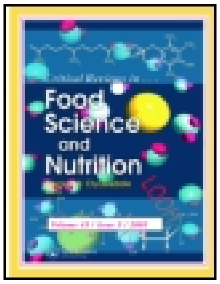

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Effects of Sugar Concentration Processes in Grapes and Wine Aging on Aroma Compounds of Sweet Wines—A Review

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Effects of Sugar Concentration Processes in Grapes and Wine Aging on Aroma Compounds of Sweet Wines – A Review

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Abstract:

Dessert sweet wines from Europe and North America are described in this review from two points of view: both their aroma profile and also their sensorial description. There are growing literature data about the chemical composition and sensory properties of these wines. Wines were grouped according to the production method (concentration of sugars in grapes) and to the aging process of wine (oxidative, biological, a combination of both and ageing in the bottle). It was found that wines natively sweets and wines fortified with liquors differ in their volatile compounds. Sensory properties of these wines include those of dried fruit (raisins), red berries, honey, chocolate and vanilla..., what is contributing to their growing sells. However, there is still a need for scientific research on the understanding of the mechanisms for wine flavour enhancement.

Keywords: Dessert sweet wines, aroma compounds, sensorial descriptors, sugar concentration processes in grapes, wine aging, market trends.

Glossary:

2M3SB	2-Methyl-3-sulfanylbutan-1-ol
2M3SP	2-Methyl-3-sulfanylpentan-1-ol
3SH	3-Sulfanylhexan-1-ol
3SHp	3-Sulfanylheptan-1-ol
3SP	3-Sulfanylpentan-1-ol
BW	Botrytized sweet wines
GC/MS	Gas chromatography/mass spectrometry
LOX	Lipoxygenase
OAV	Odour activity value
P-2M3SB	S-3-(2-methylbutan-1-ol)-l-cysteine
P-3SH	S-3-(hexan-1-ol)cysteine
P-3SHp	S-3-(heptan-1-ol)-l-cysteine
P-3SP	S-3-(pentan-1-ol)-l-cysteine
PCA	Principal component analysis
TDN	1,1,6-Trimethyl-1,2 dihydro naphthalene
TN	Touriga Nacional

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1. Types of sweet wines

During the fermentation process that transforms grapes into wine, yeast consumes the natural sugars in ripe grapes and transforms them into alcohol and carbon dioxide. Hence, most wines are "dry" (meaning, no apparent sweetness or residual sugar) or almost dry. There are, however, many sweet wines made by various processes. These constitute the world of sweet or dessert wines.

Throughout history, sweetness in wine was important for preservation, and sweet wines were prized in ancient Rome and in the Middle Ages. The Dutch and British wine trade of the early eighteenth century promoted and marketed sweet wines. Sweet Madeira was the drink of choice in Colonial America (Brook, 1987). Today, sweet dessert wines comprise a very small percentage of the overall wine trade. Nevertheless, there is a growing interest in high-quality dessert wines. An aromatic and sensorial description of sweet wines grouped by geographical origin, cultivar variety and sugar concentration process can be found in **Table 1**.

Sweet wines can be divided in two large groups: liqueur wines which are elaborated by the addition of alcohol to the must to avoid the fermentation or to stop it and naturally sweet wines obtained without the addition of alcohol (López de Lerma and Peinado, 2011).

1.1. Fortified or liqueur wines

The liqueur wines are those sweet wines obtained from so-called "base products" (grape must in fermentation; wine; a combination of both products; mixture of wine and must; or grape must or its mixture with wine) to which has been added neutral alcohol of vine origin or dried grape

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distillate and, in some cases, sweeteners products from grapes such as concentrated grape must. Their preparation necessarily requires the addition of neutral grape alcohol, to the wine during fermentation, what stops the fermentation process, and kills the yeast that consumes the sugar, in order to achieve an alcoholic content and residual sugar level according to the characteristics of each type of wine. The law states that actual alcoholic strength for these wines does not be less than 15 % vol. and a total alcoholic strength does not be less than 17.5 % vol. (Council Regulation 479/2008), except for certain liqueur wines with a designation of origin or with a geographical indication which have their own regulations.

In Spain, the most renowned fortified wines are those of Jerez (Fino, Amontillado and Oloroso) made from the Palomino Fino variety, and those obtained by mixing them with the variety Pedro Ximenez. It is also highlighted the Málaga Montilla-Moriles, Priorat, etc. In Portugal, the famous Port wine has been one of the first wines under the concept of Denomination of Origin. Other fortified wines of this country include Madeira and Moscatel Setúbal. In Italy, there are different fortified wines based on Malvasia. It should be also included the Marsala and Muscat Pantelleria. In Greece, the most famous fortified wines are Samos, Lemmos Muscat from Patras, from Rhodes and Mavrodafne.

1.2. Naturally sweet wines

Naturally sweet wines are those in what the alcohol and sweetness are exclusively from grapes. To prepare these wines grapes with particularly high sugar content are needed because

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only a part is transformed to alcohol during fermentation. These high contents in fermentable sugar are a result obtained by grape over-ripening using different procedures:

a) On the vine:

- Late harvest wines or wines of overripe grapes: These wines with a total alcoholic strength of not less than 15 % vol. and an actual alcoholic strength of not less than 12 % vol. are produced without enrichment (Council Regulation 479/2008). Grapes are left to dry on the vine until late fall to achieve full ripeness. They are very sweet wines with fruit flavors, as for example the delayed grape harvest from Alsatia, Pacherenc du Vic-Bilh and Jurançon from France; Picolit from Italy; Priorat rancid sweet, Fondillón, and Malvasia from La Palma and Lanzarote (Spain).
- Noble rot wines or botrytized wines: These wines are obtained by the work of the fungus *Botrytis cinerea* that attacks grapes when they are ripe. Botrytis can cause a destructive grey mould rot or a so-called noble rot when infected grapes are exposed to drier conditions. In the latter instance, the rotting process is slowed down by the effect of dry weather and sunshine and grapes are partially raisined. During this natural process of noble rot, water content decreases and the compounds are concentrated (sugar, acids, aroma compounds, etc.). In some cases inoculation occurs when spores are sprayed over the grapes, while some vineyards depend on natural inoculation from spores present in the environment. Botrytized wines have an exceptional range of aromas, evoking citrus and dried fruit in young wines, orange peel in older wines, and honey or waxy nuances in wines subjected to oxidative ageing (Sarrazin *et al.*, 2007a). Wines produced by this method are the French Sauternes, Barsac, Montbazillac, Côteaux du Layon, Quart de

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Chaume, Loupiac, Ste. Croix du Mont, Bonnezeaux, Vouvray, Selection of Grain Nobles from Alsace; the Hungarian Tokaj; the Italian Amarone; the German Beerenauslese and the Austrian Trockenbeerenauslese and Ausbruch.

- Ice wines: These wines are made from grapes that have been frozen while still on the vine. These grapes are harvested during a hard frost (at ≤ -8 °C) and pressed while frozen at low temperature. In the grapes there are frozen concentrated juices, separated from the water. During pressing, much of the water is retained with the grape skins as ice, while a juice highly concentrated in sugars, acids and aroma compounds is extracted (Nurgel *et al*., 2004). Eisweins or ice wines are produced in Canada, Austria and Germany where the conditions necessary for their production are achieved “naturally”. In addition, ice wines are also produced in other regions to a limited extent (such as the United States and New Zealand), but standards do not exist to ensure that they are produced without the aid of cryogenic processing (Cliff *et al*., 2002).

b) Outside the vine: Wine from raisined grapes shall be the product which is produced without enrichment from grapes left in the sun or shade for partial dehydration. These wines have a total alcoholic strength of at least 16 % vol. and an actual alcoholic strength of at least 9 % vol.

- Raisin under the sun: Málaga (from Spain), Mantonico di Bianco and Greco di Bianco (from Italy).
- Raisin under cover (**Figure 1**): Vin Santo Toscano, Trentino or from the Veneto, Recioto di Soave, di Gambellara or della Valpolicella, Torcolato and Cinque Terre Sciacchetrà

(from Italy); straw wines (Vins de Paille of Jura from France and Strohwein of Austria), and Ribeiro Toasted from Spain.

2. Influence of grape sugar concentration processes on volatiles in sweet wines

2.1. Fortified or liqueur wines

Port wine is the most famous liqueur or fortified wine of Portugal. In this case, a wine spirit of 76 to 78 % volume (known locally as 'aguardente') is used for the fortification of partially fermented grape juice. In terms of aroma, Port wine is a very complex beverage (Rogerson and De Freitas, 2002), with diverse contributions originating from the grape (primary, varietal aroma), yeast metabolites (secondary aroma), wood maturation/ageing (tertiary aroma) and a contribution from the fortification spirit (distillation aroma). The aromatic profile of five 1999 varietal Douro table wines, one aguardente, five model Ports (aguardente fortified table wines) and 15 Port wines from the 1999 vintage and aged for 7 months prior to analysis were analysed by Rogerson and De Freitas (2002). Although aguardente constitutes around one fifth of the total volume of Port, it was found to be the major contributor of numerous volatiles. Thus, a large increase in the levels of ethyl hexanoate, ethyl octanoate, ethyl decanoate (fruity, tropical aromas), ethyl hydrocinnamate (fruity, balsamic) and eugenol (spicy, clove), was observed at concentration levels above sensory thresholds, with odour activity value (OAV) > 1. By contrast, the fermented fraction (about 80 % of Port wine), contributed the majority of isoamyl acetate (fruity, banana) and 2-phenylethanol (floral). Therefore, aguardente is an exceptionally fortification agent that enhances the volatile content and adds fruity, balsamic and spicy aroma complexity to young Port wines.

A study of the phenolic and volatile composition of several Muscat lefko wines (dry, fortified and natural sweet wines as well as aged and non-aged mistelles) produced by the same winery on the island of Samos was conducted by Karagiannis *et al.* (2000). Muscat lefko is a famous white grape cultivar highly esteemed in Greece for its potential to produce high quality sweet and dry wines. Many differences in the fermentation aroma among the studied wines were observed. It was found that the dry Muscat wines contained higher quantities of terpenes and fermentation aroma compounds than the sweet wines. Dry Muscat wines showed the highest content in C6, C8, and C10 fatty acids, their ethyl esters, and acetates of higher alcohols compared to the sweet wines. The aged mistelle wines contained markedly fewer free and bound terpenes and fermentation aroma components compared to the other sweet wines. The naturally sweet wine contained relatively increased amounts of 2,3-butanediol, and glycosidically linked terpenes. The fortified sweet wines were unexceptional, exhibiting characteristics between the dry and the sweet wines in terms of the volatile compound content. These differences could be accounted for by the different vinification and conservation treatments.

Special sweet wines are produced in several Spanish and Italian regions by addition of grape syrup, which is obtained by boiling the grape must to give a dark and highly caramelised liquid. In general, the addition of grape syrup to sweet wines has a direct impact on their chromatic and aromatic characteristics. Ortega-Heras and González-Sanjosé (2009) evaluated the influence of the addition of grape syrup made from *Vitis vinifera* grapes cv. Airen on the aroma of white sweet wines (Muscat and Gewürztraminer, 85:15, w/w). While control sweet wine (a base wine fortified with a sugar solution of glucose and fructose) can be described as intense floral with fruity notes, sweet wines obtained by addition of grape syrup showed higher nuts, caramel, cooked and burnt notes. Thus, authors observed that, in general, the addition of grape syrups increase the levels of furfural related compounds but decrease the concentration of terpenes, ethyl esters, organic acids and acetates of alcohols in the sweet wine compared to the control one. These results seem to indicate that some aroma binding process occurred when grape syrup was added to the wines and this binding capacity can be attributed to the brown pigments formed during the heating treatment and present in the grape syrup. The results obtained also indicated that the intensity of the binding process was variable depending on the kind of the brown pigments present in the syrups.

2.2. Botrytized wines

Botrytized sweet wines (BW) are produced from overripe grapes affected by the *Botrytis cinerea* fungus under specific climatic conditions, alternating humid and sunny periods. Due to the unusual composition of the grapes, these specialty wines are characterized by an exceptional range of aromas, evoking not only citrus aromas, like orange peel or grapefruit, but also sweet nuances, like honey, caramel and crystallised fruit, together with walnut or spicy-curry overtones. The specific aroma of Sauternes wines, a traditional BW from France, is due to a combination of various key odorants including lactones (such as γ- and δ-lactones, γ-nonalactone, γ-decalactone, and δ-decalactone), furanones (such as 4,5-dimethyl-3-hydroxy-2(5H)-furarone, 3(2H)-furanones, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, 2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone and 2-methyl-4-hydroxy-3(2H)-furanone), ethyl 9-hydroxynonanoate,

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methional, phenylacetaldehyde, 3-mercaptohexanol, 4-methyl-4-mercaptopentanone and volatile thiols (Tominaga *et al*., 2000; Genovese *et al*., 2002; Sarrazin *et al*., 2007a; Campo *et al*., 2008; Thibon *et al*., 2009).

Recently, several works about the odorous impact of volatile thiols on botrytized sweet wines were published. Thus, Tominaga *et al*. (2000) evidenced surprisingly high concentrations of 3-sulfanylhexan-1-ol (3SH) in botrytized wines. Bailly *et al*. (2006) also demonstrated the importance of polyfunctional thiols on the aroma of Sauternes wines. These wines present a very strong "bacon-petroleum" odor that authors related with a synergetic effect of 3-methyl-3-sulfanylbutanal and 2-methylfuran-3-thiol. More recently, 3-sulfanylpentan-1-ol (3SP) and 3-sulfanylheptan-1-ol (3SHp), 2-methyl-3-sulfanylbutan-1-ol (2M3SB), and 2-methyl-3-sulfanylpentan-1-ol (2M3SP) were identified in Sauternes wines (Sarrazin *et al*., 2007b). The first two have citrus aroma whereas the other two have a raw onion odour. These volatile compounds are almost totally absent from must, mainly being released from the corresponding non-volatile S-cysteine conjugate precursors by cleavage of S-C bonds by *Saccharomyces cerevisiae* during alcoholic fermentation (Thibon *et al*., 2009). In addition, it was observed that their concentrations were drastically higher when *Botrytis cinerea* had developed on the grapes (Sarrazin *et al*., 2007b; Thibon *et al*., 2011). This positive effect, in fact, results from a strong enrichment of cysteine S-conjugate precursors in botrytized berries. For instance, levels of S-3-(hexan-1-ol)cysteine (P-3SH), the cysteinylated precursor of the most abundant volatile thiol in wine (3SH), were considerably amplified when *B. cinerea* had developed on the grapes in both on- and off-vine experiments. P-3SH levels 50-fold higher in botrytized than healthy must was found by Thibon *et al*. (2008 and 2009), suggesting the existence of a correlation between the P-

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3SH concentrations in must and 3SH levels in botrytized wines. Determination of P-3SH distribution demonstrated that *B. cinerea* was not directly responsible for precursor formation but probably stimulated the grape metabolic pathway involved in this formation (**Figure 2**). Increments in the concentrations of others cysteine S-conjugate precursors such as S-3-(pentan-1-ol)-l-cysteine (P-3SP), S-3-(heptan-1-ol)-l-cysteine (P-3SHp), and S-3-(2-methylbutan-1-ol)-l-cysteine (P-2M3SB) when *B. cinerea* had developed on the grapes were also identified (Thibon *et al*., 2010).

Moreover, it was established that the development of *B. cinerea* on grapes led also to increased concentrations of other odour-active compounds such as furanones and phenylacetaldehyde, already present in wines made from healthy grapes (Sarrazin *et al*., 2007a).

2.3. Ice wines

As stated previously, ice wines are produced using grapes frozen on the vine that are harvested and pressed while still frozen. During this process sugar, aroma and color are concentrated. The soluble solids in the juice obtained after pressing must have 35-45 °Brix.

Cliff *et al*. (2002) investigated the composition and sensory properties of 22 Canadian and 3 German ice wines. The authors identified some chemical and sensory differences between ice wines from Canada and Germany, and also between Ontario and British Columbia samples. In general, aroma and flavor attributes for the British Columbia and Ontario ice wines were similar, with only small differences in peach/apricot, tropical fruit/pineapple, and raisin/dried fruit attributes. However, German wines were characterized by a nutty/oily character and a lack of fruit or late harvest character (dried/cooked flavor, raisin/dried fruit, and honey/caramel

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attributes). A more representative study of the sensory and chemical characteristics of the Canadian ice wines was done by Nurgel and coworkers (2004). In their work, authors evaluated 52 Canadian ice wines (41 from Ontario and 11 from British Columbia) representative of a range of varieties and vintages obtained from different wineries. Ice wines from British Columbia and Ontario were significantly different for a range of chemical and sensory attributes. British Columbia ice wines had higher titratable acidity, acetic acid and glucose, and lower colour and ethyl acetate content compared with those from Ontario. Apricot, raisin, honey and oak aromas were more pronounced in Ontario ice wines, while British Columbia ice wines had higher intensities of pineapple and oxidized aromas. These results are in agreement with those obtained for Cliff *et al*. (2002) with the exception of the pineapple attribute which was rated more intensely in Ontario ice wines.

Later, Setkova *et al*. (2007) characterized and classified a large set of ice wines from Canada and Czech Republic, according to their origin, grape variety and oak or stainless steel fermentation/ageing conditions. The levels of furfural in ice wines from Czech Republic were significantly lower, as compared to the Canadian samples and therefore, furfural could be used as one of the indicator aroma components to distinguish between wines from different continents. Differences were also observed in the levels of γ-nonalactone. Levels of this compound in Czech and Ontario samples were similar to those observed for furfural while it was not detected in any of the British Columbia wine samples. In addition, a relationship between the presence of α-terpineol and the grape variety was detected. Thus, higher levels of α-terpineol were observed in the ice wines produced from Gewürztraminer, Pinot Gris, Riesling, Vidal and Ehrenfelser varieties than those from Cabernet Franc, Cabernet Sauvignon, Pinot Blanc and Chardonnay.

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Statistical evaluation of the data allowed identifying groups of aroma compounds that could be used to differentiate ice wines originated in different countries, but also between those wines from Ontario and British Columbia. In addition, differentiation between ice wines and late harvest wines of the same winery, grape variety and vintage year could be possible on basis of aroma compounds (especially phenylethyl acetate, pentadecyl 2- furancaboxylic acid, ethyl 9-decenoate and 2-propen-1-ol).

Ice wines are characterized by high concentrations of volatile acids, mainly acetic acid, which often exceeds legal limits (1.3 g/L). Wine yeasts produce acetic acid as a by-product of the hyperosmotic stress response caused by high sugar concentrations in grape must. However, it is important to keep in mind that the degree of acetic acid formation varies greatly among wine yeast strains. Because of this, the choice of yeast strain might, therefore, determine if a wine will be accepted or rejected because of legal requirements. In this sense, Erasmus et al. (2004) evaluated seven commercially available wine yeast strains (ST, N96, Vin13, Vin7, EC1118, 71B, V1116) for ice wine production. The two *Saccharomyces bayanus* strains (N96 and EC1118) were associated with the production of high-quality ice wines characterized by lower levels of perceived sulfur-like aroma and faster fermentation rates. On the contrary, ice wines produced with the strains ST and V1116 were characterized by higher perceived sulfur-like aroma. The strains Vin7 and 71B produced the highest concentrations of acetic acid and glycerol.

2.4. Late harvest and sun drying

An increment in the sugar content of grapes can be also achieved by dehydratation of grapes by either over-ripening of the grapes on the vine (late harvest) or off-vine sun drying once the

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grapes have been harvested in their optimum ripening point. In the latter case, once grapes are harvested, they are transferred to plastic mesh or esparto mats where they are allowed to dry in the sun for 5-10 days depending on the climatic conditions. In order to avoid the adverse effects of high air moisture, grape bunches are covered at night (Franco *et al*., 2004; López de Lerma and Peinado, 2011). Pressing these dried grapes gives a highly sweet must (containing > 300 g/L of sugars) that is dark, viscous and possesses a very typical aroma.

Dehydration of grapes accomplished by sun exposure has always been seen as a process of concentration of simple sugars without any regard for other quality characteristics; in particular colour and aroma, but the technology or practice of dehydrating grapes can play an important role in modulating the production and release of compounds responsible of sensorial quality. Thus, late harvest and drying of grapes determine changes in chemical and physical composition of must that influence the fermentation and the sensorial characteristics of wine (Genovese *et al*., 2007a).

The effect of off-vine sun drying on the volatile composition of must from Pedro Ximenez grape variety was evaluated by Franco *et al*. (2004). Authors compared must of ripe grapes with must obtained from ripe grapes dried off-vine by direct sun exposure. In general, the concentration of the volatile compounds analyzed was higher in must from dried grapes than must from ripe grapes with the exception of farnesol, C6 alcohols and aldehydes whose concentrations decreased during the drying process. This effect can only be explained partially by the loss of water from the grapes as showed by the variance analysis of concentration/ºBrix ratios for those volatile compounds not depending of the sampling site. Only butan-1-ol and isoamyl alcohols showed no differences, while (E)-hex-3-en-1-ol, (Z)-hex-3-en-1-ol, (E)-hex-2-

en-1-ol, (E)-hex-2-enal, hexanoic acid, isobutanol, benzyl alcohol, 2-phenylethanol, γ-butyrolactone, γ-hexalactone, and 5-methylfurfural showed significant differences between the two must types, which could be ascribed to the drying process. During ripening, grapes can change their metabolism from aerobic to anaerobic, which is reflected in the production of ethanol, CO_2, and fermentation byproducts (Franco *et al*., 2004; Costantini *et al*., 2006). Although these byproducts are the same ones as those obtained in the alcoholic fermentation carried out by yeast, their concentrations may change (Franco *et al*., 2004). Thus, the high concentrations of benzyl alcohol, 2-phenylethanol, 5-methylfurfural, γ-butyrolactone and γ-hexalactone were attributed to the anaerobic metabolism of sugars and the presence of ethanol. The undetectable contents of C6 alcohols and aldehydes in musts from dried grapes can be explained by the low lipoxygenase (LOX) activity as a consequence of the low water activity and the low oxygen diffusion of the atmosphere in the must. In addition, by grouping volatile compounds in aromatic series, it was observed an increment in the fruity, solvent, sweet, and roasted series and a decline of the herbaceous series as a consequence of the drying process (**Figure 3**).

Genovese *et al*. (2007a) evaluated by sensory descriptive analysis the odour profile of sweet wine obtained from Fiano grape, a non-aromatic cultivar widely grown in southern Italy. For the production of this sweet wine, grapes were harvested in an advanced state of maturation (26 ºBrix) with a percentage of *Botrytis cinerea* at 20 % and then were dried on racks until a sugar concentration of 32 ºBrix. The main influences of grape overripeness and drying on wines was the enhancement of dried fruits (apricot, plum, and figs), honey, citrus jam and coconut aromas. Moreover, a strong effect on free and bound volatile composition was detected. Authors observed higher levels of 35 volatile compounds in sweet Fiano wine than in base Fiano wine (**Figure 4**). These components were mostly terpenes, C-13 norisoprenoids, lactones, aldehydes and ketones. For instance, an important increment in the terpinen-4-ol and linalool content was observed with increases of about 23.7 and 10.2 times, respectively. Among C13-norisoprenoids, the higher level of β-damascenone detected in sweet wine was related not only to major concentration in overripe and dried grape but also to higher contents of its glycosidic precursors. In addition, higher levels of lactones, particularly γ-valerolactone and whisky lactones were observed in sweet Fiano wine than base Fiano wine. The high level of whisky lactones detected in sweet Fiano wine, together with other ‘‘wood compounds’’ such as eugenol, syringol and isoeugenol was linked to the high alcoholic level of the sweet wine that facilitates the extraction of these compounds from the wood. Among aldehydes, furfural and benzaldehyde showed a high increase in sweet Fiano wine of about 340.5 and 20.6 times, respectively. On the contrary, alcohols, ethyl esters, acetates and fatty acids showed lower concentration levels in sweet wine than in base Fiano wines. This fact could be correlated with the high free amino acid level, particularly glutamic acids, observed in the must from overripe grapes. On the basis of experimental data obtained, authors established a role of primary importance to the skin of grape vine berries as a source of varietal aromatic compounds when the grape is submitted to overripening and the drying process. Therefore, grape overripeness and the drying process allow concentration of varietal aromatic compounds and an easier transfer of them from skins to must during vinification.

In 2008, twenty commercial samples of Andalusian sweet wines (10 from Pedro Ximenez grapes and 10 from Muscat) were studied in order to determine the characterization of the volatile composition of these wines (Márquez *et al*., 2008). Thirty one volatile compounds were identified in the samples studied but the major volatile compounds quantified were ethyl acetate, isoamyl alcohols, ethyl lactate, acetic acid, 2-furaldehyde, linalool, diethyl succinate, α-terpineol and 2-phenylethanol. These results are in agreement with those obtained by other authors who observed higher levels of acetoin, ethyl acetate, isoamyl alcohols, γ-butyrolactone, isobutanol, 1,1-diethoxyethane and 2-phenylethanol in must from sun-dried grapes of Pedro Ximenez variety (Franco *et al*., 2004). In the study of Márquez *et al*. (2008), Muscat wines showed a high content of linalool, α-terpineol and limonene. Authors explained these high concentrations by the anaerobic metabolism of the grapes during drying by exposure to the sun. On the contrary, levels of 2-furaldehyde and 5-methyl-2-furaldehyde were lower than those observed in Pedro Ximenez wines. The C_{13} norisoprenoid, 1,1,6-trimethyl-1,2 dihydro naphthalene (TDN), was identified in both Muscat and Pedro Ximenez wines; however, Muscat wines showed a higher content. TDN in concentrations above 20 μg/L causes an unpleasant kerosene note but several authors have pointed out a positive influence in the wine aroma when TDN is present at concentrations lower than its threshold limit. The occurrence of this compound in wines is principally related to the maturation process by carotenoid-degradation (Winterhalter and Rouseff, 2002). Nevertheless, sunlight, storage time and temperature have also an important effect on its level. From the statistical analysis of the results, authors established that α-terpineol, 5-methyl-2-furaldehyde, isoamyl alcohols, ethyl decanoate, hexanal and p-cymene could be used as descriptors to differentiate Andalusian sweet wine samples according to grape variety (Márquez *et al*., 2008).

Changes in odorant compounds of musts from cv. Pedro Ximenez grapes sun-dried for 0, 2, 4, 6, 8 days, were recently studied by Ruiz and co-workers (2010) with a view to observe the changes of the most active odorant compounds during the drying process. Caramelized was the greatest aroma contributor in all musts followed by the odorant terms tree fruit, spicy, fresh and floral, that increasing their OAVs during sun-drying. Finally, lactic (3-methylbutanoic acid) and tropical fruit (γ-butyrolactone), and pungent (ethyl acetate) odors were present in the musts from grapes dried for 2 and 6 days, respectively, with OAVs slightly exceeding unity.

The study by Piombino *et al*. (2010) evaluated the impact of different sun exposures of post-harvested grapes during drying on free and bound volatiles of Malvasia delle Lipari Passito wine. Sensory analysis showed compositional differences of the wine volatiles that are reflected on their odour character. For instance, the wine obtained from the off-vine bunches dried in shaded conditions was richest in free volatiles (67 %) and exhibited the higher level of total bound terpenoids (20 %).

Moreover, a correct selection of the yeast can also influence the organoleptic characteristics of wines obtained from dried grapes. In this sense, López de Lerma and Peinado (2011) evaluated for first time two osmotolerant *Saccharomyces cerevisiae* strains (X4 strain which is characterized by its high ethanol production and resistance to high sugar concentrations and X5 strain which produces more ethanol than the X4 strain and has a similar resistance to high sugar concentration) to ferment must from Tempranillo dried grapes and their effects on the volatile composition and sensory quality of the resulting wines. Results were compared with those obtained for must of Tempranillo dried grapes fortified with ethanol up to 12 % (v/v) to avoid fermentation (traditional way) and those obtained from spontaneous fermentation of the must with the native yeast. Authors observed that fermentation of must give rise to a series of changes in the composition of the wines obtained in relation with the ones elaborated traditionally

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(control wine). In general, an increment in the aroma compound contents was observed after fermentation, highlighting those aroma compounds related with fruity, sweet and fatty aromas, emphasizing the fruity series in the samples fermented with the X4 and X5 strains. The sensorial analysis of the wine samples by a tasting panel put in evidence that the musts fermented with the osmoethanol tolerant yeasts were better valued than the rest of the wine samples (**Figure 5**). The must fermented with the X4 strain obtained the maximum score in terms of aroma and flavour. So, the use of these osmoethanol tolerant *S. cerevisiae* strains could be a suitable alternative to produce high quality sweet wines from must of dried grapes with high sugar concentration. The wines obtained by this way were chemically and organoleptically more complex than those elaborated traditionally. More recently, the same authors (López de Lerma et al., 2012) evaluated other two osmo-ethanol-tolerant *S. cerevisiae* strains (CECT 13014 and CECT 13015) to ferment must from Tempranillo dried grapes. A principal component analysis and a cluster analysis revealed that the wines obtained by fermentation with selected yeasts were very similar and differed from those fermented in the presence of the autochthonous flora or in the traditional manner. Sensory evaluation of this wines by a tasting panel led to the wines obtained by fermentation with selected yeasts being again the best scored.

2.5. Other dehydration methods

Alternatively to sun-drying, dehydration of grapes can be achieved by leaving grape clusters under the roof or in other ventilated environments with no or imprecise thermohygrometric control or with a combination of natural and artificial ventilation systems (Bellincontro *et al.*, 2004). As a general rule, the use of hot air driers avoid some typical problems of the sun-drying

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such as growth of fungi toxin producers, when the hygrometric degree is not quite low, or contamination by dust and insects (Ruiz *et al*., 2010).

Dehydration or water loss is a stressing event that induces significant modifications in the metabolism of fruits and vegetables. Several studies about the effect of the rate of water loss and their effects on the cell metabolism of postharvest grapes have been reported in the last years. For instance, the effect of different prostharvest dehydration rates on volatile compounds of Malvasia, Trebbiano and Sangiovese grapes for wine production was evaluated by Bellincontro *et al*. (2004). For this, a set of samples was submitted to fast dehydration in a dehydration tunnel (air speed of 1–1.5 m/s, 42 % of relative humidity and temperature of 21 ºC) while another set of samples used as control was kept outside the tunnel (65 % of relative humidity and temperature about 20 ºC without ventilation). Volatile compounds analysis revealed changes in the volatile profile as a result of the dehydration rates. Malvasia and Sangiovese grapes benefited from fast dehydration, not only in the increase in sugar content but also in the increase in ethanol, esters and higher alcohols. Thus, the contents of C6 compounds (mainly hexanal, hexan-1-ol, (E)-hex-2-anal and (E)-hex-2-anol), esters (mainly acetate esters), methyl butanal and methyl butanol after 18 days of treatment were higher in tunnel-treated Malvasia samples than in control samples (Bellincontro *et al*., 2004). This increment in the C6 volatile compounds was then linked to the accumulation of absciscic acid that promotes the activation of LOX, an important oxidative enzyme involved in lipid oxidation (Costantini *et al*., 2006). Therefore, LOX activity is dependent on the temperature reached during the drying process and the level of dehydration. Thus, it was observed a low LOX activity in Pedro Ximenez berries during off-vine sun dried where high temperatures were achieved (Franco *et al*., 2004) and in Sagrantino and Pecorino grapes at dehydration levels higher than 35 % of weight loss (Costantini *et al*., 2006). In addition, Belleincontro *et al*. (2004) observed that Malvasia berries after tunnel treatment showed double the content of ethyl laurate (flower and fruit note) and four times the content of isovaleraldehyde (peach note) in control samples. On the other hand, Sangiovese showed double the content of higher alcohols (isoamylic, 2-phenylethanol and methyl butanol) in tunnel-treated berries. This fact can be related with the influence of fast dehydration in the amino acids catabolism. On the contrary, Trebbiano samples were not affected by the different rates of dehydration.

Changes in odorant compounds of musts from cv. *Pedro Ximenez* grapes dried in a chamber after 5 days at controlled conditions (40 ºC and 30 % of relative humidity) were also studied by Ruiz *et al*. (2010). Acetoin was the major odorant with a concentration about 73 mg/L, followed by ethyl acetate, phenethyl alcohol, isobutanol and isoamyl alcohols, these exceeding 1 mg/L. It is important to remark that hexanal and E-2-hexenol were not detected. This fact can be related to oscillations in the LOX activity during the drying of grapes in chamber as proposed by other authors (Costantini *et al*., 2006). Musts from chamber-dried grapes exhibited the same aroma terms as those from Pedro Ximenez off-vine sun-dried grapes, although the odour activity values (OAVs) for caramelized, floral, lactic, and pungent were higher. In addition, chemical (isoamyl alcohols) odorant term, with an average OAV of 3, was only observed in chamber-dried grapes.

Moreno and co-workers (2008) also studied the effect of postharvest dehydration using a tunnel drying (air speed of 1.0–1.8 m/s, 38 % relative humidity and 22 ºC) on the volatile composition of Pinot Noir grapes (*Vitis vinifera* L.) and wine. Volatile compounds in wines made from dehydrated grapes contained more terpenes (guaiacol, citronellol, geraniol and eugenol) and norisoprenoids (β-ionone, β-damascenone) when compared to wine made from the original fruit. Therefore, it is expected that these compounds would contribute to an increase in floral and fruity characters.

The effect of oven-drying at 60 ºC on the volatile composition of the skins from Carménère and Cabernet Sauvignon grape varieties was evaluated by de De Torres and co-workers (2010). Ninety-seven volatile compounds were identified in both varieties including terpenes, sesquiterpenes, norisoprenoids, and C6 derivatives. The similarity in the volatile composition between both grape varieties was noteworthy, although the amount found for the different compounds was different. In general, the levels of terpenes, sesquiterpenes, acids, alcohols, esters and benzene derivatives in the oven-dried skins were lower than those observed in fresh skins. Of all the compound families, the C6 alcohols were most sensitive to dehydration through oven-drying, since their amount dropped by around 80 % in both varieties, probably due to C6 alcohols were evaporate together with the water in the oven-drying process. On the contrary, an increase in the total amount of norisoprenoids and derivative compounds of furan, pyran and lactones from the browning reactions was observed, caused by the increase in the amount of some of the compounds, like β-damascenone and furfural, in the dehydrated skins.

The impact of microwave vacuum dehydration on the aroma and flavor attributes of the sweet dessert wines was analyzed by Clary and coworkers (2006). Wine made from the dehydrated grapes exhibited lower fresh fruit aroma, higher fusel oils and oxidation aroma notes than those obtained by the other two methods of juice concentration (late-harvest freeze concentration and frozen grapes by refrigeration at -37 ºC) assayed. Moreover, it was associated with lower citrus/grapefruit, acidity and length of aftertaste than the other two wines (**Figure 6**). On the

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contrary, late-harvest wine had the highest fresh fruit character. However, the dried fruit aroma note was not different between the wine made from dehydrated grapes and the late-harvest fruit. Therefore, microwave vacuum dehydration could offer an alternative for concentration of grape aroma and flavor without the risk of depending on weather to freeze grapes in the vineyard to produce a late-harvest sweet dessert wine.

3. Changes in sweet wines aroma during ageing

During ageing the wine acquires aromatic complexity as a result of important modifications consequence of different phenomena, such as esterification/hydrolysis reactions, redox reactions, spontaneous clarification, CO_2 elimination, slow and continuous diffusion of oxygen through wood pores and transference of tannins and aromatic substances from wood into the wine. As it can be seen in **Table 2**, the aroma formed during the alcoholic fermentation decrease, but new compounds appear from oak wood and from the evolution of the primary and secondary aromas (Câmara et al., 2006).

3.1. Oxidative ageing

Sweet fortified wines have traditionally been elaborated from must rich in sugars which after fermentation are fortified to an ethanol content of 9 % (v/v), allowing them to stand for several months to facilitate their clarification by decantation (López de Lerma *et al*., 2010). Afterwards, the resulting wines are subjected to oxidative aging in a “criaderas” and “solera” system over long periods exceeding 10 years in some cases. In essential, this method involves mixing less aged wines with more aged ones several times per year. This method assures homogenize wine composition at each aging stage irrespective of the particular composition of each raisin vintage (Moreno *et al*., 2005; Chaves *et al*., 2007). Traditionally, sweet fortified wines are aged in barrels, often partly empty, in cellars with variable temperatures. The casks used are of very old wood to reduce the contribution of tannins and aromas from the wood; although a remarkable transference of lactones to the wine takes place (Chaves *et al*., 2007; López de Lerma *et al*., 2010). After aging, and prior to bottling, wine is again fortified to 15 % ethanol (López de Lerma *et al*., 2010). Due to their alcohol content, yeast is not involved in the aging process of sweet fortified wines.

Oxygen is assumed to play a major role in the many chemical reactions occurring during aging. Oxidation results in organoleptic modifications, likewise changing their aroma fraction to an extent that increases with aging. On the other hand, oxidation phenomena are generally considered to be favourable, or even indispensable, for the proper development of the aroma of sweet fortified wines (Cutzach *et al*., 2000; Câmara *et al*., 2006).

Chaves and coworkers (2007) observed the changes in the odorant compounds during the industrial oxidative aging of Pedro Ximenez sweet wines. For this purpose, Pedro Ximenez sweet wines, obtained following the typical “criaderas” and “solera” method for sherry wines, were subjected to oxidative aging for 0, 1.3, 4.2, 7.0, or 11.5 years. Fifteen active odorant compounds with OAV > 1 were found in the aged sweet wines that can be grouped into 6 aroma series. The fruity serie (acetaldehyde, ethyl acetate, 1,1-diethoxyethane, ethyl butanoate, isoamyl acetate, ethyl hexanoate, ethyl octanoate, decanal, linalool, and diethyl succinate) was the most important in quantitative terms followed by the balsamic (ethyl acetate and 1,1-diethoxyethane), fatty (2,3-butanedione, 2,3-pentanedione, acetoin, ethyl octanoate, decanal, and ethyl decanoate)

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and floral (linalool and diethyl succinate) series while the chemical (ethyl acetate and ethyl decanoate) and spicy (eugenol) series were the least contributors to the aroma profile of these wines. Thus, the aging process resulted in a gradual enrichment in buttery, raisin, and muscat aroma notes. However, changes in active odorants were not linearly related to aging time, being especially marked during the first 1.3 years and then less substantial up to the 7 years. The oldest wines showed sensorial properties markedly departing from all others. Authors also proposed the use of 2,3-butanedione, linalool, and decanal as reliable fingerprints of the older wines' quality for wines aged over 1.3 years.

The effect of a thermal treatment at 65 ºC for accelerating oxidative aging in Pedro Ximenez wines, in the presence or absence of oak chips, was studied in terms of volatile Maillard compounds by López-de-Lerma *et al*. (2010). Volatile Maillard products increased significantly throughout the thermal treatment in the absence of oak chips, especially furfurals (furfural, 5-methylfurfural, 5-hydroxymethylfurfural and 5-ethoxymethylfurfural), although furanones (2-methyltetrahydrofuran-3-one, 2,5-dimethyl-4-hydroxy-3(2H)-furanone and dihydro-2-methyl-3(2H)-furanone), dihydromaltol and corylon also increased. It should be noted that the content of 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-2-one increased significantly over the first 10 days and then decreased slightly by the end of the treatment. Therefore, during the thermal treatment, varietal notes (raisin, caramel and vegetable) gradually disappeared in these wines while roasted, coffee and burnt woodnotes were gradually developed. The presence of oak chips no promoted significant differences in the aromatic profiles of these wines compared with those treated for the same period of thermal treatment without chips. However, increments in the contents of 5-hydroxymethylfurfural and 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-2-one after 30 days and in dihydromaltol and furanones within the first 10 days were observed. The wines obtained after 10 days of thermal treatment were judged to be the best in terms of sensory properties due to their optimum balance between varietal and aging aromas.

According to the work of Campo *et al*. (2008), Pedro Ximenez wines were richest in 3-methylbutanal, furfural, β-damascenone, ethyl cyclohexanoate, and sotolon. These wines also had important levels of phenylacetaldehyde, methional, β-damascenone and the low levels of isobutanol. Pedro Ximenez wines showed relatively large concentrations of ethyl 2-, 3-, and 4-methylpentanonates and ethyl cyclohexanoate which are especially important in products with high alcohol content and submitted to long aging periods from different wine families (Campo *et al*., 2007 and 2008).

The oxidation of some compounds was also reported to be of fundamental importance in Muscat-type wines aroma (Arlorio *et al*., 2005). The evolution of the volatile aroma during the ageing of italian Muscat-based wines (Asti Spumante and Moscato d'Asti wines) was studied by Bordiga *et al*. (2009). The sweet floral aroma from Muscat grapes is a required sensorial quality of these wines. In one-year aged wine samples, levels of linalool, nerol and geraniol decreased respect to the young Muscat wine to become less important regarding the aroma. Therefore, α-terpineol, hotrienol, nerol oxide, furanic linalool oxides A/B and rose oxide concentration significantly increased, confirming an oxidative evolution of the aroma. Authors also identified some off-flavors, responsible of wine imperfections described as cork tones, plastic and mushroom. The presence of 2,4,6-tri-chloroanisole and 2,4,6-tribromoanisole have been highlighted in some samples.

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Already much earlier, Schneider and coworkers (1998) identified the volatile compounds involved in the aroma of the oxidized red Vins Doux Naturels from Roussillon, a sweet fortified wine from Grenache Noir. Chromatographic analyses revealed the presence of three ethyl esters (4-carbethoxy-γ-butyrolactone, ethyl 2-hydroxyglutarate, and ethyl pyroglutamate) in all the wines analyzed which were aged under different oxidative conditions. Levels of these compounds were higher than those found in young wines, suggesting that chemical esterification, lactonization, and lactamization or other unknown processes occurred and increased their levels during the oxidative aging procedure. Furthermore, the content of polar ethyl esters and related lactones increased during aging especially in barrel-aged wines. On the contrary, levels of acetals, furfural and 5-(hydroxymethyl)furfural although increased too after oxidative aging, were most important in demijohn-aged wines. Later, Cutzach *et al*. (2000) observed that wooden containers and variations in winery's temperature facilitate the formation of volatile compounds. Thus, furfural, 5-ethoxymethylfurfural, isomers of methyl-γ-octalactone and sotolon always reached concentrations above their perception thresholds in wood-aged wines, especially when a new oak was used. Among the many identifiable volatile phenols, only the vanillin content increased with aging, particularly if the container was made of wood and there was a high degree of oxidation.

The influence of the age in the volatile composition of Madeira wines made with Boal, Malvasia, Sercial and Verdelho varieties and aged in oak barrels during 1, 11 and 25 years old was studied by Câmara *et al*. (2006). The results showed the evolution of some aroma compounds during oxidative ageing. Thus, important constituents of the aromatic profile such as methanol, acethaldehyde and ethyl acetate increased with ageing. Furthermore, it was observed a great increase of ethyl esters of diprotic acids (such as monoethyl and diethyl succinate and ethyl lactate), of short-chain fatty acids (such as butanoic and isobutanoic) and also of γ-lactones (like γ-hexalactone and γ-octalactone). On the contrary, the concentration of fatty acids ethyl esters (C6-C16), acetates and medium- and long-chain fatty acids decreased significantly contributing to the loss of freshness and fruitiness (**Figure 7**). Authors also observed a strong correlation between sotolon, 2-furfural, 5-methyl-2-furfural, 5-hydroxymethyl-2-furfural, 5-ethoxymethyl-2-furfural, cis-dioxane and cis-dioxolane with wine ageing, which makes these compounds wine age markers. Similar behaviour was observed for Porto aged wines (Silva Ferreira et al., 2003a and 2003b). Among the molecules studied, sotolon [3-hydroxy-4,5-dimethyl-2(5H)-furanone] was one of the few molecules present in concentrations above the perception threshold in Madeira wines. 5-Eihoxymethyl-2-furfural formed from 5-hydroxymethyl-2-furfural and 2-furfural, derived from sugars, were also involved in the aroma of sweet fortified white wines aged in oxidative conditions.

A later research indicated that the combined use of gas chromatography/mass spectrometry (GC/MS) results, together with appropriate advanced multivariate statistical techniques, especially through principal component analysis (PCA), allow identify different types of Madeira wines in terms of their aromatic characteristics and ageing time (Pereira *et al*., 2010). It was clearly visible that PC2 is the component correlated with wine ageing, whereas PC1 is further involved in the differentiation of the wines according to their sweet/dry characteristics. Thus, similarities between Malvasia (sweet) and Boal (medium sweet) wines can be established from the biplot analysis, being both located on the PC1 positive half. In both cases, carbonyl compounds (acetoin, furfural, butyrolactone, furfuryl alcohol, 5-hydroxymethyl-2-

furancarboxaldehyde, diethyl malate, and vanillin) point out the ageing direction. In general, an increment in their contents was observed through the ageing process. Ageing trends are also similar for Sercial (dry) and Verdelho (medium dry) wines, being both located on the PC1 negative half. In these cases, the positive contribution of the higher content of the alcohol compound is remarkable. In addition, diethyl esters (diethyl succinate, diethyl malate and diethyl tartrate) showed more impact in the ageing process of “Sercial” and “Verdelho”, suggesting that esterification reactions were more extended in dry wines.

Changes in the flavor profile of Sauternes wines through maturation in oak barrels were also observed by Bailly and coworkers (2006). Thus, important increments in the concentration of *trans*-non-2-enal, β-methyl-γ-octalactone, linalool, β-damascenone, guaiacol,eugenol and vanillin were observed during maduration. *Trans*-non-2-enal, derive from unsaturated fatty acid oxidation (Collin and Noel, 1994) and it can be considered as an indicator of wine oxidative deterioration as proposed by Escudero *et al*. (2002). This compound is also responsible for the “sawdust” character of wine coming from fresh wood (Chatonnet and Dubourdieu, 1998). Eugenol and β-methyl-γ-octalactone are naturally present in wood but their concentrations increase when wood is heated (Chatonnet *et al*., 1989). Guaiacol and vanillin are formed by lignin degradation (Chatonnet *et al*., 1989). Linalool might derive from the hydrolysis of glycosidic precursors from grapes (Ribereau-Gayon *et al*., 1998) or be formed from other monoterpenes during wine storage (Pedersen *et al*., 2003). β-Damascenone might be formed through oxidative degradation of wood carotenoids (Jarauta *et al*., 2005) or by glycosides hydrolysis and chemical degradation of oxygenated C-13 norisoprenoids in acid medium (Ribereau-Gayon *et al*., 1998). The thiol profile also changed during oak maturation. 3-

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Sulfanylhexan-1-ol might be released from its cysteinylated precursors by chemical hydrolysis. 3-Sulfanylheptanal also appeared to be more relevant after maturation. On the contrary, 2-phenylethanol decreased through oxidation in the casks, as proposed by Jarauta and coworkers (2005).

Oloroso wines from southern Spain are obtained by oxidative ageing, after addition of ethanol up to a content about 18 % v/v, which prevents the growth of veil yeasts on their surface (Botella *et al*., 1990). On the basis of the discriminant analysis done by Zea *et al*. (2001), 1-decanol, propyl butanoate and methyl butanoate were the compounds most clearly distinguishing the aroma fraction of oloroso wines in analytical terms. This is because of 1-decanol and methyl butanoate, which were at higher concentrations in these wines, while propyl butanoate was not detected in them. From a sensorial point of view, and according to OAVs, Oloroso wines exhibited pineapple, balsamic, smoky and ethereal notes, mainly associated with ethyl guaiacol and ethyl acetate concentrations.

3.2. Biological ageing

Biological ageing of wines is carried out by a film of yeasts (flor) growing on the wine surface. The aerobic metabolism of yeasts causes changes in the aroma fraction of the wine which define its sensory properties (Martínez *et al*., 1997; Cortés *et al*., 1998; Moyano *et al*., 2002; Moreno *et al*., 2005).

Fino wines result from biological ageing, carried out by veil yeasts growing on the wine surface when the ethanol content is lower than 15.5 % v/v (Cortes *et al*., 1998). As observed by

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Zea et al. (2001), butanoic acid, farnesol, 3-methylbutanoic acid and γ-decalactone were the greatest contributing compounds to the flavour of Fino wines. In analytical terms, higher concentrations of these compounds distinguish Fino wines from the wines subjected to oxidative ageing. Fino wines are marked by floral and fruity (farnesol, β-citronellol and β-ionone), cheesy and rancid (butanoic acid), and pungent (acetaldehyde) notes. In addition, Z-nerolidol and ethyl isobutanoate could enhance floral and fruity notes, while hexanoic acid could contribute to the cheese and rancid notes.

Acetaldehyde production from ethanol by flor yeasts by means of the enzyme alcohol dehydrogenase in the presence of NAD^+ is typical of biological ageing (Martínez *et al*., 1997; Moreno *et al*., 2005). Acetaldehyde is responsible for the pungent character typical of Fino wine and it directly contributes with ethereal and ripe apple notes to its aroma. According to Zea and coworkers (2001), the acetaldehyde content allowed the differentiation of Fino wines from other types of sherry wines produced by oxidative ageing. Traditionally, the winemaking industry of sherry has used the acetaldehyde content as a marker for the status of biological ageing. However, one must be cautious in adopting this compound as a marker for biological ageing of Fino wines, because its production is influenced by the population and metabolic activity of the flor yeasts used, the temperature, ethanol content and the redox potential, among other factors (Martínez *et al*., 1997).

Moreno and coworkers (2005) proposed the use of sotolon, 1,1-diethoxyethane and *Z*-whisky lactone as analytical markers of the changes in Fino wines during its biological ageing. The concentrations of these three compounds were below their GC detection limits in the samples corresponding to 1 year, increasing linearly then with the ageing time. This suggests that they were synthesized exclusively during the ageing process. 1,1-Diethoxyethane and sotolon in Fino wines originate by chemical pathway from the acetaldehyde produced by the flor yeasts. 1,1-Diethoxyethane is an acetal deriving from acetaldehyde and ethanol and can be estimated as considerable odorant for wines obtained by biological ageing (Moyano et al., 2002). This compound contributes green fruit and liquorice aroma notes (Moyano *et al*., 2002) while sotolon gives nut, curry and candy cotton notes (Cutzach *et al*., 2000). On the other hand, Z-whisky lactone, also known as wood lactone, contributes vanilla notes (Moreno *et al*., 2005).

Also, the yeasts effecting biological ageing are known to consume ethyl acetate, which is used into the metabolism of fatty acids. In contrast, the ethyl acetate content of wines under chemical ageing increases by effect of the oxidation of ethanol (Moreno, 2005). Experiments carried out by Cortes et al. (1998 and 1999) on the biological ageing with pure yeast cultures and absence of wood revealed an increase in eugenol contents with ageing. In addition, no changes in ethyl lactate content were found in Sherry wines during their biological ageing in the presence of selected indigenous yeasts (Cortes et al., 1998).

The contribution of flor yeasts and wood to the aroma profile of Fino wines subjected to biological ageing was studied by Zea et al. (2007). The odour activity values for 72 aroma compounds identified in these wines were classified into eight odorant series in order to describe their aroma profile. Authors observed that the fruity, spicy and fatty series are the ones most strongly contributing to the aroma profile of Fino wines under biological ageing, while the chemical, balsamic, vegetable, empyreumatic and floral series in combination contribute in low proportion. Based on the results of applying a linear regression model to the OAVs for the eight odorant series during the ageing process, the fruity and spicy are those best describing the ageing in these wines. Taking into account that the most of the compounds contributors to the fruity series (mainly ethyl octanoate, sotolon, acetaldehyde, 1,1-diethoxyethane and ethyl acetate) are related whit the flor yeasts activity, the fruity OAVs can be used as an objective indicator of the contribution of these microorganisms to the process. On the other hand, the spicy series (eugenol, sotolon, Z-oak lactone and 4-ethylguaiacol) should represent better the contribution of wood to the biological ageing process.

3.3. Combination of chemical and biological ageing

Amontillado wines are obtained by ageing in a two-step process involving biological ageing under similar conditions to those of Fino wines, followed by an increase in the ethanol content, they are then subjected to oxidative ageing, as in Oloroso wines (Zea *et al*., 1996). Amontillado wines inherit flavour notes from both ageing processes, resulting in the more complex aroma, it being the oldest and most valued of the three types (Zea *et al*., 2001). Amontillado wines can be distinguished from Fino and Oloroso wines on the basis of their contents of 1,1-diethoxyethane, isobutanol, phenethyl alcohol, ethyl butanoate, ethyl benzoate, isobutyl isobutanoate, isoamyl laurate and E-nerolidol. Ethyl butanoate was not detected in amontillado wines and 1,1-diethoxythane was at a lower concentration in this type of wine than in the other two. Consequently, fruity notes are weaker in Amontillado wines. Compounds such as acetaldehyde, ethyl acetate, ethyl lactate, β-citronellol and β-ionone showed intermediate concentrations between Fino and Oloroso wines, revealing the participation of both types of ageing.

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Zea et al. (2008) studied the odorant activity of Amontillado wines of the Montilla-Moriles designation of origin in order to identify the compounds most markedly contributing to the respective aroma profile. A total of 16 odorant active compounds were identified and classified according to their odour descriptors into 4 groups according to their OAVs. Sotolon and eugenol were very powerful odorants, with OAVs higher than 86. A second group was formed by the esters ethyl isobutanoate, ethyl 3-hydroxybutanoate, ethyl octanoate and ethyl hexanoate, as well as acetaldehyde and its derivative 1,1-diethoxyethane (OAVs between 10 and 50). The third group included β-citronellol, Z-oak lactone, ethyl acetate and isoamyl alcohols (OAVs in the range 5-10). The last group included 4-ethylguaiacol, 2-phenylethanol, ethyl lactate and 3-methylbutanoic acid. Authors observed that acetaldehyde, ethyl acetate and eugenol were the compounds most distinguishing the Amontillado wines from the Fino and Oloroso ones. In comparison with the other wines of the Montilla-Moriles designation of origin, Amontillado wines exhibited the highest OAVs for the nutty and spicy series by effect of the increased contribution of sotolon and also the lowest OAVs for the fruity and balsamic series as the result of the decreased contribution of 1,1-diethoxyethane. For all other series (floral, fatty and chemical) Amontillado wines showed similar OAVs that those observed for the others types of wines. Because biological ageing step in Amontillado wines is shorter than their chemical ageing, the results suggested that the former influences the aroma of Amontillado wine to a greater extent than does chemical ageing.

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3.4. Ageing in the bottle

Studies focused on the fate of flavors of sweet wines in the bottle are limited in the literature. In Tokaji Aszú wine, concentrations of vitispirane, trimethyl dihydronaphtalene, 2-phenylethanol and diethyl succinate increased in the course of ageing time, while those of 3-methyl-butyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate and ethyl dodecanoate decreased (Tóth-Markus *et al*., 2002).

In Sauternes wines, most thiols were lost during the first two years in the bottle as it can be seen in **Figure 8** (Bailly *et al.*, 2009). For instance, the factor dilution (FD) value of 3-sulfanylpropyl acetate (roasted/burned flavor) dropped from 27-81 (depending of the vintage considered) to 1. Similarly, 2-sulfanylethyl acetate and 3-methyl-3-sulfanylbutanal were completely degraded (**Figure 8a**). Hydrolysis of sulfanylalcohol acetates was suspected; however, 3-sulfanylpropanol was detected in neither young nor aged wines, and 2-sulfanylethanol was only detected in fresh wines of the vintage 2002. Sulfanylaldehydes also completely disappeared (3-3.5 years after harvest; **panels b and c of Figure 8**). Oxidation is most likely responsible for this disappearance, despite the high sulfite level found in such wines. **Figure 8d** shows that the 3-sulfanylhexan-1-ol concentration also decreased through storage in both vintages, but a concentration 50 times above its threshold value (60 ng/ L, Tominaga *et al*., 1998) was still measured after more than 4 years in the bottle. Tominaga (1998) reported the hydrolysis of 3-sulfanylhexanyl acetate to its corresponding alcohol during bottle aging of dry white wines, but this ester was undetectable in the Sauternes wines analyzed by Bailly *et al*. (2009). The apparent higher stability of 3-sulfanylhexan-1-ol compared to other polyfunctional thiols might be explained by the reduction of 3,3'-disulfanyldihexan-1-ol or 3-propyl-1,2-

oxathiolane, both recently identified in Sauternes wines (Sarrazin *et al*., 2008). On the other hand, most fermentation and oak maturation-related flavors and three newly identified compounds (homofuraneol, theaspirane and γ-decalactone) characterized by sweet-honey-like descriptors proved relatively resistant to aging. In addition, abhexon, never mentioned in sweet wines before, emerged as a very interesting compound to investigate in aged Sauternes wines (Bailly *et al*., 2009).

4. Sweet wines market trends and scientific challenges

4.1. Reasons for growing sells

There are a growing number of sweet wine drinkers. There are four main reasons:

1) Distribution: Large wine producers are able to get sweet wines to large retailers at competitive prices, where many people are buying their "value" wines.

2) No stigmas since it is just "sweet": In general, they are a pleasant introduction to the varietal wines for inveterate explorers drinking globally.

3) Rising consumption and new consumers: With the rising wine consumption, there are some late converts who are surely taking the path of palate development. Muscat, for example, is tailor made for them as it evolves to Riesling and soft tannin reds.

4) Quality: Even wine enthusiasts have to admit that Muscat is an enjoyable glass of wine, pleasingly floral, typically balanced, and able to be made with some character, with reasonably low alcohol and an inexpensive price.

In sum, not just Muscat, but semi-sweet varietal wines in general, will have higher price points, but still with a "value" orientation. They won't be garishly packaged on the bottom shelf of the wine aisle, having earned a higher degree of respect in the court of wine consumer opinion. Many wine retailers feature a dessert-wine section. Nearly all fine-restaurants offer a range of dessert wines (Brostrom and Brostrom, 2009). Tawny Ports and sweet Madeiras are useful in restaurant settings, as these wines do not lose quality once the bottle is opened. Late harvest and botrytis-affected wines are offered in some forward-thinking restaurants as an aperitif or with a cheese course. Some have found it effective to offer a sweet wine as part of a feature with a particular food item, for instance, a serving of foie gras with a glass of Sauternes or a chocolate soufflé with a glass of Tawny Port, priced together as a single unit.

4.2. Optimization of wine flavor

In our understanding of grape and wine flavour, exciting opportunities exist, particularly for the development of novel analytical approaches that can be used to link metabolic profiles to gene and protein expression in plants and microorganisms. To date, many of these metabolomic studies have focused on obtaining broad chemical profiles of the non-volatiles involved in primary metabolism, for example, sugars, amino acids, and organic acids. Few studies have focused on the secondary metabolites, particularly the volatile components, which affect fruit flavor. Although not yet widely applied to grapes, it is clear that these novel "omics" approaches can yield valuable metabolic information and increase our understanding of the regulatory mechanisms involved in the biochemical production of volatiles, both in grapes during berry development and by yeast during fermentation. As a result of these many advances, the

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contributions of the wine chemist are clear, and when combined with improved understanding of human perception of odorants and odorant mixtures, it will become increasingly possible to control viticultural and winemaking practices to optimize grape and wine flavor. It is expected that wineries will employ scientists for quality control analysis, who will be involved in setting optimum parameters for grape production. Chemists involved in the winery industry will need strong analytical skills, and a good understanding of organic chemistry. They are starting to use new analytic tools to study the flavor of wine, and new science that will provide consistency and product quality to the wine industry.

Acknowledgements

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Figure 1: Grapes drying prior to wine making.

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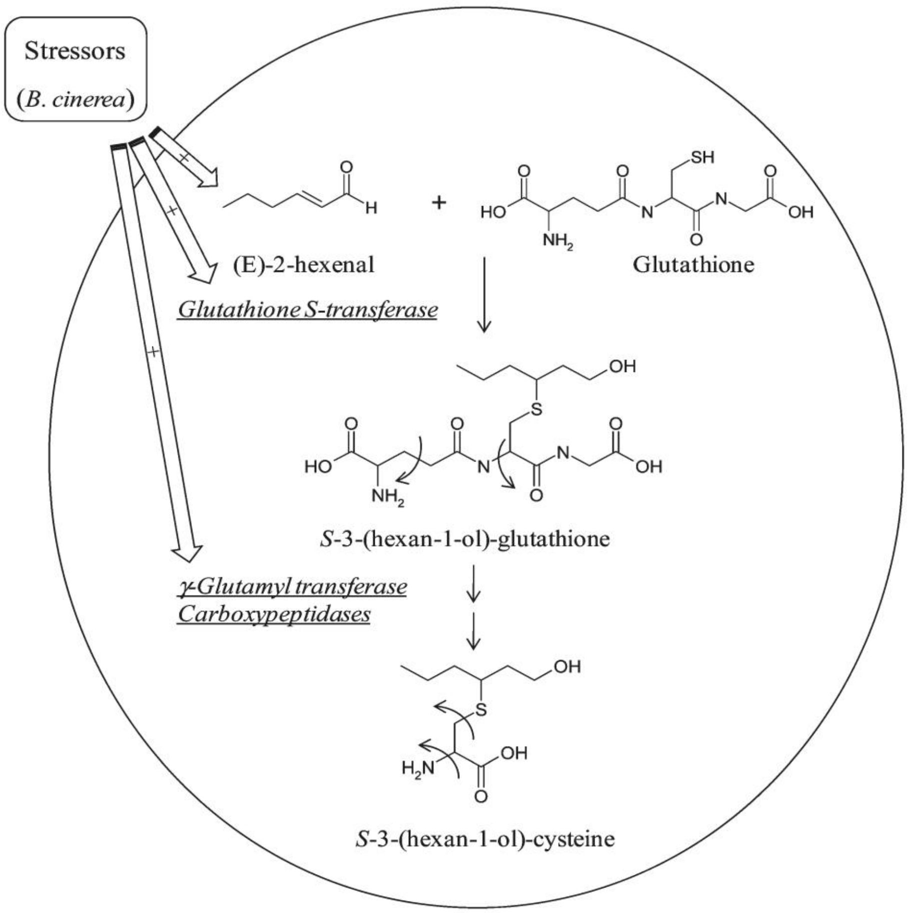


Figure 2: Hypothetical S-3-(hexan-1-ol)-glutathione (P-GSH) and S-3-(hexan-1-ol)-cysteine (P-3SH) formation pathway in grapevines, induced by abiotic or biotic (*B. cinerea*) stressors. Stressors increased glutathione S-transferase and γ-glutamyl transferase enzyme activities in grape berries (Kobayasi *et al*., 2011).

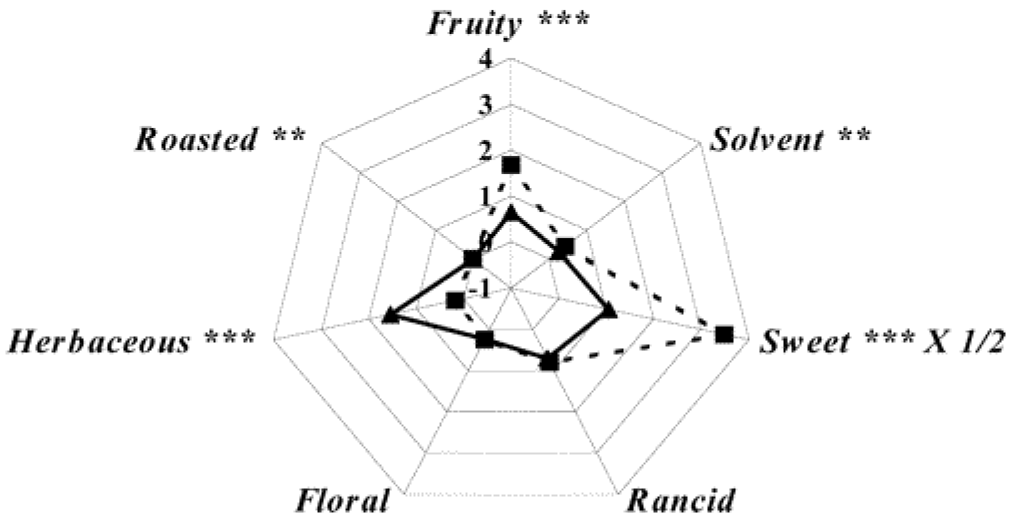


Figure 3: Mean odor activity values (OAVs), in relative unities for the odorant series in musts from ripe and off-vine-dried Pedro Ximenez grapes. Ripe grape must (triangle). Dried grape must (square). Values obtained from the ANOVA: (***) = $p \leq 0.001$; (**) = $p \leq 0.01$; (*) = $p \leq 0.05$. 1/2: Drawn values for the sweet series are one-half of the real values (Franco *et al*., 2004).

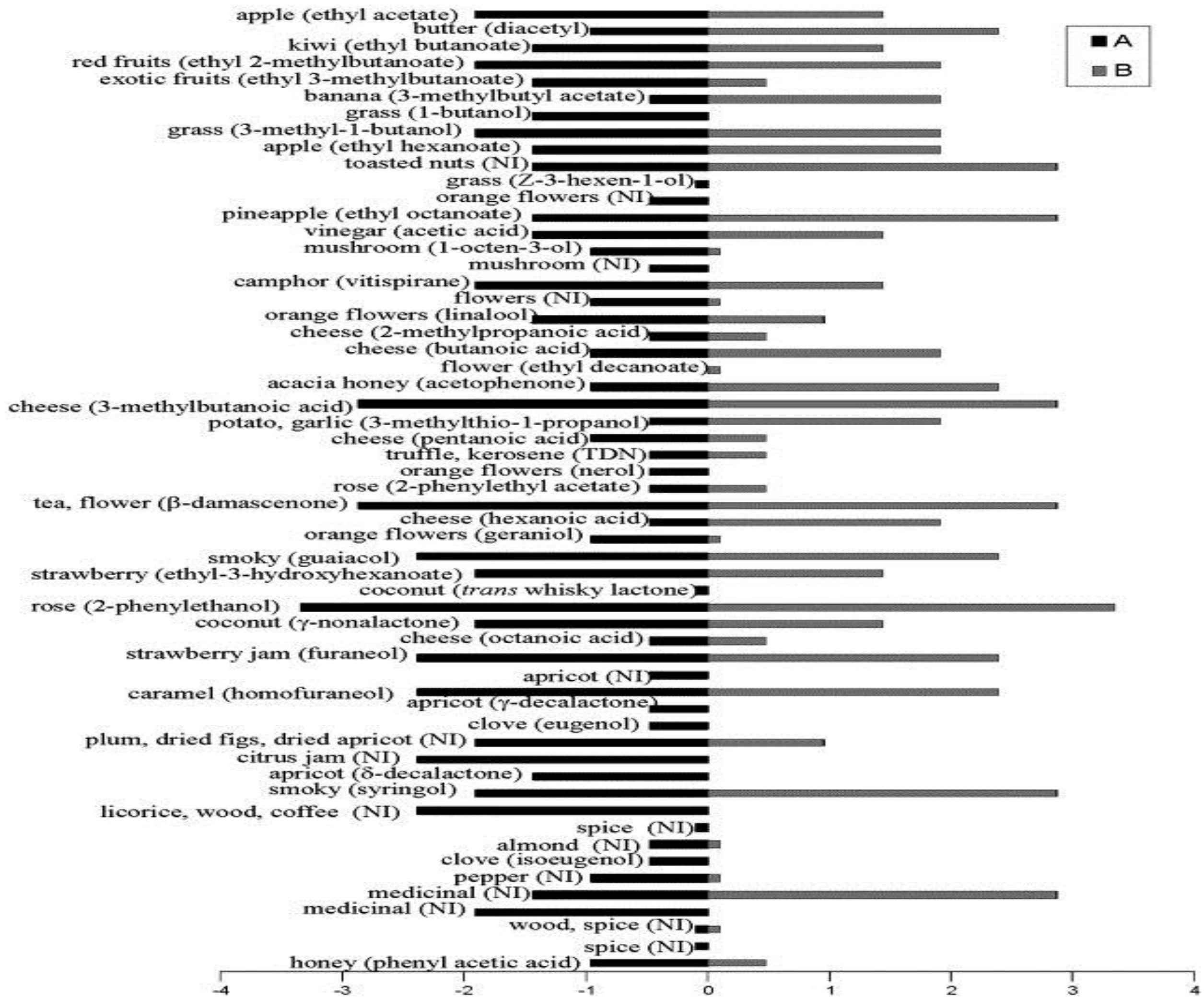


Figure 4: Aromagrams of (A) sweet Fiano wine and (B) base Fiano wine (Genovese et *al.*, 2007b).

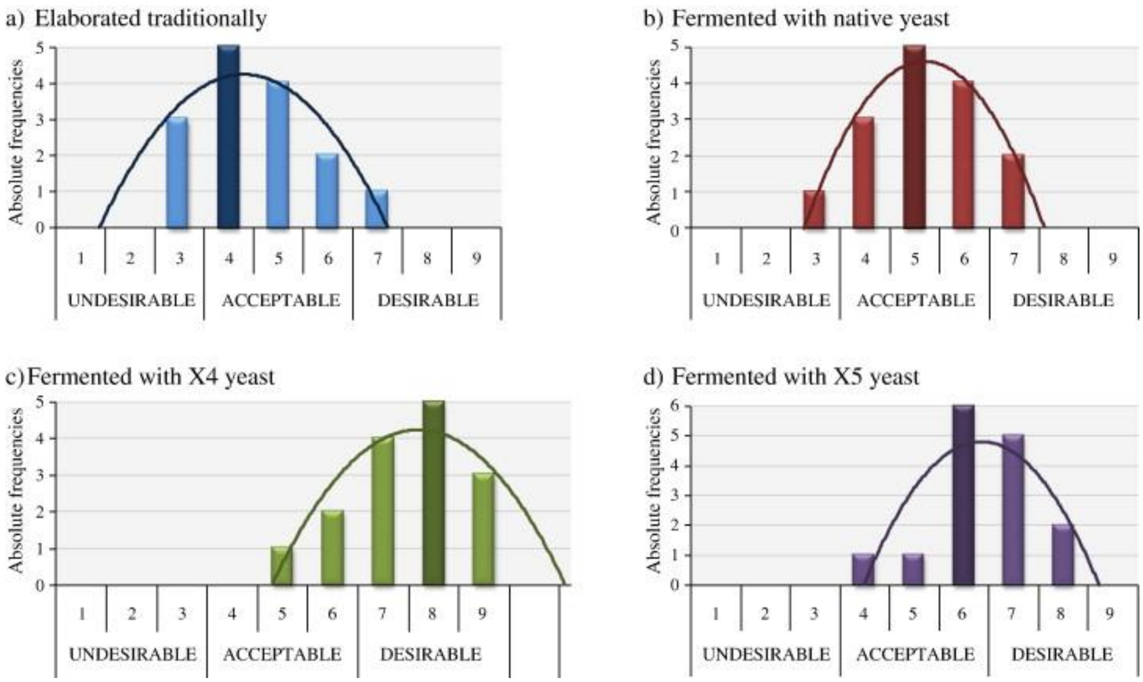
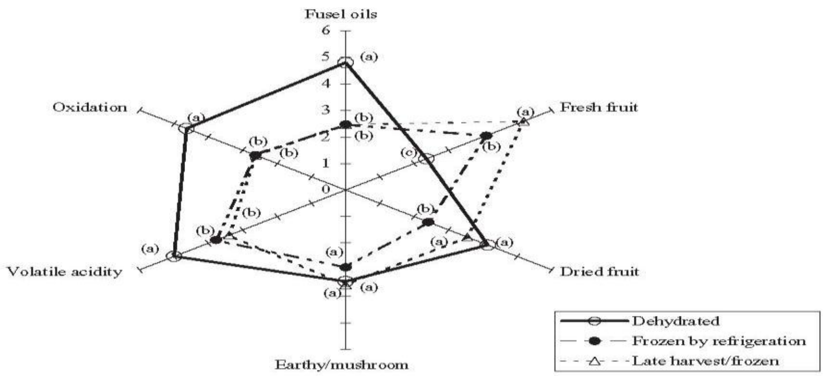


Figure 5: Distribution of absolute frequencies, medians (dark bar) and trend lines obtained for the wine aroma by a tasting panel (López de Lerma and Peinado, 2011).

(A)



(B)

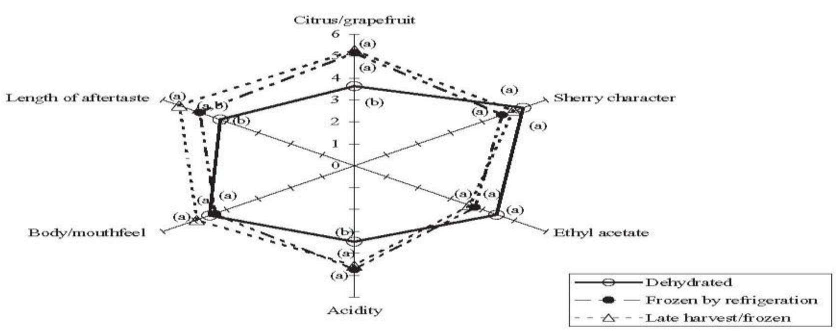


Figure 6: Levels of aroma (A) and flavor notes (B) detected by the judges for each treatment in Riesling wines. Different letters indicate significant differences between means ($P < 0.05$). Duncan's multiple range test was used (Clary *et al*., 2006).

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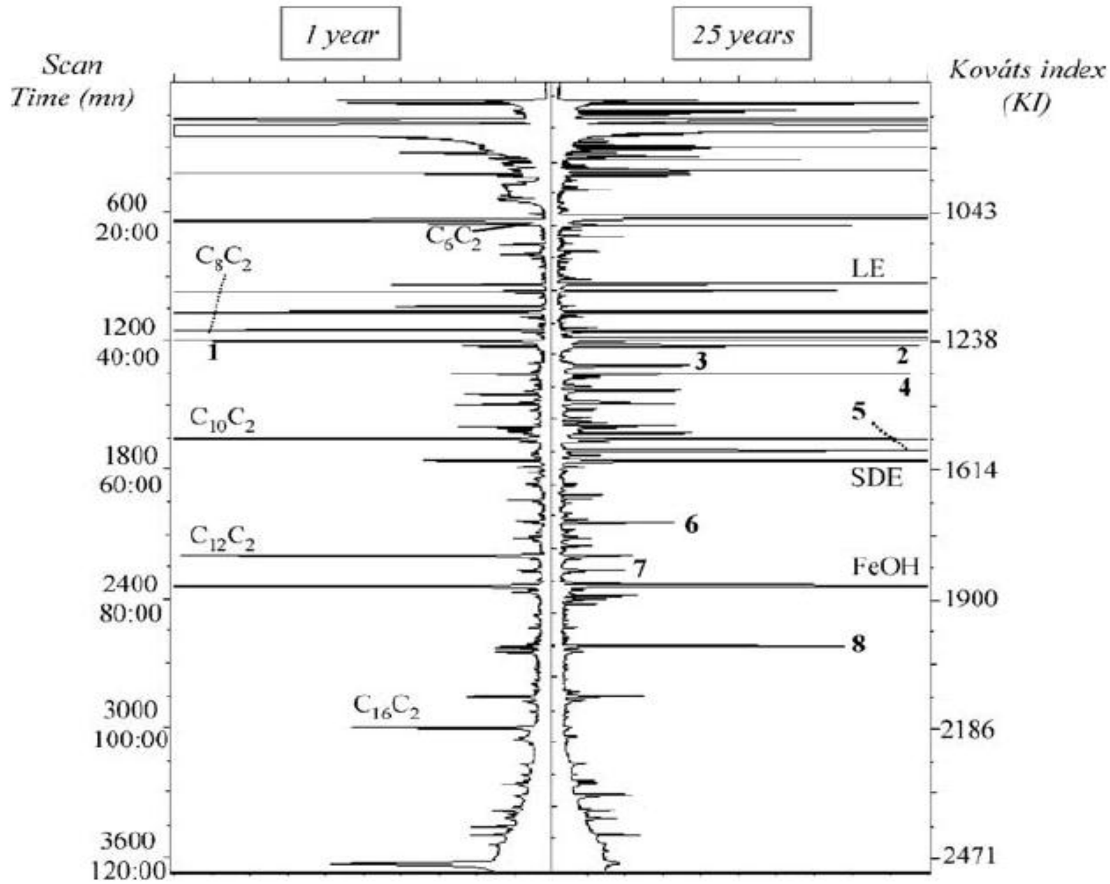

Figure 7: GC/MS chromatograms of a dichloromethane extract from a two samples of Malvasia wines with 1 and 25 years old (Câmara *et al*., 2006). Legend—(1) acetic acid; (2) 2-furfural; (3) 1,1-diethaxyethane; (4) benzaldehyde; (5) ethyl benzoate; (6) ethyl benzeneacetate; (7) benzyl alcohol; (8) ethyl 3-hydroxyhexanoate; LE: ethyl lactate; SDE: diethyl succinate; FeOH: 2-phenylethanol; C_6C_2: ethyl hexanoate; C_8C_2: ethyl octanoate; $C_{10}C_2$: ethyl decanoate; $C_{12}C_2$: ethyl dodecanoate; $C_{16}C_2$: ethyl hexanoate.

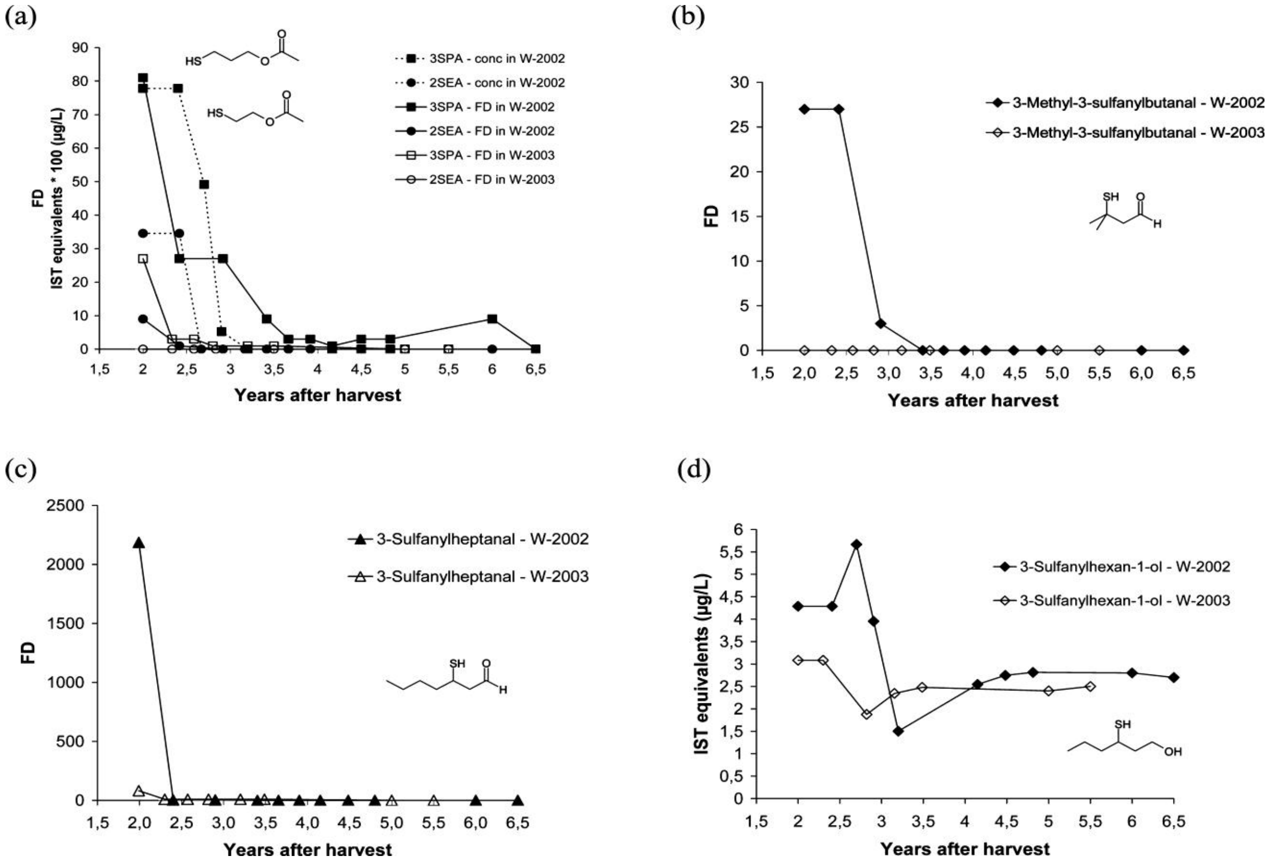

Figure 8: Fate of (a) 2-sulfanylethyl (2SEA) and 3-sulfanylpropyl (3SPA) acetates, (b) 3-methyl-3-sulfanylbutanal, (c) 3-sulfanylheptanal, and (d) 3-sulfanylhexan-1-ol through Sauternes wines aging in a cellar (2002 and 2003 vintages). FD = 3^{n-1}, with n = number of dilutions of XAD 2 extract before no detection by GC−O. conc = IST equivalents (µg/L) measured in pHMB extract by GC−PFPD (variation coefficient < 7%). The precision of the AEDA is n ± 1 (factor 3 between FD values). Assay in duplicate (Bailly et al., 2009).

Table 1: Aromatic compound and sensorial description of sweet wines grouped as a function of the sugar concentration process applied.

Cultivar variety	Geographical origin	Aromatic compound description	Sensorial description	References
Fortified wines				
Grenache Noir	Southern France (Rousillon)	Sotolon, *trans*-2-methyl-5-hydroxy-1,3-dioxane, 4-carbethoxy-γ-butyrolactone, ethyl 2-hydroxyglutarate, and ethyl pyroglutamate	Green nut, curry, chocolate, coconut , and honey	Schneider *et al*., 1998
Tinta Negra Mole	South-West Portugal (Madeira Island)	Furan compounds and acetals	Vanilla and chocolate odour descriptors	Perestrelo *et al*., 2006
Muscat and Gewürztraminer (85:15, w/w)	--	Furfural	Nutty, caramel and burnt notes	Ortega-Heras and González-Sanjosé, 2009
Botrytized wines				
Aszú	North-East Hungary (Tokaj-Hegyalja)	Higher levels of hydroxy-, oxo-, dicarboxylic acid esters, γ- and δ-lactones	Coconut, chocolate, peach, fruity, floral-honey and dried-roasted aroma character	Miklósy *et al*., 2000; Miklósy and Kerényi, 2004; Miklósy et

				al., 2004
Sauvignon blanc, Semillon	South-West France (Sauternes)	Polyfunctional thiols; α-terpineol, sotolon, fermentation alcohols (3-methylbutan-1-ol and 2-phenylethanol), esters (ethyl butyrate, ethyl hexanoate, and ethyl isovalerate), carbonyls (*trans*-non-2-enal and β-damascenone), guaiacol, vanillin, eugenol, β-methyl-γ-octalactone, and furaneol	Bacon-petroleum, feed, spicy, olive, bacon, plastic, rhubarb, lemon; Floral, musty orange, caramel, curry, chocolate, acid fruit, liquor, syrup, green apple, red fruit, peach, cardboard, rubber, wood, phenolic, hay tree, vanilla, cake, sweet, coconut, butter, cotton candy,	Bailly *et al.*, 2006
Sauvignon blanc, Semillon	South-West France (Sauternes)	3-sulfanylpentan-1-ol (3SP) and 3-sulfanylheptan-1-ol (3SHp), 2-methyl-3-sulfanylbutan-1-ol (2M3SB), and 2-methyl-3-sulfanylpentan-1-ol (2M3SP)	Citrus aroma, a raw onion odour	Sarrazin *et al.*, 2007b
Ice wines				

Riesling	South Germany (Rhine)	2-methyl-1-propanol, 3-methyl-1-butanol, benzene-ethanol, ethyl lactate, hexanoic acid, and octanoic acid	Nutty/oily character	
Riesling and Vidal	South-West Canada (British Columbia)	Threo-butanediol, octanoic acid, dihydro-2(3H)-furanone, diethyl hydroxybutanedioate, 5-(cyclohexylmethyl)-2-pyrrolidinone, and butanediol	Fruity or raisin/sherry aromas, floral, muscat, leechee, fruity, peachy, strawberry, pineapple, sweet, and perfumy attributes, honey/caramel, raisin/dried fruit, and sherry-like/oxidized characters	Cliff *et al*., 2002
Late harvest wines				
Fiano	Central Italy (Tuscany)	Terpinen-4-ol, linalool, β-damascenone, γ-valerolactone, whisky lactones, eugenol, syringol, isoeugenol, furfural, benzaldehyde	Citrus jam, dried apricot, dried figs, prune, honey and coconut	Genovese *et al*., 2007a
Sun drying wines				
Pedro Ximenez	South Spain (Andalusia)	Butane-2,3-dione, 1,1-diethoxyethane, and	Yogurt, cake, fruit, and sweets;	Franco et al., 2004

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		acetoin; benzyl alcohol, 2-phenylethanol, furfural, 5-methylfurfural, γ-butyrolactone and γ-hexalactone	burnt and caramel odor	
Muscat	South Spain (Andalusia)	Linalool, α-terpineol and limonene	--	Márquez *et al.*, 2008
Pedro Ximenez	South Spain (Andalusia)	2-furaldehyde and 5-methyl-2-furaldehyde	--	
Pedro Ximenez	South Spain (Andalusia)	Acetoin, ethyl acetate, isoamyl alcohols, 1,1-diethoxyethane, isobutanol, 1-butanol, 2,3-butanedione, γ-butyrolactone, 3-methylbutanoic acid, furfural,	Caramelized, floral, fresh, tree fruit, spicy, lactic, tropical fruit and pungent	Ruiz *et al.*, 2010
Fast dehydration in a dehydration tunnel				
Malvasia	Central Italy (Tuscany)	Hexanal, hexan-1-ol, (E)-hex-2-anal and (E)-hex-2-anol), acetate esters, methyl butanal, methyl butanol, ethyl laurate, isovaleraldehyde	Fower and fruit note, peach note	Bellincontro *et al.*, 2004
Sangiovese	Central Italy (Tuscany)	Isoamyl alcohols, 2-phenylethanol and methyl butanol	--	

Pinot Noir	Pacific Northwest region of USA (Willamette Valley of Oregon)	Guaiacol, citronellol, geraniol, eugenol, β-ionone, β-damascenone	Floral and fruity characters	Moreno *et al.*, 2008
Dried in a chamber after 5 days at controlled conditions				
Pedro Ximenez	South Spain (Andalusia)	Acetoin, ethyl acetate, phenylethyl alcohol, isobutanol and isoamyl alcohols	Chemical, caramelized, floral, lactic, and pungent	Ruiz *et al.*, 2010
Dried in a greenhouse				
Plavac mali	Central Croatia (Pelješac)	Higher alcohols (isoamyl alcohol, 1-propanol, isobutanol), 2-phenylethanol, ethyl acetate, isoamyl acetate, 2-phenylethyl acetate, ethyl lactate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, acetaldehyde,	Dried fruit (raisin, prune and strawberry jam), berries (blackberry, raspberry, strawberry, black currant, and cherry) and honey, and vanilla	Budić-Leto *et al.*, 2010

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Table 2: Evolution of the aromatic and sensorial description of sweet wines as a function of the ageing process and proposed fingerprints of the ageing process and the degree of mature.

Ageing process	Wine	Aromatic evolution	Proposed fingerprints	References
Oxidative ageing	Italian Muscat wines	Floral notes (linalool, nerol and geraniol) decreased and some off-flavours described as cork tones, plastic and mushroom were developed.		Bordiga *et al.*, 2009
	Madeira wines	Fresh and fruity notes decreased significantly during ageing.	Sotolon, 2-furfural, 5-methyl-2-furfural, 5-hydroxymethyl-2-furfural, 5-ethoxymethyl-2-furfural, cis-dioxane and cis-dioxolane as indicators of oxidative ageing.	Câmara *et al.*, 2006
	Pedro Ximenez wines	The aging process resulted in a gradual enrichment in buttery, raisin, and muscat aroma notes.	2,3-Butanedione, linalool, and decanal as indicators of oxidative ageing.	Chaves *et al.*, 2007
		During oxidative ageing at 65 ºC, varietal notes (raisin, caramel and vegetable) gradually disappeared while roasted, coffee and burnt wood notes were gradually developed (furfurals, furanones, dihydromaltol and corylon).		López de Lerma *et al.*, 2010
	Sauternes wines	Important increments in the concentration of *trans*-non-2-enal, β-methyl-γ-		Bailly *et al.*, 2006

		octalactone, linalool, β-damascenone, guaiacol, eugenol and vanillin were observed during ageing. On the contrary, 2-phenylethanol decreased through oxidation.		
	Vins Doux Naturels	The content of polar ethyl esters and related lactones increased during aging especially in barrel-aged wines. On the contrary, levels of acetals, furfural and 5-(hydroxymethyl)furfural were most important in demijohn-aged wines.		Schneider *et al.*, 1998
		Furfural, 5-ethoxymethylfurfural, isomers of methyl-γ-octalactone and sotolon always reached concentrations above their perception thresholds in wood-aged wines and also vanillin content increased with aging.	Isomers of methyl-γ-octalactone as indicators of aging in oak.	Cutzach *et al.*, 2000
Biological ageing	Fino wines	Increments in the concentrations of butanoic acid, farnesol, 3-methylbutanoic acid and γ-decalactone were observed during biological ageing. Fino wines are marked by floral and fruity (farnesol, β-citronellol and β-ionone), cheesy and rancid (butanoic acid), and pungent (acetaldehyde) notes.	Acetaldehyde as indicator of biological ageing.	Zea *et al.*, 2001
		An increment in the vainilla, nut, curry, candy cotton, green fruit and liquorice aroma notes was	Sotolon, 1,1-diethoxyethane and Z-whisky lactone as	Moreno *et al.*, 2005

		observed during ageing.	indicators of biological ageing time.	
		Fruity, spicy and fatty series are the ones most strongly contributing to the aroma profile of Fino wines under biological ageing.	Fruity OAVs can be used as an objective indicator of the contribution of flor yeasts to the process and spicy series as indicator of wood contribution.	Zea *et al.*, 2007
	Sherry wines	An increase in eugenol contents with ageing was observed.		Cortés *et al.*, 1998 and 1999
Combination of chemical and biological ageing	Amontillado wines	Fruity notes (ethyl butanoate and 1,1-diethoxyethane) are weaker in Amontillado wines.	Contents of 1,1-diethoxyethane, isobutanol, phenethyl alcohol, ethyl butanoate, ethyl benzoate, isobutyl isobutanoate, isoamyl laurate and E-nerolidol as indicators to distinguish Amontillado wines form Fino and Oloroso wines.	Zea *et al.*, 2001
		Amontillado wines exhibited the highest OAVs for the nutty and spicy series by effect of the increased contribution of sotolon and also the lowest OAVs for the fruity and balsamic series as the result of the decreased contribution of 1,1-diethoxyethane.	Contents of acetaldehyde, ethyl acetate and eugenol as indicators to distinguish Amontillado wines form Fino and Oloroso wines.	Zea *et al.*, 2008

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Ageing in the bottle	Sauternes wines	Most thiols were lost during the first two years in the bottle.		Bailly *et al.*, 2009
	Tokaji Aszú wines	During ageing the concentrations of vitispirane, trimethyl dihydronaphtalene, 2-phenylethanol and diethyl succinate increased while those of 3-methyl-butyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate and ethyl dodecanoate decreased.		Tóth-Markus *et al.*, 2002