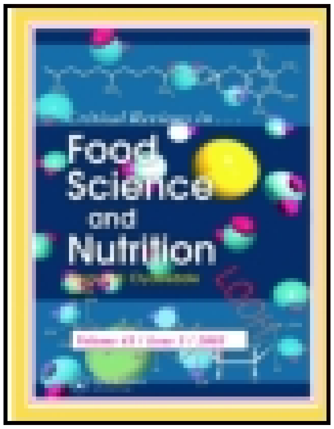

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Wine Processing: A Critical Review on Physical, Chemical, and Sensory Implications of Innovative Vinification Procedures

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Wine processing: a critical review on physical, chemical, and sensory implications of innovative vinification procedures

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Wine is one of the most popular alcoholic beverages in the world although it is mainly consumed in European and South American Countries. Several thousand years is passed since the product of grape fermentation was accidentally discovered. Over the last 100-150 years, wine making has been completely revolutionised in terms of procedures and equipment. This work was aimed to give a comprehensive overview on of consolidated use but also on winemaking innovations still in the development step or already applied to commercial products. Their effects on physical, chemical, and sensory characteristics of wines will be also discussed in comparison with those of the consolidate vinification procedures.

Keywords cryomaceration, hyperoxygenation, micro-oxygenation, reductive method, reductive winemaking, thermomaceration

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INTRODUCTION

Wine is the beverage resulting exclusively from the partial or complete alcoholic fermentation of fresh crushed or uncrushed grapes or of grape must (OIV, 2012a). *Vitis vinifera* L. is the most widely used wine grape species throughout the world (Baiano et al., 2013).

The history of wine dates back over 6000 years BC. According to an ancient Persian fable, wine was the accidental discovery of a princess seeking to end her life with what she thought was poison (http://rmc.library.cornell.edu/ewga/exhibition/introduction/). Archaeological evidence suggests the earliest production of grape wine took place at sites in Georgia and Iran. The world's oldest known winery (dated to 3000 BC) was discovered in a mountainous area of Armenia (http://en.wikipedia.org/wiki/History_of_wine). The Egyptians were the first to record the process of wine making on stone tablets and the walls of their tombs but wine was considered a privilege of the upper classes. In ancient Greece, wine was praised by historians and artist but, like the Egyptians, the ordinary citizens did not consume wine. With the Roman Empire, the production of wine spread throughout Europe and wine became available to the common citizens. The Romans did not drink pure wines but they added flavours such as fermented fish sauce, garlic, and onion. During the Dark Ages, wine production was prerogative of monasteries. The Benedictine monks, became one of European largest wine producers with vineyards in Champagne, Burgundy, and Bordeaux regions (France), as well as in the Rheingau and Franconia regions (Germany). The wine industry had a brief decline in the 17th Century, while the 19th century was the golden age of wine for many regions, although, around 1863, many French vines suffered from a disease caused by the Phylloxera aphid. When it was discovered that vines in America were resistant to Phylloxera, it was decided to graft European vines on American rootstocks (http://www.wineinmoderation.eu/en/wine-a-culture-of-moderation/history-of-wine). The resulting products were many hybrid grapes that produced a greater variety of wines. The last century have seen an overall revolution in the wine industry, with the development of a strong scientific background and innovation in equipment and processing (http://www.artmakers.com/wine/history.html).

Today, The importance of wine is proved by its statistical data. According to the report on world vitiviniculture (OIV, 2012b), in 2011, the world production of wine amounted to 265 million hectolitres and the first three producers were France (49 Mhl), Italy (41 Mhl), and Spain (33 Mhl). 2012 EU production reached 141 Mhl excluding juice and musts (compared with 157 Mhl last year), a decline of 10%/2011 (OIV, 2013). France saw its 2012 wine production decline by more than 8.5 Mhl (-16.8%), while Spain's and Italian production declined by 3.7 Mhl (-11.2%), and 2.7 Mhl (-6.3%), respectively. Although wine is one of the most popular beverages, beer is most consumed alcoholic beverage in the world. The ratio between consumption of beer and consumption of wine is 5:1.

The diversity and quality of wine result from parameters such as kind of grape, pedoclimatic conditions, location, harvest time, and the designed processes throughout the vinification (Christaki and Tzia, 2002). Technological innovations have provided for better hygiene and control of the production process, over that for the production of better quality wines. Vine cultivation and winemaking are regulated by the European Common Market Organization (CMO) in the framework of the Common Agricultural Policy (CAP) through stringent, comprehensive, and specific standards that cover the overall wine production, from soils, planting areas, authorisation of vine varieties, to wine making. Thus, the scientific innovations need a legal recognition before to pass from experimental studies to industrial and commercial applications.

This paper was intended to provide an overview of innovative winemaking procedures and of their effects on the physical, chemical, and sensory properties of wines in comparison with consolidate methods.

VINIFICATION METHODS AND STYLES

As already said, many technological innovations have been proposed in wine-making but, for sake of clarity, a systematic classification of the obtained wines is preparatory for their better understanding. Wines can be classified as red or white wines, sparkling, semi-sparkling or still wines, fortified and sweet wines (Ewing-Mulligan and McCarthy, 2005; http://en.wikipedia.org/wiki/Classification_of_wine).

In the so called traditional ózred vinificationô, the must obtained by crushing and destemming of grapes remains in contact with skins and seeds (the marc) for a more or less long time (rosé or red wines). The colouring substances of the skins are extracted by the solubilizing action of the alcohol produced during fermentation. In order to enhance contact between marc, which tends to float on the must forming a so-called ócapô, a mechanical action can exerted on the cap to submerse it in the must (pressing), or the top of the cap can be wetted with the must collected from the bottom of the vat (pump over), or a mesh screen can be introduced into the vat to avoid the emersion of the marc onto the surface (submerged cap fermentation). The colour a wine is given by the presence or absence of the grape skin during its fermentation since pulps are almost always clear. Only few grapes have coloured pulps and they are known as óteinturierô. If a so called ówhite vinificationô is carried out (a fermentation after separated of the marc), the product obtained is a white wine.

Sparkling wine have significant levels of carbon dioxide. The carbon dioxide may result from natural fermentation, either in a bottle (óChampenoiseô process), or in a large tank designed to withstand the pressures involved (óCharmatô process), or from an external injection.

Fortified wines are wines with an added distilled beverage. It includes many different styles such us Port, Sherry, Madeira, Marsala, Commandaria wine and the aromatized wine Vermouth.

Sweet wines are those wines in which high levels of residual sugar are left after fermentation. These wines can be obtained through a variety of methods. The sugar content can be increase by: harvesting grapes when they are overripe; adding sugar, either before fermentation as sugar or honey (the so called óchaptalizationô) or after fermentation as unfermented must (ñsüssreserveò); removing water to concentrate the sugar a) by air drying the grapes to make raisin wine (in warm climates), b) by freezing part of the water to make ice wine (in frosty climates), c) by using a fungal infection, *Botrytis cinerea*, to desiccate the grapes with noble rot (in damp temperate climates).

The aim of this study was to provide an overview of vinification procedures and their effects on wines. For both red and white styles, a list of vinification methods was supplied. Every vinification procedure and the effects on several wine grape cultivars in comparison with traditional winemaking were described.

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Red vinification

The most important procedures suitable to produce red wines are, in alphabetical order: addition of copigments, enzymes, tannins, and oak chips; aging on lees; carbonic maceration; co-winemaking; cryomaceration; délestage; malolactic fermentation; micro-oxygenation; extended maceration; saignée; thermovinification.

Addition of copigments, enzymes, tannins, and oak chips

Copigmentation is a hydrophobic interaction between monomeric anthocyanins and other phenolic compounds. The molecules that can interact with cofactors require a planar disposition because they need to stack with the flavilium forms of monomeric anthocyanins (Boulton, 2001). The copigmentation reactions of anthocyanins consist in conversion from monomeric to polymeric anthocyanins and cause losses in the red colour intensity, changes in tone from purpleï red to red, and an increase of the colour stability (Baranac et al., 1997). The best cofactors are flavonols, but also flavanols, hydroxycinnamoyltartaric acids and hydroxycinnamic acids can act as co-pigments if present in higher concentrations in musts and wines (Liao et al., 1992; Eiro et al., 2002). The addition of co-pigments is generally followed by a prolonged pre-fermentative maceration, in order to allow a better contact between the phenolic compounds. Álvarez et al. (2009) studied the effects of the pre-fermentative addition of co-pigments and different winemaking technologies on the polyphenolic composition of Tempranillo red wines after malolactic fermentation. In separate experiments, they added caffeic acid, rutin, (+) catechin, white grape skin tannin, and white grape seed tannin as co-pigments and compared the traditional vinifcation with the pre-fermentative cold maceration at 6ï 8 °C for 4 days and the

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pre-fermentative cold soak with dry ice at 0ï 2 °C for 4 days. The results demonstrated that pre-fermentative addition of co-pigments (of white grape tannins, in particular) increased anthocyanin co-pigmentation reactions and produced wines with a greater colour, a higher anthocyanin concentration, a higher percentage of tannins polymerised with polysaccharides and less astringency. Cold pre-fermentative maceration (in particular when it was carried out with dry ice, since it caused the disruption of the membranes and the leak of phenolic compounds) increased the extraction of polyphenols, the anthocyanin co-pigmentations and the polymerisation reactions between tannins and polysaccharides.

In the degradation of skin cell walls, different enzymatic reactions are involved, which are responsible, therefore, for the extraction and solubilisation of the vacuolar constituent (Soto Vázquez et al. 2010). The addition of pectolytic enzymes may result in a decrease of anthocyanins and in an increase of polymeric pigments that stabilize colour (Sacchi et al., 2005). The extent of extraction and the state of polymerization determines colour, structure, and aging potential of red wines. Many oenologists have questioned the effectiveness of the use of pectic enzymes during the maceration of red grapes (Bucelli et al., 2006). It is important to use purified enzyme (without cinnamoyl esterase activity) in order to avoid levels of 4-ethyl-phenol above the sensory threshold in the wine (Gerland, 2003). Amrani Joutei and Glories (1994, 1995) proposed that extraction of the anthocyanins, which are located exclusively in skin cell vacuoles, is due to degradation of the proteinaceous portions of cellular membranes caused by sulphur dioxide addition. Pectinolytic enzymes might favour the extractability of upper-middle molecular weight tannins attached to the vacuolar membranes and to the polysaccharides of the cell wall, thus improving the structure of the wine. The presence of side activities in pectic enzyme formulations, such as cellulases, hemicellulases and proteases, may also allow better extraction of grape polysaccharides, with positive effects on wine structure (Doco et al., 1995). Bucelli et al. (2006) have conducted experiments using Sangiovese grapes to understand the role of maceration enzymes during the production of red wines. They examined: the effect on wine colour of four enzymatic preparations containing different amounts of polygalacturonase, pectinase, galactanase, cellulose, pectinmethylesterase, and acid protease; the effect of enzymatic treatment during extended skin contact; the development of colour and sensory characters during wine storage. Authors observed an increase of colour stability, reflected by greater colour intensity and lower hue at 18 months after vinification and also enhanced sensory properties, particularly in terms of structure, fullness, balance, and aroma complexity. The addition of enzymes did not affect the quantity of anthocyanins extracted during fermentation but allowed the extraction of greater quantities of tannins, thus leading to the formation of greater quantities of stable polymerized pigments. Furthermore, lengthening of the maceration time to 20 days in the absence of enzymes yielded wines that were comparable to those made using enzyme additions with only 8 days of maceration. Moreno-Pérez et al. (2010) checked the effectiveness of the application of two macerating enzymes (a pectinase preparation that mainly contain pectin lyase, polygalacturonase and pectin esterase activities and a ß-galactosidase preparation) on the chromatic and phenolic parameters during the maceration period. Authors concluded that the use of maceration enzymes led to wines richer in anthocyanin compounds and showing better chromatic characteristics and that there were differences between varieties. In the case of Syrah wines, the best results were obtained with the ß-galactosidase treatment, while in the case of Cabernet-Sauvignon wines the pectinase preparation was to be preferred. Borazan and Bozan

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(2013) studied the effects of pectolytic enzyme addition on the phenolic component of Okuzgozu red wine during the winemaking and ageing processes. After 6 months in the bottle, the enzyme-treated wines had lower phenolic acid concentrations than the control. The wines treated by the pectolytic enzyme addition had lower monomeric flavan-3-ol content than the other wines, and no significant differences in terms of monomeric anthocyanins extracted.

The addition of condensed tannins (proanthocyanidins) deriving from grapes is useful to increase the anthocyanin stabilization, through the formation of polymeric pigments. Furthermore, the hydrolysable tannins (gallotannins and ellagitannins) deriving from the wood act as colour protectors. Soto Vázquez et al. (2010) studied the effects of the addition of pectolytic enzymes (with cinnamyl-esterase, polygalacturonase and pectin lyase activity), procyanidin tannins extracted from white grape pips, ellagic tannins derived from oak wood, or not toasted oak chips during alcoholic fermentation on phenolic composition and chromatic characteristics of young red wines, elaborated from Mencía grapes grown in Galicia (northwest Spain). The authors found that the main advantage of the addition of enzymes or tannins respect to the traditional winemaking was their greater ability to extract anthocyanins, as well as to facilitate the co-pigmentation reactions and thus the increase in colour. Instead, the addition of oak chips did not favour the reactions involved in anthocyanin stabilization. In conclusions, the addition of enzymes and tannins seemed to be the most adequate winemaking techniques to elaborate red wines for aging, while the addition of oak chips could be used for the elaboration of young red wines. Baiano et al. (2009) highlighted that the addition of ellagic tannins and tannins from skin and seeds allowed the increase of the phenolic content of Primitivo musts and wines in a greater amount than the other technologies (traditional, délestage, saignée, delayed punching-

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down, heating of must, cryomaceration, and prolonged maceration). The addition of tannins was also recommended to increase the radical scavenging activity of Primitivo wines. Furthermore, one-year-aged wines obtained through the addition of tannins showed high concentrations of anthocyanins sensitive to SO_2, monomeric anthocyanins, flavonoids, flavans reactive to vanillin, and coumaroylated malvidin and low content of acetylated malvidin. Neves et al. (2010) studied the effects of two highly pure commercial grape seed tannins on the phenolic composition, chromatic characteristics, and antioxidant activity of two types of red wines made with Castelão/Tinta Miúda (3/2, w/w) varieties by using two different maceration times, which corresponded to wines rich and poor in polyphenols, respectively. The results showed that the addition of grape seed tannins had the effect of increasing colour intensity and antioxidant activity only in wines poor in polyphenols. The authors also found that tannins added after alcoholic fermentation had a better effect on phenolic composition of red wine than tannins added before it. Liu et al. (2013) investigated the effects of pre-fermentative addition of exogenous condensed or hydrolysable tannins on anthocyanins and colour characteristics of Cabernet Sauvignon wines. They concluded that the application of hydrolysable tannins did not produce any influence on wine redness even after 9 months of bottle aging, while condensed tannins protected some pigment components from degradation and enhanced wine redness and yellowness since they retard the degradation of most anthocyanins and the decrease of some pyranoanthocyanins, and protect wine against oxidation or contribute to form co-pigmented anthocyanidins or polymeric pigments.

Wine aging in wood barrels requires long periods and is very expensive, but sensory properties similar to those of wines aged in barrels could be obtained using oak chips. Oak chips are small pieces of oak wood that can be added to wine fermented in stainless steel tanks, to obtain wines like those fermented in barrels (Pérez-Coello et al., 2000). Oak chips release wooden aromas in wine, although their aroma profile depends on oak variety, geographic location of the forest, wood seasoning and toasting, size, amount of chips, and contact time (Amati et l., 1999; Perez-Coello et al., 2000; Spillman, 1999). Beyond the effects on red wine volatile aroma due to the extraction of oak wood volatile compounds, oak chips could have effects on the colour stability because of their ellagic tannin content. Chips are not able to supply enough oxygen to induce the polymerization of phenols and to support the evolution of wood aromatic compounds, therefore it is often used together with micro-oxygenation to strengthen their influence on wine aroma and phenolic profiles. Parker et al. (2007) studied the effects of the addition of grape seed-derived tannins (condensed tannins) either before or after fermentation. Tannins were added in the amount of 200 mg/l. After malolactic fermentation, they observed that anthocyanin concentration decreased throughout the fermentation by about 25%, and by an additional 40% from the end of fermentation to the end of the experiment (2 years later). Tannins increased throughout fermentation. Polymeric pigments doubled from the end of fermentation to the end of the experiment as a consequence of the incorporation of anthocyanins into tannins, resulting in the formation of polymeric pigments. From a sensory point of view, the judges found that: a) the pre-fermentation and post-fermentation addition treatments significantly higher in ñoverall astringencyò than the control; b) post- and pre-fermentation treatments did not differ from each other; c) any differences were found among treatments for ñacidityò, ñbitternessò or ñfruitò attributes. According to Bowyer, the addition of oak chips provided a benefit in hue comparable to the fermentation tannins, while total phenolic load and wine colour density were superior when fermentation tannins were used. Furthermore, when the wines were shown masked to 9 independent winemakers, significant preference was shown for the wines with added fermentation tannins in terms of colour density and structural quality. According to Aiken et al., the addition of oak at the crusher in Cabernet Sauvignon wines can improve the flavour of the final wine by removing vegetal aromas, reducing astringency, and enhancing the fruit and smoothness. The increase in fruity notes was unlikely to be due to increased esters levels through assisted esterification of alcohols and acids by oak tannins, because no increase in esters were found. Oakôs ability to remove certain compounds, particularly off-odours, could explain the increased fruitiness of wines treated in this way. Furthermore, the theory that oak tannins enhance the co-pigmentation of wine phenolics has not been supported by their results. Oak chips may be added to the wine at any stage during the winemaking process, and will result in varied styles of wine depending upon when the chips were added. In a study on Bobal grapes from a vineyard in the La Mancha region of Spain, the following treatments were applied to the grape batches: wine without the addition of oak chips; addition of oak chips (a mix of French and American oak, with a medium toast) during alcoholic fermentation; addition of oak chips during malolactic fermentation; addition of oak chips post-fermentation (http://www.academicwino.com/2013/04/oak-chips-sensory-characteristics-wine.html/). From a sensory point of view, the principle component analysis grouped wines most similar to each other into two groups: 1) wines with oak chips added at alcoholic fermentation and control wines; 2) wines with oak chips added at malolactic fermentation and wines with oak chips added post-fermentation. The second group showed significantly more oak character than the first

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group and the two wines with chips added at malolactic fermentation were greater in oak aromatic intensity than the wines with oak chips added post-fermentation.

Arfelli et al. (2011) studied the single and combined effects of chips, lees, and micro-oxygenation on some flavours and sensory profile of a bottled red Sangiovese wine. At the end of aging, the main effect on selected volatile compounds was related to chips addition since they increased aromatic compounds derived from oak, such as vanilla and burnt/toasted aromas. The use of chips also led to a lower 4-ethyl guaiacol concentration than control.

Aging on lees

It consists in leaving yeast lees into the wine after alcoholic fermentation (Fornairon-Bonnefond et al., 2002). During autolysis, yeast cells release polysaccharides, nitrogen compounds, fatty and nucleic acids that enrich the wine. Furthermore, mannoproteins may stabilize wine against protein haze and tartrate crystallization and can decrease bitterness and astringency because they link tannins reducing their astringency (Dupin et al., 2000). Aging in presence of yeast lees changes the wine aroma profile (Escot et al., 2001) since the lees are able to adsorb some volatile thiols (methanethiol, ethanethiol) on their cellular walls (Lavigne and Dubourdieu, 1996) and to release aromatic compounds such as β-ionone and ethyl octanoate (Lubbers et al., 1996). The effect of the aging of red wine on lees is a novel winemaking technique. Doco et al. (2003) investigated the evolution of polysaccharides originating from the cell walls of grape berry (arabinans, arabinogalactan-proteins, RG-II, and RG-I) or released during fermentation or after autolysis of yeasts (mannoproteins) during aging on lees of a red wine from Madiran. Authors found the degradation of the pectic arabinans and of polysaccharides from grape, the latter

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consisting of dearabinosylation of arabinogalactan-proteins (AGPs). The arabinose to galactose molar ratio of AGPs decreased from 0.8 (control wine) to 0.3 (wine aged on lees). The stirring of lees during the aging of wine allowed a slight increase of mannoprotein content, which was sufficient to alter the organoleptic quality of wines. Mazauric and Salmon (2005) studied the interactions between wine polyphenols and yeast lees because these interactions have a large effect on the reactivity toward oxygen of both wine polyphenolic compounds and yeast lees. In particular, they studied the chemical composition of polyphenolic compounds remaining in solution or adsorbed on yeast lees after various contact times. According to their results, wine polyphenols adsorption on yeast lees followed biphasic kinetics. An initial and rapid fixation was followed by a slow, constant, and saturating fixation that reaches its maximum after about 1 week. Furthermore, only few monomeric phenolic compounds remained adsorbed on yeast lees. The remaining condensed tannins in the wine contained fewer epigallocatechin units than the initial tannins, thus indicating that polar condensed tannins were preferentially adsorbed on yeast lees. On the contrary, the adsorption efficiency of anthocyanin on yeast lees was unrelated to its polarity. Rodríguez et al. (2005) studied the effects of the presence of the lees during oak ageing on colour and phenolic composition of two red wines, one with a low ageing potential (low anthocyanin and proanthocyanidin concentration) and the other one with a high aging potential (high anthocyanin and proanthocyanidin concentration). Authors concluded that aging in presence of lees presented the disadvantage of producing wines with a slightly less intense colour and with lower proanthocyanidin concentration but with the advantages that colour slightly less evolved towards yellowish nuances, astringency decreased, and mouthfeel perception increased. In a study of 2009, Palomero et al. were aimed to investigate the release of polysaccharides during the autolysis of different genera of non-*Saccharomyces* wine yeasts, for their possible use in the acceleration of aging over-lees. Their effect on the stability of the anthocyanin monomer content in red wine made from *Vitis vinife*ra L. cv. Garnacha grapes was also studied. Authors found that *Schizosaccharomyces pombe* 936, *Saccharomycodes ludwigii* 980, *Pichia anomala* 930, and *Pichia membranifaciens* 956 could be used to reduce aging times since the wine content of yeast cell wall polysaccharides and mannoproteins would increase rapidly. The obtained wines had more complex molecular size profiles with beneficial effects on tartaric and protein stability, and sensory properties without any loss of colour. According to Smit and du Toit (2013), the presence of yeast lees during aging of Pinotage and Cabernet Sauvignon wines generally led to higher final concentrations of biogenic amines in wines than the absence of lees.

Synergic effects between yeast lees and micro-oxygenation or between yeast lees and oak chips are known. The combination of yeast lees and micro-oxygenation could decrease the reducing note and stabilize wine colour, because a higher amount of oxygen is necessary to balance yeast lees consumption of oxygen (Fornairon-Bonnefond and Salmon, 2003), whereas the presence of lees reduce the impact of compounds from oak wood on wine aroma (Jiménez Moreno and Ancín Azpilicueta, 2007). In the already cited work of Arfelli et al. (2011) on Sangiovese wines, the combined use of micro-oxygenation and yeast lees led to a lower amount of guaiacol and vanillin than in control.

Carbonic maceration

Carbonic maceration, also referred to as ówhole berry fermentationô or ówhole grape fermentationô is a vinification procedure in which entire bunches of grapes (with the skins, seeds and stems intact) are gently placed in a vat. Gravity causes the grapes at the bottom of the barrel to be crushed by the grapes at the top. Carbon dioxide is added to the vat of uncrushed grapes and causes fermentation of the juice while it is still within the grape skin and postpones the activity of the yeast. In particular, an ñanaerobic fermentationò occurs, which allows for various enzymatic reactions to occur inside the grapes, and for compounds to diffuse from the skins into the pulp. The resulting wine is low in tannins and high in fruit, is attractive and can be drunk immediately but does not age well. It was firstly used in the Beaujolais region but nowadays it is diffused in the world.

Miller and Howell (1989) applied various carbonic maceration treatments to Marechal Foch grapes. Two approaches were used to induce carbonic maceration. Treatments in Group 1 consisted of 15%, 30%, 60%, or 100% whole clusters in a fermenting must while they consisted in 100% whole clusters sealed under anaerobic conditions for two, four, or eight days, respectively in Group 2. Total acidity was inversely related to both increasing time of maceration and increasing percentage of whole berries. Total phenols increased with time of maceration while alcohol was inversely related to it. Salinas et al. (1996) studied the influence of the length of the anaerobiosis stage on the volatile composition of wines made from Monastrell grapes by carbonic maceration. The optimal sensory qualities were shown by wines that had undergone to a long period of maceration and then were aged in new wood, resulting in a higher concentration of ethylic esters and fatty acids and a lower alcohol concentration. The carbonic maceration was introduced in Spainôs Rioja region in late 1700ôs and it is still a common method today in some parts of Rioja - like Rioja Alavesa. The carbonic maceration practiced in Rioja uses open tanks, without addition of CO_2, and no effort is made to try to maintain as many berries intact as possible. Furthermore, another interesting practice in Rioja is the addition of small amounts of white grapes (<15%), in order to increases acidity and enhances the floral and fruity notes. Etaio et al. (2008) studied the effects of carbonic maceration and addition of white grapes (Viura cv.) on the sensory and physicochemical characteristics of young red wines. Their results showed that wines with carbonic maceration tended to have higher ethanol, free and total SO_2, red berry aroma and flavour, alcoholic flavour, and acidity. The wines with Viura grapes had significantly lower pH, dry extract, visual colour intensity and purple hue tannins, anthocyanins and total polyphenol index (which the authors attribute to a dilution effect due to the lower polyphenol levels in white grape skins), but there were no differences in total acidity and in the aroma or flavour attributes. De Leo and Massari (http://www.ismea.it/flex/AppData/Redational/Normative/pubnaz/20040514000200110.pdf) analysed several red wines, among which two Registered Designation of Origin (RDO) ñSalice Salentinoò and two Traditional Geographical Indication (TGI) ñSalentoò, produced in areas where Negroamaro vine is predominant. Each wine obtained by the traditional fermentation procedure was evaluated with respect to corresponding version, produced by carbonic maceration. The results showed that all the analysed wines have a good antioxidant activity that is comparable to that of many red Registered Designation of Origin Apulian wines as reported in literature. Moreover, the phenolic component in the wines obtained by traditional fermentation seemed to be different from that obtained by carbonic maceration, which had always lower total phenolic content.

Co-winemaking

One of the most influential factors of the sensory characteristics is the grape variety used in the elaboration of wine. Each grape variety has its own aroma profile and phenolic composition. Some grape varieties can be rich in certain compounds, while other grapes may be deficient. The content of these compounds may be modified by means of the winemaking process. An example is represented by the initial production of monovarietal wines, which are later mixed (ócoupagesö). However, the maceration and fermentation of different varieties could benefit from additional molecules provided by other varieties (Gómez García-Carpintero et al., 2010: Gómez Gallego et al., 2012), which results in a more complex formation than in monovarietal wines (Lorenzo et al., 2008a; 2008b). This complementary effect can be achieved with the co-winemaking of different grape varieties that implies both co-maceration and co-fermentation steps. In fact, interactions between phenolic compounds and stabilization reactions, and aroma extraction take place during maceration and just at the beginning of fermentation, so better results would be achieved if blending occurs at the vinification stage. Nevertheless, if this practice is carried out inadequately, it may damage wine quality due to anthocyanin dilution or pigment adsorption to the skins and pulp (Diago-Santamaría and Boulton, 2003). Co-winemaking is not commonly employed due to the different ripening periods of grapes, although this problem could be partially resolved with refrigeration of the grapes.

Gómez García-Carpintero et al. (2010) investigated the influence of co-winemaking technique on the sensory profile of wines made from minority red grape varieties cultivated in La Mancha region (Spain). Co-winemaking red wines were obtained by blending (a) Cencibel (50%) and Bobal (50%); (b) Cencibel (50%) and Moravía Agria (50%); (c) the three grape varieties Cencibel (33%), Bobal (33%), Moravía Agria (33%). Authors concluded that monovarietal Cencibel and Bobal wines presented a similar olfactory profile, while wines obtained from blending both varieties presented a complex and greater intensity in the general attributes than the monovarietal wines. The sensory profile of the wines obtained by co-winemaking of the three grape varieties was the most complex of all the co-winemaking wines.

Gómez Gallego et al. (2012) applied co-winemaking to produced red wines by pre-fermentative blend of grapes (1:1, w/w) from the predominant Cencibel (Tempranillo) variety in this region and the minor varieties Bobal, Moravia Agria, Moravia Dulce, Tortosí and Rojal. A three varieties blend (1:1:1, w/w/w) of Cencibel, Bobal, and Moravia Agria grapes was also produced. The best results were obtained using Bobal, Moravia Agria, and Moravia Dulce varieties for co-winemaking, especially in terms of colour characteristics. All co-winemaking wines significantly increased the total resveratrol content as compared to the Cencibel reference wine.

Co-winemaking of Monastrell wines with Cabernet Sauvignon or Merlot, at different proportions has been studied in terms of its odor activity value (OAV) in young and aged (in French oak barrels or in the bottle) wines by Lorenzo et al. (2008a). The co-winemaking wines were fruitier and sweeter than the monovarietal ones, enhancing their aroma characteristics. The best proportion was 60:40 in case of Merlot young and aged in barrels and in case of the bottled Cabernet sauvignon.

Cryomaceration

It is one of the most important techniques used during wine-making. While pre-fermentative cold maceration is largely used in the production of white wines, it has been only recently introduced among red grapes treatments (Parenti et al., 2006). It consists in submitting the mashed grapes to a rapid cooling (down to about 5 °C) and maintaining this temperature for hours or days, in order to improve the extraction of the compounds contained in the grape skins, such as phenolic compounds and the primary aromas (Carillo et al., 2011). If the pre-fermentation skin contact is carried out with dry ice, the skin cells are broken and disorganised. In fact, freezing increases the volume of the intracellular liquids thus disrupting the membranes and providing an easy exit for the aromatic and phenolic compounds (Couasnon, 1999). Wine produced by cryomaceration show higher aroma intensity, stability to oxidation, and stability of taste properties than wines prepared by maceration without cooling (Carillo et al., 2011).

The cryomaceration process can be performed in different ways. One of these requires the use of large-capacity refrigerator groups, which involve a high amount of energy consumption and very expensive plant costs. Besides, they very often damage the product due to friction generated in the pipes during the passage of the mashed grapes (Ribèreau-Gayon et al. 2000; Ferreira et al. 2002). A more advisable process is based on using cryogenic gas (CO_2 or N_2). It consists in injecting liquid CO_2 directly into the line that, during its evaporation, removes heat from the product to be cooled (Carillo et al., 2011). As the liquid CO_2 is injected at about $20 \cdot 10^5$ Pa, such plants present many problems and complications (Formato et al. 2010).

Parenti et al. (2006) performed experiments on Sangiovese grapes and evaluated the effects of both two different cryogenic agents (i.e., solid state carbon dioxide and liquid nitrogen) and temperatures (from -5 to +5 °C). According to their results, wines submitted to pre-fermentative cold maceration showed a better quality profile than the control. Liquid nitrogen showed a higher extraction of polyphenolic compounds than solid carbon dioxide and, for the latter, wine quality increased as the cold maceration temperature decreased.

Radeka et al. (2012) evaluate the effects of pre-fermentative cryomaceration on the aroma profile of rosé and red wines from Croatian aromatic cv. Muskat ruza porecki (*Vitis vinifera* L.). According to their results, higher concentrations of free and bound varietal aroma compounds were found in wines obtained by maceration at room temperature in relation to cryomaceration. From a sensory point of view, longer maceration treatments improved odour and overall wine quality, together with the intensity and recognisability of varietal Muscat aroma, while short-term cryomaceration was the preferable technique for the production of light rosé wines with pronounced

Muscat aroma and low phenolic content.

In 2000, Denmark was approved as a wine producing country by the EU. Fretté et al. (2012) investigated the effect of cryomaceration (liquid nitrogen) vs. a traditional pre-treatment (30°C) on the phenolic concentrations of wines produced from Rondo grapes grown on the island of Funen (Denmark). Compared to traditional pre-treatment, cryomaceration increased the content of quercetin by 6%, but reduced the content of anthocyanins, catechin and resveratrol by 11, 9, and 60%, respectively.

The effects of a pre-fermentation cold soak on extraction of colour and phenolic compounds during red wine making of Cabernet Sauvignon and Merlot wines were examined by Okubo et al. (2003). They observed that a cold soak at 10°C for 2 days resulted in higher A520 (red colour), A420 (yellow colour), and A520 (anthocyanin concentration) than the control wine.

Instead, there was no significant difference in A280 (index of total phenol concentration) between traditional and cold soaked wines.

Marais (2003) studied the effects of low-temperature skin contact (1, 2, and 4 days at 10 and 15°C) prior to fermentation on Pinotage wine composition and quality. Pinotage was bred in South Africa in 1924 as a cross between Pinot noir and Cinsaut noir (Hermitage). Polyphenols slightly increased with the increase in skin contact time. The highest quality Pinotage wines were produced by a pre-fermentative maceration at 10°C for 4 days, while the worse results were obtained at 15°C.

A study on the extraction of phenolics from berry skins and seeds of the Cabernet Sauvignon grapes during a red vinification was performed by Koyama et al. (2007). The influence of cold soak was also examined. The compounds contained mainly in berry skins such as anthocyanin, flavonol, and epigallocatechin units within proanthocyanidins were extracted during the early stage of maceration, whereas those in seeds (gallic acid, flavan-3-ol monomers, and epicatechin-gallate units within proanthocyanidins) were gradually extracted. Cold soak reduced the extraction of phenolics from the seeds.

Gambacorta et al. (2011) assessed the influence of cryomaceration (24 h at 5°C using dry ice) on the phenolic fraction of Aglianico, Montepulciano, Nero di Troia, and Sangiovese wines produced in Apulia, Southern Italy. They found that cryomaceration led to a decrease of anthocyanins (about 15%) in all cultivars. Phenols extraction from grapes was found to be dependent on the grape variety rather than on the applied winemaking technology.

Délestage

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The most difficult task for a winemaker who wants to do a red wine is to obtain a good exchange between the juice and the solid elements of the must. As fermentation begins, CO_2 bubbles pushes to the surface the solid parts in the must (skins, seeds, remains of leaves and stalks, etc.) and press the marc toward the surface, while this will be simultaneously pushed back down by the force of gravity. These phenomena contribute to create a hard cap, which only partially releases its elements to the juice. The solution would be a progressive dilution of the cap, through a replacement of this oversaturated juice with some less concentrated juice, which would produce an ideal extraction from the marc. Délestage, also called ѓrack and returnӧ, is a maceration technique designed to help optimize the exchange between the liquid and solid phase by emptying the fermentation vessel of liquid while airing the juice. Following several hours of cap draining, the liquid is gently pumped over, or returned, to the pomace. This procedure is designed to help oxygenate while minimizing mechanical grinding of the pomace and to increase the formation of acethaldehyde that induces the stabilization of the phenolic fraction of wine through the formation of bonds between tannins and anthocyans.

Zoecklein et al. (2008) compared Merlot and Cabernet Sauvignon wines obtained by a délestage involving partial seed deportation, with wines produced by manual cap punching (Merlot), and by mechanical punch-down (pigeage) systems (Cabernet Sauvignon). Fermentation reduced the percentage of colour from monomeric pigments and increased the percentage of colour from polymeric pigments for all treatments. Délestage wines generally had a higher percentage of colour derived from large polymeric pigments than either manual cap-punched or pigeage wines. Total glycosides were in greater concentration in the manual cap-punched merlot wines, and similar among the cabernet sauvignon treatments. According to Baiano et al. (2009), Primitivo wines obtained through délestage were the richest in total anthocyanidins and among the richest in the coumaroylated forms of anthocyanins if compared to traditional, saignée, delayed punching-down, addition of tannins, heating of must-wine, cryomaceration, and prolonged maceration. The importance of coumarylated forms is related to their sensory properties, since they affect the intensity of ñin-mouthò dryness.

Extended maceration

It is a method to extend the extraction of phenolic compounds (anthocyanins, flavan-3-ols, and tannins) from the solid parts of the grape beyond the period of alcoholic fermentation. The extraction of these compounds greatly changes the sensory properties and the aging possibility of wines. Winemakers can choose to extend the maceration period either by delaying the juice inoculation with yeasts or by delaying the pressing of skins after the completion of the alcoholic fermentation (Heartherbell et al., 1996; Watson et al., 1997; Boulton et al., 1998). The extension of maceration before fermentation allows to extract monomeric anthocyanins that in wine can polymerize and give rise to higher colour stability (Auw et al., 1996), while the extension of maceration after fermentation allow to extract alcohol soluble compounds such as high molecular weight astringent and bitter seed tannins (Cerpa-Calderón and Kennedy, 2008). Budic-Leto et al. (2003) studied the influence of different maceration techniques and aging on proanthocyanidins and anthocyanins of red wine cv. Babic in the Primosten vine-growing location in Dalmatia. Prolonged maceration caused an increase in the content of total phenols, vanillin index and proanthocyanidins, as well as a decrease in the content of anthocyanins in young wine. In a study published in 2008, Budic-Leto et al. investigated the effects of maceration conditions on the polyphenolic composition of red wine Plavac mali. They observed that prolonged skin contact time significantly increased the content of low molecular weight proanthocyanidins and decreased the content of anthocyanins. Weaker colour intensity of 14-month-aged wines was detected in the wine made with prolonged skin maceration time in which the ratio of proanthocyanidins/anthocyanidins was the highest. According to Baiano et al. (2009), the extended maceration was the worst winemaking technology among those assayed for the processing of Primitivo grapes (traditional, délestage, saignée, delayed punching-down, addition of grape seed tannins, addition of ellagic-skin-seed tannins, heating of must-wine, cryo-maceration, and prolonged maceration) in terms of antioxidant content. In a recent study of Casassa et al. (2013), it was checked if there may be a synergistic effect of ethanol and prolonged skin contact on the extraction of certain phenolics that may negatively impact wine sensory properties. They found that the ethanol concentration differing by 1.2% v/v had no effect on tannin and anthocyanin extraction, colour, tannin degree of polymerisation, polymeric pigment formation, and recovery of anthocyanins and tannins in the pomace after maceration. The tannin content of wines produced with extended maceration was mainly derived from seed tannins, whereas control wines had a balanced proportion of seed and skin tannins. The anthocyanin concentration was lower in extended maceration wines, whereas polymeric pigments and tannins were predictors of astringency.

Malolactic fermentation

Malolactic fermentation, i.e. the enzymatic decarboxylation of l-malic to l-lactic acid and CO_2, is an important secondary fermentation carried out by lactic acid bacteria during the

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production of red wines. In addition to the deacidification action, it contributes to complexity of the flavour and to confer a degree of microbiological stability to the wine. There are different ways to perform this fermentation including the addition of commercial lactic bacteria or the use of oak barrels. Malolactic fermentation can spontaneously occurs after alcoholic fermentation when wine conditions are favourable for the growth of lactic acid bacteria, but it is not predictable (Cabrita et al., 2008). Malolactic fermentation is mainly produced by the action of the *Oenococcus oeni* species (López et al., 2007), while other genera such as *Lactobacillus, Leuconostoc,* and *Pediococcus* may also be present and occasionally cause undesirable spoilage in wine. During recent years, in order to enhance the results of the use of malolactic bacteria, many technologies have been developed, involving the use of high densities of cells or enzymes, free or immobilized onto different matrices. Cabrita et al. (2008) evaluated the impact of malolactic fermentation (performed spontaneously or by the inoculation of two different commercial lactic bacteria) on low molecular weight phenolic compounds. The main results are related to the hydroxycinnamic acids and their derivatives, which were the main compounds modified by malolactic fermentation, independently of the use or not of commercial lactic bacteria. The decrease in concentration of caftaric, coutaric, and fertaric acids, and the increase in concentration of the corresponding free forms are linked to the lactic acid bacteria metabolism. Many studies concern the interactions between phenolic compounds and lactic acid bacteria in wines and refer to the metabolism of hydroxycinnamic acids (ferulic and coumaric acids), by different bacteria species, which results in the formation of volatile phenols such as 4-ethylguaiacol and 4-ethylphenol (Gury et al., 2004). It has been suggested that phenolic compounds can behave as activators or inhibitors of bacterial growth depending on their chemical structure (substitutions in the phenolic ring) and concentration and that they can affect the bacteria metabolism, since they favour the use of sugars and malic acid (García-Ruiz et al., 2008). Abrahamse and Bartowsky (2012) investigated the effects of inoculating Shiraz must with malolactic bacteria at various stages of the alcoholic fermentation (at the beginning of alcoholic fermentation (co-inoculation with yeast), mid-alcoholic fermentation, at pressing and post alcoholic fermentation) on wine chemical composition. Co-inoculation greatly reduced the overall fermentation time without affecting the rate of alcoholic fermentation. The fermentation-derived wine volatiles profile was different from those of the wines where bacteria were inoculated late or post alcoholic fermentation. However, there were differences in anthocyanin and pigmented polymer composition, with co-inoculation exhibiting the most distinct profile. According to López et al. (2012), the pH of the must influenced the clonal distribution of the *Oenococcus oeni* strains, which conducted the malolactic fermentation and also the concentration of amino acids in the wines after alcoholic fermentation. These aspects could account for the higher biogenic amine formation in wines with the lowest pH during spontaneous malolactic fermentation. In these wines, inoculation with a malolactic starter was favourable since it produced a lower biogenic amine concentration after malolactic fermentation. These results were confirmed by Smit and du Toit (2013), who found that the presence of indigenous lactic bacteria increased the risk of biogenic amine formation and that inoculation proved to reduce biogenic amine production over time compared to spontaneous malolactic fermentation in Pinotage and Cabernet Sauvignon wines.

Micro-oxygenation

Micro-oxygenation is a common winemaking practice for red wine, consisting of the continuous addition of small amounts of oxygen to wine in order to improve its colour, aroma, texture and conservation. Micro-oxygenation was formally developed in France in the mid 1990s in order to replicate barrel conditions for wine matured in large stainless steel and cement vessels (Ducournau and Laplace, 1995; Lemaire, 1995) although, nowadays, it has also become a powerful tool to produce colour-stable wines and it may reduce the length of production process. In terms of sensory qualities , the micro-oxygenation process increases fruity and spicy flavours, enhances the stability of red tones and decreases herbaceous aromas and astringency (Gómez-Plaza and Cano-López, 2011; Cejudo-Bastante et al., 2011a). Chemically, this technique increases both volatile compounds such as acetaldehyde, vanillin and syringaldehyde, and the non-volatile products of reaction between anthocyanins and flavanols, pyruvic acid, acetaldehyde and vinylphenols. Furthermore, it has been proved that micro-oxygenation influences the concentration of different secondary metabolites in wine (Cejudo-Bastante et al., 2011a; Gómez-Plaza and Cano-López, 2011; Waterhouse and Laurie, 2006). Anthocyanins are responsible for the purple-red colour of young wines but they are unstable and participate in reactions during fermentation and maturation to form complex pigments. Several mechanisms have been known for the formation of these new pigments, which stabilize wine colour since they partly resist discolouration by SO_2 and provide better colour stability at wine pH (Mateus et al., 2002): *a)* direct reactions between anthocyanin and flavanols (Fulcrand et al., 1996; Remy et al., 2000); *b)* reactions between anthocyanins and flavanols involving acetaldehyde, to give a compounds with an ethyl bond, that can be protonated to form a coloured compound (Atanasova et al., 2002;

Sauciere et al., 1997); *c)* formation of pyranoanthocyanins through the reaction between anthocyanins, acetaldehyde, and other compounds, such as pyruvic acid, vinylphenols and vinylflavanols (Fulcrand et al., 1996; 1997; Romero & Bakker, 2000a; 2000b). The best results can be obtained in the first 2 months of aging (Parish et al., 2000). Micro-oxygenation can be applied at any moment during vinification and maturation but, if the colour stabilization is the main goal, a distinction has been made between the influence of this procedure before or after malolactic fermentation. The differences highlighted are partially related to differences in the concentration of SO_2 and mainly attributed to the free anthocyanin concentration. Micro-oxygenation seems to be much more effective in improving wine structure before malolactic fermentation when tannins and anthocyanins are still mostly in simple monomeric form (Gómez-Plaza and Cano-López, 2011). High oxygen levels, instead, reduces wine aromatic complexity and promote wine oxidation (Moutounet et al., 2001). Another advantage of micro-oxygenation is that treatment with low doses of oxygen speeds up tannin polymerisation resulting in softer tannins, decreased astringency and vegetative and herbaceous flavours of wine (Parish et al., 2000; Paul, 2002; Blackburn, 2004), and an overall improvement in mouthfeel. Cejudo-Bastante et al. (2011a) investigated the effects of micro-oxygenation and oak chip treatments on colour-related phenolics, volatile composition and sensory characteristics of Petit Verdot wines. Micro-oxygenation treatment promoted the stabilization of red wine colour by increasing the formation of pyranoanthocyanins and anthocyanin-ethyl-flavan-3-ol adducts and increased the scores for the plum/currant and spicy attributes, and for the tobacco and nutty notes wines. The typical oak chip aromas (vanilla and woody) were reduced by micro-oxygenation. In the already cited work of Arfelli et al. (2011) on Sangiovese wines, micro-oxygenation combined with the use of oak

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chips and yeast lees reduced astringency, increased balance, and enhanced vanilla perception. Devatine et al. (2007) investigated the incidence of dissolved carbon dioxide in wine on oxygen transfer. This parameter must be considered when the micro-oxygenation is applied during or after alcoholic fermentation. Authors established that the presence of dissolved carbon dioxide affected the efficiency of the transfer of oxygen to the liquid by decreasing it of one order of magnitude when carbon dioxide concentration changed from 0 to 1.4 g/L.

Saignée

Saignée (or bleeding) is the removal of juice from a red must immediately after destemming/crushing. Usually, it is performed to concentrate flavours and phenols in the wine made from the remaining must (Ritchie, 2010). It is based on the matter that, when the juice is released from a crushed red grape, it contains water, sugars, and acids, and only little amounts of aroma compounds, anthocyanins, and other phenolic compounds because the majority is found in the skins. After 30 minutes to one hour, however, the skins start to release these compounds thus, to concentrate must, saignée should be carried out as soon as possible after crushing. The percentage of juice removed is in the range 5-30% depending on the raison of the saignée. In some cases, this technique should be applied with caution. For example, when the must concentration is made to counterbalance the impossibility for grapes to reach optimum maturity, saignée could also concentrate undesirable vegetal flavours responsible for bitterness and astringency. Furthermore, juice also contains organic acids and yeast assimilable nitrogen, thus a nitrogen addition or an acidity correction could be necessary (Ritchie, 2010). Baiano et al. (2009) compared the effects of saignée to those of other winemaking procedures (traditional, délestage, saignée, delayed punching-down, addition of grape seed tannins, addition of ellagic tannins, heating of must, cryomaceration, and prolonged maceration) on the phenolic content and antioxidant activity of Primitivo musts and wines. Authors concluded that the wines obtained by the application of other procedures (for example, the addition of tannins) showed higher antioxidant contents also after 1 year of storage. Nevertheless, saignée was recommended to increase the radical scavenging activity of Primitivo wines.

Thermovinification

It consists in heating grapes and must to near-boiling temperatures prior to fermentation and it is used to rise up the extraction of colour and tannin from grapes relatively deficient in one or the other or as a sanitizing agent to reduce the *Brettanomyces* incidence. Some bulk white wines have utilized thermo as well, in order to get the most out of over-cropped fruit. Applying heat also inhibits troublesome enzymes such as polyphenol oxidase and laccase. The effects of heating deal with its ability to break down the cell structures. Hot or thermo- vinification cuts drastically the waiting time required, since colour migration from the skins to the liquid phase is obtained in minutes. After crushing and destemming, the must is heated for a few minutes up to 80-85°C. The heating product is sent to a flash cooling system where the temperature is lowered to 35-40°C. Probably, the flash cooling causes the intercellular explosion of the grape skins thus favouring a better extraction. Nevertheless, the effectiveness of thermovinification greatly depends on the grape variety. After cooling, the must is decanted and clarified before fermentation.

Chiaromonti et al. (1999) studied the phenolic content of musts and wines of Niellucciu vinified according to two different techniques (thermo-maceration and the classic maceration). According to their results, the wines obtained by the two techniques showed similar anthocyanin contents, but the structure of the pigments differed. In fact, the thermo-maceration determined an extraction of anthocyanins in the form of quinonic, carbinol bases and chalcone, while the classic maceration gave a wine richer in anthocyanins in the form of flavylium cations. Atanackovic et al. (2012) studied the influence of winemaking techniques and cultivars on the resveratrol content, total phenolic content and antioxidant potential of red wines made from the cultivars Merlot, Cabernet Sauvignon, Pinot Noir and Prokupac. Authors did not establish a clear correlation between the winemaking technique and the resveratrol content of wines. Nevertheless, thermo-vinification increased the total phenolic content and antioxidant potential of all samples. In an already cited research, Fretté et al. (2012) compared the effects of thermovinification (70 °C) to those a traditional pre-treatment (30°C) on the content of phenolic compounds in Rondo wines. Compared to traditional pre-treatment, thermovinification increased the content of anthocyanins, catechin and resveratrol by 62%, 69% and 260%, respectively.

White vinification

The most interesting types of white vinification include: addition of enzymes and tannins; aging on lees; carbonic maceration (although unusual for white wines); cryomaceration; hyper-oxygenation; reductive winemaking.

Addition of enzymes and tannins

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Enzymes can be added also during aromatic white winemaking. The utilization of aromatic enzymes (activities of β-glucosidase, rhamnosidase, arabinosidase, furanosidase) permits to enhance the aromas by transformation of non smelling precursors, often composed of sugars linked to the odorant aromatic molecule (like terpenol, norisoprenoides). Those enzymes are used on grapes like Muscat, Gewürztraminer, Riesling, which are known to contain those aromas in free and bound forms, but also on other varieties like Chardonnay, and also low aromatic varieties like Muscadet and Ugni blanc, with effective results (Gerland, 2003). Espejo and Armada (2010) evaluated the effects of two commercial pectolytic enzymes (one containing mainly polygalacturonase activity, indicated for the extraction of phenolic and aromatic compounds, and another with primary pectinase (pectinesterase and polygalacturanase) activity and secondary cellulose and hemicellulase activities on some oenological parameters of musts and wines from sun-dried grapes of the Pedro Ximenez variety. The enzyme preparations, combined with dynamic maceration, increased the degrees Brix of the musts and improved the total juice yield but did not affect the total phenolic index. The effects of the enzyme addition, instead, were greatly appreciated in the sensory evaluation since it increased intensity of the typical aroma (note of raisins, figs, honey, caramel, and toffee). LaurenŞu Itu et al. (2011) enzymatically treated white grapes of Muscat Ottonel variety with pectolytic enzyme preparation. The enzymatic treatment presented a beneficial effect on the alcoholic fermentation and the final wine composition. By using maceration enzymes, the wine aromatic intensity is emphasized, because the enzymatic preparation contains high concentrations of glycosidase, acting on the first stage of the enzymatic mechanism, and ϐ-glucosidase, acting on the second phase of enzyme mechanism able to release the aromatic constituents. Addition of enzymes that hydrolyse β-glycosidic bonds can be used to increase the potential of aromatic white grapes, since they allow the release of odoriferous aglycons from non-volatile glycosides. In a work of Dziadas and JeleŒ(2011), two white grape varieties, Nachodka (Traminer × Müller Thurgau) and Perğa Zali (Siewiernyj × Odeskij Ustojczcziwyj), grown in Golesz vineyard in Jasğo were used for winemaking. Two commercial enzymes, containing different enzymatic activities, were added to the must before fermentation. Addition of glycosidases resulted in increase in investigated monoterpenes in both the varieties. Total amount of monoterpenes (linalool, nerol, geraniol, ϐ-citronelol, Ŭ-terpineol) decreased after 6 months storage, although their levels in enzyme treated wines were significantly higher than in control samples. From a sensory point of view, enzyme treated wines were perceived different from control samples with more pronounced fruity and floral notes.

Cíchová et al. (2008) studied the effects of the addition of four tannin preparations in white wine (Müller Thurgau, Welschriesling, Chardonnay, Sauvignon blanc, Rheinriesling, Sauvignon blanc, and Pinot blanc). According to their results, the addition of all tannins was helpful for Sauvignon wine, which was roundness without expressive losses of fruity in smell. On the contrary, the addition of tannins was inappropriate in Chardonnay, because the tannin addition determined a decrease in the sample fruity flavour. Thus the use of tannin cannot be generalised.

Aging on lees

Sotolon (4,5-dimethyl-3-hydroxy-2(5)H-furanone) is a volatile compound with an intense odour of curry, which contributes to the aromas of ñvins jaunesò from the Jura, sherries, French fortified wines (Vins Doux Naturels, VDN), and port. Its concentration increases during the barrel aging of sweet wines or during the aging with yeast óflorô of wines from grapes Savagnin. It is also well known that oxidation phenomena are involved in the generation of sotolon in wine (Silva Ferreira et al., 2003). According to Lavigne et al. (2008), yeast lees were capable of minimizing the formation of sotolon in dry white wines during aging. Moretti et al. tested various kinds of aging of ñMalvasia Puntinata of Latiumò: contact with yeast lees at different temperatures, several mannoproteinic preparations, β-glucanase or β-glucosidase enzymes, inactivated yeasts, French or American oak. They found that the different treatments did non affect neither the basic physical-chemical parameters nor the wine catechins and benzoic acids concentration. The wine aged with inactivated yeast and β-glucanase gave the best results, obtaining higher scores for floral and fruity aroma.

Carbonic maceration

The carbonic maceration of white wines is unusual, but experiments in this field were performed. In a work of Carroll (1996), grapes of four muscadine (*Vitis rotundifolia* Michaux) cultivars were subjected to carbonic maceration. When compared to the standard wines, the carbonic macerated white wines had lower pH values, higher titratable acidity and phenols, lower alcohol, were yellower in colour and were judged significantly lower in sensory quality. The carbonic maceration is not recommended for white wine production.

Cryomaceration

Pre-fermentative skin cryomaceration is used by winemakers to enhance the varietal character of white wines through the extraction of terpenes, thiols, and other aromatic compounds present in the grape skins. According to Peinado et al. (2004), cryomaceration provides well-balanced and better-rounded wines having a stronger body in the mouth. Nevertheless, this strengthening effect could also alter the wine typicity and introduces heavy, coarse aromas (Delteil et al., 2000). Cryomaceration also increases the phenolic extraction from skins, and phenolics influence the perception of volatile thiols. For example, (+)-catechin and quercitin increase the concentration required to perceive 3-mercaptohexan-1-ol, whereas the opposite happen for 3-mercaptohexyl acetate and (+)-catechin.

Carillo et al. (2011) tested an innovative plant prototype for rapid grape cooling for production of a white wine from Bianchello del Metauro. They also set up a numerical model for the cooling tunnel, and performed numerical simulations to investigate the operative parameters of the machine. According to their results, all phenolic parameters were higher in the cryomacerated wines, while alcohol, reducing sugars, acids, and volatile acidity were less affected by the different winemaking technique. The cryomacerated wines also have a deeper yellow colour and was preferred by panelists for their rich and delicate aroma.

Peinado et al. (2004) applied the pre-fermentative cryomaceration to produce young white wines from Airen and Macabeo grapes, two Spanish varieties. According to their results, pre-fermentative cryomaceration significantly increased the solvent, floral, fruity and balsamic flavour in the Airen variety, whereas only the solvent series was affected in the Macabeo variety.

Esti and Tamborra (2006) submitted Fiano grapes (a white, not aromatic vine native of the South Italy) to a maceration before fermentation at 10 °C for 10 h. The concentration of aglycons, liberated by enzymatic hydrolysis, was much higher in the Fiano wines that had undergone the skin maceration. The prefermentative maceration also led to the presence in the wines of acid generated free forms of actinidol 1 and 2.

Piñeiro et al. (2006) found that winemaking practices devoted to increase the aromatic properties of wines produced different results depending on the variety of grape. More specifically, cold soaking produced very different results when applied on aromatic varieties such as Palomino fino and Traminer or on non-aromatic ones such as Viura. In fact, the differences between cold soaking and fermentation without maceration were related to the higher extraction of terpenes.

Piombino et al. (2010) studied the effects of cryomaceration on free and glycosilated flavours of Malvasia delle Lipari, a high quality passito wine produced in the Aeolian island of Salina (Sicily, Italy). They found that total free volatiles and total bound volatiles of the cryomacerated wine were respectively 45 and 36% higher than those of the traditional wines. Among the free volatile, two alcohols significantly increased namely 3-methyl-1-butanol and 2-phenilethanol. Among the bound volatile, four terpenols significantly increased namely linalool, α-terpineol, geraniol, and nerol. Only epoxylinalool decreased.

Baiano et al. (2012) investigate the effects of cryomaceration and reductive vinification on chemical and physical indices and on antioxidant compounds of Sauvignon blanc wines. The strongest changes were for organic acid concentrations (tartaric, in particular) and phenolic content. Cryomaceration caused a noticeable precipitation of tartaric acid and protected flavans reactive with vanillin from the action of oxidative enzymes.

Hyper-oxygenation

One of the most important problems in white wine production is the browning of the must, due to the oxidation reactions that alter wine organoleptic characteristics, mainly colour and aroma.

As it will see in one of the following paragraphs, enologists traditionally recommended the addition of sulphur dioxide, although it could provoke toxic and allergenic effects on human health. Nowadays, a new system aimed to avoid further oxidation is based on the oxygen addition. The hyper-oxygenation is a pre-fermentative technique based on either oxygen or air addition to a non-sulphited must until saturation and before the beginning of the fermentation in order to reduce the content of phenolic compounds and to increase the colour stability of wine produced from this must. Phenolic precursors are enzymatically oxidized to brown high molecular weight polymers, which precipitate and must be removed from the must before alcoholic fermentation, due to their high solubility in alcohol (Castro and García-Barroso, 2000). Different scientific results have been reported concerning the effects of hyper-oxygenation on white wines aroma to highlight the importance of the grape variety submitted to hyper-oxygenation procedures. According to Dubourdieu and Lavigne (1990), C6 alcohols concentration decreased in Semillon musts due to hyper-oxygenation, while they found marked decreases of isoamylic alcohols, acetaldehyde and ß-damascenone in Chardonnay white wines (Cejudo-Bastante et al., 2011b). Instead, Artajona et al. (1990) and Schneider (1994) observed increases of free terpenes, acetates of large-chain alcohols, and fatty acids and their esters in Spanish, French, and German white wines, while Cheynier et al. (1989; 1991) proved the positive effect of must hyper-oxygenation on the aroma quality of Chardonnay, Moscatel of

Alexandría, Macabeo, Parrellada, and Grenache wines. The effectiveness of hyper-oxygenation depends on the amount of oxygen required to fully oxidise the flavonoid phenols in the juice, the pH and temperature, and the fraction of phenols that will oxidise under polyphenoloxidase activity. To successfully manage hyper-oxigenation, polyphenoloxidase activity should be maximised. Aside from avoiding SO_2, this also means the juice should not be fined or clarified. The juice should be sparged with pure oxygen or compressed air. Around 20-30 mg/l oxygen (15-23 ml/l oxygen) or 95-140 mg/l air (70-105 ml/l air) are required. Repeating the sparging procedure is recommended. The juice should then be separated from the precipitated oxidised phenols and SO_2 may be added after clarification, but it is usually avoided (http://www.brsquared.org/wine/Articles/SO2/SO2.htm). Cejudo-Bastante et al. (2012) applied hyper-oxygenation to Macabeo and Airén white wines and studied its effects on colour characteristics, phenolic and volatile composition. Hyper-oxygenation treatment significantly decreases all the phenolic compounds in must, young and one-year-aged wines. In particular, this treatment reduces hydroxycinnamic acid derivatives, flavonols, and the phenolic compounds of recent identification (derived from 2-S-glutathionyl-caftaric acid or grape reaction product (GRP) derivatives). Nevertheless, the contribution of the yellow colour component (b*) of white wines derived from hyper-oxygenated musts was significantly higher in comparison with untreated ones. Furthermore, the concentration of major volatile compounds and some alcohols (namely, C6 alcohols, terpenes, and lactones) was higher in wines derived from hyper-oxygenated musts. These results were substantially confirmed by Cejudo-Bastante et al. in a work performed on Airén whirw wines in 2013.

Reductive winemaking

Reductive vinification is increasingly common in France and Europe for the production of white and rosé wines with aromatic varietal characteristics. It is particularly suited to grape varieties rich in varietal aromas that are sensitive to oxidation such as Sauvignon, Colombard, Petit Manseng, Chenin, Gewürztraminer, or like Grenache, Cabernet franc and Merlot with regards to rosé wines (Ardilouze). In these wines, secondary characters, such as those caused by oak, malolactic fermentation and extended yeast lees contact, are avoided. Reductive vinification is mainly carried out by limiting the contact with oxygen and early addition of SO_2 combined with ascorbic acid. Reductive vinification ensures a good protection against enzymatic oxidations during the pre-fermentation stage, but the simultaneous presence of ascorbic acid and sulphur dioxide does not guarantee a lasting total protection against oxidation. Furthermore, ascorbic acid may favour the transition from a protective to an oxidative phase during wine aging (Peng et al. 1998). The hyper-reductive vinification technique applies inert gases such as CO_2 and N_2 to ensure the continuing protection against oxidation also during the crushing phase. This also ensures a satisfactory extraction of desirable organoleptic compounds, which are mainly located in the skin. Reductive winemaking is used alone or in combination with a prefermentative cryomaceration step. Antonelli et al. (2010) performed an explorative study to verify the applicability of reductive winemaking on a semi-aromatic white grape (Sauvignon blanc) and a white neutral one (Trebbiano romagnolo). All phenolic parameters were higher in wines produced under reductive conditions, while other substances such as alcohol, reducing sugars, acids, and volatile acidity acids were less affected by the different winemaking techniques. A deeper yellow colour was a direct consequence of the higher phenolic content of wines, while the optical density at 320 nm was related to caftaric acid integrity. Panelists preferred the wines produced under reductive conditions, since they were characterized by a richer and more delicate aroma. Mattivi et al. (2011) found positive effect of reductive winemaking also on Lugana wines, a traditional white wine from the Garda Lake region (Italy), produced from a native grape variety, Trebbiano di Lugana. According to Baiano et al. (2012), the vinification in reductive conditions obtained through the addition of a mixture of potassium metabisulfite and ascorbic acid, alone or combined with a cryomaceration step, gave wines with high solids content. Moreover, it caused a greater extraction of phenolic compounds from skins compared to the traditional white vinification or cryomaceration alone, due to SO_2 solubilising effect. Baiano et al. (in press) compared the traditional white vinification with a combined cryomaceration-vinification in reductive conditions of Falanghina and Bombino bianco, two wine grape cultivars of Southern Italy. According to their results, vinification in reductive conditions combined with cryomaceration enhanced the oenological potential of grapes by increasing the content of sugars, phenolic compounds (and also the yellow colour), and aroma of white wines and protecting them from oxidation. Titratable acidity decreased with cryomaceration due to the tartrate precipitation, whereas the malic acid was greatly extracted from pulps and skins. The reductive conditions applied allowed to obtain a protection of the SO_2 by the presence of ascorbic acid, thus the wines exhibited higher free/total SO_2 ratio.

CONCLUSIONS

Scientific and technical advances have been of enormous importance in wine history. Many winemaking procedures have been developed in order to enhance quality and to offer highly diversified wines from a same grape variety. Furthermore, the different wineries formulate customised winemaking procedures according to their needs. The choice of a vinification method cannot be accidental but it must calibrate on the oenological aptitudes of grapes, in order to exploit their strengths and minimize their weaknesses.

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