and white wines explained 34% and 35% of total variation, respectively. As it is shown in Figure 4, no distinct separation between wines produced from PIWI and *V. vinifera* varieties based on their overall chemical composition was observed. The two groups of genotypes are actually sharing the same metabolomic space.

Then, OPLS-DA analysis was performed to investigate the major variations between disease tolerant varieties and references. The score plots for red and white wines are presented in Fig. 5a and b, respectively. Application of OPLS-DA clearly distinguished the two groups of wine samples (PIWI and *V. vinifera* varieties). According to the PLS-DA loading plot applied to red wine samples (Fig. 6a), the most significant metabolites distinguishing between PIWI and *V. vinifera* varieties included the five diglucoside forms of anthocyanins, monoglucoside coumaroyl anthocyanins (delphinidin, petunidin and cyanidin), zinc, tartaric acid and *cis*-linalool oxide. These compounds were found in higher amounts in wines from disease tolerant varieties. On the other hand, red wines from *V. vinifera* cultivars contained higher amounts of sodium, thiocysteine, gallocatechin, malvidin-3-*O*-glucoside, catechin, cysteine-glycine, isorhamnetin-3-*O*-glucoside, homocysteine and epicatechin.

The OLPS-DA loading plot for the chemical compounds of white wines is presented in Fig. 6b. This plot showed decreased levels of shikimic acid, cysteine-glycine, copper, potassium, malic acid, thiocysteine, sodium, hydrogen sulfide, isorhamnetin-3-*O*-glucoside, methanol, cysteine, 2,3-butanediol and calcium and increased levels of magnesium, ethyl isobutanoate, 2-phenylethanol, catechin gallate + epicatechin gallate, methyl gallate, succinic acid, 3-methyl butanol + 2-methyl butanol, *S*-methyl thioacetate, ethanol, quercetin, astringin, epicatechin and epicatechin (extension units) in wines produced from disease tolerant varieties as compared to references.

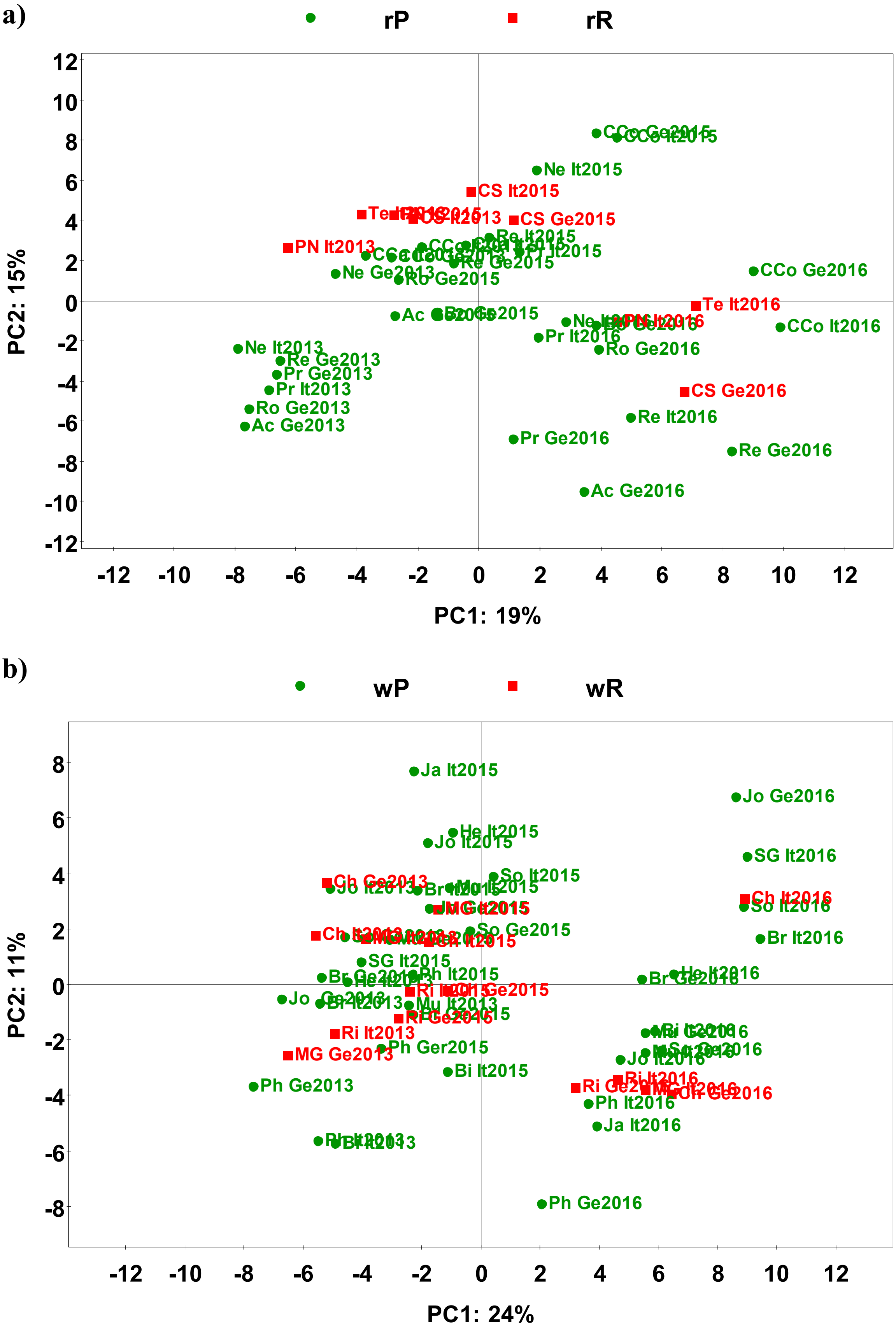


Figure 4. PCA plot of red (a) and white (b) wines. Abbreviations: rP, red PIWI variety; rR, red reference variety; wP, white PIWI variety; wR, white reference variety.

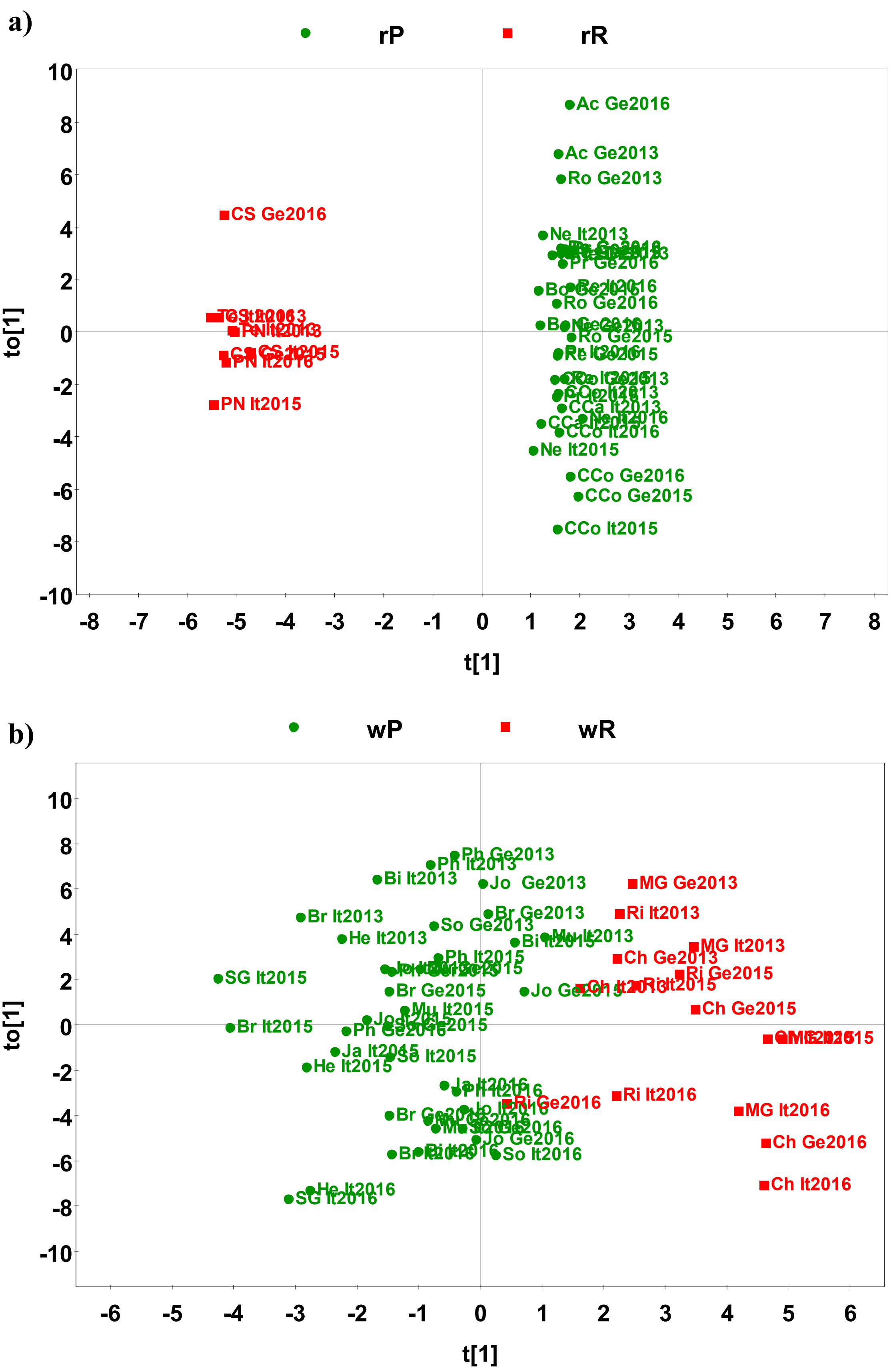


Figure 5. OPLS-DA score plot of red wines (a) and white wines (b). Abbreviations: rP, red PIWI variety; rR, red reference variety.

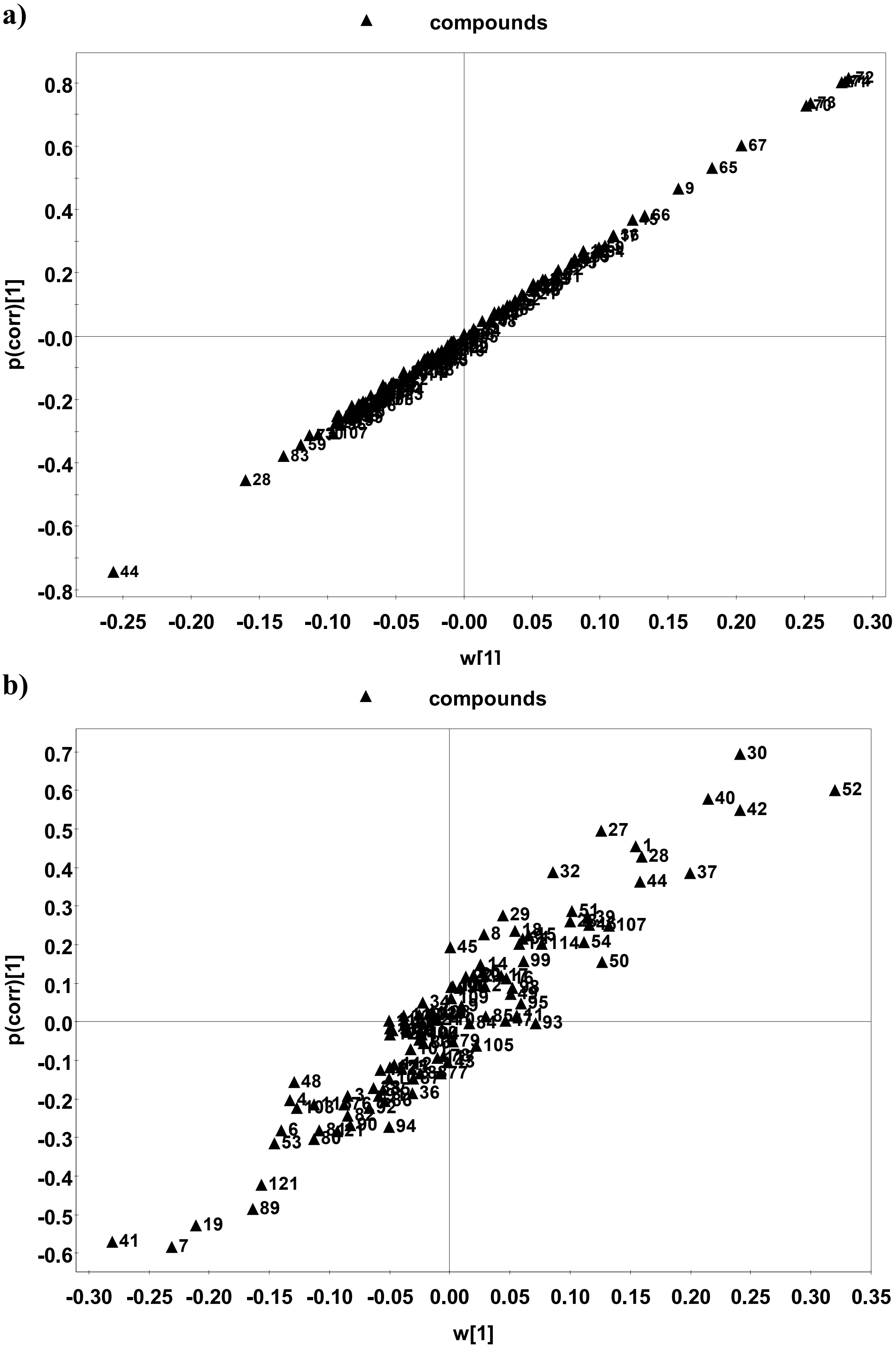


Figure 6. OPLS-DA loading plot of composition variables for red (a) and white (b) wines. Compounds are represented by numbers for visualisation purposes and the list is reported in the caption above Figure 3.

4.3.2 Non-volatile composition

Oenochemical parameters

The basic oenochemical parameters in the wines studied are summarised in Table S3. The alcoholic strength was included between 8.0 and 15.5% in red wines, while it ranged between 9.0 and 17.5% in white wines (Fig. 7a). White wines made from disease tolerant varieties showed a larger range of total alcohol content than *V. vinifera* varieties. In particular, wines made from disease tolerant varieties Solaris, Souvignier Gris, Jasmine and Muscaris were characterised by a high average alcoholic grade (14.67%, 14.21%, 13.65% and 13.14%, respectively). With regards to Solaris, it is acknowledged that this variety produce wines with a high total alcohol and prefers to be cultivated at an altitude higher than 700 meters above sea level (Lieselehof, 2017). Therefore, the alcoholic grade observed for Solaris wines was suitable for this type of white wine even though it was found to be higher than that detected in wines produced from varieties grown in Denmark (Liu et al., 2015). As regards red wines, the mean total alcohol content was found in similar amounts between PIWI and reference varieties with the exception for Rondo and Bolero.

Among alcohols, methanol is well known as a toxic and harmful substance to human health. In wines, methanol is produced before and during the alcohol fermentation from the degradation of pectic substances, naturally present in crushed grapes, by pectinase enzymes. More methanol is produced when must is fermented on grape skins which are rich in pectins (Cordonnier, 1987). In fact, higher levels of methanol are found in red wines as compared to white wines. The range for methanol found in both red and white wines under study was quite similar to that found in commercial wines from Australia (Hodson, Wilkes, Azevedo, & Battaglene, 2017). It was observed that red wines from PIWI varieties were characterised by a wider range of methanol than those made from reference varieties (Fig. 7b). The increased concentration observed may be attributable to the higher pectin content of red grape skins of these varieties. On the contrary, the methanol content of white wines made from PIWI varieties fell into the range of that found for reference varieties (Fig. 7b). According to the International Organisation for Vine and Wine (OIV), maximum acceptable level for methanol in red wines is 400 mg/L, while it is 250 mg/L in white and rosé wines. In this study, none of the wines analysed exceeded these limits (Table S3). pH values ranged from 3.30 to 3.80 and from 3.00 to 4.10 in red PIWI and reference varieties, respectively. In white wines pH was, in some cases, lower than the mean value but within the normal range. It varied from 2.70 to 3.60 and from 2.80 to 3.50 in white PIWI and reference varieties, respectively.

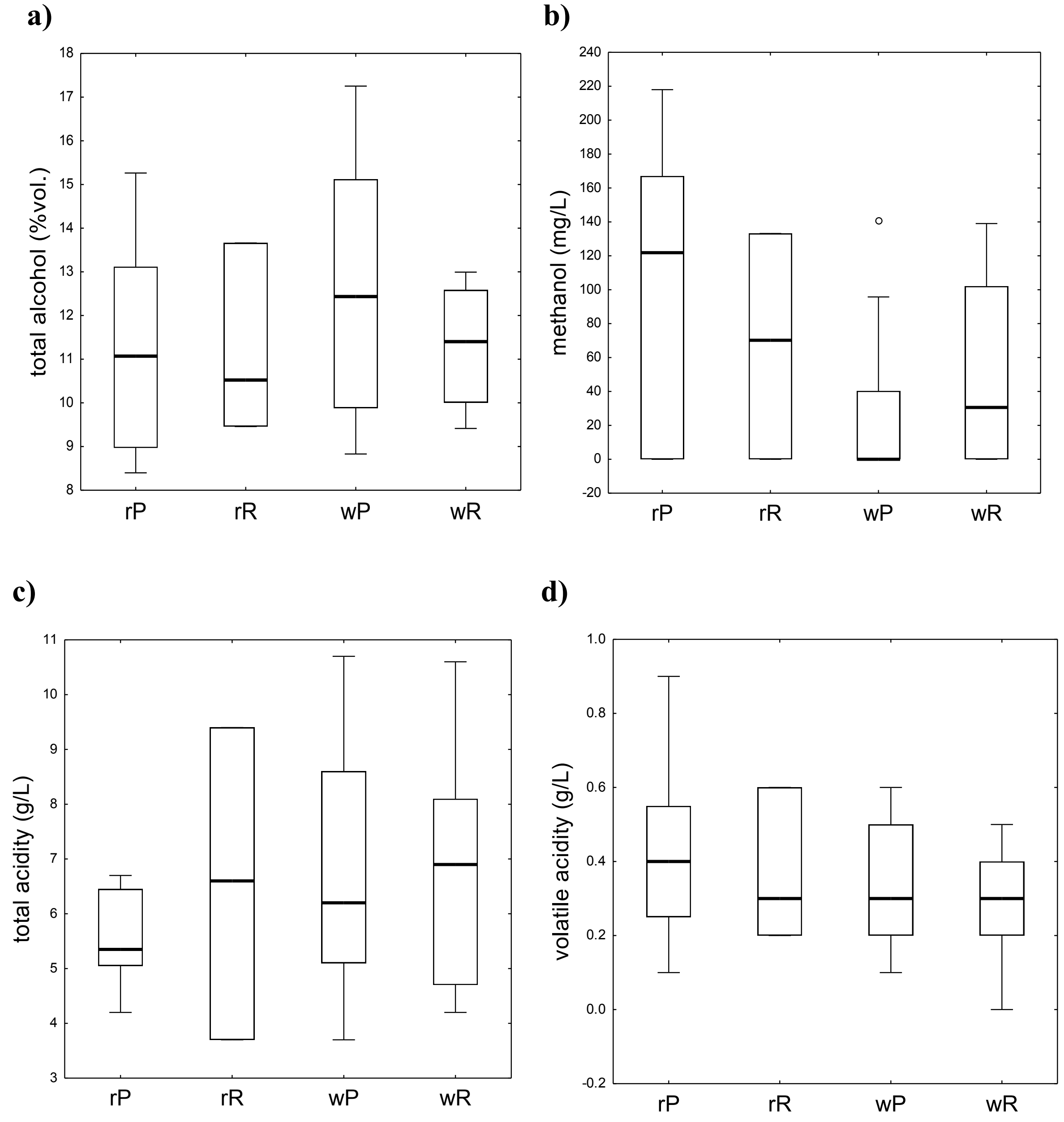


Figure 7. Boxplots illustrating the total alcohol (a), methanol content (b), total acidity (c) and volatile acidity (d). Abbreviations: rP, red PIWI varieties; rR, red reference varieties; wP, white PIWI varieties; wR, white reference varieties.

The levels of total acidity varied from 3.70 to 8.80 g/L in red wines and from 4.30 to 11.20 g/L in white wines. In particular, it was observed that the total acidity (TA) of red wines made from PIWI varieties fell into the range of that found for reference varieties; while the range observed for TA was comparable between white wines produced from PIWI and reference varieties (Fig. 7c). Previous studies (Okamoto et al., 2002; Liang et al., 2012) have reported that the berries of wild *Vitis* species and most disease tolerant hybrids are relatively high in acid resulting in wines relatively poor in alcohol and not well balanced for acid. In our study, red wines made from Regent, Cabernet Cortis and Cabernet Carbon varieties resulted being the best balanced in terms of acid and alcohol content. The mean total alcohol and acid content accounted respectively for 11.66% and 5.28 g/L in Regent, 12.21% and 5.73 g/L in Cabernet Cortis and 11.90% and 5.35 g/L in Cabernet Carbon. On the other hand, Johanniter and Bronner were the white wines with a well-balanced amount of total acidity and total alcohol. The mean total alcohol and acid content accounted respectively for 12.11% and 7.02 g/L in Johanniter and, 11.15% and 7.75 g/L in Bronner.

Volatile acidity in wine consists of free and combined forms of volatile acids. It ranged from 0.10 to 0.90 g/L and from 0.20 to 0.60 g/L in red and white wines, respectively. Red wines from PIWI varieties showed a wider range of volatile acidity in comparison to reference wines, while in white wines it was comparable between wines made from PIWI and reference varieties (Fig. 7d).

Low molecular weight phenols

The levels of the phenolic compounds detected in the wines analysed are given in Table S4. Among the red wines studied, Cabernet Carbon and Teroldego were characterised by the highest mean level of total low molecular weight phenols (129.92 and 126.17 mg/L, respectively). Accent, Rondo, Prior and Regent were the PIWI varieties with a lower average amount of total phenols compared to references. With respect to white wines, the highest levels of total phenols were recorded in wines from Chardonnay (96.94 mg/L) and Muscaris (95.07 mg/L). Wines produced from disease tolerant Bianca and Phoenix varieties were found to contain a low amount of total phenols as compared to *V. vinifera* references.

Caftaric and *trans*-coutaric acids were the most common phenolic acids found in the wines analysed. These results were expected being this class of phenols ubiquitary in grapevine, and are in agreement with those reported by the analysis of disease tolerant varieties growing in Poland (Samoticha et al., 2017). However, some red and white PIWI wines of 2016 vintage from Italy showed a low level of *trans*-coutaric acid when compared to the other wine samples produced from the same variety in the other vintages. The other phenolic acids quantified (p-hydroxybenzoic, vanillic, gallic, ellagic and ferulic acids, and methyl gallate) occurred in small amounts in all wines. Phenolic acids are important wine phenolics because they are good wine co-pigments and play an important role in oxidative discoloration of wines (Lago-Vanzela et al., 2014). In red wines, the lowest and highest amount of phenolic acids was detected in Regent and Cabernet Carbon. Phoenix and Muscaris were found to contain the highest and lowest level of phenolic acids among white wines. Among flavonols, quercetin derivatives and taxifolin were the most common compounds in all wines studied. Kaempferol derivatives were found in traces and not in all the wines analysed. A higher level of kaempferol was observed in varietie red Polish wines when compared with our results (Socha et al., 2015).

Stilbenes were detected in low amounts and not in all the wine samples studied. Resveratrol forms, astringin, isorhapontin and pallidol were the most common compounds detected. In wines studied, resveratrol was mostly as glycoside rather than as aglycone. In fact, *cis*-and *trans*-resveratrol were present in traces and not in all samples, whereas *cis*-and *tran*s-piceide (the glucoside forms) were detected in higher amounts in the majority of both red and white wines. These results are in agreement with those reported by Pedastsaar et al. (2014). In our study, the highest amounts of piceide (including both *cis*- and *trans*- forms) were found in Cabernet Cortis from Germany 2016 and Johanniter from Germany 2015. With respect to red wines, Cabernet Carbon and Rondo were the varieties with a higher mean total amount of stilbenes as compared to references; Muscaris and Chardonnay contained the highest mean total level of stilbenes among white wines.

Anthocyanins

A total of 20 anthocyanins were detected and quantified in this study (Table S5). The total anthocyanins were in the range 204.82- 2318.00 mg/L and 75.49-711.89 mg/L in red wines made from PIWI and reference varieties, respectively. Previous authors have reported that disease tolerant varieties contain high levels of anthocyanins as compared to *V. vinifera*. In this study, PIWI varieties with a high mean level of total anthocyanins were Rondo, Accent, Regent, and Bolero. These results are in agreement with the findings of Antoce et al. (2008) who observed that the level of anthocyanins found in Regent was 3 times higher as compared to Cabernet Sauvignon. In our study, the anthocyanin concentrations of Regent and other disease tolerant varieties (Rondo, Accent and Bolero) were almost 2 times higher in comparison to *V. vinifera* varieties. Rondo was found to be richest source of anthocyanins in agreement with Socha et al. (2015). However, Pedastsaar et al. (2014) observed that Rondo from Estonia had the lowest concentration of total anthocyanins among the varieties studied. It is generally understood that the concentration of anthocyanin in wine is affected by grape variety, terroir and also winemaking practices.

On the contrary, Cabernet Carbon and Nero contained a lower or similar anthocyanin amount in comparison to references. Furthermore, differences in the total anthocyanins were observed in of different vintages. As reported by many authors, the relative amounts of the anthocyanin families can change significantly depending on the grape cultivar and within a specific cultivar on endogenous and exogenous factors that include plant age, vine cultivation, vintage, and climate conditions (Mattivi et al., 2006; Picariello, Ferranti, Chianese & Addeo, 2012; Rodríguez-Delgado, González-Hernández, Conde-González, & Pérez-Trujillo, 2002). Malvidin derivatives were the most abundant anthocyanins present in all wines as previously described (Wrolstad, 2000). On the other hand, cyanidin derivatives were detected in low amounts in the majority of wines studied. Coumaroyl derivatives were the most abundant forms in Cabernet Cortis, Nero, Accent and Bolero while in the other wine samples the acetyl derivatives were predominant (Table S5). Both these forms of anthocyanins can participate in the formation of both inter- and intra-molecular copigmentation complexes, thus contributing to the stability of anthocyanins and intensity of the red colour of wine (Figueiredo-González et al., 2012).

On the basis of the results obtained from the characterisation of the chemical composition of grapes from disease tolerant varieties described in chapter 3, diglucoside anthocyanins were detected in wines made by PIWI varieties. Out of the eight disease tolerant varieties, one produced wine which contained diglucosides for less than 8% of the total amount of anthocyanins (variety Nero). In wines of the seven remaining PIWI varieties more than 50% of total anthocyanins was found to be diglucosides.

The predominance of 3,5-diglucosides may preserve anthocyanins against further reactions leading to colour stabilisation in aged red wine, including those that give rise to the more stable red-orange pigments called pyranoanthocyanins, which are often observed in wines made from *Vitis vinifera* (Lago-Vanzela, Da-Silva, Gomes, García-Romero, & Hermosín-Gutiérrez, 2011). Furthermore, the monomeric anthocyanins in red wines are not particularly stable, are easily oxidized and tend to decrease significantly with aging, with a concomitant increase in condensed products. On the other hand, diglucoside anthocyanins are more stable than their monoglucoside counterparts, but are more susceptible to browning and are less coloured (He et al., 2012).

In this study, diglucoside anthocyanins were found in the majority of the wines studied and traces of these compounds were also found in Nero and some *V. vinifera* references although they were not detected in their corresponding grapes as reported in chapter 3. As previously described (He et al., 2012), anthocyanin composition in red wines depends not only on the original anthocyanin profile of grape berries, but also on the winemaking techniques employed. Indeed, for a better assessment of the anthocyanin profile, some adjustments were taken into account in the winery for the vinification of grapes harvested in 2016 vintage. In particular, wine samples for chemical analysis were collected before the filtration. The results obtained from the investigation of the anthocyanin profile of reference wines of 2016 vintage have shown that diglucoside anthocyanins were not present in Pinot Noir and Teroldego whereas traces were detected in Cabernet Sauvignon. This observation is in agreement with a previous study which showed and confirmed the presence of anthocyanin 3,5-diglucosides in grape berries of Cabernet Sauvignon (Xing et al., 2015). Furthermore, also other *V. vinifera* cultivars have been found to contain diglucosides as described in the literature (Liang, Owens, Zhong, & Cheng, 2011; Yang et al. 2014).

In order to better visualise and compare the anthocyanin composition of red wines made from disease tolerant varieties and *V. vinifera* varieties, PCA analysis was performed. Fig. 8 shows the biplot for the first two principal components which accounted for 69% of total variance (42% and 27% for PC1 and PC2, respectively). All anthocyanins were explained by the loadings of PC1. Two main groups of wine samples were distinguished: on the bottom right of the plot there were the wines produced from PIWI grapes (with the exception of Pinot Noir from Italy of 2015) while on the top left-middle p those made from *V. vinifera* varieties and PIWI variety Nero. Therefore, diglucoside anthocyanins contributed to this distribution of the wine samples. It was then possible to note that wines made from grapes collected in both Italy and Germany in different vintages were located close. According to the literature, the anthocyanin profile is relatively stable and characteristic for each cultivar (Mattivi et al., 2006).

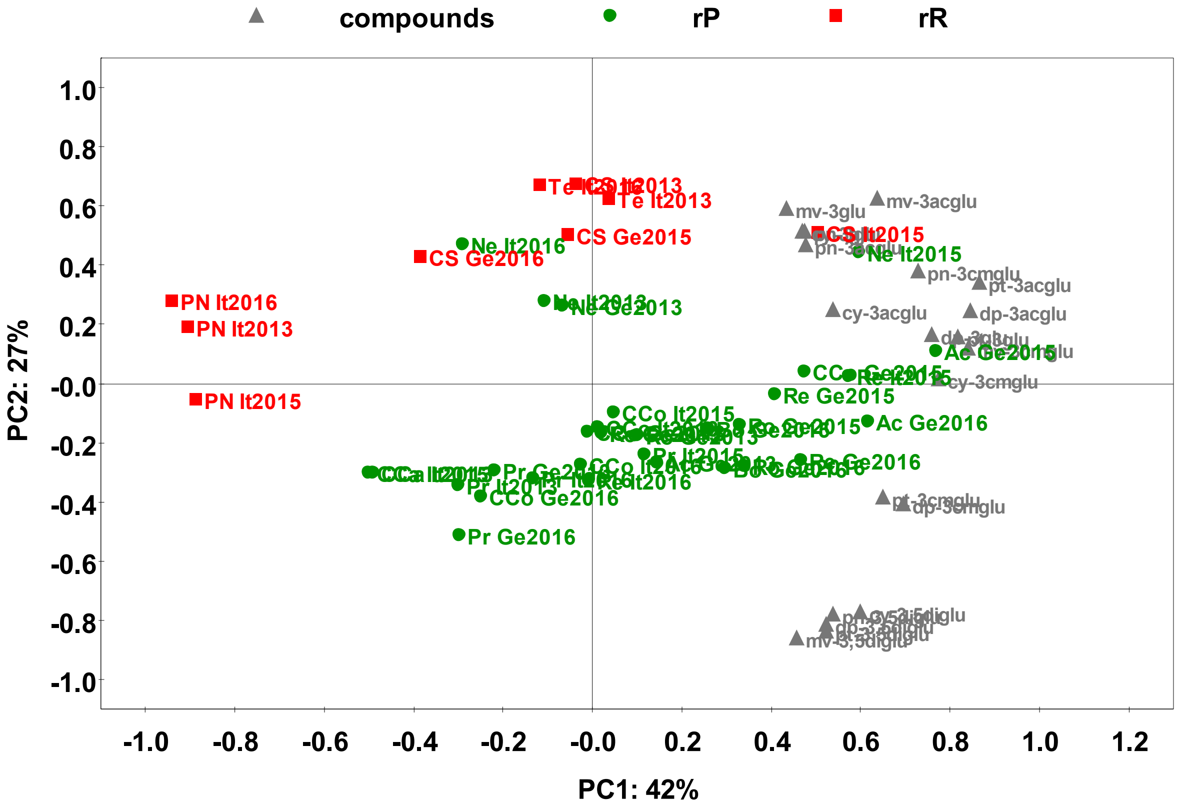


Figure 8. PCA biplot of anthocyanin profile of red wines. Abbreviations: rP, red PIWI variety; rR, red reference variety.

Flavan-3-ols and their polymers

Flavan-3-ol monomers (catechin, epicatechin, epigallocatechin, epicatechin gallate, catechin gallate and epigallocatechin gallate) and their oligomers and polymers, were identified and quantified in both red and white wines (Table S6). The analysis of the composition of red wines showed that catechin and epicatechin were the main flavan-3-ol monomers in agreement with the literature (Mattivi, Vrhovsek, Masuero, & Trainotti, 2009; Gris et al. 2011). Gallocatechin and epigallocatechin were present at lower concentrations. Procyanidin B1 was the most abundant dimer in all wine samples. The total flavan-3-ols momomers ranged from to 7.26 to 366.77 mg/L and from 21.29 to 248.00 mg/L in red PIWI and *V. vinifera* wines, respectively. The dimer concentrations were in the range of 6.69-208.03 mg/L in PIWI and 34.36-159.24 mg/L in reference wines. The mean total amount of flavanols, including both monomers and dimers, was found to be the highest in Pinot noir and Nero. In white wines, catechin, epicatechin and dimer B1 were present in small amounts as compared to red wines, due to the lack of maceration with the solid parts during the winemaking procedure. However, these metabolites were found to be the most abundant compounds of the class as well. Total flavan-3-ol monomers were in the range 0.42-20.71 mg/L and 1.02-9.33 mg/L in PIWI and reference wines, respectively. The dimer concentrations ranged from 0.03 to10.87 mg/L and from 0.12 to 10.68 mg/L in PIWI and in *V. vinifera* wines. The absolute amount of total flavanols was very variable among vintages for the majority of red wine samples.

Proanthocyanidins found in wine samples comprised catechin, epicatechin, gallocatechin, epigallocatechin, catechin gallate and epicatechin gallate as terminal and extension units. In our study, the terminal and extension units found in both red and white wines were mainly comprised of catechin. This is in part in agreement with Gris et al. (2011) who observed that in Brazilian *V. vinifera* red wines terminal and extension units were mainly of catechin and epicatechin, respectively. In the composition of red wines, proanthocyanidins play a crucial role being the major group of polyphenols responsible for wine astringency. A lower tannin concentration in wine made by disease tolerant varieties in comparison to *V. vinifera* wines has been reported by Springer et al. (2014). In particular, the low amount of PAs in wines from disease tolerant varieties was attributable to tannin-binding molecules, such as proteins and pectins, present in the cell wall.

In our study, it was observed that one PIWI variety (Cabernet Cortis) contained the highest amount of total proanthocyanidins; three varieties (Accent, Rondo and Bolero) contained a lower level of PAs as compared to traditional varieties. In the remaining three disease tolerant varieties (Regent, Cabernet Carbon and Prior) the mean amount of proanthocyanidins fell into the range of that found in the wine references Pinot Noir and Cabernet Sauvignon. Furthermore, it is worth to note that there were differences in total proanthocyanidins in wines produced from a given variety in different vintages.

As it shown in Fig. 9a, the percentage of galloylation (%G) of red wines produced by disease tolerant varieties was comparable to that observed in those made from *Vitis vinifera* varieties. It ranged from 1.06% to 9.06% in red wines under study in agreement with the literature (Monagas, Gómes-Cordovée, Begoña, Laureano, & Ricardo da Silva, 2003).

These values were higher than those reported by Gris et. al. (2011) although values even higher than those presented in our study have previously been reported in the literature (Cosme, Ricardo-da-Silva, & Laureano, 2009). As with red wines, the range of the percentage of galloylation was found to be similar between wines made from PIWI and reference varieties (Fig. 9b). The mean degree of polymerisation (mDP) reveals the polymerisation degree of proanthocyanidins. The mDP varied from 3.88 to 13.73 in *V. vinifera* wines in accordance with previous studies (Monagas et al., 2003). In red wines produced from mildew tolerant varieties, it ranged from 2.81 to 9.18. Therefore, it was observed that the range of mDP was also comparable between reference and PIWI varieties for both red and white wines (Fig. 9b).

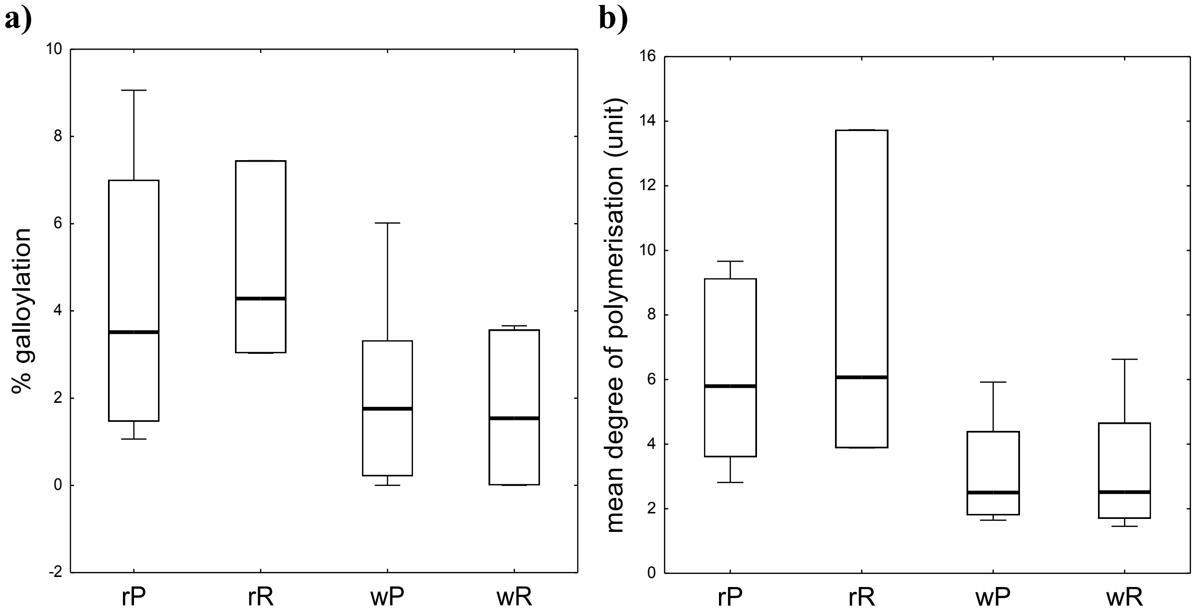


Figure 9. Boxplots illustrating the percentage of galloylation (a) and the mean degree of polymerisation (b) of the wines analysed. Abbreviations: rP, red PIWI varieties; rR, red reference varieties; wP, white PIWI varieties; wR, white reference varieties.

Measurement of total phenolic content by the Folin-Ciocalteu's assay

The total phenolic content (TPC) in wines under study was evaluated using the Folin-Ciocalteu method. The obtained results demonstrated a high variability of the TPC among the wines analysed (Table S3). In red wines, the TPC ranged from 1080 to 4116. mg/L for Pinot Noir Italy 2016 and Accent Germany 2016, respectively; in white wines, it varied from 124.50 to 355.50 mg/L for Phoenix Germany 2015 and Helios Italy 2013, respectively. It is clear that red wines were characterised by a significantly higher level of TPC than white wines in agreement with previously published results (Minussi et al., 2003; Socha, Gałkowska, Robak, & Fortuna, 2015). This is attributable to clear differences in wine making process (including maceration for red wines) as well as differences in the phenolic composition between red and white grapes. The range of total phenolic content of both red and white wines produced from PIWI varieties (1219.00-4116.50 mg/L in red wines and 100.00- 355.50 mg/L in white wines) was higher when compared to *V. vinifera* varieties (1080.00-2294.00 mg/L in red wines and 135.00-239.50 mg/L in white wines). Accent and Cabernet Cortis were the PIWI varieties with an average amount of total phenols higher than *V. vinifera* varieties. Considering that anthocyanins can be present in high levels in wines made from PIWI varieties, they can represent a contributing factor in determining the high content of phenols. Furthermore, the level of TPC of both white and red PIWI wines analysed in the present study was found to be higher as compared to that found in Polish wines made from PIWI grapes (Socha et al., 2015). As previously reported, polyphenolic composition in wine depends on grape variety, atmospheric conditions, viticulture and winemaking techniques (Mazza, Fukumoto, Delaquis, Girard, & Ewert, 1999; Rodríguez-Delgado et al., 2002).

Measurement of antioxidant activity

Antioxidant activity measured by TEAC assay ranged from 13.10 to 49.70 mmol/L in red wines and from 2.10 to 4.80 mmol/L in white wines (Table S3). Red wines showed higher antioxidant activity than white wines in agreement with literature (Fernández-Pachón, Villaño, Garc, & Troncoso, 2004). The range of AA in white wines made from PIWI varieties was comparable to that of references (from 2.10 to 4.80 mmol/L in wines from PIWI varieties and from 2.30 to 4.20 mmol/L in references) whereas it was slightly higher in red wines produced from mildew tolerant varieties as compared to *V. vinifera* varieties (from 15.20 to 49.70 mmol/L in PIWI wines and from 13.10 to 31.00 mmol/L in reference varieties). Since TEAC values greater than 11 are considered very high (Fernández-Pachón et al., 2004), all red wines tested in our study showed an evident antioxidant effect. In particular, Accent and Cabernet Cortis were the varieties with high mean TEAC values (38.50 and 32.47 mmol/L, respectively) and also high amounts of total phenolic content. It is known that wines with higher total phenol levels are better radical-scavengers than those with lower amounts. Indeed, the existence of a positive correlation between the antioxidant capacity of wines and their total phenolic content has been described in previous studies (Rigo et al., 2000; Minussi et al., 2003; Fernández-Pachón et al., 2004; Cimino, Sulfaro, Trombetta, Saija, & Tomaino, 2007).

Mineral composition

Potassium was the major ion present in all the wines analysed as reported in the literature (Kondrashov, Ševčík, Benáková, Koštířová, & Štípek, 2009). The concentration of potassium was higher in red wines than white wines ranging from 831.00 to 1878.00 mg/L and from 331.00 to 959.00 mg/L, respectively (Table S7). Calcium and magnesium were among the other most abundant cations. Other minerals, such as copper, iron, sodium and zinc were found in traces.

It has been reported that the mineral composition can be used as fingerprint to determine the geographical origin (or authenticity) of a wine taking into account the relationship between the metallic content in samples and soil composition (Frías et al., 2002; Burin et al., 2010). However, in our study it was not possible to characterise and obtain a separation of wine samples according to the vineyard location even if the wines were produced from grapes grown in different soils, countries (Italy and Germany) and in different climatic conditions.

Low-molecular-weight thiols

The amino acid cysteine is the main product of plant sulfur assimilation and also the main component of thiol-containing proteins, low-molecular-weight thiol compounds and other sulfur-containing molecules. Glutathione and related compounds, such as cysteine, γ-glutamylcysteine, cysteine-glycine, homocysteine, thiocysteine and N-acetylcysteine were identified and quantified (Table S8). Cysteine, glutathione and N-acetylcysteine were detected in all wines under study. The range of glutathione was higher in white wines as compared to red wines. In particular, it was found in the range of 0.10-5.03 mg/L and 0.24-3.81 mg/L in wines from mildew tolerant varieties and reference varieties, respectively. These results are in agreement with Marchand et al. (2010) who found glutathione ranged from 1.7 to 7.1 mg/L in Sauvignon Blanc and Chardonnay white wines. It has been demonstrated that glutathione plays an important role in the development of white wine aroma during bottle-aging (Ribéreau-Gayon et al., 2006).

Among red wines, the level of glutathione varied from 0.14 to 1.71 mg/L in disease tolerant varieties and from 0.09 to 1.05 mg/L in *V. vinifera* varieties. This range was found to be higher than that reported by Marchand et al. (2010) who observed that commercial red wines from the Bordeaux areas of different vintages contained small GSH amounts due to the wine aging. In fact, it is acknowledged that the amount of glutathione in wine decreases inevitably during aging because of its strong propensity for reacting with oxygen and oxidized phenolic compounds (Ribéreau-Gayon et al., 2006). In this study, it was possible to note that the GSH concentration for the majority of wines of 2013 vintage was lower as compared to the values quantified in the corresponding wines of 2015 and 2016 vintages.

4.3.3 Volatile composition

Knowledge of the components that are responsible for the aroma and flavour characteristics in wines is very important. To better compare and visualise the volatile composition of the wines under study, PCA analysis was performed. Fig. 10a shows the biplot of red wines where PC1 explained 39% and PC2 13% of total variance. On the other hand, the PCA of white wines explained 55% of total variation of the chemical variables, with 43% and 12% explained by the first and second component, respectively (Fig. 10b).

Clear separation of both red and white wines in three distinct groups according to the harvest vintage of the grapes was observed. Red wines of 2013 vintage had a strong positive correlation with some aroma compounds, such as dimethyl sulfide (DMS), diethyl succinate, ethyl isobutanoate, ethyl lactate, α-terpineol, diethyl succinate, cis- and *trans*-linalool oxide. With respect to white wines of 2013 vintage, they also were correlated to diethyl succinate and dimethyl sulfide. According to the literature, levels of DMS in freshly bottled wines are low but they increase during aging As previously reported, dimethyl sulfide tends to increase in concentration as wine ages probably due to the amounts of DMS precursors remaining in the wine (Segurel et al., 2004). Diethyl succinate tend to increase with time as well and its formation is promoted by temperature elevation (Shinohara & Watanabe, 1981). In this study, the presence of high amounts of these volatile compounds in wines of 2013 vintage can be explained considering that the chemical analysis of wines was carried out together with those of 2015 vintage.

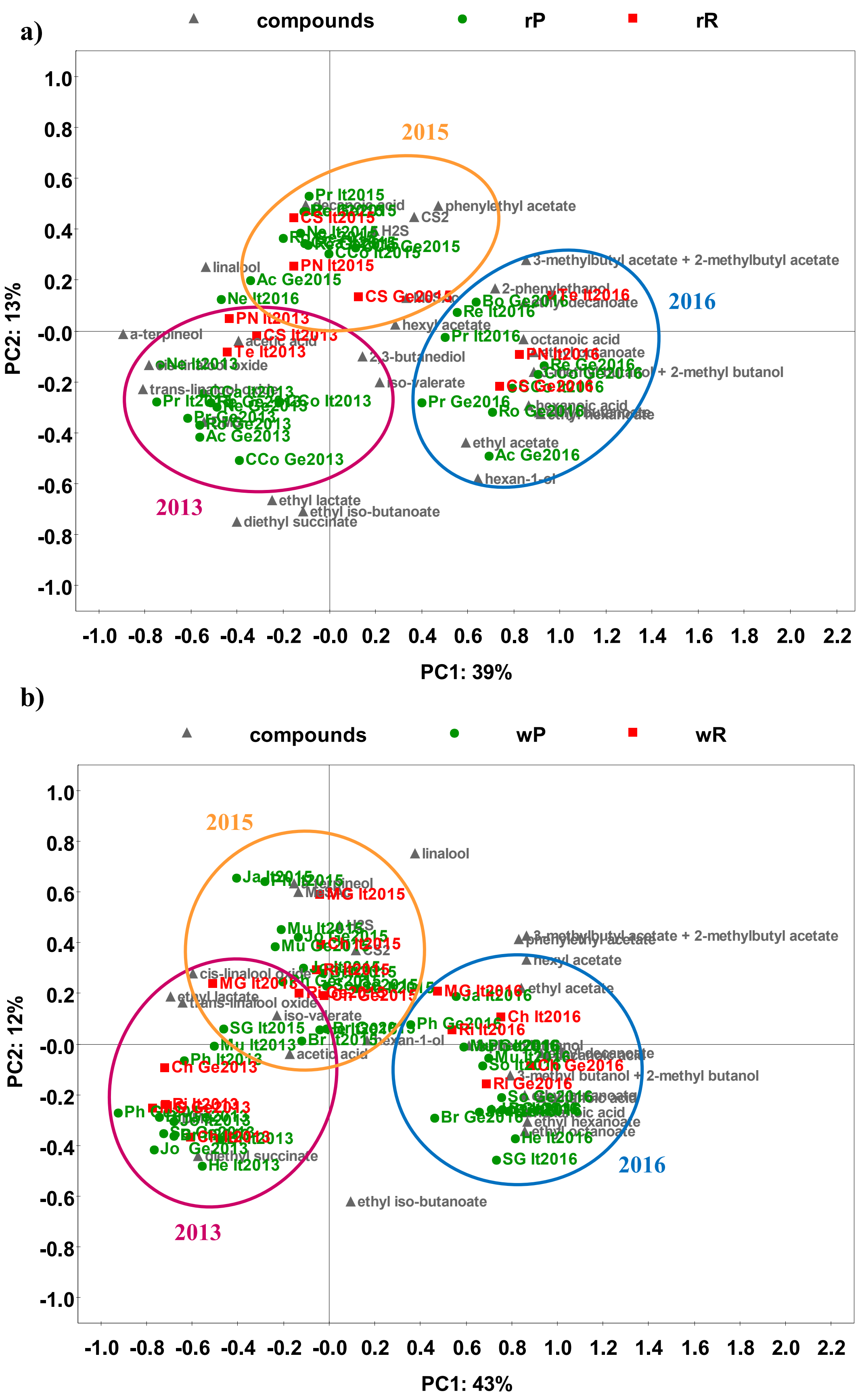


Figure 10. PCA biplot of volatile compounds for red (a) and white (b) wines. Abbreviations: rP, red PIWI variety; rR, red reference variety; wP, white PIWI variety; wR, white reference variety.

Fermentation derived aroma compounds

Twenty-three fermentation derived aroma compounds in wines produced out of *V. vinifera* and PIWI varieties were identified and quantified (Table S9). The volatiles belonged to different classes, namely: acids, alcohols, esters and monoterpenols. Esters constitute one of the most important classes of aroma compounds and are largely responsible for the fruity aromas of wines (Styger, Prior, & Bauer, 2011). The ethyl esters of fatty acids are formed from ethanolysis of acyl-CoA which is an intermediate metabolite of fatty acid metabolism. As can be seen in Table S9, ethyl lactate and diethyl succinate were quantitatively the main ethyl esters present in red and white wines. The esterification of lactic acid and succinic acid with ethanol is typically occurring during malolactic fermentation (García-Carpintero Gómez, Gallego Gómez, Sánchez-Palomo, & Viñas González, 2012). High levels of these compounds were found in PIWI white wines of the variety Solaris which had undergone malolactic fermentation; diethyl succinate was also found to be present at high level in wines without malolactic fermentation (Liu et al., 2015). In this study, Accent and Solaris had the highest mean amount of ethyl lactate in red and white wines, respectively. The level of diethyl succinate was found to be higher in all wines of 2013 vintage in comparison to those of other vintages because of the longer aging of these wines.

The other group of esters, the acetate esters are products of the reaction of acetyl-CoA with higher alcohols that are formed from the degradation of amino acids or carbohydrates (Perestrelo et al., 2006). The ethyl acetate, with a fruity odour of "pineapple", was the acetate ester found in high concentrations in all wines.

Another class of fermentative volatile compounds is the higher alcohols which are typically formed by yeast via the anabolic pathway from glucose or catabolic pathway from their corresponding amino acids. Among alcohols, 3 methyl-1-butanol and 2 methyl-1-butanol were found in high amounts ranging from 113.06 to 487.45 mg/L in red wines and from 121.25 to 534.56 mg/L in white wines. Hexanol is an alcohol which when found in high concentration can have a negative effect on the quality of the wine, because of a vegetable and herbaceous odour. Among red wines, higher mean levels of 1-hexanol were found in Rondo and Prior; while Jasmine and Phoenix were the white varieties with a higher amount in comparison to references. On the other hand we have to take this result with care, since differences during the pressing can greatly influence the formation of this pre-fermentative alcohol. A complete standardisation of this process is always critical in small plot winemaking. Monoterpenols play an important role in the aroma of white wines, being this group responsible for the floral and fruity aromas associated with the primary aroma of the wines. The monoterpenols identified in this study were linalool, α-terpineol and the oxide forms of linalool. The wine made by Nero had the highest total content of monoterpenols among red wines. As expected, wines of Moscato Giallo contained high concentrations of terpenols since these compounds are known to be key odourants in determining their aroma. However, Bianca was found to contain the highest amount of monoterpenols in comparison to all white wines.

The fatty acids hexanoic, octanoic, decanoic and acetic were identified in this study. It is known that high levels of acetic acid can impart a vinegar-off odour to wines. In our study, the wines made with the cultivar Nero resulted in the highest mean level of acetic acid.

Hexanoic, octanoic and decanoic can impart cheese, sweat and rancid notes to wine aroma. Lower levels of these compounds were found in red wines than white wines. Decanoic was present in low amounts in both red and white wines. In our study, Helios wines had the highest level of hexanoate and possessed high levels of octanoic and decanoic acids.

Low volatile sulfur compounds

Low volatile sulfur compounds are known to be able to create unappealing flavours in wine ranging from rotten eggs to cooked cabbage. Hydrogen sulfide (H_2S), carbon disulfide (C_2S) and dimethyl sulfide (DMS) were the most frequently occurring compounds in the wines under study. Methanethiol (MeSH) was not detected in all red wines while some occurrences were found in white wines. *S*-methyl thioacetate (MeSAc) were found in few occurrences in both white and red wines. The quantitative results are collected in Table S10. Of the volatile sulfur compounds examined, DMS had the largest overall concentration range with 0.50-42.60 µg/L in red wines and 0.60-13.80 µg/L in white wines. DMS is an interesting sulfur compound which can contribute to the wine aroma bouquet at low levels (perhaps up to 100 µg/L), increasing the perceived fruitiness as previously reported (Lopez, Lapeña, Cacho & Ferreira, 2007; Segurel, Razungles, Riou, Salles, & Baumes, 2004). On the other hand, at high levels it may mask fruity aromas and impart unpleasant canned corn, cooked cabbage, or vegetal type aromas (Francis & Newton, 2005). In this study, higher levels of DMS were found in wines of 2013 vintage which were analysed together with the wines of vintage 2015 (2 years later). As previously reported, dimethyl sulfide tends to increase in concentration as wine ages probably due to the amounts of DMS precursors remaining in the wine (Segurel et al., 2004). Carbon disulfide was detected in the majority of wine samples studied with concentrations up to 23.30 and 23.90 µg/L for white and red wines, respectively. In the literature there is an aroma threshold study of CS_2 but it was observed that its concentration at almost 38 µg/L have no effect on the wine aroma (Siebert, Solomon, Pollnitz, & Jeffery, 2010). Although the impact of CS_2 on wine aroma is not well understood, the main descriptors relating to carbon disulfide are rubber and sulfidy.

With regards to red wines, the highest levels of hydrogen sulfide was found in Cabernet Sauvignon from Germany 2016 (42.60 µg/L) while for white wines it was found in Chardonnay from Italy 2015 (12.70 µg/L). It has been reported that at low levels, H_2S may add complexity to wine aroma but higher levels remaining after fermentation may lead to undesirable traits, such as “rotten egg” or “sewage-like” odours. Different aroma thresholds for hydrogen sulfide in wine have been previously reported (Mestres et al., 2000; Rauhut 2009). The aroma detection threshold was revisited and found to be 1.1 and 1.6 µg/L in red and white wine, respectively (Siebert et al., 2010). Additionally, it was reported that commercial wines with up to 30 µg/L of H_2S were not characterised by noticeable sulfur off-flavours (Lopez, Lapeña, Cacho, & Ferreira, 2007). In our study, the levels encountered in some of the wines analysed could be expected to affect the aroma composition.

Methanethiol was present in only six white PIWI wines with the highest level detected in Jasmine from Italy 2016 (4.60 µg/L). The aroma detection thresholds reported for MeSH in white and red wines were 3.10 and 1.80 µg/L, respectively (Siebert et al., 2010). This indicates that MeSH could contribute to “reductive” traits in 6 white wines analysed in this study. The concentration of MeSAc was up to 22.6 and 20.30 µg/L for red and white wines, respectively. In both cases its amount was below the aroma detection threshold of 50 µg/L determined in beer (Siebert et al., 2010). Therefore, with the exception of hydrogen sulfide which was found in a larger range in wines produced from mildew tolerant varieties than references, all the other volatile sulfur compounds were found at concentrations lower than those necessary to create “off-odours”. Therefore, they can also contribute, as previously described in the literature, to the wine aroma complexity.

4.4 Conclusions

In this study, the volatile and non-volatile composition of 17 disease tolerant varieties compared to 6 *V. vinifera* reference varieties grown in Italy and Germany in three different vintages (2013, 2015 and 2016) was investigated. PCA analysis of the overall chemical composition for both red and white wines revealed three observations: (i) the clear separation of wines according to the colour, (ii) the strong influence of the vintage on the chemical composition of wines and, (iii) the good stability of the metabolomic profile of wines produced from grape varieties grown in different vineyards. By comparing wines made from PIWI and V. *vinifera* varieties, PCA analysis showed a not clear separation between them based on their overall composition, with the exception of anthocyanins. In general, and not considering the anthocyanins in red wines, the wines produced from PIWI and *V. vinifera* grapes share the same metabolomic space. Furthermore, by means of OPLS-DA analysis it was possible to measure the major variations in terms of metabolites in the wines analysed according to the vintage, country of origin and type of variety (PIWI or reference).

The analysis of the non-volatile compounds showed differences in the total phenols since i) some of the disease tolerant varieties had a higher amount in comparison to references; ii) the presence of diglucoside anthocyanins characterised the majority of red PIWI wines and, iii) variations in the concentration and composition of tannins were more evident for some disease tolerant varieties than others. The investigation of the volatile profile revealed that the presence of low volatile sulfur compounds at lower concentrations than their aroma detection threshold could contribute to the wine aroma complexity rather than to create undesirable "off-flavours" in the wines analysed.

In conclusion, this study provides a clear picture of the chemical profile of the wines made from a selection of some PIWI varieties. It appears that with the exception of the anthocyanins, the wine produced from the modern disease tolerant varieties have a general composition closely resembling that of the well know *V. vinifera* wines. Therefore, PIWI varieties face as equally valuable varieties that are promised to produce high quality wines. Additionally, the information gained increased our knowledge on the composition of their wines and it could also serve for further breeding programs as well as to winegrowers and winemakers. As an example, for those high quality red varieties having particular richness of tannins in grapes, shortening the duration of the maceration would allow to produce red wines with the desired amount of tannins.

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Table S1. List of the non-volatile compounds and oenochemical parameters investigated.

	Unit	Method	Ref.
Oenochemical parameters			
glycerol	mg/L	NMR analysis	4.2.3.1
methanol	mg/L	NMR analysis	4.2.3.1
proline	mg/L	NMR analysis	4.2.3.1
trigonelline	mg/L	NMR analysis	4.2.3.1
ethanol	mg/L	NMR analysis	4.2.3.1
ethanol	vol.%	NMR analysis	4.2.3.1
total alcohol	mg/L	NMR analysis	4.2.3.1
total alcohol	vol.%	NMR analysis	4.2.3.1
relative density	20/20	FTIR analysis	4.2.3.1
extract	g/L	FTIR analysis	4.2.3.1
sugar-free extract	g/L	FTIR analysis	4.2.3.1
fermentable sugar	g/L	FTIR analysis	4.2.3.1
total acidity	g/L	FTIR analysis	4.2.3.1
pH		FTIR analysis	4.2.3.1
volatile acidity	g/L	FTIR analysis	4.2.3.1
free SO_2	mg/L	FTIR analysis	4.2.3.1
total SO_2	mg/L	FTIR analysis	4.2.3.1
total phenols	mg/L	Folin–Ciocalteau assay	4.2.3.1
TEAC	mmol/L	TEAC	4.2.3.1
Phenols			
p-hydroxybenzoic acid	mg/L	UPLC-MS/MS	4.2.3.2
vanillic acid	mg/L	UPLC-MS/MS	4.2.3.2
gallic acid	mg/L	UPLC-MS/MS	4.2.3.2
caftaric acid	mg/L	UPLC-MS/MS	4.2.3.2
fertaric acid	mg/L	UPLC-MS/MS	4.2.3.2
trans-coutaric acid	mg/L	UPLC-MS/MS	4.2.3.2
phloridzin	mg/L	UPLC-MS/MS	4.2.3.2
luteolin-7-*O*-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
quercetin	mg/L	UPLC-MS/MS	4.2.3.2
taxifolin	mg/L	UPLC-MS/MS	4.2.3.2
kaempferol-3-*O*-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
quercetin-3-*O*-glucoside + quercetin-3-*O*-galactoside	mg/L	UPLC-MS/MS	4.2.3.2
isorhamnetin-3-*O*-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
quercetin-3-*O*-glucuronide	mg/L	UPLC-MS/MS	4.2.3.2
kaempferol-3-*O*-glucuronide	mg/L	UPLC-MS/MS	4.2.3.2
arbutin	mg/L	UPLC-MS/MS	4.2.3.2
trans-resveratrol	mg/L	UPLC-MS/MS	4.2.3.2
cis-resveratrol	mg/L	UPLC-MS/MS	4.2.3.2
piceatannol	mg/L	UPLC-MS/MS	4.2.3.2
trans-piceide	mg/L	UPLC-MS/MS	4.2.3.2
cis-piceide	mg/L	UPLC-MS/MS	4.2.3.2

astringin	mg/L	UPLC-MS/MS	4.2.3.2
isorhapontin	mg/L	UPLC-MS/MS	4.2.3.2
caffeic acid+catechin condensation	mg/L	UPLC-MS/MS	4.2.3.2
pallidol	mg/L	UPLC-MS/MS	4.2.3.2
ampelopsin D+quadrangularin A	mg/L	UPLC-MS/MS	4.2.3.2
isohopeaphenol	mg/L	UPLC-MS/MS	4.2.3.2
methyl gallate	mg/L	UPLC-MS/MS	4.2.3.2
ellagic acid	mg/L	UPLC-MS/MS	4.2.3.2
syringetin-3-glucoside + syringetin-3-galactoside	mg/L	UPLC-MS/MS	4.2.3.2
Anthocyanins			
delphinidin-3-*O*-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
cyanidin-3-*O*-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
petunidin-3-*O*-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
peonidin-3-*O*-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
malvidin-3-*O*-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
delphinidin-3-*O*-(6"-acetyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
cyanidin-3-*O*-(6"-acetyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
petunidin-3-*O*-(6"-acetyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
peonidin-3-*O*-(6"-acetyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
malvidin-3-*O*-(6"-acetyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
delphinidin-3-*O*-(6"-*p*-coumaroyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
cyanidin-3-*O*-(6"-*p*-coumaroyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
petunidin-3-*O*-(6"-*p*-coumaroyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
peonidin-3-*O*-(6"-*p*-coumaroyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
malvidin-3-*O*-(6"-*p*-coumaroyl)-glucoside	mg/L	UPLC-MS/MS	4.2.3.2
delphinidin-3,5-*O*-diglucoside	mg/L	UPLC-MS/MS	4.2.3.2
cyanidin-3,5-*O*-diglucoside	mg/L	UPLC-MS/MS	4.2.3.2
petunidin-3,5-*O*-diglucoside	mg/L	UPLC-MS/MS	4.2.3.2
peonidin-3,5-*O*-diglucoside	mg/L	UPLC-MS/MS	4.2.3.2
malvidin-3,5-*O*-diglucoside	mg/L	UPLC-MS/MS	4.2.3.2
Flavan-3-ols and proanthocyanidins			
procyanidin B1	mg/L	UPLC-MS/MS	4.2.3.3
procyanidin B2	mg/L	UPLC-MS/MS	4.2.3.3
catechin	mg/L	UPLC-MS/MS	4.2.3.3
catechin (extension units)	mg/L	UPLC-MS/MS	4.2.3.3
catechin (terminal units)	mg/L	UPLC-MS/MS	4.2.3.3
epicatechin	mg/L	UPLC-MS/MS	4.2.3.3
epicatechin (extension units)	mg/L	UPLC-MS/MS	4.2.3.3
epicatechin (terminal units)	mg/L	UPLC-MS/MS	4.2.3.3
gallocatechin	mg/L	UPLC-MS/MS	4.2.3.2
gallocatechin (extension units)	mg/L	UPLC-MS/MS	4.2.3.3
gallocatechin (terminal units)	mg/L	UPLC-MS/MS	4.2.3.3
epigallocatechin	mg/L	UPLC-MS/MS	4.2.3.3
epigallocatechin (extension units)	mg/L	UPLC-MS/MS	4.2.3.3

epigallocatechin (terminal units)	mg/L	UPLC-MS/MS	4.2.3.3
catechin gallate + epicatechin gallate	mg/L	UPLC-MS/MS	4.2.3.3
catechin gallate + epicatechin gallate (extension	mg/L	UPLC-MS/MS	4.2.3.3
catechin gallate + epicatechin gallate (terminal units)	mg/L	UPLC-MS/MS	4.2.3.3
catechin + epicatechin (upper units)	mg/L	UPLC-MS/MS	4.2.3.3
epigallocatechin(upper units)	mg/L	UPLC-MS/MS	4.2.3.3
epicatechin gallate (upper units)	mg/L	UPLC-MS/MS	4.2.3.3
Minerals			
calcium	mg/L	AAS	4.2.3.4
potassium	mg/L	AAS	4.2.3.4
magnesium	mg/L	AAS	4.2.3.4
copper	mg/L	AAS	4.2.3.4
iron	mg/L	AAS	4.2.3.4
sodium	mg/L	AAS	4.2.3.4
zinc	mg/L	AAS	4.2.3.4
Low-molecular-weight thiols			
cysteine (cys)	mg/L	HPLC-FLD	4.2.3.5
thiocysteine (cysT)	mg/L	HPLC-FLD	4.2.3.5
homocysteine (Hcys)	mg/L	HPLC-FLD	4.2.3.5
cysteine-glycine (cys-gly)	mg/L	HPLC-FLD	4.2.3.5
γ-glutamylcysteine (γ-Glu-Cys)	mg/L	HPLC-FLD	4.2.3.5
glutathione (GSH)	mg/L	HPLC-FLD	4.2.3.5
N-acetylcysteine (NAC)	mg/L	HPLC-FLD	4.2.3.5
Organic acids			
acetic acid	mg/L	NMR analysis	4.2.3.1
shikimic acid	mg/L	NMR analysis	4.2.3.1
succinic acid	mg/L	NMR analysis	4.2.3.1
tartaric acid	g/L	FTIR analysis	4.2.3.1
malic acid	g/L	FTIR analysis	4.2.3.1
lactic acid	g/L	FTIR analysis	4.2.3.1
Sugars			
glucose	g/L	FTIR analysis	4.2.3.1
fructose	g/L	FTIR analysis	4.2.3.1

Table S2. List of the volatile compounds analysed in this study.

	Unit	Method	Ref.	Odour description
Volatile acids				
hexanoic acid	mg/L	GC-MS	4.2.4.1	sweat
octanoic acid	mg/L	GC-MS	4.2.4.1	sweat, cheese
decanoic acid	mg/L	GC-MS	4.2.4.1	rancid, fat
acetic acid	mg/L	NMR	4.2.3.5	sour
Higher alcohols				
3-methyl butanol + 2-methyl butanol	mg/L	GC-MS	4.2.4.1	whiskey, malt, burnt
hexan-1-ol	µg/L	GC-MS	4.2.4.1	resin, flower, green
2,3-butanediol	mg/L	NMR	4.2.3.5	fruit, onion
2-phenylethanol	mg/L	GC-MS	4.2.4.1	honey, spice, rose, lilas
Acetate esters				
ethyl acetate	mg/L	GC-MS	4.2.4.1	pineapple
3-methylbutyl acetate + 2-methylbutyl acetate	µg/L	GC-MS	4.2.4.1	banana
hexyl acetate	µg/L	GC-MS	4.2.4.1	fruit, herb
2-phenylethyl acetate	µg/L	GC-MS	4.2.4.1	rose, honey, tabacco
Ethyl esters				
ethyl *iso*butanoate	µg/L	GC-MS	4.2.4.1	sweet, rubber
ethyl butanoate	µg/L	GC-MS	4.2.4.1	apple
ethyl lactate	mg/L	GC-MS	4.2.4.1	fruit
iso-valerate	µg/L	GC-MS	4.2.4.1	fruit
ethyl hexanoate	µg/L	GC-MS	4.2.4.1	apple peel, fruit
diethyl succinate	µg/L	GC-MS	4.2.4.1	wine, fruit
ethyl octanoate	µg/L	GC-MS	4.2.4.1	fruit, fat
ethyl decanoate	µg/L	GC-MS	4.2.4.1	grape
Monoterpenols				
linalool	µg/L	GC-MS	4.2.4.1	flower, lavender
α-terpineol	µg/L	GC-MS	4.2.4.1	oil, anise, mint
Monoterpenol oxides				
trans-linalool oxide	µg/L	GC-MS	4.2.4.1	flower, lavender
cis-linalool oxide	µg/L	GC-MS	4.2.4.1	flower, lavender
Low volatile sulfur compounds				
hydrogen sulfide (H_2S)	µg/L	HS-GC-PFPD	4.2.4.2	rotten egg, sewage-like, vegetal
methanethiol (MeSH)	µg/L	HS-GC-PFPD	4.2.4.2	rotten cabbage, burnt rubber, putrefaction
dimethyl sulfide (DMS)	µg/L	HS-GC-PFPD	4.2.4.2	black currant, cooked cabbage, canned corn, asparagus
carbon disulfide (CS_2)	µg/L	HS-GC-PFPD	4.2.4.2	sweet, ethereal, slight green, rubber, sulfidy
S-methyl thioacetate (MeSAc)	µg/L	HS-GC-PFPD	4.2.4.2	sulfurous, cheesy, egg

Table S3. Oenochemical compositions in the wines analysed.

Variety	Country	Vintage	density (20/20)	alcohol (g/L)	extract (g/L)	sugar free extract(g/L)	fermentable sugar(g/L)	glucose (g/L)	fructose(g/L)	total acidity (g/L)	tartaric acid (g/L)	malic acid (g/L)	lactic acid (g/L)	volatile acidity (g/L)	glycerin (g/L)	free SO_2 (mg/L)	total SO_2 (mg/L)	pH	acetic acid (mg/L)	ethanol (mg/L)	ethanol (vol.%)	glycerol (mg/L)	methanol (mg/L)	total alcohol (mg/L)	total alcohol (vol.%)	TPC (mg/L)	TEAC (mol /L)
Regent	Germany	2013	1.00	81.20	22.80	22.80	n.d.	n.d.	n.d.	5.50	2.60	n.d.	2.90	0.40	7.50	5.00	43.00	3.30	485.56	91397.41	11.58	8488.51	218.00	91583.29	11.60	1546.00	20.40
Cabernet Cortis	Italy	2013	0.99	108.20	28.60	28.00	0.60	n.d.	0.60	5.30	2.90	0.40	1.30	0.50	9.10	2.00	50.00	3.50	268.99	75300.42	9.54	6636.91	145.65	75492.23	9.56	2477.00	30.40
Cabernet Cortis	Germany	2013	0.99	94.60	26.90	26.80	0.10	n.d.	0.10	6.30	2.90	0.10	2.80	0.50	8.40	1.00	35.00	3.40	253.49	102115.25	12.94	8519.33	117.33	102452.09	12.98	2064.00	27.10
Cabernet Carbon	Italy	2013	0.99	93.40	26.40	26.30	0.10	n.d.	0.10	5.10	1.80	0.20	2.50	0.50	8.30	7.00	51.00	3.60	259.42	89352.05	11.32	7895.65	104.99	89577.54	11.35	2241.50	25.40
Prior	Italy	2013	1.00	84.60	26.70	26.60	0.10	n.d.	0.10	5.10	1.50	0.50	3.50	0.60	7.80	n.d.	18.00	3.70	380.04	84032.25	10.65	8149.30	152.31	84477.89	10.70	1789.00	20.50
Prior	Germany	2013	1.00	76.80	23.90	23.90	n.d.	n.d.	n.d.	6.00	1.80	0.30	5.00	0.60	6.60	n.d.	18.00	3.60	459.94	75509.05	9.57	7458.27	172.44	75640.31	9.58	1219.00	15.20
Nero	Italy	2013	0.99	81.50	22.60	22.60	n.d.	n.d.	n.d.	4.20	2.20	0.20	2.50	0.50	7.60	2.00	30.00	3.70	388.03	68621.85	8.69	5826.18	173.23	68847.56	8.72	1792.00	22.80
Nero	Germany	2013	0.99	100.90	22.00	21.90	0.10	n.d.	0.10	5.10	2.30	n.d.	2.80	0.30	8.10	4.00	29.00	3.50	323.08	71966.79	9.12	6875.65	116.76	72100.76	9.14	1397.00	19.40
Johanniter	Italy	2013	0.99	101.80	17.40	14.70	2.70	n.d.	2.60	5.70	2.80	1.80	0.10	0.30	5.50	8.00	70.00	3.10	230.45	91591.74	11.60	7587.82	95.74	91848.25	11.64	247.50	3.70
Johanniter	Germany	2013	0.99	93.30	19.20	19.20	n.d.	n.d.	n.d.	9.40	4.10	3.70	0.30	0.30	5.80	4.00	33.00	2.80	104.65	92968.41	11.78	5500.25	n.q.	94029.87	11.91	178.00	2.40
Solaris	Germany	2013	0.99	111.20	21.90	21.60	0.30	0.30	0.10	9.20	3.90	2.80	0.30	0.20	6.50	18.00	97.00	2.80	406.87	128967.10	16.34	8481.50	n.q.	131021.55	16.60	165.00	3.30
Phoenix	Italy	2013	0.99	87.40	17.40	17.30	0.10	0.10	n.d.	4.30	1.30	1.70	0.30	0.30	5.70	11.00	71.00	3.40	134.02	103039.92	13.06	6956.00	n.q.	103426.70	13.10	150.00	2.60
Phoenix	Germany	2013	0.99	77.00	20.90	20.90	n.d.	n.d.	n.d.	9.20	3.90	3.60	0.40	0.30	5.20	14.00	75.00	2.80	125.40	77639.52	9.84	5480.76	40.28	77981.78	9.88	100.00	2.20
Bronner	Italy	2013	0.99	93.20	18.30	18.10	0.20	0.10	0.10	7.10	3.60	2.00	0.40	0.30	5.50	9.00	67.00	3.00	n.q.	69584.99	8.82	5191.45	34.61	69689.50	8.83	210.50	3.10
Bronner	Germany	2013	0.99	95.90	23.20	22.80	0.40	n.d.	0.40	10.70	4.50	4.00	0.40	0.30	5.40	25.00	131.00	2.80	127.32	86522.91	10.96	5381.74	n.q.	86778.17	10.99	151.00	3.30
Helios	Italy	2013	0.99	99.20	17.00	16.80	0.20	n.d.	0.20	6.80	3.40	1.50	0.20	0.20	5.40	4.00	44.00	2.90	134.60	88002.42	11.15	5852.68	n.q.	88400.24	11.20	355.50	4.00
Bianca	Italy	2013	0.99	99.90	17.20	16.90	0.30	0.30	n.d.	5.10	2.00	2.20	0.20	0.30	5.70	3.00	53.00	3.40	n.q.	92481.51	11.72	5493.90	n.q.	92703.88	11.75	131.00	2.10
Muscaris	Italy	2013	0.99	122.60	19.80	17.70	2.10	0.60	1.40	5.60	2.20	1.40	n.d.	0.20	7.30	5.00	94.00	3.20	177.17	92278.09	11.69	5197.79	n.q.	92489.27	11.72	192.00	3.30
Accent	Germany	2013	0.99	82.00	22.60	22.20	0.40	0.40	n.d.	5.50	2.40	n.d.	3.30	0.50	7.10	4.00	36.00	3.40	194.16	119773.87	15.18	7375.10	n.q.	120455.03	15.26	2134.00	24.50
Rondo	Germany	2013	0.99	82.00	22.10	22.10	n.d.	n.d.	n.d.	6.00	2.50	n.d.	3.50	0.50	6.80	1.00	29.00	3.30	396.24	75903.23	9.62	6691.42	124.52	76076.76	9.64	1682.00	20.20
Pinot noir	Italy	2013	0.99	110.50	22.70	22.70	n.d.	n.d.	n.d.	3.70	1.40	n.d.	1.70	0.30	8.60	n.d.	140.00	3.70	342.09	75767.16	9.60	6030.95	133.16	75909.68	9.62	1519.50	19.80
Cabernet Sauvignon	Italy	2013	0.99	113.30	26.80	26.20	0.60	0.30	0.30	4.80	2.10	0.30	1.30	0.20	8.90	4.00	26.00	3.60	252.30	85181.23	10.79	6908.99	80.31	85431.08	10.82	1960.50	24.90
Teroldego	Italy	2013	1.00	99.70	33.20	33.20	n.d.	n.d.	n.d.	4.20	1.20	1.20	4.50	0.50	10.60	1.00	36.00	4.40	470.48	82491.01	10.45	7124.23	62.35	83054.27	10.52	2115.50	25.90
Chardonnay	Italy	2013	0.99	103.50	19.90	18.40	1.50	n.d.	1.50	6.90	2.60	2.20	n.d.	0.30	7.20	4.00	59.00	3.00	477.99	89624.07	11.36	10263.82	102.09	89802.94	11.38	222.00	3.30
Chardonnay	Germany	2013	0.99	92.80	23.60	23.10	0.50	0.40	0.10	10.60	3.20	6.80	0.10	0.40	5.70	14.00	97.00	2.80	150.20	96738.69	12.26	7172.18	31.19	97408.57	12.34	167.00	3.30
Riesling	Italy	2013	0.99	96.90	19.70	19.60	0.10	n.d.	0.10	7.10	2.90	2.00	0.20	0.30	6.90	6.00	83.00	2.90	194.91	85804.59	10.87	5301.12	n.q.	86053.66	10.90	162.00	2.80
Moscato Giallo	Italy	2013	0.99	103.40	19.80	18.90	0.90	0.30	0.60	5.10	1.40	2.50	n.d.	0.40	6.50	17.00	132.00	3.40	150.08	89755.43	11.37	6858.82	30.99	89992.74	11.40	207.50	3.90
Moscato Giallo	Germany	2013	1.00	76.50	22.20	22.20	n.d.	n.d.	n.d.	11.20	4.40	5.20	0.30	0.40	4.90	4.00	57.00	2.80	330.10	96546.58	12.23	6598.17	36.91	96948.01	12.28	135.00	2.30
Regent	Italy	2015	0.99	102.90	25.60	25.40	0.20	0.20	n.d.	5.20	2.50	n.d.	1.60	0.30	8.60	138.00	179.00	3.50	462.66	97343.25	12.33	7538.61	153.90	97612.44	12.37	2833.00	33.20
Regent	Germany	2015	0.99	85.90	24.30	24.30	n.d.	n.d.	n.d.	6.10	3.30	n.d.	2.80	0.20	7.10	83.00	150.00	3.30	216.71	80439.30	10.19	6777.18	119.14	80617.05	10.21	2002.00	25.00
Cabernet Cortis	Italy	2015	0.99	109.80	29.40	27.90	1.50	n.d.	1.50	6.10	3.60	0.20	1.40	0.50	9.10	23.00	52.00	3.40	387.34	104011.59	13.18	8896.24	101.40	104332.54	13.22	3334.50	41.70
Cabernet Cortis	Germany	2015	0.99	100.40	27.00	25.60	1.40	n.d.	1.40	6.10	4.00	n.d.	1.70	0.40	8.30	23.00	51.00	3.30	246.77	95373.74	12.08	7495.72	53.98	95467.90	12.10	2935.50	34.40
Cabernet Carbon	Italy	2015	0.99	102.90	25.90	24.70	1.20	0.10	1.10	5.60	2.50	0.50	1.20	0.40	8.10	16.00	125.00	3.50	329.62	97839.77	12.40	8330.58	102.29	98285.78	12.45	2188.50	26.80
Prior	Italy	2015	0.99	98.00	29.00	27.50	1.50	0.50	1.00	5.30	2.30	0.90	2.40	0.30	8.00	21.00	52.00	3.80	398.62	91706.92	11.62	8154.43	161.67	91851.35	11.64	2838.00	32.60
Nero	Italy	2015	0.99	117.10	28.20	27.00	1.20	0.70	0.50	5.10	2.20	0.10	1.50	0.40	1n.d.	74.00	133.00	3.60	477.97	112933.69	14.31	8936.46	126.60	113454.33	14.37	2695.50	34.20
Souvignier gris	Italy	2015	0.99	106.80	23.70	18.90	4.80	n.d.	4.80	8.30	3.90	1.90	0.30	0.60	6.70	19.00	83.00	2.80	437.08	101220.66	12.82	6877.05	n.q.	103019.40	13.05	177.00	3.00
Johanniter	Italy	2015	0.99	104.50	16.60	15.90	0.70	n.d.	0.70	5.90	3.10	1.10	n.d.	0.30	7.90	41.00	103.00	2.90	439.85	103025.81	13.05	6787.41	n.q.	104882.56	13.29	205.00	3.50
Johanniter	Germany	2015	0.99	93.40	20.0	19.20	0.80	n.d.	0.80	8.10	4.00	3.00	n.d.	0.30	7.30	25.00	85.00	2.70	169.62	99773.65	12.64	7243.45	n.q.	99976.85	12.67	166.50	3.00
Solaris	Italy	2015	0.99	119.70	18.20	17.30	0.90	n.d.	0.90	5.60	3.20	0.70	n.d.	0.40	7.40	25.00	106.00	3.00	108.67	87903.49	11.14	6172.58	n.q.	88178.74	11.17	230.00	3.60
Solaris	Germany	2015	0.99	118.00	24.10	18.80	5.30	n.d.	5.30	7.40	4.40	1.70	n.d.	0.40	8.30	23.00	98.00	2.70	308.11	116028.14	14.70	6774.89	n.q.	116167.90	14.72	195.00	3.20
Phoenix	Italy	2015	0.99	90.70	21.00	20.50	0.50	n.d.	0.50	6.00	2.80	1.30	0.10	0.10	9.50	30.0.	118.00	2.80	221.32	114878.74	14.56	7335.34	n.q.	116633.89	14.78	139.50	2.90
Phoenix	Germany	2015	0.99	81.40	18.50	18.20	0.30	n.d.	0.30	7.50	4.70	2.50	n.d.	0.20	8.00	22.00	94.00	2.80	n.q.	84639.74	10.72	8670.83	42.59	85307.85	10.81	124.50	2.50

Bronner	Italy	2015	0.99	110.40	22.40	16.70	5.70	n.d.	5.70	6.80	3.60	1.70	0.10	0.50	6.90	30.00	95.00	2.90	191.86	74694.50	9.46	6381.09	n.q.	74994.64	9.50	276.50	4.80
Bronner	Germany	2015	0.99	90.40	18.80	18.40	0.40	n.d.	0.40	8.60	4.50	3.10	n.d.	0.30	6.90	31.00	93.00	2.80	348.82	105125.65	13.32	6916.87	n.q.	107245.97	13.59	149.00	2.80
Muscaris	Italy	2015	0.99	122.40	20.50	17.80	2.70	0.10	2.70	6.00	2.20	1.40	n.d.	0.30	9.50	44.00	117.00	3.20	123.44	83548.93	10.59	5772.35	n.q.	83595.51	10.59	228.00	4.00
Muscaris	Germany	2015	0.99	92.70	21.80	21.30	0.50	n.d.	0.50	9.30	4.40	3.40	0.20	0.20	8.60	46.00	110.00	2.80	299.45	118493.35	15.01	9625.95	n.q.	119332.32	15.12	155.50	3.10
Accent	Germany	2015	1.00	77.10	27.10	25.60	1.50	0.80	0.70	6.60	4.90	0.40	2.10	0.30	7.20	33.00	61.00	3.00	126.69	84709.61	10.73	7758.20	n.q.	84828.75	10.75	2729.50	41.30
Rondo	Germany	2015	1.00	73.90	23.50	23.20	0.30	n.d.	0.30	5.20	2.90	0.80	2.70	0.40	6.70	31.00	57.00	3.50	300.01	69392.56	8.79	6150.88	160.79	69480.08	8.80	1901.50	23.70
Bolero	Germany	2015	0.99	96.40	24.00	22.50	1.50	0.80	0.80	6.00	3.40	0.40	1.40	0.30	7.00	14.00	51.00	3.30	362.01	66125.81	8.38	6070.26	100.15	66291.29	8.40	1740.00	21.40
Helios	Italy	2015	0.99	104.70	19.50	17.90	1.60	n.d.	1.60	6.50	3.80	1.20	0.10	0.20	8.00	22.00	73.00	2.80	254.07	89635.15	11.36	6648.76	140.65	89860.88	11.39	250.00	4.20
Bianca	Italy	2015	0.99	116.30	23.00	21.70	1.30	0.40	0.90	6.30	1.90	1.80	n.d.	0.10	9.80	61.00	134.00	3.20	n.q.	98846.03	12.52	7112.04	n.q.	99203.85	12.57	154.00	3.10
Jasmine	Italy	2015	0.99	106.40	17.30	16.70	0.60	n.d.	0.60	5.10	2.20	1.20	n.d.	0.20	8.00	39.00	98.00	3.20	n.q.	113600.15	14.39	9353.81	n.q.	114050.33	14.45	291.00	4.90
Pinot noir	Italy	2015	0.99	95.30	23.80	23.80	n.d.	n.d.	n.d.	3.70	1.00	0.60	3.00	0.60	8.40	71.00	130.00	4.10	219.17	91725.72	11.62	6421.32	n.q.	91973.08	11.65	1245.00	18.50
Cabernet Sauvignon	Italy	2015	0.99	103.90	26.80	26.60	0.20	n.d.	0.20	4.70	2.00	0.30	2.40	0.30	9.00	49.00	78.00	3.90	214.20	74578.32	9.45	6617.07	70.17	74647.31	9.46	2294.00	31.00
Cabernet Sauvignon	Germany	2015	0.99	83.30	23.10	22.50	0.60	0.40	0.30	6.60	2.90	n.d.	2.80	0.30	7.70	20.00	143.00	3.20	309.42	96312.84	12.20	8162.14	112.23	96691.48	12.25	1155.00	17.70
Chardonnay	Italy	2015	0.99	99.90	18.30	17.90	0.40	n.d.	0.40	5.70	2.20	2.60	n.d.	0.30	6.10	39.00	143.00	3.30	402.67	97415.24	12.34	8987.82	139.05	98151.77	12.44	164.00	3.40
Chardonnay	Germany	2015	0.99	94.60	20.70	20.40	0.30	n.d.	0.30	7.00	2.00	3.90	0.10	0.30	7.10	7.00	106.00	3.20	157.49	94415.96	11.96	5695.83	n.q.	94909.89	12.03	151.00	2.90
Riesling	Italy	2015	0.99	90.60	18.40	17.80	0.60	n.d.	0.60	7.00	3.70	2.40	n.d.	0.20	6.40	26.00	122.00	2.70	n.q.	88554.41	11.22	6649.65	n.q.	88940.10	11.27	181.00	3.40
Riesling	Germany	2015	0.99	83.00	18.30	17.70	0.60	n.d.	0.60	7.30	6.70	3.20	n.d.	n.d.	9.50	9.00	83.00	2.80	135.88	84405.63	10.69	5637.68	35.77	84698.10	10.73	161.00	2.80
Moscato Giallo	Italy	2015	0.99	93.90	18.10	17.40	0.70	n.d.	0.70	5.50	2.20	2.70	n.d.	0.20	7.30	16.00	88.00	3.10	106.75	78776.04	9.98	5838.24	36.83	78981.25	10.01	164.00	3.10
Regent	Italy	2016	0.99	93.10	26.40	24.00	2.40	1.60	0.70	4.40	2.00	0.40	2.50	0.30	7.80	14.00	31.00	3.80	n.q.	71422.49	9.05	7810.86	148.04	87543.23	11.09	2044.00	23.60
Regent	Germany	2016	0.99	106.30	27.40	24.10	3.40	2.20	1.20	5.20	3.00	0.40	1.00	0.10	8.70	27.00	50.00	3.30	193.19	102436.04	12.98	8973.09	133.27	102761.53	13.02	2387.50	27.60
Cabernet Cortis	Italy	2016	0.99	104.20	30.80	28.40	2.40	1.20	1.20	5.20	2.30	0.50	2.00	0.40	9.60	10.00	57.00	3.80	323.60	99084.14	12.55	9533.01	n.q.	99294.60	12.58	2837.50	31.30
Cabernet Cortis	Germany	2016	0.99	104.50	29.80	26.70	3.10	1.60	1.50	5.40	2.50	0.20	1.50	0.20	9.20	9.00	52.00	3.50	171.93	101047.62	12.80	9134.49	83.60	101113.74	12.81	2758.50	29.90
Prior	Italy	2016	1.00	87.60	26.60	24.30	2.20	1.60	0.70	5.00	1.90	0.50	2.50	0.50	7.70	17.00	56.00	3.80	414.30	81728.90	10.36	7411.34	68.45	81853.73	10.37	1313.50	15.40
Prior	Germany	2016	1.00	82.20	28.60	26.20	2.40	1.70	0.70	5.40	1.40	0.70	3.40	0.50	7.80	24.00	115.00	3.80	410.18	76296.76	9.67	7336.33	130.11	76477.29	9.69	1270.00	15.30
Nero	Italy	2016	1.00	88.40	28.90	26.30	2.60	1.50	1.00	6.70	1.90	3.20	0.50	0.90	7.10	n.d.	64.00	3.60	628.82	80844.08	10.24	6879.63	86.65	82417.80	10.44	1502.00	16.80
Souvignier Gris	Italy	2016	0.99	117.10	29.00	18.70	10.20	1.80	8.40	6.40	2.80	1.70	0.10	0.50	7.10	16.00	89.00	3.30	409.07	117768.86	14.92	6681.75	n.q.	121230.52	15.36	226.00	3.20
Johanniter	Italy	2016	0.99	90.30	19.30	17.70	1.60	0.80	0.90	6.50	2.50	2.10	0.30	0.30	6.70	37.00	111.00	3.20	113.05	86429.74	10.95	5658.47	n.q.	86565.64	10.97	155.50	2.80
Johanniter	Germany	2016	0.99	99.40	19.50	17.40	2.20	1.20	1.00	6.50	2.80	1.90	0.10	0.20	6.30	90.00	188.00	3.10	n.q.	96144.14	12.18	5986.91	n.q.	96368.78	12.21	155.50	3.40
Solaris	Italy	2016	0.99	107.90	21.20	19.10	2.10	1.10	1.00	6.10	2.50	1.20	0.40	0.40	7.50	22.00	107.00	3.20	205.54	107240.61	13.59	6991.61	n.q.	107368.32	13.60	173.00	3.00
Solaris	Germany	2016	0.99	130.10	27.90	19.60	8.40	2.30	6.10	5.90	2.80	1.00	n.d.	0.30	8.20	13.00	107.00	3.30	323.79	133783.35	16.95	8532.73	n.q.	136164.37	17.25	216.00	3.40
Phoenix	Italy	2016	0.99	87.00	19.10	17.20	2.00	1.30	0.70	5.70	2.20	2.00	0.20	0.20	5.90	30.00	105.00	3.20	n.q.	82874.59	10.50	5767.82	32.87	83478.47	10.58	161.00	3.00
Phoenix	Germany	2016	0.99	81.40	18.30	17.00	1.30	1.10	0.20	5.80	2.30	1.70	0.30	0.20	6.40	72.00	159.00	3.20	n.q.	76704.64	9.72	5786.51	n.q.	76898.83	9.74	120.00	2.70
Bronner	Italy	2016	0.99	100.90	20.10	17.90	2.20	1.40	0.80	5.90	2.50	1.90	0.20	0.30	6.60	23.00	95.00	3.30	119.37	96576.76	12.24	5900.23	n.q.	97061.75	12.30	183.00	2.80
Bronner	Germany	2016	0.99	96.60	19.80	18.00	1.80	1.10	0.60	7.40	3.20	1.90	0.10	0.20	6.90	82.00	174.00	3.00	n.q.	91937.19	11.65	6475.74	n.q.	92018.63	11.66	143.50	3.10
Muscaris	Italy	2016	0.99	114.20	25.50	20.10	5.40	1.70	3.70	7.00	2.20	2.40	n.d.	0.30	8.00	24.00	107.00	3.20	193.55	113758.52	14.41	7813.58	33.21	115108.84	14.58	243.00	3.80
Muscaris	Germany	2016	0.99	110.10	23.20	19.20	4.00	1.70	2.30	6.90	2.80	1.70	0.10	0.20	7.90	89.00	184.00	3.10	n.q.	107160.04	13.58	7690.95	n.q.	107870.10	13.67	184.00	3.80
Accent	Germany	2016	1.00	93.60	36.40	30.40	5.90	3.90	2.00	6.00	3.60	0.80	2.50	0.30	6.90	3.00	28.00	3.40	405.66	86655.73	10.98	7897.18	n.q.	86683.63	10.98	4116.50	49.70
Rondo	Germany	2016	1.00	96.90	32.50	29.10	3.30	1.90	1.50	5.40	2.50	0.60	2.40	0.40	8.80	21.00	62.00	3.70	401.74	90871.81	11.51	8590.46	145.20	91242.28	11.56	2864.00	30.80
Bolero	Germany	2016	0.99	91.60	25.30	22.30	3.10	1.90	1.20	5.20	2.80	0.30	1.40	0.30	7.20	13.00	64.00	3.40	192.44	86841.48	11.00	7299.49	138.06	87199.07	11.05	1452.00	17.90
Helios	Italy	2016	0.99	106.10	19.40	16.40	3.10	1.40	1.60	5.10	2.40	1.30	n.d.	0.30	6.70	28.00	105.00	3.40	149.56	103759.78	13.15	6491.38	n.q.	104303.79	13.22	261.50	4.10
Bianca	Italy	2016	0.99	115.50	21.50	18.60	2.90	1.90	1.00	5.20	1.70	2.20	n.d.	0.20	7.50	25.00	104.00	3.60	158.69	111303.17	14.10	6942.46	n.q.	111662.98	14.15	183.00	3.20
Jasmine	Italy	2016	0.99	103.60	17.60	15.80	1.80	1.40	0.40	4.30	1.80	0.90	n.d.	0.20	7.50	38.00	120.00	3.40	n.q.	101294.97	12.83	6373.81	n.q.	101420.26	12.85	194.00	3.50
Pinot noir	Italy	2016	0.99	113.20	28.10	25.00	3.10	2.20	0.90	5.50	1.30	2.50	0.30	0.40	9.40	13.00	70.00	3.70	146.90	107051.81	13.56	8927.12	69.75	107824.84	13.66	1080.00	13.10
Cabernet Sauvignon	Germany	2016	1.00	86.90	27.10	25.20	1.90	1.10	0.80	8.80	4.00	2.40	0.50	0.30	7.80	2.00	14.00	3.00	251.75	79108.54	10.02	8227.42	61.49	79137.08	10.03	1240.00	15.20
Teroldego	Italy	2016	1.00	90.10	28.10	25.50	2.60	1.80	0.80	7.00	2.00	4.10	0.30	0.20	7.80	5.00	44.00	3.50	131.23	81310.84	10.30	7834.31	88.62	81470.15	10.32	1629.00	18.80
Chardonnay	Italy	2016	0.99	106.80	22.80	19.60	3.20	1.60	1.60	4.70	1.30	1.40	0.10	0.40	7.90	148.00	299.00	3.50	404.83	102053.68	12.93	7535.63	n.q.	102554.26	12.99	207.00	4.40
Chardonnay	Germany	2016	0.99	100.20	22.00	19.70	2.30	1.60	0.70	6.90	2.30	3.00	0.10	0.20	6.90	84.00	187.00	3.30	n.q.	96576.22	12.24	6592.05	n.q.	96809.96	12.27	147.00	3.30
Riesling	Italy	2016	0.99	103.40	23.20	19.50	3.60	1.30	2.30	6.60	2.90	1.30	0.20	0.30	8.20	17.00	100.00	3.10	184.00	98545.07	12.49	8557.42	n.q.	99314.63	12.58	190.00	3.10
Riesling	Germany	2016	0.99	93.90	21.20	19.00	2.10	1.20	0.90	8.10	3.60	2.40	0.30	0.30	6.30	66.00	153.00	3.00	n.q.	88169.75	11.17	5862.77	30.56	88383.86	11.20	239.50	4.20
Moscato Giallo	Italy	2016	0.99	81.30	20.10	17.80	2.30	1.40	0.90	5.60	1.80	2.20	0.10	0.30	7.50	8.00	112.00	3.30	108.23	74079.86	9.39	7430.53	n.q.	74301.54	9.41	148.50	2.90

Abbreviations: TPC, total phenolic content; TEAC, trolox equivalent antioxidative capacity; n.q., not quantifiable; n.d., not detected.

Table S4. Quantitative results of the phenolic compounds detected in the wines studied. The results are expressed as mg/L.

Variety	Country	Vintage	*p*-hydroxybenzoic acid	vanillic acid	gallic acid	caftaric acid	fertaric acid	*trans*-coutaric acid	phloridzin	luteolin-7-*O*-glu	quercetin	taxifolin	kaemp-3-*O*-glu	que-3-*O*-glu + que-3-*O*-gal	Isorhamn-3-*O*-glu	que-3-*O*-glucur	kaemp-3-*O*-glucur	arbutin	*trans*-resveratrol	*cis*-resveratrol	piceatannol	*trans*-piceide	*cis*-piceide	astringin	isorhapontin	caff acid + cat cond	pallidol	amp D + quadrangularin A	isohopeaphenol	methyl gallate	ellagic acid	syr-3-*O*-glu + syr-3-*O*-gal
Regent	Germany	2013	0.12	0.41	10.15	49.05	2.70	15.42	0.11	n.d.	0.20	2.05	n.d.	n.d.	n.d.	0.77	n.d.	n.d.	n.d.	0.01	0.06	0.01	0.02	0.01	0.01	4.78	0.20	n.d.	n.d.	0.01	1.31	0.81
Cabernet Cortis	Italy	2013	0.10	0.13	16.42	102.25	4.58	32.71	0.21	n.d.	0.19	0.51	n.d.	n.d.	n.d.	3.13	0.01	0.01	n.d.	0.01	n.d.	0.04	0.72	0.01	n.d.	12.66	0.53	0.05	0.15	0.01	1.40	0.80
Cabernet Cortis	Germany	2013	0.09	0.21	16.00	74.64	2.54	21.36	0.21	0.01	0.16	1.03	0.05	0.02	0.19	3.11	0.04	0.01	n.d.	n.d.	n.d.	0.10	0.44	0.02	0.02	7.54	0.14	n.d.	0.04	0.01	1.34	0.58
Cabernet Carbon	Italy	2013	0.11	0.42	12.44	76.59	3.27	17.01	0.16	0.01	0.13	4.51	n.d.	0.04	n.d.	5.58	0.15	0.01	0.02	n.d.	n.d.	0.02	0.16	0.01	0.01	6.51	0.07	0.02	n.d.	0.01	1.24	0.63
Prior	Italy	2013	0.06	0.10	5.35	24.92	1.46	4.54	0.02	n.d.	0.05	0.36	n.d.	n.d.	0.01	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	5.22	0.04	n.d.	n.d.	0.01	1.22	0.51
Prior	Germany	2013	0.05	0.12	6.16	46.84	1.70	11.15	0.05	0.01	0.06	0.58	0.05	n.d.	n.d.	0.22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.01	0.01	4.09	0.05	n.d.	n.d.	0.01	1.20	0.61
Nero	Italy	2013	0.12	0.32	9.08	44.02	2.40	14.12	0.10	n.d.	0.27	1.84	n.d.	n.d.	0.02	1.22	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	0.02	0.01	0.01	3.74	0.14	n.d.	n.d.	0.01	1.23	0.74
Nero	Germany	2013	0.09	0.22	9.05	46.43	1.10	15.07	0.16	n.d.	0.08	0.73	n.d.	0.01	0.06	2.64	0.02	0.01	n.d.	0.01	n.d.	0.10	0.55	0.02	0.04	4.80	0.33	n.d.	0.10	0.01	1.24	0.86
Johanniter	Italy	2013	0.03	0.01	1.13	53.41	3.57	8.96	0.04	n.d.	0.04	0.25	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.01	0.01	n.d.	2.16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Johanniter	Germany	2013	0.01	0.01	0.89	47.20	2.69	4.98	0.03	n.d.	0.04	0.13	n.d.	0.01	0.01	0.03	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.01	n.d.	0.01	1.38	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Solaris	Germany	2013	0.01	n.d.	0.50	47.75	1.33	5.78	0.04	n.d.	0.04	0.19	n.d.	n.d.	n.d.	0.04	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.02	0.01	0.01	1.11	0.02	n.d.	n.d.	0.09	n.d.	n.d.
Phoenix	Italy	2013	0.02	0.02	0.77	0.35	0.79	0.51	0.01	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.03	n.d.	n.d.	n.d.	n.d.	n.d.
Phoenix	Germany	2013	0.02	0.01	0.59	4.56	1.05	1.30	0.01	0.01	0.04	0.08	0.01	n.d.	n.d.	0.02	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	1.17	n.d.
Bronner	Italy	2013	0.05	0.01	0.55	39.58	1.97	7.05	0.04	0.01	0.04	0.33	0.01	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.66	0.02	0.01	n.d.	0.01	1.18	n.d.
Bronner	Germany	2013	0.02	0.01	0.38	33.64	1.25	5.39	0.04	n.d.	0.04	0.27	n.d.	n.d.	0.01	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.01	0.01	n.d.	0.62	0.02	n.d.	n.d.	0.03	n.d.	n.d.
Helios	Italy	2013	0.02	0.01	0.52	44.19	1.85	10.14	0.04	n.d.	0.04	0.53	n.d.	0.01	0.01	0.06	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	1.43	n.d.	n.d.	n.d.	0.02	1.18	n.d.
Bianca	Italy	2013	0.02	0.02	0.50	4.59	1.46	1.12	0.01	n.d.	0.04	n.d.	n.d.	0.01	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Muscaris	Italy	2013	0.01	0.02	0.54	65.54	3.44	9.73	0.06	0.01	0.04	0.26	n.d.	0.01	0.01	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.03	0.02	n.d.	0.97	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Accent	Germany	2013	0.09	0.47	7.34	34.61	1.69	7.27	0.06	n.d.	0.89	2.43	n.d.	0.01	n.d.	1.60	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	1.40	0.04	n.d.	n.d.	0.01	1.46	0.81
Rondo	Germany	2013	0.06	0.23	7.69	43.75	1.66	13.18	0.14	n.d.	0.23	1.54	n.d.	n.d.	0.22	0.65	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.02	n.d.	0.01	3.34	0.04	n.d.	n.d.	0.01	1.41	0.81
Pinot noir	Italy	2013	0.20	0.72	5.13	92.32	4.04	23.91	0.30	n.d.	0.06	8.48	n.d.	n.d.	0.17	4.73	0.03	0.02	n.d.	0.01	0.06	0.17	0.10	n.d.	0.01	21.29	2.20	0.06	0.47	0.01	1.20	2.18
Cabernet Sauvignon	Italy	2013	0.10	0.35	10.52	94.41	4.27	21.04	0.30	n.d.	0.50	1.00	n.d.	0.30	15.35	15.98	0.35	n.d.	0.02	n.d.	n.d.	0.02	0.08	n.d.	0.01	13.69	0.06	n.d.	0.05	0.01	1.29	2.95
Teroldego	Italy	2013	0.10	0.35	17.36	50.86	2.15	11.76	0.17	0.01	0.20	1.26	0.01	n.d.	0.05	1.40	0.03	n.d.	0.02	0.01	n.d.	0.01	0.07	0.01	0.01	4.20	0.40	0.02	0.19	0.01	2.95	2.00
Chardonnay	Italy	2013	0.02	0.01	0.75	62.89	2.45	8.16	0.06	n.d.	0.04	0.68	0.01	n.d.	0.01	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.03	n.d.	n.d.	2.26	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Chardonnay	Germany	2013	0.09	0.03	0.81	35.07	1.56	3.62	0.03	n.d.	0.04	0.35	n.d.	0.01	0.01	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.05	n.d.	0.01	0.85	0.03	n.d.	n.d.	n.d.	n.d.	n.d.
Riesling	Italy	2013	0.02	0.03	0.47	42.53	6.44	4.41	0.04	n.d.	0.04	0.20	n.d.	n.d.	0.02	0.03	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.06	0.02	n.d.	0.68	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Moscato Giallo	Italy	2013	0.07	0.03	1.05	40.78	1.82	3.80	0.06	n.d.	0.04	0.40	n.d.	n.d.	n.d.	0.01	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.06	0.01	0.01	1.12	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Moscato Giallo	Germany	2013	0.01	0.01	0.30	52.45	0.95	5.90	0.01	n.d.	0.04	0.20	n.d.	n.d.	0.01	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.02	0.01	n.d.	1.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Regent	Italy	2015	0.07	0.11	9.16	31.79	2.16	7.11	0.14	n.d.	0.13	1.51	n.d.	0.05	0.26	3.86	0.04	0.01	0.02	0.01	n.d.	0.05	0.39	0.02	0.01	9.09	0.23	n.d.	0.03	0.01	1.82	0.87
Regent	Germany	2015	0.13	0.22	8.31	64.93	3.00	20.88	0.17	n.d.	0.79	n.d.	n.d.	n.d.	n.d.	5.73	0.02	0.01	n.d.	0.01	n.d.	0.06	0.27	0.03	0.01	4.97	0.13	0.02	0.02	0.01	1.50	0.95
Cabernet Cortis	Italy	2015	0.06	0.04	9.51	87.41	4.12	28.04	0.51	n.d.	0.22	0.40	n.d.	3.16	3.12	9.18	0.16	0.01	0.02	n.d.	n.d.	0.21	0.99	0.04	0.03	15.48	0.14	n.d.	0.03	0.01	1.33	1.12
Cabernet Cortis	Germany	2015	0.08	0.07	15.01	121.45	5.08	38.46	0.38	0.01	0.16	1.05	0.05	0.66	n.d.	8.88	0.17	0.02	0.02	0.01	n.d.	0.18	1.29	0.02	0.02	11.20	0.17	0.02	0.05	0.01	1.27	0.67
Cabernet Carbon	Italy	2015	0.09	0.13	11.12	124.44	4.38	29.09	0.24	n.d.	0.20	8.10	n.d.	0.54	3.46	4.37	0.06	0.03	0.02	0.01	0.06	0.05	0.74	0.03	0.01	6.62	0.16	n.d.	0.01	0.01	1.27	1.64
Prior	Italy	2015	0.04	0.06	4.16	78.85	2.63	18.01	0.24	n.d.	0.27	0.23	n.d.	0.08	0.39	4.54	0.04	n.d.	0.02	0.01	n.d.	n.d.	0.03	0.01	0.01	4.32	0.03	n.d.	0.01	0.04	1.31	1.60
Nero	Italy	2015	0.09	0.13	12.65	31.91	1.29	7.17	0.19	n.d.	0.15	0.65	n.d.	0.22	1.32	4.39	0.06	0.02	n.d.	0.01	n.d.	0.27	1.37	0.08	0.04	5.53	0.32	0.01	0.38	0.01	1.34	2.05
Souvignier Gris	Italy	2015	0.01	0.01	0.63	18.19	3.16	2.60	0.03	n.d.	0.04	0.11	n.d.	n.d.	0.01	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.16	n.d.	n.d.	n.d.	0.07	1.17	0.04
Johanniter	Italy	2015	0.02	0.01	1.02	38.16	4.72	8.97	0.03	n.d.	0.04	0.10	n.d.	0.01	n.d.	0.05	n.d.	0.01	n.d.	n.d.	n.d.	0.02	0.03	0.01	0.01	0.96	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Johanniter	Germany	2015	0.02	0.01	0.75	45.86	3.09	6.29	0.05	n.d.	0.04	0.25	n.d.	0.01	n.d.	0.03	n.d.	0.01	0.02	n.d.	n.d.	n.d.	0.03	0.02	n.d.	0.34	0.03	n.d.	n.d.	0.01	1.18	n.d.
Solaris	Italy	2015	0.02	0.01	0.36	31.40	2.13	6.38	0.04	n.d.	0.04	0.25	n.d.	0.01	n.d.	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.06	0.04	n.d.	0.33	n.d.	n.d.	n.d.	0.14	n.d.	n.d.
Solaris	Germany	2015	0.01	0.01	0.59	41.02	1.52	5.03	0.03	n.d.	0.04	0.15	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.03	0.04	n.d.	0.14	0.03	n.d.	n.d.	0.14	1.18	n.d.
Phoenix	Italy	2015	0.01	0.01	0.72	11.39	1.35	1.65	0.02	0.01	0.04	0.05	n.d.	0.01	0.01	0.01	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.13	0.08	0.01	n.d.	0.02	n.d.	n.d.	0.01	n.d.	n.d.

Phoenix	Germany	2015	n.d.	0.01	0.71	14.20	1.48	1.38	0.02	n.d.	0.04	0.14	n.d.	n.d.	n.d.	0.01	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.03	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Bronner	Italy	2015	0.02	0.01	0.43	76.46	2.52	17.45	0.08	n.d.	0.04	0.36	n.d.	n.d.	0.01	0.04	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.02	0.06	0.01	1.63	0.03	n.d.	n.d.	0.20	1.18	n.d.
Bronner	Germany	2015	0.02	0.01	0.30	35.55	1.49	5.73	0.04	0.01	0.04	0.31	0.01	n.d.	n.d.	0.02	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.02	0.03	n.d.	0.20	n.d.	n.d.	n.d.	0.11	n.d.	n.d.
Muscaris	Italy	2015	0.02	0.02	0.72	79.42	4.12	11.44	0.06	n.d.	0.05	0.29	n.d.	n.d.	0.02	0.07	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.04	0.04	0.01	0.32	0.03	n.d.	n.d.	n.d.	1.17	n.d.
Muscaris	Germany	2015	0.01	0.01	0.43	37.49	2.45	4.99	0.04	0.01	0.04	0.20	n.d.	n.d.	0.01	0.01	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.02	n.d.	n.d.	0.28	0.02	n.d.	n.d.	0.01	1.18	n.d.
Accent	Germany	2015	0.06	0.48	7.86	47.89	2.94	10.22	0.08	n.d.	0.89	3.98	n.d.	n.d.	n.d.	0.95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.01	2.13	0.07	0.01	0.01	0.03	1.75	1.27
Rondo	Germany	2015	0.07	0.11	9.16	68.63	2.32	17.89	0.09	0.01	0.19	1.62	n.d.	0.01	n.d.	2.24	0.01	0.01	n.d.	0.01	n.d.	0.01	0.08	0.02	0.01	3.11	0.03	n.d.	n.d.	0.01	1.48	0.71
Bolero	Germany	2015	0.07	0.07	5.23	54.54	3.00	18.47	0.16	n.d.	0.47	4.25	n.d.	0.20	0.40	5.70	0.10	0.01	0.02	n.d.	n.d.	0.04	0.16	0.02	0.01	2.64	0.02	n.d.	n.d.	0.01	1.19	0.53
Helios	Italy	2015	0.03	0.02	0.57	52.01	2.64	17.64	0.08	n.d.	0.04	0.40	n.d.	0.01	0.03	0.05	n.d.	0.01	n.d.	n.d.	n.d.	0.02	0.04	n.d.	0.01	0.63	n.d.	n.d.	n.d.	0.02	n.d.	0.01
Bianca	Italy	2015	0.01	0.02	0.49	8.79	2.83	1.93	0.02	n.d.	0.04	0.13	n.d.	0.01	0.01	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.07	0.02	n.d.	n.d.	n.d.	1.18	n.d.
Jasmine	Italy	2015	0.03	0.03	0.55	74.60	6.09	9.73	0.11	n.d.	0.05	0.55	n.d.	0.01	0.02	0.09	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.04	n.d.	0.01	0.65	n.d.	n.d.	n.d.	0.01	1.18	0.01
Pinot noir	Italy	2015	0.20	0.57	8.72	7.28	0.44	1.37	0.15	0.01	0.05	5.18	n.d.	0.01	0.03	2.03	0.02	0.01	0.02	0.01	n.d.	0.06	0.32	0.02	0.01	2.81	0.48	0.07	0.03	0.01	1.20	0.59
Cabernet Sauvignon	Italy	2015	0.08	0.14	5.76	29.89	2.14	8.37	0.20	n.d.	0.24	2.69	n.d.	0.57	1.86	11.92	0.17	0.01	0.02	0.01	n.d.	0.10	0.49	0.02	0.01	8.97	0.22	n.d.	0.06	0.01	1.97	1.41
Cabernet Sauvignon	Germany	2015	0.09	0.16	7.11	43.84	1.56	12.69	0.30	n.d.	0.18	1.48	n.d.	0.05	0.76	4.05	0.07	0.02	n.d.	n.d.	n.d.	0.90	3.82	0.28	0.10	2.75	0.13	0.03	n.d.	0.01	1.24	0.60
Chardonnay	Italy	2015	0.02	0.01	0.48	21.93	2.33	3.24	0.02	0.01	0.05	0.30	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.23	n.d.	n.d.	n.d.	n.d.	1.18	n.d.
Chardonnay	Germany	2015	0.02	0.02	0.50	28.24	1.53	4.50	0.02	n.d.	0.04	n.d.	n.d.	0.01	0.01	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.16	n.d.	0.01	n.d.	0.02	n.d.	n.d.	n.d.	1.17	n.d.
Riesling	Italy	2015	0.01	0.02	0.43	50.57	5.77	4.77	0.04	n.d.	0.04	0.07	n.d.	n.d.	0.01	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01	0.03	0.02	0.01	0.11	n.d.	n.d.	n.d.	n.d.	1.18	n.d.
Riesling	Germany	2015	0.02	0.02	0.39	43.44	4.48	5.62	0.03	n.d.	0.04	0.36	n.d.	n.d.	0.01	0.01	n.d.	0.01	n.d.	0.01	n.d.	0.01	0.10	0.03	0.01	0.07	n.d.	0.01	n.d.	0.01	n.d.	n.d.
Moscato Giallo	Italy	2015	0.02	0.02	0.81	39.90	1.39	3.42	0.03	n.d.	0.04	0.18	n.d.	0.01	0.03	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.01	0.01	0.34	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Regent	Italy	2016	n.d.	0.03	0.62	2.98	2.28	1.57	n.d.	n.d.	1.10	0.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	0.48	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
Regent	Germany	2016	n.d.	0.01	0.37	24.81	1.59	3.68	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	0.54	n.d.	n.d.	n.d.	n.d.	n.d.	0.25	n.d.	n.d.
Cabernet Cortis	Italy	2016	n.d.	0.01	0.72	2.30	4.25	1.73	n.d.	n.d.	n.d.	0.23	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	0.96	n.d.	n.d.	0.08	n.d.	n.d.	0.08	0.40	0.02
Cabernet Cortis	Germany	2016	0.13	0.36	22.27	35.36	1.86	10.66	0.03	n.d.	1.14	0.47	n.d.	0.89	0.01	1.06	0.02	0.13	n.d.	n.d.	n.d.	0.62	12.41	1.05	n.d.	n.d.	0.38	n.d.	0.12	0.01	0.46	0.73
Prior	Italy	2016	0.06	0.60	15.10	72.13	3.38	11.64	0.45	0.08	2.94	6.60	n.d.	n.d.	0.19	9.67	0.02	n.d.	n.d.	n.d.	n.d.	0.15	0.27	0.47	n.d.	0.70	0.13	n.d.	n.d.	0.03	5.16	3.10
Prior	Germany	2016	n.d.	0.02	0.39	54.93	2.56	7.46	n.d.	n.d.	1.11	0.27	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.39	n.d.
Nero	Italy	2016	n.d.	n.d.	0.51	38.74	1.75	3.86	n.d.	n.d.	1.10	0.13	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	0.53	n.d.	n.d.	0.14	n.d.	n.d.	0.09	0.39	n.d.
Souvignier Gris	Italy	2016	0.26	0.77	20.94	79.08	4.43	29.13	0.19	0.02	1.17	3.12	n.d.	0.62	n.d.	5.32	0.01	n.d.	n.d.	n.d.	n.d.	0.33	1.24	0.70	0.05	0.69	0.71	n.d.	0.15	0.02	0.65	3.25
Johanniter	Italy	2016	n.d.	0.01	0.34	49.34	5.99	5.24	n.d.	n.d.	1.10	0.08	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.48	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.39	n.d.
Johanniter	Germany	2016	0.15	1.62	13.82	56.75	4.25	11.47	0.18	n.d.	1.13	8.31	n.d.	0.74	n.d.	1.37	0.01	0.39	0.12	0.21	0.54	2.01	18.56	2.22	0.08	0.55	7.58	0.09	1.02	0.01	n.d.	1.05
Solaris	Italy	2016	0.09	0.41	21.04	103.41	2.93	41.90	0.52	0.03	n.d.	3.11	n.d.	0.39	0.05	7.45	0.02	n.d.	n.d.	n.d.	n.d.	0.18	0.55	n.d.	0.09	0.48	0.33	n.d.	n.d.	0.01	n.d.	2.69
Solaris	Germany	2016	n.d.	0.04	0.56	58.13	6.97	4.93	n.d.	n.d.	1.12	0.19	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.05	0.43	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.38	n.d.
Phoenix	Italy	2016	n.d.	0.03	1.42	4.10	1.66	1.33	n.d.	n.d.	n.d.	0.06	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.14	0.76	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.39	n.d.
Phoenix	Germany	2016	n.d.	0.01	0.51	16.84	2.04	2.92	n.d.	n.d.	1.11	0.31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.42	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
Bronner	Italy	2016	0.15	0.21	16.05	90.04	3.76	37.86	0.31	0.03	1.59	3.73	n.d.	1.07	n.d.	18.32	0.10	n.d.	n.d.	n.d.	n.d.	0.66	1.51	0.81	0.04	0.45	0.65	n.d.	n.d.	0.02	5.81	2.95
Bronner	Germany	2016	0.01	0.24	9.13	78.48	2.36	17.10	0.04	n.d.	1.17	0.66	n.d.	0.36	n.d.	1.73	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.76	0.42	n.d.	0.34	0.08	n.d.	n.d.	0.06	0.69	0.94
Muscaris	Italy	2016	n.d.	0.02	0.89	91.33	7.79	7.67	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	0.47	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.38	n.d.
Muscaris	Germany	2016	n.d.	0.03	1.09	116.52	4.36	14.84	0.01	n.d.	1.10	0.35	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.17	0.73	n.d.	n.d.	0.11	n.d.	n.d.	0.04	n.d.	n.d.
Accent	Germany	2016	n.d.	0.02	0.72	52.61	3.96	5.94	n.d.	n.d.	n.d.	0.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.39	n.d.
Rondo	Germany	2016	0.08	0.95	9.12	71.04	3.32	15.38	0.23	n.d.	1.19	7.70	n.d.	0.59	0.03	4.16	0.03	0.12	n.d.	n.d.	n.d.	1.24	8.74	1.04	0.04	0.24	1.42	n.d.	n.d.	n.d.	1.67	0.89
Bolero	Germany	2016	n.d.	0.14	10.76	64.56	1.52	18.53	0.28	0.01	1.67	0.81	0.01	1.31	0.54	10.10	0.27	n.d.	n.d.	n.d.	n.d.	0.27	1.39	n.d.	0.02	0.31	0.10	n.d.	n.d.	0.02	3.05	2.21
Helios	Italy	2016	n.d.	0.03	0.50	4.30	1.48	1.01	n.d.	n.d.	1.10	0.05	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.54	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Bianca	Italy	2016	n.d.	0.03	0.46	22.22	2.38	4.17	n.d.	n.d.	1.10	0.38	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	0.09	0.52	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	n.d.
Jasmine	Italy	2016	n.d.	0.01	0.40	42.96	2.19	6.10	n.d.	n.d.	n.d.	0.28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	n.d.	n.d.
Pinot noir	Italy	2016	0.06	0.45	17.53	66.04	1.64	21.02	0.27	0.01	1.27	1.17	n.d.	0.46	0.22	6.82	0.11	n.d.	n.d.	n.d.	n.d.	0.05	0.31	0.42	n.d.	0.22	0.18	n.d.	n.d.	0.02	2.92	1.36
Cabernet Sauvignon	Germany	2016	n.d.	0.02	1.03	46.36	5.31	6.23	n.d.	n.d.	1.11	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.43	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Teroldego	Italy	2016	0.02	0.23	9.67	112.32	2.57	26.06	0.13	0.01	1.18	0.32	n.d.	0.29	n.d.	1.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.19	0.46	n.d.	0.35	0.09	n.d.	n.d.	0.05	0.39	1.05
Chardonnay	Italy	2016	0.07	0.14	24.60	180.31	7.64	70.92	0.39	0.03	1.27	0.82	0.01	1.39	0.23	8.68	0.14	n.d.	n.d.	n.d.	n.d.	0.25	2.10	n.d.	n.d.	0.49	0.27	n.d.	n.d.	0.02	1.51	1.18
Chardonnay	Germany	2016	n.d.	0.03	0.29	65.58	7.85	6.90	n.d.	n.d.	n.d.	0.40	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Riesling	Italy	2016	0.08	0.05	2.28	2.69	2.27	0.42	n.d.	n.d.	n.d.	0.05	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.01	n.d.	0.01
Riesling	Germany	2016	n.d.	0.01	0.26	70.46	3.15	3.95	n.d.	n.d.	n.d.	0.12	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.52	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Moscato Giallo	Italy	2016	n.d.	0.04	0.50	27.86	2.01	11.69	n.d.	n.d.	n.d.	0.76	n.d.	0.03	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.13	0.52	n.d.	n.d.	0.08	n.d.	n.d.	0.01	0.38	n.d.

Abbreviations: glu, glucoside; kaemp, kaempferol; gal, galactoside; glucur, glucuroside; caffeic acid, caffeic acid; cat cond, catechin condensation product; amp D, ampelosin D; syr, syringetin; n.d., not detected.

Table S5. Quantitative results of anthocyanins detected in red wines. The results are expressed as mg/L.

Variety	Country	Vintage	dp-3-*O*-glu	cy-3-*O*-glu	pt-3-*O*-glu	pn-3-*O*-glu	mv-3-*O*-glu	dp-3-(6”-acetyl)-*O*-glu	cy-3-(6”-acetyl)-*O*-glu	pt-3-(6”-acetyl)-*O*-glu	pn-3-(6”-acetyl)-*O*-glu	mv-3-(6”-acetyl)-*O*-glu	dp-3-(6”-p-coumaroyl)-*O*-glu	cy-3-(6”-p-coumaroyl)-*O*-glu	pt-3-(6”-p-coumaroyl)-*O*-glu	pn-3-(6”-p-coumaroyl)-*O*-glu	mv-3-(6”-p-coumaroyl)-*O*-glu	dp-3.5-*O*-diglu	cy-3.5-*O*-diglu	pt-3.5-*O*-diglu	pn-3.5-*O*-diglu	mv-3.5-*O*-diglu
Regent	Germany	2013	25.01	n.d.	26.14	6.05	80.56	1.21	0.49	1.23	2.77	3.29	1.50	0.29	2.33	1.12	7.51	6.87	4.63	17.18	26.85	99.13
Cabernet Cortis	Italy	2013	7.12	n.d.	14.91	7.38	52.17	1.37	1.07	1.76	7.24	5.43	2.27	0.54	2.64	1.05	7.18	7.01	2.14	20.34	13.18	136.79
Cabernet Cortis	Germany	2013	18.96	n.d.	17.86	4.27	53.42	2.96	1.07	2.70	1.55	6.19	2.01	0.21	1.17	0.60	4.40	4.70	4.62	12.10	28.57	85.30
Cabernet Carbon	Italy	2013	n.d.	n.d.	3.17	4.26	20.44	0.32	1.35	0.49	1.81	2.25	2.88	0.17	0.23	0.31	1.29	3.13	0.39	9.03	24.85	173.20
Prior	Italy	2013	0.34	n.d.	7.84	3.42	37.32	0.58	0.98	0.57	6.07	1.13	1.17	0.03	1.16	0.24	5.82	9.55	2.66	40.25	19.95	340.01
Prior	Germany	2013	7.75	n.d.	11.67	1.73	52.97	1.03	0.42	1.04	2.13	2.48	1.18	n.d.	1.16	0.27	4.82	13.16	3.31	21.91	19.47	178.08
Nero	Italy	2013	8.47	1.15	22.83	3.85	130.14	2.02	0.57	3.13	1.61	15.86	n.d.	0.33	1.53	1.10	7.51	n.d.	0.22	1.81	3.01	9.80
Nero	Germany	2013	13.97	2.97	25.43	5.16	117.39	1.73	0.66	2.60	1.16	8.65	1.18	0.20	1.73	1.13	8.76	n.d.	0.17	1.67	0.68	9.57
Accent	Germany	2013	32.19	n.d.	29.11	12.21	43.82	7.66	1.90	5.31	4.91	4.03	3.46	n.d.	1.82	0.78	2.87	25.77	28.85	71.78	161.35	197.20
Rondo	Germany	2013	14.30	n.d.	20.85	4.62	74.82	3.22	1.80	3.36	2.93	7.54	2.28	0.18	2.35	1.09	7.72	11.15	4.70	19.75	47.88	218.79
Pinot noir	Italy	2013	0.21	0.29	4.38	11.16	132.19	0.03	n.d.	0.36	0.15	0.71	0.93	n.d.	0.01	0.12	0.43	n.d.	n.d.	n.d.	0.15	0.67
Cabernet Sauvignon	Italy	2013	17.70	2.15	23.46	14.47	133.52	6.91	1.08	6.33	8.06	36.70	n.d.	0.59	1.17	3.67	7.49	n.d.	n.d.	n.d.	n.d.	n.d.
Teroldego	Italy	2013	6.63	26.35	22.01	7.59	150.10	12.93	3.97	12.16	10.74	62.35	n.d.	0.04	1.24	2.19	10.37	n.d.	0.05	n.d.	4.47	n.d.
Regent	Italy	2015	34.81	4.99	57.48	26.57	142.90	4.92	1.38	6.87	2.26	13.99	18.82	5.29	6.54	9.19	53.21	11.24	5.75	36.16	45.51	188.60
Regent	Germany	2015	31.62	2.54	46.63	15.28	149.48	2.77	0.41	3.72	0.63	7.54	13.88	3.15	5.01	4.71	51.51	8.13	3.99	27.16	26.96	157.16
Cabernet Cortis	Italy	2015	9.30	0.73	11.75	2.91	50.49	3.81	0.51	4.64	0.77	12.19	1.74	0.51	0.71	1.17	10.19	10.41	1.77	24.78	8.32	131.26
Cabernet Cortis	Germany	2015	40.48	8.05	40.85	24.80	69.89	13.98	3.70	12.12	3.83	12.36	7.21	3.00	1.73	3.56	12.21	10.38	6.04	27.99	40.12	136.10
Cabernet Carbon	Italy	2015	1.30	0.08	2.19	0.85	17.87	0.45	0.08	0.73	0.20	3.50	0.32	0.08	0.17	0.41	5.00	1.96	0.58	6.29	30.98	175.56
Prior	Italy	2015	11.13	0.47	24.71	3.21	96.42	1.47	0.15	2.13	0.17	4.33	7.31	1.05	0.02	2.08	42.06	29.55	6.40	89.00	48.68	539.88
Nero	Italy	2015	26.76	4.27	62.28	24.99	378.80	8.29	4.75	21.97	12.65	129.30	7.19	5.02	0.12	13.23	96.59	2.58	0.58	6.71	4.75	51.41
Accent	Germany	2015	63.39	20.92	87.39	64.88	134.37	29.28	10.57	28.91	12.35	21.80	10.09	5.74	2.80	7.46	17.48	22.36	24.95	67.45	150.52	171.82
Rondo	Germany	2015	7.35	0.20	19.05	2.21	100.92	6.31	0.70	8.35	1.59	20.99	9.02	1.37	3.66	3.53	53.91	12.46	3.29	37.44	57.65	437.54
Bolero	Germany	2015	18.40	1.47	31.75	3.24	79.26	4.36	0.78	6.02	0.55	8.96	5.51	1.64	1.98	1.01	18.20	9.67	11.28	35.32	31.10	195.16
Pinot noir	Italy	2015	0.46	0.04	1.50	3.48	63.65	0.14	0.01	0.14	n.d.	0.35	0.43	0.05	0.12	0.08	1.24	0.13	0.03	0.37	0.26	3.00
Cabernet Sauvignon	Italy	2015	31.83	1.43	38.44	18.01	268.14	18.32	3.87	29.00	19.56	200.74	4.09	1.33	1.53	7.57	51.94	1.27	0.14	1.47	2.03	11.16
Cabernet Sauvignon	Germany	2015	11.19	1.41	10.74	13.72	100.13	3.82	1.10	4.23	5.52	29.23	0.59	0.34	0.29	3.02	15.63	0.28	n.d.	n.d.	0.27	1.63
Regent	Italy	2016	21.00	2.00	56.00	11.00	148.00	1.00	n.d.	1.00	n.d.	4.00	4.00	n.d.	2.00	n.d.	12.00	22.00	7.00	96.00	146.00	539.00
Regent	Germany	2016	71.00	8.00	117.00	24.00	226.00	1.00	n.d.	2.00	n.d.	5.00	23.00	4.00	18.00	3.00	44.00	41.00	11.00	175.00	202.00	760.00
Cabernet Cortis	Italy	2016	14.40	0.70	20.10	3.10	48.70	1.90	0.30	2.80	0.60	8.90	1.10	0.30	1.00	n.d.	4.70	25.70	4.60	80.10	45.80	264.80
Cabernet Cortis	Germany	2016	10.50	0.50	13.90	1.60	32.90	1.00	0.20	1.50	0.20	4.20	0.70	n.d.	0.60	n.d.	2.60	25.20	4.70	82.40	48.70	270.90
Prior	Italy	2016	8.80	0.60	14.00	2.50	55.10	1.10	0.40	1.20	0.50	4.80	0.60	0.20	0.50	n.d.	5.00	32.20	4.00	90.10	64.40	335.10
Prior	Germany	2016	4.30	n.d.	13.50	1.40	50.70	0.40	n.d.	0.70	0.20	2.40	0.90	0.10	1.10	n.d.	6.60	41.90	5.00	122.90	77.90	357.50
Nero	Italy	2016	7.20	0.80	19.80	9.00	67.40	0.70	0.80	1.80	2.10	12.20	0.20	0.70	0.50	0.90	5.00	n.d.	n.d.	n.d.	n.d.	n.d.
Accent	Germany	2016	35.60	12.10	71.20	39.50	70.00	5.70	4.50	10.80	6.30	12.10	4.50	5.30	7.40	3.40	12.90	71.50	62.40	271.70	272.50	351.50
Rondo	Germany	2016	16.00	1.00	41.00	6.00	140.00.	3.00	n.d.	5.00	1.00	15.00	7.00	1.00	5.00	1.00	27.00	50.00	9.00	167.00	358.00	1465.00
Bolero	Germany	2016	22.90	1.60	42.40	4.80	63.20	2.80	0.80	4.50	0.50	6.90	4.90	2.30	5.80	0.50	12.10	42.50	19.70	139.60	109.80	308.10
Pinot noir	Italy	2016	6.00	1.00	14.00	15.00	96.00	n.d.	n.d.	n.d.	n.d.	2.00	n.d.	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	n.d.	n.d.	n.d.
Cabernet Sauvignon	Germany	2016	20.00	2.00	26.00	12.00	126.00	2.00	n.d.	2.00	2.00	2n.d.	n.d.	n.d.	n.d.	n.d.	8.00	n.d.	n.d.	n.d.	3.00	6.00
Teroldego	Italy	2016	22.00	3.00	39.00	14.00	145.00	5.00	1.00	7.00	5.00	35.00	2.00	n.d.	n.d.	1.00	11.00	n.d.	n.d.	n.d.	n.d.	n.d.

Abbreviations: dp, delphinidin; cy, cyanidin; pt, petunidin; pn, peonidin; malvidin, malvinidin; glu, glucoside; diglu, diglucoside; n.d., not detected.

Table S6. Levels of flavan-3-ols and proanthocyanidins in the wines studied. The results are expressed as mg/L.

Variety	Country	Vintage	catechin	epicatechin	gallocatechin	epigallocatechin	cat gallate + epicat gallate	procyanidin B1	procyanidin B2	cat (extension units)	cat (terminal units)	epicat (extension units)	epicat (terminal units)	gallocat (extension units)	gallocat (terminal units)	epigallocat (extension units)	epigallocat (terminal units)	cat gallate + epicat gallate (extension units)	cat gallate + epicat gallate (terminal units)	cat + epicat (upper units)	epigallocat (upper units)	epicat gallate (upper units)	%G	mDP
Regent	Germany	2013	13.54	6.52	0.24	0.46	0.04	11.20	3.26	53.66	40.12	24.20	17.68	5.93	5.69	5.12	4.66	0.12	0.08	75.71	45.19	2.82	2.28	2.81
Cabernet Cortis	Italy	2013	16.32	8.18	0.91	0.90	0.06	16.99	6.43	131.52	115.20	69.81	61.63	19.08	18.17	22.33	21.43	0.61	0.55	329.74	250.21	14.76	2.48	3.74
Cabernet Cortis	Germany	2013	18.18	13.22	1.18	1.30	0.05	32.44	14.85	99.71	81.53	70.03	56.82	16.40	15.22	19.19	17.89	0.48	0.44	313.19	263.91	16.17	2.73	4.45
Cabernet Carbon	Italy	2013	17.98	8.30	1.08	0.61	0.04	21.34	6.33	134.10	116.12	60.35	52.04	20.55	19.47	16.44	15.82	0.40	0.36	315.85	187.74	21.41	4.08	3.58
Prior	Italy	2013	7.50	3.07	1.28	0.53	n.d.	21.66	3.23	46.67	39.18	11.78	8.71	10.64	9.36	7.01	6.48	0.10	0.10	126.99	66.84	2.87	1.46	4.08
Prior	Germany	2013	9.78	3.38	2.04	0.95	n.d.	17.86	2.79	52.73	42.95	15.01	11.63	15.38	13.35	9.68	8.74	0.12	0.12	139.18	94.08	3.48	1.47	4.08
Nero	Italy	2013	11.72	5.44	0.73	0.53	n.d.	9.40	2.92	44.03	32.31	19.59	14.15	4.81	4.08	5.28	4.75	0.11	0.11	87.96	54.85	1.75	1.21	3.61
Nero	Germany	2013	39.49	14.91	2.20	1.30	n.d.	38.59	8.16	79.85	40.36	29.82	14.91	10.82	8.63	10.83	9.53	0.15	0.15	171.42	214.86	9.15	2.31	6.37
Johanniter	Italy	2013	5.82	0.88	0.45	0.16	n.d.	2.73	0.15	20.97	15.15	2.03	1.15	2.46	2.02	2.01	1.85	0.06	0.06	6.12	10.23	0.55	3.28	1.84
Johanniter	Germany	2013	0.83	0.11	0.09	0.04	0.01	0.06	0.02	5.20	4.36	0.34	0.23	0.96	0.87	0.45	0.41	0.07	0.06	0.96	7.50	0.38	4.29	2.49
Solaris	Germany	2013	2.71	0.94	0.14	0.09	0.03	0.21	0.06	7.69	4.98	1.69	0.75	0.65	0.51	0.67	0.58	0.08	0.05	1.59	8.14	0.32	3.14	2.46
Phoenix	Italy	2013	0.54	0.09	0.10	0.04	n.d.	0.47	0.05	2.37	1.83	0.27	0.18	0.35	0.25	0.28	0.23	n.d.	n.d.	2.11	7.14	0.29	3.07	4.81
Phoenix	Germany	2013	0.88	0.31	0.06	0.04	n.d.	0.05	0.03	3.00	2.12	0.86	0.54	0.24	0.18	0.27	0.23	n.d.	n.d.	1.60	8.53	0.33	3.18	4.40
Bronner	Italy	2013	3.73	1.03	0.08	0.05	n.d.	1.50	0.10	9.95	6.21	1.41	0.38	0.29	0.21	0.57	0.51	n.d.	n.d.	3.03	11.37	0.23	1.55	3.00
Bronner	Germany	2013	3.08	0.99	0.09	0.06	0.01	0.52	0.05	8.12	5.04	1.69	0.69	0.31	0.22	0.47	0.41	0.05	0.04	3.58	8.06	0.27	2.28	2.86
Helios	Italy	2013	2.06	0.44	0.05	0.04	0.01	0.20	0.04	8.40	6.34	1.21	0.77	0.36	0.30	0.54	0.50	0.06	0.05	2.94	8.71	0.25	2.13	2.50
Bianca	Italy	2013	0.57	0.15	0.02	0.03	n.d.	0.06	0.03	1.76	1.19	0.43	0.28	0.18	0.16	0.27	0.24	n.d.	n.d.	1.39	7.40	0.36	3.90	5.92
Muscaris	Italy	2013	2.34	0.64	0.02	0.03	0.01	0.46	0.05	6.09	3.75	1.13	0.49	0.09	0.07	0.46	0.43	n.d.	n.d.	1.57	9.06	0.21	1.94	3.29
Accent	Germany	2013	4.44	2.11	0.37	0.34	n.d.	4.96	1.73	17.64	13.20	7.00	4.89	3.52	3.15	2.97	2.63	0.07	0.07	103.73	67.08	5.17	2.94	8.35
Rondo	Germany	2013	12.18	3.39	0.56	0.37	0.04	18.39	4.45	26.39	14.21	9.54	6.15	1.59	1.03	2.78	2.41	0.09	0.05	114.33	53.46	3.57	2.08	8.19
Pinot noir	Italy	2013	69.55	35.72	1.67	0.69	n.d.	69.70	18.97	87.81	18.26	39.89	4.16	6.26	4.59	6.25	5.56	0.12	0.12	264.96	134.54	16.76	4.03	13.73
Cabernet Sauvignon	Italy	2013	20.69	4.62	4.37	1.52	0.06	30.53	3.83	96.65	75.97	20.48	15.87	39.81	35.44	16.46	14.94	0.58	0.52	284.92	468.66	23.55	3.03	6.44
Teroldego	Italy	2013	38.62	32.51	2.86	3.67	0.04	37.41	23.97	111.54	72.92	80.91	48.40	17.61	14.75	23.53	19.86	0.26	0.21	244.71	190.81	22.92	5.00	3.94
Chardonnay	Italy	2013	1.54	0.23	0.04	0.04	0.01	0.18	0.05	10.71	9.17	1.30	1.07	0.56	0.52	0.59	0.55	0.06	0.05	5.64	7.70	0.51	3.66	2.22
Chardonnay	Germany	2013	7.38	1.04	0.78	0.13	0.01	4.68	0.17	23.44	16.06	1.65	0.61	3.37	2.60	1.43	1.31	0.05	0.04	6.93	9.25	0.33	2.03	1.80
Riesling	Italy	2013	1.18	0.20	0.03	0.05	n.d.	0.10	0.02	3.50	2.31	0.38	0.18	0.18	0.14	0.35	0.30	0.05	0.05	1.63	9.17	0.16	1.50	4.66
Moscato Giallo	Italy	2013	2.71	0.13	0.24	0.04	n.d.	0.27	0.03	13.92	11.21	0.74	0.61	1.64	1.40	0.94	0.90	0.05	0.05	1.80	7.95	0.18	1.81	1.70
Moscato Giallo	Germany	2013	1.22	0.15	0.03	0.03	n.d.	0.11	0.02	4.16	2.94	0.35	0.20	0.15	0.12	0.27	0.24	n.d.	n.d.	2.22	7.13	0.30	3.10	3.77
Regent	Italy	2015	42.38	28.02	2.60	2.70	0.05	75.76	16.88	118.74	76.36	57.31	29.29	14.83	12.23	9.51	6.80	0.53	0.48	276.44	288.89	29.08	4.89	5.75
Regent	Germany	2015	49.67	29.67	4.00	2.12	0.04	71.09	17.90	113.54	63.87	53.22	23.55	17.92	13.92	7.42	5.30	0.56	0.51	153.45	112.11	12.87	4.62	3.60
Cabernet Cortis	Italy	2015	37.11	20.18	4.25	5.30	0.39	81.86	22.98	192.29	155.18	95.28	75.10	59.07	54.82	48.12	42.81	4.57	4.18	1016.12	1343.50	52.40	2.17	8.26
Cabernet Cortis	Germany	2015	41.68	25.78	6.21	6.46	0.14	76.27	24.63	185.56	143.88	105.56	79.79	72.33	66.12	51.88	45.41	4.01	3.87	737.13	1427.80	80.89	3.60	7.62
Cabernet Carbon	Italy	2015	9.00	7.44	0.83	0.60	0.06	12.16	5.27	75.19	66.19	51.59	44.14	14.25	13.42	6.25	5.65	1.19	1.13	302.51	276.73	25.60	4.23	5.63
Prior	Italy	2015	21.34	18.81	2.98	1.84	0.04	69.19	14.38	112.52	91.18	46.62	27.81	41.52	38.54	16.78	14.94	0.46	0.42	551.52	508.46	26.37	2.43	7.28
Nero	Italy	2015	87.81	63.65	4.37	2.69	0.04	100.38	37.25	204.15	116.34	118.69	55.04	25.13	20.75	11.32	8.63	0.59	0.54	457.31	484.39	33.40	3.43	5.84
Souvignier Gris	Italy	2015	3.88	3.68	0.02	0.03	0.03	1.36	0.52	7.72	3.84	4.75	1.07	0.12	0.10	0.69	0.66	0.06	0.03	4.00	9.26	0.85	6.02	3.48
Johanniter	Italy	2015	5.99	1.47	0.33	0.14	0.02	8.88	0.47	17.34	11.35	2.05	0.57	1.58	1.25	1.40	1.27	0.12	0.09	10.38	10.75	0.73	3.33	2.50
Johanniter	Germany	2015	4.87	1.33	0.39	0.06	0.01	3.81	0.27	11.40	6.54	1.37	0.04	1.46	1.06	1.02	0.96	0.05	0.05	3.48	8.05	0.20	1.72	2.36
Solaris	Italy	2015	8.18	4.02	0.23	0.12	0.04	9.83	1.03	21.46	13.27	5.38	1.36	0.81	0.57	1.37	1.25	0.12	0.09	9.60	8.46	0.23	1.23	2.11
Solaris	Germany	2015	3.18	1.82	0.16	0.10	0.03	2.30	0.32	7.53	4.35	2.55	0.73	0.50	0.34	0.71	0.61	0.09	0.06	3.70	8.35	0.21	1.67	3.01

Phoenix	Italy	2015	2.44	1.37	0.09	0.07	0.01	1.86	0.21	5.24	2.80	1.50	0.13	0.31	0.22	0.64	0.57	0.05	0.05	2.10	5.99	0.20	2.39	3.20
Phoenix	Germany	2015	1.74	0.98	0.06	0.04	0.01	1.98	0.19	4.62	2.88	0.94	n.d.	0.21	0.15	0.31	0.28	0.05	0.04	1.23	7.82	0.20	2.18	3.80
Bronner	Italy	2015	5.00	1.64	0.11	0.11	0.02	4.42	0.40	11.83	6.82	2.11	0.47	0.59	0.49	1.40	1.28	0.07	0.05	11.83	15.07	0.33	1.21	3.99
Bronner	Germany	2015	2.62	0.88	0.02	0.03	0.01	1.26	0.09	5.11	2.50	0.80	n.d.	0.14	0.12	0.54	0.50	0.05	0.04	3.42	9.94	0.17	1.22	5.40
Muscaris	Italy	2015	3.22	1.16	0.06	n.d.	0.01	4.01	0.32	23.05	19.83	3.55	2.39	0.69	0.63	1.16	1.16	0.10	0.09	7.12	8.26	0.18	1.16	1.65
Muscaris	Germany	2015	1.13	0.59	0.02	0.04	0.01	0.52	0.06	10.20	9.06	4.30	3.71	0.49	0.47	0.55	0.51	0.10	0.09	1.38	8.59	0.22	2.20	1.74
Accent	Germany	2015	12.73	9.46	1.05	0.84	0.04	34.00	10.66	54.14	41.42	29.66	20.20	8.32	7.26	9.28	8.44	0.41	0.37	141.20	92.35	8.98	3.70	4.12
Rondo	Germany	2015	26.85	16.19	1.77	1.11	0.05	54.15	15.67	85.08	58.23	41.44	25.25	9.48	7.70	13.21	12.11	0.57	0.52	181.57	75.24	15.12	5.56	3.62
Bolero	Germany	2015	8.67	4.10	1.04	1.15	0.06	15.91	3.69	48.46	39.79	15.37	11.28	8.63	7.60	9.72	8.57	0.84	0.78	121.49	105.38	16.44	6.76	4.58
Helios	Italy	2015	8.68	5.84	0.09	0.10	0.03	6.10	2.27	19.22	10.54	8.58	2.74	0.44	0.35	1.92	1.82	0.13	0.10	20.89	13.53	0.91	2.57	3.27
Bianca	Italy	2015	0.28	0.09	0.01	0.03	n.d.	0.01	0.02	3.01	2.73	0.50	0.41	0.17	0.16	0.39	0.36	n.d.	n.d.	2.19	6.55	0.17	1.87	3.44
Jasmine	Italy	2015	4.45	1.37	0.11	0.07	0.03	7.52	0.60	44.79	40.34	8.69	7.31	1.63	1.51	1.73	1.66	0.34	0.31	35.35	12.41	1.19	2.42	1.96
Pinot noir	Italy	2015	147.81	97.27	1.77	1.15	n.d.	106.05	53.19	241.32	93.51	145.25	47.97	12.10	10.33	30.29	29.13	0.32	0.32	369.66	179.52	24.58	4.28	4.17
Cabernet Sauvignon	Italy	2015	36.55	21.66	2.57	2.19	0.05	74.51	15.74	124.50	87.95	53.37	31.71	22.16	19.59	23.22	21.03	0.89	0.84	329.36	377.74	31.39	4.25	5.58
Cabernet Sauvignon	Germany	2015	47.50	22.83	8.59	2.23	0.05	48.39	12.74	119.70	72.20	51.97	29.14	36.62	28.03	16.42	14.19	0.53	0.48	172.47	227.54	15.06	3.63	3.88
Chardonnay	Italy	2015	4.37	1.79	0.07	0.04	n.d.	3.97	0.37	10.47	6.10	2.52	0.72	0.32	0.25	0.76	0.72	0.05	0.05	3.13	13.74	0.20	1.17	3.18
Chardonnay	Germany	2015	3.86	1.17	0.10	0.04	n.d.	4.55	0.13	11.36	7.50	1.43	0.26	0.38	0.28	0.62	0.58	0.05	0.05	3.75	9.13	0.25	1.88	2.51
Riesling	Italy	2015	1.97	0.72	0.08	0.04	n.d.	0.92	0.08	4.38	2.41	0.78	0.06	0.31	0.23	0.47	0.42	0.05	0.05	0.72	16.88	0.27	1.54	6.63
Riesling	Germany	2015	0.67	0.30	0.02	0.03	n.d.	0.29	0.04	5.37	4.70	0.93	0.64	0.24	0.23	0.38	0.35	n.d.	n.d.	0.85	18.28	0.36	1.83	4.30
Moscato Giallo	Italy	2015	6.59	1.67	0.26	0.06	n.d.	9.83	0.85	20.57	13.98	3.15	1.47	1.25	0.99	1.21	1.15	0.05	0.05	9.03	9.05	0.21	1.14	2.04
Regent	Italy	2016	31.87	21.54	1.90	1.43	0.05	58.89	22.39	104.08	72.21	56.96	35.42	10.03	8.13	5.41	3.98	0.84	0.79	518.48	168.01	28.74	4.02	6.93
Regent	Germany	2016	12.97	9.71	1.22	0.72	0.08	42.49	8.32	67.01	54.04	31.29	21.58	12.20	10.99	4.10	3.39	1.92	1.84	528.81	228.53	29.96	3.81	9.57
Cabernet Cortis	Italy	2016	47.24	45.91	2.79	3.55	0.07	105.31	50.44	215.88	168.65	146.49	100.58	36.39	33.61	17.04	13.49	5.84	5.77	1630.41	627.49	205.23	8.31	6.86
Cabernet Cortis	Germany	2016	17.90	17.90	3.63	3.82	0.10	50.55	20.15	123.60	105.70	88.57	70.68	54.93	51.30	26.13	22.31	5.04	4.94	1403.99	832.48	175.40	7.26	9.10
Prior	Italy	2016	13.56	6.76	3.31	n.d.	n.d.	54.48	7.88	75.39	61.83	19.37	12.61	22.89	19.58	8.64	8.64	0.26	0.26	620.86	204.37	16.26	1.93	9.18
Prior	Germany	2016	12.13	9.35	2.83	2.26	n.d.	42.24	10.58	54.24	42.11	23.73	14.38	15.47	12.64	7.69	5.43	0.18	0.18	235.48	80.00	3.38	1.06	5.27
Nero	Italy	2016	115.11	86.18	2.86	2.03	n.d.	143.69	64.34	241.86	126.75	166.74	80.56	10.63	7.77	3.86	1.83	0.68	0.68	597.82	202.30	79.70	9.06	5.04
Souvignier Gris	Italy	2016	2.77	3.13	0.15	0.05	n.d.	7.03	2.11	11.46	8.69	6.92	3.80	0.40	0.26	0.18	0.13	0.06	0.06	11.08	0.27	0.09	0.77	1.88
Johanniter	Italy	2016	1.81	0.76	0.24	0.04	n.d.	8.08	0.56	10.08	8.27	2.24	1.48	0.79	0.54	0.10	0.06	0.06	0.06	9.45	0.52	0.02	0.22	1.96
Johanniter	Germany	2016	1.75	1.02	0.62	0.09	n.d.	6.92	0.58	7.67	5.92	2.53	1.51	1.52	0.90	0.26	0.18	0.07	0.07	6.30	0.57	0.02	0.23	1.80
Solaris	Italy	2016	1.41	1.94	0.05	0.02	n.d.	5.73	1.02	6.48	5.07	5.22	3.28	0.17	0.12	0.11	0.09	n.d.	n.d.	7.79	0.28	0.03	0.39	1.95
Solaris	Germany	2016	1.22	1.58	0.08	0.01	n.d.	3.71	0.75	6.18	4.97	3.23	1.66	0.36	0.28	0.15	0.13	0.08	0.08	6.60	0.23	0.12	1.80	1.98
Phoenix	Italy	2016	0.54	0.54	0.45	0.06	n.d.	9.01	1.04	4.81	4.26	2.72	2.18	1.26	0.81	0.21	0.15	n.d.	n.d.	15.57	1.30	0.04	0.21	3.28
Phoenix	Germany	2016	0.22	0.70	0.04	0.01	n.d.	3.08	0.40	1.42	1.20	1.97	1.27	0.19	0.15	0.05	0.04	n.d.	n.d.	3.57	0.13	n.d.	n.d.	2.40
Bronner	Italy	2016	1.22	0.93	0.02	0.01	n.d.	3.70	0.58	4.44	3.21	2.57	1.64	0.15	0.13	0.05	0.04	n.d.	n.d.	6.10	0.24	n.d.	n.d.	2.26
Bronner	Germany	2016	1.18	1.19	0.10	0.03	0.02	3.42	0.39	6.16	4.97	3.09	1.90	0.42	0.32	0.08	0.05	0.09	0.07	4.86	0.35	n.d.	n.d.	1.71
Muscaris	Italy	2016	1.61	1.81	0.04	0.02	0.01	9.02	1.14	9.87	8.26	4.33	2.52	0.42	0.38	0.11	0.09	n.d.	n.d.	18.47	0.74	0.07	0.37	2.71
Muscaris	Germany	2016	0.64	1.09	0.05	0.02	0.02	6.51	0.66	5.38	4.74	2.93	1.84	0.35	0.30	0.09	0.08	0.10	0.08	14.40	2.39	0.48	2.76	3.45
Accent	Germany	2016	4.53	3.55	0.23	0.31	0.05	23.03	7.01	34.58	30.06	18.21	14.66	6.16	5.93	2.89	2.58	0.45	0.40	319.08	127.89	17.54	3.78	9.66
Rondo	Germany	2016	21.81	8.43	0.73	0.42	n.d.	46.77	14.28	79.18	57.36	29.56	21.13	8.08	7.35	2.75	2.33	0.57	0.57	548.63	131.20	21.00	3.00	8.90
Bolero	Germany	2016	12.09	9.16	1.34	1.61	0.16	55.92	13.74	58.52	46.43	25.57	16.42	9.48	8.14	5.97	4.36	1.67	1.51	368.84	141.30	31.20	5.76	8.04
Helios	Italy	2016	9.12	11.27	0.15	0.16	0.01	19.00	15.76	39.57	30.46	28.21	16.94	0.61	0.46	0.70	0.55	0.07	0.06	48.43	2.19	0.36	0.70	2.05
Bianca	Italy	2016	2.38	4.55	0.12	0.07	n.d.	5.59	2.73	8.97	6.59	9.31	4.76	0.48	0.36	0.28	0.21	0.07	0.07	12.15	0.98	0.14	1.07	2.11
Jasmine	Italy	2016	1.30	1.38	0.02	0.01	n.d.	7.60	1.10	6.45	5.16	3.47	2.09	0.15	0.14	0.05	0.04	0.06	0.06	11.20	0.22	0.05	0.43	2.53
Pinot noir	Italy	2016	45.32	37.21	1.34	0.74	n.d.	69.57	22.49	113.79	68.47	66.47	29.26	7.26	5.92	1.88	1.14	0.32	0.32	401.99	92.70	38.17	7.16	6.07
Cabernet Sauvignon	Germany	2016	7.82	5.63	5.84	1.85	0.16	38.19	5.81	54.70	46.88	22.50	16.88	42.12	36.28	5.27	3.42	1.18	1.02	487.94	417.07	72.81	7.45	10.36
Teroldego	Italy	2016	18.57	10.41	6.51	4.59	n.d.	50.02	10.79	88.47	69.90	31.49	21.08	45.11	38.60	11.38	6.79	0.49	0.49	743.20	516.43	89.37	6.62	10.86
Chardonnay	Italy	2016	1.17	1.41	0.02	0.02	n.d.	4.02	1.47	5.49	4.32	3.61	2.20	0.20	0.18	0.13	0.11	0.06	0.06	10.32	0.51	n.d.	n.d.	2.58
Chardonnay	Germany	2016	1.19	1.25	0.04	0.02	n.d.	5.16	0.53	6.33	5.14	2.83	1.58	0.24	0.20	0.07	0.06	0.06	0.06	8.03	0.20	n.d.	n.d.	2.17
Riesling	Italy	2016	2.07	1.11	0.05	0.02	n.d.	2.28	0.57	8.31	6.24	3.21	2.10	0.33	0.27	0.07	0.04	n.d.	n.d.	5.15	0.26	0.02	0.35	1.46
Riesling	Germany	2016	0.73	0.82	0.19	0.03	0.02	4.60	0.60	3.22	2.49	2.39	1.57	1.07	0.88	0.11	0.08	0.08	0.06	12.72	3.88	0.62	3.57	3.52
Moscato Giallo	Italy	2016	1.03	0.59	0.04	0.01	n.d.	3.65	0.47	6.89	5.86	2.09	1.50	0.35	0.31	0.07	0.06	n.d.	n.d.	9.64	0.33	n.d.	n.d.	2.06

Abbreviations:cat, catechin;epicat, epicatechin; gallocat, gallocatechin; epigallocat, epigallocatechin; %G, percentage of galloylation; mDP, mean degree of polymerisation, n.d., not detected.

Table S7. Mineral composition of the wines studied. The results are expressed as mg/L.

Variety	Country	Vintage	Ca	K	Mg	Cu	Fe	Na	Zn
Regent	Germany	2013	83.00	1084.00	84.00	0.12	1.04	4.30	0.34
Cabernet Cortis	Italy	2013	80.00	1115.00	130.00	0.14	0.86	3.70	0.61
Cabernet Cortis	Germany	2013	91.00	1109.00	88.00	0.08	1.16	5.90	0.46
Cabernet Carbon	Italy	2013	61.00	1244.00	129.00	n.q.	0.98	3.50	0.64
Prior	Italy	2013	97.00	1813.00	88.00	0.15	0.76	3.00	0.33
Prior	Germany	2013	82.00	1474.00	71.00	0.13	1.13	2.80	0.36
Nero	Italy	2013	62.00	1377.00	85.00	0.13	0.58	2.70	0.32
Nero	Germany	2013	58.00	1151.00	79.00	0.13	0.90	6.70	0.30
Johanniter	Italy	2013	62.00	446.00	75.00	n.q.	0.23	4.70	0.36
Johanniter	Germany	2013	71.00	427.00	63.00	0.07	0.52	10.60	0.39
Solaris	Germany	2013	110.00	480.00	93.00	n.q.	1.00	14.20	0.68
Phoenix	Italy	2013	62.00	883.00	87.00	0.11	0.24	4.10	0.20
Phoenix	Germany	2013	67.00	833.00	67.00	0.13	0.62	7.30	0.45
Bronner	Italy	2013	60.00	469.00	88.00	0.11	0.30	3.70	0.35
Bronner	Germany	2013	77.00	572.00	81.00	0.10	0.75	12.90	0.72
Helios	Italy	2013	66.00	392.00	114.00	n.q.	0.67	4.40	0.23
Bianca	Italy	2013	48.00	729.00	92.00	0.15	0.62	4.40	0.29
Muscaris	Italy	2013	88.00	675.00	99.00	0.13	0.39	4.00	0.67
Accent	Germany	2013	63.00	899.00	93.00	0.07	1.13	3.60	0.32
Rondo	Germany	2013	51.00	871.00	77.00	0.09	0.88	4.30	0.33
Pinot noir	Italy	2013	61.00	1609.00	74.00	0.12	0.36	5.80	0.12
Cabernet Sauvignon	Italy	2013	60.00	1518.00	103.00	0.07	1.10	6.83	0.54
Teroldego	Italy	2013	87.00	2463.00	84.00	0.10	1.11	7.20	0.30
Chardonnay	Italy	2013	86.00	508.00	62.00	0.10	0.83	6.57	0.15
Chardonnay	Germany	2013	85.00	710.00	71.00	0.27	1.13	8.37	0.52
Riesling	Italy	2013	75.00	515.00	76.00	0.12	0.58	6.79	0.15
Moscato Giallo	Italy	2013	68.00	959.00	69.00	0.16	1.70	8.45	0.75
Moscato Giallo	Germany	2013	89.00	640.00	58.00	0.12	0.69	10.20	0.53
Regent	Italy	2015	56.00	1008.00	96.00	0.23	1.20	4.40	0.40
Regent	Germany	2015	75.00	1058.00	70.00	0.11	1.01	5.00	0.26
Cabernet Cortis	Italy	2015	79.00	871.00	127.00	0.20	1.69	4.10	0.95
Cabernet Cortis	Germany	2015	86.00	1024.00	103.00	0.36	1.41	3.50	0.28
Cabernet Carbon	Italy	2015	68.00	1000.00	109.00	0.10	0.96	3.20	0.21
Prior	Italy	2015	62.00	1533.00	78.00	0.33	0.65	2.60	0.22
Nero	Italy	2015	64.00	1073.00	125.00	0.14	1.00	4.30	0.55
Souvignier Gris	Italy	2015	64.00	355.00	90.00	0.07	1.17	6.00	0.50
Johanniter	Italy	2015	92.00	487.00	67.00	n.q.	0.84	4.80	0.35
Johanniter	Germany	2015	78.00	486.00	73.00	0.13	0.73	7.90	0.62
Solaris	Italy	2015	48.00	331.00	117.00	0.07	0.56	14.42	0.56
Solaris	Germany	2015	68.00	375.00	96.00	0.10	0.24	8.74	0.24
Phoenix	Italy	2015	95.00	678.00	85.00	0.13	0.70	3.74	0.70
Phoenix	Germany	2015	81.00	513.00	76.00	0.12	0.21	5.68	0.21
Bronner	Italy	2015	65.00	345.00	100.00	0.07	0.41	3.56	0.41
Bronner	Germany	2015	90.00	373.00	91.00	n.q.	0.21	7.38	0.21
Muscaris	Italy	2015	65.00	543.00	83.00	n.q.	0.89	8.71	0.89
Muscaris	Germany	2015	118.00	439.00	67.00	0.07	1.03	4.24	1.03
Accent	Germany	2015	93.00	1080.00	83.00	0.13	2.79	2.32	2.79
Rondo	Germany	2015	63.00	1347.00	65.00	0.14	2.86	5.14	2.86
Bolero	Germany	2015	65.00	847.00	103.00	0.13	0.66	3.20	0.39
Helios	Italy	2015	64.00	376.00	123.00	0.08	0.74	3.80	0.47
Bianca	Italy	2015	95.00	696.00	101.00	n.q.	0.43	6.10	0.44
Jasmine	Italy	2015	71.00	589.00	80.00	n.q.	0.66	6.10	0.13
Pinot noir	Italy	2015	63.00	1745.00	77.00	0.08	1.26	8.90	0.42
Cabernet Sauvignon	Italy	2015	63.00	1618.00	102.00	0.17	0.74	5.90	0.33
Cabernet Sauvignon	Germany	2015	96.00	831.00	78.00	0.09	0.96	7.70	0.31
Chardonnay	Italy	2015	71.00	635.00	66.00	0.22	0.52	7.00	0.63
Chardonnay	Germany	2015	90.00	633.00	68.00	n.q.	0.39	8.30	0.52
Riesling	Italy	2015	81.00	519.00	63.00	0.22	0.30	8.20	0.46
Riesling	Germany	2015	100.00	517.00	65.00	0.19	0.33	6.90	0.45
Moscato Giallo	Italy	2015	75.00	799.00	67.00	0.43	0.59	8.00	0.63
Regent	Italy	2016	60.00	1498.00	90.00	0.20	0.40	1.50	0.30
Regent	Germany	2016	82.00	939.00	90.00	n.q.	0.40	6.90	0.30
Cabernet Cortis	Italy	2016	98.00	1431.00	126.00	n.q.	0.70	2.30	0.70
Cabernet Cortis	Germany	2016	106.00	1139.00	100.00	n.q.	0.60	2.40	0.30
Prior	Italy	2016	79.00	1796.00	84.00	0.20	0.50	1.40	0.20
Prior	Germany	2016	75.00	1878.00	65.00	0.10	0.50	2.40	0.30

Nero	Italy	2016	135.00	1421.00	118.00	n.q.	0.80	5.00	0.90
Souvignier Gris	Italy	2016	50.00	453.00	108.00	0.10	0.30	3.30	0.60
Johanniter	Italy	2016	61.00	473.00	81.00	n.q.	0.40	3.80	0.60
Johanniter	Germany	2016	81.00	510.00	81.00	0.11	0.40	7.30	0.60
Solaris	Italy	2016	42.00	335.00	103.00	0.11	0.20	3.40	1.00
Solaris	Germany	2016	57.00	449.00	97.00	0.24	0.40	7.80	0.70
Phoenix	Italy	2016	89.00	601.00	96.00	0.12	0.30	3.70	0.40
Phoenix	Germany	2016	69.00	660.00	77.00	n.q.	0.50	4.90	0.20
Bronner	Italy	2016	74.00	442.00	119.00	n.q.	0.20	2.40	0.50
Bronner	Germany	2016	86.00	470.00	91.00	n.q.	0.50	6.80	0.50
Muscaris	Italy	2016	78.00	488.00	121.00	n.q.	0.10	3.90	0.80
Muscaris	Germany	2016	85.00	451.00	89.00	n.q.	0.50	4.90	0.30
Accent	Germany	2016	71.00	1348.00	86.00	0.20	1.20	3.70	0.30
Rondo	Germany	2016	66.00	1606.00	79.00	0.20	0.80	3.50	0.40
Bolero	Germany	2016	77.00	1163.00	88.00	0.10	0.40	5.10	0.30
Helios	Italy	2016	47.00	384.00	127.00	n.q.	0.20	2.30	0.30
Bianca	Italy	2016	44.00	678.00	113.00	0.10	0.30	2.30	0.30
Jasmine	Italy	2016	66.00	584.00	73.00	n.q.	0.20	2.90	0.30
Pinot noir	Italy	2016	101.00	1228.00	92.00	n.q.	0.30	9.20	0.10
Cabernet Sauvignon	Germany	2016	120.00	891.00	73.00	0.10	0.40	7.40	0.30
Teroldego	Italy	2016	131.00	1258.00	85.00	0.10	1.10	6.00	0.10
Chardonnay	Italy	2016	71.00	810.00	88.00	0.20	0.30	9.40	0.50
Chardonnay	Germany	2016	89.00	719.00	74.00	0.10	0.20	10.50	0.60
Riesling	Italy	2016	85.00	515.00	81.00	0.10	0.20	6.60	0.40
Riesling	Germany	2016	88.00	534.00	78.00	n.q.	0.70	8.80	0.60
Moscato Giallo	Italy	2016	51.00	798.00	54.00	0.10	n.q.	3.40	0.30

Abbreviations: Ca, calcium; K, potassium; Mg, magnesium, Cu, copper; Fe, iron; Na, sodium; Zn, zinc; n.q., not quantifiable.

Table S8. Concentrations of low-molecular-weight (LMW) thiols detected in the wines studied. The results are expressed as mg/L.

Variety	Country	Vintage	Cys	CysT	HCys	Cys-Gly	γ-Glu-Cys	GSH	NAC
Regent	Germany	2013	0.29	0.01	0.10	0.11	0.04	0.21	0.03
Cabernet Cortis	Italy	2013	0.48	n.d.	0.34	0.08	0.19	1.56	0.03
Cabernet Cortis	Germany	2013	0.26	n.d.	0.09	0.11	0.06	0.31	0.01
Cabernet Carbon	Italy	2013	0.20	n.d.	0.08	0.03	0.09	0.25	0.01
Prior	Italy	2013	0.24	n.d.	0.13	0.11	0.09	0.31	0.02
Prior	Germany	2013	0.21	n.d.	0.10	0.11	0.03	0.23	0.02
Nero	Italy	2013	0.34	0.01	0.30	0.13	0.06	0.14	0.04
Nero	Germany	2013	0.26	n.d.	0.07	0.07	0.05	0.25	0.02
Johanniter	Italy	2013	0.25	0.01	0.04	0.19	0.04	0.24	0.04
Johanniter	Germany	2013	0.34	0.01	0.09	0.13	0.07	0.77	0.02
Solaris	Germany	2013	0.65	0.01	0.68	0.29	0.11	1.74	0.03
Phoenix	Italy	2013	0.30	n.d.	0.10	0.29	0.07	0.10	0.12
Phoenix	Germany	2013	0.24	n.d.	0.07	0.03	0.10	0.57	0.01
Bronner	Italy	2013	0.34	n.d.	0.10	0.06	0.10	0.29	0.03
Bronner	Germany	2013	0.73	n.d.	0.10	0.17	0.27	1.36	0.02
Helios	Italy	2013	0.46	n.d.	0.09	0.06	0.18	0.97	0.02
Bianca	Italy	2013	0.36	n.d.	0.16	0.03	0.07	0.12	0.02
Muscaris	Italy	2013	0.92	n.d.	0.09	0.43	0.24	2.81	0.04
Accent	Germany	2013	0.13	n.d.	0.08	0.08	0.02	0.31	0.01
Rondo	Germany	2013	0.16	n.d.	0.06	0.06	0.07	0.17	0.10
Pinot noir	Italy	2013	0.28	0.01	0.28	0.14	0.08	0.09	0.01
Cabernet Sauvignon	Italy	2013	0.15	n.d.	0.08	0.03	0.08	0.54	0.01
Teroldego	Italy	2013	0.26	0.01	0.25	0.21	0.02	0.33	0.02
Chardonnay	Italy	2013	0.13	0.01	0.03	0.03	0.08	0.24	n.d.
Chardonnay	Germany	2013	0.42	0.01	0.17	0.31	0.06	1.48	0.02
Riesling	Italy	2013	0.64	0.01	0.23	0.26	0.15	0.91	0.04
Moscato Giallo	Italy	2013	0.60	0.01	0.17	1.19	0.19	0.67	0.05
Moscato Giallo	Germany	2013	0.36	0.01	0.14	0.32	0.12	1.14	0.01
Regent	Italy	2015	0.11	n.q.	0.04	0.01	0.07	0.19	0.12
Regent	Germany	2015	0.15	n.q.	0.06	0.05	0.08	0.47	0.12
Cabernet Cortis	Italy	2015	0.34	n.q.	0.17	0.04	0.20	1.39	0.03
Cabernet Cortis	Germany	2015	0.25	n.q.	0.09	0.03	0.12	0.96	0.02
Cabernet Carbon	Italy	2015	0.17	n.q.	0.10	0.01	0.08	0.47	0.01
Prior	Italy	2015	0.17	n.q.	0.07	0.02	0.10	0.42	0.02
Nero	Italy	2015	0.17	n.q.	0.11	0.03	0.14	0.81	0.03
Souvignier Gris	Italy	2015	0.22	n.d.	0.10	0.02	0.11	0.41	0.01
Johanniter	Italy	2015	0.59	0.01	0.28	0.13	0.14	0.97	0.02
Johanniter	Germany	2015	0.80	0.01	0.21	0.30	0.18	2.29	0.02
Solaris	Italy	2015	1.11	0.01	0.69	0.19	0.52	2.42	0.02
Solaris	Germany	2015	0.70	0.01	0.24	0.15	0.26	2.21	0.03
Phoenix	Italy	2015	0.38	0.01	0.29	0.12	0.11	0.81	0.02
Phoenix	Germany	2015	0.27	n.d.	0.05	0.05	0.09	0.48	0.01
Bronner	Italy	2015	0.25	n.d.	0.06	0.03	0.12	0.39	0.03
Bronner	Germany	2015	0.38	0.01	0.03	0.06	0.14	0.72	0.02
Muscaris	Italy	2015	0.47	0.01	0.16	0.11	0.20	1.23	0.02
Muscaris	Germany	2015	0.49	0.01	0.06	0.12	0.11	0.84	0.02
Accent	Germany	2015	0.24	0.01	0.18	0.09	0.32	1.21	0.03
Rondo	Germany	2015	0.23	0.01	0.23	0.06	0.50	0.85	0.03
Bolero	Germany	2015	0.22	0.01	0.08	0.04	0.06	0.35	0.02
Helios	Italy	2015	0.41	0.01	0.13	0.13	0.22	1.43	0.02
Bianca	Italy	2015	1.23	0.02	0.79	0.30	0.37	2.06	0.06
Jasmine	Italy	2015	0.27	0.01	0.19	0.03	0.16	0.30	0.03
Pinot noir	Italy	2015	0.47	0.01	0.26	0.36	0.26	0.32	0.05
Cabernet Sauvignon	Italy	2015	0.34	0.01	0.13	0.04	0.14	0.40	0.01
Cabernet Sauvignon	Germany	2015	0.59	0.01	0.13	0.07	0.12	1.05	0.02
Chardonnay	Italy	2015	0.81	0.01	0.20	0.58	0.10	1.83	0.03
Chardonnay	Germany	2015	0.91	0.01	0.25	0.40	0.11	2.27	0.04
Riesling	Italy	2015	0.47	0.01	0.08	0.41	0.13	1.40	0.02
Riesling	Germany	2015	0.63	0.01	0.15	0.22	0.13	2.20	0.03
Moscato Giallo	Italy	2015	0.56	0.01	0.19	0.28	0.16	2.19	0.02
Regent	Italy	2016	0.32	n.d.	0.04	0.05	0.11	0.70	0.29
Regent	Germany	2016	0.52	n.d.	n.d.	n.d.	n.d.	0.44	0.14
Cabernet Cortis	Italy	2016	0.48	n.d.	0.06	0.03	0.16	1.24	0.18
Cabernet Cortis	Germany	2016	0.58	n.d.	0.03	0.03	0.11	0.74	0.08
Prior	Italy	2016	0.48	n.d.	0.09	0.04	0.19	1.04	0.33

Prior	Germany	2016	0.44	n.d.	0.10	0.07	0.25	1.71	0.13
Nero	Italy	2016	0.18	n.d.	0.06	0.02	0.06	0.66	0.09
Souvignier Gris	Italy	2016	0.42	0.01	0.08	0.09	0.31	2.31	0.69
Johanniter	Italy	2016	0.67	0.01	0.23	0.22	0.18	2.69	0.36
Johanniter	Germany	2016	0.74	0.01	0.38	0.28	0.25	3.01	0.27
Solaris	Italy	2016	1.27	0.01	1.34	0.32	0.53	5.03	0.40
Solaris	Germany	2016	0.48	n.d.	0.85	0.09	0.23	3.35	0.42
Phoenix	Italy	2016	0.32	0.01	0.07	0.10	0.10	1.57	0.47
Phoenix	Germany	2016	0.20	0.01	0.08	0.07	0.13	0.99	0.41
Bronner	Italy	2016	0.59	0.01	0.38	0.22	0.16	2.77	0.44
Bronner	Germany	2016	0.50	0.01	0.23	0.19	0.17	2.07	0.58
Muscaris	Italy	2016	0.72	0.02	0.17	0.19	0.03	2.52	0.52
Muscaris	Germany	2016	0.65	0.01	0.40	0.29	0.24	2.81	0.40
Accent	Germany	2016	0.81	n.d.	n.d.	n.d.	n.d.	0.25	n.d.
Rondo	Germany	2016	0.66	n.d.	n.d.	n.d.	n.d.	0.37	n.d.
Bolero	Germany	2016	0.17	n.d.	n.d.	0.01	0.11	0.26	0.08
Helios	Italy	2016	0.71	0.01	0.20	0.18	0.20	2.37	0.32
Bianca	Italy	2016	0.71	0.01	0.08	0.22	0.15	2.64	0.52
Jasmine	Italy	2016	0.46	0.01	0.26	0.13	0.10	2.00	0.69
Pinot noir	Italy	2016	0.34	n.d.	0.11	0.11	0.07	0.72	0.18
Cabernet Sauvignon	Germany	2016	0.20	n.d.	0.04	0.02	0.05	0.24	0.06
Teroldego	Italy	2016	0.38	n.d.	0.05	0.03	0.07	0.77	0.12
Chardonnay	Italy	2016	1.69	0.01	0.37	0.85	0.49	3.81	0.22
Chardonnay	Germany	2016	1.22	0.01	0.60	0.45	0.36	3.58	0.49
Riesling	Italy	2016	1.22	0.01	0.61	0.24	0.41	3.60	0.42
Riesling	Germany	2016	0.51	0.01	0.11	0.18	0.16	1.87	0.60
Moscato Giallo	Italy	2016	1.41	0.01	0.35	0.32	0.70	3.50	0.23

Abbreviations: Cys, cysteine; CysT, thiocysteine; HCys, homocysteine; γ-Glu-Cys , γ-glutamylcysteine; GSH, gluthathione; NAC, N-acetylcysteine; n.d., not detected.

Table S9. Concentrations of fermentation derived aroma compounds in the wines studied.

Variety	Country	Vintage	3-methyl butanol + 2-methyl butanol (mg/L)	hexan-1-ol (µg/L)	ethyl acetate (mg/L)	3-methylbutyl acetate + 2-methylbutyl acetate (µg/L)	hexyl acetate (µg/L)	ethyl isobutanoate (µg/L)	ethyl butanoate (µg/L)	ethyl lactate (mg/L)	iso-valerate (µg/L)	ethyl hexanoate (µg/L)	diethyl succinate(µg/L)	ethyl octanoate(µg/L)	ethyl decanoate (µg/L)	*trans*-linalool oxide (µg/L)	*cis*-linalool oxide (µg/L)	linalool (µg/L)	α-terpineol (µg/L)	2-phenylethanol (mg/L)	phenylethyl acetate (µg/L)	octanoic acid (mg/L)	decanoic acid (mg/L)	hexanoic acid (mg/L)
Regent	Germany	2013	150.95	1658.88	19.06	3.83	n.d.	122.83	103.22	205.93	1794.70	203.68	4606.00	127.79	18.24	12.11	7.09	2.91	12.74	17.37	8.54	1.69	0.16	5.40
Cabernet Cortis	Italy	2013	212.45	1751.00	46.63	16.92	n.d.	141.76	178.76	154.80	1913.18	327.25	8367.24	200.43	22.19	8.98	4.47	2.55	14.09	33.91	19.86	1.74	0.18	5.83
Cabernet Cortis	Germany	2013	230.63	2317.85	32.84	11.06	2.73	183.05	127.50	234.97	2202.29	224.92	7173.20	109.69	22.53	10.32	4.91	4.11	18.58	38.01	18.11	1.35	0.15	5.42
Cabernet Carbon	Italy	2013	265.46	1645.36	39.33	20.08	n.d.	126.99	92.31	147.71	1918.23	165.08	9108.79	55.05	17.95	14.93	7.74	21.68	38.19	47.85	20.61	0.92	n.d.	4.94
Prior	Italy	2013	163.83	1990.38	47.05	8.80	n.d.	86.79	75.25	160.02	1635.40	178.44	5753.16	49.41	8.74	22.12	14.04	24.45	37.34	18.41	7.06	0.96	n.d.	4.81
Prior	Germany	2013	130.84	2238.84	45.68	4.40	n.d.	92.38	97.72	244.78	1557.61	222.87	5325.25	102.92	9.44	13.97	6.27	4.34	14.48	12.07	4.77	1.13	0.12	4.95
Nero	Italy	2013	138.31	2176.57	26.24	5.53	n.d.	82.49	91.74	134.86	1621.42	158.26	4323.93	80.39	21.42	27.27	26.41	38.69	54.43	16.58	5.80	1.20	0.12	4.93
Nero	Germany	2013	219.42	1968.51	19.68	12.15	0.39	152.62	137.39	218.55	2133.72	279.21	6994.03	171.57	43.80	27.77	25.61	51.10	105.45	32.93	18.49	1.41	0.14	5.45
Johanniter	Italy	2013	134.72	292.83	n.d.	n.d.	16.87	98.41	158.52	3.12	1504.22	463.25	8090.38	577.28	62.88	18.34	8.85	n.d.	14.40	27.21	12.48	2.74	0.19	5.89
Johanniter	Germany	2013	121.25	568.06	n.d.	n.d.	74.54	127.28	148.89	9.68	1470.16	382.53	8650.69	494.36	84.86	20.06	9.45	n.d.	4.04	14.15	n.d.	2.63	0.28	5.60
Solaris	Germany	2013	160.06	997.94	5.25	n.d.	36.90	152.91	214.58	25.59	1585.20	462.06	11128.32	548.72	90.20	75.20	29.93	n.d.	7.67	21.92	n.d.	2.59	0.31	6.00
Phoenix	Italy	2013	189.35	1045.50	n.d.	61.73	62.80	98.02	116.51	3.38	1819.16	257.12	3688.04	365.98	60.12	22.06	10.60	22.68	48.30	27.83	39.13	2.51	0.22	5.46
Phoenix	Germany	2013	139.41	1574.00	n.d.	n.d.	10.96	107.92	95.10	11.99	1458.56	260.86	5965.28	322.86	47.44	103.46	39.88	n.d.	7.48	13.05	n.d.	2.19	0.18	5.11
Bronner	Italy	2013	192.43	692.39	n.d.	n.d.	30.02	167.12	147.13	5.52	1663.12	324.89	6932.11	474.90	86.78	61.35	29.22	n.d.	5.20	33.71	12.21	2.62	0.26	5.45
Bronner	Germany	2013	108.87	897.56	n.d.	n.d.	2.97	97.27	182.24	10.32	1458.07	526.69	8548.32	657.12	108.77	132.20	60.23	n.d.	3.99	6.74	n.d.	3.06	0.33	6.13
Helios	Italy	2013	141.63	727.02	n.d.	n.d.	76.75	132.37	168.65	2.39	1564.72	520.70	10320.02	686.78	103.51	11.43	5.58	n.d.	4.13	34.41	3.05	2.99	0.35	6.30
Bianca	Italy	2013	181.34	956.07	10.61	5.34	n.d.	141.86	194.99	6.83	1823.18	397.28	5252.15	594.05	93.36	4.44	2.32	2.46	8.54	28.42	17.62	2.93	0.27	5.82
Muscaris	Italy	2013	150.84	495.48	16.84	2.07	17.03	96.82	255.34	20.83	1550.81	646.60	7239.59	691.45	179.67	141.34	76.21	30.40	122.90	11.90	15.54	3.01	0.43	6.85
Accent	Germany	2013	186.95	1893.85	48.68	7.76	n.d.	136.17	92.08	198.26	1726.32	164.55	7800.44	65.83	9.32	8.62	8.44	4.21	13.83	28.23	9.82	1.15	n.d.	4.94
Rondo	Germany	2013	113.05	2245.23	25.26	5.65	n.d.	129.59	100.60	189.97	1610.00	240.09	7374.93	132.80	19.96	8.78	7.65	3.10	15.41	17.45	6.46	1.26	0.14	5.02
Pinot noir	Italy	2013	162.22	1002.82	10.92	16.53	n.d.	93.86	121.14	97.92	1877.87	188.17	4342.91	131.90	17.63	3.16	2.37	6.01	8.64	30.82	19.12	1.22	0.13	4.94
Cabernet Sauvignon	Italy	2013	267.04	793.98	13.09	9.86	23.28	81.71	122.07	134.62	1625.97	247.67	8308.66	188.22	14.67	2.21	n.d.	5.60	11.32	52.97	19.75	1.14	0.12	5.00
Teroldego	Italy	2013	154.66	1821.29	51.87	61.66	61.09	45.87	98.57	140.51	1591.17	210.65	4131.19	119.66	22.38	2.79	2.29	11.81	9.40	12.74	11.47	1.13	0.13	4.96
Chardonnay	Italy	2013	182.05	861.47	3.47	n.d.	9.02	110.32	119.18	2.93	1599.77	330.16	12190.32	378.06	81.74	5.35	3.42	n.d.	4.54	45.42	8.04	2.30	0.28	5.64
Chardonnay	Germany	2013	129.45	1092.39	7.69	n.d.	88.24	95.27	154.82	7.88	1483.45	430.73	5340.67	594.74	97.26	173.04	77.58	2.08	88.06	9.42	3.52	2.84	0.25	5.94
Riesling	Italy	2013	126.39	1341.52	n.d.	n.d.	n.d.	86.33	173.56	10.63	1497.55	515.08	7555.66	550.66	109.33	92.69	40.91	n.d.	31.32	7.50	1.24	2.98	0.37	6.33
Moscato Giallo	Italy	2013	136.99	722.43	46.49	417.67	n.d.	116.40	157.87	11.37	1614.35	433.70	3728.20	599.48	88.97	252.68	115.30	131.06	346.78	11.58	43.42	2.84	0.25	5.93
Moscato Giallo	Germany	2013	94.26	717.80	n.d.	n.d.	11.13	84.57	114.25	5.20	1446.26	378.95	4311.85	480.34	79.16	129.44	54.61	n.d.	6.74	7.81	n.d.	3.12	0.32	5.76
Regent	Italy	2015	218.30	1094.20	35.61	246.23	180.34	62.10	102.28	105.18	2157.01	176.06	486.72	143.22	53.51	2.58	3.10	15.04	8.07	40.12	59.50	1.49	0.24	5.05
Regent	Germany	2015	199.81	1522.03	13.26	150.34	218.15	62.22	110.60	134.75	1900.63	192.83	485.57	154.41	43.60	1.99	2.55	5.43	6.13	29.55	28.62	1.85	0.23	5.19
Cabernet Cortis	Italy	2015	248.06	1175.66	43.57	915.94	76.74	80.42	135.70	103.77	2139.02	245.81	1928.13	217.64	51.18	4.04	4.26	18.71	14.82	54.23	135.63	1.60	0.19	5.31
Cabernet Cortis	Germany	2015	235.75	1365.33	22.52	688.17	113.32	52.98	136.77	112.31	1989.09	304.26	1091.81	270.23	52.55	3.13	2.19	7.25	7.52	48.90	88.39	1.99	0.24	5.69
Cabernet Carbon	Italy	2015	288.90	826.58	21.53	299.97	82.03	54.94	94.35	69.45	2411.20	193.51	961.39	156.94	42.06	3.61	2.54	22.67	11.38	63.77	81.28	1.51	0.20	5.24
Prior	Italy	2015	208.11	1223.51	4.39	159.12	n.d.	30.90	91.48	66.23	2105.47	198.80	926.56	168.92	51.61	2.40	1.68	5.50	4.61	43.57	34.88	1.62	0.22	5.18
Nero	Italy	2015	265.35	1134.79	29.35	403.51	n.d.	67.13	87.80	83.10	2589.58	184.81	805.42	184.77	63.14	4.43	5.44	24.17	14.65	51.12	83.23	1.49	0.22	5.00
Souvignier Gris	Italy	2015	203.82	1727.47	56.79	22.56	n.d.	120.61	64.25	3.05	1951.83	169.74	1914.57	140.28	74.83	9.73	4.34	6.31	7.61	41.50	48.38	1.74	0.27	5.02
Johanniter	Italy	2015	176.85	387.64	22.36	1430.74	n.d.	58.33	206.68	6.45	1547.71	443.68	864.40	571.41	232.31	3.13	2.83	12.69	9.10	30.39	174.95	3.68	0.83	5.92
Johanniter	Germany	2015	142.31	698.35	20.17	1856.41	n.d.	54.35	199.61	8.37	1532.71	431.96	581.94	589.05	146.70	9.75	6.41	53.26	28.35	24.28	224.30	4.13	0.59	6.34
Solaris	Italy	2015	206.59	628.25	66.78	3084.28	n.d.	114.59	271.08	7.99	1866.30	677.34	570.54	844.02	321.77	10.11	33.00	94.62	45.12	44.54	775.24	4.65	1.07	6.87
Solaris	Germany	2015	189.49	767.06	44.76	1603.30	n.d.	99.97	217.08	9.93	1757.81	539.39	1405.17	635.94	257.98	6.87	2.92	15.46	12.29	39.80	332.24	3.87	0.85	6.42
Phoenix	Italy	2015	194.05	1179.11	32.17	306.19	n.d.	49.33	134.79	9.91	1463.23	243.28	832.57	247.03	128.35	12.32	6.71	133.00	74.28	27.96	101.30	2.49	0.58	5.21

Phoenix	Germany	2015	204.85	1815.61	13.06	360.99	n.d.	93.65	76.24	2.46	1842.72	242.21	378.80	275.86	168.98	11.64	6.15	31.24	21.84	41.23	122.38	2.83	0.81	5.18
Bronner	Italy	2015	250.78	644.82	41.56	283.56	n.d.	110.98	87.90	1.99	1881.41	270.74	1262.41	508.32	253.22	12.98	6.68	4.45	5.30	66.45	198.65	2.96	0.82	5.21
Bronner	Germany	2015	226.89	1099.63	8.49	1519.46	n.d.	98.17	145.45	2.20	1958.71	436.39	806.09	566.20	272.18	25.24	13.58	4.92	6.00	53.79	334.49	5.02	1.05	6.45
Muscaris	Italy	2015	227.37	434.27	23.32	736.21	n.d.	47.72	158.67	7.71	1773.49	364.27	1372.36	417.53	215.53	22.83	34.47	188.97	75.11	49.42	128.75	3.16	1.07	5.70
Muscaris	Germany	2015	256.49	984.18	8.67	727.40	n.d.	86.18	124.76	12.42	1754.34	298.33	1402.29	343.74	161.75	42.43	29.67	97.89	79.53	44.40	119.69	3.45	0.97	5.77
Accent	Germany	2015	150.60	1190.52	16.01	8.00	n.d.	46.41	90.35	126.14	1679.06	162.87	973.78	116.59	25.88	2.47	5.48	4.33	5.57	19.87	8.78	1.75	0.22	5.16
Rondo	Germany	2015	136.68	1837.79	11.53	33.03	n.d.	29.42	84.07	99.90	1738.28	178.22	710.92	126.75	28.01	2.04	3.22	4.20	5.68	19.33	14.99	1.90	0.28	5.24
Bolero	Germany	2015	203.02	825.74	24.85	64.65	n.d.	79.74	88.93	72.31	1900.36	168.32	1271.73	106.60	27.72	n.d.	n.d.	7.97	6.48	38.69	56.25	1.37	0.19	4.80
Helios	Italy	2015	196.51	891.59	4.59	733.73	n.d.	111.90	194.29	4.28	1547.25	504.76	1511.64	638.25	223.09	3.35	n.d.	6.04	6.86	37.02	127.41	3.92	0.78	6.19
Bianca	Italy	2015	227.87	1202.31	42.15	1553.30	n.d.	65.51	233.39	14.66	1640.22	428.23	1441.55	488.31	158.88	n.d.	n.d.	14.98	9.35	36.69	231.60	3.02	0.49	5.99
Jasmine	Italy	2015	244.43	866.39	4.62	723.23	n.d.	79.29	136.57	4.62	1928.76	250.61	718.50	240.17	90.23	103.86	393.72	921.59	436.31	46.91	158.64	1.87	0.27	5.02
Pinot noir	Italy	2015	199.78	1437.37	30.01	10.98	n.d.	27.97	89.64	54.78	1914.49	169.76	2406.14	130.82	27.52	n.d.	n.d.	1.84	4.45	36.64	20.94	1.36	0.18	5.03
Cabernet Sauvignon	Italy	2015	277.14	983.16	30.40	263.21	n.d.	40.08	101.24	80.01	2184.17	184.16	479.59	146.80	37.40	5.39	3.78	46.48	13.86	60.84	71.62	1.43	0.17	4.96
Cabernet Sauvignon	Germany	2015	175.28	2975.56	65.44	378.34	n.d.	58.09	121.30	135.66	1511.23	246.98	1079.72	175.34	41.27	n.d.	n.d.	4.16	6.09	31.05	53.08	1.67	0.16	5.32
Chardonnay	Italy	2015	179.24	809.25	45.95	3317.04	n.d.	26.30	231.47	1.21	1563.66	437.61	42.38	596.37	63.92	8.03	2.96	16.97	8.40	34.18	537.37	4.01	0.25	6.58
Chardonnay	Germany	2015	117.80	1519.13	63.00	2272.14	n.d.	32.84	232.13	3.30	1463.00	490.38	601.20	622.21	235.07	9.45	5.85	37.45	17.16	15.98	273.45	4.01	0.72	6.42
Riesling	Italy	2015	142.41	663.57	9.63	1344.11	n.d.	47.07	171.67	5.80	1548.09	414.33	517.56	590.30	214.69	6.02	3.14	17.84	17.00	32.27	280.57	4.23	0.73	5.98
Riesling	Germany	2015	145.14	1208.25	23.55	1469.73	11.31	39.21	182.34	8.03	1544.07	406.74	636.46	554.08	118.39	12.14	4.78	19.14	18.58	22.34	241.97	4.18	0.61	6.46
Moscato Giallo	Italy	2015	139.44	732.34	29.57	2149.64	n.d.	30.71	233.11	1.69	1590.85	510.54	226.58	636.78	161.44	94.20	42.29	615.95	172.18	22.45	223.98	4.26	0.69	6.92
Regent	Italy	2016	432.71	1865.39	66.28	194.38	n.d.	67.46	231.06	120.95	2008.11	453.36	1803.44	442.26	72.59	n.q.	n.q.	5.76	n.q.	58.17	12.12	n.q.	n.q.	5.48
Regent	Germany	2016	487.45	2831.87	98.80	1654.82	n.d.	95.83	340.37	157.00	2105.45	716.37	1730.24	649.12	162.40	n.q.	n.q.	9.42	n.q.	60.14	120.32	n.q.	n.q.	6.41
Cabernet Cortis	Italy	2016	524.26	3174.85	108.17	2221.24	n.d.	69.56	290.05	148.21	1959.35	608.74	2967.56	536.06	78.07	n.q.	n.q.	8.20	n.q.	77.87	100.47	n.q.	n.q.	6.12
Cabernet Cortis	Germany	2016	517.43	3513.75	92.50	2182.56	n.d.	87.48	300.45	145.72	2068.00	695.89	1922.36	555.97	93.27	n.q.	n.q.	8.74	n.q.	70.65	140.51	n.q.	n.q.	6.37
Prior	Italy	2016	337.24	2752.00	70.42	454.19	n.d.	54.47	197.59	126.75	2824.23	469.31	2087.12	363.72	50.33	n.q.	n.q.	5.16	n.q.	48.04	19.26	n.q.	n.q.	6.02
Prior	Germany	2016	327.75	3684.24	134.99	350.15	n.d.	73.01	196.32	160.00	1739.23	498.75	1820.88	326.57	61.17	n.q.	n.q.	7.41	n.q.	29.63	n.q.	n.q.	n.q.	5.86
Nero	Italy	2016	285.22	2502.84	220.86	164.73	n.d.	103.72	88.88	n.q.	n.q.	168.18	2001.13	n.q.	n.q.	n.q.	n.q.	130.38	48.47	39.28	20.56	n.q.	n.q.	4.19
Souvignier Gris	Italy	2016	452.41	1270.91	164.14	3927.65	132.04	199.24	404.28	n.q.	1665.38	1046.37	2579.01	1324.12	412.73	n.q.	n.q.	2.65	n.q.	72.09	598.47	6.81	2.57	8.71
Johanniter	Italy	2016	276.02	259.62	94.04	5581.38	69.56	97.15	516.75	n.q.	1665.88	1089.35	281.25	1461.13	527.19	n.q.	n.q.	4.98	n.q.	31.52	421.68	8.03	3.02	8.01
Johanniter	Germany	2016	282.57	925.42	106.98	4915.84	246.18	90.75	547.87	n.q.	1445.91	1230.82	611.99	1337.32	452.63	n.q.	n.q.	10.53	n.q.	28.19	310.13	8.74	2.81	8.30
Solaris	Italy	2016	376.64	1065.07	193.93	7053.04	182.13	142.65	611.78	n.q.	1675.63	934.71	1008.56	1271.66	343.70	n.q.	n.q.	99.27	30.23	45.17	685.98	6.89	2.16	7.59
Solaris	Germany	2016	481.45	1056.10	195.22	6025.81	196.50	122.11	617.45	34.95	1891.02	1182.15	1548.56	1619.24	757.80	n.q.	n.q.	40.20	20.96	71.44	666.49	7.06	3.63	7.98
Phoenix	Italy	2016	373.83	1649.72	23.93	3780.90	87.88	89.83	377.43	n.q.	1859.74	950.88	n.q.	1208.14	372.44	n.q.	n.q.	36.37	14.33	59.17	573.42	7.27	2.64	7.48
Phoenix	Germany	2016	534.56	2801.53	12.38	1336.72	58.97	183.14	173.84	n.q.	2150.15	552.59	n.q.	569.64	257.84	19.06	n.q.	161.50	83.32	62.95	114.78	4.83	2.12	6.05
Bronner	Italy	2016	347.55	696.14	126.13	6879.08	110.05	97.41	594.13	n.q.	1729.08	1205.95	727.35	1507.84	481.66	13.28	n.q.	n.q.	n.q.	49.14	680.09	9.19	3.43	8.71
Bronner	Germany	2016	365.01	1561.96	13.51	2566.25	107.99	136.27	411.46	n.q.	1525.39	982.35	1790.76	809.72	311.04	19.89	n.q.	n.q.	n.q.	51.92	210.84	7.27	2.57	7.70
Muscaris	Italy	2016	395.97	522.95	103.59	4299.05	103.01	157.92	542.41	n.q.	1935.79	1295.31	1768.40	1573.41	477.66	28.77	25.66	219.14	107.65	59.75	402.27	8.56	2.87	8.84
Muscaris	Germany	2016	380.56	1232.87	79.15	3583.45	99.45	124.40	551.29	n.q.	1543.32	1172.59	1837.82	1088.74	472.79	27.67	23.13	138.26	86.70	50.03	253.98	7.70	3.11	8.11
Accent	Germany	2016	457.11	3371.32	167.48	323.51	n.d.	101.26	266.35	246.75	5711.89	531.14	2048.76	446.22	108.38	n.q.	n.q.	n.q.	n.q.	56.50	12.42	3.53	n.q.	6.06
Rondo	Germany	2016	373.64	4157.27	256.91	1160.91	n.d.	94.42	304.87	178.49	1951.85	556.63	1781.46	403.75	78.91	n.q.	n.q.	n.q.	n.q.	34.93	22.67	3.03	n.q.	5.99
Bolero	Germany	2016	353.53	2563.53	62.79	1231.82	17.73	70.46	230.47	128.56	n.q.	445.83	1921.84	401.46	69.03	n.q.	n.q.	n.q.	n.q.	45.18	86.99	2.61	n.q.	5.61
Helios	Italy	2016	286.19	876.40	97.05	5883.93	216.67	134.73	542.70	n.q.	n.q.	1413.66	1739.73	1544.24	563.49	n.q.	n.q.	15.48	n.q.	47.15	675.49	8.21	3.18	9.55
Bianca	Italy	2016	376.68	999.42	119.40	6067.17	105.60	77.73	547.60	n.q.	n.q.	1222.54	2119.57	1484.22	458.06	n.q.	n.q.	n.q.	n.q.	58.47	549.01	6.95	2.64	8.91
Jasmine	Italy	2016	453.79	1571.34	81.20	6183.21	246.08	148.06	500.59	n.q.	n.q.	931.15	2541.80	1033.11	373.41	92.10	119.61	694.01	323.53	68.23	790.31	5.84	2.26	7.33
Pinot noir	Italy	2016	485.75	3791.17	145.95	439.64	n.d.	69.07	271.66	n.q.	2681.66	633.70	728.40	472.75	88.30	n.q.	n.q.	n.q.	n.q.	77.09	31.66	2.03	n.q.	6.11
Cabernet Sauvignon	Germany	2016	366.20	3509.95	74.23	717.87	14.72	184.00	215.19	32.90	3579.48	546.83	1957.40	420.34	71.09	n.q.	n.q.	n.q.	n.q.	53.64	46.77	3.03	n.q.	6.31
Teroldego	Italy	2016	413.62	2918.76	126.32	1380.49	n.d.	87.58	321.13	n.q.	n.q.	681.36	1961.85	624.94	116.15	n.q.	n.q.	n.q.	n.q.	62.03	50.50	4.74	0.70	6.53
Chardonnay	Italy	2016	331.85	730.13	167.56	5973.08	305.43	45.88	540.85	n.q.	1761.90	1189.84	n.q.	1197.47	493.15	n.q.	n.q.	68.56	24.32	26.30	480.19	8.17	3.49	8.35
Chardonnay	Germany	2016	271.96	1423.42	120.91	6816.63	520.39	101.58	772.57	n.q.	1518.85	1438.12	n.q.	1411.30	490.02	n.q.	n.q.	25.06	n.q.	34.45	518.10	8.07	2.70	9.00
Riesling	Italy	2016	305.04	1090.68	121.64	3701.01	140.46	95.90	554.80	32.19	1600.71	1218.66	1410.78	1276.97	445.26	n.q.	n.q.	62.02	41.26	38.27	456.29	5.99	2.29	8.13
Riesling	Germany	2016	401.81	1655.28	40.19	3552.79	90.53	110.61	422.59	n.q.	1676.29	964.33	1082.43	1269.93	544.54	n.q.	n.q.	25.42	24.13	48.18	295.68	8.33	3.48	8.23
Moscato Giallo	Italy	2016	178.84	1040.32	59.11	3110.25	294.55	50,00.	497.94	n.q.	n.q.	1236.58	1380.41	1359.74	382.46	171.46	98.86	788.45	368.49	15.55	253.15	7.60	2.39	9.10

Abbreviations: n.q., not quantifiable; n.d., not detected.

Table S10. Quantitative results of low volatile sulfur compounds expressed as μg/L in the wines studied.

Variety	Country	Vintage	H_2S	MeSH	DMS	CS_2	MeSAc
Regent	Germany	2013	5.40	n.d.	14.50	3.70	n.d.
Cabernet Cortis	Italy	2013	9.50	n.d.	79.60	13.40	8.70
Cabernet Cortis	Germany	2013	n.d.	n.d.	49.20	3.60	n.d.
Cabernet Carbon	Italy	2013	5.30	n.d.	23.00	n.d.	8.80
Prior	Italy	2013	n.d.	n.d.	8.30	n.d.	n.d.
Prior	Germany	2013	4.10	n.d.	11.60	2.70	n.d.
Nero	Italy	2013	4.80	n.d.	16.10	4.50	n.d.
Nero	Germany	2013	6.90	n.d.	15.20	4.50	n.d.
Johanniter	Italy	2013	n.d.	n.d.	5.20	4.00	17.10
Johanniter	Germany	2013	n.d.	n.d.	7.00	2.50	8.50
Solaris	Germany	2013	5.30	n.d.	10.30	3.90	n.d.
Phoenix	Italy	2013	n.d.	n.d.	9.50	1.10	11.90
Phoenix	Germany	2013	n.d.	n.d.	3.50	2.10	20.30
Bronner	Italy	2013	n.d.	n.d.	5.90	4.20	7.30
Bronner	Germany	2013	4.00	n.d.	8.00	9.30	n.d.
Helios	Italy	2013	n.d.	n.d.	5.90	1.40	12.30
Bianca	Italy	2013	n.d.	n.d.	6.90	n.d.	13.50
Muscaris	Italy	2013	4.90	n.d.	5.50	3.70	12.90
Accent	Germany	2013	n.d.	n.d.	16.00	1.30	n.d.
Rondo	Germany	2013	n.d.	n.d.	12.70	1.70	22.60
Pinot noir	Italy	2013	8.00	n.d.	12.10	1.20	n.d.
Cabernet Sauvignon	Italy	2013	7.20	n.d.	56.40	4.60	11.10
Teroldego	Italy	2013	n.d.	n.d.	48.90	5.00	19.00
Chardonnay	Italy	2013	n.d.	n.d.	2.90	1.40	9.7
Chardonnay	Germany	2013	3.70	n.d.	10.40	3.80	n.d.
Riesling	Italy	2013	4.50	n.d.	3.60	1.00	n.d.
Moscato Giallo	Italy	2013	4.70	n.d.	13.80	2.80	n.d.
Moscato Giallo	Germany	2013	n.d.	n.d.	n.d.	1.20	8.6
Regent	Italy	2015	20.40	n.d.	3.00	21.00	n.d.
Regent	Germany	2015	7.60	n.d.	2.70	11.20	n.d.
Cabernet Cortis	Italy	2015	13.30	n.d.	12.60	23.30	7.3
Cabernet Cortis	Germany	2015	34.80	n.d.	5.40	7.20	n.d.
Cabernet Carbon	Italy	2015	n.d.	n.d.	2.50	7.40	n.d.
Prior	Italy	2015	20.90	n.d.	0.80	13.40	n.d.
Nero	Italy	2015	8.30	n.d.	4.90	15.30	n.d.
Souvignier Gris	Italy	2015	n.d.	n.d.	n.d.	23.90	n.d.
Johanniter	Italy	2015	3.70	n.d.	0.60	15.30	n.d.
Johanniter	Germany	2015	13.80	4.1	2.30	5.70	n.d.
Solaris	Italy	2015	7.10	3.4	3.30	8.20	n.d.
Solaris	Germany	2015	5.10	n.d.	1.1	13.70	n.d.
Phoenix	Italy	2015	7.90	n.d.	n.d.	17.00	14.20
Phoenix	Germany	2015	n.d.	n.d.	n.d.	2.10	n.d.
Bronner	Italy	2015	n.d.	n.d.	n.d.	6.00	n.d.
Bronner	Germany	2015	n.d.	n.d.	n.d.	n.d.	n.d.
Muscaris	Italy	2015	n.d.	n.d.	n.d.	19.60	n.d.
Muscaris	Germany	2015	n.d.	n.d.	n.d.	6.10	n.d.
Accent	Germany	2015	3.90	n.d.	2.20	5.60	n.d.
Rondo	Germany	2015	4.40	n.d.	2.40	11.00	n.d.
Bolero	Germany	2015	6.20	n.d.	n.d.	21.00	n.d.
Helios	Italy	2015	n.d.	n.d.	n.d.	17.20	n.d.
Bianca	Italy	2015	n.d.	n.d.	n.d.	5.20	n.d.
Jasmine	Italy	2015	5.10	n.d.	n.d.	6.80	n.d.
Pinot noir	Italy	2015	5.60	n.d.	4.40	6.80	n.d.
Cabernet Sauvignon	Italy	2015	4.70	n.d.	6.10	9.90	n.d.
Cabernet Sauvignon	Germany	2015	3.10	n.d.	2.90	6.20	n.d.
Chardonnay	Italy	2015	12.70	n.d.	2.00	20.00	n.d.
Chardonnay	Germany	2015	2.90	n.d.	1.60	1.10	n.d.
Riesling	Italy	2015	3.70	n.d.	n.d.	5.30	n.d.
Riesling	Germany	2015	2.70	n.d.	0.80	3.00	n.d.
Moscato Giallo	Italy	2015	15.40	n.d.	0.30	4.80	n.d.
Regent	Italy	2016	10.80	n.d.	n.d.	10.00	16.40
Regent	Germany	2016	n.q.	n.d.	n.q.	19.20	n.d.
Cabernet Cortis	Italy	2016	n.d.	n.d.	9.50	7.50	14.80
Cabernet Cortis	Germany	2016	n.d.	n.d.	4.60	17.80	11.80

Prior	Italy	2016	9.10	n.d.	n.d.	7.30	16.10
Prior	Germany	2016	n.q.	n.d.	n.q.	9.60	12.30
Nero	Italy	2016	n.d.	n.d.	n.d.	2.80	n.d.
Souvignier Gris	Italy	2016	n.d.	n.d.	n.d.	3.30	n.d.
Johanniter	Italy	2016	n.d.	n.d.	n.d.	2.40	n.d.
Johanniter	Germany	2016	n.d.	n.d.	n.d.	2.80	n.d.
Solaris	Italy	2016	n.d.	n.d.	n.d.	4.70	n.d.
Solaris	Germany	2016	n.d.	n.d.	n.d.	n.q.	n.d.
Phoenix	Italy	2016	n.d.	n.d.	n.d.	2.70	n.d.
Phoenix	Germany	2016	n.d.	n.d.	n.d.	2.70	n.d.
Bronner	Italy	2016	3.80	4.10	n.d.	12.50	n.d.
Bronner	Germany	2016	4.40	n.d.	n.d.	5.90	n.d.
Muscaris	Italy	2016	n.d.	n.d.	n.d.	12.70	n.d.
Muscaris	Germany	2016	n.d.	n.d.	n.d.	5.40	n.d.
Accent	Germany	2016	6.90	n.d.	2.40	3.80	n.d.
Rondo	Germany	2016	9.90	n.d.	3.50	19.10	n.d.
Bolero	Germany	2016	11.20	n.d.	n.d.	15.50	n.d.
Helios	Italy	2016	3.10	3.80	2.00	8.80	n.d.
Bianca	Italy	2016	6.90	4.20	n.d.	13.30	n.d.
Jasmine	Italy	2016	5.80	4.60	n.d.	4.20	n.d.
Pinot noir	Italy	2016	7.80	n.d.	1.50	1.10	n.d.
Cabernet Sauvignon	Germany	2016	42.60	n.q.	3.10	8.00	n.d.
Teroldego	Italy	2016	11.90	n.d.	0.50	1.10	11.50
Chardonnay	Italy	2016	6.00	n.d.	n.d.	1.00	n.d.
Chardonnay	Germany	2016	6.80	n.q.	n.q.	4.50	n.d.
Riesling	Italy	2016	7.30	n.q.	n.q.	4.00	n.d.
Riesling	Germany	2016	n.q.	n.d.	n.q.	4.30	n.d.
Moscato Giallo	Italy	2016	n.q.	n.q.	n.q.	6.00	n.d.

Abbreviations: H_2S, hydrogen sulfide; MeSH, methanethiol; DMS, dimethyl sulfide; CS_2, carbon disulfide;.MeSAc, *S*-methyl thioacetate; nq., not quantifiable; n.d., not detected.

Concluding remarks

The current study provides information on some promising disease tolerant varieties recently introduced to the cultivation. In particular, it gives a clear picture of the chemical profile of wine made by PIWI varieties grown in Italy and Germany in three different vintages. It appears that with the exception of the anthocyanins, the wine produced from these varieties have a general composition closely resembling that of the well know *V. vinifera* wines. It follows that mildew tolerant varieties are promised grape varieties to produce high quality wines.

The information gained contribute to increase knowledge about the composition of wine made by mildew tolerant varieties and may be useful to change the bad reputation of these varieties in the wine industry. Furthermore, this information could also serve to suggest the most appropriate winemaking style allowing the improvement of the wine quality and also the valorisation of the characteristics of each grapevine variety. Considering that grape quality is crucial for wine quality, the analysis of the chemical profile of the grapes from disease tolerant varieties has also contributed to better characterise these varieties.

Finally, the investigation of the metabolomic profile of red non-*V. vinifera* genotypes allowed to characterise their chemical composition highlighting the presence of a significant genotypic diversity between the genotypes. The knowledge of their composition can be useful to provide the basis wider choices for further breeding programs.

Summary of PhD experiences

This PhD project is included in the “Agriculture Science and Biotechnology” PhD school of University of Udine with partner institution the Fondazione Edmund Mach (FEM). I was selected and awarded of a PhD scholarship by the University of Udine to undertake research in the following topic: “Chemical characteristics of wine made by disease tolerant varieties”. In November 2014, I started my PhD project at the Department of Food Quality and Nutrition (DQAN) of Fondazione Edmund Mach.

My supervisor is Dr. Urska Vrhovsek of the Department of Food Quality and Nutrition (DQAN), Research and Innovation Center, of Fondazione Edmund Mach (San Michele all’Adige, Italy) and my co-supervisor is Prof. Doris Rauhut of Hochschule Geisenheim University (Geisenheim, Germany).

During my PhD, I had the opportunity to spend approximately 8 months at Hochschule Geisenheim University in Germany. Grape harvest of PIWI and *V. vinifera* grapes was conducted at the experimental vineyards in San Michele all’Adige and Geisenheim. The non-volatile profile was studied in the Department of Food Quality and Nutrition of Fondazione Edmund Mach. The analysis of the volatile compounds was performed in the Department of Microbiology and Biochemistry at Hochschule Geisenheim University. Furthermore, in 2016 I was awarded to an Erasmus+ Traineeship scholarship to support my mobility experience abroad.

I attended a course on statistical analysis and a summer school centered on the R environment organized by Fondazione Edmund Mach and University of Udine, respectively. I also participated to international symposia, such as the IX In Vino Analytica Scientia Symposium –IVAS– (Mezzocorona, Trento, Italy, 2015, 14-17 July), Macrowine 2016 (Nyon, Switzerland, 2016, 27-30 June) and the X In Vino Analytica Scientia Symposium –IVAS– (Salamanca, Spain, 2017, 17-20 July). Finally, I gave two oral presentations in both Macrowine 2016 and IVAS 2017 presenting respectively the following communications: “Metabolomic profile of red non-*V. vinifera* genotypes” and “Investigation of volatile and non-volatile compounds of wines from interspecific varieties cultivated in Italy and Germany”.

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