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REVIEW ARTICLE

Grape, wine and pomace anthocyanins: winemaking biochemical transformations, application and potential benefits

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ABSTRACT

Anthocyanins are polyphenols found in red grapes, wines and their by-products. This scientific paper reviews their physiological significance in grape tissues, the biochemical transformations they undergo during winemaking and wine aging, their potential application in the food industry, and the health benefits associated with them. The paper sheds light on the factors influencing their extraction, stability and composition in wines, and explores their applications in various food products and the possibility of sustainable winemaking using pomace. The paper focuses on the broad impact of anthocyanins on product quality and consumer preferences, and highlights potential preventive and therapeutic applications for human health conditions. Overall, this comprehensive overview provides valuable insights into the multifaceted roles of anthocyanins, paving the way to future research on the application of anthocyanin in agriculture, food science and medicine.

KEYWORDS: grape, wine, anthocyanins, polyphenols, winemaking, biochemical transformations, application, health benefits

INTRODUCTION

Since ancient times, grape growing has been closely intertwined with human culture, making it one of the world's oldest and most significant agricultural traditions. The cultivation of grapes and the production of wine have played pivotal roles in various civilisations, spanning continents and centuries. Till now, a total of about 10,000 grapevine varieties are known according to OIV reports (International Organisation of Vine and Wine); however, approximately 50 % of the vineyard area worldwide contains 33 grapevine varieties (OIV, 2017). These findings underscore the significant dominance and widespread cultivation of a relatively small number of grapevine varieties (known as "international varieties") on a global scale (OIV, 2017). On the other hand, local indigenous varieties are cultivated in specific regions of numerous winemaking countries. These local, autochthonous or native varietals are currently increasing in importance for the wine industry due to their enhanced adaptability to the escalating challenges posed by climate change (Otto *et al*., 2023). A large percentage of global grape production is dedicated to wine production; the wine industry plays a major role in world economy with global grape production estimated to be 7.2 million hectares in 2023, and global wine production to be 237 million hectoliters (OIV, 2024). As a result of numerous chemical and biochemical reactions and mechanisms, wine production is a synergy of several different elements, such as grape variety, terroir and winemaking techniques (Razungles, 2022).

The quality of red wine is directly proportional to its content in aromatic compounds, proanthocyanins, and anthocyanins. Moreover, the colour of red wine is one of the prime sensory characteristics in which anthocyanins have a crucial role (Paissoni *et al*., 2018). Anthocyanins are natural water-soluble pigments that are found in a wide range of plants and appear red, blue or purple (Winefield *et al*., 2009). Grapevine anthocyanins have an important role in winemaking, since they are responsible for the red colour of wine. The stimulation of anthocyanin molecules by visible light influences their colours (Li *et al*., 2021). Anthocyanins also have a special physiological role in the grapevine linked to, for example, free radical scavenging and antioxidative capacity, defence against pathogens, seed dispersal, and the proposed modulation of signaling cascades (He *et al*., 2010) which has to date not been thoroughly explained and requires further investigation (Roubelakis-Angelakis, 2009). Anthocyanins are found in the skin of the black and purple varieties of grape berries; white grape varieties do not usually synthesise anthocyanins, although some studies have shown that synthesis can occur in white berries due to mutations of the genes that are responsible for the synthesis of anthocyanins (He *et al*., 2010; Ivanova *et al*., 2011a). 'Teinturier' grape varieties are known as dyer grapes, because anthocyanins are contained in the flesh of their berries (Kőrösi *et al*., 2022). Biochemically, anthocyanins are highly reactive and unstable bioactive compounds, which undergo degradative changes, depending on, for example, the pH of the medium, temperature, light, presence of oxygen, presence of dry matter and water content (Moreno-Arribas & Polo, 2009). Due to their structure and instability, anthocyanins undergo transformation processes during red winemaking, with changes to their chemical structure and various complexes being formed with other compounds (sugars, organic acids, phenolic compounds and halogens). Anthocyanins often exhibit positive effects on human health (Zia ul Haq *et al*., 2016); as a result, their presence in winemaking waste (*i.e*., pomace and its constituents) is being increasingly valorised and they are further used in different food industry sectors (García-Lomillo & González-SanJosé, 2017). For example, different types of encapsulations have been developed to increase the use of anthocyanins in food technology, as well as their stability and bioavailability (Zuidam & Nedovic, 2010; Popović *et al*., 2019; Milinčić *et al*., 2019; Milinčić *et al*., 2022b).

This review manuscript aims to consolidate all the research related to grape anthocyanins in several subsections, which address the 1) behaviour of anthocyanins during physiological processes in grapevine, 2) presence of anthocyanins in different international and indigenous black grape varieties, 3) biochemical transformations of anthocyanins during the winemaking process and wine aging, 4) effect of anthocyanins on wine sensory properties, 5) valorisation of anthocyanins in winemaking waste and further applications in the food industry, and 6) health benefits of anthocyanins and *in vivo/ in vitro* transformation after their consumption.

OVERVIEW AND CHEMISTRY OF ANTHOCYANINS

Anthocyanins are the most important group of water-soluble plant pigments. Plant pigments have different roles, such as attracting pollinators and fruit dispersers, tracking the time of the day and photoprotection. In epidermal plant cells, anthocyanins are accumulated in vacuoles (Li *et al*., 2021; Crang *et al*., 2018). The anatomy, morphology and structure of the berries and clusters are key parameters in ampelography for grapevine variety distinction. The development and composition of mature berries and anthocyanin transformation is mostly genetically influenced, but environmental conditions may also have an influence (Ribéreau-Gayon *et al*., 2006).

In chemical and biochemical terms, anthocyanins are bioactive compounds belonging to polyphenols, and more specifically to a subclass of secondary metabolites known as flavonoids (Li *et al*., 2021). Anthocyanins have amphoteric properties due to their structure. They change colour with a change in pH of the medium. The flavylium cation consists of two benzene rings (A, B) connected by an unsaturated cationic oxygenated heterocycle (C), which originates from the 2-phenyl-benzopyrylium nucleus, thus giving anthocyanins amphoteric properties (Ribéreau-Gayon *et al*., 2006). Anthocyanins exist in many different forms, which affect their colour and stability. Glycosylation of anthocyanidins usually occurs at the C_3 position of the 2-phenyl-benzopyrylium nucleus (C), giving 3-monoglucoside. In the case of glycosylation with the second sugar, it is mostly a 5-hydroxyl position. The most common sugar is glucose, but there can also be other monosaccharides, such as galactose, arabinose and xylose (Vermerris & Nicholson, 2006). Furthermore, acylation also increases anthocyanin stability and occurs at the C_6 position of the sugar moieties by esterification with acetic, *p*-coumaric and caffeic acids (Moreno-Arribas & Polo, 2009).

1. Anthocyanins-biosynthesis

Anthocyanins are synthesised *via* the flavonoid pathways (He *et al*., 2010), encoded by two groups of genes: structural and regulatory. The biosynthesis of anthocyanins is intersected by many different products that act as precursors for other related compounds, involving a considerable number of enzymes (Ivanova *et al*., 2011b) [Figure 1].

Enzymes that are responsible for anthocyanin biosynthesis are encoded by structural genes (Yang *et al.*, 2023). Regulatory genes, also known as transcription factors, control the expression of structural genes, regulating the synthesis of anthocyanins (Holton & Cornish, 1995; Moreno-Arribas & Polo, 2009). Anthocyanin synthesis occurs during the phenological ripening phase, and is controlled by the VvMYBA1 anthocyanin biosynthesis transcription factor, which controls the expression of anthocyanin-specific biosynthetic gene 3-O-glucosyltransferase [UFGT] (Cutanda-Perez *et al.*, 2009). Anthocyanin accumulation occurs in most cases after veraison, but recent research has shown that it depends largely on the grapevine variety (Wang *et al.*, 2024). Other than genetic factors, environmental factors, such as low temperature and light, also affect gene expression during anthocyanin biosynthesis (Azuma, 2018). However, some research has shown that anthocyanin biosynthesis may not be dependent on light, since, in some varieties, flesh coloration occured after skin coloration (Lu *et al.*, 2023). Recent studies have given new insights into the metabolic pathway and biosynthesis of anthocyanins, and the genes involved. Some have suggested that the pathways of anthocyanin components have large effects on different levels of grape berry development (Zia ul Haq *et al.*, 2016). This implies that some levels of development of the grape berry may, to a greater or lesser extent, depend on anthocyanin precursor compounds and the genes and enzymes responsible for their biosynthesis. Regarding ‘teinturiers’, these varieties have shown a high tendency to direct the methylation of cyanidin but a low readiness for its hydroxylation (Papoušková *et al.*, 2011). Furthermore, it has recently been proven that anthocyanin biosynthesis in grape flesh is independent of anthocyanin biosynthesis in the skin (Lu *et al.*, 2023). These investigations were carried out on new teinturier varieties, such as ‘ZhongShan-HongYu’ (Yang *et al.*, 2023), ‘Mio Red’ (Lu *et al.*, 2023) and the medicinal *Vitis vinifera* L. variety ‘SuoSuo’ (Wang *et al.*, 2023).

Immediately after synthesis, the aglycone forms of anthocyanins, anthocyanidins (Figure 2A), are unstable and undergo modifications, such as glycosylation, methylation and acylation (He *et al.*, 2010). Glycosylation increases the hydrophilicity and stability of anthocyanidins, resulting in their transformation into anthocyanins. In *Vitis vinifera* L. varieties, O-glycosylated anthocyanins are only present at the C3 position, with methylation of the hydroxyl groups occuring at C3’ or both C3’ and C5’ on the B rings of the anthocyanins (Grotewold, 2006) [Figure 2B]. Acylation is a modification that occurs on the C6’’ positions of the

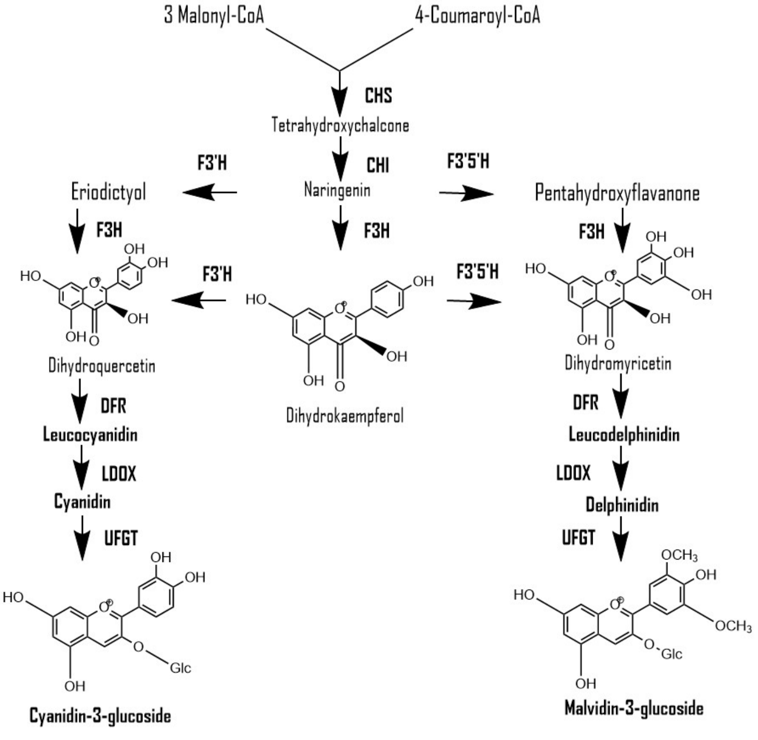

FIGURE 1. Biosynthesis pathway of anthocyanins in red grapes.

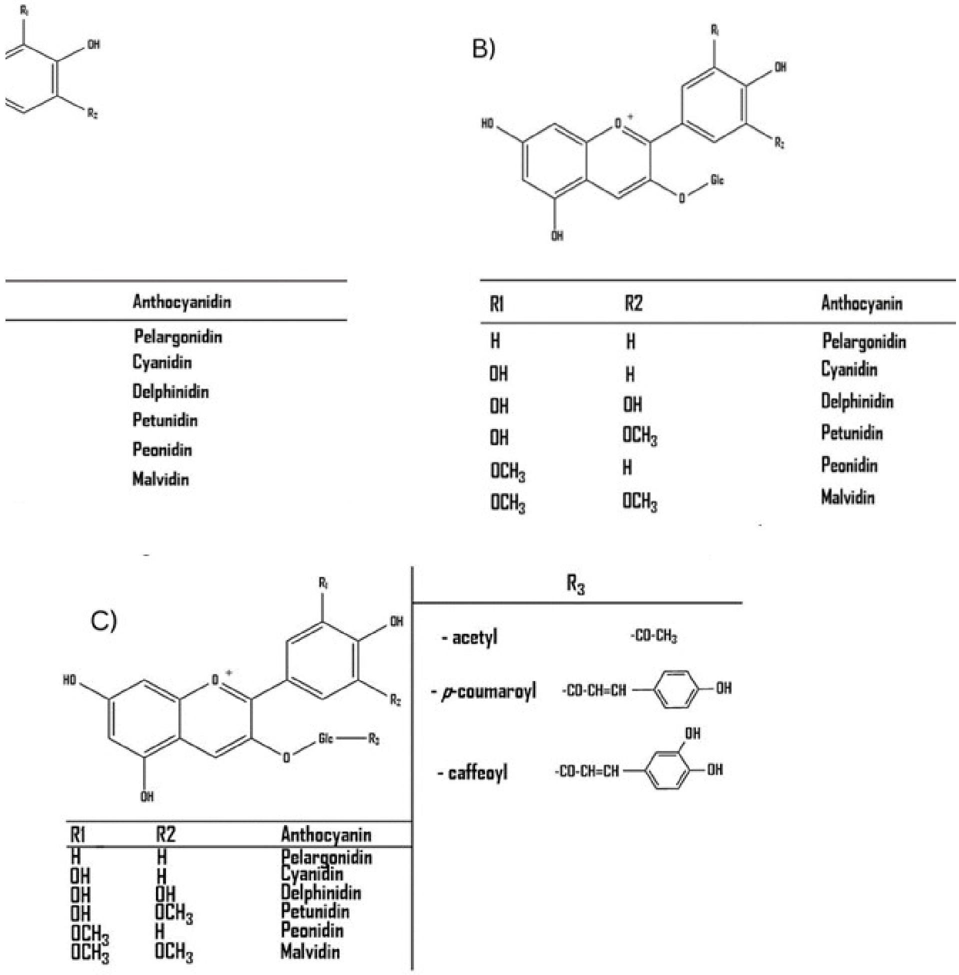

FIGURE 2. Structural formulas of A) Anthocyanidins, B) Anthocyanins, and C) Acylated anthocyanins.

glycosyl groups, involving the addition of the aromatic and/or aliphatic group (He *et al.*, 2010; Holton & Cornish, 1995; Grotewold, 2006) [Figure 2C]. All these modifications increase the stability of anthocyanins, which is particularly important during intracellular transport. Because anthocyanins are unstable in the cytosol, this is where modifications mostly occur (Wang *et al.*, 2024).

The biosynthesis of anthocyanins occurs in the endoplasmic reticulum (Alfenito *et al*., 1998), after which they are transported to the vacuole (Grotewold, 2004). Two types of anthocyanin transport in the cells take place: ligandin transport (LT) and vesicular transport [VT] (Zhao & Dixon, 2010). The sequestration of anthocyanins inside the vacuoles is the last step of anthocyanin accumulation, where their colour will depend not only on their molecular structure but also on the vacuolar pH and the concentration of metal ions and co-pigments (Grotewold, 2006). These kinds of insights provide valuable information regarding the molecular structure and bioavailability of anthocyanins.

2. Anthocyanins in red grapes

The mature red grape berry has a complex anatomical structure characterised by distinct tissues and structures within the berry and the cluster. The outermost layer of the berry, known as the exocarp or skin, is composed of multiple layers of epidermal cells rich in anthocyanins (Figure 3A). Under the exocarp is mesocarp or flesh, comprising parenchyma cells that store sugars, organic acids and water, which contribute to the berry's juiciness and flavour. The berries of teinturier varieties are morphologically different to other varieties, as their flesh is red and their mesocarp contains anthocyanins (Kőrösi *et al*., 2022) [Figure 3B].

The exact role of anthocyanins in grapevine is still not clear (Roubelakis-Angelakis, 2001). Other than dispersing seed and being potential UV-protectants, red and black grape anthocyanins are responsible for the colour of the wine, which, their first most important role. The concentration, composition and distribution of anthocyanins and their derivatives significantly vary among red grape varieties of *Vitis vinifera* L. Moreover, these characteristics also differ among other grape north American and Asian species, including *Vitis labrusca*, *Vitis rotundifolia* and *Vitis amurensis*, and hybrid varieties resulting from crossing of *Vitis vinifera* L. cultivars with other species (Teissedre, 2018).

Much research has been conducted to identify and quantify the polyphenolic compounds of red grape varieties, including both vinifera and non-vinifera varieties. Important

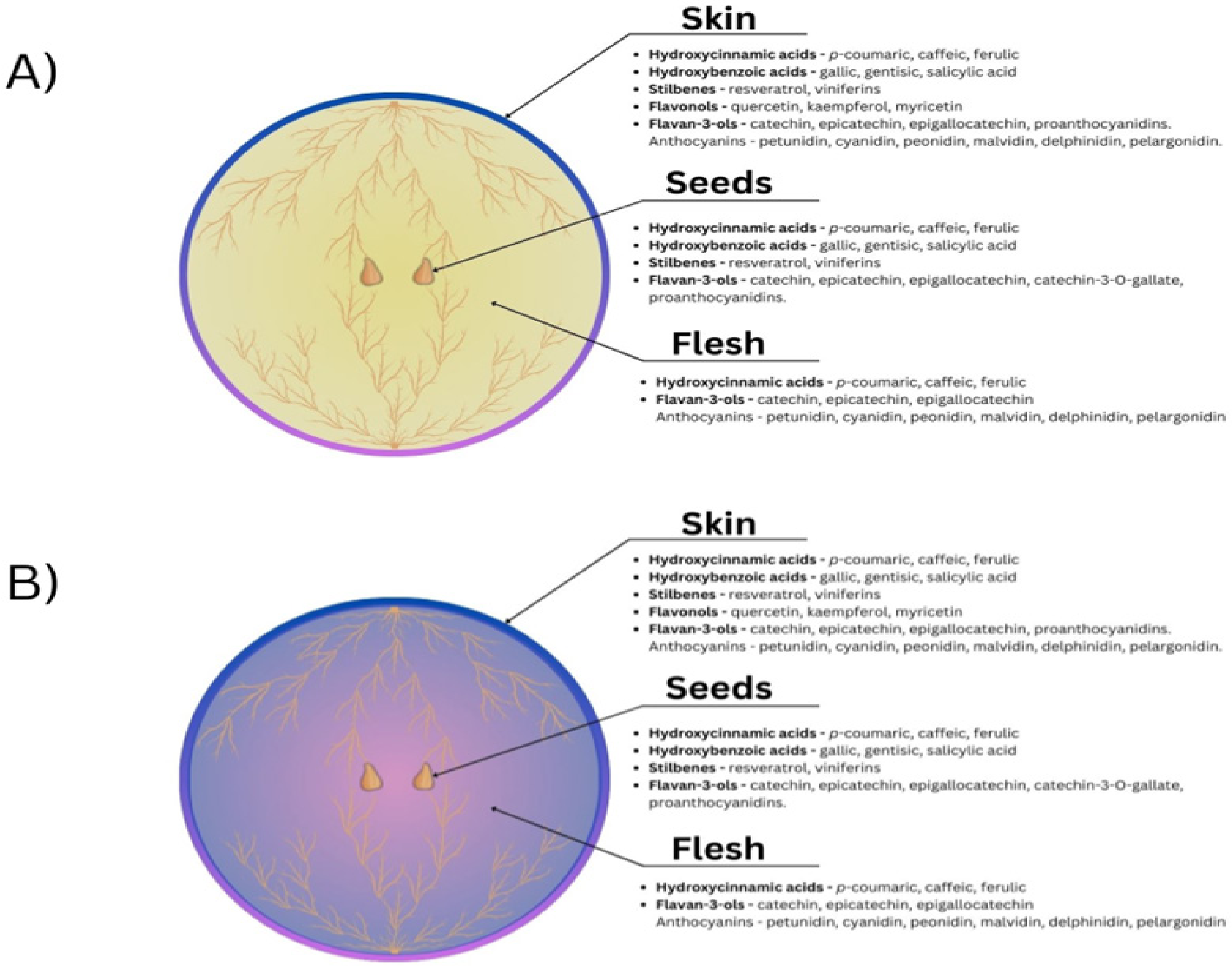

FIGURE 3. Anatomy of the red grapevine berry: A) varieties without anthocyanins in the mesocarp, and B) 'teinturier' varieties.

differences in their composition regarding anthocyanins have been reported, and they also vary in concentration. According to Lamikanra (1989), *Vitis vinifera* L. varieties contain mainly acylated and non-acylated anthocyanins, *Vitis rotundifolia* and its hybrids have non-acylated 3,5-*O*-di-glucosides, and *Vitis labrusca* cultivars have a mixture of acylated and non-acylated mono- and di-glucosides of anthocyanidins, as previously reported by many studies (Ehrhardt *et al*., 2014; Zhu *et al*., 2012; Wojdyło *et al*., 2018; Tassoni *et al*., 2019; Milinčić *et al*., 2021a; Forino *et al*., 2022; Tampaktsi *et al*., 2023; Milinčić *et al*., 2023b).

The most analysed anthocyanin profiles are those of the French international varieties 'Cabernet-Sauvignon' and 'Merlot' (Chira *et al*., 2011; Chira *et al*., 2012; Zhao *et al*., 2023), which have been investigated and compared in every winegrowing region worldwide. Many results have shown that 'Cabernet-Sauvignon' and 'Merlot' are predominant in malvidin-3-*O*-glucoside, which show potential for chemotaxonomic purposes (Garcia-Beneytez *et al*., 2003). In addition, they are rich in acetylglucosides, with a 1.5- to 3-fold higher concentration of acetyl anthocyanins in 'Cabernet-Sauvignon' than in 'Merlot' (Lorrain *et al*., 2011). Cinnamoyl derivatives (*p*-coumaroylglucosides and caffeoylglucosides) have also been identified in these two varieties (Costa *et al*., 2014). Other *V. vinifera* L. varieties have been investigated. Garcia-Beneytez *et al*. (2003) worked on the different red grapevine varieties mainly grown in Spain, namely alicante Bouschet, Bobal, Carinena, Crujidera, Garnacha Peluda, Monastrell, Moristel, Morrastel-Bouschet, petit Bouschet, Prieto Picudo, Tempranillo and Vitidillo. HPLC-MS identification of anthocyanins in grape extracts has been done and the presence of 3-*O*-glucoside derivatives, acetyl glucosides, and cinnamoyl derivatives of delphinidin, cyanidin, petunidin, peonidin, and malvidin has been confirmed. For most of these varieties, malvidin-3-*O*-glucoside was the major anthocyanin, except for the teinturier varieties alicante Bouschet, Morrastel Bouschet and petit Bouschet, in which the main anthocyanin was peonidin-3-*O*-glucoside, which is specific to teinturier cultivars. Portuguese varieties showed similar results in the research done by Costa *et al*. (2014). They investigated Portuguese *V. vinifera* L. varieties (Camarate, Monvedro, Moreto Boal, Negro Mole, Negro Mouro, Alfrocheiro, Alvarilhao, Bastardo, Cornifesto, Jean, Malvasia Petra, Rufete, Sausao, Tinta Amarela, Tinta Barca, Tinta Barroca, Tinta Miuda and Tinto Cao) in comparison to some of the international varieties (Gewurztraminer, Aramon, Cabernet franc, Carignan noir, Gamay and Grenache). The main individual anthocyanin in the skin composition of these varieties was malvidin-3-*O*-glucoside, followed by the cinnamoyl derivative, malvidin-3-*p*-coumaroyl glucoside. These slight differences in composition and concentration of the most predominant individual anthocyanins in grape skin of *V. vinifera* L. cultivars are thought to be genetically determined, which has been confirmed by other authors (Obreque-Slier *et al*., 2013; Perez-Navarro *et al*., 2019; Guerrero *et al*., 2009; Arozarena *et al*., 2002; Lingua *et al*., 2016; Sikuten *et al*., 2021; Ivanova *et al*., 2011a; Šuković *et al*., 2020; Đorđević *et al*., 2018; Milinčić *et al*., 2021a; Ćirković *et al*., 2022; Lakićević *et al*., 2022; Milinčić *et al*., 2023b). Table 1 lists the phenolic compounds found in different grape skins and their concentrations in mg/kg dry matter (DM).

Non-vinifera cultivars (hybrids or PIWI varieties), which are resistant to most grapevine pathogenic fungi and phylloxera, represent the future for sustainable viticulture and winemaking. They are known for having different phenolic compositions to the *V. vinifera* L. varieties. The potential significance of this fact is reflected in the need to increase the stability of the colour of grape juice and wine, due to the increasing industrial demand for natural colorants. Research carried out to date has resulted in the detection and identification of anthocyanins that are not specific to *V. vinifera* L., namely anthocyanidin-3,5-diglucosides (Lamikanra, 1989). Although some researchers have detected anthocyanidin-3,5-diglucosides in certain *V. vinifera* L. varieties (Pantelić *et al*., 2016; Perez-Navarro *et al*., 2019), they have been found to be different to those identified in non-vinifera cultivars and present in non-measurable concentrations. Through recent research on the different *Vitis amurensis* cultivars and hybrids, Zhu *et al*. (2021) discovered a new type of anthocyanin, which is believed to be 3,5,7-*O*-triglucosides. They also report the results of the anthocyanin composition of *V. amurensis* to show a high content of diglucoside anthocyanins and a low content of acylated anthocyanins, which is consistent with previous research (Zhao *et al*., 2010). For further valorisation of the potential usage of non-vinifera cultivars in winemaking, and their contribution to human health, the red grape varieties ‘Rondo,’ ‘Regent,’ and ‘Cabernet-Cortis’ were investigated by different authors. Wojdylo *et al*. (2018) detected in ‘Rondo’ and ‘Regent’ the presence of 3,5-diglucosides of delphinidin, cyanidin, petunidin, peonidin and malvidin. Meanwhile, Ehrhardt *et al*. (2014) reported the presence of pelargonidin-3,5-diglucoside as well in both ‘Cabernet-Cortis’ and ‘Regent.’, which is mostly found in traces, and could therefore be an important distinguishing marker of the anthocyanin profiles of PIWIs. On a technological level, 3,5-diglucosides are largely preferable in winemaking and superior to monoglucosides, since they show greater stability to heat and light (Lamikanra, 1989); therefore, hybrids are quickly finding their place in grape juice production and winemaking.

ANTHOCYANINS IN RED WINE

Red winemaking is a complex process that involves the transformation of red grapes into red wine through a series of biochemical reactions. The production of red wine can be divided into several key stages, including harvesting and crushing the grapes, maceration, fermentation, aging and bottling. Each step contributes to the development of the wine’s colour, flavour and aroma. The most vital step is maceration, involving the contact of grape skins, seeds and pulp with the fermenting juice for a certain amount of time. This contact facilitates the extraction of anthocyanins, tannins and flavour compounds from the grape solids into the wine. The duration of maceration can vary depending on winemaker preference and grape variety. Anthocyanins are released into the wine, contributing to its characteristic red hue, while tannins affect its structure, astringency and aging potential (Razungles, 2022). As a result of fermentation, maceration, aging, and bottling, the wine develops its characteristic colour, flavour and aroma profile. The interaction between grape solids, phenolic compounds (anthocyanins), yeast and various winemaking techniques contributes to the complexity and diversity of red wines which influence their phenolic composition (Table 1). The anthocyanin composition of red wine is subject to various factors, primarily determined by the concentration and specific content of anthocyanins present in grape varieties. However, additional factors, such as environmental conditions, and viticultural and agrotechnical practices employed in the vineyard, can also impact the anthocyanin profile of red wine (Morgani *et al*., 2023; Haselgrove *et al*., 2000; Sivilotti *et al*., 2020; Kyraleou *et al*., 2016a; Ju *et al*., 2021).

1. Effect of maceration time, skin contact, extraction methods and fermentation temperature on anthocyanins and their transformation

During winemaking, anthocyanins undergo different biochemical processes and transformations, changing their chemical and physio-chemical properties (Ribéreau-Gayon *et al*., 2006). The extraction of anthocyanins and phenolic and non-phenolic compounds, as well as colour stability, depend on maceration time and fermentation conditions (Ribéreau-Gayon *et al*., 2006). Maceration, as an extraction process, is a key step in red wine production, because it directly influences anthocyanin content. For this reason, different maceration lengths and techniques have been studied. Despite the importance of maceration as a step in red winemaking, there is a constant need to develop new methods to improve the sustainability and cost-effectiveness of winemaking. Reducing maceration time while ensuring appropriate wine quality would save energy use and reduce financial losses. Previous research on maceration length has shown that it influences the colour, and chemical and sensory properties of wines, since colour and anthocyanin concentration decrease with maceration length (Gil *et al*., 2012). It has been recorded in the literature anthocyanin increases to its maximum concentration in the first five or six days of maceration (Ribéreau-Gayon, 1982).

TABLE 1. List of phenolic compounds found in different wines of different ages and their concentrations (in mg/L), as well as anthocyanins (% of total monomeric anthocyanins).

Phenolic compounds		Concentration	Wine age (months)	Wine variety	Winemaking technique	Source
Flavan-3-ol monomers		102.65–242.90	24	Syrah	Conventional winemaking	Garcia *et al.*, 2024
		130.9	3	Teran	Cold pre-fermentative maceration	Lukić *et al.*, 2017
		185.3			Pre-fermentative heating followed by traditional maceration	
		192.2			Post-fermentative maceration	
Flavan-3-ol dimers		75.29–156.90	24	Syrah	Conventional winemaking	Garcia *et al.*, 2024
		123.8	3	Teran	Cold pre-fermentative maceration	Lukić *et al.*, 2017
		157.3			Pre-fermentative heating followed by traditional maceration	
		163.1			Post-fermentative maceration	
Pyranoanthocyanins (vitisin A and B)		0.27–1.1	24	Syrah	Conventional winemaking	Garcia *et al.*, 2024
		Concentration (% of total anthocyanins)				
Anthocyanins	Glucosides	64.4–72.3	24	Syrah	Conventional winemaking	Garcia *et al.*, 2024
		83.13	3	Teran	Cold pre-fermentative maceration	Lukić *et al.*, 2017
		82.95			Pre-fermentative heating followed by traditional maceration	
		85.81			Post-fermentative maceration	
	Acetyl-glucosides	17.4–24.1	24	Syrah	Conventional winemaking	Garcia *et al.*, 2024
		9.26	3	Teran	Cold pre-fermentative maceration	Lukić *et al.*, 2017
		9.47			Pre-fermentative heating followed by traditional maceration	
		6.11			Post-fermentative maceration	
	p-coumaroyl glucosides	9.05–14.4	24	Syrah	Conventional winemaking	Garcia *et al.*, 2024
		7.67	3	Teran	Cold pre-fermentative maceration	Lukić *et al.*, 2017
		7.66			Pre-fermentative heating followed by traditional maceration	
		8.11			Post-fermentative maceration	

As far as we know, to our knowledge, the kinetics of anthocyanin extraction and its result depend mostly on the berry skin properties, content and anthocyanin concentration of a given variety (Otteneder *et al*., 2004). Numerous studies have reported an extended extraction duration to result in a decreased total anthocyanin content (Gil *et al*., 2012; Sipiora *et al*., 1998). Another has confirmed that maximum values for colour parameters and anthocyanin concentrations are obtained in wine that has been subjected to maceration for a duration of three to six days (Jagatić Korenika *et al*., 2023). Opposite results were found by Alencar *et al*. (2017), who investigated the effect of maceration time on anthocyanin extraction in Syrah must and wine and showed that the extractions increased until the 20th day. The authors explained this phenomenon as being due to a markedly higher concentration of anthocyanins in the investigated Syrah grape skin because of its good adaptation to the agroecological conditions of the northeastern region of Brazil. The effectiveness of anthocyanin extraction during maceration, phenolic composition and colour characteristics might all be influenced by other factors, such as grape maturity, presence of seeds and grape solids, addition of oak and tannin, fermentation temperature or the implementation of different chemical and physical agents. Research has been conducted to ascertain new ways of speeding up extraction, of inducing better co-pigmentation and complexation of anthocyanins with other compounds, and of increasing colour stability, all while enhancing the sustainability of red winemaking. In this context, wines from very mature and ripe grapes contain a higher percentage of skin proanthocyanidins, and the extraction process is shorter (Gil *et al*., 2012). Early seed removal caused a decrease in monomeric anthocyanin concentration, as well as gallic acid and flavan-3-ols (Jagatić Korenika *et al*., 2023). The application of high hydrostatic pressure (HHP) at moderate pressure combined with oak chip maceration enhances the phenolic content and colour intensity of wine (Tao *et al*., 2016). Giacosa *et al*. (2023) investigated seed impact on anthocyanin extraction kinetic of four Italian varieties, ‘Aglianico’, ‘Nebbiolo’, ‘Primitivo’, and ‘Sangiovese’. The results showed that the presence of seeds increased the polymerization rate, which is important for obtaining colour stability in mature wines. Concerning maceration and fermentation temperature, results in the literature differ in terms of temperature regimes and length of exposure to given temperatures. A study in California on three clones of Pinot noir showed that higher fermentation temperature (25 °C for 14 days) resulted in better anthocyanin extraction and higher anthocyanin concentrations (Reynolds *et al*., 2022). The authors hypothesise that raising the fermentation temperature augments the extraction of phenolic compounds, and increases tannin extraction and the formation of polymeric pigments. These results are consistent with previous findings. Conversely, cold maceration has been shown through numerous studies to result in a decrease in anthocyanin concentration (Leong *et al*., 2020; Kuchen *et al*., 2018; Casassa *et al*., 2019).

Techniques such as carbonic maceration, thermovinification, cold maceration (cryomaceration), pulsed electric field (PEF) treatment, microwave treatment, ohmic heating and enzymatic treatment are among the winemaking methods that have been investigated (Tong *et al*., 2023; Portu *et al*., 2023; Zhang *et al*., 2019; Pace *et al*., 2014; Aleixandre-Tudo & Du Toit, 2018; Bianchi *et al*., 2023; Fanzone *et al*., 2022; López-Giral *et al*., 2023; Gordillo *et al*., 2021; Maza *et al*., 2020; Wojdyło *et al*., 2021; Río Segade *et al*., 2015; Zhang *et al*., 2021).

Being a water-soluble pigment, the extraction of anthocyanin occurs very quickly; meanwhile, the extraction of the other phenolic compounds starts with increased alcohol content during fermentation (Bautista-Ortín *et al*., 2004). It has been previously reported that the concentration and content of anthocyanins extracted during maceration primarily depend on the characteristics of the grape variety. However, for other phenolic compounds and complex compounds co-pigmented with anthocyanins, the extraction method during winemaking plays a major role. It has been proven that different pre-treatment maceration techniques affect anthocyanin content (Wojdyło *et al*., 2021).

Carbonic maceration is a winemaking process during which whole grape clusters are fermented in an anaerobic environment saturated with carbon dioxide. This technique initiates intracellular fermentation within the intact grapes, leading to unique biochemical transformations that influence the wine’s phenolic composition, aroma and flavour profile. Multiple studies on carbonic maceration have consistently demonstrated that this winemaking technique leads to a decrease in the concentration of individual anthocyanins, mostly monoglucosides and total phenols. Despite the reduced content of individual anthocyanins, research on carbonic maceration has indicated an increased potential for polymerization, which gives wines a higher hue (Chinnici *et al*., 2009). Gonzalez-Arezana *et al*. (2020) have confirmed this by comparing the aromatic and phenolic composition of 84 commercial Tempranillo wines produced *via* carbonic maceration with wines produced by the standard (traditional) method of destemming and crushing. They reported the wines obtained *via* carbonic maceration to have higher colour intensity due to higher rates of ionization and polymerization. Additionally, the authors found coumaroyl derivatives and the vitisins A and B to be in higher concentrations in the wines made by carbonic maceration, which has also been confirmed by other researchers (Chinnici *et al*., 2009; Portu *et al.*, 2023). Carbonic maceration results in wines with a lower average content in total phenolics, anthocyanins and resveratrol, but a higher concentration of catechins, as well as oligomeric and polymeric proanthocyanidins; therefore, the wines are less saturated but more brighter in colour due to higher chroma values (Zhang *et al*., 2019). Wines made *via* carbonic maceration have greater colour intensity, more reddish hues and a high content in flavanols, hydroxycinnamic acids, ethyl-bridged anthocyanin isomers because of ionization of the pigments (Shmigelskaya *et al*., 2021).

Thermovinification is a winemaking process that involves heating grape must to a temperature typically lower than 85 °C before fermentation for a certain controlled period of time. This thermal treatment enhances the extraction of phenolic compounds, such as anthocyanins and tannins, from the grape skins and seeds, and it is thought to expeditiously result in wines with intensified colour, improved stability, and modified tannin structure. Research has been conducted to determine the validity of this theory. As a time- and temperature-dependent maceration method, thermomaceration has demonstrated its suitability for achieving higher concentrations of phenolic compounds compared to other methods (Aguilar *et al*., 2016). However, in their review article, Maza *et al*. (2019) stated that thermovinification is associated with a range of issues stemming from the heating of the grapes, adversely affecting wine quality. Thermomaceration has shown different results depending on the grape variety. Some researchers have reported the use of thermal maceration to improve anthocyanin extraction, especially in Pinot noir (Girard *et al*., 1997). Ntuli *et al*. (2023) investigated the impact of flash détente (FD) treatment on the chemical composition, colour stability and sensory profile of Merlot wines. The technique involved heating must to 85 °C, and the vacuum chamber was maintained at –0.94 bar. The temperature dropped to 32 °C, when the must entered the vacuum chamber. Results showed that the wine had significantly higher concentrations of caftaric acid, malvidin-3-*O*-glucoside and quercetin glycoside. While high temperatures caused the rapid pre-fermentation extraction of anthocyanins into must, the authors found that approximately 40 % of the colour was lost during fermentation. They also suggested that FD can be used to improve the body and astringency of the wine by extracting the polysaccharides and proanthocyanidins.

Ohmic heating is a relatively new pre-fermentative maceration technique based on the application of an electric field. Also known as the Moderate Electric Fields method, it induces electroporation of plant cell membranes. Ohmic heating generates an electric field of less than 1 kV/cm and the little research that has been conducted to date has shown it to be a promising method for shortening the maceration period and thereby conserving energy (Junqua *et al*., 2021). The aforementioned authors report that, in comparison to conventional heating and no treatment of Aglianico and Barbera musts, ohmic heating resulted in a phenolic compound content twice as high as that before treatment. This indicates that the pre-fermentation process could be significantly shortened and simplified. The same research demonstrated that the total polyphenolic content in the finished wines was 17 % higher than in conventionally heated samples and 30 % higher than in untreated samples. Research conducted by Pereira *et al*. (2020) yielded similar results, postulating ohmic heating to be an environmentally sustainable technology for food processing. Their investigation of aqueous extracts from grape skin winemaking residues of the 'Vinho Verde' variety demonstrated that, irrespective of the temperature applied, ohmic heating increases the concentration of total phenolic compounds, soluble solids and colour intensity. Notably, total anthocyanin concentration increased from 756 to 1349 µg/g, primarily comprising malvidin-3-*O*-glucoside. These authors consider the internal heating generated by ohmic heating to be advantageous, as it means that chemical solvents are not required, the treatment duration and water usage are reduced, and energy consumption is lower than during thermovinification.

Pulsed electric field (PEF) winemaking is a non-thermal processing technique that involves the application of short bursts of high-voltage electric fields to grape must. This process disrupts the cell membranes through electroporation, enhancing the extraction of intracellular compounds, such as phenolics and anthocyanins. Studies have shown that PEF treatment improves juice yield, accelerates maceration and preserves the sensory and nutritional qualities of wine, providing an energy-efficient alternative to conventional thermal methods (López *et al*., 2008; López-Giral *et al*., 2023). El Darra *et al*. (2016) has reported a 56 % increase in colour intensity of Cabernet-Sauvignon wine treated by PEF compared to that treated using other methods (thermovinification and enzymatic treatment). Additionally, total phenolic content was 18 % higher and total flavonol content 48 % higher. They also suggest that the higher intensity and difference in colour composition between the control and pretreated freshly-fermented model wines are not solely due to a higher content of residual native anthocyanins but also to co-pigmentation and the formation of derived pigments. Leong *et al*. (2020) investigated the effect of a continuous PEF system operated at high-intensity electric field strengths exceeding 30 kV/cm during a 4-day cold maceration of Merlot. This study is the first in the literature to apply such high-intensity electric fields. The results indicate that malvidin derivatives were the most significant anthocyanins to contribute to changes in colour intensity. Furthermore, it was noted that PEF at high-intensity electric field strengths and under continuous operation caused sufficient damage to grape cells, leading to the release of various types of anthocyanins. This technique could be particularly useful for the maceration of grape varieties with impermeable skins.

The use of the microwave technique in winemaking involves the application of microwave radiation to grape must or wine. This method generates heat through the dielectric heating of water molecules, leading to rapid and uniform heating. The microwave technique enhances the extraction of phenolic compounds and other desirable constituents from grape skins, improves colour stability, and accelerates the maceration process. It is a time-efficient and energy-saving alternative to conventional thermal methods, with the potential benefits of enhancing the sensory attributes and quality of the final wine. Carew *et al*. (2014) studied the influence of microwave maceration on phenolic extraction and fermentation kinetics of Pinot Noir in combination with early pressing. They reported the microwave pre-treatment to show significant cellular and phenolic integrity degradation and to accelerate the anthocyanin extraction. The results indicate that this technique could be an alternative solution to fermenting Pinot noir for seven days. After six months, the microwave wine had a higher anthocyanin content, which allowed colour to develop. Furthermore, other authors have reported the physical force employed by this method to cause cell wall disruption, resulting in faster extraction kinetics. Additionally, this method can be advantageous when extracting acetylated anthocyanins, as they can become trapped within the matrix or form hydrogen bonds with polysaccharides (Sommer & Cohen, 2018). The same research found similar results for the application of the ultrasound technique. The use of ultrasound technique in winemaking involves applying high-frequency sound waves to grape must or wine. This process induces cavitation, which creates microbubbles that collapse and generate localized high temperatures and pressures. These effects enhance the extraction of phenolic compounds, improve maceration efficiency and facilitate the homogenization of the wine. Like the microwave treatment, ultrasound treatment can reduce processing times, improve the extraction of desirable compounds and preserve the sensory and nutritional qualities of the wine, making it an efficient and environmentally friendly alternative to traditional winemaking methods. Bautista-Ortín *et al*. (2017) investigated the application of high-power ultrasound in Monastrell red winemaking. The study examined maceration periods of 3, 6, and 8 days, and compared the results to a control vinification process involving 8 days of skin maceration without pre-treatment: in the initial must, the sonicated samples exhibited significantly higher levels of total phenols, total anthocyanins and colour intensity. These elevated levels persisted throughout the entire winemaking process, with the sample subjected to just three days of skin contact showing a higher concentration of anthocyanins than the control. After fermentation, the sonicated sample that underwent 3-day maceration maintained the highest amounts of total and polymeric anthocyanins and the highest colour intensity. Regarding the influence of sonication on anthocyanin composition, the anthocyanins present in the highest concentrations initially were dihydroxylated, cyanidin-3-*O*-glucoside and peonidin-3-*O*-glucoside. Following skin contact and fermentation, malvidin-3-*O*-glucoside was found in the greatest quantity. The authors reported that high-power ultrasound treatment was favourable for the extraction of skin tannins, as evidenced by the high concentrations of total tannins, the mean degree of polymerization, the percentage of galloylation and the concentration of epigallocatechin. This has been was corroborated by recent studies, which investigated the effects of high-power ultrasound on the colour and aroma of Monastrell rosé wines: the sonicated wines exhibited higher colour intensity and increased total polyphenol and anthocyanin content (Labrador Fernandez *et al*., 2023).

The use of high hydrostatic pressure (HHP) in winemaking involves subjecting grape must or wine to extremely high pressures, typically ranging from 100 to 600 MPa, in a liquid medium. This non-thermal technique deactivates spoilage microorganisms and enzymes, enhances the extraction of phenolic compounds and preserves the sensory and nutritional qualities of the wine. HHP treatment can improve wine stability, colour and the flavour profile while maintaining the integrity of heat-sensitive compounds, providing an innovative and efficient alternative to traditional winemaking processes. Given its potential applications in winemaking, the high hydrostatic pressure (HHP) technique has been investigated to improve winemaking sustainably. Tao *et al*. (2012) conducted a study to investigate the influence of high hydrostatic pressure (HHP) on the physicochemical and sensorial properties of the 2010 vintage of the Nero d'Avola Syrah red wine. The treatment involved subjecting the wine to 650 MPa for durations of 0.25, 0.5, 1 and 2 hours. The results showed a shift in the equilibrium of chemical reactions within the wine, with an enhancement of its organoleptic properties and acceleration of the aging process. In terms of phenolic composition, the treatment resulted in a decrease in content of total phenols, total anthocyanins, tartaric esters, flavonols and tannins, mirroring changes that occur during natural aging. Regarding anthocyanin composition, the levels of monomeric and polymerized anthocyanins decreased post-pressurization, while the level of co-pigmented anthocyanins showed a slight increase, likely due to condensation reactions induced by HHP. Another study demonstrated the influence of high hydrostatic pressure (HHP) processing combined with oak chip maceration on the physicochemical and sensory properties of young red Sangiovese and Merlot blend (Tao *et al*., 2016). The results showed that young wine subjected to 250 MPa, 450 MPa and 650 MPa for 45 min and macerated with oak chips had higher total phenolics, tartaric esters and flavonols in comparison to the untreated control wine. The concentration of total monomeric and polymeric anthocyanins increased, probably due to HHP influence on potential desorption of anthocyanins from the oak chips, and the tannic compounds extracted from the oak chips reacted with anthocyanins to form new polymeric compounds. This technique is noted as potentially beneficial for both red wine quality and the costs associated with its production, since it increases colour stability by influencing the formation of polymeric pigments and accelerates wine aging without the need for the use of oak barrels. Other researchers have also reported that HHP can influence long-term red wine physicochemical and sensorial characteristics, increasing the condensation reactions of phenolics (Santos *et al*., 2013; Christofi *et al*., 2020).

Enzymatic treatment in red winemaking involves the adding specific enzymes, such as pectinases, cellulases and hemicellulases, to the grape must. These enzymes catalyze the breakdown of complex polysaccharides in the grape cell walls, facilitating the release of phenolic compounds, anthocyanins and other desirable constituents. This process enhances colour extraction, improves juice yield, accelerates clarification and stabilizes the wine. Enzymatic treatment is a controlled and efficient method for optimizing the maceration process, improving sensory attributes, and increasing the overall quality of the red wine. Enzymatic maceration depends highly on choice of enzymes (Wang *et al*., 2016) and the thickness and structure of the berry skin of the 'Syrah' and 'Cabernet-Sauvignon' grape (Apolinar-Valiente *et al*., 2016). Scientific research has demonstrated that the addition of commercial enzymes, including polygalacturonase and cellulase, does not increase the concentration of anthocyanins relative to other winemaking techniques. In the comparative study of enzymatic maceration with thermomaceration in 'Lachryma

Christi' and 'País' winemaking, thermomaceration resulted in the extraction of higher concentrations of phenolic compounds. The low anthocyanin content after the enzymatic treatment might be due to the formation of an enzyme polyphenol complex as a result of hydrophobic interactions (Aguilar *et al*., 2016; Wang *et al*., 2016). However, it is noted that the addition of pectolytic enzymes might influence the greater concentration of iron, calcium and magnesium in wines (Soto Vázquez *et al*., 2013).

Cryomaceration in winemaking is a cold maceration technique in which grape must is subjected to low temperatures, typically around 5-10 °C, before fermentation. This process slows down enzymatic activity and microbial growth, resulting in a prolonged extraction of aromatic compounds, phenolics and colour from the grape skins without the risk of oxidation. However. Aleixandre-Tudo and Du Toit (2017) have found that the efficiency of this method depends on the variety, maturity of the grapes, the temperature applied, the maceration length and potential combination with other techniques, such as enzyme or dry ice addition. In a comparative study of the effect of different alternative winemaking techniques on the pigment profile of red Tannat wines, Gonzalez-Neves *et al*. (2010) did not find cold pre-fermentation maceration to significantly increase anthocyanin content. The reason for these results might be the low extractability of the pigments in the Tannat grapes. Casassa *et al*. (2016) reported that a cold prefermentative soak affects colour and wine phenolics of Barbera D'asti and Malbec wine only with the addition of SO_2 of 100 mg/L. This method positively influenced colour intensity and violet hue. In their study on thermal pre-fermentative treatment of André wine, Ševcech *et al*. (2015) found that the cold soak gave the best results regarding anthocyanin concentrations.

2. Wine aging biochemical transformation and colour changes

During winemaking and aging, anthocyanins undergo different chemical reactions and transformations, being influenced by various factors (grape variety, maceration time, yeasts, winemaking technique, amount of SO_2, wine aging, fining agents and micro-oxygenation). More complex polyphenolic compounds are formed through co-pigmentation, condensation and polymerization reactions (Boulton *et al*., 2001). The compounds formed in these reactions are condensed tannin (flavan-3-ol) products, better known as polymeric pigments, and different groups of pyranoanthocyanins (vitisin A, vitisin B, vinylphenolic pyranoanthocyanins, vitisin A derivatives, and other types of pyranoanthocyanins–oxovitisins, methylpyranoanthocyanins and pyranoanthocyanin dimers). Vinlylphenolic pyranoanthocyanins include pinotins and flavanol-pyranoanthocyanins, while portisins are a distinct class of derived pigments usually found in Port wine (Waterhouse & Zhu, 2019). Numerous studies have demonstrated that these biochemical transformations affect the phenolic composition, colour intensity and hue, colour stability and sensory properties of red wine, which have been thoroughly reviewed by Qualglieri *et al*. (2017). The complexation of anthocyanins with various molecules (other anthocyanins [self-association], tannins, proteins and ions) during fermentation leads to an increase in colour intensity due to the co-pigmentation phenomenon (Moreno-Arribas & Polo, 2009). Co-pigmentation causes hyperchromic effect and bathochromic shift, leading to higher colour density and a richer purple hue of the wine (Zhang *et al*., 2022). The percentage of the contribution of intermolecular co-pigmentation to colour has been estimated to be up to 30-50 % in young red wines (Boulton *et al*., 2001), while that of monomeric anthocyanins, in the form of flavylium cation, is 30-70 % (Brouillard *et al*., 1982). Polymerized pigments are the main contributors of colour to aged wines, contributing to 35-63 % of the wine colour (Han *et al*., 2008). Many authors have used well-known CIELAB parameters to define the colour of wine, namely lightness (L^*), redness (a^*), blueness (b^*), chroma (C^*), hue angle (H^*) and ΔE^* (colour difference). Young wines are dark, with a high colour density, and they are predominantly violet-red. Han *et al*. (2008) applied principal component analysis of the relationship between CIELAB colour and monomeric anthocyanins in young Cabernet-Sauvignon wines: various monomeric anthocyanins exhibited negative correlations with the L^*, b^*, and H^* values, and positive correlations with the a* and C^* values. During wine aging the value of L^*, b^*, and H^* parameters increases due to the decrease in colour density, loss of violet hue and accumulation of tawny tones (McRae *et al*., 2012). Chromatically, the colour of red wine during wine aging changes from bright red and deep purple to pale red (Apolinar-Valiente *et al*., 2016), and thusred wine colour can be used as an indicator of age (Wang *et al*., 2023). Furthermore, it has been observed by (Zhang *et al*., 2021) that the tawny characteristics of aged wines are attributable to pyranoanthocyanins, excluding vitisin B, with a particular emphasis on pinotins. Being more stable phenolic compounds that are formed during the aging process through direct cycloaddition of malvidin and caffeic acid, pinotins maintain colour intensity and add to the complexity of wine's hue. Chromatically, they are connected to the tawny and brick-red colours of the well-aged red wines. The colour density associated with aging is closely linked to the concentration of vitisin A and flavanyl-pyranoanthocyanins (Zhang *et al*., 2021). The same group of authors noted that evolution and stability patterns differ among anthocyanin derivative classes, with pinotins as the most stable anthocyanin derivative compound, followed by flavanyl-pyranoanthocyanins, vitisin A, monomeric anthocyanin and direct anthocyanin-flavan-3-ol condensation products, and then vitisin B and anthocyanin ethyl-linked flavan-3-ols products as the least stable. They were investigating the anthocyanin derivatives and chromatic characteristics of 234 different vintage red wines (of the varieties Cabernet-Sauvignon, Syrah, Merlot, Cabernet franc, Tempranillo, Zinfandel, Pinotage, Carmenere, and Marselan) from 13 countries. Chromatic changes in wine correspond to biochemical changes, including alterations in the ratio between non-acylated and acylated anthocyanins. Acylation, a process that occurs during wine aging, significantly impacts anthocyanins–which are crucial sensory constituents of red wine–and plays an important role in the formation of pyranoanthocyanins and polymeric pigments, leading to colour changes as acylated and non-acylated anthocyanins are lost (Wang *et al*., 2023). The same authors reported that the younger wines had higher concentrations of acylated anthocyanins than non-acylated anthocyanins due to the slow degradation of acylated ones. Moreover, the decrease in both acylated and non-acylated anthocyanins was accompanied by the development of pyranoanthocyanins and polymeric pigments, with a reduction in the a^* value and an increase in the b^* and H^* values.

Generally, after fermentation, anthocyanins continue to react with other polyphenolic compounds, including the derived pigments and tannic compounds extracted from the grapes (Boulton, 2001). Each step after fermentation can cause a different reaction and result in the formation of different phenolic compounds; therefore the treatments and wine aging vessels should be chosen appropriately. Numerous researchers have investigated the effects of aging wine in oak barrels, adding oak chips and micro-oxygenation on red wine's phenolic composition and colour. Red wines typically undergo a maturation process, primarily in wooden barrels or bottles, which constitutes a critical stage in their production (Teissedre & Jourdes, 2013). Consequently, monitoring the physicochemical properties of wine throughout the aging period is essential. Watrelot and Waterhouse (2018) investigated the percentage of the degradation and loss of monomeric anthocyanins and the percentage of the formation of pigmented tannins in 'Cabernet-Sauvignon' red wines, aged 8 and 12 months in barrels of different toasting levels (low LTP, medium MTP, and high HTP). Being the most reactive monomeric anthocyanin, malvidin coumaroyl glucoside was found, and its loss was significant. The loss of coumaroylated anthocyanins is a result of the reaction of ester hydrolysis with the acyl group or its precipitation, and is not a result of oxidation. Red wine aged in barrels toasted at lower temperatures exhibited higher levels of ellagitannins, as higher temperatures lead to their degradation. Meanwhile, the wines that contained lower concentrations of ellagitannins showed a higher percentage in loss of monomeric anthocyanins. These results indicate that ellagitannins protect anthocyanins and stabilize wine colour by forming new compounds with them, as was also suggested by Chassaing *et al*. (2010). The aging process in oak barrels imposes significant financial costs on wineries due to both the expense of the barrels and the extended duration required. Substantial efforts have been made to develop alternative, cost-effective methods to reduce the aging period while minimizing financial expenditures and maintaining the high quality of the wines (Ferreiro-Gonzales *et al*., 2019). Some of these efforts include the addition of oak chips, micro-oxygenation treatments and high hydrostatic pressure (HHP) treatment, the latter of which is still undergoing validation.

The addition of oak chips can influence wine characteristics, depending on the timing of their addition. When added during fermentation, oak chips do not favorably affect ellagitannin extraction and anthocyanin stabilization, but the wines can contain wood-extracted volatiles, such as lactones, ramified ethyl esters, and acetates. The addition of the chips after fermentation may give wines greater aging potential and increase the condensation reactions of tannins and anthocyanins (Kyraleou *et al*., 2016b). Comparative studies have been conducted to evaluate the differences between the influence of oak barrels, the addition of oak chips, micro-oxygenation and high hydrostatic pressure (HHP) on the polyphenolic complexation and colour characteristics of wine. Cano-Lopez *et al*. (2010) reported that, like oak barrel aging in the same aging period (3 months), micro-oxygenation improves quality and colour of Monastrell wine. Nevertheless, when analyzed after aging for six months in a bottle, the wines showed different chromatic characteristics, with a higher percentage of yellow tint. The assumption is that ellagitannins, phenolic acids and wood aldehydes extracted from wood during barrel aging form anthocyanin-tannin complexes which stabilize the colour. Gonzales-Sais *et al*. (2014) carried out similar research on the Spanish variety Tempranillo to determine the effect of different treatments that advance the aging process. Namely, they used different oxygen doses, oak chip dose, wood origin (French and American oak), different toasting degree and maceration time. The objective was to investigate the influence of controlled doses of oxygen and the addition of oak chips to wine by mimicking the conditions of oak barrel aging. The results showed that changes in anthocyanin content during aging are associated with numerous processes that compete for the same substrates: monomeric anthocyanins. The final state of anthocyanin content results from a complex equilibrium of these reactions and mechanisms, which are highly sensitive to variations in experimental conditions. More specifically, the higher degree of toasting had an advantage over the maceration time, due to higher extraction and formation of complex polymeric anthocyanin with flavan-3-ols and proanthocyanidins, and the formation of pyranoanthocyanidins. Meanwhile, high oxygen doses in combination with medium to medium-plus toasting levels showed the best results, with the formation of anthocyanin derivative complex compounds; however, when medium to high oxygen doses were combined with heavy-plus toasted chips a relatively high level of anthocyanins remained. According to Ćurko *et al*. (2021), micro-oxygenation enhances polymerization reactions between flavanols and anthocyanins *via* acetaldehyde mediation.

As already mentioned, high hydrostatic pressure (HHP) is one of the new sustainable winemaking techniques for accelerating the extraction of anthocyanins and other polyphenolic compounds during maceration. Like the other techniques described, its influence on the physicochemical and sensorial properties of red wine has been investigated. It has been employed for producing high-quality wines and reducing manufacturing costs with effective inhibition of spoilage microorganisms. Tao *et al*. (2012) investigated the influence of HHP processing of 650 MPa at an ambient temperature of around 18 °C, for 0.25, 0.5, 1, and 2 h, respectively, on the phenolic complex of Nero D'avola Syrah wine. The aim was to investigate the possibility of using HHP as a technique for accelerating the wine aging process. The best results were obtained for the 2 h treatment, with a reduction in the intensity of the wine colour and in phenolic compound content; it also enhanced the sourness, astringency, alcoholic and bitter taste of the wine. The authors suggest this method is useful for the aging of wines with low aging potential (low anthocyanin and tannin content).

3. Influence of anthocyanins on red wine astringency

Wine phenolics influence the flavour and mouthfeel of the wines (Setford *et al*., 2017). While astringency might be defined as a tactile sensation (Breslin *et al*., 1993) of the oral cavity triggered by harsh food compounds [*i.e*., tannins] (Gibbins *et al*., 2013), it is perceived more as a feeling (Pires *et al*., 2020). To characterize astringency as a complex sensation, Gawel *et al*. (2000) developed terminology linked to a "mouth-feel wheel" to systematically describe the sensory attributes of red wine. A total of 33 astringency characteristics, are classified into 7 classes: particulate, surface smoothness, complex, drying, dynamic, harshness and unripness. During red wine tasting, astringency occurs due to the tannins-salivary protein interaction (Breslin *et al*., 1993), which involves the precipitation of proteins, leaving a puckering sensation and oral dryness as an aftertaste (Green, 1993). The most studied mechanism of astringency is the interaction between salivary proteins rich in proline (PRPs) and astringent compounds (Pires *et al*., 2020). Proline-rich proteins are very reactive and are divided into three groups: acidic (aPRPs), basic (bPRPs) and glycosylated (gPRPs). It has been previously reported that their presence in mammals' saliva is connected to the consumption of food rich in tannins (Bennick, 1982). In biochemical terms, astringency might occur because of noncovalent binding interactions; for example, the hydrophobic effect and hydrogen bonds that occur between PRPs and tannins (García-Estévez *et al*., 2018; Delić *et al*., 2023). Because anthocyanins interact with tannins during the production of red wine to form anthocyanin-tannin complexes, the question arises of whether there is an interaction mechanism between anthocyanins and salivary proteins (Paissoni *et al*., 2018; Ferrer-Gallego *et al*., 2014; Ferrer-Gallego *et al*., 2015; Paissoni *et al*., 2020; Mattioli *et al*., 2020). Some studies have shown that there are anthocyanin-salivary protein complexes, but the interaction between them has not yet been explained (Ferrer-Gallego *et al*., 2015). Many recent studies have worked on determining the influence of anthocyanins on enhancing or reducing the astringency of red wine (Paissoni *et al*., 2018). Previous studies have shown that, during wine aging, anthocyanins undergo reactions with tannins to form polymeric pigments. When their sensorial effect was investigated, these polymeric pigments were found to interact with salivary proteins and show decreased astringency levels (Villamor *et al*., 2009). Additionally, polysaccharides in aged wines can bind to anthocyanins and tannins, decreasing the perception of astringency (Escot *et al*., 2001). Therefore, molecular investigations are needed in order to better understand the interaction between anthocyanins and salivary proteins necessitates.

The affinity between plant pigments and salivary proteins has been investigated and found to probably depend on the functional groups and molecular weight of pigments (Yao *et al*., 2011). The effect of different anthocyanin fractions (glucoside, acetylated and cinnamoylated fractions) on oral sensory properties and astringency have also been studied, with the conclusion that cinnamoylated anthocyanins are the most reactive anthocyanins to salivary proteins rich in proline (Paissoni *et al*., 2018). Soares *et al*. (2019) carried out research to determine whether the co-pigmentation of malvidin-3-*O*-glucoside and epicatechin could affect the ability of flavonols to interact with PRPs, *via* saturation-transfer difference (STD)-NMR and isothermal titration calorimetry (ITC). The epicatechin-malvidin-3-*O*-glucoside mixture showed the same affinity for PRPs as individual compounds; in addition, epicatechin was found to involve hydrophobic and hydrophilic interactions, while malvidin-3-*O*-glucoside involved electrostatic interactions. Meanwhile, recent studies have investigated the role of anthocyanins in the interaction between salivary mucins and wine astringent compounds (Torres-Rochera *et al*., 2023), with the results showing that, when isolated, anthocyanin (namely malvidin-3-*O*-glucoside) had the strongest affinity for salivary mucins compared to catechin, epicatechin and quercetin-3-β-glucopyranoside. Additionally, according to the authors, the co-pigmentation phenomenon might have a larger purpose, since the presence of malvidin-3-*O*-glucoside modified the intensity and characteristics of the interactions between the mucins and other phenolic compounds. Similarly, Mao *et al*. (2024) studied the interactions between oral mucins and cyanidin-3-*O*-glucoside, emphasizing the effect of oxidized quinone. They explain that when the anthocyanins oxidize into quinones they covalently bind with mucins in the oral cavity and form a tighter cross-linkage, enhancing oral astringency. Some researchers went further by developing different oral models and investigating the interactions of phenolic compounds in conditions similar to the human oral cavity. Soares *et al*. (2020) developed oral epithelia comprising buccal mucosa and tongue, human saliva and the mucosal pellicle in order to investigate the interactions with anthocyanin red wine extract and green tea flavanol extract. They reported that anthocyanins had higher interaction with oral cells only, but the studied anthocyanins (delphinidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, petunidin-3-*O*-glucoside and malvidin-3-*O*-glucoside) all showed the same level of interaction ability. Additionally, it was shown that various oral constituents can perform distinct functions at different phases of phenolic compound intake. These findings may serve as an useful starting point for future investigations into the influence of anthocyanins on red wine astringency.

APPLICATION OF ANTHOCYANINS IN THE FOOD INDUSTRY

The antioxidant properties of anthocyanins make them essential in food technology. They can serve as natural food colorants or specific indicators for food quality control. The estimated daily intake (ADI) for humans is 2.5 mg/kg body weight per day (Clifford, 2000). Enhancing the stability of anthocyanins would increase their use in food technology (Mattioli *et al*., 2020). To improve the stability and ingestion of these compounds, encapsulation techniques have been developed. This method is also widely used to enhance the quality of food in terms of colour, aroma, smell and taste. Various studies have explored different types of encapsulations, materials, matrices and carriers for polyphenol-loaded microparticles (Popović *et al*., 2019; Milinčić *et al*., 2019; Milinčić *et al*., 2022b; Milinčić *et al*., 2023a; Đorđević *et al*., 2015; Popović *et al*., 2019). Micro- and nanoencapsulation are among the most effective methods for incorporating anthocyanins within bioactive compounds and facilitating their introduction into the human body. Researchers are addressing challenges such as low stability, low bioavailability and controlled release of anthocyanins *via* new micro- and nanoencapsulation techniques (Milinčić *et al*., 2019; Milinčić *et al*., 2022b; Milinčić *et al*., 2023a). For example, Lavelli *et al*. (2019) investigated the microencapsulation of grape skin phenolics and its controlled release, utilising calcium chloride as a hardening agent. Their findings indicate that alginate is effective as a pH-controlled release system for grape skin phenolics. Additionally, seed/skin extracts are frequently added to various products, such as meat, cereal-based infant formula (Pešić *et al*., 2019), goat milk yogurt (Milinčić *et al*., 2021b; Milinčić *et al*., 2022b; Milinčić *et al*., 2024) and biscuits (Kammerer *et al*., 2005) to enhance techno-functional and functional properties, or to examine the bioavailability of phenolic compounds in these matrices.

1. Anthocyanins as natural food colorants and additives

Food colour is constantly being improved, especially with the development of new technologies for the use of natural colours. Increased awareness of the harmful health effects of synthetic colorants can be achieved by utilising anthocyanins as natural food colorants. For these purposes, different encapsulation techniques have been used (Lavelli & Sri Harsha, 2019; Ghosh *et al*., 2021) and studied, namely coacervation, spray drying, freeze drying, liposomal systems, electro spraying and electrospinning, inclusion complexation, emulsification, ionic gelation, and extrusion (Shaddel *et al*., 2018; Kanha *et al*., 2020; Adali *et al*., 2020; Zhang *et al*., 2020; Atay *et al*., 2018; Forghani *et al*., 2021; Fernandes *et al*., 2018; Norcino *et al*., 2022; De Moura *et al*., 2018; Mohammadalinejhad *et al*., 2023). In micro- (particle size between 1 µm and 1,000 µm per unit) and nanoencapsulation (particles of 50 nm and 500 nm in size), the most common encapsulation techniques are spray drying and electrospinning, which have been thoroughly reviewed by Sharif *et al*. (2020). Recent research on the microencapsulation of anthocyanins combined different wall materials and different encapsulation techniques to achieve higher stability of encapsulates, better preservation of microcapsule colour, a longer storage period, higher antioxidant capacity, sustained release of the bioactive compound, and high encapsulation efficiency. The use of different wall materials, such as alginate (Lević *et al*., 2015), gelatin (Gao *et al*., 2022), inulin (Enache *et al*., 2022), pectin (Pereira Souza *et al*., 2017), chitosan (Wang *et al*., 2016) and whey protein isolate (Wang *et al*., 2022), has improved existing encapsulation techniques and provided new solutions for the development of strategies and methods for producing microparticles containing anthocyanins. Two different paths of scientific research are associated with the use of anthocyanin nanoencapsulation (Milinčić *et al*., 2019): one focussing on the fabrication of nanofibers or films for developing new, smart/intelligent food packaging using anthocyanins as biosensors of food spoilage and microbiological activity (Almasi *et al*., 2022); and the other to find new ways of producing anthocyanin-loaded nanoparticles increase their use in food technology and potentially give a new perspective on their use (Nivetha *et al*., 2022). The encapsulating base material is very important since the concentration and molecular structure of the anthocyanins will depend on it. Grapes, pomace and wine have been actively investigated as sources of anthocyanins (Tikhonova *et al*., 2021; Lavelli & Sri Harsha, 2019; Brezoiu *et al*., 2019), using varieties such as Ancellota and Aspirant Bouchet wines to produce encapsulated natural colorant powders because of their high anthocyanin content. The encapsulate properties of the colouring powder was evaluated, and the results showed that the increase from 135 to 145 °C in inlet air temperature did not influence the anthocyanin profile in the wine powder; thus indicating that the encapsulates were appropriate for potential use as natural food colorants (Alvarez Gaona *et al*., 2022). Other authors have reported that using spray drying to produce powders resulted in encapsulates with low moisture content, low hygroscopicity, high solubility and stable colour (De Souza *et al*., 2015). A widely-used anthocyanin-rich extract obtained from grape pomace called Enocianina is one of the most important colorants in the food industry, being rich in polyphenols and anthocyanins (mostly malvidin derivates) and also showing anti-inflammatory properties (Della Vedova *et al*., 2022).

2. Grape pomace as source of anthocyanins

Economically, grapevine production is one of the most important productions in the world. According to the statistical data reported by the Food and Agriculture Organization (FAO) for 2022, grape production was almost 75 million tons (FAO, 2022). The International Organization for Vine and Wine (OIV) reported that in 2023 world wine production was the lowest it had ever been in 60 years, with a decrease of 7 % compared to 2022 (OIV, 2024). They stated that extreme climatic conditions have significantly impacted vineyard output worldwide. Overcoming meteorological problems that occur during grapevine production is often costly, which further increases the costs of wine production in general.

Many wineries have turned to sustainable winemaking, trying to use as much waste as possible from their production, namely pomace. Not only is the practice of using different by-products cost-effective, but it is also environmentally friendly and contributes to the fight against climate change, and air, soil and water pollution. Grape pomace is a by-product of vinification and winemaking. Soceanu *et al*. (2021) state that as a by-product of winemaking, pomace should be considered as a starting point for creating new products that are nutritionally and industrially valuable. At the same time, this would decrease the harmful ecological impacts of winemaking related to inconsistent waste disposal practices. Since it is rich in phenolic compounds (listed in Table 2), grape pomace can be used in many different industries. The composition and concentration of anthocyanins within grape pomace vary depending on grape variety, growth conditions and winemaking methodology. To extract anthocyanins from grape pomace, several techniques such as solvent extraction, enzymatic hydrolysis, microwave-assisted extraction and supercritical fluid extraction have been employed (Milinčić *et al*., 2021a; Valls *et al*., 2017; Castellanos-Gallo *et al*., 2022; Monteiro *et al*., 2021; Muñoz *et al*., 2021; Peixoto *et al*., 2018; Milinčićč *et al*., 2023b). Extraction parameters, such as solvent selection, temperature, pH and extraction duration, play a critical role in influencing the yield of anthocyanins (Peixoto *et al*., 2018). Hoss *et al*. (2021) have noted that grape pomace contains a high content of bioactive molecules, which, once extracted, can be used in cosmetic products due to the antioxidant, antiaging, anti-hyperpigmentation and photoprotective effects of the phenolic compounds. According to Gomez-Brandon *et al*. (2021) grape pomace can potentially be used for the production of vermicompost, which increases the content of macro- and micronutrients in the soil. Another group of scientists studied the potential use of winemaking pomace as a new source of compounds for antibacterial agents: due to their bacteriostatic and/or bactericidal properties, phenolic compounds that have synergistic action with antibiotics might prevent bacterial resistance to the antibiotic (Silva *et al*., 2021).

Anthocyanins from grape pomace can be successfully used in the formulation of different nutraceuticals and functional foods. Nutraceutical products (*i.e*., dietary supplements, capsules and powders) can be formulated to deliver concentrated anthocyanin extracts. The enrichment of food products with grape pomace powder or extracts has been shown to improve the functional properties of the food and to have health benefits (Troilo *et al*., 2022). The incorporation of grape pomace into these products not only increases their anthocyanin content, but also imparts desirable attributes related to, for example, colour, flavour and texture (Monteiro *et al*., 2021, Tikhonova *et al*., 2021). A comparative study of white wine Pinot noir pomace flour and white wine Pinot noir pomace extracted in hot water, showed the higher potential of the extracts for use as an antioxidant dietary ingredient. The extracts had higher mineral and soluble fibre content, and human digestion simulation showed that digested fractions had higher bioactive value, with gallic, vanillic and seringic acid as the main bio-accessible phenolic compounds (Beres *et al*., 2019). Adding grape pomace (specifically, 5 % of grape seed flour) as an ingredient to bread gave interesting results regarding sensorial analysis and customer acceptance. The panelists found it to be very similar to black bread (Oprea & Gaceu, 2020). Troilo *et al*. (2022) studied the addition of different particle sized fractions of pomace powder to flour and their influence on the chemical, technological and sensorial characteristics of functional muffins. They reported that particle size was not the decisive factor when 15 % of grape pomace powder was added. The functional muffins were valuable sources of fiber with high content of antioxidants. The utilization of grape pomace as a source of anthocyanins and dietary fibre promotes sustainability within the agri-food industry (Milinčić *et al*., 2020; Milinčić *et al*. 2021a). Finally, the valorization of grape waste by using it for obtaining highly valuable bioactive compounds is environmentally friendly and is one of the principles of circular economy (Rajković *et al*., 2020).

3. Anthocyanins as smart/intelligent food packaging bio-compounds

Being bioactive compounds, anthocyanins can be used as incorporated agents for the fabrication of nanofibers or films and the development of new, smart/intelligent food packaging (Forghani *et al*., 2021; De Silva *et al*., 2022). For this purpose, anthocyanins are used as biosensors of food spoilage and microbiological activity, because they easily change colour when pH changes (Almasi *et al*., 2022). There are two different types of intelligent food packaging: food freshness indicators (FFI) and time-temperature indicators [TTI] (Forghani *et al*., 2024; Almasi *et al*., 2022). There are different methods of preparation of food freshness indicators, as well as different intelligent food packaging. Recent advances have been made in research on 3D printing technology combined with incorporating anthocyanins in intelligent packaging. Bao *et al*. (2024) conducted research on a starch based 3D printed intelligent colorimetric film with blueberry anthocyanin-phycocyanin incorporated (with chondroitin sulfate as a co-pigment). Colorimetric film exhibited high sensitivity to ammonia response, high antioxidant activity, biosafety and degradability, showing efficacy in maintaining the freshness of salmon and beef. Li *et al*. (2024) developed a composite film made of soybean protein isolate/carboxymethyl cellulose sodium/blueberry anthocyanin by *in situ* incorporation of anthocyanin, which showed UV-shielding, gas barrier and water resistance performance. Developing an intelligent edible electrospun nanofiber film for shrimp preservation, Wu *et al*. (2024) incorporated anthocyanin and thymol into polymer fibers of gelatin and zein. The results showed that the film had high mechanical properties and decreased water vapour permeability, excellent sensitivity to change of the pH solutions, high antioxidant properties and antibacterial responses. Additionally, it extended shelf life for packaged shrimps by 11 days when at 4 °C. Qin *et al*. (2024) developed highly pH-sensitive film for quantifying fish freshness in real-time based on a chitosan/gelatin matrix and incorporating *Zingiber striolatum* Diels anthocyanin extract. When tested, the film showed greater melting temperature

TABLE 2. List of phenolic compounds found in grape pomace (skins, seed stems) and their concentrations expressed as mg/g dry weight (DW).

Phenolic compounds	Concentration	Grape variety/Pomace type	Source
Gallic acid	0.07	Prokupac seed, skin and stem pomace	Milinčić *et al.*, 2021a
	0.01–0.03	Grenache, Syrah, Carignan noir and Mouvedre skin pomace	Ky *et al.*, 2014
Catechin	0.19	Prokupac seed, skin and stem pomace	Milinčić *et al.* 2021a
	0.02–0.08	Syrah, Merlot and Cabernet-Sauvignon pomace	Lingua *et al.*, 2016
	0.003–0.01	Grenache, Syrah, Carignan noir, Mouvedre skin pomace	Ky *et al.*, 2014
Epicatechin	0.12	Prokupac seed, skin and stem pomace	Milinčić *et al.*, 2021a
	0.02–0.1	Syrah, Merlot and Cabernet-Sauvignon pomace	Lingua *et al.*, 2016
Quercetin	0.01	Prokupac seed, skin and stem pomace	Milinčić *et al.*, 2021a
Resveratrol	0.04	Prokupac skin and stem pomace	Milinčić *et al.*, 2021a
Anthocyanin glucosides	2.9–9.0	Grenache, Syrah, Carignan noir and Mouvedre skin pomace	Ky *et al.*, 2014
	1.35	Prokupac skin and stem pomace	Milinčić *et al.*, 2021a
	0.05–0.14	Syrah, Merlot and Cabernet-Sauvignon pomace	Lingua *et al.*, 2016
Anthocyanins acylated	0.05	Prokupac skin pomace	Milinčić *et al.*, 2021a
	0.2–0.8	Grenache, Syrah, Carignan noir and Mouvedre skin pomace	Ky *et al.*, 2014
	0.02–0.2	Syrah, Merlot and Cabernet-Sauvignon pomace	Lingua *et al.*, 2016
Anthocyanins *p*-coumaroylated	0.15	Prokupac skin pomace	Milinčić *et al.*, 2021a
	0.7–5.2	Grenache, Syrah, Carignan noir and Mouvedre skin pomace	Ky *et al.*, 2014
	0.07–0.4	Syrah, Merlot and Cabernet-Sauvignon pomace	Lingua *et al.*, 2016
Total Tannins	31.8 – 56.1	Grenache, Syrah, Carignan Noir and Mouvedre skin pomace	Ky *et al.*, 2014

and a lower weight loss at melting temperature, with a visible colour change from red to yellow green in a pH 1-14 buffer. Teixeira Gomez *et al*. (2024) reported that the sensitivity of the films and their behaviour depends on the source of the extract of anthocyanins. They developed gelatin/polyvinyl alcohol films incorporated with different blueberry extracts (raw blueberry extract, purified fractions of phenolic extract and anthocyanin extract). The film with anthocyanin extract was more sensitive to acidic vapours, changing the colour from green to purple, while the film with raw blueberry extract was more sensitive to basic conditions. This might be because of the presence of other phenolic compounds in the raw blueberry extract, which are less susceptible to acidic conditions in comparison to anthocyanins. Therefore, the phenolic composition of the extract is of high importance when developing the food indicator film. The use of anthocyanin extracts in the development of novel and intelligent indicator food film and packaging is vast and still to be thoroughly explored, with high potential in food industry.

BENEFITS OF GRAPE AND WINE ANTHOCYANINS FOR HUMAN HEALTH

Anthocyanins have multiple protective and therapeutic properties for human health (Zia ul Haq *et al*., 2016). Being bioactive compounds, anthocyanins have a wide range of properties; they are, for example, antioxidants (Monteiro *et al*., 2021) and anti-inflammatories (Della Vedova *et al*., 2022), and they also regulate blood lipids (Bayram *et al*., 2024). Furthermore, they show insulin resistance, and anti-mutation and anti-tumour properties (Li *et al*., 2021). Many studies have confirmed that anthocyanins can also improve visual (Liu *et al*., 2024) and brain functions (Baek *et al*., 2023; Hasan *et al*., 2023). Their role in the prevention of diseases is based on their antioxidant capacity and regulatory function in the human immune system.

1. *In vitro* studies for evaluation functionality of anthocyanin

In vitro testing of anthocyanin health benefits for humans is a scientific approach that investigates the biological effects and potential therapeutic properties of anthocyanin compounds isolated from different sources (grapes or pomace) through experiments conducted in a laboratory setting. During *in vitro* testing, anthocyanins are isolated from their sources and exposed to controlled conditions to evaluate their interactions with various cellular and molecular components (Corrêa *et al*., 2017; Lingua *et al*., 2018; Pešić *et al*., 2019). The health benefits of the grape and the mechanisms of anthocyanin activity are analysed, improving the understanding of the correlation between the grape, anthocyanins and human health (Zhou *et al*., 2022). As anthocyanins are sensitive to oxidation and susceptible to isomerisation, their bio-efficacy will depend on their bioavailability and bioaccessibility (Pešić *et al*., 2019). Various factors, such as temperature, pH, light, food and gastrointestinal conditions (temperature, pH of digestive fluid and enzymes), influence the ability of anthocyanins to absorb, convert and metabolise (Moreno-Arribas & Polo, 2009; Milinčić *et al*., 2022a; Milinčić *et al*., 2023a). Several researchers have studied the effect of simulated digestion on the phenolic components of red grapes and wines. Corrêa *et al*. (2017) investigated the in vitro-simulated digestion and bioactivity of bioactive compounds from Merlot variety grape pomace. Anthocyanin content decreased after gastrointestinal digestion. After cologne digestion, it did not change. However, characteristic metabolites originated from anthocyanins in the colon phase (Corrêa *et al*., 2017). According to some researchers, anthocyanins from grapes and wine are less affected by the human gastrointestinal tract, which explains their high antioxidant capacity (Lingua *et al*., 2018). These results are consistent with previous studies by the same group of authors, who reported that changes that occur from grape to wine during the winemaking process are responsible for the differences in phenolic content, especially anthocyanin concentration and antioxidative capacity. Therefore, grape will have higher antioxidative capacity due to its content in kaempferol-3-O-glucoside and fertaric acid, and wine and pomace will have lower antioxidative capacity due to the presence of ethyl-gallate (Lingua *et al*., 2016).

2. *In vivo* studies for evaluation functionality of anthocyanin

The *in vivo* evaluation of the effects of anthocyanins on human health has very often been conducted on a living organism, whether animal or human, to study physiological effects, mechanisms of action and any health benefits associated with the consumption of anthocyanins. Grimes *et al.* (2018) investigated the the effect of anthocyanins from table grape on cancer cell inhibition, and the results showed inhibition of cancer cells in three human cancer cell lines. Anthocyanins from both grape and red wine have beneficial effects on human health (Grimes *et al*., 2018). In their review regarding the health benefits of grape bioactive molecules, Sabra *et al.* (2021) noted that whole grapes and their derivatives may have blood pressure-lowering potential. Meanwhile, in their review of the chemical properties of anthocyanins and their health effects on cardiovascular and neurodegenerative diseases, Mattioli *et al.* (2020) pointed out their protective effects on CVDs and neurodegenerative diseases. The protective effects of anthocyanins for both diseases are related to their antioxidant and anti-inflammatory properties (Kyraleou *et al*., 2016b). In a recent study, Radeka *et al.* (2022) investigated the bioactive compounds of Croatian white and red wines and the effect of their consumption on human health. The results showed that regular moderate wine consumption (200 mL per day) decreases systolic and diastolic blood pressure, total cholesterol and LDL. Ferrer-Gallego and Silva (2022) suggested that food enriched with wine by-products can prevent chronic human diseases, since they are rich in anthocyanins, phenolic acids, flavonols, proanthocyanidins and stilbenes. Many researchers have worked on the estimation and valorization of the health benefit potentials of new functional foods as detailed in a comprehensive review by Iuga and Mironeasa (2020). According to Teissedre *et al*. (2018) in their review, the moderate and regular consumption of wine has cardioprotective effects due to anthocyanins and other polyphenolic compounds. It is thus necessary to find the best way to preserve the stability of anthocyanins and to increase their bioavailability so that they can be used to the maximum against various human diseases.

CONCLUSION

Although anthocyanins from red grape and wine have been widely investigated, this is the first comprehensive overview on their biosynthesis and transformations during winemaking and wine aging, their effects on sensorial properties and application in the food industry, and the valorization in order to benefit human health.−Anthocyanins are red grape and wine pigments that are responsible for wine colour. In our in-depth analysis of winemaking processes, we have unravelled the complex biochemical transformations undergone by anthocyanins during fermentation and maceration, offering insights into factors influencing their extraction and stability, and co-pigmentation and polymerization in wines. Being very susceptible to changes, they undergo numerous transformations during wine aging that influence colour intensity, colour density and hue. They influence the sensorial properties of wine by interacting with salivary proteins during wine tasting. The increasing application of anthocyanins in the food industry as natural colorants and functional ingredients highlight their versatility and potential for enhancing the aesthetic and nutritional qualities of various food products. Our investigation into the health benefits of anthocyanins reveals their promising therapeutic potential due to their antioxidant, anti-inflammatory and cardioprotective properties. This not only substantiates the significance of the role of anthocyanins in preventive healthcare but also paves the way to novel interventions that address a spectrum of human health conditions. In summary, this comprehensive review synthesises current knowledge on grape, wine and pomace anthocyanins in the fields of plant physiology, winemaking science, food technology and human health. The findings discussed here serve as a foundation for future research endeavours, inspiring further exploration into the intricate interplay of anthocyanins across disciplines.

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