SCIENTIA AGRICOLA

DOI: http://dx.doi.org/10.1590/1678-992X-2019-0233

ISSN 1678-992X

Research Article

Characterization of Brazilian Syrah winter wines at bottling and after ageing

Renata Vieira da Mota[1]*, Isabela Peregrino[1], Stephanie Patricia Teran Rivera[2], Neuza Mariko Aymoto Hassimotto[2], André Luiz de Souza[3], Claudia Rita de Souza[1]

[1]Empresa de Pesquisa Agropecuária de Minas Gerais/Núcleo Tecnológico Uva e Vinho. Av. Santa Cruz, 500, C.P. 33 – 37780-000 – Caldas, MG – Brasil.

[2]Universidade de São Paulo/Faculdade de Ciências Farmacêuticas/Centro de Pesquisas em Alimentos – Depto. de Alimentos e Nutrição Experimental, Av. Prof. Lineu Prestes, 580 – Bloco 14 – 05508-000 – São Paulo, SP – Brasil.

[3]Universidade Federal de Alfenas – Depto. de Química, Rod. José Aurélio Vilela, 11999 – 37715-400 – Poços de Caldas, MG – Brasil.

*Corresponding author <rvmota@epamig.br>

Edited by: Luís Guilherme de Lima Ferreira Guido

Received August 29, 2019
Accepted December 27, 2019

ABSTRACT: Double pruning extended the harvest season of wine grape (*Vitis vinifera* L.) to dry winter, enabling production of high quality wines in the southeastern Brazil. Winter harvest allows grapes to fulfill not only technological maturation, but also phenolic ripeness. Winter wines from Syrah grapes harvested from eight vineyards in southeastern Brazil during three harvests were analyzed for their chemical and aromatic composition after bottling and after ageing for 20, 30, and 42 months in bottle. Winter wines have high content of total phenolic compounds, which remained almost constant through ageing, as well as color intensity. Malvidin 3-*O*-glucoside stood out among anthocyanins, remaining 5-10 % after 39 months of ageing. Moreover, malvidin 3-*O*-glucoside-pyruvic acid was the main pyranoanthocyanin identified in winter wine. Polymerized pigments index ranged from 54 % at bottling to 80 % after 42 months of ageing. Young winter wines are rich in ester and monoterpene, as well as alcoholic volatile compounds responsible for ethereal, fruity, flowery, fresh and sweet aromas. Aged winter wines showed higher contents of furfural, geranyl ethyl ether, isoamyl decanoate, α-muurolene and α-calacorene, contributing to sweet, fruity and woody aromas. Syrah winter wines are characterized by high content of phenolic compounds and color stability, and keep good sensorial characteristics after ageing in bottle.

Keywords: double-pruning, composition, color, phenolics, aroma

Introduction

The use of double pruning enables to harvest grapes under climatic conditions that favor grape ripening (Favero et al., 2011; Palliotti et al., 2017; Toda et al., 2019). In southeastern Brazil, this technique allowed vineyard dissemination for high quality fine wine production (Favero et al., 2011).

Wines elaborated from grapes harvested at winter season under low water availability and high thermal amplitude have higher alcoholic and phenols content as well as color intensity than summer wines (Mota et al., 2009). Similar results were obtained with controlled water deficits in 'Cabernet sauvignon' vines (Cáceres-Mella et al., 2018). The authors observed that wines from less irrigated vines exhibited high levels of total phenols, anthocyanins and chroma and therefore showed higher color intensity and sensorial perception of more fullness. Phenolic compounds are the main component of color and mouthfeel in wine, also affecting its ageing ability. Double pruning favors phenolic maturation mainly by high thermal amplitude and low rainfall during autumn-winter season (Favero et al., 2011).

Besides color, aroma is a wine characteristic immediately observed and highly appreciated by consumers. The presence of compounds, such as alcohols, acids, aldehydes, lactones, benzenes, esters, ketones, terpenes, originating from grapes or formed during the fermentation process and ageing, are responsible for the aroma profile of the wine (Vidal and Segurel, 2005; Belda et al., 2017).

Among the cultivars tested under double-pruning management in the southeastern Brazil (Mota et al., 2010, 2011), Syrah vines showed the best adaptation to this management. Winter Syrah wines have been well accepted by consumers, which increased the interest in management of this vineyard in Brazil (Salettes, 2016); however, there is little information on the composition of these wines and the effect of ageing.

As far as the authors know, there is no information in the literature about aromatic profile of Syrah wines from winter harvest. Therefore, this work investigated the volatile aroma compounds in Syrah wines from winter harvest and the effect of bottle ageing in the composition of these wines.

Materials and Methods

Wine samples

Wines were elaborated from grapes harvested in the 2013, 2014 and 2015 seasons from non-irrigated commercial vineyards in Indaiatuba, SP (23°05′ S, 47°13′ W, altitude of 701 m), Santo Antônio do Amparo, MG (20°95′ S, 44°91′ W;, altitude of 990 m), São Bento do Sapucaí, SP (22°41′ S, 45°43′ W, altitude of 886 m), São Sebastião do Paraíso, MG (20°54′ S, 47°06′ W, altitude of 860 m), Três Pontas, MG (21°12′ S, 45°35′ W, altitude of 881 m), Vargem, SP (22°53′ S, 46°24′ W, altitude of 845 m), Itobi, SP (21°42′ S, 46°55′ W, altitude of 840 m) and Três Corações, MG (21°36′ S, 45°07′ W, altitude of 865 m) in the southeastern region of Brazil. All vineyards were over 6 years old of 'Syrah' clone 174 ENTAV-INRA, grafted onto 1103 Paulsen, at vertical shoot position trellis managed under double pruning. The first pruning to induce the vegetative cycle was carried out in September and all bunches at bunch closure stage were removed to avoid harvest in the summer season. In January of the subsequent year, the lignified shoots were pruned to allow the productive cycle during the autumn-winter season (Favero et al., 2011).

Grapes were harvested on average with 23.1 °Brix, pH 3.61 and total acidity 5.92 g L^{-1} tartaric acid. Not all vineyards were represented in the three seasons due to environmental damages or erroneous management that compromised vine production.

Harvested bunches were stored at 4 °C for 24 h at the winery. For each region, 200 kg of grape clusters were destemmed, crushed and placed in 200 L inox fermentation tanks. The musts were inoculated with rehydrated wine yeast *Saccharomyces cerevisiae* × *S. kudriavzevii* and added with 80 mg SO_2 kg^{-1}.

Wine density was determined daily during alcoholic fermentation performed at 21 °C. When the density reached approximately 990 g L^{-1}, wines were racked to 100 L stainless steel tanks. Malolactic fermentation was carried out with native bacteria flora at 21 °C and the presence of malic acid was routinely followed by the paper chromatography method (Amerine and Ough, 1980). When malic acid was not detected by paper chromatography, wines were carefully racked to avoid lees, added with 35 mg SO_2 L^{-1} and kept at 3 °C for 15 d to allow tartaric stabilization. The wines were bottled in 750 mL green glass bottles closed with natural cork and allowed to age in lying position at 15 °C in a dark cell for 20, 30 or 42 months.

Wine composition

The physicochemical analyses consisted of alcohol, fixed acidity (g L^{-1} tartaric acid), pH, residual sugars (g L^{-1}) and ashes (g L^{-1}) (Amerine and Ough, 1980). Color intensity (CI) ($A_{420}+A_{520}+A_{620}$), color hue (A_{420}/A_{520}), color composition (the contribution of each color component in the overall color expressed by the general equation OD n (%) = OD n / CI × 100) and polymerized pigments were evaluated by spectrophotometry (Ribéreau-Gayon et al., 2006; Harbertson and Spayd, 2006). Total flavanoid content was evaluated by Bate-Smith reaction (Ribéreau-Gayon et al., 2006). Anthocyanins and phenolics were measured by the pH differential method (Giusti and Wrosltad, 2000) and Folin-Ciocalteu method (Amerine and Ough, 1980), respectively. Each sample was analyzed in triplicate at bottling and after ageing.

Monomeric Anthocyanin extraction

Anthocyanins and polymeric anthocyanins identification were performed in Syrah winter wines produced in São Bento, Três Pontas, Indaiatuba, Santo Antônio do Amparo and São Sebastião do Paraíso at bottling and after 19 and 36 months of ageing.

Identification and quantification of monomeric anthocyanins were performed by the HPLC-DAD and LC-ESI-MS/MS analyses. Wines samples (5 mL) were concentrated under vacuum at 40 °C on a rotary evaporator to remove the alcohol, and filled up to 10 mL with ultrapure water prior to application to a solid-phase extraction polyamide column (1 g) previously conditioned with methanol and ultrapure water. The de-alcoholized sample (2 mL) was loaded into the column and washed with ultrapure water and eluted with 0.3 % HCl in methanol. The eluates were completely dried using a rotary evaporator under vacuum at 40 °C, resuspended in 5 % acetic acid in methanol and filtered through a 0.45 µm PTFE filter. For the polymeric anthocyanin analysis, wine was filtered through a 0.45 µm PTFE and injected directly.

LC-ESI-MS/MS and HPLC-DAD conditions

Anthocyanins were identified by LC-ESI-MS/MS using a Prominence Liquid Chromatograph attached to an ion trap Esquires-LC mass spectrometer with an electrospray ionization (ESI) interface. We used a 5-µ Prodigy ODS3 column (4.60 × 250 mm) with a flow rate of 1 mL min^{-1} at 25 °C. The mobile phase consisted of solvent A, water ultrapure, formic acid and acetonitrile (95:1:3, v/v/v) and solvent B, water, formic acid and acetonitrile (48:1:51, v/v/v). Anthocyanins were detected at 525 nm (Teixeira et al., 2015). For application to the mass spectrometer after DAD detection, the flow rate was reduced to 0.2 mL min^{-1} Mass spectrometer operated with collision energies of -3500 V and N_2 like dry gas with ESI in the positive mode using a full scan from *m/z* 100 to 1500. Compounds were identified according to comparison with the retention time of authentic standards when possible, as well as by absorption spectrum similarity, mass spectral characteristics and by comparison with the literature data. The calibration curve was performed by injecting the standards malvidin 3-*O*-glucoside, peonidin 3-*O*-glucoside, petunidin 3-*O*-glucoside, delphinidin 3-*O*-glucoside three times at five different concentrations. The acylated form of anthocyanins with coumaroyl and acetyl groups were quantified using the calibration curve of their respective O-glucoside form. The results were expressed as mg 100 mL^{-1}.

Pyranoanthocyanins analysis by LC-qTOF-MS/MS and HPLC-DAD conditions

The identification of the polymeric anthocyanins was performed using a Prominence Liquid Chromatograph linked to a qTOF mass spectrometer Compact model. The LC condition was reverse phase Luna 3 µ C18 (150 × 3.0 mm) at 25 °C. The solvent gradient condition was: phase A: 0.5 % formic acid in ultrapure water and phase B: 0.5 % formic acid in acetonitrile at a flow rate of 0.5 mL min^{-1}. The mass spectrometer conditions were: positive mode, N_2 like dry gas, capillary -3500 V, scan *m/z* 50-1500. The polymeric anthocyanins were identified comparing the mass spectra with data available in the literature (Blanco-Vega et al., 2014).

Volatile extraction and analysis

For the isolation and concentration of volatiles, the headspace solid-phase microextraction technique (HS-SPME) was used according to Gürbüz et al. (2006)

with some modifications. All extractions were carried out using a DVB/CAR/PDMS fiber, of 50/30 μm film thickness. An aliquot of 10 g of wine was placed in 20 mL vials closed with Teflon cap. Vials were heated to 30 °C under agitation with a magnetic stir bar for 10 min for headspace equilibrium. Adsorption time was 45 min at the same temperature. The SPME fiber was then injected directly into a gas chromatograph mass spectrometer operating with ChemStation software. The SPME fiber was held for 10 min at 250 °C for desorption of volatile compounds, which were separated in HP-5MS (30 m × 0.25 mm × 0.25 μm) capillary column with helium as carrier gas at constant flow of 1 mL min^{-1}. Initial oven temperature was 40 °C held for 5 min, then increased to 160 °C at 3 °C min^{-1} and to 250 °C at 10 °C min^{-1} and kept for 10 min before returning to 40 °C, in a total cycle of 64 min; transfer line temperature at 250 °C; MS detector in SCAN mode 30-500 *m/z*.

Volatile compounds were tentatively identified by comparison with the NIST library considering 70 % similarity as the cut-off, further confirming the results with the retention indexes calculated according to the Kovats Index and compared to data reported on Nist Webbook (https://webbook.nist.gov), Chemspider (www.chemspider.com) or PubChem (www.pubchem.ncbi.nlm.nih.gov) websites. Only aromatic compounds with difference in Kovats Retention Indices lower than 70 units up or down were accepted. All analyses were carried out in triplicate.

Statistical analysis

The Partial Least Squares Discriminant Analysis (PLS-DA) was performed to investigate the trends or group formations of wines from different ageing times on all volatile compounds in the wine samples analyzed by the MetaboAnalyst Program (www.metaboanalyst.ca).

Results

At bottling, winter wine composition was on average 14 % alcohol, pH 4.0, fixed acidity 5.4 g L^{-1} tartaric acid, residual sugar 3.1 g L^{-1}, ashes 3.9 g L^{-1}, total anthocyanin content 380 mg L^{-1}, total phenolics 2.4 g L^{-1}, total flavanols 2.7 g L^{-1}, color intensity of 13.5, color hue 0.75, and polymerized pigments 54 % (Table 1).

Ageing decreased the total monomeric anthocyanin content and increased color hue and the polymerized pigments index, with no changes in color intensity (Tables 2 and 3). The monomeric anthocyanins identified in the Brazilian Syrah winter wine were the malvidin-3-O-glucoside (*m/z* 493), peonidin-3-O-glucoside (*m/z* 463), petunidin-3-O-glucoside (*m/z* 479) and delphinidin-3-O-glucoside (m/z 465) and the respective acylated form with coumaroyl and acetyl groups. The malvidin 3-*O*-glucoside was the main anthocyanin for all wine samples (Table 4), remaining 5-10 % of the concentration at bottling after 36 months of ageing.

Contribution of yellow component to the overall wine color was on average 38 % at bottling reaching 41 % after 42 months of ageing, while red color changed from 49 % to 46 % in the same period. Blue component (OD 620) was almost constant during ageing (Tables 1 and 3).

Polymerized pigments ranged from 54 % at bottling to 80 % after 42 months of ageing (Tables 1 and 3). Although not all wine samples were analyzed at 30 and 42 months after ageing, it seems that polymerized pigments reached maximum values after 30 months of ageing and remained constant afterwards.

Among polymerized anthocyanins, 14 pyranoanthocyanins were identified in wine samples, mainly carboxy-pyranoanthocyanins (Vitisin type), hydroxyphenyl pyranoanthocyanin and flavan-3-ol pyranoanthocyanin (Table 5). Vitisin A (*m/z* 561) formed

Table 1 – Physicochemical parameters of Syrah winter wine samples at bottling.

Parameter	2013 winter season						2014 winter season			2015 winter season		
	VAR13*	IND13	SB13	SAA13	SSP13	TP13	VAR14	TC14	SSP14	ITO15	TC15	TP15
Alcohol (% vol)	13	13	14	14	15	13	14	15	16	14	15	14
pH	3.83	3.83	3.99	3.73	3.94	3.99	4.08	3.96	4.27	4.27	4.03	4.21
Fixed acidity (g L^{-1})	6.57	6.75	5.64	6.24	6.22	5.18	5.07	5.56	4.46	4.35	4.85	4.05
Residual sugar (g L^{-1})	3.46	3.46	3.67	3.00	3.60	2.93	2.87	3.47	2.00	2.87	3.34	2.40
Ashes (g L^{-1})	3.75	4.14	3.72	3.21	3.94	3.96	3.54	3.70	4.24	4.76	3.61	4.47
Total polyphenols (g L^{-1})	2.41	2.51	3.30	2.86	2.80	2.49	2.28	1.78	2.50	2.30	1.74	1.95
Total anthocyanins (mg L^{-1})	540.11	427.18	414.61	399.20	443.29	363.80	358.47	200.98	306.50	451.22	293.31	360.70
Total flavanols (g L^{-1})	2.71	2.87	2.98	2.97	3.63	3.53	2.34	1.98	2.88	2.56	1.95	2.42
Color intensity	14.32	15.48	15.49	15.72	17.59	12.73	12.42	10.63	14.98	10.90	10.18	11.82
Color hue	0.61	0.64	0.71	0.65	0.70	0.73	0.71	0.78	0.86	0.86	0.82	0.88
OD 420 %	33	34	36	34	36	36	36	39	40	39	39	40
OD 520 %	54	53	51	53	51	50	50	49	46	46	48	46
OD 620 %	12	12	13	13	13	13	14	12	14	15	13	14
Polymerized pigments (%)	47	52	52	51	54	53	45	64	61	52	59	60

Average values of three samples per region. *Number represents the harvest season; OD = optical density at 420, 520, or 620 nm; VAR = Vargem (SP); IND = Indaiatuba (SP); SB = São Bento do Sapucaí (SP); SAA = Santo Antônio do Amparo (MG); SSP = São Sebastião do Paraíso (MG); TP = Três Pontas (MG); TC = Três Corações (MG); ITO = Itobi (SP).

Table 2 – Physicochemical parameters of Syrah winter wine samples after 20 months of ageing in bottle.

Parameter	2013 winter season						2014 winter season			2015 winter season		
	VAR13*	IND13	SB13	SAA13	SSP13	TP13	VAR14	TC14	SSP14	ITO15	TC15	TP15
Alcohol (% vol)	14	14	14	14	15	13	14	15	16	14	15	14
pH	3.78	3.79	3.91	3.75	3.93	3.85	4.09	3.90	4.16	4.14	3.99	4.13
Fixed acidity (g L^{-1})	5.75	6.16	5.60	5.90	5.43	5.33	5.27	5.99	5.12	4.80	5.47	5.00
Residual sugar (g L^{-1})	3.40	2.53	2.14	3.27	3.33	2.93	2.20	3.20	2.94	2.80	3.13	2.87
Ashes (g L^{-1})	4.09	4.26	3.80	3.34	4.10	4.15	3.56	3.63	4.41	4.71	3.64	4.43
Total polyphenols (g L^{-1})	2.06	2.36	2.40	2.51	2.87	1.90	2.09	1.82	2.54	2.29	1.89	2.13
Total anthocyanins (mg L^{-1})	167.83	147.76	136.82	155.87	156.50	116.27	112.85	57.21	122.97	187.25	100.55	135.74
Total flavanols (g L^{-1})	2.68	3.11	2.90	3.02	3.65	2.85	2.50	1.98	3.30	2.61	2.10	2.52
Color intensity	14.33	14.67	14.90	15.12	17.22	12.43	12.32	12.63	14.98	12.73	11.73	12.86
Color hue	0.72	0.73	0.76	0.75	0.77	0.78	0.88	0.84	0.89	0.89	0.84	0.89
OD 420 %	37	37	38	37	38	38	40	40	41	40	40	41
OD 520 %	50	50	49	50	49	49	45	48	46	46	47	46
OD 620 %	13	13	13	13	14	13	15	12	13	14	13	13
Polymerized pigments (%)	69	69	72	68	73	72	73	83	78	72	78	77

Average values of three samples per region. *Number represents the harvest season; OD = optical density at 420, 520, or 620 nm; VAR = Vargem (SP); IND = Indaiatuba (SP); SB = São Bento do Sapucaí (SP), SAA = Santo Antônio do Amparo (MG); SSP = São Sebastião do Paraíso (MG), TP = Três Pontas (MG), TC = Três Corações (MG); ITO = Itobi (SP).

Table 3 – Physicochemical parameters of Syrah winter wine samples after 30 and 42 months of ageing in bottle.

Parameter	30 months ageing		42 months ageing				
	SSP14*	TC14	IND13	SB13	SAA13	SSP13	TP13
Alcohol (% vol)	16	15	14	14	14	15	13
pH	4.11	3.84	3.79	3.89	3.72	3.92	3.83
Fixed acidity (g L^{-1})	4.99	6.03	5.86	5.37	5.58	5.57	5.84
Residual sugar (g L^{-1})	2.73	2.80	2.93	1.87	2.73	4.00	2.53
Ashes (g L^{-1})	4.25	3.57	4.07	3.62	3.05	3.85	3.83
Total polyphenols (g L^{-1})	2.57	1.77	2.41	2.54	2.60	3.00	2.18
Total anthocyanins (mg L^{-1})	90.06	42.32	74.94	67.26	82.71	82.25	55.17
Total flavanols (g L^{-1})	2.96	1.88	3.08	3.36	3.43	3.74	2.64
Color intensity	15.65	12.42	14.61	14.79	14.72	17.45	12.91
Color hue	0.93	0.86	0.86	0.88	0.87	0.89	0.89
OD 420 %	42	41	40	41	40	41	41
OD 520 %	45	47	46	46	46	46	46
OD 620 %	13	12	13	13	13	13	12
Polymerized pigments (%)	80	85	80	83	79	81	83

Average values of three samples per region. *Number represents the harvest season. OD = optical density at 420, 520, or 620 nm; IND = Indaiatuba (SP); SB = São Bento do Sapucaí (SP); SAA = Santo Antônio do Amparo (MG); SSP = São Sebastião do Paraíso (MG); TP = Três Pontas (MG); TC = Três Corações (MG).

Table 4 – Mass spectra and concentration of monomeric anthocyanins of Syrah winter wine of five regions at bottling and after 19 and 36 months of ageing in bottle.

		Peak	RT	[M]$^+$ (*m/z*)	MS/MS (*m/z*)	SB13	TP13	IND13	SAA13	SSP13
			min							
T_0	Delphinidin-3-glu	1	12.3	465	303	17.9 ± 1.2	nd	10.4 ± 0.1	15.4 ± 0.6	19.2 ± 0.8
	Petunidin-3-glu	3	14.3	479	317	34.3 ± 2.12	24.6 ± 1.7	23.4 ± 0.2	26.0 ± 0.3	35.0 ± 0.6
	Malvidin-3-glu	5	15.6	493	331	269.0 ± 19.3	266.0 ± 22.9	163.7 ± 1.7	114.5 ± 2.1	168.2 ± 0.8
	Petunidin-3-acgly	8	21.8	521	317	10.3 ± 0.5	nd	6.6 ± 0.1	nd	7.2 ± 0.5
	Malvidin-3-acgly	10	22.2	535	331	nd	nd	22.0 ± 1.2	15.3 ± 0.9	nd
	Peonidin-3-cmgly	14	25.6	609	301	22.4 ± 1.0	20.3 ± 1.6	17.5 ± 0.3	16.0 ± 0.1	9.1 ± 1.1
T_{19}	Malvidin-3-glu	5	15.6	493	331	42.1 ± 2.3	37.8 ± 3.8	31.0 ± 0.9	25.7 ± 2.7	28.6 ± 1.3
	Petunidin-3-acgly	8	21.8	521	317	7.5 ± 0.7	3.2 ± 0.01	7.5 ± 0.4	nd	9.6 ± 0.3
T_{36}	Malvidin-3-glu	5	15.6	493	331	16.3 ± 1.1	15.3 ± 0.4	nd	11.7 ± 1.1	17.6 ± 1.8
	Petunidin-3-acgly	8	21.8	521	317	3.7 ± 0.2	2.9 ± 0.0	4.5 ± 0.2	nd	5.1 ± 0.5

RT = retention time; glu = glucoside; acgly = 6''-acetyl-glycoside; cmgly = (6-p-coumaroyl) glycoside; nd = not detected; T_0 = wine at bottling; T_{19} = wine after 19 months of ageing; T_{36} = wine after 36 months of ageing. Petunidin-3-acgly, malvidin-3-acgly and peonidin-3-cmgl were expressed as petunidin-3-glucoside, malvidin-3-glucoside and peonidin-3-glucoside equivalent, respectively. Results expressed as mg 100 mL^{-1}; IND = Indaiatuba; SB = São Bento do Sapucaí; SAA = Santo Antônio do Amparo; SSP = São Sebastião do Paraíso; TP = Três Pontas.

from malvidin 3-*O*-glucoside and pyruvic acid reaction was the most abundant pyranoanthocyanins (He et al., 2012). Ageing decreased the content of vitisin A on average by 10-30 % in most samples, while 10-HP-pymv-3-gly (*m/z* 609) increased during ageing (Table 6).

The Partial Least Squares Discriminant Analysis (PLS-DA) accounted for 63 % of the total data variance. The two-dimensional graph showed a clear separation of aromatic compounds from bottled wines to those over 30 months ageing (Figure 1).

Table 7 summarizes all the aromatic volatile compounds tentatively identified in the samples, regardless of vineyard and ageing. Esters represented the principal class of compounds with 40 aromatic volatile compounds identified, followed by terpenes (17 compounds), benzene (14), and alcohol (12). Esters were found mainly at bottling, but their concentration increased slightly at 30 months ageing.

Discussion

Winter wines composition resemble that of Syrah wines from traditional regions, such as Australia (Antalick et al., 2015), Italy (Condurso et al., 2016), California (Brillante et al., 2018), and South Africa (Hunter and Volschenk, 2018) confirming the great potential of this technique for Brazilian viticulture.

The anthocyanins identified in the Brazilian Syrah winter wines were 3-*O*-glucoside and acylated forms of malvidin, peonidin, petunidin, and delphinidin also described in Syrah wines from Spain (Blanco-Vega et al., 2014).

Table 5 – Mass spectra of pyranoanthocyanins of Syrah winter wine of five regions at bottling and after 19 and 36 months of ageing in bottle.

	Compound	RT	MS (m/z)	MS2 (m/z)
		min		
A-type vitisins (10-carboxy-pyranoanthocyanins)	10-Carboxy-pymv-3-glc (vitisin A)	18.3	561	399
	10-Carboxy-pymv-3-acglc (ac-vitisin A)	19.9	603	399
	10-Carboxy-pymv-3-cmglc (cm-vitisin A)	23.6	707	399
	10-Carboxy-pypn-3-glc	16.9	531	369
	10-Carboxy-pypn-3-cmglc	22.9	677	369
	10-Carboxy-pypt-3-glc	14.4	547	385
	10-Carboxy-pydp-3-glc	10.4	533	371
B-type vitisins (pyranoanthocyanins)	pymv-3-glc (vitisin B)	19.4	517	355
10-Hydroxyphenyl-pyranoanthocyanins	10-HP-pymv-3-glc	34	609	447
	10-HP-pymv-3-acglc	36.5	651	447
	10-HP-pymv-3-cmglc	38.6	755	447
	10-DHP-pymv-3-glc	31.3	625	463
10-Flavanol-pyranoanthocyanins	10-(+)-Catechin-pypn-3-acglc	28.4	817	665, 613, 461
	10-(-)-Epicatechin-pypn-3-acglc	30.5	817	665, 613, 461

glc = glucoside; acglc = 6''-acetyl-glycoside; cmglc = (6-p-coumaroyl) glycoside; pymv = pyranomalvidin; pypn = pyranopeonidin; pypt = pyranopetunidin; pydp = pyranodelfinidin.

Table 6 – Relative percentage of polymeric anthocyanins in winter wine of five regions at bottling and after 19 and 36 months of ageing in bottle.

	SB13			TP13			IND13			SAA13			SSP13		
	T_0	T_{19}	T_{36}	T_0	T_{19}	T_{36}	T_0	T_{19}	T_{36}	T_0	T_{19}	T_{36}	T_0	T_{19}	T_{36}
10-Carboxy-pypt-3-gly	3	4	3	1	2	nd	2	5	5	3	4	4	3	7	7
10-Carboxy-pypn-3-gly	6	6	5	4	4	4	5	7	7	6	6	6	7	8	7
10-Carboxy-pymv-3-gly (vitisin A)	45	41	32	25	20	17	45	54	50	32	32	26	44	45	41
10-Carboxy-pymv-3-acgly (ac-vitisin A)	5	4	3	6	4	3	6	14	14	9	7	5	12	11	9
10-Carboxy-pypn-3-cmgly	2	2	2	2	2	nd	15	3	3	3	3	3	3	3	3
10-Carboxy-pymv-3-cmgly (cm-vitisin A)	7	8	8	6	5	5	3	8	9	7	7	8	8	8	10
TOTAL Carboxy-	68	65	53	44	37	29	76	91	88	60	59	52	77	82	77
10-(+)-Catechin-pypn-3-acgly	2	2	5	4	3	4	4	3	2	5	3	3	3	3	3
10-(-)-Epicatechin-pypn-3-acgly	6	5	6	nd	nd	nd	nd	nd	nd	8	10	9	nd	nd	nd
TOTAL Flavanol-	8	7	11	4	3	4	4	3	2	13	13	12	3	3	3
10-HP-pymv-3-gly	17	17	25	31	34	36	8	9	7	17	17	22	13	10	13
10-HP-pymv-3-acgly	3	2	3	6	5	5	3	2	2	5	4	4	4	2	3
10-HP-pymv-3-cmgly	3	3	5	8	7	6	2	nd	2	5	4	5	4	3	3
10-DHP-pymv-3-gly	-	4	4	8	16	19	nd	nd	nd	nd	3	4	nd	1	3
TOTAL Hydroxyphenyl-	23	26	37	53	62	66	13	11	11	27	28	35	21	16	22

T_0 = wine at bottling; T_{19} = wine after 19 months of ageing; T_{36} = wine after 36 months of ageing. Gly = glycoside; acgly = 6''-acetyl-glycoside; cmgly = (6-p-coumaroyl) glycoside; pymv = pyranomalvidin; pypn = pyranopeonidin; pypt = pyranopetunidin; pydp = pyranodelphinidin; IND = Indaiatuba; SB = São Bento do Sapucaí; SAA = Santo Antônio do Amparo; SSP = São Sebastião do Paraíso; TP = Três Pontas.

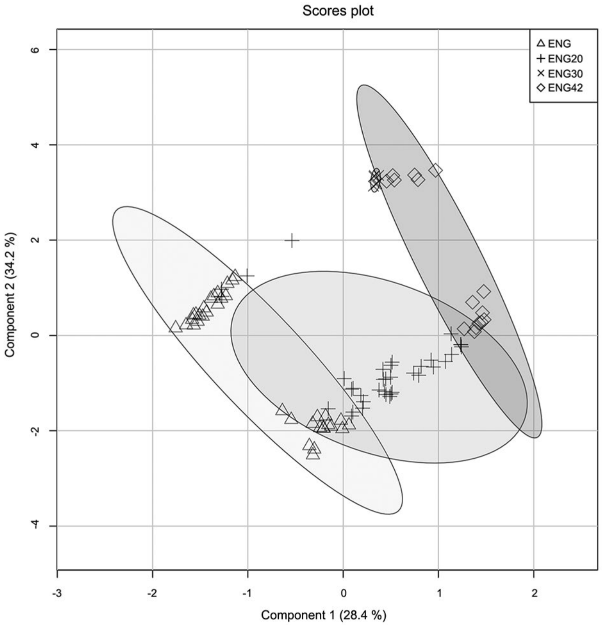

Figure 1 – Discriminant Analysis of aromatic volatile compounds of Syrah wines at bottling (ENG) and after ageing for 20 months (ENG20), 30 months (ENG30), or 42 months (ENG42).

It is well known that a fraction of the anthocyanin pigments disappears rapidly few months after fermentation. These pigments may be either broken down by external factors (temperature, light, oxygen), precipitated in colloidal coloring matter, combined and condensed with tannins, and also forming stable anthocyanin derived pigments, named pyranoanthocyanins. These pigments are produced by reaction between anthocyanins and acetaldehyde, pyruvic acid or vinylphenols, by-products of yeast, in young wine and also from condensation between anthocyanin and/or flavan-3-ols in aged wine (He et al., 2012). The elimination of anthocyanins leads to color loss and is detrimental to wine while pyranoanthocyanins production form more stable molecules responsible for color maintenance (Cheynier et al., 2006).

A reduction in total anthocyanins from 490 to 60 mg L^{-1} followed by an intense reduction in color intensity from bottling to 17 months aged was observed in Italian Syrah wines (Condurso et al., 2016). Color intensity in Brazilian Syrah winter wines, on the other hand, was not affected during ageing as well as total phenolic compounds and flavanols, which remained almost constant through ageing. Moreover, there was an increase in hydroxyphenyl pyranoanthocyanins and

Table 7 – Aromatic volatile compounds tentatively identified in the Syrah winter wine samples.

Compound	Code	CAS	Kovats^a	Odor^b
Acids				
Hexanoic acid	BF	142-62-1	997	Rancid, sour, sharp, pungent, cheesy, fatty
n-decanoic acid	BJ	334-48-5	1374	Unpleasant rancid, sour, fatty, citrus, soapy
Octanoic acid	BC	124-07-2	1194	Fruity-acid
Alkanes				
hexadecane	BW	544-76-3	1599	Mild wax
tetradecane	CH	629-59-4	1400	Mild wax
Alcohols				
1-decanol	AQ	112-30-1	1275	Sweet, fat-like
1-heptanol	AM	111-70-6	977	Woody, oily, fatty
1-hexanol	AL	111-27-3	877	Herbaceous, woody, sweet, green fruit, banana, flower, grass
1-hexanol, 2-ethyl	X	104-76-7	1035	Oily, sweet, flowery, rose, green
1-nonanol	BH	143-08-8	1178	Rose-orange, fat, floral, green, oil
1-octanol	AO	111-87-5	1076	Fresh, orange-rose, sweet, bitter almond, burnt matches, fat, floral
1-octen-3-ol	CT	3391-86-4	984	Sweet, earthy, herbaceous lavender, rose, cucumber, fat, floral, mushroom
2-heptanol	BV	543-49-7	905	Brassy, herbaceous, fruity, green, citrus, earth, mushroom, oil
2-nonanol	CG	628-99-9	1102	Waxy, green, creamy, citrus, orange, cheese, fruity
Cis-3-hexen-1-ol	CK	928-96-1	865	Grassy-green, herbaceous, leafy
3-nonen-1-ol, (Z)	DB	10340-23-5	1158	Fresh, waxy, green, melon, rind, tropical, mushroom
3-octanol	BY	589-98-0	998	Sweet, oily, nutty, herbaceous
Aldehydes				
Decanal	AR	112-31-2	1209	Sweet, waxy, flowery, citrus, fatty
Furfural	N	98-01-1	841	Sweet, woody, almond, fragrant, baked, bread
Nonanal	BD	124-19-6	1105	Fatty, citrus-like
benzeneacetaldehyde	AV	122-78-1	1047	Harsh, green
Benzenes				
benzaldehyde	T	100-52-7	964	Bitter almond

Continue.

Table 7 – Continuation.

Benzene, 1, 2-dimethoxy	G	91-16-7	1151	Sweet, creamy, vanilla, phenolic, musty
Benzeneacetic acid, ethyl ester	U	101-97-3	1247	Sweet, floral, honey, rose, balsam, cocoa
benzofuran	BI	271-89-6	995	Sweet
Ethyl salicylate	AT	118-61-6	1271	Sweet, wintergreen, mint, floral, spicy, balsam
Ethyl benzoate	I	93-89-0	1173	Fruity, dry, must, sweet, wintergreen
Benzyl alcohol	S	100-51-6	1036	Fruity, pungent
Benzyl nitrile	BE	140-29-4	1141	Bitter almonds, spicy, floral
Naphthalene	H	91-20-3	1179	Pungent, resinous
1, 2-Dihydro-1, 1, 6-trimethylnaphthalene	DK	30364-38-6	1351	Licorice (wine off-flavour on ageing)
o-xylene	J	95-47-6	871	Geranium
Phenylethyl alcohol	A	60-12-8	1115	Flowery-rose, bitter, fruity-peach
p-xylene	AF	106-42-3	874	Sweet
Styrene	R	100-42-5	892	Sweet, balsam, floral, plastic
Ketones				
2-nonanone	CJ	821-55-6	1094	Fresh, sweet, green, weedy, earthy, herbal
(E)-beta-damascenone	DH	23726-93-4	1385	Apple, rose, honey, tobacco, sweet
Alkyl sulfide				
1-propanol, 3-(methylthio)-	BS	505-10-2	983	Sulfurous, onion, sweet, soup, vegetable
Ester				
1-butanol, 2-methyl-, acetate	CB	624-41-9	886	Over ripe fruit, sweet banana, juicy, fruit
1-butanol, 3-methyl-, acetate	BA	123-92-2	884	Fruity – banana, pear, apple, glue
Ethyl crotonate	CW	6776-19-8	854	Found in alcoholic beverages. Component of strawberry aroma, guava fruit, pineapple, yellow passion fruit
2-ethylhexyl salicylate	AS	118-60-5	1805	Mild, orchid, sweet, balsam
2-hexenoic acid, ethyl ester	CL	1552-67-6	1051	Fruity – pineapple, apple, green
Phenethyl acetate	W	103-45-7	1259	Floral, rose, sweet, honey, fruity, tropical
Acetic acid, hexyl ester	BG	142-92-7	1019	Fruity – apple, cherry, pear
Octyl acetate	AP	112-14-1	1216	Green, earthy, mushroom, herbal, waxy
Diethyl succinate	AX	123-25-1	1188	Mild, fruity, cooked, apple, ylang
Ethyl 2-methyl butyrate	CZ	7452-79-1	860	Sharp, sweet, green, apple, fruity
Ethyl isovalerate	AH	108-64-5	863	Fruity, sweet, apple, pineapple, tutti frutti
Isoamyl butyrate	AB	106-27-4	1062	Fruity, green, apricot, pear, banana
Ethyl butyrate	Y	105-54-4	808	Fruity, juicy, pineapple, cognac
Ethyl decanoate	AI	110-38-3	1399	Sweet, waxy, fruity, apple, grape, oily, brandy
Methyl decanoate	AJ	110-42-9	1327	Oily, wine, fruity, floral
Propyl decanoate	DL	30673-60-0	1492	Waxy, fruity, fatty, green, vegetable, woody, oily
Ethyl laurate	AE	106-33-2	1595	Sweet, waxy, floral, soapy, clean
Methyl laurate	AN	111-82-0	1526	Waxy, soapy, creamy, coconut, mushroom
Ethyl 9-decenoate	DU	67233-91-4	1390	Fruity, fatty
Ethyl heptanoate	AC	106-30-9	1100	Fruity, pineapple, cognac, rum, wine
Ethyl palmitate	CF	628-97-7	1917	Mild, waxy, fruity, creamy, milky, balsam
Hexanoic acid, 2-methylbutyl ester	CS	2601-13-0	1257	Ethereal
Isobutyl hexanoate	Z	105-79-3	1156	Sweet, fruity, pineapple, green, peach, tropical
Hexanoic acid, ethyl ester	AZ	123-66-0	1003	Fruity – pineapple, banana
Hexanoic acid, methyl ester	AG	106-70-7	933	Ether-like
Hexanoic acid, propyl ester	CD	626-77-7	1098	Sweet, fruity, juicy, pineapple, green, tropical
Isoamyl lactate	DF	19329-89-6	1073	Fruity, creamy, nutty
Isopentyl hexanoate	CP	2198-61-0	1254	Fruity, banana, apple, pineapple, green
n-caprylic acid isobutyl ester	CU	5461-06-3	1351	Fruity, green, oily, floral
Nonanoic acid, ethyl ester	AY	123-29-5	1298	Fruity, rose, waxy, rum, wine, natural, tropical
Nonanoic acid, methyl ester	CM	1731-84-6	1229	Sweet, fruity, pear, waxy, tropical, wine
Isoamyl octanoate	CO	2035-99-6	1449	Sweet, oily, fruity, green, soapy, pineapple, coconut
Octanoic acid, ethyl ester	AD	106-32-1	1204	Fruity, wine, waxy, sweet, apricot, banana, brandy, pear
Octanoic acid, methyl ester	AK	111-11-5	1129	Winy, fruity – orange, oily
Isoamyl decanoate	CR	2306-91-4	1649	Waxy, banana, fruity, sweet, cognac, green

Continue.

Table 7 – Continuation.

Pentadecanoic acid, ethyl ester	DN	41114-00-5	1871	Honey, sweet
Ethyl lactate	M	97-64-3	821	Sharp, tart, fruity, buttery, butterscotch
Propyl octanoate	CA	624-13-5	1294	Coconut, caco, gin
Tetradecanoic acid, ethyl ester	BB	124-06-1	1796	Sweet, waxy, violet, orris
Undecanoic acid, ethyl ester	CE	627-90-7	1496	Soapy, waxy, fatty, cognac, coconut
ether				
Geranyl ethyl ether	DM	40267-72-9	1290	Diffusive, ethereal, fruity, green
Volatile phenols				
Phenol, 2, 4-bis (1, 1-dimethylethyl)	L	96-76-4	1513	phenolic
Phenol, 2-methoxy-	F	90-05-1	1090	Phenolic, smoke, spice, vanilla woody
Phenol, 4-ethyl-	AW	123-07-9	1174	Phenolic, castoreum, smoke, guaiacol
Furans				
Ethyl 2-furoate	BZ	614-99-3	1059	Ethyl benzoate, fruity, floral
Lactones				
butyrolactone	K	96-48-0	917	Sweet, aromatic, buttery, creamy, oily, fatty, caramel
Monoterpenes				
.alpha.-terpineol	O	98-55-5	1191	Pine-like, woody, resinous
Laevo-camphor	BL	464-48-2	1145-NF	Camphor
citronellol	AA	106-22-9	1232	Flowery - rose
menthol	DE	15356-70-4	1176	Mint-like
(±) menthone	D	89-80-5	1155	Mint-like
D-Limonene	CV	5989-27-5	1030	Citrus, orange, fresh, sweet
Levomenthol	CQ	2216-51-5	1174	Peppermint, cooling, mentholic, minty
l-menthone	DD	14073-97-3	1155	Deep menthol, peppermint, herbal, camphor
Methyl salicylate	AU	119-36-8	1193	Wintergreen, mint
p-Cymene	P	99-87-6	1026	Fresh, citrus, terpene, woody, spice
Terpinen-4-ol	BX	562-74-3	1177	Pepper, woody, earth, musty, sweet
Linalool	B	78-70-6	1100	Citrus, floral, sweet, bois de rose, woody, green, blueberry
Eucalyptol	BM	470-82-6	1033	Camphoraceous
Beta-cyclocitral	BK	432-25-7	1222	Tropical, saffron, herbal, clean, rose, oxide, sweet, tobacco, damascene, fruity
Sesquiterpenes				
Calamenene	BO	483-77-2	1522	Herb, spice
.alpha.-Calacorene	DG	21391-99-1	1543	woody
.alpha.-Muurolene	DA	10208-80-7	1499	woody
Pirane				
Nerol oxide	CN	1786-08-9	1158	Green, weedy, cortex, herbal, diphenyl oxide, narcissus, celery
Tetrahydrothiophene				
Blackberry thiophenone	DC	13679-85-1	988	Sulfur, fruity, berry

[a]Linear retention indices calculated on the capillary HP-5MS column according to the Kovats equation. Data were considered within the mean ± 70 units as reported on Nist, Chemspider or PubChem websites - NF Kovats index not identified in the literature; [b]Odors extracted from Good Scents (www.thegoodscentscompany.com) or PubChem (http://pubchem.ncbi.nlm.nih.gov) websites.

flavan-3-ol pyranoanthocyanins in aged wine, pigments probably responsible for the red color of wine.

The polymerized pigment index, applied to define the percentage of free and combined anthocyanins producing color in wine (Harbertson and Spayd, 2006), increased from 54 % at bottling to 80 % after 42 months of ageing, corroborating the contribution of copigmentation reactions to preserve color of winter wines.

The literature does not report aroma compounds in Syrah winter wines. According to Condurso et al. (2016), tipicity and quality of the wine are closely related to volatile aroma compounds from grape and those formed during the vinification process. Syrah wine has been described with spicy, dark fruit, or berry like flavors depending on the terroir. Therefore, studies report different volatile data. For example, rotundone, the sesquiterpene compound responsible for the peppery character of Syrah wines, requires an optimized procedure of extraction and therefore is not always found in Syrah wines samples (Siebert et al., 2008; Cincotta et al., 2015; Condurso et al., 2016).

Freshly fermented wines from vineyards in southeastern Brazil were combined in the left part of the PCA plot while aged wines were displaced to the right part, with positive scores (Figure 1). Loscos et al. (2010) also observed such tendency. The second component reflects vineyard site importance, which will be discussed in another study.

In an attempt to differentiate wine varieties by their volatile compounds profile, Fabani et al. (2013) selected four ester compounds ethyl caprylate (106-32-1), diethyl succinate (123-25-1), ethyl caproate (123-66-0), and isopentyl acetate (123-92-2), one benzene compound, benzyl alcohol (100-51-6) and one alcohol, 1-hexanol (111-27-3) as representative volatile compounds in wines. All these compounds were also found in Syrah winter wines. As mentioned by these authors, ethyl caprylate was also found through wine ageing, but mainly at bottling and in winter wines aged 20 months.

Volatile esters play a significant role in wine aroma, as they are associated to "fruity" and "floral" flavors. Numerous esters compounds were identified in wine samples from thinned and control plants of Syrah vineyards located in Palermo, Italy (Condurso et al., 2016). The most represented esters identified by these authors, ethyl hexanoate (CAS 123-66-0), ethyl octanoate (CAS 106-32-1), and ethyl decanoate (CAS 110-38-3) were also present in Syrah winter wines from southeastern Brazil. However, those with the most contrasting patterns among ageing were 1-butanol, 2-methyl-acetate (624-41-9), 2-hexenoic acid, ethyl ester (1552-67-6), acetic acid, hexyl ester (142-92-7), ethyl heptanoate (106-30-9), hexanoic acid, propyl ester (626-77-7), n-caprylic acid isobutyl ester (5461-06-3), isoamyl decanoate (2306-91-4) identified as fruity aroma compounds, and hexanoic acid, methylbutyl ester (2601-13-0) and hexanoic acid, methyl ester (106-70-7) with ether-like notes.

Diethyl succinate (123-25-1), an ester mentioned as a chemical marker of wine ageing (Fabani et al., 2013) was found after 30 and 42 months ageing, mainly in winter wines aged for 30 months. Isopentyl acetate (123-92-2) another ester, responsible for the banana bouquet, was present at bottling and after 30 months of ageing. Fabani et al. (2013) reported a tendency to find lower levels with ageing in Syrah wines. As our results are qualitatively, we were not able to measure its content in the samples; however, it was found from bottling throughout ageing, with lower amounts after 42 months in the bottle.

Furfural (98-01-1), an aldehyde responsible for almond and caramel aroma, was found in Syrah winter wines over 30 months of age. This volatile compound is formed from carbohydrates during wine ageing; however, it can also be generated from hemicelluloses of the barrels (Condurso et al., 2016).

Among benzene class, benzyl alcohol (100-51-6) and ethyl benzoate (93-89-0) associated to 'flowery' and 'sweet' aromas were also found mainly at 30 months of ageing as well as 1, 2-Dihydro-1, 1, 6-trimethylnaphthalene (30364-38-6), a benzene compound known as off-flavor of ageing. Benzene levels decreased from bottle to 20 months ageing and then increased at 30 months with great loss at 42 months.

The presence of leafy and herbaceous aromas from C6 compounds such as cis-3-hexen-1-ol (928-96-1) released from the enzymatic degradation of lipids from grape cell membrane (Brillante et al., 2018) is related to fresh grape processing. Indeed this compound was found mainly at bottling in Syrah winter wines. Volatile compounds belonging to alcohol, alkyl sulfide, and acids classes were found mainly in young wines.

The volatile phenols associated with smoke, spice, and phenolic aromas (Loscos et al., 2010), guaiacol (90-05-1), and 4-ethylphenol (123-07-9) increased their concentration during ageing.

Terpenes are synthesized during grape maturation. They have pleasant flavor perceived even at low concentrations due to its very low olfactory threshold. The fermentation process has little contribution on terpene levels and therefore their content depends on vineyard management (Condurso et al., 2016). Syrah winter wines showed an increase in monoterpenes until 30 months ageing with a sharp decrease at 42 months, as observed by Loscos at al. (2010) under accelerated ageing process. Citronellol (106-22-9), the rose-like aroma, was found at bottling while D-limonene (5989-27-5) and p-cymene (99-87-6), both contributing to fresh, citrus-like aroma, increased at 30 months ageing. Pepper and peppermint aromas of terpinen-4-ol (562-74-3) and levomenthol (5989-27-5) were found mainly at bottling and at 30 months of ageing, while l-menthone (14073-97-3) content was higher in wines for 30 months aged.

The monoterpene linalool (78-70-6) and the ketone β-damascenone (23726-93-4) characterized as 'floral' and 'fruity' aromas were also present in winter wines, mainly at 30 months of ageing. Norisoprenoids, such as β-damascenone, are formed by an enzymatic reaction of carotenoids that are further subjected to catalytic reactions during wine ageing (Brillante et al., 2018).

Wine health benefits have been attributed to antioxidant, anti-inflammatory, anticarcinogenic, and antibacterial properties of sesquiterpenes (Siebert et al., 2008). Sesquiterpenes α-Muurolene (10208-80-7) and α-calacorene (21391-99-1), which contributes to woody, floral, and herbal aromas, were found mainly after 30 months of ageing.

Acknowledgements

Authors thank the Minas Gerais State Agency for Research and Development (FAPEMIG) and the Brazilian National Council for Scientific and Technological Development (CNPq) for funding, the São Paulo Research Foundation (FAPESP) for the scholarship and the southeast winter wine viticulturists for providing the grapes.

Authors' Contributions

Conceptualization: Mota, R.V.; Souza, C.R.; Peregrino, I.; Hassimotto, N.M.A. **Data acquisition:** Mota, R.V.; Peregrino, I.; Rivera, S.P.T.; Souza, A.L. **Data analysis:** Mota, R.V.; Rivera, S.P.T.; Hassimotto, N.M.A. **Design of methodology:** Mota, R.V.; Peregrino, I.; Hassimotto, N.M.A. **Writing and editing:** Mota, R.V.; Peregrino, I.; Souza, C.R.; Hassimotto, N.M.A.

References

Amerine, M.A.; Ough, C.S. 1980. Methods for Analysis of Musts and Wines. John Wiley, New York, NY, USA.

Antalick, G.; Šuklje, K.; Blackman, J.W.; Meeks, C.; Deloire, A.; Schmidtke, L.M. 2015. Influence of grape composition on red wine ester profile: comparison between Cabernet Sauvignon and Shiraz cultivars from Australian warm climate. Journal of Agricultural and Food Chemistry 63: 4664 – 4672.

Belda, I.; Ruiz, J.; Esteban-Fernández, A.; Navascués, E.; Marquina, D.; Santos, A.; Moreno-Arribas, M.V. 2017. Microbial contribution to wine aroma and its intended use for wine quality improvement. Molecules 22: 189. doi: https://doi.org/10.3390/molecules22020189

Brillante, L.; Martínez-Lüscher, J.; Kaan Kurtural, S. 2018. Applied water and mechanical canopy management affect berry and wine phenolic and aroma composition of grapevine (Vitis vinifera L., cv. Syrah) in central California. Scientia Horticulturae 227: 261–271.

Cáceres-Mella, A.; Ribalta-Pizarro, C.; Villalobos-González, L.; Cuneo, I.F.; Pastenes, C. 2018. Controlled water deficit modifies the phenolic composition and sensory properties in Cabernet Sauvignon wines. Scientia Horticulturae 237: 105–111.

Cheynier, V.; Dueñas-Paton, M.; Salas, E.; Maury, C.; Souquet, J-M.; Sarni-Manchado, P.; Fulcrand, H. 2006. Structure and properties of wine pigments and tannins. American Journal of Enology and Viticulture 57: 298-305.

Cincotta, F.; Verzera, A.; Tripodi, G.; Condurso, C. 2015. Determination of sesquiterpenes in wines by HS-SPME coupled with GC-MS. Chromatography 2: 410-421.

Condurso, C.; Cincotta, F.; Tripodi, G.; Sparacio, A.; Giglio, D.M.L.; Sparla, S.; Verzera, A. 2016. Effects of cluster thinning on wine quality of Syrah cultivar (Vitis vinifera L.). European Food Research and Technology 242: 1719-1726.

Fabani, M.P.; Ravera, M.J.A.; Wunderlin, D.A. 2013. Markers of typical red wine varieties from the Valley of Tulum (San Juan-Argentina) based on VOCs profile and chemometrics. Food Chemistry 141: 1055–1062.

Favero, A.C.; Amorim, D.A.; Mota, R.V.; Soares, A.M.; Souza, C.R.; Regina, M.A. 2011. Double-pruning of 'Syrah' grapevines: a management strategy to harvest wine grapes during the winter in the Brazilian Southeast. Vitis 50: 151–158.

Giusti, M.M.; Wrosltad, R.E. 2000. Characterization and Measurement of Anthocyanins by Uv-Visible Spectroscopy: Current Protocols in Food Analytical Chemistry. John Willey, New York, NY, USA.

Gürbüz, O.; Rouseff, J.M.; Rouseff, R.L. 2006. Comparison of aroma volatiles in commercial Merlot and Cabernet Sauvignon wines using gas chromatography-olfactometry and gas chromatography-mass spectrometry. Journal of Agricultural and Food Chemistry 54: 3990-3996.

Harbertson, J.F.; Spayd, S. 2006. Measuring phenolics in the winery. American Journal of Enology and Viticulture 57: 280-288.

He, F.; Liang, N.; Mu, L.; Pan, Q-H.; Wang, J.; Reeves, M.J.; Duan, C-Q. 2012. Anthocyanins and their variation in red wines. II. Anthocyanin derived pigments and their color evolution. Molecules 17: 1483-1519.

Hunter, J.J.; Volschenk, C.G. 2018. Chemical composition and sensory properties of non-wooded and wooded Shiraz (*Vitis vinifera* L.) wine as affected by vineyard row orientation and grape ripeness level. Journal of the Science of Food and Agriculture 98: 2689–2704.

Loscos, N.; Hernández-Orte, P.; Cacho, J.; Ferreira, V. 2010. Evolution of the aroma composition of wines supplemented with grape flavor precursors from different varietals during accelerated wine ageing. Food Chemistry 120: 205–216.

Mota, R.V.; Amorim, D.A.; Fávero, A.C.; Gloria, M.B.A.; Regina, M.A. 2009. Physico-chemical characterization and bioactive amines in Syrah wines. I. Influence of growing season. Ciência e Tecnologia de Alimentos 29: 380-385 (in Portuguese, with abstract in English).

Mota, R.V.; Favero, A.C.; Silva, C.P.C.; Purgatto, E.; Shiga, T.M.; Regina, M.A. 2011. Wine grape quality of grapevines grown in the cerrado ecoregion of Brazil. Journal International des Sciences de la Vigne et du Vin 45: 101-109.

Mota, R.V.; Silva, C.P.C.; Favero, A.C.; Purgatto, E.; Shiga, T.M.; Regina, M.A. 2010. Physico-chemical composition of wine grapes berries in summer and winter growing seasons. Revista Brasileira de Fruticultura 32: 1127-1137 (in Portuguese, with abstract in English).

Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D. 2006. Phenolic compounds. p. 141-204. In: Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D., eds. Handbook of enology 2. The chemistry of wine: stabilization and treatments. John Wiley, New York, NY, USA.

Salettes, S. 2016. Minas Gerais (Brazil) wine in the country of coffee. = Minas Gerais (Brésil): du vin au pays du café. La Revue du Vin de France 599: 50-53 (in French).

Siebert, T.E.; Wood, C.; Elsey, G.M.; Pollnitz, A.P. 2008. Determination of Rotundone, the pepper aroma impact compound, in grapes and wine. Journal of Agriculture and Food Chemistry 56: 3745–3748.

Vidal, S.; Segurel, M. 2005. Knowledge of aromas of Grenache and Syrah = Connaissance des arômes du Grenache et de La Syrah. Guide de la Vinification Rhodanienne 9: 44-46 (in French).