Food Research International 57 (2014) 234–241

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Criteria to discriminate between wines aged in oak barrels and macerated with oak fragments

Purificación Hernández-Orte [a,*], Ernesto Franco [b], Carlos González Huerta [c], Juana Martínez García [d], Mariano Cabellos [e], Julián Suberviola [f], Ignacio Orriols [g], Juan Cacho [a]

[a] Laboratory for Flavor Analysis and Enology, Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, 50009 Zaragoza, Spain
[b] Unidad de Enología, Gobierno de Aragón, Movera, Zaragoza, Spain
[c] Estación Enológica de Castilla y León, Rueda, Valladolid, Spain
[d] Centro de Investigación y Desarrollo Tecnológico Agroalimentario, Logroño, Spain
[e] Instituto Madrileño de Investigación y Desarrollo Rural, Agrario y Alimentario, Madrid, Spain
[f] Estación enológica de Navarra, Olite, Navarra, Spain
[g] Estación enológica de Galicia, Leiro, Orense, Spain

ARTICLE INFO

Article history:
Received 31 October 2013
Accepted 19 January 2014

Keywords:
Discriminate wines
Barrel oak
Oak chips
Aroma compounds

ABSTRACT

Wine aging in barrels is carried out to increase stability and achieve more complex aromas. In the last few years, however, the practice of macerating wine with small fragments of toasted oak (chips) has become increasingly common. This conveys similar tastes, aromas, and wooden notes to the wine as those obtained with traditional barrel aging, but much faster and at a fraction of the cost. Without proper regulation, this could lead to fraud if wine macerated with chips is offered as barrel aged wine.

In the present study, 75 volatile compounds have been determined by applying gas chromatography–mass spectrometry (MS) and flame ionization detection (FID). It has been found that compounds directly related to the wood have greater discriminative power for telling apart wines aged in barrels from those macerated with oak fragments, but no single compound permits flawless classification. Therefore, we have studied the effect of the addition of oak fragments of different origins, different oak types, different formats and subjected to different toasting processes on a set of 231 samples from 6 Spanish Denominations of Origin wines (DOs), and compared them to those same wines aged in oak barrels. In light of the results, we have developed a set of criteria which allows distinguishing with high degree of accuracy between wines which have been aged in barrels and those macerated with oak fragments. The application of these criteria to different wines allows correct classification in over 90% of cases.

1. Introduction

Wine aging is a technique commonly used in wineries to increase the stability of wines, spontaneously clarify them, and achieve more complex aromas. Normally, oak barrels are used. The composition of the wine in direct contact with the barrel is modified as the wine extracts compounds from the wood such as tannins, phenolic acids and volatile compounds. Moreover, the coloring elements in wine stabilize due to the micro-oxygenation produced when air flows through the barrel staves, increasing the quality of the wine. However, this method is expensive and requires long periods of time. In the last few years, the practice of macerating wine with small fragments of toasted oak has become increasingly common, as it conveys similar tastes and aromas to the wine as those obtained with traditional barrel aging, but much faster and at a fraction of the cost (wine macerated with oak fragments can be up to 10 times cheaper than the same wine aged in barrel). The increased surface area of the fragments accelerates the extraction of the compounds.

The use of oak fragments for macerating wines is already an alternative to oak barrel aging. New wine-producing countries such as Chile, Argentina, South Africa, Australia or the United States have been using these techniques for several years. A great variety of systems are used to elaborate wines this way, all based on adding pieces of oak of different sizes, wood\ types and degree of toasting to the wine. Some of them are introduced directly in the tank, and some of them to reuse old barrels.

Oak fragments can be found in a variety of forms (del Alamo Sanza, 2006). These include shavings, known as *oak fragments*; cut into dices, named *cubes* or *oak beans*; *oak powder*; pieces of granulated wood called *pencil shavings* or *granulates*; *dominoes*; or square pieces referred to as *blocks* or *segments*. Additionally, bigger pieces designed to be placed in the tank can also be found on the market, usually in the form of staves, hence being called *tank staves*, *winewood* or *infusion staves*. Old barrels can also be used by adding wooden pieces such as *oak chains*, *sticks*, or *barrel inserts*.

* Corresponding author. Tel.: +34 976 761290; fax: +34 976 761292.
E-mail address: puhernan@unizar.es (P. Hernández-Orte).

0963-9969/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodres.2014.01.044

All the above-mentioned products are made from different kinds of oak wood (American, French, Hungarian, and Pyrenean) and are subjected to a variety of toasting methods (fire, hot air, and infrared radiation) and degrees of toasting (in addition to the well known light, medium and strong levels, toasting is also offered as simple or double, or performed at specific temperatures).

The effects produced by the addition of wooden pieces into wine depend on several factors, which define the characteristics of the wine. These include the origin of the wood (Chatonnet & Dubourdieu, 1998; Fernandez de Simon, Cadahia, & Jalocha, 2003; Frangipane, De Santis, & Ceccarelli, 2007), the type of drying (Masson, Baumes, Moutounet, & Puech, 2000; Vivas & Glories, 1996), the toasting process (Fernandez de Simon, Cadahia, del Alamo, & Nevares, 2010; Fernandez de Simon et al., 2003; Franco, Castells, Martínez, & Pérez, 2007), the amount of fragments added to the wine (Fan, Xu, & Yu, 2006), the contact time between wine and oak (Bautista-Ortin et al., 2008), the size of the wooden pieces, and the age of the barrel (Arapitsas, Antonopoulos, Stefanou, & Dourtoglou, 2004; Mosedale, Puech, & Feuillat, 1999; Singleton, 1995).

The aromas that the wood conveys to the wine come from the degradation of compounds from the wood during its toasting process, or from the wood itself. Eugenol and oak lactones add spicy character and oak flavor. When the lignin degrades during the toasting process, volatile phenols such as guaiacol and aromatic aldehydes such as vanillin and syringaldehyde are generated (Chatonnet, Cutzach, Pons, & Dubourdieu, 1999; Diaz-Maroto, Sanchez-Palomo, & Perez-Coello, 2004). Also, the degradation of hemicelluloses produces furanic compounds such as furfural and 5-methyl furfural (Garde-Cerdan & Ancin-Azpilicueta, 2006; Perez-Coello, Gonzalez-Vinas, Garcia-Romero, Cabezudo, & Sanz, 2000) which are reminiscent of toasted almond and nuts. These compounds appear preferentially at a specific temperature so if the toasting is precise and homogeneous, clearly definable aromatic characteristics can be achieved. If wooden pieces toasted at different temperatures are mixed, the compounds conveyed by the wood will be more diverse.

In Europe the use of oak fragments to macerate wines is an alternative to oak barreling. This enological practice is approved by EU regulations (CE) No 2165/2005 and (CE) No 1507/2006 which define the terms of use of oak fragments in wine.

Oak fragments are able to give wine a wooden touch without the need to use barrels. Without proper regulation, this could lead to fraud if such wine is offered as barrel aged wine. European regulations on wine protect specific labelings (crianza, reserva) for wines which have obtained exclusively through aging in barrels. OIV resolutions in this matter explicitly forbid wines with particular indications (crianza and reserva among others) to be treated with wood fragments. Therefore, analytical tools must be found in order to distinguish between these two types of treatments and so avoid possible frauds.

The main objective of this study is to find markers that allow us to discriminate between wines aged in barrels and wines fermented or macerated with oak fragments. The aim is to tell the difference between wines that have been made following two quite different enological practices described in the enological CODEX published by the International Organization of Vine and Wine (2006 edition) as “Ageing in small capacity wooden containers (OENO 8/01)” and as “usage of pieces of oak wood in winemaking (OENO 9/01)”.

2. Materials and methods

2.1. Reagents and standards

The aroma standards were supplied by Aldrich (Gillingham, UK), Fluka (Buchs, Switzerland), Sigma (St. Louis, MO, USA), Lancaster (Strasbourg, France), PolyScience (Niles, USA), Chemservice (West Chester, USA), Interchim (Monluçon, France), International Express Service (Allauch, France) and Firmenich (Geneva, Switzerland). LiChrolut EN resins (styrene–divinylbenzene) and polypropylene cartridges were obtained from Merck (Darmstadt, Germany). Dichloromethane and methanol of LiChrosolv quality were purchased from Merck (Darmstadt, Germany); absolute ethanol, and ammonium sulfate were obtained from Panreac (Barcelona, Spain), all of them of ARG quality. Pure water was obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). Semi automated Solid Phase Extraction (SPE) was carried out with a VAC ELUT 20 station supplied by Varian (Walnut Creek, CA, USA).

2.2. Samples

The grapes and wines used in the assay were of the vintages 2008 and 2009, vinified in 6 experimental centers in 6 different regions of Spain.

The first assay was made at the Centro de Transferencia Agroalimentaria de Aragón (CTA), with wines of the “Garnacha Tinta” variety. The wines of the 2008 vintage were vatted in 12 American oak barrels of 225 L capacity. Three of them were new and the other 9 semi new from the third, fifth and seventh years of usage, respectively. With the wine from the same batch as mentioned above, 6 tanks of 250 L capacity were filled and 2 different types of oak fragments were added in 6 g/L doses. The wines and fragments were in contact during 60 days, after which the oak fragments were removed by racking and 75 L was bottled. With the rest of the macerated wine, 6 7-year old American oak barrels were filled. Six and twelve months after vatting the wine in the barrels, corresponding 50 L samples were taken and bottled. In the second year of experiment, with the wine of 2009 vintage, 15 American oak barrels of 225 L capacity were filled, 3 new and 12 semi new from the assay of the previous year, which now were 2, 4, 6 and 8 years old, respectively. In the same way as the first year but with 2009 vintage wine, three 250 L tanks were filled and other American oak fragments were added. In addition, Pyrenean fragments were added to three other 250 L tanks, in both cases in doses of 6 g/L. The assay was repeated in the same way as for the first year, except for the wines macerated with oak fragments that were vatted in 8-year old barrels.

The second assay was made at the Instituto Tecnologico Agrario, Estación enologica de Castilla y León (ITACYL), with wines of the Tinta del Pais (Tempranillo) variety. In the two years of the assay, wines of the 2008 and 2009 vintages were vatted in nine 225 L French oak barrels, 3 new and 6 semi new (3 3-year old and 3 5-year old barrels). Six 250 L tanks were filled with the same wine, to which two different types of French oak fragments were added in 6 g/L doses. The working protocol was the same as that used in the CTA on the first assay.

The third assay was made at the Centro de Investigacion y Desarrollo Agrario de la Rioja (CIDA), with wine of the Tempranillo variety. In the first year, 2 new French oak barrels and 3 American oak barrels, all of 225 L capacity, were filled with wine of the 2008 vintage. Twelve 250 L tanks were filled with wine from the same vinification batch, to which 2 different types of French oak fragments and 2 different types of American oak were added, all in 6 g/L doses.

During the second year, 3 new French oak barrels and 3 American oak barrels were filled with wine of the 2009 vintage. In addition, twelve 250 L tanks were filled with wine from the same batch to which French, American and Pyrenean oak fragments were added in 6 g/L doses. In 2009, six 250 L tanks containing French and American oak hogshead staves in 0.33 m^3/hl doses were also filled with wine. The wine was macerated with the hogshead staves during 12 months. At six and twelve months the samples were taken and bottled.

The fourth assay was made at the Instituto Madrileño de Investigacion y desarrollo Rural Agrario. During the first year, grapes of the Tempranillo variety, 2008 vintage, were fermented in nine 50 L tanks with American oak fragments added in 3, 6 and 9 g/kg doses. Once the fermentation concluded, 50 L of each treatment were bottled.

Similarly, grapes were fermented without fragments and the wine obtained was placed in three new 225 L American oak barrels and