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# Chemical Constituents of Fruit Wines as Descriptors of their Nutritional, Sensorial and Health-Related Properties

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## Abstract

Functional foods are foods that provide positive health effects apart from the provision of essential nutrients. Along with nutraceuticals, they represent the top trends in the food industry. Fruit wines are considered functional foods. When assessing the fruit wine quality, a wide range of descriptors are taken into consideration, namely physico-chemical and sensorial properties of fruit wine. Furthermore, within the context of the new food products development (e.g. functional products), functional properties of fruit wines are also taken into consideration. Functional properties are determined by the content of the biologically active components, such as polyphenols, vitamins and micro- and macrominerals. It is also important to consider the food-safety issues regarding the fruit wines consumption, that is, the presence of pesticides, mycotoxins and biogenic amines in different fruit wines. This chapter aims to give an overview of various factors used to evaluate the quality and the functional properties of fruit wines.

**Keywords:** fruit wine, functional food, biologically active compounds, phenolic compounds, mineral composition, volatile compounds, food safety

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## 1. Introduction

The past decade has seen the rapid development of fruit wine production in many countries, which may be attributed to the enhanced consumers' interest in functional foods that may help to promote health and help reduce the risk of disease. However, there is literature gap data

regarding the production, properties and health benefits of different fruit wines, compared to grape wines. With the ageing of the population, the incidence of chronic diseases that can be linked to caloric excess and the cost of health-care both increase, and so is the consumers' preference towards self-care, instead of pharmaceutical management of disease [1]. The utilisation of functional foods for health-care can lead to the reduction of the use of pharmaceuticals or their replacement. According to the Functional Food and Nutraceuticals market report [2], many consumers were prompted to turn to preventive or alternative health-care practices due to the increase of health-care costs [3]. Consequently, the consumption of functional foods and nutraceuticals increased substantially. Moderate consumption of grape wine (mainly red) has a beneficial health effects when combined with balanced diet, which is confirmed by many studies [4–9]. Some of the reported effects regarding health effects include the protection of the incidence of cardiovascular diseases, ischaemic stroke, hypertension, diabetes, dietary cancers, peptic ulcers, kidney stones and macular degeneration, as well as stimulation of resistance to infection and bone density retention [10–14]. However, apart from grapes, a whole range of other fruits that differ in shape, taste, colour and nutritive value can also be utilised for the production of wine [9], which are nowadays gaining the full acceptance at the market [15]. Fruit wines have proved to be an excellent dietary source of antioxidants, phytonutrients and minerals [16]. According to the European regulations, fruit wines must be obtained by the fermentation of fruits (or respective juices) other than grape. Based on the carbon dioxide retention and content, fruit wines can be classified either as still or sparkling, while their permitted alcoholic strength lies between 1.2 and 14% by volume [14]. Winemaking technology of fruit wines is mostly similar to that of grape wines, except for the variations based on the fruit used, that usually involves the adjustment of fruit juice for winemaking, for example, sugar content or acidity. Geographical area, that is, the fruit cultivars typically grown in that specific area, mainly determines the production and consumption of different fruit wines. Non-grape fruits successfully used for the production of fruit wines in different parts of the world include blackberries, strawberries, currants, apples, wild apricots, pears, kiwifruit, plums, peaches, cherries, bananas, pineapples, cashew nuts, pomegranates, lemons, tangerines, oranges, dates, figs, and so on [17, 18]. There is a large volume of published studies describing chemical composition, with the particular emphasis on various bioactive compounds, of different fruits and fruit juices [19–32]. However, comprehensive reviews of respective fruit wines are still scarce, as well as the comparison of different fruit wines regarding their bioactive compounds. The primary focus of this chapter includes three most popular fruit wines in Croatia, produced from three different groups of fruit, namely berries (blackberry wine), stone fruit (sour cherry wine) and pome fruit (apple wine), in respect to chemical constituents affecting their nutritional, sensorial and health-related properties. Furthermore, food-safety issues, that is, the presence of pesticides, mycotoxins and biogenic amines, are also tackled.

## **2. Chemical constituents of fruit wines**

### **2.1. Alcohol, sugars and organic acids**

Fruit wine consists of two primary ingredients—water and ethanol, the latter being the primary product of alcoholic fermentation, essential for both flavour and stability of wine.

Fermentation is an anaerobic process carried out by yeast in which yeast converts the relatively high level of sugars present in fruits into ethanol and carbon dioxide [14]. Ethanol production is controlled by three main factors: sugar content, fermentation temperature and yeast strain. Particular types of yeast are used in wine production that can both tolerate and produce high alcohol levels (in some cases up to 14%, or even higher). The alcohol content is usually expressed as a volume percentage. Under standard fermentation conditions, ethanol can accumulate to up to 14–15%, while higher ethanol levels can be achieved by the sequential addition of sugar during fermentation. However, to achieve ethanol concentrations above 15%, the wine has to be fortified [33]. The role of ethanol in wine is multiple: it acts as an essential cosolvent (along with water) in extracting fruits constituents, it serves as a reactant in the generation of important volatile compounds (e.g. ethyl esters) and is crucial to the sensory properties, stability and ageing of wine [33]. The secondary products of yeast metabolism include higher alcohols (containing more than two carbons), also known as fusel alcohols or fusel oils [34]. Some of the representatives of higher alcohols are *n*-propanol, isobutyl alcohol (2-methyl-1-propanol), 2-methyl butanol (optically active amyl alcohol), isoamyl alcohol and 2-phenyl ethanol. Glycerol is the primary fermentation product of yeast, besides ethanol and carbon dioxide, and can indirectly contribute to the sensory character of the wine [35]. It is a colourless, odourless, non-volatile compound, without aromatic properties. However, it contributes significantly to the sweetness, as well as to the full and round mouth-feel of wine and wine texture [36]. There is a difference in the levels of glycerol formed by various yeast strains, and therefore glycerol production should be considered in the selection of wine yeast strains [37, 38]. Glycerol is mainly produced during glyceropyruvic fermentation at the start of alcoholic fermentation, and its degradation can be detrimental to the wine quality – partly because of the decrease of its concentration and partly because of the resulting metabolic products [39]. Glycerol concentrations of 5.976 and 4.491 were determined in two blackberry wines, produced on a small scale (in microfermentation experiments) by two commercial wine yeasts [40]. The reported glycerol concentrations in cider are 3–6 g/L [41]. Furthermore, glycerol can be metabolised by lactic acid bacteria during cider maturation, decreasing its final sensorial quality. Selection of yeast strains for secondary fermentation of sparkling ciders has been made by Suárez Valles et al. [42]. Glycerol level was 4.7 g/L in base cider while sparkling ciders produced using four different yeast strains for secondary fermentation contained 5.1–5.2 g/L. Besides ethanol and glycerol, methanol can also be present in measurable concentrations in some types of fruit wines (e.g. plum wine). However, being toxic to humans, methanol content of commercially available fruit wines should not exceed 200–250 mg/L, as regulated in different countries [14]. Fructose, glucose and, in some fruits, sucrose are the major sugars present in fruits. They are fermented by yeast during fruit wine fermentation, producing previously mentioned major metabolites: ethanol, carbon dioxide and glycerol. However, fruits other than grapes are often much lower in sugar content compared to grapes, which makes them unsuitable for winemaking unless sugar content is adjusted by the addition of (most often) sucrose [14]. Sugars may also be metabolised to higher alcohols, fatty acid esters, and aldehydes, which mostly define the primary aromatic character of wine [33]. The sugars that remain unfermented (i.e. the sugars in wine) are referred to as residual sugars. Amidžić Klarić et al. [43] reported the wide range of residual (reducing) sugars from 13.5 to 177.6 g/L in investigated blackberry wines. The authors noted that sugar (mostly sucrose) is often added during different stages of the blackberry wine production, so the wide range

of reducing sugars concentration found in investigated samples is probably the result of the applied technological procedure. Sun et al. [44] studied the suitability of different yeast strains for the production of cherry wine and reported the concentration of total reducing sugars in wine ranging from 0.7 to 1 g/L. Initial analysis of must revealed the initial concentration of total sugars of 165 g/L, achieved by the addition of sucrose to the crushed and deseeded cherries. The discrepancy in the residual sugar content between the blackberry wines and cherry wines can be attributed to the production technology and consumers' preferences—low acidity and high sugar fruit wines seem to be the most acceptable [14]. Fruit species, climate and geomorphological character of soil determine the content of organic acids in fruit. Consequently, the acidity of fruits affects the fruit wine acidity. Total acidity is the wine-quality parameter that gives the measure of the wine acidity, a parameter influencing the wine taste and the overall quality [43]. The total acidity of blackberry wines reported by Amidžić Klarić et al. [43] ranged from 6.7 to 18.1 g/L (as tartaric acid), while the reported total acidities of cherry wines ranged from 5.94 to 6.71 g/L [44]. When it comes to grape wine tasting, a high level of acidity refers to excessively tart, sour and sharp wine attributes, while a low total acidity results in a flat-tasting wine that is more susceptible to infection and spoilage by microorganisms [45]. Organoleptic properties of musts and fruit wines are strongly influenced by organic acids [46]. The major organic acid present in blackberry, cherry and apple wines is malic acid, with reported concentrations of 3.5, 6.8 and 6.2 g/L, respectively. The second most abundant is citric acid [14], while the predominant volatile acid is acetic acid, often expressed as the wine-quality parameter called volatile acidity. Acetic acid is a secondary metabolite derived from a pyruvic acid, which is always formed during alcoholic fermentation. Its accumulation in wine is usually the result of the secondary infection of the fruit, that is, the acetic acid bacteria activity, which is promoted by excessive oxygen uptake. The secondary infection can occur during the vinification process or after bottling [47]. Higher concentrations of acetic acid can detrimentally affect the organoleptic properties of wine, because of bitter taste and smell-like vinegar [39]. Besides acetic acid, as already mentioned, malic acid also contributes to the acidity of fruit wine. However, its degradation by malolactic fermentation (MLF) can reduce the acidity of the wine. MLF can occur spontaneously during or at the end of alcoholic fermentation or can be induced by the addition of lactic acid bacteria starter cultures, namely *Oenococcus oeni* as the primary species used in MLF. Compared to malic acid, lactic acid has a softer flavour, which results in the more desirable flavour profile of wine [48]. Furthermore, the conversion of malic acid to lactic acid results in reduced wine acidity and improved stability and quality of high-acid wines [49].

## 2.2. Volatile (aroma) compounds

Knowledge of the volatile composition of wine is of great interest; since these compounds are responsible for the quality of wine aroma. The aroma of fruit wines is mainly determined by volatile compounds produced by the fruit itself (varietal wine aroma), as by-products of alcoholic and malolactic fermentation (fermentative wine aroma), and formed during bottling, ageing and storing (post-fermentative wine aroma) [50]. Esters, higher alcohols, acetates, organic acids and other compounds are the groups of volatile compounds that most commonly contribute to the flavour and/or aroma profile of fruit. Apart from the listed groups of

volatiles, there are also many minor volatile and non-volatile compounds adding to the aroma of fruit wines, such as aldehydes, ketones, lactones, terpenes and phenols [51]. A fast, selective and sensitive method for the determination of volatile compounds in blackberry wine samples using an HSS-GC-FID method was presented by Mornar et al. [52]; still, the study encompassed a limited number of compounds as well as samples. Therefore, Amidžić Klarić et al. [53] analysed volatile compounds in the 15 blackberry wine samples produced from conventionally and organically grown blackberries using a GC-FID method. The amount of ethyl acetate in the investigated samples ranged from 53.8 to 188.4 mg/L, while propane-1-ol was found in three organic samples. Although isoamyl alcohol was found in all samples, the measured values ranged from 56.7 to 226.9 mg/L. A GC-MS technique was used by Wang et al. [54] for the investigation of the fermentation process influence (primary and secondary) on volatile compounds of blackberry wine. Fifty-five volatile compounds were detected in blackberry fruit juice before fermentation, while nine new aroma components such as octanoate, benzenepropanoic acid ethyl ester, ethyl benzoate, dodecyl ethyl, *n*-propanol, *n*-butanol, D-citronellol, benzaldehyde and cedrol were detected in natural ageing wine which appeared during secondary fermentation. These findings emphasise the importance of natural ageing for the formation of aroma components of blackberry wine. Due to the high popularity of cherry wine, the volatile compounds of this fruit wine were in focus of several investigations as indicators of aroma profile of fruit wines. Niu et al. [55] have applied descriptive sensory analysis to describe the aroma attributes of different cherry wines by GC-olfactometry, an analytical technique that uses human assessors as a sensitive and selective detector for odour-active compounds. Fifty-one compounds were detected and subsequently quantified by GC-MS. The conducted research revealed that the aroma-active compound profiles were dominated by ethyl 2-methyl propionate, 2,3-butanedione, ethyl butyrate, ethyl pentanoate, 3-methyl-1-butanol, ethyl hexanoate, 3-hydroxy-2-butanone, ethyl lactate, 1-hexanol, (Z)-3-hexen-1-ol, ethyl hydroxyacetate, acetic acid, furfural, 2-ethyl-1-hexanol, benzaldehyde, propanoic acid, butanoic acid, guaiacol, beta-citronellol, hexanoic acid, 2-methoxy-4-methylphenol, 2-ethyl-3-hydroxy-4H-pyran-4-one, ethyl cinnamate and 2-methoxy-4-vinylphenol. Afterwards, Xiao et al. [56] have determined 75 volatiles in 9 cherry wine samples using an improved sample preparation technique HS-SPME. The cluster analysis results suggested that esterification reactions and fermentation process were more extended during the ageing period and the production process could have a significant influence on volatile profile of cherry wines. The similar conclusion was obtained by Xiao et al. [57] using multivariate classification of cherry wines. The research revealed the major volatile components of investigated cherry wines: isoamylol, ethyl acetate, benzyl alcohol, benzaldehyde and diethyl succinate. More recently, the research of Xiao et al. [58] have shown that the Chinese cherry wines from different price segments have the different aroma-active compounds profile as well as various aroma attributes. Furthermore, the correlation between the composition of aroma-active compounds and cherry wine from different regions was established by Xiao et al. [59]. Wang et al. [60] have proposed a new, rapid method for analysis of volatile compounds in apple wine using HS-SPME-GC-MS technique. Forty-three volatile compounds (alcohols, esters, lower fatty acids, carbonyls, alkenes, terpenes and phenols) were quantified in 'Fuji' apple wine. The most abundant aroma compounds were esters, alcohols and lower fatty acids; total concentrations were 242.1, 479.3 and 297.4 mg/mL, respectively. Still, the

dominant aroma component was isoamyl alcohol (232.0 mg/mL). The same technique was used for the investigation of the temperature effect during apple winemaking on both the critical aroma compounds and sensory properties of wine. The concentration of all aroma compounds was changed with a temperature increase, and sensory analysis showed the highest acceptance of apple wine fermented at 20°C [61]. The influence of apple variety (Šampion, Idared and Gloster) harvested from the orchard in Poland on the volatile composition, and sensory characteristics of apple wine were investigated by Satora et al. [62]. The high concentration of acetaldehyde, ethyl acetate and methanol was found in Šampion wines, while Gloster wines contained a higher concentration of fusel alcohols. The Idared wines had the best results of the sensory evaluation and high levels of butanol and acetic acid. As mentioned earlier, the majority of investigations were performed using sample preparation procedures such as HS and/or SPME, while gas chromatography with FID and MS detectors was shown to be the analytical technique of choice for the determination of volatile compounds in fruit wine. Ye et al. [63] have developed and applied a new rapid method for the identification of volatile compounds in apple wine using FT-NIR spectroscopy. To provide the greater insight into yeast metabolism and flavour formation of mulberry wine, Butkhup et al. [64] have developed a new HS-SPME-GC-MS method to characterise various volatile compounds of in-house-made mulberry wine. Eighty volatile compounds belonging to groups of higher alcohols, fatty acids, esters and phenols were quantified. These compounds were present in various amounts from 0.1 mg/L (benzene carboxaldehyde) to 138.4 mg/mL (isoamyl alcohol). Feng et al. [65] have extended their research on other fruit wines produced from mulberry as well as raspberry and strawberry. Alcohols formed the most abundant group, followed by esters and acids. Comparing to investigated grape wine, two alcohols, 4-methyl-2-pentanol and 2,3-butanediol, were not found in the three fruit wines. While the number of esters in raspberry (1.5%) and mulberry (2.1%) wines were higher than those of strawberry (0.8%) wine, there were no significant differences in acid content. Song et al. [66] have used the same sample preparation and analytical techniques to determine 78 volatile compounds in wild strawberry wine sample from a southern region of China. Odour activity values were detected for 21 compounds while 6 of them were identified as the particular aroma substances for wild strawberry wine, in particular, methyl 2-methylbutyrate, ethyl 2-methylbutyrate, methyl 3-methylbutyrate, (E)-3-hexen-1-ol, 1-octen-3-ol and phenylacetaldehyde.

### *2.2.1. Volatile compounds containing sulphur*

The formation of off-flavours represents the core problem of high-quality fruit wine production. The main compounds responsible for off-flavours of fruit wines are sulphur-containing volatiles, acetic acids and free amino nitrogen [14]. The volatile compounds containing sulphur, formed as a part of sulphur metabolism, include both molecules positively correlated to the aromatic profile of the wine (volatile thiols), as well as those responsible for wine defects, such as notes described as cabbage, onion, rotten egg, garlic, sulphur and rubber. Hydrogen sulphide and mercaptans (e.g. dimethyl sulphide, dimethyl disulphide, dimethyl trisulphide) are the most often linked to the formation of off-odours in wine, and they are usually present in very low concentration [67]. However, their perception threshold is also low [68].

### 2.3. Phenolic compounds

Wine quality is significantly influenced by phenolic compounds, namely anthocyanins, flavonols, catechins and other flavonoids since they have an enormous impact on the sensory characteristics of wines, mainly colour and astringency [69]. Furthermore, they exhibit a range of antioxidant and pharmacological effects. Phenolic compounds can be classified in different ways because they are constituted at a large number of heterogeneous structures that range from simple molecules to highly polymerised compounds. A review of the composition and content of phenolic compounds in various fruit wines is presented in **Table 1**. Based on the total phenolic content, wines are commonly categorised to three major groups: (i) high in total phenolics, (ii) moderately high in total phenolics and (iii) low in total phenolics. The total phenolic content of cherry, raspberry, black currant, bilberry, elderberry and sea buckthorn fruit wines proved to be comparable or even higher than that of grape red wines, while apple, plum and peach fruit wines had a lower total phenolic content than red grape wines [20, 87–89]. Among the phenolic compounds with known antioxidant activity, flavonoids, phenolic acids and tannins are highlighted [26].

*Flavonoids*, the most studied phenolics, are important components of the human diet. They are also the most widely present in plants and are among the most potent antioxidants in plants. Different members of certain classes of flavonoids can be either colourless or coloured (e.g. anthocyanins), such as pigments of flowers and other plant parts [26]. Important subclasses of flavonoids are, among others, anthocyanins and flavanols. Anthocyanins are important polyphenolic components of fruits, especially berries [90]. The anthocyanins are conjugated anthocyanidins, and they provide the unique colours of dark berries. There are six anthocyanidins distributed throughout the plant kingdom: cyanidin, malvidin, delphinidin, peonidin, pelargonidin and petunidin. The significant anthocyanins in blackberries are cyanidine derivatives. In nature, anthocyanins are mainly found as heterosides. The aglycone form of anthocyanin, known as anthocyanidin, is structurally based on the flavilium or 2-phenylbenzopyrylium cation, with methoxyl and hydroxyl groups present at different positions of the basic structure. Numerous studies have shown that anthocyanins are absorbed in their original glycosylated forms in humans [14, 91, 92]. Anthocyanins are predominant phenolic components or comprise a considerable portion of the total polyphenol content of blackberry as well as cherry juice [76, 84, 93–95]. They are found in berry wines and some fruit wines and presented as total anthocyanin content (TAC). The TAC values found in some blackberry and blueberry wines were 75.56 and 20.82 mg/L (expressed as ellagic acid equivalents), respectively [79]. Mudnić et al. [96] determined high TAC values in blackberry wines, comparable to that measured in red grape wine and ranging from 134 to 164 mg/L (expressed as malvidin 3-glucoside equivalents). Flavonols, another important class of flavonoids, are characteristic for the cool climate fruits and their respective wines [14]. Myricetin and quercetin have been recognised as the first flavonols detected in red berry wines [5]. The results of a study conducted by Mudnić et al. [73] that compared flavanol and procyanidin B<sub>2</sub> contents of several grape wines (red and white), with four commercially available blackberry wines, revealed that the highest concentrations of catechin (45.2 mg/L) and epicatechin (34.7 mg/L) were determined in two blackberry wines. The content of procyanidin B<sub>2</sub> (77.1 mg/L) of the



Phenolic compound	Blackberry wine (no. of samples) [Ref.]	Cherry wine (no. of samples) [Ref.]	Apple wine (no. of samples) [Ref.]	Wine [Ref.]
Total phenolics*	733–2698 (17) [70]	584–743 (6) [44]	160–470 (4) [71]	932–1055 [72]
	1697–22,789 (4) [73]	1081–2711 (9) [74]	225–645 (3) [74]	190–1215 [75]
	1055–2704 (13) [74]	850–1300 (5) [76]	451 (6) [20]	
	1052–3621 (6) [73]	991 (6) [20]	228–639 (3) [62]	
	1122–1400 (10) [77]	1940 (1) [78]	471–801 (40) [77]	
Total anthocyanins	1.3–125.3 (17) [70]		NF	61–125 [72]
	13–164 (4) [73]	17.9–27.9 (6) [44]		
	23–217 (13) [74]	55–483 (9) [74]		
	18.5–192.0 (6) [79]	120 (1) [78]		
	52–105 (19) [77]			
Flavonoids*	924–1417 (4) [73]	NF	NF	NF
Tannin*	1010–1312 (10) [77]	741–901 (6) [44]	NF	266–414 [72]
<b>Individual phenolic compounds</b>				
<i>Flavonol</i>				
Quercetin	0.4–17.9 (13) [74]	0.3–3.9 (9) [74]	0.4–0.9 (3) [74]	<LOD–13.4 [80–83]
	0.8–21.7 (15) [43]	ND (1) [78]		
Quercetin-4-glucoside	ND-2.6 (4) [73]	NF	<LOD-0.1 (3) [62]	NF
Quercetin-3-O-rutinoside (Rutin)	NF	0.2 (1) [78]	NF	6.8–20.2 (67) [82]
<i>Flavan-3-ol</i>				
(+)-Catechin	1.7–10.3 (13) [74]	0.4–11.2 (9) [74]	1.5–15.2 (3) [74]	13.4–95.8 (6) [81]
	9.1–45.2 (4) [73]	12.0–15.2 (4) [84]	1.6–3.5 (3) [79]	
		1.3 (1) [78]		
(-)-Epicatechin	ND-34.7 (4) [73]	0.5–24.1 (9) [74]	4.1–25.9 (3) [74]	4.4–68.5 [80–83]
	0.1–61.4 (13) [74]	10.3–20.91 (4) [84]	3.5–6.6 (3) [62]	
		3.91 (1) [78]		
Epigallocatechin gallate	ND-148.8 (4) [73]	ND (1) [78]	NF	<LOD-15.6 [85]
(-)-Epigallocatechin	NF	1.01 (1) [78]	NF	NF
Procyanidin B2	6.1–77.1 (4) [73]	24.7–69.1 (4) [84]	2.9–7.4 (3) [62]	3.0–83.2 (67) [82]
<i>Flavanone</i>				
Naringenin	NF	0.15 (1) [78]	NF	NF
<i>Flavone</i>				
Apigenin	NF	0.06 (1) [78]	NF	NF

Phenolic compound	Blackberry wine (no. of samples) [Ref.]	Cherry wine (no. of samples) [Ref.]	Apple wine (no. of samples) [Ref.]	Wine [Ref.]
<i>Anthocyanins</i>				
Cyanidin	<LOD-3.2 (15) [43]	ND-4.2 (5) [84]	NF	<0.4-12.3 [86]
Cyanidin 3-glucoside	0.39-25.51 (13) [74]	0.36-0.68 (6) [44]	NF	NF
	8-18 (10) [77]	0.78-12.07 (9) [74]		
		<LOQ-3.78 (5) [84]		
Cyanidin 3-rutinoside	1.9-119.3 (13) [74]	10.7-15.1 (6) [44]	NF	NF
	25-69 (10) [77]	3.2-91.4 (9) [74]		
		1.3-10.2 (5) [84]		
Cyanidin 3-glucosylrutinoside	NF	17.6-25.4 (6) [44]	NF	NF
		7.4-361.3 (9) [74]		
		10.1-44.6 (5) [84]		
Pelargonidin	<LOD-1.46 (15) [43]	NF	NF	NF
Peonidin 3-rutinosid	NF	1.06-1.64 (6) [44]	NF	11.4-128.0 (67) [82]
<i>Phenolic acids</i>				
Gallic acid	45.4-59.0 (4) [73]	<LOQ-5.7 (9) [74]	0.1-1.4 (3) [74]	6.7-104.8 [80-83]
	10.8-52.3 (13) [74]	1.1 (1) [78]		
	28.1-122.4 (17) [70]			
Caffeic acid	2.0-4.8 (17) [70]	0.4-1.7 (6) [44]	1.1-5.4 (3) [74]	0.2-30.8 [80-83]
		1.7-46.3 (9) [74]	0.6-2.5 (3) [62]	
		13.9 (1) [78]		
		16.3-25.6 (5) [76]		
Chlorogenic acid	1.0-3.9 (17) [70]	21.7-29.6 (6) [44]	13.3-25.7 (3) [74]	NF
		12.2-110.5 (9) [74]		
		3.6 (1) [78]		
		27.3-81.0 (5) [76]		
Neochlorogenic acid	NF	12.8-18.5 (6) [44]	NF	NF
		44.5-71.4 (5) [76]		
<i>p</i> -Hydroxybenzoic acid	NF	4.0-4.7 (6) [44]	NF	0.4-0.7 (6) [81]
		6.7 (1) [78]		
<i>p</i> -Coumaric acid	0.1-79.7 (13) [74]	3.3-7.0 (6) [44]	<LOQ-0.2 (3) [74]	0.2-14.2 [80-83]
	1.0-4.4 (17) [70]	0.2-22.2 (9) [74]	0.1-0.9 (3) [62]	
		23.4 (1) [78]		
		0.6-15.2 (5) [76]		

Phenolic compound	Blackberry wine (no. of samples) [Ref.]	Cherry wine (no. of samples) [Ref.]	Apple wine (no. of samples) [Ref.]	Wine [Ref.]
<i>p</i> -Coumarylquinic acid	NF	NF	0.3–4.3 (3) [62]	NF
Protocatechuic acid	13.8–62.6 (13) [74]	<LOQ–15.4 (9) [74] 23.9 (1) [78]	NF	NF
Ferulic acid	NF	ND-4.2 (5) [76] 1.9–13.4 (9) [74]	NF	0.1–0.2 (6) [81]
<i>Stilbene</i>				
<i>trans</i> -Resveratrol	0.5–0.9 (4) [73]	NF	ND (1) [78]	0.02–1.46 (6) [81]
<i>cis</i> -Resveratrol	ND-1.5 (4) [73]	NF	NF	NF
Astringin	ND-12.1 (4) [73]	NF	NF	NF
(E)-Piceid	2.0–6.5 (4) [73]	NF	NF	NF

All concentrations are expressed in mg/L.

ND, not detected; NF, not found; LOD, limit of detection; LOQ, limit of quantification.

\*Values are expressed as gallic acid equivalents (milligrams of gallic acid per litre of fruit wine).

**Table 1.** A review of the composition and content of phenolic compounds in various fruit wines.

same wines was sevenfold higher than in red grape wine (12.3 mg/L). Cherry wines proved to be a much more potent source of flavonols than grape wines, with almost 10 times higher values (from 24.2 to 69.08 g/L for procyanidin B<sub>2</sub>) [84]. The flavanol profile of cherry wine is similar to its grape counterparts, with values up to 3.92 mg/kg for epicatechin, followed by smaller amounts of catechin and epigallocatechin [78]. The major flavanol in apple wines is epicatechin, followed by catechin and their polymerisation product procyanidin B<sub>2</sub> [62].

*Phenolic acids.* P (Phenolic acids) are usually divided into hydroxybenzoic acid derivatives (such as gallic, hydroxybenzoic, salicylic and protocatechuic) and diverse hydroxycinnamic acids and their derivatives. Blackberry and wine made from this edible fruit are known to have high concentrations of benzoic and cinnamic acids [19, 21], especially gallic acid, chlorogenic acid, *p*-coumaric acid and caffeic acid [70]. Cherry wines have a significantly higher content of phenolic acids in comparison to grape wine and almost 10 times higher content of caffeic acid. The prevalent hydroxycinnamic acids in apple wines are chlorogenic and *p*-coumaroylquinic acid. However, they are susceptible to very fast oxidation catalysed by enzyme polyphenol oxidase, giving *o*-quinone, a compound responsible for the browning of apple must, as the principal product [62]. It has been reported in the literature that organically produced fruits may have a higher level of phenolic compounds. This can probably be explained by the enhanced synthesis of endogenous natural defence substances (phenolics) enriching plant defence mechanisms, that is, produced as a response to biotic and abiotic stress [97], in the absence of fertilisers and pesticides, commonly used during conventional production [98–100]. Even though there are generally recognised differences between the conventionally and organically grown food, namely the yield, the size and the pesticide residues, the data on the impact of the practices mentioned earlier on nutritional quality are scarce

and often contradictory. Amidžić Klarić et al. [43] evaluated the quercetin content, colour and selected physicochemical quality parameters of Croatian blackberry wines produced using organically and conventionally grown blackberries. Quercetin content of organic wine samples group was slightly higher than that of conventional wine samples group. No significant overall differences were found in case of colour. Phenolic compounds, in general, are not well absorbed, and it is supposed that the presence of ethanol enhances their bioavailability. This can explain the reported results, indicating that (grape) wines offer somewhat higher health benefits than the preparation of isolated phenolic extracts alone or dealcoholised wine [101, 102]. Similar investigations of fruit wines are still lacking. A progressive loss of phenolic compounds can occur during the winemaking process, as a result of chemical reactions, such as degradation, oxidation, precipitation of phenolics with polysaccharides, condensation with tannins and the formation of other stable anthocyanin-derived pigments. All these reactions can result in significant changes in colour and flavour of red (grape) wines [103, 104]. The same could be applied to other fruit wines. Rommel et al. [93] investigated the processing and storage effects on the composition of anthocyanin, colour and appearance of blackberry juice and wine. They reported 85–100% degradation of juice total anthocyanins, caused by fermentation in combination with depectinising and storage time.

#### 2.4. Vitamins

Vitamins are compounds essential for both plant and animal metabolism, and their deficiencies in humans often lead to different disorders and diseases. Because of their ability to synthesise vitamins, plants (namely fruits and vegetables) are an excellent source of the vitamins in the diet. The stability of vitamins in different foods is often at risk due to various technological practices used during the processing of food, namely changes in temperature regimes (e.g. thermal treatments) and oxygen levels [105, 106]. Since fruits are a good source of vitamins, consequently the vitamins can also be found in fruit juices. However, the concentration of vitamins decreases during the winemaking (fermentation and ageing), so their levels in wine are inadequate to be of significance in human nutrition. On the other hand, their levels are usually enough or more than enough to support microbial growth. Biotin (vitamin H) and nicotinic acid (niacin, vitamin B<sub>3</sub>) contents are adequate for most yeast strains [33]. Low levels of vitamins determined in grape wines are probably the reason for the absence of relevant studies regarding the vitamins in fruit wines. Grape wines are reported to contain some B vitamins (thiamine, riboflavin and vitamin B<sub>12</sub>) and very small amounts of vitamin C and fat-soluble vitamins A, D and K. Some vitamins, such as vitamin C, may be primarily destroyed during processing and storage, whereas others, for example, B vitamins, are also produced by the action of yeast and may be present in measurable quantities in the final product [107]. Thiamine (vitamin B<sub>1</sub>) is utilised by yeast during fermentation, so its levels in wine are insignificant. In addition, thiamine levels are lowered by reaction with SO<sub>2</sub> during fermentation as well as the absorption by bentonite. Riboflavin (vitamin B<sub>2</sub>) is oxidised on exposure to light [33]. Free riboflavin (RF) is naturally present in raw and processed fruits and fermented beverages. Flavin-adenine dinucleotide (FAD) and sometimes flavin mononucleotide (FMN) are present together with RF in significant amounts in fruit juices, while RF is the only form of riboflavin present in important quantities in wine [108]. Since some yeasts synthesise RF

during cell growth as an extracellular by-product of the fermentation process, its content can increase in wine. *p*-aminobenzoic acid (PABA), classified into a group of vitamin-like substances, although often referred to as a vitamin [109], is the only compound to increase substantially during fermentation [33]. Folic acid (pteroylglutamic acid) is a water-soluble B vitamin, essential for healthy growth and development of humans, can be found in significant amounts in berries [110] and can reach up to 1 mg/100 mL in some berry wines [14]. During the process of alcoholic fermentation, this vitamin is not subject to change because it has no significant effect on yeast, while for lactic acid bacteria, it is essential [111]. Vitamin C is one of the essential nutritional quality factors of fruits and has many vital biological roles in the human body, such as cell division and proliferation, photosynthesis, hormone biosynthesis and signalling [112, 113]. It is a crucial antioxidant that is produced by plants response to various biotic and abiotic stresses. Vitamin C plays a fundamental role in scavenging reactive oxygen species (ROS) due to its potent antioxidant properties [113]. Fruits and vegetables provide more than 90% of the vitamin C in human diets [112]. The reported vitamin C concentration ranges in blackberries, cherries and apples are 87–696 mg/L [114], 43–177 mg/L [115] and 3–25 mg/100 mg of fresh weight [116], respectively. Previous investigation has indicated that the content of ascorbic acid varied for organically and conventionally cultivated fruits and vegetables [117], as well as for different environmental conditions under which the plant was grown, such as temperature, water availability, pathogenic attack and nutrients [118]. Taken together, the facts listed earlier lead to a conclusion that moderate wine consumption is very far from providing an adequate intake of vitamins for maintaining optimal nutritional status and overall health [14].

## 2.5. Antioxidant capacity

Fruits contain various dietary phytonutrients with strong antioxidant capacities, such as phenolics (which include flavonoids and phenolic acids), carotenoids and vitamins. Many phenolic substances present in fruits influence sensory properties of fruit wine such as taste, astringency, bitterness as well as colour. Since fruit wines are processed in the same way as wine made from grapes, significant compositional changes take part in winemaking [119]. Both fermentation and ageing result in the transformation of starting compounds present in musts into secondary metabolites that determine the quality of the final product [119, 120]. Berries, grape and their processed products such as wines contain a wide range of flavonoids and other phenolic compounds that possess antioxidant activity. Heinonen et al. [71] evaluated the antioxidant activity of over 44 different fruit wines, mainly berry wines, but also apple wines. The results of the study showed that all the investigated wines possessed a significant antioxidant activity. However, the total phenolic content did not correlate with the antioxidant activity. On the other hand, several other studies confirmed a strong positive correlation between the total antioxidant activity of fruit wines and total phenolics [26, 28, 31, 69, 95, 121]. When compared to red (grape) wines, blackberry, blueberry and sour cherry wines proved to have 30–40% more superoxide radical-scavenging activity [122], which makes them very potent natural antioxidants beneficial to human health [74, 76, 84, 94]. Yoo et al. [12] compared the levels of enzymes superoxide dismutase (SOD) and catalase in fresh cherries,

cherry juice and cherry wines and concluded that cherry wine had enhanced levels of the mentioned enzymes. Superoxide dismutases (SODs) are the major antioxidant defence systems against superoxide anion, the most common free radical in the body [123]. SODs reduce the cellular damage caused by superoxide anion. When comparing different fruit wines, it has been reported that berry fruit wines (blackberry, elderberry, blueberry and raspberry) in general had higher total antioxidant capacities than apple and pear wines (as representatives of pome wines) [14, 20].

## 2.6. Mineral composition

Minerals are inorganic ingredients of food, required by the body in small amounts for a variety of different metabolic processes important for the functioning of human body. Since some minerals are needed in more substantial quantities than others, they can be divided to three groups, based on their recommended daily intake: macrominerals (over 50 mg/day), trace minerals and ultratrace minerals (lower than 50 mg/day) [124–126]. Nowadays, a mineral deficiency occurs very often without its noticeable signs. The sufficient intake of minerals depends on their quantities consumed with food, but even more on their bioavailability, which depends on the food composition and properties. The mineral content of fruits can vary significantly depending on the genetic and climate factors, cultivation procedures, soil composition, ripeness and many other factors. Furthermore, changes in mineral content usually occur as a result of applied technological procedures, for example, the removal of a portion of the raw material [125, 126]. The sources of minerals (metals) in alcoholic beverages are various: raw materials, process equipment, applied technological procedures, fermentation, bottling, ageing, storage and adulteration [127]. The soil on which fruits are grown is a source of metals of natural origin (primary metals) present in wine. The concentration of primary metals is characteristic and comprises the most significant part of the total metal content in wine [128, 129]. External impurities present in fruits, as well as those that occur during different stages of winemaking, are the source of metals of secondary origin. For example, the prolonged contact of wine and the construction materials used for the oenological equipment (stainless steel, aluminium, brass, glass and wood) can be a source of contamination of wine with Al, Cd, Cr, Cu, Fe and Zn [128–130]. Fining and clarifying substances (e.g. bentonites) used during winemaking can be a source of contamination with Na, Ca or Al [129–132]. Furthermore, individual metals have a significant effect on the organoleptic properties of wine (i.e. Al, Zn, Cu and Fe) and, therefore, their concentration must be monitored [133]. The total amount of minerals in a sample of fruits and fruit wines can be expressed as the ash content. Ash is the inorganic residue remaining after the water, and organic matter has been removed. A higher ash content in a fruit wine implies a higher amount of minerals and a higher quality of the wine [134]. The literature regarding grape wines proposes that the mineral profile of wines could be used as a 'fingerprint', used for the characterisation of wines based on their geographical origin [20, 135]. While there is a significant volume of available data on the mineral content of blackberries, cherries and apples, far too little attention has been paid to the mineral composition of respective fruit wines. A review of metal concentrations in fruit wines is given in **Table 2**. As it could be seen from the table,

Metal	Blackberry wine (no. of samples) [Ref]	Cherry wine (no. of samples) [Ref]	Apple wine (no. of samples) [Ref]	Grape wine [Ref]
Ag	0.34–2.76 µg/L (15) [134]	NF	NF	0.008–2.77 µg/L (31) [128]
Al	6–16 mg/L (15) [134] 37–1110 µg/L (22) [136]	0.200 mg/kg (1) [78]	NF	0.017–14.3 µg/mL [129]
As	<0.9 µg/L (15) [134]	0.093 µg/kg (1) [78]	NF	1.7–15.2 µg/L (31) [128]
B	NF	2.760 mg/kg (1) [78]	NF	2.1–12.1 mg/L (68) [137]
Ba	0.48–1.46 mg/L (15) [134]	NF	NF	0.01–0.48 µg/mL [129]
Ca	86–457 mg/L (32) [134, 138] 115–555 mg/L (22) [136]	0.084 g/kg (1) [78] 69 µg/g (6) [20]	8–28 mg/L (3) [9] 45 µg/g (6) [20]	7–241 µg/mL [129]
Cd	0.3–9.9 µg/L (32) [134, 138]	0.093 µg/kg (1) [78]	<0.026–3.72 µg/L (3) [9]	ND-0.054 µg/mL [129]
Co	1.3–11.9 µg/L (32) [134, 138] 2–40 µg/L (22) [136]	0.577 µg/kg (1) [78]	NF	ND-0.045 µg/mL [129]
Cr	2.3–18.7 µg/L (32) [134, 138]	0.016 mg/kg (1) [78]	NF	ND-0.2 µg/mL [129]
Cu	0.06–0.77 mg/L (32) [134, 138] 0.05–3.83 mg/L (22) [136]	0.030 mg/kg (1) [78]	NF	ND-2.60 µg/mL [129]
Fe	0.082–8.4 mg/L (32) [134, 138] 0.093–5.49 mg/L (22) [136]	2.192 mg/kg (1) [78] 1.2 µg/g (6) [20]	<0.027–0.508 mg/L (3) [9] 0.4 µg/g (6) [20]	0.06–23.7 µg/mL [129]
Hg	NF	NF	<0.036 µg/L (3) [9]	NF
K	564–2014 mg/L (32) [134, 138] 615–1760 mg/L (22) [136]	1.373 g/kg (1) [78] 834 µg/g (6) [20]	233–353 mg/L (3) [9] 958 µg/g (6) [20]	265–3056 µg/mL [129]
Li	13–21 µg/L (15) [134] 1–40 µg/L (22) [136]	0.678 µg/kg (1) [78]	NF	0.002–0.098 µg/mL [129]
Mg	706–381 mg/L (32) [134, 138] 77–238 mg/L (22) [136]	0.072 g/kg (1) [78] 50 µg/g (6) [20]	13–19 mg/L (3) [9] 38 µg/g (6) [20]	7–718 µg/mL [129]
Mn	0.7–11.5 mg/L (32) [134, 138] 0.5–11.3 mg/L (22) [136]	0.632 mg/kg (1) [78] 0.2 µg/g (6) [20]	0.2 µg/g (6) [20]	ND-5.5 µg/mL [129]
Mo	NF	0.093 µg/kg (1) [78]	NF	0.7–64 µg/L (88) [139]
Na	12–213 mg/L (32) [134, 138] 3–13 mg/L (22) [136]	1.65 mg/kg (1) [78] 38 µg/g (6) [20]	31 µg/g (6) [20]	ND-310 µg/mL [129]
Ni	60–278 µg/L (15) [134]	0.054 mg/kg (1) [78]	NF	ND-0.5 µg/mL [129]
P	32–119 mg/L (15) [43]	0.179 g/kg (1) [78] 54 µg/g (6) [20]	68 µg/g (6) [20]	0.3–47.3 mg/L (31) [128]
Pb	13.6–52.8 µg/L (15) [134] 17–54 µg/L (22) [136]	4.4 µg/kg (1) [78]	75.3–116.3 µg/L (3) [9]	ND-1.1 µg/mL [129]
Rb	90–1470 µg/L (22) [136]	NF	NF	0.03–9.90 µg/mL [129] 96–2470 µg/L (31) [128]

Metal	Blackberry wine (no. of samples) [Ref]	Cherry wine (no. of samples) [Ref]	Apple wine (no. of samples) [Ref]	Grape wine [Ref]
S	NF	0.089 g/kg (1) [78] 136 µg/g (6) [20]	80 µg/g (6) [20]	NF
Sb	NF	0.093 µg/kg (1) [78]	NF	0.18–29.7 µg/L (31) [128]
Se	<1.5 µg/L (15) [134]	0.011 mg/kg (1) [78]	NF	NF
Si	1.82–8.24 mg/L (15) [134]	NF	NF	5.30–33.3 mg/L (68) [137]
Sn	12.7–22.0 µg/L (15) [134]	NF	<32.5 µg/L (3) [9]	0.02–1.0 mg/L (68) [137]
Sr	165–1445 µg/L (22) [136]	NF	NF	0.12–3.22 µg/mL [129] 0.27–1.84 mg/L (54) [140]
V	NF	6.86 µg/kg (1) [78]	NF	ND-0.40 µg/mL [129]
Zn	0.25–6.65 mg/L (32) [134, 138] 0.30–1.96 mg/L (22) [136]	0.3 mg/kg (1) [78] 0.1 µg/g (6) [20]	36–105 µg/L (3) [9] 0.2 µg/g (6) [20]	ND-8.9 µg/mL [129]

ND, not detected; NF, not found.

**Table 2.** A review of metal concentrations in blackberry, cherry and apple wines.

the mineral content of blackberry, cherry and apple wine is in accordance with that of grape wines. Predominant metal in all reviewed fruit wines is K, its concentration being the highest in blackberry wine. Na is a widespread metal in food since the industrially processed food is a particularly important source of this macroelement. The sodium concentrations of blackberry wines varied over a wide range when compared to other fruit wines (**Table 2**). Still, the low-sodium/high-potassium levels found in all three types of fruit wine indicate that fruit wines can be considered as effective sources of potassium. Due to irregular diet and large intake of refined sugars, coffee and alcohol, the insufficient intake of magnesium may occur. Amidžić Klarić et al. [141] investigated the mineral composition of commercially available Croatian blackberry wines. The results indicated that 17 investigated Croatian blackberry wines could be considered as an excellent additional source of magnesium, manganese and potassium. When compared to cherry and apple wines (**Table 2**), blackberry wine seems to be a better source of Ca, Mg, Fe and Mn. The literature data show that calcium and phosphorus absorption is closely related, but due to an unbalanced diet dominated by a high phosphorus intake, homeostasis is compromised and contributes to low serum calcium levels (hypocalcaemia). For this reason, it has been suggested that the calcium-phosphorus ratio in foods should be between 1:1 and 2:1. As can be seen from **Table 2**, the calcium-phosphorus ratio of reviewed blackberry wine samples was higher than 1 in favour of calcium. Iron deficiency is one of the most common nutritional deficiencies, characterised by signs and symptoms such as unusual tiredness, paleness, shortness of breath and anaemia. In Croatia, blackberry wine is traditionally called ‘ferrous wine’, and it has been used as a popular medicine for anaemia and iron deficiency. Some of the metals exhibit not only beneficial effects on the human body but also deleterious ones that made them a cause of concern for wine producers and consumers for years now. Heavy metals are some of the most critical chemicals found in the environment,



and the exposure through the consumption of food is frequent, regardless of the mode of food production (conventional or organic) [142]. Amidžić Klarić et al. [134] examined mineral and heavy metal content of blackberry wines made from conventionally and organically grown blackberries. The comparison between these two groups of investigated blackberry wines showed the statistically significant difference in the content of Si and Li, whereas the organic wines group contained higher levels of these compounds. Toxic metals (As, Cd, Hg, Pb) are frequently found to be the primary food contaminants [126], and they can be poisonous and harmful. Therefore, the metal content of grape wine is regulated according to the national legislation and the European Union legislation [141, 143]. Above optimal level, elements, such as Al, Cu, K, Fe, Mn, Zn, may have detrimental effects on wine stability and its commercial acceptability [144].

### 3. Food-safety issues regarding fruit wines

#### 3.1. Pesticides residues

Pesticides comprise a numerous and diverse group of chemical compounds with a common characteristic of eliminating pest in agriculture and households. They are widely used in agricultural practice, not only during cultivation but also in post-harvest storage. Pesticide residues may end up in fruit pulp and juices since they can penetrate plant tissues. However, their concentrations are lower than those in the intact fruit [145]. Pesticide residues in fruit wine, like those found in juice, can also be introduced by planting and preservation process [146]. In wine-making, the activity of yeast can be affected by pesticides. The presence of pesticides has been associated with stuck and sluggish fermentation [147]. Most of the pesticides can pass from fruit/grape to must and wine, but the extent to which they pass is different [148, 149]. Organic products, compared to those produced by conventional practices, present some advantages in respect to well-known toxicants, such as pesticides and nitrates [142]. However, caution is needed concerning the problem of pesticide because the number of chemicals to trace is very high [142]. The research, which included the analysis of 25 pesticides in Croatian grape wines, conducted by Vitali Čepo et al. [150], indicated significantly lower total pesticide concentrations and the average number of pesticides per sample of organic grape wines, compared to conventional wines. Pesticide residues not only result in potential health risks for the consumers but also lead to a decrease in the fruit wine quality. Because of the health risk of pesticide residues in juice and fruit wine, it is of particular importance to provide the precise, accurate and reliable result of residues as the scientific basis for ensuring food safety. Determination of pesticides is challenging, because of their chemical diversity and lack of collective analytical methods, which probably explains the fact that the reports regarding the pesticide residues in different fruit wines are still missing. Since the diet is the primary source of exposure of the general population to pesticide residues, the regulatory controls on pesticides by different organisations aim at minimisation of exposure to pesticide residues in food. The great variety of applied pesticides, both within European Union countries (EU) and non-EU countries, as well as the arrival of new plant protectors and chemicals, calls for an ever-expanding list of pesticides along with their accompanying maximum residue limits (MRLs) [151].

### 3.2. Mycotoxins

Mycotoxins are secondary metabolites of filamentous fungi that naturally occur in food. Mycotoxins can be present in food when fungi are no longer present, which means that the fungal growth is not necessarily associated with the mycotoxins synthesis [152]. Fruits are susceptible to fungal growth, whose development occurs in between harvest and fermentation process. During fermentation, the fungal growth is inhibited by ethanol and the anaerobic conditions [153]. Organic acids present in fruits (malic, citric and tartaric acids) slow down the bacterial spoilage of fruits by lowering the pH. However, the acidic pH of fruit that varies from <2.5 to 5.0 is tolerable for many fungal species [152]. Different practices applied in fruit cultivation (such as the use of pesticides and different cultivars) and in winemaking (period and conditions of storage, type of maceration, time and temperature of fermentation) can have an impact on mycotoxins accumulation [154]. It seems that organic production could be more affected by mycotoxins since no synthetic fungicides are applied [142]. Several mycotoxins have been reported in fruit juices and wine (the list, however, is not exhaustive): *Alternaria* mycotoxins are produced by *A. alternata*, byssochlamic acid produced by *Byssochlamys nivea* in prune, grape and apple juices, citrinin produced by *Penicillium expansum* in apple juice, ochratoxin A, the most crucial mycotoxin in wine, secreted by *Aspergillus carbonarius* present in harvested grapes and juices and finally patulin (PAT), the most critical mycotoxin in fruit juices, produced by several species such as *B. fulva*, *B. nivea* and *P. expansum* [155]. The most critical mycotoxin in grape wine is the ochratoxin A (OTA), which is produced by *A. carbonarius* and is not degraded during winemaking, fermentation process and storage [155]. OTA has been detected in cherries and strawberries and their associated juices. Since the fungus grows on the exterior surfaces of the fruit, the concentration of OTA tends to be higher in wines that are produced by the increased skin contact that is necessary to extract pigments and tannins. OTA concentration in wine is highest after maceration and tends to diminish during the yeast and malolactic fermentations, probably due to adsorption to yeast cells or degradation by lactic acid bacteria [156]. Toxicological studies have determined that OTA may have several effects on health, such as genotoxicity, carcinogenicity, immunosuppressive properties and nephrotoxicity, and for that reason, the EU regulation (EC no. 1881/2006) [157] has set the acceptable limit for OTA in wine to 2 µg/L. Patulin (PAT), which is the most important mycotoxin in fruit juices, has been studied mainly in fruit juices and particularly in apple juices, although the presence of the compound was also described in the brown rot of other fruits [155]. It is produced by the fungi belonging to the genera *Penicillium*, *Aspergillus* and *Byssochlamys*, and its presence in foodstuffs may be a health hazard since this mycotoxin can cause severe acute (convulsions, nausea and ulceration) and chronic (carcinogenic, genotoxic and immunotoxic) effects in humans [158]. The removal of the damaged or rotten fruit could help reduce the levels of PAT in the juices, but the complete elimination of PAT is not possible since PAT diffuses into the healthy parts of the fruit [152]. Stinson et al. [159] reported the 99% reduction of PAT levels as a result of alcoholic fermentation of apple juice. The Codex Alimentarius [160] and the EU Commission Regulation (EC no. 1881/2006) [157] have established limits for patulin maximum level of 50 µg/kg for apple products intended for human consumption. When it comes to winemaking, it seems that the use of sound manufacturing practices (e.g. fruit selection, handling, sorting, storage, culling and washing) could keep the residual mycotoxin levels of the fruit juices and wine under the maximum allowed limits [155].

### 3.3. Biogenic amines

Fermentation by-products, biogenic amines, are low molecular nitrogen compounds formed mainly by decarboxylation of amino acids or by amination and transamination of aldehydes and ketones. In food and beverages, they are synthesised by the enzymes from raw material or are generated by decarboxylation of amino acids by microorganisms [161, 162]. Biogenic amines are undesirable in all foods and beverages because if absorbed at too high concentrations, they may cause adverse physiological effects in sensitive humans, especially in the presence of alcohol and acetaldehyde. The most studied biogenic amine is histamine [33, 163]. Biogenic amines, particularly histamine, the most frequently found in wines, often reduce the sensory quality of grape wines. Different microorganisms present in wine can synthesise biogenic amines from their respective amino acid precursors, at any stage of wine production, ageing or storage. Therefore, their presence in wines can serve as an indicator of spoilage and authenticity [164, 165]. Biogenic amines associated with grape wine are putrescine, histamine, tyramine and cadaverine, followed by phenylethylamine, spermidine, spermine, agmatine and tryptamine [162]. Lactic acid bacteria present in wine (e.g. *Lactobacillus*, *Leuconostoc* and *Oenococcus* spp.) are mainly responsible for the occurrence of biogenic amines in wine (and in other fermented products) since they produce enzymes that decarboxylate the respective precursor amino acids [166]. To prevent the problem of a high biogenic amine concentration in wines, the length of the processes of maceration and the contact of wine and lees should be reduced to a minimum, because those are the processes that incorporate amino acids to must or wine. This is hard to achieve when age wines are produced. Another way of solving the problem is to inhibit the growth of indigenous lactic acid bacteria and use the selected *O. oeni* strains unable to produce biogenic amine [167]. Biogenic amines present in fruits also contribute to their level in the wine. It has been reported that fruit cultivation conditions and management technique play essential roles in the accumulation of biogenic amines in fruits, for example, the accumulation of putrescine in grapes as a response to a potassium deficiency in soil [168]. While data are available on the concentrations of biogenic amines in grape wines, rare investigations have been conducted to evaluate their concentrations in fruit wines. Ouyang et al. [169] observed a noticeable difference in the profile of biogenic amines in the wines made from different fruits. A high level of the total biogenic amines (28.11–67.48 mg L<sup>-1</sup>) was detected in red grape wines, followed by the strawberry wine (14.60 mg L<sup>-1</sup>) and the raspberry wine (8.75 mg L<sup>-1</sup>). The total content of BA in the white grape wines ranged from 5.42 to 7.21 mg L<sup>-1</sup>, while the level of total biogenic amines of other fruit wines was below 2.5 mg L<sup>-1</sup>. When individual biogenic amines were analysed, the results revealed that spermidine was present in most of the wines, while putrescine was present in all the grape wine samples. However, the levels of putrescine in blueberry, raspberry, schisandrae and strawberry wines were higher than that in the grape wines. Blueberry wine and raspberry wine also contained tyramine.

### 3.4. Sulphur dioxide

The most common preservative in wine production used to control both oxidative processes and unwanted spontaneous fermentations is sulphur dioxide (SO<sub>2</sub>) [39]. This is due to its potent antioxidant and antimicrobial properties. However, when present in high concentrations in wine, SO<sub>2</sub> can have unfavourable health effects, for example, diarrhoea, urticaria and abdominal pain [170]. The International Organisation of Vine and Wine (OIV) has been gradually reducing the maximum advisable levels of total SO<sub>2</sub> in wines [143]. The maximum acceptable limit for

total SO<sub>2</sub> in grape wine is set between 150 and 300 mg/L depending on the wine type and the level of reducing substances in wine. One of the challenges for scientists and winemakers who are striving to meet today's consumer demands for SO<sub>2</sub>-free high-quality wines is the application of new technologies to replace the use of SO<sub>2</sub> [171]. The alternatives to SO<sub>2</sub> investigated so far include treatments with lysozyme, dimethyl dicarbonate (DMDC), the addition of reduced glutathione (up to 20 mg/L) and the addition of commercial oenological tannins [170, 172–176].

## 4. Conclusions

The role of fruits in the human diet is well established due to various important nutritive and biologically active components intrinsic to fruits. Consequently, fruit wines tend to preserve these components, along with developing new desirable ones in the final product. Fruit wines proved to be a good source of different antioxidants, phytonutrients and minerals, which classify them with the functional food. The production of fruit wines is growing steadily in recent years, probably driven by the demand for new functional products. However, having in mind the fact that most fruits can be used for fruit wines production, it is evident that they comprise a vast and diverse group of fermented beverages. Compared to grape wines, the comprehensive reviews of specific fruit wines are still scarce, as well as the comparison of different fruit wines regarding their production, composition, nutritional, functional and health-related properties. Hopefully, this chapter will contribute to the body of knowledge, as well as to diversification, standardisation and, consequently, commercialisation of quality fruit wine production.

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