CHAPTER 5

Port Wine

N. Moreira and **P. Guedes de Pinho**[1]

Contents

I. Introduction 120
II. The Douro Demarcated Region 122
A. Soil and climate 124
B. The grape varieties 125
III. The Benefício 129
IV. Wine Production 130
V. Types of Port Wines 133
A. Special categories of port wines 136
VI. Chemical Composition 137
A. Polyphenols profile 137
B. Volatiles in port wines 138
Acknowledgments 143
References 143

Abstract

Port wine is a fortified wine with its origin in the Douro Demarcated Region but also includes Oporto city and the *Entreposto* of Gaia. Soil, climate, and viticultural conditions are important parameters used to classify and select the best vineyards to produce port wine. Taking into account the winemaking process, two major groups of wines can be distinguished: The wood ports and the bottle-aged ports. These distinct conditions and processes ensure that there is not an unique port wine but, several ports, whose colors range from white to deep purple and that present a wide variety of flavors: *vintage*, *late-bottled vintage*, *crusted*, *indication of age*, *colheita*, *reserve*, *white*, *tawny*, *ruby*, and *rosé*.

REQUIMTE—Toxicological Laboratory, Biological Science Department of Faculty of Pharmacy, University of Porto, Porto, Portugal
[1] Corresponding author: P. Guedes de Pinho, *E-mail address:* pguedes@ff.up.pt

Advances in Food and Nutrition Research, Volume 63
ISSN 1043-4526, DOI: 10.1016/B978-0-12-384927-4.00005-1

I. INTRODUCTION

Port wine has been produced for centuries. Its winemaking procedures, based on traditional methods, include stopping must fermentation by adding grape spirits, making lots of wines when desired, and letting them age in bottle or in wood cooperage.

The name of ''vinho do Porto'', ''vin de Porto'', ''Porto'', or port wine comes from the city of Oporto (Porto), the second largest in Portugal. Curiously, port wine is more related to the city of Gaia, located in the south side of the estuary of the Douro River, and the Douro Demarcated Region (DDR), located a few hundred kilometers east of Oporto city.

The vineyards of this region are located beyond the Marão and Montemuro mountains. These mountains help to retain much of the moisture coming from the Atlantic. This steeply sloped region possesses a landscape completely different from Oporto region: it is sunnier and less humid, being divided into a succession of linear, almost vertical terraces (Fig. 5.1).

The *Entreposto* of Gaia, that functions as an extension of the DDR, was created in 1926 (Cardoso and Silva, 2007). At that time, Oporto was the site for banks, residences, offices, or clubs of wine traders, but no longer

FIGURE 5.1 The *socalcos*—terraced vineyards of Douro Demarcated Region. Photography of Victor Ribeiro from the collection of the IVDP, IP.

for wine storage (Guichard *et al.*, 2003). All companies connected to port wine trade were forced to build cellars within this Gaia for aging their wines. In practice, this was the end of all trade directly from the DDR. The *Entreposto* provided a junction point between fluvial and marine navigation. Boats (*rabelo*) brought the wines down from the Douro Region, and the port at Gaia facilitated shipping to external markets (Fig. 5.2). Indeed, Gaia presents excellent natural conditions for wine conservation. It storage facilities are constructed on a sloping terrain that is less sensitive to the diurnal variations of temperature and is protected from the sea winds.

The exportation of wines directly from the DDR has been authorized since 1986. This measure allowed the production of different and new wines. However, the finest and most prestigious port wine continues to be matured in the old *Entreposto* of Gaia.

Ports are subject of an extensive set of legislation. According to the Decree-Law nº173/2009 of 3rd of August, 2009, the ''Instituto dos Vinhos do Douro e do Porto'' (IVDP, IP), located in the city of Oporto, has the duty of promoting quality control, as well as the amount of port wine produced, regulating the production process, and the defense and protection of the Douro and Port denominations of origin and the geographical indication of the Douro Region. The panel of tasters of

FIGURE 5.2 The *Rabelo* boats. Photography of Victor Ribeiro from the collection of the IVDP, IP.

FIGURE 5.3 Guarantee seal (IVDP, IP, collection).

IVDP is responsible for the certification, approval of the wines and the grape spirits, as well as the granting of the guarantee seal (Fig. 5.3).

II. THE DOURO DEMARCATED REGION

The DDR is located in Northeast Portugal, in a very mountainous region within the Douro River Basin. It is characterized topographically by sloping vineyards arranged in various terraced configurations (Figs. 5.1 and 5.4). The region was the first demarcated and controlled winemaking region in the world (Cardoso and Silva, 2007; Mayson, 2003; Pereira, 1991). The demarcation dates back to 10th of September, 1756. In December 2001, 24,000 ha of DDR were added to the UNESCO World Heritage List as an ''evolved continuing cultural landscape'' (Andersen *et al.*, 2004).

The region presents an area of approximately 250,000 ha, 39,000 ha being covered with vines. The region is divided in three distinct subregions based on physical characteristics and human occupation: Lower Corgo (*Baixo Corgo*), Upper Corgo (*Alto Corgo*), and Upper Douro (*Douro Superior*; Fig. 5.5).

The Lower Corgo is the most westerly subregion, being less mountainous and the oldest viticultural area of the region. It still possesses the largest proportion covered with vines—37% of its total area and

FIGURE 5.4 The vineyards planted along *patamares.* Photography of João Paulo Sottomayor from the collection of the IVDP, IP.

FIGURE 5.5 The Lower Corgo, the Upper Corgo, and the Upper Douro (IVDP, IP, collection).

represents 15% of the DDR (Guichard *et al.*, 2003). The soil is fertile and schistous, with a high percentage of clay. The climate is characterized by moderate, average annual temperatures, with peaks in the summer, high

humidity, and favorable demographic indices (Cardoso and Silva, 2007). These conditions make the Lower Corgo an area of great productivity that produces less-concentrated and less-complex wines (Martins, 2001).

The central subregion, classified as the Upper Corgo, occurs upstream from the Lower Corgo. It consists of steep slopes along the river Douro. Its vines cover 19.8% of the region, which comprises 38% of total DDR region. It contains most of the largest and more famous *quintas* (states). It produces the most distinct, superior quality, port wines. This quality is derived from a set of factors, the main one being the combination of the schistous soil and the more hostile climate. They generate vine stress, lowering yield but raising quality.

The Upper Douro, situated further eastward, encompassing the largest portion of the region (47%). Nonetheless, it produces the least amount of vine in the entire DDR, equivalent to 7.5% coverage (Guichard *et al.*, 2003). This region is the driest zone, with scarce water supplies. It is also characterized by the greatest temperature fluctuations and is least densely populated. It was incorporated into the Demarcated Region of the Douro in the twentieth century (Cardoso and Silva, 2007). The great distances that separate the subregion from Oporto and Gaia, as well as transport and communication difficulties, were the main reasons why the area was not explored for many years. Recently, Upper Douro has experienced the greatest expanse in vine coverage, being considered the subregion of the future. It has already begun to produce some exceptional wines (Guichard *et al.*, 2003). The vineyards are easily mechanized, reducing production costs, and the high quality of its wines remains consistent from year to year (Martins, 2001).

A. Soil and climate

The soil and climatic condition in the DDR are the major factors that contribute to port's distinctive characteristics, and ensure that these attributes are unreproducible elsewhere (Guichard *et al.*, 2003).

From a geological point of view, schist is the predominating rock type in the region (Fig. 5.6). The surface rock formation has excellent properties for viticulture: it holds water well, enabling the roots to penetrate deeply into the subsoil, resisting to erosion. In addition, the soil retains heat during the day and transmits it to the vine at night (Martins, 2001). The vast schistous countryside of the Douro is supplemented by granite outcrops in certain areas, namely in the Upper Douro, and some of the more fertile alluvial soils in the Lower Corgo. This geological formation is indispensable to the quality of port. Although the amount of wine produced is always small, it enables vines to live longer and increases must quality.

FIGURE 5.6 The schistous soil of the Douro Demarcated Region (IVDP, IP, collection).

The soil is also characterized by low organic content (0.6–1.6%), an acidic pH (4.6–5.5), and low potassium and phosphorus levels (Guichard *et al.*, 2003).

The Douro's climate is best illustrated by a local saying that describes the weather as ''9 months of winter and 3 months of hell.'' In winter, the temperature often falls several degrees below zero, while in July and August, the temperatures rise above 40 °C (Guichard *et al.*, 2003). Such contrasting weather has a marked effect on the wines produced and makes the vines behave distinctly, depending on where they are planted. For example, a very wet year may spoil the quality of the wines from the Lower Corgo but not necessarily have the same effect in the Upper Douro. In general, vineyards that face south and west receive abundant sunlight and heat, whereas north-facing vineyards favor more uniform ripening (Martins, 2001). Vine age is an important factor in such a harsh climate. Old vines, with their extensive root system, are better able to endure particularly hot summers as their roots penetrate deeply into the subsoil to obtain water.

B. The grape varieties

The extensive number of cultivars in the Douro and their adaptation to its different climatic conditions are proof of the region's ability to offer optimal conditions for vine growth and fruit maturation. There are more than 150 grape varieties, a substantial portion of which originated in the region (Cardoso and Silva, 2007). However, the grape varieties that

may be planted in the region are regulated by Decree-Law nº104/85, 10th of April, 1985. It lists the recommended varieties and the percentage to which each may be planted (Table 5.1).

Of authorized red grape cultivars, the six most important are Touriga Nacional, Touriga Franca, Tinta Roriz, Tinta Barroca, Tinto Cão, and Tinta Amarela. For white cultivars, Malvasia Fina, Viosinho, Donzelinho Branco and Verdelho (Gouveio) are the most significant (Cardoso and Silva, 2007).

Normally, port wine is considered to be a red wine. Nonetheless, white grape varieties represent 34% of the vine coverage (Guénaël, 2005). Some of the enologically important parameters of the red cultivars are presented in Table 5.2. They are the most studied cultivars.

Touriga Nacional is a traditional *Vitis vinifera* cultivar in the DDR, where it is thought to have been originated. It is the most valuable and finest grape for producing port. However, it only represents 4% of the vineyard coverage (Guénaël, 2005). In spite of its recognized quality, plantation of the variety was progressively abandoned during the twentieth century. Its low yield, irregular production, and extreme sensitivity to ''desavinho'' and ''bagoinha,'' two physiological vine disorders discouraged its planting. The disorders result in grapes either not developing or being seriously deformed (Andersen *et al.*, 2004). Using clonal selection,

TABLE 5.1 Grape varieties recommended and the percentage according to which each may be planted to the production of red and white port wines

Red varieties		White varieties	
Minimum 60%	Bastardo	Minimum 60%	Esgana Cão (Sercial)
	Mourisco Tinto		Folgosão
	Tinta Amarela		Verdelho (Gouveio)
	Tinta Barroca		Malvasia Fina
	Tinta Francisca		Viosinho
	Tinta Roriz (Aragonez)		
	Tinto Cão	Maximum 40%	Arinto
	Touriga Nacional		Boal
	Touriga Franca		Côdega
Maximum 40%	Cornifesto		Moscatel Galego
	Donzelinho		Donzelinho Branco
	Malvasia		Samarrinho
	Periquita		
	Rufete		
	Tinta Barca		

TABLE 5.2 Enological parameters of recommended red grape varieties (adapted from Abade and Guerra, 2008)

Parameter	Probable alcohol (v/v)	pH	Total polyphenols index	Anthocyanins (mg/l)	Dry extract (g/l)	Intensity of color
Bastardo	13.0	3.87	23.94	98	28.6	2.78
Mourisco Tinto	11.6	3.61	16.99	85	24.1	1.70
Tinta Amarela	12.7	3.46	36.4	429	28.7	10.4
Tinta Barroca	13.5	3.58	48.4	436	27.3	11.0
Tinta Francisca	12.6	3.71	52.7	451	28.5	11.1
Tinta Roriz	11.8	3.65	48.71	453	27.0	8.64
Tinto Cão	12.7	3.75	52.33	500	28.8	10.1
Touriga Nacional	13.3	3.69	71.06	703	30.8	17.3
Touriga Franca	13.6	3.78	76.24	707	33.0	18.0

it has been possible to select vines that are resistant to these disorders, and possess acceptable yields and resolve irregular production problems. Often, the yield of Touriga Nacional is about half or a third of other varieties (Oldenburg, 1999).

The blue-black grapes of Touriga Nacional are small, but deep in color and rich in tanninic compounds (Oldenburg, 1999). This variety is considered one of the most aromatic of the region (Guedes de Pinho *et al.*, 2007). The wines possess deep coloration (ruby tending to violaceous) and a complex and intense aroma reminiscent of red fruit (raspberry and cherry), jammy black fruits (plum), berries (blackberry), raisin, and floral (especially rose and violet) essences (Almeida and Laureano, 2007; Andersen *et al.*, 2004). The floral aroma is due to the high content of free terpenols, including α-terpineol, nerol, and geraniol, as well as to the high contents of β-ionone, a violet aroma descriptor (Guedes de Pinho *et al.*, 2007; Oliveira *et al.*, 2006). In the mouth, the wines are well balanced, very well structured, with rounded tannins (Andersen *et al.*, 2004).

Touriga Nacional is also known under various synonyms, such as Preto Mortágua, Mortágua, Azal Espanhol, Touriga Fina, Tourigão, Tourigo Antigo, or Elvatoiriga (Almeida and Laureano, 2007).

Touriga Franca is the most widely grown variety, representing about 22–26% of vineyard hectarage of the Douro (Guénaël, 2005; Oldenburg, 1999). Touriga Franca is a popular variety, recognized by its adaptation to hot and fertile soils. As it possesses an extremely thick skin, it is notorious for being extremely difficult to crush properly in treading tanks. According to Guichard *et al.* (2003), at first sight, this is not an immediately attractive or elegant variety, due to its rough appearance. Nonetheless, it is a very important component in port blends.

The wines produced from Touriga Franca are characterized by an intense color (ruby tending to violaceous), associated with a complex, fine, and fruity aromas. Red fruits (such as raspberry and cherry), berries (blackberry), and floral notes are dominant attributes of its aroma. Previous work has shown that wines from Touriga Franca possess a high concentration of free terpenols, but lower than those that characterize Touriga Nacional wine (Oliveira *et al.*, 2006). The wines also possess a light herbaceous taste combined with a full-bodied structure. These wines have fine sensory qualities (Bohm, 2007).

The Touriga Franca is also known as Touriga Francesa.

Tinta Roriz is the second most widely grown variety (12%; Guénaël, 2005). It is remarkably resistant to hot weather and gives high yields, two to three times that of Touriga Nacional. Tinta Roriz is sensitive to mildew and fungal diseases and is intolerant of soils with high mineral contents (Oldenburg, 1999). Thus, judicious positioning in the vineyard is essential to ensure consistent quality. Its best quality coincides with years when the vine carries few grapes and there is no rain at harvest (Guichard *et al.*, 2003). Under these conditions, the wines are as well structured as Touriga Nacional and possess flavors and tannins of similar quality.

Tinta Barroca constitutes 11.6% of the coverage in the Douro (Guénaël, 2005). It is resistant to the cold weather and is often planted on northern slopes, in sheltered areas, and at high altitudes (Guichard *et al.*, 2003; Oldenburg, 1999). It is high yielding, produces large clusters of grapes possessing high sugar contents. Traditionally, it is used with other varieties to improve the quality of grapes ripened at low elevations. It produces a robust wine with an aroma often described as flowery, in contrast to the more fruity aroma in port's other classical grape varieties (Oldenburg, 1999).

Tinto Cão has been cultivated in the Douro since the sixteenth century, and possibly longer (Oldenburg, 1999). However, it represents less than 1% of all red varietal hectarage (Guénaël, 2005). It is resilient and grows without problems, possessing limited disease susceptibility. Although its yield is low it is a consistent producer. The grapes are rather small and loose, but develop a high sugar contents. Its high natural acidity is an important contributor to port blends, donating longevity and quality wines destined for extended aging (Guichard *et al.*, 2003).

Guichard *et al.* (2003) refers to Tinta Amarela as one of the most popular varieties in the region. However, it represents only 6% of the planted hectarage, consisting mainly of old vines (Guénaël, 2005). Due to its thin skin, the variety is very susceptible to *Botrytis cinerea*. This is the main reason why it is not incorporated in new vineyard plantations. Wines from this variety are highly structured and possess good aromas, being an excellent contributor to port blends.

III. THE BENEFÍCIO

The IVDP is responsible for verifying the suitability of vineyards for port wine production. The vineyards are classified taking into account soil, climate, and viticultural conditions (Portaria nº 413/2001 of 18th April). The method used to classify each vineyard is unique to Portugal. It was conceived by Álvaro Moreira da Fonseca and first applied in 1947. Features that influence grape quality, such as location, altitude, slope, bedrock, rough matter, exposure, shelter, grape variety, vine age, yield, planting density, and trellising are graded relative to a scale of positive and/or negative points (Table 5.3). The sum permits the classification of vineyards into quality categories, ranging from A to I (Table 5.4). Vines placed in group A are of the best quality. Grape must from vineyards of class F are frequently excluded from the *benefício* (benefit; Cardoso and Silva, 2007).

The scoring system is used to allocate annual authorizations (licenses) to produce port wine (*beneficio*). The *benefício* indicates the amount of grape spirits that can be added to the fermenting must (Cardoso and Silva, 2007). This is an indicator of the amount of port that can be produced. This not only regulates wine quality but also ensures that the market complies with the laws of supply and demand. It empowers the ''Conselho Interprofissional da Região Demarcada do Douro,'' an interprofessional organization under the responsibility of the IVDP, to

TABLE 5.3 Criteria of vineyard classification using the scoring method (adapted from Guichard *et al.*, 2003 and Portaria nº 413/2001 of 18th of April)

	Minimum score	Maximum score
Soil and climate		
Location	−50	600
Altitude	−900	240
Exposure	−30	100
Slope	1	101
Shelter	0	60
Bedrock	−400	100
Rough matter	0	80
Viticulture		
Varieties	−150	150
Age	0	60
Yield	−900	120
Planting density	−50	50
Trellising	−500	100

TABLE 5.4 Classification of the vineyards according to total score (adapted from Guichard *et al.*, 2003 and Portaria nº 413/2001 of 18th of April)

Class	Scoring (points)
A	>1200
B	1001–1200
C	801–1000
D	601–800
E	401–600
F	201–400
G	1–200
H	−201–0
I	−401 to −200

establish the volume of wine permitted to be used in port production. When the decision is made on how much port is to be permitted each year, the IVDP notifies each wine producer of their quota (Mayson, 2003; Oldenburg, 1999). The licenses are established according to the relative scoring of each vineyard. Vineyards in the highest categories (class A and class B) are authorized to fortify a greater proportion of their wine to make port. Those in the lowest categories are allocated little *benefício* and can fortify little wine for port production.

The *benefício* varies from year to year, reflecting current stocks, export volumes, and market trends. To have an idea of the quantities involved, 313,943 pipes (a cooperage volume) of wine were produced in 2005, of which only 155,125 were given a *benefício* (Cardoso and Silva, 2007).

IV. WINE PRODUCTION

Once the grapes arrive at the winery, a sample of the juice is assessed chemically for parameters such as probable alcohol and sugar content. Grapes must have fall within the range of 12–14 °Baumé. Wines can be made separately by variety or mixed together.

Red port is made by first removing the stalks (destemming), followed by crushing the grapes. The grape juice is subjected to intensive maceration to ensure maximal color extraction from the skins, to give the wine a deep red color. Simultaneously, the must ferments until the amount of grape sugars remaining reach the desired degree of sweetness. Normally, fermentation takes a very short period, varying from 2 to 3 days. Fermentation is normally spontaneous, and under the control of natural yeasts on

the grapes and/or derived from winery equipment. During fermentation, yeast generated carbon dioxide brings the skins to the surface to form a cap, or *manta* as it is known in the Douro. Fermentation temperatures vary between 25 and 30 °C. When the decision is taken to terminate fermentation, the juice is separated from the pomace (solid matter) and grape spirits added. The alcohol added quickly stops yeast fermentation. The pomace is pressed to extract the remaining juice and, in the case of red port, supplied additional anthocyanins and tannins. These first steps of port wine production are similar for red and white ports; however, white ports have little if any fermentation on the skins.

The addition of grape spirits (77.0 ± 0.5% ethanol) at 20 °C to the fermenting must is an essential step in the port production. The average proportions of grape spirit added are 115 L for each 435 L of grape must (IVDP, 2009). This step stops yeast metabolism due to the toxicity of the high ethanol content. In addition, grape spirits favor polyphenol solubilization and triggers the precipitation of insoluble matter (Silva Ferreira, 1998).

The grape spirits permitted are subjected to rigorous quality standards, performed by the laboratories and tasters panel of the IVDP. Turbidity, color, aroma, and taste are evaluated. Ethyl carbamate, total higher alcohols, acetaldehyde, ethyl acetate, methanol, 2-butanol, 1-butanol, allylic acid, and cyanidric acid concentrations are analyzed; calcium, copper, and iron contents determined; and the alcohol content, total acidity, and density assessed. All must be below designated limits (Regulamento nº 84/2010).

Some wines are still made using traditional methods, where total or partial removal of the stalks as well as grape crushing is almost exclusively done by treading the fruit in *lagares*. These are granite tanks having a maximum height of 60 cm (Fig. 5.7). There are fewer *lagares* at work today because it is becoming increasingly difficult to obtain the requisite manual labor. For this reason, several firms have adopted a range of alternative solutions, one of which is use of a robot fitted with large blades to crush the grapes (Martins, 2001). Currently, treading is usually reserved for the best grapes, those that will potentially become superior port. The remaining grapes are vinified in stainless steel tanks similar to those used for table wines. In the tanks, the winemaker can control fermentation temperature and adjust the frequency with which juice is pumped from the bottom and sprayed over the cap to accentuate color extraction.

Young wines may remain in the Douro, or be transported directly to cellars in the *Entreposto* in Gaia. Transport is carried out at the end of the vintage year or early in the following year. Unlike in the past, it is mainly under strict supervision by road (Fonseca *et al.*, 1998).

On arrival at the *Entreposto* in Gaia, or in the Douro itself, the wines undergo racking and fining. The alcoholic strength is checked and raised,

FIGURE 5.7 Crushing the grapes in the *lagar*. Photography of Rui Cunha from the collection of the IVDP, IP.

if necessary, by further addition of grape spirits. At this time, the production of each type of port wine begins.

Each wine must be submitted to the taster panel of the IVDP for classification. The best lots from a single year may be declared appropriate for designation as a *vintage*, *late-bottled vintage* (*LBV*), or *colheita*. The remainder and majority is used for blending. Blending can involve port wines from different *quintas* sited in different subregions, and from different harvests. However, where wines possess a date of origin, only wines of that vintage may be used.

After classification, all port wines are matured in oak barrels for a period that depends on the style and category. The wines are subsequently matured in wood casks or vats if oxidative aging (contact with oxygen) is desired, or in bottle when reductive aging is intended (without contact with oxygen). These different aging procedures affect both the polyphenolic and volatile profile of the wines.

Wood casks possess a volume that varies from 600 to 650 L (Zamith, 2001). They are used to age wines that will become *tawny* ports, whether *reserve* or *colheita*. In the casks, the young port, possessing a red color and fruity aromas, is transformed into a golden brown wine with dried fruit aromas.

Vats, or *balseiros*, are wooden containers of larger capacity, between 10,000 and 100,000 L (Fig. 5.8). They are used to age full-bodies and fruity wines such as *ruby*, *LBV*, and *vintage* ports. The wines age more slowly than those conserved in wooden casks, retaining their structure and fresh fruity aromas that are the main characteristics of these wines (Guichard *et al.*, 2003).

FIGURE 5.8 The *balseiros* in Gaia. Photography of Luís Ferreira Alves from the collection of the IVDP, IP.

Bottle aging is reserved for *vintage*, *LBV*, and *crusted* ports (Fig. 5.9). These wines are chosen for their quality and structure. After an initial period in wood, the wines are matured in dark glass bottles laid on their sides in cool dark cellars. Temperature, ventilation, and humidity are strictly controlled (Fonseca *et al*., 1998). Once bottled, these wines do not come in contact with oxygen.

V. TYPES OF PORT WINES

The expression ''port wine'' is a unique brand, well established and known throughout the world. However, within this brand are a variety of categories and subtypes, varying according to sweetness, alcohol content, and color.

The classification of port wines according to sugar content is presented in Table 5.5. The sweetness level depends on when grape spirits were added to stop fermentation. The probable alcoholic degree of the juice

FIGURE 5.9 Vintage cellar. Photography of Luís Ferreira Alves from the collection of the IVDP, IP.

TABLE 5.5 Classification of port wines according to sweetness (Regulamento nº 242/2010)

Sweetness	Sugar content (g/l)
Extra dry	<40
Dry	40–65
Semi dry	65–85
Sweet	85–130
Very sweet	>130

must be at least 11%, and the wine between 19% and 22% alcohol by volume, excluding white semidry ports. The latter must have minimum alcohol percentage of 16.5 by volume (Regulamento nº 242/2010, March 15).

FIGURE 5.10 The colors of port wine. Photography of João Paulo Sottomayor from the collection of the IVDP, IP.

In terms of color, red ports vary from deep purple to light gold (Fig. 5.10). Designations of full, medium full or ruby, medium tawny, tawny, and light tawny are used to define each type. White ports come in various shades (pale yellow, straw, and golden white), all intimately related to the winemaking technique used.

Red ports can be designated as ruby or tawny.

Wines chosen to produce a ruby port usually possess a deep color, straight forward fruity aromas, full-bodied and rich tannins in the mouth (Mayson, 2003). Generally, ruby blends are composed of wines from several vintages, aged for up to 3 years, and bottled young. Ruby is a wine in which the winemaker seeks to restrain the evolution of its deep red color and maintain the fruit and strength of a young wine. It is the simplest version, and can be one of the most satisfying styles of port wine.

Tawny ports are derived from blending separate lots of wine that have been aged for different periods in wood casks or in vats. They are aged in wood for considerably longer than ruby ports. With age, the color of wines slowly develops into tawny, medium tawny, or light tawny color, with a bouquet resembling dried fruits and wood—the older the wine, the stronger the aromas.

White ports vary in style, depending on the duration of maturation. When aged in oak barrels for many years, the wine acquires a golden color that resembles a very old tawny wine and picks up a nutty character from the wood (Mayson, 2003). White ports destined to be drunk young are crisp, with an intense bouquet that combines aromas of melons and peach, with hints of citrus fruit, camomile, and lemon balm flowers. In contrast, white ports aged in wood present a complex aroma of tropical fruits, such as pineapple and banana, with a touch of almond and vanilla.

Recently, a new style of port wine has been created, the Rosé. This is a pink-colored wine, obtained by light maceration of red grapes. These are highly aromatic, with notes of cherry, raspberry, and strawberry, as well as appearing soft and pleasant on the palate.

A. Special categories of port wines

According to Regulamento nº 242/2010 (March 15), there are several special categories of port, designated *vintage*, LBV, *crusted*, *colheita*, *Indicação de Idade* (*indication of age*), and *reserve*. Besides these special categories, there are tawny reserve, ruby reserve, white reserve, tawny, ruby, white, and rosé (Table 5.6).

Vintage port is of superior quality with all the wine coming from a single vintage. To be recognized as *vintage*, the wines must be very full-bodied and deep in color. They are matured in wood for 2–3 years before they are bottled. The label must indicate the year of harvest. Aging in bottle can take from 10 to 50 years or more before consumption. As it ages, it retains the intense ruby of its original color, exuberant aromas of red fruits and wild berries, and a taste of black chocolate, all of which is balanced with strong tannins. After 10 years in bottle, in addition to forming a light deposit, *vintage* ports take on garnet tones and ripe fruit aromas and flavors. It is said that the origin of the *vintage* goes back to the last third of the eighteenth century when cylindrical bottles first appeared (Cardoso and Silva, 2007).

LBV is special, single vintage, version of a ruby port. It is aged in wood for longer than a *vintage* port—between 4 and 6 years. The vintage year is always indicated on the label. Most *LBV* ports can be drunk with pleasure as soon as they are purchased, but some continue to age well in bottle. The port has a deep, ruby red color, is extremely full-bodied and rich in the mouth. As other vintage-dated wines, it expresses the particular style and personality of a wine produced that year.

Crusted ports are high quality, very full-bodied, deep colored wines. Crusted ports are a blend of wines from several vintages, aged for a minimum of 2 years in wood and then in bottle for 3 years before release

TABLE 5.6 Traditional port names and sensorial appreciation level

Traditional designation	Classification
Vintage	Superior
Late-bottled vintage (LBV)	High
Crusted	
Colheita	
Indication of age	
Tawny reserve	Very good
Ruby reserve	
White reserve	
Tawny, *ruby*, *white*, or *rosé*	With quality

from the cellars. *Crusted* port is bottled without fining or filtration and laid down to mature like a *vintage* port. Similar to *vintage* ports, they develop a ''crust'' of sediment in the bottle. The year in which it was bottled must be indicated on the label. *Crusted* ports are much closer in style to a *vintage* than most *LBV* ports (Mayson, 2003).

Colheita or *Data de Colheita* is a red or white port with high sensory qualities. Like *vintage* and *LVB*, *colheita* is the product from a single harvest but are aged in wood for a minimum of 7 years. During the oak cask maturation, the young, fruity, and fresh aromas change through oxidation to donate a bouquet in which aromas of dried fruits, roasting, wood, and spices dominate. The wine also takes on a smooth mouthfeel. *Colheita* ports may possess a wide range of colors—from golden red to tawny, depending on duration of aging. Two dates appear on the label—the date of harvest and the date of bottling.

Port wine with *indication of age* (10-, 20-, 30-, or over 40-*year-old*) is a red or white wine of high quality, obtained by blending wines aged in wood from different years. The age indicated on the label corresponds to the approximate average age of the wines used in the blend. In mouth, the wine is smooth and well balanced with a persistent aroma. Gradual exposure to air concentrates and intensifies the original fruit character of the wines, creating complex flavors resembling honey and spices with essences of dry peaches, hazelnuts, and vanilla.

Reserve port is another quality version, being a blend of wines made from red or white grapes aged in wood. If the red or white wine is aged in wood for more than 6 years, it can be, respectively, designated as tawny or white port.

VI. CHEMICAL COMPOSITION

A. Polyphenols profile

Red wine possesses a very complex matrix because of the extraction of a wide variety of compounds from the skins. Among red wines, port wine has a higher complexity, owing to the addition of grape spirits (to induce a premature termination of fermentation). This augments its potential to form new compounds (Pissarra *et al.*, 2005).

The phenolic compounds extracted from the fruit contribute to the development and stability of the wine's red color. The color evolution during vinification and aging is mainly due to chemical transformations to the phenolic compound derived from the fruit. Anthocyanins, responsible for the purple-red color of young wines, participate in reactions with other phenolic compounds to generate other, more chemically stable molecules. These changes involve oxidation, polymerization, and other

complex interactions, in which anthocyanins are involved in producing high-molecular-weight compounds. The pigments so formed change the wine's color and provide it with stability.

According to some studies, the compounds form as reaction by-products between anthocyanins and flavan-3-ols, such as catechins and proanthocyanidins (condensed tannins). These reactions may also involve other molecules such as acetaldehyde, pyruvic acid, acetoacetic acid, vinylphenol, vinylguaiacol, vinylcatechol, and dimerization of anthocyanins (Asenstorfer *et al*., 2001; Atanasova *et al*., 2002; Bakker and Timberlake, 1997; Brouillard and Dangles, 1994; Fulcrand *et al*., 1996, 1998; He *et al*., 2006; Liao *et al*., 1992; Remy *et al*., 2000; Salas *et al*., 2004; Schwarz *et al*., 2003; Timberlake and Bridle, 1976).

The most rapid changes in wine color composition appear to occur during the first year, when the wine is normally in bulk storage (Somers, 1971). This phase is considered to be distinct from reactions occurring latter when the wine is in bottle and well protected from further contact with air (Ribéreau-Gayon *et al*., 1983).

Oxidative cycloaddition products between pyruvis acid and anthocyanins have been identified in port after 1 year of aging (Mateus and Freitas, 2001; Mateus *et al*., 2002). Identification is complicated by their presence is trace amounts. Nevertheless, advances in analytical techniques are permitting their identification (Mateus *et al*., 2002). These stable malvidin–pyruvic acid adducts have been reported in both red wines and grape pomace (Bakker *et al*., 1993; Bakker and Timberlake, 1997; Fulcrand *et al*., 1998). These pigments are more resistant to bisulphate bleaching than the original anthocyanins (Bakker and Timberlake, 1997). Recently, a new class of yellowish pigments has been identified in aged port (He *et al*., 2010). These are derived from anthocyanin secondary products (vitisins A), which are precursors of these new pigments (oxovitisins). They begin to appear in the latter stages of wine aging and may contribute to the evolution of aged ports.

B. Volatiles in port wines

The aroma profile of a young port differs markedly from that of an aged tawny port and bottle-aged wines. Notes such as floral, bergamot-like, violet, jasmine, present in young wines, change during maturation in oak barrels (Falqué *et al*., 2004; Silva Ferreira *et al*., 2006). The typical flavors developed during aging may be described by terms such as maderized, rancio, burnt, dry fruit, nutty, and spicy (Freitas *et al*., 1999; Silva Ferreira *et al*., 2005). The volatile profile expressed using gas chromatography/mass spectrometry is also very different (Fig. 5.11). The commercial value of aged tawny is related to the aroma characteristics developed during its prolonged aging in vats permeable to the entrance of

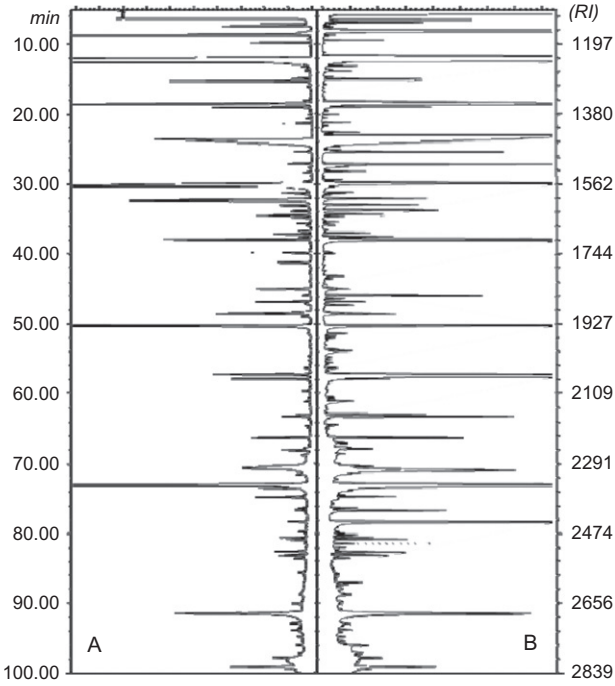

FIGURE 5.11 Chromatogram of a DCM extract of (A) young ruby port wine (3-years-old) and (B) 40-*years-old* tawny port wine.

oxygen. Features such as oxygen, temperature, and pH are important parameters that influence these oxidative transformations.

Bottle-aged ports, such as *vintage* port, develop floral and violet notes that could be related to the presence of some nor-isoprenoid molecules. For example, the presence of β-damascenone, β-ionone, 2,2,6-trimethyl-cyclohexanone (TCH), 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), and vitispirane was found to differ markedly between young and aged samples (Silva Ferreira and Guedes de Pinho, 2004). TCH is responsible for a ''rock-rose-like'' aroma (Freitas *et al.*, 1999). Precursors of nor-isoprenoids such as carotenoids, β-carotene, lutein, neoxanthin, and violaxanthin can be present in port wines due to the short period of fermentation (Falqué *et al.*, 2004; Guedes de Pinho *et al.*, 2001; Mendes Pinto *et al.*, 2005).

Additional studies by Silva Ferreira *et al.* (2008) have investigated the influence of features such as dissolved O_2, free SO_2 levels, pH, and time/temperature on nor-isoprenoid presence. Of these effects, temperature and pH had the largest effects. Oxygen saturation (>10 mg/l) decreased their presence. However, in traditional barrel aging TDN, vitispirane, and

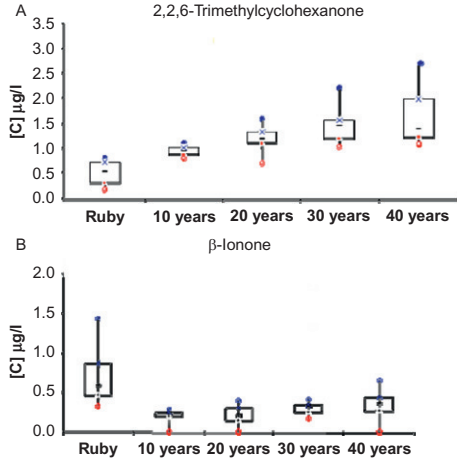

FIGURE 5.12 Levels of (A) 2,2,6-trimethylcyclohexanone and (B) β-ionone in ruby port wine and oak barrels aged port wines.

TCH increased (Fig. 5.12A), whereas the levels of β-ionone (Fig. 5.12B) and β-damascenone decreased. Over *40-year-old* ports had, respectively, 15, 5, and 3 times higher levels of TDN, vitispirane, and TCH than young ports.

Young ports possess higher concentrations of volatile sulfur compounds than do aged ports (Fig. 5.13; Silva Ferreira *et al.*, 2003a). As shown in Tables 5.7 and 5.8, sulfur compounds, such as 2-mercaptoethanol (rubber/burnt odor), 2-(methylthio)ethanol (French bean aroma), ethyl 3-(methylthio)propionate (metallic, sulfur aroma), 3-(methylthio)-1-propanol (cauliflower aroma), *cis*-(odorless), and *trans*-2-methyltetrahydrothiophen-3-ol (onion, chive-like aroma), 3-(ethylthio)-1-propanol (rancid, sweaty odor), 4-(methylthio)-1-butanol (metallic-bitter, grassy, earthy odor), dimethyl sulfone (odorless), benzothiazole (rubber odor), 3-(methylthio)-1-propionic acid (butter, rancid odor) and *N*-3-(methylthiopropyl) acetamide (odorless) are absent or present in lower contents in old tawnys than in young ports. Due to their sensory thresholds, the long-aged ports are unlikely to develop sulfur off-flavors as may occur in young ports (Ferreira *et al.*, 1997; Mestres *et al.*, 2000; Silva Ferreira *et al.*, 2003a).

The effect of dissolved oxygen, free SO_2, pH, and time/temperature influences on the content of dimethyl sulfide (DMS), 2-mercaptoethanol, dimethyl sulfone, methional, and 3-(methylthio)-1-propanol in ports was studied by Silva Ferreira *et al.* (2003a). They found that 3-(methylthio)-1-propanol decreased significantly in the presence of O_2, and no methional formed. 2-Mercaptoethanol also decreased in the presence of O_2, whereas

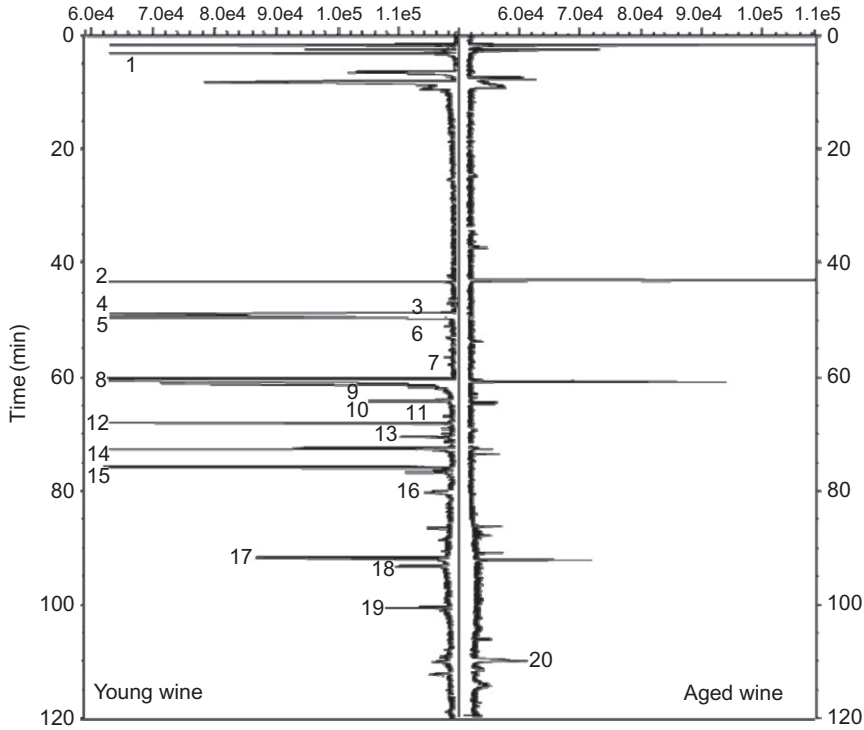

FIGURE 5.13 Chromatogram of a dichloromethane extract of a Touriga Nacional (1999 vintage) and of a 20-year-old tawny port wine: 1, dimethyl sulfide; 2, internal standard, ethyl (methylthio)acetate; 3, 2-mercaptoethanol; 4, 2-(methylthio)ethanol; 5, 2-methyltetrahydrothiophen-3-one; 6, ethyl 3-(methylthio)propionate; 7, acetic acid 3-(methylthio)propyl ester; 8, 3-(methylthio)-1-propanol; 9, *cis*-2-methyltetrahydrothiophen-3-ol; 10, 3-(ethylthio)-1-propanol; 11, *trans*-2-methylhydrothiophen-3-ol; 12, 4-(methylthio)-1-butanol; 13, 3-(methylthio)-1-hexanol; 14, dimethyl sulfone; 15, benzothiazole; 16, unidentified; 17, 3-(methylthio)-1-propionic acid; 18, unidentified; 19, *N*-3-(methylthiopropyl)acetamide; 20, *bis*(2-hydroxydiethyl) disulfide.

the respective disulfide was formed. In contrast, DMS and dimethyl sulfone were formed in the presence of O_2. An increase in DMS during bottle aging has been observed by other authors (Anocibar Beloqui, 1998; Spedding *et al.*, 1980). DMS contributes to aromas such as quince, truffle, and metallic.

Oxidative reactions, occurring during aging of port in barrels, increase aldehyde, methyl ketone (Silva Ferreira and Bertrand, 1996), acetal, and lactone contents. Of these, acetaldehyde was the major aliphatic aldehyde detected and showed the most significant increase during barrel aging. Due to glycerol being a major wine constituent, acetal formation from a

TABLE 5.7 Concentrations of volatile sulfur compounds in young ruby ports

Compound (μg/l)	Average (15 wines)[a]	Max.	Min.	SD
2-Mercaptoethanol	48.4	134	7.0	35.0
2-(Methylthio)ethanol	436	1336	70	362
Ethyl 3-(methylthio)propionate	5.6	9.1	nd	2.5
3-(Methylthio)-1-propanol	1055	2144	493	436
cis-2-Methyltetrahydrothiophen-3-ol	20	25	2	8
3-(Ethylthio)-1-propanol	19	45	5	11
trans-2-Methyltetrahydrothiophen-3-ol	21	23	5	1
4-(Methylthio)-1-butanol	27	33	21	4
Dimethyl sulfone	119	175	45	45
Benzothiazole	233	513	70	145
3-(Methylthio)-1-propionic acid	700	1811	500	354
N-3-(Methylthiopropyl)acetamide	189	899	10	309

[a] Wines coming from 1999 vintage, from five different varieties, from two different subregions, with different winemaking procedures; nd, not detected; SD, standard deviation.

TABLE 5.8 Concentrations of volatile sulfur compounds in old tawny port wines

Compound (μg/l)	Average (12 wines)[a]	Max.	Min.	SD
2-Mercaptoethanol	nd	23	nd	4
2-(Methylthio)ethanol	4	70	23	9
Ethyl 3-(methylthio)propionate	nd	nd	nd	nd
3-(Methylthio)-1-propanol	174	206	149	17
cis-2-Methyltetrahydrothiophen-3-ol	nd	nd	nd	nd
3-(Ethylthio)-1-propanol	nd	nd	nd	nd
trans-2-Methyltetrahydrothiophen-3-ol	nd	nd	nd	nd
4-(Methylthio)-1-butanol	nd	nd	nd	nd
Dimethyl sulfone	17	75	nd	31
Benzothiazole	nd	nd	nd	nd
3-(Methylthio)-1-propionic acid	109	448	nd	197
N-3-(Methylthiopropyl)acetamide	nd	nd	nd	nd

[a] Tawny wines coming from different ages between 10 and 30 years old; nd, not detected; SD, standard deviation.

reaction between acetaldehyde and glycerol is considered an indicator of wine age (Silva Ferreira *et al.*, 2002, 2003b). More recently, sotolon has being suggested as being a key odorant in the aroma of aged port, there being good correlation between the age of a tawny and sotolon

concentration (Silva Ferreira *et al.*, 2005). This odor active molecule has been shown to contribute to the aroma of Jura wines, ''vin jaunes,'' ''vins doux naturels,'' Tokay wines, botrytized wines, and sherries (Cutzach *et al.*, 1999, 2000; Williams *et al.*, 1983).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from FCT (via a postgraduate fellowship ref. SFRH/BPD/63851/2009) and the photos provided for publication by the IVDP, IP. Special thanks to Sandra Bandeira, from IVDP library's, for her attention and availability.

REFERENCES

Abade, E. and Guerra, J. (2008). Método de pontuação das parcelas de vinha—Contributos para a sua revisão. Centros de estudos Vitícolas do Douro, Régua, Portugal.

Almeida, M. J. and Laureano, P. (2007). Memórias do Vinho. Civilização Editora, Portugal.

Andersen, T., Aguiar, F. B., and Curado, M. J. (2004). The Alto Douro region greenway. *Landsc. Urban Plan.* **68**, 289–303.

Anocibar Beloqui, A. (1998). Contribution a' l'e´tude des compose´s soufre´s volatiles des vins rouges. Thèse de Doctorat de l'Universite´ de Bordeaux II, France.

Asenstorfer, R. E., Hayasaka, Y., and Jones, G. P. (2001). Isolation and structures of oligomeric wine pigments by bisulfite-mediated ion-exchange chromatography. *J. Agric. Food Chem.* **49**, 5957–5963.

Atanasova, V., Fulcrand, H., Cheynier, V., and Moutounet, M. (2002). Effect of oxygenation on polyphenol changes occurring in the course of wine-making. *Anal. Chim. Acta* **458**, 15–27.

Bakker, J. and Timberlake, C. (1997). Isolation, identification, and characterization of new color stable anthocyanins occurring in some red wines. *J. Agric. Food Chem.* **45**, 35–43.

Bakker, J., Picinelli, A., and Bridle, P. (1993). Model wine solutions: Color and composition changes during aging. *Vitis* **32**, 111–118.

Böhm, J. (2007). Portugal Vitícola—O grande livro das castas. Chaves Oliveira. Publicações, SA, Lisboa, Portugal.

Brouillard, R. and Dangles, O. (1994). Anthocyanin molecular interactions: The first step in the formation of new pigments during wine aging? *Food Chem.* **51**, 365–371.

Cardoso, A. and Silva, F. R. (2007). Porto do Vinho. Civilização Editora, Porto, Portugal.

Cutzach, I., Chatonnet, P., and Dubordieu, D. (1999). Study of the formation mechanisms of some volatile compounds during the aging of sweet fortified wines. *J. Agric. Food Chem.* **47**, 2837–2846.

Cutzach, I., Chatonnet, P., and Dubordieu, D. (2000). Influence of storage conditions on the formation of some volatile compounds in white fortified wines (*Vins doux Naturels*) during the aging process. *J. Agric. Food Chem.* **48**, 2340–2345.

Decree-Law nº104/85, 10th of April. Ministério da Agricultura. Diário da República, 1ª série, no. 83..

Decree-Law nº173/2009 of 3rd of August. Ministério da Agricultura, do desenvolvimento rural e das pescas. Diário da República, 1ª série, no. 148..

Falqué, E., Silva Ferreira, A. C., Hogg, T., and Guedes de Pinho, P. (2004). Determination of aromatic descriptors of Touriga Nacional wines by sensory descriptive analysis. *Flavour and Fragr. J.* **19**, 298–302.

Ferreira, V., Escudero, A., Fernández, P. E., and Cacho, J. (1997). Changes in the profile of volatile compounds in wines stored under oxygen and their relationship with the browning process. *Z. Lebensm. Unters. Forsch* **205**, 392–396.

Fonseca, A. M., Galhano, A., Pimentel, E. S., and Rosas, J. R. P. (1998). Port Wine—Notes on its history, production & technology. Edited by Instituto do Vinhos dos Porto. Lipografia Nacional, Porto, Portugal.

Freitas, V., Ramalho, P., Azevedo, Z., and Macedo, A. (1999). Identification of some volatile descriptors of the rock-rose like aroma of fortified red wines from Douro Demarcated Region. *J. Agric. Food Chem.* **47**, 4327–4331.

Fulcrand, H., Cameira dos Santos, P. J., Sarni-Machado, P., Cheynier, V., and Favre-Bonvin, J. (1996). Structure of new anthocyanin-derived wine pigment. *J. Chem. Soc. Perkin Trans. 1* **I**, 735–739.

Fulcrand, H., Benabdeljalil, C., Rigaud, J., Cheynier, V., and Moutounet, M. (1998). A new class of wine pigments generated by reaction between pyruvic acid and grape anthocyanins. *Phytochemistry* **47**, 1401–1407.

Guedes de Pinho, P., Ferreira, A. C., Gomez Benitez, J., Mendes Pinto, M., and Hogg, T. (2001). Determination of carotenoid profiles in grapes. *J. Agric. Food Chem.* **49**, 5484–5488.

Guedes de Pinho, P., Falqué, E., Castro, M., Oliveira e Silva, H., Machado, B., and Silva Ferreira, A. C. (2007). Further insights into the floral character of Touriga Nacional wines. *J. Food Sci. I* **72**, S396–S401.

Guénaël, R. (2005). La bible du Porto. Les Publications Modus Vivende Inc., Montreal, Canada.

Guichard, F., Pereira, G. M., Guimaraens, D., Peixoto, F., Almeida, A. R., Lopes, T. S., Sandeman, G., and Carvalho, M. (2003). O Vinho do Porto. Edited by Instituto dos Vinhos do Douro e do Porto. Porto, Portugal.

He, J., Santos-Buelga, C., Silva, A. M., Mateus, N., and Freitas, V. (2006). Isolation and structural characterization of new anthocyanin-derived yellow pigments in aged red wines. *J. Agric. Food Chem.* **54**, 9598–9603.

He, J., Oliveira, J., Silva, A. M., Mateus, N., and Freitas, V. (2010). Oxovitisins: A new class of neutral pyranone–anthocyanin derivatives in red wines. *J. Agric. Food Chem.* **58**, 8814–8819.

IVDP, (2009). Instituto dos Vinhos do Douro e do Porto, Comunicado de Vindima 2009. Ministério da Agricultura, do Desenvolvimento Rural e das Pescas.

Liao, H., Cai, Y., and Haslam, E. (1992). Polyphenol interactions. Anthocyanins co-pigmentation and colour changes in red wines. *J. Food Agri.* **59**, 299–305.

Martins, J. P. (2001). A Wine Lover's Guide to Port—The Inside Story of a Unique Fortified Wine. Publicações Dom Quixote, Lisboa, Portugal.

Mateus, N. and Freitas, V. (2001). Evolution and stability of anthocyain-derived pigments during port wine aging. *J. Agric. Food Chem.* **40**, 5217–5222.

Mateus, N., Pascual-Teresa, S., Rivas-Gonzalo, J., Santos-Buelga, C., and Freitas, V. (2002). Structural diversity of anthocyanin-derived pigments in port wines. *Food Chem.* **76**, 335–342.

Mayson, R. (2003). The wines and vineyards of Portugal. Edited by Beazley, M.Octopus Publishing Group Ltd, London, Great Britain.

Mendes Pinto, M. M., Silva Ferreira, A. C., Caris-Veyrot, C., and Guedes de Pinho, P. (2005). Carotenoid, chrorophyll and chlorophyll-derived compounds in grapes and port wines. *J. Agric. Food Chem.* **53**, 10034–10041.

Mestres, M., Martí, M. P., Busto, O., and Guasch, J. (2000). Analysis of low volatility organic sulphur compounds in wines by solid phase microextraction and gas chromatography. *J. Chromatogr. A* **881**, 583–590.

Oldenburg, H. (1999). Port. Smag & Behag, Copenhagen, Denmark.

Oliveira, C., Silva Ferreira, A. C., Barbosa, A., Guerra, J., and Guedes de Pinho, P. (2006). Carotenoid profile in grapes related to aromatic compounds in wines from Douro region. *J. Agric. Food Chem.* **71**, S001–S007.

Pereira, G. M. (1991). O Douro e o Vinho do Porto—de Pombal a João Franco. Edições Afrontamento, Lda, Porto, Portugal.

Pissarra, J., Lourenço, S., Machado, J. M., Mateus, N., Guimarães, D., and Freitas, V. (2005). Contribution and importance of wine spirit to the port wine final quality—Initial approach. *J. Sci. Food Agric.* **85**, 1091–1097.

Portaria nº 413/2001 of 18th April. Ministério da Agricultura, do desenvolvimento rural e das pescas. Diário da República, 1º série-B, no. 91.

Regulamento nº 242/2010 of 15th March. Instituto dos Vinhos do Douro e do Porto, I. P. Diário da República, 2ª série, no. 51.

Regulamento nº 84/2010 of 8th of February. Diário da República, 2ª série, no. 26.

Remy, S., Fulcrand, H., Labarbe, B., Cheynier, V., and Moutounet, M. (2000). First confirmation in red wine of products resulting from direct anthocyanin-tannin reactions. *J. Sci. Food Agric.* **80**, 745–751.

Ribéreau-Gayon, P., Pontallier, P., and Glories, Y. (1983). Some interpretations of colour changes in young red wines during their conservation. *J. Sci. Food Agric.* **34**, 505–516.

Salas, E., Atanasova, V., Poncet-Legrand, C., Meudec, E., Mazauric, J. P., and Cheynier, V. (2004). Demonstration of the occurrence of flavanol–anthocyanin adducts in wine and in model solutions. *Anal. Chim. Acta* **513**, 325–332.

Schwarz, M., Wabnitz, T. C., and Winterhalter, P. (2003). Pathway leading to the formation of anthocyanin–vinylphenol adducts and related pigments in red wines. *J. Agric. Food Chem.* **51**, 3682–3687.

Silva Ferreira, A. (1998). Caracterisation du vieillissement du Vin de Porto. Approche chimique et statistique. Role aromatique du sotolon. Thèse de Doctorat de l'Université Victor Segalen, Bordeaux II, France.

Silva Ferreira, A. C. and Bertrand, A. (1996). Evolution de quelques constituants du vin de Porto au cours du vieillissement. Etude particulière des composés carbonylés. *In* ''Œnologie 95, 5ème Symposium International d'Œnologie''. pp. 520–523. Lavoisier, Paris, France.

Silva Ferreira, A. C. and Guedes de Pinho, P. (2004). Nor-isoprenoids profile during port wine ageing—Influence of some technological parameters. *Anal. Chim. Acta* **513**, 169–176.

Silva Ferreira, A. C., Barbe, J. C., and Bertrand, A. (2002). Heterocyclic acetals from glycerol and acetaldehyde in port wines: Evolution with aging. *J. Agric. Food Chem.* **51**, 4356–4363.

Silva Ferreira, A. C., Rodrigues, P., Hogg, T., and Guedes de Pinho, P. (2003a). Influence of some technological parameters on the formation of dimethyl sulfide, 2-mercaptoethanol, methionol, and dimethyl sulfone in Port wines. *J. Agric. Food Chem.* **51**, 727–732.

Silva Ferreira, A. C., Hogg, T., and Guedes de Pinho, P. (2003b). Identification of key odorants related to the typical aroma of oxidation-spoiled white wines. *J. Agric. Food Chem.* **51**, 1377–1381.

Silva Ferreira, A. C., Avila, I., and Guedes de Pinho, P. (2005). Sensorial impact of sotolon as the ''perceived age'' of tawny port wines. Chap 10. *In* ''Natural Flavors and Fragrances, Chemistry, Analysis and Production'', (Frey Carl and Rouseff Russell, Eds). published by American Chemical Society (ACS). **908**, 141–159.

Silva Ferreira, A. C., Falqué, E., Castro, M., Oliveira e Silva, H., Machado, B., and Guedes de Pinho, P. (2006). Identification of key odorants related with high quality Touriga Nacional wine. *Dev. Food Sci.* **43**, 217–220.

Silva Ferreira, A. C., Monteiro, J., Oliveira, C., and Guedes de Pinho, P. (2008). Study of major aromatic compounds in port wines from carotenoid degradation. *Food Chem.* **110**, 83–87.

Somers, T. C. (1971). The polymeric nature of wine pigments. *Phytochemistry* **10**, 2175–2186.

Spedding, D. J., Eschenbruch, R., and Purdie, A. (1980). The distribution of dimethyl sulphide in some New Zealand wines. *Vitis* **19**, 240–246.
Timberlake, C. F. and Bridle, P. (1976). Interactions between anthocyanins phenolic compounds and acetaldehyde. *Am. J. Enol. Viticult.* **27**, 97–105.
Williams, A. A., Lewis, M. J., and May, H. V. (1983). The volatile flavour components of commercial port wines. *J. Sci. Food Agric.* **343**, 311–319.
Zamith, A. F. (2001). The Port Wine guide. Chaves Ferreira, Publicações, SA, Lisboa, Portugal.