Evaluation of the Influence of Vineyard Age, Grape Ripening Stage and Storage Temperature on the Ester Profile of Palomino Fino White Wines

José M. Muñoz-Redondo[1], M. Victoria Jiménez-Povedano[2], Belén Puertas[2], Emma Cantos-Villar[2], Manuel J. Valcárcel-Muñoz[3], Beltrán Peña-Parra[3], José M. Moreno-Rojas[1]

[1]Department of Food Science and Health - Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA), Avenida Menéndez-Pidal, SN, 14004 Córdoba, Spain

[2]Department of Food Science and Health - Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA), Ctra. Cañada de la Loba PK 3.1 (CA-3102), 11471 Jerez de la Frontera, Spain

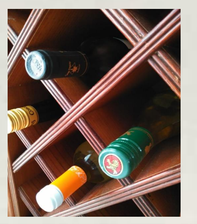
[3]Bodegas Fundador, S.L.U., C/ San Ildefonso, 3, 11403 Jerez de la Frontera, Spain

INTRODUCTION

Wine is an alcoholic beverage made from grapes and composed of hundreds of chemical compounds. Among them, volatile compounds are considered to be responsible for their aroma. This attribute is linked to the quality of a wine and related to the consumer preferences[1]. Esters are an important volatile family that greatly influence on the aroma directly or throughout complex synergistic interactions[2]. This family has been described as an important contributor to the fruity aroma of wines[3]. Likewise, some of them were described as one of the main contributors to the fundamental aroma of the wines[4]. The composition of those volatile compounds can be modulated during winemaking. The aim of this study was to evaluate the influence of vineyard age, grape ripening stage and storage temperature on the ester profile of Palomino Fino white wines using HS-SPME-GC-MS and chemometrics.

Vineyard Age

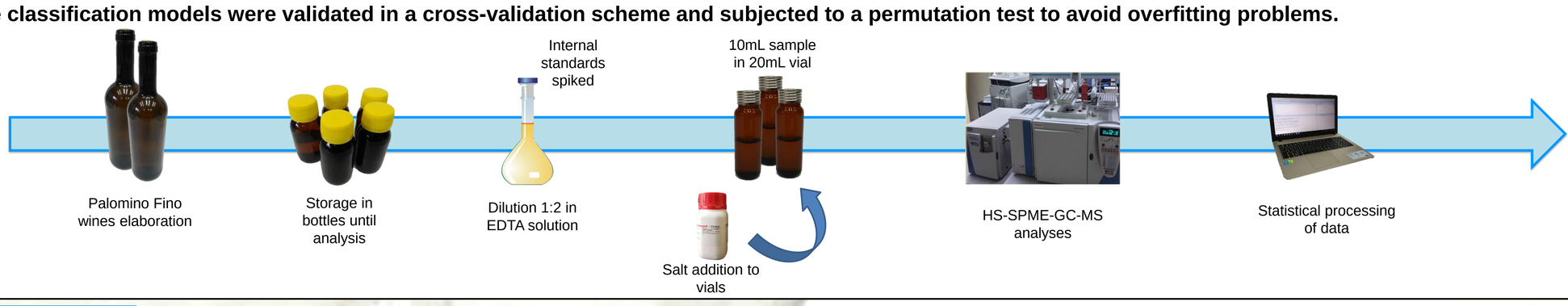
Ripening Stage



Storage Temperature

MATERIALS AND METHODS

Palomino Fino white wines were elaborated from three different vineyard ages (4, 13 and 21 years) and harvested grapes at three different ripening stages (8.5, 10.5 and 12.5 °Baumé). Additionally, all the wines from harvested grapes at 12.5 °Baumé were conserved at refrigerated (conventional) and room temperatures to evaluate the impact over the ester composition. Ester compounds were identified using the reference standards and comparing the retention index with those found in bibliography. Their quantification was performed using head space solid phase micro-extraction method (HS-SPME) followed by gas chromatography – mass spectrometry (GC–MS) as previously described[5]. Data were treated in an univariate (analysis of variance, ANOVA) and multivariate approach (principal component analysis, PCA; (orthogonal) partial least squares discriminant analysis, (O)PLS-DA) to highlight potential volatile markers responsible for the studied factors. The classification models were validated in a cross-validation scheme and subjected to a permutation test to avoid overfitting problems.



RESULTS

A total of 26 compounds belonging to the ester family were identified and quantified. The first two latent variables of the PLS-DA/O-PLS-DA models for each factor were plotted in Figure 1. Classification models were satisfactory in terms of error and overfitting. Wines displayed differences in their ester composition depending on the vineyard age. Ethyl esters of branched acids (EEBAs) were the most impacted compounds due to this factor. In addition, most of the analysed esters increased their concentration with the maturity of the grapes which the wine was made with. However, hexyl acetate and methyl hexanoate esters decreased their concentrations with the maturity of the grapes while ethyl decanoate and palmitate esters reached the higher concentrations in the intermediate maturity stage. Higher alcohol acetates HAAs were found as important contributors for the differentiation of the wines according to the grape ripening stage. Additionally, we could add that the storage temperature revealed great concentration changes in the ethyl esters of fatty acid (EEFA) family.

Table 1. Two-way Analysis of Variance (ANOVA) carried out on the vineyard age and grape ripening stage factors for the subfamilies of esters.

Compounds	Vineyard Age				Ripening Stage				Interactions
	A1	A2	A3	p-value	S1	S2	S3	p-value	p-value
EEFAs	4250	4399	4716	ns	4070b	4784a	4512a	*	ns
HAAs	6718a	4381c	5834b	***	4201c	5705b	7026a	***	***
EEBAs	37b	41a	35c	***	33b	40a	40a	***	***
Cinnamates	0.73	0.74	0.71	ns	0.54c	0.71b	0.93a	***	ns
MEFAs	6.2a	5.4b	5.6b	**	6.0a	5.7ab	5.5b	*	*
Miscellaneous	286a	292a	267b	**	173c	288b	383a	***	***

EEFAs: Ethyl esters of branched acids; HAAs: Higher Alcohol Acetates; EEBAs: Ethyl Esters of Branched Acids; MEFAs: Methyl Esters of Fatty Acids. A1, A2, A3: vineyard age corresponding to 4, 13 and 21 years respectively. S1, S2 and S3: wines elaborated from grapes harvested at 8.5, 10.5 and 12.5 °Baumé respectively.

Table 2. One-way Analysis of Variance (ANOVA) carried out on the storage temperatura factor for the subfamilies of esters.

Compounds	Conservation Temperature		
	Refrigerated	Room	p-value
EEFAs	4512b	7547a	*
HAAs	7026	5784	ns
EEBAs	40b	50a	*
Cinnamates	0.93b	1.09a	**
MEFAs	5.5a	5.0b	**
Miscellaneous	383	484	ns

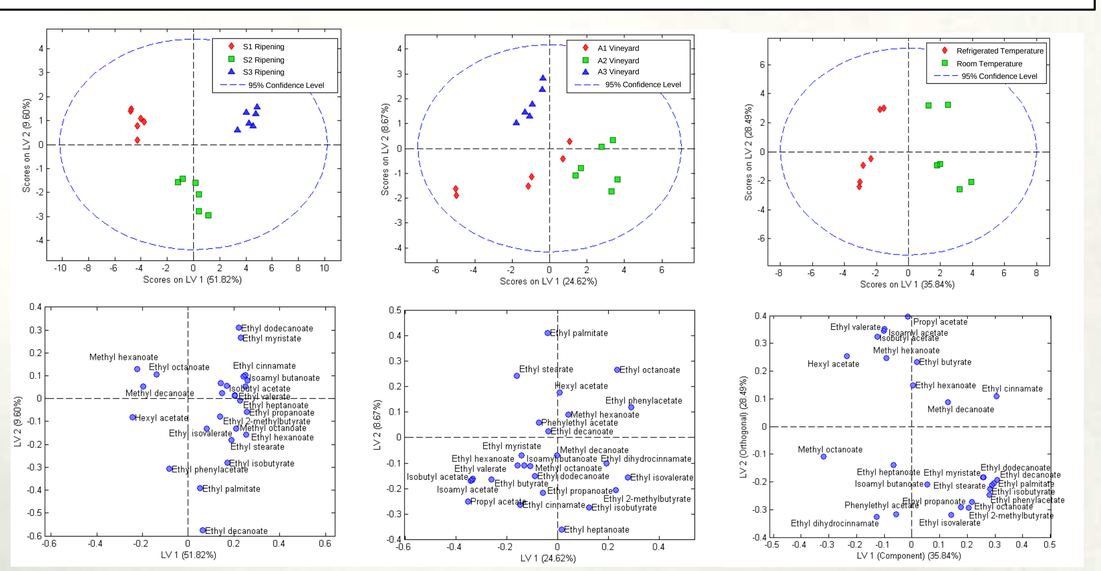


Figure 1. PLS-DA/O-PLS-DA performed for the three factors studied: ripening stage, vineyard age and storage temperature.

CONCLUSIONS

The HS-SPME-GC-MS methodology was successfully used to identify and quantify 26 ester compounds in Palomino Fino white wines. The chemometric approach allowed us to study differences between wines from a holistic point of view. Differences in the ester profile of these wines were observed and related to three factors: vineyard age, grape maturity stage and storage temperature. The results gave a detailed profile of this important volatile family modulation by means of these three factors.

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