Aging of Port Wine: Chemical and Perceptual Changes

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Port wines from the Douro region in northern Portugal are made from various varieties of *Vitis Vinifera* grapes, with Souzao and Trousseau generally making higher-quality ports and Carignane and Grenache making lower-quality ports (Singleton 1964). The native Touriga Nacional grape may be used in every type. Port wine commonly faces descriptors such as “maderized,” “burnt,” “dry fruit,” “nutty,” “spicy,” and most notably, “*rancio*,” a twist on the concept of “rancid” but in favorable presentation: controlled oxidation and aging effects produce a specific type of flavor associated with browning seen in all port wines and many sherries and madeiras. Concerning production of port wine, after harvesting the chosen grapes, sulfur dioxide is normally added and maceration and fermentation follow. Port’s higher sweetness is obtained by draining and pressing the mash before fermentation completes and then adding brandy spirits to the must, a process known as *benefecio*. The brandy spirits used may be 77% ethanol by volume or higher, making the final mixture between 18 and 22% ethanol and preventing any further fermentation (Bakker 1986). This halted fermentation greatly decreases the wines’ risk of oxidation and results in a high level of residual sugars. There are several types of port currently manufactured, with the primary determinant factors for each type being the quality of the average harvest for all vineyards and length of time stored in casks before release. Vintage years of port are named by the Instituto dos Vinho do Douro y Porto (IVDP); true port wine cannot be labeled “vintage” unless it is fermented exclusively from grapes from a vintage year. According to IVDP practices, the wine is first tasted immediately after it has been racked from the lees during the winter following the year in which it was made (IVDP 2008a). Some port winemakers set aside all vintage production for vintage release, but most major manufacturers set aside only a portion and use the rest in blends that appeal to a larger market due to their lower price points. Vintage port is meant to be aged in the bottle for 10–50 years before consumption; its market price reflects its age in addition to its quality. Late-bottled vintage (LBV) port is stored in casks for a longer period of time (4–6 years, compared to 2–3 years for vintage) before market release, speeding up the maturation process and allowing the bouquets to develop upon bottling. LBV ports are meant to be consumed upon release but may be aged in the bottle for up to 5 years. Port with an Indication of Date is a mixture of wine from various years, with the average of all harvest years being indicated on the bottle (IVDP 2008a). The latter two types of port are generally considered slightly inferior to vintage port but contribute to about 50% of a manufacturer's sales. White port is also manufactured but comprises a much smaller portion of the market share and is not discussed in this paper due to a lack of available data.

Many of the changes that take place in the appearance, aroma, and taste of a port wine are the same as those for red table wines. In the same way that many young red wines are not palatable, ports consumed before at least three years of maturing would appear and taste much different from those that are usually marketed. Young red wines derive much of their pigmentation from anthocyanins, but these chemicals, when they lose stability after leaving the fruit, undergo a series of reactions leading to their degradation. Because of this, anthocyanins are found less frequently in older wines and polymeric pigmentation accounts for most of the red color in well-aged wines. This has been determined by gel chromatographic separation (Somers 1971) and thin-layer chromatography (Timberlake and Bridle 1976). It has also been shown that well-aged wine color and pigmentation are correlated: the disappearance of much of the bitterness, astringency, and harshness during aging has been attributed to the reactions of chemicals that result in the formation of pigmentation polymers. Thus, color may plausibly be loosely used as a reflection of wine age and quality for the casual drinker. A particular entity, the cationic version of flavylium, has been well documented as a result of anthocyanin condensation during aging (Jurd 1967). The concentration of flavylium cations relative to hydrated anthocyanins is determined by pH, anthocyanin to tannin ratio, and oxygen availability. While pH is dependent on the grapes' maturity and fermentation potential, maceration practices can greatly affect the proportions of anthocyanins and tannins, as increased skin contact will lead to increased anthocyanin absorption by the must (Fulcrand et al. 2005).

In addition to the normal reactions between anthocyanins and phenolic compounds, a phenomenon known as copigmentation has an appreciable amount of impact on red wine color development. Copigmentation is a process by which pigments and noncolored organic compounds (cofactors) form molecular associations (Boulton 1996). These associations can cause the pigments to exhibit far greater color than would be expected from their concentrations. Some authors believe that copigmentation accounts for 50% of color in red wines (Neri and Boulton 1996). Potential for copigmentation is a quality intrinsic to the molecules themselves; the actual degree of copigmentation is dependent upon pigment concentration, ratio of cofactor to pigment, pH, and ions in solution (Boulton 1996). Wine varietals such as Pinot Noir or Sangiovese presumably have a lower concentration of cofactors, as determined either by the grapes' maturity or maceration practices, and appear lighter than they would if they had been exposed to a higher concentration of cofactors; this is an example of how lighter colored wines can result from darker berries. Concerning aging, since many of the flavenoids found in red wines can act as relatively good cofactors, a significant fraction of their total concentration may be involved in the copigmentation reactions at any given time. This usage of flavenoids may draw many molecules from the pool that could potentially be involved in aging reactions such as formation of flavenoid macromolecules, meaning slower rates of spoilage, but also slower rates of maturation for wines that must be aged. If anthocyanins are also involved in the same reactions, the reaction could be second-order, creating a dramatic effect on reaction kinetics. Berg (1975) even suggested that a wine's susceptibility to oxidation was directly related to the degree of association of its pigments with their cofactors, but not much data could be found by the author of this paper to either support or refute Berg's hypothesis. Flavylium cations are the most widely documented molecules in red wine copigmentation; it is unclear whether all or some of the others also participate in the phenomenon, and whether copigmentation is a less important factor in fortified wines such as port because the higher ethanol fraction may interfere with anthocyanin condensation.

Most of the chemical changes that take place during the aging of port wine mirror those of red table wines discussed previously, but there is an added complexity in the manufacture and storage of port: the brandy spirits used to arrest fermentation can have a substantial impact on the speeds and frequencies of reactions that occur. The two major chemicals resulting in appearance and aroma changes in port, as with many table and dessert wines, are anthocyanins and free aldehydes (largely in the form of acetaldehyde, which contains natural pigments) (Bakker 1986). Multiple studies have confirmed that the deep red pigmentation of ports is a function of free aldehyde concentration (Berg and Akiyoshi, Timberlake and Bridle). Two other key chemicals, 3-hydroxy-4,5-dimethyl-2(5H)furanone (henceforth sotolon) and the heterocyclic acetals resulting from glycerol and aldehyde reactions, have been identified as important in fortified wine aging and studied specifically in port wines and will also be discussed in this paper (Silva Ferreira et al. 2003, Silva Ferreira et al. 2002).

Generally, concerning appearance, ports made from the same grape cultivars tend to age in similar ways: their color vibrancies increase during the same months, reach a plateau, and then decreas to create a browner appearance. The color density of a port without any added acetaldehyde or sulfur dioxide increases linearly for roughly 16 weeks (Bakker 1986). Bakker and her associates noticed that this color increase was correlated with a loss of total aldehyde, creating the hypothesis that consumption of aldehyde results in increased color, which has provided the basis for many of the more recent research in port aging. Since aldehyde can only react in the free form, i.e., not bound to SO_2, tests were performed to analyze color density with varying levels of aldehyde and SO_2. The researchers found that when free aldehyde was zero (an environment created by adding a plethora of SO_2), there was no increase in port color and no reaction of acetaldehyde. Only when free aldehyde appeared was there an increase in color. As SO_2 normally becomes oxidized to sulfate during aging, it is argued that the characteristic brown appearance of port begins to evolve only after the SO_2 decreases enough to allow free aldehyde to provide pigmentation (Bakker 1986). This evolution in most port wines happens after four to five months of storage with normal racking (Mateus and Freitas 2001). To assess the impact of these aging-related color changes on perceived wine quality, Bakker and Arnold (1993) enlisted trained tasters to analyze 39 port samples ranging from low pigmentation to high pigmentation as a function of aldehyde and anthocyanin content in a controlled environment assuring no visual cues. Regression analysis showed that quality ratings from independent tastings consistently reflected that browner ports were indeed perceived to be of higher quality.

Because of the route by which they are formed, Silva Ferreira et al. (2003) argue that certain compounds accumulate predictably and can be used as indicators of age. The nutty, tawny, or *rancio* aromas are used by the IVDP as indicators of potential quality as they are analyzed directly from the casks. The presence of aldehydes and methyl ketones were shown to be related to the *rancio* odor, but the aforementioned chemical sotolon, often found in other specialty wines such as *vins doux*, sherry, and botrytized wines, was recently shown to be more important in sensory analysis of particular "old port" aromas (Silva Ferreira et al. 2003). The flavor threshold of sotolon was determined to be 19 micrograms/L in port wine, roughly the same as in sherry (Martin et al. 1992). This odorant plays a strong role not only in the establishment of port "smelling like port," but also in the analysis of quality for each particular wine, especially for wines 10 years or older (Silva Ferreira et al. 2003). Researchers have correlated the levels of sotolon found in certain lots with the typical aroma of aged port wine by providing trained tasters, deprived of visual and gustatory cues, with ports with varying levels of sotolon. It was found that sotolon was the main chemical in evaluating the age of the wines, and that samples supplemented with extra sotolon were consistently ranked as older.

In a study contemporaneous with the sotolon study, it was found that the condensation reaction between glycerol and aldehyde in port leads to the formation of four isomers, all of which have already been identified in sherry (Silva Ferreira 2002). Isomers of heterocyclic acetaldehyde acetals were found in port wine at contents between 9.4 to 175.3 mg/L. The most abundant of the four, *cis*-5-hydroxy-2-methyl-1,3-dioxane, had already been reported in higher concentrations in older red dessert wines (Simpson 1980). Oxidative reactions occurring during the aging process of port wine stored in barrels increases the contents of acetaldehyde, and glycerol is a component of essentially all wines, so it is not unexpected that acetals could be formed. Silva Ferreira and his colleagues (2002) attempted to isolate the four resulting acetal isomers and determine their evolution during the aging of port wine. They analyzed perceptual differences in wines containing varying levels of each of the four isomers using both olfactometry and a 10-person panel. The concentrations of the four isomers did indeed increase with time, with *cis*-5-hydroxy-2-methyl-1,3-dioxane being the most prominent, as with other oxidative wines. After 10 years of barrel aging, up to 75% of the heterocyclic acetals were in the 1,3-dioxane form. This proportion remained constant thereafter, implying kinetic equilibrium is reached after roughly ten years. The mechanism of isomerization has been documented previously in other food products, summarized by the formation of an acetal carbocation which leads exclusively, through intramolecular reactions, to the dioxalanes first; however, the 1,3-dioxane form concentration increases over time due to its higher thermodynamic stability. The authors determined through human odor evaluation that the 1,3-dioxanes had the highest intensity aroma and were described as “old” and “port-like”. High acetaldehyde quantities are consumed by this reaction, with 30-40% of total aldehyde content being accounted for by heterocyclic acetals. Glycerol thus protects the wine against excessive acetaldehyde content and plays an essential role in port wine aging. Silva Ferreira and his colleagues, in the same study, also noticed that the concentrations of the four acetals were higher in the samples without free SO_2, whereas no acetal formation appeared at all in samples supplemented with SO_2. The authors hypothesized that SO_2 combined with acetaldehyde and blocked the acetalization reaction, underlining the importance of sulfur dioxide in port wine storage and the oxidative aging process. However, as free SO_2 is absent in proper in-bottle port wine storage conditions, the acetaldehyde-acetal balance changes so predictably with bottle age that Silva Ferreira and his colleagues argue they may be able to be used as an effective indicator of actual port wine age.

Secondary to the anthocyanin and aldehyde reactions that take place in the wine itself, the mechanisms of port wine production can have a large effect on aging temperament, color development, and aroma and taste descriptors. The short period available for anthocyanin extraction during port production makes the obtaining of adequate color a problem for many ruby port producers and occasionally for vintage port producers. Singleton and Guyman (1963) reported that red color was considerably greater for a lot of port fortified with aldehyde-spiked brandy than for another portion of the same base wine made with the same brandy lacking added aldehyde. This could seem contradictory to the previous claim that acetaldehyde reacts with anthocyanins and other components, causing a decrease in red color, so Singleton et al. (1964) decided to determine whether the presence of aldehydes in the added spirit increases the red pigment in ports. They collected multiple grape varieties commonly used in port wine (Trousseau, Mission, Grenache, Carignane) and produced port wine in the standard fashion until the spirits were added. Their lot was divided into two portions, one of which was treated with normal brandy and the other with high-aldehyde brandy. After spectral analysis at multiple-week intervals, the wine produced from each grape variety showed considerably more absorbance at 520nm (the characteristic adsorbance wavelength of port-style wines) than the control. Singleton and his colleagues concluded that fortification with spirits containing higher aldehyde concentrations produces a more intensely colored port, creating differences large enough to be seen by the eye, perhaps explaining why the reason that panelists rated the former wine as both older and of better quality. The authors of the study hypothesized that the added spirit aldehydes caused a reaction which modified a portion of the anthocyanins so that they became resistant to further color change yet adsorbed light to remain red. Reactive carbonyl compounds such as acetaldehyde can react with anthocyanins via an acid-catalyzed reaction that produced phenolic compounds -a process that produces a color change by its own mechanism, without encouraging further anthocyanic ("true") color development in the bottle. Thus, it could be possible for a port wine producer to halt fermentation using high-aldehyde spirits to make the wine appear older than it truly is by simply mirroring the color changes that take place during aging, or, worse, actually fraudulently label the wine as older. The IVDP has added clauses in the mandatory production rules of port wine to account for this nuance, but producers of port-style wines in other regions are usually not required to abide by any restrictions concerning aldehyde concentration in spirits. It could be possible that many of the red dessert wines on the market do not produce the typical port color by the standard aging mechanism, but rather are deep purple or brown because of added spirits spiked with extra acetaldehyde. The author of this paper, however, could not find any documented scandals or consumer complaints to account for this possibility. Singleton and colleagues (1965), after measuring the same samples 3 months after fermentation halt, discovered that the effects of added aldehyde diminish slightly with aging in the bottle, but also produce other "chemical and sensory effects" that were not discussed in the paper.

Another production process that differs from producer to producer is the technique used to crush the grapes before fermentation. The traditional method of crushing is to allow a human to tread the grapes in a lagar until he determines the desired consistency is reached, while more modernized houses use automated mechanical crushing. As the cost of labor has increased and several accidents through human treading have been recorded, most port houses now use mechanical crushing. The mechanized tanks are also able to pump the juice over the top of the partially crushed berries, a more consistent and better method of the punching down of the cap used by traditional manufacturers. Bakker et al. (1996) compared the two techniques with regard to sensory perception and aging temperament. They measured the amino acid concentration, sugars, ethanol, and pigmentation at different intervals during fermentation and barrel aging. Total phenols and total pigments in the two lots showed only small differences during fermentation; the must in the lagar lot was slightly higher in both by the end of the fermentation. Hence, at wine pH, the lagar wine was darker than the tank wine, measured by spectrophotometry. Hue angle and tint, the two components producing what is perceived as brownness, were the same for both wines. As the wine matured over six months to two years, the differences in color decreased.

After the two year measurement, the wines were both measured by machine and human to be identical in color. At the first analysis interval, just after fermentation was halted and the wines were barreled, a tasting panel scored the lagar wine considerably higher. However, when the tasters were asked to score appearance, aroma, and taste independently, the lagar wine scored higher only in appearance, while the mechanically crushed wine scored higher in aroma. Differences in taste scores were not significant. After two years, differences in appearance, aroma, and taste were imperceptible to the panel. The authors suspect that during maturation and aging the wines gradually lost their aroma and flavor derived mainly from the fruit and acquired the more typical port characteristics due to flavor acquirement in barrels. This study has implications for production of different types of port: for instance, a producer of tawny port that releases the wine shortly after fermentation may want to employ laborers to crush the grapes by treading, as the color development is better in the short-term, but vintage port manufacturers gain no appreciable advantage in quality by using lagar crushing because vintage port is aged for decades in barrels and bottles. However, a weakness of Bakker's 1996 study is that it only measured changes for one grape variety, Touriga Nacional, while we have already seen that at least four other varieties.

A third production process that appreciably affects aging reactions is the addition of pyruvic acid during port maturation in the barrel. During storage, while all port samples change from purplish-red to brownish-red, those with pyruvic acid added during maturation tended to have a lower incidence of hue angle change, meaning a longer duration of time of retention of purple coloring. Without added pyruvic acid, the hue angle tended to increase at least twice as much (Romero and Bakker 2000). After seven months, the port wines with pyruvic acid were lighter and redder than the controls. Evidently, during the first year of port wine aging, when most of the monomeric anthocyanins are degraded and polymeric compounds provide the majority of pigmentation, addition of pyruvic acid can be used to manipulate potential future color density. The reaction mechanism of this interaction was not speculated by the authors, and it is noteworthy that they do not discuss whether addition of pyruvic acid is a favorable decision, presumably because brownness of a port is desirable in some varieties but undesirable in others. Ruby ports, for instance, as their name implies, are perceived as highest quality when their color is deep red to purple, but older ports such as vintage or those bearing an indication of date are often desired to be browner because that color is reflective of controlled oxidation.

While the science of port wine aging is exciting to many, some economic and social parameters can be equally so, and provide an interesting note on which to end. Recently, commensurate with the increase in general table wine sales, revenue from aged and vintage port has seen an increase in both consumption and price. Trends in market price of aged port support this idea: a bottle of 1955 Graham's currently retails for about $995 (cf. $820, 1998), while a bottle of Dow's 1963 retails for about $395 (cf. $210, 1998) (IVDP 2008b). The same producers' 2000 vintages cost $140 and $100 respectively, while recent LBV or tawny varieties run $10–20. Clearly, as indicated by market prices, aged vintage port appeals to many people, probably for a number of different reasons. It is possible that the $970 price difference between an old vintage and a young LBV can be smelled or tasted by a select few, but it is the opinion of the author that it is more likely the aura of luxury and the impression begotten by a fine, old product that commands such a high pricetag. One of the most interesting articles that the author discovered was not published in a food science journal; rather, it was in the Journal of Applied Statistics that Fernando and Ramos (1999) reported "The parameters of [our recently developed sales] model...apply to a real data set from a Portuguese marketing survey. We find that purchases of bottles of port wine increase significantly with income class and the size of the household." Summarized, the article elucidated a solid yet predictable social trend: wealthy people drink a greater quantity of expensive port wine. This may not seem at all surprising, but it encourages one to wonder whether the finest ports are in the most deserving of hands. Wine critic Hugh Johnson recently claimed that "Sweet or dry, port was the most-drunk wine in Britain from the early 18th century to the early 20th" (Prial 2008). While its popularity across the world does not mirror that of 19th century Britain, there is, and will most likely remain, a huge market for aged port wine and a host of continuing scientific research into the changes during aging in order to maximize the quality of a product that has been a favorite of millions of people since 1692.

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