ENOLOGICAL POTENTIAL OF AUTOCHTHONOUS GRAPE CULTIVARS FROM CASTILLA Y LEÓN (SPAIN) TO ELABORATE SPARKLING WINES: POLYPHENOLIC AND BIOGENIC AMINES AND AMINO ACID COMPOSITION OF BASE WINES•

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1. INTRODUCTION

Castilla y León has an important number of autochthonous grape cultivars with good characteristics to obtain quality sparkling wines. The employment of these cultivars will allow to obtain wines with their own personality and different from the rest of the sparkling wines that exist in the market.

The aim of this work was to analyse monomeric polyphenols, proanthocyanidins, biogenic amines and amino acids of white and rosé base wines in order to select the more adequate grapes to elaborate quality natural sparkling wines.

2. MATERIALS AND METHODS

The base wines were prepared using the traditional white or rosé winemaking process in stainless steel tanks of 150 liters by duplicate. Seven cultivars were studied, five white: ‘Verdejo’ and ‘Viura’ from the Rueda Denomination Origin (D.O.), ‘Malvasía’ from the Toro D.O., ‘Albarín’ from the Tierras de León, and ‘Godello’ from the Bierzo D.O.; and two red cultivars: ‘Garnacha’ from the Cigales D.O. and ‘Prieto picudo’ from the Tierras de León. Monomeric polyphenols were directly analysed by HPLC-DAD (Gómez Alonso *et al*., 2007

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a), tannins were fractionated by GPC (Guadalupe *et al*., 2006) and further analysed by HPLC-DAD (Kennedy *et al*., 2001), and finally biogenic amines and amino acids were analysed by simultaneous HPLC-DAD analysis (Gómez Alonso *et al*., 2007 b). All the analyses were performed in triplicate.

3. RESULTS AND DISCUSSION

No significant differences among cultivars were detected as concerns the content of proanthocyanidins (tab. 1).

Tab. 1 - Content of proanthocyanidins (mg L^{-1}) and mean Degree of Polymerization (mDP) in base wine.

cv	PA[1]	% Cat[1]	% Epi[1]	% Epigal[1]	mDP[1]
Malvasía	$24.15^{a}\pm0.26$	$5.51^{b}\pm2.39$	$7.57^{a}\pm0.45$	$0.00^{a}\pm0.00$	$7.04^{d}\pm0.78$
Godello	$35.43^{a,b}\pm11.38$	$10.13^{a}\pm1.81$	$5.22^{a}\pm1.99$	$1.44^{a}\pm1.58$	$4.91^{a,b,c}\pm0.36$
Verdejo	$26.49^{a}\pm0.93$	$12.43^{d}\pm0.14$	$6.67^{a}\pm0.21$	$7.38^{b,c}\pm5.23$	$3.95^{a,b}\pm1.30$
Viura	$31.39^{a,b}\pm4.88$	$10.82^{a,d}\pm0.52$	$5.82^{a}\pm1.36$	$0.00^{a}\pm0.00$	$6.68^{c,d}\pm2.35$
Albarín	$45.51^{b}\pm10.35$	$8.96^{a,c}\pm0.63$	$3.87^{a}\pm1.24$	$3.61^{a,b}\pm0.65$	$3.75^{a,b}\pm0.35$
Prieto picudo	$41.92^{b}\pm14.10$	$9.68^{a}\pm1.15$	$7.53^{a}\pm5.79$	$9.49^{c}\pm0.94$	$3.03^{a}\pm0.60$
Garnacha	$89.48^{c}\pm2.98$	$7.30^{b,c}\pm0.31$	$3.18^{a}\pm1.88$	$3.82^{a,b}\pm1.14$	$5.51^{b,c,d}\pm0.55$

[1]PA: proanthocyanidins as the sum of all the subunits, extension subunits (phloroglucinol adducts) and terminal subunits (catechin, epicatechin and epicatechin gallate); %Cat: % of catechin terminal subunits; %Epi: % of epicatechin terminal subunits; %Epigal: % of epicatechin gallate terminal subunits; mDP: mean degree of polymerization.
In this table as in the following ones values are means ± standard deviations ($n = 6$) and different letters in the same column indicate that means significantly differ at $p < 0.05$.

Two groups could be observed regarding their degree of polymerisation: Malvasía and Viura, with a high degree of polymerisation, and Verdejo and Albarín, with a low degree of polymerisation. Although both groups showed significant differences, these differences were small (4 units) and thus they will not probably affect in a sensory level. Regarding rosé wines, the proanthocyanidin content was significantly higher in Garnacha. However, the ratio tannin/anthocyanin was approximately 6, while it was 3 in Prieto picudo. It is known that the best ability to stabilize the red color and ageing occurs when the relationship anthocyanin/tannin is close to 1. In this sense Prieto picudo seems to be the best suitable for the stabilization of color and ageing.

The content in amino acids and biogenic amines in base wine shows that Verdejo had significantly higher values in total amino acids followed by Albarín and Godello and finally Malvasía and Viura showed the lowest values (tab. 2). Regarding to rosé wines, Prieto picudo had twelve times higher values than Garnacha wine in total amino acids. This difference could be attributed to varietal differences rather than to different levels of ripening or vinification. The percentage of neutral amino acids in relation to total amino acids was lower than 50 % in Viura, Malvasía and Garnacha wines due to a low content in proline, whose percentage was lower than 7 %. In the rest of the wines, the percentage of neutral amino acids was 70-90 % and proline was 50-80 % of the total content. After proline, the major neutral amino acids were α-alanine and GABA. Total biogenic amine content was low (tab. 2) and the content of histamine was near to 0 mg L^{-1} in all the cases (data not shown). Therefore, all base wines were healthy as the histamine content was lower than the limits set by several European countries (8 mg L^{-1} in France and 2 mg L^{-1} in Germany). Putrescine, usually associated with poor sanitary conditions, was the predominant biogenic amine in all the analyzed wines (55 % to 75 % of total content) although its content was not high in any case.

No significant differences were observed in the profile or in the total content of anthocyanins in Garnacha and Prieto picudo rosé wines (tab. 3). Unlike what it was observed in total amino acids, Garnacha wine had higher values in total hydroxycinnamic acid, gallic acid, monomeric proanthocyanidins (catechin) and total flavonols.

Tab. 2 – Content of amino acids and biogenic amines (mg L^{-1}) in base wine

Cv	Total aas[1]	Neutral aas[1]	Basic aas[1]	Acid aas[1]
Malvasía	$14.25^{a}\pm3.58$	$7.41^{a}\pm2.21$	$6.10^{a}\pm1.32$	$0.74^{a}\pm0.05$
Godello	$109.27^{b}\pm3.10$	$99.55^{b}\pm4.18$	$9.04^{a,b}\pm1.31$	$0.67^{a}\pm0.03$
Verdejo	$183.79^{d}\pm11.01$	$147.42^{c}\pm10.41$	$32.58^{d}\pm0.70$	$3.79^{d}\pm0.05$
Viura	$16.31^{a}\pm0.24$	$7.91^{a}\pm0.08$	$7.23^{a}\pm0.33$	$1.18^{b}\pm0.04$
Albarín	$136.07^{b}\pm20.51$	$108.69^{b}\pm21.45$	$25.57^{c}\pm1.22$	$3.33^{c}\pm0.20$
Prieto picudo	$429.14^{e}\pm24.05$	$364.54^{d}\pm18.51$	$59.61^{e}\pm5.19$	$5.00^{e}\pm0.40$
Garnacha	$34.05^{a}\pm0.27$	$11.32^{a}\pm1.23$	$14.38^{a,b}\pm7.06$	$0.76^{a}\pm0.04$

cv	Proline	α- alanine	Gaba	Total amines[1]	Putrescine
Malvasía	$0.72^{a}\pm0.12$	$1.21^{a,b}\pm0.81$	$0.84^{a}\pm0.38$	$2.47^{a}\pm0.11$	$1.37^{a}\pm0.05$
Godello	$89.74^{b,c}\pm4.49$	$1.12^{a,b}\pm0.14$	$1.18^{a}\pm0.03$	$2.80^{a}\pm0.11$	$1.62^{b}\pm0.06$
Verdejo	$113.37^{c}\pm10.36$	$7.15^{c}\pm0.52$	$6.28^{b}\pm0.37$	$3.65^{d}\pm0.05$	$2.20^{c}\pm0.04$
Viura	$1.38^{a}\pm0.09$	$0.66^{a}\pm0.05$	$0.68^{a}\pm0.02$	$2.09^{c}\pm0.05$	$1.20^{a}\pm0.02$
Albarín	$68.34^{b}\pm36.39$	$8.65^{d}\pm0.49$	$5.45^{b}\pm0.31$	$6.15^{e}\pm0.50$	$4.48^{f}\pm0.20$
Prieto picudo	$323.43^{d}\pm14.52$	$10.77^{e}\pm0.28$	$8.83^{c}\pm1.54$	$4.13^{b}\pm0.09$	$2.68^{e}\pm0.03$
Garnacha	$1.55^{a}\pm0.06$	$1.73^{b}\pm0.32$	$1.47^{a}\pm0.24$	$4.11^{b}\pm0.05$	$2.47^{d}\pm0.21$

[1]Total Aas: total amino acids as sum of acid, neutral and basic amino acids. Neutral Aas: neutral amino acids: serine, HO-proline, glycine, threonine, α-alanine, β-alanine, GABA, proline, tyrosine, valine, methionine, cysteine, isoleucine, leucine, phenylalanine. Basic Aas: basic amino acids: asparagine, glutamine, histidine, arginine, tryptophan, ornithine, lysine. Acid Aas: acid amino acids: aspartic acid, glutamic acid. Total amines: total biogenic amines: histamine, agmatine, spermidine, tyramine, putrescine, tryptamine, cadaverine, phenylethylamine, isoamylamine.

Tab. 3 - Content of anthocyanins, hydroxycinnamic acids and flavonols (mg L^{-1}) in base wine.

Cv	TAn[1]	GluA[1]	AceA[1]	CumA[1]	TAc[1]	Gal[1]
Garnacha	15.34^a±0.97	14.29^a±0.57	0.37^a±0.04	0.68^a±0.37	90.52^b±7.51	3.29^b±0.11
Prieto picudo	15.46^a±6.18	13.16^a±4.83	1.61^b±0.65	0.69^a±0.70	13.39^a±1.97	2.23^a±0.02

cv	Cat[1]	TFlavo[1]
Garnacha	14.91^b±2.16	2.40^b±1.22
Prieto picudo	7.54^a±2.83	0.26^a+±0.11

[1]TAn: total anthocyanins is the sum of GluA, AceA and CumA. GluA: glucoside anthocyanins is the sum of delphinidin, cyanidin, petunidin, peonidin and malvidin-3-glucosides; AceA: acetyl-glucoside anthocyanins is the sum of delphinidin, cyanidin, petunidin and malvidin-3-(6-acetyl)-glucosides; CumA: coumaryl-glucoside anthocyanins is the sum of delphinidin, petunidin, and malvidin-3-(6-p-coumaryl)-glucosides; TAc: total hydroxycinnamic acids is the sum of trans-caftaric (trans-caffeoyl-tartaric acid), cis-caftaric (cis-caffeoyl-tartaric acid), trans-coutaric (trans-p-coumaryl-tartaric acid), cis-coutaric (cis-p-coumaryl-tartaric acid), caffeic and trans-p-coumaric acid; Gal: gallic acid; Cat: catechin; TFlavo: total flavonols is the sum of myricetin 3-glucoside, quercetin 3-rutinoside, quercetin 3-galactoside, quercetin 3-glucoside, quercetin 3-glucuronide, isorhamnetin 3-rutinoside, kaempferol 3-glucoside, isorhamnetin 3-glucoside, myricetin, quercetin, kaempferol and isorhamnetin.

Abstract

In white wines, Verdejo wine stands out because of its high content in total amino acids. The total content in biogenic amines was low in all wines analyzed and putrescine was the predominant biogenic amine. No significant differences were observed in the total proanthocyanidin content among white wines. Regarding to rosé wines, Prieto picudo had the highest values of total amino acids and significantly lower values in total hydroxycinnamic acids, total flavonols and proanthocyanidins. However, its ratio tannin/anthocyanins was more nearby to 1 than in Garnacha wine and thus Prieto picudo seemed to be the most adequate variety regarding to the stabilization of red color and for ageing.

Literature cited

Gómez Alonso S., García Romero E., Hermosín Gutiérrez I. – 2007a - HPLC analysis of diverse grape and wine phenolics using direct injection and multidetection by DAD and fluorescence. *Journal of Food Composition and Analysis*, 20, 618-626.

Gómez Alonso S., Hermosín-Gutiérrez I., García-Romero E. – 2007b - 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.

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.