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# Location effects on the polyphenolic and polysaccharidic profiles and colour of Carignan grape variety wines from the Chilean Maule region

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ABSTRACT

This paper reports on a study of chemical characterization and colour parameters of cv. Carignan red wines from six locations and two production years of the Chilean Maule valley. The chemical study was performed on polyphenolic composition (benzoic acids, hydroxycinnamic acid derivatives, stilbenes, flavan-3-ols, flavonols and anthocyanins) and several fractions of proanthocyanidins and polysaccharides. Results revealed that although significantly ($p < 0.05$) different content of anthocyanins were observed according to the production year, it could be possible to establish fingerprints of the different locations of the Maule valley wines. Thus, wines from zones closer to the Andes Mountains had higher content of procyanidin B3 (Caliboro), polysaccharides and *cis*-resveratrol-glucoside (Loncomilla and Melozal), whereas the proximity to the Pacific Ocean provoked a unifying effect in chemical and colorimetric terms (Cauquenes, Sauzal and Huerta del Maule).

## 1. Introduction

In the past few years, there is a new tendency about valuing new-style vinifications, betting on minority and indigenous grapevines, potenting their use as complementary varieties with different sensorial characteristics to the renowned grape varieties. That fact could be the case of Carignan grape variety, with a natural lesser acidity compared with other varieties such as Cabernet Sauvignon or Carménère (Úbeda, del Barrio-Galán, Peña-Neira, Medel-Marabolí, & Durán-Guerrero, 2017). This characteristic could improve the chemical and microbiological stability, confer mouth freshness and deep violet-red colour to the resulting wines.

Some studies in terms of colour parameters and general chemical characteristics of French and Spanish Carignan red wines have been developed. Carignan wines from the north of Spain contained low anthocyanin total content in comparison with other grape varieties (Arozarena, Casp, Marín, & Navarro, 2000), although Edo-Roca, Nadal, Snchez-Ortiz, and Lampreave (2014) affirmed that a strong dependency on the plant vigour exists. Carignan wines cultivated in France also showed low values of total anthocyanins and polyphenols, with not very high amounts of (+)-catechin, (−)-epicatechin and hydroxycinnamic acids (Jensen, Demiray, Egebo, & Meyer, 2008). However, in other countries such as Turkey, the content of anthocyanins and phenols was intermediate compared to other grape varieties of the country (Orak, 2007). With regard to polysaccharides, Ducasse, Williams, Meudec, Cheynier, and Doco (2010), Doco, Quellec, Moutounet, and Pellerin (1999) and Doco, Williams, Meudec, Cheynier, and Sommerer (2015) developed an accurately identification of oligosaccharides and polysaccharides in Carignan red wines cultivated in France. However, in spite of the importance in terms of winemaking, very scarce studies about Carignan grape variety have been published in the main vinicultural countries.

Chile is a long and narrow country, whose territory presents a tremendous diversity of landscapes. The central region, with a Mediterranean climate, is the traditional wine region of the country. In 2016, Chile was the fourth largest exporter of wines in the world, and the eighth largest producer (Organización Internacional de la Viña y el Vino, OIV, http://www.oiv.int/). Over thirty grape varieties in production (72% of world red varieties) are grown in Chile, such as Carménère, Cabernet Sauvignon and Syrah, among others.

Most of Chile's premium wine regions are dependent on irrigation to sustain vineyards, getting the necessary water from melting snow caps in the Andes. However, nowadays, the strategic plan of Wines of Chile 2020 includes an item to promote dry-farmed and old-vine wines. In this sense, Carignan vines are mainly cultivated in the dry-farmed or Secano Costero in the Maule Valley (350 km to the south of Santiago de Chile), with vineyards with > 60 year old vine-age. Although each year Carignan is increasingly used in the blends of different commercial

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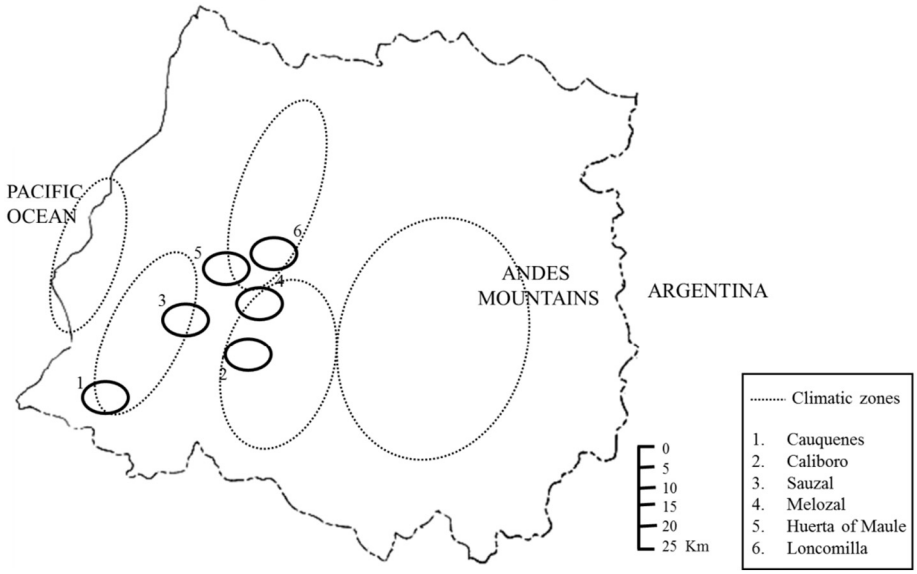


**Fig. 1.** Climatic zones of the Chilean Maule region and locations studied (Cauquenes, Caliboro, Sauzal, Melozal, Huerta del Maule and Loncomilla).

wines in Chile and in the world, very scarce previous scientific studies to typify Carignan wines has been developed, especially from the Maule region that concentrates more than the 70% of the total Carignan vineyard area (≈857 ha) in Chile (SAG, Servicio Agrícola y Ganadero, http://www.sag.gob.cl/).Only Martínez-Gil, Gutiérrez-Gamboa, Garde-Cerdán, Pérez-Álvarez, and Moreno-Simunovic (2018), Úbeda et al. (2017) and Gutiérrez-Gamboa et al. (2018) have been very recently published about phenolic, volatile and amino acid composition of different locations of the Chilean Maule Valley.

Climate conditions and geographical sites influence on the final quality of the wines, in terms of sugar content, aromas and colour (Van Leeuwen et al., 2004). In this way, the wines from the Chilean Maule Valley, with a heterogeneous orography, are greatly influenced by the proximity to the Andes Mountains and the Pacific Ocean. In fact, Montes, Perez-Quezada, Peña-Neira, and Tonietto (2012) divided the Maule Valley into five climatic zones (Fig. 1) employing three climate indexes (Huglin Index, the Cold Night Index and the Drought Index). These indexes estimate the potential climate of a particular place to ensure the maturation of different grape varieties (Huglin & Schneider, 1998). Moreover, they also suppose a climate classification system for wine regions which permits the grouping of regions according to their similarities (Montes et al., 2012; Tonietto & Carbonneau, 2004).

To the best of our knowledge, this is the first attempt to deeply and jointly characterise Chilean Carignan wines from the Maule Valley from a colour and chemical (phenolic, proanthocyanins, anthocyanin and polysaccharides) points of view. Besides, in the light of the influence of the climatic conditions on the wine quality, different locations and years of production of Carignan red wines have been taken into account. This work would not only suppose a diversification of the oenological market that could permit to elaborate young monovarietal wines, coupages or even with a short aging, but also contribute to the social and economic development of a Chilean vinicultural area poorly developed as the Maule valley.

## 2. Material and methods

### 2.1. Chemical and solvents

Methylcellulose (1500 cP viscosity at 20 g/L) and standards of caffeic acid, *p*-coumaric acid, (+)-catechin and (−)-epicatechin (purity > 98%), gallic acid and caftaric acid (purity > 97%), quercetin (purity > 95%) and malvidin-3-glucoside (purity > 90%) were purchased from Sigma Chemical Co. (St Louis, MO, USA).

Polyethylene membranes of 0.22 μm pore size were acquired from EMD Millipore (Billerica, MA, USA). Merck (Darmstadt, Germany) supplied sodium sulphate (anhydrous), vanillin (990 g/L), ethyl acetate, potassium metabisulfite, diethyl ether, sodium hydroxide, hydrochloric acid, sulfuric acid, high-performance liquid chromatography (HPLC)-grade acetonitrile, acetic acid, formic acid and methanol. All reagents were of analytical grade or higher. Sep-Pack Plus Environmental $C_{18}$ cartridges (900 mg) and Sep-PackPlus Short $C_{18}$ cartridges (400 mg) were obtained from Waters (Milford, MA, USA). Phosphate buffer (pH 7) was acquired from Mallinckrodt Baker (Phillipsburg, NJ, USA). Nitrogen gas was supplied by Indura SA (Santiago, Chile).

### 2.2. Red wines samples

Twenty-eight commercial monovarietal cv. Carignan red wines corresponding to two vintages (2012 and 2014) and different areas of the Maule Valley (in the VII region of Chile) were analyzed. Vines were > 50 years old, without irrigation, ungrafted and growing in good phytosanitary conditions. All the cellars followed traditional winemaking methods, in which maceration was developed until the alcoholic fermentation finished (three days at 10 °C), punched down twice a day until breaking the cap fully. Fermentation progress was tracked monitoring the relative density. Sulphur dioxide was used for all the assays.

The samples were collected from wine cellars from six different areas: Caliboro (8) (35°49′S; 71°54′W), Melozal (8) (35°42′S; 71°48′W); Cauquenes (2) (35°58′S; 72°21′W), Huerta of Maule (2) (35°40′S; 71°57′W), Loncomilla (4) (35°34′S; 71°45′W), and Sauzal (4) (35°45′S; 72°07′W) (Fig. 1). Once supplied, wines were stored at 10 °C until their analysis.

### 2.3. Spectrophotometric measurement

Wine conventional analytical data were obtained by O.I.V. official methods. Absorbance measurements were made with a Hewlett-Packard UV–Vis 1700 Pharmaspec spectrophotometer (Shimadzu, Kyoto, Japan).

Colour measurements were determined using the whole visible spectrum (380–770 nm) at constant intervals ($\Delta\lambda$ = 2 nm), with 2-mm path length glass cells. Distilled water was used as reference. The CIELAB colour parameters ($L^*$, $C^*_{ab}$ and $h_{ab}$) were determined according to Pérez-Magariño and González-Sanjosé (2003), following the