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Location effects on ripening and grape phenolic composition of eight 'Carignan' vineyards from Maule Valley (Chile)

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ABSTRACT

Among the forgotten varieties within the Chilean wine industry, 'Carignan' grapevines (*Vitis vinifera* L.) in the Maule Valley, Chile, have been rediscovered by viticulturist and winemakers, producing very interesting wines and well recognized worldwide. Phenolic compounds are secondary metabolites, and there has been much interest in potential health benefits of polyphenols as antioxidants. The aim of this work was to study grape phenolic composition from 'Carignan' vineyards growing in eight different sites of the Maule Valley during the 2016 vintage. Phenolic compounds were analyzed by HPLC-DAD. The results showed that, as expected, the most abundant anthocyanin, flavonol, flavanol and hydroxycinnamic acid in 'Carignan' grapes were malvidin-3-glc varying from 279.56 to 428.68 mg kg^{-1}, quercetin-3-glucoside+rutin ranging from 27.64 to 82.69 mg kg^{-1}, procyanidin B1 varying from 39.13 to 72.84 mg kg^{-1} and *trans*-coutaric acid varying from 27.14 to 72.76 mg kg^{-1}, respectively. *trans*-Piceid was the only stilbene identified, which ranged from 1.06 to 7.67 mg kg^{-1}. Climate conditions more than soil characteristics affected grape ripening. Generally, grapes from Curtiduría (Cur) and El Peumal (Peu) presented a faster ripening, in terms of technological maturity, than grapes harvested from the rest of the sites, regarding day of season. In most of the phenolic compounds, grapes from Peu, presented higher concentration than grapes from the rest of the sites. Thus, location conditioned phenolic composition in grapes. These findings are of importance for the Chilean wine industry in relation to the viticultural management of the 'Carignan' variety, regarding climatic conditions, soil characteristics and ripening within the Maule Valley.

Key words: 'Carignan', climatic conditions, Maule Valley, rainfed, ripening, soil characteristics, *Vitis vinifera*.

INTRODUCTION

During the last years, several forgotten varieties within the Chilean wine industry have been resurged due to their oenological potential, the new marketing strategies of wine companies and to the changes in wine consumer's habits, allowing their economic and social recovery. This is the case of the Carignan grapevine variety, which has attracted the attention of winemakers and consumers, producing very interesting wines being known worldwide. Due to the aforementioned, 'Carignan' grapes are increasing annually its transaction price to a level twice or three times higher than that of 'Cabernet Sauvignon' and 'Carménère', the most important varieties for the Chilean wine industry. This variety belongs to the Chilean heritage viticulture, being managed by small winegrowers in an ancestral way in Maule Valley. The 'Carignan' grapevines are growing in rainfed conditions and trained to a traditional bush system. The origin of 'Carignan' in Chile is diffuse, however most of the oenologists and winegrowers are in agreement that the first vine cuttings were introduced from the South of France after the earthquake of Chillan in 1939, which

devastated the vitiviniculture of the Maule, Biobío, and Itata valleys (Hernández and Moreno, 2011). The variety has a high anthocyanin content, low level of acidity and rustic tannins (Hernández and Moreno, 2011), characteristics that were used in those years to increase the productivity of the vineyards of the area, very affected after the great earthquake (Moreno and Vallarino, 2011). Maule Valley holds around 600 ha of a total of 722 'Carignan' hectares planted in the country (SAG, 2014). 'Carignan' vineyards are located within the Central Valley and near to the coastal range, thereby differences in wine styles are attributed mainly to variations in climate (Úbeda et al., 2017; Martínez-Gil et al., 2017; Gutiérrez-Gamboa et al., 2018).

The analysis of phenolic compounds in grapes has become interesting since they are responsible for the typical sensory attributes of wines, particularly color, bitterness and astringency (Heras-Roger et al., 2017). Polyphenolics are bioactive compounds with antioxidant and anticarcinogenic properties (Amararathna et al., 2016; Chen et al., 2016). Moreover, flavonoids seem to address neuroprotective action in neurodegenerative diseases by means of different mechanism of action, improving and promoting memory, learning and cognitive functions (Alañon et al., 2017). In this way, several factors influence grape phenolic composition such as variety, degree of grape maturation at harvest, climatic conditions, soil characteristics and viticultural practices (Downey et al., 2006; Martínez-Gil et al., 2017; Gutiérrez-Gamboa et al., 2017).

Regarding the study of phenolic compounds in different wine-growing sites within a particular valley, to our knowledge, there are few reports studying their composition. Van Leeuwen et al. (2004) studied the influence of soil characteristics, climate conditions and variety on yield and grape composition. These authors reported that the impacts of climate and soil were greater than the cultivar, suggesting that that the effects of climate and soil on fruit quality are mediated through their influence on vine water status. Edo-Roca et al. (2013) studied the effects of terroir in ripening and berry composition in 'Carignan' and 'Grenache' from Tarragona (Spain), reporting that pulp maturity is less influenced by terroir than phenolic maturity, and 'Carignan' does not achieve a complete phenolic ripening in cold mesoclimates. Recently, Martínez-Gil et al. (2017) characterized phenolic compounds in 'Carignan' grapes from six sites of the Maule Valley reporting that the synthesis of anthocyanins and flavonols in grapes were related with a high accumulation of biologically effective degree days, while hydroxycinnamic acids and flavanols abundance in grapes were related with cooler temperatures during the warmest productive month.

Due to the aforementioned, the aim of this research was to study the influence of climatic conditions and soil characteristics on ripening and grape phenolic composition of 'Carignan' vineyards from the Maule Valley (Chile).

MATERIALS AND METHODS

Study site, plant material and harvest

An experimental research was performed along the Maule Valley, Región del Maule, Chile, during the 2016 vintage. Eight different sites from the Maule Valley were selected for this study, based on geological and geomorphological information provided by CIREN (1997), as shown in Table 1. 'Carignan' vineyards were located in El Peumal (Peu), Ciénaga de Name (Cdn), Pocillas (Poc), Santa Sofía (Sso), Truquilemu (Tru), Sauzal (Sau), Curtiduría (Cur) and Caliboro (Cal). In each of the sites was chosen a representative vineyard, where three replicates were arranged randomly within the vineyard, accounting around 18-22 grapevines per replicate. The selection of the vineyards was made based on the following characteristics: 'Carignan' ungrafted grapevines with more than 30 yr old, located in rainfed conditions, trained to a bush system, growing in good phytosanitary conditions and with an active leaf surface. For each replicate within an experimental site, around of 70 kg grapes were manually harvested, considering all bunches from the grapevines, when berries reached the following parameters: Content of soluble solids of approximately 22-26 °Brix, titratable acidity between 5 and 8 g L^{-1} tartaric acid, and pH level between 3.25 and 3.75. Then, 200 berries for each replicate were frozen at -20 ºC for the subsequent phenolic composition determination.

Climate and soil characteristics

In each of the selected sites, a test pit of 2 m was made to evaluate chemical and physical characteristics of the soil. Surface and deep texture, soil depth, water holding capacity, organic matter, and soil total N analysis were

Table 1. Geographic location, seasonal temperature and soil characteristics of the 'Carignan' vineyards along Maule Valley (Chile): El Peumal (Peu), Ciénaga de Name (Cdn), Pocillas (Poc), Santa Sofía (Sso), Truquilemu (Tru), Sauzal (Sau), Curtiduría (Cur), and Caliboro (Cal).

	Geographic location		Seasonal temperature					Soil characteristics			
Site	Location	Elevation	Average	Min	Max	Soil classification	Surface and deep texture	Soil depth	Water holding capacity	Organic matter	Total N
		m a.s.l.	——— ºC ———					cm	cm	%	%
El Peumal (Peu)	241168X, 6062193Y	50	18.6	1.0	38.4	Inceptisol	Sandy loam, sandy loam	200	19.3	0.59	0.09
Ciénaga de Name (Cdn)	214893X, 6039258Y	161	23.5	0.8	32.2	Inceptisol	Sandy loam, sandy loam	180	13.1	1.41	0.09
Pocillas (Poc)	204651X, 5994901Y	152	19.0	0.5	40.7	Alfisol	Sandy loam, sandy clay	200	23.0	0.64	0.08
Santa Sofía (Sso)	198627X, 6014491Y	141	17.2	0.7	37.2	Inceptisol	Loam, sandy loam	100	10.8	1.07	0.05
Truquilemu (Tru)	214508X, 6047719Y	246	16.1	0.4	35.8	Inceptisol	Sandy loam, sandy clay	200	17.5	0.46	0.12
Sauzal (Sau)	210645X, 6031381Y	159	16.9	-0.5	38.5	Alfisol	Sandy loam, sandy loam	150	12.7	0.79	0.10
Curtiduría (Cur)	230886X, 6068369Y	47	19.5	2.3	41.4	Inceptisol	Sandy loam, sandy clay loam	140	10.4	1.07	0.10
Caliboro (Cal)	237313X, 6034015Y	108	17.9	0.2	39.3	Alfisol	Sandy loam, sandy clay loam	200	15.0	0.52	0.10

made according to methodology exposed by Soil and Crop Technological Center (CTSyC, 2017). The rest of soil descriptive information for each selected site was collected from to the described by CIREN (1997). Information about climatic variables was recorded *in situ*, from temperature and relative humidity sensors (HOBO Pro V2, Onset, Bourne, Massachusetts, USA) located at the beginning of the most representative row of each of the sites along the Maule Valley. Location, seasonal temperature, and soil characteristics are shown in Table 1.

Analysis of technological maturity

From each of the replicates arranged in the eight selected vineyards, 200 grapes were harvested weekly from first week of February to harvest. Grape technological maturity, such as ºBrix, pH and total acidity (g L^{-1} tartaric acid) of the samples obtained were determined according the methodology established by OIV (2003).

Extraction of grape samples

Grape extraction of the samples was performed according to the exposed by Portu et al. (2015). Around 50 g each frozen grape sample were immersed in 50 mL aqueous methanol solution (50% v/v) at pH 2, which was adjusted with formic acid (> 96%). Subsequently, grape samples were homogenized using an Ultra-Turrax T-18 (IKA, Staufen, Germany) at 18 000 rpm during 1 min, obtaining a smooth paste in which there were not visible pieces of seeds or skin. After, the samples were then maintained in an ultrasonic bath (JP Selecta, Barcelona, Spain) for 10 min and were centrifuged at 5000 rpm at 10 ºC for 10 min. A second and a third extraction of the resulting pellets was completed using the same volume of the solvent mixture (50 mL). The supernatants were combined and the volume was annotated. Each sample was maintained at -20 ºC until the analyses were carried out.

Extraction of non-anthocyanin compounds in grapes

Isolation of non-anthocyanin compounds from the samples was carried out according to the methodology exposed by Castillo-Muñoz et al. (2007) and Portu et al. (2015). Extraction was performed on PCX SPE cartridges (500 mg, 6 mL Bond Elut Plexa, Agilent, Palo Alto, California, USA). Firstly, 3 mL of the aforementioned grape extract were diluted with 9 mL 0.1 N HCl. The PCX SPE cartridges were previously conditioned using 5 mL methanol and 5 mL water. Then, the diluted samples were passed through the PCX SPE cartridges and a washing step was carried out using 5 mL 0.1 N HCl and 5 mL water. The anthocyanin-free fraction was eluted with 3 per 5 mL methanol. The adsorbed anthocyanins were removed by passing methanol with 2% HCl until the eluate was colorless. The latter step

also regenerates the cationic exchange sites for a new use of the cartridges. The eluate containing the anthocyanin-free fraction was dried in a rotary evaporator at 35 ºC (Hei-VAP Advantage HL/G5, Heidolph, Schwabach, Germany) and re-solved in 1.5 mL 20% (v/v) methanol aqueous solution. The anthocyanin free fraction was used to analyze non-anthocyanin flavonoid compounds (flavonols, flavanols, hydroxycinnamic acids, and *trans*-piceid).

Analysis of phenolic compounds by HPLC in grapes

The analysis of grape phenolic compounds was made using a liquid chromatograph Agilent 1260 Infinity, equipped with a diode array detector (DAD). Anthocyanins were analyzed by direct injection of 10 µL grape extract previously filtered (0.22 µm, Chromafil PET 20/25, Machery-Nagel, Düren, Germany). Non-anthocyanin compounds, such as flavonols, flavanols, hydroxycinnamic acids and *trans*-piceid were analyzed by injection of 20 µL anthocyanin-free grape fractions previously filtered (0.22 µm, Chromafil PET 20/25, Machery-Nagel, Düren, Germany). Separation was achieved on a narrow-bore column Zorbax Eclipse XDB-C18 (2.1 × 150 mm; 3.5 µm particle; Agilent), with a pre-column Zorbax Eclipse XDB-C8 (2.1 × 12.5 mm; 5 µm particle; Agilent). Both were thermostated at 40 ºC. The eluents used were (A) acetonitrile/water/formic acid (3:88.5:8.5 v/v/v), and (B) acetonitrile/water/formic acid (50:41.5:8.5 v/v/v). The linear solvents' gradient for anthocyanin analysis was as follows: zero min, 6% B; 10 min, 30% B; 30 min, 50% B; 34 min, 100% B; 36 min, 100% B; 42 min, 4% B; 50 min, 4% B. For non-anthocyanin analysis, free-anthocyanin fractions were filtered (0.20 µm, Machery-Nagel) and injection volume was 20 µL. The same column was used while eluents were (A) acetonitrile/water/formic acid (3:88.5:8.5 v/v/v), (B) acetonitrile/water/formic acid (50:41.5:8.5 v/v/v), and (C) methanol/water/formic acid (90:1.5:8.5 v/v/v). The linear solvents gradient for non-anthocyanin analysis was as follows: zero min, 2% B and 0% C; 8 min, 4% B and 0% C; 37 min, 17% B and 13% C; 51 min, 30% B and 20% C; 51.5 min, 40% B and 30% C; 56 min, 50% B and 50% C; 57 min, 50% B and 50% C; 64 min, 4% B and 0% C. The use of a narrow-bore column allowed to establish a slow flow rate (0.19 mL min^{-1}). The identification of all compounds was performed according to the retention times of pure compounds and the UV-Vis characteristics obtained from authentic standards or those published in previous studies (Lago-Vanzela et al., 2011). (–)-Epicatechin, (+)-catechin, quercetin, quercetin-3-*O*-glucoside, quercetin-3-*O*-galactoside, kaempferol and myricetin standards were purchased from Sigma-Aldrich. Malvidin-3-*O*-glucoside, quercetin-3-*O*-glucuronide, procyanidin B1, procyanidin B2, (–)-epigallocatechin and (–)-epicatechin gallate standards were purchased from Extrasynthèse (Genay, France). Compound quantification was made using DAD chromatograms recorded at 520 nm (anthocyanins), 360 nm (flavonols), 320 nm (hydroxycinnamic acids and *trans*-piceid), and 280 nm (flavan-3-ols) and the calibration graphs of the respective standards ($R^2 > 0.999$). Quantification of non-commercial compounds was made according to the calibration graphs of the most similar compounds. Hence, anthocyanins were expressed as mg kg^{-1} of malvidin-3-*O*-glucoside, flavonols were expressed as mg kg^{-1} of quercetin-3-*O*-glucoside, and hydroxycinnamic acid derivatives were expressed as mg kg^{-1} of *trans*-caftaric acid. In addition, *trans*-piceid was expressed as mg kg^{-1} of its corresponding isomer, procyanidins B1 and B2 were expressed as mg kg^{-1} catechin, while epicatechin-3-gallate were expressed as mg kg^{-1} epicatechin. The treatments were performed in triplicate, so the results for phenolic compounds correspond to the average of three analyses (n = 3).

Statistical analysis

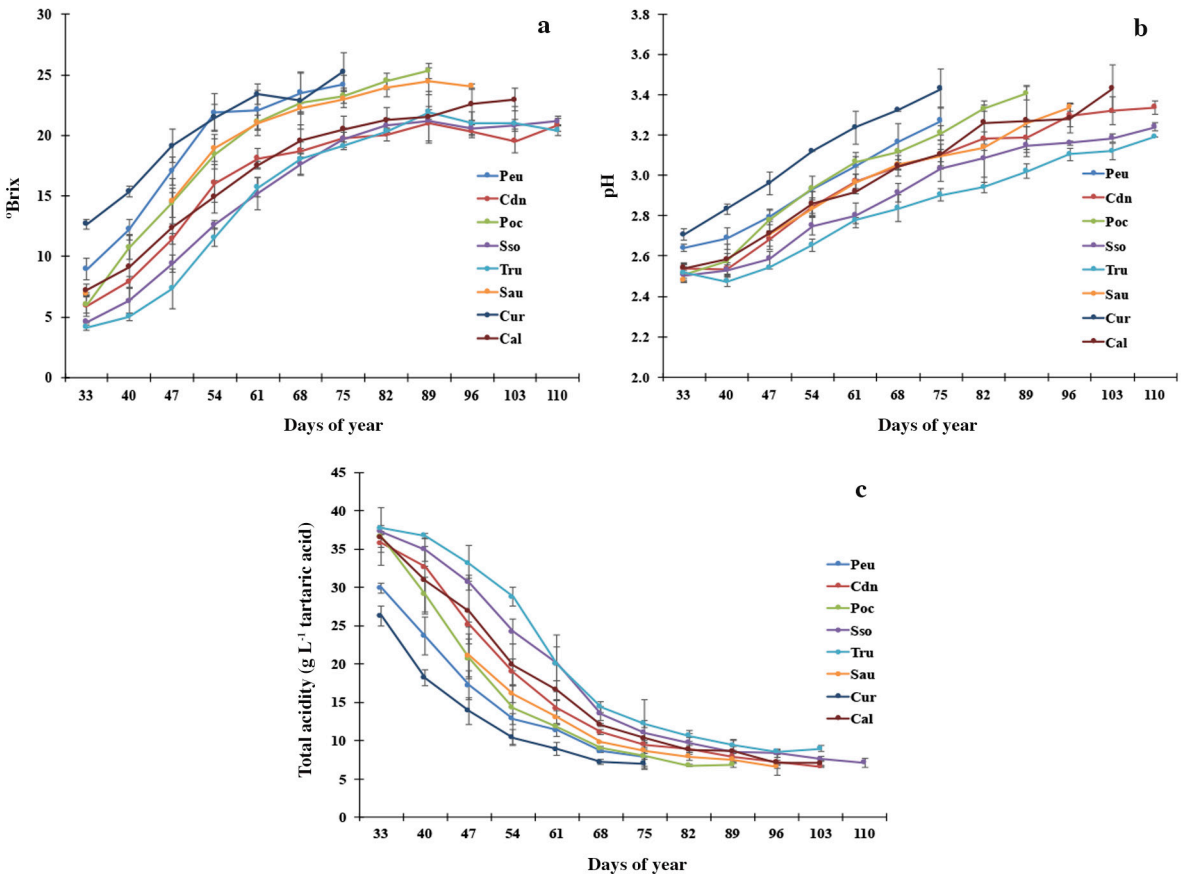
The statistical analysis of oenological parameters and phenolic compounds was performed using one-way ANOVA by (Statgraphics Centurion XVI.I, The Plains, Virginia, USA). Differences between samples were compared using the Tukey test at 95% probability level.

RESULTS AND DISCUSION

Grapevine ripening from 'Carignan' vineyards of Maule Valley

Figure 1 shows the evolution of technological maturation in terms of ºBrix, pH and total acidity of 'Carignan' grapes from eight locations of the Maule Valley: El Peumal (Peu), Ciénaga de Name (Cdn), Pocillas (Poc), Santa Sofía (Sso), Truquilemu (Tru), Sauzal (Sau), Curtiduría (Cur) and Caliboro (Cal). The results showed that location had

Figure 1. Evolution of technological maturity in terms of a) ºBrix, b) pH and c) total acidity (g L^{-1} tartaric acid) of the Carignan vineyards along Maule Valley (Chile): El Peumal (Peu), Ciénaga de Name (Cdn), Pocillas (Poc), Santa Sofía (Sso), Truquilemu (Tru), Sauzal (Sau), Curtiduría (Cur), and Caliboro (Cal).



a considerable effect on the evolution of technological maturity in 'Carignan' vineyards within the Maule Valley. The grapes from Peu and Cur presented the fastest evolution of ºBrix, while the samples from Sso and Tru were the slowest. Respect to pH, the grapes from Cur presents the fastest evolution, while the samples from Sso and Tru were the slowest. In relation to total acidity, Sso and Tru grapes presented the fastest evolution, while Cur grape, the slowest. In this way, according to the technological maturity, Cur and Peu grapevines were harvested at 75 day of the year. The vineyard from Poc was harvested at 89 day of year, and the grapevines from Sau were harvested at 96 day of year. The vineyard from Cal was harvested at 103 day of year, while the grapevines from Cdn, Sso and Tru were harvested at 110 day of year. The grape from the aforementioned sites did not reach the optimal technological maturation for 'Carignan'. In accordance with Table 1, Cur site presented the highest maximum and minimum temperatures, while Tru showed the lowest average temperature. The results aforementioned exposed are similar to those obtained by Edo-Roca et al. (2013) for 'Carignan' vineyards growing in cool mesoclimates from Tarragona (Spain). These authors reported that during ripening on 'Carignan' and 'Grenache' grapevine, berry composition is more influenced by terroir in terms of early or late ripening, than bunch uniformity. Besides, Martínez-Gil et al. (2017) showed that in the warmer sites planted with 'Carignan' vineyards, the grapes presented a more advanced technological maturation at harvest than the coldest places. Moreover, van Leeuwen et al. (2004) reported that ripening speed was more influenced by cultivar and vintage compared to soil factor.

Grape anthocyanins content

Table 2 shows the concentration of anthocyanins in 'Carignan' grapes from vineyards planted along the Maule Valley. The major contributor to total anthocyanins in 'Carignan' grapes was the non-acylated forms, varying from

Table 2. Grape anthocyanin concentration from 'Carignan' vineyards planted along Maule Valley (Chile): El Peumal (Peu), Ciénaga de Name (Cdn), Pocillas (Poc), Santa Sofía (Sso), Truquilemu (Tru), Sauzal (Sau), Curtiduría (Cur), and Caliboro (Cal).

	Peu	Cdn	Poc	Sso	Tru	Sau	Cur	Cal
	mg kg^{-1}							
Df-3-Glc	132.19±16.76b	75.59±16.93ab	116.63±8.82ab	68.54±1.87a	121.31±9.90ab	122.79±13.14ab	100.55±32.68ab	82.11±19.57ab
Cn-3-Glc	27.29±4.77b	9.08±4.30a	11.18±1.95a	5.60±0.49a	13.65±1.91a	10.62±1.66a	12.76±4.78a	9.98±2.79a
Pt-3-Glc	120.86±16.71b	77.99±15.31ab	114.12±8.92ab	65.73±2.25a	108.97±8.31ab	121.99±10.42b	97.48±28.94ab	76.63±16.06ab
Pn-3-Glc	69.83±11.73b	26.39±9.85a	35.04±3.22a	19.07±1.13a	38.92±7.95a	35.61±4.40a	37.36±10.48a	35.83±4.44a
Mv-3-Glc	417.87±43.36a	306.08±45.50a	407.59±34.27a	279.56±13.94a	389.89±49.19a	428.68±21.22a	363.84±62.18a	366.83±60.60a
Total non-acylated	768.05±90.48b	495.14±91.25ab	684.54±51.64ab	438.50±17.49a	672.74±72.90ab	719.69±49.47ab	612.00±137.61ab	571.38±101.63ab
Df-3-Acglc	0.67±0.16a	0.75±0.14a	0.46±0.02a	0.76±0.12a	0.54±0.04a	0.56±0.09a	0.67±0.04a	0.50±0.05a
Pt-3-Acglc	4.76±1.67a	3.64±0.46a	4.39±0.74a	3.56±0.29a	4.63±0.07a	5.60±0.65a	4.58±1.01a	3.08±0.36a
Pn-3-Acglc	3.24±0.54b	1.74±0.68a	1.49±0.48a	1.50±0.44a	1.65±0.35a	1.97±0.31ab	1.69±0.05a	1.02±0.19a
Mv-3-Acglc	22.26±1.03b	16.24±0.81a	19.63±1.95ab	15.60±1.53a	16.33±1.07a	22.99±2.43b	20.90±1.90ab	19.00±1.94ab
Total acetylated	30.94±1.66bc	22.37±1.85a	25.96±2.70abc	21.42±1.29a	23.15±0.86a	31.13±3.07c	27.60±2.67abc	23.59±1.98ab
Df-3-Cmglc	20.73±1.01ab	14.86±2.14ab	18.13±1.81ab	15.04±1.09ab	16.76±1.73ab	20.06±2.31ab	21.43±4.57b	13.17±1.20a
Cn-3-Cmglc	5.10±0.75b	2.43±0.29a	3.34±0.43ab	2.04±0.11a	2.82±0.44a	3.80±0.86ab	3.33±0.78ab	2.41±0.33a
Pt-3-Cmglc	21.72±1.02bcd	17.23±0.26abc	22.29±2.41cd	16.38±1.89ab	19.42±0.30abcd	24.36±0.62d	21.49±2.53bcd	15.44±1.42a
Pn-3-Cmglc	13.43±1.86b	6.04±0.93a	8.48±1.07a	5.39±0.30a	7.94±1.20a	9.49±1.50ab	8.83±1.88ab	8.51±1.19a
Mv-3-Cmglc	103.98±3.14a	98.72±5.55a	109.13±12.26a	96.91±8.95a	100.49±9.26a	118.85±0.78a	108.41±7.38a	103.42±11.29a
Mv-3-Cis-Cmglc	3.72±0.13ab	3.51±0.28ab	4.04±0.55ab	3.57±0.19ab	3.29±0.23a	4.62±0.46b	4.05±0.61ab	3.44±0.22ab
Total coumaroylated	168.68±5.79ab	142.79±5.93ab	165.41±17.07ab	139.32±12.19a	150.71±7.95ab	181.18±4.22b	167.53±15.55ab	146.39±14.70ab
Mv-3-CfGlc	1.30±0.21ab	1.09±0.11ab	1.50±0.22ab	0.76±0.04a	0.89±0.24ab	1.56±0.37b	1.49±0.31ab	1.13±0.16ab
Total anthocyanins	968.97±96.30b	661.39±91.19ab	877.41±70.87ab	600.01±30.55a	847.49±81.23ab	933.56±54.59b	808.62±154.59ab	742.50±113.44ab

All parameters are given with their standard deviation (n = 3). Different letters in the same row indicate significant differences ($p \leq 0.05$) between treatments.
Df: Delphinidin; Cn: cyanidin; Pt: petunidin; Pn: peonidin; Mv: malvidin; Glc: glucoside; Acglc: acetyl-glucoside; Cfglc: caffeoyl-glucoside; Cmglc: p-coumaroyl-glucoside.

438.50 to 768.05 mg kg^{-1} (Sso and Peu sites, respectively), followed by the coumaroylated forms, which ranged 139.32 to 181.18 mg kg^{-1} (Sso and Sau, respectively), being the acylated derivatives, the minor forms varying from 21.42 to 31.13 mg kg^{-1} (Sso and Sau sites). The major acylated form was the coumaroylated, which has already been described in 'Carignan' grapes (Martínez-Gil et al., 2017). Malvidin-3-glucoside was the most abundant anthocyanin in 'Carignan' grapes varying from 279.46 to 428.68 mg kg^{-1} (Sso and Sau sites, respectively), while cyanidin-3-glucoside was the least abundant anthocyanin ranging from 5.60 to 27.29 mg kg^{-1} (Sso and Peu sites, respectively). Total anthocyanins ranged from 600.01 to 968.97 mg kg^{-1} (Sso and Peu sites, respectively).

Respect to the grapes from eight different locations along the Maule Valley, the concentration of malvidin-3-glc, delphinidin-3-acglc, petunidin-3-acglc and malvidin-3-cmglc did not show significant differences among the sites. Peu samples showed the highest concentration of cyanidin-3-glc and peonidin-3-glc. Besides, the grapes from Peu presented higher content of delphinidin-3-glc, petunidin-3-glc, peonidin-3-acglc, malvidin-3-acglc, cyanidin-3-cmglc and peonidin-3-cmglc than the grapes from the most of the sites. The grapes from Cdn, Sso, Tru and Cal sites presented lower concentration of several of anthocyanins than the samples from Peu and Sau sites. Grapes from this last site showed higher content of petunidin-3-glc, malvidin-3-acglc, petunidin-3-cmglc, malvidin-3-*cis*-cmglc and malvidin-3-cfglc than the grapes from the most of the sites, except Peu. Thus, total non-acylated content was higher in Peu samples than in Sso grapes. Cur samples presented only a higher concentration of delphinidin-3-cmglc than the Cal berries. Total acetylated concentration was lower in grapes from Cdn, Sso, Tru, and Cal than the samples from Sau. Total coumaroylated content in berries was higher in Sau site than the grapes from Sso. Total anthocyanins concentration was higher in grapes from Peu and Sau sites than in berries from Sso.

Generally, the grapes which reached a slower ripening, presented a lower concentration of anthocyanins at harvest. Castellarin et al. (2007) reported that early water deficits accelerate ripening and induce changes in gene expression regulating flavonoid biosynthesis in grapes, increasing anthocyanin content. On the other hand, it has been showed that high temperatures reduced total anthocyanin concentration however, anthocyanin biosynthetic genes were not strongly down-regulated at high temperature (Mori et al., 2007). It is probably that the high temperatures reached in

Cur sites, did not allow a greater accumulation of anthocyanins despite having a more rapid grape ripening than the other sites. Besides, Martínez-Gil et al. (2017) found that anthocyanins concentration in 'Carignan' grapes at harvest were related to the accumulation of biologically effective degree days. Andrés-de Prado et al. (2007) showed that the soils with higher water holding capacity (Whc), produced wines with lower color intensity and shade, as well as lower total phenolic composition than the wines from the rest of soils. In this way, Poc vineyard showed the highest Whc however, its anthocyanin concentration did not showed differences among the sites. In addition, van Leeuwen et al. (2004) showed that soil characteristics and vintage were the principal factors on grape anthocyanin content compared to cultivar and their interaction. Therefore, grapevine maturity has an important influence on the synthesis of anthocyanins in grape berries as is showed in Figure 1 and Table 2.

Grape flavonols content

Table 3 shows the concentration of flavonols found in 'Carignan' grapes from vineyards planted along the Maule Valley. The most abundant flavonol derivative in 'Carignan' grapes was quercetin-3-glc+rutin, ranging from 27.64 to 82.69 mg kg^{-1} (Cal and Sso sites, respectively), followed by myricetin-3-glc which varied from 58.43 to 59.79 mg kg^{-1} (Peu and Sso sites, respectively). The least abundant flavonol was laricitrin-3-gal ranging from 0.17 to 0.46 mg kg^{-1} (Cal and Poc sites, respectively). Total flavonols concentration in 'Carignan' grapes varied from 137.43 to 249.27 mg kg^{-1} (Cal and Sso sites, respectively). Martínez-Gil et al. (2017) showed that 'Carignan' grapes from Sau and Cur sites presented higher total flavonols than the grapes from Tru, Sau, Peu and Sso sites during the 2015 vintage.

Respect to the grapes from the different locations from the Maule Valley, it was showed that the content of myricetin-3-glucu and isorhamnetin-3-gal did not show significant differences among the sites. Peu samples showed lower concentration of myricetin-3-glc than Tru and Cur, and Sso and Tru samples, respectively. However, Peu grapes showed higher content of all quercetin derivatives, kaempferol-3-gal, kaempferol-3-glucu and isorhamnetin-3-glc than the samples from the most of the sites, mainly Cur and Cal grapes. Berries from Poc, Sso, Tru and Sau sites presented higher concentration of some of flavonols than the grapes from some of the sites, mainly of Cur and Cal sites. 'Carignan' grapes from Peu and Sso sites showed higher total flavonols concentration than the grapes from Cur and Cal sites. It seems to be that grape maturity had less influence on the synthesis of flavonols than the anthocyanin accumulation in 'Carignan' grapevines. On the other hand, Cur and Cal sites presented higher

Table 3. Grape flavonol concentration from 'Carignan' vineyards planted the along Maule Valley (Chile): El Peumal (Peu), Ciénaga de Name (Cdn), Pocillas (Poc), Santa Sofía (Sso), Truquilemu (Tru), Sauzal (Sau), Curtiduría (Cur), and Caliboro (Cal).

	Peu	Cdn	Poc	Sso	Tru	Sau	Cur	Cal
	mg kg^{-1}							
M-3-Gal	1.48 ± 0.08ab	1.86 ± 0.12bc	1.89 ± 0.30bc	1.49 ± 0.56ab	2.55 ± 0.44c	2.46 ± 0.29c	1.35 ± 0.19ab	0.77 ± 0.12a
M-3-Glucu	8.86 ± 0.22a	7.72 ± 1.84a	9.94 ± 2.74a	10.06 ± 1.16a	6.14 ± 3.32a	10.00 ± 2.53a	5.79 ± 0.87a	4.74 ± 1.68a
M-3-Glc	58.43 ± 0.18a	59.01 ± 0.11ab	59.26 ± 0.78ab	59.79 ± 0.12b	59.67 ± 0.23b	59.01 ± 0.10ab	59.19 ± 0.18ab	59.66 ± 0.56b
M-3-Acglc	1.07 ± 0.16bc	0.67 ± 0.22ab	1.31 ± 0.40bc	0.91 ± 0.09abc	0.97 ± 0.18abc	1.38 ± 0.15c	0.82 ± 0.24abc	0.46 ± 0.10a
Q-3-Gal	3.63 ± 0.59c	2.11 ± 0.60abc	2.34 ± 0.95abc	3.49 ± 0.48c	3.22 ± 0.34bc	3.06 ± 0.63bc	1.66 ± 0.42ab	1.15 ± 0.47a
Q-3-Glucu	55.41 ± 2.89c	37.22 ± 3.38abc	39.66 ± 18.20abc	48.70 ± 3.24bc	55.41 ± 6.05c	48.14 ± 7.13bc	30.94 ± 4.33ab	25.47 ± 5.66a
Q-3-Glc+Rut	78.18 ± 12.48c	52.81 ± 13.48abc	55.65 ± 22.91abc	82.69 ± 11.29c	70.39 ± 10.79bc	70.62 ± 8.72bc	39.30 ±3.69ab	27.64 ± 9.76a
L-3-Gal	0.38 ± 0.09bc	0.29 ± 0.08abc	0.46 ± 0.16c	0.29 ± 0.04abc	0.25 ± 0.03abc	0.29 ± 0.05abc	0.24 ± 0.05ab	0.17 ± 0.01a
L-3-Glc	7.27 ± 0.54ab	6.92 ± 1.17ab	8.94 ± 2.13b	7.17 ± 0.60ab	5.28 ± 0.31a	8.81 ± 0.79b	6.26 ±0.75ab	4.58 ± 0.56a
K-3-Gal	5.33 ± 0.59d	2.56 ± 0.94ab	3.02 ± 1.00abc	5.00 ± 0.44cd	4.30 ± 0.80bcd	3.72 ± 1.77abcd	1.80 ± 0.47a	1.97 ± 0.19a
K-3-Glucu	1.74 ± 0.19c	0.89 ± 0.27abc	0.92 ± 0.54abc	1.47 ± 0.13bc	1.52 ± 0.12bc	1.23 ± 0.51abc	0.81 ± 0.15ab	0.48 ± 0.18a
K-3-Glc	16.97 ± 4.40bc	10.89 ± 3.79ab	10.87 ± 3.72ab	20.60 ± 2.76c	17.08 ± 3.35bc	13.88 ± 3.57abc	11.29 ± 0.99ab	5.27 ± 1.05a
I-3-Gal	0.24 ± 0.07a	0.32 ± 0.12a	0.22 ± 0.07a	0.16 ± 0.02a	0.27 ± 0.08a	0.27 ± 0.02a	0.19 ± 0.07a	0.17 ± 0.01a
I-3-Glc	5.45 ± 1.81b	3.80 ± 1.32ab	4.54 ± 1.89ab	4.72 ± 0.50ab	3.84 ± 0.70ab	5.28 ± 0.79ab	3.18 ± 0.02ab	2.18 ± 0.42a
S-3-Glc	3.41 ± 0.26bc	2.69 ± 0.39ab	4.49 ± 0.99c	2.75 ± 0.22ab	1.87 ± 0.38a	3.01 ± 0.21ab	3.16 ± 0.33b	2.74 ± 0.09ab
Total flavonols	247.84 ± 20.40c	189.53±26.25abc	203.50±56.48abc	249.27 ± 19.73c	232.77±19.42bc	229.93±24.03bc	165.98±11.94ab	137.43±19.26a

All parameters are given with their standard deviation (n = 3). Different letters in the same row indicate significant differences ($p \leq 0.05$) between treatments.
M: Myricetin; Q: quercetin; L: laricitrin; K: kaempferol; I: isorhamnetin; S: syringetin; Glc: glucoside; Glucu: glucuronide; Gal: galactoside; Rut: rutin; Acglc: acetylglucoside.

maximum temperatures than the most of the sites. Thus, probably, these high temperatures allowed a degradation of flavonol compounds in 'Carignan' grapes.

Flavonol synthesis occur in grapes around flowering and during ripening of the developing berries due to the expression of the VvFLS1 gene (Downey et al., 2003). These compounds, mainly in their deglycosylated form, are labile molecules and may be degraded upon exposure to heat, enzymes, and oxidative chemical species, such as free radicals (Makris et al., 2006). The accumulation of flavonols in grapes is activated in response to treatments with UV and sunlight (Haselgrove et al., 2000). Light interception at fruit zone is determined by the training system, and its management can increase sunlight exposure improving grape quality (Pascual et al., 2017). In this way, temperature appears to have a less influence on flavonol synthesis, compared to sunlight (Makris et al., 2006; Flamini et al., 2013). Thus, Downey et al. (2004) reported that in shading berries, the levels of flavonols in grape skins were reduced, while in the exposed fruit, flavonol concentration was highest around flowering then declined as the berries grew, but there was an increase in flavonols per berry during ripening. Azuma et al. (2012) found that total flavonols concentration were higher for a daytime temperature of 15 °C under light treatments, with small variations regarding temperature. Martínez-Gil et al. (2017) reported that flavonol accumulation in 'Carignan' grapes was related to a high accumulation of biologically effective degree days. However, compared to the results obtained in the present manuscript the warmer sites did not present more flavonol concentration than the rest of sites and probably its content depended more on other factors such as sunlight exposure.

Grape flavanols, hydroxycinnamic acids and *trans*-piceid content

Table 4 shows the concentration of flavanols, hydroxycinnamic acids (HCAs) and *trans*-piceid in 'Carignan' grapes from vineyards planted along the Maule Valley. The most abundant flavanol derivative found in 'Carignan' grapes was procyanidin B1, ranging from 39.13 to 72.84 mg kg^{-1} (Cdn and Cur sites, respectively), followed by catechin, which varied from 4.27 to 30.76 mg kg^{-1} (Cur and Peu sites, respectively) and by epicatechin gallate ranging from 5.60 to 31.64 mg kg^{-1} (Cur and Sau sites, respectively). Total flavanols concentration varied from 86.09 to 158.57 mg kg^{-1} (Cdn and Tru sites, respectively). The most abundant HCA found in 'Carignan' grapes was *trans*-coutaric acid ranging from 27.14 to 72.76 mg kg^{-1} (Cur and Tru sites, respectively), followed by *trans*-caftaric acid varying from 24.82 to 57.87 mg kg^{-1} (Cur and Tru sites, respectively). Total content of HCAs varied from 51.96 to 130.63 mg kg^{-1} (Cur and Tru sites, respectively). *trans*-Piceid was the only stilbene identified in 'Carignan' grapes, and its content ranged from 1.06 to 7.67 mg kg^{-1} (Cdn and Peu sites, respectively).

Nonsignificant differences were found in the concentration of procyanidin B1 among the sites. The grapes from Peu showed higher concentration of catechin and epicatechin than the berries from Cdn and Cur. The content of

Table 4. Grape flavanol, hydroxycinnamic acids (HCAs), and stilbene concentration from Carignan vineyards planted the along Maule Valley (Chile): El Peumal (Peu), Ciénaga de Name (Cdn), Pocillas (Poc), Santa Sofía (Sso), Truquilemu (Tru), Sauzal (Sau), Curtiduría (Cur), and Caliboro (Cal).

	Peu	Cdn	Poc	Sso	Tru	Sau	Cur	Cal
	mg kg^{-1}							
Flavanols								
Procyanidin B1	65.91 ± 9.79a	39.13 ± 17.21a	45.14 ± 14.56a	55.92 ± 18.87a	70.28 ± 6.20a	55.07 ± 7.51a	72.84 ± 20.37a	49.72 ± 7.58a
Procyanidin B2	4.83 ± 1.28a	7.98 ± 1.46ab	6.75 ± 2.71ab	9.39 ± 0.51abc	14.11 ± 2.71c	10.88 ± 2.26bc	4.59 ± 1.66ab	6.16 ± 2.63ab
Catechin	30.76 ± 1.13d	10.08 ± 3.30ab	17.70 ± 5.30bc	20.23 ± 1.79bcd	26.11 ± 3.34cd	25.19 ± 5.84cd	4.27 ± 1.25a	20.12 ± 3.60bcd
Epicatechin	21.20 ± 3.68c	9.31 ± 3.52ab	12.27 ± 2.74abc	18.00 ± 2.98abc	17.37 ± 4.58abc	18.66 ± 2.80bc	7.02 ± 0.18a	12.41 ± 5.07abc
Epicatechin Gallate	19.78 ± 2.90bc	21.98 ± 5.43bc	15.24 ± 5.34ab	21.05 ± 0.98bc	28.03 ± 5.26c	31.64 ± 3.66c	5.60 ± 0.31a	10.98 ± 5.21ab
Total flavanols	143.33 ± 12.53bc	86.09 ± 23.09a	98.52 ± 29.65ab	125.64 ± 19.40abc	158.57 ± 5.55c	142.32 ± 11.65bc	94.56 ± 20.29ab	100.12 ± 19.58ab
Hydroxycinnamic acids								
trans-Caftaric acid	38.73 ± 1.69ab	36.77 ± 12.22ab	26.99 ± 8.73a	38.59 ± 7.51ab	57.87 ± 6.77b	42.41 ± 9.13ab	24.82 ± 1.84a	34.60 ± 7.49a
trans-Coutaric acid	42.28 ± 5.24a	44.72 ± 11.63a	31.62 ± 11.13a	48.24 ± 7.52a	72.76 ± 8.42b	47.72 ± 7.93a	27.14 ± 1.74a	35.24 ± 4.27a
Total HCAs	81.01 ± 6.92a	81.49 ± 23.83a	58.61 ± 19.87a	86.83 ± 14.27a	130.63 ± 15.09b	90.13 ± 16.82ab	51.96 ± 2.06a	69.84 ± 11.66a
Stilbenes								
trans-Piceid	7.67 ± 1.63c	1.06 ± 0.19a	1.95 ± 0.30ab	1.97 ± 0.33ab	3.84 ± 1.49b	1.35 ± 0.06ab	3.18 ± 1.10ab	4.04 ± 1.02b

All parameters are given with their standard deviation (n = 3). Different letters in the same row indicate significant differences ($p \leq 0.05$) between treatments.

procyanidin B2 and epicatechin gallate was higher in the grapes from Tru site than the samples from the most of the sites. Cdn, Poc, Cur and Cal grape samples presented lower concentration of several flavanols than the most of the sites. Total flavanols concentration was higher in the berries from Tru than in the samples from Cdn, Poc, Cur and Cal. Respect to HCAs, the grapes from Tru presented the highest *trans*-coutaric acid concentration, and a higher content of *trans*-caftaric acid than the berries from Poc, Cur and Cal sites. Total HCAs concentration in 'Carignan' grapes was higher in the samples from Tru than the rest of the sites, except Sau. Grapes from Peu site presented the highest concentration of *trans*-Piced.

Flavanols or tannins are considered responsible for astringency, one of the most important sensory attributes of wines (Peleg et al., 1999). These compounds usually are colorless and form copigmentation complexes with the anthocyanins. Thus, flavanols acting as copigments contributing to color in red wines. Ripening has an important influence on phenolic compounds including flavanols. In this way, at early stages of berry development, procyanidins and quercetin were the major flavonoids, but the levels decreased dramatically during the progress of ripening, however during the later stages of ripening, the content of anthocyanins increased strongly and they were the major flavonoids in the ripe berry (Jaakola et al., 2002). Some studies shown a positive association between temperature and number of seeds and total proanthocyanidin amounts per berry at harvest (Pastor del Rio and Kennedy, 2006; Teixeira et al., 2013). Martínez-Gil et al. (2017) reported that flavanols and HCAs synthesis is favored by cooler temperatures during the warmest month. Tru presented the lowest average and maximum temperature. Therefore, it is possible that colder climates provide a slow ripening of grapes allowing a synthesis of flavanols and HCAs in grapes. *trans*-Piceid found in 'Carignan' grapes is higher than to those exposed by some authors (López-Hernández and Rodríguez-Bernaldo de Quirós, 2016; Portu et al., 2016), mainly in the grapes collected from Peu site. It has been showed that the concentration of stilbenes increased after plant diseases (Chong et al., 2009). Probably it is possible that the grapevines from Peu presented some abiotic stress not visually detected at the vineyard.

CONCLUSIONS

Climate conditions more than soil characteristics affected grape ripening in 'Carignan' grapes from eight sites of Maule Valley. Besides, these characteristics together with grape maturation altered grape phenolic composition in 'Carignan' vineyards during the 2016 vintage. The grapevines from Curtiduría (Cur) presented the fastest evolution of technological maturity and their grapes were harvested early in the season. The vineyards located from Santa Sofía (Sso) and Truquilemu (Tru) showed the lowest evolution of technological maturity, regarding day of season. These sites did not reach the optimal technological maturity for 'Carignan' grapevine variety. The grapes harvested from El Peumal (Peu) and Sauzal (Sau) presented higher total anthocyanins content than the berries collected from Sso. This last site showed lower maximum and average temperature than the most of the sites. The grapes obtained from Peu and Sso sites presented higher total flavonols concentration than the berries collected from Cur and Caliboro (Cal). These last sites presented higher maximum temperatures than the most of the sites. The grapes harvested from Truquilemu presented higher total flavanols and hydroxycinnamic acids concentration than the samples obtained from the most of the sites. Therefore, climate conditions more than soil characteristics had an important influence on grapevine ripening affecting phenolic composition in 'Carignan' grapes from the Maule Valley.

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