Received: 29 June 2020 | Accepted: 27 January 2021 | Published: 15 March 2021
DOI:10.20870/oeno-one.2021.55.1.3865

Volatile and phenolic composition of monovarietal red wines of Valpolicella appellations

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ABSTRACT

The volatile and phenolic compositions of nine monovarietal wines from the following grape varieties allowed in the Valpolicella appellation were investigated: Corvina, Corvinone, Rondinella, Molinara, Oseleta, Raboso, Croatina, Sangiovese and Cabernet-Sauvignon. Different clones were also investigated for Corvina and Corvinone, the two main varieties of the appellation. All grapes were harvested from a single experimental block and vinified following a standard protocol. Wines from different clones of Corvina were characterised by higher monoterpenols content, including linalool, α-terpineol and geraniol, as well as by a peculiar pattern of C6-alcohols. Relatively high levels of monoterpene alcohols were also found in Corvinone wines, while Oseleta showed the highest concentration of terpinen-4-ol and cis- and trans- isomers of linalool oxide. The evaluation of the wine aroma profile by means of different aromatic series indicated higher values for the "floral", "fruity" and "ripe fruit" series for Corvina and Corvinone wines. Major differences in phenolic composition were found between the different varieties of wine. The total phenolics and total tannins values for Corvina, Corvinone, Rondinella and Molinara wines indicated relatively low phenolic content in comparison with Croatina, Oseleta, Cabernet-Sauvignon. There were also major differences in the content of individual phenolic compounds, in particular anthocyanins, between the monovarietal wines.

KEYWORDS

wine aroma, red wine, monoterpenols, Valpolicella

INTRODUCTION

In traditional wine producing countries, such as Italy, France and Spain, the appellation of origin system is well-established and plays a central role in the economic success of local wines in international markets (Dorfmann, 2016). This system aims to convey to the consumer a message of uniqueness of individual products, which reflects the relationship between the characteristics of a given wine and the geographical area in which it is produced. As such, appellations of origin have been considered of primary importance for the sustainable and cultural development of producing areas (FAO, 2018). Among the many specifications that define the characteristics of individual appellations of origin, the grape varieties used in winemaking are a major element of distinction. While many appellations restrict grape selection to one single variety, others allow a number of varieties, so that within certain limits producers can opt for different blends, with the aim of optimising the final wine style. In the current context of climate change, there is great interest in revisiting the characteristics of different grape varieties (Hannah *et al.,* 2013), including the so-called 'minor' varieties that are often limited to particular regions as part of specific appellations.

Valpolicella is a hilly area of about 240 km^2 in north-eastern Italy, which is located in the province of Verona between the city of Verona (south) and the Lessini mountains (north). The renowned Denomination of Controlled and Guaranteed Origin (DOCG) Amarone and Recioto are produced in this region, as well as Denomination of Controlled Origin (DOC) Valpolicella Classico and Ripasso. These wines are obtained using local grape varieties, mainly Corvina and Corvinone, with smaller portions of other local varieties like Molinara, Rondinella, Oseleta. A maximum of 10 % of other grape varieties authorised in the province of Verona can be used, with Raboso, Croatina, Sangiovese and Cabernet-Sauvignon being most frequently used. Although Valpolicella wines are an example of blended wines where minor local varieties contribute to the production of wines with distinctive character and value (Paronetto & Dellaglio, 2011), little is known about the chemical composition of the wines obtained from grapes typically used in the Valpolicella appellation.

There are a few available data to date with regards phenolic characterisation (Nicolini & Mattivi, 1993; Mattivi *et al.,* 2002) and the study of certain grape-derived Corvina and Corvinone wines (Slaghenaufi & Ugliano 2018; Slaghenaufi*et al.,* 2019). Moreover, an evaluation of different percentages of a combination of Corvina, Corvinone and Rondinella has been carried out for the production of Amarone wine (Bellincontro *et al.,* 2016). Nevertheless, a comparative study that can set the ground for improved vinicultural and winemaking practices within the appellation has not been carried out to date.

The aim of this paper is to characterise the volatile and polyphenolic profile of different monovarietal wines obtained from Valpolicella varieties, including different clones of Corvina and Corvinone, in order to provide useful information for winemakers with view to improving the production of Valpolicella wines.

MATERIALS AND METHODS

1. Reagents and materials

2-Octanol (97 %), 1-hexanol (99 %), *cis*-3-hexenol (98 %), *trans*-3-hexenol (97 %), *cis*-2-hexenol (95 %), vanillin (99 %), 2,6-dimethoxyphenol (99 %), linalool (97 %), terpinen-4-ol (≥ 95 %), α-terpineol (90 %), nerol (≥ 97 %), geraniol (98 %), linalool oxide (≥ 97 %), β-citronellol (95 %), β-damascenone (≥ 98 %), isoamyl alcohol (98 %), 1-pentanol (99 %), benzyl alcohol (≥ 99 %), 2-phenylethanol ((≥ 99 %), vanillyl alcohol (≥ 98 %), ethyl butanoate (99 %), ethyl 3-methyl butanoate (≥ 98 %), isoamyl acetate (≥ 95 %), ethyl hexanoate (≥ 95 %), n-hexyl acetate (≥ 98 %), ethyl lactate (≥ 98 %), ethyl octanoate (≥ 98 %), ethyl decanoate (≥ 98 %), furfural (≥ 99 %), benzaldehyde (≥ 99.5 %), hexanoic acid (≥ 99 %), octanoic acid (≥ 98 %), 3-methylbutanoic acid (99 %), α-ionone (90 %), β-ionone (96 %), methionol (≥ 98 %), α-ionol (≥ 90 %), 1-butanol (≥ 99 %), 4-ethyl guaiacol (≥ 99%), 4-vinyl guaiacol (≥ 98 %), methyl vanillate (99 %) and ethyl vanillate (99 %) were supplied by Sigma Aldrich (Milan, Italy). Dichloromethane (≥ 99.8 %) and methanol (≥ 99.8 %) were provided by Honeywell (Seelze, Germany).

2. Wines

Grapes were harvested from one single experimental plot of about 1 hectare, located in the town of San Pietro in Cariano (VR; 45.515264°, 10.908528°). Three clones of Corvina (ISV-CV 7, ISV-CV 48 and VCR 446), four clones of Corvinone (ISV-CV 2, ISV-CV 3, ISV-CV 4 and ISV-CV 6), as well as Rondinella (clone VCR 38), Molinara (clone ISV-CV 100), Oseleta (clone VITIVER 1), Sangiovese (clone APSG5), Croatina (clone MICR 9), Raboso del Piave (clone VCR 19) and Cabernet-Sauvignon (clone FV6) were selected for the study. All grapes were in healthy condition. Five kilograms of each grape sample were destemmed and one single pool of berries was obtained. Potassium metabisulfite (100 mg/kg) was added to 800 g of grape berries. The berries were then hand-crushed and transferred to 1.5 L glass containers. Fermentations were carried out at 22 ± 1 °C in a temperature-controlled room. The temperature of the liquid was measured twice a day and the weight loss monitored daily. *Saccharomyces cerevisiae* VL3 (Laffort, Floirac, France) was used for inoculation. The yeast was rehydrated in 37 °C water for 20 min and was added to individual fermentation batches at a rate of 20 g/hL, as recommended by the manufacturer. The cap was mixed twice a day by gently pushing it down with a dedicated plunger, and fermentations were considered complete when no change in weight was observed for two consecutive days. At the end of fermentation, the wine was separated from the skins by pressing at 1.5 bar for 10 min with a pneumatic press. Potassium metabisulfite was added in order to reach a concentration of 25 mg/L of free SO_2. The samples were then clarified by centrifugation at 4500 rpm for 10 min at 5 °C and stored at 4 °C until analysis. All fermentations were conducted in duplicate. Sulphur dioxide, ammonia and primary amino nitrogen (PAN) were determined using an automatic analyser Y15 Biosystems (Barcelona, Spain). The pH was monitored with a Crison Basic 20+ pHmeter (Barcelona, Spain). Grape juice sugar content was monitored using a HI96801 refractometer (Hanna Instruments, USA).

3. Volatile compounds analysis

Volatile compounds were extracted and analysed as described by Slaghenaufi *et al.* (2020a) with minor modification. Fifty milliliters of sample were added with 20 µL of internal standard solution (2-octanol at 42 mg/L in ethanol) and diluted with 50 mL of distilled water. The solution was loaded onto a BOND ELUT-ENV, SPE cartridge, containing 1 g of sorbent (Agilent Technologies, USA), previously activated with 20 mL of methanol and equilibrated with 20 mL of water. The cartridge was then washed with 15 mL of water. Free volatile compounds were eluted with 10 mL of dichloromethane, and then concentrated under gentle nitrogen stream to 200 µL prior to GC injection. GC–MS analysis was carried out on an HP 7890A (Agilent Technologies) gas chromatograph coupled to a 5977B quadrupole mass spectrometer equipped with a Gerstel MPS3 auto sampler (Mülheim/Ruhr, Germany). Separation was performed using a DB-WAX UI capillary column (30 m × 0.25, 0.25 µm film thickness, Agilent Technologies) and helium as the carrier gas at 1.2 mL/min constant flow rate. The GC oven was programmed as follows: at 40 °C for the first 3 min, then increasing to 230 °C at 4 °C/min, at which it was maintained for 20 min. The transfer line was set at 200 °C. The mass spectrometer operated in electron ionisation (EI) at 70 eV with an ion source temperature of 250 °C and quadrupole temperature of 150 °C. Mass spectra were acquired in Scan mode.

Calibration curves were prepared for each analyte using seven concentration points and three replicate solutions per point in the model wine (12 % v/v ethanol, 3.5 g/L tartaric acid, pH 3.5). 20 µL of internal standard 2-octanol (42 mg/L in ethanol) were added to the solution. SPE extraction and GC-MS analysis were performed as described above for the samples. Calibration curves were obtained using Chemstation software (Agilent Technologies, Inc.) by linear regression, plotting the response ratio (analyte peak area/internal standard peak area) against concentration ratio (analyte added concentration/internal standard concentration). Method characteristics are reported in Supplementary S.1. The analysis of 3-oxo-α-ionol, 8-hydroxylinalool, 3-hydroxy-β-damascone and 3-hydroxy-7,8-dehydro-α-ionol was semi-quantitative and they were expressed as µg/L of 2-octanol equivalent (internal standard), because no commercial standards were available for these compounds .

4. Polyphenols analysis

Folin-Ciocalteu reagent was used to quantify the total phenolics, according to the procedure described by Singleton & Rossi (1965). Total tannins were determined by methyl cellulose precipitation (Sarneckis *et al.,* 2006). Total anthocyanins were determined using the bisulfite bleaching method. Quantification of individual flavonoids, anthocyanins, flavan-3-ols and phenolic acids was performed by liquid chromatography as described by Gonzales *et al.* (2018).

A Jasco HPLC system (Jasco, Oklahoma City, USA) was used, constituting an AS-2057 autosampler and PU-2089+ pumps coupled to a MD-2010+ photodiode array detector. Chromatographic separation was achieved using an Aces 5 C_{18}

250 x 4.6 mm column (Advanced Chromatography Technologies, Aberdeen, Scotland).

Quantification was done on the 280, 320, 360 and 520 nm recorded chromatograms. A binary gradient consisting of 0.4 % formic acid in water (v/v, solvent A) and 0.4 % formic acid in acetonitrile 80 % (v/v, solvent B) were used as the mobile phase. Elution was performed with a flow rate of 1 mL/min and the following gradient programme (v/v): starting at 10 % solvent B for 2 min, increasing from10 to 45 % in 18 min, then from 45 to 100 % in 1 min, and finally maintained at 100 % for 5 min. The column was re-equilibrated for 6 min before the next injection. An amount of 10 µL of wine or calibration standards was injected into the column. All the samples were filtered through 0.20 µm Microliter PTFE membrane filters (Wheaton, NJ, USA) into dark glass vials and immediately injected into the HPLC system.

5. Data treatment

Data treatment, ANOVA and Tukey post-hoc test were performed using XLSTAT 2017 (Addinsoft SARL, Paris, France).

RESULTS AND DISCUSSION

1. Standard oenological parameters of musts and wines

The main oenological parameters of musts and wines are shown in Table 1. Although all the grapes were harvested on the same date and grown in the same experimental field with the same agronomical practices, differences in °Brix and nitrogen levels were observed. This could be a reflection of varietal differences in grapevine response to the pedoclimatic conditions of the experimental vineyard. Differences in grape berry nitrogen content were observed between clones of the same varieties, as in the case of Corvina and Corvinone.

2. Volatile compounds

The 46 volatile compounds analysed in the wine samples are shown in Table 2. Depending on their chemical structure, they are grouped into alcohols, C_6-compounds, esters, terpenes and norisoprenoids, acids and benzenoids.
Despite a certain degree of volatilisation occurring due to the small size of the fermentation batches, it should be noted that fermentation length was similar in all the batches (varying between 8 and 9 days); therefore major differences in the CO_2 stripping rates are likely to be negligible.

2.1. Higher Alcohols

Higher alcohols are a major group of volatile compounds produced during alcoholic fermentation by yeast either from amino acid via the Ehrlich pathway or directly from sugars. Higher alcohols have an odour of solvent, with the exception of 2-phenylethanol and methionol that are described as being like roses and potatoes respectively. 3-methyl-1-butanol and 2-phenylethanol showed the highest concentrations in all studied wines, their concentrations always exceeding the odour threshold (Supplementary S.4.). However, De-La-Fuente-Blanco *et al.* (2016) showed that the aroma contribution of methionol and 2-phenylethanol to model wines was insignificant, even at concentrations well above the odour threshold; whereas 3-methyl-1-butanol was reported to contribute to the green character of wine (Sáenz-Navajas *et al.,* 2018). The highest concentration of total higher alcohols was observed in Sangiovese and the lowest in Rondinella and Cabernet-Sauvignon. The same behaviour was observed for the level of 3-methyl-1-butanol. The highest and the lowest content of 2-phenylethanol were found in Oseleta and Corvina 48 respectively. Croatina and Cabernet-Sauvignon showed the lowest levels of methionol, and Molinara and Corvinone 2 the highest, being up to 3 times higher. No statistical differences were observed between the wine varieties for 1-pentanol.

2.2. Acids

Fatty acids are associated with cheesy, fatty and rancid aromas. They are formed during fermentation as by-products of yeast metabolism. Their concentration in wine is influenced by must composition, oxygen availability and temperature. Differences in the concentrations of hexanoic, octanoic, and 3-methyl butanoic acids across wines were relatively minor except for octanoic acid, which was detected in considerably lower concentrations in Oseleta and Cabernet-Sauvignon. In all samples, these compounds exceeded their odour threshold, therefore potentially contributing to wine aroma. These compounds are characterised by fatty and cheesy odors and contribute to the generic vinous character of wine.

2.3. C_6 alcohols

C_6 alcohols such as 1-hexanol, *cis*-3-hexenol and *trans*-2-hexanol are formed during berry crushing by the enzymatic oxidation of unsaturated fatty acids in the grape (Ugliano, 2009); they have been reported in association with the "leafy"

TABLE 1. Musts and wine enological parameters.

	MUSTS					WINE			
	°Brix	pH	Ammonia (mg/L)	PAN (mg/L)	YAN [a] (mg/L)	Alcohol (% v/v)	Glucose + fructose (g/L)	Free SO_2 (mg/L)	Total SO_2 (mg/L)
Corvina 446	24.6 ± 0.4	2.98 ± 0.01	24 ± 1	63 ± 2	88 ± 3	13.5 ± 0.1	0.1 ± 0.02	28 ± 1	100 ± 1
Corvina 48	22.9 ± 0.3	3.17 ± 0.01	30 ± 4	87 ± 12	117 ± 15	13.2 ± 0.2	0.22 ± 0.03	26 ± 2	107 ± 3
Corvina 7	23.9 ± 0.7	2.97 ± 0.01	34 ± 6	74 ± 5	108 ± 11	13.7 ± 0.1	0.39 ± 0.06	29 ± 2	106 ± 2
Corvinone 2	19.1 ± 0.5	3.12 ± 0.01	33 ± 8	60 ± 10	93 ± 18	11 ± 0.1	0.33 ± 0.05	24 ± 1	100 ± 3
Corvinone 3	20.4 ± 0.7	3.04 ± 0.01	36 ± 3	69 ± 9	105 ± 12	11.5 ± 0.1	0.3 ± 0.05	25 ± 1	99 ± 4
Corvinone 4	22.4 ± 0.2	3.02 ± 0.01	19 ± 1	50 ± 2	69 ± 3	12.8 ± 0.2	0.37 ± 0.06	27 ± 2	108 ± 2
Corvinone 6	21.8 ± 0.3	2.98 ± 0.01	24 ± 3	53 ± 2	77 ± 5	12.5 ± 0.2	0.4 ± 0.06	23 ± 1	111 ± 2
Croatina	21.8 ± 0.1	3.17 ± 0.01	39 ± 3	68 ± 3	108 ± 7	12.3 ± 0.1	0.31 ± 0.05	25 ± 1	105 ± 2
Molinara 100	22.9 ± 0.5	3.08 ± 0.01	6 ± 1	53 ± 0	59 ± 1	13 ± 0.3	0.3 ± 0.05	25 ± 3	100 ± 2
Oseleta	22 ± 0.1	3.33 ± 0.01	15 ± 4	69 ± 2	84 ± 5	12.5 ± 0.1	0.19 ± 0.03	22 ± 1	100 ± 4
Rondinella 38	23.2 ± 0.5	3.23 ± 0.01	14 ± 6	61 ± 8	76 ± 14	13.1 ± 0.2	0.44 ± 0.07	26 ± 1	99 ± 4
Raboso	24.3 ± 0.6	2.77 ± 0.01	9 ± 5	56 ± 6	65 ± 1	13.5 ± 0.2	0.5 ± 0.08	30 ± 3	106 ± 2
Sangiovese	23.4 ± 0.8	2.88 ± 0.01	23 ± 3	90 ± 2	114 ± 4	13.2 ± 0.1	0.21 ± 0.03	25 ± 2	98 ± 1
Cabernet-Sauvignon FV6	24 ± 0.4	3.33 ± 0.01	8 ± 0	61 ± 7	69 ± 7	13.6 ± 0.2	0.15 ± 0.02	24 ± 2	104 ± 2

[a] YAN (Yeast Assimilable Nitrogen, calculated as sum of PAN+Ammonia)

and “herbaceous” odours of wines (Benkwitz *et al.,* 2012). *trans*-3-Hexenol and *cis*-2-hexanol have also been reported by different authors (Oliveira *et al.,* 2006; Benkwitz *et al.,* 2012; Bindon *et al.,* 2013; Jouanneau *et al.,* 2010), but their origin is less clear. The concentration of C_6 compounds in finished wines may be linked to grape variety (Versini *et al.,* 1994; Nicolini *et al.,* 1995) and maturity (Kalua & Boss, 2009), as well as technological factors, such as timing of SO_2 addition (Nicolini *et al.,* 1996) and duration of pre-fermentative skin contact (Ramey *et al.,* 1986). In the present study, differences were observed in all C_6 alcohols across different wines, with wines from Corvinone clones generally displaying the highest values, while the Molinara sample was nearly three times lower. Considering that the vinification protocol was the same for all the samples, these differences may be related to either grape variety or maturity. With regard to the latter, in a recent study it was found that wines with higher 1-hexanol concentrations were produced from early-harvested grapes (Bindon *et al.,* 2013). In our experimental samples, a negative correlation ($R^2 = 0.719$) between grape °Brix values and 1-hexanol concentrations was only observed in the Corvinone clones subset. Given that Corvinone had generally lower °Brix values, it is possible that this relationship is true for early-harvested grapes (e.g., < 20 °Brix), whereas it is less relevant once full maturity approaches or is achieved. Garcia *et al.* (2003) and, more recently, Vilanova *et al.* (2012) reported that C_6 compounds during the ripening period tend to initially increase, after which they stabilise and then decrease; this behaviour occurred in a delta of sugar level that depends on grape variety. In any case, our results indicate a strong varietal component in wines C_6 alcohols content and profile.

Of particular interest was that Corvina wines exhibited *cis*-3-hexenol concentrations that were much higher than those detected in all the other wines, with this characteristic being consistent for all the tested Corvina clones. As a consequence, 3-hexenol isomers distribution could be used to distinguish Corvina, Rondinella and Raboso wines from the other samples. In fact, the *cis/trans* ratio was 11.7 (± 1.2) in Corvina wines, 11 (± 0.1) in Rondinella, 2.2 (± 0.02) in Raboso, and less than 1 in the remaining varieties. These results confirm previous observations in studies by Nicolini *et al.* (1996) and Oliveira *et al.* (2006) on the possible role of 3-hexanol isomers as varietal markers

TABLE 2. Volatile compound mean concentration (µg/L) and standard deviation (SD) of the studied wines.

		Corvina 7		Corvina 48		Corvina 446		Corvinone 2		Corvinone 3		Corvinone 4		Corvinone 6	
		mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Higher Alcohols	1-Butanol	104.8	± 1.21^{d}	117.4	± 3.13^{de}	82.6	± 0.7^{c}	137	± 0.71^{fg}	155.5	± 2.65^{h}	82.16	± 2.28^{bc}	123.3	± 7.09^{ef}
	3-Methyl-1-butanol	42255	± 2225^{cd}	37231	± 1274^{abc}	36776.3	± 539^{abc}	38949	± 2354^{bcd}	39899.2	± 1206.6^{cd}	37457.8	± 1.49^{abc}	38582	± 2076^{bcd}
	1-Pentanol	35.32	± 1.08^{a}	51.13	± 1.65^{a}	29.64	± 1.3^{a}	67.88	± 4.74^{a}	31.82	± 0.08^{a}	39.02	± 402^{a}	41.21	± 0.08^{a}
	2-Phenylethanol	24592	± 996^{abc}	19802	± 1116^{a}	21209	± 853^{ab}	23819	± 1095^{abc}	26671	± 1678^{bc}	24679.8	± 2721^{abc}	21589	± 710^{ab}
	Methionol	191	± 5.66^{cd}	192.5	± 7.78^{cd}	167.5	± 25^{bc}	241	± 12.73^{d}	181.5	± 20.51^{cd}	166.5	± 17.7^{bc}	222.5	± 27.6^{cd}
Acids	3-Methylbutanoic acid	1491	± 66.4^{ab}	1284	± 6.23^{ab}	1317.59	± 4.5^{ab}	1559	± 25.72^{ab}	1153	± 52.08^{a}	1195	± 8.43^{a}	1370	± 76.1^{ab}
	Hexanoic acid	1477	± 110de	1395	± 98.5^{bcde}	1442.67	± 34^{cde}	1493	± 26.57^{de}	1764	± 3.46^{f}	1315	± 6.31^{abcd}	1456	± 40.8^{de}
	Octanoic acid	1444	± 3.75^{g}	1052	± 13.6^{bc}	1314.84	± 32^{defg}	1113	± 13.34^{bc}	1199	± 79.57^{cde}	1058	± 5.88^{bc}	1423	± 41.8^{fg}
C_6-alcohols	1-Hexanol	1751	± 125^{fg}	1516	± 25.5^{def}	1476.97	± 30de	2037	± 65.03^{h}	2144.7	± 22.74^{h}	1615.48	± 0.04^{ef}	1368	± 38de
	trans-3-Hexenol	18.99	± 0.49^{a}	15.87	± 0.35^{a}	18.41	± 0.3^{a}	65.1	± 0.52^{bcd}	67.11	± 0.32^{bcd}	52.05	± 13.7^{b}	58.98	± 0.07^{bcd}
	cis-3-Hexenol	215	± 15.3^{e}	209	± 14.7^{e}	197.02	± 3.4^{e}	34.54	± 0.49^{b}	30.64	± 0.91^{b}	16.49	± 1.25^{ab}	13.32	± 0.75^{ab}
	cis-2-Hexenol	7.41	± 0.47^{bc}	5.01	± 0.1^{a}	6.54	± 0^{ab}	11.58	± 0.16^{efg}	11.01	± 0.45^{defg}	9.48	± 0.48^{cde}	10.77	± 0.14^{def}
	trans-2-Hexenol	<LOQ		<LOQ		<LOQ		1.71	± 1.41	1.52	± 0.42	1.43	± 0.1	1.66	± 0.18
Esters	Ethyl butanoate	101.7	± 1.34^{fg}	80.79	± 0.45^{c}	82.48	± 0.2^{cd}	97.93	± 1.23^{ef}	151	± 0.54^{I}	91.58	± 0.61^{de}	98.36	± 1.41^{ef}
	Ethyl 3-methyl butanoate	25.22	± 0.75^{ef}	17.15	± 1.7^{cd}	20.37	± 0.2^{de}	30.28	± 1.56^{fg}	19.3	± 3.57^{d}	6.37	± 0.8^{a}	19.57	± 0.06^{d}
	Isoamyl acetate	1319	± 4.06^{f}	896.1	± 12.2^{abc}	1102.32	± 18^{e}	1039	± 34.21^{cde}	1786.56	± 65.53^{g}	922.44	± 26.6^{bcd}	1400	± 1.05^{f}
	Ethyl hexanoate	177	± 0.63^{h}	133.2	± 2.64^{cde}	128.95	± 4^{cd}	149.7	± 4.24^{def}	163.23	± 13.21^{fgh}	92.34	± 6.12^{b}	172.6	± 0.14^{gh}
	n-Hexyl acetate	1.86	± 0.05^{b}	0.16	± 0.03^{a}	4.45	± 0.7^{c}	0.51	± 0.05^{a}	0.66	± 0.13^{a}	0.33	± 0.09^{a}	0.43	± 0.11^{a}
	Ethyl lactate	1147	± 11.5^{fgh}	735.2	± 10.7^{bcd}	1022.2	± 60^{efg}	1220	± 22.17^{gh}	890.95	± 11.41^{cde}	670.9	± 18.5^{bc}	991.2	± 116^{efg}
	Ethyl octanoate	126	± 0.14^{h}	98.6	± 0.63^{fg}	75.79	± 3.9^{d}	105.9	± 1.97^{g}	84.63	± 2.12^{de}	65.55	± 4.07^{c}	131.3	± 2.41^{h}
	Ethyl decanoate	115	± 100^{a}	32.69	± 1.69^{a}	31.96	± 2.1^{a}	36.34	± 1.77^{a}	22.04	± 1.41^{a}	29.91	± 2.38^{a}	44.69	± 1.85^{a}
Terpenes	*cis*-Linalool oxide	1.38	± 0.01^{ab}	1.34	± 0.07^{ab}	1.47	± 0.1^{abc}	1.31	± 1^{ab}	0.1	± 0.02^{a}	1.21	± 0.08^{ab}	0.15	± 0.07^{a}
	trans-Linalool oxide	0.42	± 0.04^{b}	0.7	± 0.03^{cd}	0.53	± 0^{bc}	0.13	± 0.01^{a}	0.08	± 0.01^{a}	0.01	± 0.06^{a}	0.08	± 0.01^{a}
	Linalool	25.93	± 1.3^{g}	18.18	± 0.57^{f}	23.59	± 0.9^{g}	14.28	± 0.93^{e}	19.16	± 0.78^{f}	12.2	± 0.98^{de}	14.1	± 0.71^{e}
	Terpinen-4-ol	0.85	± 0.02^{bc}	0.51	± 0.01^{ab}	0.98	± 0.1^{cd}	0.18	± 0.01^{a}	0.29	± 0.08^{a}	0.51	± 0.05^{ab}	0.48	± 0.11^{ab}
	α-Terpineol	8.43	± 0.54^{g}	4.83	± 0.4^{f}	8.2	± 0.3^{g}	3	± 0.03^{cde}	4.45	± 0.16^{f}	2.95	± 0.42^{cde}	3.97	± 0.02^{ef}
	β- Citronellol	17.05	± 1.99^{def}	18.87	± 1.54^{ef}	15.8	± 1.1^{de}	16.93	± 1.37^{def}	18.48	± 0.07^{def}	14.39	± 0.62^{cd}	9.03	± 0.01^{ab}
	Nerol	6.07	± 0.89^{defg}	6.77	± 0.35^{fg}	3.46	± 0.3^{ab}	4.63	± 0.45^{bcd}	5.42	± 0.18^{cdef}	3.68	± 0.01^{abc}	4.66	± 0.6^{bcde}
	Geraniol	8.49	± 0.05^{e}	8.55	± 0.76^{e}	7.1	± 0.7^{cde}	6.49	± 0.05^{cd}	7.65	± 0.18^{de}	5.68	± 0.62^{bc}	6.38	± 0.52^{cd}
	8-Hydroxylinalool	0.3	± 0.28^{a}	0.03	± 0.02^{a}	0.1	± 0^{a}	0.02	± 0.01^{a}	0.01	± 0.01^{a}	0.01	± 0^{a}	<LOQ	^{a}
Norisoprenoids	β-Damascenone	3.36	± 0.37^{ef}	2.76	± 0.25^{de}	2.61	± 0de	4.3	± 0.13^{g}	3.94	± 0.07^{fg}	3.34	± 0.21^{ef}	4.23	± 0.38^{g}
	α-Ionone	0.59	± 0.02^{cd}	0.72	± 0.22^{d}	0.55	± 0^{cd}	0.56	± 0.01^{cd}	0.04	± 0.01^{a}	0.04	± 0.01^{a}	0.02	± 0.01^{a}
	α-Ionol	7.61	± 0.03^{g}	0.28	± 0.01^{a}	1.45	± 0^{cd}	2.55	± 0.13^{e}	0.13	± 0^{a}	1.63	± 0.08^{cd}	2.01	± 0.22^{de}
	β-Ionone	0.24	± 0.01^{cde}	0.31	± 0.06^{e}	0.07	± 0^{ab}	0.28	± 0.01^{de}	0.35	± 0.05^{e}	0.01	± 0^{a}	0.03	± 0.04^{a}
	3-Hydroxy-β-damascone	0.13	± 0.13^{a}	0.05	± 0.01^{a}	0.04	± 0^{a}	0.04	± 0^{a}	0.04	± 0^{a}	0.02	± 0^{a}	<LOQ	
	3-Oxo-α-ionol	1.06	± 0.99^{a}	0.41	± 0.02^{a}	0.28	± 0^{a}	0.3	± 0^{a}	0.31	± 0^{a}	0.12	± 0.01^{a}	0.25	± 0^{a}
	3-Hydroxy-7,8-dehydro-α-ionol	0.09	± 0.08^{a}	0.03	± 0^{a}	0.02	± 0^{a}	0.01	± 0^{a}	0.01	± 0^{a}	<LOQ		<LOQ	
Benzenoids	Vanillin	13.29	± 0.01^{bc}	15.94	± 0.58^{c}	12.61	± 0.4^{bc}	25.26	± 1.51^{d}	27.63	± 0.66^{d}	16.61	± 1.97^{c}	25.03	± 2.5^{d}
	Vanillyl alcohol	1.3	± 0.01^{ab}	2.96	± 0.06^{de}	1.74	± 0.1^{bc}	2.82	± 0.01^{de}	2.81	± 0.06^{de}	1.35	± 0.14^{ab}	0.48	± 0.4^{a}
	Methyl vanillate	8.92	± 0.51^{b}	8.57	± 0.25^{b}	8.95	± 0.4^{b}	14.06	± 0.46^{c}	13.07	± 0.36^{c}	14.23	± 0.34^{c}	12.44	± 0.04^{c}
	Ethyl vanillate	62.19	± 8.66^{bc}	78.64	± 2.9^{ab}	59.71	± 4^{ab}	81.58	± 2.61^{bc}	64.78	± 0.73^{cd}	86	± 1.03^{cd}	59.74	± 2.14^{cd}
	Benzaldehyde	42.18	± 2.31^{g}	13.97	± 2.38^{cd}	41.82	± 1.3^{g}	17.78	± 1.36^{de}	14.25	± 1.27^{cd}	13.52	± 0.75^{cd}	26.62	± 2.31^{f}
	Benzyl alcohol	222	± 2.04^{e}	278.6	± 21.9^{f}	148.43	± 4.7^{d}	48.22	± 0.66^{ab}	22.64	± 1.78^{ab}	32.13	± 0.18^{ab}	18	± 1.12^{a}
	4-Ethylguaiacol	0.02	± 0.01^{a}	0.07	± 0.01^{a}	0.01	± 0.1^{a}	0.14	± 0.07^{a}	0.02	± 0.01^{a}	0.02	± 0.01^{a}	0.01	± 0.03^{a}
	4-Vinylguaiacol	15.8	± 0.72^{cd}	19.73	± 1.1^{def}	15.87	± 0.1^{cd}	44.66	± 1.11^{I}	24	± 0.03^{fgh}	25.68	± 1.78^{gh}	23.61	± 2.1^{fg}
	2,6-Dimethoxyphenol	1.33	± 0.05^{c}	0.9	± 0.04^{abc}	1.16	± 0.1^{bc}	5.18	± 0.14^{e}	0.68	± 0^{abc}	0.69	± 0.06^{abc}	1.23	± 0.19^{bc}

		Molinara			Rondinella			Oseleta			Raboso			Croatina			Sangiovese			Cabernet-Sauvignon		
		mean	SD		mean	SD		mean	SD		mean	SD		mean	SD		mean	SD		mean	SD	
Higher Alcohols	1-Butanol	66.9	± 3.7	b	33.9	± 2.4	a	69.6	± 9.2	bc	67.8	± 0.5	bc	35.5	± 3.5	a	139.9	± 3.7	g	42.1	± 0.6	a
	3-Methyl-1-butanol	38432	± 796	bcd	31794	± 2383	a	33569	± 346	ab	36566	± 2129	abc	38615	± 999	bcd	44311	± 667	d	32276	± 1390	a
	1-Pentanol	37.8	± 1.9	a	35.5	± 1.1	a	31.7	± 1.2	a	36.1	± 4.1	a	20.4	± 0.1	a	37.3	± 1.5	a	22.6	± 1.7	a
	2-Phenylethanol	21557	± 1118	ab	21473	± 1144	ab	28547	± ###	c	27080	± 2766	bc	23534	± 384	abc	26553	± 725	bc	22376	± 823	abc
	Methionol	233.5	± 13	cd	204.5	± 10.6	cd	104.98	± 20	ab	110.5	± 36.06	ab	82	± 5.66	a	209	± 4.24	cd	84.5	± 0.71	a
Acids	3-Methylbutanoic acid	1459	± 26	ab	1350	± 62	ab	1542	± 64	ab	1213	± 57	a	1434	± 56	ab	1653	± 351	b	1220	± 53	a
	Hexanoic acid	1390	± 81	bcde	1224	± 42	abc	1356	± 22	bcd	1100	± 70	a	1221	± 55	ab	1583	± 13	ef	1184	± 24	ab
	Octanoic acid	1355	± 56	efg	1193	± 49	cd	693	± 16	a	975	± 36	b	1018	± 34	b	1281	± 69	def	793	± 16	a
C_6-alcohols	1-Hexanol	790	± 29	a	966	± 37	ab	1990	± 132	gh	1275	± 72	cd	1290	± 55	cd	1894	± 67	gh	1062	± 15	bc
	trans-3-Hexenol	26.4	± 3.2	a	13.2	± 0.3	a	108.4	± 6.3	e	27.4	± 1.1	a	69.7	± 3.7	cd	75.6	± 1.1	d	54.3	± 2	bc
	cis-3-Hexenol	3.4	± 0.1	a	146.6	± 5.8	d	21.6	± 1	ab	59.9	± 2.8	c	15.9	± 0.4	ab	33.7	± 2.3	b	22.9	± 0.9	ab
	cis-2-Hexenol	9.36	± 0.8	cd	7.78	± 0.08	bc	20.34	± 1	h	7.43	± 0.78	bc	12.99	± 0.04	g	10.42	± 0.35	de	12.63	± 1.04	fg
	trans-2-Hexenol	<LOQ			<LOQ			<LOQ			<LOQ			<LOQ			2.97	± 0.68		1.82	± 1.06	
Esters	Ethyl butanoate	68.4	± 1.6	b	62.3	± 2.9	ab	53.9	± 1	a	98.7	± 2.1	ef	156.3	± 7.7	I	124.5	± 1.8	h	109	± 1.7	g
	Ethyl 3-methyl butanoate	17	± 0.8	cd	11.9	± 0.3	bc	12.8	± 0.1	bc	19.5	± 2	d	15.6	± 0.7	cd	32.1	± 1.3	g	9.6	± 0.4	ab
	Isoamyl acetate	1085	± 31	de	748	± 41	a	904	± 12	abc	970	± 6	bcde	957	± 54	bcde	2234	± 115	h	823	± 2	ab
	Ethyl hexanoate	130.7	± 13	cd	118.4	± 2.3	c	56.4	± 0	a	66.6	± 2	a	119	± 2.7	c	154.3	± 2.8	efg	52.3	± 0.7	a
	n-Hexyl acetate	0.4	± 0.3	a	0.8	± 0.2	a	0.4	± 0	a	0.2	± 0	a	0.2	± 0	a	0.6	± 0.2	a	0.2	± 0	a
	Ethyl lactate	705	± 16	bc	564	± 14	ab	407	± 14	a	971	± 40	def	543	± 7	ab	1273	± 177	h	512	± 20	ab
	Ethyl octanoate	96	± 1.8	fg	90.4	± 1.2	ef	33.5	± 2.9	a	45.6	± 0.5	b	82.3	± 3.7	de	77	± 3.5	d	38	± 0.7	ab
	Ethyl decanoate	27	± 0.5	a	27.9	± 0.9	a	14.9	± 0.2	a	16.5	± 0.1	a	33.2	± 0.6	a	27.8	± 0.7	a	15.1	± 0.5	a
Terpenes	*cis*-Linalool oxide	1.4	± 0.3	ab	1.6	± 0.5	abc	3.5	± 0.8	d	3	± 0.2	cd	1.6	± 0.4	abc	2.5	± 0.3	bcd	1.3	± 0.1	ab
	trans-Linalool oxide	0.8	± 0	d	0.1	± 0	a	1.4	± 0.2	e	0.1	± 0.1	a	0	± 0	a	0	± 0	a	1.8	± 0	f
	Linalool	12.6	± 1.9	de	9.7	± 1.2	cd	6.5	± 0.1	bc	7	± 0.1	bc	5.4	± 0.3	ab	7.6	± 0.2	bc	2.2	± 0.1	a
	Terpinen-4-ol	1.7	± 0.1	e	1.7	± 0.1	e	2.4	± 0.2	f	0.1	± 0.1	a	0.9	± 0.1	bc	1	± 0	cd	1.4	± 0.2	de
	α-Terpineol	3.8	± 0.2	def	2.1	± 0.3	abc	1.7	± 0.1	ab	2.2	± 0	bc	1.6	± 0	ab	2.9	± 0.1	cd	1.1	± 0.1	a
	β- Citronellol	20.7	± 1.5	f	19	± 1.9	ef	10.9	± 1	bc	6.7	± 0.4	ab	10	± 0.5	bc	8.4	± 0.6	ab	4.8	± 0.4	a
	Nerol	6.5	± 0.7	fg	3.4	± 0.6	ab	6.5	± 0.5	efg	2.5	± 0.2	a	7.5	± 0.2	g	5.4	± 0.5	cdef	3.4	± 0.1	ab
	Geraniol	6.7	± 0.6	cd	8.5	± 0.4	e	6.5	± 0.1	cd	2.5	± 0.5	a	4.1	± 0.1	ab	5.5	± 0.1	bc	3	± 0.1	a
	8-Hydroxylinalool	<LOQ		a	<LOQ		a	<LOQ		a	<LOQ		a	0.1	± 0	a	<LOQ		a	<LOQ		a
Norisoprenoids	β-Damascenone	3.2	± 0.2	ef	2.3	± 0.3	cd	0.6	± 0.2	a	1.1	± 0.1	ab	1.6	± 0.3	bc	1.7	± 0.1	bc	2.6	± 0.1	de
	α-Ionone	<LOD			0.6	± 0	ab	0.2	± 0.1	cd	0.1	± 0	f	0.2	± 0	cd	0.3	± 0.1	a	0	± 0	bc
	α-Ionol	0.04	± 0	a	0.5	± 0.04	d	0.47	± 0.3	ab	0.08	± 0.04	a	0.6	± 0.31	ab	0.04	± 0.01	bc	0.12	± 0.03	a
	β-Ionone	<LOD			<LOD			<LOD			<LOD			0.2	± 0	bcd	0.2	± 0	bc	<LOD		
	3-Hydroxy-β-damascone	0.1	± 0	a	0.1	± 0	a	0.1	± 0	a	0.1	± 0.1	a	0	± 0	a	0.3	± 0.3	a	0.1	± 0	a
	3-Oxo-α-ionol	0.4	± 0.1	a	0.4	± 0	a	0.8	± 0.2	a	0.7	± 0.2	a	0.3	± 0	a	0.5	± 0.1	a	0.5	± 0	a
	3-Hydroxy-7,8-dehydro-α-ionol	<LOD			<LOD			<LOD			<LOD			<LOD			0.1	± 0.1	a	<LOD		
Benzenoids	Vanillin	17.1	± 1.1	c	41.5	± 2.9	e	0.6	± 0.1	a	0.2	± 0	a	9.8	± 0.4	b	12	± 0.3	bc	0.3	± 0.1	a
	Vanillyl alcohol	2.6	± 0.1	cde	3.5	± 0.2	e	15.3	± 0.5	f	2.1	± 0.2	bcd	1.2	± 0.3	ab	2.4	± 0.4	cd	1.8	± 0	bc
	Methyl vanillate	4.08	± 0	a	3.67	± 0.07	a	61.26	± 1.9	f	30.72	± 0.27	e	14.01	± 0.28	c	22.18	± 0.77	d	8.69	± 0.16	b
	Ethyl vanillate	25.83	± 0.9	ef	77.32	± 1.23	f	112.43	± 3.1	ef	38.5	± 1.27	f	48.22	± 0.72	de	38.14	± 5.99	g	49.38	± 4.19	a
	Benzaldehyde	18.8	± 1	de	9.8	± 0.3	bc	22.2	± 1	ef	7.1	± 0.6	ab	16.3	± 1	d	7.3	± 0.8	ab	3.5	± 0	a
	Benzyl alcohol	56.2	± 1.3	b	277.8	± 7.7	f	787.5	± 8.9	g	39.7	± 2.2	ab	94.6	± 5.1	c	259.5	± 1.3	f	210.3	± 17.9	e
	4-Ethylguaiacol	<LOQ		a	<LOQ		a	<LOQ		a	<LOQ		a	<LOQ		a	<LOQ		a	0.1	± 0	a
	4-Vinylguaiacol	13.4	± 1.1	bc	23.6	± 1.7	efg	28.3	± 1.1	h	7.9	± 0.5	a	11.1	± 0.2	ab	19	± 0.3	de	9.3	± 1.5	ab
	2,6-Dimethoxyphenol	0.1	± 0	a	3.1	± 0.3	d	6.4	± 0.7	f	0.2	± 0.1	a	0.4	± 0	ab	3.5	± 0.2	d	4.6	± 0	e

Values in the same row with different letters indicate statistically significant differences ($p < 0.05$).
<LOQ: Value bellow the limit of quantification

of certain wines, which would appear to be of particular relevance in the case of Valpolicella red wines. Likewise, 2-hexenol isomers also seem to be varietal markers; in particular, the highest concentration of *cis*-2-hexenol was found in Oseleta, almost double that in other samples. Moreover, on average, Corvinone showed a concentration that was about 69 % higher than Corvina. Clonal variations for the *cis*-2-hexenol concentration were quite low: < 20 % in Corvina and < 10 % in Corvinone. *trans*-2-Hexenol could only be quantified in Corvinone, Sangiovese and Cabernet.

2.4. Esters

Esters are mainly produced during fermentation and they are related to the fruity character of wines. Out of all the esters analysed, ethyl butanoate, ethyl 3-methyl butanoate, ethyl hexanoate, ethyl octanoate and isoamyl acetate exceeded their odour threshold in all wine samples (Francis & Newton, 2005), and their concentrations varied considerably across individual samples. The production of esters by yeast during alcoholic fermentation is influenced by several factors, such as those related to must composition; more specifically, sugar content, yeast available nitrogen (YAN, the sum of primary amino nitrogen and ammonia), fermentation temperature, insoluble solids concentration, oxygen availability and yeast strain (Antalick *et al.*, 2015). As the vinification conditions were the same for all wines, it is likely that the differences in ester content were a result of variations in grape must YAN. Positive correlations were observed between ammonia and ethyl butanoate, ethyl hexanoate and ethyl octanoae (Table 3). A tendency for increasing PAN (Primary AminoNitrogen) and isoamyl acetate and ethyl 3-methylbutanoate was also observed. YAN was mostly correlated with ethyl butanoate, ethyl 3-methyl-butanoate, isoamyl acetate and ethyl hexanoate. Although these correlations confirm the importance of YAN fractions in modulating wine esters content, other grape compositional factors may also contribute to wine ester diversity; for example, grape lipids availability, which is also linked to variety (Pérez-Navarro *et al.,* 2019), can influence the production of ester using yeast (Rosi & Bertuccioli, 1992).

The sugar level of musts may play an important role in yeast ester production (Ugliano & Henschke, 2009; Antalick *et al*., 2015; Slaghenaufi *et al*., 2020a). However, within the whole dataset, no correlation emerged between °Brix in musts and ester content in wines. Grape °Brix was observed to be negatively correlated with ethyl 3-methyl butanoate ($R^2 = 0.701$) and ethyl lactate ($R^2 = 0.605$) concentrations in the Corvinone clones subset only. Antalick *et al.* (2015) observed that the influence of grape maturity level on wine ester concentrations varied in relation to grape variety.

Interestingly, different clones of either Corvina or Corvinone showed rather large variations in ester content, which should be further investigated.

2.5. Terpenes and C_{13}-norisoprenoids

Terpene compounds are associated with floral notes and are characteristic of aromatic grape varieties such as Muscat (Jackson, 2008). They are generally considered to potentially contribute to the aroma of white wines (Jackson, 2008). Terpene alcohols, in particular linalool and α-terpineol, were found in higher concentrations in Corvina wines. β-citronellol also varied significantly across wines, with Corvina, Rondinella, Molinara and most of the Corvinone samples generally showing the highest concentrations. Conversely, the highest concentrations of terpinen-4-ol and *cis*- and *trans*- isomers of linalool oxide were observed in the Oseleta sample. In comparison with the data recently reviewed by Black *et al.* (2015), these observations indicate that the terpene content of wines from certain Valpolicella varieties, in particular Corvina and to a lesser extent Corvinone, is not negligible. This should also be considered in light of the observation that terpene alcohols (i.e., linalool, geraniol, α-terpineol and terpinen-4-ol) in Corvina wines can act as precursors to the potent balsamic aroma compounds 1,4- and 1,8-cineole during wine aging (Slaghenaufi & Ugliano, 2018).

Grape-derived terpenes are produced by both the 1-deoxy-D-xylulose-5-phosphate/methylerythritol phosphate (DOXP/MEP) pathway and the mevalonic acid (MVA) pathway. In the case of non-aromatic varieties, such as the ones investigated here, terpenes mostly accumulate as non-volatile glycosidic precursors (Black *et al.,* 2015; Slaghenaufi *et al.,* 2019). Part of these precursors are converted to free aroma compounds during fermentation by both acid and enzymatic hydrolysis, and the liberated compounds can be further transformed by chemical rearrangements or yeast activity (Ugliano *et al.,* 2006; Slaghenaufi *et al*., 2020b; Slaghenaufi & Ugliano, 2018; Rapp *et al.,* 1985). Terpene precursors tend to accumulate in the berry during ripening (Wilson *et al.,* 1984; Costantini *et al.,* 2017); however, for non-aromatic varieties complex terpene accumulation

TABLE 3. Pearson correlations between esters and ammonia, PAN and YAN.

	Ammonia	PAN[a]	YAN[b]	Sugar (°Brix)
Isoamyl acetate	0.331	0.471	0.478	-0.118
n-Hexyl acetate	0.157	0.027	0.114	0.387
Ethyl butanoate	0.597	0.233	0.481	-0.266
Ethyl 3-methyl butanoate	0.430	0.457	0.524	-0.189
Ethyl lactate	0.367	0.233	0.349	-0.069
Ethyl hexanoate	0.651	0.279	0.538	-0.309
Ethyl octanoate	0.528	0.065	0.335	-0.279
Ethyl decanoate	0.457	0.177	0.362	0.089

[a] PAN (Primary Amino Nitrogen)

[b] YAN (Yeast Assimilable Nitrogen, calculated as sum of PAN+Ammonia)

patterns have been observed in response to variety and vintage conditions (Luo *et al.*, 2019). From this point of view, although maturity levels varied across the different grapes used in the present study, out of the group of grapes harvested in the 23-24 °Brix range (namely Corvina, Molinara, Rondinella, Raboso, Sangiovese and Cabernet), Corvina was clearly characterised by increased content of monoterpene compounds; nevertheless, the possibility that Corvinone can also attain equally high terpene levels with a delayed harvest still needs to be investigated.

In the wines of the present study, a positive correlation (Supplementary S.3.) was observed between terpinen-4-ol and *trans*-linalool oxide content (r = 0.609), whereas the r value for the isomers *cis*- was considerably lower (0.430). Linalool concentration was correlated with the level of α-terpineol (r = 0.945), geraniol (r = 0.723), and β-citronellol (r = 0.660). Despite nerol being the *cis*- isomer of geraniol, no strong correlation was observed with the other terpenes.

C_{13}-norisoprenoids are very powerful odour compounds due to their low odour threshold. β-Damascenone was quantitatively the most abundant norisoprenoid in the studied wines, largely exceeding the odour threshold. The concentration of β-damascenone seemed to be related to wine variety: the highest concentrations were found in Corvinone, followed by Molinara, Corvina and Rondinella; while Cabernet showed a concentration similar to Corvina and Rondinella, and Croatina, Raboso and Oseleta were found to be 2 to 7 times less abundant than Corvinone. Small variations in concentrations of β-damascenone between clones of the same variety (Corvina or Corvinone) were observed (Coefficient of variation between 11 and 13.5 %).

2.6. Benzenoid compounds

Relatively low concentrations of vanillin, vanillic alcohol, ethyl vanillate and methyl vanillate were found in the experimental wines, which may be due to the fact that the adopted experimental protocol did not involve any oak contact. These benzenoids can contribute to aromas of sweet spices. However, in our samples they were observed at concentrations below the olfactory thresholds, although it is possible that some synergistic interactions occured between compounds with similar properties contributing to the spicy aroma notes (Cameleyre *et al.*, 2020). From a chemical point of view these compounds seemed to be characteristic of some varieties; for example, vanillin was virtually absent in Cabernet-Sauvignon, Oseleta and Raboso, whereas in most of the other wines it was detected in the range of 11-25 µg/L and reached 41 µg/L in Rondinella.
Benzenoid alcohols, such as vanillic and benzyl alcohol, were higher in Oseleta, Rondinella and Corvina 48, whereas Corvinone 6 exhibited low concentrations for both compounds. Corvina always showed a higher level of benzyl alcohol compared to Corvinone, but this differentiation was not observed for vanillic alcohol.

Oseleta was by far the richest variety in ethyl and methyl vanillate, whereas Molinara was characterised by lower concentrations. No difference was observed between Corvina and Corvinone for ethyl vanillate content. Conversely, a higher methyl vanillate level was found in Corvinone than in Corvina. Finally, the volatile phenols, 4-ethylguaiacol and 4-vinylguaiacol, were found at a very low concentrations in all samples.

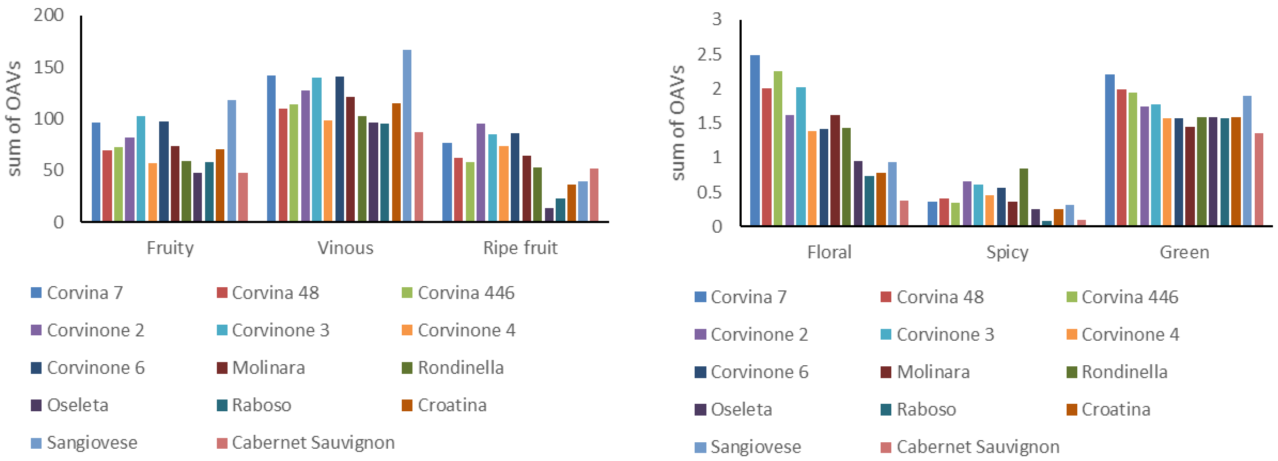

FIGURE 1. Aromatic series in Valpolicella wines.

3. Evaluation of wine aroma profile based on aromatic series

Odour activity values (OAV) is often used to identify the compounds that contribute the most to wine aroma. Compounds with a concentration higher than the olfactory threshold (OAV > 1) are considered to have an impact on wine aroma. However, compounds below their odour threshold should also be considered as they can contribute to wine aroma through synergistic effects (Lopez *et al.,* 1999).

In order to estimate the olfactory profile of studied wines, the compounds were grouped into different aromatic series according to their odour descriptor, and the OAV were summed to give the intensity for each series. The six series were formed according to Sánchez-Palomo *et al.* (2019) with some modification: fruity, floral, vinous, green, spicy and ripe fruit (Supplementary S2). The "fatty" and "sweet" series proposed by Sánchez-Palomo *et al.* (2019) were replaced by "vinous", including all fermentative aromas. The "Ripe fruit" series included norisoprenoids and vanillin. The "green" series included C_6 compounds, as well as 3-methyl-1-butanol as it was recently reported to contribute to the green character of wine (Sáenz-Navajas *et al.,* 2018). The "floral" series was composed of terpenes. These modifications were made in order to obtain a better representation of the aroma descriptors commonly used in wine tasting, and they also took into account the aroma families proposed by Ferreira *et al.* (2007).

As can be seen in Figure 1, the vinous, fruity and ripe fruit series contributed the most to the aroma profile of all the studied wines. The main Valpolicella varieties, Corvina and Corvinone, showed high values for all the aromatic series. In particular, Corvina wines showed the highest floral value (mainly due to the high linalool concentration), followed by Corvinone. In general, local varieties had higher floral levels than Raboso, Croatina, Sangiovese and Cabernet. Corvina also showed the highest value for the green series, which was even higher than Corvinone, despite it being well-recognised that green/herbaceous notes are more characteristic of Corvinone aroma than of Corvina (Nicolini & Mattivi, 1993). This may be due to the possible contribution of some compounds responsible for the green aroma, like methoxy pyrazines (Heymann *et al.,* 1986; Kotseridis *et al.,* 1998), which were not analysed in the present study. Sangiovese was also characterised by high values for the green series, less than Corvina, but more than Corvinone.

Sangiovese showed the highest value for the fruity series. This high value was related to the ester content and, more specifically, to the concentration of isoamyl acetate, which was twice as high as in the other wines. Corvinone 3, Corvinone 6 and Corvina 7, in that order, showed the next highest fruity values. High diversity was observed between the clones of Corvinone, with Corvinone 3 and 6 showing a value almost the double of Corvinone 4, and clone Corvinone 2 being in the middle. In Corvina, clone 7 showed higher fruity levels, but clonal differences were less prominent. In the vinous series, sample behaviour was similar to that of the "fruity" series.

Of the Verona local varieties, Corvina, 1Corvinone, Molinara and Rondinella were characterised by "ripe fruit"; in particular, Corvinone showed the highest value in this series, followed by Corvina, Molinara and Rondinella, which showed more or less the same values. Oseleta showed by far the lowest level of ripe fruit.

Cabernet-Sauvignon showed the lowest values in almost all of the aromatic series, except for the ripe fruit series for which it showed a higher value than the other varieties due to its β-damascenone content. The variety that seemed to have values similar to Corvina were Molinara and Rondinella, even though both varieties showed lower values for the floral and green series. Furthermore, Rondinella were characterised by the highest level of spicy aromas in the whole data set.

4. Phenolic compounds

Polyphenols play an important role in red wine quality, in terms of, for example, colour, astringency and protection from oxidation. Phenolic data are shown in Table 4. Corvina and Corvinone are generally characterised as having low polyphenolic content; likewise, in our experimental wines, Corvina and Corvinone had low total polyphenol content, and only that of Molinara was lower. The amount of total polyphenols found in Oseleta, Croatina, Raboso and Cabernet-Sauvignon was 3-, 2.5-, 2- and 2-fold higher respectively than in the main Valpolicella varieties, Corvina and Corvinone. Wine tannin content was relatively low for most Valpolicella varieties, the only exception being Oseleta and Croatina. Oseleta wines also exhibited the highest concentration of the monomers catechin and epicatechin, while epicatechin gallate was absent in this variety. Corvinone was generally richer in monomers than Corvina

Looking at flavonols, kampferol was detected only in Croatina, Molinara and Cabernet-Sauvignon. Quercetin-3-glucoside was found to be below 10 mg/L in all the Corvina, Corvinone and Molinara samples, while Oseleta and Sangiovese were the richest with a concentration of 51.5 and 37 mg/L respectively. Phenolic acids were almost absent in Corvina and Corvinone, but they were present in all the other varieties.

The anthocyanin content of Corvina, Corvinone and Rondinella wines was generally rather low, which is in agreement with previous findings (Bellincontro *et al.,* 2016). Conversely, Oseleta, Raboso and Croatina wines were characterised by high anthocyanin content (Mattivi *et al.,* 1990; De Rosso *et al.,* 2010). Total anthocyanin content depended on the clone; this was very apparent for Corvinone where clone "2" had almost twice as many anthocyanins as clone "3" (the lowest Corvinone). As regards monomers, Raboso, Croatina, Oseleta, Cabernet and Sangiovese had a high concentration of malvidin-3-glucoside (between 400 and 600 mg/L), which was 4-6 times higher than that found in Corvina. Corvinone showed an intermediate level of malvidin-3-glucoside with a great variability between clones (between 216 and 373 mg/L) with Corvinone 4 reaching the level of Sangiovese. Peonidin was detected only in Oseleta, Raboso, Croatina, Rondinella and Sangiovese. Oseleta and Raboso were characterised by very high levels of delphinidin (more than 300 mg/L), which is over one order of magnitude higher than that in the other varieties. Peonidin and delphinidin have previously been reported as markers of Oseleta and Raboso (De Rosso *et al.,* 2010).

5. Oenological implications for the volatile and phenolic composition of the monovarietal wines

The current regulation of the Valpolicella appellation stipulates that Corvina and Corvinone must be the two main varieties in the final blends, varying from a minimum of 45 % to a maximum of 95 %. Rondinella is limited to the 5-30 % range, and other varieties to a maximum of 25 %, with a maximum limit of 10 % for each grape variety. Figure 2 summarises some of the main characteristics of the monovarietal wines studied. Based on their phenolic and aroma features, it was possible to categorise the wines into two main groups. The first group, characterised by high values in the aromatic series, but with lower polyphenols content, included wines from Corvina, Corvinone, Rondinella and Molinara grapes, which are the main varieties of the Valpolicella blends. These wines are likely to exhibit an aroma profile leaning towards floral, fruity and spicy aroma attributes, but their content in phenolic compounds which contribute to colour, mouthfeel and longevity is rather low.

Conversely, the second group was characterised by a high level of tannins and anthocyanins, but lower values for aroma features, and it included Oseleta, Croatina, Raboso, Sangiovese and Cabernet-Sauvignon. Interestingly, the varieties of the first group have also been reported to be phylogenetically related (Vantini *et al.,* 2003; Cipriani *et al.,* 2010), implying that their chemical proximity reflects a common genetic background. It was therefore surprising to observe that Oseleta, which is also genetically related to the varieties of the first group (Vantini *et al.,* 2003;

TABLE 4. Phenolic composition of studied wines: mean (mg/L) and standard deviation (SD).

	Corvina 7				Corvina 48				Corvina 446				Corvinone 2				Corvinone 3				Corvinone 4				Corvinone 6			
	means		SD		means		SD		means		SD		means		SD		means		SD		means		SD		means		SD	
Total Polyphenols (mg/L of gallic acid equivalent)	1067	±	16.5	bc	1029.67	±	46.67	abc	1221.67	±	127.75	bcd	1035.67	±	57.98	bc	986	±	19.8	ab	1171.33	±	25.5	bc	931.33	±	27.34	ab
Tannins (mg/L of catechin equivalent)	910.56	±	172.19	bcd	633.92	±	4.98	abcd	1006.08	±	132.6	de	544.16	±	48.65	abc	716.32	±	39.6	abcd	617.6	±	74.22	abcd	586.08	±	65.85	abc
Total Anthocyanins (mg/L malvidin-3-glucoside equivalent)	169.3	±	4.3	ab	204.8	±	39.6	ab	236.3	±	6.2	ab	442.3	±	76.1	ab	222.2	±	11.1	ab	334.6	±	1.42	ab	267.3	±	0.6	ab
T/A	5.4	±	0.8	e	3.2	±	0.5	cd	4.3	±	0.5	de	1.2	±	0.2	ab	3.2	±	0.2	cd	1.8	±	0.2	ab	2.2	±	0.2	abc
Malvidin-3-glucoside	123.7	±	14.844	ab	103.8	±	12.456	ab	134.6	±	16.152	ab	216.4	±	25.968	bc	234.9	±	28.188	bc	373.2	±	44.784	cde	256.3	±	30.756	bcd
Delphinidin	22.4	±	2.688	ab	18.2	±	2.184	ab	31.8	±	3.816	ab	22	±	2.64	ab	14.9	±	1.788	ab	35.8	±	4.296	ab	24.7	±	2.964	ab
Peonidin	<0.7			a	<0.7			a	<0.7			a	<0.7			a	<0.7			a	<0.7			a	<0.7			a
Quercetin-3-glucoside	8.6	±	1.032	ab	6	±	0.72	ab	4.5	±	0.54	ab	<0.8			a	3.2	±	0.384	ab	<0.8			a	9.4	±	1.128	abc
Myricetin	3	±	0.36	abc	3	±	0.36	abc	2.7	±	0.324	abc	3	±	0.36	abc	2.6	±	0.312	abc	4.6	±	0.552	bc	4.8	±	0.576	bc
Kaempferol	<0.9			a	<0.9			a	<0.9			a	<0.9			a	<0.9			a	<0.9			a	<0.9			a
Catechin	34	±	4.08	bcd	9	±	1.08	a	26.1	±	3.132	abc	39.7	±	4.764	cd	33	±	3.96	bcd	34.3	±	4.116	bcd	27.6	±	3.312	bc
Epicatechin	3.9	±	0.468	b	4.8	±	0.576	b	4.8	±	0.576	b	10	±	1.2	de	8	±	0.96	cd	4.7	±	0.564	b	5.9	±	0.708	bc
Epicatechin gallate	3	±	0.36	ab	8.2	±	0.984	de	3.5	±	0.42	abc	3.8	±	0.456	abcd	16.1	±	1.932	f	17.1	±	2.052	f	<1.2			a
Caffeic acid	5.4	±	0.648	de	0.9	±	0.108	a	3.4	±	0.408	bcd	0.5	±	0.06	a	1.1	±	0.132	ab	1	±	0.12	a	0.7	±	0.084	a
p-Coumaric acid	0.9	±	0.108	b	<0.2			a	<0.2			a	<0.2			a	<0.2			a	<0.2			a	<0.2			a
Feluric acid	2.8	±	0.336	ab	<0.5			a	<0.5			a	<0.5			a	<0.5			a	<0.5			a	<0.5			a
Gallic acid	3.7	±	0.444	bc	4	±	0.48	bc	4.2	±	0.504	bc	9.5	±	1.14	d	4.9	±	0.588	bc	4.6	±	0.552	bc	2.6	±	0.312	ab

	Molinara				Rondinella				Oseleta				Raboso del piave				Croatina				Sangiovese				Cabernet-Sauvignon			
	means		SD		means		SD		means		SD		means		SD		means		SD		means		SD		means		SD	
Total Polyphenols (mg/L of gallic acid equivalent)	681	±	92.87	a	1562	±	29.23	d	3318	±	261.63	g	2192	±	66.47	e	2626	±	33.94	f	1347	±	54.74	cd	2070	±	16.03	e
Tannins (mg/L of catechin equivalent)	388.32	±	141.42	a	504	±	92.77	ab	2190.08	±	26.25	g	1675.84	±	238.95	f	2203.36	±	12.89	g	957.28	±	40.96	cd	1385.12	±	49.1	ef
Total Anthocyanins (mg/L malvidin-3-glucoside equivalent)	46.8	±	6.8	a	222.7	±	19.2	ab	2448.3	±	260.5	e	1810.8	±	69.9	d	1490.6	±	280.2	cd	540.3	±	6	b	1283.6	±	73	c
T/A	8.3	±	2.7	f	2.3	±	0.4	bc	0.9	±	0.1	a	0.9	±	0.1	a	1.5	±	0.2	ab	1.8	±	0.1	ab	1.1	±	0.1	ab
Malvidin-3-glucoside	22.1	±	2.652	a	213.8	±	25.656	bc	465.8	±	55.896	efg	605.3	±	72.636	g	557.2	±	66.864	fg	410	±	49.2	def	473.7	±	56.844	efg
Delphinidin	3.1	±	0.372	a	47.7	±	5.724	ab	540.9	±	64.908	d	332.1	±	39.852	c	87.7	±	10.524	b	63.1	±	7.572	ab	46.3	±	5.556	ab
Peonidin	<0.7			a	1	±	0.12	a	13.7	±	1.644	c	5.7	±	0.684	b	4.2	±	0.504	b	1	±	0.12	a	<0.7			a
Quercetin-3-glucoside	<0.8			a	18.8	±	2.256	cd	51.5	±	6.18	f	13.1	±	1.572	bc	25.4	±	3.048	d	37	±	4.44	e	25	±	3	d
Myricetin	<1.1			a	<1.1			a	5.6	±	0.672	c	2.2	±	0.264	ab	15.2	±	1.824	d	2.6	±	0.312	abc	18.2	±	2.184	d
Kaempferol	5.4	±	0.648	c	<0.9			a	<0.9			a	<0.9			a	15.2	±	1.824	d	<0.9			a	3.2	±	0.384	b
Catechin	26.9	±	3.228	bc	35.1	±	4.212	bcd	67.4	±	8.088	e	45.2	±	5.424	d	18.7	±	2.244	ab	40.3	±	4.836	cd	29.3	±	3.516	bcd
Epicatechin	<1			a	5	±	0.6	bc	11.6	±	1.392	e	4.5	±	0.54	b	10.2	±	1.224	de	4.5	±	0.54	b	4.1	±	0.492	b
Epicatechin gallate	<1.2			a	4.6	±	0.552	bcd	<1.2			a	7.9	±	0.948	cde	10.3	±	1.236	e	18.1	±	2.172	f	4.1	±	0.492	abcd
Caffeic acid	2.6	±	0.312	abc	5.1	±	0.612	de	7	±	0.84	e	12	±	1.44	f	5.5	±	0.66	de	4.4	±	0.528	cd	4.3	±	0.516	cd
p-Coumaric acid	<0.2			a	1.3	±	0.156	b	4.1	±	0.492	d	3.3	±	0.396	c	0.7	±	0.084	ab	0.8	±	0.096	b	1	±	0.12	b
Feluric acid	0.8	±	0.096	a	5.9	±	0.708	b	13.3	±	1.596	cd	14.7	±	1.764	d	13.6	±	1.632	cd	10.1	±	1.212	c	10.7	±	1.284	c
Gallic acid	2.6	±	0.312	ab	2.6	±	0.312	ab	17.7	±	2.124	e	4	±	0.48	bc	<1			a	5.6	±	0.672	bc	6.6	±	0.792	cd

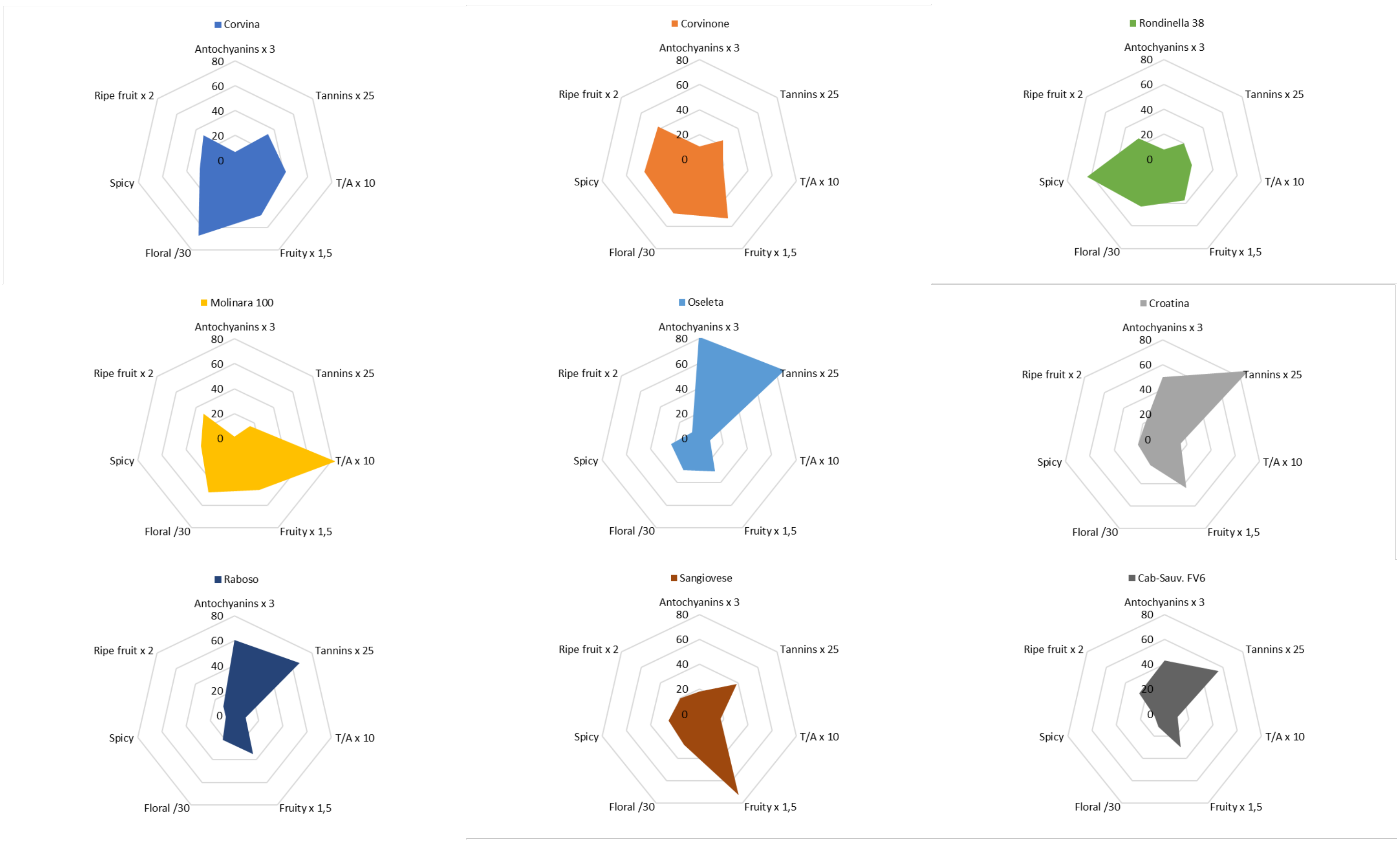

FIGURE 2. Spider charts summarising the main monovarietal wines features.

T/A = tannins/anthocyanins ratio. For better visualisation, the values of "ripe fruit", "anthocyanins", "tannins", "T/A" and "fruity" have been multiplied by 2, 3, 25, 10 and 1.5 respectively, while floral value has been divided by 30. Corvina and Corvinone values are averages of the respective clones.

Cipriani *et al.,* 2010), showed such a different chemical profile, having in particular very high values for phenolic parameters.

Also of particular relevance was the high variability of the anthocyanins/tannin ratio, indicating different potential for colour stabilisation during aging (Gambuti *et al.*, 2017). This component must be carefully considered, particularly in the case of wines destined for aging, such as Valpolicella Superiore which should be aged in the cellar for at least 12 months.

CONCLUSIONS

The present paper characterises aroma and phenolic compounds of monovarietal red wines included in the Valpolicella appellations. The main Valpolicella varieties Corvina and Corvinone have a relatively low phenolic content, but compared to the other varieties they generally had a higher amount of volatile compounds, such as terpenes and norisoprenoids. Terpene richness appears to be a common characteristic of most Valpolicella local varieties, as Rondinella and Molinara also exhibited relatively high terpene levels. Vice-versa, wines produced from the grape varieties Oseleta, Raboso, Croatina and Cabernet-Sauvignon generally had reduced terpene content and higher phenolic levels. As regards Corvina and Corvinone, a certain degree of variability in terms of both volatile and phenolic composition was also observed across clones; this constitutes potentially useful information for new vineyard planting.

The present study was carried out using grapes from a single experimental block, and therefore it did not take into account the variability potentially associated with the complex interaction between different varieties/clones and the pedoclimatic conditions of different sub-regions. These aspects will need to be further investigated. Nevertheless, the results reported in the present paper provide a useful approach to the study of the characteristics of blend-based appellation of origins. As such, in the case of Valpolicella, they indicate that terpenes could play an important role in defining the aroma character of Valpolicella wines - this feature being mostly associated with Corvina. Attention should be paid to the relatively low phenolic content of the main Valpolicella varieties, especially in terms of wines produced for longer aging; winemakers should thus carefully consider the potential contribution of minor varieties, such as Croatina and Oseleta, in order to create distinctive wine styles.

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