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Grape and Wine Metabolites: Biotechnological Approaches to Improve Wine Quality

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Abstract

Grape metabolites can be affected by many extrinsic and intrinsic factors, such as grape variety, ripening stage, growing regions, vineyard management practices, and edaphoclimatic conditions. However, there is still much about the *in vivo* formation of grape metabolites that need to be investigated. The winemaking process also can create distinct wines. Nowadays, wine fermentations are driven mostly by single-strain inoculations, allowing greater control of fermentation. Pure cultures of selected yeast strains, mostly *Saccharomyces cerevisiae*, are added to grape must, leading to more predictable outcomes and decreasing the risk of spoilage. Besides yeasts, lactic acid bacteria also play an important role, in the final wine quality. Thus, this chapter attempts to present an overview of grape berry physiology and metabolome to provide a deep understanding of the primary and secondary metabolites accumulated in the grape berries and their potential impact in wine quality. In addition, biotechnological approaches for wine quality practiced during wine alcoholic and malolactic fermentation will also be discussed.

Keywords: grape physiology, grape metabolites, wine biotechnology, alcoholic fermentation, malolactic fermentation, microbial metabolites

1. Introduction

Grape berry chemical composition is complex, containing hundreds of compounds. Water (75–85%) is the main component followed by sugars and then organic acids. Other important compounds include amino acids, proteins, and phenolic compounds. Berry sugar composition

has a key role in wine quality, since it determines alcohol content in wines [1]. Grape sugar, acidity, pH, and color are considered to mark harvest. *Bouquet* and flavor are related to the winemaker's expertise, stabilization, and storage processes, but primarily they are related to grape varietal character and its particular expression in a given *terroir*.

Nowadays, wine fermentations are driven mostly by single-strain inoculations, allowing greater fermentation control, leading to more predictable outcomes and decreasing the risk of spoilage by other yeasts [2]. During must fermentation, *Saccharomyces cerevisiae* produces a plethora of active-aroma secondary metabolites and releases many aroma compounds from inactive precursors present in grape juice, which significantly affect the sensory quality of the final wine [3, 4]. Besides yeasts, lactic acid bacteria (LAB) are members of the normal microbiota that appears in all type of wines (white and red), and, therefore, they also play an important role in their final quality. Malolactic fermentation (MLF), a long-standing process of deacidification in winemaking carried by LAB, is a reaction of L-malic acid decarboxylation to L-lactic acid. Complex metabolic activities also occur, thus suggesting that MLF can positively or negatively affect the final wine quality [5, 6].

2. Grape berry physiology and metabolome

2.1. Morphology and anatomy of grape berries

After successful pollination and fertilization of ovules within a flower berry development initiates [7]. The formation and growth of grape (*Vitis vinifera*) berries follows a double sigmoid pattern with three distinct phases [8]: I, rapid cell division and expansion in green berries; II or lag phase, in which cell expansion ceases; and III, in which growth is reinitiated and the fruit matures. The berry fruit comprises up to four seeds surrounded by the inner endocarp, the middle mesocarp, pulp or flesh, and the outer exocarp or skin [8, 9] (**Figure 1**).

Figure 1. Structure of a ripe grape berry. Illustrated by Silvia Afonso.

The exocarp consisting of a cuticle-covered epidermis, which represents 5–18% of the fresh weight of the fruit [10] and several layers of underlying thick-walled cells of hypodermis,

contains most of the skin flavonoids [11], notably anthocyanins in the outermost layers of the red grape varieties [8], interspersed with cells rich in needle-like crystals (raphides) [12]. Epidermis has non-photosynthetic cells with vacuoles containing large oil droplets [8]. Small berries have greater color, tannins, and flavor compounds than large berries because skin has a higher percentage of the total mass of small berries [7]. Scanning electron microscopy showed very few but functional stomata on young berries and wax-filled stomata on older berries [13], which accumulate polyphenolics and abnormally high concentrations of silicon and calcium in the peristomatal protuberances of up to 200 μm diameter [14].

At harvest, the cuticle of grape berry had an amorphous outer region and a mainly reticulate inner region [15]. During fruit development, the composition of the cuticular waxes changed, being oleanolic acid the main constituent, representing 50–80% of the total weight [16]. The soft wax was a mixture of long chain fatty acids (C_{16} and C_{18} fatty acid esters [17]), alcohols, aldehydes, esters, and hydrocarbons [18].

The mesocarp consists of thin-walled parenchyma [12]. The cells are round to ovoid and contain large vacuoles, which are the primary sites for the accumulation of sugars and phenolics [8], water, and organic acids [9] during grape berry ripening. According to Coombe [19], the translucent and hydrated mesocarp composes 85–87% of the berry's spherical volume. Altogether these make up 99.5% of the juice mass and hence are the major determinants of berry size and quality [9, 20]. The remaining 0.5% of berry components are phenolics, terpenoids, lipids, cellulose, and pectin [20]. The endocarp consists of crystal-containing cells (druses) and an inner epidermis [12].

Grape seeds are contained in locules (**Figure 1**), and are composed of an outer seed coat, the endosperm, and the embryo [9]. As with most seeds, the endosperm comprises the bulk of the grape seed and serves to nourish the embryo during early growth. The normal or perfect number of seeds in the grape is four [9], but lack of ovule fertilization or ovule abortion reduces the number of developing seeds, generally resulting in smaller berry size [7]. Based upon recent molecular evidence, auxin is synthesized in the ovule and transported to the pericarp upon fertilization, where it induces gibberellin (GA) biosynthesis. The GA then degrades DELLA proteins that repress ovary growth and fruit initiation [21]. The size of mature berries at harvest is also a function of the number of cells divisions before and after flowering, extent of growth of these cells [22], and the extent of preharvest shrinkage [23].

High level of tannins is observed in the seed coat [9, 11]. Similar to the tannins and phenols found in the flesh, these tannins also decline greatly on a per-berry basis after *véraison* [24].

Berry vascular tissue develops directly from that of the ovary. It consists primarily of a series of peripheral bundles that ramify throughout the outer circumference of the berry and axial bundles that extend directly up through the stem [8]. Grape berry is provided through the berry stem or pedicel by a vascular system composed of xylem and phloem vessels [25]. Water, minerals, hormones, and nutrients are transported from the root system throughout the vine by the xylem tissue [25]. Present evidence indicates that in the final stages of grape development, water movement through the xylem vessels decreases markedly [25]. But, it seems that the fruit is not hydraulically isolated from the parent grapevine by xylem occlusion then,

rather, is “hydraulically buffered” by water delivered via the phloem [9]. Berry is also supplied by the phloem, which is the vasculature involved in photosynthate (sucrose) transport from the canopy to the vine [25].

2.2. Grape primary and secondary metabolites

2.2.1. Sugars

One of the main features of the grape-ripening process is the accumulation of sugars in the form of glucose and fructose within the cellular medium, specific in vacuole. In addition, sugar content is an important indicator often used to assess ripeness and to mark grape harvest. But, it is also possible to quantify small traces of sucrose in *V. rotundifolia* and hybrids between *V. labrusca* and *V. vinifera* grapevines [26]. Liu et al. [27] analyzed sugar concentration of 98 different grape cultivars and concluded that glucose (45.86–122.89 mg/mL) and fructose (47.64–131.04 mg/mL) were the predominant sugars in grape berries. During grape berry maturation, sucrose is produced in leaves by photosynthetic carbon assimilation and is transported to the berry in the phloem [24]. Sucrose is loaded into the phloem by either a symplastic or apoplastic mechanism [28]. However, it is at *véraison* that begins the sugar accumulation and the imported sucrose is converted into hexoses as a result of the activity of invertases [29].

Grape berries accumulate glucose and fructose in equal amounts at a relatively constant rate during ripening [29]. In addition, after *véraison* there is a considerable accumulation of glucose and fructose in the vacuoles of mesocarp cells, while 20 days after this period, the hexose content of the grape berry is close to 1 M, with a glucose/fructose ratio of 1 [19, 30]. Grape sugar concentration and composition is mainly determined by several factors, such as genotype [26, 31], vineyard management [32, 33], and climatic conditions [34, 35]. Moreover, in last years, as a result of climate change, there is a tendency for a sugar increase in grapes [36]. But, according to Mira de Orduña [35], the extremely high sugar levels reached at harvest today, especially in warm climates, may be rather associated with the desire to optimize technical or polyphenolic and/or aromatic maturity.

2.2.2. Organic acids and nitrogenous compounds

L-Tartaric and L-malic acids contribute to around 90% of the organic acid content in mature grapes [37, 38]. Minor amounts of citric, succinic, lactic, and acetic acids are also present in ripened grapes [39]. Despite L-tartaric and L-malic acids having similar chemical structures, they are synthesized and degraded by evidently different metabolic pathways in the grape berries. L-Tartaric acid synthesis in grape berries occurs during the period of grape growth [19, 40]. Tartaric acid pathway using L-ascorbic acid (vitamin C) is considered to be responsible for >95% of grape L-tartaric acid production [41]. L-Malic acid synthesis indicates that-carboxylation of pyruvate or of phosphoenol pyruvate is the most important pathway [42]. Accumulation of acids usually occurs at the beginning of berry development. The organic acid content increases up to *véraison* and then declines. The content of organic acids is determined by a balance between their synthesis and degradation. L-Tartaric acid was the most prominent acid from *véraison* until the fruits were fully mature. L-Malic acid content increased gradually

until *véraison*, after which it decreased with fruit ripening [37]. Grape acid composition is influenced by many factors such as grape variety, environmental conditions, and cultural practices [43]. High malate-producing grape varieties have been identified, such as Carignane, Chardonnay, Grenache, Malbec, and Pinot Noir, as well as high tartrate-producing grape varieties such as Merlot, Semillon, Riesling, and Thompson Seedless [44]. Temperature is a key factor in the rate of L-malic acid degradation during the berries ripening; with low temperatures, higher concentration of L-malic acid was observed [43]. L-Tartaric acid is presumed to be more stable when exposed to higher temperature, being the slight decreases during ripening due to dilution from berry expansion [45, 46].

Grapes nitrogenous compounds include ammonium cations and organic nitrogenous compounds such as amino acids, hexose amines, peptides, nucleic acids, and proteins. As maturation happens, organic nitrogen progressively increases while ammonia slightly declines. The synthesis of amino acids, peptides, and protein occurs during the last 6–8 weeks of berry ripening [47]. In grapes, the main free amino acids include proline (up to 2 g/L), arginine (up to 1.6 g/L), and to a lesser extent, alanine, aspartic acid, and glutamic acid [48]. However, compositional differences in amino acids were observed by Stines et al. [49] among grape varieties, proline and arginine always being the major grape amino acids. In all grape varieties, most of the proline accumulation happened late in ripening, nearby 4 weeks of post-*véraison*. In opposite, arginine accumulation started before *véraison* and continued to maturity, excluding grape varieties in which a great level of proline accumulated [49]. The variation of amino acid profile and their concentration in grapes depends on grape variety, but also on viticultural management and environmental conditions [43, 50, 51].

According to Hsu and Heatherbell [52], grapes contain naturally a wide range of different proteins, up to 41 protein fractions with molecular mass ranging from 11.2 to 190 kDa and isoelectric point from 2.5 to 8.7 [53, 54]. Soluble proteins in grape are globular proteins, mainly albumins [55, 56]. There is a significant increase in grape total protein content after *véraison* being a small content of proteins synthesized significantly during grape ripening [55, 57]. The most abundant grape proteins synthesized during ripening are pathogenesis-related proteins, including chitinases (32 kDa) and thaumatin-like proteins (24 kDa) [29, 57, 58].

2.2.3. Aroma and flavor compounds

Free and bound terpene grape content has been used to measure berry flavorant development and potential. Numerous types of flavorants existed in the form of glycosidic precursors. Analysis of the total precursor content by assessment of the glycoside glucose (GG) content of the grapes may yield a more complete depiction of the grape flavorant potential [59]. During grape maturity, changes in the concentration and diversity of aroma precursors and volatile compounds occurred [60, 61]. Lacey et al. [60] observed that grapes grown under cool temperatures showed higher grape methoxypyrazine concentration than grapes grown under hot temperatures. Grape methoxypyrazine levels were relatively high at *véraison* but decreased markedly with grape ripening. However, since grape maturation is genetically controlled, it is considerably influenced by environmental conditions [60].

2.2.4. Phenolic compounds

Phenolic compounds are very important for wine quality because they are responsible for most of the wine sensory characteristics, particularly color and astringency. These groups of compounds constitute a diverse group of secondary metabolites that exist in grapes, mainly in the grape berries' skins and seeds [62] and also in grape stems [63]. The phenolic compounds in *V. vinifera* grapes include two classes of phenolic compounds: non-flavonoids and flavonoids. The non-flavonoid compounds include phenolic acids divided into hydroxybenzoic acids and hydroxycinnamic acids, but also other phenol derivatives such as stilbenes (Figure 2). Non-flavonoids incorporate C₆-C₃ hydroxycinnmates acids, C₆-C₁ hydroxybenzoic acids, and C₆-C₃-C₆ stilbenes *trans*-resveratrol, *cis*-resveratrol, and *trans*-resveratrol glucoside.

Figure 2. Main non-flavonoid compounds found in *V. vinifera* grapes.

For flavonoid compounds, there are a large number of subclasses, such as flavonols, flavanols, and anthocyanins [64]. Flavonols are the most abundant phenolic compounds in grape skins [65], while grape seeds are rich in flavan-3-ols [66]. Flavonoids are characterized by a basic structure of 15 carbon atoms comprising two aromatic rings bound through a three carbon chain (C₆-C₃-C₆). The major C₆-C₃-C₆ flavonoids in grapes include conjugates of flavonols quercetin, and myricetin; flavan-3-ols (+)-catechin and (-)-epicatechin; and malvidin-3-O-glucoside and other anthocyanins (Figure 3a–c).

According to Pastrana-Bonilla et al. [67], the average concentration of the total phenolic compounds in different grape fractions varied from 2178.8 mg/g gallic acid equivalent in seeds

to 374.6 mg/g gallic acid equivalent in skins. In addition, it is also possible to found low concentrations of phenolic compounds in pulps (23.8 mg/g gallic acid equivalent).

Figure 3. (a) Main flavonoid compounds (anthocyanidins) found in *V. vinifera* grape varieties. (b) Main flavonoid compounds (flavan-3-ols and procyanidins) found in *V. vinifera* grape varieties. (c) Main flavonoid compounds (flavonols) found in *V. vinifera* grape varieties.

In general, the phenolic composition of grapes is influenced by different factors, such as grape variety [68, 69], sunlight exposition [70], solar radiation [71] altitude [72], soil composition [73], climate [70, 74–76], cultivation practices [43, 74], exposure to diseases [77], and the degree of grape ripeness [63, 69].

The quantification of phenolic acids, stilbenes, monomeric anthocyanins, flavan-3-ols, and proanthocyanidins in red grape varieties is summarized in **Tables 1–3** and the quantification of phenolic acids, stilbenes, flavan-3-ols, and proanthocyanidins in white grape varieties is summarized in **Table 4**.

Phenolic compounds	Grape variety	Concentration	References
Phenolic acids	Negroamaro	7.3 ^a	
Gallic acid	Susumaniello	45.0 ^a	Nicoletti et al. [78]
	Malvasia Nera	77.3 ^a	
	Aglianico	151.9 ^a	
	Merlot	66.6 ^a	Obreque-Slier et al. [79]
	Carménère	2.8 ^b	
	Cabernet Sauvignon	3.5 ^b	
	Merlot	9.8 ^c	Montealegre et al. [80]
	Cencibel	7.3 ^c	
	Cabernet Sauvignon	9.0 ^c	
	Shiraz	6.8 ^c	
Protocatechuic acid	Negroamaro	42.0 ^a	Nicoletti et al. [78]
	Susumaniello	8.5 ^a	
	Malvasia Nera	46.0 ^a	
	Aglianico	37.4 ^a	
	Cesanese	31.1 ^a	
	Merlot	328.7 ^a	Montealegre et al. [80]
	Cencibel	1.5 ^b	
	Cabernet Sauvignon	2.4 ^b	
	Merlot	1.7 ^b	
	Shiraz	2.4 ^b	
	Merlot	8.7 ^c	Montealegre et al. [80]
	Cencibel	3.3 ^c	
	Cabernet Sauvignon	7.1 ^c	
	Shiraz	6.2 ^c	
	Primitivo	1.89 ^a	
Caftaric acid	Negroamaro	8.5 ^a	Nicoletti et al. [78]
	Susumaniello	171.7 ^a	
	Malvasia Nera	171.9 ^a	
	Aglianico	320.4 ^a	
	Cesanese	28.8 ^a	
	Alphonse	645.0 ^a	
	Merlot	746.3 ^a	
	Carménère	0.6 ^b	
			Obreque-Slier et al. [79]

Phenolic compounds	Grape variety	Concentration	References
Stilbenes <i>Trans</i> -piceid	Cabernet Sauvignon	0.7 ^b	Nicoletti et al. [78]
	Primitivo	30.7 ^a	
	Negroamaro	4.14 ^a	
	Susumaniello	150.3 ^a	
	Uva di Troia	15.3 ^a	
	Malvasia Nera	98.0 ^a	
	Aglianico	75.7 ^a	
	Cesanese	12.0 ^a	
	Merlot	26.3 ^a	
	Alphonse Lavallée	24.1 ^a	
<i>Trans</i> -resveratrol	Castelão	67.24 ^c	Sun et al. [81]
	Syrah	10.43 ^c	
	Tinta Roriz	11.57 ^c	
	Primitivo	13.9 ^a	Nicoletti et al. [78]
	Negroamaro	3.6 ^a	
	Susumaniello	63.0 ^a	
	Uva di Troia	4.6 ^a	
	Malvasia Nera	48.5 ^a	
	Aglianico	61.1 ^a	
	Cesanese	8.1 ^a	
	Merlot	9.2 ^a	
	Alphonse Lavallée	40.0 ^a	Mikeš et al. [82]
	Blauer Burgunder	0.5 ^d	
	Lemberger	0.3 ^d	
	Saint Laurent	1.0 ^d	
	Saint Laurent	2.3 ^d	Balík et al. [83]
	Blauer Portugieser	0.4 ^d	
	Andre	0.4 ^d	
	Castelão	6.8 ^d	Sun et al. [81]

^amg/kg of berry dry weight.

^bmg/kg of fresh grape skin.

^cmg/kg of fresh grape seed.

^dmg/kg dry skin.

Table 1. Quantification of phenolic acids and stilbenes in red grape varieties.

Monomeric anthocyanins	Grape variety	Concentration	References
Delphinidin 3- <i>O</i> -glucoside	Cabernet-Sauvignon	431.6 ^a	Ortega-Regules et al. [84]
	Merlot	231.7 ^a	
	Syrah	258.0 ^a	
	Cabernet Sauvignon	4.67 ^b	Revilla et al. [85]
	Garnacha	2.26 ^b	
	Graciano	6.81 ^b	
	Mencia	5.13 ^b	Jordão et al. [86]
	Merlot	7.53 ^b	
	Tempranillo	10.9 ^b	
	Castelão Francês	6.2 ^c	
	Touriga Francesa	0.9 ^c	
Cyanidin 3- <i>O</i> -glucoside	Cabernet-Sauvignon	53.1 ^a	Ortega-Regules et al. [84]
	Merlot	48.2 ^a	
	Syrah	27.9 ^a	
	Cabernet Sauvignon	0.90 ^b	Revilla et al. [85]
	Garnacha	1.02 ^b	
	Graciano	1.28 ^b	
	Mencia	2.15 ^b	Jordão et al. [86]
	Merlot	5.52 ^b	
	Tempranillo	3.26 ^b	
	Castelão Francês	2.6 ^c	
	Touriga Francesa	0.1 ^c	
Petunidin-3- <i>O</i> -glucoside	Cabernet-Sauvignon	337.4 ^c	Ortega-Regules et al. [84]
	Merlot	270.9 ^a	
	Syrah	385.2 ^a	
	Cabernet Sauvignon	4.21 ^b	Revilla et al. [85]
	Garnacha	3.73 ^b	
	Graciano	7.21 ^b	
	Mencia	6.68 ^b	Jordão et al. [86]
	Merlot	7.0 ^b	
	Tempranillo	11.11 ^b	
	Castelão Francês	8.5 ^c	
	Touriga Francesa	2.5 ^c	
Peonidin 3- <i>O</i> -glucoside	Cabernet-Sauvignon	259.5 ^a	Ortega-Regules et al. [84]

Monomeric anthocyanins	Grape variety	Concentration	References
Malvidin 3-O-glucoside	Merlot	381.9 ^a	Revilla et al. [85]
	Syrah	299.2 ^a	
	Cabernet Sauvignon	4.87 ^b	
	Garnacha	12.69 ^b	
	Graciano	12.79 ^b	
	Mencia	14.85 ^b	
	Merlot	14.27 ^b	
	Tempranillo	7.81 ^b	Jordão et al. [86]
	Castelão Francês	11.7 ^c	
	Touriga Francesa	3.6 ^c	
	Cabernet-Sauvignon	2506.3 ^a	Ortega-Regules et al. [84]
	Merlot	1834.7 ^a	
	Syrah	2889.7 ^a	Revilla et al. [85]
	Cabernet Sauvignon	41.45 ^b	
	Garnacha	64.69 ^b	
	Graciano	53.69 ^b	
	Mencia	47.40 ^b	
	Merlot	35.54 ^b	
	Tempranillo	46.35 ^b	Jordão et al. [86]
	Castelão Francês	59.2 ^c	
	Touriga Francesa	46.3 ^c	

^aµg/g grape skin.

^bRelative amount of anthocyanidins (%).

^c% weight of anthocyanins/weight grape.

Table 2. Quantification of monomeric anthocyanins in red grape varieties.

Phenolic compounds	Grape variety	Concentration	References
Flavan-3-ols	Baboso Negro	51.61 ^a	Pérez-Trujillo et al. [87]
(+) -Catechin	Listán Negro	54.25 ^a	
	Negramoll	51.31 ^a	
	Tintilla	50.10 ^a	
	Vijariego Negro	49.09 ^a	
	Touriga Nacional	0.012–0.021 ^b	Mateus et al. [88]
	Touriga Francesa	0.012 ^b	

Phenolic compounds	Grape variety	Concentration	References
(-)-Epicatechin	Merlot	240.0 ^c	Montealegre et al. [80]
	Cencibel	82.0 ^c	
	Cabernet Sauvignon	270.0 ^c	
	Shiraz	120.0 ^c	
	Baboso Negro	16.50 ^a	Pérez-Trujillo et al. [87]
	Listán Negro	13.77 ^a	
	Negramoll	15.07 ^a	
	Tintilla	20.55 ^a	
	Vijariego Negro	16.13 ^a	
	Touriga Francesa	0.010 ^b	Mateus et al. [88]
Proanthocyanidins	Merlot	210.0 ^c	Montealegre et al. [80]
	Cencibel	60.0 ^c	
	Cabernet Sauvignon	130.0 ^c	
	Shiraz	130.0 ^c	
	Touriga Nacional	0.013 ^b	Mateus et al. [88]
Procyanidin B3	Merlot	64.0 ^c	Montealegre et al. [80]
	Cencibel	43.0 ^c	
	Cabernet Sauvignon	50.0 ^c	
	Shiraz	55.0 ^c	
	Baboso Negro	15.95 ^a	Pérez-Trujillo et al. [87]
Procyanidin B1	Listán Negro	15.00 ^a	
	Negramoll	14.69 ^a	
	Tintilla	13.64 ^a	
	Vijariego Negro	13.39 ^a	
	Touriga Nacional	0.184–0.260 ^b	Mateus et al. [88]
	Touriga Francesa	0.090–0.138 ^b	
	Merlot	170.0 ^c	Montealegre et al. [80]
	Cencibel	74.0 ^c	
Procyanidin B4	Cabernet Sauvignon	150.0 ^c	
	Shiraz	100.0 ^c	
	Merlot	80.0 ^c	Montealegre et al. [80]
	Cencibel	39.0 ^c	
	Cabernet Sauvignon	57.0 ^c	
	Shiraz	33.0 ^c	

Phenolic compounds	Grape variety	Concentration	References
Procyanidin B2	Baboso Negro	10.39 ^a	Pérez-Trujillo et al. [87]
	Listán Negro	5.74 ^a	
	Negramoll	7.55 ^a	
	Tintilla	9.92 ^a	
	Vijariego Negro	7.44 ^a	
	Touriga Nacional	0.020 ^b	Mateus et al. [88]
	Touriga Francesa	0.011–0.015 ^b	
	Merlot	37 ^c	Montealegre et al. [80]
	Cencibel	21.0 ^c	
	Cabernet Sauvignon	41.0 ^c	
	Shiraz	23.0 ^c	

^aMolar percentages.

^bmg/g dry weight.

^cmg/kg of fresh grape seed.

Table 3. Quantification of flavan-3-ols and proanthocyanidins in red grape varieties.

Phenolic compounds	Grape variety	Concentration	References
Phenolic acids	Grüner Veltliner	3.9 ^a	Mikeš et al. [82]
Gallic acid	Hibernal	4.0 ^a	
	Malverina	3.5 ^a	
	Müller Thurgau	2.6 ^a	
	Rheinriesling	2.1 ^a	
	Welschriesling	1.8 ^a	
	Neuburger	3.9 ^a	
Protocatechuic acid	Chardonnay	4.8 ^b	Montealegre et al. [80]
	Sauvignon Blanc	4.4 ^b	
	Moscato	3.6 ^b	
	Gewürztraminer	6.0 ^b	
Caftaric acid	Moscato	48.4 ^c	Nicoletti et al. [78]
Stilbenes	Chardonnay	1.1 ^a	Balík et al. [83]
<i>Trans</i> -piceid	Welschriesling	0.4 ^a	Nicoletti et al. [78]
	Pinot Gris	0.6 ^a	
<i>Trans</i> -resveratrol	Moscato	3.89 ^c	
	Grüner Veltliner	0.1 ^a	Mikeš et al. [82]
	Hibernal	0.3 ^a	

Phenolic compounds	Grape variety	Concentration	References
	Malverina	0.3 ^a	Balík et al. [83]
	Müller Thurgau	0.3 ^a	
	Rheinriesling	0.2 ^a	
	Welschriesling	0.5 ^a	
	Neuburger	1.5 ^a	
	Chardonnay	0.3 ^b	
	Welschriesling	1.6 ^b	
Flavan-3-ols	Pinot Gris	1.1 ^b	Balík et al. [83]
	Chardonnay	123 ^a	
(+) -Catechin	Welschriesling	61.0 ^a	De Freitas and Glories [89]
	Pinot Gris	481 ^a	
	Ugni blanc	2.6–222.0 ^d	
	Sémillon	12–35.2 ^d	
	Chardonnay	390.0 ^c	
	Sauvignon Blanc	200.1 ^c	
	Moscatel	350.0 ^c	
(–) -Epicatechin	Gewürztraminer	500.0 ^c	Montealegre et al. [80]
	Riesling	400.0 ^c	
	Viogner	120.0 ^c	
	Chardonnay	144 ^a	
	Welschriesling	84.3 ^a	
	Pinot Gris	251 ^a	
	Ugni blanc	0.04–3.0 ^d	
	Sémillon	0.03–1.6 ^d	
	Chardonnay	310.0 ^c	
	Sauvignon Blanc	130.0 ^c	
	Moscatel	120.0 ^c	
	Gewürztraminer	150.0 ^c	
Proanthocyanidins	Riesling	160.0 ^c	De Freitas and Glories [89]
	Viogner	110.0 ^c	
	Ugni blanc	0.2–0.3 ^d	
	Sémillon	0.01–0.2 ^d	
Procyanidin B3	Chardonnay	52.0 ^c	Montealegre et al. [80]
	Sauvignon Blanc	52.0 ^c	
	Moscatel	39.0 ^c	
	Gewürztraminer	56.0 ^c	

Phenolic compounds	Grape variety	Concentration	References
Procyanidin B1	Riesling	43.0 ^c	De Freitas and Glories [89]
	Vioigner	51.0 ^c	
	Ugni blanc	1.1–1.9 ^d	
	Sémillon	0.02–0.4 ^d	
	Chardonnay	380.0 ^c	Montealegre et al. [80]
	Sauvignon Blanc	250.0 ^c	
	Moscatel	330.1 ^c	
	Gewürztraminer	460.0 ^c	
Procyanidin B4	Riesling	620.0 ^c	De Freitas and Glories [89]
	Vioigner	200.0 ^c	
	Ugni blanc	0.04 ^d	
	Chardonnay	71.5 ^c	
	Sauvignon Blanc	54.0 ^c	Montealegre et al. [80]
	Moscatel	40.0 ^c	
	Gewürztraminer	70.0 ^c	
	Riesling	95.0 ^c	
Procyanidin B2	Vioigner	53.0 ^c	De Freitas and Glories [89]
	Ugni blanc	0.06–0.2 ^d	
	Chardonnay	33.0 ^c	
	Sauvignon Blanc	19.0 ^c	
	Moscatel	15.0 ^c	Montealegre et al. [80]
	Gewürztraminer	22.0 ^c	
	Riesling	33.0 ^c	
	Vioigner	19.0 ^c	

^amg/kg fresh grape weight.
^bmg/kg of fresh grape seed.
^cmg/kg of berry dry weight.
^dmg/g dry weight.

Table 4. Quantification of phenolic acids, stilbenes, flavan-3-ols, and proanthocyanidins in white grape varieties.

3. Biotechnological approaches for wine quality

More than 800 volatile compounds have been identified in wines, with a concentration range from hundreds of mg/L to the µg/L or ng/L [90]. The wine bouquet is formed by secondary metabolites synthesized by an extensive range of microbial species (yeasts and bacteria). Wine alcoholic fermentation (AF) is the key for innovation or creation of biotechnology that will change the expanding market [91] (**Figure 4**).

Figure 4. Grape juice is converted into wine by the action of wine yeast and bacteria during alcoholic and malolactic fermentations. Some wine components are wholly generated by these microorganisms as part of metabolism, while others are essentially synthesized by the grapevine. Wine quality and style is determined by the quality and quantity of compounds produced or modified by must/wine microflora.

In addition to yeasts, LAB also appears in all type of wines, being responsible for MLF that normally occurs after AF but may also occur simultaneously [92]. During the winemaking process, indigenous populations of LAB vary quantitatively and qualitatively [93], through a succession of species and strains before, during and after the AF [94]. After a phase of latency, the surviving cells begin to multiply and entering the exponential growth phase, reaching populations from 10^6 to 10^8 cfu/mL, almost exclusively, constituted by strains of *Oenococcus oeni*, species that dominate this stage and performs the MLF. Normally, a great diversity of strains of *Oenococcus oeni* at the beginning of the MLF is detected, while at the end only one or two predominate [95].

3.1. Yeasts metabolites: the imperceptible search of perfection

Wine yeasts contribute to wine aroma by a number of mechanisms: (i) they utilize grape juice constituents and transform them into flavor-impacting components, then (ii) they produce enzymes capable to transform neutral grape compounds into flavor-active compounds, and finally (iii) they can synthesize many flavor-active compounds such as primary and secondary metabolites [96].

Esters, in wine, are mainly originated from yeast metabolism during AF. But, some esters are also found in grape berry [97], where they occur in small amounts, contributing to the aroma of *V. vinifera* varieties [98]. Esters are formed via an intracellular process, catalyzed by an acyl transferase or ester synthase [99]. The concentration of esters usually found in wine is mostly well above their sensory threshold levels. Fruity and floral terms in Chardonnay wines were related to 2-phenylethyl acetate, as a rose-like/honey aroma [100] (Table 5). In red wines, ethyl butyrate (pineapple aroma), ethyl 2-methylbutyrate (sweet, floral, fruity, and apple), ethyl 3-methylbutyrate (strawberry, ethereal, buttery, and ripe), isoamyl acetate (banana-like aroma), ethyl hexanoate (anise seed, apple, or pineapple aroma), and ethyl octanoate (sweet, cognac, and apricot aroma) made a main contribution to the fruity character of wines [101] (Table 5).

These esters also appear in higher levels in wines after bio-reduction (deacidification) of wine's volatile acidity [102]. A study of overexpression *S. cerevisiae* alcohol acetyltransferases genes, ATF1p, ATF2p, and Lg-ATF1p, was performed by Verstrepen et al. [103]. Analysis of the fermentation products confirmed that the expression levels of ATF1 and ATF2 greatly affected the production of ethyl acetate and isoamyl acetate. But, factors such as oxygen and temperature that allow ester and higher alcohol synthesis must be monitored during AF [104].

Compounds	Odor description	Det. Threshold (µg/L)	References
Isoamyl acetate	Banana	30	Guth [115]
2-Phenylethylacetate	Roses, honey	250	Guth [115]
Ethylpropionate	Ethereal, fruity, rum-like	1800	Etievant [116]
Ethylisobutyrate	Strawberry, ethereal, buttery, ripe	15	Etievant [116]; Ong and Acree [117]
Ethyl butyrate	Pineapple	20	Guth [115]
Ethyl 2-methylbutyrate	Sweet, floral, fruity, apple	1–18	Guth [115]; Ferreira et al. [118]
Ethylisovalerate	Fruity	3	Ferreira et al. [118]
Ethyl hexanoate	Anise seed, apple, pineapple	5–14	Guth [115]; Ferreira et al. [118]
Ethyl octanoate	Sweet, cognac, apricot	2–5	Guth [115]; Ferreira et al. [118]
Diethylsuccinate	Fruity, melon	1200	Peinado et al. [119]
Acetaldehyde	Grass, green, apple, sherry	100,000	Carlton et al. [120]
Benzaldehyde	Almond	3500	Delfini et al. [121]
Linalool	Rose, lavender	25	Ferreira et al. [118]
α-Terpineol	Lily of the valley	300	Mateo and Jiménez [122]
Citronellol	Citronella	100	Guth [115]
Geraniol	Rose-like; geranium flowers	~75	Pardo et al. [109]
2-phenylethanol	Roses	10,000	Guth [115]
Isoamyl alcohol	Marzipan, burnt, whisky-like	30,000	Guth [115]
Butyric acid	Rancid, cheese	173	Ferreira et al. [118]
Isovaleric acid	Rancid, sweaty	33.4	Ferreira et al. [118]
Hexanoic acid	Sweaty, cheesenotes	420–3000	Guth [115]; Ferreira et al. [118]
Octanoic acid	Grass acid- like	500–8800	Etievant [116]; Ferreira et al. [118]
Decanoic acid	Soapy	1000–15,000	Guth [115]; Ferreira et al. [118]

Table 5. Major wine-yeast aromatic compounds, odor description, and detection thresholds in white and red wines.

Ethanol and glycerol are quantitatively the largest group of alcohols found in wine. Both contribute to the textural aspects of wines [1]. The search of yeast that can impart specific desirable characteristics to wines led to investigations such as the production of optimal levels of glycerol (the overexpression of GPD1, GPD2, and FPS1, together with the deletion of the ALD6 acetaldehyde dehydrogenase gene) [105].

Medium-chain fatty acids and their ethyl esters are natural components of alcoholic beverages. Fatty acids (butyric, isovaleric, hexanoic, octanoic, and decanoic acids, among others; **Table 5**) are produced by yeasts as intermediates in the biosynthesis of long-chain fatty acids, important components of yeast membrane [106]. Their aroma goes from vinegar to pungent, rancid, and soapy, sweetie, fruit and butter [106] (**Table 5**). One of the major problematic volatile acids is acetic acid. It can be formed as a by-product of AF, MLF, or as a product of the metabolism of acetic bacteria. Acetic acid affects the quality of certain types of wine when it is present above a given concentration [107] due to its unpleasant vinegar aroma.

Terpenes are one of the major grape components that contribute to wine aroma. This is especially valid to wines of Gewürztraminer and Muscat varieties, but these flavor compounds are also present in other grape varieties, where they supplement other varietal flavors and aromas. They are present in two forms: a free volatile and a non-volatile sugar-conjugated [108]. Geraniol (geranium flowers aroma) and linalool (rose or lavender-like aroma) are considered to be the most important of the monoterpene alcohols as they are present in higher levels and have lower perception thresholds than other major wine monoterpenes [109]. Monoterpenes can be released from their glycosides either by acid or by enzymatic hydrolysis. Hydrolysis during winemaking is caused by grape [110] or microorganisms enzymes taking part in the process [111]. In the yeasts that were selected in the past years, glycosidase activities have been used for the hydrolysis of glycoconjugated aromatic precursors in order to enhance wine sensorial quality [112]. Fungi are considered a promising genetic source for commercial production of recombinant β -glucosidase [113]. In a work by Zietsman et al. [114], an yeast strain (*S. cerevisiae* VIN13) was built to express and secrete the *Aspergillus awamori* encoding a B-type α -l-arabinofuranosidase (AwAbfB) in combination with either the β -glucosidases BGL2 from *Saccharomycopsis fibuligera* or the BGLA from *Aspergillus kawachii*. Coexpression of AwAbfB and BGL2 in VIN13 increased free monoterpenes in wines. Panelists confirmed wine aroma profile improvement, mainly in floral character [114]. Recently, Pardo et al. [109] found that the expression of *Ocimum basilicum* (sweet basil) geraniol synthase (GES) gene in an *S. cerevisiae* wine strain greatly changed terpene profile of wine made from a non-aromatic grape variety.

3.2. Lactic acid bacteria metabolites: beyond malolactic fermentation

The complexity and diversity of LAB metabolic activities in wine illustrates that MLF is more than a mere decarboxylation of L-malic acid into L-lactic acid, and it may affect positively and/or negatively the quality of wine [123] (**Table 6**). Besides to the decrease in acidity, MLF also improves sensorial characteristics and increases wines microbiological stability that undergone this important second fermentation [124, 125].

Aromatic modifications are due to L-lactic acid, less aggressive, and due to the increase of a number of other compounds such as diacetyl, acetoin, 2,3-butanediol, esters mainly ethyl lactate and diethyl succinate, and some higher alcohols and aromatic aglycones released by the action of β -glucosidases [126–128]. Sumby et al. [129] have verified the impact that different strains of *O. oeni* had on wine aroma and related that to their ester hydrolysis and synthesis abilities. For the aromatic complexity of wines, the production of volatile sulfur compounds,

particularly 3-methylsulfanyl-propionic acid with chocolate and toasted odors [130], and the activity of taninoacil hydrolase enzyme, commonly termed tannase, reducing wine astringency and turbidity [131], also contribute.

Compounds	Odor description	Det. threshold ($\mu\text{g/L}$)	References
4-Ethylguaiacol	Bacon, spice, clove, or smoky aromas	33	Dai et al. [26]; Bartowsky [123]
4-Ethylphenol	Horse and barnyard odor	440	Barthelmebs et al. [147], [148]
Tetrahydropyridines	Mousy off-odor	60	Swiegers et al. [149]; Harrison and Dake [150]
3- Methylsulfanyl-propionic acid	Chocolate and toasted odors	244	Pripis-Nicolau et al. [151]
Ethyl lactate	Lactic, raspberry	154–636	Ferreira et al. [118]; Bartowsky [152]
Diethyl succinate	Fruity, melon	1200	Peinado et al. [119]; Bartowsky [152]
Diacetyl	Butter	200–2800	Martineau and Henick-Kling [153]; Bartowsky and Henschke [154]
Acetoin	No negative organoleptic influence. Unpleasant buttery flavor at concentrations higher than threshold	150	Swiegers et al. [155]; Ehsani et al. [156]
2,3-Butanediol	Neutral sensory qualities	150	Swiegers et al. [155]; Romano and Suzzi [157]

Table 6. Major LAB aromatic compounds, odor description, and detection thresholds in wine.

Concerning to negative effects on wine quality, LAB may be responsible for the formation of ethyl carbamate by the degradation of arginine [124] and for the formation of biogenic amines such as histamine, tyramine, and putrescine by the degradation of precursor amino acids [132, 133]. Also, although less frequent nowadays, bitterness by acrolein formation from glycerol

degradation [134], butter aroma due to excessive production of diacetyl [135], flocculent growth [136], mannitol taint [137], ropiness [138], tartaric acid degradation [137], mousy off-odor by acetamide production of tetrahydropyridines [139], the geranium off-odor [140], and the formation of 4-ethylguaiacol and 4-ethylphenol volatile phenols [141, 142] are spoilage phenomenons that may occur after malolactic fermentation. Nevertheless, it is thought that the time between the completion of alcoholic fermentation and the start of malolactic fermentation is the most likely time that *Brettanomyces* multiplies and produces “Brett character,” 4-ethylphenol of flavor, in wine [143].

As what happens to other food products, some researchers defend the use of autochthones LAB strains, more adapted and efficient to regional vinification conditions, for keeping the typicity of wines, instead of using universal ones that may impart similar characteristics and thus leading to final products that are too similar and also for preserving the local microbial biodiversity [144, 145]. According to Marcobal and Mills [146], the knowledge of some wine LAB whole genome, including the PSU1 *O. oeni* strain, allows deeper phylogenetic analyses and their relation with key pathways involved in carbon and nitrogen metabolism, which will foster modeling of *O. oeni* growth and metabolism in order to predict optimum strategies for efficiently performing the MLF with a desired flavor outcome.

4. Composition of grapes and wines: new analytical techniques

Several different analytical approaches are increasingly used to profile the volatile, non-volatile, and elemental composition of grapes and wines (see recent reviews, e.g., [158, 160]).

According to a review made by Ebeler [159], we can group these analytical approaches in (i) targeted analysis of compounds, (ii) non-targeted analysis and profiling of metabolites, (iii) elemental analysis, and (iv) relating chemical composition and sensory attributes (**Table 7**).

Therefore, wine composition and hence wine origin are possible by combining several analytical techniques (**Table 7**) that offer significant advantages for trace quantification of important aroma-active volatiles [174], [175] and taint compounds [163]. It is also possible to comprehensively profile metals [178], including those that affect chemical stability and oxidative reactions, and to characterize aroma qualities of complex mixtures [182]. Each of these tools, alone and in combination, is providing significant new insights into variables influencing grape and wine composition and flavor. Moreover, concerning to specific grape compounds, in past years, several methodologies were also developed focused on the identification, quantification, and also in extraction techniques. For example for phenolic compounds, substantial developments for individual phenolic analysis, such as benzoic and cinnamic acid, coumarins, tannins, lignins, lignans, and flavonoids, have occurred over the last 25 years. Thus, several extraction techniques have been employed namely for grape phenolic compounds, such as ultrasounds and microwaves [183], supercritical fluid extraction [184], subcritical water extraction [185], high hydrostatic pressure extraction [186], pulsed electric fields [187], and enzymatic treatment [188].

Analytical approaches	Analytical techniques	Examples and references
Targeted analysis of compounds (i)	Selected ion monitoring and tandem mass spectrometric, MS/MS or MS ⁿ	Analysis of trace analytes, with important sensory properties—Ebeler [160] and Robinson et al. [161, 162]—such as 2,4,6-trichloroanisole (TCA)—Hjelmeland et al. [163]
	Combination of liquid chromatography, LC with mass spectrometry, MS. MS/MS is the combination of two mass analyzers in one mass spectrometry instrument, LC-MS/MS/LC-MS/MS.	Smoke-derived volatile phenols—guaiacol and their glycoside precursors, and anthocyanins from grapes and wines—Kennison et al. [164–166], Hayasaka et al. [167], and Pati et al. [168].
	Supercritical fluid chromatography (SFC)	Polyphenols from grape seed extracts—Kamangerpour et al. [169]
Non-targeted analysis and profiling of metabolites (ii)	Ultra-high performance liquid chromatography, UHPLC wish operates in the 20,000 psi range, combined with quadrupole time-of-flight mass spectrometry, qTOF and UHPLC-qTOF-MS	Varietal classification of wines—Vaclavik et al. [170] and Flamini [171]
	Ion cyclotron resonance mass spectrometry, ICR-MS	Characterization of Pinot Noir grapes and wines and chemodiversity comparison of different appellations: Vintage vs terroir effects—Roullier-Gall et al. [172, 173]
	Gas chromatography combined with time-of-flight mass spectrometry, GC GC-TOF-MS	Identification of over 350 volatile compounds in Australian Cabernet Sauvignon wines—Robinson et al. [174, 175]
	Nuclear Magnetic Resonance, NMR	¹ H NMR metabolite profiling to relate chemical composition to sensory perception of body and mouthfeel of white wines—Kogerson et al. [176]
Elemental analysis (iii)	Inductively coupled plasma mass Spectrometry, ICP-MS	Relating elemental composition of wines to the vineyard that the grapes were grown or in wish winery they were made—Hopfer et al. [177]. Leaching of metals from stainless steel containers and from closures—Hopfer et al. [178]
Relating chemical composition and sensory attributes (iv)	Categorical principal components analysis, CATPCA; principal components analysis, PCA and partial least squares analysis, PLS	One or more compounds that correlate with specific aroma or flavor attributes—Polaskova et al. [179] and development of a flavor lexicon using new statistical nonparametric approaches—Vilela et al. [180] and Monteiro et al. [181]
	In-instrument gas chromatography recomposition-olfactometry, GC-RO	Perceptual characterization and analysis of aroma mixtures—Johnson et al. [182]

Table 7. Analytical approaches, analytical techniques used to profile the volatile, non-volatile and elemental composition of grapes and wines.

5. Final remarks

The study of the grape berry physiology and metabolome will provide a deep understanding of the primary metabolites including sugars, organic acids and amino acids, and some secondary metabolites accumulated in the grape berries such as phenolic compounds. This issue is of particular importance for viticulturists and oenologists in order to know how grape composition could affect wine quality. In addition, biotechnological approaches for wine quality, practiced during wine AF and MLF, are also a promising tool available for oenologists that improve wine quality, namely, their sensorial value.

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References

- [1] Jordão AM, Vilela A, Cosme F: From sugar of grape to alcohol of wine: sensorial impact of alcohol in wine. *Beverages*. 2015;1(4):292–310. Doi: 10.3390/beverages1040292.
- [2] Bisson LF: The biotechnology of wine yeast. *Food Biotechnology*. 2004;18(1):63–96. Doi: 10.1081/FBT-120030385.
- [3] Swiegers JH, Pretorius IS: Modulation of volatile sulfur compounds by wine yeast. *Applied Microbiology and Biotechnology*. 2007;74:954–960. Doi: 10.1007/s00253-006-0828-1.
- [4] Chambers PJ, Pretorius IS: Fermenting knowledge: the history of winemaking, science and yeast research. *EMBO Reports*. 2010;11(12):914–920. Doi: 10.1038/embor.2010.179.

- [5] Inês A, Tenreiro T, Tenreiro R, Mendes-Faia A: Review: The lactic acid bacteria of wine- Part I. *Ciência e Técnica Vitivinícola*. 2008;23:81–96.
- [6] Inês A, Tenreiro T, Tenreiro R, Mendes-Faia A: The lactic acid bacteria of wine- Part II. *Ciência e Técnica Vitivinícola*. 2009;24:1–23.
- [7] Hellman EW: Grapevine structure and function. Oregon Viticulture. Hellman, EW (ed.). Oregon State University Press, Corvallis, 2003; pp. 5–19.
- [8] Jackson RS: Grapevine Structure and Function, Chapter 5 in *Wine Science*, 2nd ed. Academic Press, San Diego, 2000; pp. 66–71.
- [9] Keller M: *The Science of Grapevines: Anatomy and Physiology*. 2nd ed. Academic Press, Oxford, 2015; pp. 522.
- [10] Wilson B, Strauss CR, Williams PJ: The distribution of free and glycosidically-bound monoterpenes among skin, juice and pulp fractions of some white grape varieties. *American Journal of Enology and Viticulture*. 1986;37:107–111.
- [11] Teixeira A, Eiras-Dias J, Castellarin SD, Gerós H: Berry phenolics of grapevine under challenging environments. *International Journal of Molecular Sciences*. 2013;14(9): 18711–18739. Doi: 10.3390/ijms140918711.
- [12] Hardie WJ, O'Brien TP, Jaudzems VG: Morphology, anatomy and development of the pericarp after anthesis. *Australian Journal of Grape and Wine Research*. 1996;2(2):97–141.
- [13] Rogiers SY, Hatfield JM, Jaudzems VG, White RG, Keller M: Grape berry cv. Shiraz epicuticular wax and transpiration during ripening and pre harvest weight loss. *American Journal of Enology and Viticulture*. 2004;55:121–127.
- [14] Blanke MM, Pring RJ, Bake, EA: Structure and elemental composition of grape berry stomata. *Journal of Plant Physiology*. 1999;154:477–481. Doi: 10.1016/S0176-1617(99)80286-7.
- [15] Comménil P, Brunet L, Audran J-C: The development of the grape berry cuticle in relation to susceptibility to bunch rot disease. *Journal of Experimental Botany*. 1997;48:1599–1607.
- [16] Yamamura H, Naito R: The surface wax of several grapes in Japan. *Journal Japan Society of Horticultural Science*. 1983;52:266–272.
- [17] Walton TJ, Kolattukudy PE: Determination of the structures of cutin monomers by a novel depolymerization procedure and combined gas chromatography and mass spectrometry. *Biochemistry*. 1972;11:1885–1897.
- [18] Kolattukudy PE: Plant waxes. *Lipids*. 1969;5:259–275.
- [19] Coombe B: Research on development and ripening of the grape berry. *American Journal of Enology and Viticulture*. 1992;43:101–110.

- [20] Tilbrook J, Tyerman SD: In: Finishing the job—Optimal ripening of Cabernet Sauvignon and Shiraz, Water, sugar and acid: How and where they come and go during berry ripening. Oag D., DeGaris K., Partridge S., Dundon C., Francis M., Johnstone R., Hamilton R (Eds.). Austral. Soc. Viticult. Oenol. Adelaide, Australia, 2006; pp. 4–12.
- [21] Sundberg E, Ostergaard L: Distinct and dynamic auxin activities during reproductive development. Cold Spring Harbor Perspective Biology. 2009;1:a001628. Doi: 10.1101/cshperspect.a001628.
- [22] Coombe BG: The development of fleshy fruits. Annual Review of Plant Physiology. 1976;27: 507–528.
- [23] Gerling C: Environmentally Sustainable Viticulture: Practices and Practicality. Apple Academic Press, Canada, 2015; 424 pp.
- [24] Conde BC, Silva P, Fontes N, Dias ACP, Tavares RM, Sousa MJ, Agasse A, Delrot S, Geros H: Biochemical changes throughout grape berry development and fruit and wine quality. Food. 2007;1:1–22. <http://hdl.handle.net/1822/6820>.
- [25] Kalliopi A, Roubelakis-Angelakis KA (eds.). Grapevine Molecular Physiology and Biotechnology, 2nd ed. Springer Dordrecht Heidelberg London New York 2009; 599 pp. Doi: 10.1007/978-90-481-2305-6.
- [26] Dai ZW, Ollat N, Gomès E, Decroocq S; Tandonnet J-P, Bordenave L, Pieri P, Hilbert G, Kappel C, Van Leeuwen C, Vivin P, Delrot S: Ecophysiological, genetic, and molecular causes of variation in grape berry weight and composition: a review. American Journal of Enology and Viticulture. 2011;62:413–425.
- [27] Liu HF, Wu BH, Fan PG, Li SH, Li LS: Sugar and acid concentrations in 98 grape cultivars analyzed by principal component analysis. Journal of the Science of Food and Agriculture. 2006;86:1526–1536. Doi: 10.1002/jsfa.2541.
- [28] Boss PK, Davies C: Molecular biology of sugar and anthocyanin accumulation in grape berries. In: Molecular Biology and Biotechnology of the Grapevine, Roubelakis-Angelakis KA (ed.). Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001; pp. 1–33.
- [29] Robinson SP, Davies C: Molecular biology of grape berry ripening. Australian Journal of Grape and Wine Research. 2000;6:175–188. Doi: 10.1111/j.1755-0238.2000.tb00177.x
- [30] Fillion L, Ageorges A, Picaud S, Coutos-Thevenot P, Lemoine R, Romieu C, Delrot S: Cloning and expression of a hexose transporter gene expressed during the ripening of grape berry. Plant Physiology. 1999;120:1083–1093. Doi: <http://dx.doi.org/10.1104/pp.120.4.1083>.
- [31] Esteban MA, Villanueva MJ, Lissarrague JR: Relationships between different berry components in Tempranillo (*Vitis vinifera* L.) grapes from irrigated and non-irrigated vines during ripening. Journal of the Science of Food and Agriculture. 2002;82:1136–1146. Doi: 10.1002/jsfa.1149

- [32] Jordão AM, Ricardo-da-Silva JM, Laureano O: Influence of irrigation on phenolic composition of the French Touriga red wine-grapes variety (*Vitis vinifera* L.). *Ciência e Tecnologia dos Alimentos*. 1998;2:60–73.
- [33] Van Leeuwen C, Tregoat O, Choné X, Bois B, Pernet D, Gaudillère J-P: Vine water status is a key factor in grape ripening and vintage quality for red Bordeaux wine. How can it be assessed for vineyard management purposes? *Journal International des Sciences de la Vigne et du Vin*. 2009;43:121–134. <http://prodinra.inra.fr/record/33055>.
- [34] Hawker JS: Effect of temperature on lipid, starch and enzymes of starch metabolism in grape, tomato and broad bean-leaves. *Phytochemistry*. 1982;21:33–36. Doi: 10.1016/0031-9422(82)80009-5.
- [35] Mira de Orduña R: Climate change associated effects on grape and wine quality and production. *Food Research International*. 2010;43:1844–1855. Doi: 10.1016/j.foodres.2010.05.001.
- [36] García-Martín N, Perez-Magariño S, Ortega-Heras M, González-Huerta C, Mihnea M, González-Sanjosé ML, Palacio L, Prádanos P, Hernández A: Sugar reduction in musts with nanofiltration membranes to obtain low alcohol-content wines. *Separation and Purification Technology*. 2010;76:158–170. Doi: 10.1016/j.seppur.2010.10.002.
- [37] Kanellis AK, Roubelakis-Angelakis KA: Grape. In: *Biochemistry of Fruit Ripening*, Seymour G, Taylor J, Tucker G (Eds.). London: Chapman & Hall, 1993; pp. 189–234.
- [38] Lamikanra O, Inyang ID, Leong S: Distribution and Effect of Grape Maturity on Organic Acid Content of Red Muscadine Grapes. *Journal of Agricultural and Food Chemistry*. 1995;43(12):3026–3028. Doi: <http://dx.doi.org/10.1021/jf00060a007>.
- [39] Kliewer WM: Sugars and Organic Acids of *Vitis vinifera*. *Plant Physiology*. 1966;41:923–931.
- [40] Rüffner HP: Metabolism of tartaric and malic acid in *Vitis*: a review—Part B. *Vitis*. 1982;21:346–358.
- [41] DeBolt S, Cook DR, Ford CM: L-Tartaric acid synthesis from vitamin C in higher plants. *Proceedings of the National Academy of Sciences USA*. 2006;103:5608–5613.
- [42] Ruffner HP, Possner D, Brem S, Rast DM: The physiological role of malic enzyme in grape ripening. *Planta*. 1984;160:444–448.
- [43] Jackson DI, Lombard PB: Environmental and management practices affecting grape composition and wine quality—a review. *American Journal of Enology and Viticulture*. 1993;44:409–430.
- [44] Kliewer WM, Howarth L, Omori M: Concentrations of tartaric acid and malic acids and their salts in *Vitis vinifera* grapes. *American Journal of Enology and Viticulture*. 1967;18:42–54.

- [45] Hale CR: Relation between potassium and the malate and tartrate contents of grape berries. *Vitis*. 1977;16: 9–19.
- [46] Saito K, Kasai Z: Conversion of labeled substrates to sugars, cell wall polysaccharides, and tartaric acid in grape berries. *Plant Physiology*. 1978;62(2):215–219.
- [47] Wermelinger B: Nitrogen Dynamics in Grapevine. *Physiology and Modeling. Proc. Int. Symp. Nitrogen in grape and wines*, Seattle WA, USA (Ed J. M. Rantz) 1999; pp. 23–31.
- [48] Huang Z, Ough CS: Amino acid profiles of commercial grape juices and wines. *American Journal of Enology and Viticulture*. 1991;45:261–267.
- [49] Stines AP, Grubb J, Gockowiak H, Henschke PA, Høj PB, van Heeswijck R: Proline and arginine accumulation in developing berries of *Vitis vinifera* L. in Australian vineyards: Influence of vine cultivar, berry maturity and tissue type. *Australian Journal of Grape and Wine Research*. 2000;6:150–158. Doi: 10.1111/j.1755-0238.2000.tb00174.x
- [50] Feuillat M: The nitrogenous constituents of grapes and wines. *Le Vigneron Champenois*. 1974;5:201–210.
- [51] Spayd SE, Andersen-Bagge J: Free amino acid composition of grape juice from 12 *Vitis vinifera* cultivars in Washington. *American Journal of Enology and Viticulture*. 1996;47:389–402.
- [52] Hsu JC, Heatherbell DA: Isolation and characterization of soluble proteins in grapes, grape juice, and wine. *American Journal of Enology and Viticulture*. 1987;38:6–10.
- [53] Anelli G: The proteins of must. *American Journal of Enology and Viticulture*. 1977;28:200–203.
- [54] Yokotsuka K, Yoshii M, Aihara T, Kushida T: Isolation and characterization of soluble glycoproteins in red wine. *Journal of Fermentation Technology*. 1977;55:510–515.
- [55] Murphey JM, Spayd SE, Powers JR: Effect of grape maturation on soluble protein characteristics of Gewürztraminer and White Riesling juice and wine. *American Journal of Enology and Viticulture*. 1989;40:199–207.
- [56] Yokotsuka K, Ebihara T, Sato T: Comparison of soluble proteins in juice and wine from Koshu juice. *Journal of Fermentation Technology*. 1991;71:248–253. Doi: 10.1016/0922-338X(91)90276-M
- [57] Tattersall DB, Heeswijck R, Høj PB: Identification and characterization of a fruit-specific, thaumatin-like protein that accumulates at very high levels in conjunction with the onset of sugar accumulation and berry softening in grapes. *Plant Physiology*. 1997;114:759–769. Doi: <http://dx.doi.org/10.1104/pp.114.3.759>
- [58] Waters EJ, Hayasaka Y, Tattersall DB, Adams KS, Williams PJ: Sequence analysis of grape (*Vitis vinifera*) berry chitinases that cause haze formation in wines. *Journal of Agricultural and Food Chemistry*. 1998;46:4950–4957. Doi: 10.1021/jf980421o

- [59] Williams PJ, Francis IL: Wine flavor research: Experiences from the past offer a guide to the future. Proceedings of the ASEV 50th Anniversary Annual Meeting, Seattle, American Society for Enology & Viticulture, Davis, CA, 2000; pp. 191–195.
- [60] Lacey MJ, Allen MS, Harris RLN, Brown WV: Methoxypyrazines in Sauvignon Blanc grapes and wines. American Journal of Enology and Viticulture. 1991;42:103–108.
- [61] Dunlevy JD, Kalua CM, Keyzers RA, Boss PK: The production of flavour and aroma compounds in grape berries. In Grapevine Molecular Physiology and Biotechnology. K.A. Roubelakis-Angelakis (ed.), Springer, Dordrecht, Netherlands, 2009; pp. 293–340.
- [62] Lorrain B, Chira K, Teissedre P-L: Phenolic composition of Merlot and Cabernet-Sauvignon grapes from Bordeaux vineyard for the 2009-vintage: Comparison to 2006, 2007 and 2008 vintages. Food Chemistry. 2011;126:1991–1999. Doi: 10.1016/j.foodchem.2010.12.062
- [63] Jordão AM, Ricardo-da-Silva JM, Laureano O: Evolution of proanthocyanidins in bunch stems during berry development (*Vitis vinifera* L.). Vitis. 2001;40:17–22.
- [64] Hernandez-Jimenez A, Gomez-Plaza E, Martinez-Cutillas A, Kennedy JA: Grape skin and seed proanthocyanidins from Monastrell x Syrah grapes Journal of Agricultural and Food Chemistry. 2009; 57:10798–10803. Doi: 10.1021/jf903465p
- [65] Cheynier V, Rigaud J: HPLC separation and characterization of flavonols in the skins of *Vitis Vinifera* var. Cinsault. American Journal of Enology and Viticulture. 1986;37:248–252.
- [66] Jordão AM, Ricardo-da-Silva JM, Laureano O: Evolution of catechins and oligomeric procyanidins during grape maturation of Castelão Francês and Touriga Francesa. American Journal of Enology and Viticulture. 2001;53:231–234.
- [67] Pastrana-Bonilla E, Akoh, CC, Sellappan S, Krewer G: Phenolic content and antioxidant capacity of Muscadine grapes. Journal of Agriculture and Food Chemistry. 2003;51:5497–5503. Doi: 10.1021/jf030113c
- [68] Monagas M, Gómez-Cordovés C, Bartolomé B, Laureano O, Ricardo-da-Silva JM: Monomeric, oligomeric, and polymeric flavan-3-ol composition of wines and grapes from *Vitis vinifera* L. Cv. Graciano, Tempranillo, and Cabernet Sauvignon Journal of Agricultural and Food Chemistry. 2003;51:6475–6481. Doi: 10.1021/jf030325
- [69] Obreque-Slier E, Peña-Neira A, Lopez-Solís R, Zamora-Marín F, Ricardo-da-Silva JM, Laureano O: Comparative study of the phenolic composition of seeds and skins from Carménère and Cabernet Sauvignon grape varieties (*Vitis vinifera* L.) during ripening. Journal of Agricultural and Food Chemistry. 2010;58:3591–3599. Doi: 10.1021/jf904314u
- [70] Bergqvist J, Dokoozlian N, Ebisuda N: Sunlight exposure and temperature effects on berry growth and composition of Cabernet Sauvignon and Grenache in the Central San Joaquin Valley of California. American Journal of Enology and Viticulture. 2001;52:1–7.

- [71] Madeira FC: Effect of ultraviolet radiation b on the behavior of the wine variety (*Vitis Vinífera* L.) Cabernet Sauvignon in São Joaquim, Santa Catarina. Master Thesis (Mestrado em Recursos Genéticos Vegetais), University Federal of Santa Catarina, Florianópolis, Brasil. 2011.
- [72] Mateus N, Marques S, Gonçalves AC, Machado JM, De Freitas V: Proanthocyanidin composition of red *Vitis vinifera* varieties from the Douro Valley during ripening: Influence of cultivation altitude. *American Journal of Enology and Viticulture*. 2001;52:115–121.
- [73] Ubalde JM, Sort X, Alicia Zayas A, Poch RM: Effects of soil and climatic conditions on grape ripening and wine quality of Cabernet Sauvignon. *Journal of Wine Research* 2010;21:1–17. Doi: 10.1080/09571264.2010.495851.
- [74] Downey MO, Dokoozlian NK, Krstic MP: Cultural practice and environmental impacts on the flavonoid composition of grapes and wine: a review of recent research. *American Journal of Enology and Viticulture*. 2006;57:257–268.
- [75] Costa E, Cosme F, Jordão AM, Mendes-Faia A: Anthocyanin profile and antioxidante activity from 24 grape varieties cultivated in two Portuguese wine regions. *Journal International des Sciences de la Vigne et du Vin*. 2014;48:51–62.
- [76] Costa E, Da Silva JF, Cosme F, Jordão AM: Adaptability of some French red grape varieties cultivated at two different Portuguese terroirs: comparative analysis with two Portuguese red grape varieties using physicochemical and phenolic parameters. *Food Research International*. 2015;78:302–312. Doi: 10.1016/j.foodres.2015.09.029
- [77] Bruno G, Sparapano L: Effects of three esca-associated fungi on *Vitis vinifera* L. Changes in the chemical and biological profile of xylem sap from diseased cv. Sangiovese vines. *Physiological and Molecular Plant Pathology*. 2007;71:210–229. Doi: 10.1016/j.pmpp.2008.02.005
- [78] Nicoletti I, Bello C, De Rossi A, Corradini D: Identification and quantification of phenolic compounds in grapes by HPLC-PDA-ESI-MS on a semimicro separation scale. *Journal of Agricultural and Food Chemistry*. 2008;56:8801–8808. Doi: 10.1021/jf801411m.
- [79] Obreque-Slier E, Peña-Neira A, Lopez-Solís R, Zamora-Marín F, Ricardo-da-Silva JM, Laureano O: Comparative study of the phenolic composition of seeds and skins from Carménère and Cabernet Sauvignon grape varieties (*Vitis vinifera* L.) during ripening. *Journal of Agricultural and Food Chemistry*. 2010;58:3591–3599. Doi: 10.1021/jf904314u.
- [80] Montealegre RR, Peces R., Vozmediano JLC, Gascueña JM, Romero EG: Phenolic compounds in skins and seeds of ten grape *Vitis vinifera* varieties grown in a warm climate. *Journal of Food Composition and Analysis*. 2006;19:687–693. Doi: 10.1016/j.jfca.2005.05.003.
- [81] Sun B, Ribes AM, Conceição ML, Belchior AP, Spranger MI: Stilbenes: quantitative extraction from grape skins, contribution of grape solids to wine and variation during

- wine maturation. *Analytica Chimica Acta*. 2006;563:382–390. Doi: 10.1016/j.aca.2005.12.002.
- [82] Mikeš O, Vrchotová N, Tríska J, Kyseláková M, Šmidrkal J: Distribution of major polyphenolic compounds in vine grapes of different cultivars growing in South Moravian vineyards. *Czech Journal of Food Sciences*. 2008;26:182–189.
- [83] Balík J, Kyseláková M, Vrchotová N, Tríska J, Kumšta M, Veverka J, Híc P, Totušek J, Lefnerová D: Relations between polyphenols content and antioxidant activity in vine grapes and leaves. *Czech Journal of Food Sciences*. 2008;26(Special Issue):S25-S32.
- [84] Ortega-Regules A, Romero-Cascales I, López-Roca JM, Ros-García JM, Gómez-Plaza E: Anthocyanin fingerprint of grapes: environmental and genetic variations. *Journal of Science of Food and Agriculture*. 2006;86:1460–1467. Doi: 10.1002/jsfa.2511.
- [85] Revilla E, García-Beneytez E, Cabello F, Martín-Ortega G, Ryan JM: Value of high-performance liquid chromatographic analysis of anthocyanins in the differentiation of red grape cultivars and red wines made from them. *Journal of Chromatography A*. 2001;915:53–60. Doi: 10.1016/S0021-9673(01)00635-5.
- [86] Jordão AM, Ricardo-da-Silva JM, Laureano O: Evolution of anthocyanins during grape maturation of two varieties (*Vitis vinifera* L.), Castelão Francês and Touriga Francesa. *Vitis*. 1998;37:93–94.
- [87] Pérez-Trujillo JP, Hernández Z, López-Bellido FJ, Hermosín-Gutiérrez I: Characteristic phenolic composition of single-cultivar red wines of the Canary Islands (Spain). *Journal of Agricultural and Food Chemistry*. 2011;59:6150–6164. Doi: 10.1021/jf200881s.
- [88] Mateus N, Marques S, Gonçalves AC, Machado JM, De Freitas V: Proanthocyanidin composition of red *Vitis vinifera* varieties from the Douro Valley during ripening: Influence of cultivation altitude. *American Journal of Enology and Viticulture*. 2001;52:115–121.
- [89] De Freitas VAP, Glories Y: Concentration and compositional changes of procyanidins in grape seeds and skin of white *Vitis vinifera* varieties. *Journal of the Science of Food and Agriculture*. 1999;79:1601–1606. Doi: 10.1002/(SI-CI)1097-0010(199909)79:12<1601::AID-JSFA407>3.0.CO;2-1.
- [90] Li H: Wine tasting. China Science Press, Beijing, China. 2006.
- [91] Fleet GH: Wine Yeasts for the Future. *FEMS Yeast Research*. 2008;8:979–995. Doi: <http://dx.doi.org/10.1111/j.1567-1364.2008.00427.x>
- [92] Lonvaud-Funel A: Lactic acid bacteria in the quality improvement and depreciation of wine. *Antonie van Leeuwenhoek*. 1999;76:317–331. Doi: 10.1023/A:1002088931106.
- [93] Wibowo D, Eschenbruch R, Davis C, Fleet G, Lee T: Occurrence and growth of lactic acid bacteria in wine: a Review. *American Journal of Enology and Viticulture*. 1985;36:302–313.

- [94] Fleet GH, Lafon-Lafourcade S, Ribéreau-Gayon P: Evolution of yeasts and Lactic Acid Bacteria during fermentation and storage of Bordeaux Wines. *Applied and Environmental Microbiology*. 1984;48:1034–1038.
- [95] Reguant C, Bordons A: Typification of *Oenococcus oeni* strains by multiplex RAPD-PCR and study of population dynamics during malolactic fermentation. *Journal of Applied Microbiology*. 2003;95:344–353. Doi: 10.1046/j.1365-2672.2003.01985.x.
- [96] Styger G, Prior B, Bauer FF: Wine favour and aroma—review. *Journal of Industrial Microbiology & Biotechnology*. 2011;38:1145–1159. Doi: 10.1007/s10295-011-1018-4.
- [97] Perestrelo R, Fernandes A, Alburquerque FF, Marques JC, Camara JS: Analytical characterization of the aroma of Tinta Negra Mole red wine: identification of the main odorants compounds. *Analytica Chimica Acta*. 2006;563:154–164. Doi: 10.1016/j.aca.2005.10.023.
- [98] Swiegers JH, Pretorius IS: Yeast modulation of wine flavour. *Advances in Applied Microbiology*. 2005;57:131–175. Doi: 10.1016/S0065-2164(05)57005-9.
- [99] Saerens SMG, Delvaux FR, Verstrepen KJ, Thevelein JM: Production and biological function of volatile esters in *Saccharomyces cerevisiae*—minireview. *Microbial Biotechnology*. 2010;3(2):165–177. Doi: 10.1111/j.1751-7915.2009.00106.x.
- [100] Lee SJ, Noble AC: Characterization of odor-active compounds in Californian Chardonnay wines using GC–olfactometry and GC–mass spectrometry. *Journal of Agricultural and Food Chemistry*. 2003;51:8036–8044. Doi: 10.1021/jf034747v.
- [101] Li H, Tao Y, Wang H, Zhang L: Impact odorants of Chardonnay dry white wine from Changli County (China). *European Food Research and Technology*. 2008;227:287–292. Doi: 10.1007/s00217-007-0722-9.
- [102] Vilela-Moura A., Schuller D, Mendes-Faia A, Silva RF, Chaves SR, Sousa MJ, Côrte-Real M: The impact of acetate metabolism on yeast fermentative performance and wine quality: reduction of volatile acidity of grape-musts and wines—minireview. *Applied Microbiology and Biotechnology*. 2011;89:271–280. Doi: 10.1007/s00253-010-2898-3.
- [103] Verstrepen KJ1, Van Laere SD, Vanderhaegen BM, Derdelinckx G, Dufour JP, Pretorius IS, Winderickx J, Thevelein JM, Delvaux FR: Expression levels of the yeast alcohol acetyltransferase genes ATF1, Lg-ATF1, and ATF2 control the formation of a broad range of volatile esters. *Applied Environmental Microbiology*. 2003;69(9):5228–37. Doi: 10.1128/AEM.69.9.5228-5237.2003.
- [104] Procopio S, Qian F, Becker T: Function and regulation of yeast genes involved in higher alcohol and ester metabolism during beverage fermentation. *European Food Research and Technology*. 2011;233:721–729. Doi: 10.1007/s00217-011-1567-9.
- [105] Pretorius IS: Tailoring wine yeast for the new millennium: novel approaches to the ancient art of winemaking. *Yeast*. 2000;16:675–729. Doi: 10.1002/1097-0061(20000615)16:8<675::AID-YEA585>3.0.CO;2-B.

- [106] Lambrechts MG, Pretorius IS: Yeast and its importance to wine aroma. A review. South African Journal of Enology and Viticulture. 2000;21:97–129.
- [107] Vilela-Moura A, Schuller D, Mendes-Faia A, Côrte-Real M: Effects of acetic acid, ethanol and SO₂ on the removal of volatile acidity from acidic wines by two *Saccharomyces cerevisiae* commercial strains. Applied Microbiology and Biotechnology. 2010;87(4):1317–1326. Doi: 10.1007/s00253-010-2558-7.
- [108] Gunata Z, Bayonove C, Baumes RL, Cordonnier R: The aroma of grapes. Extraction and determination of free and glycosidically bound fractions of some grape aroma components. Journal of Chromatography. 1985;331:83–90.
- [109] Pardo E, Rico J, Gil, JV, Orejas M: De novo production of six key grape aroma monoterpenes by a geraniol synthase-engineered *S. cerevisiae* wine strain. Microbial Cell Factories. 2015;14:136. Doi: 10.1186/s12934-015-0306-5.
- [110] Biron C, Cordonnier R, Glory O, Gunata Z, Sapis JC: Study, in grapes, of the beta-glucosidase activity. Connaissance de la Vigne et du Vin. 1988;22:125–134.
- [111] Delcroix A, Gunata, Z, Sapis JC, Salmon JM, Bayonove C: Glycosidase activities of three enological yeast strains during winemaking: effect on the terpenol content of Muscat wine. American Journal of Enology and Viticulture. 1994;45:291–296.
- [112] Palmeri R, Spagna G: β -Glucosidase in cellular and acellular form for winemaking application. Enzyme and Microbial Technology. 2007;40:382–389. Doi: 10.1016/j.enzmictec.2006.07.007.
- [113] Van Rensburg P, Stidwell T, Lambrechts MG, Otero RC, Pretorius IS: Development and assessment of a recombinant *Saccharomyces cerevisiae* wine yeast producing two aroma-enhancing β -glucosidases encoded by the *Saccharomycopsis fibuligera* BGL1 and BGL2 genes. Annals of Microbiology. 2005;55(1):33–42. Doi: <http://hdl.handle.net/10019.1/11876>.
- [114] Zietsman A, Klerk JJD, van Rensburg P. Coexpression of α -l-arabinofuranosidase and β -glucosidase in *Saccharomyces cerevisiae*. FEMS Yeast Research. 2011;11:88–103. Doi: 10.1111/j.1567-1364.2010.00694.x.
- [115] Guth H: Identification of character impact odorants of diferente white wine varieties. Journal of Agricultural and Food Chemistry. 1997;45:3027–3032. Doi: 10.1021/jf9608433
- [116] Etievant PX: Volatile compounds in foods and beverages. In: Wine, Maarse H (ed.). 2nd ed. Marcel Dekker, New York, 1991; pp 483–546
- [117] Ong PKC, Acree TE: Similarities in the aroma chemistry of Gewürztraminer variety wines and lychee (*Litchi chinesis* Sonn.) fruit. Journal of Agricultural and Food Chemistry. 1999;47:665–670. Doi: 10.1021/jf980452j
- [118] Ferreira V, Lopez R, Cacho JF: Quantitative determination of the odorants of young red wines from different grape varieties. Journal of the Science of Food and Agriculture.

- 2000;80(11):1659–1667. Doi: 10.1002/1097-0010(20000901)80:11<1659::AID-JSFA693>3.0.CO;2-6.
- [119] Peinado RA, Moreno J, Bueno JE, Moreno JA, Mauricio JC: Comparative study of aromatic compounds in two young white wines subjected to pre-fermentative cryomaceration. *Food Chemistry*. 2004;84:585–590. Doi: 10.1016/S0308-8146(03)00282-6.
- [120] Carlton WK, Gump B, Fugelsang K, Hasson AS: Monitoring acetaldehyde concentrations during micro-oxygenation of red wine by headspace solid-phase microextraction with on-fiber derivatization. *Journal of Agricultural and Food Chemistry*. 2007;55:5620–5625. Doi: 10.1021/jf070243b.
- [121] Delfini C, Cocito C, Bonino M: A review: biochemical and molecular mechanisms in *Saccharomyces cerevisiae* that are involved in the formation of some volatile compounds in wines. *Journal International des Sciences de la Vigne et du Vin*. 1999;33(4):195–211.
- [122] Mateo JJ, Jiménez M: Monoterpenes in grape juice and wines. *Journal of Chromatography A*. 2000;881:557–567. Doi: 10.1016/S0021-9673(99)01342-4.
- [123] Bartowsky E: *Oenococcus oeni* and malolactic fermentation—moving into the molecular arena. *Australian Journal Grape and Wine Research*. 2005;11:174–187. Doi: 10.1111/j.1755-0238.2005.tb00286.x.
- [124] Liu S: A review: malolactic fermentation in wine – beyond deacidification. *Journal of Applied Microbiology*. 2002;92:589–601. Doi: 10.1046/j.1365-2672.2002.01589.x.
- [125] Arnink K, Henick-Kling T: Influence of *Saccharomyces cerevisiae* and *Oenococcus oeni* strains on successful malolactic conversion in wine. *American Journal of Enology and Viticulture*. 2005;56:228–237.
- [126] Bartowsky E, Burvill T, Henschke P: Diacetyl in wine: Role of malolactic bacteria and citrate. *The Australian Grapegrower and Winemaker*. 1997; (25th Technical Issue 402a): 130–135.
- [127] Bartowsky E, Henschke P: Management of malolactic fermentation for the ‘buttery’ diacetyl flavour in wine. *The Australian Grapegrower and Winemaker*. 2000;(28th Technical Issue 438a)58–67.
- [128] Bartowsky E., Henschke P: The ‘buttery’ attribute of wine—diacetyl-desirability, spoilage and beyond. *International Journal of Food Microbiology*. 2004;96:235–252. Doi: 10.1016/j.ijfoodmicro.2004.05.013.
- [129] Sumby KM, Jiranek V, Grbin PR: Ester synthesis and hydrolysis in an aqueous environment, and strain specific changes during malolactic fermentation in wine with *Oenococcus oeni*. *Food Chemistry*. 2013;141:1673–1680. Doi: 10.1016/j.foodchem.2013.03.087.

- [130] Pripis-Nicolau L, De Revel G, Bertrand A, Lonvaud-Funel A: 2004. Methionine catabolism and production of volatile sulphur compounds by *Oenococcus oeni*. Journal of Applied Microbiology 96:1176–1184. Doi: 10.1111/j.1365-2672.2004.02257.x.
- [131] Vaquero I, Marcobal A, Munoz R: Tannase activity by lactic acid bacteria isolated from grape must and wine. International Journal of Food Microbiology. 2004;96: 199–204. Doi: 10.1016/j.ijfoodmicro.2004.04.004.
- [132] Arena M, Manca de Nadra M: Biogenic amine production by *Lactobacillus*. Journal of Applied Microbiology. 2001; 90:158–162. Doi: 10.1046/j.1365-2672.2001.01223.x.
- [133] Lonvaud-Funel A: Biogenic amines in wines: role of lactic acid bacteria. FEMS Microbiology Letters. 2001;199:9–13. Doi: 10.1111/j.1574-6968.2001.tb10643.x.
- [134] Claisse O, Lonvaud-Funel A: Detection of lactic acid bacteria producers of 3-hydroxypropionaldehyde (acrolein precursor) from glycerol by molecular tests. Lait. 2001;81:173–181. Doi: <10.1051/lait:2001121>.<hal-00895470>.
- [135] Martineau B, Henick-Kling T: Performance and diacetyl production of commercial strains of malolactic bacteria in wine. Journal of Applied Bacteriology. 1995;78:526–536. Doi: 10.1111/j.1365-2672.1995.tb03095.x.
- [136] Amerine M, Kunkel RE: Microbiology of winemaking. Annual Review of Microbiology. 1968;22:323–358.
- [137] Sponholz WR: Wine spoilage by microorganisms. In: Wine Microbiology and Biotechnology. Editor Fleet, G.H., Harwood Academic Publishers, Chur, Switzerland, 1993; pp. 395–420.
- [138] Walling E, Gindreau E, Lonvaud-Funel A: The biosynthesis of exopolysaccharide by strains of *Pediococcus damnosus* isolated from wine: development of molecular detection tools. Lait. 2001;81,289–300. Doi: <http://dx.doi.org/10.1051/lait:2001132>.
- [139] Costello P, Henschke P: Mousy off-flavor of wine: precursors and biosynthesis of the causative N-heterocycles 2-ethyltetrahydropyridine, 2-acetyltetrahydropyridine, and 2-acetyl-1-pyrroline by *Lactobacillus hildargii* DSM 20176. Journal of Agricultural and Food Chemistry; 2002;50:7079–7087. Doi: 10.1021/jf020341r.
- [140] Crowell EA, Guymon JF: Wine constituents arising from sorbic acid addition, and identification of 2-ethoxyhexa-3,5-diene as source of geranium-like off-odor. American Journal of Enology and Viticulture. 1975; 26:97–102.
- [141] Chatonnet P, Viala C, Dubourdieu D: Influence of polyphenolic components of red wines on the microbial synthesis of volatile phenols. American Journal of Enology and Viticulture. 1997;48:443–448.
- [142] Barthelmebs L, Divies C, Cavin J: Molecular characterization of the phenolic acid metabolism in the lactic acid bacteria *Lactobacillus plantarum*. Lait. 2001;81:161–171.

- [143] Lin W, You W, Feng T: Review of *Brettanomyces* of grape wine and its inhibition methods. In: Advanced Engineering and Technology, Xie and Huang (eds.), CRC Press, London, 2014; pp 635–640. Doi: 10.1201/b16699-99.
- [144] Zapparoli G, Moser M, Dellaglio F, Tourdot-Marechal R, Guzzo J: Typical metabolic traits of two *Oenococcus oeni* strains isolated from Valpolicella wines. Letters in Applied Microbiology. 2004;39:48–54. Doi: 10.1111/j.1472-765X.2004.01541.x
- [145] Pramateftaki P, Metafa M, Kallithraka S, Lanaridis P: Evolution of malolactic bacteria and biogenic amines during spontaneous malolactic fermentations in a Greek winery. Letters in Applied Microbiology. 2006;43:155–160. Doi: 10.1111/j.1472-765X.2006.01937.x
- [146] Marcobal A, Mills DA: Genomics of *Oenococcus oeni* and other lactic acid bacteria. In: Biology of Microorganisms on Grapes, in Musts and Wine. Editor Koning, H., Uden, G., Frohlich, J., Springer, New York, 2008; pp. 351–360. Doi: 10.1007/978-3-540-85463-0_19
- [147] Barthelmebs L, Divies C, Cavin J: Molecular characterization of the phenolic acid metabolism in the lactic acid bacteria *Lactobacillus plantarum*. Lait. 2001;81:161–171.
- [148] Barthelmebs L, Lecomte B, Divies C, Cavin J: Inducible metabolism of phenolic acids in *Pediococcus pentosaceus* is encoded by an autoregulated operon which involves a new class of negative transcriptional regulator. Journal of Bacteriology. 2000;182:6724–6731.
- [149] Swiegers J., Bartowsky E., Henschke P, Pretorius I: Yeast and bacterial modulation of wine aroma and flavour. Australian Journal of Grape and Wine Research. 2005;11:139–173. Doi: 10.1111/j.1755-0238.2005.tb00285.x.
- [150] Harrison T.J., Dake G.R: An expeditious, high-yielding construction of the food aroma compounds 6-acetyl-1,2,3,4-tetrahydropyridine and 2-acetyl-1-pyrroline. The Journal of Organic Chemistry. 2005;70:10872–10874. Doi: 10.1021/jo051940a.
- [151] Pripis-Nicolau L., De Revel G., Bertrand A., Lonvaud-Funel A: Methionine catabolism and production of volatile sulphur compounds by *Oenococcus oeni*. Journal of Applied Microbiology. 2004;96:1176–1184.
- [152] Bartowsky E: 2005. *Oenococcus oeni* and malolactic fermentation—moving into the molecular arena. Australian Journal of Grape and Wine Research. 2005;11:174–187.
- [153] Martineau B., Henick-Kling T: Performance and diacetyl production of commercial strains of malolactic bacteria in wine. Journal of Applied Microbiology. 1995;78:526–536. Doi: 10.1111/j.1365-2672.1995.tb03095.x.
- [154] Bartowsky E., Henschke P: The ‘buttery’ attribute of wine—diacetyl—desirability, spoilage and beyond. The International Journal of Food Microbiology. 2004;96:235–252.

- [155] Swiegers J., Bartowsky E., Henschke P., Pretorius I: Yeast and bacterial modulation of wine aroma and flavour. *Australian Journal of Grape and Wine Research*. 2005;11:139–173.
- [156] Ehsani M, Fernandez MR, Biosca JA, Julien A, Dequin S: Engineering of 2,3-butanediol dehydrogenase to reduce acetoin formation by glycerol-overproducing, low-alcohol *Saccharomyces cerevisiae*. *Applied and Environmental Microbiology*. 2009;75:3196–3205. Doi: 10.1128/AEM.02157-08.
- [157] Romano P., Suzzi G: Origin and production of acetoin during wine yeast fermentation – a review. *Applied and Environmental Microbiology*. 1996;62:309–315.
- [158] Lambert M, Meudec E, Verbaere A, Mazerolles G, Wirth J, Masson G, Cheynier V, Sommerer N: A high-throughput UHPLC-QqQ-MS method for polyphenol profiling in rosé wines. *Molecules*. 2015;20:7890–7914. Doi: 10.3390/molecules20057890.
- [159] Ebeler SE: Analysis of Grapes and Wines: An Overview of New Approaches and Analytical Tools. In: *Advances in Wine Research*, ACS Symposium Series; American Chemical Society, Washington, DC, 2015; pp. 3–12. Doi: 10.1021/bk-2015-1203.ch001.
- [160] Ebeler SE. Chapter 30 – Gas Chromatographic Analysis of Wines: Current Applications and Future Trends. In: *Gas Chromatography*, Poole, C. F., Elsevier, New York, 2012; pp 689–710. Doi: 10.1016/B978-0-12-385540-4.00030-4.
- [161] Robinson AL, Boss PK, Solomon PS, Trengove RD, Heymann H, Ebeler SE: Origins of grape and wine aroma. Part 1. Chemical components and viticultural impacts. *American Journal of Enology and Viticulture*. 2014;65:1–24. Doi: 10.5344/ajev.2013.12070.
- [162] Robinson AL, Boss PK, Solomon PS, Trengove RD, Heymann H, Ebeler SE: Origins of grape and wine aroma. Part 2. Chemical and sensory analysis. *American Journal of Enology and Viticulture*. 2014;65:25–42. Doi: 10.5344/ajev.2013.13106.
- [163] Hjelmeland AK, Collins TS, Miles JL, Wylie PL, Mitchell AE, Ebeler SE: High-throughput, sub ng/L analysis of haloanisoles in wines using HS-SPME with GC-triple quadrupole MS. *American Journal of Enology and Viticulture*. 2012;63:494–499. Doi: 10.5344/ajev.2012.12043.
- [164] Kennison KR, Wilkinson KL, Williams HG, Smith JH, Gibberd MR: Smoke-derived taint in wine: effect of postharvest smoke exposure of grapes on the chemical composition and sensory characteristics of wine. *Journal of Agricultural and Food Chemistry*. 2007;55:10897–10901. Doi: 10.1021/jf072509k.
- [165] Kennison KR, Gibberd MR, Pollnitz AP, Wilkinson KL: Smoke-derived taint in wine: The release of smoke-derived volatile phenols during fermentation of merlot juice following grapevine exposure to smoke. *Journal of Agricultural and Food Chemistry*. 2008;56:7379–7383. Doi: 10.1021/jf800927e.
- [166] Kennison KR, Wilkinson KL, Pollnitz AP, Williams HG, Gibberd MR: Effect of timing and duration of grapevine exposure to smoke on the composition and sensory prop-

- erties of wine. *Australian Journal of Grape and Wine Research*. 2009;15:228–237. Doi: 10.1111/j.1755-0238.2009.00056.x.
- [167] Hayasaka Y, Dungey KA, Baldock GA, Kennison KR, Wilkinson KL: Identification of a β -d-glucopyranoside precursor to guaiacol in grape juice following grapevine exposure to smoke. *Analytica Chimica Acta*. 2010;660:143–148. Doi: 10.1016/j.aca.2009.10.039.
- [168] Pati S, Liberatore MT, Gambacorta G, Antonacci D, La Notte E: Rapid screening for anthocyanins and anthocyanin dimers in crude grape extracts by high performance liquid chromatography coupled with diode array detection and tandem mass spectrometry. *Journal of Chromatography A*. 2009;1216:3864–3868. Doi: 10.1016/j.chroma.2009.02.068.
- [169] Kamangerpour A, Ashraf-Khorassani M, Taylor LT, McNair HM, Chorida L: Supercritical fluid chromatography of polyphenolic compounds in grape seed extract. *Chromatographia*. 2002;55:417–421. Doi: 10.1007/BF02492270.
- [170] Vaclavik L, Lacina O, Hajslova J, Zweigenbaum J: The use of high performance liquid chromatography–quadrupole time-of-flight mass spectrometry coupled to advanced data mining and chemometric tools for discrimination and classification of red wines according to their variety *Analytica Chimica Acta*. 2011;685:45–51. Doi: 10.1016/j.aca.2010.11.018.
- [171] Flamini R: Recent Applications of Mass Spectrometry in the Study of Grape and Wine Polyphenols. *ISRN Spectroscopy Article*. 2013;2013:Article ID 813563, 45 pages. <http://dx.doi.org/10.1155/2013/813563>.
- [172] Roullier-Gall C, Lucio M, Noret L, Schmitt-Kopplin P, Gougeon RD: How Subtle Is the “Terroir” Effect? Chemistry-Related Signatures of Two “Climats de Bourgogne”. *PLoS One*. 2014;9(5):e97615. Doi: 10.1371/journal.pone.0097615.
- [173] Roullier-Gall C, Boutegrabet L, Gougeon RD, Schmitt-Kopplin P: A grape and wine chemodiversity comparison of different appellations in Burgundy: Vintage vs terroir effects. *Food Chemistry*. 2014;152:100–107. Doi: 10.1016/j.foodchem.2013.11.056.
- [174] Robinson AL, Adams DO, Boss PK, Heymann H, Solomon PS, Trengove RD: The relationship between sensory attributes and wine composition for Australian Cabernet Sauvignon wines. *Australian Journal of Grape and Wine Research*. 2011;17:327–340. Doi: 10.1111/j.1755-0238.2011.00155.x.
- [175] Robinson AL, Boss PK, Heymann H, Solomon PS, Trengove RD: Influence of Yeast Strain, Canopy Management, and Site on the Volatile Composition and Sensory Attributes of Cabernet Sauvignon Wines from Western Australia *Journal of Agricultural and Food Chemistry*. 2011;59:3273–3284. Doi: 10.1021/jf104324d.
- [176] Kogerson K, Runnebaum R, Wohlgemuth G, de Ropp J, Heymann H, Fiehn O: Comparison of gas chromatography-coupled time-of-flight mass spectrometry and ^1H nuclear magnetic resonance spectroscopy metabolite

- identification in white wines from a sensory study investigating wine body. *Journal of Agricultural and Food Chemistry*. 2009;57:6899–6907. Doi: 10.1021/jf9019322.
- [177] Hopfer H, Nelson J, Collins TS, Heymann H, Ebeler SE: The combined impact of vineyard origin and processing winery on the elemental profile of red wines. *Food Chemistry*. 2015;172:486–496. Doi: 10.1016/j.foodchem.2014.09.113.
- [178] Hopfer H, Nelson J, Mitchell AE, Heymann H, Ebeler SE: Profiling the trace metal composition of wine as a function of storage temperature and packaging type. *Journal of Analytical Atomic Spectrometry*. 2013;28:1288–1291. Doi: 10.1039/c3ja50098e.
- [179] Polaskova P, Herszage J, Ebeler SE: Wine flavor: chemistry in a glass. *Chemical Society Reviews*. 2008;37:2478–2489. Doi: 10.1039/B714455P.
- [180] Vilela A, Monteiro B, Correia E: Sensory profile of port wines: categorical principal component analysis, an approach for sensory data treatment. *Ciência e Técnica Vitivinícola*. 2015;30(1):1–8. <http://dx.doi.org/10.1051/ctv/20153001001>.
- [181] Monteiro B, Vilela A, Correia E: Sensory profile of pink port wines: development of a flavour lexicon. *Flavour and Fragrance Journal*. 2014;29:50–58. Doi: 10.1002/ffj.3178.
- [182] Johnson AJ, Hirson GD, Ebeler SE: Perceptual characterization and analysis of aroma mixtures using gas chromatography recomposition-olfactometry. *PLoS One*. 2012;7(8):e42693. Doi: 10.1371/journal.pone.0042693.
- [183] Casazza AA, Aliakbarian B, Mantegna S, Cravotto G, Perego P: Extraction of phenolics from *Vitis vinifera* wastes using non-conventional techniques. *Journal of Food Engineering*. 2010;100:50–55. Doi: 10.1016/j.jfoodeng.2010.03.026.
- [184] Vatai T, Skerget M, Knez, Z: Extraction of phenolic compounds from elder berry and different grape marc varieties using organic solvents and/or supercritical carbon dioxide. *Journal of Food Engineering*. 2009;90:246–254. Doi: 10.1016/j.jfoodeng.2008.06.028.
- [185] Luque-Rodríguez JM, Luque de Castro MD, Pérez-Juan P: Dynamic superheated liquid extraction of anthocyanins and other phenolics from red grape skins of wine making residues. *Bioresource Technology*. 2007;98:2705–2713. Doi: 10.1016/j.biortech.2006.09.019.
- [186] Corrales M, Toepfl S, Butz P, Knorr D, Tauscher B: Extraction of anthocyanins from grape by-products assisted by ultrasonics, high hydrostatic pressure or pulsed electric fields: A comparison. *Innovative Food Science and Emerging Technologies*. 2008;9:85–91. Doi: 10.1016/j.ifset.2007.06.002.

- [187] López N, Puértolas E, Condón S, Álvarez I, Raso J: Effects of pulsed electric fields on the extraction of phenolic compounds during the fermentation of must of Tempranillo grapes. *Innovative Food Science and Emerging Technologies*. 2008;9:477–482. Doi: 10.1016/j.ifset.2007.11.001.
- [188] Maier T, Goppert A, Kammerer DR, Schieber A, Carle R: Optimization of a process for enzyme-assisted pigment extraction from grape (*Vitis vinifera* L.) pomace. *European Food Research and Technology*. 2008;227:267–275. Doi: 10.1007/s00217-007-0720-y.