STUDY OF VARIETAL WINES FROM THE QUALIFIED ORIGIN DENOMINATION RIOJA (SPAIN): ANALYSIS OF WINE COLOUR, POLYSACCHARIDES, POLYPHENOLS, BIOGENIC AMINES AND AMINO ACIDS•

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1. INTRODUCTION

La Rioja has an important number of autochthonous grape cultivars with good characteristics to obtain high quality red wines. The use of these cultivars will allow to obtain wines with their own personality and different from the rest of wines that exist in the market.

The objective of this work was to analyse the wine colour components, oenological parameters, colour attributes, CIELAB parameters, polysaccharides, polyphenolic compounds, proanthocyanidins and biogenic amines and amino acids of red wines elaborated from different autochthonous grape cultivars from the qualified origin denomination Rioja (D.O.Ca. Rioja): 'Tempranillo', red 'Maturana', red 'Monastel' and red 'Maturana Navarreteña'.

2. MATERIALS AND METHODS

Four grape cultivars from the D.O.Ca. Rioja were harvested at commercial maturity: *Vitis Vinífera* L. red 'Tempranillo', red 'Maturana', red 'Monastel' and red 'Maturana Navarreteña'. The winemaking was made in 500 litres French oak barrels in duplicate. After one month of alcoholic fermentation samples of the barrels were taken and a descriptive study of each wine was made. All the analyses were performed in triplicate. The analyses carried out were:

- analysis of wine colour by spectrophotometry following the method of Boulton;
- biogenic amines, amino acids and ammonium ion by simultaneous HPLC analysis (Gómez-Alonso *et al*., 2007 a);
- polysaccharides were recovered by precipitation after ethanolic dehydration and analysed by HRSEC-RID (Guadalupe *et al*., 2007);
- tannins were fractionated by GPC (Guadalupe *et al*., 2006) and further analysed by HPLC-DAD as described by Kennedy *et al*., 2001;

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- analysis of enological parameters following the methods described by the Office International de la Vigne et du Vin (1990). CIELAB parameters.

3. RESULTS AND DISCUSSION

Monastel was the most alcoholic wine and showed the highest values in color intensity, total polyphenol index, wine colour, total anthocyanins, *t*-resveratrol and in gallic acid.

Tempranillo had the highest values in pH, total hydroxycinnamic acids and total proanthocyanidins and it showed the greatest mean degree of polymerization (mDP). On the contrary, it showed the lowest values in total anthocyanins and *t*-resveratrol.

Maturana showed the lowest pH and the highest titratable acidity, total flavonol content and biogenic amines content. It showed the lowest values in gallic acid, catechin, amino acids and high molecular weight polysaccharides.

Maturana Navarreteña reached the highest values in catechin, amino acids and in high molecular weight polysaccharides and showed the lowest values in wine colour, flavonols, total proanthocyanidin content and mDP.

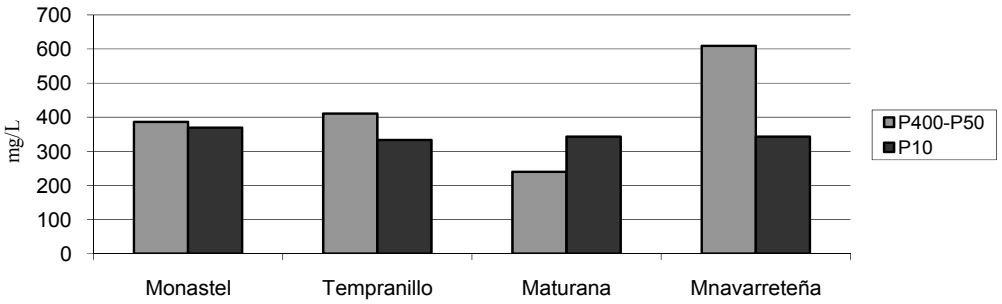

Fig. 1 - Polysaccharide content after alcoholic fermentation. Σ(P400-P50) polysaccharides with an average molecular weight between 404 KDa and 47.3 Kda; P10: polysaccharides with an average molecular weight of 11.8 Kda.

Tab. 1 - Oenological parameters and colour attributes after alcoholic fermentation.

Cv	Alcohol[1]	pH	TA[1]	VA[1]	H_2M[1]	CI[1]	Hue[1]	TPI[1]	a*[1]	b*[1]	L*[1]
Monastel	15.02	3.46	6.75	0.29	1.64	21.48	0.52	80.00	48.04	5.83	53.94
Tempranillo	14.58	3.64	6.01	0.28	2.64	19.41	0.55	75.26	45.93	4.02	55.30
Maturana	14.28	3.41	6.96	0.38	2.22	19.83	0.47	71.82	49.62	-1.51	54.72
MNavarreteña	13.95	3.51	5.63	0.30	1.25	19.81	0.50	71.04	44.75	3.27	57.55

[1] Alcohol: mL ethanol for 100 mL of wine at 20 ºC; TA: titratable acidity as g of tartaric acid per litre; VA: volatile acidity as g of acetic acid per litre; H_2M: malic acid (g L-1); CI, colour intensity as sum of absorbances at 420, 520 and 620 nm; Hue: A420/A520; TPI: total polyphenol index; a*: from green to red; b*: from blue to yellow; L*: lightness.

Tab. 2 - Colour components (absorbance units) after alcoholic fermentation.

Cv	WC[1]	MAC[1]	CC[1]	BSC[1]	SC[1]
Monastel	11.96±0.11^{a}	5.37±0.08^{a}	4.36±0.11^{ab}	2.24±0.01^{a}	6.60±0.10^{a}
Tempranillo	11.02±0.04^{ab}	5.23±0.08^{a}	3.79±0.04^{a}	1.99±0.01^{b}	5.78±0.04^{a}
Maturana	11.53±0.05^{ab}	5.11±0.10^{ab}	4.94±0.06^{b}	1.49±0.01^{c}	6.40±0.30^{a}
MNavarreteña	10.46±0.09^{b}	4.62±0.06^{b}	4.03±0.09^{a}	1.81±0.01^{d}	5.83±0.09^{a}

[1]WC: wine color; MAC: monomeric anthocyanin color; CC: copigmentation color; BSC: bisulphite stable color; SC: stable color calculated as the sum of CC and BSC. Values are means ± standard deviations (n =6). In this table and in the following ones different letters in the same column indicate that means significantly differ at $p < 0.05$.

Tab. 3 - Content of Proanthocyanidins (mg L^{-1}) and mean Degree of Polymerization (mDP) after alcoholic fermentation.

cv	T(mg/L)[1]	%Cat[1]	%Epicat[1]	%Epctgal[1]	mDP[1]
Monastel	1013±19^{a}	5.61±0.02^{a}	3.47±0.03^{a}	3.22±0.02^{a}	10.53±0.00^{a}
Tempranillo	1078±46^{a}	5.06±0.06^{b}	1.77±0.06^{b}	1.61±0.06^{b}	15.57±0.01^{b}
Maturana	723±27^{b}	5.38±0.05^{ab}	2.66±0.05^{ab}	2.78±0.08^{c}	12.12±0.00^{c}
MNavarreteña	585±36^{b}	5.18±0.09^{b}	5.2±0.1^{c}	3.18±0.07^{d}	9.57±0.00^{d}

[1] T: proanthocyanidin concentration (mg/L), as the sum of extension and terminal subunits; %Cat: % catechin terminal subunits; %Epicat: % epicatechin terminal subunits; %Epctgal: % epicatechin gallate terminal subunits; mDP: mean degree of polymerization. Values are means ± standard deviations (n = 3).

Tab. 4 - Content of amino acids and biogenic amines (mg L^{-1}) after alcoholic fermentation.

Cv	Total Aas[1]	Neutral Aas[1]	Basic Aas[1]	Acid Aas[1]	Proline	α-alanine	Gaba
Monastel	1690±362^{a}	1616±362^{a}	49.2±0.4^{a}	24.5±0.3^{a}	1548±60^{a}	5.5±0.8^{a}	25.9±0.8^{a}
Tempranillo	1422±134^{b}	979±87^{b}	129±2^{b}	52±1^{b}	841±32^{b}	32.1±0.5^{b}	48±1^{b}
Maturana	814±109^{b}	767±109^{b}	32±1^{a}	14.6±0.8^{a}	716±36^{b}	10.2±0.8^{a}	14.2±0.9^{bc}
MNavarreteña	1802±220^{a}	1763±220^{a}	26.7±0.7^{a}	12.7±0.4^{a}	1713±96^{a}	8.4±0.9^{a}	10.7±0.5^{c}

Cv	Glycine	Glutamine	Arginine	GluAc[1]	Total Amines[1]	Putrescine
Monastel	9.19±0.33^{a}	18.59±0.26^{a}	8.4±0.2^{a}	22.4±0.3^{a}	15.3±0.5^{a}	2.75±0.05^{ab}
Tempranillo	17.62±0.22^{c}	48.8±1.5^{b}	28.1±0.8^{b}	46±1^{b}	15±1^{a}	2.39±0.07^{a}
Maturana	3.82±0.8^{b}	10.20±1.1^{a}	6.3±0.8^{a}	12.8±0.8^{a}	23±2^{b}	3.5±0.1^{b}
MNavarreteña	6.07±0.28^{ab}	6.66±0.54^{a}	6.1±0.2^{a}	11.3±0.4^{a}	14±0.7^{a}	5.7±0.2^{c}

[1] Total Aas: total amino acids as sum of acid, neutral and basic amino acids. Neutral Aas: neutral amino acids. Basic Aas: basic amino acids. Acid Aas: acid amino acids. GluAc: glutamic acid. Total amines: total biogenic amines. Values are means ± standard deviations (n = 6).

Tab. 5 -. Content of anthocyanins, hydroxycinnamic acids and flavonols (mg L^{-1}) after alcoholic fermentation.

	TAn[1]	GluA[1]	AceA[1]	CumA[1]	TAc[1]
Monastel	439±3[b]	329±2[b]	75.1±0.5[b]	35±0.2[b]	56.4±0.5[b]
Tempranillo	308±3[a]	271±2[a]	14.9±0.1[a]	22±0.2[a]	67.4±0.7[a]
Maturana	402±4[c]	304±3[c]	78.1±0.7[c]	20±0.2[c]	64.6±0.6[c]
MNavarreteña	358±3[d]	241±2[d]	98.7±0.8[d]	19±0.2[c]	63.9±0.6[c]

	t-res[1]	t-res-gl[1]	c-res[1]	Gal[1]	Cat[1]	TFlavo[1]
Monastel	4.66±0.05[b]	5.29±0.05[a]	0.20±0.00[b]	56.4±0.6[b]	75.9±0.8[b]	42.3±0.4[a]
Tempranillo	1.47±0.01[b]	3.00±0.03[b]	0.17±0.00[a]	45.6±0.5[a]	78.5±0.8[a]	42.7±0.4[a]
Maturana	2.15±0.02[c]	6.45±0.06[c]	0.28±0.00[c]	39.5±0.4[c]	66.4±0.7[c]	69.3±0.7[b]
MNavarreteña	2.23±0.02[d]	3.78±0.04[d]	0.03±0.00[d]	46.2±0.5[b]	90.7±0.9[d]	33.6±0.3[c]

[1] TAn: total anthocyanins. GluA: glucoside anthocyanins. AceA: acetyl-glucoside anthocyanins. CumA: coumaryl-glucoside anthocyanins. TAc: total hydroxycinnamic acids; t-res: trans-resveratrol; t-res-gl: trans-resveratrol glucoside; c-res: cis-resveratrol. Gal: gallic acid. Cat: catechin. TFlavo: total flavonols. Values are means ± standard deviations (n = 6).

Abstract

The cultivar with a greater oenological potential was 'Monastel', which showed overall better values than 'Tempranillo' in colour intensity, total polyphenol index, wine colour, total anthocyanins, resveratrol and gallic acid. 'Maturana' showed the lowest pH and the highest values in biogenic amines. 'Maturana Navarreteña' showed the highest values in amino acids and in polysaccharides and the lowest values in proanthocyanidin content and mDP. Neither 'Maturana' nor 'Maturana Navarreteña' seem to be interesting in comparison with 'Tempranillo'.

Literature cited

Gómez-Alonso S., Hermosín-Gutiérrez I., García-Romero E. – 2007 - Simultaneous HPLC analysis of biogenic amines, amino acids, and ammonium ion as aminoenone derivatives in wine and beer samples. *Journal of Agricultural and Food Chemistry*, 55, 608-613.

Guadalupe Z., Soldevilla A., Sáenz Navajas M.P., Ayestarán B. – 2006 - Analysis of polymeric phenolics in red wines using different techniques combined with gel permeation chromatography fractionation. *Journal of Chromatography A*, 1112, 112-120.

Guadalupe Z., Ayestaran B. – 2007 - Polysaccharide profile and content during the vinification and ageing of Tempranillo red wines. *Journal of Agricultural and Food Chemistry*, 55, 10720-10728.

Kennedy J. A., Jones G. P. – 2001 - Analysis of proanthocyanidin cleavage products following acid-catalysis in the presence of excess phloroglucinol. *Journal of Agricultural and Food Chemistry*, 49, 1740-1746.