**Resurgence of minority and autochthonous grapevine varieties in South America:
A review about their oenological potential**

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ABSTRACT

Contrary to the general trend to produce wine from the most famous grapevine varieties, associated to the French paradigm, such as Cabernet-Sauvignon, Merlot, Pinot Noir, Syrah, Sauvignon Blanc and Chardonnay, there is a slight tendency to revalorize and preserve the minority or autochthonous grapevine varieties within the world wine scenario. South American wine region is not exempt from this reality, where most of the varieties derived from the varieties brought after European colonization. This has allowed to provide new wines with distinctive identity that has provided a marked differentiation of quality to the current homogenized wine production. Moreover, the varietal homogenization increases the vineyard genetic vulnerability in relation to the emergence of grapevine diseases, which the commonly cultivated varieties are not

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resistant. This review summarizes the oenological potential of minority or autochthonous grapevine varieties cultivated within the South American wine region, focused on Argentina, Chile and Bolivia, according to the current revalorization of the viticultural heritage.

Keywords: Carignan; Carmenère; Cereza; Grosse Méridle; Listán Prieto; Moscatel de Alejandría; Torrontés Riojano; Vicchoqueña

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INTRODUCTION

Traditionally, the existence of up to 24,000 different grapevine variety denominations has been considered.¹ Currently, important studies lead to the conclusion that the number of grapevine varieties can be much smaller.²⁻⁸ In that sense, the world wine market is limited to the production of a small amount of grapevine varieties coming mostly from Spain, France and Italy. According to the International Organization of Vine and Wine⁹ these countries of the European Union, are the largest producers of wine in the world, respectively devoting 1,021, 793, and 705 thousand hectares (Kha) of cultivable land to this purpose. In this way, few grapevine varieties such as Cabernet-Sauvignon, Chardonnay, Merlot, Malbec, Tempranillo, Sangiovese, among others, account for a large surface of the vineyard planted worldwide.¹⁰ However, the introduction and spread of the aforementioned grapevine varieties, mostly in South America, has caused a massive loss of minority and autochthonous grapevine varieties traditionally grown in different wine growing regions.¹¹⁻¹⁶ Moreover, the disappearance of a large number of old grapevine varieties and the varietal homogenization of the vineyard entail an increase in genetic vulnerability in relation to the spread of pathogens against which the cultivated varieties are not resistant.^{15,17-19}

Over the last years, a new productive tendency has gradually been introduced in the world wine industry in favor of the production and preservation of minority grapevine varieties.^{15,16,20-29} In contrast to the general trend to produce wine from globally disseminated grapevine varieties, associated to the French paradigm, there is a slight tendency to increase the number of studies about minority or autochthonous

grapevine varieties. The aim is to seek distinct products, different from the current homogenized wine production.³⁰⁻⁴⁰ Despite the above, there are few studies that evaluate the oenological potential of these varieties and most of them focus on regions with a great winemaking tradition such as Aragón, Galicia, La Rioja and La Mancha (Spain), including other countries such as Georgia and Azerbaijan that seek to maintain and provide products linked to the territory with different organoleptic characteristics.^{15,25,38-40} Additionally, emerging studies about minority, autochthonous or wild grape varieties have been recently conducted in South America and in others wine-growing regions in order to provide productive alternatives to traditional varieties and diversify the range of products offered in the wine market.^{24,26-28,31-33,37,41-44} Therefore, this review summarizes the studies that evaluate the oenological potential of minority and autochthonous grapevine varieties located in different South American, focused on Argentina, Chile and Bolivia wine growing regions as alternative to the traditional varieties on the world wine scenario, and provides additional information about the management of these varieties with an oenological perspective.

MINORITY AND AUTOCHTHONOUS VARIETIES

Argentina

Argentine wine scenario is not very different to the aforementioned, in which most of the winemaking production is aimed at international commonly used varieties such as Malbec, Cabernet-Sauvignon, Merlot, Pinot Noir, Chardonnay and Sauvignon Blanc.⁴⁵⁻⁵³ Around the 17th and 18th century, the varieties Criolla Chica (96.4 %),

Moscatel de Alejandría, Moscatel Blanco and Moscatel Rosado (3.5 %), Mollar Cano (0.1 %) and others such as Ferral de America, Cereza de América and Criolla Grande dominated the viniculture in Argentina.^{7,8} However, as in Chile, was carried out a rapid transformation of the wine industry during the 90s when there was a reconversion of these old grapevine varieties to varieties of high wine value mainly coming from France.⁵⁴⁻⁵⁶ According to the exposed by Prieto et al.,⁵⁷ Argentina holds around 74,195 ha cultivated with autochthonous varieties, representing about 33% of the national vineyard surface, which accounts a total of 220,848 ha. These authors reported that the most cultivated autochthonous varieties are Cereza (29,190 ha), Criolla Grande (15,970 ha), Pedro Giménez (11,389 ha) and Torrontés Riojano (8,221 ha). Aliquó et al.⁸ reported that European cultivars, such as Moscatel de Alejandría, Muscat à Petits Grains, Listán Prieto, Mollar Cano and Malbec, were involved in natural crossings resulting in different South American cultivars as the exposed above (Fig. 1). Nowadays, the oenological potential of these varieties is questioned due to their possible low aptitude, especially for the elaboration of red wines. However, the study about oenological potential of these varieties are scarce and it seems to be that Torrontés Riojano variety presents a high oenological potential to produce high quality wines.

Cereza

Cereza (*Vitis vinifera* L.) (Fig. 2) is the most abundant criolla variety and the second most cultivated in Argentina, after Malbec, accounting a 12.5 % of the total vineyard area planted in the country.⁵⁷ This autochthonous variety comes from a natural

crossing between Moscatel de Alejandría and Listán Prieto (Fig. 1).⁸ Cereza variety is cultivated mainly in Mendoza (53.5%) and San Juan (40.9%) but it is also present in other provinces (5.5%), among which Catamarca and La Rioja stand out (Fig. 3).⁵⁸ Cereza is a very vigorous variety, rustic and resistant to soil salinity, reasons why, it has been used as a rootstock for other varieties when retrofitting a vineyard.⁵⁸ Cereza is susceptible to *Plasmopara viticola* and the incidence of *Botrytis cinerea*.⁵⁸ Generally, Cereza and Criolla Grande productivity are associated to a low oenological potential and despite that Cereza is considered of multipurpose, most of its productivity is destined to the elaboration of wines and concentrated musts.⁵⁸

Torrontés Riojano

Torrontés Riojano (*Vitis vinifera* L.) (Fig. 2) is an aromatic white autochthonous grape variety cultivated in Argentina that commonly produces dry wines with distinct Muscat flavor.⁵⁹ This autochthonous variety resulted from a natural crossing between Moscatel de Alejandría and Listán Prieto varieties that arrived in Argentina during the Spanish colonization (Fig. 1).^{8,60} Previous researches reported that Torrontés Riojano is characterized by being an aromatic variety, presenting a high terpenoid content compared to Muscat.⁶¹ Additionally, Romano et al.⁶² reported that the most abundant free monoterpenes found in this variety were β -citronellol, geraniol, hotrienol, limonene, linalool, nerol and α -terpineol, which gives honey, rose and azahar aromas to the producing wines. Viticultural managements in grapevines slightly affect monoterpenoids content in grapes, and the concentration of these compounds in wines,

is mostly affected by their extraction from grapes and by transformations of precursors or free volatiles during fermentation and storage.⁶³ Therefore, pre-fermentative macerations, harder pressing or the use of pectolytic enzymes may to increase the extraction of free and bound monoterpenoids.⁶³

Currently, more researches have been carried out to evaluate the enological potential of this autochthonous variety with the aim to diversify the Argentine varietal offer of wines.⁵⁷ However, the reported works that evaluate oenological potential of this variety are scarce. Pérez et al.⁶⁴ showed that as the intensity of pressing increased, total acidity decreased, while pH and soluble solids extraction increased in Torrontés Riojano grapes. In this way, 0.7 bars applied in crushing grapes allowed the maximum extraction of soluble solids, while this same pressure on grapes achieved an extraction of 80% of them. Additionally, draining Torrontés Riojano musts reached the lowest concentration of varietals and fermentative volatile compounds compared to press must, and linalool and ethyl octanoate were the most abundant volatile compounds in wines. Linalool confers flowery and Muscat aromas to wines, while ethyl octanoate contribute to banana and pear aroma of the wine.⁶⁵ Fanzone et al.⁶⁶ characterized chemically and sensory Torrontés Riojano wines from different location in Argentina (see Fig. 3). These authors reported that the wines from Cafayate and Luján de Cuyo presented higher level of terpenes and acetates of higher alcohols, while wines from Colalao del Valle showed an important abundance of medium-chain fatty acids and their corresponding ethyl esters. Respect to sensory analysis, Torrontés Riojano wines from Cafayate, Luján de Cuyo and Chilecito were characterized by floral, citrus and acid,

while Pocito and Colalao del Valle wines were described with greater bitterness and volume in the mouth, presenting honey and fresh fruit aromas. Pérez et al.⁴⁴ reported that the Torrontés Riojano musts fermented at 14 °C, supplemented with ammonium salts at the middle point of alcoholic fermentation, showed the maximal concentration of terpenes and lower levels of pH and volatile acidity in the produced wines. These authors also reported that the musts from Torrontés Riojano fermented at 22 °C, supplemented with ammonium salts, resulted in the most aromatic wines qualified by a sensory panel, identifying pineapple and banana notes, which was related to their greater amounts of higher alcohol acetates.

Pedro Giménez

Pedro Giménez (*Vitis vinifera* L) (Fig. 2) is an indigenous grapevine variety, and the most abundant white variety cultivated in Argentina.⁶⁷ Ampelographic differences and microsatellites markers allowed the distinction between Pedro Giménez and the Spanish Pedro Ximénez, mostly cultivated in Jerez, Spain.^{68,69} Pedro Giménez is the progeny from Moscatel de Alejandría and Listán Prieto, being the latest one the most likely female progenitor (Fig. 1).⁶⁹ Pedro Giménez variety produces wines with high intensity fruit aromas such as apple and pear.⁶⁸ To our knowledge, few studies have been carried out about the oenological potential of Pedro Giménez grape variety. Maturano et al.⁷⁰ reported that certain volatile compounds such as β -damascenone, α -ionone, β -linalool, geraniol, ethyl butanoate, ethyl hexanoate and ethyl octanoate were the most prevalent aroma-active compounds in Pedro Giménez grapes. These authors

suggested that, according to the monoterpene levels achieved by this variety, it is possible to indicate that Pedro Giménez can be considered as a neutral variety. To our knowledge, until now, this is the only report describing the main potential free aroma contributors of Pedro Giménez grapes from vines grown in Argentina.

Among the C₁₃ norisoprenoids, β -damascenone, β -ionone and TDN (1,1,6-trimethyl-1,2-dihydronaphthalene) are the most important contributor to wine aroma.⁶³ β -damascenone can enhance fruitiness character associated to esters, whereas decrease green characters from methoxypyrazines.^{63,71} Carotenoids are precursors of C₁₃ norisoprenoids, which can be formed from glycosylated intermediates and by direct degradation of carotenoids such as β -carotene, lutein, neoxanthin and violaxanthin.⁷²⁻⁷⁴ Biostimulation to grapevines through nitrogen applications such as urea or phenylalanine, and elicitors such as methyl jasmonate or a yeast extract can improve lutein, zeaxanthin and β -carotene content, but the effectiveness of these treatments mostly depends of the variety factor.⁷⁵ Leaf removal may up-regulate flavonol synthase and to stimulate deoxyxylulose-5-phosphate activity pathway, leading to the synthesis of monoterpenes and isoprenoids.⁷⁶⁻⁷⁷ Contrary to this, Ristic et al.⁷⁸ reported that β -damascenone and β -ionone concentration was not affected by canopy manipulation. Certain grape-growing zones in Argentina such as Lujan de Cuyo and Rio Negro (Fig. 3) are classified as warm viticultural regions, accounting 2,568 and 2,566 values of Heliothermal index.⁷⁹ Therefore, leaf remove can be a detrimental practice to grapevines cultivated in these Argentinean valleys, since under these conditions, berry

temperature tends to increase, leading to sunburn and dehydrated fruit, and subsequently, the degradation of several secondary metabolites.

According to the investigations performed by the Instituto Nacional de Tecnología Agropecuaria (INTA, Argentina), who have extensive experience in this type of varieties, the autochthonous national varieties have a wide genetic diversity and oenological potential not yet exploited. Based on the aforementioned, they selected some autochthonous varieties, such as Uva Anís (white variety: Listán Prieto × Moscatel de Alejandría), Picanta (white variety: Moscatel de Alejandría × unknown), Moscatel Amarillo (white variety: Listán Prieto × Moscatel de Alejandría), Canela (red variety: Listán Prieto × Muscat à Petit Grains), Blanca Oval Cuyana (white variety: Listán Prieto × Moscatel de Alejandría), Moscatel Rosado (rose-white variety: Moscatel de Alejandría × unknown), Criolla N°1 (red variety: Criolla Grande Sanjuanina × Malbec), Criolla Chica (Listán Prieto), among others, with promising oenological potential due to their polyphenolic composition, aromatic profile and acidity. Currently, these varieties are under study by these researchers.

Chile

As was aforementioned, cultivation of vines in America dates back to the early 16th century along with the Spanish colonization.^{7,8} According to the mentioned by Lacoste et al.⁸⁰ the vine introduction to the Kingdom of Chile took place at the beginning of the Spanish conquest, in the middle of the 16th century. However, the incipient Santiago de Nueva Extremadura (Santiago de Chile) population was besieged

and burned by the natives (Mapuche-Picunche) led by the Toqui Michimalonco in September 1541, who opposed with a tenacious resistance to the conquest of their territories by the Spanish, and all the wine and other items related to its elaboration were lost.^{81,82} Later in the 16th century, the Viceroyalty of Peru became an important secondary center for vine cultivation, which spread to other regions of the Spanish kingdom and surrounding territories.⁷ During the first steps of South American viticulture until the middle of the 19th century, the Spanish cultivar Listán Prieto (Argentina: cv. Criolla Chica or Criolla de Vino; Chile: cv. País; Bolivia: cv. Misionera; Perú: cv. Negra Corriente or Rosa del Perú; México: cv. Misión; USA: cv Mission) was the predominant.^{8,80} Then, other criolla varieties such as Torontel, Pedro Giménez, Corinto and Moscatel Rosada were also important.⁸⁰ The introduction of recognized varieties such as Malbec, Cabernet-Sauvignon, Pinot Noir, Malbec, among others, led to a competition that lasted for more than a century.⁸⁰ Around 1990, most of these old grapevine varieties were uprooted and replaced by these recognized varieties.⁵⁴ This type of viticulture based on the cultivation of these renowned grapevine varieties is the one that currently prevails in Chile, accounting a total vineyard surface of 144,619 ha.⁸³ According to the last viticultural report, the grapevine varieties most cultivated in Chile for wine production are Cabernet-Sauvignon (41,156 ha), Sauvignon Blanc (15,162 ha), Merlot (11,703 ha), Chardonnay (11,297 ha) and Carmenère (10,250 ha), whereas the least cultivated grapevine varieties for this same purpose are Gros Colman (0.35 ha), Ahmeur Bou Ahmeur (0.30 ha), Moscatel Rosada (0.25 ha), Gros Manseng (0.04 ha) and Muscat à Petits Grains (0.02 ha).⁸³ Additionally, it is important to consider that

phylloxera is distributed in most major viticultural regions with the exception of Chile and the Australian states of South Australia and Western Australia.⁸⁴

Listán Prieto

Listán Prieto or País variety (*Vitis vinifera* L.) (Fig. 4) was the first established in Chile, incorporated by the Spanish in the 16th century. Its original name is Listán Prieto, although it is also believed that it could correspond to Negro or Mollar, cultivated in Portugal and Canary Island.⁸⁵ This variety has been traditionally cultivated by small wine-growers with unirrigated vines trained to a traditional bush system, accounting 10,056 ha of the national surface. Maule and Biobío hold 6,036 and 3,877 ha of cultivated País surface, respectively (Fig. 5).

País is a very rustic grapevine variety that tolerates cryptogamic diseases, nematodes and other soilborne pests.²⁸ This variety cultivated under rainfed conditions performs better than most of the *Vitis vinifera* varieties.^{28,86} For these reasons and due to the low price of its grapes, it has been used as a rootstock for other grapevine varieties when retrofitting a vineyard.²⁸ According to the OIV⁸⁷ descriptors, País leaves are generally medium to large in size, yellowish-green in color and partially red in autumn. Depending on the edaphoclimatic conditions and viticultural management, País vines can reach great leaf development in terms of leaf area index.^{82,86} País is considered as variety of long cycle and requires of high temperature to reach an adequate technological maturity.^{82,86}

During the last decade, certain oenologists consider the País variety as not priority for wine production since its productivity usually results in low quality wines, mainly due to its roughness and unbalance.⁸⁸ However, these characteristics indicate the presence of a wide amount of phenolic compounds, which could bring it a commercial resurgence. Villarroel⁸⁹ showed that País grapes from Itata Valley, Chile (Fig. 5) presented higher concentration of proanthocyanidins than Carmenère and Pinot Noir grapes, which may have positive implications for human health. In this way, higher inhibitory power of País skin extract against angiotensin I-converting enzyme, that is responsible to the increments of blood pressure, was associated with greater –OH availability, higher mean degree of polymerisation (mDP) and the presence of epicatechin-gallate (ECG), expressed as percentage of galloylation (%G).⁹⁰ Aguilar et al.⁹¹ studied the extraction process and the quality of musts enriched in the phenolic compounds extracted from grape skins, seeds and flesh, autumn leaves and canes of País and Aspirant Bouschet (*Lachryma Christi*) varieties (*Vitis vinifera* L.) (Fig. 4). These authors reported that thermovinification of a mixture of must and pomace at 60 °C allowed a higher extraction of polyphenols than the maceration carried out with pectolytic enzymes. In addition, must enriched by vine leaves and grape pomace from Aspirant Bouschet presented higher antioxidant properties than País ones. Martínez et al.⁹² studied the aroma characterization of musts enriched with País and Aspirant Bouschet by-products using thermomaceration. In this work, País musts showed high contents of esters, contributing to fruity odor, while benzenoids prevailed in Aspirant Bouschet musts, giving them phenolic and balsamic odors. Additionally, these authors

showed that thermomaceration allowed to increase the concentration of certain free and bound volatile compounds, as well as isoeugenol, phenol, vanillin and 2-ethyl-1-hexanol. Aguilar et al.⁹³ reported that grape pomace from País and Aspirant Bouschet variety was a good source of anthocyanins (malvidin-3-glucoside), while flavonols (quercetin-3-hexoside) and phenolic acids (caftaric acid) were the main phenolic compounds in leaf extracts. These by-products could provide extra desirable ingredients for health-food applications, improving juice quality. These findings offer new opportunities for this variety with the aim to revalorize and diversify its productivity.

Chilean oenologists, together with the national researchers have been tested and evaluate País variety to produce high quality sparkling wines in response to revalorize this relegated variety within the Chilean wine industry. Ubeda et al.⁴² showed that along the second fermentation and aging of País sparkling wines, there was a significant loss of esters, that might be related to their adsorption on lees, ester volatility or their hydrolysis. However, the concentration of certain volatile compounds such as diethyl succinate, ethyl lactate, and ethyl isovalerate increased during aging, reason why these authors suggested that these volatile compounds could be used as aging markers in País sparkling wines. In addition, vitispiranes were identified as the best C₁₃-norisoprenoids aging markers for young sparkling wines, and time of aging on lees affected mostly esters and terpenes.⁴² On the other hand, Ubeda et al.²⁴ studied the influence of ripening and location on free and bound aroma of País grapes. These authors reported that during ripening, the concentration of aroma precursors increased in the different locations. In addition, it was found that *cis*-2-hexenol could be a good candidate to

assess maturity, and that terpene content seemed to be strongly related to the vineyard location and cultivar conditions.

Currently, País variety has been revalorized due to the production of qualified sparkling wines. However, there is little available information about the effects of viticultural managements to obtain a desirable grape berry quality for sparkling wine production.⁹⁴ Generally, grapes destined for the sparkling wine production are commonly harvested at relative lower pH, higher total acidity and lower soluble solids than the grapes destined for the table wine production.⁹⁵ Climate conditions limit grapevine ripening stage, widely affecting volatile concentration of grapes destined to the production of sparkling wines, rather than soil conditions. Monoterpenoids tends to increase along the ripening, whereas sesquiterpenes and C₁₃ norisoprenoids showed an increase from early harvest to harvest and a decrease at late harvest.⁹⁶ Polyphenols, polysaccharides and soluble proteins affects foam behavior in sparkling wines. Most of the studies carried out point to a positive influence of total polysaccharides on both, foamability and foam stability.⁹⁷⁻¹⁰¹ López-Barajas et al.⁹⁸ reported that must quality determines the foam capacity of base wine, establishing a maturation index between 4.0 to 5.5. Riu-Aumatell et al.¹⁰² showed that grapes obtained with yields higher than 10,500 kg ha⁻¹ presented higher content of soluble proteins and lower content of polysaccharides than the grapes obtained from yields below to 10.500 kg ha⁻¹. País is a rustic variety and its cultivation is more suited into granitic soils of low fertility and moderate water supply than into fertile soils, with high content of organic matter and water availability, conditions in which País considerably increase its yield, widely

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delaying its ripening. Canopy management, leaf removal and yield manipulation for the production of table wines might indicate a potential for application and development to optimize grapes for the production of sparkling wines.⁹⁴ Therefore, viticultural practices that allow to adjust yield might to modify ripening, and subsequently grape polysaccharides composition, which could benefit the production of País sparkling wines.

Currently, there are important public and private initiatives in Chile that seek to add value to País grapevine variety. According to this, it is possible to mention the elaboration of different styles of wines, such as carbonic maceration wines, organic wines, low calorie wines, white wines, *pipeño* wines, *pajarete* wines, aging wines, rosé wines, late harvest wines, *chicha* and distillates, some of which achieved an important insertion in the national market. Around 2015 year, the Instituto Nacional de Investigaciones Agropecuarias (INIA), the Cooperativa Agrícola Vitivinícola Loncomilla, and the Foundation for Agrarian Innovation (FIA), developed the first dealcoholized wine in Chile based on País variety.

Carignan

During the last few years, certain neglected grapevine (*Vitis vinifera* L.) varieties within the Chilean wine industry have emerged mainly due to their oenological potential and the changes in wine consumer's habits.^{29,103} This resurgence has allowed the economic and social recovery of a part of the small wine-growers of the Maule Valley, who cultivate the oldest grapevine Chilean varieties.¹⁶ Carignan variety (Fig. 4)

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is one of those minor cultivars that has had a major resurgence within the Chilean wine industry, attracting the attention of winemakers and consumers alike, which has allowed to increase its transaction prices to a level twice or three times higher than the selling price of the rest of grapevine varieties.^{16,26-28,29,104} Most of the oenologist and viticulturist agree that the first Carignan vine cuttings were introduced from the South of France after the Earthquake of Chillán occurred in 1939.^{16,29} This devastated the viticulture of the Valleys of Maule, Biobío and Itata (Fig. 5).¹⁶ The aim was to improve the color and freshness of the wines produced from the País variety, that dominated the viticulture of the area.¹⁶ However, there are precedents from a grapevine nursery that indicates the presence of Carignan in Chile towards the end of the 19th century, long before the 1939 Chillán earthquake. As the País variety, Carignan has also been traditionally cultivated by small wine-growers with unirrigated vines. Maule Valley (Fig. 5) holds approximately 83% of cv. Carignan, accounting 707 ha of a total of 851 ha planted in the country.⁸³

Viticulturally, Carignan is a rather late-budding cultivar, decreasing the risk of damage from spring frosts.¹⁶ This variety has fertile basal nodes, so it is spur pruned and trained in goblet system.¹⁶ Carignan usually tolerates warm climates, long dry summers, and soils with moderate to low fertility.¹⁶ Hillsides or other soils with limited depth or fertility provide it a good vegetative/productive balance, optimizing fruit quality.¹⁰⁵ Carignan adapts very well to windy conditions and its shoots lignify early in the season and mature well.¹⁶ This variety is very sensitive to *Uncinula necator*, which is controlled through preventive programs targeting this disease.¹⁶

Maule Valley is the largest wine region in Chile, and it expands from east to west from the foothills of The Andes Mountains to the Coast Range closer to Pacific Ocean (Fig. 5).^{16,106} These large variations in the soils, as well as the prevailing climatic conditions, allow differences in the composition and style of the Carignan wines produced.^{16,26-28,43,103,106} Martínez-Gil et al.²⁹ showed that as in most of the grapevine varieties, the most abundant anthocyanin was malvidin-3-glucoside (glc). Respect to anthocyanin composition, non-acylated forms were the most important contributor to total anthocyanins, followed by the coumaroylated forms, while the acetylated derivatives were the minor forms in grapes and wines from Carignan.^{27,29,103} Myricetin-3-glc and catechin were the most important flavonol and flavanol, respectively in Carignan grapes located within the Maule Valley.^{29,103} In addition, Martínez-Gil et al.²⁹ mentioned that anthocyanin concentration in Carignan grapes from Maule Valley is higher than those observed by Jensen et al.¹⁰⁷ in Carignan grapes from the South of France and by Fernandes de Oliveira et al.¹⁰⁸ in Carignan grapes from Sardinia, Italy. Respect to edaphoclimatic conditions, anthocyanin and flavonol concentration in Carignan grapes was related with biologically effective degree days, exhibiting a direct relationship between grape maturity and thermal accumulation.^{16,29} On the other hand, flavanol and hydroxycinnamic acid content was inversely correlated to the average maximum temperature of the warmest month, showing that their synthesis is favored by cooler temperatures during the warmest month.²⁹ Gutiérrez-Gamboa et al.²⁸ reported that Carignan behaved as proline accumulator grapevine and this amino acid was the most abundant in most of the studied samples. These authors

also reported that cool night index (CI) was inversely related to the concentration of several amino acids in Carignan grapes. Therefore, amino acid synthesis is improved under low minimum temperatures during the last month before harvest.^{26,28} Carignan grapevines located in the highest altitude sites with the influence of the Pacific Ocean, such as Truquilemu and Ciénaga de Name locations presented the highest concentration for several amino acids and total amino acid content in grapes, which led to a faster alcoholic fermentation.^{16,28} Gutiérrez-Gamboa et al.²⁶ reported that higher alcohols were the chemical family of volatile compounds most abundant in Carignan wines. In addition, certain ethyl esters and β -damascenone were the most odoriferous compounds according to their odorant activity value, and no varietal compounds were detected. Respect to the effects of edaphoclimatic and viticultural management on the concentration of volatile compounds in wines, the dominant factor was season, whereas rootstock (Carignan grapevines ungrafted and grafted onto cv. País) did not have a significant effect on wine volatile composition.²⁶ Cold nights during the month prior to harvest were related with high concentration of certain volatile compounds such as linalool, α -terpineol and *trans*-3-hexen-1-ol content.²⁶ On the other hand, the accumulation of biologically effective degree-days was inversely related with the concentration of some esters such as isoamyl acetate and 2-phenylethyl acetate, while the Huglin's heliothermal and the average mean temperature of the warmest month indices were inversely related with ethyl vanillate, ethyl hexanoate and ethyl octanoate content.²⁶ Water restriction of Carignan grapevines cultivated in Melozal, Sauzal and Cauquenes sites within the Maule Valley due to the shallow soil depth and the warm

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climate conditions limits the production of small grape berries, determining a higher skin to pulp ratio than the Carignan grapes harvested in Truquilemu, Ciénaga de Name, Huerta de Maule and Santa Sofía sites, favoring the extraction of polyphenols and anthocyanins by the fermentative maceration.^{16,109} During cold seasons, Truquilemu and Ciénaga de Name sites lead to a delay in technological maturity of Carignan grapevines.²⁹ In these conditions, cluster thinning or pruning leaving one bud, could be interesting viticultural practices that may control the relationship between productivity and quality, allowing improvements on berry ripening.¹¹⁰ Cover crops establishment into the vineyards could be a useful practice to control excessive vigor and yield, improving grape and quality.¹¹¹

Commercial wines also were studied, in this way Ubeda et al.²⁴ reported that Carignan wines from sites closer to the Andes Mountains showed significantly lower contents of esters and acids. Additionally, the studied wines were correctly classified regarding location, being esters the chemical family of volatile compounds that mostly contributed to the correct classification of the samples. Moreover, Cejudo-Bastante et al.⁴³ reported that Carignan wines from sites closer to the Andes Mountains had higher content of procyanidin B3, polysaccharides and *cis*-resveratrol-glc, whereas the proximity to the Pacific Ocean provoked a unifying effect in chemical and colorimetric terms. To our knowledge, Carignan vineyards planted in the sites closer to Pacific Ocean with high altitude such as Truquilemu and Ciénaga de Name provides grapes and wines with a high concentration of several amino acids and volatile compounds, being the late ripening sites.¹⁶ In contrast, Carignan vineyards located in the sites into the

Entre Cordillera area, towards The Andes Mountains, provides grapes and wines with a high alcohol and phenolic concentration, being the sites of early maturation.¹⁶

Generally, the grape must from Carignan grapevines cultivated on most of the sites into the Maule Valley have low yeast assimilable nitrogen and high content of proline respect to arginine.¹⁶ Proline is the only free amino acid that is not assimilable by yeasts and one of the most abundant amino acid found in Carignan grape musts.^{28,112,113} Therefore, an accurate prevention and diagnostic of stuck and sluggish fermentations must be carried out in this variety at the wine cellar, to avoid wine spoilage. The addition of diammonium phosphate (DAP) is a common practice performed into wine cellar that increase fermentation rate, decreasing fermentation duration.¹¹⁴⁻¹¹⁶ However, the addition of DAP lead to an increase in ammonium content that provoke a higher evolution of hydrogen sulfide (H₂S) compared to non-supplemented DAP musts.¹¹⁷ H₂S contributes to the spoilage character of wines, giving them undesirable rotten egg and sewage aromas.^{118,119}

Certain viticultural practices could be performed at the vineyard as alternative to wine cellar procedures to improve the nitrogen content of the must and to prevent the aforementioned problems. Garde-Cerdán et al.¹²⁰ reported that phenylalanine and urea foliar applications to the grapevines increased the concentration of several amino acids in grape musts. Gutiérrez-Gamboa et al.¹²¹ reported that, commercial nitrogen products and a urea supplemented with sulfur treatment, increased the concentration of several amino acids in grape musts. Gutiérrez-Gamboa et al.⁶⁵ reported that these treatments applied to grapevines allowed to increase ethyl hexanoate, ethyl octanoate and ethyl

decanoate content in wines. Ancín-Azpilicueta et al.¹²² showed that total concentration of higher alcohols in wines decreased with the application of urea in the vineyard, whereas the concentration of ethyl hexanoate, ethyl octanoate and ethyl decanoate were highest in the wine obtained from grapevines treated with 4 kg N ha⁻¹ of urea. However, the effectiveness of these applications mainly depends of vine nitrogen needs and the edaphoclimatic conditions of the site, which could determinate grape maturity, and thus to condition nitrogen composition of grapes.¹²³ On the other hand, certain viticultural practices negatively affect nitrogen composition of grapes. Oliva et al.¹²⁴ reported that the application of famoxadone and fenhexamid fungicides in grapevines decreased the concentration of several amino acids in grapes.

Carmenère

Carmenère (*Vitis vinifera* L.) (Fig. 4) is an emblematic red grapevine variety of Chile originating from the Médoc, Bordeaux (France) that was believed to be extinguished after the catastrophic effects of *Daktulosphaira vitifoliae* that ravaged the French vineyard in the mid 19th century.¹²⁵ Carmenère was identified and rediscovery in Chile by the French ampelographer Jean-Michel Boursiquot, who differentiated it from Merlot and Cabernet Franc.¹²⁶⁻¹²⁸ Currently, it has established itself as the emblematic variety that produces quality Chilean wines.¹³⁷ In this way, at 2012, around of 40 Chilean wineries (about 20% of the total) were making, marketing and exporting their own brands of luxury Carmenère, defined as retailing at US\$50 or more per 750 mL bottle according to the stated by Beverland,¹²⁹ or Carmenère-blend wines.¹³⁰ The

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reported area of Carmenère has been increasing over the last years,^{131,132} and according to the last viticultural report, the Carmenère surface accounting 10,250 ha, being the fifth most cultivated variety in Chile after Cabernet-Sauvignon, Chardonnay, Sauvignon Blanc and Merlot.⁸³ Although, nowadays this variety has an important relevance within the Chilean wine scenario, we have included it in this review, since Carmenère was believed extinct and was rediscovered and revalorized by the Chilean wine industry.

Respect to the viticultural behavior, Carmenère is a very vigorous cultivar that is characterized by late entering into production, presenting a low fertility in their basal buds.¹³³ These problems force to prune the vines to cane pruning instead spur pruning or to girdling the canes.^{127,133,134} In addition, Carmenère exhibits a high tendency to fruitlet abscission that seriously affect productivity.¹³⁵ This is a viticultural hazard problem, in which there is an incomplete fertilization in fruit set, so that the grape bunches contain berries that differ greatly in size and maturity.^{133,135} Respect to its oenological potential, Carmenère presents a high content of tannins, generally soft and round, even though it is sometimes possible to obtain a small degree of bitterness.¹²⁶ Also, it has been mentioned that the first Carmenère wines that appeared in the market presented harsh and green aromas, resulting in notes of green bell pepper, celery, and green beans.¹³⁶

In previous works, it has been reported that Carmenère grape seeds showed a lower concentration of monomeric flavanols and (+)-catechin, presenting higher mean degree of polymerization, percentage of galloylation, average molecular weight of the flavanol fraction, and contents of (-)-epicatechin, epicatechin-3-*O*-gallate, gallic acid,

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and dimeric procyanidins esterified with gallic acid than Cabernet-Sauvignon grape seeds.¹³⁷ In addition, Merlot seeds presented a high concentration of flavanol monomers and some proanthocyanidins such as trimer 1, B3 and B4, while Carmenère seeds exhibited high concentrations of other proanthocyanidins such as B1, B4G and B2.¹³⁸ The sum of glucoside and cumaroylglucoside anthocyanins in Carmenère was higher than in Cabernet Franc and Cabernet-Sauvignon in some sampling date throughout ripening.¹³⁹ Carmenère wines enriched with grape commercial oenological tannins resulted in the highest values of (+)-catechin, (-)-epicatechin, and monomers and polymers of flavanols, whereas others wines enriched with wood commercial oenological tannins presented the highest values of total phenols, total tannins, dihydroflavonols, proanthocyanidin gallates, syringic acid and flavanol oligomers.¹⁴⁰ Moreover, the main chemical markers contributing to antioxidant capacity of Carmenère wines were the fraction of color given by free and co-pigmented anthocyanins (39.1%) for DPPH and gallic acid (30.7%) for ORAC-FL.¹⁴¹ These authors suggested that these results are good indicators of the complexity of the wine matrix, and the wide variety of substances possibly contributing to antioxidant capacity of Carmenère wines.

Vegetal and green aromas are recurrent aromatic attributes that define Carmenère wines, which suggests that methoxypyrazines could be present in important amounts in these wines. 3-isobutyl-2-methoxypyrazine (IBMP) concentration in Carmenère wines ranged from 5.0 to 44.4 ng L⁻¹ hugely higher than most of the Cabernet-Sauvignon wines.¹³⁶ These authors reported that genotype widely influenced

methoxypyrazine content of Carmenère wines. In this way, some clones presented three-fold more than others. In addition, climatic conditions, rather than maturity or terroir, had a critical effect upon IBMP concentration in grapes.¹³⁶ On the other hand, almost 150 volatile compounds were identified in Carmenère wines, corresponding to aliphatic and aromatic alcohols, organic acids, acetate and ethyl esters, lactones, terpenes, norisoprenoids, pyrazines, thiols and phenolic compounds.¹²⁵ These authors reported that 3-mercaptopentyl acetate (3MHA), 3 mercaptopentan-1-ol (3MH), benzenemethanethiol (BM), 2-furanmethanethiol (2FM) and IBMP showed significant odorant properties. Contrary to this, 2-isopropyl-3 methoxypyrazine (IPMP) and 4-mercaptopent-4 methylpentan-2-one (4MMP) were not detected.¹²⁵ β -damascenone, several thiols, ethyl octanoate, 2-phenylethanol, and 2-isobutyl-3-methoxypyrazine, showed significant odor activities values (OAV), and were correlated with different attributes such as cooked fruits, berries-like and herbaceous notes characteristics of Carmenère wines.¹²⁵ Additionally, certain thiols, such as 2-furanylmethanethiol, 3-sulfanylhexyl acetate, 3-sulfanyl-1-hexanol, and 2-methyl-3 sulfanyl-1-butanol, with potential to influence the overall aroma, were identified in Carmenère wines.¹⁴² On the other hand, Carmenère wines macerated with Colombian oak chips (*Quercus humboldtii*) for 90 days presented higher concentration of 5-methylfurfural, guaiacol, *trans*-isoeugenol and syringol and lower content of furfural and *cis*- β -methyl- γ -octalactone than the Carmenère wines macerated with *Q. alba* and *Q. petraea*.¹⁴³ These authors reported that a sensory analysis showed that the wines treated with Colombian oak presented more notes of smoked and less of coconut. Laqui-Estaña et al.¹⁴⁴ reported that Carmenère and

Cabernet-Sauvignon wines in contact with oak wood presented a high amount of caffeic acid, gallic acid, ellagic acid and ellagitannins, while the wines in contact with staves were characterized by total phenols, vanillic acid and higher color intensity. Additionally, these authors reported that the Carmenère and Cabernet-Sauvignon wines aged with chips presented a large amount of proanthocyanidin gallates, while the wines aged in barrels showed high contents of ellagitannins and ethyl gallates. Therefore, it is possible to reduce the gustatory and olfactory vegetable character of Carmenère wines by using different types or species of oak woods, such as chips, staves or oak barrels during the wine aging.

Methoxypyrazines are a group of heterocyclic aromatic organic compounds that are present in green plant tissues contributing to green, vegetal or herbaceous character.¹⁴⁵ Several environmental factors such as cluster shading, water availability and nitrogen fertilization can affect the synthesis and accumulation of IBMP content in grapes.¹⁴⁶ Scheiner et al.¹⁴⁶ reported that timing of basal leaf removal performed at 10 to 40 days after anthesis reduced IBMP accumulation compared to control. These authors suggested that early leaf removal is a more effective viticultural management to decrease IBMP accumulation in grapes than the leaf removal performed later in ripening stage. Sala et al.¹⁴⁷ reported that cluster shading resulted in wines with lower IBPM concentration than the sun exposed samples. Additionally, these authors showed that vine trellis system also can affects the synthesis of IBMP, reporting that the wines from goblet-trained vines contained lower IBMP concentration than the wines from bilateral cordon trained vines. Ryona et al.¹⁴⁸ showed that IBMP concentration analyzed at 2

weeks before veraison was highly correlated to its levels at harvest, suggesting that light exposure conditions, mostly influenced IBMP accumulation, but not IBMP degradation.

Moscatel de Alejandría

Moscatel de Alejandría (Fig. 4) together with Listán Prieto came to South America in the second third of the sixteenth century, brought by the Spanish conquerors, who began to quickly find the cities in Peru and Chile.^{7,8,80,82,149} In both territories, they began to cultivate the first vines simultaneously.¹⁴⁹ Subsequently, La Serena city (Chile) was founded to facilitate communications between Peru and Chile.¹⁰⁶ The cultivation of Moscatel de Alejandría began due to its easy adaptation, together with the production of wines and spirits, mainly in the Valleys of Copiapó, Huasco, Elqui and Limarí.¹⁴⁹

Moscatel de Alejandría is a variety of singular interest within the Chilean wine industry, since is the most commonly used variety to the Pisco elaboration, the most important Denomination of Origin of South America.¹⁵⁰ Pisco is a brandy derived from grape distillate, typical of the northern zone of Chile, and can only be produced from certain grapevine varieties, such as Moscatel de Alejandría and its successors.¹⁵⁰ Based on this, most of the cultivated surface destined to Pisco elaboration corresponds to Moscatel de Alejandría (14.0 % or 1,120.5 ha) and criolla varieties such as Moscatel de Austria, Moscatel Rosada, Moscatel Negra and Pedro Giménez (85.7% or 6,838.3 ha), with low percentage of varieties corresponding to the French paradigm (0.21% or 16.85 ha).⁸³ Studies carried out using DNA markers have shown that the crossing of Moscatel

de Alejandría with Listán Prieto has originated the main criolla varieties, such as Moscatel Amarilla, Moscatel de Austria, Moscatel Rosada, Cereza, Criolla Media, Pedro Giménez, among others, which are mostly used to the Pisco elaboration (Fig.1).

^{7,59,69,150,151} Viticulturally, Moscatel de Alejandría presents leaves of medium to small size, while its bunches tend to be large and loose. Grape berries are elliptical, large, golden and medium-thick skin. Due to these characteristics, grapes are used also to fresh consumption and to produce raisins. ¹⁵² This variety adapts better to warm climates, in particular during flowering and fruiting, which allows to avoid coulure and millerandage problems. ¹⁵²

Currently, the interest to elaborate monovarietal, sparkling and late harvest wines from this variety is increasing due to its interesting aromatic composition and freshness. ²³ Muscat grape cultivars are known for the strong aromatic properties that they confer to wines, mainly due to its high presence of terpenes, which present low odors threshold. ¹⁵³ Belancic et al. ¹⁵⁴ reported that Moscatel de Alejandría and Moscatel Rosada presented similar total free terpenoids around to 2,100 $\mu\text{g L}^{-1}$, although Moscatel de Alejandría contained abundant concentrations of total bound terpenols. These authors reported that free terpenols was higher in Moscatel Rosada treated with artificially semi-shaded cluster than vines treated with shaded cluster. Shaded grapes had the lowest concentration of terpenols, with poor Muscat typicity, while linalool was the most sensitive volatile compound to sun exposure. Agosin et al. ¹⁵⁵ reported that Moscatel de Alejandría and Moscatel Rosada are highly aromatic, according to their linalool, nerol and geraniol content in grapes. These authors showed that Early Muscat

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and Moscatel Amarilla varieties could contribute much to the aroma of Pisco, due to their high levels of free monoterpenes and its glycoside bound fraction. According to the odor activity values (OAV), the most active compounds in commercial Piscos were isovaleric acid, isoamyl alcohol, 1-heptanol, linalool, hotrienol, β -ionone, isoamyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, isoamyl acetate, ethyl heptanoate and *cis*-3-hexenyl acetate.¹⁵⁶ Pascual et al.²³ reported that linalool was the most prevalent volatile compound in Moscatel de Alejandría clusters exposed to sun. These authors reported that treatment with the highest defoliation of Moscatel de Alejandría vines allowed an important increase of the linalool concentration compared to control treatment. However, Moscatel de Alejandría grapevines located in the Itata Valley presented high levels of sunburn, which conditioned berry quality, decreasing fruity aromas and increasing bitterness.¹⁵⁷ Therefore, it is important to perform viticultural practices that allow to obtain a good vegetative-productive balance in Moscatel de Alejandría grapevines, with the aim to maximize the aromatic potential of this variety.

Grosse Méridle

There is little available information about Verdot or Chilean Verdot (Grosse Méridle) grapevine variety (Fig. 4), which is considered as an old and rare French variety.¹⁵⁸ Ampelographic studies allow to differentiate this variety from Petit Verdot.^{152,158} Currently, the Grosse Méridle is found only in varietal collections in France and should not be confused with the Méridle, which could sometimes be considered as one

of its synonymies.¹⁵⁸ Simple sequence repeat analysis allowed to confirm that the Chilean Verdot variety, is the French Grosse Méridle, with which it is ruled out that it is a synonymous of Petit Verdot variety.¹⁵⁸ According to the reported by Pszczółkowski et al.,¹⁵⁸ it is probable that Grosse Méridle or Verdot was introduced in the 19th century with other varieties of the same origin, before the phylloxera crisis. Around 1980s, it was common to find Grosse Méridle grapevines, within the old vineyards along central valleys of Chile.¹⁵⁸ According to the last Chilean vitivinicultural register,⁸³ the national vineyard surface holds 2.68 ha of Verdot variety, whereas in 2014 there were 3.98 ha of this variety (SAG, 2014). This register accounted 7.2 ha of Verdot in 2006.¹⁵⁹ Therefore, the decrease in the cultivated surface of Verdot in Chile, indicates an imminent risk of disappearance in the current Chilean wine scenario.¹⁵⁸

A viticultural description of this variety has been reported by Pszczółkowski et al.¹⁵⁸ Grosse Méridle is a vigorous grapevine variety that presents an early budbreak and high productivity due to the presence of fertile basal buds.¹⁵⁸ Grosse Méridle grapevines cultivated in depth and fertile soils under high water availability, lead to an over-productivity, delaying its ripening, and decreasing wine color.¹⁵⁸ Regulated deficit irrigation at the beginning of berry development could result in an important reduction of both vegetative growth and berry weight with an increase in anthocyanins and phenolic compounds.¹⁶⁰ Berry size reductions increase the skin to pulp ratio and consequently the concentration of several phenolic compounds, except total tannins.¹⁰⁹ Cold climates lead to poor fruit set in Grosse Méridle grapevines, which might result in an early bunch necrosis.¹⁵⁸ This variety requires a minimum thermal accumulation of

1,372-degree days and is very sensitive to boron deficiency, such as that found in granitic soils of the Coastal Range.¹⁵⁸ Additionally, Grosse Méridle does not present particular sensitivities to grapevine diseases and pests.¹⁵⁸ On the other hand, wines from this variety are characterized by a moderate color intensity, with an intense and peculiar aroma, that sometimes recalls tropical fruits, such as cherimoya.¹⁵⁸ Gustatory phase is characterized by a fresh flavor due to its high level of acidity, moderate alcohol and low astringency, similar to Pinot Noir wines.¹⁵⁸ Occasionally, Grosse Méridle wines are used to obtain assembled with other grapevine varieties.¹⁵⁸ Currently, rosé and varietal red wines have been produced, taking advantage of their distinctive flavor, with an intense aroma of tropical fruits.¹⁵⁸

Currently, to propose the possibility to elaborate wines from criolla grapevine varieties (Fig. 4), such as Blanca Ovoide, Pedro Giménez or Torontel, is considered as an innovation and not an idea without a future, as it was previously occurred.¹⁸² Additionally, the possibility to produce wines from European varieties scarcely cultivated in Chile, such as Carignan, Garnacha, Cinsaut or Portugais Blue, is seen as a positive innovation.¹⁸²

Bolivia

Bolivian viticulture, began with the arrival of the Spanish conquerors around 1570, in order to supply Augustinians and Jesuits wine needs, who due to the inflexibility of the Catholic religion, were obliged to use wine in the Eucharist.¹⁶¹ According to the crown interests, silver mines were discovery by in 1545 until 1549 to

the aim to brought to Spain silver to fill the royal treasury.¹⁶² By 1630, silver miners' needs were mainly supplied with wine, distillates, wheat and maize produced from Uruba, Chaqui, Puna and Mataka valleys.¹⁶² This historical context allowed the emergence of a specific group of Andean spirits: the Singani of Bolivia, the Pisco of Peru and the Pisco of Chile.¹⁵¹ Vicchoca locality (Cotagaita Valley, Potosí) is designated as the first site where the vine would have been cultivated in this country, originating the criolla Vicchoqueña variety (Fig. 2), probably as a natural crossbreeding between Listán Prieto (Criolla Negra or Misionera) and Moscatel de Alejandría. Then, Bolivian firsts vineyards were cultivated at Río de la Paz and then were expanded along Mecapaca, Sapahaqui, Caracato, and Luribay valleys (La Paz); Mizque, Sipe-Sipe and Capinota valleys (Cochabamba); Tupiza and Sinkani (Potosí); Nor and Sur Cinti (Chuquisaca); Entre Ríos, Sella, Santa Ana, Concepción, La Compañía de Jesús, Juntas del Rosario and Central Valley of Tarija (Tarija) and in the mesothermic valleys of Santa Cruz (Fig. 5).¹⁶¹ Around 1690, the Society of Jesus acquired lands in the Camacho valley and contributed to the extension of the grapevine cultivation in the valley.¹⁶³ Bolivian viticulture development was threatened by the emancipation of the Guaraní Indians, who usually devastated the vineyards and other winemaking items, reason by which the vineyard cultivation emigrates to the valleys less prone to the assaults of Guaraní.¹⁶¹ Already towards to the end of the 20th century, new fine grapevine varieties were imported from Europe such as Malbec, Merlot, Syrah, Cabernet-Sauvignon, Tannat, Chardonnay, Sauvignon, among others, which were mostly cultivated in Central Valley of Tarija (Fig. 5).¹⁶⁴ Currently, the most important

wine-growing regions in Bolivia is the Central Valley of Tarija, the Cinti Valley and the Valleys of Santa Cruz, accounting 2,400, 300 and 100 ha, respectively (Fig. 5).¹⁶⁴ Due to the particularities of the Bolivian vitiviniculture we display the information in a differentiated way to the exposed in the previous sections.

Bolivian vitiviniculture

Bolivia viticulture is characterized by its subtropical climates, and mainly to the vineyard altitude, ranging from 1,600 to 2,800 meters above sea level (m a. s. l).^{164,165} The most widely planted grapevine variety in Central Valley of Tarija is Moscatel de Alejandría, which is mostly used as table grape and also for wine and Singani production, accounting the 85% of the total cultivated surface.^{161,164} This variety is well adapted to sub-tropical climatic conditions. Singani is a distilled beverage produced only in the Bolivian high valleys and is considered as the national liquor of Bolivia.¹⁶¹ Red Globe and Italia Piróvano 65 are important table grape varieties, which are grown in the same areas where vitiviniculture is developed, including others such as Chaco Tarijeño at 400 m a. s. l.¹⁶⁵ Vineyards are manually harvested and most of the grapevines are grafted onto resistant rootstocks such as 1103 P, 110 R, 99 R and SO4 due to the salinity of the soils and the presence of phylloxera (*Daktulospharia vitifoliae*), and certain nematodes such as southern root-knot nematode (*Meloidogyne incognita*), Walnut root-lesion nematode (*Pratylenchus vulnus*) and dagger nematode (*Xiphinema index*).¹⁶⁵ Due to the novelty of this topic, we displayed differently the following sections compared to the previous ones.

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Along to the Central Valley of Tarija, grapevine productivity is widely variable from one area to another and from season to season.¹⁶⁶ These variations are strongly influenced by climatic adversities, such as spring frosts, hail and summer rains that favor the development of cryptogamic diseases and a low accumulation of chilling hours.¹⁶⁶ The physico-chemical soil characteristics also influence the grapevine variability, since they present very alkaline pH and high levels of carbonates and sodium salts, which makes it mandatory to apply high corrective doses of calcium and sulfur.¹⁶⁵ Additionally, pHs of irrigation water range between 7.8 and 8.5.¹⁶⁶ The variability on grapevine production is also affected by certain viticultural managements, such as pruning severity, availability of water for irrigation and fertilization rates of the vineyards which determines premature aging of the vines.¹⁶⁶

Grapevine varieties cultivated under subtropical conditions lack of cold accumulation during dormancy in autumn and winter.¹⁶⁶ Chilling requirements is defined as the period of low temperature (sum of hours recorded at an air temperature below to 7.2 °C) that is necessary to reach 100% of buds to break.¹⁶⁷ In these conditions, grapevine cultivation is only possible at a sufficient altitude, taking advantage of winter cooling by adiabatic effect.¹⁶⁵ Chilling hours registered in the Central Valley of Tarija during the last 45 years are lower than 340 h, with a clear tendency to decrease in the last years, whereas the maximum average temperatures during winter in the Central Valley of Tarija are close to 25 °C.¹⁶⁶ These climatic conditions favor problems of grapevine budbreak uniformity. Hydrogen cyanamide (H₂CN₂) in form of calcium cyanamide (CaCN₂) is commonly applied two at four

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weeks before the intended time of budbreak to end dormancy and promote budbreak.¹⁶⁸ However, under the edaphoclimatic conditions of Bolivian vineyards, the application of H_2CN_2 is not a viable solution since by advancing budbreak, the grapevines may be affected by late spring frosts.¹⁶⁹ The rolling up and the re-pruning of the one-year-old full-length canes (non-tipping shoots) are used to improve budbreak.¹⁶⁹ When grapevine reach around of 30 to 70% of budbreak, these canes are re-pruning.¹⁶⁹ The H_2CN_2 use is potentially possible in Chaco Tarijeño and in the mesothermal valleys of Santa Cruz, where an emergent viticulture of table grapes is developing.¹⁶⁹ In addition, *bourrillon* pruning and spur pruning to a one bud can attenuate the effects of the acrotony and to favor the budbreak of basal buds.¹⁷⁰ On the other hand, the vine-growers utilize anti-hail nets because they allow the mechanization of certain viticultural practices, such as pre-pruning, application of phytosanitary products and harvest, decreasing the incidence of cryptogamic diseases and reducing the production costs.¹⁶⁶

Autochthonous varieties

Due to the absence or lack accumulation of cold during winter, a series of physiological problems such as null dormancy, heterogenous budbreak and a markedly acrotony vegetative development are commonly observed in most of the *Vitis vinifera* L., grapevine varieties cultivated.¹⁶⁵ However, it is interesting to highlight that the Tannat grapevine variety has adapted very well to the edaphoclimatic conditions of Bolivia, granting wines with great oenological potential.^{165,169} Others *Vitis* species and

its varieties have a better adaptation to subtropical climates than most of the *Vitis vinifera* L., varieties. Favorita Diaz and Monte Rico (Concord $\times$ *V. labrusca*) red varieties are adapted to the Central Valley of Tarija viticulture.^{165,169} Additionally, criolla varieties, such as Vicchoqueña, Criolla Negra, Blanca Redonda, Rosada Criolla, Moscatel Sanjuanina, Mollar, Alphonse Lavallée, Cereza, Pedro Giménez and Torrontes are also adapted to these climatic conditions and represent near to 5 % of the total planted surface.^{165,169}

According to a study about phenolic composition of Bolivian grapevine varieties,¹⁷¹ it has been showed that Vicchoqueña grapes (Fig. 2) harvested in Chuquisaca showed higher concentration of anthocyanins than the Vicchoqueña grapes obtained from Potosí (62.17 and 215.09 mg L⁻¹, respectively). In this location, Criolla Negra grapes presented higher monomeric anthocyanins content than Vicchoqueña grapes (62.17 and 224.90 mg L⁻¹, respectively).¹⁷¹ In Chuquisaca, the Vicchoqueña and Alphonse Lavallée grapes presented higher monomeric anthocyanins than Red Globe, Criolla Negra, Merlot and Cabernet-Sauvignon.¹⁷¹ These differences seem to be due to the genotype of the grapevine variety rather than climatic conditions since the vineyards presented similar altitudes. Chalcone synthase may compete with stilbene synthase, decreasing the ability to synthesize resveratrol in response to UV-radiation as a consequence to a rise in the anthocyanin biosynthesis.¹⁷² However, the high incident radiation in Bolivian vineyards might to active stilbene synthase more than chalcone synthase.

Stilbenes are vine phytoalexins present in grapes and its consumption is associated to healthy beneficial effects.¹⁷³ Stilbene synthesis is widely related to biotic or abiotic stress in grapevines, mostly of cryptogamic diseases affection and high UV-radiation exposure.¹⁷² Resveratrol is the main stilbene and is characterized to contribute to several healthy properties such as anticancer, antioxidant, anti-inflammatory and cardioprotective activity.¹⁷⁴ Stilbenes are produced by grapevines, as glucosides, in response to infection of biotic pressure. Grapes appear to synthesize the *trans* form and light causes *trans/cis* isomeration.⁶³ Taquichiri et al.¹⁷⁵ reported that *trans*-resveratrol concentration in grapes harvested from autochthonous and introduced Bolivian grapevine varieties was 10-fold higher than the reported data from the literature. Additionally, Osorio-Macías et al.¹⁷⁶ reported that Bolivian wines were correlated with high concentration of resveratrol, total antioxidant capacity and total flavonoids compared to Argentinean, Chilean and Uruguayan wines. Ultraviolet radiation reaching at the earth's surface increases with altitude and varies with latitude.¹⁷⁷ Moderate levels of UV-B radiation can stimulate protective mechanisms in grapevines, including the accumulation of stilbenes, as response to cellular damage. Martínez-Lüscher et al.¹⁷⁸ showed that grapevines exposed to UV-B radiation presented a decrease in the concentration of threonine, isoleucine, methionine and glycine in grapes. These amino acids are precursor of certain volatile fermentative compounds. Gil et al.¹⁷⁹ reported that grapevines subjected to high UV-B reached the highest content of terpenoids with antioxidant properties, diterpenes α and γ tocopherol and phytol, the sesquiterpene E-nerolidol and the monoterpenes carene, α -pinene and terpinolene. These authors

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reported that low UV-B treatment increased the levels of the membrane-related triterpenes sitosterol, stigmasterol and lupeol, more notable in young leaves, suggesting the UV-B elicitation as a mechanism for grapevine acclimation.¹⁷⁹ Gil et al.¹⁸⁰ reported that UV-B radiation allowed to increase the content of monoterpenes, some aldehydes, alcohols and ketones applied at pre-harvest stage. UV-B radiation-specific signaling pathway is activated in the skin of grapes grown at mid-altitudes.¹⁸¹ Most of these studies have been carried out in Mediterranean climatic conditions and in vineyards cultivated at low altitude and it would be interesting to evaluate these researches under the climatic conditions of the Bolivian viticulture. Therefore, grapes and wines from Bolivian valleys have distinctive characteristics in relation to a high content of phenolic compounds and a high antioxidant capacity, providing more healthy products for the consumers.

Moscatel de Alejandría

Moscatel de Alejandría (Fig. 4) is the most cultivated grapevine variety in the Central Valley of Tarija, accounting 346 ha (47.6%) of the total national surface.¹⁶⁴ Moscatel de Alejandría is a multipurpose white grape variety within the Bolivian vitiviniculture since it is used to fresh consumption, to produce table wines and Singani.¹⁶⁴ Because the oenological potential of this variety for wine production was previously described, we will focus on its potential to the production of Singani, the most emblematic Bolivian alcoholic beverage. Singani is a wine distillate, a member of the family of the ancient spirits of the Peru Viceroyalty, and its origin is associated to the

exploitation silver mines of the Cerro Rico de Potosí.¹⁶² Due to the difficult climatic conditions, the Spaniards and indigenous people demanded a higher alcohol content in beverages, and together with the coca, the Singani allowed to fight the ravages caused by the hunger and the rigor of the climate, and provided the necessary energies to fulfill the work of the mines.¹⁶² Singani is an aromatic distillate made exclusively with Moscatel de Alejandría wines, a variety well adapted to the edaphoclimatic conditions of the Central Valley of Tarija and Cinti Valley.¹⁵¹ These attributes allowed the Singani to be established as a product of Appellation of origin, whose delimitation is reinforced by the fact that this distillate develops from vineyards cultivated in significant altitude.

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According to the exposed by Pszczółkowski et al.,¹⁶⁵ Singani distillates seem to present distinctly 'velvety' and 'nutmeg' attributes, whereas Chilean Piscos offer more diversity. This could be linked to the fact that Pisco grapevine varieties contribute to a wide range of typicity such as 'green pepper' notes attribute to Pedro Giménez variety, or 'floral, nutmeg, spicy' attributed to Muscat's grapevine varieties. These authors also showed that, Peruvian Piscos had a wide sensory diversity attributed to the different grapevine varieties used, presenting notes of 'aromatic herbs' (Quebranta variety), 'floral, nutmeg, spicy' (Muscat's varieties) and empyreumatic characters related to Pisco aging, contributing to strong structures in the mouth. Bordeau et al.¹⁸² standardized and describe differences among a wide range of Piscos, showing that descriptors such as vanilla, burning, raisins, linalool, charcoal, prunes, caramel, ethanol, honey, sweet, banana, apple, pear, parched, rose, almond, rancid, peach, mouth-coat and artichoke

were frequently used by a trained panel of oenologists. These authors suggested that the terminology proposed is aimed at young spirits and so should apply equally to Peruvian Pisco or Bolivian Singani.

Adulteration of the Singani through alcohols of a diverse origin usually occurred. Tin artisanal alembics to produce Singani is a particularly delicate fact because they enrich of lead the final product.¹⁶⁵ Distillate process decisions and equipment selection might have many effects on distillate composition since a higher degree of rectification indicates lower congener concentrations.⁶³ Continuous still spirits have lower levels of head components such as acetaldehyde, diethyl acetal, ethyl acetate, as well as furfural, whereas pot still marc spirits presents higher levels of methanol and heads components.⁶³ However, some differences in the concentration of a number of congeners between spirits produced from continuous stills is evident due to the wide variations in still design.⁶³ Spirits produced from pot stills are normally perceived to be more aromatic than spirits elaborated from continuous stills.¹⁸³ Generally, spirits are aging into oak barrels where some phenolics and volatile compounds are extracted.¹⁸⁴ Aging on oak barrels accelerate the acid-catalyzed reactions like ester hydrolysis and formation compared to those aged in glass.¹⁸⁵ Additionally, a long temp aging of old brandies decreases alcohol along time due to evaporation and may already be at the appropriate strength at the time of blending and bottling so no reduction is required.⁶³

European varieties

The Cabernet-Sauvignon grapevine variety accounts 86 ha (11.8%) of the Central Valley of Tarija vineyard surface, being the second most cultivated grapevine variety in this valley after Moscatel de Alejandría.¹⁶⁴ The third variety in importance, in the Central Valley of Tarija, is Syrah, covering 39 ha (5.4%) of the cultivated surface, following by Malbec, which holds 35 ha of the Central Valley of Tarija surface (4.8%).

¹⁶⁴ As it was mentioned, there is little available information about oenological potential of the grapevine varieties cultivated in Bolivia and most of the reports are related to the effects of UV-radiation on grape and wine quality due to the particularities of the Bolivian vitiviniculture.^{175,176,186,187} Ayarde Mogro et al.¹⁸⁷ studied total antioxidant content and total polyphenols in Carignan, Moscatel de Alejandría, Syrah and Cabernet-Sauvignon varieties subjected under three different levels of solar ultraviolet radiation using anti-hail nets. These authors reported that total antioxidant content in the grapes increased in grapevines subjected to anti-hail nets treatments. Ceppi de Lecco and Castillo¹⁸⁸ characterized the wines from Syrah and Cabernet-Sauvignon grapevines located in different sites of the Central Valley of Tarija. These authors reported that Cabernet-Sauvignon wines from Pampa Colorada and Santa Ana sites presented higher alcohol degree, total phenols and anthocyanins than the Cabernet-Sauvignon wines from Pampa la Villa and La Compañía sites. In this report, Syrah wines from Pampa la Villa and La Compañía sites presented higher anthocyanins than the Syrah wines from Pampa Colorada and Santa Ana sites. Total phenols and color index in Syrah wines were not affected by the edaphoclimatic differences of the sites. According to these results, it

seems to be that the edaphoclimatic conditions of the sites could considerably affect the wine quality with a varietal dependence.

As has been shown, scarce available information there is about oenological potential of Bolivian grapevine varieties and most of the studies are published in national scientific and technical journals or divulgated in local congresses. Currently, viticultural and oenological research is incipient. Bolivia vitiviniculture has a great potential for develop, which is differentiated from the rest of the South American countries by the altitude that the vineyards are located. Bolivia also has a historical heritage, which gives it a significant added value.

CONCLUSIONS

Currently, there is an important tendency to revalorize and preserve the minority or autochthonous grapevine varieties in different wine-growing zones, as well as in South America. This is of a wide importance if we considered the historical context of the traditional products elaborated in South America, since the hegemony of the French paradigm, which has dominated the consumption patterns since the mid-19th century, made almost all typical products disappear, being replaced by imported drinks and foods or their imitations elaborated in Chile and Argentina. At present, there is little information available about the oenological potential of these varieties since the current wine industry is focused on the production of the most famous grapevine varieties associated to the French paradigm, such as Cabernet-Sauvignon, Merlot, Pinot Noir, Syrah, Sauvignon Blanc and Chardonnay, among others. The knowledge about the

oenological potential of minority or autochthonous South American varieties gives us a valuable possibility to generate production alternatives to the current wine market. The oenological potential of these varieties strongly depends on the origin of the variety and edaphoclimatic conditions. Canopy and crop load management can modify grape quality in accordance to the productive goal of the winegrower. However, most of these grapevine varieties are cultivated under rainfed conditions and defoliation could be a detrimental practice to grape quality. *Vitis vinifera* L., rustic varieties have distinctive oenological characteristics compared to the commonly *V. vinifera* L., cultivated grapevine varieties, presenting wide differences on their anthocyanins, tannin and volatile composition with imbalances in their sensory attributes in some cases. However, the researches carried out has allowed to find appropriate productive alternatives for these varieties and a large part of them are still being studied. Lastly, the current progress towards the development of a sustainable viticulture opens an important opportunity to these varieties, which are mostly resistant to pests and diseases. Therefore, viticulturists and winemakers must to consider these outstanding opportunities, in order to provide to the competitive world wine market, a wide range of wine products with a distinctive identity.

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Figure Captions

Figure 1. Natural crossings resulting in different South American cultivars. *Footnote:* Information obtained to the reported by Aliquó et al.⁸

Figure 2. Autochthonous and minority varieties cultivated in Argentina and Bolivia: 1) Grape cluster of Cereza variety. 2) Grape cluster of Vicchoqueña variety. 3) Grape cluster of Torrontés Riojano variety. 4) Leaves and grape clusters of Pedro Giménez variety. 5) Leaves and grape clusters of Cereza variety. 6) Leaves and grape clusters of Torrontés Riojano variety. *Footnote:* Elaborated using own information and the reported by different available sources^{58,190}

Figure 3. Wine Regions of Argentina.¹⁸⁹

Figure 4. Grape clusters of the following autochthonous and minority varieties cultivated in Chile: 1) Listán Prieto. 2) Carignan. 3) Carmenère. 4) Moscatel de Alejandría. 5) Grosse Méridle. 6) Blanca Ovoide. 7) Torontel. 8) Cinsault. 9) Aspirant Bouschet. *Footnote:* Elaborated using own information and the reported by Pszczółkowski et al.¹⁵⁸

Figure 5. Wine Regions of Chile.¹⁸⁹

Figure 6. Wine Regions of Bolivia.¹⁶⁴

Table 1. Summary of the oenological potential of minority and autochthonous varieties cultivated in South America.

Variety	Colour	Description	References
Argentina			
Torrontés Riojano	White	Aromatic variety with a high terpenoids content.	61
		Abundant free monoterpenoids such as β -citronellol, geraniol, hotrienol, limonene, linalool, nerol and α -terpineol.	62
Pedro Giménez	White	High intensity fruit aromas such as pear and apple.	68
		Prevalence of β -damascenone, α -ionone, β -linalool, geraniol, ethyl butanoate, ethyl hexanoate and ethyl octanoate in wines.	70
Chile			
País	Red	Unbalanced and rough wines.	88
		Abundance of proanthocyanidins.	89
		High – OH availability, higher mean degree of polymerisation (mDP) and presence of epicatechin-gallate (ECG).	90
		Grape pomace contains a good source of malvidin-3-glucoside, while leaves have abundant amounts of quercetin-3-hexoside and caftaric acid.	93
		Diethyl succinate, ethyl lactate, and ethyl isovalerate could be used as aging markers in País sparkling wines.	42
		Vitispiranes were identified as the best C ₁₃ -norisoprenoids aging markers for young sparkling wines.	42
		<i>cis</i> -2-Hexenol could be a good candidate to assess maturity in País.	24
Carignan	Red	High anthocyanin concentration compared to Carignan cultivated in other valleys.	29
		Cool climate provides grapes with high amino acid content and fermentative volatiles in wines.	16,26,28
		Ethyl esters and β -damascenone were the most odoriferous compounds.	26
Carmenère	Red	Presence of soft and round tannins, even though it is sometimes possible to obtain a small degree of bitterness.	126
		Seeds present low concentration of monomeric flavanols and (+)-catechin.	137
		Seeds present high degree of polymerization, percentage of galloylation, molecular weight of the flavanol fraction, among others.	137
		Seeds present high concentrations proanthocyanidin B1, B4G and B2.	138
		Important concentrations of 3-isobutyl-2-methoxypyrazine (IBPM) in grapes and wines.	136
		β -damascenone, several thiols, ethyl octanoate, 2 phenylethanol, and 2-isobutyl-3- methoxypyrazine presented significant odor activities values (OAV): cooked fruits, berries-like and herbaceous notes characterized Carménère wines.	125
		Presence of 2-furanylmethanethiol, 3-sulfanylhhexyl acetate, 3-sulfanyl-1-hexanol, and 2-methyl-3 sulfanyl-1-butanol wines.	142
Moscatel de Alejandría	White	High total free and bound terpenoids.	154
		Linalool is the most prevalent volatile compound in Moscatel de Alejandría clusters exposed to sun.	23

Bolivia

Autochthonous varieties	Red-White	High content of phenolic compounds, mainly of stilbenes.	175,186
European varieties	Red	High content of phenolic compounds, mainly of stilbenes.	175,186
		High concentration of resveratrol, total antioxidant capacity and total flavonoids compared to Argentinean, Chilean and Uruguayan wines	176
	Red	Differences on anthocyanins and phenolic compounds content in Cabernet Sauvignon and Syrah grapes widely depended on variety and edaphoclimatic conditions	188

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

WINES OF CHILE MAP AND REGIONS

Coquimbo

- Elqui valley
- Limari valley
- Choapa valley

Aconcagua

- Aconcagua valley
- Casablanca valley
- San Antonio & Leyda valley

Central Valley

- Maipo valley
- Cachapoal valley
- Colchagua valley
- Curico valley
- Maule Valley

Southern Chile

- Itata valley
- Bio-Bio
- Malleco valleys

Figure 6.