Chapter 1
Introduction

1.1 Scope of the book

The primary meaning of the word 'wine' is the product of the aqueous fermentation by yeasts of the sugars in the juice of grapes. The fermented juices of many other fruits are sometimes also called wines, though they do not enjoy the same popularity or prestige as the grape wines. Fermented liquids from materials containing starch or cereals are usually called 'beers'. The term wine is incorrectly used, for example, in rice wines, since the sugars in rice are stored as starch. Since fermenting yeasts can only convert sugars into alcohol, raw materials containing starch need to be processed so that, first, sugars are generated, for example, by hydrolytic cleavage of the starch. Uniquely, grapes contain tartaric acid, which has preservative qualities, and which, in addition to the presence of fermentable sugars, gives wines both a relatively high acid and alcohol content.

This book is solely concerned with wine from grapes. The focus is on the chemistry and flavour of table wines, which are normally consumed with meals. These wines have an alcohol content of 9–15% v/v (percent by volume), typically 11.5–14% v/v for red wine. Many red wines from hot wine regions exceed this percentage since the grapes are picked more mature with higher sugar levels. Wines consumed before a meal (aperitifs) are usually 'dry' (low sugar content) and often fortified to raise the alcohol content to about 20% v/v. Wines consumed after a meal tend to be sweet, for example, made by fortification with alcohol before the yeasts have converted all the sugar into alcohol, giving fortified wines such as Port as made in the Douro region in northern Portugal. Such fortified sweet wine styles are also made in other regions, and will be referred to as Port style. Fortification of dry wine followed by a special maturation process gives Sherry, as made in the Jerez region in Spain. Some other wine regions also use variants of this production to make Sherry style wines. Sherry can either be kept dry to be served before a meal or sweetened to be served after

Wine Flavour Chemistry, Second Edition. Jokie Bakker and Ronald J. Clarke.

a meal. The wine-making process of the classic wines Port, Sherry and the less popular Madeira will be described separately.

There is a very wide range of types of table wines, from sweet to dry and from still to sparkling, including its most famous example, Champagne. Table wines can be red, rosé or white, the colours depending on the choice of grapes and the wine-making processes used. The wines can be sweet or dry, although red wines tend to be always dry, while white wines are produced from dry to very sweet, with a range of different sweetness levels in between. A most remarkable sweet white wine is made from grapes infected by *Noble Rot* that is caused by a mould (*Botrytis cinerea*). The term 'wine' will be restricted to the main species of the vine plant, *Vitis vinifera*, which covers about 98% of the total wine production from grapes.

1.2 Historical background

There is much historical information on wine, for example, Johnson's (1989) excellent writing and McGovern (2003). It is generally considered that vines originated from the Caucasus area of Russia, between the Baltic and the Caspian Seas. After the Stone Age, some 6000 years ago, settled agricultural practices developed in the 'Fertile Crescent' of Mesopotamia and Egypt. Wild vines, botanically known as *Vitis vinifera sylvestris*, became domesticated and strictly speaking became the so-called *Vitis vinifera L. sativa*.

The *Vitis* genus contains many similar species, with other names such as *Vitis labrusca* (see the next paragraph). From those very early origins in Mesopotamia and Egypt, vines and wine-making methods were exported to the Greek- and Latin-speaking world of the Mediterranean. After the decline of these civilizations, wine production in Europe was not established until late medieval times. Wines were shipped in barrels and even countries with little or no wine production could enjoy drinking wine. Fortified wines such as Sherries (the Sack of Shakespeare's Falstaff) developed as a result of the Arabian invention of distillation, which gave the required skills to prepare fortifying spirit that could be added to wines. In the late nineteenth century wine production was fully established in France. France, Italy and Spain are still the three largest wine producers.

Speculation remains, however, about the flavour of these early wines compared with the wines we know today. Grape juice is fairly easily fermented by ubiquitous yeasts, and the fermented product can be reasonably stable due to its relatively high alcohol and acid content. However, there are longer-term storage problems and it is likely that wine spoilage was a frequent problem. This was due to a lack of understanding of the actual processes involved in vinification and their effective application. For example, it was not until the days of Louis Pasteur in the 1860s that the role of yeasts in wine fermentation, in addition to the role of some lactic acid bacteria in wine spoilage, was uncovered. The scientific achievements of Pasteur regarding the discovery of the microbiological processes involved in wine-making laid the foundations for the modern wine industry.

As late as the eighteenth century, wines were mostly sweet, although even from these more recent times we have little information regarding the sensory properties of the wines. Roman wines are thought to have been more like syrups. Wines were stored and transported in amphorae, which were long earthenware vessels fitted with stoppers, often made of waxy materials. The Romans used glass decanters to bring wine to the table but glass was too fragile for storing wine. An especial boost came with the invention of glass bottles in the early seventeenth century that were sufficiently strong to allow the transport and storage of wine. Once corks started to be generally used to seal wine bottles, it was a relatively small step to mature the wine in bottles, which had to lie at a fairly even temperature to prevent leaking. Wines have long been imported to the UK, where there was an appreciative market for so-called fine wines. For example, there was a marked interest in red wines from Bordeaux in the early twentieth century, to accompany the lengthy Edwardian dinners.

The native vine plant is confined to certain latitudes of the world and its domesticated version similarly requires favourable growing conditions. In particular, vines thrive in a climate with the right combination of sun and rain, although varieties/cultivars have been adapted to suit various climatic conditions. The type of soil is important, with adequate drainage being a prerequisite for successful vine cultivation. The areas of growth include North and South America, outside the tropics and excluding the very temperate zones. The commercial production of wines in many regions outside Europe did not really develop until the late nineteenth century. White settlers in Australia and New Zealand were interested in wine-making but only after World War II did the wine industry really develop. The spread of vine and wine is probably also closely linked to social and cultural aspects of communities.

Viticulture in Europe and elsewhere, like the production of other domesticated plants cultivated for food and drink, has been closely associated with the activities of plant breeders. Hence, over the centuries many varieties/cultivars of the species *Vitis vinifera* have been selected, e.g. *Vitis vinifera* Pinot Noir, and are responsible for the various wines that are available in the market place. An important part of the history of wine is the disease caused by *Phylloxera*, a root louse pest accidentally imported from America that struck nearly all vines in Europe in the 1870s, devastating many vineyards by killing the vines and thereby ruining the wine industry. It was not until the discovery that grafting local European vines onto American imported root-stocks conferred resistance to the disease that the wine industry in Europe started to recover. Ironically, *Phylloxera* eventually attacked vines in California around 1980, damaging many vineyards.

1.3 Wine flavour

The smell and taste of a wine are directly associated with the chemistry of the entire wine-making process. The word flavour usually indicates the combination of smell (or odour) and taste. However, when assessing the

sensory properties of wine, the word 'tasting' is used to indicate that the flavour of the wine is being judged. The flavour of wine originates from (1) the grapes, (2) the treatment of the must (grape juice) and its fermentation and (3) the maturation process of the wine. The chemistry of the flavour compounds derived from these three sources will be discussed in some detail for both non-volatile (Chapter 3) and volatile (Chapter 4) compounds.

Wine writers in numerous books and articles, many in the English language, have dealt with the subject of wine flavour. Some texts are aimed at the marketing aspects of wine and emphasize the opinions of expert wine tasters. Other texts are more critical, such as Barr (1988). Of course, there are also numerous texts in French and German, dealing with all aspects of wine. The number of technical texts which directly relate the flavour of the wine to its chemistry is much more limited, though there are some chapters in books on food and beverage flavour in general (see Bibliography). Many scientific papers describe only individual aspects of wine flavour and its chemistry. None of these texts are complete; they omit to raise many questions and fail to answer many others. An exception is the comprehensive scientific book of Jackson (1994, revised for the second and third edition in 2000 and 2008 respectively), which discusses in detail the three interrelated topics of wine science: grapevine growth, wine production and wine sensory analysis. Ribéreau *et al*. (2006) have published a similar work in two volumes (in English).

The term 'wine tasting' is often used and suggests ignorance of the essential nature of wine flavour, which is a combination of (a) the five taste sensations (sweet, salt, sour, bitter, umami) from non-volatile substances perceived on the tongue and (b) the aroma (or smell) sensation from volatile substances perceived by the olfactory organs behind the nose. Volatile substances reach the olfactory organs by two routes, sometimes referred to as the nasal and retronasal routes. Nasal means that volatile compounds will reach the olfactory organ through the nostrils of the nose during the period of 'nosing' the wine from the glass. Nosing is the traditional sniffing of the air space above the glass of wine, before any sample is placed in the mouth. Once in the mouth, the wine is warmed up, moved around in the mouth and there is the option of noisily sucking air through the mouth. All these actions help the volatile compounds to escape from the wine and to travel retronasally via the back of the mouth to the olfactory organ. Volatile compounds detected during nosing are often described separately, and may or may not be similar or identical to those detected on the palate. Wine tasting will be discussed in Chapter 5.

There is no consensus in the use of terms like bouquet, aroma, etc. and different wine writers may use them with different meanings. The term 'aroma' is most commonly used to describe the smell of the wine derived from the grapes, while the term 'bouquet' tends to refer to the smell of the wine formed as part of the development during maturation.

The quality and quantity of colour as well as the clarity of the wine are assessed entirely by eye, usually before the tasting. Next, our sense of smell

and taste are used to assess the flavour of the wine. The depth of intensity and the multicomponent detection of flavour notes in wines (usually described in terms of flavour notes from other fruit/vegetable/mineral/animal sources) that are used to describe wine attributes by many expert wine tasters is surprising to the non-expert wine-drinker, and at times stretches credulity. In addition to flavour recognition and description, there are also the perceptions of mouthfeel, temperature, bubbles, etc., which all are registered and assessed by our senses. Over and above the enjoyment of the wine flavour, wine is also drunk for its stimulant properties, derived from up to 15% v/v ethyl alcohol, formed by the fermentation of sugars in the must by fermenting yeasts.

The flavour of wine is determined by the grape variety (or varieties), in combination with the growing conditions, such as climate, agronomic factors during growth and harvest, and these are reflected in the composition and organic chemistry of the must. Perhaps equally important is the process of vinification used; in particular, must treatment, temperature, yeast strain, use of fermentation aids, filtration and other processes used, together with any maturation (ageing) process. The relative importance of these factors is a moot point, but they are all determined by chemical causes. Interestingly, for example, French wines are essentially characterized by the region in which they are produced, as referred to in the Appellation *d'Origine Contrôlée* (AC), usually without mention of the grape varieties used (although some French wines nowadays list the grape(s) used on the label). Although the grape varieties are defined in the AC, the proportions used may vary from year to year. As from 1 May 2009 the term 'Appellation d'Origine Contrôlée AOC or AC' has, with resistance from some producers, been progressively replaced with the new European standard, Appellation d'Origine Protégée (AOP). In contrast wine makers in many other countries, especially in the 'New World', make a feature of characterizing their wines by the grape variety used. In short, currently the French emphasize the '*terroir*', while in many relatively new wine-making countries the emphasis is on grape variety. A particular grape variety (e.g. Chardonnay, Cabernet Sauvignon) can, evidently, produce a rather different wine flavour as a result of the method of vinification and maturation, even though, usually, the characteristics of the wine flavour for the grape *variety* remain recognizable. A given variety grown in a certain region is also claimed to give a different wine than when grown in another region, even though the process of vinification is essentially the same. This subject is further explored in Chapter 5.

Therefore the flavour of the wine derived from the grape has to be considered in terms of its complex chemical composition, which is detailed in subsequent chapters. Current wine-making practice is outlined in Section 1.5 to give a better understanding of the background in which chemical changes related to flavour occur. Formation pathways of flavour compounds during vinification are discussed in Chapter 7. Some physiological aspects of wines related to wine chemistry will be described briefly.

1.4 Wine colour

Wines are primarily distinguished by their colour and fall into three groups (1) white wines, which include most sparkling wines, (2) red wines, including most fortified Port style wines and (3) rosé wines, essentially an intermediate between white and red wines. A wine's colour is determined by the choice of grape and the vinification process. White grapes, which usually have pale yellow skins, give white wines, while black grapes, which have blue, red or even black skins, depending on the amount of colouring matter in the skins, give mostly red wines. Red grapes can give a range of wine colours, from deep red to rosé, depending on the wine-making process, and by careful handling they can even yield white wines, for example the 'blanc de noirs' in Champagne production. Since most of the colour is in the grapes' skin, the choice of the vinification technique for red grapes allows a lesser or greater extraction of colour into the wine.

Within each colour, however, there will be differences between wines, which are easily perceived in the wine glass. The clarity may also differ, due to very small amounts of very finely suspended insoluble matter (not desired), although nowadays most wines are clarified before reaching the consumer. The changes in colour that occur during ageing, whether the wine is stored in-bottle or in-cask, are determined by chemical composition; the colour of red wines depends on the content and composition of anthocyanins. Colour and the chemistry of the changes in colour during maturation will be discussed briefly in Chapter 3.

1.5 Vinification

Traditionally good wines were made in regions where the conditions were frequently just right to give healthy, ripe grapes, with somewhat cooler weather during vinification. Although undoubtedly much knowledge was collected over many years, there was limited control over the process and wine-making was, to an extent, considered to be an art. With the advance of our scientific knowledge of many aspects of wine-making and the improvements of technology used in wine-making, in particular the use of refrigeration at various stages, there is now much control over the process. Nonetheless, the wine maker still faces many choices that determine the properties of the wine, and so the art still remains in making the best possible wine that is typical for the grapes and the region. The use of modern technology has also enabled good quality wines to be made in many more regions, including ones once thought to be too warm.

A basic understanding of the wine-making process ('vinification') is necessary in any study of wine chemistry and wine flavour. Grapes are the key ingredients, and they should be healthy, mature and in good condition. The choice of grape variety will influence the wine flavour and colour and to an

extent depends on the region. Grape varieties and some of the main growing regions are discussed in Chapter 2. In essence the grapes are picked, crushed to form a 'must' (grape juice) and fermented by yeasts to convert the sugars present into alcohol. There are three stages in wine-making, all of which can influence the flavour and colour of the wine:

(1) Pre-fermentation, during which various pre-fermentation treatments of the grapes or must can be given (such as sulfur dioxide addition, sugar or acid adjustments, nitrogen contents and possible addition, clarification of must, contact time with the skins or 'maceration' and cooling).
(2) Fermentation of the must, during which several factors have to be managed (such as choice of fermenting yeast, fermentation temperature, maceration time and pressing conditions).
(3) Post-fermentation, during which several different treatments are available. Some are probably essential (such as racking to remove the spent yeast or 'lees'), while others are optional, depending on the desired characteristics of the wine (such as filtration, cold stabilization). Wines can be made to drink when young, or after maturation (or ageing) in different types of vessels (such as old vats, new oak barrels or bottles).

Several general rules of modern wine-making have emerged. The production of both red and white quality wines requires attention to the following, as emphasized in many wine-making publications:

(1) Grapes should be picked at optimum ripeness, in sound and healthy condition, at as low a temperature as possible (in very warm conditions, they should be cooled) and transported to the winery with minimal delay for immediate processing. The must for white wines should be cooled both before and during fermentation.
(2) Strict adherence to cleanliness of all wine-making equipment; to prevent the growth of spoilage organisms on the grapes, in the must or in the wine at all stages of fermentation and maturation. A particular risk are *Acetobacter* bacteria, which convert alcohol into acetic acid, hence spoiling the wine into vinegar.
(3) Non-oxidizing atmospheres should be used, especially in the early stages of vinification of white wines, for example by blanketing the must or wine with inert gas and/or by addition(s) of sulfur dioxide.
(4) The temperature of the fermentation should be controlled. Heat produced during fermentation (an exothermic process) in stainless steel tanks should be removed by efficient cooling and refrigeration. This is usually done by cooling the outside of the tank or sometimes by pumping the must through an external heat exchange unit. Fermentation in barrels may lose heat through the relatively larger surface area; however, barrels are difficult to cool, though ice is sometimes used.

The success of wines produced in regions such as Australia, California and South Africa has been attributed to careful attention in controlling the vinification process, especially to the factors listed above. Of course, great care is also given to planning the vineyard (site selection, considering soil, climate and choice of the most appropriate grape) and vineyard management (pruning, fertilization, preventing disease and picking at grape maturity). Modern scientific methods of wine-making analysis and control have also been adopted. Nevertheless, traditional wine makers in Europe have not been slow to adopt modern practices and the overall quality of wine now available to consumers has improved significantly.

The equipment used for fermentation and details of that used for both pre- and post-fermentation stages have been well described in detail (Jackson, 2008; Ribéreau-Gayon *et al.*, 2006), while Robinson (1995) has given a good account for the general reader. The actual equipment used differs between wineries, depending on local conditions and the style of wine that is made.

Spoilage of wine is what all wine-makers want to avoid. This risk is present at all stages of wine-making, and can be both microbiological and chemical in nature. Under the wrong conditions, *Acetobacter* bacteria can change wine into vinegar in a very short time. Yeasts also pose a risk, as reviewed by Loureiro & Malfeito-Ferreira (2003), pointing out that understanding the ecosystems of wineries is crucial in prevention of spoilage. Excess air is also a known enemy, possibly causing chemical spoilage by oxidation of the wine, and enhancing the risk of microbial spoilage.

1.5.1 Vinification process

The basic wine-making process described here, highlighting those parts that greatly influence the resulting end product, covers many components that are common to both red and white wines. Recent textbooks by Jackson (2008) and by Ribéreau-Gayon *et al.* (2006) offer the reader a more in-depth treatment. The formation of specific flavour compounds during vinification (Chapter 7, devoted to reaction pathways) and volatile compounds (Chapter 4) are discussed elsewhere. A recent review on red wine-making reviews steps of wine-making affecting colour (Sacchi *et al.*, 2005), and interestingly cold soaks and the addition of sulfur dioxide tended to have an effect on the wine only over a short time, after some maturation the differences became minimal. Other parameters, such as yeast selection and carbonic maceration showed that the grape varieties affected the results.

Flow charts for both the production of red and white wines (Figs. 1.1 and 1.2 respectively) give a helpful overview of the various wine-making steps. Figures 1.1 and 1.2 reflect the headings below, as appropriate. Specific information for the production of red (Section 1.5.2) and white (Section 1.5.3) wines is included below. These brief descriptions focus on the differences from the general vinification process and, therefore, not all captions will be used in Sections 1.5.2 and 1.5.3.

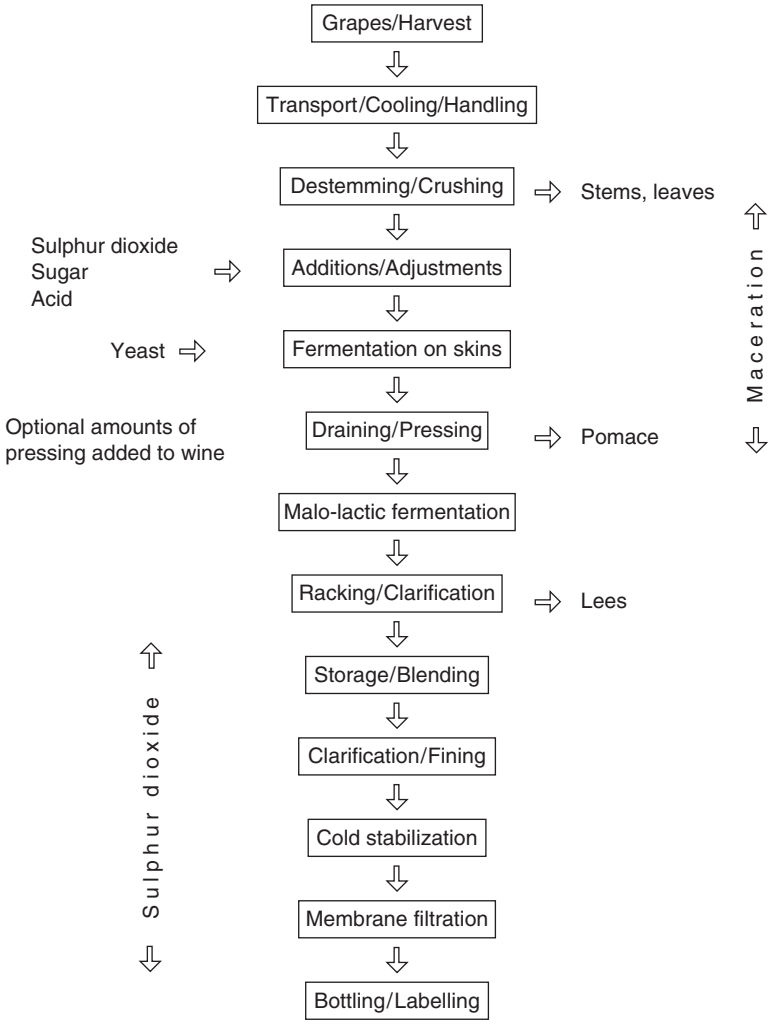

Figure 1.1 Typical processing sequence in vinification of red wines. Some steps are optional (see text). Oak contact can occur during fermentation and/or storage. Prolonged storage in-barrel or tank will mature wines.

The production of specialized wines is described separately, briefly emphasizing the part of the process that makes these wines different. As stressed above, some wine-making steps are essential, but the wine maker can make numerous decisions that will determine the overall style of the wine.

Pre-fermentation

Grapes/harvest

The first important step is the grape harvest. The grapes are picked at commercial maturity, which is usually determined by both their acid and the sugar content. The maturity of the grape will also affect the aroma and

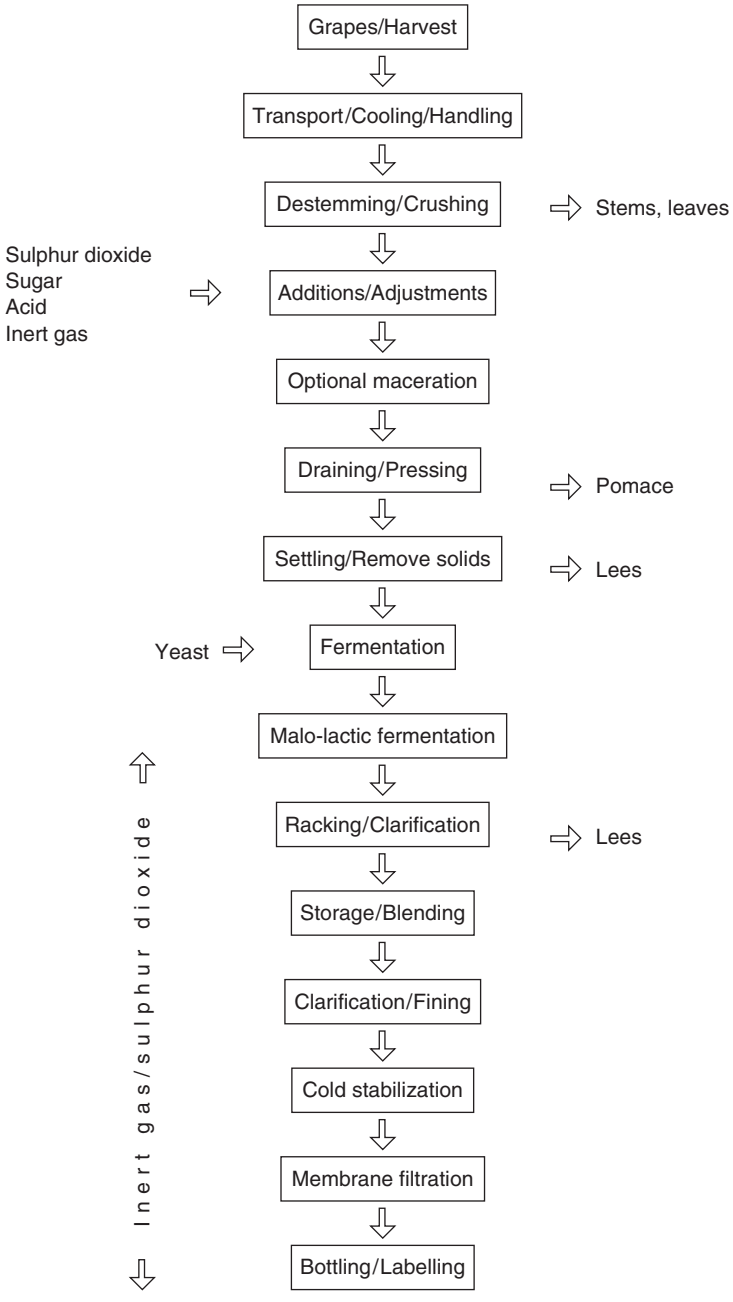

Figure 1.2 Typical processing sequence in vinification of white wines. Some steps are optional (see text). Oak contact can occur during fermentation and/or storage. Prolonged storage in-barrel or tank will mature wines.

phenolic composition typical for the variety, an aspect of increasing importance since they affect the varietal character and quality of the wine. As grapes mature, their acid content decreases and their sugar content increases. In hotter climates, the mature grapes tend to be high in sugar and low, sometimes even too low, in acid. In cooler climates the reverse happens: the grapes may struggle to reach full maturity and remain low, sometimes even too low, in sugar content and high, sometimes too high, in acid content.

The grapes can be picked by hand or by mechanical harvester. Hand picking allows access in even the most inaccessible vineyards (steep slopes, very soft soils), does not restrict the pruning style of the vines and some selection in the vineyard can be made (rejection of immature fruit and overripe, mouldy fruit). However, hand picking has a high labour cost. Machine picking is fast, costs much less in labour and can be done at night, which is attractive in hot regions to keep the fruit as cool as possible. Fast picking may help to ensure that the grapes can all be picked at optimum maturity, especially important in hot climates where a short delay in picking may give overripe and shrivelled grapes. However, mechanical picking has specific requirements on vineyard lay-out, access and vine pruning and training, etc. No selective picking of individual grape bunches is possible and it may not be desirable to pick grape varieties with very thin skins.

Transport/handling/cooling

Grapes should be handled with care to avoid damage that would encourage the growth of undesirable micro-organisms and lead to oxidative browning. Hence, hand-picked grapes are generally placed in shallow containers to prevent them being pressed under their own weight. The fruit must be kept cool and transported to the winery for processing with minimal delay. When using a mechanical harvester, it is important to avoid damaging the fruit.

De-stemming/crushing

Next, the grapes are usually de-stemmed and crushed. De-stemming involves the removal of stems, grape stalks and leaves, thereby minimizing the extraction of phenols and other compounds considered undesirable in the wines. Some of these phenols may impart bitterness and astringency to wine (Chapter 3), whilst some of the other compounds can give off-flavours or a haze in the wine.

The grapes are crushed, usually immediately after de-stemming, as gently as possible since excess pressure may damage the seeds, which will lead to the extraction of an excess of compounds (phenols) that, due to their bitter and astringent properties, would tend to give a harsh wine. With crushing the grapes are broken open, thus releasing the juice from the grapes. This facilitates the onset of fermentation, since the yeast has easy access to the sugar-containing juice. Most modern wine-making equipment carries out both stages, and it is generally thought that de-stemming before crushing gives the least extraction of undesirable compounds in the wine. In the past the stems were, notably, not removed, and their presence in the fermentation of red

wine facilitated the pressing procedure. Modern equipment for pressing the wine does not require the presence of stems. Some traditional wine makers may still choose to leave the stems in during the fermentation stage, although any vine leaves should always be removed.

Additions/adjustments

Additions of sulfur dioxide, sugar, acid, nitrogen and enzymes can be made but also acid adjustments can be made. Dependent on the soundness of the grapes, sulfur dioxide may be added at crushing. Sulfur dioxide has several functions; it protects the must against both browning reactions and, to an extent, unwanted micro-organisms. It suppresses the growth of wild yeasts and delays the onset of the fermentation. It is probably most effective in its use to protect against undesirable spoilage bacteria, especially if the pH of the must is low. However, it can also inhibit the malo-lactic fermentation, so its use should be avoided if an early malo-lactic fermentation is desired. It also damages the grape skin, and therefore enhances extraction of compounds from the skins.

Just prior to fermentation several adjustments may be made to the must, depending on local conditions and regulations. Grapes from cool regions containing insufficient sugar to ensure an adequate final alcohol content in the finished wine may receive an addition of dry sugar (sucrose, in crystal form). This process is called *chaptalization*, and was first introduced in France by M. Chaptal in 1801. Usually no more sugar than the equivalent of 2% v/v alcohol may be added. In addition, if the must contains excess acid, which tends to be a risk in cool climates, it may need to be de-acidified, often by the use of 'Acidex®', a form of calcium carbonate. In the same way, must prepared from grapes from hot regions containing insufficient acid may need to be acidified, usually by an addition of tartaric acid, otherwise the wines may taste flat and may have a high pH, which is undesirable for both chemical and microbiological stability.

When it is suspected that insufficient nitrogen is available to complete the yeast fermentation, an addition of diammonium phosphate can be made to the must to ensure an adequate concentration of nitrogen for yeast growth and maintenance. In particular highly clarified juice for white wine fermentation or must made from *Botrytis* infected grapes may not have a sufficient nitrogen concentration. There are two reasons for this addition. Firstly to avoid the fermentation getting stuck before the process is finished and secondly to avoid the production of hydrogen sulfide by yeasts, which is produced when the yeasts have prematurely depleted nitrogen in the fermenting must, as reviewed by Bell & Henschke (2005) and Ugliano *et al*. (2007). However, Jackson (2008) considers the addition of diammonium phosphate unnecessary and suggests that it does not prevent the formation of hydrogen sulfide. Possibly other yeast nutrients may also be inadequate in the fermenting must, not just nitrogen, for more detailed discussion see Ugliano *et al*. (2007). They suggest that cleaner, fruitier style wines may be obtained if wine-makers ensure that there is between 250 and 300 mg L^{-1} nitrogen available for yeast

fermentation. During the last decade much more information regarding the interaction of yeast and nutrients in the must and the effect on the formation of flavour has become apparent and is further discussed in Chapter 7.

Additions of enzymes, including pectolytic enzymes to enhance colour extraction can also be made, however, the review by Sacchi *et al.* (2005) concluded that pectinases do not seem to increase anthocyanins in wines but only increase the extraction of other phenolic compounds in wines. Presumably, anthocyanins were rapidly lost by the naturally occurring maturation reactions these compounds participate in, as suggested by the increased polymeric pigment formation observed in pectinase treated wines.

Additions of enzymes can also be made to stimulate the hydrolyses of glycosides from terpenes, since only the non glycosilated terpenes contribute to the volatile varietal aroma characteristics of the must, or more importantly the wine. The review by Maicas & Mateo (2005) gives an in depth overview of the current enzymes available, which gives wine makers potential tools to enhance the varietal aroma. The authors also warned against some potential adverse effects, such as the production of off-flavour as a result of vinyl phenols, resulting from the presence of undesirable cinnamate decarboxylase activity. Overall, with further studies on both the definition of desirable varietal wine aroma and precisely defined action of added enzymes, the use of these glucolytic enzymes give scope in the future to manipulate the wine aroma.

Enzymes can also be added as processing aids, such as enhancing the ease of pressing or aiding juice clarification.

Maceration

This is the process of steeping or soaking the skins and seeds of the grapes in the grape juice that was released from the grapes during crushing. It forms an important part of red wine-making, since during maceration the phenols, including the coloured ones (anthocyanins) and the flavour compounds from the grape skins, the seeds and the residual grape stems are dissolved into the juice, or into the fermenting must. The efficiency of the maceration depends on the temperature, the length of time and the amount of agitation the macerating mash receives. A recent review of Sacchi *et al.* (2005) lists the various techniques commonly used and their effects on the extraction of colour of red wines.

The maceration of a red wine typically starts before the onset of fermentation, and continues during part or the entire fermentation, and in some instances even after fermentation. The extraction of compounds will change in the presence of an increasing concentration of ethanol. How much maceration the wine should get is decided by the wine maker. Generally, longer macerations will lead to darker, more phenolic wines, requiring longer maturation before the wine is ready to drink. Red wines made to be drunk young tend to have short maceration times and are run off the skins before the fermentation has finished. Most of the anthocyanins are extracted during the first five days, whilst prolonged extraction increases the phenolic

compounds in wines. Astringency of red wines is mostly attributable to phenols, hence longer extraction of red grapes tends to give more astringent wines. Many of the flavour compounds are in the skins of the grapes; hence maceration also increases the extraction of flavour compounds into the wine, although little information is available on red wines.

Temperature of maceration can also be varied, and before the fermentation starts some wine-makers elect to do cool (about 15°C) to cold (4°C) macerations; temperature effects on colour and flavour have been reported (see Jackson, 2008), although increased risks of spoilage due to the adaptation the indigenous flora has also been reported.

As well as the temperature and duration of the maceration, during fermentation the agitation is also usually controlled. Without agitation, solids (grape skins, seeds, etc.) would float to the top with the stream of carbon dioxide produced during the fermentation and form a thick surface layer, known as the 'cap'. Obviously there would be no extraction from such a cap, and the risk of spoilage organisms growing in the cap (which is warm once the fermentation gets on the way from the heat released from the fermenting yeasts) is extremely high. Therefore it is imperative to keep the cap wet by some way of 'working' the must. Probably the most commonly used method is known as 'pumping over', in which juice is drawn from underneath the cap and quite literally pumped over it. Often such a process can be done semi-automatically every few hours, the time required depending on the size of the fermentation vessel, temperature, etc.

Of the several other methods used to keep the cap wet, some are quite simple, although labour intensive, while others rely on more sophisticated fermentation equipment. If the fermentation is performed in a shallow open vat, the cap can physically be punched down with the aid of simple punching sticks. If the fermentation takes place in a tank, a physical restraint (a metal grill or wooden beams) can be fitted just under the expected level of the must when the tank is full, to keep the cap submerged. There are also fermentation vats designed specially to keep the cap wet, such as autovinification vats (using pressure from the carbon dioxide released during fermentation to pump over the must) and roto-fermenters (using rotation of the tank, usually the tank being fitted in brackets on its side). A combination of colour extraction, must cooling and aeration can also be achieved by a technique of rack and return, a widely used method also known as *délestage*. After the start of the fermentation and the formation of the cap, the juice is drained into a holding tank, sprayed into a second tank and then pumped back into the fermentation tank. At the drainage stage seeds can be removed, desirable if grapes are immature to avoid excess extraction of extractable phenols.

Another maceration technique discussed was the use of freezing to enhance extraction (Sacchi *et al.*, 2005). They reported that freezing tended to enhance the extraction of both anthocyanins and phenols, presumably because freezing damages both the skin of the berries, allowing easier extraction of the coloured anthocyanins and the seeds of the fruit, thus aiding the extraction of phenols. The authors also suggested that the use of dry ice has the added advantage of

protecting the berries from oxygen. However, although such studies add greatly to our understanding of the processes in wine-making, currently it would seem that freezing is too expensive to have commercial applications.

Fermentation

Fermentation process

The next major step is the fermentation, in which the fermentable sugars (glucose and fructose) present in the grape juice (including any added sugar) are converted by yeasts into ethanol (ethyl alcohol) and carbon dioxide, with the generation of heat, the excess of which needs to be removed. The fermentation temperature is an important variable. The fermentation also produces many of the aromatic characteristics of the finished wine. The fermentation is usually carried out in large, closed stainless steel tanks (capacity 2000 L up to 2000 hL), which are temperature controlled so as to lower the fermentation temperature as appropriate. Open fermentation vats are also used, although not for modern white wines. The fermentation time increases with decreasing temperature. The effect of fermentation temperature on the formation of volatile flavour compounds, in particular esters, is discussed in Chapter 7.

Yeasts are unicellular micro-organisms that are classified taxonomically as 'fungi'. Yeasts have several commercial applications, and they are used also for beer brewing, baking and biomass production. Yeasts used in wine-making generally belong to the *Saccharomyces* genus, the most important species of which, *cerevisiae*, has some unique characteristics – perhaps one of the most useful ones being its tolerance to ethanol (up to 15% v/v), a very toxic compound for most other micro-organisms. Naturally occurring fermenting yeasts will start the fermentation at 18°C, though, increasingly, cultured yeasts are used. Some wine makers rely on fermenting yeasts that naturally occur in the winery, to start the fermentation and do not add any yeasts, allowing the natural yeasts to ferment the must, in order to achieve wines with a character believed to be more typical for the region. Generally, a strain of *S. cerevisiae* is added to the must, ensuring that the fermentation will start without much delay. The fermentation in wine-making may include several other types of yeast, some indigenous ones, although most yeasts will only grow at very low levels of ethanol (Chapter 7), and they tend to be more sensitive to sulfur dioxide. The fermenting yeast, inoculated or from the winery, will in most cases take over from all other organisms that may have become established during the early part of the fermentation and ferment the must to 'dryness' (low residual sugar).

Once dried fermenting yeasts became commercially available, most wine-makers deciding to inoculate the must did so mostly to avoid problems such as slow or even stuck fermentations and exert greater control over the fermentation, whilst minimizing the potential role of indigenous yeasts. An inoculum of active fermenting yeasts generally guarantees a rapid fermentation, also reducing the risk of spoilage. However wine-making knowledge has grown substantially over the last decades regarding the role of

the yeasts in wine fermentation and its effect on wine aroma and quality. There are recent reviews discussing and summarizing the role of yeasts in wine fermentation, wine aroma and wine quality giving details of current knowledge (Fleet, 2008; Swiegers *et al.*, 2008; Ugliano & Henschke, 2009; Bisson & Karpel, 2010). The current view is that the fermentation is more complex than previously assumed, with indigenous wild yeasts contributing significantly to the fermentation and the resulting wine quality, whereas it was assumed that these organisms died soon after the fermenting *S. cerevisiae* took over.

Further studies on flavour modulation by yeasts and the use of a mixture of yeasts to inoculate fermentation, may give in future yeasts even better tailored to fermentation and flavour production than currently available. The selection of yeast strains with suitable characteristics for wine-making, the use of mixed strains allowing a succession of fermentations to take place, and making these commercially available will in the long run give the wine-maker many more opportunities to select the yeast according to the desired wine style and quality, and create the wine most suited to the current consumer preferences. This further future exploitation of yeasts requires detailed information regarding the attributes valued in wines, so accurate selection criteria for the fermenting yeasts can be developed. Aspects regarding the effect of yeasts on wine aroma are discussed in more detail in Chapter 7.

Draining/pressing

The juice is taken from the grape skins *w*hen sufficient maceration has occurred (the fermentation may or may not have finished; to be decided by the wine maker) either by running off the juice without exerting any pressure on the grape skins (free run juice) or by pressing further juice (pressed juice) out of the remaining grape mash, usually referred to as pomace. The pressed juice tends to contain more tannins than the free run juice. The wine maker can choose either to keep pressed juice separate from the free run juice or to mix some or all of the pressed juice with the free run juice. For lighter wines, made to drink early, the pressed juice is kept separate, and often used for distillation. White wines are pressed *before* the fermentation (Section 1.5.3), while red wines are pressed *after* (or possibly during) the fermentation stage (Section 1.5.2).

There are various designs of presses available, and there is some variation in the properties of the pressed juice depending on the press, most important variables seem to be an excess of suspended solids in the juice, requiring extra fining to remove, and increasing amounts of anthocyanins and phenols in higher press run fractions. It is up to the wine-maker how the pressed wine fractions should be used.

Malo-lactic fermentation

A type of second fermentation, usually referred to as the malo-lactic fermentation, often occurs in wine, in which lactic acid bacteria convert the harsh-tasting malic acid into the softer tasting lactic acid, producing a small amount of carbon dioxide gas and raising the pH value of the wine. This fermentation can take place either approximately concurrently with the yeast

fermentation or in the young wine. It seems still a matter of debate what the optimum time for this process is. Malo-lactic fermentation tends to be encouraged in wines with an excess acidity and almost without exception is carried out for red wines. However, this acid conversion is not desirable in wines already high in pH or low in acidity. Wines can be inoculated with selected micro-organisms, or the wine maker may rely on the indigenous flora of lactic acid bacteria for the malo-lactic fermentation. Inoculation with malo-lactic organisms does not automatically mean this fermentation will occur, since this process does not appear to be controlled easily. Wines kept at 20°C or above are likely to undergo the malo-lactic fermentation, while high levels of sulfur dioxide and high acidity tend to inhibit the process. Malo-lactic fermentation also changes the flavour in the wine due to the volatile compounds produced, which may or may not be desirable, depending on the style of wine the wine maker is aiming to produce. A comprehensive review by Bartowsky & Henschke (2004) describes current knowledge on malo-lactic fermentation, and in particular its contribution to the buttery flavour in wine. Bottle ageing of red wines is also reported to affect the aroma compounds formed during malo-lactic fermentation (Boido *et al.*, 2009).

Post-fermentation

Racking/clarification

Young wines are stored and matured in small (225 L) or large wooden barrels, or in wooden, stainless steel or concrete vats. Whatever the mode of storage, a few weeks after the fermentation has ceased the wine will, usually, clarify and the yeasts be deposited at the bottom of the container. The wine is then usually taken off the lees (i.e. the precipitate of mostly yeast cells) and placed in a clean container. Thus, racking involves drawing off the wine from the barrel or tank to just above the level of the sediment or lees and transferring the wine to clean barrels or vats. This process may need to be repeated, depending on how long the wine is left to mature. Wines should be racked as required, more frequently when the wines are very young, and possibly annually when the wines are a few years old.

Oxygen

Aeration of the wine due to racking is thought to be crucial to the development of the flavour and colour of red wine but is generally detrimental to that of white wine. The higher phenol content in red wines, in particular the flavonoids, use oxygen for complex chemical reactions, leading to a softening of the wine. In contrast, white wines have much lower concentrations of phenols, mostly based on tartrate esters of hydroxycinnamic acids, prone to oxidation and forming hydrogen peroxide in the process, which can oxidize other compounds in wine, such as ethanol being oxidized into acetaldehyde. These oxidation processes were first reported by Wildenradt & Singleton (1974). Hence care should be taken when pumping white wine around at various stages post fermentation to protect the wine from the uptake of oxygen, often achieved

by using a blanket of inert gas and adding some sulfur dioxide if required. In contrast, red wine can be deliberately aerated, often by pumping over the wine or storage in wooden barrels which allow the slow ingress of oxygen, to enhance the reactions involving phenolic compounds, which lead to softening the wine and colour changes and has impact on the formation of the typical red wine aroma. Another technique used to allow a controlled amount of oxygen uptake is referred to as micro-oxygenation. This is used when the extraction of oak flavours into the wine is to be avoided and hence, inert vessels for wine storage are preferred. A specially designed cooperage can be used to allow controlled oxygen uptake of red wine, or silicone tube diffusers can be used to supply oxygen below the rate of consumption. Various instruments are also available to supply oxygen at selected rates via microporous diffusers.

An excess of oxygen in wines can lead to oxidative browning, a process avoided by ensuring minimal contact with oxygen, in particular in the case of white wines, and/or the use of sulfur dioxide as an antioxidant to control browning. Enzymic browning occurs primarily in must, whereas non-enzymic browning generally occurs in wines. A recent review (Li *et al.*, 2008) describes the pathways involved in browning, and discusses the central role of iron and copper in initiating non-enzymic browning, suggesting that control of these metals may help to avoid browning.

Oxygen in must, during fermentation and during storage impacts on red wine aroma and quality, in addition to the above mentioned effect on phenolic compounds (Kilmartin, 2009; Toit *et al.*, 2006). In red wine maturation it is thought that oxygen can lower undesirable vegetative aromas and enhance some of the varietal fruity aromas. However, more studies are needed to unravel the interaction between the chemical changes occurring in the group of phenolic compounds, and the accompanying changes in aroma volatiles.

Bulk storage

Wines can be stored and matured in large stainless steel tanks, although the flavours that develop on maturation are different from those formed during maturation in oak vats or barrels. Both red and white wines can be 'aged' before bottling, so-called maturation and the changes that occur are discussed in detail in Chapters 3 and 4. The chemical changes that occur affect the colour, the non-volatile and volatile compounds and contribute to the changes of flavour in the wine. This use of maturation is practiced for red wines, and to a lesser extent for white wines, to accomplish changes in flavour and colour. Oxygen uptake needs to be avoided for white wines, and controlled for red ones (see the earlier paragraph). Storage temperature is typically 18°C or below, and will affect the rate of chemical ageing changes.

Barrel ageing

The main reason to use oak is for the wine to extract aroma compounds from oak into the wine. There are various ways of achieving this. Normally maturation may take place in large wooden barrels, but if a typical wood

flavour is required the process is more effective in small barrels (225 L), although this is much more expensive due to the extra cost of labour and barrels. Such barrels are usually made of oak (mainly French or American, each imparting a distinct and different oak character to the wine) and may be used when either new or old. Various pretreatments of the wood (charring) have different effects on the flavour of the matured wine. Maturation in such vessels takes place over periods ranging from three months to three years, and the maturing wines should preferably be kept at about 15°C, a temperature prevalent in underground cellars.

The addition of oak chips to wines stored in stainless steel vats as been investigated as a cheaper alternative to the used of small wooden barrels (Campbell *et al.*, 2006). However, despite the numerous experiments done on potential variables, such as time of addition, size of shavings and using planks, the resulting wines tend not to have the same sensory properties as those matured in traditional small oak barrels. More research on the relationship between the composition of wines and the sensory properties will lead to a better understanding on how the process can be influenced. Not all wine regions allow the use of oak shavings, etc.

Blending

Of course, in addition to all these possible treatments, another very important aspect of wine-making is blending. Blending can be done simply to sweeten a wine, by adding some specially prepared sweetening wine, or to colour a wine, by adding some specially prepared colouring wine. However, in many wine-making industries, highly skilled blending experts prepare blends to ensure a consistency of wine character. Blending is also done to improve the wine flavour. The character of wines such as Champagne, fortified Port and Sherry depend heavily on the preparation of blends, often drawing on wines from both different years and different locations. European table wines are blended to a much lesser extent, thereby usually showing annual differences from the same producer due to differences in growing conditions (climate) as well as differences in any particular year arising from where the grapes were grown. Some wines can even be made from one particular year and one particular vineyard, so blending is not part of the process.

In contrast, for example, Australian table wines tend to rely heavily on the preparation of blends, often using wines from regions quite far apart, giving the wine maker a range of wines with which to make the desired blend. It is important to prepare the final blend some time before the pre-bottling treatments so as to allow time for compounds that are insoluble in the blend to precipitate.

Clarification/fining

Most wines clarify themselves during storage, being racked off their lees during the maturation before bottling. However, before bottling, several treatments are used to ensure the wine's stability, so that it remains clear, without the development of unsightly hazes or deposits in the bottle. Wines may be fined,

to precipitate specifically compounds that may affect the long-term stability of the wine, or they may be filtered or both. Fining involves using a coagulant, which is carefully stirred through the wine and then slowly descends to the bottom of the vat, removing suspended solids or specific compounds from the wine and forming a deposit. The wine may be racked off the thus-formed deposit and filtered or centrifuged to remove all particulate material.

Many fining agents have been used by wine-makers for a long time, and can be considered as 'traditional' wine-making aids (protein based compounds, such as egg white, gelatine, casein, or clay-based such as bentonite, or others such as activated carbon). Whatever the fining agent used, all fining agent added is removed from the wine; it is not an additive which remains in the wine, but a wine-making aid, only temporarily present in wine during its fining stage.

Care should be taken not to expose the wine to air (oxygen), which will affect the flavour and the colour of the wine. By carefully choosing the type of fining, the flavour of the wine may also be modified, for example, by using polyvinylpolypyrrolidone some of the phenolic compounds that impart excess astringency to red wines can be removed.

Clarification/cold stabilization

Without further treatment, some of the tartrate salts may not remain soluble during storage, leading to the occurrence of glass-like crystals of tartrates in the wine that are sometimes found on the cork or at the bottom of the bottle. These crystals may be considered unsightly, but are completely harmless and do not affect the quality of the wine in any way. To prevent any deposit of the salts of tartaric acid, and other compounds that may not remain soluble in the wine during short- to medium-term storage in-bottle, the wine can also be cold stabilized. Usually this involves chilling the wine to near its freezing point, keeping the wine at this low temperature up to two weeks, during which time tartrates and other compounds will generally form a deposit which are then removed by filtration or centrifugation.

Clarification/(membrane) filtration/centrifugation/pasteurization

There are numerous filtration methods used, based on thicker layers of fibrous filters generally designed to remove the larger particles, whereas membrane type filters can be employed to remove large molecules and colloids. Centrifugation is another way of removing particulate matter from a wine, and can even used instead of racking, particularly when wines are intended to be drunk young. Care has to be taken to avoid oxidation, often achieved by blanketing the wine with inert gas.

Just prior to bottling, all yeasts and other micro-organisms have to be removed to ensure the microbial stability of the wine. This may be done by sterile filtration, using a narrow pore membrane to ensure the removal of yeasts and bacteria. Bottling needs to be conducted under sterile conditions, using sterile bottles to avoid contaminating the wine with micro-organisms. In addition, the bottles may be injected with nitrogen to minimize exposure to oxygen.

Instead of sterile filtration, the wines can also be pasteurized by one of numerous heat treatments to reduce the risk of spoilage, for example, by heating for a short time (a few seconds) at a relatively high temperature (95°C), or for longer (about one minute) at a lower temperature (85°C), etc. These more brutal heat treatments are unlikely to be used for expensive quality wines.

Bottling/labelling

Often, a small addition of sulfur dioxide is made just before bottling, to protect the wine from oxygen, to prevent browning and to reduce the risk of contaminating micro-organisms. The wine bottle is sealed with either a cork or a screw cap. After the initial uptake of oxygen from the cork, wine sealed with a cork usually has an 'airtight' seal especially if the bottle is stored lying down at a cool (about 16°C) and even temperature. The use of cork as a closure has been reported to have a small effect on the oxidation of wines, and has been recently reviewed (Karbowiak *et al.*, 2010). However, faulty corks can leak (which gives a risk of wine spoilage) or give unpleasant off-flavours (see also Chapter 5). Therefore artificial 'corks' are also used; however, they are often difficult to extract.

An alternative closure is a screw cap, although it does not traditionally suit the image of the bottle of wine or its drinkers. However, a screw cap protects the wine well, since it retains the added sulfur dioxide and allows minimal uptake of oxygen, thus preventing oxidation in-bottle. Wines can be stored upright and maintain their character. One problem associated with the use of screw caps is the development of reduced sulfur odours attributed to the low redox potential developing in the wine. This problem does not occur in wines closed with high quality corks. Debate regarding formation of these off-odours and prevention of their formation is still a matter of debate (see Jackson, 2008). There is no reported risk of screw cap failure and wines developing off-flavors as a result. There is a gradual shift towards its use becoming more acceptable and not just for entry level wines but also for some of the more expensive wines produced in the New World.

Bottle labels vary from country to country (some of the information may be regulated locally) and come in various styles. The bottle label will give the year in which the grapes were harvested and the wine made, but not usually when the wine was bottled. The absence of a year on the label for a table wine usually indicates that the wine is a blend from different years. This is generally only done for cheaper table wines and helps to produce a consistent product. However, many Champagnes, most Ports and nearly all Sherries are blends of different years, which in no way reflect any inferiority in quality. Wines from the same production year from the Southern Hemisphere are half a year older than those from the Northern Hemisphere. The wine label usually gives information regarding its origin and its producer. Many New World wines tend to give information about grape variety, and sometimes even some technical information about grape growing, fermentation and maturation of the wine. Some wine-makers even give tasting notes on the back label.

Bottle ageing

A further type of maturation that may be used is bottle ageing. Many white wines and most red wines are sold ready to drink and do not require any further maturation in the bottle. However, some wines are expected to age in the bottle, resulting in changes in flavour. Some delay between bottling and the sale of the wine is inevitable, resulting in some bottle ageing. However, deliberate bottle ageing is practiced by wine merchants and consumers to affect the quality of the wine. The chemical changes in bottle maturation differ from those during in-cask maturation, primarily because there is no oxygen take up or extraction from wood in-bottle maturation. The chemical changes known to be involved are discussed in Chapters 3 and 4.

1.5.2 Red wines

Pre-fermentation

Crushing/de-stemming

White and red wine-making differ significantly at the stage immediately after crushing; for red wines the skins and seeds are not removed, and maceration (i.e. contact between the skins and the juice of the grapes after crushing) on the skins is given both before and during fermentation and occasionally even after fermentation. Red wine production, including both maturation in large stainless tanks and/or maturation in small casks is outlined in Figure 1.1. The stems can be removed, or left in the must.

Maceration

The amount of anthocyanins and other phenolic compounds extracted into red wine directly affects the colour of the wine, even after some years of maturation. It has to be borne in mind that the extraction will depend on the composition of these compounds in the grapes. The environmental factors and vineyard practices impacting on the flavonoid composition in grapes and the resulting wine has been reviewed (Downey *et al.*, 2006), and the grape composition determines the wine quality more than the choice of extraction parameters. Numerous factors other than grape variety are thought to influence the biosynthesis of flavonoids, hence viticultural aspects should to be considered as part of the wine-making process.

The subsequent potential of the wine to age depends on the phenol content of the red wine. Mouthfeel of red wines, one of the key differences in sensory properties between red and white wine, is thought to be determined by both the amount and composition of phenolic compounds in wine. It is therefore not surprising that there are numerous different techniques in use to aid the extraction of anthocyanins and to a lesser extent other phenolic compounds, during red wine-making. Such techniques can be typical for a wine-making region, for example carbonic maceration is typical for Beaujolais Nouveau, giving a light and fruity wine intended to be consumed young. Maceration also may be a choice made by the wine maker to an extent independent of the wine region.

A recent review by Sacchi *et al.* (2005) clarified the methods currently in use for red wine-making and summarized the effects on the extraction methods on colour due to the anthocyanins and other phenols in wines. They reported no long term effects on phenol contents as a result of levels of sulfur dioxide during maceration or a so-called *cold soak* (keeping the must cool for several days before the fermentation is started) and neither did the use of pectolytic enzymes lead to increased colour in the wine. Thermovinification, whereby the must is heated to 60–70°C, followed by cooling and fermentation, tended to extract more colour, without a significant increase in other phenolic compounds. So-called 'punch downs' or 'pump overs' are frequently used in red wine-making, since during fermentation the carbon dioxide formed brings the solids to the top of the fermentation vessel, forming the cap, thus reducing the effectiveness of extraction, risking excessive heat being trapped and spoilage due to *Acetobacter* contamination. Hence the cap is often pushed down by physical punching or by taking must from the bottom of the fermentation vessel and spraying this over the top to wet the cap.

The effectiveness of extraction of these methods varies, possibly depending on the grape variety used. Interestingly, the reviewers found that studies on carbonic maceration gave conflicting results and suggested the success of this technique may well depend on the varieties used. Longer maceration times tended to increase the phenolic content in the wine, since the anthocyanin extraction tends to peak after 4–5 days. Thus both the type and the extent of the maceration can be varied, according to the desired style of wine. It would be interesting to see studies on the sensory properties of red wines made with different maceration methods and fermentation temperatures, in particular relating the phenol composition to perceived mouthfeel and astringency.

Fermentation

Yeast fermentation

The wines may be fermented to low residual sugar content on the skins, thus allowing maceration during the entire fermentation period. The grapes may spend only 2–3 days on the skins and either before or shortly after fermentation has started the juice can be run off the skins, the pomace pressed and the fermentation allowed to continue in the absence of the skins, leading to light red wines. In the presence of skins, and possibly the stems, it is preferred to ferment at 24–28°C (no higher than 30°C) for up to two weeks. In this way, the classic and traditional red wines are produced, with dark colours, a high tannin content and flavours, which generally need some maturation to develop fully. The higher fermentation temperatures typical for red wines tend not to produce the fruity fermentation esters. Red wines made for early drinking, more typical for some red wines from, for example, Australia tend to be fermented at a lower temperature (17–24°C).

The review by Sacchi *et al.* (2005) reported that generally higher fermentation temperatures increased phenolic extraction, which the reviewers suggested tend to lead to higher polymeric pigment contents in the mature wines.

Also a new group of anthocyanins, called vitisins and currently referred to as belonging to the group of pyranoanthocyanins, was first isolated, identified and reported by Bakker & Timberlake (1997). This is a very stable group of anthocyanins, which plays an important role in the colour of wines (Rentzsch *et al.*, 2007). Recent reseach from Morata *et al.* (2006) shows that the fermentation temperature, the levels of sulfur dioxide and the pH during fermentation determine to an extent the formation of these colour stable anthocyanins in wines. This is further discussed in Chapter 3.

Malo-lactic fermentation

Malo-lactic fermentation is commonly practiced in red wines, and can be allowed to take place by naturally occurring lactic acid bacteria or by a specially prepared inoculum. It is desirable in red wines, which benefit from a conversion of the sharp tasting malic acid into lactic acid.

Post-fermentation

Maturation

One good reason for red wines to be aged is to allow changes in the phenolic composition to occur due to chemical reactions and precipitation, which will affect the colour of the wine as well as the sensory properties related to astringency and mouthfeel. These colour changes, which are a consequence of complex chemical reactions between the various anthocyanins and mostly non-coloured phenolic compounds occur as long as the wine is stored, although the rate will depend on various other factors, such as storage temperature and available oxygen. In addition the fermentation aroma is gradually lost or modified and the aroma often referred to as bottle aged bouquet is formed.

Bulk storage

Red wine should be kept with low sulfur dioxide concentrations and at a relatively low storage temperature. The extent of ageing required depends on the initial maceration given and also on the grape variety, other wine characteristics, local custom, etc. Red wines are often sold with some ageing, and many are not intended to be aged further. Wines generally need a fair amount of acidity to withstand, or improve with, ageing. Only some red wines (and even fewer white wines) will improve on prolonged ageing.

Some aeration of red wines, often achieved when the wine is racked off its lees and pumped over into a clean vat, is thought to benefit their development. Generally, the darker wines with higher tannin contents are thought to improve more with maturation than the lighter, less tannic wines. The amount of maturation needed to optimize red wine quality is still a subject of research. The wine maker can influence the wine properties depending on the amount of aeration given to a wine. Excess oxygen can cause oxidative browning (Li *et al.*, 2008), as discussed above.

Barrel ageing

Red wines can be made with some *in-cask* ageing, usually in small oak barrels, often in addition to maturation in large stainless steel vats. Traditional ageing usually means storing in oak barrels or vats from three months up to about three years, possibly even using some new oak for a short duration, followed by bottle storage. Only some 10% of wines are actually aged in casks (Robinson, 1995). For example in commercial practice Spanish Rioja red wines are traditionally aged in oak barrels, usually made of American oak, to provide characteristic flavours (see Chapter 4). The choice of oak (American or French, new or old) and duration of barrel ageing, in addition to the amount of aeration during barrel ageing, will determine the sensory properties of the wine.

Bottle ageing

Wine merchants and consumers also practice maturation by deliberate bottle ageing to affect the quality of some wines. Wines given a prolonged period of bottle ageing before consumption are of great interest to wine experts, as indicated by the charts and tables produced on the condition of wines from a range of vintages, indicating wines that need further bottle ageing, wines ready to drink and wines past their optimum drinking quality. A current, common classification system used to indicate the 'drinkability' of such wines is 'not ready', 'just ready', 'at peak' and 'fading'. These designations include information on the different qualities to be expected of the wines in given vintage years.

Tasting notes are often made using a numerical scoring system, the most commonly used systems are from 0–20 or from 0–100. All wine experts have their own defined version of making notes and scoring the wines, published in annual wine tasting books and increasingly on the web. The scores experts allocate to wines may well add to the value of the wines, depending on the status of the expert of course! One example of information on the web is the www.wineanorak.com site, which has tasting notes prepared by Jamie Goode on wines from many prestigious wine producers around the world, typically grouped by region. Wines scored on this site typically average between 85–95 points, defined as good to very good but the author stresses that only good quality wines do get recorded. Tasting comments of such wines usually include an indication regarding readiness for drinking, such as 'drinking well now', 'at its peak' or 'do not keep much longer'. An example is the list of tasting notes on 60 years of classic Clarets, dating back to 1947, with all wines assessed scoring 92 points or more. Unfortunately, no prices are given! However, top wines from Bordeaux do demand very high prices.

There are actual distinct chemical changes occurring in red wines during ageing in-bottle, discussed in Chapter 4.

1.5.3 White wines

There are a number of differences for the white wine-making process. Firstly wines tend to be fermented off the skins. Secondly, air (oxygen) must be excluded as much as possible during white wine-making to prevent the

development of a brown colour, due to oxidative browning, as a result of enzymic and chemical reactions of the phenolic compounds (Li *et al.*, 2008). Oxidation also needs to be avoided to prevent losing the often delicate fruity white wine aroma. Typically, this is done by adding a small amount of sulfur dioxide to the must, combined with careful wine-making practice thus avoiding oxygen uptake.

Surprisingly, one technique often practiced to protect white wine from oxidation is making it less sensitive to oxygen, achieved by oxidation of the must. The deliberate excess oxidation of the must, so-called hyperoxidation, promotes enzymic oxidation (browning) of phenols in white musts, compounds which precipitate during the fermentation. The resulting wine is less bitter and less sensitive to accidental oxidation. Not all grape varieties are suited to the use of hyperoxidation, since there can be a negative effect on the aroma development. Also, the chemical process of hyperoxidation varies with phenolic precursor concentration present in the grape variety and is discussed in detail by Ribéreau Gayon *et al.* (2006).

Additions of sulfur dioxide can be used to protect the wine, in addition to the use of an inert gas to prevent the uptake of oxygen. Thirdly, temperature control during the entire process is necessary, especially in the warmer wine-making regions, which lack natural cooling conditions during harvest.

Pre-fermentation

Harvesting/grapes

Figure 1.2 outlines the production steps involved for a standard white wine prepared for drinking young and made without subsequent maturation in oak casks. To produce fruity white wines it is especially important to pick the grapes cool (early morning, or even at night). The grapes are, preferably, kept cool and crushed with minimal delay, often with an addition of sulfur dioxide. Some white grapes are picked and immediately cooled in the vineyard. White wines are usually produced from white grapes, but can also be made from red grapes (Section 1.5.1), when great care is needed not to damage the skins since this would lead to a red coloration of the juice (and wine).

Crushing/de-stemming/pressing

The special feature of white wine production is the removal of grape skins, seeds and stems, usually immediately after crushing and draining of the grapes. Part of the juice runs out of the crushed grapes (free run juice) without added pressure (draining) and is followed by immediate pressing. Sometimes white grapes are not crushed, but immediately pressed, to minimize extraction of compounds from the skins, seeds or stalks. The fermentation is carried out on the must or grape juice, without the skins, etc.

Maceration

Often white wines are made with minimal maceration, and the crushed grapes are pressed immediately. As harder pressing generally causes greater extraction from the skins, care is often taken to press the grapes very gently

to make the wines fresh and fruity and is intended to be drunk young. The free run juice generally has the highest quality, and the addition of more or less pressed juice to the free run juice affects the chemical composition of the wine and its resulting colour and flavour.

However, with some grape varieties it may be desired to extract the maximum amount of aromatic compounds from the skins, the so-called primary aromas (mainly terpenes). Here, limited maceration before the fermentation is given to assist the extraction. It is important, however, that no excess in tannin is extracted, since this would make the wine more susceptible to browning and increase its bitterness and astringency. Generally, maintaining a low maceration temperature combined with a minimal maceration time gives fresh and fruity wines, while increasing temperatures and maturation time gives a darker wine with a less fruity character.

Settling/clarification

To obtain white wines with a fresh fruity character, the grape juice (or must) is usually clarified before fermentation by 'cold settling'. The must is kept cold (10–15°C), possibly with an addition of sulfur dioxide to prevent the onset of fermentation and the suspended solids that subsequently fall to the bottom of the tank are removed by racking and/or filtering and/or centrifugation. Usually, not all solids are removed, as that tends to hinder the subsequent fermentation. Of course, any combination of pre-fermentation treatments already described in the vinification procedure (Section 1.5.1) can be given.

Fermentation

Yeast fermentation

In modern white wine-making, the fermentation is carried out in large stainless steel vessels at between 15 and 20°C, although even lower temperatures are used. Some of the Old World white wines are fermented at slightly higher temperatures, between 20 and 25°C. Fermentation takes at least 2–3 weeks or even a month or more, depending on the temperature. Precise control of the temperature is important since it governs the production of esters, the compounds responsible for the fruity character typical for modern young white wines, with lower temperatures giving a greater concentration of esters (see also Chapters 4 and 7).

Certain fine white wines are still made by fermentation in the barrel, rather than in a large tank. They are often subjected to many of the treatments described, followed by ageing in oak barrels (e.g. aged Chardonnays, as in Meursault).

The malo-lactic fermentation can also be induced at some stage of the processing. However, changes in aroma accompany this conversion, which may not be desired in fresh white wines. The sharper acidity of white wines is usually valued as adding to the freshness of the taste, another reason to avoid malo-lactic fermentation.

Post-fermentation

Racking

Often, young wines are stored briefly in large wooden barrels or vats or in stainless steel vats. They need to be racked off the lees but aeration should be avoided since this is generally detrimental to the flavour and colour of white wine. Careful monitoring of the concentration of sulfur dioxide and making a further addition when required, helps to protect the fresh and fruity character of the wine.

Clarification

Most white wines are to be bottled and drunk young, without any ageing, in order to enjoy their fresh and fruity character and therefore need clarification, stabilization and filtering before bottling (Section 1.5.1).

Bottle ageing

The fruity and fresh character of such white wines disappears during ageing and only a few white wines will improve on ageing (Chapter 4 and Chapter 7). After bottling, some fine white wines may continue to develop during bottle ageing, although white wines generally cannot be aged in-bottle as long as some reds.

1.5.4 Specialized wines

Rosé wines

Rosé wines are made from red grapes, which are crushed and de-stemmed as usual, but the maceration period is very short, often less than 24 hours. The wine-making resembles the process used for white wines. In general the maceration is stopped before fermentation has started and the desired amount of anthocyanins (giving the red-pink colour to the must and wine) has been extracted from the skins. If the juice is run off after the start of the alcoholic fermentation, the resulting wine will have a higher phenolic content.

Next the mash is pressed and the resulting juice is processed further in the same way as white wine, using juice settling and a cool fermentation. The resulting wine is much lower in tannin than red wine and generally treated more like white wine. Ageing in oak is usually avoided, the wine is stored cool, protected from oxidation and bottled for early drinking. Rosé wine can also be made using carbonic maceration (see the section on *Wines by carbonic maceration* later in this section), ensuring free run juice does not extract the grapes, thus preventing the extraction of excess colour but allowing the development of the fruity aroma typical for this fermentation method.

An array of red grape varieties is used for rosé production, not just the lighter red varieties, including blends of red and white grapes. Blending red and white wine to produce rosé table wine is not allowed in EU countries, however, pink Champagne can be made by adding red wine during the blending (or assemblage) stage of champagne production.

Wines made from organically farmed grapes

There is an expanding consumer demand for organic produce, including wine. Although there are good quality 'organic wines' available, the label organic is by no means signifying any information regarding the quality of the wine, it just refers to the production methods used in viticulture and to a lesser extent in vinification. Indeed there is a range of qualities of wines on the market, made from organically produced grapes and non-organically produced ones.

Organic wine is wine made from organically grown grapes, which means the grapes are grown without artificial fertilizers or chemicals to control weeds, pests and diseases. The correct wine label will state 'wine made from organically grown grapes', rather than 'organic wine'. The wines are made in much the same way as non-organic wines. In order for wine to be called 'wine made from organically grown grapes' the vineyard management has to comply with EU standards, including the required conversion time during which the grapes have been produced according to the organic standard. There are organic inspection bodies to verify the organic production and only certified organic producers can legally sell wines from organically produced grapes.

Organic viticultural methods focus on keeping the soil in good condition and reducing the risk of pests and diseases. The production of healthy grapes will be stimulated by selecting grapes suitable for the climatic conditions and providing growing conditions which will encourage strong and healthy vines and stimulating natural predators to keep pests in check. No doubt all viticulturists adhere to this general principle.

The production of good quality grapes requires correct vineyard fertility, which in organic grape production is done without the use of artificial fertilizers. In order to achieve correct fertility and adequate nutrients in the soil both green manure and animal manure can be used, depending on local soil requirements. Growers are selective in the use of their source of manure to prevent accidental introduction of pests and diseases, as well as the introduction of high levels of heavy metals. Mulches have been used traditionally to control weeds and to preserve water. Generally organic manures improve the soil structure, for example influencing water retention, enrich the nutrient content of the soil and enhances biological activity, such as influencing soil bacteria aiding nitrogen availability by fixing nitrogen.

The control of pests and diseases is done without the use of manmade chemicals. Generally dryer climates may have less trouble with mildew and kinds of rot typical for grapes than wetter ones. Many techniques used for such problems are based on environmental modifications, such as ensuring light and air access towards grape bunches by having a more open canopy and the removal of leaves around the bunches. Weed control may prevent the carriers of the infections. Specific pests are controlled using biological control, either by introducing specific predators or enhancing the environment thus stimulating the occurrence of natural predators. Control of numbers of predators can also be controlled with pheromones, interfering with the reproduction of predators. In depth knowledge of the micro environment is

required to ensure the right measures are taken. Knowledge regarding the weather forecast may allow preventative measures to be taken, without treating the grapes unnecessarily. Organically produced grapes can be treated with sulfur and copper to prevent moulds, but its use is regulated and restricted.

Wine-making is done much in the same way as for other wines. There are no current EU standards for organic wine-making, however, the standard set by the Soil Association in Britain requires wines to be made with lower levels of sulfur dioxide (total and free sulfur dioxide) than current EU standards for non-organic wines (organic red wine 90 mg L^{-1} total and 25 mg L^{-1} free sulfur dioxide, organic white wine 100 mg L^{-1} total and 30 mg L^{-1} free sulfur dioxide). No other processing aids are regulated, so these wines are not necessarily suitable for vegetarians. The label specifies suitability for vegetarians or vegans only if no animal derived fining aid has been used.

There are also cost implications. For example it may be easy to spray against an infection, however, if the loss of the crop without treatment would have been small, the costs associated with treatment may not have been justifiable. In addition, there may also be health aspects to be considered, for example the production of toxins by excessive mould growth if grapes were left untreated. Generally farming methods for producing of organically grown grapes is more labour intensive and results in lower yields, hence justifying the increase in the premium on the price of a bottle.

Wines with added resin

In ancient times a major problem was to keep wine drinkable, by stopping it from going vinegary and protecting it from oxidation. Since the use of sulfur dioxide to protect wine was not generally known, other methods were also used. The use of pine resin or pitch is thought to date back to the ancient Greeks and Romans, and traces of resin have been found in old Greek amphorae. Additions were made to wine to extent the shelf life of the wine, although it may also have been added to mask off-flavours. The use of these additions has been maintained until today, although now its use is for flavouring purposes only, giving wines a fresh turpentine-like flavour.

Most Retsinas are made from two grape cultivars, Savatianó and Roditis. Savatianó is a white grape, well adapted to the dry conditions and relatively easy to grow. Grown in large quantities, especially in Central Greece, it produces a rather bland and low acid wine, traditionally flavoured to produce Retsina. Roditis is a red grape, although the many clones available vary in skin colour from pink to red, grown widely in the northern Peleponese. A selection of the rosé wines are flavoured to produce Retsina.

There was a sudden surge in the popularity of Retsina in the 1960s, when Retsina suddenly became the national beverage, and the production was expanded rapidly to meet demand from increases in tourism and the local market. Currently its popularity seems to be mainly in Greece.

Wines with low alcohol content

In order to produce wines with low alcohol content, typically wines are made using standard wine-making techniques, followed by the removal of part of the formed ethanol. Older methods still widely used are vacuum distillation and reverse osmosis; techniques which remove the fruity volatile compounds and tend to accentuate the more unpleasant odours (see Jackson, 2008, for more information on these methods). Current methods gaining ground are based on membrane filtration and spinning cones, and processing at lower temperatures and are reviewed by Pickering (2000) and also discussed by Jackson (2008). It is claimed that these methods are superior and these production methods may lead to improved sensory properties of low alcohol wines. For example, the spinning cone column method is fast and the disruption of the wine flavour is minimal, however, the equipment is expensive and the method has not been legalized in all wine producing countries, also leading to potential export hurdles. Adding water to the wine would be the easiest method of reducing the alcohol content but this is usually not allowed.

The retention of aroma and the recovery of aroma compounds can prevent flavour inbalance, although no doubt ethanol acts as a solvent for typical wine flavour volatiles, and its significant reduction from typically between 11.5–13.5% v/v will affect the release and perception of wine flavour (see Chapter 4, Section 4.1.2). Alcohol at higher concentrations may give an apparent sweetness, which low alcohol wines lack, possibly making the low alcohol wines more tart than the natural level alcohol wine. There are no current sensory research data confirming perception differences between low and natural alcohol wines, with comparable flavour volatile compositions.

Further research in dealcoholization methods showed a viability study using a polypropylene membrane contractor (Diban *et al.*, 2008), this investigation showed large and unacceptable flavour losses for total dealcolization of model and real wines but a reduction of 2% alcohol gave acceptable aroma losses that did not damage the final perceived quality of wine. Another approach is the use of engineered yeast strains, which in future may also give fermenting yeasts producing an acceptable flavour but with a reduced alcohol production (Ehsani *et al.*, 2009).

Sweet wines

Several methods are in use to produce sweet wines, many of which have evolved into specialized products with very distinctive flavours. The fermentation can be stopped if sweet wines are required, for example by the addition of alcohol to about 18% v/v, as is done in the production of Port wine. Sweet wines can also be made by sweetening the dry wine with an especially made sweetening juice, such as the use of Süssreserve, an unfermented sterilized grape juice, in the production of some German wines. Other methods use sun-dried grapes, or late-harvested grapes infected with *Botrytis* (see below).

Sweet wines from *Botrytis cinerea* infected grapes

The more interesting of specialized wines include the sweet wines derived from grapes infected by a mould. Many wines made from mouldy grapes result in unpalatable wines, but from Sémillon given the correct conditions for mould infection, highly sought after wines can be made, with appealing sensory properties. Grapes can be infected by several micro-organisms, usually resulting in so-called bunch rot grapes that are unfit for human consumption. In several areas where climatic conditions are right, a particular mould (*Botrytis cinerea*) attacks the grapes and causes what is often referred to as *Noble Rot*. This mould can also be the cause of undesirable grape rot.

Botrytis cinerea mould generally causes desirable changes in grapes grown in river valleys, where autumn mists develop at night and linger during the morning. The mists should clear and give way to sunny afternoons. During the dry conditions the grapes will shrivel and the juice will become more concentrated, reaching 30–40% sugar w/v. These mould-infected grapes can be vinified and produce wines with desirable flavours.

Late-ripening grape varieties with relatively thick skins are less susceptible to bunch rot but are suited to developing Noble Rot. Riesling and Sémillon Chapter 2) are the main varieties used, although Chenin Blanc (Loire, France), Furmint (Hungary) and, occasionally, Gewürztraminer (Alsace, France) are all susceptible to Noble Rot and can give excellent wines. Especially, the Sauternes district in France is famous for its wines made from the Sémillon grape that has been attacked by *Botrytis cinerea*. New World wines made from *Botrytis* infected grapes are now also appearing. The chemical changes taking place in the grape are discussed further in Chapter 7.

Sparkling wine in Champagne

Champagne is the classic sparkling wine, and the name Champagne is legally protected so as to be applied only to wines from the Champagne region in Northern France. Champagne is made from one white grape variety, Chardonnay and two black ones, Pinot Noir and Pinot Meunier. Because black grapes are used for the Champagne production of white wine it is important to avoid the extraction of coloured pigments from the skins and, for all grapes, to minimize the extraction of grape solids. Hence in traditional sparkling wine production the grapes are pressed whole, without either crushing them or removing their stems.

Dry white wines are made separately from the different varieties from the numerous vineyards. Malo-lactic fermentation of these young high acidity wines is usually encouraged. Over the winter all the young wines are tasted and assessed and blends are prepared (a blend is called a cuvée). The cuvée is thought to determine to a considerable extent the character of the Champagne; hence much skill is needed to achieve the appropriate composition of wines in the cuvée. After the wines have clarified, a calculated amount of sugar and a specially selected yeast (*liqueur de tirage*) are added to the cuvée before bottling the wine in extra strong bottles, closed with a special closure. The

second fermentation consumes the added sugar and raises the alcohol content from about 11% to 12.5% v/v. The released carbon dioxide needs to stay trapped to give a sparkling wine.

The dead yeast cells of this second fermentation remain in the bottle during maturation, a process that contributes significantly to the typical flavour of Champagne. Bottles are matured on their sides, in cool, dark conditions, for a legal minimum of 15 months but for great Champagnes the maturation may take 3–5 years. Finally the dead yeast cells must be removed to clarify the Champagne. The process starts with riddling (*rémuage*). The bottles are stored in inclined racks and, over time, the inclination is increased until the bottles are upside down. The yeast debris accumulates on the closure in the neck of the bottle, which is frozen and the slightly slushy yeast sediment is removed from the bottle (*disgorgement*). The wine has to be topped up and is usually sweetened with some sugar syrup (*liqueur d'expédition*).

Sparkling wine by other methods

The wine-making process developed in Champagne is used in many other sparkling wine-making regions, and is often referred to as the 'classical method' or 'bottle fermented' or, as in Spain, *método por cava*. The process is quite expensive and other methods have also been developed that differ mainly in the second fermentation, including the removal of the yeasts and adding of the sugar, without losing the carbon dioxide.

In-tank carbonation

Eugène Charmat developed this method in Bordeaux at the beginning of the twentieth century. It is cheaper, faster and less labour intensive than the traditional method. Secondary fermentation is carried out in a pressure tank and the wine is usually matured for a short period. The wine is filtered, removing the lees pumped off under pressure. This method is best used for wines made from grapes with a strong varietal flavour, which can be preserved, such as Muscat (as used in Asti).

Transfer process

This process was developed in the 1940s to reduce costs by avoiding the manual riddling process. Secondary fermentation is done in the bottle but then the contents are emptied in a pressurized tank, filtered to remove the yeast cells, sweetened and re-bottled under pressure with an inert gas. The quality of the wine should not suffer much, assuming the wines are kept cool and handled hygienically.

Bicycle pump method

This is the most elementary method, involving carbonation by injecting carbon dioxide into a tank of wine under pressure. It is only used for the cheapest sparkling wines; there is no flavour development due to maturation on the yeast cells and the bubble release of carbon dioxide is usually rapid.

Wines by carbonic maceration

A variant wine-making method for wines to be drunk young is the so-called 'carbonic maceration', which is designed to extract the red colour from the skins, but less tannin than in normal red wine-making procedures. This is the common red wine-making technique for the Gamay grape in the Beaujolais area. The bright red wines with a distinctive fruity aroma are suitable for early drinking (e.g. Beaujolais Nouveau). They are made by carefully placing the whole bunches in a tank, which is then sealed. Oxygen is excluded, usually by using carbon dioxide. Fermentation by grape enzymes occurs in the intact berries, though some grapes will be crushed by their own weight.

The metabolism in the grapes is anaerobic. Under these conditions the grape berry can produce a small amount of alcohol, with a slightly higher temperature enhancing this mechanism. After about a week the process stops. The grape bunches, containing 1.5–2% v/v alcohol are then pressed and the juice is fermented by yeasts, usually at 15–20°C. The pressed juice can be kept separate or added to the free run juice, and gives a more aromatic and darker wine than the free run juice. Carbonic maceration is most suited to red grapes, and typical aroma descriptors are fruity, with notes of cherry, plums and stone fruits.

Wines by thermovinification

Thermovinification requires the intact or crushed grapes, usually for red wine-making, to be heated to between 50–87°C. The cell structure, in particular of the grape skins, is disrupted, facilitating the extraction of skin components. The holding time of the heated pulp (maceration time) decreases with increasing temperature, ranging from 2 min at 87°C to several hours at lower temperatures. The grapes are then pressed, the must is usually inoculated with a fermenting yeast, and fermented. The wine maker can decide to leave the skin and seeds in during fermentation but usually just the juice is fermented. The fermentation is usually rapid, thus requiring the fermentation temperature to be controlled.

Thermovinification efficiently extracts the red skin pigments (anthocyanins), as reviewed by Sacchi *et al.* (2005) which is advantageous for lighter red grapes grown in cooler wine regions, or for the production of deeply red wines, for example some Port wines. Another advantage is that grapes attacked by mould can be processed. When grapes have been attacked by a mould (*Botrytis cinerea*) they may contain laccase, a very stable enzyme that causes browning. Laccase is difficult to control during wine-making but thermovinification above 60°C inactivates its enzymic action. Also naturally present polyphenol oxidase in grapes is denatured, potentially reducing the risk of browning. After holding the must, the pulp is pressed, sometimes without pre-cooling, but sometimes the hot pulp is cooled by the incoming cold grapes.

The choice of the vinification temperature, the maceration time, fermentation on or off the skins and the seeds and the selection of the fermenting yeast all

affect the composition of the wine, and the wine maker can influence to an extent the sensory properties of the wine (see also Chapter 7).

Wines matured *Sur Lie*

Sur Lie is the French expression for 'on the lees'. Dry white Muscadet wines (France) made from Melon du Bourgogne grapes were traditionally given maturation on the lees, gaining a hint of yeasty flavour. Keeping wine in contact with the yeast lees for an extended period after the fermentation has finished will influence the wine aroma. Autolysis of the yeast cells, whereby the cells burst and release their contents into the wine, is thought to influence the development of aroma compounds. Chardonnay wines aged on their lees develop a less buttery and more toasty aroma. This method of maturation has become more widespread, and in red wines it has been reported to reduce astringency. Most typically, this type of maturation is used for sparkling wines, to give the toasty flavour after the second yeast fermentation in-bottle, and in Fino Sherry maturation in the solera system.

Lees bind to many undesirable compounds, so the removal of lees has many practical advantages, such as removing toxic compounds, undesirable volatiles produced by spoilage yeasts and reducing the risk of the formation of undesirable volatile sulfur compounds, as reviewed by Perez-Serradilla & Luque de Castro (2008). The lees also forms a reservoir of micro-organisms and amino acids, and it is well documented that maturation on lees can lead to higher concentrations of biogenic amines, which can have adverse effects. Ageing in the presence of lees affects the phenolic composition, and in general wines are less astringent, slightly less intensely coloured with a more yellow hue. The authors also discussed effects of released polysaccharides and lipids but there is not yet sufficient evidence to determine these effects on the sensory properties of wine. The chemistry involved in the positive effects on wine quality reported in the development of flavours of wines aged on lees does not yet seem to be well documented.

1.5.5 Fortified wines

The general processes of fortified Port wine, Sherry and Madeira are outlined here, while the underlying chemistry that affects the flavour and colour of wine, Sherry and Madeira will be discussed in Chapter 6, specifically focusing on where these processes differ from those of table wines.

Numerous countries make Port-style wines. Australia and South Africa make sweet red wines of good quality, although different grapes are used. Portuguese production of typical Port wine is outlined below. Some countries make Sherry-style wine; in particular, California has made this style of wine, although often with different grapes. The Spanish production of typical Sherry styles is outlined below. Within the EU the names Port and Sherry can only be used for wines from the designated Port and Sherry production regions.

Port wine

Port wine is named after Oporto, a large coastal town in northern Portugal. Therefore *Port* or *Port wine* comes from Portugal, although some other wine-making regions may also produce sweet red wines, possibly using a comparable wine-making process. Port wine is a naturally sweet fortified wine, made by adding fortifying spirit to stop the fermentation approximately halfway to 'dryness' and thereby leaving some glucose and fructose in the wines.

Port wine grapes are grown in a warm climate, and the young wines produced tend to have high phenolic contents, resulting in astringency and making them very suitable for maturation. Port wines are made from grapes grown in a demarcated area that covers the eastern part of the river Douro and its tributaries in the region of the Douro valley in northern Portugal. Although there are numerous varieties recommended or permitted for Port production, there are now five red and four white varieties generally regarded as superior. Many older vineyards are terraced with hand-built slopes, and planted with a mixture of varieties that are harvested and vinified together.

Many of the steps involved in the production of a standard Port wine (outlined in Fig. 1.3) are similar to red table wine vinification. Red grapes are picked, transported to the winery, and crushed and at least a proportion of the stems is removed. The crushed grapes are pumped into a fermentation tank, often with an addition of sulfur dioxide. In this warm climate, the acid level of the grapes may be low, giving a high pH; hence the must may be adjusted to about pH 3.6 using tartaric acid. Fermentation takes place mostly with the naturally occurring yeasts and the fermentation temperature is kept under 28°C. Unlike red wine, fortified red Port wine employs a very short maceration time and so it is very important to 'work' the must before and during the fermentation, for example, by using a robotic leg that simulates traditional treading by foot or more commonly by pumping the must over in the tank. Traditional treading by foot has almost entirely disappeared. The fermentation time on the skins is short; approximately halfway through the fermentation the 'mash' is pressed and the juice is fortified with spirit containing 77% v/v ethanol, to give a final concentration of about 18% v/v ethanol, which prevents further fermentation and results in a naturally sweet fortified wine.

Port wines are normally stored and matured in old oak vats, ranging from about 550 L capacity (pipes) to up to 200 000 L. The young wines are frequently racked as they need to be taken off the yeast. Chemical changes during maturation modify the colour and flavour of the Port wine; the young red Port wine becomes browner, changing from a deep red colour with a purple edge at the rim of the glass, to a brick red or even amber tawny colour. The flavour changes from an intensely fruity, even spirity, character when the wines are very young to a rich fruity ruby wine after three to five years maturation in wood. Wines left an average of ten years or so in wooden containers evolve into tawny wines, having an amber colour and a flavour reminiscent of nuts, raisins and crisp apples.

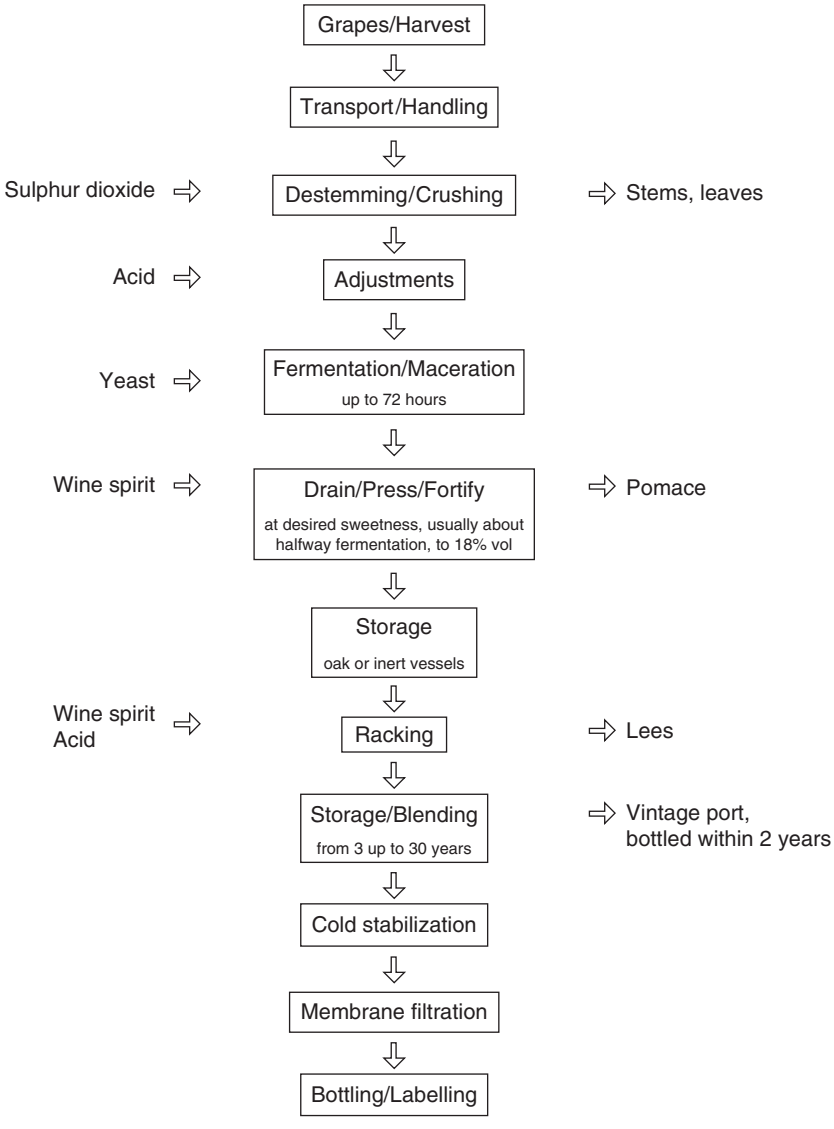

Figure 1.3 Typical processing sequence for the production of fortified Port wines. Some steps are optional (see text).

In contrast with table wines, where wines from each vintage are marketed separately, most Port wines are blended. Annual differences in climate that affect the quality of the grapes and the resulting wines can be corrected by blending. The use of especially made sweetening wines (*jeropiga*) and dry wines allows the final blends to be adjusted to the required sweetness. This allows the shipper to produce a consistent product. The indication of age on most Ports is an average age. Wines sold have an average age of at least three years, with many wine styles being much older.

Vintage Port, being the premium red wine and all from one vintage year, is matured in wood for two years, followed by a considerable period (often several decades) of bottle ageing and so it develops a different character from those wines matured solely in vats or barrels. Vintage Port is sold with a harvest date on the label, and is not treated before bottling; consequently, it will need decanting before drinking to take the wine off the considerable deposit in the bottle.

White Port wines are made in much the same way as the red ones but there is a trend to reduce the skin contact and even to fermenting clarified juice at a low temperature (18–20°C), to obtain a fruity aroma. The wines are aged in old oak vats for a minimum of three years before they are drunk.

Sherry

Sherry is the name given to several related fortified wines made from grapes grown in Jerez de la Frontera, in the province of Cadiz in the south of Spain. The white wine in this region is fairly neutral and lacking in acidity, but it forms an excellent base wine for the delicate flavours produced by the maturation and blending procedures evolved to make Sherry. There are three main types of Sherry, made from the base wine by three different maturation techniques. Sherry can be matured under *flor* (i.e. a layer of yeasts growing on top of the wine), developing into 'Fino' Sherry, or matured without *flor* yeasts, developing into 'Oloroso' Sherry. A combination of *flor* maturation followed by a period of ageing without *flor*, results in 'Amontillado' Sherry.

The climate in Jerez de la Frontera is generally warm and rainfall is moderate. The best vineyards consist of rather chalky soils, known as *Albariza* (very white soil, high in chalk). Palomino Fino is the main grape variety grown. Figure 1.4 outlines the steps involved in the production of base wine, which is fed into the maturation system to produce the Fino (or Amontillado) and Oloroso wine styles. At harvest, the grapes are picked, crushed and pressed. It is at this stage that the types of juice are separated for the intended wine styles. The free run juice and early pressings are the most suitable to make Fino, while juice containing pressed juice is more appropriate for Oloroso or Amontillado. The juice is settled to reduce the solids to about 1% before the fermentation stage. An addition of tartaric acid is made to juices with low acidity. Sulfur dioxide may also be added to the juice. Fermentation to 'dryness' takes place in large cylindrical fermentation tanks at about 25°C. Commercial yeast inocula are not normally used.

The dry wines are classified on the basis of their quality and fortified accordingly. Fino is usually made from the lighter dry wines and Oloroso is usually made from the darker wines, containing more phenols. Fino and Oloroso wines are fortified to 15.5 and 18.5% v/v alcohol, respectively. The wines are matured in seasoned oak casks (500–600 L) in 'bodegas', which are tall, well-ventilated buildings, designed to stay relatively cool.

Fino wines are stored in the coolest part of the bodega and, hopefully, develop *flor*. These wines are kept in vats only 80% full, providing a relatively

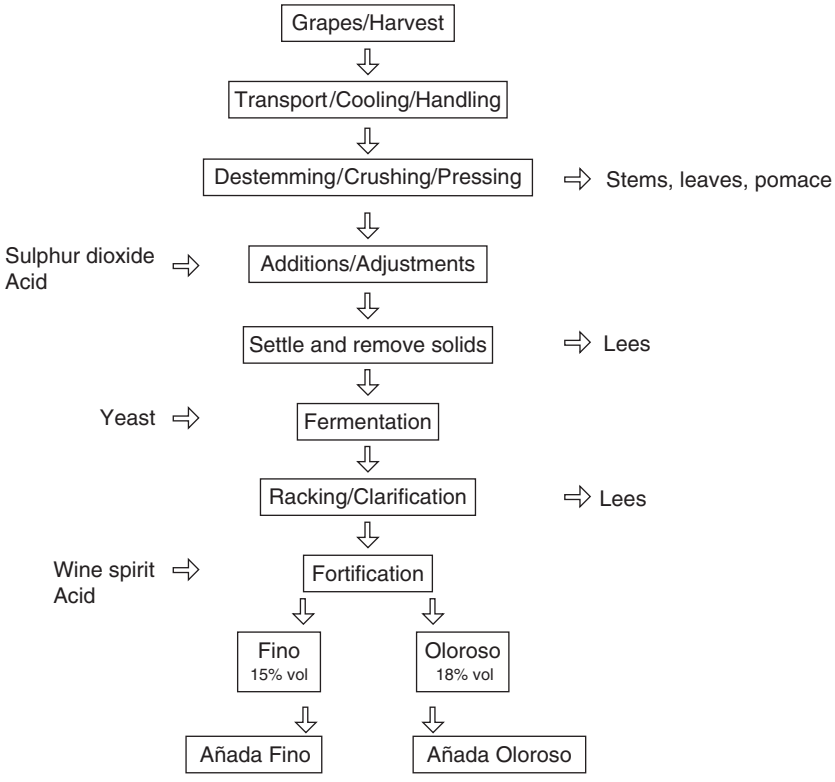

Figure 1.4 Typical schematic processing sequence for the vinification of Sherry. Maturation in butts in the solera system follows from añada (see text for further explanation).

large wine–air interface on which *flor* can develop. The origin of the *flor* yeasts and their taxonomy is still debated, although several are *Saccharomyces* species. The organisms in the *flor* layer consume oxygen, thus protecting the wine from the uptake of oxygen and preventing the oxidative browning of phenolic compounds to which the wine is very susceptible. The *flor* results in numerous biochemical changes, which greatly influence the flavour of the wine.

Young Oloroso wines, which contain more phenolic compounds than Fino wines, are kept in casks 95% full and stored in the warmer part of the bodega. To produce a good Oloroso, the neutral base wine needs to contain sufficient oxidizable phenols and is stored in warmer parts of the bodega, under oxidative conditions. The dark golden colour of the Oloroso can be attributed to the oxidation of phenols. The higher alcohol concentration, usually combined with a higher storage temperature, may increase the extraction of phenols from the wood during maturation of Olorosos and so partly explain the higher concentrations of phenols. Oloroso takes a long time to develop and requires about 7–8 years of maturation.

Some wines mature initially under *flor* and develop all the characteristics of a Fino. However, when the wine starts to lose its *flor*, it is further fortified to about 17.5% v/v alcohol and matured in a second solera system (see below) in casks, about 95% full. The maturation processes then change, with oxidation changing the initially pale yellow wine to amber and dark gold, together with the development of a nutty, complex flavour typical for this wine, called Amontillado.

Large quantities of wines with a consistent quality are obtained by an elaborate fractional blending system, referred to as the 'solera system' (Fig. 1.5), that contains blends of wines of different ages and vintages, and aims to mature wines to achieve a steady supply of comparable and consistent quality. The very complex blending procedure of the solera system involves many transfers of wine. The labour cost is high and it is not easy to make a rapid, significant change to the character of the wine.

The youngest Sherries are stored in the *añada* (wines up to one year old) and wines from the añada are gradually fed into a solera system. The solera system consists of several stages of ageing wines, called *criaderas*. Some of the oldest wine is periodically taken out of the criadera containing the oldest wine (also referred to as the solera) and prepared for bottling and shipping. Wines from the second oldest criadera are used to replace the volume of wine taken from the oldest criadera and basically the topping up of older wines with younger wines continues sequentially throughout the solera system. The volume of wine in the youngest criadera is replenished with a suitable añada wine. Each criadera may consist of a hundred or so butts, and usually the wine drawn from the butts in each criadera is blended before being used to top up the butts in the next criadera stage. There are from three to about 14 criaderas in each solera system, with Fino Sherries generally having more than the other styles. Up to about of 1/3 of the wine can be drawn from the solera system in one year, without affecting the quality of the wine. Fino Sherry needs to be removed regularly from the solera system, to allow the butts to be topped up regularly and so supply nutrients to maintain a healthy growth of *flor*.

Special colouring and sweetening wines are prepared, so that dry Sherries can be blended to the desired colour and level of sweetness before stabilization procedures and bottling. There are two sweetening wines, PX, made from the juice of Pedro Ximenez grapes and Mistela, made from Palomino grapes. The Pedro Ximenez grapes are usually dried, pressed and the juice is fortified to 9% v/v alcohol, and the wine contains 40% sugar. After settling, it is aged in special soleras. Mistela is made from pressed juice of the Palomino grape, which is fortified to 15% v/v alcohol and contains about 15% sugar. It is not usually aged in a solera.

Madeira

In addition to Port and Sherry, Madeira is the third 'classic' fortified wine. The island of Madeira is part of Portugal, lies in the Atlantic about 1000 km from the Portuguese mainland and about 600 km off the coast of North Africa. The

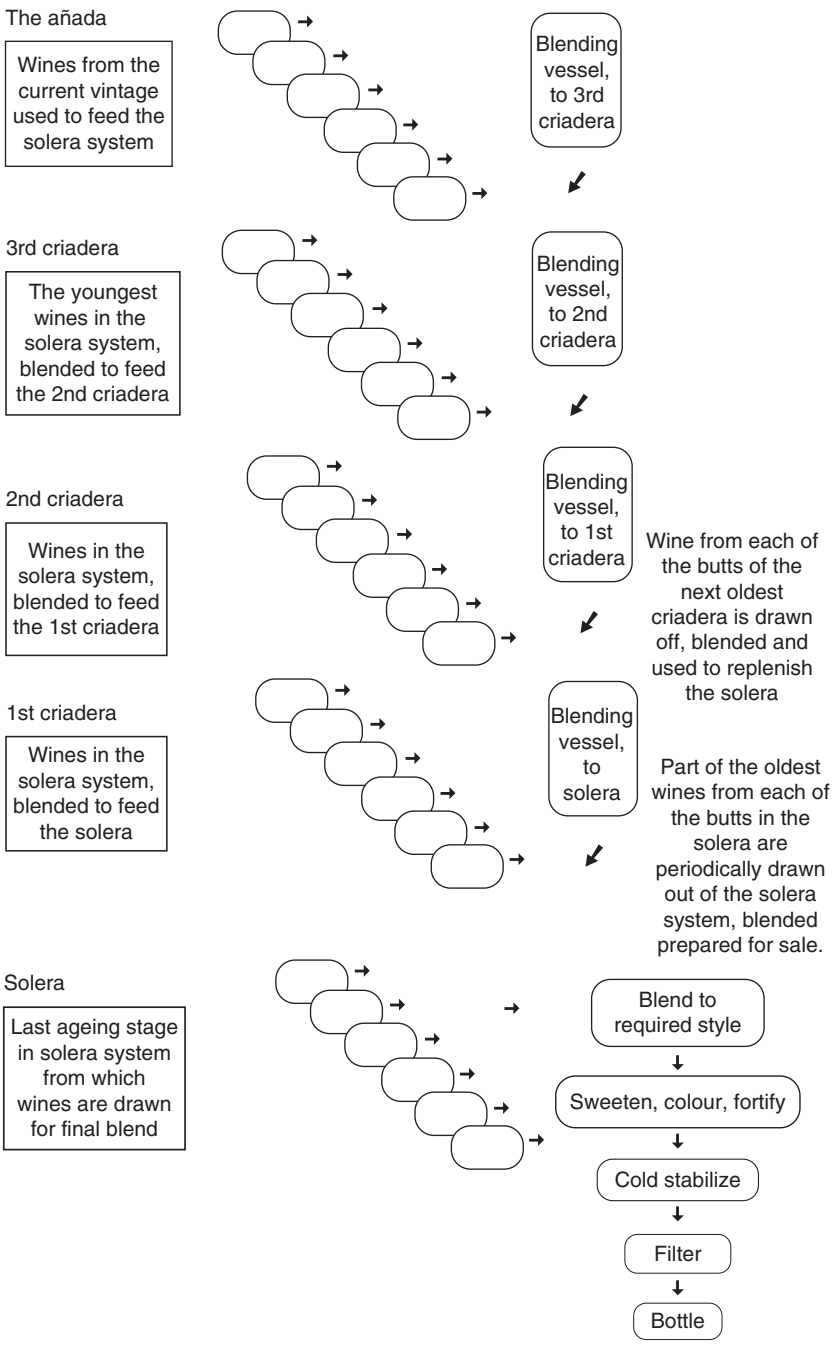

Figure 1.5 Schematic solera blending system for Sherry ageing, showing Sherry butts in añada, three criaderas and solera stage. The number of stages depends on the style: typically Oloroso, three; Fino, eight and Amontillado, five stages (see text). There can be about 100 butts in each criadera. Up to 1/3 of the wine can be drawn from the solera system each year.

wines are essentially shaped by their maturation, which involves heating them up to 50°C. This heating process is commonly referred to as the *estufagem* and confers a strong and characteristic flavour on the wine.

There are four traditional 'noble' grape varieties (Sercial, Verdelho, Bual and Malmsey) but these account for only some 12% or so of the grapes used for Madeira. However, several others are also grown, and the main grape variety planted is Tinta Negra Mole, in many wine books referred to as Madeira's workhorse. Temperature does not vary much over the year, the winters are relatively warm (average about 14°C) and the summers are relatively cool (average about 23°C). The soil is fertile and light red, consisting of volcanic basalt bedrock. The vineyards tend to be small and on terraces on steep slopes.

The grapes are picked, crushed and pressed. Fermentation, in fermentation tanks, is by the natural yeast population. Several wine-making techniques are in use. Some wines are made by stopping the fermentation by the addition of 95% v/v grape spirit to about 18% v/v alcohol, thus preserving some of the sweetness of the grapes (a process similar to Port wine-making). Other wines are fermented to dryness and fortified after the estufagem.

After fermentation and fortification of the wine, the estufagem process begins. Most wines are matured in this way. The wine is stored in an inert tank (ca. 20 000 L) and heated to ~45°C for three months. Smaller lots of wines are heated in wooden butts (600 L), kept in the warehouse and warmed by the main estufagem. This process tends to take place at between 30 and 40°C. Clear wines are then obtained by fining, and a minimum of 13 months further maturation is needed before the wines can be prepared for shipping.

Many wines are aged considerably longer and after about two years most shippers start preparing a blend to obtain their house style. Ageing typically takes between 13 months and five years. Small lots of wines from exceptional years are called vintage and aged 20 years in wood and two years in-bottle. The wines are orange-amber to deep brown, have a high acidity, and a typical aroma sometimes described as smoky or rancio. Classic grapes (Sercial, Verdelho, Bual and Malmsey) each produce a unique style of wine, and the wines should be made of 85% of the named variety if the grape name appears on the bottle. Sweetening wine is used to sweeten the wine. The wines are sold ready to drink but due to the high alcohol, high acidity and the estufagem process they have a very long shelf-life, remaining in good condition.

1.6 Physiological effects

Wine is primarily drunk for pleasure, consequent upon a mixture of its stimulant activity and its flavour, to which there seems to be early biblical reference: 'and wine that maketh glad the heart of man,' (Psalms 104:15). However, despite the primarily sociable and pleasurable aspects of a moderate consumption of wine, there is increasing evidence of beneficial physiological health aspects, both due to ethanol and some of the phenolic compounds; in

particular, reservatrol. Over the last ten years or so more scientific evidence of the health aspects of wine compounds, mostly phenolic compounds, has become available and is briefly discussed below. There are also negative effects, in particular an excess intake of alcohol can lead to both social and health problems and these issues are well documented. However, other attributed negative effects, such as migranes induced by wine, are scientifically less well documented.

1.6.1 Attributed negative effects

Wines are sometimes associated with allergic reactions and the development of migraines for particular people, believed to be triggered by histamine (and some other so-called amines), although some studies suggest that the levels of histamine in wine are generally too low to have a significant biological effect on most humans. After normal vinification the levels of histamine in wine tend to be low, although the concentration is enhanced by prolonged maceration, low fermentation temperatures and the growth of certain bacteria (some belonging to the bacteria inducing malo-lactic fermentation). Migraine is also often attributed to sulfur dioxide in wines, though there appears to be no scientific evidence to support this.

Methyl alcohol (methanol) is definitely toxic, leading to blindness and death, so that drinking 25–100 ml of pure methanol has been reported to be fatal (LD 50=350 mg per kg bodyweight). Wines made by normal wine-making procedures have very low concentrations of naturally formed methanol, although some cases of adulteration leading to toxic levels have been reported. Higher alcohols, for example amyl alcohol, known as fusel oils, are a product of the fermentation and their concentrations in wines vary.

The chemistry and physiological effects of wines were investigated by the International Agency for Research on Cancer (IARC) in Lyon, and reported in *Alcohol Drinking* (1988). This report prompted the US Government to issue 'health warnings' on the labels of wine produced in California. The monograph on *Alcohol and Health* by Stuttaford (1997) provides further reading on this topic.

1.6.2 Wine ethyl alcohol (ethanol)

Wine ethyl alcohol (ethanol), the most important physiologically active compound of wine, has stimulating properties when ingested. However, alcohol is essentially a poison that the body detoxifies. The negative effects of excessive alcohol consumption have been well documented. Many social problems, accidents and illnesses are associated with an excessive intake of alcohol, either as a result of chronic long-term overexposure or excessive intake in a relatively short time. Heavy consumption of alcohol causes cardiomyopathy (heart muscle disease) and cirrhosis of the liver. However, many other medical conditions can also, to an extent, be attributed to an excessive intake of alcohol, such as cancer of the mouth and larynx, nerve and

muscle wasting, blood disorders, skin problems and increased infertility. Excessive consumption of alcohol during pregnancy may lead to abnormal babies (fetal alcohol syndrome).

Alcoholism is a physical dependence on the consumption of alcohol, so that sudden deprivation may cause withdrawal symptoms; tremors, anxiety, hallucination and delusions. Alcohol dependence takes time to evolve and is not induced after a few binge drinking excesses. Several years of excessive alcohol intake is needed for alcoholism to develop (*Oxford Concise Medical Dictionary*, 1985). Alcoholism impairs intellectual functions, physical skills, memory and judgement, though social skills such as conversation are preserved until a late stage. Even an occasional moderate intake of alcohol affects intellectual functions, physical skills, memory and judgement, hence the need to legislate against the intake of alcohol when driving. In the UK the legal limit for 'drink-driving' has been set at a maximum 80 mg d L^{-1} (or 17.4 mmol L^{-1}) for samples taken from blood, breath or urine. Whilst highly dependent upon individual response and related to time elapsed since the last meal, it is generally considered that about 180 ml of wine will cause these limits to be reached in a short time. It is of interest to note that the accepted minimum of a trade measure of wine in the UK is 125 ml.

The effects of alcohol intake on the human body engendered the Temperance movements in the nineteenth century. Especially in the USA, several different organizations emerged, one of which was the Order of the Rechabities derived from the biblical Rechabite house, who denied the use of wine (Jeremiah Chapter 35, verses 5–6). The Temperance movement in the USA led to the Prohibition (1920–1933), which prohibited the production or use of any drink containing alcohol, with devastating effects on the wine industry. It took many years to restore the consumer market and the wine-producing industry.

There are also positive aspects related to a moderate intake of alcohol and some such references are already made in the Bible. Saint Paul said: 'Drink no longer water, but use a little wine for thine often infirmities,' (1 Tim. 5:23). However, there are also some additional warnings against excess, instructing not to be 'a wine bibber' (Tit. 1:7), nor to be 'drunk with wine' (Eph. 5:18). Modern medical research and opinion to date appear to endorse that a moderate consumption of alcohol, in particular red wine, may have positive health benefits compared with total abstinence. A regular moderate consumption of alcohol, in particular wine, is associated with a decrease in mortality. The protective action of wine against some infections of the intestine has long been known and was exploited by wine-drinking cultures, for example the Romans. The antibiotic action of wine is thought to be associated with the presence of certain phenols, particularly in red wines, in addition to any effect of alcohol, and is discussed in the next section.

Alcohol is now also believed to have beneficial anti-cancer effects and has long been thought to have a protective effect against certain heart problems but only for a regular and moderate consumption. There are two mechanisms that seem to decrease the risk of these heart problems associated with a moderate intake of alcohol. The first is an increase in plasma high-density

lipoprotein cholesterol (HDL), which is generally associated with a lower risk of heart disease. The second is a reduced activity of the platelets in the blood, which reduces the development of atherosclerosis and coronary thrombosis, thus reducing the onset of angina or infarction. It is stressed that any health benefits ever reported from the intake of alcohol are only applicable in regular moderate alcohol consumption.

1.6.3 Effects of phenols

Numerous studies have shown that red wine may have antibacterial or even antiviral effects; however, there is very little direct scientific proof linking identified compounds with mechanisms of such action. The binding of proteins to phenols is thought to inhibit certain enzymic actions. Although direct proof is limited, phenols (flavonoids and particularly reservatrol) have antioxidant properties and limit the action of free radicals in the body and, therefore, are thought to have anti-carcinogenic effects (Stuttaford, 1997). Supporting evidence comes from research on green tea, consumed in great quantities in the Far East and which has been reported to have beneficial anti-cancer effects due to compounds similar to those in wine.

Epidemiological studies have suggested a moderate consumption of alcoholic beverages, particularly red wine, is associated with a reduction in overall mortality attributed mostly to a reduced risk of coronary heart disease. In particular the so-called French Paradox survey, where the incidence of heart disease was low, despite the high intake of saturated fats and cholesterol, attributed to a daily intake of red wine. Further studies have suggested that plant-derived dietary constituents of food, in particular phenolic compounds in wine, can play an important role in the prevention of disease. However, although the potential role of phytochemicals, compounds having a positive effect on health in our diet, has been discussed and researched, it still remains difficult to get scientific proof of their role on disease prevention, for example heart disease (Visioli *et al.*, 2000). Despite the apparent difficulties, there been numerous studies *in vivo* and *in vitro* to determine physiological effects of specific phenolic compounds in order to unravel effects of these compounds in our diet, and some of the more recent literature reviews have summarized research of phenolic compounds focusing on particular health benefits.

A recent review on the role of wine polyphenols and the promotion of health (Cooper *et al.*, 2004) discusses the effects of wine, in particular its polyphenolic content, on early indicators of coronary heart disease and examines whether it is the wine or the alcohol which affects the onset of heart disease. They concluded that red wine polyphenols have little effect on plasma lipid concentrations, which at elevated concentrations, in particular of the so-called low density lipids, are a risk factor in the onset of heart disease. However, red wine consumption may lower the susceptibility of low density lipids to oxidation, indicating a protection of wine phenols against heart disease. They also found evidence that alcohol has a positive synergistic effect with wine polyphenols on platelet aggregation and adhesion, a heart disease risk factor, and they

suggested that this may be relevant after red wine consumption, since the concentration of wine flavonoids in the circulation is usually lower than those found to be effective in platelet aggregation and adhesion. Overall, Cooper *et al.* (2004) concluded that despite the great research input over the last decade in this area, we are still some way of understanding the health benefits of wine; there are still many questions regarding the functions of the individual compounds and there is little research done on the metabolism and biological activities of phenolic compounds at cellular, molecular and biochemical levels.

The beneficial effects of numerous polyphenolic compounds has been attributed to their antioxidant and free radical scavenging properties, although in many instances direct links between identified compounds and their effects is tentative. A number of studies *in vitro* support the concept that flavonoids are involved in the decrease of age related disease, however, a review by Halliwell *et al.* (2005) on the health promoting effects of flavonoids, found little substantive evidence to link the protective effects of flavonoids to their anti-oxidant activity *in vivo*. They suggested the following reasons for the lack of evidence. Firstly, foods rich in flavonoids may not necessarily give the desired action of the flavonoids in the body, there may be other interactions required to obtain an effect. Secondly flavonoids are complex molecules with multiple potentially biological activities, for example, they are known to inhibit numerous enzymes in the body and interact with cellular drug transport systems. Thirdly, due to our rapid metabolism, aided by colonic bacteria, the plasma concentrations of phenols are usually low, the authors suggested they may be too low to exert any systemic antioxidant action in the body, although this suggestion should be backed up by further research. Fourthly, many flavonoids have cytotoxic effects both *in vitro* and *in vivo*, although the relevance of these observations is still poorly understood. These authors concluded that despite the enormous interest in flavonoids and other non-flavonoid phenolic compounds having a potential role in protecting against disease, there were no unambiguous data to show their beneficial effects on maintaining human health, nor data to support any mechanisms of how they may protect health. Antioxidant effects are found *in vitro*, but consistent evidence *in vivo* is lacking. They suggested that the biological effects of these compounds and their metabolites may be in the gastrointestinal tract.

A number of chemical groups have been studied for their specific health benefits, for example anthocyanins have been attributed with a wide range of biological activities. In young wines anthocyanins may still be present but in most red wines the anthocyanins will have polymerized to larger molecules. Further information on anthocyanins (Pascual-Teresa & Sanchez-Ballesta, 2008) and on flavonoids (Anderson & Markham, 2006) is documented elsewhere.

Resveratrol

There has been a long history of interest in the potential health effects of resveratrol and according to the review by Aggarwal *et al.* (2004), its use in the form of grape extracts for human health can be traced back over

2000 years, to a well known Indian herbal preparation *Ayurvedic*, with *Vitis vinifera* grapes as main ingredient, used for heart as well as other disorders. Although sourced from other plants, resveratrol has been used in traditional Chinese and Japanese medicine. To date numerous studies indicate that resveratrol, a non-flavonoid phenolic compound found in red grapes, wine and grape derived products, has a number of pharmacological properties and can protect against heart disease and cancer.

Aggarwal *et al*. (2004) also review the occurrence of resveratrol and related stilbenes in numerous sources. Resveratrol (3,5,4′-trihydroxystilbene) is a phytoalexin naturally produced in plants as a result of stress, such as fungal infection, ultraviolet radiation or injury and is also occurs in grapes. It has been identified in the skins of fresh grapes, with concentrations between 50–100 mg g^{-1} and in wines between 0.2–7.7 mg L^{-1}.

Aggarwal *et al*. (2004) review the role of resveratrol in the prevention and therapy of cancer, both preclinical and clinical studies. Clearly resveratrol has great potential in the prevention and therapy of a wide variety of tumors. It has antiproliferative effects through the induction of cell death (apoptosis) *in vitro* of cells from cell lines of carcinomas of breast, prostrate, colon, pancreas, head and neck and leukemias. Most studies indicated that no cell death was induced in normal cell lines.

Two recent reviews by Ahtar *et al*. (2007) and Bishayee (2009) on cancer prevention and treatment with resveratrol, ranging from rodent studies to clinical trials, focused on the use of on resveratrol, a compound now attributed with health benefits as well as having the potential to be used as a drug in treatment of cancers. The anti-cancer property of resveratrol has been demonstrated in a wide variety of human tumor cells *in vitro*. Bishayee (2009) summarizes the *in vivo* studies and their proposed mechanisms. It seems that resveratrol influences the three stages of carcinogenesis (initiation, promotion and progression) due to its influence on cell division and growth. Resveratrol affects the vascular system by suppressing the growth of new blood vessels, a process involved in the initiation, development and progression of many diseases, including cancer. However, since the growth of blood vessels forms an important part of wound healing, resveratrol delays wound healing.

A recent study on the role of resveratrol on liver cancer cancer (Bishayee & Dihr, 2009) showed that resveratrol can inhibit cell proliferation and there were significant effects of resveratrol on the development of liver cancer *in vivo*. The primary mechanism of resveratrol was attributed in part to the inhibition of cell proliferation and induction of cell death, although further studies are required to confirm the underlying mechanisms. Even low exposure to resveratrol in the diet may be effective in protecting against liver cancer in certain instances. The authors suggested that since resveratrol has very low toxicity, it can potentially be developed as a drug against human liver cancer.

According to a recent study by Kazuhiko *et al*. (2009) even dimers and tetramers of resveratrol isolated from parts of the vines were shown to have cell death effects on heart cells and the authors suggested that one of the tetramers may have use in clinical care for the prevention of acute heart infarcts.

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