17 November 2018; Accepted : 7 February 2019; Published : 10 March 2019
DOI : 10.20870/oeno-one.2019.53.1.2348

Terroir and typicity of Carignan from Maule Valley (Chile): the resurgence of a minority variety

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ABSTRACT

Carignan is one of those minor cultivars that have had a major resurgence in the Chilean wine industry, and its production is sold at a price well above the national average. This variety, together with other autochthonous grapevine varieties, makes up a unique heritage in Chilean winemaking, which has given a new identity to the country on the world wine scene. Chilean viticulture is based on the production of the most recognized grapevine varieties such as Cabernet Sauvignon, Merlot, Chardonnay and Sauvignon blanc. However, this has caused a massive loss of minority and autochthonous grapevine varieties in certain wine growing regions. Thus, this review summarizes the effects of terroir of the Maule Valley on the typicity of Carignan. Carignan grapevines growing in the sites closer to the Pacific Ocean, such as Truquilemu and Ciénaga de Name, present a high concentration of several amino acids and volatile compounds in grapes and wines, while Carignan grapevines growing in the sites further east, towards the Andes Mountains, provide grapes and wines with a high alcohol and phenolic concentration. Therefore, Maule Valley provides unique edaphoclimatic conditions that allow differences in the composition and style of the Carignan wines.

KEYWORDS

Carignan, Maule Valley, minority cultivar, terroir, grape composition, wine style

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Over the last few decades, the introduction and spread of recognized grapevine varieties has caused a massive loss of minority and autochthonous grapevine varieties traditionally grown in several wine growing regions (Martínez de Toda *et al*., 2004; Xu *et al*., 2010; García-Carpintero *et al*., 2011; Martínez-Pinilla *et al*., 2012; Meng *et al*., 2012; Vilanova *et al*., 2012; Liang *et al*., 2013; Pedneault *et al*., 2013; Cejudo-Bastante *et al*., 2015; Slegers *et al*., 2015; Loureiro *et al*., 2016; Balda and Martínez de Toda, 2017; Nicolle *et al*., 2018). Additionally, the disappearance of a large number of old grapevine varieties and the varietal homogenization of the vineyards entail an increase in genetic vulnerability in relation to the spread of pathogens against which the cultivated varieties are not resistant (Balda and Martínez de Toda, 2017). *Vitis vinifera* vines were brought to Chile by Spanish conquistadors and missionaries in the 16th century around 1554 (Hernández and Moreno, 2011). Since then, it is considered that Criolla viticulture originated from some foundational genotypes considering País (Listán Prieto) and Moscatel de Alejandría (Milla-Tapia *et al*., 2013; Aliquó *et al*., 2017). During several centuries (Spanish colonization), both in the Kingdom of Chile and in other territories of the vast Spanish empire, most of the vineyards were cultivated with red varieties, called simply "black grapes" (Lacoste *et al*., 2010). Around 1990, most of these old grapevine varieties were uprooted (Knowles and Sharples, 2002). In this way, the Cabernet Sauvignon surface doubled from 11,000 to 20,000 hectares. Merlot vineyard acreage quadrupled between 1994 and 1999. With respect to white varieties, Chardonnay and Sauvignon blanc exploded, while the "old" grape varieties stagnated (Knowles and Sharples, 2002). This type of viticulture based on renowned grapevine varieties is the one that currently prevails in Chile.

However, in the last decade, several grapevine varieties overseen for years by the Chilean wine industry have emerged due mainly to changes in wine consumer's habits and the oenological potential of these grapevines. This has allowed the economic and social recovery of the small vine growers, who grow most of the minority and autochthonous grapevine varieties in Chile (Pascual *et al*., 2017; Ubeda *et al*., 2017a; Gutiérrez-Gamboa *et al*., 2018a; Martínez-Gil *et al*., 2018a). Carignan is one of those minor cultivars that have had a major resurgence, and its production is sold at a price well above the national average (Gutiérrez-Gamboa *et al*., 2018b, 2018c; Martínez-Gil *et al*., 2018a). Carignan, together with most of the minority and autochthonous national grapevine varieties, makes up a unique heritage in Chilean winemaking, which has given a new identity to the country on the world wine scene (Gutiérrez-Gamboa *et al*., 2018c). These grapevine varieties have been cultivated mostly in Maule, Itata and Bio Bio Valleys, the largest wine-producing areas of Chile, with unirrigated vines trained to a traditional bush system and managed by small wine growers (Pascual *et al*., 2017; Gutiérrez-Gamboa and Moreno-Simunovic, 2018; Gutiérrez-Gamboa *et al*., 2018a, 2018c). In particular, Maule Valley holds approximately 700 (83%) of the 843 hectares of Carignan noir planted in the country (Gutiérrez-Gamboa *et al*., 2018c). Maule Valley is the largest wine region in Chile. It extends from the foothills of the Andes Mountains in the east to the Coastal Range in the west, closer to the Pacific Ocean. 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 (Ubeda *et al*., 2017b; Cejudo-Bastante *et al*., 2018; Gutiérrez-Gamboa *et al*., 2018b, 2018d). The origin of Carignan in Chile is diffuse. However, most of the winemakers and vine growers agree that the first vine cuttings were brought from the South of France after the Chillán earthquake of January 24, 1939, which devastated the viticulture of the Valleys of Maule, Bio Bio and Itata (Gutiérrez-Gamboa and Moreno-Simunovic, 2018). The goal of importing French Carignan vines, at that time, was to improve the color and freshness of the wines produced from País grapevines, a variety that dominated the viticulture of the area. Currently, Carignan wines are mainly associated with the collective brand "VIGNO", which has attracted the attention of wine critics and specialists, who visit the area year after year and enjoy its economic, social and environmental characteristics. This has benefited the rural sector of the region. Thus, this review exposes the collective efforts of the Chilean academia, government, and grape and wine industry in the recovery of a minority grapevine variety, namely Carignan, which improved the economic and social conditions of one of the most vulnerable areas of the country. Knowledge of the chemical composition can provide opportunities for the adaptation of the characteristics of this minority

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grape variety to the winemaking processes defined by the consumer□s preferences. In this way, this review summarizes the effects of terroir on the typicity of the Carignan grapevine variety.

TERROIR OF THE CARIGNAN VINEYARDS

1. Geology of Maule region's interior dryland

As shown in Figures 1 and 2, the interior dryland of Maule Valley consists of three large geological units with identifiable and homogenous features (Pinochet, 1983). The first is the Granitic Intrusive unit, which crops out over most of the zone. It is particularly prominent in the western hills and mountain chains present in the area, and is also part of the Coastal Batholith. Approximately 340 to 290 ± 40 million years old, this formation evolved from the ancient magma chambers of the coastal volcanic chain during the Paleozoic era (Carboniferous-Permian) (Escobar *et al*., 1977; Alfaro-Soto, 2011). After the migration of the volcanic arc to the east, these chambers began to cool and solidify, and as the upper layers eroded, they were gradually exposed to the surface. In addition to granitic rocks, one can identify various other intrusive rocks in this unit such as granodiorites and tonalites, which are composed of four types of minerals: quartz, plagioclase (sodium-calcium) feldspars, orthoclase (potassium) feldspars, and micas. In the study region, Muscovite mica can be identified by its golden and pearly white translucent sheets. These rocks have evolved into soils in situ that were generated from mechanical weathering processes owing to the ambient humidity and rapid temperature shifts. These successive expansion and compression forces broke down the original basement rock, giving rise to maicillo type soils, which correspond to an aggregation of individual minerals such as quartz, feldspars and micas. As these soils evolve, their chemical processes accelerate, affecting the surface of the most susceptible minerals such as feldspars and micas. This process leads to clay minerals such as Kaolinite and Smectite. Thus, a high clay content in the soils indicates a more evolved state than that of soils with less clay. Some examples of soils derived in situ for this unit can be found in some Carignan vineyards located in Loncomilla, Sauzal, Pilén and Cauquenes. The second geomorphological unit corresponds to Sedimentary Rocks or stratified rocks of volcanic-sedimentary origin known as the Pocillas-Coronel de Maule-Quirihue strata, which were deposited on top of the Coastal Batholith around 250 million years ago during the Triassic period. These rocks form part of the discontinuous outcroppings found throughout the region, primarily to the south of the area under study. While they are a significant geological formation in the region, there are not many Carignan vineyards associated with them. The third large unit is Sedimentary Fill, which includes sediments associated with fill deposited in basins located on flat zones or rolling hills. These are characterized by rock fragments of different sizes as well as fine sediments, which form a heterogeneous matrix and correspond to alluvial and/or colluvial fill zones. The colluvial deposits are associated with sectors close to more elevated hills and receive sediments from both natural gravitational collapse and large-scale movement of earth, giving rise to abundant angular fragments in a sandy matrix. For their part, alluvial sediments are associated with watercourses (currently active or not). These sediments are characterized by rounded or partially rounded fragments in a matrix with abundant clay. In both cases, the fragments present in the soils correspond to intrusive rocks such as granite, granodiorite and tonalite, all belonging to the intrusive basement surrounding these depressed zones. Because these soils are found in low-lying zones, they tend to accumulate more water than other sectors. In combination with the already fine matrix, this accelerates chemical weathering processes, leading to a higher presence of clay. Some examples of soils derived from these kinds of sediment can be found in the Carignan vineyards located in Huerta de Maule, Truquilemu, Melozal, Ciénaga de Name, Cauquenes and Pocillas.

2. Soils of Maule region's interior dryland

The various soils of the Maule region developed over a broad timeframe ranging from just over 400 million years ago to a few thousand or even hundreds years ago (Figure 2). While their material origin is also very diverse, in Maule it is possible to identify the four geomorphological areas characteristic of Chile's central zone: a) Marine terraces with some schist and micro schist from the Quaternary period; 2) the Coastal Range, which has the oldest soils in the region, originating primarily in the Mesozoic and even Paleozoic eras, and having two predominant source materials-granitic and metamorphic rocks; 3) the Central Valley, containing the

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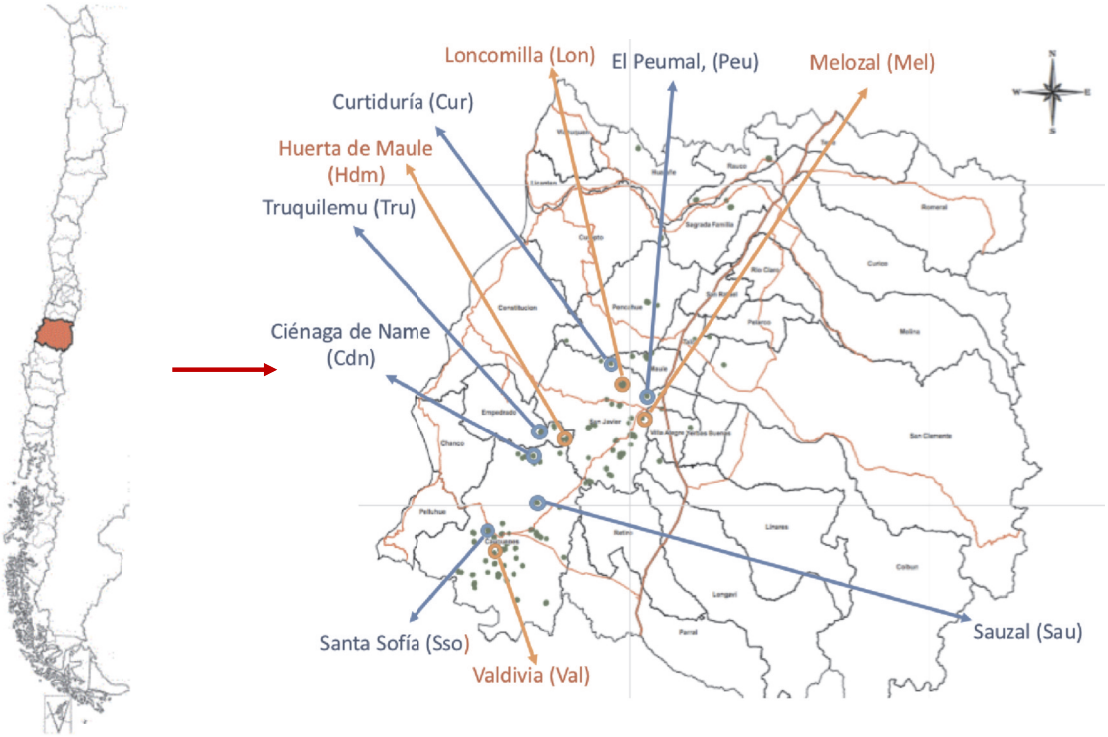


FIGURE 1. Locations of the most important sites cultivated with Carignan grapevines in the Maule Valley (Chile).

youngest soils, generated by fluvioglacial, alluvial and volcanic processes during the Tertiary and Quaternary periods; and 4) the Andean foothills, where the predominant soils are the product of recent volcanic ash deposits from the Tertiary and Quaternary periods (Thiele, 1980; Rauld, 2002). In the dryland area, where the Carignan vineyards are found, analyses of physico-hydric, morphological and stratigraphic properties have enabled the classification of five broad Morphological Units (MUs). These MUs are delineated primarily by their water retention capacity, which is determined by the depth and texture of the soil profile at the point of maximum root exploration of the vines. Within each MU, evolved and unevolved soils can be identified, meaning soils of ancient or recent geological origin, respectively. The soils of the zone under study correspond primarily to highly evolved soils formed from granitic and metamorphic rocks from the Paleozoic and Mesozoic eras. Among these soils, the Alfisol order and Cauquenes and Pocillas soil associations predominate. There are also smaller proportions of less evolved soils, corresponding to the Quaternary period of the Cenozoic era. In these soils, the Inceptisol order and Melozal, Ninhue and Totoral soil series predominate. MU 1 has soils with a high water retention capacity and a very high effective depth, a predominance of moderately coarse textures on the surface and fine to moderately fine textures at depth, and a high clay content. MU 2 soils are deep, with a high water retention capacity and predominantly moderate to medium textures throughout the profile. MU 3 soils have a medium water retention capacity, are moderately deep to deep and display moderately coarse textures on the surface and fine textures at depth. MU 4 displays deep soils with medium water retention capacity, and very coarse to moderately coarse textures throughout the soil profile. Lastly, MU 5 corresponds to marginally deep soils with low water retention capacity and a soil profile comprised of moderately coarse and moderately fine textures throughout. Soils from these MUs are described by Gutiérrez-Gamboa and Moreno-Simunovic (2018), Gutiérrez-Gamboa *et al*. (2018b, 2018c, 2018d) and Martínez-Gil *et al*. (2018b).

3. Viticultural conditions of Maule region's interior dryland

The geomorphology of Chile's central zone south of 34° S latitude presents three morpho-structural units running parallel from NNW to SSW - the Coastal Range, the Central Depression, and the Andes Mountains (Pinochet, 1983). The interior dryland is located on the

eastern flank of the Coastal Range, in a zone dominated by intrusive basement rock known as "Coastal Batholith". This formation corresponds to a large chain of mountains running north-south that transitions into a relatively flat geomorphology on the east side, where a zone of alluvial and colluvial fill marks the western edge of the large basin that is Chile's Central Depression. In the interior dryland, the Coastal Range comprises two chains running north-south at altitudes ranging between 300 and 600 meters above sea level (m a.s.l.) and occasionally reaching 900 m a.s.l. in the easternmost range. Between these two chains are intermontane basins such as Empedrado and Cauquenes, which are sheltered from the coastal breezes. As it is exposed to the cool, humid winds from the ocean, the eastern watershed of the Coastal Range has greater temperature oscillations, and being in the rainshadow of the Coastal Range, summer rainfall is reduced by approximately 200 mm during the vine's active growth period (from October to March). In terms of topography, the zone consists of rolling hills and swampy grasslands (vegas) that offer a diverse array of landscapes favorable for viticulture. Most of the Carignan vineyards are located between 40 and 250 m a.s.l., and while one can hardly speak of high altitude vineyards here, the altitude of vineyards in the zone does vary by up to 200 m, which influences the mesoclimatic growing conditions of Maule Carignan. In general, sectors close to the eastern watershed of the Coastal Range are at higher altitudes and have lower heat summations during the growing season, while those on the west and north are at the lowest altitudes and have the greatest heat summations. Hydrographically, the principal watercourses in the zone include the Maule and Loncomilla Rivers. The former is the fourth largest river in Chile, with a hydrographic basin that covers an area of 20,295 km^2 and has a mean flow rate of 467 m^3/s. Originating in the Coastal Range, the Cauquenes River flows eastward before joining the Perquilauquén River, which crosses part of Cauquenes Province. When it crosses the city of Cauquenes, the river joins up with the Tutuvén River, which is another major water source for local agriculture. As a transition zone between the Valdivian temperate rainforest biome and the Chilean sclerophyllous scrubland, the ecosystems of Maule are known globally for their uniqueness and biodiversity (Amigo and Ramírez, 1998;

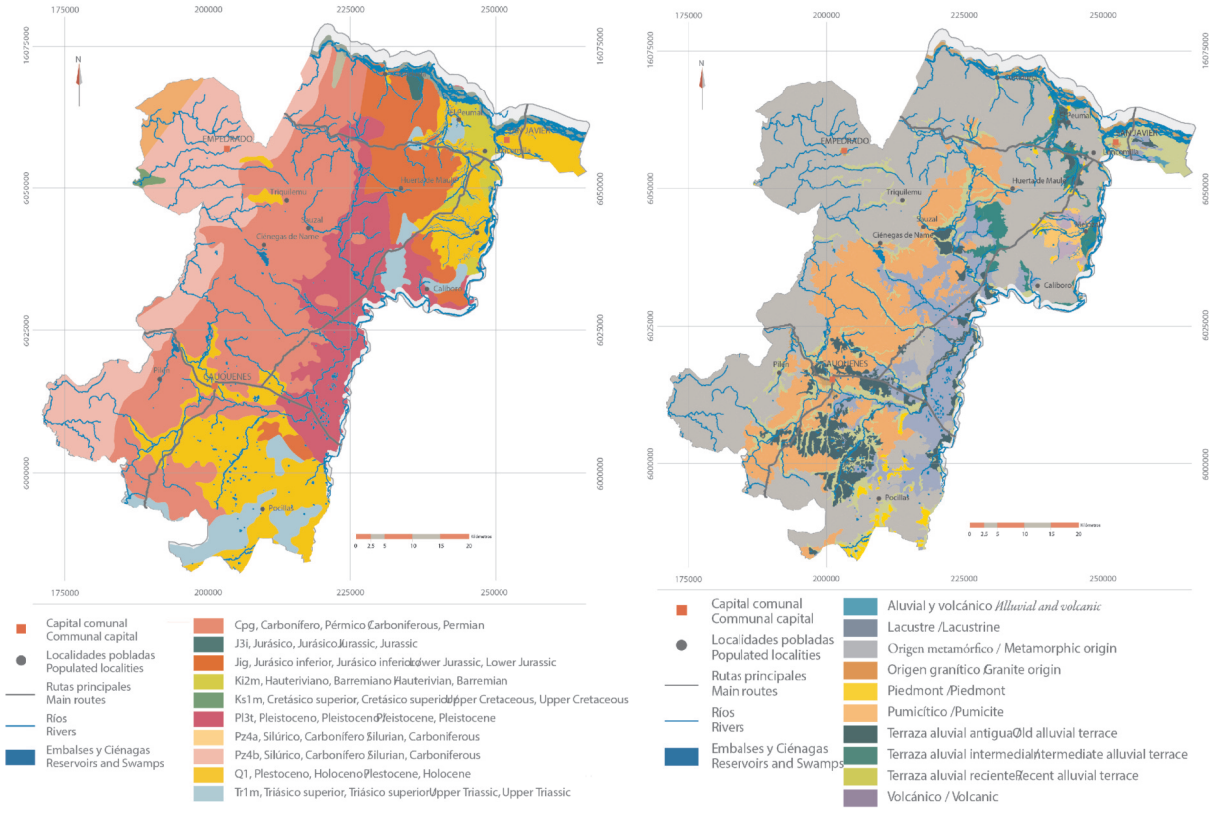


FIGURE 2. Geological (left) and soil (right) information of the Maule Valley.

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Luebert and Pliscoff, 2006; Ramírez *et al*., 2014). The zone's endemic vegetation is dominated by Aromo (*Acacia caven*) steppe. Towards the eastern limit of the Coastal Range and in sectors with deeper soils, there is sclerophyllous scrub with species such as Quillay (*Quillaja saponaria*), Boldo (*Peumus boldus*) and Peumo (*Cryptocarya alba*). In sectors that are cooler and at higher altitudes it is possible to find small tracts of species such as Maitén (*Maytenus boaria*), Quila (*Chusquea quila*), Quillay, Peumo and Boldo.

4. Mesoclimate of Maule region's interior dryland

The Heliothermal Index (HI) expresses the favorability of thermal conditions during the daylight period, which affects the growth of plants and their ability to ripen the fruit (Huglin, 1978; Blanco-Ward *et al*., 2007; Jones *et al*., 2010; Köse, 2014; Gutiérrez-Gamboa *et al*., 2018b). The HI includes average and maximum temperatures during the active vegetative period, corrected for the length of the day (Huglin, 1978; Köse, 2014). For the zone in question, HI values fall into two categories: Warm Temperate climate (HI>2100) for Truquilemu, and Warm climate (HI>2400) for the rest of the Carignan vineyards studied. These values ensure the complete ripening of this cultivar's fruit (Huglin, 1978; Ubeda *et al*., 2017a; Cejudo-Bastante *et al*., 2018; Gutiérrez-Gamboa *et al*., 2018c). Another factor with a marked impact on the fruit is the nighttime temperature regime during the final ripening period. In vigorous vineyards, low nighttime temperatures slow the growth of shoots, generating surplus carbohydrates that can accumulate in the fruit. Cool nights also support the synthesis of secondary metabolites, improving color intensity and preserving fruit aromas in the must (Tonietto and Carbonneau, 2004; Blanco-Ward *et al*., 2007; Montes *et al*., 2012; Bonnefoy *et al*., 2013; Gutiérrez-Gamboa *et al*., 2018c). From this perspective, the Cool Night Index (CI) expresses the mean minimum air temperature during the 30 days prior to harvest. In this zone the CI presents two sectors classified as having Cold Nights ($12 \leq CI < 13.9$) and Very Cold Nights ($CI < 11.9$), which correspond to the occurrence of two distinctive aromatic profiles. The heat summation in this zone, measured in terms of Cumulative Effective Degree Days (CEDD) and corrected for maximum daily temperature and latitude, fluctuates between 1,061 and 1,927 degree days. Virtually the entire zone achieves values well above the minimum threshold established for Carignan (1,050 to 1,100 degree days), allowing the fruit to ripen completely (Matthews *et al*., 1987; Jones *et al*., 2010; Campbell, 2013). For the Carignan vineyards located near the eastern watershed of the Coastal Range and at a higher altitude in Truquilemu and Pilén, the heat summation values are generally lower, approaching the minimum advisable threshold in cold seasons. Thus, at these sites, the fruit load is carefully adjusted each year by pruning to achieve a vegetative-reproductive balance that will ensure adequate ripening (Gutiérrez-Gamboa *et al*., 2018c). Finally, the Mean Temperature of the Warmest Month of the year (MTWM) allows a vitivinicultural zone to be characterized in terms of the potential style of wine to be produced (Smart and Dry, 1980; Jackson and Cherry, 1988; Villiers, 1997; Martínez-Gil *et al*., 2018b). In this way, sectors with a lower index, meaning those with a cooler summer, produce wines with high acidity, low pH, and a distinctive varietal character. Each of these attributes is different at higher temperatures. The zone under study presents three very well-defined sectors: Moderate Climate, with mean temperatures fluctuating between 21 and 22.9°C, including vineyards in the locations of Curtiduría, El Peumal, Loncomilla, Melozal, Majuelo, Caliboro, Cauquenes and Pocillas; Cold Climate, with mean temperatures fluctuating between 19 and 20.9°C, including vineyards in the locations of Huerta de Maule, Truquilemu, Sauzal, Santa Sofía, Pilén and Cauquenes; and Very Cold Climate, with mean temperatures fluctuating between 17 and 18.9°C, including vineyards near Ciénaga de Name.

5. Carignan vineyards of the Maule Valley

The Carignan cultivar is characterized by young, open-tipped buds with very dense trichomes and stalks with internodes and reddish striations. The young leaves are a shiny yellow-green, while the mature leaves are very large, five-lobed, and green to dark green in color, with a narrow V-shaped petiolar sinus (Galet, 1998; Moreno and Vallarino, 2011). The lateral sinuses range from shallow to deep. The mature leaves have a warped blade with significant puckering and the underside is rather glabrous, with sparse trichomes. Most Carignan vineyards found in the Maule dry-farmed area are ungrafted, meaning that they grow on their original rootstock

(Gutiérrez-Gamboa and Moreno-Simunovic, 2018). The exception to this consists of a small fraction of vineyards that have been grafted onto other traditional cultivars such as País (4%) or Torontel (1%) (Gutiérrez-Gamboa *et al*., 2018a, 2018c). Despite the changes that dry-farmed viticulture has undergone in the past 50 years, most Carignan vineyards have maintained a high level of varietal purity over time and, as a result, other traditional cultivars such as País, Muscat of Alexandria, Cinsault, or Torontel are found in only 5% of these vineyards. In terms of cluster architecture, the bunches are compact, cylindroconical and medium to large in size (OIV, 2001). Each cluster comprises 300 to 350 medium-sized spherical black-blue berries that are quite uniform and weigh between 1.1 and 1.5 g each (OIV, 2001). From an agronomical perspective, Carignan is a rather late-budding cultivar (approximately 10 days later than Chardonnay), which decreases the risk of damage from spring frosts (Moreno and Vallarino, 2011). It grows erect and has extremely fertile basal nodes, so it is spur-pruned and head- or Gobelet trained. It is tolerant of warm climatic conditions, long dry summers, and soils with moderate to low fertility. Hillsides or other soils with limited depth or fertility thus provide a vegetative/productive balance, which optimizes fruit quality (Edo-Roca *et al*., 2013). Carignan adapts very well to windy conditions and its shoots lignify early in the season and mature well. It is very sensitive to *Uncinula necator* (powdery mildew), which is controlled through preventive programs targeting this disease. Under the growing conditions of the Maule region's interior dryland, Carignan displays great color potential and firm tannins (Martínez-Gil *et al*., 2018b). In older vineyards, with careful management of winter pruning, shoot removal, and cluster thinning, it is possible to balance vegetative expression and yield per vine to obtain wines of very high quality, with prominent but fine tannins, refreshing acidity and subtle aromas with cherry and floral notes (Ubeda *et al*., 2017b; Gutiérrez-Gamboa *et al*., 2018c, 2018d).

TYPICITY OF THE CARIGNAN VINEYARDS

1. Nitrogen composition

Nitrogen composition of grapes affects the growth and metabolism of the yeasts, which is directly related to the kinetics of alcoholic fermentation and subsequently the formation of fermentative volatile compounds responsible for the aroma of the wine (Bell and Henschke, 2005). The yeasts of the genus *Saccharomyces* are not able to assimilate inorganic nitrogen sources such as nitrates, nitrites, proteins and polypeptides, which are usually present in the must (Carrascosa *et al*., 2011). In this way, ammonium ions and amino acids (excluding proline) are the main nitrogenous sources used by yeasts to carry out a complete alcoholic fermentation (Bell and Henschke, 2005). It is known that a concentration greater than 140 mg N/L of assimilable nitrogen is generally considered as the threshold nitrogen content to carry out a correct alcoholic fermentation, avoiding stuck or sluggish fermentation (Bisson and Butzke, 2000). In this sense, considering amino acid fraction, the grapes from the different sites of the Maule Valley have a concentration below the lower threshold (Gutiérrez-Gamboa *et al*., 2018c). It is important to highlight that the availability of nitrogen for Carignan vines growing in rainfed conditions depends on the presence of water in the soil, which is mainly accumulated during the winter or early spring rains (Christensen and Peacock, 2000; Gutiérrez-Gamboa *et al*., 2018c). Therefore, the addition of inorganic nitrogen such as diammonium phosphate (DAP), or organic nitrogen such as amino acids, in addition to corrections through foliar fertilization in the vineyard, can be an alternative to prevent problems associated with nitrogen deficiencies in the must (Arias-Gil *et al*., 2007; Garde-Cerdán and Ancín-Azpilicueta, 2008; Lacroux *et al*., 2008; Mendes-Ferreira *et al*., 2010; Garde-Cerdán *et al*., 2014; Hannam *et al*., 2014; Verdenal *et al*., 2015; Hannam *et al*., 2016; Verdenal *et al*., 2016; Garde-Cerdán *et al*., 2017; Gutiérrez-Gamboa *et al*., 2017, 2018e, 2019).

Arginine is an important source of nitrogen for yeasts (Bely *et al*., 1990; Stines *et al*., 2000; Bell and Henschke, 2005; Vilanova *et al*., 2007). In contrast, proline is not usually metabolized by yeast and only a small amount of this amino acid is absorbed by yeast in nitrogen de-repression environments when oxygen is present (Watson, 1976; Ough *et al*., 1991; Bell and Henschke, 2005; Arias-Gil *et al*., 2007). The concentration of arginine in the Carignan grape varied from 20.3 to 219.3 mg/L in the Loncomilla and Ciénaga de Name sites, respectively, while the proline content varied from 212.0 to 484.8 mg/L

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in the Loncomilla and El Peumal sites, respectively (Gutiérrez-Gamboa *et al*., 2018c). In this way, grapevine varieties can be classified into two categories based on their nitrogen behavior in relation to the accumulation of one of these amino acids versus the other (Huang and Ough, 1991; Stines *et al*., 2000; Bell and Henschke, 2005; Bouzas-Cid *et al*., 2015). Consequently, two varieties may have the same total amino acid content; however, the cultivar that accumulates a high amount of proline in relation to arginine will have a smaller amount of easily assimilable nitrogen than the variety that accumulates a higher concentration of arginine in relation to proline (Bell and Henschke, 2005). The proline to arginine ratio in the Carignan grape samples varies from 2 to 10 for the Ciénaga de Name and Loncomilla sites, respectively, so this cultivar tends to behave as a proline accumulator variety (Gutiérrez-Gamboa *et al*., 2018c). However, this is less apparent when calculated in terms of berry assimilable nitrogen, since arginine contains four atoms of N per molecule (Stines *et al*., 2000). In this way, the grapevines growing in cold sites such as Ciénaga de Name and Truquilemu tended to behave as an arginine accumulator variety, while in the rest of the sites, the grapevines tended to behave as a proline accumulator variety. It is possible to suggest that edaphoclimatic conditions could impact on the amino acid uptake of grapevines and in this way modify the nitrogen behavior of a specific grapevine variety with respect to its proline to arginine ratio. Despite this, Carignan grapevines from most of the sites of Maule Valley presented small amounts of easily assimilable nitrogen. Therefore, in Carignan grapevines it is important to develop preventive strategies for the management of possible stuck or sluggish fermentations. These troubles result in logistical problems in the winery and the production of undesirable aromas in wines, especially when easily assimilable nitrogen is low (Carrau *et al*., 2008). As was mentioned, Gutiérrez-Gamboa *et al*. (2018c) reported that the most abundant amino acid found in Carignan grapes was proline, whereas arginine, which is one of the most important nitrogen sources for yeasts, was the second most abundant amino acid (Figure 3). In addition, these authors reported that the most abundant amino acids found in Carignan noir grapevines grafted onto cv. País were, in decreasing order, proline, gamma-aminobutyric acid, arginine, glutamine and serine, while in ungrafted vines they were proline, arginine, gamma-aminobutyric acid, glutamine and serine.

As reported by several authors, amino acids are differently consumed by yeasts and therefore have been categorized into different groups (Cooper, 1982; Gorinstein *et al*., 1984; Large, 1986; Jiranek *et al*., 1991; Ough *et al*., 1991; Henschke and Jiranek, 1993; Jiranek *et al*., 1995; Bisson and Butzke, 2000; Soufleros *et al*., 2003; Valero *et al*., 2003; Bell and Henschke, 2005; Hernández-Orte *et al*., 2006; Arias-Gil *et al*., 2007; Garde-Cerdán *et al*., 2011; Gutiérrez-Gamboa *et al*., 2018c). In this way, amino acids

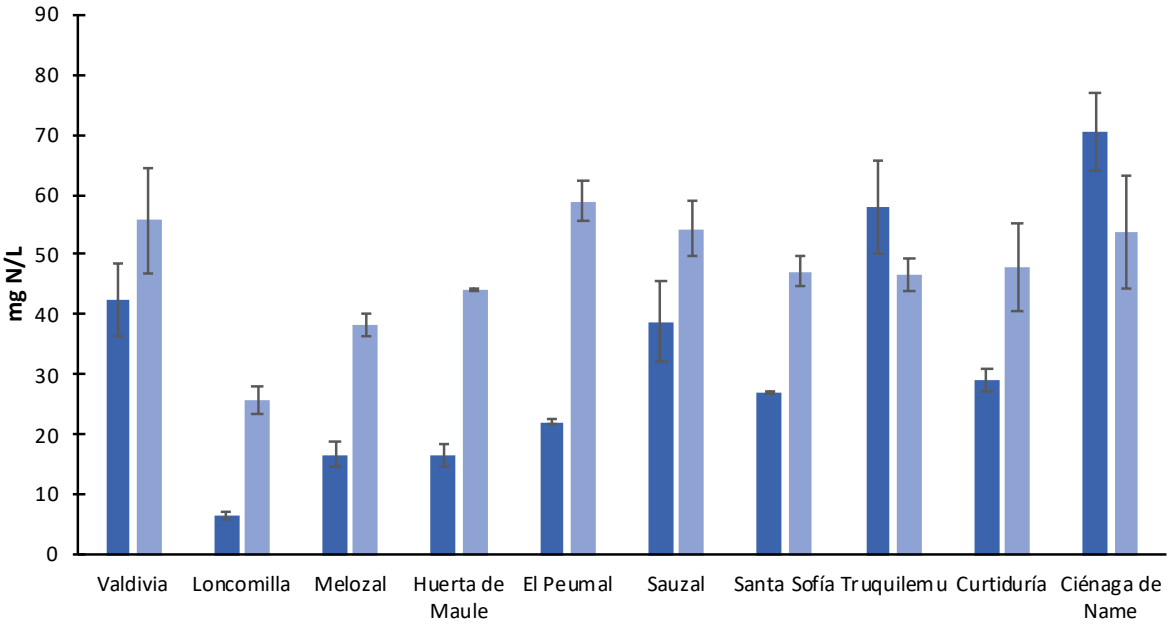


FIGURE 3. Arginine and proline concentration (mg N/L) in grapes from different sites of the Maule Valley.

such as arginine, aspartic acid, asparagine, glutamine, lysine, serine, threonine, methionine, isoleucine and leucine are considered amino acids easily assimilated by yeast. Histidine, valine, glutamic acid, alanine, phenylalanine, alpha and gamma aminobutyric acid are considered as fairly assimilable amino acids. Glycine, tyrosine, citrulline, ornithine and cysteine are poorly assimilable amino acids. Finally, proline and hydroxyproline are not assimilable by yeasts under normal fermentation conditions. The Carignan grape presents a greater proportion of amino acids that cannot be assimilated by the yeasts; in percentage, it varies from 30.4 to 49.7% of the total amino acids in the Ciénaga de Name and Loncomilla sites, respectively (Gutiérrez-Gamboa *et al*., 2018c). The proportion of easily assimilable amino acids form the second most important group in terms of quantity, which, in percentage, varies between 24.6 and 54.0% of the total amino acids in the Ciénaga de Name and Loncomilla sites, respectively (Gutiérrez-Gamboa *et al*., 2018c). The non-assimilable or slowly assimilating amino acids vary from 15.6 to 25.7% in the Ciénaga de Name and Loncomilla sites, respectively (Gutiérrez-Gamboa *et al*., 2018c). Finally, the total amino acid concentration varied between 369.6 and 1042.1 mg/L, while the total amino acid concentration without proline ranged from 157.6 to 599.7 mg/L in the Loncomilla and Ciénaga de Name sites, respectively (Gutiérrez-Gamboa *et al*., 2018c). Gutiérrez-Gamboa *et al*. (2018c) reported that the most abundant amino acids found in Carignan noir wines were proline, glutamic acid, gamma-aminobutyric acid, asparagine and cysteine. Proline was excreted by yeast to a concentration that varied from 17.86 to 816.66 mg/L for the wines from Loncomilla and Melozal sites, respectively. These authors showed that grape amino acid composition conditioned alcoholic fermentation, which was faster for musts coming from the colder sites such as Truquilemu and Ciénaga de Name compared to the rest of the sites.

2. Phenolic composition

Anthocyanins are responsible for the color of red wines and are involved in polymerization reactions that occur in wine aging (Boulton, 2001). In general, they are located inside the vacuoles of the grape skin cells in the three or four first cellular layers of the hypodermis (Ortega-Regules *et al*., 2008). As is shown in Figure 4, total anthocyanin concentration in Carignan grape from the Maule Valley varied between 1,582.59 and 2,271.31 mg/kg in Ciénaga de Name and Sauzal sites, respectively (Martínez-Gil *et al*., 2018b). The most abundant anthocyanin in Carignan grapes was malvidin-3-glucoside, which varied between 653.80 and 897.69 mg/kg in Ciénaga de Name and Sauzal sites, respectively (Martínez-Gil *et al*., 2018b). The concentrations mentioned above are higher than those reported by several authors in Carignan located in other wine growing regions such as southern France and Sardinia, Italy (Jensen *et al*., 2008; Fernandes de Oliveira *et al*., 2015). In this context, in warm vintages, Maule Valley can provide the ideal conditions to favor the synthesis of anthocyanins in Carignan grapevines. With respect to the anthocyanin composition of Carignan grapes and wines from the Maule Valley, the non-acylated form was the most abundant, followed by the coumaroylated form, while the acetylated form was the lowest (Gutiérrez-Gamboa *et al*., 2018b; Martínez-Gil *et al*., 2018b). These results are typical of the variety and agree with those reported by Fernandes de Oliveira *et al*. (2015) in Carignan grapes.

Flavonols are located mainly in the skins of grapes, and most of them are present in the glycoside, galactoside, rhamnoside, rutinoside or glucuronide forms or in the four aglycones such as quercetin, myricetin, kaempferol and isorhamnetin (Makris *et al*., 2006). However, other compounds derived from laricitrin and syringetin have been identified (Makris *et al*., 2006; Castillo-Muñoz *et al*., 2007). In wine, they can be found in free form due to the hydrolysis of glycosides during the winemaking process (Castillo-Muñoz *et al*., 2007). In Carignan grapes from the Maule Valley, myricetin-3-glucuronide, myricetin-3-galactoside, myricetin-3-glucoside, quercetin-3-glucuronide, quercetin-3-galactoside+rutin, laricitrin-3-glucoside, kaempferol-3-glucoside, isorhamnetin-3-glucoside and syringetin-3-glucoside have been identified (Martínez-Gil *et al*., 2018b). Total flavonol concentration of Carignan grapes from the Maule Valley varied from 152.14 to 279.64 mg/kg in Santa Sofía and Sauzal sites, respectively (Martínez-Gil *et al*., 2018b). Additionally, the most abundant flavonol derivative in Carignan grapes and wines was quercetin (Gutiérrez-Gamboa *et al*., 2018b; Martínez-Gil *et al*., 2018b). Flavanols (commonly called “tannins”) play a crucial role

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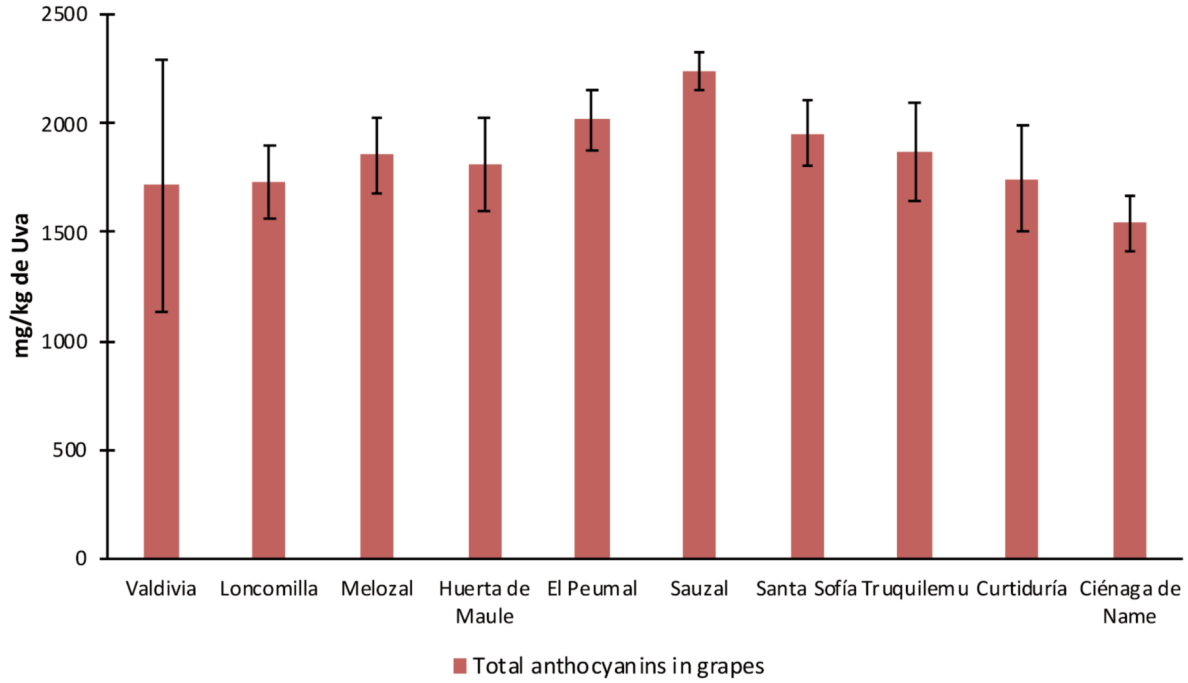


FIGURE 4. Total anthocyanin concentration (mg/kg) in grapes from different sites of the Maule Valley.

in the quality of wines because they confer properties of astringency, color and structure (Ma *et al*., 2014; Soares *et al*., 2017). In addition, they contribute to the stabilization of color during the aging process (Zamora, 2003). Six flavanols have been identified in Carignan grapes from the Maule Valley, namely dimer B1, dimer B2, epigallocatechin, catechin, epicatechin and epicatechin gallate (Martínez-Gil *et al*., 2018b). The most abundant flavanol in Carignan grapes was catechin, which varied from 27.36 to 46.55 mg/kg in Santa Sofía and Truquilemu sites, respectively, while total flavanol concentration varied from 96.08 to 156.72 mg/kg in El Peumal and Truquilemu sites, respectively (Martínez-Gil *et al*., 2018b).

Therefore, Maule Valley provides ideal conditions to improve the quality of Carignan grapes and wines in terms of phenolic composition. The edaphoclimatic conditions of the sites and the particular management of the grapes in the vineyard together with the winemaking processes in the wine cellar provide a wide variety of wine styles for Carignan. Martínez-Gil *et al*. (2018b) reported that cold sites influence the synthesis of flavanols and hydroxycinnamic acids in Carignan grapes, while warm sites allow to improve the synthesis of anthocyanins and flavonols. Gutiérrez-Gamboa *et al*. (2018b) showed that the water holding capacity and soil depth affected the berry weight of Carignan grapes and consequently the phenolic composition of the wines. In addition, these authors reported that climatic conditions affected alcoholic degree more than phenolic compounds in wines. Cejudo-Bastante *et al*. (2018) reported that the most abundant concentration of benzoic acids corresponded to wines elaborated in the Huerta del Maule site, whereas Cauquenes was found to be the zone with the lowest amount. These authors suggested that the Andes Mountains produced a wide range of Carignan red wines, with high content of polysaccharides, *cis*-resveratrol-glucoside and procyanidin B3, while the proximity to the ocean seemed to produce a unifying effect in chemical and colorimetric terms. However, these location effects were evaluated in commercial Carignan wines. In this way, these suggestions are in contrast to those reported by Martínez-Gil *et al*. (2018b) and Gutiérrez-Gamboa *et al*. (2018b, 2018c, 2018d), which showed that the cold sites influenced by the altitude, deep soils and sea breeze from the Pacific Ocean (Figure 5) resulted in more differentiated grapes and wines (non-commercial) in terms of amino acid, phenolic and volatile composition compared to the rest of the sites.

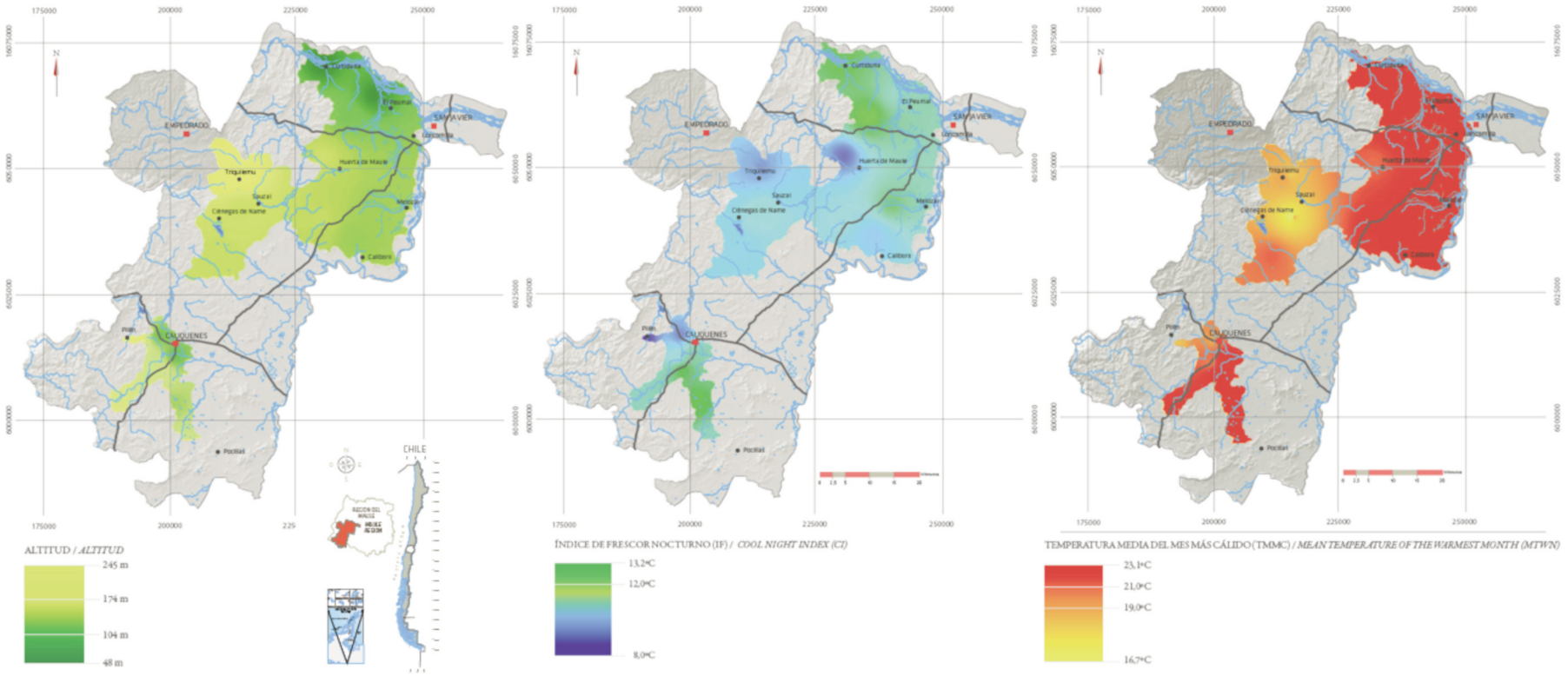


FIGURE 5. Altitude, Cool Night Index and Mean Temperature of the Warmest Month for Carignan grapevines from different sites of the Maule Valley.

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3. Volatile composition

Wine aroma is composed of a series of chemical families of volatile compounds that contribute differentially to its aroma (González-Barreiro *et al*., 2015). Higher alcohols are alcohols that have more than two carbons, a high molecular weight and a high boiling point (Boulton *et al*., 1996). These compounds are formed in low amount by the metabolism of yeasts during alcoholic fermentation (Bell and Henschke, 2005). Higher alcohols are formed anabolically by sugars and catabolically by amino acids through the Ehrlich pathway (Bell and Henschke, 2005). In this sense, amino acids such as leucine, isoleucine, valine, threonine and phenylalanine are precursors of 3-methyl-1-butanol, 2-methyl-1-butanol, 2-methyl-1-propanol, *n*-propanol and 2-phenylethanol, respectively (Bell and Henschke, 2005). The beneficial role of these alcohols in wines is uncertain; however, it has been shown that a concentration above 400 mg/L has a detrimental effect on wine quality (Rapp and Versini, 1991). Rose is the aroma descriptor usually defined as 2-phenylethanol (Gutiérrez-Gamboa *et al*., 2018f). The concentration of higher alcohols in Carignan wines from Maule Valley ranged from 272.87 to 482.76 mg/L and 2-phenylethanol varied from 72.99 to 111.12 mg/L in Loncomilla and Huerta de Maule sites, respectively (Gutiérrez-Gamboa *et al*., 2018d). Esters contribute fruity and floral aromas to the wines (Culleré *et al*., 2004). They are mostly formed from the metabolism of sugars and amino acids by yeast, while other esters are derived from the glycosylated fraction of the grape (Bell and Henschke, 2005; González-Barreiro *et al*., 2015). In terms of aromatic quality, acetate esters give more fruity aromas, while ethyl esters can give fruit and floral aromas at the same time (Bell and Henschke, 2005). Total ester concentration in Carignan wines from Maule Valley varied from 1.40 to 3.19 mg/L (Gutiérrez-Gamboa *et al*., 2018d). Carignan wines from Truquilemu presented the highest ethyl octanoate content, while the wines from Santa Sofía presented the highest 2-phenylethyl acetate content. Carignan wines from Melozal presented the highest concentration of ethyl decanoate and isoamyl acetate, while the wines from Sauzal presented the highest content of ethyl hexanoate (Gutiérrez-Gamboa *et al*., 2018d). Terpene compounds are present in wines at very low concentrations and are constituents responsible for the floral and fragrant characteristics of Muscat grapes and wines. These are isoprenoids and are derived from a 5-carbon unit with the formula C_5H_8. There are multiple units, with the most predominant in grapes and wines being the monoterpenes (González-Barreiro *et al*., 2015). These compounds are present in the grape as glycoconjugates, while a very low proportion is in the free form (González-Barreiro *et al*., 2015). C_{13}-norisoprenoids are a diverse class of aromatic compounds that contribute to the varietal character of many wines, including those of aromatic varieties. These compounds come from the degradation of carotenoids such as *ß*-carotene and lutein and are synthesized during the ripening of the grape (Gutiérrez-Gamboa *et al*., 2018g). Gutiérrez-Gamboa *et al*. (2018d) reported that *ß*-damascenone was the most odoriferous compound in Carignan wines from Maule Valley. This volatile compound contributes strongly to the fruity aroma and its content was the highest in the wines from Melozal. Linalool content in Carignan wines from Maule Valley varied from 6.25 to 11.95 µg/L in Valdivia and Truquilemu sites, while citronellol ranged from 5.12 to 11.30 µg/L in Huerta de Maule and Loncomilla sites, respectively (Gutiérrez-Gamboa *et al*., 2018d). Despite the aforementioned findings, it has been reported that Truquilemu and Ciénaga de Name sites, whose locations are closer to the Pacific Ocean, were correlated with high concentration of several fermentative volatile compounds, mainly esters, in non-commercial Carignan wines. These results matched those reported in amino acids for this variety (Gutiérrez-Gamboa *et al*., 2018c, 2018e). This agrees with the work of Ubeda *et al*. (2017b), who reported that commercial Carignan wines from locations closer to the Andes Mountains showed significantly lower contents of esters and acids. Therefore, based on the aforementioned findings and Figure 6, Carignan can be classified as a neutral variety from the aromatic point of view.

In summary, Carignan grapevines generally behave as a proline accumulator variety with the exception of the vines planted in cold sites. Considering terroir, Carignan grapevines growing in the sites closer to the Pacific Ocean and at high altitude, such as Truquilemu and Ciénaga de Name, present a high concentration of several amino acids and volatile compounds in grapes and wines, being the late-ripening sites. On the contrary, Carignan grapevines growing in the sites of the Entre Cordillera area, towards the Andes Mountains, provide grapes and wines

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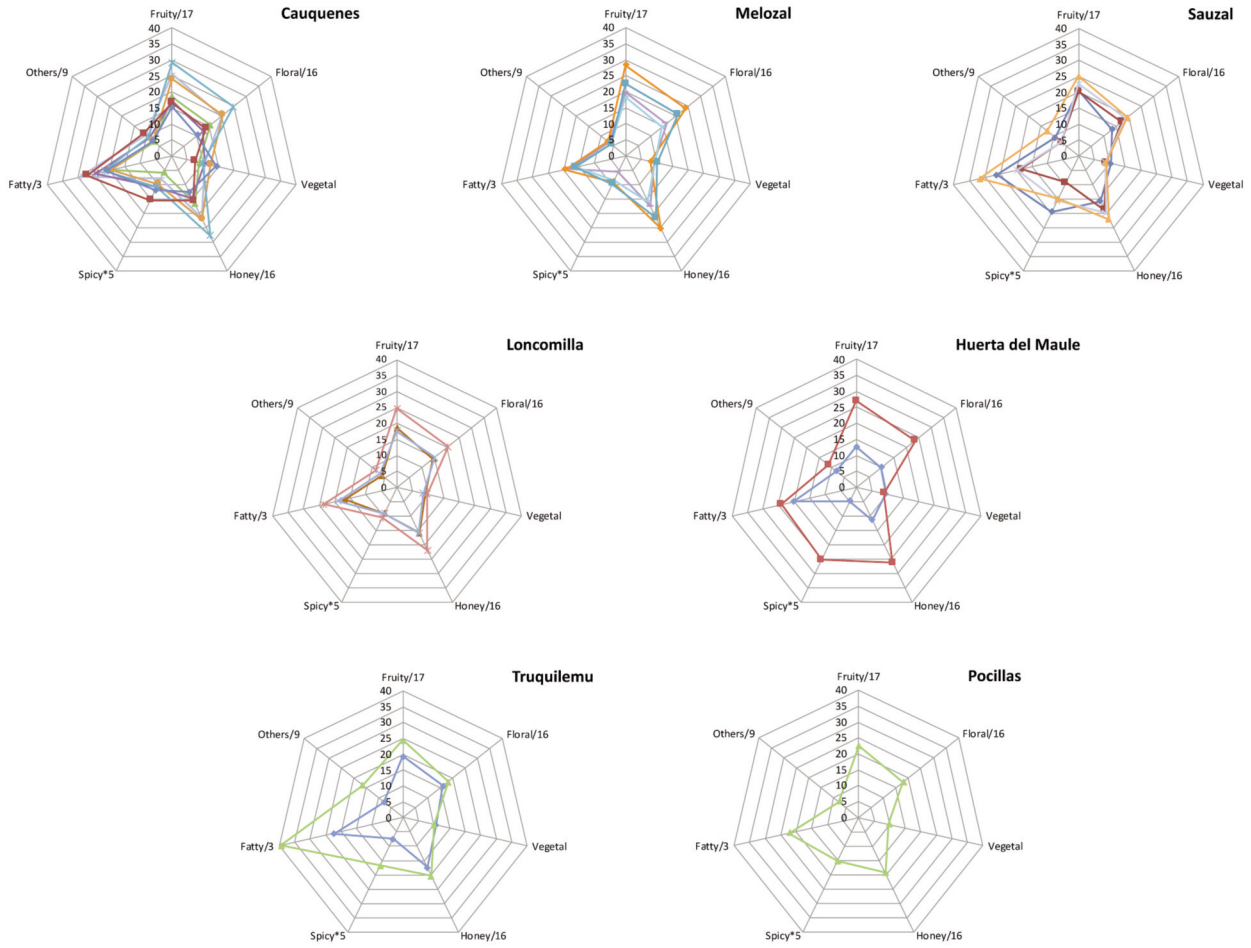


FIGURE 6. Aromatic profile of young wines from Carignan grapevines from different sites of the Maule Valley based on the odorant activity values for each volatile compound studied.

with a high alcohol and phenolic concentration, being the early-ripening sites. The anthocyanin concentration in Carignan grapes from Maule Valley is higher than that reported by some authors for this variety in other viticultural areas. With respect to volatile composition, Carignan is classified as a neutral variety.

CONCLUSIONS

Maule Valley provides unique differentiated characteristics that allow to offer different styles of Carignan wines. Carignan vineyards are inserted into the Coastal Batholith, the heart of the Coastal Range, which is an ancient mountainous cord of volcanic origin formed by an intrusive rock. There is also a flat area with gentle hills that is formed from the erosion of that Coastal Batholith, with deposits of alluvial and colluvial rocks. The most evolved soils in this sector are richer in clay. Coastal Batholith is between 300 and 400 million years older than the Andes Mountain. Due to this, it is considered one of the oldest soils in Chile for viticulture. In its composition there is also a mixture of granites, with quartz veins. Soils from Maule Valley are very poor, with less than 1% of organic matter and low content of nitrogen, potassium, phosphorous and magnesium.

With respect to typicity, Carignan vineyards located in the Sedimentary Fill unit that presents alluvial and colluvial fill zones provide differentiated conditions compared to the Granitic Intrusive unit and Sedimentary Rocks that are inserted on the Coastal Batholith. The soils of these geological units tend to accumulate clay and present high water holding capacity. Additionally, the Sedimentary Fill unit is inserted near the Pacific Ocean, and the Carignan vineyards located in Truquilemu and

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Ciénaga de Name into the Coastal Range are influenced by the ocean currents, providing cooler conditions than other sites, according to the bioclimatic indices measured. These edaphoclimatic conditions allow deeper rooting, increase vegetative growth, vigor and yield, and delay grape ripening. Carignan grapevines located in these sites behaved as an arginine accumulator variety. Additionally, Carignan grapevines from Truquilemu and Ciénaga de Name present a high concentration of several amino acids and volatile compounds in grapes and wines. The wines from these sites present a wide diversity of floral and fruity sensory attributes. On the contrary, most of the Carignan vineyards are located in the Central Valley, which contains the youngest and shallowest soils, generated by fluvioglacial, alluvial and volcanic processes during the Tertiary and Quaternary periods. According to the bioclimatic indices, these sites present warm conditions. These edaphoclimatic conditions limit rooting depth and restrict vegetative growth and yield, advancing grape ripening. The vines from Central Valley in the Entre Cordillera area, towards the Andes Mountains, behaved as a proline accumulator variety, providing grapes and wines with high alcohol and phenolic concentration, as in Melozal, Cauquenes and Sauzal. The wines from these sites present ripe fruit aromas and a marked astringency.

These results are of oenological and viticultural interest for the Carignan wine growers of the Chilean wine industry since understanding the effects of the edaphoclimatic conditions of the Maule Valley on the typicity of Carignan may be useful in optimizing viticultural practices and winemaking processes to improve grape and wine quality.

Acknowledgements:

This work was funded by FIC BIP 30.345.677-0, Vigno (Vignadores de Carignan A.G.), Vinos de Chile A.G., Viña Casas Patronales, and Viñedos de Loncomilla. We appreciate the contribution of all small Carignan wine growers from the Maule Valley region. G. G.-G. thanks the financial support from CONICYT, BCH/Doctorado-72170532.

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