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Factors Influencing the Aroma Composition of Chardonnay Wines

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ABSTRACT: Chardonnay is one of the oldest and most widely distributed wine grape cultivars and is of commercial importance for the world's wine-producing nations. It is an extremely flexible variety that has adapted to different regions with varied weather and soil characteristics. Somewhat uniquely among white wines, Chardonnay lends itself to a wide variety of production styles, which can be tailored to the target market. Techniques such as skin maceration, barrel and stainless steel fermentation, use of selected or indigenous yeasts, malolactic fermentation, and aging in barrels with or without lees are all applicable and lead to different compositional outcomes. A number of research papers have been published with a view to understanding Chardonnay composition and quality as well as the impact of different enological techniques on the final product. This review summarizes current knowledge, explaining the influence of viticultural and production techniques on aroma composition, and poses directions for further research into Chardonnay wines.

KEYWORDS: *Chardonnay, grape, wine aroma, volatile compounds, winemaking, aging, viticulture*

INTRODUCTION

Chardonnay can be found in every wine-producing region of the world, from both the Casablanca and San Antonio valleys in Chile to the Barossa and Yarra valleys in Australia. It is the most widely planted variety in California,[1,2] the most important white wine grape in Australia (almost 25% of total Australian grape production),[3] and the main white variety and second most important grape cultivar in Chile (Table 1). In the United States, which is currently the world's main wine-consuming nation and export destination, Chardonnay accounts for 13.3% of all the wine consumed.[4]

Table 1. Hectares of Chardonnay Vines Planted and Percentage of Total Vineyard Area in Selected Wine-Producing Countries[1−3,5−11]

country	surface planted (ha)	% total vineyard area for country
France	47487	6.3
USA (California)	38475	19.9
Australia	25491	17.2
Chile	10970	8.7
South Africa	8278	6.5
Spain	6957	0.7
Argentina	6473	3.0
Germany	1388	1.4

Chardonnay first appeared in Burgundy, France, approximately 500 years ago, making it one of the oldest cultivars in the world.[12] This "ancient" variety originated from the crossing of Pinot and Gouais blanc.[13] Several clones of Chardonnay are available, some of which are favored by winemakers depending on the environmental conditions (e.g., temperature, rainfall, soil type) and the wine characteristics being sought.[12] However, according to Riaz et al.,[12] most of the variability observed among clones of the same grape variety is simply chimeric. These authors reported polymorphic markers in nine genotypes among Chardonnay clones, none of which were unique at more than one marker.[12]

Chardonnay can be considered a vigorous variety with a moderate grape yield; on average it produces 4−10 T/ha of grapes when cultivated on reasonably fertile soils. This is an early-ripening variety, better adapted to the Winkler climatic regions I (such as Burgundy, Tasmania, and Oregon; heat summation below 2500 degree days) and II (such as Bordeaux and the Yarra Valley; heat summation between 2501 and 3000 degree days).[14] Nonetheless, Chardonnay is very versatile and can adapt to different climates and soils, as evidenced by the varied sites and conditions where it is cultivated. When planted in cool regions, cropping levels should be monitored to ensure adequate ripening.[15] Disease-wise, Chardonnay is susceptible to powdery mildew, botrytis, and crown gall.[15]

This variety is genetically predisposed to a low percentage fruit set and millanderage (excessive numbers of small, ripe berries within a cluster), particularly when climatic conditions are adverse.[16] Budburst occurs relatively early in Chardonnay, around 3 days before the average onset of budburst for other varieties and 11 days before that for Semillon. Flowering also takes place early, as much as 9 days before the mean in hot regions such as the Barossa Valley in South Australia.[16] The lower buds of Chardonnay vines are sterile, so cane-pruning is more suitable for this variety than spur-pruning.[14,16] Additionally, this type of pruning is well suited for machine harvesting.[14]

Chardonnay berry clusters are small, cylindrical, and winged and can range from well-filled to compact. Berries are small, thin-skinned, round, and usually contain only one seed.[14,17] In most clones, seedless berries account for only 2% of the total bunch weight, although this percentage is higher for the Mendoza clone.[16] Chardonnay is an anisohydric variety, which

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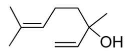
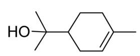
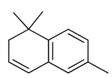
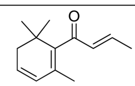
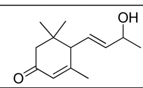
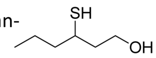
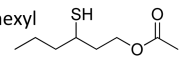
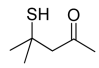
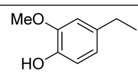
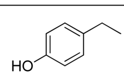
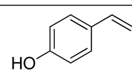
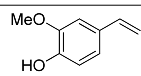
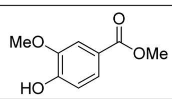
Table 2. Characteristics of Grape-Derived Odorants Important to Chardonnay Wine Typicity[a]

name and structure	aroma descriptor(s)	threshold (μg/L)	reported content in Chardonnay (μg/L)
linalool 	fruit, citrus[28,29]	25[30b]	2.0 – 142[31,32]
α-terpineol 	floral, musty, orange[33]	250[30 b]	0.3 – 181[31,34]
1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) 	kerosene, petrol[35]	2[36c]	1 – 30[37]
β-damascenone 	stewed fruit, apple, peach[28,33]	0.05[38d]	66 –170[39]
3-oxo-α-ionol 	spicy[40]	N.A.[e]	19 – 2674[32,40]
3-sulfanylhexan-1-ol 	passionfruit, grapefruit[41]	0.06[41f]	0.010 – 0.148[42]
3-sulfanylhexyl acetate 	box tree, passion fruit[43]	0.004[43f]	0.006 – 0.100[42]
4-methyl-4-sulfanyl-pentan-2-one 	box tree[41]	0.0008[41f]	0.0007 – 0.023[42]
4-ethylguaiacol 	spice, phenolic[44]	33[30b]	0.2 – 50[40,45]
4-ethylphenol 	horse stable, medicinal, leather, phenolic[46,47]	440[48g]	<1 – 1194[49,50]
4-vinylphenol 	spicy, pharmaceutical[29]	180[51 g]	44 – 638[29]
4-vinylguaiacol 	smoke, phenolic[52]	40[38 d]	2.9 – 410.6[34,53]
methyl vanillate 	vanillin[46]	3,000[54f]	N.A.[e]

[a]Compounds are included in this table on the basis that they are present in grape berries or, more often, have precursors which are present in berries that are modified during fermentation or aging; that is, they are not produced de novo by winemaking microorganisms. Nonetheless, they may also be associated with other aspects of wine production, for example, storage in oak barrels. [b]11% aqueous ethanol solution containing 7 g/L glycerol and 5 g/L tartaric acid; pH adjusted to 3.4. [c]Calculated in a Chardonnay wine. [d]10% aqueous ethanol solution. [e]N.A., data not available. [f]10% aqueous ethanol solution; pH adjusted to 3.5. [g]Model aqueous alcohol solution.

means that the pathway for water to move back from the berry to the vine closes as cell vitality decreases, effectively stopping water backflow and late-ripening weight loss (shriveling).[16] Due to its anisohydric character, Chardonnay possesses a higher hydraulic conductance, which enables it to recover more rapidly from water stress after irrigation. Under water stress conditions, the decrease in stomatal conductance that Chardonnay undergoes is lower when compared to that of isohydric varieties, which in turn enables this variety to sustain a higher photosynthetic level and capacity.[18]

Chardonnay is undoubtedly a commercially important variety for the world's wine-producing nations, and its popularity among consumers is driven by the underlying chemical composition of the wines. In particular, aromas and flavors, resulting from volatile compounds derived from grapes, fermentation, and aging, are important to the quality of Chardonnay wines and, therefore, contribute to consumer liking.[19−22] The reported impacts of different viticultural and production practices that influence the aroma and flavor profiles and perceived quality of Chardonnay wines are summarized in this review. Future directions for research into factors that contribute to the differences in Chardonnay aroma composition are also outlined.

■ WINE AROMA AS AN INDICATOR OF QUALITY

Quality is a very subjective notion that, among other factors, drives the price a bottle of wine might fetch in the market. Wine quality depends not only on the physicochemical composition of the wine but also on what the consumer expects from it. Expectation will vary depending on the type of wine and from which standpoint quality is viewed from: young wine versus aged wine; producer versus consumer; low involvement versus high involvement level consumer.[23] Individual consumers will define this concept differently depending on their expectations and needs.[24] Various authors describe wine quality in terms of its fitness for purpose and the absence of faults,[19,23,25−27] but these terms are more related to production and establish only a very basic level of quality.

Table 3. Characteristics of Odorants Important to Chardonnay Wine Typicity Formed during Alcoholic and Malolactic Fermentation

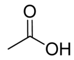
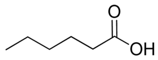
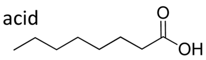
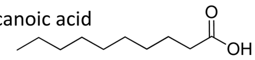
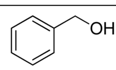
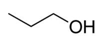
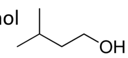
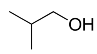
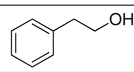
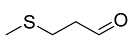
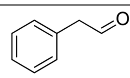
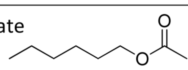
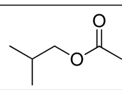
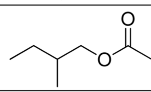
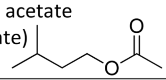
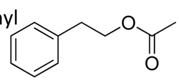
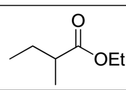
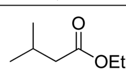
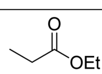
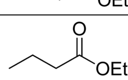
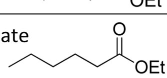
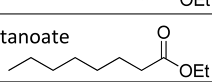
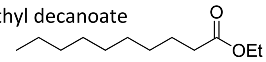
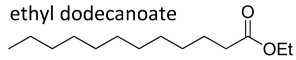
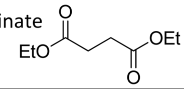
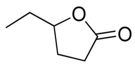
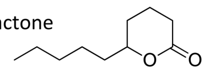
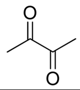
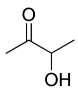
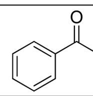
name and structure	aroma descriptor(s)	threshold (μg/L)	reported content in Chardonnay (μg/L)
acetic acid 	vinegar[68]	200000[38a]	6460 – 925000[40,62]
hexanoic acid 	rancid, pungent, green[28,52]	420[30b]	50 – 10430[67]
octanoic acid 	animal, spicy, cheese[29,44]	500[30b]	1150 – 50600[40,67]
decanoic acid 	vinegar, animal, fatty[29]	1000[30b]	40 – 14150[40,60]
benzyl alcohol 	fruity, floral[29]	10000[69c]	12 – 679[53,70]
1-propanol 	alcohol, ripe fruit[71]	306000[71d]	40 – 149000[40,67]
3-methyl-1-butanol (isoamyl alcohol) 	alcohol, harsh[72]	30000[38a]	50300 – 394900[59,67]
2-methylpropan-1-ol (isobutanol) 	green, fresh, fusel[73]	40000[38a]	160 – 45400[74,75]
2-phenylethanol 	rose[28,33]	14000[30b]	930 – 153800[40,70]
methional 	cooked vegetables[76]	0.5[76e]	N.A.[f]
phenylacet-aldehyde 	green, honey, floral, spicy[29,77]	1.0[78e]	4 – 28[29]
hexyl acetate 	apple[79]	1500[79a]	24 – 1590[63,80]
2-methylpropyl acetate 	strawberry[44]	1600[28b]	25 – 4600[59,62]
2-methylbutyl acetate 	banana, pear[81]	N.A.[f]	33 – 671[62,82]
3-methylbutyl acetate (isoamyl acetate) 	banana[29]	30[38a]	59 – 14900[63,67]
2-phenylethyl acetate 	floral, rose[73]	250[38a]	40 – 2000[67,82]
ethyl 2-methyl-butanoate 	strawberry, berry[44]	18[30b]	0.5 – 3.6[82]
ethyl 3-methyl-butanoate 	red fruit[33]	3[30b]	1.5 – 92[40,82]
ethyl propanoate 	sweet, ethereal, fruity[83]	1800[79a]	3 – 546[80,82]
ethyl butanoate 	fruity, strawberry[29,44]	20[38,84a]	60 – 1970[67]
ethyl hexanoate 	green apple, fruity, strawberry[29,33,44]	14[30b]	30 – 3960[63,70]
ethyl octanoate 	fruity, sweet[44]	5[30,38b]	30 – 3700[63,80]

Table 3. continued

name and structure	aroma descriptor(s)	threshold (µg/L)	reported content in Chardonnay (µg/L)
ethyl decanoate 	oily, fruity, floral[83]	200[30b]	17 – 496[63,70]
ethyl dodecanoate 	oily, fruity, floral[83]	500[85g]	1 – 3100[62,63]
diethyl succinate 	caramel[29]	200000[79a]	90 – 4580[67]
γ-hexalactone 	coconut, fruit[86]	13000[79a]	N.A.[f]
δ-decalactone 	coconut, floral[29]	386[30b]	3 – 53[29]
diacetyl (2,3-butanedione) 	butter, cream[28,73]	100[38a]	173[87]
acetoin (3-hydroxy-2-butanone) 	fatty, wet, flowery, butter, cream[28,44,46,88]	150000[79a]	250 – 4800[40]
acetophenone 	flower, almond, fruity[33,89]	65[69h]	N.A.[f]

[a]10% aqueous ethanol solution. [b]11% aqueous ethanol solution containing 7 g/L glycerol and 5 g/L tartaric acid; pH adjusted to 3.4. [c]Hydroalcoholic solution. [d]10% hydroalcoholic solution, pH 3.5. [e]10% aqueous ethanol solution containing 5 g/L tartaric acid; pH adjusted to 3.2. [f]N.A., data not available. [g]14% aqueous ethanol solution; pH adjusted to 3.5 with tartaric acid. [h]Aqueous ethanol solution.

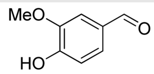
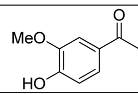
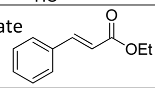
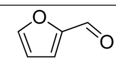
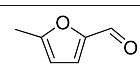
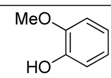
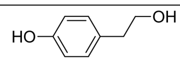
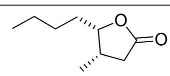
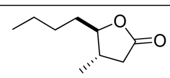
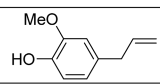
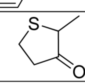
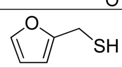
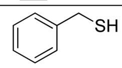
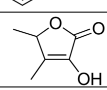
Consumers also rate quality according to how much pleasure it affords them[23] (which is too subjective to use as a parameter for production), ongoing trends, and wine flavor in particular.[23]

The flavor or "style" of a wine depends on its chemical composition; this relates to perceptions of astringency, bitterness, and acidity, among others, due to nonvolatile components, but relies particularly on the type and concentration of volatile molecules contributing to wine aroma. For Chardonnay wines, the most relevant aroma compounds are listed in Tables 2–4. A recent, but somewhat limited, study by Saliba et al.[21] of 21 commercial Australian Chardonnay wines identified at least five distinct styles (A–E), which are outlined in Figure 1. The presence of particular odorants such as diacetyl, thiols, and esters above their aroma thresholds allows the perception of attributes such as "butter", "tropical fruit", and "citrus" (Tables 2–4). These attributes in turn characterize the different styles described by Saliba et al.[21] and consequently have a major impact on Chardonnay quality and acceptance by consumers. However, the identification of strong links between Chardonnay grape and wine composition remains a holy grail. If wine producers are to fully exploit the capability of producing wines of a targeted style and quality for a specific market segment, a detailed understanding of Chardonnay impact odorants and the contribution of grape precursors and winemaking inputs is paramount in helping to address this need.

The advancement in extraction and analytical techniques has allowed scientists to delve further into the precursors and volatile molecules that contribute to the aroma of most wine varieties. However, given the wide array of existing styles and production techniques available to winemakers, the makeup of Chardonnay wine aroma and its relationship to quality have yet to be completely comprehended. Nonetheless, despite all of the possible combinations of enological techniques, studies by authors such as Jaffre et al.[55] and Ballester et al.[56] have demonstrated that a common olfactory representation (or prototype, as Ballester et al.[56] described it), independent of vintage and origin, does exist for Chardonnay wines among industry experts. It should be remembered, however, that it is the opinions and perceptions of consumers that matter in the marketplace, and these are underpinned by their notions of quality.

Ongoing research appears to be delving deeper into the understanding of Chardonnay wine quality and the different factors that affect it. The literature covers an array of fields, from studies on how quality is perceived by consumers[55,57,58] to the effect of winemaking techniques to incorporate more flavor, character, and uniqueness, such as the use of new yeast strains and sequential inoculation and thermotreatment of grapes, among others.[59−63] Particular interest exists among researchers in understanding "minerality", which is an essential (although somewhat poorly characterized) attribute of some of the most famous Chardonnay wines in the world such as those from Chablis and Burgundy.[64] Given the changes in global climate, studies are also required into the adaptation of viticultural practices and clone selection to continue producing high-quality wines, particularly as related to a drive to reduce alcohol levels. Even though anecdotal knowledge exists among producers as to the quality and style of fruit that can be obtained from each different Chardonnay clone available, there is a lack of scientific information as to the characteristics of these clones, and studies are needed on how they adapt to different terroirs and rootstocks.

Table 4. Odorants Derived from Oak Contact or Formed during Aging That Are Important to the Typicity of Chardonnay Wines

name and structure		aroma descriptor(s)	threshold (μg/L)	reported content in Chardonnay (μg/L)
vanillin		vanilla[33]	200[38a]	3.9 – 1223[40,53]
acetovanillone		floral, clove, vanilla[46]	1000[54b]	N.A.[c]
ethyl cinnamate		cinnamon, sweet, floral, strawberry, plum[28,44,99]	1.1[30d]	1 – 33[40]
furfural		almond[48]	14100[46d]	1 – 21190[40,45]
5-methyl-furfural		warm, spicy[100]	20000[101]	trace – 37.5[45]
guaiacol		phenolic, chemical, spice[28,33,44]	9.5[30d]	1.6 – 284[40,45]
tyrosol		N.A.	N.A.[c]	600 – 17040[59,70]
cis-oak lactone		coconut[77]	24[102e]	33 – 382[40]
trans-oak lactone		coconut, oak[103]	172[102e]	10.2 – 1355 [40,45]
eugenol		clove[48]	6[30d]	10 – 362[40,49]
2-methyltetrahydro-thiophen-3-one		metallic, natural gas[104]	0.09[105a]	18000[106g]
2-furan-methanethiol		roasted coffee[107]	0.0004[107f]	0.014[108]
benzene-methanethiol		smoky, gunflint[109]	0.0003[109f]	0.03 – 0.04[109]
sotolon		burnt, curry[28,33]	5[38a]	1.1 – 4.7[110]

[a]10% aqueous ethanol solution. [b]10% aqueous ethanol solution; pH adjusted to 3.5. [c]N.A., data not available. [d]11% aqueous ethanol solution containing 7 g/L glycerol and 5 g/L tartaric acid; pH adjusted to 3.4. [e]Neutral white wine. [f]12% aqueous ethanol solution containing 5 g/L tartaric acid; pH adjusted to 3.5. [g]As 1-octanol equivalents.

■ CHARDONNAY AROMA PROFILES

The headspace of Chardonnay wines has been tentatively determined to contain 243 volatiles detected through GC×GC-time-of-flight-mass spectrometry (TOF-MS),[65] which belong to a complex mixture of diverse chemical families including, but not restricted to, C_{13}-norisoprenoids, esters, alcohols, polyfunctional thiols, lactones, monoterpenoids, phenols, and acids.[39] Of these, the compounds derived from the grapes, winemaking, and aging listed in Tables 2−4 have been reported as having a positive relationship to the typicity of Chardonnay wines (i.e., the extent to which a wine is typical of the variety and is a good example of the Chardonnay wine concept), and some can be considered as character-relevant compounds for this variety.[29,55,56,66,67]

Not all of the compounds present in Tables 2−4 have an odor activity value (OAV) >1, which is normally taken as the value required for a compound to be a likely contributor to characteristic aroma. Their apparent importance to typical Chardonnay wine aroma highlights the fact that OAVs based on threshold values in a specific matrix (e.g., neutral white wine or 10% v/v aqueous ethanol) act merely as a guide when determining the importance of a compound to wine aroma, due to a significant effect of the matrix.[90−92]

When dealing with the typicity of a wine, with Sauvignon blanc being a good example, rather than search for impact compounds alone, researchers are also looking for those odorants that are essential for the wine to fit within a perceptual concept for that variety.[93] Similarly to quality, defining typicity requires a sensory analysis of samples; a number of sensory techniques are available for this purpose such as requiring the panelists to rate how well a wine belongs to a certain category and descriptive analysis or sorting of the samples, culminating with pairing and discrimination of the results based on the volatile composition of good and bad samples.[55,56,93] Other strategies to target relevant compounds include reconstitution analysis, which reveals the importance of certain volatiles to the overall aroma of the wine in question.[40] Consideration also needs to be given to the interactions among odorants, where differing concentrations of compounds in a mixture may have

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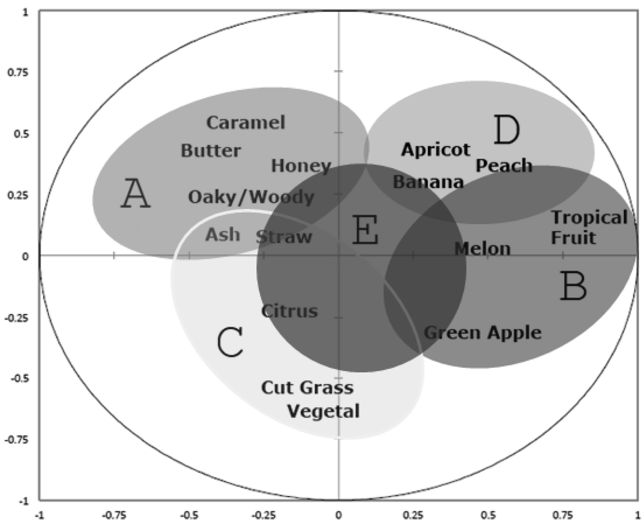

Figure 1. Representation of Chardonnay flavor profiles. A−E denote different commercial wine styles (based on data from Saliba et al.[21]).

synergistic or antagonistic effects and aromas may be enhanced or suppressed or odor quality altered as a result.[94−98]

Along the lines of seeking a perceptual concept for varietals, Louw et al.[67] analyzed 125 young unoaked Chardonnay wines, among other monovarietals from South Africa, using liquid−liquid extraction (LLE) and GC-flame ionization detection (FID), together with multivariate analysis and a "most used subset" of compounds to determine characteristic molecules that could be used to discriminate among cultivars. They showed that Chardonnay wines can be discriminated (with 74% correctly classified) by using the following eight volatile compounds: 2-phenylethanol, decanoic acid, diethyl succinate, ethyl hexanoate, ethyl decanoate, ethyl octanoate, hexyl acetate, and 1-propanol (Table 3). This prediction model, however, remains to be used to classify other sets of Chardonnay wines, particularly more developed ones, and the links between grape and wine composition for these eight specific compounds need clarification. They also observed that unlike most yeast-derived compounds (i.e., alcohols, acids, and esters such as those in Table 3), 2-phenylethanol, acetic acid, ethyl hexanoate, hexanoic acid, isoamyl alcohol, and 1-propanol were not affected by vintage, which could signify that their concentrations are characteristic of the Chardonnay cultivar. More work has to be done to confirm this, however.

Chardonnay juice does not possess any distinct aroma; however, certain precursors can be found in the must as well as the following volatile hydrolysis products: C_{13}-norisoprenoids, benzene derivatives, monoterpenoids, and aliphatic compounds as isolated by Sefton et al.[111] by reverse-phase chromatography followed by LLE and GC-MS. Although monoterpenoids (such as linalool and α-terpineol, Table 2) characterize the aroma of grape varieties such as Gewürztraminer and Muscats, Chardonnay is mostly deficient in these compounds, instead being dominated by C_{13}-norisoprenoids.[111] Studies by Lee and Noble,[40] Sefton et al.,[111] and Simpson et al.[39] suggest that the most relevant C_{13}-norisoprenoids to this variety's overall aroma are β-damascenone, 3-oxo-α-ionol, 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), and vitispirane.

C_{13}-Norisoprenoids such as β-damascenone and TDN are formed downstream from the oxidative cleavage of carotenoids (particularly lutein and β-carotene, with minor amounts of violaxanthin, neoxanthin, and several others), which occurs during grape berry ripening (e.g., Figure 2).[112−114] Although C_{13}-norisoprenoids can be found in their free form in the juice, they are usually present as glycoconjugates and easily degraded under acidic conditions.[115] β-Damascenone is a powerful odorant (odor threshold in model wine of 50 ng/L, Table 2) and aroma enhancer that, depending on concentration, can exhibit different odor qualities. At perithreshold concentrations, β-damascenone exhibits a "lemon balm" aroma, whereas at a concentration some 2 orders of magnitude higher it can be characterized as having "apple", "rose", and "honey" nuances.[116] Although β-damascenone is a ubiquitous wine component,[117] TDN, which possesses a "kerosene" aroma (Table 2), is typically associated with aged Riesling wines.[118] As determined by Lee and Noble[40] using GC−olfactometry (GC-O), 3-oxo-α-ionol possesses "spicy" notes at the concentrations found in Chardonnay wines (Table 2).

Polyfunctional thiols such as 3-sulfanylhexan-1-ol (3-SH), 3-sulfanylhexyl acetate (3-SHA), and 4-methyl-4-sulfanylpropan-2-one (4-MSP) are extremely potent odorants with very low aroma thresholds (60, 4.2, and 0.8 ng/L, respectively; Table 2) and aromas reminiscent of "box-tree", "grapefruit", and "passion fruit".[119,120] Both 3-SH and 4-MSP occur naturally in grapes as odorless glutathione and cysteine conjugates, which are released by yeast during alcoholic fermentation; 3-SHA is formed during alcoholic fermentation by esterification of 3-SH by alcohol acetyltransferase (AAT).[43,121,122] Although of particular significance to the typicity of Sauvignon blanc wines, these compounds are not as abundant in Chardonnay, yet still appear to be important.[42,119,123,124] The presence of other thiols such as benzenemethanethiol (BM) and 2-furanmethanethiol (FFT) at concentrations above their perception thresholds (0.3 ng/L[109] and 0.4 ng/L,[107] respectively) must also be noted (Table 4). BM has been described as having "flinty" and "smoky" (i.e., empyreumatic) notes, which may be related to Chardonnay wines' "mineral" character[64] and has an inconclusive formation

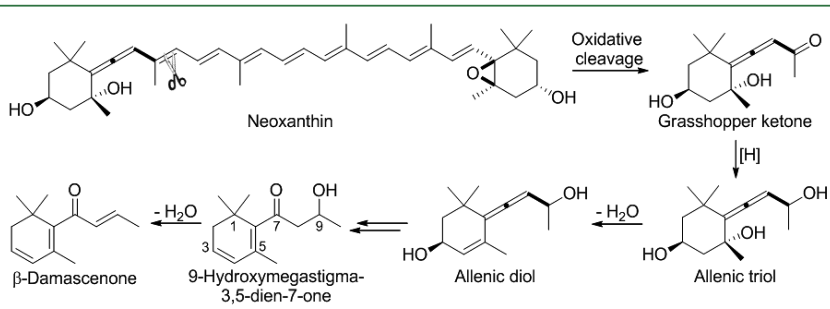

Figure 2. Formation of C_{13}-norisoprenoid β-damascenone from the carotenoid neoxanthin via oxidative cleavage, carbonyl reduction [H], and acid-catalyzed reactions. Although not depicted, glycosylated intermediates are also featured in this pathway.

pathway. On the other hand, FFT, with its strong "roast coffee" aroma, is formed from the furfural released by oak barrels and hydrogen sulfide formed during alcoholic fermentation.[125] Using a specific thiol extraction method (*p*-hydroxymercuribenzoate) together with GC-MS analysis, Tominaga et al.[109] determined that among wines from several appellation regions in France, Chardonnay possessed the highest concentrations of BM (30−32 ng/L), at 100 times above its detection threshold and 2−3 times more than all other assayed varieties. Mateo-Vivaracho et al.[42] have also confirmed the presence of suprathreshold concentrations of BM in Chardonnay (0.6−1.4 ng/L) through solid-phase extraction (SPE) and GC-MS analysis with negative chemical ionization (NCI). The different methodologies as well as the different origins of the wines employed by both research groups may account for the differences in quantities of BM found and in the hierarchy between Sauvignon blanc and Chardonnay in terms of these compounds. Comparison of Sauvignon blanc wines from different origins by Mateo-Vivaracho et al.[42] emphasized the importance that origin has on the content of all polyfunctional thiols (3-SH, 3-SHA, 4-MSP, BM, and FFT); BM concentration was highest in New Zealand wines, and FFT contents were found to be highest in French wines and lowest in those from Chile. However, these differences may be also due to viticultural and enological practices in each region. These two compounds have also been found at concentrations well above their perception thresholds in aged French Champagnes and have been shown to increase during aging.[126] Unfortunately, as with other polyfunctional thiols, analysis of BM and FFT is not a trivial undertaking (e.g., low abundance and reactive), and this may account for the fact that they have not been reported as characteristic of certain Chardonnay styles as yet.

Other important compounds are the esters (Table 3), which constitute the second most significant chemical group in the volatile fraction of Chardonnay wines. The esters are formed in excess during alcoholic fermentation by yeast metabolism and are responsible for "fruity" and "floral" aromas.[127,128] Wines contain two main types of odor-active esters: acetates of higher alcohols (formed by yeast AAT enzymes Atf1p and Atf2p, via condensation of their corresponding higher alcohols and acetyl CoA[129−131]) and ethyl esters of fatty acids (thought to be formed by esterification of the activated fatty acids (acyl CoA) during lipid biosynthesis mediated by acyl CoA:ethanol *O*-acyltransferase (EAT) enzymes Eeb1 and Eht1 together with other as yet unidentified enzymes[132]). Acetates are synthesized at higher concentrations than ethyl esters, and the ratio between both, as well as the concentration at which acetates are produced, is affected particularly by fermentation temperature, must nutrient content, and yeast strain rather than grape variety. Although both acetates and ethyl esters are liposoluble, excretion of ethyl esters through the yeast cell membrane becomes more difficult as chain length increases (only 8−17% of all ethyl decanoate produced by yeast is excreted into wine during alcoholic fermentation),[133] whereas 100% of all acetates produced are released.

The production of esters is modulated by the presence of cosubstrates and the activity of related synthesis and hydrolysis enzymes (esterases).[134] Formation of acetates depends on the concentration of unsaturated fatty acids (which inhibit AAT activity) available in the medium and carbon-to-nitrogen ratio.[134] A dynamic equilibrium exists between acetates and their corresponding acids and alcohols, which depends on the conditions of the medium.[135] Ethyl esters respond to the modification of most winemaking parameters in a similar way as acetates (albeit increases in nitrogen content or fermentation temperature have more pronounced effects on acetate formation). Higher concentrations of unsaturated fatty acids decreased ethyl ester production; however, inclusion of an additional carbon source to the medium increased only acetate production. Unlike acetates, synthesis of ethyl esters depends more on the availability of substrate (medium-chain fatty acids) rather than on enzyme expression level;[134] in turn, the amount and type of fatty acids available[136] depend on agricultural conditions and grape variety, making ethyl ester profiles more variety-dependent than that of acetates (except for hexyl acetate).[137] According to Smyth,[66] the most relevant esters for unwooded Chardonnay aroma appear to be ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl 2-methylpropanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, hexyl acetate, 2-methylbutyl acetate, and 3-methylbutyl acetate.

Moio,[138] Lorrain,[29] and Lee and Noble[40] all agree on the importance of volatile compounds such as guaiacol, *cis*- and *trans*-oak lactones, 4-ethylphenol, 4-ethylguaiacol, 4-vinylphenol, vanillin, methyl vanillate, and 5-methylfurfural (Tables 2 and 4) to the typicity of Chardonnay wines. These compounds derive mainly from aging in oak barrels, and some of them are even considered to be off-odors if they are present at concentrations above their perception threshold, as they are commonly associated with the metabolism of *Brettanomyces*/*Dekkera*.[47] However, some of these compounds, such as 4-vinylguaiacol, can also be found in wines that have had no contact with oak. 4-Vinylguaiacol is responsible for "smoke" and "phenolic" notes,[79] and although usually associated with aging in barrels, higher concentrations of this compound have been detected in some Chardonnay wines aged in stainless steel.[40] Spillman et al.[49] refer to 4-vinylguaiacol, 4-ethylguaiacol, 4-ethylphenol, and 4-vinylphenol as fermentation products rather than as compounds derived from oak contact. They are formed through decarboxylation of natural grape components ferulic and *p*-coumaric acids by *Saccharomyces cerevisiae* enzymatic activity[139] (hence their inclusion in Table 2). The concentration of these compounds appears to depend more on factors such as higher fermentation temperature and contact with lees than on the influence of oak wood.[140]

In their assessment of Australian Chardonnay wines, Saliba et al.[21] observed that five distinct styles resulted from the sensory analysis (Figure 1); among these, style A (a more "traditional/oaky" Chardonnay style, marked by "caramel", "butter", "honey", and "oak" attributes) and style B (a "crisp/fruity" style, with "tropical fruit", "melon", and "green apple" notes) seem to dominate the current market. From a volatile compound perspective, style A wines were marked by "woody", "smoky", "vanilla", "spicy", and "clove" odors, which are attributed to the presence of vanillin, guaiacol, 4-vinylguaiacol, furfural, and *cis*- and *trans*-oak lactones (Tables 2 and 4).[40,87] From the correlation matrix by Spillman et al.,[49] it can be inferred that the "smoky" notes present in Chardonnay wines aged in oak barriques are caused by the combined presence of guaiacol, 4-methylguaiacol, furfural, 5-methylfurfural, and, to a lesser extent, 4-ethylguaiacol and vanillin. Other oak-related aromas such as "cinnamon" and "coconut" were positively correlated to vanillin and *cis*-oak lactone (followed by guaiacol), respectively.

Unlike what might have been expected, the difference in resulting overall aroma between such A and B styles is not necessarily due to a different composition of characteristic

Table 5. Concentration (Micrograms per Liter) and Comparison of Volatile Compounds in Two Styles of Chardonnay Wines ("Fruity" and "Oaky") As Determined in Separate Studies

	Buettner et al.[87]			Lee and Noble[40]		
	fruity	oaky	factor of difference	fruity	oaky	factor of difference
ethyl isobutyrate	72.2	99.9	1.4	31		
ethyl butanoate	263	341.5	1.3	844	1040	1.2
ethyl isovalerate	9.2	19.9	2.2	42	41	1.0
3-methylbutyl acetate	943.7	163.5	0.2	519	349	0.7
ethyl hexanoate	757.2	737.5	1.0	843	600	0.7
linalool				50	31	0.6
2-phenylethanol	12415	24971	2.0	153840	116850	0.8
acetic acid	434232	489370	1.1	10000	11290	1.1
butanoic acid	1839	1611	0.9	1824	1505	0.8
trans-oak lactone	7.1	131.1	18.5	173	996	5.8
cis-oak lactone	17	214.8	12.6	33	382	11.6
2-methoxyphenol	2.7	9.9	3.7	25	284	11.4
ethyl cinnamate	1.5	3.1	2.1	3	6	2.0
eugenol	1.6	8.9	5.6	21	362	17.2
4-vinylguaiacol	50.5	49.3	1.0	1356	380	0.3
vanillin	48.5	241.6	5.0	107	1223	11.4

volatile molecules. A study by Buettner[87] of the potent odorants identified in two Chardonnay wines representative of a "traditional/oaky" and a "crisp/fruity" style (i.e., styles A and B according to Saliba et al.[21] in Figure 1) showed that they were both composed of the same volatiles, but each contained different amounts, leading to different time persistence levels for each attribute. Retronasal sensory assessment of both samples showed that the notes related to "oak" in style A were more persistent when judged by time−dilution analysis than the "fruity" ones in style B. Table 5 shows some of the results of this study, revealing that the concentration of *cis*-oak-lactone ("coconut" notes, Table 4) as measured by high-resolution (HR) GC-MS using stable isotope dilution analysis (SIDA) was almost 13 times higher in the A style wine than in the B style wine, and 3-methylbutyl acetate ("banana" notes, Table 3) was 6 times more abundant in the B style wine.

Lee and Noble[40] studied an array of California Chardonnay wines, two of which were characterized as belonging to the "crisp/fruity" and "traditional/oaky" styles (Figure 3). A comparison of their results to those obtained by Buettner[87] demonstrates similarities for certain compounds (Table 5). Both studies found concentrations of *cis*-oak lactone in the A styles that were approximately 13 times higher than in style B, as well as twice the concentration of ethyl cinnamate in the woodier styles than in the fruitier ones. The differences observed in the content of compounds related to fruity attributes were not as high as expected, and in some cases the difference found between both styles was not significant (i.e., ethyl hexanoate and ethyl butanoate). The use of aroma models and similarity tests by Lee and Noble[31] showed that even when trying to replicate wines with a high intensity of "fruity" aroma attributes, it was also necessary to incorporate "oak/spicy" volatiles (e.g., vanillin, furfural, 2-acetylfuran, *cis*- and *trans*-oak lactone, eugenol). The wines to which only "fruity" related aroma molecules (ethyl butanoate, 3-methylbutyl acetate, linalool, α-terpineol, and 2-phenylethyl acetate) were added were less representative and closer in profile to the base wine rather than the original "crisp/fruity" wine sample.

This highlights the potential importance of "oak" and "spicy" attributes to Chardonnay aroma even for "crisp/fruity" styles and explains the predominance of "woody" and "spicy" notes in

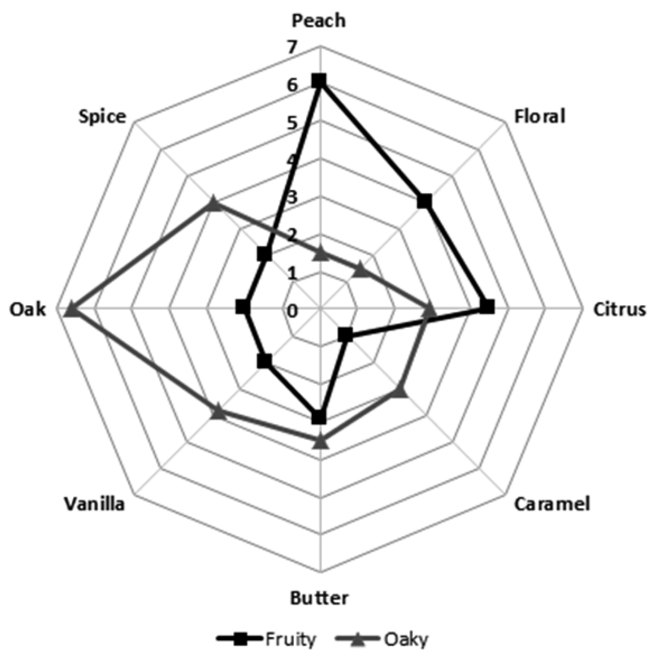

Figure 3. Aroma profiles of "fruity" and "oaky" Chardonnay wines (data from Lee and Noble[40]).

the "oaky" wine and lack thereof in the "fruity" style in the study by Buettner et al.[87] The only compounds not detected by tasters in the "fruity" sample were *cis*- and *trans*-oak lactone and eugenol; likewise, 3-methybutyl acetate was not detected by the tasters in the "oaky" wine and was, in fact, less abundant in the "oaky" style by a factor of 5.[87] The "fruity" style was also characterized by a higher detection frequency of linalool and α-terpineol,[40] which have been described as having "citrus" and "floral" notes.[40,79] Wines described as being "oaky" are seldom described as "fruity", and the work of Arrhenius et al.[37] showed a very significant negative correlation existed between the attributes "citrus" and "caramel/pumpkin" (this term is positively correlated to the presence of TDN). On the other hand, esters, which contribute "fruity" aromas, are often present in Chardonnay wines at concentrations well above their detection thresholds; therefore, no significant differences have been observed in the detection frequency of most of these compounds between both wine styles.[40]

■ FACTORS AFFECTING AROMA DEVELOPMENT

A range of factors determine the aroma composition of a wine, including but not limited to grape maturity, vine nutrition, harvest method, alcoholic and malolactic fermentation, and aging. Among these, grape maturity and alcoholic fermentation are considered the most critical stages.[26] Compounds related to grape variety and typicity, such as monoterpenoids, C_{13}-norisoprenoids, pyrazines, and polyfunctional thiols, which derive from the berry itself, can vary in concentration and can be found either in free form or bound as glycosides or amino acid conjugates, depending on the grape variety.[141−143] During fermentation, *S. cerevisiae* metabolism produces many of the olfactory compounds identified as being important to wine, such as esters and fusel alcohols, from the nutrients, elements, and different compounds present in the juice or must.[141,144,145]

Juice Composition and Nutrient Content. A balanced content of nutrients in the juice (nitrogen, amino acids, lipids, vitamins, and metal cations), as well as optimum oxygen and pH levels before the start of fermentation,[62] are determinant of yeast biomass formation, yeast metabolism, and alcoholic fermentation rate. Chardonnay appears to be the variety with the most reported cases of difficult fermentations in Australia as per Schmidt et al.,[146] most probably due to low pH and, in some cases, low potassium (K) concentration. The pH of juice appears to affect yeast performance in one of three ways; either the strain is unaffected, or its performance is affected (negatively) but can be corrected by adding K to the medium, or it is affected and K cannot correct the problem. A low pH combined with a low K concentration alters the redox potential of the medium, which is then corrected by an excess production of acetic acid, which is itself inhibitory for yeast metabolism and thereby further compromises the progression of fermentation.[146]

Nutrient deficiencies increase the risk of incomplete fermentations, leading to the appearance of off-odors (e.g., H_2S and other sulfur compounds) and unstable wines prone to bacterial spoilage. By supplementing a juice deficient in yeast assimilable nitrogen (YAN), usually in the form of diammonium phosphate (DAP) as an ammonium source, lower amounts of higher alcohols (for example, those in Table 3) and branched-chained acids (isoacids) are produced, and a higher concentration of esters is synthesized, improving overall sensory quality.[75] However, an excessive addition of DAP will tend to produce wines with an undesirable "solvent" character and higher ethyl acetate and acetic acid contents.[82,147]

In terms of the type of nitrogen supplement used, Torrea et al.[82] demonstrated that the addition of inorganic ammonium nitrogen (as NH_4Cl) to Chardonnay juices resulted in an increased concentration of acetic acid in the corresponding wines, but lower quantities of higher alcohols than with other forms of nitrogen (i.e., amino acids and ammonium). When the amount of ammonium supplementation was increased, the final wine had low fruit-related aromas and high "acetic" and "nail polish remover" notes, due to acetic acid and ethyl acetate, respectively; of 16 aroma descriptors evaluated, 14 changed significantly when different types and quantities of nitrogen were supplied.[82] These results can be explained on the basis of yeast metabolism, in which amino acids may play a role in certain metabolic pathways or may act as precursors to esters.[148]

If nitrogen is supplied in the form of amino acids, greater amounts of esters will be produced and higher alcohol concentrations will decrease.[75,82] In general, higher amino acid content improves the capacity of yeast to adapt to and/or work under anaerobic conditions, activating the synthesis of fatty acids and increasing the amount of ethyl esters produced.[75] However, there appears to be no correlation between higher alcohol acetates and amino acid levels; the extent of utilization of a particular amino acid by yeast will depend on the nature of the amino acid. As an example, greater amounts of leucine (a precursor to 3-methyl-1-butanol) were utilized in fermentations in which it was supplemented, but the final concentration of 3-methylbutyl acetate was similar to that of control fermentations.[149]

It should be mentioned that not all yeasts are equally sensitive to every nitrogen source. Certain strains were revealed to be insensitive to specific sources, whereas strain 254D, which is a moderate ester producer, was very responsive to changes in nitrogen source. For example, the content of ethyl and 3-methylbutyl acetates produced by 254D was significantly higher when using DAP than when nitrogen was incorporated as amino acids. Furthermore, use of amino acids when working with 254D yielded the lowest maximum and final concentrations of acetate esters and fatty acid ethyl esters determined in the study when compared to DAP-supplemented and control fermentations.[149]

Nutrients other than nitrogen are important to fermentation performance and metabolite profile. Varela et al.[62] demonstrated that aroma composition can be affected through lipid and oxygen supplementation, thereby influencing ester and higher alcohol production in Chardonnay wines while limiting production of fatty acids, especially of acetic acid, as well as lowering acetaldehyde concentrations.[62] Furthermore, supplementation of musts with these nutrients not only stimulated yeast growth and metabolism but improved fermentation rates significantly and diminished the amount of residual sugar in the final product. Addition of either oxygen or lipids changed the proportions of acetate to ethyl esters and of branched-chain to medium-chain fatty acids while, unfortunately, also increasing, by approximately 2-fold, the amount of higher alcohols to levels oscillating between 320 and 400 mg/L. This means higher alcohols were above the value indicated by Rapp and Mandery[68] as contributing positively to wine complexity (300 mg/L). These authors also suggested that concentrations of higher alcohols in excess of 400 mg/L no longer contribute positively to the overall aroma of a wine but rather detract from it. Addition of lipids (as unsaturated fatty acids) and sterol yielded Chardonnay wines with more esters overall, whereas incorporation of oxygen (with and without addition of lipids) increased acetate esters but strongly diminished the total content of ethyl esters. In either case there was a reduction in hexanoic acid but an increase in 3-methylpropanoic acid and variable effects on the other volatile acids (excluding acetic acid, which was reduced as mentioned above). Addition of lipids can also improve the fermentation progress of overly clarified juices and avoid stuck fermentations and high acetic acid concentrations.[62,146,150]

Use of Enzymatic Preparations. Endogenous grape glycosidases have a low enzymatic activity at the pH and/or sugar content of most grape juices and are therefore capable of only a limited level of aroma release through glycoside cleavage.[151,152] In addition, different enzymes are required to release bound volatiles such as monoterpenoids and C_{13}-norisoprenoids from their different glycosidic forms (i.e., β-D-glucosides and disaccharides).[153,154] Winemaking yeasts possess glycosidase activity[155] as highlighted by Chassagne et al.,[152] who revealed differences in the extent of glycoside hydrolysis during fermentation of a Chardonnay must. Model fermentations containing a Chardonnay glycosidic extract also showed that yeast glycosidases exhibited different extents of hydrolysis depending on the type of sugar involved (mostly glucose, arabinose, and rhamnose); by the end of fermentation 47% of glucose contained within the glycoside pool had been hydrolyzed, whereas glycosides containing rhamnose and arabinose had been almost completely metabolized.[61]

The use of enzymatic preparations with glycosidase activity has been demonstrated to increase the content of total monoterpenoids and C_{13}-norisoprenoids,[153,154] and enological preparations (of fungal origin) are available for use in winemaking to help improve aroma profiles.[155,156] Enzymes are typically added prior to fermentation during commercial winemaking (i.e., preparations used for juice extraction and clarification containing glycosidase side activities), but in a study of Chardonnay wines, glycosidases were added postfermentation, leading to increases of around 50% or more in total monoterpenoids and C_{13}-norisoprenoids.[32] Unlike grape glycosides, fungal glycosides are not inhibited under normal wine conditions[151] and have even been shown to enhance aroma characteristics when applied to dealcoholized wine containing grape aroma precursors.[157]

Winemaking Techniques. In response to current market trends and the popularity of certain wines, two marked tendencies exist now for Chardonnay aroma profiles: fruity and light styles are opposed by more flavored and complex (and possibly more evolved) styles. These disparate styles are targeted through choices made during winemaking, which have a strong influence on the overall aromas of Chardonnay wine, perhaps more so than any other white wine variety. Yeast produces esters during alcoholic fermentation, and given that they constitute one of the main groups of sensorially important compounds in Chardonnay, the choice of fermentation conditions and yeast strain will play a major role in overall wine aroma.[145] This explains why some non-Chardonnay wines, produced in the same style as a Chardonnay, have been confused by experts as belonging to the latter category during tasting.[55] In particular, Chardonnay aroma is marked by the presence of the ethyl esters of fatty acids (i.e., butanoate, hexanoate, octanoate, and decanoate) along with hexyl acetate (Table 3); the "fruity" nuances derived from variation in the concentrations of these compounds will be dependent on yeast strain, providing uniqueness to wine aroma.[158]

Chardonnay is one of the few white varieties that can endure a prolonged maceration.[159] This is fortuitous, because as shown with various grape varieties, a number of aroma compounds and precursors are located preferentially in grape skins; among them are monoterpenoids and their glycosides and precursors to β-damascenone and polyfunctional thiols.[53,160−163] Extended skin contact increases the total aroma content both in terms of concentrations of volatile molecules and as evaluated by sensory analysis.[34,164,165] Increased concentrations of linoleic and linolenic acids (precursors to C_6 compounds such as hexenals and, ultimately, 1-hexanol) have also been revealed through extended skin contact of Chardonnay musts,[166] and maceration with skins produced wines that were described as being more intense and "fruitier".[34,164] Macerated wines were also shown to be richer in C_6 compounds, particularly 1-hexanol.[34] According to Colagrande et al.,[167] the effect of C_6 alcohols and aldehydes depends on their concentration; when at low concentrations (<0.5 mg/L) their contribution is actually positive, adding to the typical aroma of Chardonnay wines, but they are also responsible for herbaceous flavors when their content is higher. The production of fruitier wines can be partly explained by the results of Dennis et al.,[137] which confirmed the role of certain C_6 compounds (1-hexanol, hexanal, (*E*)-2-hexenal, (*E*)-2-hexen-1-ol, and (*Z*)-3-hexen-1-ol) as precursors to hexyl acetate after the respective reduction and/or acetylation. Hexyl acetate, with its pleasant "apple" aroma (Table 3), is typical of unwooded Chardonnay wines.[66]

It is worth noting that skin maceration will necessarily increase the extraction of grape phenolic compounds (i.e., nonvolatiles associated with taste, mouthfeel, and color (browning of white wine)), potentially having an adverse effect on white wine sensory properties. However, despite total phenolics being increased linearly with maceration time, no significant differences in bitterness or astringency of Chardonnay wines were found in studies employing different times for maceration treatments. After 16 or 24 h of maceration, the sensory effect of an increased level of phenolics was no different from the wines that did not undergo skin contact.[164,165] Temperature plays an important role, however, such that cooler temperatures minimize the extraction of phenols without overly affecting the extraction of aroma components.[168] Furthermore, maceration affected the pH, titrable acidity, total nitrogen and amino acid contents, and potassium, calcium, and magnesium levels.[164,165] Some of these parameters will influence fermentation performance and contribute to differences in aroma profiles.

Thermotreatment of grapes is usually reserved for red wines, where higher polyphenol and anthocyanin contents are sought for their effects on color and mouthfeel. Chardonnay juices or wines may also benefit from thermotreatments to improve the extraction of determinate compounds from grapes and accelerate the level of hydrolysis of glycosylated aroma precursors. A study by Francis et al.[61] showed that heat treatments of Chardonnay wines at around 45 °C for several weeks resulted in wines with sensory properties similar to those of wines that had been bottle-aged for several years. Thermal treatment reduced "floral", "pineapple", and "grassy" characters of the resulting wines and intensified their "oak", "honey", and "smoky" characteristics. On the contrary, heating of juices or wines for a short time (i.e., around 2−12 min) at 90 °C on a pilot scale (250 L) was shown not to produce any discernible sensory differences when compared to the unheated control wine. In either case, there were no oxidized, cooked, or maderized aromas. Thermal treatment of Chardonnay juice or wine using mild temperatures could be envisaged as a more rapid and economical alternative to ordinary aging of wines to obtain a more "evolved" profile.

A choice of fermentation vessels is available to winemakers when producing Chardonnay wines. Tanks constructed of steel, cement, or plastic as well as oak barrels and vats may be used, depending on the desired style, available infrastructure, and budget. Unlike stainless steel, barrels are not inert and interact with the juice during fermentation, resulting in higher concentrations of certain volatile compounds. According to González-Marco et al.[70] the total concentration of about 186 mg/L for higher alcohols in wines produced in new French oak barrels was 42% greater than for stainless steel, but below the 400 mg/L total suggested as detrimental to wine aroma.[68] Ethyl acetate formed in oak barrels was approximately 32% higher, whereas other esters totaled almost 18 mg/L and were up to 4 times higher, particularly those of short- and medium-chain fatty acids, 3-methylbutyl acetate, and diethyl and monoethyl succinate, compared to stainless steel tanks. Hexanoic, octanoic, and decanoic acids were up to 6 times higher in oak barrel fermentations as well.

These outcomes can be rationalized by considering compositional differences between the fermentations in each type of vessel. Wood contains even-numbered saturated fatty acids (C2:0−C26:0), among a range of other volatile and nonvolatile compounds, which are extracted during fermentation, thus increasing the amount of esters and acids in the wine. The improved production of higher alcohols seemed to relate to a reduced consumption of amino acids in barrel-fermented wines, with the biggest differences being observed for 2-phenylethanol, benzyl alcohol, 1-hexanol, 1-propanol, 3-(methylthio)-1-propanol, methanol, tyrosol, and tryptophol.[70] Fermentation of wines in oak barrels also favors the extraction of typical oak-related volatiles such as oak lactones and furfurals, which undergo reduction to the corresponding furan alcohols because of a prolonged contact with lees.[140]

Yeast Influences. Yeasts affect the aroma composition and therefore quality of a wine in a number of ways. They synthesize odorant molecules de novo, such as esters and higher alcohols, release odorless precursors, and alter wine perception and flavor through the production of ethanol and the release of yeast constituents such as mannoproteins.[169] As well, the level of stress a yeast strain may tolerate will influence the amount of sulfur-containing malodorous compounds that will be formed in low-nitrogen situations. As outlined earlier, esters formed during fermentation comprise an important class of "fruity" aroma compounds in Chardonnay wine. Genetic variation between wine yeast strains and must composition leads to differences in expression of genes related to ester synthesis and hydrolysis.[149,169] Yeasts are also responsible for the cleavage of cysteinyl and glutathionyl conjugates and release of the corresponding polyfunctional thiols 3-SH, 3-SHA, and 4-MSP (see Table 2).[169] Typically, winemakers inoculate with selected strains of *Saccharomyces cerevisiae*, but a large diversity of yeast genera which can affect ester production exist as indigenous microflora.[170] A quick analysis of Australia's and America's major fine Chardonnay producers (based on wines with scores above 92 points as defined by James Halliday[171] and *Wine Spectator*) shows that many winemakers are choosing "natural" (i.e., wild or spontaneous) fermentations with indigenous yeasts (dominated initially by non-*Saccharomyces* yeast)[172] as a vehicle to incorporate more complexity and uniqueness into their wines. Wines from "natural" fermentations are not always scored better than inoculated wines, despite often possessing a higher aromatic intensity. This is because the use of non-*Saccharomyces* yeasts produces higher intensities of both positive and negative aromas, so scoring of the wine will depend on the balance between these compounds and the preference of the wine judge or consumer.[173]

Medina et al.[59] found that the use of commercial yeasts together with highly standardized procedures results in wines with uniform characteristics. Richter et al.[158] studied and characterized the metabolic footprint of 69 commercial yeast strains in Chardonnay wines. Despite the large number of strains studied, only four clusters, and therefore four wine aroma profiles, were identified through hierarchical clustering of their metabolites. Each cluster was identified by its particular ratio of acetate to ethyl esters, primarily due to a fluctuation in acetates. Each type of ester arises from discrete sets of precursors and enzymes, highlighting phenotypic differences among the clusters as a result of potential genetic variations. The final concentrations of esters in the wine depend on the maximum level attained during alcoholic fermentation, and the rate of formation, volatilization, and hydrolysis thereafter.[149] Esters are formed at different rates during fermentation, in particular, hexyl acetate and ethyl hexanoate, which derive from the modification of C_6 compounds by yeast. The earlier onset of production of these esters was suggested to depend on yeast cell growth, which relates to both the yeast strain and the medium conditions;[174] concentrations of hexyl acetate and ethyl hexanoate dropped significantly as fermentation progressed and ester degradation or volatilization overcame formation.[149]

New yeasts are still being selected and/or developed to provide winemakers with greater options to introduce complexity and increase diversity in aroma profiles. Strategies for the development of new strains include hybridization, mutagenesis, directed evolution, and genetic modification techniques such as the overexpression and introgression of genes related to the formation of specific aroma molecules or specific metabolic pathways.[169,175] Although genetically modified organisms are not currently permitted for use in the majority of wine-producing countries, and are anyhow met with high reticence by the public, they do constitute a very useful research tool. Gene deletions allow for metabolic pathways involved in the formation of key metabolites to be identified and comprehended, as has been the case in the elucidation of the mechanisms leading to the formation of polyfunctional thiols.[176] Even under the most favorable conditions (optimum fermentation temperature, extended skin maceration[177,178]), commercial yeast strains are able to release only 10% of all polyfunctional thiol precursors available. In response to this limitation, both Swiegers et al.[179] and Holt et al.[180] have developed yeast strains capable of releasing higher amounts of polyfunctional thiols due to enhanced carbon−sulfur (CS) lyase activity, through the insertion of the *Escherichia coli tna*A gene and by overexpressing the yeast gene *STR3*, respectively, in the commercial yeast VIN13 (considered to impart a high yield of thiols). Swiegers et al.[179] achieved a strain capable of releasing up to 25 times more 4-MSP and 3-SH than the original VIN13 strain, and Holt et al.[180] were able to confirm the CS β-lyase role of *STR3* gene product as well as design a yeast strain capable of releasing close to 10 times as much 3-SH as the original strain. Unfortunately, neither of these strains can be commercially applied.

Saberi et al.[63] isolated and studied two unique Burgundian strains individually and in cofermentations using Chardonnay juice, showing they were similar to each other and generally produced intermediate levels of higher alcohols, and ethyl and acetate esters, compared to the six commercial strains, which were more disparate to one another. The sensory profiles of the wines were estimated from descriptors and OAVs, showing the Burgundian strains produced higher alcohols (in particular, 1-butanol, 1-hexanol, and isobutanol) with OAVs of much less than 1 (minimizing fusel characters) and ethyl esters, responsible for pleasant "fruity" aromas, above their perception threshold (OAV > 1). Fermentations with mixed Burgundian strains tended to produce greater diversity in their profile of

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volatile compounds, indicating some form of metabolic interaction.

Likewise, Orlic et al.[60] isolated seven indigenous strains of *Saccharomyces paradoxus* from the Zagreb region in Croatia. These strains have the capacity to produce higher levels of glycerol than *S. cerevisiae* and lower total amounts of higher alcohols. When used to ferment Chardonnay juice, *S. paradoxus* produced wines of similar or better organoleptic quality than those in which *S. cerevisiae* was used, with higher concentrations of 1-propanol and 1-hexanol and lower concentrations of isobutanol, capric acid, and ethyl acetate. However, they also produced lower amounts of 3-methylbutyl acetate and total volatile esters. Cell−cell communication and modification of gene expression through quorum sensing have been raised previously and may explain this phenomenon.[172] The results of Miller et al.[149] showed that no one yeast strain possesses a higher rate of accumulation for all of the desirable esters, so a choice has to be made according to the compounds that are to be maximized. Fermentations with mixed yeast populations therefore provide a potential means to better achieve the desired aroma outcome.

Unlike inoculated fermentations in which a single *S. cerevisiae* strain dominates throughout the whole process, spontaneous fermentations resemble more a relay course where different species and strains of yeast succeed one another as alcohol content increases and nutrients become scarcer. Sequential inoculations with chosen strains seek to imitate this progression while affording the winemaker more control over the process than in spontaneous fermentations; however, these schemes rarely incorporate more than two different yeasts. Medina et al.[59] used the apiculate yeast *Hanseniaspora vineae* (as a starter culture) together with *S. cerevisiae* to barrel ferment Chardonnay; this approach produced wines with more intense "fruity" characters and flavors than the wines fermented with only *S. cerevisiae*. Similarly, Soden et al.[181] produced Chardonnay wines with more intense desirable attributes such as "floral", "honey", and "apricot" when including *Candida stellata*. However, in both cases the concentration of ethyl acetate in the wine resulting from the sequential inoculation was almost double that of the control fermented with only *S. cerevisiae*, at levels above the perception threshold of this compound. When above its perception threshold, ethyl acetate possess a "solvent"/"varnish" aroma that is considered a fault and decreases wine quality. Contreras et al.[182] proved that sequential inoculation of Chardonnay musts with *Metschnikowia pulcherrima* and *S. cerevisiae* produced wines with lower ethanol contents as well as higher contents of esters (particularly the "pear" and "banana" smelling 2- and 3-methylbutyl acetate; see Table 3). Sequential inoculation with *M. pulcherrima* increased the concentration of higher alcohols, however, although these remained below their perception threshold, and augmented ethyl acetate 6.5-fold to a level above its perception threshold, at which it is negative to overall wine quality. As observed above, sequential inoculations can be used for a number of purposes, be it to incorporate more aroma complexity into the wine or to produce a wine with a certain desired characteristic, such as reduced ethanol content.

Unlike *S. cerevisiae*, where strains have been isolated, selected, and industrialized to minimize the production of off-odors and negative secondary products such as higher alcohols, acetic acid, and ethyl acetate, while ensuring the consumption of all fermentable sugars, similar work is still being undertaken for alternative yeasts. When using yeasts other than *S. cerevisiae*, a compromise is usually made by the winemaker in favor of the desired characteristic (e.g., trade-off with suboptimal fermentation performance). Parameters such as the optimum ratio between yeast strains and the ideal moment of inoculation with *S. cerevisiae*, depending on the desired style, have yet to be determined, and any possible synergistic effects among the different yeast species requires study. Ciani et al.[183] stated that using more than one yeast species may have unpredictable results, such as unexpected compounds or anomalous levels of components that can alter the final aroma of the wine; all of which must be tested before they can be commonly applied industrially.

White wine fermentations are typically conducted at cool temperatures (i.e., 10−18 °C), and bisulfite is a common winemaking additive used to eliminate indigenous yeasts on grapes prior to inoculation with *S. cerevisiae*. Fermentation temperature and sulfite addition are crucial when indigenous yeasts are used, however, as they are more sensitive to higher temperatures and the presence of sulfite than *S. cerevisiae*. At 21 °C, *S. cerevisiae* is 10 times more viable than any indigenous yeast, whereas an addition of 50 mg SO_2/L (as bisulfite) reduces any non-*Saccharomyces* population by a factor of 10.[173] Furthermore, for inoculated fermentations, ester formation will be affected by the level of inoculum and the sugar content (total soluble solids, TSS) of the must. When lower TSS are present, yeast should be inoculated at a higher level to maximize the ester formation potential. Due to a higher cell count and maximum percentage of viable cells, a high level of inoculation doubles the amount of esters produced in a low TSS situation compared to a low level of inoculation; however, this means that no differences can be detected from a per cell point of view. When TSS is higher and carbon energy sources sufficient, higher inoculation levels do not produce any significant effects on ester production.[127]

Despite the interesting aroma characteristics that may be obtained from using autochthonous yeasts, widespread preference for commercial options can be easily explained by the certainty they give the winemaker for the strain being inoculated and the favorable characteristics they will impart to the wine. Indigenous microflora can include a number of yeasts that produce undesired characteristics (i.e., elevated quantities of acetic acid and ethyl acetate, haziness, off-odors, etc.), that can induce wine spoilage such as *Kloeckera apiculata*, *Metschnikowia pulcherrima*, and *Brettanomyces* spp. For example, *Zygosaccharomyces bailli* produces elevated quantities of acetoin and *Saccharomyces prostoserdovii*, *Saccharomyces bayanus*, and *Zygosaccharomyces fermentati* generate flor-like films under aerobic conditions.[184]

Good hygiene and sound enological practices together with inoculation with selected commercial yeasts have basically eradicated problems with any of the aforementioned yeasts. However, given their resistance to high alcohol and SO_2 levels and low sugar content, *Brettanomyces* spp. pervade all winemaking regions. Contamination with *Brettanomyces* spp. results in higher concentrations of volatile phenols and isobutyric, isovaleric, and 2-methylbutyric acids (sweaty and cheesy aromas). Volatile phenols possess "smoky", "barnyard", "horse sweat", and "spicy" odors and arise from the decarboxylation of hydroxycinnamic acids into vinylphenols, which are then reduced into their corresponding ethylphenols.[47,184] Some strains such as *Brettanomyces intermedius* and *Brettanomyces lambicus* also have the ability to produce "mousy"-smelling 2-acetyltetrahydropyridine/pyrroline from amino acid precursors;[185] others may produce high amounts of octanoic and decanoic acids (also known as "toxic fatty acids") that inhibit *S. cerevisiae* metabolism when present at the start of alcoholic fermentation.[184]

Bacterial Influences. Malolactic fermentation (MLF) of Chardonnay wines is a common practice in regions such as Burgundy and contributes the typical "buttery", "hazelnut", and "fresh bread" notes (and diminishes the intensity of "fresh" varietal odors such as "apple" and "grapefruit–orange")[186] associated with this variety from lactic acid bacteria (LAB) metabolites, particularly diacetyl and acetoin (Table 3). The contributions from MLF can differ due to grape variety[186] and, to some extent, the relative amounts of diacetyl and acetoin also relate to variety (thus, wine composition), with work by Flamini et al.[187] showing Chardonnay had a higher acetoin/diacetyl ratio than Cabernet Sauvignon. The desirability of this process depends on the style of wine being produced; winemakers have the choice of completely suppressing MLF, allowing it to occur only partially or on a portion of the wine, letting it take place naturally or encouraging it by adding LAB in the form of strains of *Oenococcus oeni*. In addition to deacidifying and helping stabilize wine by transforming malic acid into lactic acid, LAB also possess enzymatic activity, which further modifies wine aroma during MLF.[188] Grimaldi et al.,[189] D'Incecco et al.,[190] and Hernandez-Orte et al.[191] have confirmed the existence of glycosidase activity in *O. oeni* and its ability to release terpenes, C_{13}-norisoprenoids, and other glycoconjugates in model wine, even when MLF does not take place. This means that LAB not only contribute to the aroma of a wine through the production of diacetyl and acetoin but can also increase the amount of desirable compounds that are related to its typicity.[189]

As with yeast, development of indigenous bacteria can also have detrimental effects on the quality of the wine if production is not properly monitored and hygiene is not strictly observed. Several factors contribute to the spoilage of wines by bacteria such as high wine pH, elevated storage temperatures, insufficient SO_2, duration of MLF, strain of LAB present, and presence of residual sugar or O_2 during storage and aging.[184,192] Certain LAB, in particular *Pediococci* and *O. oeni*, possess enzymes that can decarboxylate amino acids into biogenic amines in wines with a high pH; these enzymes remain active even after the bacteria die.[193,194] These two strains are also responsible for the occurrence of "ropiness", in which high amounts of mucilaginous exopolysaccharides such as β-1,3-glucans are produced, conferring to the wine an oily appearance and a viscous texture, albeit no anomalous tastes or smells.[184,192] *Lactobacillus brevis* and *O. oeni* can cause what is known as "Tourne" disorder by fermenting tartaric acid into oxaloacetic acid, and subsequently succinic acid, or acetic acid and CO_2, causing a rise in pH, off-odors ("sauerkraut" and "mousy"), and a flat taste.[184] "Mousy" odors can also appear when 2-acetyltetrahydropyridine, 2-acetyl-1-pyrroline, and 2-ethyltetrahydropyridine are metabolized from ornithine and lysine.[195,196]

Of the eight known acetic acid bacteria (AAB) species, only *Acetobacter* sp. and *Gluconobacter* sp. are commonly found in grapes and wines.[184] These bacteria oxidize glucose and ethanol into acetic acid, acetaldehyde, and ethyl acetate.[192] Spoilage of musts occurs during pressing, when grapes are moldy and exhibit high levels of AAB.[184] Wines exposed to oxygen during aging (under *ullage* or with insufficient SO_2) are also susceptible to the development of AAB.

Contributions from Oak, Aging, and Lees. Chardonnay allows winemakers more stylistic choices than any other white wine variety; depending on the desired style, wines can be aged in oak and stored after bottling for long periods of time. Storage encompasses a number of variables (temperature, time, storage vessel, exposure to light, and closure) of which time and temperature are the most important ones,[74] because these promote and accelerate determinate chemical reactions among the different volatile and nonvolatile molecules in the wine. Unlike most other white wine varieties that are not aged, Chardonnay wines commonly spend a period of time, which may vary between several weeks and a year, in oak barrels. During barrel aging, furfural, 5-methylfurfural, furfuryl alcohol, guaiacol, 4-methylguaiacol, 4-propylguaiacol, eugenol, syringol, and oak lactone (both isomers) are extracted into wine from barrels (Table 4); the contents of 2-phenylethanol, 4-vinylguaiacol, and diethyl succinate also increase.[197]

Freshly cut oak does not contain the compounds that are desired in barrels and has too high a percentage of water; therefore, it must be seasoned and toasted before it can come into contact with wine.[198] Seasoning allows the wood to dry and prevents any shrinkage once the barrel has been formed. Compounds such as oak lactone and eugenol are formed during seasoning, and their concentration will depend on the wood's origin and where and for how long the wood is dried.[199,200] Furan aldehydes (furfural, 5-methylfurfural), vanillin, guaiacol, eugenol, and 4-methylguaiacol are degradation products formed by heat during wood cooperage from cellulose, hemicellulose, and lignin.[199] All of these oak compounds are responsible for the "smoky" and "spicy" aromas associated with barrel-aged Chardonnay wines.[140] Moio et al.[138] determined that guaiacol, derived from contact with oak, is one of Chardonnay's main impact odorants, denoting the relevance if this treatment for the typicity of certain styles of wine for this grape variety.

The amount of volatiles extracted from oak will vary according to the pH and ethanol content of the wine, as well as the barrel lot, its origin, and the number of years in use.[140] Although new French oak possesses on average 2–4 times more total volatile phenols than American oak, these compounds are formed during toasting and will depend on the degree of toasting rather than the origin of the wood. Certain compounds such as syringol, eugenol, and 4-methylguaiacol can decrease drastically between new and 2-year-old barrels to the point where no eugenol or 4-methylguaiacol may be found in wines aged in second-use barrels. Oak lactones are mainly formed from (3*S*,4*S*)-3-methyl-4-*O*-(6′-*O*-galloyl)-β-D-glucopyranosyloctanoic acid (galloylglucoside) and (3*S*,4*S*)-*cis*- and (3*S*,4*R*)-*trans*-3-methyl-4-*O*-β-D-glucopyranosyloctanoic acid during toasting and wine aging.[201] Oak lactones seem to be the exception to the general trend observed for most oak-derived compounds in wines, as the concentration of both isomers increased after 1 year of barrel use, with a more pronounced augmentation of the *cis*- rather than the *trans*-isomer. The ratio at which the *cis*- and *trans*-isomers are present will primarily depend on the origin of the wood, although seasoning can also play a role.[199] Among the oak lactones, the *cis*-isomer is more relevant to wine aroma and represents 57–90% of all oak lactones present,[202] and as highlighted by Maga,[203] only one enantiomer of each isomer can be found naturally in oak, that is, (4*S*,5*S*)-*cis*- and (4*S*,5*R*)-*trans*-oak lactones. *cis*-Oak lactone has been correlated with the intensity of "coconut" aroma in Chardonnay wine;[204] it is usually extracted at concentrations above its perception

Table 6. Concentration (Micrograms per Liter) and Standard Deviation (in Parentheses) of Odorants Relevant to Chardonnay Wine Typicity (Young, Bottle-Stored, and under Accelerated Aging Conditions)[a]

compound	young wine			stored wine (1 year; 18 °C)			accelerated aging		
hexyl acetate	72.7	(23)	a	5.6	(0.6)	b	14.1	(0.06)	c
ethyl butyrate	87.1	(7.9)		103	(11)		92.7	(1.7)	
ethyl hexanoate	674	(27)		871	(82)		830	(3.8)	
ethyl octanoate	1247	(199)		763	(48)		864	(2.7)	
ethyl decanoate	479	(35)	a	96.7	(16)	b	36.3	(1)	c
ethyl 4-oxopentanoate			a	4.52	(0.3)	b	3.40	(0.13)	a
ethyl dodecanoate	605	(47)	a	123	(10)	b	125	(14)	b
diethyl succinate	828	(47)	a	8930	(846)	b	4331	(135)	c
2-phenylethyl acetate	446	(117)	a	27.5	(9.1)	b	6.24	(3.4)	c
2-methyl-1-propanol	155	(11)	a	205	(38)	ab	286	(8.2)	b
1-butanol	15.2	(2.1)		18.4	(3.1)		22	(2.3)	
3-methyl-3-buten-1-ol	0.74	(0.2)							
1-hexanol	268	(88)		401	(98)		299	(0.9)	
(*E*)-3-hexen-1-ol	13.6	(2.7)		13.1	(4.7)		18.1	(0.4)	
(*Z*)-2-hexen-1-ol	1.56	(0.6)	a			a	4.13	(0.4)	b
linalool	5.93	(1.2)		3.35	(0.96)		2.16	(0.3)	
citronellol	4.33	(0.3)	a			b			b
geranic acid	67.1	(9.9)	a			b			b
benzaldehyde	11.5	(2.7)		4.91	(0.92)		12.9	(1.7)	
benzyl alcohol	112	(13)	a	169	(20)	b	108	(2.1)	ab
phenylethyl alcohol	5353	(13)	a	7876	(715)	b	6136	(250)	c
benzofuran			a	8.55	(1.34)	b	9.71	(0.25)	b
4-vinylguaiacol	126	(15)	a	226	(20)	b	212	(10)	b
γ-butyrolactone	19.9	(0.7)	a	18.3	(3)	a	0.06	(0.01)	b
γ-caprolactone			a	13.1	(1.49)	b	9.09	(0.42)	b
δ-decalactone	21	(2.8)	a	15.5	(2)	a	4.94	(1.2)	b
γ-undecalactone	226	(30)	a	436	(31)	b	552	(1.9)	b
furfural	5.52	(0.1)	a	69.2	(13)	b	92.8	(1.8)	b
5-methylfurfural			a	13.4	(1.8)	b	13.9	(3.0)	b
hexanoic acid	694	(8.1)	a	1019	(66)	b	827	(25)	c
octanoic acid	2545	(6.2)		2635	(7.8)		2718	(8.7)	
decanoic acid	558	(1.4)	a	381	(32)	b	400	(8.9)	b
dodecanoic acid	148	(0.7)	a	41.5	(13)	b	65.6	(2.4)	b
β-damascenone	13	(3.7)	a	14.4	(2.9)	a	45	(3.6)	b
3-oxo-α-ionol	154	(27)	a			b	99.5	(0.2)	a
3-hydroxy-β-damascenone	28.1	(5.4)	a			b	9.68	(0.28)	c
TDN			a	6.15	(0.86)	b	16.5	(0.8)	c

[a]Data from Cejudo-Bastante et al.[74] Where present, different letters across a row indicate significant differences ($p < 0.05$).

threshold (24 μg/L in white wine[102]) and at a low concentration is responsible for the "oaky" and "vanilla" aromas and of "coconut" notes when its concentration increases. The *trans*-isomer possesses a higher detection threshold of 172 μg/L (in white wine) and even when present at high levels does not seem to have an important influence on the overall aroma of the wine.[102,140,205]

As can be observed in Figure 1, Chardonnay wines can either have "smoky", "caramel", and "butter" attributes characteristic of a wine aged in oak or a more "fruity/crisp" character, dominated by "green apple" and "tropical fruit" notes. The Spearman rank-order correlation matrix by Spillman et al.[49] appears to support this claim. From the ranking of attributes the "green apple" attribute appears as very negatively correlated to guaiacol, 4-ethylguaiacol, furfural + furfuryl alcohol, and maltol and less significantly negatively correlated to 4-methylguaiacol, 5-methylfurfural, and furfuryl alcohol. "Green apple" was found to be highest in the control wine that had no contact with oak and exhibited a particularly significant negative correlation to "smoky"; the degree to which the "green apple" attribute was suppressed depended directly on the level of toasting of the barrel.

It is worth mentioning that oak barrel alternatives[45,206−208] (i.e., powders, chips, staves, plastic tanks lined with new or reclaimed oak staves) and different woods[209,210] (e.g., chestnut, beech, pine, cherry) have received attention from researchers. Although not specific to Chardonnay alone, as a whole, the use of oak barrel alternatives in particular offers an economical means of incorporating some of the desirable aroma compounds from oak without the time or expense associated with storing wine in oak barrels. The main factors to be considered when employing oak alternatives are the amount and surface area (shape and size) of the materials used. Chip-treated and barrel-aged wines differ in their contents of a range of volatiles, including vanillin, guaiacol, and furfural,[211] which translates accordingly into different aromas and flavors such as more pronounced "coconut" and "vanilla" together with more bitterness and astringency in white wines treated with chips.[45,212] Use of chips may also decrease the amount of perceived "fresh" and "unripe fruit" aromas and increase the overall concentration of esters and wood-related compounds as well as the intensity of "oak" aromas in the treated wine.[213] In general, relative to unoaked wines, the use of oak chips improved the liking of wines by the assessors in a number of studies,[45,211,213] which makes it a useful and cost-effective technique for incorporation of oak into certain Chardonnay wines.

Unlike oak, glass is inert, and once a wine is bottled, it is deemed ready to be consumed. Nonetheless, bottle-aging encompasses a different set of changes from those taking place when wine is stored in barrels. For instance, from studies performed on Champagne wines, it is known that the concentration of FFT increases proportionally to the time spent in the bottle, whereas BM reaches a peak at 13−15 years, after which its concentration falls.[126] With regard to other aging phenomena, esters are particularly affected due to their acid−ester equilibria;[214,215] for a wine that had spent 1 year stored in a bottle at 18 °C, Cejudo-Bastante et al.[74] found a significant decrease in the concentration of acetates and certain short-chain fatty acid ethyl esters (C_8−C_{12}) responsible for "fruity" aromas of Chardonnay wines. As evidenced by those results (Table 6), time (storage period) and temperature (accelerated aging) introduced several of these changes in the aromatic profile of Chardonnay wines. Modifications included a decrease in acetates and short-chain fatty acid ethyl esters of octanoic, decanoic, and dodecanoic acid, and the disappearance of 3-methyl-3-buten-1-ol, citronellol, geranic acid, (*Z*)-2-hexen-1-ol, 3-hydroxy-β-damascenone, and 3-oxo-α-ionol (for the latter three the disappearance was true only in the case of storage time), thereby changing the aromatic profile of the wine. Storage time and accelerated aging induced the appearance of benzofuran, ethyl 4-oxopentanoate, 4-hydroxyhexanoic acid lactone (i.e., γ-caprolactone), 5-methyl-2-furancarboxaldehyde (i.e., 5-methylfurfural), and TDN. These compounds are responsible for some of the tertiary aromas of wine, and therefore wines containing high quantities of these volatiles are referred to as more "evolved".

Aging can take place in the presence or absence of yeast lees (autolyzed yeast cells). Aging on lees (often in barrel, but also in tank or bottle as is the case for Champagne) improves the organoleptic score of wines (including overall quality, persistence, color, and taste, as well as aroma) and attenuates the impact of wood on the wine's aroma.[106] During yeast autolysis, polysaccharides (mainly mannoproteins), amino acids, assimilable nitrogen, and other cell contents are released into the wine.[216,217] The presence of lees contributes to the formation of "floral" and "fruity" scented ketones and lactones and to an increase in monoterpenoid concentrations due to the release of β-glucosidase enzymes acting on precursors.[106] However, this technique also results in wines with a lower global ester content as yeast autolysis releases esterases, which hydrolyze some of the esters present, into the medium.

During aging, lees both adsorb positive compounds such as esters and glycosylated compounds and strip the wine of off-odors such as volatile phenols and malodorous sulfur compounds (e.g., methanethiol and ethanethiol; however, hydrogen sulfide, dimethyl sulfide, and thiophene were not absorbed).[218,219] In general, aging on lees creates a highly reductive environment that both protects the wine from oxidation and increases the possibility that these negative sulfur volatiles will be formed. This latter effect can be countered by frequent stirring to resuspend lees and create a limited oxidation, as well as by performing an early racking of the gross lees before any reduction odors appear. With time, lees do lose their ability to generate foul-smelling sulfur volatiles as sulfitoreductase activity progressively subsides.[220] Furthermore, both adsorption and hydrolysis reactions are enhanced when lees are stirred.[152,217] When volatile compounds are present at low concentrations, mannoproteins have been observed to enhance the perceived intensity of a number of aroma attributes in Chardonnay wines.[216] However, this effect on overall aroma and individual aroma attributes is not discernible when volatile compound concentrations are high.[106]

The presence of lees also affects the absorption of wood volatiles. Towey and Waterhouse[197] showed that during the last 60 days of a 150 day aging trial, the adsorption on lees of oak volatiles exceeded that of extraction by the wine. This implies that aging on lees decreased the overall oak volatile content in wine, which can be either positive or negative depending on the style of wine sought, the degree of toasting, and the age of the barrel.

Terroir: Regional and Environmental Effects. Terroir has been proven to be an important element in wine aroma profiles. Enological variables aside, each wine-producing region will impart certain aromatic characteristics to the wines produced through the unique combination of weather, soil composition, latitude, longitude, altitude, and viticulture practices.

Fruit set, ripening, and the accumulation and concentration of aroma precursors and free compounds in the berry are affected by environmental and agronomic practices such as canopy management, fertilization, and yield.[26,221−224] Berry development is very susceptible to changes in solar radiation, temperature, rainfall, irrigation, soil composition, and altitude.[225] In particular, sunlight seems to have the most impact on monoterpenoid and C_{13}-norisoprenoid concentrations among all cited parameters; an increase in sun exposure increases the amount of glycosidic aroma precursors present.[116,226] As mentioned previously, C_{13}-norisoprenoids arise from the enzymatic breakdown of carotenoids; if the berry receives a higher amount of sun exposure before veraison, the concentration of carotenoids will increase. If exposure to sunlight is higher after veraison, it will generally accelerate carotenoid breakdown and induce an increase in the amount of glycosylated C_{13}-norisoprenoids present.[227,228] Likewise, higher sunlight exposure increases monoterpenoid concentrations, with this effect being more pronounced in cooler years.[229] It must be noted, however, that the opposite seems to be true for the ubiquitous C_{13}-norisoprenoid β-damascenone, at least in the case of Cabernet Sauvignon. As Lee et al.[228] observed, concentrations of β-damascenone were highest and those of TDN, lowest, at lower sunlight exposure and temperature.

Arrhenius et al.[37] showed that within wines of a higher quality, sensory attributes were significantly correlated to the wine's origin. In turn, they found that aroma attributes were correlated only to secondary volatiles, such as 3-methylbutyl acetate with the term "green-apples/pears", TDN with "honey", and ethyl 2-hydroxypropanoate with "buttery". In fact, high-quality Chardonnay wines from the Carneros and Napa regions in California could be discriminated from other California wines on the basis of the concentration of 3-methylbutyl acetate, the level of which is unique to each of these regions. Environmental factors could be responsible for differentiating the regions; for example, the Carneros region has a different photoperiod from the Central Coast of California that may affect the rate of formation and accumulation of certain compounds. This region could further be differentiated from the rest because of higher linalool content.[37] Williams et al.[230] and Marais et al.[231] observed that certain degradation products of carotenoids can be used as geographic markers for Chardonnay wines, because their concentrations vary depending on the temperature of the region; this is likely to be true of Australian Chardonnays, which seem to possess a distinct concentration of C_{13}-norisoprenoids that yield characteristic sensory attributes.[111,230]

Changes in environmental conditions between different vintages also affect the volatile composition of wines from a single vineyard (i.e., vintage effect). Louw et al.[67] showed that, with the exception of 2-phenylethanol, acetic acid, ethyl hexanoate, hexanoic acid, 3-methyl-1-butanol, and propanol, the level of 20 of 26 volatiles varied significantly during three consecutive South African vintages. That is, changes to fatty acids and their ethyl esters, along with higher alcohols and their acetates, were deemed to be caused by vintage effects. These compounds are associated with the volatiles derived from fermentation, implying an underlying change in grape composition (e.g., differences in amino acids and other nutrients) that was materialized upon fermentation.

Depending on intensity and timing, water deficit induces a reduction in Chardonnay wine quality, generating wines with high pH and low acidity and prone to atypical aging (i.e., wines with a lower intensity of varietal aromas and evident faults reminiscent of "acacia blossom", "furniture polish", "medicinal", and "naphthalene").[232,233] Atypical aging can be caused by suprathreshold levels of 2-aminocetophenone and other compounds such as sotolon that remain to be conclusively identified.[233−235] Research conducted by Reynolds et al.[236] showed that Chardonnay wines made from vines irrigated for different lengths of the season possessed higher intensities of "apple" and "citrus" compared to the nonirrigated controls and lower "earthy" aromas in three of four cases; however, consistent with the controls, wines showed greater atypical aging potential when the vines were subjected to irrigation up until lag phase or veraison. From their results, water stress could have interfered with the ability of grape berries to synthesize and accumulate monoterpenoids and ester precursors and may have promoted accumulation of compounds responsible for the atypical age character depending on the timing of water stress.

The characteristics of the soil where vines are planted is another environmental variable to consider when effects on wine composition are evaluated.[237] Soil properties can influence the depth that roots can penetrate, the availability of micronutrients, the retention of water, and therefore the level of hydric stress the plant is subjected to. All of these variables can affect the overall aroma of the subsequent wines. As Reynolds et al.[238] demonstrated, vineyards with high clay textures tended to yield Chardonnay wines with "vegetal", "earthy", and "citrus" characteristics, whereas wines made from grapes grown in sandy soils had "floral" and "melon" aromas. Although this study provides some guidance, at times there was a relationship between vine size and soil texture, and it was possible that vines in high-clay zones experienced some level of water stress. However, the results highlight the need to consider the impacts of the multiple facets of terroir on wine quality.

Weather can be partly countered through different agricultural techniques such as leaf removal and crop thinning. Leaf removal is particularly recommended in cold and cool climates to decrease the presence of "green" and "unripe" sensory attributes in the wine.[239] Under these conditions, leaf removal has been shown to increase the positive "floral" and "fruity" attributes. The effect of this treatment depends on when in the berry development cycle it is practiced; when applied during fruit set and veraison, the results are similar.[239] In areas with a high luminosity and potential for sunburn, a shaded bunch zone is preferable because a combination of high light intensity and temperature of the berry surface between 40 and 43 °C for only 5 min is enough to cause sunburn of mature Chardonnay berries. Sunburn damages the skin of the berry, decreasing quality and increasing concentrations of total phenolics, hydroxycinnamates, flavonoids, and tannins,[240−242] whereas under high light intensity and temperature conditions, shading can lead to crisper and more elegant wines that have more "citrus", "apple", and "quince" aromas.[16,224]

■ FUTURE DIRECTIONS

Given the popularity of Chardonnay wines and the global economic relevance of this variety, producers are always striving to produce better wines that cater to the current market trends. Understandably then, much work has been done to comprehend the volatile compounds present and the impact of each production step on the final aroma of Chardonnay wines. Over the years, quality has improved such that, for consumers, finding a good-quality wine is now extremely easy, but at the same time a certain homogeneity of flavor has appeared in the market, with two dominant styles arguably being responsible for most Chardonnays available in the market. In an industry where brand recognition goes only so far, uniqueness of the product is necessary. Determining whether this uniqueness is achieved at the vineyard level or via increased extraction of grape aroma compounds or through the use of different winemaking techniques requires more emphasis and understanding of the terroir dimension as well as a search for originality through the use of different yeast strains while preserving the typicity of Chardonnay.

Despite the definite existence of a typicity concept for Chardonnay, this has only started to be comprehended and requires deeper studies as this is a variety that can express itself in a multitude of profiles; Chardonnay is not as straightforward as other varieties (i.e., Sauvignon blanc or Muscats), which are dominated by distinct varietal compounds. Tackling its typicity requires multidisciplinary studies that analyze a number of variables responsible for the final product, rather than a one-directional focus.

Excellent advances in compositional knowledge have been detailed above, yet studies need to be carried out to confirm whether vintage-related changes between fatty acids and higher alcohols and their corresponding esters also occur in Chardonnay produced in different parts of the world and whether a trend can be determined. A better comprehension of the fate of aroma compound precursors extracted from the grapes is still required, as is the combined effect of the many components of terroir and how the most important ones are best manipulated and controlled. More work is therefore needed to correlate viticulture management with aroma/sensory profiles of the wines. In addition, very little is known of the potential of currently available Chardonnay clones, their interrelation with rootstocks, and any new clones that might be in development as related to other parameters such as yield, salt and drought tolerance, and vigor. Climate change will demand transformation and adaptation to new weather conditions with new choices that preserve the current quality standards.

Due to health concerns and taxation implications, as well as in response to the augmentation of alcoholic strength due to global warming and opting for riper fruit, low-alcohol wines and dealcoholization techniques have become a prime concern for the industry. Viable and cost-effective techniques that yield palatable and high-quality wines need to be formulated and tested on Chardonnay to determine the best alternative for producers. In a similar way, higher rates of individuals being susceptible to SO_2 and other industry additives, as well as dietary restrictions, pose new challenges for the wine industry, which will require the help of researchers to be solved.

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Notes

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■ ABBREVIATIONS USED

T, tonnes; ha, hectares; TDN, 1,1,6-trimethyl-1,2-dihydronaphthalene; GC, gas chromatography; GC-O, gas chromatography−olfactometry; TOF, time-of-flight; OAV, odor activity value; LLE, liquid−liquid extraction; SPE, solid phase extraction; NCI, negative chemical ionization; FID, flame ionization detector; HR, high resolution; SIDA, stable isotope dilution analysis; 3-SH, 3-sulfanylhexan-1-ol; 3-SHA, 3-sulfanylhexyl acetate; 4-MSP, 4-methyl-4-sulfanylpropan-2-one; BM, benzenemethanethiol; FFT, 2-furanmethanethiol; YAN, yeast assimilable nitrogen; DAP, diammonium phosphate; TSS, total soluble solids; MLF, malolactic fermentation; LAB, lactic acid bacteria; AAB, acetic acid bacteria

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