AJEV | American Journal of Enology and Viticulture

Research Report
DOI: 10.5344/ajev.2023.22059

Aging of Malbec Wines from Mendoza and California: Evolution of Volatile Composition

Rocío B. Pellegrino Vidal[1], Roger B. Boulton[2], Alejandro C. Olivieri[3], and Fernando Buscema[1*]

Abstract

Background and goals

The search for strategies to improve the quality of Argentine Malbec wines has led to experimentation with production of wines that achieve superior sensory properties after prolonged bottle aging. During aging, a series of complex oxidation-reduction and polymerization reactions occur. These reactions, responsible for changing the sensory aspects of wines, can be influenced by a variety of factors (terroir, winemaking practices, storage conditions, etc.). Thus, understanding the chemical processes that take place during bottle aging could significantly impact the enology industry. This work evaluates the evolution of aromatic profiles over time in Malbec wines from Mendoza and California.

Methods and key findings

Wines from Mendoza and California were obtained under standardized conditions. Determination of volatile profiles was carried out on young wines by gas chromatography-mass spectrometry and, subsequently, after seven years of aging. The effect of time and region on volatile profiles was investigated. The aging time showed a significant effect on the aromatic composition. While the profiles obtained after seven years were less diverse than at bottling, they retained a significant number of desirable volatile compounds. Additionally, the volatile profiles of the aged wines still permitted differentiation of samples by region of origin.

Conclusions and significance

The information obtained enabled us to assess the evolution of aromatic profiles during bottle aging of Malbec wines from Mendoza and California, and could be useful in decision-making regarding the blending, marketing, and storage of these wines.

Key words: bottle aging, gas chromatography, Malbec, wine aroma

Introduction

Bottle aging can improve the sensory properties of some wines (Gambuti et al. 2013). This process can range from a few years to more than a century, depending on the nature and composition of the wine. While some wines evolve favorably over time, many others are made to be consumed young. The property that defines whether a wine can withstand long aging is the aging potential (AP), defined as the ability of a given wine to improve its sensory quality over time (Jaffré et al. 2009).

Argentina is the largest producer of Malbec wines in the world, with 86% of its production in the province of Mendoza. During the 20th century, this variety was established as the insignia of the country. The incessant search for new tools and strategies that allow the local wine industry to continue to improve the quality of Argentinian Malbec has led winemakers to experiment with production of age-worthy wines.

Terroir, understood as the environmental, edaphic, and cultural factors of a grapegrowing region (Baker and Clarke 2012), can have a great impact on the chemical composition and sensory attributes of young wines and, consequently, on their AP. In turn, factors associated with winemaking (pH, antioxidant concentration, access to O_2, phenolic composition, and ripening conditions, among others) and external factors (aging temperature, closure type, bottle size, humidity, light exposure, etc.) are expected to also have a major impact on sensory changes.

The evolution of a wine over time can be divided into three stages, during which various electron transfer (oxidation-reduction), hydrolysis, condensation, and polymerization reactions take place. These reactions, which change the sensory aspects of wines, are initiated by the catalytic activation of dissolved O_2. In the presence of tartaric acid and other ligands, and complexes of Fe (II) and possibly other metal cations (Cu, Mn, Cr, Co, Ni), an auto-oxidative process is triggered, leading to formation of various oxidation products (among them acetaldehyde), which become involved in subsequent polymerizations between

---

[1]Catena Institute of Wine, Bodega Catena Zapata, Agrelo, Luján de Cuyo, Mendoza, Argentina; [2]Department of Viticulture and Enology, University of California, Davis, CA, USA; [3]Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Instituto de Química de Rosario (IQUIR-CONICET), Rosario, Argentina.

*Corresponding author (fbuscema@catenainstitute.com)

Manuscript submitted Sept 2022, accepted March 2023, published May 2023

flavanols and anthocyanins (Fulcrand et al. 2006). In the first stage, known as development, chemical changes occur that improve wine sensory quality, characterized by reduced astringency and increased color stabilization. During the second maturity stage, the wine reaches its maximum sensory impact, which is the ideal time for consumption. Finally, a period of deterioration begins, in which the wine loses color and body, often becoming drying on the palate (Ribéreau-Gayon et al. 2006, Linsenmeier et al. 2022).

Storing a bottle of wine for an adequate time allows it to reach its full sensory impact: a more rounded palate and the development of aromatic bouquet. Aromas associated with wood, vanilla, dried fruit, chocolate, and cooked fruit (Ribéreau-Gayon et al. 2006) replace the aromas of young wines (fruity and floral), and color stabilizes from intense purple to reddish hues (Ribéreau-Gayon et al. 2006).

Currently, it is not possible to objectively determine the storage time and conditions necessary to achieve maximum sensory improvement from wine composition, therefore, the future AP of a wine is estimated using sensory analysis. A new strategy for estimating AP has been proposed; applying cognitive definitions from professional tasters regarding the aging potential of champagne reserve wines, this strategy is based on a three-dimensional scale and sensory analysis method (Le Menn et al. 2021). Estimating wine resistance to oxidation is also critical to assess wine aging capacity (Waterhouse and Miao 2021). The information gathered from such an approach, while useful, provides enologists with only a partial view of the aging process. Consequently, studying the link between initial composition and the chemical changes that occur during wine aging is considered central to understanding this process and to predicting AP.

Several authors have investigated the evolution of physicochemical indicators with storage time. The aromatic profile as determined by a panel of tasters provided some clues to define the aging capacity of Burgundy wines (Langlois et al. 2010). This study determined that young wines with low acidity and high astringency had greater AP. It concluded that the concept of *vin de garde* (from French, referring to a wine that is meant for aging) involves a wide variety of sensory aspects such as color, aroma, and flavor. Physicochemical indicators, including the profiles of volatile compounds, phenolics and organic acids, and antioxidant capacity, were determined for a wide range of Cabernet Sauvignon and Merlot vintages from different areas of Bordeaux (Chira et al. 2011). Similar studies have been published on Spanish Tempranillo, Graciano, and Cabernet Sauvignon wines (Monagas et al. 2006), Chilean Cabernet Sauvignon (Lissi et al. 2014), and Treixadura wines (Vázquez-Pateiro et al. 2020). In general, these studies suggest a significant decrease in the concentration of total anthocyanins with aging and a decrease in the concentrations of catechin and proanthocyanidins, consistent with the loss of low-molecular weight phenols and the formation of higher molecular weight tannin polymers. In a more recent publication, Maioli et al. (2022) monitored the chemical and sensory properties of Sangiovese red wines after six and 12 months of aging in different types of tanks and six months in glass bottles. This study found that bottle aging enhanced chemical and sensory differences between wines aged in different types of tanks, and that they were characterized by a higher content of varietal volatiles such as norisoprenoids and terpenes. However, an exhaustive compilation of available studies on the temporal evolution of polyphenols and antioxidant activity in different wines concluded that there is no consistent pattern in the reported results (Lissi et al. 2014).

The sensory and chemical properties of young Malbec wines have been examined (King et al. 2014, Buscema and Boulton 2015, Nelson et al. 2015, Urvieta et al. 2018, 2021). Changes in polyphenol and anthocyanin profiles and elemental composition in wines from different regions of Mendoza and California were also evaluated after five years of aging (Agazzi et al. 2018). However, no previous publications have studied changes in aromatic profile during aging of Malbec wines and the effect of regionality in the aging process. This study analyzed the evolution of the volatile composition of different Malbec wines, made under identical winemaking conditions, from Mendoza and California, and compared the initial aromatic profile with that obtained after seven years of aging under controlled storage conditions.

Materials and Methods

Wine samples

Twenty-six Mendoza wines produced from grapes grown in six different districts within the departments of Luján, San Carlos, and Tupungato were studied. The study also included 15 California wines produced from grapes grown in seven districts within the counties of Napa, Sonoma, Monterey, and Yolo (Table 1; Buscema and Boulton 2015). Plots were selected to provide a representative sample of Malbec grapes from each department. The samples were harvested by hand, in uniform 500 kg batches at 24 to 25 Brix and without perceptible herbaceous notes. The trial was conducted during the 2011 harvest. Wines from Mendoza were made at the Catena Institute of Wine (Mendoza, Argentina) and the California wines were made in the pilot winery at the University of California, Davis (Davis, CA). Subsequently, the wines were stored at 16.5 ± 0.2°C in the UC Davis bottle

Table 1 Wine regions from Mendoza, Argentina and California, USA included in the study.

Region	State, Country	# Viticultural sites assessed
Luján	Mendoza, Argentina	4
Maipú	Mendoza, Argentina	2
San Carlos	Mendoza, Argentina	11
Tupungato	Mendoza, Argentina	9
Lodi	California, USA	2
Monterrey	California, USA	2
Napa	California, USA	4
Sonoma	California, USA	4
Yolo	California, USA	3

cellar. Winemaking practices were comparable for both sample sets, with details as described (Buscema and Boulton 2015). The volatile profiles of the wines were analyzed right after bottling and are identified as '*t*0 wines' (data reported in King et al. 2014). The same wines were then bottle-aged for seven years at 16.5 ± 0.2°C and re-analyzed (the aged wines are referred to as "*t*7 wines").

Volatile profile analysis

The aromatic profiles of the wines were analyzed as described (Hjelmeland et al. 2013). This method is based on the solid-phase microextraction of volatile compounds present in the headspace (HS SPME) and its subsequent analysis by gas chromatography coupled to mass spectrometry (GC-MS). Fifty-seven volatile compounds of interest were semi-quantified using undecanone as the internal standard. As previously reported, these compounds are important contributors to aroma in a wide variety of red wines, including Malbec (Kotseridis et al. 2000, Campo et al. 2005, Goldner and Zamora 2007), and are associated with aroma attributes such as berries (ethyl and acetate esters), violets (ionones), herbal (C6 alcohols), sweet-caramel (phenyl acetaldehyde, linalool), and woody (oak lactone) (Escudero et al. 2007).

Chemical analyses of the identified compounds were performed in triplicate (Table 2). Chemical spectra, calculated retention times, and experimental retention times were compared to those obtained for the reference compounds in a previous work, with the exception of three compounds (vitispirane I and II and α-cedrene), due to unavailability (Hjelmeland et al. 2013). Experimental and reference retention indices and the ions selected for SIM detection are shown (Table 2).

The analysis was carried out as follows: 10 mL wine sample was combined with 50 ng L-1, 2-undecanone, and 3 g NaCl in a glass vial with magnetic crimp caps (Supelco). The samples were then exposed to a 2 cm divinylbenzene/

Table 2 A list of the compounds measured using headspace solid-phase microextraction gas chromatography-mass spectrometry, their CAS number, retention time, retention index (RI), calculated retention index (CRI), and selected ion monitoring (SIM) qualifying ions.

	Volatile compound	CAS #	Ret. time (min)	RI	CRI	SIM ions
1	Ethyl acetate	141-78-6	3,105	907[a]	915	43, 61, 88
2	Ethyl isobutyrate	97-62-1	4,559	955[a]	960	43, 71, 116
3	Diacetyl	431-03-08	4,794	970[a]	967	43, 86
4	α-Pyrene	80-56-8	5,939	1032[a]	1003	93, 121, 136
5	Ethyl butyrate	105-54-4	6,599	1028[a]	1022	116, 88, 71
6	Ethyl 2-methylbutyrate	7452-79-1	7,168	1050[a]	1038	57, 102, 130
7	Ethyl isovalerate	108-64-5	7,769	1069[b]	1055	85, 88, 130
8	Hexanal	66-25-1	8,150	1084[a]	1066	56, 72, 100
9	Isobutanol	78-83-1	8,825	1099[a]	1101	43, 74, 55
10	Isoamyl acetate	123-92-2	9,926	1132[b]	1126	55, 87, 130
11	α-Terpinene	99-86-5	12,212	1178[a]	1178	93, 121, 136
12	Limonene	138-86-3	13,060	1178[a]	1197	68, 93, 136
13	Eucalyptol	470-82-6	13,480	1213[a]	1206	93, 108, 154
14	Isoamyl alcohol	123-51-3	13,910	1205[a]	1216	57, 70, 88
15	Ethyl hexanoate	123-66-0	14,890	1220[a]	1238	88, 99, 144
16	*p*-Cymene	99-87-6	16,260	1261[a]	1269	91, 119, 134
17	Hexyl acetate	142-92-7	16,654	1270[a]	1278	43, 84, 144
18	Acetoin	513-86-0	16,898	1287[a]	1284	43, 45, 88
19	Octanal	124-13-0	17,236	1280[a]	1297	56, 84, 128
20	Hexanol	111-27-3	20,503	1360[a]	1366	56, 69, 102
21	(Z) -3-Hexenol	928-96-1	21,761	1391[a]	1395	67, 82, 100
22	Ethyl octanoate	106-32-1	23,797	1436[a]	1443	88, 101, 172
23	*cis*-Linalool oxide	5989-33-3	24,083	1420[a]	1450	59, 68, 170
24	Furfural	98-01-1	24,730	1455[a]	1465	67, 95, 96
25	*trans*-Linalool oxide	23007-29-6	25,279	1453[b]	1478	59, 68, 170
26	Camphor	76-22-2	26,626	1491[a]	1510	95, 108, 152
27	Vitispirane I	99944-79-3	27,273	1515[c]	1526	93, 177, 193
28	Vitispirane II	99881-85-3	27,396	1515[c]	1560	93, 177, 194
29	Linalool	78-70-6	28,629	1537[a]	1560	71, 93, 154
30	α-Cedrene	469-61-4	28,747	1570[b]	1562	119, 161, 204
31	5-Methylfurfural	620-02-0	29,157	1560[a]	1573	53, 109, 110
32	Phenylacetaldehyde	122-78-1	31,701	1625[a]	1637	91, 92, 120
33	Ethyl decanoate	110-38-3	32,003	1636[a]	1645	88, 101, 200

Continued on next page.

carboxen/polydimethylsiloxane (DVB/CAR/PDMS) (Supelco) 23 gauge SPME fiber for 30 min at 40°C with agitation. Chromatographic analysis was performed using an SPME inlet liner (0.7 mm i.d.; Supleco) and a DB-Wax (polyethylene glycol) capillary column (30 m, 0.25 mm i.d., and 0.25 μm film thickness; J&W Scientific). The inlet temperature was maintained at 240°C and the SPME fiber was desorbed in split mode, using a split ratio of 20:1. Helium was used as the carrier gas with a constant flow of 1 mL/min. An oven temperature gradient was used to achieve resolution of the analytes. An initial oven temperature of 40°C was held for 5 min, then increased by 3°C/min to 180°C, and then by 30°C/min to 240°C. Finally, the oven temperature was kept at 240°C for another 10 min. An electron ionization source was used, with a source temperature of 230°C and an electron energy of 70 eV. The samples were analyzed using a 6890 gas chromatograph coupled to a 5975 MSD set at 240°C (Agilent Technologies), equipped with an MPS2 autosampler (Gerstel). The instrument was controlled by Maestro (version 1.2.3.1, Gerstel) and the data were analyzed using ChemStation software (E.01.01.335, Agilent Technologies).

Statistical analyses

The factors studied were age and origin: (i) aging time, indicated by *t*0 (after five to six months of aging for California wines, or seven to nine months for Mendoza wines) and *t*7 (after seven years of aging); and (ii) geographic origin of the vineyards. This factor was examined both as the effect of region (Mendoza versus California) and of the subregions or departments (see Table 1). Principal component analysis (PCA) was used as a multivariate technique for the characterization and exploration of the samples. The confidence ellipses were calculated at a significance level of $\alpha = 0.05$. Partial least squares-discriminant analysis (PLS-DA) was used to build a classification model of the samples based on their volatile profiles, using software developed by Zontov et al. (2020).

Results and Discussion

Evolution of volatile profiles

The wine volatile profiles at *t*0 were analyzed in a previous study (King et al. 2014). There were significant differences between the volatile compositions of Malbec wines from Mendoza and California. Mendoza wines were characterized by a greater presence of terpenes associated with floral and fruity aromas (eugenol, ionones, syringol, camphor and cymene, among others) and by volatile phenols and lactones associated with woody and spicy aromas. California wine volatile profiles were similar to each other, with a predominance of terpenes (linalool, limonene, and damascenone)

Table 2 *continued* A list of the compounds measured using headspace solid-phase microextraction gas chromatography-mass spectrometry, their CAS number, retention time, retention index (RI), calculated retention index (CRI), and selected ion monitoring (SIM) qualifying ions.

	Volatile compound	CAS #	Ret. time (min)	RI	CRI	SIM ions
34	Methionol	505-10-2	34,929	1723[a]	1722	61, 73, 106
35	β-Citronellol	106-22-9	36,939	1762[a]	1778	69, 82, 156
36	2-Phenethyl acetate	103-45-7	38,235	1829[a]	1814	91, 104, 121
37	β-Damascenone	23726-93-4	38,454	1813[a]	1820	69, 121, 190
38	α-Ionone	127-41-3	39,471	1809[a]	1850	93, 121, 192
39	Guaiacol	90-05-1	39,828	1859[a]	1860	81, 109, 124
40	Benzyl alcohol	100-51-6	40,477	1865[b]	1879	79, 107, 108
41	*cis*-Oak lactone	55013-32-6	40,609	1886[a]	1883	87, 99, 156
42	2-Phenethyl alcohol	60-12-8	41,678	1925[a]	1916	65, 103, 122
43	β-Ionone	79-77-6	42,475	1912[a]	1940	135, 177, 192
44	*trans*-Oak lactone	39212-23-2	42,918	1933[a]	1954	87, 99, 156
45	4-Methylguaiacol	93-51-6	43,060	2067[a]	1958	95, 123, 138
46	γ-Nonalactone	104-61-0	45,236	2042[a]	2027	85, 99, 156
47	2-Ethylphenol	90-00-6	46,971	2054[b]	2085	77, 107, 122
48	*trans*-Ethyl cinnamate	103-36-6	48,522	2139[a]	2138	103, 131, 176
49	Eugenol	97-53-0	49,772	2141[a]	2182	103, 149, 164
50	4-Ethylphenol	123-07-9	50,080	2200[b]	2193	77, 107, 122
51	4-Vinilguayacol	7786-61-0	50,566	2198[a]	2110	107, 135, 150
52	Syringol	91-10-1	52,419	2296[a]	2279	111, 139, 154
53	Isoeugenol	97-54-1	53,438	2250[a]	2340	103, 149, 164
54	Farnesol	106-28-5	53,606	2350[a]	2363	69, 81, 164
55	γ-Dodecalactone	2305-05-7	53,679	2350[a]	2363	85, 100, 128, 198
56	Vanillin	121-33-5	55,417	2569[a]	2584	109, 151, 152

[a] Acree and Arn 2004.
[b] El-Sayed 2023.
[c] Humpf and Schreier 1991.

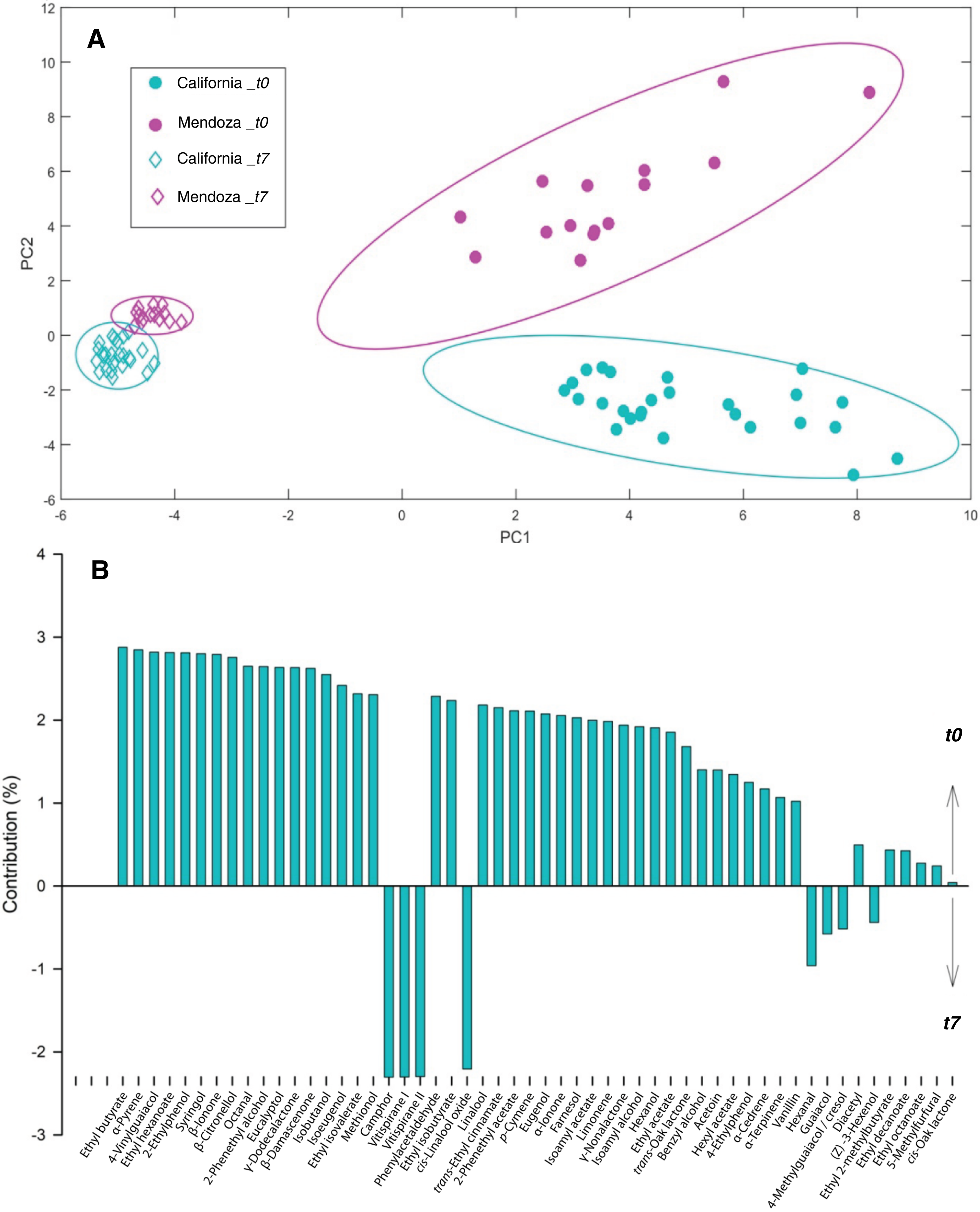

Figure 1 **A**) Principal component analysis (PCA) separation of samples by aging time and region using volatile composition. Mendoza_*t0* are shown as pink dots; California_*t0*, as cyan dots; Mendoza_*t7*, as pink diamonds; and California_*t7*, as cyan diamonds. Confidence ellipses were calculated at a significance level of α = 0.05. **B**) Percentage contribution of variables (volatile compounds) to PC1 in PCA of young versus old wine samples.

and several esters. Multivariate analysis showed that it is possible to differentiate Mendoza wines from California wines based on volatile composition. However, the wines could not be separated more finely by department/county of origin.

This study compares the volatile profiles of the Malbec wines at *t*0 with the *t*7 profiles, generated after seven years aging in the bottle using PCA (Figure 1). The profile of aromatic compounds in the Malbec wines changed significantly after seven years aging (confidence ellipses with a significance of $\alpha = 0.05$). On the other hand, the *t*7 profiles clustered closer together than those of the *t*0 samples, demonstrating that the differences in volatile profiles decreased considerably over time. Component 1 (PC1, the abscissa) represents 98% of the explained variance.

The changes in concentrations of volatile compounds contributing to PC1 represent chemical changes in wines after seven years aging (Figure 1B, Table 3). Over time, in general there were lower concentrations of compounds associated with fruity, fresh, and floral aromas, and a simultaneous increase in the concentration of volatile compounds related to spicy, woody, and toasted aromas. This development of the so-called bouquet, bottle bouquet, or bottle-aged character, is in concordance with similar studies performed on other wine varieties (Pereira et al. 2014, Moreira et al. 2016, Cassino et al. 2019).

A recent study analyzed the effect of temperature, closure type, and aging time on the phenolic and volatile composition of Mendoza Malbec wines during 24 months of aging (Giuffrida de Esteban et al. 2019). While the aging times in that study were significantly shorter than the aging period applied in this work, similar trends were observed in the levels of different families of compounds: both studies show a decrease in the levels of terpenoids, volatile phenols, and esters over time. Similar results were found in a 20-month aging study of Pinot noir wines (Cantu et al. 2021).

Finally, it is important to note that although the wines studied here were never in contact with wood during the winemaking process, *t*0 wines showed the presence of numerous compounds usually associated with oak maturation, including vanillin, oak lactones, whiskey lactone, furfural, and guaiacol. Consistent with these results, descriptive sensory analysis found woody aromas in Malbec samples from Mendoza at *t*0, as reported by King et al. (2014) and Heymann et al. (2015). This finding demonstrates that contact with wood is not the only source of such compounds in Malbec wines, although it may be the most significant. Analysis of the same samples after seven years of aging showed that the concentrations of some of these components decreased with time. Although these findings are contrary to some reports (Morata 2019), there are no previous studies on the evolution of volatile composition in Malbec wines without oak aging and more studies are needed on this topic. A recent study evaluated aromatic profiles of Pinot noir wines with no oak exposure after eight and 20 months of bottle aging (Cantu et al. 2021). This study found no oak lactones, vanillin guaiacol, or other wood-related compounds, suggesting the phenomena observed in our study could be specific to Malbec wines.

Further data treatment was performed to assess the differences in volatile profiles between *t*0 and *t*7, and between region of origin. The full data set was divided into two subsets: a training set (70% of the samples) and a test set (the remaining 30% of the samples). The data were subjected first to mean centering. Next, the training set was used to build a PLS-DA classification model between the four classes (Mendoza_*t*0, California_*t*0, Mendoza_*t*7, and California_*t*7). Five latent variables were needed to achieve proper classification. While a high percentage of variation was explained by only two PCs in the PCA, three extra components were necessary in the PLS-DA, showing that minor components also influenced the classification. The PLS-DA model was then employed to predict the classes of the samples in the test set, achieving a successful classification of 100% of samples and demonstrating that there were significant differences in the volatile profiles of the studied samples, owing to both sample origin and bottle aging time.

Regionality after aging

Once the temporal evolution of the samples was analyzed, we compared the volatile profiles of the Malbecs

Table 3 Predominant volatile compounds at *t0* and *t7* in Malbec wines from Mendoza and California, with origin and associated aromatic descriptors.

	Compound family	Examples	Origin	Aromas[a]
t0	Esters	Ethyl butylate, hexyl acetate, ethyl 2-methylbutyrate, ethyl hexanoate, vinylguaiacol	Alcoholic and malolactic fermentations	Fruity, floral
	Terpenes	Ionones, damascenones, β-citronellol, eucalyptol, linalool, limonene, eugenol	Berries	Fruity, floral, fresh
	Phenols	2-Ethylphenol, 2-phenethyl alcohol	Malolactic fermentation	Spicy
t7	Aldehydes	Furfural	Berries, malolactic fermentation	Vanilla, toasted
	Terpenes	Camphor, linalool oxides, and vitispiranes	Berries	Fresh, woody, earthy

[a] Peinado et al. 2004, Escudero et al. 2007, and Morata 2018.

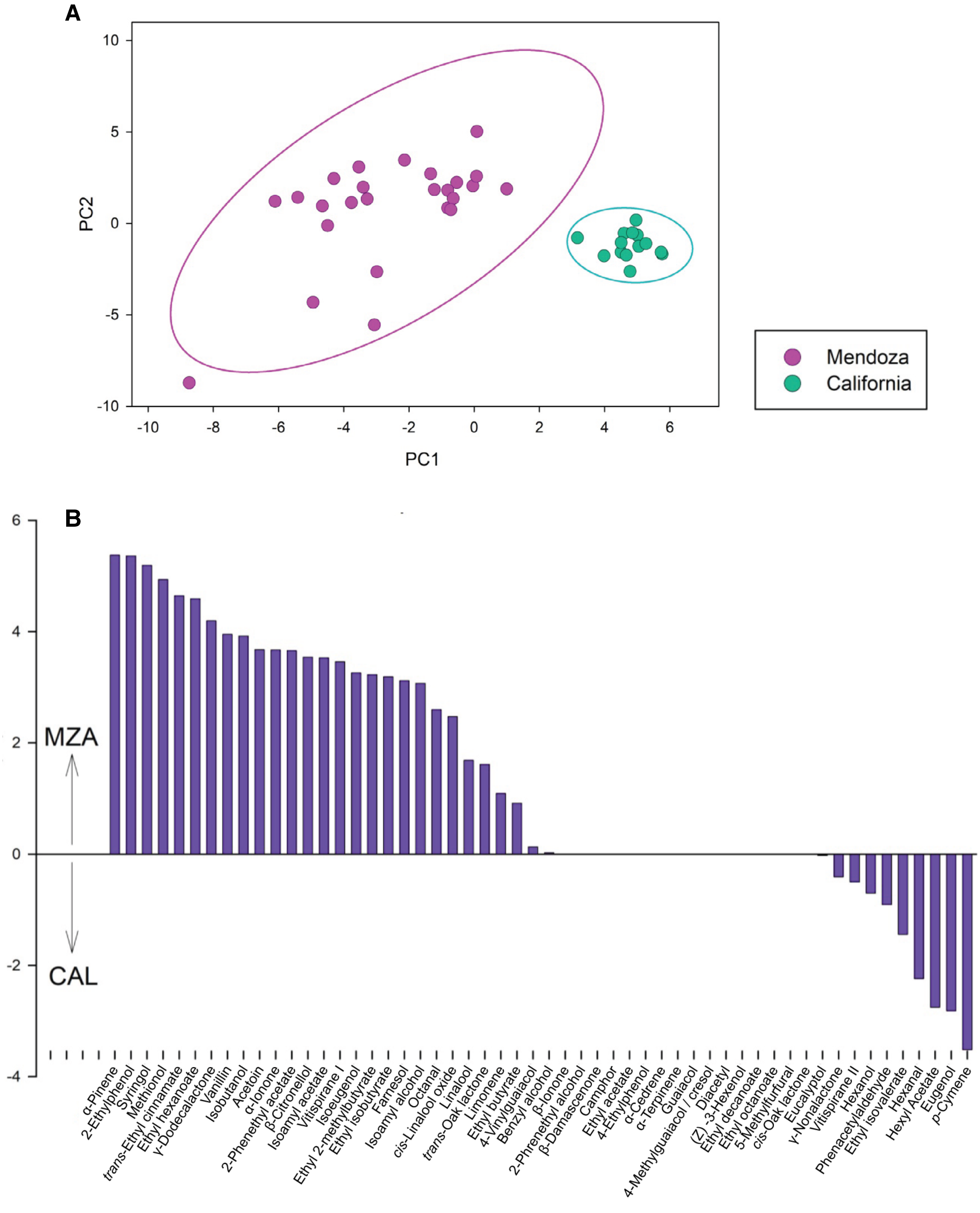

Figure 2 (**A**) Principal component analysis (PCA) separation of samples by region of origin at *t7*, using volatile composition. Argentinian wines are shown as pink dots and California wines, as cyan dots. Confidence ellipses were calculated at a significance level of α = 0.05. **B**) Percentage contribution of variables (volatile compounds) to PC1 in PCA comparing wine regions (Mendoza versus California) after seven years of aging.

from Mendoza with those of the Malbecs from California, after seven years of aging. The analysis by PCA is shown in Figure 2A. There were significant differences in the profiles of aromatic compounds at *t*7 according to the region of origin. There was a greater diversity of profiles in the Mendoza samples, evidenced by the greater dispersion of the sample scores in the PCA graph. In this analysis, PC1 represented 99% of the explained variance. The individual chemicals contributing to PC1 were also determined (Figure 2B).

The more significant contributions to the volatile profiles of the analyzed wines at *t*7 are presented (Table 4). Wines from Mendoza were characterized by many compounds of interest, associated with a broad variety of aromas such as fruity and fresh, spicy, woody, and vanilla (Peinado et al. 2004, Escudero et al. 2007, Morata 2019). For their part, California wines were characterized by less complex aromatic profiles, with compounds associated with fruity, spicy, and woody descriptors. Some characteristic compounds were present in wines from both origins, but most of these were more abundant in Argentinean Malbecs. While the difference in aromatic diversity observed in this study is mostly associated with regionality, the aromatic profiles could also have been influenced by the California vines being grafted, while those from Argentina were own-rooted. Rootstock has been reported to have an impact on the volatile composition of wines (Romero et al. 2019, Wang et al. 2019, Vilanova et al. 2021).

Further analysis of the volatile compositions of the seven-year-old wines showed that there was no differentiation by subregion or department. As previously mentioned, the same results were obtained when analyzing the aromatic data at *t*0, i.e., no particular trends or clustering by department or subregion was observed. However, it is important to point out that our previous studies have been able to discriminate these and other similar Malbec samples from different departments, using descriptive sensory analysis and polyphenolic profiles, in both young and aged Malbec samples (Agazzi et al. 2018, Urvieta et al. 2018, 2021). This shows there is a significant effect of season and/or site on sensory perception and chemical composition of the same set of wines.

Finally, ionones, a group of compounds of particular importance in Malbec that are associated with violet aroma, was recorded at *t*0 in the wines from both regions, but only the Mendoza samples showed detectable concentrations at *t*7. These compounds not only are associated with desirable floral aromas, but also interact with other volatile components, enhancing and/or masking the perception of other aromas (Escudero et al. 2007, Ferreira et al. 2016).

Table 4 Predominant volatile compounds at *t7* in Malbec wines from Mendoza and California, and associated aromas.

	Mendoza		**California**	
Family	**Compound**	**Aromas**[a]	**Compound**	**Aromas**[a]
Acetates	Ethyl acetate	Fruity, sweet	Ethyl acetate	Fruity, sweet
Alcohols	(Z) -3-Hexenol[b]	Fresh, herbal	(Z) -3-Hexenol	Fresh, herbal
	Hexanol	Herbaceous, resin	Hexanol	Herbaceous, resin
	Isoamyl alcohol	Malt, whisky	Isoamyl alcohol	Malt, whisky
Aldehydes	Hexanal[b]	Herbaceous	Hexanal	Herbaceous
	5-Methyl furfural	Spice, caramel	5-Methyl furfural	Spice, caramel
Esters	Ethyl decanoate	Sweet, brandy	Ethyl decanoate	Sweet, brandy
	Ethyl octanoate[b]	Sweet, brandy	Ethyl octanoate[b]	Sweet, brandy
	Ethyl 2-methylbutyrate[b]	Apple, berries	Ethyl 2-methylbutyrate	Apple, berries
Phenols	Guaiacol	Smoky, spicy	Guaiacol	Smoky, spicy
	4-Methylguaiacol[b]	Spicy, leathery	4-Methylguaiacol	Spicy, leathery
	Vanillin*	Vanilla		
Lactones	γ-Nonalactone	Coconut, peach		
	cis-Oak lactone	Coconut, spicy	*cis*-Oak lactone	Coconut, spicy
Terpenes	α-Ionone	Floral, violets		
	Vitispirane I[b]	Wood, floral	Vitispirane I	Wood, floral
	Vitispirane II[b]	Woody, floral	Vitispirane II	Woody, floral
	Camphor[b]		Camphor	
	α-Terpinene	Woody, herbal	α-Terpinene	Woody, herbal
	α-Cedrene	Woody	α-Cedrene	Woody
	Linalool oxides[b]	Fresh, floral, earthy	Linalool oxides[b]	Fresh, floral, earthy
Others	Acetoin	Butter, cream		
	Diacetyl	Butter	Diacetyl	Butter

[a] Peinado et al. 2004, Escudero et al. 2007, and Morata 2018.
[b] Significantly different concentration between one region and the other.

Since the aroma compounds were only semiquantified, their absolute concentrations are unknown and cannot be compared with the thresholds of perception. However, the presence of ionones and other compounds of interest (furfural, camphor, vanillin, eugenol, etc.) after seven years of aging shows that the Malbec wines maintained a rich volatile profile, characteristic of their region of origin, suggesting high AP.

The authors propose to continue this study by evaluating the contribution of volatile compounds to aged Malbec wine aroma using gas chromatography coupled with olfactometry (Welke et al. 2021) and descriptive sensory analysis. However, our current findings could have a direct impact on decision making for wineries in Mendoza and California. For example, the shorter lifespan of desirable volatile compounds in California Malbecs suggests that California wineries could benefit from using less oak and selling their wines more rapidly to preserve a distinctive volatile fingerprint. California Malbecs could be used as a blender if a longer AP is desired. In contrast, this study indicates that Malbec wines from Mendoza could be used both as a blender and as a single varietal. Finally, these results should encourage California growers to try different plant materials to search for Malbec wines that better preserve their unique volatile profiles.

Conclusions

The evolution of aromatic compounds during a relatively long period of bottle-aging (i.e., seven years) of Malbec wines was examined for the first time. When comparing the results obtained at the beginning and after seven years of aging, it was observed that there is a significant time effect on the volatile profiles of Malbec wines. Several compounds associated primarily with fruity and floral aromas are predominant in the younger wines, while the *t*7 wines are characterized by an abundance of compounds related to woody, smoky, fresh, vanilla, and earthy aromas. Even after seven years of aging, the wines are easily differentiated by region of origin. Although a loss of diversity is observed in the aromatic profiles over time, it is not very significant in Mendoza wines. Furthermore, a large variety of aromatic compounds considered 'desirable' or 'of interest' were present in the Mendoza Malbecs after seven years of bottle aging. Thus, the Malbec wines from Mendoza were more suitable for aging than the wines from California. The results obtained in this study could prove helpful to wineries when making decisions about winemaking, aging, and commercialization of Malbec wines.

Acknowledgments

The authors thank Roy Urvieta and Martha Stoumen for their assistance in winemaking and the Catena Zapata family for financial support. R.B.P.V. thanks CONICET for a postdoctoral fellowship. The authors declare that there are no conflicts of financial and personal relationships in this work. F.B. and A.C.O. should be considered joint senior authors.

References

Acree T and Arn H. 2004. Flavornet and Human Odor Space. www.flavornet.org

Agazzi FM, Nelson J, Tanabe CK, Doyle C, Boulton RB and Buscema F. 2018. Aging of Malbec wines from Mendoza and California: Evolution of phenolic and elemental composition. Food Chem 269:103-110. DOI: 10.1016/j.foodchem.2018.06.142

Baker J and Clarke JR. 2012. Wine: Flavour Chemistry. 2d ed. Wiley-Blackwell, New Jersey.

Buscema F and Boulton RB. 2015. Phenolic composition of Malbec: A comparative study of research-scale wines between Argentina and the United States. Am J Enol Vitic 66:30-36. DOI: 10.5344/ajev.2014.14006

Campo E, Ferreira V, Escudero A and Cacho J. 2005. Prediction of the wine sensory properties related to grape variety from dynamic-headspace gas chromatography-olfactometry data. J Agric Food Chem 53:5682-5690. DOI: 10.1021/jf047870a

Cantu A, Lafontaine S, Frias I, Sokolowsky M, Yeh A, Lestringant P et al. 2021. Investigating the impact of regionality on the sensorial and chemical aging characteristics of Pinot noir grown throughout the U.S. West coast. Food Chem 337:127720. DOI: 10.1016/j.foodchem.2020.127720

Cassino C, Tsolakis C, Bonello F, Gianotti V and Osella D. 2019. Wine evolution during bottle aging, studied by ^{1}H NMR spectroscopy and multivariate statistical analysis. Food Res Int 116:566-577. DOI: 10.1016/j.foodres.2018.08.075

Chira K, Pacella N, Jourdes M and Teissedre PL. 2011. Chemical and sensory evaluation of Bordeaux wines (Cabernet-Sauvignon and Merlot) and correlation with wine age. Food Chem 126:1971-1977. DOI: 10.1016/j.foodchem.2010.12.056

El-Sayed AM. 2023. The Pherobase: Database of Pheromones and Semiochemicals. https://www.pherobase.com

Escudero A, Campo E, Fariña L, Cacho J and Ferreira V. 2007. Analytical characterization of the aroma of five premium red wines. Insights into the role of odor families and the concept of fruitiness of wines. J Agric Food Chem 55:4501-4510. DOI: 10.1021/jf0636418

Ferreira V, Sáenz-Navajas M-P, Campo E, Herrero P, de la Fuente A and Fernández-Zurbano P. 2016. Sensory interactions between six common aroma vectors explain four main red wine aroma nuances. Food Chem 199:447-456. DOI: 10.1016/j.foodchem.2015.12.048

Fulcrand H, Dueñas M, Salas E and Cheynier V. 2006. Phenolic reactions during winemaking and aging. Am J Enol Vitic 57:289-297. DOI: 10.5344/ajev.2006.57.3.289

Gambuti A, Rinaldi A, Ugliano M and Moio L. 2013. Evolution of phenolic compounds and astringency during aging of red wine: Effect of oxygen exposure before and after bottling. J Agric Food Chem 61:1618-1627. DOI: 10.1021/jf302822b

Giuffrida de Esteban ML, Ubeda C, Heredia FJ, Catania AA, Assof MV, Fanzone ML et al. 2019. Impact of closure type and storage temperature on chemical and sensory composition of Malbec wines (Mendoza, Argentina) during aging in bottle. Food Res Int 125:E108553. DOI: 10.1016/j.foodres.2019.108553

Goldner MC and Zamora MC. 2007. Sensory characterization of *Vitis Vinifera* cv. Malbec wines from seven viticulture regions of Argentina. J Sens Studies 22:520-532. DOI: 10.1111/j.1745-459X.2007.00123.x

Heymann H, Robinson AL, Buscema F, Stoumen ME, King ES, Hopfer H et al. 2015. Effect of region on the volatile composition and sensory profiles of Malbec and Cabernet Sauvignon wines. *In* Advances in Wine Research. ACS Symposium Series. Ebeler SE et al. (eds.), pp. 109-122. American Chemical Society, Washington, DC. DOI: 10.1021/bk-2015-1203.ch007

Hjelmeland AK, King ES, Ebeler SE and Heymann H. 2013. Characterizing the chemical and sensory profiles of United States Cabernet Sauvignon wines and blends. Am J Enol Vitic 64:169-179. DOI: 10.5344/ajev.2012.12107

Humpf HU and Schreier P. 1991. Bound aroma compounds from the fruit and the leaves of blackberry (*Rubus laciniata* L.). J Agric Food Chem 39:1830-1832. DOI: 10.1021/jf00010a028

Jaffré J, Valentin D, Dacremont C and Peyron D. 2009. Burgundy red wines: Representation of potential for aging. Food Qual Prefer 20:505-513. DOI: 10.1016/j.foodqual.2009.05.001

King ES, Stoumen M, Buscema F, Hjelmeland AK, Ebeler SE, Heymann H et al. 2014. Regional sensory and chemical characteristics of Malbec wines from Mendoza and California. Food Chem 143:256-267. DOI: 10.1016/j.foodchem.2013.07.085

Kotseridis Y, Razungles A, Bertrand A and Baumes R. 2000. Differentiation of the aromas of Merlot and Cabernet Sauvignon wines using sensory and instrumental analysis. J Agric Food Chem 48:5383-5388. DOI: 10.1021/jf000401y

Langlois J, Ballester J, Campo E, Dacremont C and Peyron D. 2010. Combining olfactory and gustatory clues in the judgment of aging potential of red wine by wine professionals. Am J Enol Vitic 61:15-22. DOI: 10.5344/ajev.2010.61.1.15

Le Menn N, Marchal R, Demarville D, Casenave P, Tempere S, Campbell-Sills H et al. 2021. Development of a new sensory analysis methodology for predicting wine aging potential. Application to champagne reserve wines. Food Qual Prefer 94:104316. DOI: 10.1016/j.foodqual.2021.104316

Linsenmeier AW, Rauhut D and Sponholz WR. 2022. Aging and flavor deterioration in wine. *In* Managing Wine Quality, Volume Two: Oenology and Wine Quality. 2d ed. Reynolds AG (ed.), pp. 559-594. Woodhead Publishing, Cambridge, MA.

Lissi E, Campos AM, Calderón C, Lobato S and López-Alarcón C. 2014. Effects of aging on the antioxidant capacity of red wines. *In* Processing and Impact on Antioxidants in Beverages. Elsevier, Amsterdam, Netherlands. DOI: 10.1016/B978-0-12-404738-9.00008-8

Maioli F, Picchi M, Guerrini L, Parenti A, Domizio P, Andrenelli L et al. 2022. Monitoring of Sangiovese red wine chemical and sensory parameters along one-year aging in different tank materials and glass bottle. ACS Food Sci Technol 2:221-239. DOI: 10.1021/acsfoodscitech.1c00329

Monagas M, Gómez-Cordovés C and Bartolomé B. 2006. Evolution of the phenolic content of red wines from *Vitis vinifera* L. during aging in bottle. Food Chem 95:405-412. DOI: 10.1016/j.foodchem.2005.01.004

Morata A (ed.). 2019. Red Wine Technology. Elsevier Inc, Cambridge, MA.

Moreira N, Lopes P, Ferreira H, Cabral M and de Pinho PG. 2016. Influence of packaging and aging on the red wine volatile composition and sensory attributes. Food Packag Shelf Life 8:14-23. DOI: 10.1016/j.fpsl.2016.02.005

Nelson J, Hopfer H, Gilleland G, Cuthbertson D, Boulton R and Ebeler SE. 2015. Elemental profiling of Malbec wines under controlled conditions using microwave plasma-atomic emission spectroscopy. Am J Enol Vitic 66:373-378. DOI: 10.5344/ajev.2015.14120

Peinado RA, Moreno J, Bueno JE, Moreno JA and Mauricio JC. 2004. Comparative study of aromatic compounds in two young white wines subjected to pre-fermentative cryomaceration. Food Chem 84:585-590. DOI: 10.1016/S0308-8146(03)00282-6

Pereira V, Cacho J and Marques JC. 2014. Volatile profile of Madeira wines submitted to traditional accelerated aging. Food Chem 162:122-134. DOI: 10.1016/j.foodchem.2014.04.039

Ribéreau-Gayon P, Glories Y, Maujean A and Dubourdieu D. 2006. Handbook of Enology Volume 2: The Chemistry of Wine Stabilization and Treatments. 2d ed. John Wiley & Sons, Ltd., New Jersey. DOI: 10.1002/0470010398

Romero P, Botía P, del Amor FM, Gil-Muñoz R, Flores P and Navarro JM. 2019. Interactive effects of the rootstock and the deficit irrigation technique on wine composition, nutraceutical potential, aromatic profile, and sensory attributes under semiarid and water limiting conditions. Agric Water Manage 225:105733. DOI: 10.1016/j.agwat.2019.105733

Urvieta R, Buscema F, Bottini R, Coste B and Fontana A. 2018. Phenolic and sensory profiles discriminate geographical indications for Malbec wines from different regions of Mendoza, Argentina. Food Chem 265:120-127. DOI: 10.1016/j.foodchem.2018.05.083

Urvieta R, Jones G, Buscema F, Bottini R and Fontana A. 2021. Terroir and vintage discrimination of Malbec wines based on phenolic composition across multiple sites in Mendoza, Argentina. Sci Rep 11:1-13. DOI: 10.1038/s41598-021-82306-0

Vázquez-Pateiro I, Arias-González U, Mirás-Avalos JM and Falqué E. 2020. Evolution of the aroma of Treixadura wines during bottle aging. Foods 9:1419. DOI: 10.3390/foods9101419

Vilanova M, Genisheva Z, Tubío M, Alvarez K, Lissarrague JR and Oliveira JM. 2021. Rootstock effect on volatile composition of Albariño wines. Appl Sci 11:2135. DOI: 10.3390/app11052135

Wang Y, Chen W-K, Gao X-T, He L, Yang X-H, He F et al. 2019. Rootstock-mediated effects on Cabernet Sauvignon performance: Vine growth, berry ripening, flavonoids, and aromatic profiles. Int J Mol Sci 20:401. DOI: 10.3390/ijms20020401

Waterhouse AL and Miao Y. 2021. Can chemical analysis predict wine aging capacity? Foods 10:654. DOI: 10.3390/foods10030654

Welke JE, Hernandes KC, Nicolli KP, Barbará JA, Biasoto ACT and Zini CA. 2021. Role of gas chromatography and olfactometry to understand the wine aroma: Achievements denoted by multidimensional analysis. J Sep Sci 44:135-168. DOI: 10.1002/jssc.202000813

Zontov YV, Rodionova OY, Kucheryavskiy SV and Pomerantsev AL. 2020. PLS-DA- A MATLAB GUI tool for hard and soft approaches to partial least squares discriminant analysis. Chemo Intel Lab Sys 203:104064. DOI: 10.1016/j.chemolab.2020.104064