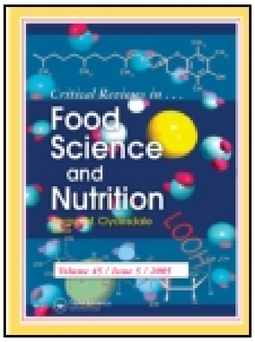

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Wine Aroma Compounds in Grapes: A Critical Review

CARMEN GONZÁLEZ-BARREIRO, RAQUEL RIAL-OTERO, BEATRIZ CANCHO-GRANDE, and JESÚS SIMAL-GÁNDARA
Nutrition and Bromatology Group, Department of Analytical and Food Chemistry, Faculty of Food Science and Technology, University of Vigo—Ourense Campus, E-32004 Ourense, Spain

Volatile organic compounds are vital to wine quality, determining their aroma and varietal characteristics. Which are present, and in what quantity, depends on the cultivar, the situation and soil of the vineyard, weather, cultivation methods, and wine-making practices. Here, we review the literature on the development of wine aroma compounds in grapes, and how it is affected by the above-named factors. Increasing understanding of these processes at the molecular level will aid vine growers in the optimal selection of harvest dates and other decisions favoring the consistent production of balanced, flavorful berries.

Keywords grapes, wines, volatiles, aroma, ripening, soil type, seasonal weather, vineyard practices

GRAPE BERRY DEVELOPMENT

From a wine-making perspective, the grape berry has three major types of tissue (Fig. 1): flesh, skin, and seed, the bulk of wine deriving from the flesh. These tissues differ considerably in composition, and accordingly contribute differently to overall wine composition. Because of this, the composition of wine can be manipulated by simply changing berry size: as a rule, wines made from smaller berries will have a greater proportion of compounds derived from skin and seed. The number of seeds in the berry can also influence the proportion of seed-derived components in wine. The perfectly formed grape has four seeds (Bioletti, 1938), but the actual number is usually smaller because environmental and nutritional conditions at flowering time limit the success of fertilization and hence the number of seeds per berry (Coombe, 1973; Ewart and Kliewer, 1977; Ebadi et al., 1995a, 1995b).

It is well known that grape berry development consists of two successive sigmoidal growth periods separated by a lag phase (Fig. 2): berry formation and berry ripening (Coombe and McCarthy, 2000). During the first period, which lasts for approximately 60 days after flowering, the berry is formed and the seed embryos are produced. Cell division is rapid in the first few weeks, and by the end of this period the total number of cells within the berry has been established (Harris et al., 1968). The extent of cell division has some bearing on the eventual size of the berry. The beginning of the second sigmoidal growth phase is characterized by the berry becoming softer and changing color (*véraison*). Overall, it approximately doubles in size during this period.

The needs of the grape berry are supplied through its stem or pedicel via a vascular system composed of xylem and phloem elements (Fig. 1). Xylem vessels transport water, minerals, growth regulators, and nutrients from the root system to the rest of the vine. Current evidence indicates that xylem is functional in grape berries early in development (up to *véraison*), but has reduced or zero functionality later (Greenspan et al., 1994). Phloem, which transports photosynthate (sucrose) from the canopy, is of small importance early in berry development, but becomes the primary supply line after *véraison* (Greenspan et al., 1994). Although increases in berry volume after *véraison*, primarily due to increased water content, are associated with increases in sugar content, there are grape varieties (notably Syrah) in which an increase in sugar content during the latter stages of ripening is not accompanied by increased berry volume but is instead due to berry shrinkage, apparently because of transpirational loss of water (McCarthy, 1997; McCarthy, 1999; McCarthy and Coombe, 1999). This inability of the berry to stay well-hydrated suggests that at this point in the season the phloem vessels feeding the berries of these varieties become blocked.

Research on the formation phase of berry development has been limited by the complex nature of this type of study, and

Address correspondence to Simal-Gándara Jesús, Nutrition and Bromatology Group, Department of Analytical and Food Chemistry, Faculty of Food Science and Technology, University of Vigo—Ourense Campus, E-32004 Ourense, Spain. E-mail: jsimal@uvigo.es
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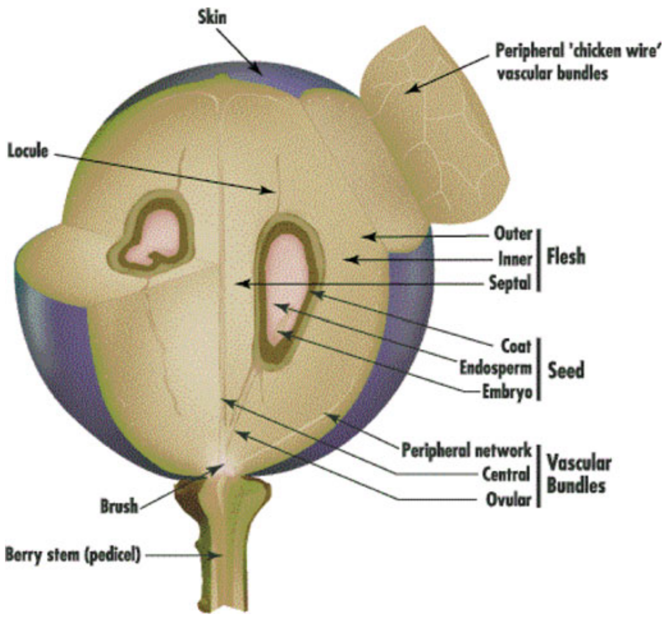

Figure 1 Structure of a ripe grape berry partially sectioned on the long and central axis to show internal parts (taken from Kennedy, 2002).

by the mistaken assumption that compounds produced or assimilated during this stage are of little interest from a sensory standpoint. It is nevertheless known that as the berry expands in volume, several solutes accumulate, all of which reach an apparent maximum around *véraison* (Possner and Kliewer, 1985). Among these compounds, particular interest attaches to tartaric acid, which accumulates in the skin early in development, and to malic acid, which accumulates in the flesh just prior to *véraison*. These acids (the accumulation of which may have evolved to dissuade foraging) are related to wine acidity, and are therefore critical for wine quality. Hydroxycinnamic acids also accumulate during the first growth period (Romeyer et al., 1983), as do monomeric catechins and other tannins (Kennedy et al., 2000a, 2000b; Kennedy et al., 2001). Hydroxycinnamic acids are dispersed in the flesh and skin, and are important because of their involvement in browning reactions and because they are precursors of volatile phenols (Licker et al., 1999). Tannins are present in skin and seed tissues – they are almost totally absent from the flesh – and are responsible for bitterness and astringence in red wine. These compounds are also believed to be important for the stability of the color of red wine. Other compounds relevant to wine quality that are produced or taken up during the first growth period include minerals (Possner and Kliewer, 1985), amino acids (Stines et al., 2000), micronutrients, and aroma compounds such as methoxypyrazines (Allen et al., 1989; Allen and Lacey, 1999). It is a mistake to believe that first-period compounds are of no sensory interest; many remain at harvest (though at lower concentration due to increased berry volume), and all the above are critically important for overall wine quality.

At *véraison*, the berry begins to accumulate sugar, taking up photosynthetic sucrose and hydrolyzing it to glucose and fructose (Robinson and Davies, 2000). Glycolysis is downregulated, and stored malate becomes the major carbon source for respiration (Coombe, 1992). The final sugar concentration depends on crop load, canopy size, plant health, hydration, and how long the grape is allowed to stay on the vine. Other determinants of wine quality that are established during this second growth phase are secondary metabolites, including most of the volatile flavor components (e.g., terpenoids, which are important for the pleasant aroma of varieties such as Riesling and Muscat) and also precursors (often glycosides) that become transformed into volatiles as the wine ages (Marais, 1983; Dimitriadis and Williams, 1984; Wilson et al., 1984; Park et al., 1991; Marais, 1994; Francis et al., 1999). Coombe and McCarthy (1997) referred to the period during which precursors are produced as "gestation." Aroma compounds are distributed in both the flesh and the skin of the berry, though mostly in the latter. By contrast, anthocyanins, which are determinant of red grape varieties and are also produced in the second growth period, are generally restricted to skin tissue.

Though the concentrations of most compounds produced during the first growth phase fall during the second due to dilution, reduction in concentration is in some cases also due to actual loss of quantity per berry. As noted above, this is the case of malic acid, especially in grapes grown in warmer regions, which accordingly tend to have less malic acid than those grown in cooler regions. Other examples include several methoxypyrazines that contribute to herbaceous ("vegetal") characteristics in varieties such as Cabernet Sauvignon and Sauvignon Blanc (Hashizume and Samuta, 1999). This decrease in pyrazines is thought to be linked to sunlight levels in the cluster, so if these characteristics are deemed to be undesirable (the current prevailing opinion), then canopy management can be used to reduce them.

Tannins also decline considerably on a per-berry basis during the second growth phase. In the case of seed tannins, the decrease appears to be due to oxidation as the tannins become fixed to the seed coat (Kennedy et al., 2000a, 2000b), a change that, in particular, reduces the levels of the most bitter tannins. Skin tannins, too, can decline, and also undergo modifications that increase their size, including association with pectins and anthocyanins, a modification with implications for wine texture and color stability (Kennedy et al., 2001).

FAMILIES OF VOLATILE COMPOUNDS RESPONSIBLE FOR GRAPE AROMA

Although a number of the odorant compounds contributing to wine quality are produced from nonvolatile compounds by the yeasts during fermentation, or are derived from precursors during the aging of wine, a good many are already present in the grape and come through fermentation unaltered or with only minor modifications. These compounds are responsible for the varietal aroma of wines. The term "varietal aroma" does not imply that each grape variety has specific volatile compounds; a

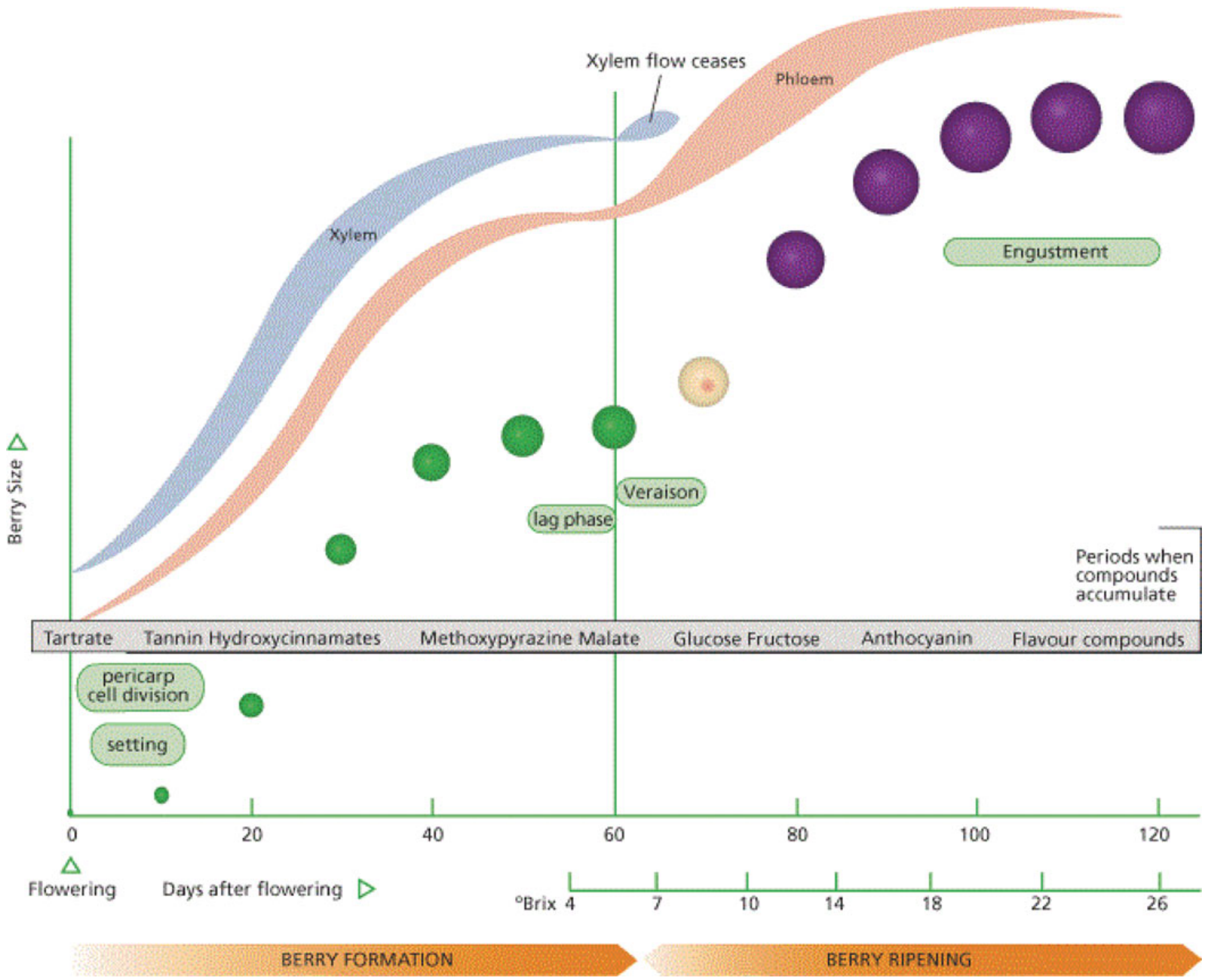

Figure 2 Diagram showing relative size and color of berries at 10-day intervals after flowering, the periods when various types of compound accumulate, juice °Brix, and an indication of the inflow of sap into the berry via xylem and phloem (taken from Kennedy, 2002).

given odoriferous compound or precursor is generally found in the musts and wines of several grape varieties. The individual aromatic personality of each grape variety is due to its particular combination of the various compounds (Ribéreau-Gayon et al., 2006). The accumulation of these compounds, of which several hundred have been identified, does not seem to be closely correlated with sugar concentration. The most important families of aroma and flavor compounds are organic acids, proanthocyanidins (tannins), terpenoids (monoterpenoids, sesquiterpenoids, and C_{13} norisoprenoids), and various precursors of aromatic aldehydes, esters, and thiols. Grape berries seem to lack anatomical structures for storage of lipophilic volatile organic compounds, which instead tend to be stored as water-soluble glycosides or conjugates with amino acids such as cysteine (Peyrot des Gachons et al., 2000). The glycosidases and peptidases that release volatile aroma compounds from these water-soluble forms play a vital role in wine flavor and aroma.

Terpenes are the varietal compounds that have been most extensively studied in *Vitis vinifera* grapes (see Table 1 for a description of volatiles in wine, though the text below focuses on the main volatiles in grapes). About 40 terpenes have been identified in grapes; they can occur as hydrocarbons, alcohols, aldehydes, ketones, or esters, and their olfactory impact is synergistic. Compounds of this family are largely responsible for fruity (citric) and floral aromas, though a number have resin-like odors (α-terpinene, *p*-cimene, myrcene, and farnesol). Some of the most odoriferous are monoterpene alcohols, notably linalool, α-terpineol, nerol, geraniol, citronellol, and hotrienol. Free terpenol composition varies a great deal in the different parts of grapes; geraniol and nerol, for example, have higher concentrations in skin than in flesh or juice (Ribéreau-Gayon et al., 2006). Although monoterpenes are present in most grapes and wines, they are particularly prevalent in certain varieties of Muscat and Riesling.

Table 1 Characteristics of the chemical classes of volatile compounds in wines

Volatile classes	Subtypes	Origin and aroma nuances
Pyrazines		- Originate in grapes - Vegetal characters: bell pepper, chili, bean, carrot, potato, peanut, roasted barley
Terpenes - Formed from isoprene units - Monoterpenes (C10) and higher terpenes (>C10)	Monoterpenes: - Hydrocarbons - Alcohols - Aldehydes - Ketones - Esters: free or bound (as glycosides)	- Generally originate in grapes - Can be produced by some yeasts and moulds (but not *Saccharomyces*) - Only free terpenes can be detected sensorially - Fruity/floral aromas
	Higher terpenes (includes naphthalene derivatives)	- Originate in the plants - Fruity and fuel-like characters
Shikimic acid derivatives		- Produced by aromatic amino acid metabolism - Originate in the plants, microbes, and oak barrels
Lactones	Oxygen-containing 5- or 6-member cyclic compounds	- Originate in grapes, microbes, and oak barrels - Typical characters: candy floss, generic sweet stuff, generic fruit, coconut, butter
Esters	- Alcohol: ethanol or alcohol from degradation of amino acids, purine, and pyrimidine - Acid: acetic acid or acid from degradation of amino acids or biosynthesis of fatty acids	In general: - Short chain: fruity, floral - Long chain: perfume, soap - Lower concentrations: fruity, floral - Higher concentrations: perfume Specific examples: - Ethyl acetate: nail polish remover - Ethyl laurate: soap - Isoamyl acetate: banana - Phenethyl acetate: rose oil
Higher alcohols or fusel oils	From amino acid degradation or biosynthesis	- Made mostly by microbes, can be made by plants
Acids		- From the plant or microbes - Sourness - Other characters: rancid (butyric acid) or pungent (acetic acid)
Phenolic compounds	Flavonoids and non-flavonoids	- Produced by plant -Can be converted into vinyl phenols by microbes (spoilage characters) -Bitterness, astringency
Sulfur-containing compounds	Sulfides	- Hydrogen sulfide: rotten egg - Dimethyl sulfide: cabbage, canned corn - Dimethyl disulphide: clam
	Thiols	- Methanethiol: rubber - Ethanethiol: onion, rubber, skunk
	Sulfoxides	- Dimethyl sulfoxide: plastic, rubber hose
	Thio alcohols	- Mercaptoethanol: barnyard - Thiomethylbutanol: garlic, chive - Methionol: raw potato, soy

Terpene glycosides were found in grapes in the early 1980s (Williams et al., 1982a, 1982b; Dimitriadis and Williams, 1984; Günata et al., 1985). In fact, glycosylated forms are frequently more common than the free terpenes, the relative proportions of free and bound forms depending on the grape variety (Ribéreau-Gayon et al., 2006); Muscat-flavored varieties have the highest concentrations of terpene glycosides. During fermentation, terpene glycosides are hydrolyzed to free volatile terpenes by yeast glycosidases and by the acidic fermentation conditions (pH $\sim$ 3.5). Overall, grape skins have a higher concentration of free and glycosylated monoterpenes than the flesh or juice.

C13-Norisoprenoids are a diverse group of aroma compounds derived from grape carotenoids. Although they are only present at trace levels, sensory thresholds for most norisoprenoids are very low (e.g. 700 ng/L for β-ionone and 200 ng/L for β-damascenone). These compounds can therefore contribute significantly to the aroma potential of many wine varieties, including Chardonnay, Chenin Blanc, Semillon, Sauvignon Blanc, Cabernet Sauvignon, and Syrah. Many new norisoprenoids were identified in grapes and wines during the 1970s and 1980s thanks to advances in gas chromatographic analysis (Ebeler and Thorngate, 2009). Like monoterpenes, many norisoprenoids are present in grapes as nonvolatile glycosides. Hydrolysis during fermentation and storage releases the free aroma compounds. Chemically, grape norisoprenoids adopt two main forms (Ribéreau-Gayon et al., 2006):

- Megastigmane. The megastigmane norisoprenoids include β-damascenone, β-ionone, 3-oxo-α-ionol, β-damascone, and 3-hydroxy- β-damascone.
- Non-megastigmane. The most important nonmegastigmane C_{13}-norisoprenoids are TDN (1,1,6-trimethyl-1,2-dihydronaphthalene), which has a distinctive kerosene-like odor; TPB ((*E*)-1-(2,3,6-trimethylphenyl)buta-1,3-diene), which can contribute a strong green or cut-grass aroma to white wines, particularly Semillon; and actinidiols and vitispirane, which have odors reminiscent of camphor.

Methoxypyrazines are nitrogenated heterocyclic products of amino acid metabolism which originate in the grape and are associated with vegetal characteristics of wine; 3-isobutyl-2-methoxypyrazine (IBMP), 2-*sec*-butyl-3-methoxypyrazine (SBMP), and 3-isopropyl-2-methoxypyrazine (IPMP) have been identified in both. The aroma of IBMP is described as like that of bell peppers or green gooseberries, that of IPMP like asparagus or green bean, and that of SBMP like pea or bell pepper (Sala et al., 2004).

Many *thiols (mercaptans)* cause defective aromas, but not all sulfur-containing compounds – nor even all thiols – are deleterious to wine quality. In fact, since the early 1990s, the highly odoriferous thiols 4-mercapto-4-methylpentan-2-one, 3-mercaptohexyl acetate, 3-mercaptohexan-1-ol, and 3-mercapto-2-methylpropanol have been identified as potentially having an important positive impact – the first three in Sauvignon Blanc wines, the latter three in Merlot and Cabernet Sauvignon. Like monoterpenes and norisoprenoids, these compounds have non-volatile precursors, in this case cysteine conjugates or related compounds. The musts of these wines are almost devoid of volatile thiols, which are assumed to be released during fermentation by the C-S β-lyase activity of *Saccharomyces cerevisiae*. It has been suggested that the cysteine conjugates themselves are breakdown products of glutathionyl conjugates, commonly formed as detoxification products. Recently, Subileau et al. (2008) demonstrated that the glutathionyl conjugate, and not the cysteine conjugate, is the major precursor of 3-mercaptohexan-1-ol (Ebeler and Thorngate, 2009).

THE ACCUMULATION OF AROMA DURING GRAPE RIPENING

General Ripening Processes

Ripening is an important physiological period that in grapes starts at *véraison* and lasts about 40 days, depending on variety, environment and agricultural practices. While it is well-established that in climacteric fruits such as tomato the gaseous hormone ethylene is a key activator of ripening, it is not known how ripening is triggered in non-climacteric fruits such as grape. Grape ripening influences the composition of grapes (and consequently their wine), and thereby contributes to the development of varietal characteristics. The properties altered to different extents in different parts of the grape are both physical (weight, volume, rigidity, and color) and chemical (pH, acidity, concentrations of sugars, phenolics, and volatiles) (Coelho et al., 2007). The rapid change in a wide variety of transport and metabolic processes suggests coordinated regulation and cross-talk among the relevant signaling pathways. Thus key targets for the gene and protein discovery programmes in grapevine are molecules thought possibly to be involved in inter- and intracellular signaling. Enzymes involved in the biosynthesis and storage of acids and glycone terpenoid compounds are also being targeted.

The skin of the grape not only constitutes a fundamental protective barrier against damage by physical injury and attack by pathogens, but also plays a central role in the synthesis of many compounds of interest (e.g., anthocyanins and aroma volatiles). Negri et al. (2008) studied its role during ripening by using 2-DE to follow protein expression changes in the skin of the red cultivar Barbera. Two-way hierarchical clustering of 80 protein spots showing changes in expression brought out a clear difference between the first 2 weeks post-*véraison* and weeks 5–7, the most important changes occurring during the former period. LC-ESI-MS/MS allowed characterization of 69 proteins with altered expression, many of them involved in responses to stress (38%), in glycolysis and gluconeogenesis (13%), in the metabolism of carbohydrates and other C-compounds (13%), or in amino acid metabolism (10%). Notably, among other enzymes involved in primary metabolism, those of the last five steps of the glycolytic pathway were induced, whereas previous studies had observed their downregulation in the whole fruit. The marked changes in the levels of many proteins involved in abiotic stress responses suggest that their expression depends on developmental stage as well as stress.

To monitor grape ripening, classical parameters based on percentage of soluble solids, sugar, titratable acidity, pH, and color are used. The utility of these indices is limited, as they provide only the most basic information relevant to the potential quality of wines made from the monitored grapes. Controlling them is nonetheless essential. For example, every year, millions of euros are spent worldwide in preventing acidity at harvest from being too high, as it tends to be in cooler climes such as Canada and Germany, or too low, as it tends to be in warmer climes such as much of Spain and Australia, where malate is metabolized faster. For more specific information on the development of varietal characteristics during grape ripening, analyses of phenolics, carotenoids, and/or volatile compounds have been used (Coelho et al., 2007).

Accumulation of Grape Aroma

The accumulation of aroma in the grape berry, which Coombe and McCarthy (1997) have suggested be termed "engusting," appears to differ significantly from the accumulatory processes normally associated with berry ripening. A distinctive feature is the increase in concentration of free and glycosylated aroma compounds in the advanced stages of ripening, when sugar

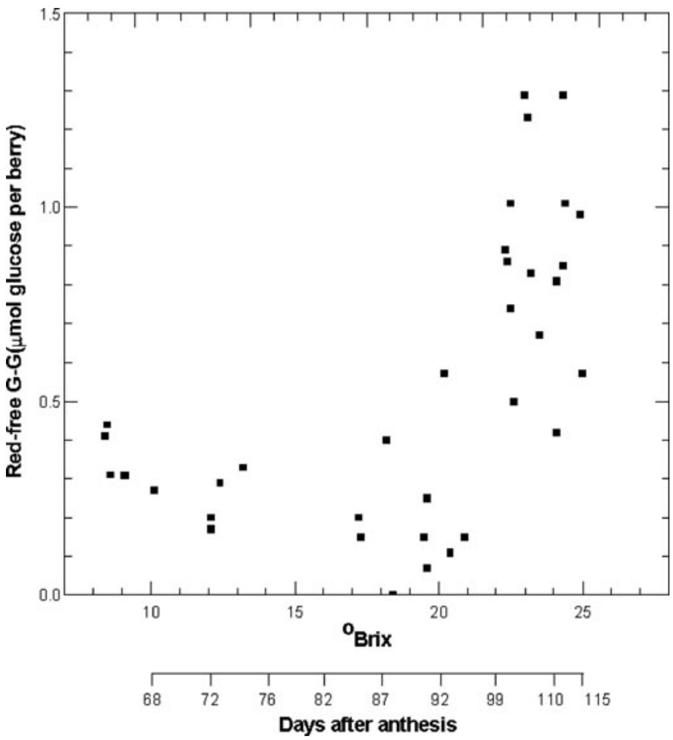

Figure 3 Red-free glycosyl glucose content ("red-free G-G," as μmol glucose per berry) plotted against juice total soluble solids content (°Brix) and "days after flowering" of Syrah grape berries. Samples were taken in 1995 from fully irrigated grapevines at Waikerie, Riverland, South Australia (taken from Coombe and McCarthy, 1997). Red-free G-G includes only a small proportion of aroma compound glycosides, may be correlated with wine aroma.

increase per berry has slowed; this pattern is shown, for example, by nonanthocyanin glycosides ("red-free glycosyl glucose" or "red-free G-G") in Syrah grapes (Fig. 3).

Red Grapes

In red grapes, maximum varietal volatile compounds content is reached at maturity as established by the sugar/acidity ratio, and remains constant in the following weeks (Salinas et al., 2004; Coelho et al., 2006). In Cabernet Sauvignon, esters are characteristic of early berry development, aldehydes of middle development stages, and alcohols of late development (Kalua and Boss 2009); also, terpenes (predominantly eucalyptol, β-caryophyllene, and *R*-humulene) are prevalent during early development, while benzene derivatives such as 2-phenylethanol and 2-phenylethanal tend to appear later. The late dominance of alcohols is desirable, because alcohols usually have not only higher herbaceous odor thresholds than related aldehydes, but also a greater propensity to form fruity esters in the presence of carboxylic acids during vinification. Chemically, the evolution of volatile compounds during berry development suggests a greater dependence on enzyme activity and specificity than on the extent of fatty acid unsaturation; in particular, the dependence on accumulation of the products of alcohol dehydrogenase, alcohol acetyl transferase, and enal isomerase activity in the lipoxygenase pathway raises possibilities for the manipulation of aroma profiles in grapes and wines. More immediately perhaps, the successive dominance of aldehydes and alcohols suggests the possibility of using the alcohol:aldehydes ratio for timing harvest to maximize grape and wine aroma.

In Muscat Hamburg grapes, the major aroma compounds that accumulate during ripening are linalool, geraniol, citronellol, nerol, diendiol I, and diendiol II in the free fraction, and geraniol, linalool, citral, nerol, citronellol, α-terpineol, diendiol I, diendiol II, linaloloxide I, linaloloxide II, benzyl alcohol, and 2-phenylethanol in the bound (glycoside) fraction (Fenoll et al. (2009). Most Muscat aroma compounds have higher bound form levels than free form levels at this stage.

In Baga grapes monitored at two Bairrada vineyards over 7 weeks following half-*véraison* (the point at which 50% of berries are changing color), the main group of free varietal and related prefermentative volatile compounds (those arising in the first 2 h after the grapes are crushed) consisted of sesquiterpenoids (40 at one vineyard, 23 at both, accounting at maturity for 56–80% of total varietal gas-chromatographic peak area) (Coelho et al. 2006). They included (+)-cycloisosativene, γ-elemene, α-ylangene, β-bourbonene, β-cubenene, β-caryophyllene, 3,7-guaiadiene, (−)-isoledene, (+)-aromadendrene, α-amorphene, (−)-δ-selinene, germacrene D, epizonarene, β-cadinene, γ-cadinene, δ-cadinene, α-muurolene, and α-calacorene. Other compounds detected at both vineyards were 13 monoterpenoids, 6 norisoprenoids, 2 aromatic alcohols, and a diterpenoid. Maximum gas-chromatographic peak area was reached at maturity, and remained constant until postmaturation.

In Monastrell grapes, Salinas et al. (2004) studied the evolution during ripening of 34 volatile compounds that they classified broadly as of pleasant aroma (acetates, terpenes, norisoprenoids, 2-phenylethanol, nonanal, and decanal) or unpleasant aroma (C_6 compounds and acids). The ratio of pleasant to unpleasant compounds reached its maximum at week 5 of ripening.

White Grapes

In white varieties, changes in the concentrations of volatile compounds during ripening differ with variety, making it more difficult to determine maturity on the basis of varietal volatiles content (García et al., 2003). In the white varieties Airén, Macabeo, and Chardonnay, grown in La Mancha (Spain), C_6 aldehyde and alcohol concentrations reach 9–11° Baumé in Airén grapes, and 11–13° in Macabeo and Chardonnay; these results are in keeping with the observation of higher lipoxygenase activity in the middle of ripening period (Zamora et al., 1985). Terpenic compounds also increase progressively, to 6° Baumé in Airén and 9–11° Baumé in Macabeo and Chardonnay. The most characteristic volatile compounds are *cis*-3-hexenol in Airén musts, *trans*-3-hexenol and 2,4-hexadienal in Macabeo, and benzaldehyde, phenylacetaldehyde, and benzyl alcohol in Chardonnay, although skins have more volatiles than musts in all three varieties. Airén skins had the highest levels of nerol, and were the only skins with citronellol, while low concentrations of eugenol are found in the Chardonnay skins but not in the other two varieties.

The pre-fermentation variety-related volatiles of Fernao-Pires grapes (16 monoterpenoids, two C_{13} norisoprenoids, two aromatic alcohols, two C_6 aldehydes, and three C_6 alcohols) increase for about 3 weeks after *véraison*, and then decrease sharply (Coelho et al. 2007). In this study, the peak coincided with the optimal harvest time for white table wine production, as indicated by the sugar/acidity ratio. Potentially favorable volatiles with fruity, sweet, floral, or citric notes (monoterpenoids, C_{13} norisoprenoids, and aromatic alcohols) peak at the same time as those with potentially herbaceous notes (C_6 compounds). The evolution of the terpenoids with the greatest gas chromatography (GC) peak areas (linalool, α-terpineol, and geraniol) is representative of the varietal volatile compounds.

Reynolds et al. (1993) found that Müller-Thurgau, Muscat Ottonel, Gewürztraminer, and Kerner grapes lost substantial amounts of free volatile terpenes (FVTs) and potentially volatile terpenes (PVTs) between the berry and press-juice stages, although PVTs were higher in press juices of Gewürztraminer and Muscat Ottonel than in free-run juices, and Kerner, Müller-Thurgau, Optima, and Siegerrebe juices had higher FVT and PVT levels if left in contact with skins than if grape crushing was immediately followed by pressing. Also, Müller-Thurgau, Muscat Ottonel, Kerner, Optima, Pearl of Csaba, and Siegerrebe juices had higher FVT and PVT contents if the grapes were harvested 10–20 days after the initially designated date. Sensory evaluation found aroma differences between wines from free-run and press juices of Müller-Thurgau and Muscat Ottonel, aroma and flavor differences due to harvest date for all the above cultivars except Pearl of Csaba, and aroma and flavor differences due to skin contact for Siegerrebe.

Sánchez Palomo et al. (2007) found that wines obtained from less ripe Albillo and Muscat grapes had higher ester and fatty acid concentrations but lower concentrations of terpene and benzene derivative than wines from highly mature grapes. Coelho et al. (2009) found similar total volatiles contents of *ca.* 11 mg L^{-1} in wines from grapes picked at maturity or 1 week earlier or later, and the total ester and total alcohol contents of wines from grapes harvested during this period were also unchanged, but monoterpenoid content tended to increase progressively with ripening, while other varietal chemicals (sesquiterpenoids and C_{13} norisoprenoids) increased up to maturity and decreased thereafter, as previously reported for Fernao-Pires grapes (Coelho et al., 2007). By contrast, 1-hexanol, which derives from lipoxygenase activity in the grape and/or from aeration of the must, fell by *ca.* 60% with increasing harvest time delay, probably due to enzyme activity (since unripe fruit, like 1-hexanol, are usually associated with grassy, herbaceous aromas). Gómez-Míguez et al. (2007) likewise found white wines produced from grapes in early maturity to exhibit more intense herbaceous notes than those obtained from riper grapes.

MAIN FACTORS AFFECTING AROMA QUALITY IN GRAPES (TABLE 2)

Effect of Site on Volatile Compounds

The view that the vine needs to "suffer" to produce fine quality fruit is long established in wine folklore. Regions where grapevine vigor is restrained by local conditions – enhanced by vineyard practices – are noted for their better-quality wines. The topographical, agro-pedological, and climatic environmental conditions that influence grape and wine composition and quality are referred to collectively by means of the French term "terroir" (Jackson and Lombard, 1993). An understanding of the influence of the terroir allows grape growers not only to produce better-quality grapes in traditional wine-producing regions, but also to expand production into new viticultural areas in a rational fashion.

According to the work by Robinson et al. (2011), site had the most significant influence on sensory scores and wine composition, followed by canopy management. Probably the first feature recognized as favoring finer grape was limited soil fertility. Soils with just adequate nutrient levels restrict vegetative growth and permit a higher proportion of photosynthate to be directed toward fruit maturation; they thus favor flavor formation, which as we have seen, tends to develop near the end of ripening. Many low-nutrient soils are also highly porous, which results in periods of mild water deficit that further limit vegetative growth, and also favors the rapid warming of, and radiation of heat from, the soil; this, in turn, can improve the microclimate around the vine and delay or minimize frost severity. Good drainage also promotes early spring growth and limits fruit cracking following heavy rains. Finally, the skin of grape berries grown on well-drained soil develops fewer micro- and macro-fissures, and thus affords greater protection against infection by fungi and bacteria.

In consonance with the benefits of mild water deficit, another feature recognized early on as benefiting grape quality is medium to low rainfall. Dry conditions enhance the resistance of vines to several pathogens. Although water stress must be avoided in the spring and early summer (up to *véraison*), dry conditions later tend to improve fruit quality and advance ripening for the reasons noted above. Because grapevines tend to root deeply, dry conditions during ripening generally do not cause serious water stress on deep soil (deep rooting probably also prevents nutrient deficiencies in impoverished soils by tapping subsoil nutrient sources). Grapevines are one of the few crops that do well on relatively poor soils. For Nero d'Avola wines, the increase in soil salinity enhanced color intensity, purple reflexes, salty, citrus, and fruit in the aroma (Scacco et al., 2010).

It was possibly during the expansion of viticulture into central Europe during Roman times that the benefits of growing cultivars near the northern limit of fruit ripening became apparent. Wines from cooler mountainous sites in Italy were already known to classical Romans as having superior quality. Cool conditions are now known to retain fruit acidity, which improves

Table 2 Revision of the main factors affecting aroma quality in grapes

Factors	Affecting features	Effects on aroma qualities	References
		(a) Site	
Soil	Limited soil fertility	Higher fruit maturation vs. vegetative growth, what favors flavor formation	Jackson, 2008
	Potassium-rich soils	Wines from the potassium-rich soils have higher concentrations of C_{13} norisoprenoids such as β-ionone and fermentative aroma compounds such as ester acetates (mainly isoamyl acetate)	Falcao et al., 2008
	Well-drained gravelly soils vs. limestone soils and clay-silt soils	Grapes grown on well-drained gravelly soils have mild water deficit, with rapid warming of soil and vine. This helps to lower concentrations of methoxypyrazines	Ribéreau-Gayon et al., 2006
	Clayey soils vs. sandy soils	Clayey soils have better water retention capacity and volumetric wetness than sandy soils. Wines from clayey soils had greater contributions from the floral, sweet and fruity series, and wines from sandy soils greater contributions from the solvent and green series	Gómez-Míguez et al., 2007
	Calcareous clay soils vs. sandy soils and clay soils	Concentrations of monoterpenoids, sesquiterpenoids and C_{13} norisoprenoids in wines of calcareous clay origin were higher than in those of clay and sandy origin	Coelho et al., 2009
Weather	Dry conditions at the end of Summer	Improve fruit quality and advance ripening, what favors flavor formation	Jackson, 2008
	Temperate conditions	Development of higher β-damascenone and geraniol concentrations	Sabon et al., 2002
		Retention of higher concentrations of monoterpenes	Ji and Dami, 2008
		(b) Cultivation practices	
Sunlight	Different percentage of exposure to sunlight of grape clusters	In Muscat cultivars, Moscatel de Alejandria and Moscatel rosada, the highest concentration of free terpenols was found in the artificially semi-shaded (50%) treatment. Linalool appeared to be very sensitive to exposure to sunlight.	Belancic et al., 1997
		In Muscat of Frontignan and Syrah bunches shaded by 90% shade cloth had lower levels of monoterpenols and C_{13} norisoprenoids.	Bureau et al., 2000a, 2000b
		Extreme shading of Syrah berries decreased the glycosides of β-damascenone and TDN in the wine.	Ristic et al., 2007
		The concentrations of TDN and Riesling acetal in White Riesling increase with sunlight exposure above a threshold of about 20%.	Gerdes et al., 2002
Training and canopy management	Different training systems	ADC of Riesling vines afforded higher FVT and PVT contents.	Reynolds et al., 1996a
		Viognier grapes had higher levels of free volatiles (linalool, α-terpineol, β-damascenone and *n*-hexanol) if subjected to Smart-Dyson training.	Zoecklein et al., 2008
		Levels of geraniol and other monoterpenes in Traminette juice were higher following vertical shoot-positioning training.	Ji and Dami, 2008
	Different canopy manipulation practices	Basal leaf removal tended to increase FVT and PVT in Gewürztraminer vines and that wines from the vines so treated were generally richer in muscat and floral aroma and flavor.	Reynolds et al., 1996b
		FVT and PVT found to be higher in the berries of Chardonnay Musqué vines following cluster thinning and basal leaf removal.	Roberts et al., 2007
Water	Water stress	Cabernet Sauvignon made from minimal irrigation treatment were significantly higher in red/blackberry aroma, jam/cooked berry aroma, dried fruit/raisin aroma, and fruit by mouth than the wines from the irrigated treatments.	Chapman et al., 2005
		Grapes from Sauvignon Blanc vines subjected to moderate water stress also have higher concentrations of cysteinylated aroma compound precursors than those with unlimited water supply.	Ribéreau-Gayon et al., 2006
		In Agiorgitiko vines limited water availability seems to increase the levels of the glycoconjugates of the main aromatic components.	Koundouras et al., 2006
		Wines from own-rooted Merlot vines that were supplied with only 35% of their estimated crop evapotranspiration requirement throughout the berry development had more vitispiranes, β-damascenone, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4 vinylguaiacol than wine produced from well-watered vines.	Qian et al., 2009
Nitrogen fertilization	Variation of the nitrogen supply	In Sauvignon Blanc increasing the nitrogen supply leads to higher cysteine precursor levels in grape juice.	Choné et al., 2006
		N fertilization of a Riesling vineyard increased 1-butanol, *trans*-3-hexen-1-ol, benzyl alcohol, and the majority of esters in wines.	Webster et al., 1993
Fungicide treatment	Fungicide residues in grape juice and wine	Such traces can affect aroma quality by altering fermentation kinetics.	Noguerol-Pato et al., 2011 González-Rodríguez et al., 2011 González-Álvarez et al., 2012a, 2012b

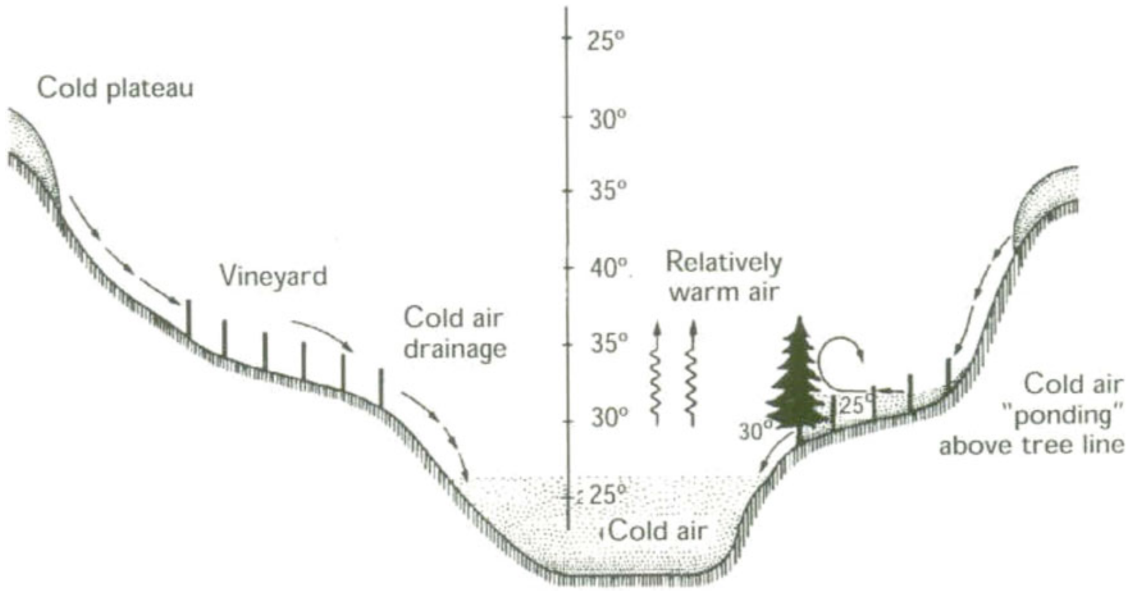

Figure 4 Site considerations for vineyard establishment: topography (both elevation and slope) and air movement (conditioned by water body and tree line) (taken from Fiola, 2010).

the microbial and color stability of wines. Temperate conditions likewise appear to favor the development and retention of grape aroma compounds, and do so differentially: in the Rhone Valley, for example, Grenache wines produced on the southernmost, warmest soils, where maturation occurs early, have the highest β-damascenone and geraniol concentrations, whereas wines obtained from soils on which grapes mature later are poorer in β-damascenone but richer in β-ionone (Sabon et al., 2002); and Traminette grapes develop higher concentrations of C_6 aldehydes at cool sites, but higher concentrations of monoterpenes at warm sites (Ji and Dami, 2008). However, growing at the high-altitude limit also increases the chances of frost damage and of crop failure (due to the shorter growing season), making sites on slopes or in the proximity of large bodies of water preferable (Fig. 4). For all these reasons, the typical number of annual and seasonal growing degree days at a site must be borne in mind when establishing a vineyard (Fig. 5).

Soil Type

Soil type, though closely related to soil water status, has long been considered less important for wine aroma than climate or variety; furthermore the depth, water-holding capacity, and drainage of soils have been considered more important than their composition (Jackson and Lombard, 1993; Koundouras et al., 2006). However, according to some researchers soil may have an independent effect on grape aroma quality.

Soil may affect the availability of water and nutrients to the plant through its retaining capacity; microclimate through its heat-retaining and light reflecting capacity; and root growth through its penetrability (Jackson and Lombard, 1993). In general, clayey soils have better water retention capacity and volumetric wetness than sandy soils. On the other hand, sandy soils have better drainage (Hillel, 1998; Gerrard, 2000). On balance, clay and calcareous clay soils with good water-holding capacities and drainage should produce wines that are richer in volatiles than sandy soils. Wines from cover crop also had higher contents of impact odorants compared with a clean tillage control (Xi et al., 2011). For different cover crops, alfalfa sward yielded the highest levels, followed by the tall fescue treatment.

In Merlot, Cabernet Franc and Cabernet Sauvignon wines of the Bordeaux region, soil has a decisive influence on methoxypyrazine concentrations due to its effect on vegetative growth. Grapes grown on well-drained gravelly soils have lower concentrations than those grown on limestone or clay-silt soils (Ribéreau-Gayon et al., 2006).

In white wines of the variety Zalema, soil type had significant effects on aromas of the solvent series ($p \leq 0.01$) and the green series ($p \leq 0.05$) if the grapes had been harvested early, and on all aromas except the fatty series if they were harvested on the date determined for industrial production (Gómez-Míguez et al., 2007). Wines from clayey soils had greater contributions from the floral, sweet and fruity series, and wines from sandy soils greater contributions from the solvent and green series.

Together with seasonal weather differences, soil composition is the principal determinant of differences among the aromas of Cabernet Sauvignon wines from four sites in Santa Catarina State (Brazil), a new grape growing region. Wines from the potassium-rich Bom Retiro soils have higher concentrations of α-ionone and ester acetates (mainly isoamyl acetate) than those from the other three sites (Falcao et al., 2008).

Coelho et al. (2009) reported that calcareous clay soils produce sparkling wines with higher concentrations of varietally relevant compounds than sandy soils or clay soils. Specifically,

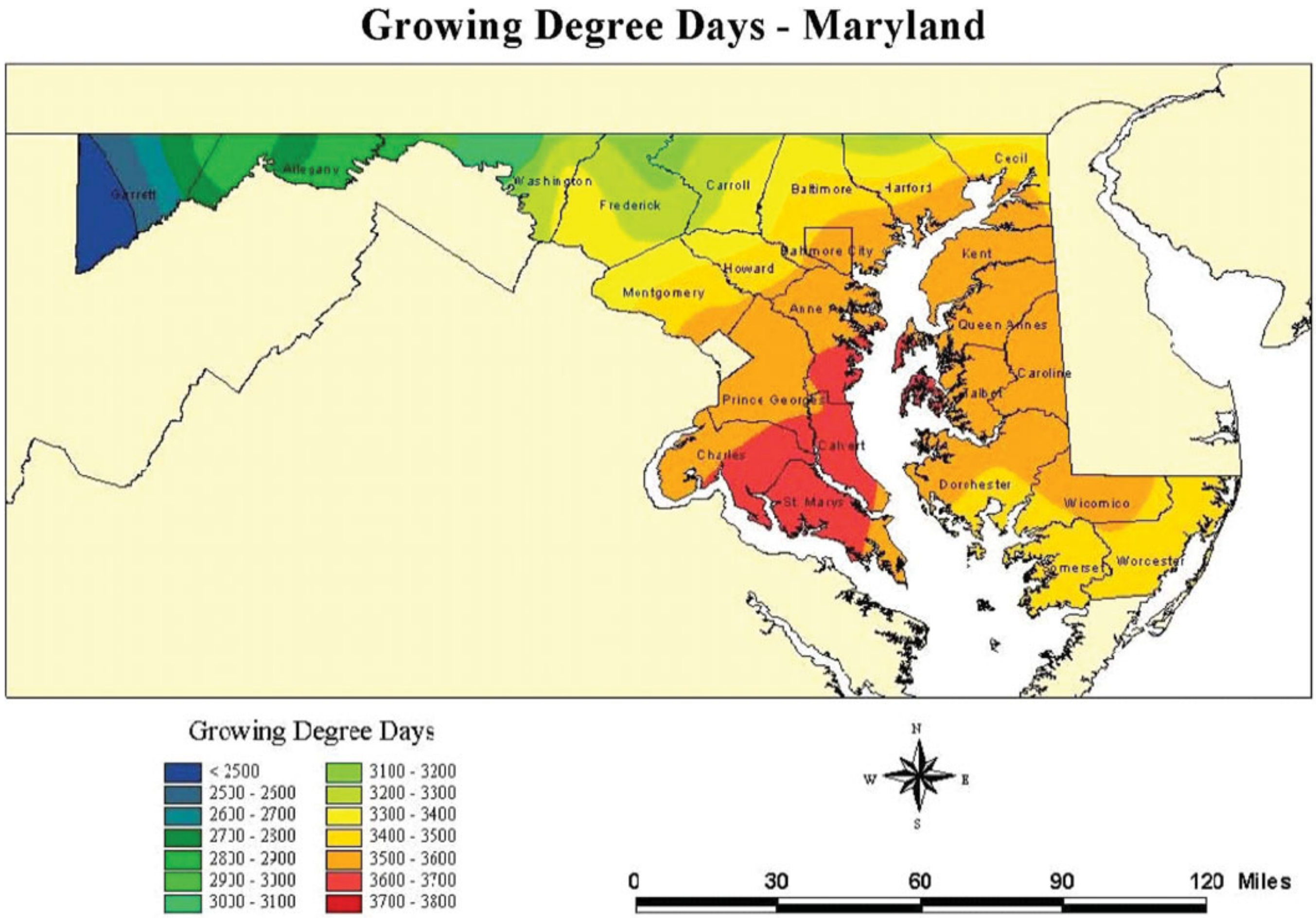

Figure 5 Typical annual growing degree days values (GDD) in Maryland (taken from Fiola, 2010). Each day's GDD is calculated as the average of the maximum and minimum temperatures, expressed relative to a base temperature (usually 10°C): GDD = $\frac{T_{\max}+T_{\min}}{2} - T_{\text{base}}$.

in their study, the concentrations of monoterpenoids, sesquiterpenoids and C_{13} norisoprenoids in wines of calcareous clay origin were respectively 2.1, 1.4, and 1.3 times higher than in those of clay origin, and respectively 1.6, 1.4, and 2.7 times higher than in wines from sandy soils. However, clay soil wines had total volatiles contents similar to those of wines from calcareous clay soils.

Seasonal Weather

Caven-Quantrill and Buglass (2008) reported that the analytical flavor profiles of English-grown Huxelrebe, Madeleine Angevine 7672, Ortega, Schönburger and Siegerrebe grapes varied considerably from year to year, depending on ripeness as judged by sugar (and hence on weather). The C_6 aldehydes hexanal and *(E)*-2-hexenal, as well as other carbonyl compounds, *(E)*-anethole and estragole were all most abundant in less ripe juices, although the concentrations of these last two were in all cases low. Riper juices tended to have higher concentrations of decanoic and dodecanoic acids, and larger aliphatic/aromatic ester ratios. The vintage dependence of aliphatic alcohols and most terpenoids depended on variety. Variations in linalool content seemed likely to have the greatest organoleptic impact on Schönburger and Siegerrebe juices, and variations in *(E)*-β-damascenone content the greatest impact on Huxelrebe and Ortega juices, but very few variations of individual components seemed likely to have much organoleptic impact by themselves.

The study by Kalua and Boss (2010) suggests that some compounds that contribute to grape aroma may be produced pre-*véraison*, and not simply accumulate after *véraison*. Understanding the timing of volatile compound production and cultivar differences will guide viticulture researchers and growers in the optimization of vineyard strategies to enhance grape aroma attributes that may, in turn, contribute to wine aroma.

Effect of Vineyard Cultivation Practices on Volatile Compounds

Vineyard cultivation practices can affect the development of aroma compounds in a variety of ways (Kobayashi et al., 2010).

Firstly, through their influence on the amount of sunlight to which the vine is exposed, which depends not only on the site of the vineyard but also on management factors such as the way the vines are trained. The training system affects both total leaf area and the percentage of leaf area that is well-exposed to light, and hence influences the ability of the vine to photosynthesize efficiently, as well as numerous other relevant events and variables, such as fruit bud differentiation, cluster exposure, leaf transpiration, and vine water status (Reynolds and Vanden Heuvel, 2009). Water conditions, as noted in the previous subsection, have long been recognized as important for grape quality, and many papers – most concerning irrigation trials – have reported extensively on the effects of water deficit on the accumulation of various grape metabolites. It is also well known that vine nitrogen deficiency can have a negative impact on aroma in white wines, and that treatments such as fungicides can cause changes in aroma profiles. In the remainder of this subsection, we review each of these factors in turn.

Sunlight

The effect of exposure to sunlight on grape metabolism and the development of aroma compounds is complex. Direct sunlight can cause stress due to dehydration or temperature increase, but can also induce beneficial changes in photosynthetic pigment levels. For instance, in green berries light appears to increase the concentration of carotenoids, which are considered to be precursors of C_{13} norisoprenoids (Bureau et al., 2000a, 2000b). Sunlight likewise seems to increase the concentration of glycosides of terpenols and phenols, and to reduce the concentration of methoxypyrazines, which are light-sensitive (Heymann et al., 1986; Maga, 1989). Electronic noses can be used as a tool for quick analysis that can help wine makers to decide the optimum drying time, taking into account the concentration of volatile compounds (López de Lerma et al., 2012).

In an experiment in which grape clusters of the Muscat cultivars Moscatel de Alejandria and Moscatel rosada were subjected to 20%, 50%, and 100% exposure to sunlight, the highest concentration of free terpenols was found in the semi-shaded (50%) treatment, although in Moscatel de Alejandria the difference with respect to fully exposed grapes was negligible (Belancic et al., 1997). Linalool, one of the most important terpenols for aroma, appeared to be the most sensitive to exposure to sunlight. These effects on monoterpene levels (and hence Muscat flavor) were attributed to the influence of sunlight on berry temperature.

Bureau et al. (2000a, 2000b) reported that bunches of Muscat of Frontignan grapes that were shaded naturally by the vine foliage had levels of free volatiles and glycoconjugates similar to those of berries exposed to the sun, but that bunches shaded by 90% shade cloth had lower levels of monoterpenols and C_{13} norisoprenoids. Shading the whole vine with 50% or 70% shade cloth had less effect than the 90% shading of bunches. Similarly, Syrah bunches that were shaded naturally (by vine foliage) or by 90% shade bags had lower levels of glycoconjugates, particularly phenolic and C_{13}-norisoprenoid glycosides, than bunches exposed to sunlight, and 30% or 50% shading of whole vines reduced the concentrations of glycosides of terpenols, phenols, and C_{13}-norisoprenoids, although bunch shading appeared to have a greater effect than vine shading (Bureau et al., 2000a, 2000b). Ristic et al. (2007) also found that extreme shading of Syrah berries decreased the glycosides of β-damascenone and TDN in the wine (as well as color, anthocyanins, and tannins), and although there was no significant difference in aroma attributes the wines made from shaded fruit were rated lower for astringency, fruity flavor, and the persistence of flavor in the mouth.

Again, the concentrations of TDN (1,1,6-trimethyl-1,2-dihydronaphthalene) and Riesling acetal (2,2,6,8-tetramethyl-7,11-dioxatricycloundec-4-ene) in White Riesling increase with sunlight exposure above a threshold of about 20%, possibly due in part to the effect on berry temperature (Gerdes et al., 2002).

Training and Canopy Management

Because of the influence of vine training and canopy management on exposure to sunlight and related grape production variables (Kok, 2011; Robinson et al., 2011), many training systems have been devised to exploit this influence. Unfortunately, few have been compared with each other in regard to their influence on aroma and flavor under equitable conditions. Fair comparison would need to involve vines of the same cultivar, age, and level of canopy management, and such conditions are difficult to establish. Furthermore, the influence of training no doubt depends on vine growth habit, which in turn depends on both genetics and the local environment. Accordingly, such knowledge as there is regarding the effects of training systems often concerns only particular varieties in particular locations. Moreover, studies of the influence of training have often been concerned less with maximizing aroma, flavor and other quality parameters than with minimizing production costs. Nevertheless, several studies of the influence of training systems on volatiles in grapes and wines can be found in the recent literature, and in this section, we review them.

Reynolds et al. (1996a) found that alternate double cross-arm training (ADC) of Riesling vines afforded lower °Brix, but also lower titratable acidity and pH and higher FVT and PVT contents, than the Lenz Moser, low cordon, low-V and pendelbogen training systems. FVT and PVT were also increased, and titratable acidity reduced, by removing basal leaves approximately 45 days postbloom, but vine spacing had little influence on fruit yield and composition. These authors also found that basal leaf removal similarly tended to increase FVT and PVT in Gewürztraminer vines grown in British Columbia, and that wines from the vines so treated were generally richer in muscat and floral aroma and flavor than those from vines that were unhedged or hedged to *ca.* 14 leaves per shoot (Reynolds et al., 1996b).

In the berries of Chardonnay Musqué vines grown in Ontario, Roberts et al. (2007) found FVT and PVT to be higher following cluster thinning and basal leaf removal than if only thinning or hedging was performed, with highest values if thinning was performed at *véraison*. Wines from vines so treated generally had more intense muscat and floral/scented aromas.

Zoecklein et al. (2008) reported that juice and wines from Viognier grapes grown in northern Virginia had higher levels of most of the free volatiles considered (linalool, α-terpineol, β-damascenone, and n-hexanol) if subjected to Smart-Dyson training than if the vertical shoot-positioning (VSP) or Geneva double curtain (GDC) systems were used. However, GDC, which afforded greater fruit zone sunlight interception, fruit exposure, cluster numbers and crop yield, and lower cane pruning weights per meter of cordon, often afforded wines with the highest concentration of phenol-free glycosides. GDC wines generally had more intense fruity and floral aromas than those produced using the other systems. By contrast, Ji and Dami (2008) found that the levels of geraniol and other monoterpenes in Traminette juice were higher following VSP training than following Scott Henry, Smart-Dyson, high cordon or GDC training, and, following Reynolds et al. (1996b) and Belancic et al. (1997), attributed this to VSP affording less extreme exposure to sunlight than GDC or HC.

Finally, a combination of leaf thinning and removal of side-shoots in the fruiting zone has been found to be particularly effective in enhancing the aromatic maturity of Cabernet Saugvignon and Saugvignon Blanc grapes in Bordeaux vineyards (Ribéreau-Gayon et al., 2006).

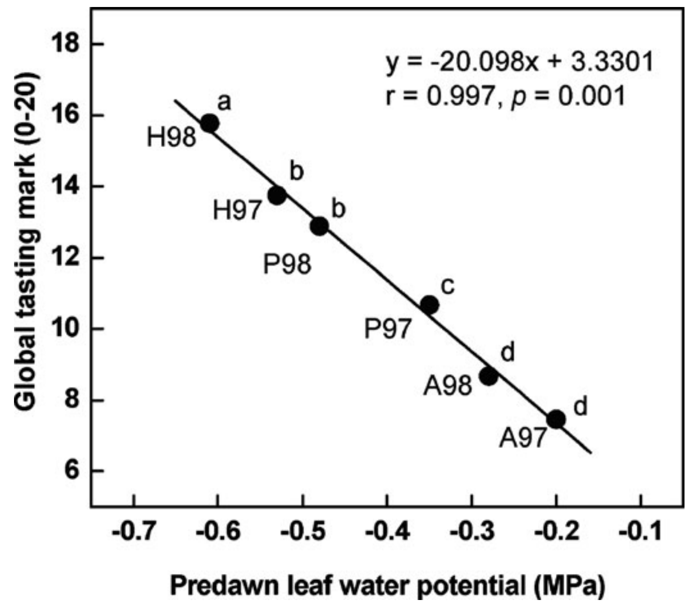

Figure 6 Relationship between average predawn leaf water potential between fruit set and harvest, and wine sensory evaluation. Data labels refer to three sites (P, H, and A) and two seasons (1997 and 1998). Data points labeled with different letters differ significantly in overall tasting mark ($p < 0.05$) according to a Newman-Keuls test with all years and sites considered together (taken from Koundouras et al., 2006).

Water

As has already been noted in relation to the effects of vineyard soil and weather, moderate water deficit can improve wine quality, enhancing color, flavor, and/or aroma (Deluc et al., 2009; Ou et al., 2010) (Fig. 6). As is natural, most studies of the influence of water status have concerned the evaluation of irrigation needs and protocols. Findings have depended on cultivar.

Cabernet Sauvignon vines that were not irrigated unless the midday leaf water potential dropped below –1.6 MPa have been reported to have given wines with significantly more fruitiness in the mouth, significantly more intense red/blackberry, jam/cooked berry and dried fruit/raisin aromas, and significantly less astringency and vegetal, bell pepper and black pepper aromas, than those from vines that were irrigated with 32–64 L of water per vine per week (Chapman et al., 2005). Similarly, in central Greece, Cabernet Sauvignon on 1103P and SO4 rootstocks have greater aroma potential at harvest if water supply is limited (Koundouras et al., 2009).

Grapes from Sauvignon Blanc vines subjected to moderate water stress also have higher concentrations of cysteinylated aroma compound precursors than those with unlimited water supply (Ribéreau-Gayon et al., 2006). However, for maximum aroma expression in Sauvignon Blanc grapes, water deficit stress should be no more than mild (Peyrot des Gachons et al., 2005).

In Agiorgitiko vines growing in the Nemea appellation area (Greece), limited water availability seems to increase the levels of the glycoconjugates of the main aromatic components, and wines produced from grapes from stressed vineyards have been preferred in tasting trials (Koundouras et al., 2006).

Again, Qian et al. (2009) reported that wines from own-rooted Merlot vines in Idaho that were supplied with only 35% of their estimated crop evapotranspiration requirement throughout the berry development had more vitispiranes, β-damascenone, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-vinylguaiacol than wine produced from well-watered vines, although irrigation deficit had no effect on the concentrations of volatile esters and terpenes.

Somewhat in contrast to the above, Reynolds et al. (2007) found that wines made from irrigated grapes from an Ontario Chardonnay vineyard had more intense apple, citrus and floral aromas and flavors, and less earthy aroma and flavor, than unirrigated controls, suggesting the possibility of simultaneously favoring sensory attributes, soluble solids, and yield.

The mechanisms by which water deficit modifies the production of aroma compounds in the red grape cultivar Cabernet Sauvignon and the white grape cultivar Chardonnay have been analyzed by Deluc et al. (2009) by means of integrated transcript and metabolite profiling. In Chardonnay, which lacks significant anthocyanin content, water deficit induced photoprotective mechanisms, activating parts of the phenylpropanoid, energy, carotenoid, and isoprenoid pathways that contribute to production of antheraxanthin, flavonols, and aroma volatiles, and lowering the concentration of abscisic acid (ABA) following *véraison*. In Cabernet Sauvignon, water deficit increased ABA concentrations, and also proline, sugar and anthocyanin concentrations (which were not increased in Chardonnay, suggesting their dependence on ABA). Water deficit increased the transcript abundance of lipoxygenase and hydroperoxide lyase in the fatty metabolism pathway, which is known to affect berry and wine aromas.

Nitrogen Fertilization

Soil nitrogen fertilization can lead to excessive vine vigor and susceptibility to grey rot, but can also enhance aroma expression. In Sauvignon Blanc, for example, increasing the nitrogen supply leads to higher cysteine precursor levels in grape juice, and late application (at berry set) to higher levels of aroma-protective glutathione and lower levels of phenolics (Choné et al., 2006). Furthermore, although application of nitrogen to the soil or the foliage brings about similar leaf N-tester values, leaf yeast available nitrogen levels, the concentrations of volatile thiols and glutathione in wine, and the Sauvignon Blanc varietal aroma intensity of wine are higher if a foliar spray is used, especially if nitrogen and sulfur are applied together (Lacroux et al., 2008). González-Marco et al. (2010) demonstrate that when juice is sufficient in nitrogen, the addition of amino acids does not improve the volatile composition of wine. Under these conditions, the amino acids would have probably been used for other cellular processes that do not produce volatile compounds.

Webster et al. (1993) found that N fertilization of the vineyard reduced the concentrations of amyl alcohols and 2-phenylethanol in Riesling wines aged for 3–5 years, and increased those of 1-butanol, *trans*-3-hexen-1-ol, benzyl alcohol, and the majority of esters. Sensorially, wines from unfertilized vines and vines fertilized with 224 kg N/ha differed significantly.

Fungicide Treatments

The biggest difficulty in growing grapes for wine is, without doubt, to protect the vines against fungal diseases such as botrytis, powdery mildew, and downy mildew. Although non-chemical viticultural techniques can help minimize the incidence of these diseases, the most effective means of prevention is prophylactic application of fungicides. However, fungicide components can persist in trace levels in grape juice and wine, to the direct detriment of both toxicological safety and sensory quality, and such traces can also affect aroma quality by altering fermentation kinetics (González-Álvarez et al., 2011; González-Rodríguez et al., 2011; Noguerol-Pato et al., 2011; González-Álvarez et al., 2012a, 2012b). Since the European Union now prioritizes the sustainable use of pesticides, it will phase out those with the worst toxicological and environmental behavior; but the development of resistance to existing fungicides by their target pathogens means that there is a periodic need for replacement of one generation of fungicides by another.

Given the above background, it is of paramount importance to perform field studies of the behavior of fungicides in vineyards under various management regimes, to investigate the dynamics of residual fungicide during vinification, and to determine how trace levels of these compounds affect wine flavor profiles. Together with considerations of fungicidal efficacy, the results of such studies will orient the preferences of wine growers for one or another fungicide (Noguerol-Pato et al., 2009).

FUTURE SCENARIO DUE TO GREENHOUSE GASES

The continued increase in CO_2 and other greenhouse gases in the atmosphere is expected to raise average global surface temperatures, evaporative demand, and the frequency and intensity of drought. On the other hand, the predicted changes in CO_2 would tend to increase carbon assimilation by C_3 plants, and hence their growth rate and yield. For example, high atmospheric CO_2 concentrations have been reported to increase net photosynthetic rate, intrinsic water use efficiency, leaf thickness, Mg concentration and the C/N, K/N and Mg/N ratios, and to reduce stomatal density and N concentration, in Touriga Franca grapevine, although stomatal conductance, transpiration rate, photochemical efficiency, leaf water potential, and the red/far-red ratio transmitted by leaves were not significantly affected (Moutinho-Pereira et al., 2009).

Though it will be necessary for optimizing the quality of wine in a future scenario of climate change, information about changes in the volatiles composition, phenolic content, and antioxidant activity of wines produced at elevated CO_2 concentrations is limited. The only study we know of once more concerns Touriga Franca. Gonçalves et al. (2009) found that in general high CO_2 (500 $\pm$ 16 ppm as against ambient concentrations in open-top chambers or an outside plot) did not affect berry characteristics – in particular, total anthocyan and tannin concentrations were unaltered – but did alter the balance among the thirty-five volatile compounds identified in the wines (with minor exceptions, the same set under all treatments): in one year, ethyl 2-methylbutyrate, isoamyl acetate, ethyl hexanoate, ethyl octanoate, butyric acid, and isovaleric acid all increased under high CO_2, while ethyl acetate decreased; while in the following year it was ethyl lactate and linalool that increased and methionol, 1-octanol, and 4-ethylguaiacol that decreased. C_6 alcohols, citronellol, carbonyl compounds, and β-damascenone concentrations were unaffected. Overall, the effects of increased CO_2 were not negative as regards wine quality.

THE CHALLENGE OF SCIENTIFIC QUALITY MANAGEMENT IN VINEYARDS

As we have seen, the many chemical compounds that contribute to flavor and aroma in wines are determined in part in the vineyard through complex and poorly understood interplay among the natural environment, vineyard management practices, and vine genotypes, including the rootstocks (Jackson and Lombard, 1993; van Leeuwen et al., 2004). Such complexity has meant that the consistent production of high-quality grapes for wine-making has traditionally been more an art than a science. However, in practicing this art, many wine producers are increasingly guided by science.

There may be dozens or even hundreds of chemical compounds in grape berries that, like methoxypyrazines and norisoprenoids, are present in exceedingly small quantities and have yet to be discovered and characterized. Their discovery will require advances in extraction protocols and the application of increasingly sensitive analytical techniques such as Fourier transform ion cyclotron resonance, mass spectrometry, and nuclear magnetic resonance; while discovering their contribution, if any, to wine flavor and aroma will require the scientifically rigorous use of human sensory analyses (Campo et al., 2005).

It is desirable to know not only which compounds are responsible for grape and wine flavor and aroma, but also their origins and roles in the metabolism of the plant, and how environmental conditions affect the regulation of the genes and enzymes involved in their production. A better understanding of exactly how temperature, light, and water and nutrient availability affect allozyme production and activity will help in the development of molecular diagnostic tools that will assist viticulturalists in fine-tuning pruning, cluster thinning, irrigation, and fertilization practices from season to season in each vineyard. To achieve such understanding, complex networks of signaling and metabolic pathways must be characterized at the gene, protein, and metabolite levels in varied, controlled environments. As a first step, gene cloning and the functional characterization of enzymes that are important for the formation of volatile organic compounds in grapes have recently been carried out (Lücker et al., 2004; Martin and Bohlmann, 2004; Mathieu et al., 2005). Specifically, it seems that the complex metabolic profiles of volatile terpenoids and isoprenoids may be largely orchestrated by numerous terpenoid synthases (TPSes; Lücker et al., 2004; Martin and Bohlmann, 2004) and carotenoid cleavage dioxygenases (Mathieu et al., 2005).

For the future, it may be anticipated that wine-related genomic, proteomic, and metabolomic research will not be limited to *Vitis vinifera* cultivars that are currently commercially important, but extended to other cultivars, to the many other *Vitis* species (Wang and De Luca, 2005), and to the yeasts employed in fermentation.

CONCLUSIONS

Many advances have been made in understanding how the grape berry develops, and which of its chemical components are important for wine aroma and flavor. The quality of wines has doubtless improved as a direct result of being able to manipulate the grape berry through production practices. However, much remains to be learnt regarding what to manipulate, and when, given the complex interplay among the relevant factors. Ongoing molecular research will hopefully afford new insights allowing optimal decisions at the time of vineyard establishment (e.g., optimal matching of genotype to mesoclimate) and better control of berry ripening and flavor.

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ABBREVIATIONS

ABA	= Abscisic acid
ADC	= Alternate double cross-arm
ADH	= Alcohol dehydrogenase
AAT	= Alcohol acetyl transferase
CCD	= Carotenoid cleavage dioxygenase
2-DE	= Two-dimensional electrophoresis
FVT	= Free volatile terpene
FT-ICR	= Fourier transform – ion cyclotron resonance
GC	= Gas chromatography
GDC	= Geneva double curtain
HC	= High cordon
IBMP	= 3-isobutyl-2-methoxypyrazine
IPMP	= 3-isopropyl-2-methoxypyrazine
LC	= Low cordon
LC-ESI/MS/MS	= Liquid chromatography electrospray ionization tandem mass spectrometry
LM	= Lenz-Moser
LV	= Low-V
OAV	= Odor activity value
PB	= Pendelbogen
PVT	= Potentially volatile terpene
Red-free G-G	= Red-free glycosylglucose
RH	= Relative humidity
SBMP	= 2-*sec*-butyl-3-methoxypyrazine
SD	= Smart-Dyson
SH	= Scott Henry
TDN	= 1,1,6-trimethyl-1,2-dihydronaphthalene
TPB	= ((E)-1-(2,3,6-trimethylphenyl)buta-1,3-diene
TPS	= Terpenoid synthase
VSP	= Vertical shoot-positioned

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