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THE ROLE OF PROCYANIDINS IN GRAPES AND WINES: EFFECTS ON QUALITY AND COMPOSITION

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Abstract. Proanthocyanidins in grapes and wine are oligomers and polymers of flavan-3-ols, predominantly connected through C4−C8 and/or C4−C6 bonds (B-type). These compounds significantly influence red wine's sensory profile, particularly its color and mouthfeel. In addition, proanthocyanidins are recognized for their antioxidant and radical-scavenging properties, capable of neutralizing reactive oxygen species and preventing cellular damage caused by oxidative stress. These properties give them an important role in protecting health, with beneficial effects on the body by reducing the risk of cardiovascular diseases and cancer. The aim of the article is to explore the role of proanthocyanidins in grapes and wine, focusing on their contributions to wine's sensory characteristics such as color, astringency, and mouthfeel. It aims to examine the factors influencing their composition, the transformations they undergo during winemaking and aging, and their broader implications for wine quality, stability, and health benefits. The objectives of the study are to investigate the physical, chemical, and biochemical properties of procyanidins, as well as the influence of factors such as grape variety, ripeness, health status, climatic conditions, viticultural techniques, grape processing methods, wine stabilization, and aging techniques on their content.

Keywords: *procyanidins, grapes, wine, antioxidant and antiradical activities.*

Rezumat. Proantocianidinele din struguri și vinuri sunt oligomeri și polimeri ai flavan-3-olilor, conectați predominant prin legături C4−C8 și/sau C4−C6 (tip B). Acești compuși influențează semnificativ profilul senzorial al vinului roșu, în special culoarea și senzația la gust. În plus, proantocianidinele sunt recunoscute pentru proprietățile lor antioxidante și antiradicalice, fiind capabile să neutralizeze specii reactive de oxigen și să prevină deteriorarea celulară cauzată de stresul oxidativ. Aceste proprietăți le conferă un rol important în protejarea sănătății, având un efect benefic asupra organismului prin reducerea riscului de boli cardiovasculare și cancer. Scopul articolului este de a explora rolul proantocianidinelor în struguri și vin, concentrându-se pe contribuția acestora la caracteristicile senzoriale ale vinului, cum ar fi culoarea, astringența și senzația în gură. Acesta își propune să examineze factorii care influențează compoziția lor, transformările pe care le suferă în timpul vinificației și învechirii și implicațiile lor mai largi pentru calitatea vinului, stabilitate și beneficiile pentru sănătate. Obiectivele studiului constau în investigarea proprietăților fizice, chimice și biochimice ale procianidinelor, precum și influența unor factori precum soiul de struguri, gradul de maturitate, starea de sănătate, condițiile climaterice, tehnicile viticole utilizate, metodele de prelucrare a strugurilor, stabilizarea vinurilor și tehnicile de maturare a acestora, asupra conținutului lor.

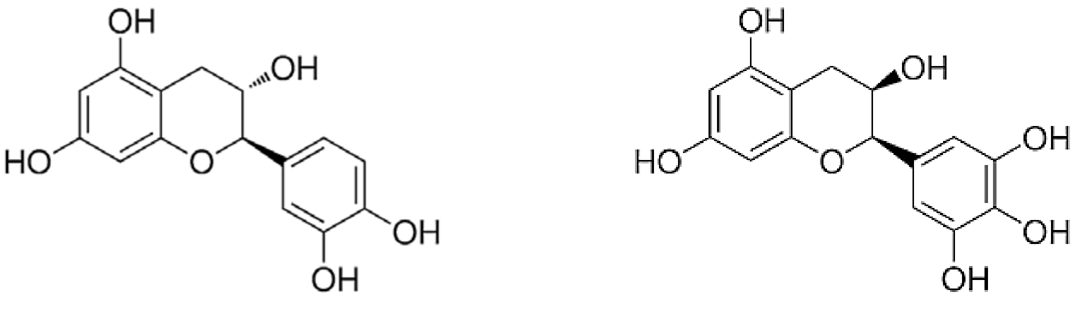
Cuvinte-cheie: *procianidine, struguri, vin, activitate antioxidantă și antiradicalică.*

1. Introduction

Proanthocyanidins are a vital group of polyphenolic compounds found abundantly in grapes and wine, especially red varieties, and are known for their significant contributions to wine's sensory characteristics, including color, astringency, and mouthfeel. Structurally, proanthocyanidins are composed of flavan-3-ol units, forming complex oligomers and polymers linked through specific bonds [1,2]. Their levels and composition in wine vary widely due to factors like grape variety, ripening stage, environmental conditions, viticultural practices, and winemaking methods. These compounds not only enhance the sensory appeal of wines but also possess antioxidant properties, which can affect the aging stability and health benefits associated with moderate wine consumption [3,6]. As wine ages, particularly in oak barrels, interactions between proanthocyanidins, anthocyanins, and wood-derived compounds lead to further transformations, impacting both the chemistry and sensory profile of the final product. This article explores the nature of proanthocyanidins in grapes and wine, examining their roles in sensory perception, their evolution during winemaking and aging, and the broader implications for wine quality and consumer experience [4,5].

2. Structure of proanthocyanidins

Procyanidins are a class of flavan-3-ol oligomers and polymers that are part of the larger flavonoid family. These compounds are found in various fruits (e.g., grapes, apples, and berries), cocoa, and wine [6]. Their structure is based on the catechin and epicatechin monomers linked by carbon-carbon bonds [7].



a) b)

Figure 1. Structure of catechin (a) and epicatechin (b) [8].

The chemical structure of procyanidins is based on monomeric units of catechin and epicatechin, which are flavan-3-ols characterized by a three-ring structure (A-ring, B-ring, and C-ring) with hydroxyl groups attached at specific positions [8,9].

The monomeric units can link together through carbon-carbon bonds to form oligomers and polymers. These linkages occur primarily between the carbon atoms at positions C4 and C8 (or sometimes C4 and C6) of the flavan-3-ol units. This bonding pattern is typical of B-type procyanidins (Figure 3), the most common form [7,8]. In contrast, A-type procyanidins (Figure 2) have an additional ether bond, such as a C2-O-C7 linkage, which provides a distinct structural variation [8,9].

Procyanidins are classified by their degree of polymerization (DP), which refers to the number of monomer units in the compound. Dimers, trimers, and tetramers (DP = 2−4) are called oligomeric procyanidins, while those with a higher DP are considered polymers. Oligomeric forms are more soluble in water and tend to have higher biological activity, particularly as antioxidants. As the polymerization increases, solubility and bioavailability decrease, but the compounds may still contribute to dietary fiber and other functional properties [7,8].

The hydroxyl groups present on the aromatic rings of procyanidins contribute significantly to their chemical reactivity and biological activity. These groups make procyanidins powerful antioxidants, capable of scavenging free radicals and chelating metal ions. Some procyanidins also contain gallate groups, which enhance their antioxidant potential [6,10].

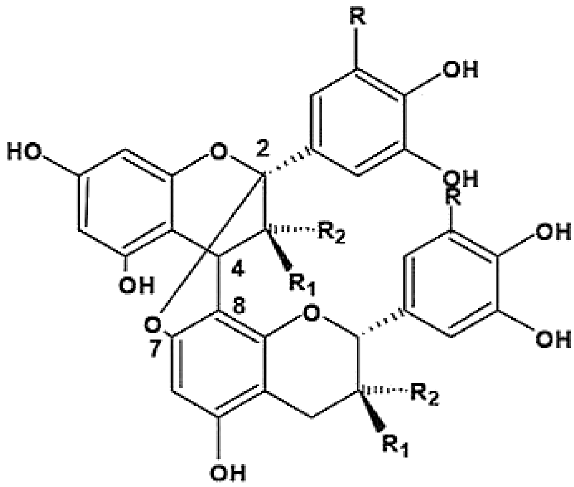


Figure 2. A-type proanthocyanidin [8].

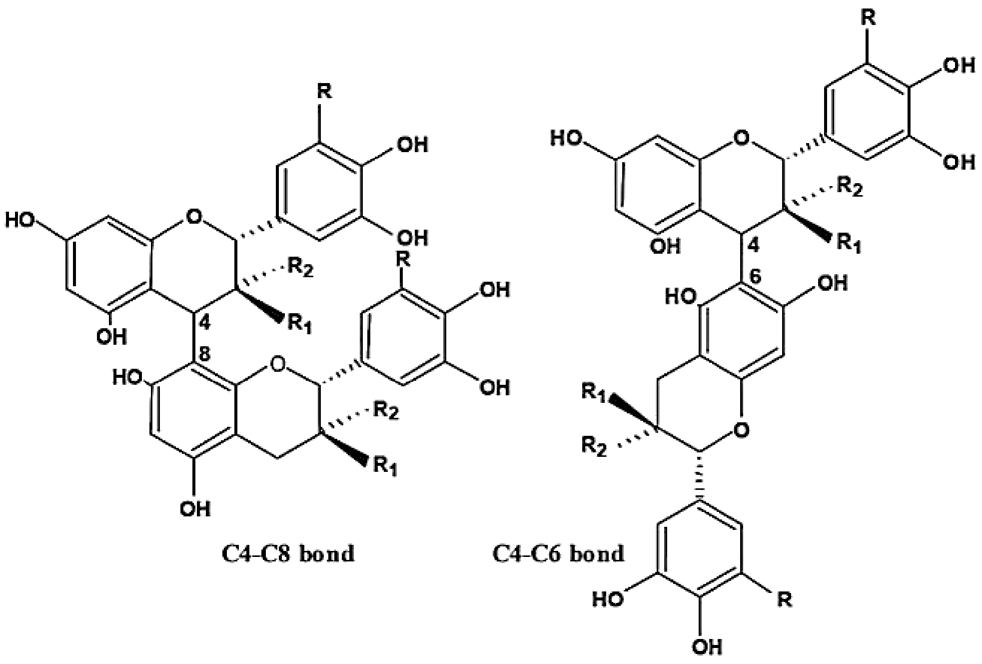


Figure 3. B-type proanthocyanidin [8].

The identification of procyanidins in grapes and wine is essential for understanding the role of these compounds in wine quality, health benefits, and aging potential. Several analytical methods, such as HPLC, LC-MS, NMR, and spectrophotometry, can be employed to quantify and characterize procyanidins, each with its own strengths and limitations [10-14]. A combination of these techniques is often used to gain a comprehensive understanding of procyanidin content and structure in winemaking.

3. The physical, chemical, biochemical, and physiological properties of procyanidins

Procyanidins are a diverse group of polyphenolic compounds with significant physical, chemical, biochemical, and physiological properties. These properties make them essential in food science, nutrition, and pharmacology [15].

Procyanidins display unique physical characteristics that influence their solubility, stability, and interaction with other compounds.

Table 1

Physical Properties

Property	Description	References
Solubility	Low molecular weight procyanidins (dimers, trimers) dissolve readily in water and polar solvents. Larger polymers are insoluble in water but dissolve in alcohols like ethanol.	[15]
Appearance	In pure form, procyanidins are colorless or pale yellow. In foods and beverages, they contribute to browning through oxidation.	[9,15]
Thermal stability	Procyanidins are stable at moderate temperatures but degrade or polymerize when exposed to prolonged heat.	[8,16]
Optical Activity	Due to chiral centers in their monomeric units, procyanidins are optically active, with measurable enantiomeric rotations.	[7,16]

The chemical properties of procyanidins are shaped by their unique structural features and their interactions with other compounds, which are critical to their functionality in food and biological systems [6,15].

- *Structure:* Procyanidins are composed of catechin and epicatechin monomers linked by C4-C8 or C4-C6 bonds, forming B-type procyanidins. Some forms, known as A-type procyanidins, include an additional ether bond, providing structural diversity [8,15].
- *Antioxidant Activity:* The numerous hydroxyl groups present in procyanidins make them highly effective at scavenging free radicals. This antioxidant property protects cells and food products from oxidative damage [17].
- *pH Sensitivity:* Procyanidins exhibit stability in acidic environments, which is why they remain functional in acidic foods and beverages like wine and fruit juices. However, they degrade in alkaline conditions, limiting their stability in such environments [18].
- *Protein Binding:* Procyanidins have a strong affinity for proteins, particularly salivary proteins. This interaction contributes to the astringent sensation experienced in foods and drinks such as red wine, enhancing sensory attributes [19].

These chemical properties underline the significance of procyanidins in food preservation, sensory quality, and health-related benefits.

At a molecular level, procyanidins demonstrate biochemical properties that significantly affect enzymatic activity, oxidative processes, and their interactions with biomolecules. These compounds play a crucial role in inhibiting lipid peroxidation, thereby protecting cell membranes from oxidative damage and ensuring cellular stability. They also modulate enzymatic activity, with the ability to inhibit digestive enzymes such as amylase and lipase [20]. This enzymatic inhibition can slow the metabolism of carbohydrates and fats, contributing to potential therapeutic benefits. Additionally, procyanidins undergo polymerization through oxidative reactions, forming larger polymers. While this polymerization can reduce their bioavailability, it may simultaneously enhance specific functional properties in foods, such as texture or stability. These biochemical properties highlight the multifaceted roles of procyanidins in both biological systems and food applications [8,20].

Procyanidins provide numerous health benefits, making them valuable in nutrition and therapeutic applications [21].

Table 2

Physiological properties

Benefit	Description	References
Cardiovascular health	Improve blood vessel function by increasing nitric oxide levels, lowering blood pressure, and reducing LDL oxidation.	[21]
Anti-inflammatory effects	Reduce inflammation by downregulating pro-inflammatory cytokines like TNF-α and IL-6.	[22]
Gut microbiota support	Promote the growth of beneficial gut bacteria, acting as prebiotics, while smaller procyanidins are absorbed in the intestine.	[23,24]
Anticancer Activity	Inhibit cancer cell growth, induce apoptosis, and reduce angiogenesis through antioxidant and anti-inflammatory mechanisms.	[17,21]
Neurological protection	Cross the blood-brain barrier to protect neurons, reduce oxidative stress, and enhance cognitive functions.	[21]
Skin health	Protect against UV damage, enhance collagen stability, and combat signs of aging.	[25]

In conclusion, procyanidins are a versatile group of polyphenolic compounds with remarkable physical, chemical, biochemical, and physiological properties that make them highly valuable in food science, nutrition, and pharmacology. Their structural diversity, antioxidant activity, and interactions with proteins and enzymes allow them to enhance food stability, sensory quality, and health benefits. Physically, their solubility and stability characteristics influence their functionality in different environments, while chemically, their pH sensitivity and protein binding contribute to their role in food and beverages. Biochemically, their ability to modulate enzymatic activity and protect cells underscores their potential therapeutic uses [17,25].

Procyanidins' physiological benefits, such as promoting cardiovascular health, reducing inflammation, supporting gut microbiota, and offering neurological and skin protection, further emphasize their importance in nutrition and medical research. This multifaceted nature ensures that procyanidins remain a focus of interest for their applications in improving food quality and human health [21, 23].

Procyanidin's antioxidant effects are primarily due to their ability to neutralize free radicals, which are unstable molecules that can damage cells, proteins, and DNA. This damage is often linked to various chronic diseases, such as cancer, cardiovascular conditions, and aging. By scavenging these free radicals, procyanidins help to reduce oxidative stress and protect the body from these harmful effects [25,26].

In addition to scavenging free radicals, procyanidins can also chelate metal ions like iron and copper, which are known to promote the formation of reactive oxygen species (ROS) [27]. By binding to these metals, procyanidins prevent the initiation of oxidative damage. They also exhibit anti-inflammatory properties, which further complement their antioxidant actions. Since chronic inflammation can exacerbate oxidative stress, procyanidins' ability to reduce inflammation adds an extra layer of protection for the cells [24,28].

Studies suggest that procyanidins can enhance the body's own antioxidant defenses by stimulating the production of endogenous antioxidant enzymes, such as superoxide dismutase and glutathione peroxidase [29]. This strengthens the overall defense against oxidative damage. Moreover, procyanidins are effective at preventing lipid peroxidation, a process that leads to the oxidation of lipids and the formation of harmful compounds like malondialdehyde. This helps preserve the integrity of cell membranes and protects cells from oxidative damage [30].

By neutralizing free radicals, procyanidins also protect DNA from oxidative damage, which could otherwise lead to mutations and cancer. They also help protect proteins from oxidation, ensuring that proteins maintain their proper function and supporting overall cell health [25,31]. The antioxidant properties of procyanidins are believed to offer various health benefits, including promoting cardiovascular health, providing neuroprotection, and potentially reducing cancer risk [30,32].

In the winemaking industry, the presence of procyanidins in grape skins and seeds contributes to the health benefits associated with red wine. These compounds help preserve the wine's freshness and stability, contributing to its antioxidant-rich content. The antioxidant capacity of procyanidins in grapes also plays a role in the overall quality and aging potential of wine [33].

Procyanidins exhibit strong antiradical activity due to their ability to neutralize reactive oxygen species (ROS) such as hydroxyl radicals, superoxide anions, and peroxyl radicals. Their multiple hydroxyl groups donate hydrogen atoms, stabilizing these reactive species and preventing oxidative damage. They also chelate transition metals like iron and copper, reducing the formation of radicals via catalytic processes such as the Fenton reaction [33].

Additionally, procyanidins interrupt lipid peroxidation by stabilizing peroxyl radicals, thus protecting cellular membranes. The degree of polymerization influences their antiradical efficacy, with oligomeric procyanidins showing higher activity due to better bioavailability, while polymeric forms provide robust local antioxidant effects. Compared to simpler phenolics, procyanidins have superior scavenging capacity, amplified by their structural complexity and ability to act synergistically with other antioxidants [34].

Key Antiradical Mechanisms [34]:

- Free Radical Scavenging: Procyanidins effectively neutralize reactive oxygen species (ROS) such as hydroxyl radicals (·OH), superoxide anions ($O_2^{-}\cdot$), and peroxyl radicals (ROO·), thereby preventing oxidative damage to lipids, proteins, and DNA.

- Metal Chelation: Procyanidins chelate transition metals like iron (Fe^{2+}) and copper (Cu^{2+}), which catalyze the generation of free radicals through Fenton or Haber-Weiss reactions. This reduces the formation of highly reactive hydroxyl radicals.
- Regeneration of Antioxidants: Procyanidins can regenerate other antioxidants like vitamin C and vitamin E, enhancing the overall antioxidant defense system in cells.
- Inhibition of Lipid Peroxidation: Procyanidins interrupt the chain reactions of lipid peroxidation by stabilizing peroxyl radicals, protecting cell membranes and lipoproteins from oxidative damage [35].
- Antiradical Strength: The antiradical activity of procyanidins is influenced by their degree of polymerization (DP):
  - ✓ Oligomeric Procyanidins (low DP): Exhibit higher free radical scavenging efficiency due to better bioavailability and interaction with radical species.
  - ✓ Polymeric Procyanidins (high DP): Though less bioavailable, they possess strong local antioxidant effects in the gastrointestinal tract.
- Health Impacts of Antiradical Properties:
  - ✓ Cardiovascular Health: Procyanidins protect LDL cholesterol from oxidative modification, reducing the risk of atherosclerosis.
  - ✓ Anti-Aging Effects: Their ability to combat oxidative stress helps mitigate aging-related cellular damage.
- Neuroprotection: Procyanidins protect neurons by reducing oxidative stress, potentially lowering the risk of neurodegenerative diseases like Alzheimer's.

Table 3 is presenting the procyanidin content (measured in mg/100 g or mg/L) in various natural sources. The values may vary depending on the source, variety, and processing method [36-38].

Table 3

Procyanidin content in various natural sources and the impact of processing methods

Source	Procyanidin content	Unit	Processing Method	Impact on Procyanidins	References
Grapes (seeds)	350 - 500	mg/100 g	Crushing, extraction, drying	Minimal loss if carefully dried; extraction concentrates procyanidins	[39]
Grapes (skins)	10 - 25	mg/100 g	Fermentation, drying	Loss during fermentation unless skins are retained	[39]
Red wine	200 - 300	mg/L	Fermentation, maceration	Longer maceration increases content	[39]
White wine	10 - 20	mg/L	Fermentation without skin contact	Minimal procyanidins due to lack of maceration	[39]

Continuation Table 3

Apples	40 - 120	mg/100 g	Fresh, juice production, drying	Peeling reduces content; drying concentrates procyanidins	[40]
Cranberries	200 - 400	mg/100 g	Fresh, juice production, drying	Processing (juicing) may reduce content; drying retains high levels	[41]
Blueberries	50 - 100	mg/100 g	Fresh, freezing, drying	Freezing preserves content; heat drying may lead to slight loss	[41]
Cocoa beans	300 - 1200	mg/100 g	Fermentation, drying, roasting	Fermentation and roasting reduce content but release bioactive forms	[42]
Dark chocolate	200 - 500	mg/100 g	Grinding, conching, tempering	Higher cocoa content correlates with higher procyanidin levels	[42]
Green tea	50 - 100	mg/100 g	Drying, steaming, brewing	Steaming preserves content; prolonged brewing may increase extraction	[43]
Almonds	50–60	mg/100 g	Roasting, blanching, drying	Roasting may reduce content; raw almonds have slightly higher levels	[44]

Table 3 highlights the variation in procyanidin content across different natural sources, emphasizing the significant levels found in grapes and their derivatives, particularly red wine. Grapes, especially their seeds, are among the richest sources of procyanidins, with content ranging from 350–500 mg/100 g in seeds and 10–25 mg/100 g in skins.

This high concentration makes them a valuable raw material for health-promoting polyphenols.

Red wine, produced through maceration and fermentation processes that extract procyanidins from grape skins and seeds, contains 200–300 mg/L of these compounds. The prolonged contact with grape solids during winemaking contributes to its higher procyanidin levels compared to white wine, which undergoes minimal skin contact, resulting in only 10–20 mg/L [44].

The table underscores the critical role of processing in preserving and enhancing procyanidin content. For grapes and wine, proper handling during fermentation and maceration is essential to maximize the health benefits of these potent antioxidants. As such, grape-based products, particularly red wine, stand out as both a cultural and nutritional asset, providing significant amounts of bioactive compounds with antioxidant properties [45].

The biosynthesis of proanthocyanidins usually starts after flowering and fruit setting at 3~9 weeks post grape fruit anthesis. The biosynthesis of procyanidins in grapes begins in the phenylpropanoid pathway, where phenylalanine is converted into 4-coumaroyl-CoA through the action of enzymes like phenylalanine ammonia-lyase (PAL), cinnamate-4-hydroxylase (C4H), and 4-coumarate-CoA ligase (4CL). This intermediate then enters the flavonoid pathway, where it is used to synthesize naringenin chalcone through the activity of chalcone synthase (CHS). The chalcone is then isomerized into naringenin by chalcone isomerase (CHI) [46,47].

Next, naringenin undergoes hydroxylation by flavonoid 3'-hydroxylase (F3'H) or flavonoid 3',5'-hydroxylase (F3'5'H), leading to the formation of dihydroflavonols like dihydroquercetin or dihydromyricetin. These dihydroflavonols are then reduced by dihydroflavonol-4-reductase (DFR) to produce leucoanthocyanidins, which are further converted into flavan-3-ols, such as catechins and epicatechins, by the action of leucoanthocyanidin reductase (LAR) or anthocyanidin reductase (ANR) [46,47].

Procyanidins are then formed through the polymerization or oligomerization of these flavan-3-ol monomers. This process can occur enzymatically or non-enzymatically, leading to the creation of dimers, trimers, and larger procyanidin molecules. These procyanidins are transported and accumulated primarily in grape skins and seeds, where they serve various roles, including contributing to the grape's defense mechanisms and influencing the organoleptic properties of wine.

The biosynthesis of procyanidins is tightly regulated by environmental factors such as sunlight and temperature, as well as genetic factors. The final accumulation of procyanidins in the grape seeds and skins is important not only for the plant's defense but also for the sensory qualities of wine, especially red wines, where procyanidins play a key role in color, astringency, and antioxidant properties [48].

Procyanidins are a versatile and valuable group of polyphenolic compounds with significant physical, chemical, biochemical, and physiological properties. They are most notably found in grapes, particularly in seeds and skins, where they contribute to the antioxidant, astringent, and color characteristics of wine. Their physical properties, such as solubility and stability, influence their functionality in food and beverages, while their chemical properties—such as antioxidant activity, pH sensitivity, and protein binding—make them important for food preservation, sensory attributes, and health benefits.

The content of procyanidins varies significantly across different natural sources, with grapes and their derivatives (especially red wine) being rich sources of these compounds. The processing methods, such as fermentation and maceration in winemaking, play a critical role in enhancing or reducing procyanidin content. Grapes, particularly when processed into red wine, remain an important source of these bioactive compounds, contributing to the overall health benefits associated with moderate wine consumption [39,48].

In addition to their beneficial effects in human health, procyanidins' antioxidant and anti-inflammatory properties underscore their potential in therapeutic applications, making them essential in both nutrition and pharmacology. The understanding of their biosynthesis in grapes also provides insight into how environmental and genetic factors can influence the quantity and quality of procyanidins in grape-based products, especially wines [47].

4. Effects of climate, soil, and grape variety on procyanidin accumulation in red wines

The accumulation of procyanidins in red wines is significantly influenced by environmental and cultivation factors, including climate, soil, and grape variety. Procyanidins, key polyphenolic compounds contributing to the astringency, color, and antioxidant properties of wines, are synthesized in grape skins and seeds, with their levels varying depending on several viticultural conditions. Understanding these factors is essential for optimizing wine quality, especially in relation to the desired sensory characteristics and health benefits associated with red wines [49].

Table 4

Effects of climate, soil, and grape variety on procyanidin accumulation in red wines

Factor	Description	Impact on procyanidin levels	References
Climate:			
Temperature	High temperatures increase anthocyanin synthesis and the rate of procyanidin polymerization. However, excessive heat can degrade procyanidins	Optimal temperatures (15-25°C) promote balanced synthesis of polyphenols.	[50]
Sunlight	UV exposure stimulates the production of phenolic compounds in grape skins.	Higher sunlight exposure enhances procyanidin content, especially in grape skins.	[50,52]
Rainfall	Excessive rainfall before harvest can dilute grape components, affecting polyphenol concentration.	Moderate rainfall allows procyanidin accumulation; excess rain may reduce levels.	[51,53,55]
Soil:			
pH	Soil pH affects nutrient availability and grape metabolism. Acidic soils tend to favor the synthesis of flavonoids, including procyanidins.	Slightly acidic soils (pH 5.5-6.5) are optimal for procyanidin production.	[54,58]
Nutrients	Rich soils with adequate nitrogen and potassium promote vine health and polyphenol synthesis.	High nutrient availability supports optimal vine growth and procyanidin synthesis.	[56,58]
Drainage	Well-drained soils prevent waterlogging, which can dilute phenolic content in grapes.	Good drainage ensures higher concentration of procyanidins in grape skins and seeds.	[57,58]

Continuation Table 4

Grape Variety	Different grape varieties naturally accumulate varying levels of procyanidins.	Red grape varieties, such as Cabernet Sauvignon, Merlot, and Pinot Noir, are known for higher procyanidin levels in their skins and seeds.	[59-61]

The balance between environmental conditions like climate and soil properties significantly impacts the polyphenolic content of grapes, especially procyanidins. For instance, optimal temperature and sunlight conditions enhance the production of polyphenolic compounds, while excessive rainfall or poor drainage can reduce their concentrations. Additionally, the choice of grape variety plays a crucial role, with certain varieties naturally yielding higher levels of procyanidins due to genetic factors [56,62].

5. The influence of winemaking technology on the accumulation of procyanidins in wines

Winemaking technology plays a crucial role in determining the levels of procyanidins, a class of polyphenolic compounds, in wines. These compounds, primarily found in grape skins and seeds, contribute to the astringency, color, and antioxidant properties of the final product. The winemaking process, including grape handling, fermentation techniques, maceration, and aging, significantly impacts procyanidin extraction and polymerization, influencing both the sensory and health-related properties of the wine [63-66].

Grape handling methods before fermentation can affect procyanidin extraction. The way grapes are crushed, sorted, and processed determines the extent to which procyanidins are released from the skins and seeds into the must [67].

Crushing is essential for releasing the polyphenols from grape skins and seeds. Mechanical crushing, if too aggressive, may lead to the breakdown of seeds and the release of undesirable compounds. However, moderate crushing facilitates the release of procyanidins, enhancing their concentration in the wine [67].

Cold soaking involves macerating the crushed grapes at low temperatures before fermentation. This technique allows the extraction of phenolic compounds, including procyanidins, without initiating fermentation. Cold soaking has been found to increase procyanidin content, especially in red wines, by promoting the diffusion of polyphenols from the skins into the must [68,69].

Fermentation is a pivotal step in the winemaking process that influences the solubility, polymerization, and degradation of procyanidins [69].

Fermentation temperature is critical for procyanidin extraction. Higher temperatures (25-30 °C) facilitate the release of polyphenols from grape skins and seeds. However, temperatures above this range may lead to the degradation of sensitive phenolic compounds, including procyanidins. Therefore, maintaining optimal fermentation temperatures is key to maximizing procyanidin levels [70].

The choice of yeast strain during fermentation can also influence the procyanidin content of the wine. Some yeast strains have been shown to enhance the extraction of polyphenols, while others may result in lower concentrations. Additionally, yeast-derived metabolites can interact with phenolic compounds, modifying the sensory properties of the wine.

Longer fermentation times, especially in red wines, allow for more extended contact between the juice and grape skins, increasing the extraction of procyanidins. Extended fermentation and maceration times are beneficial for extracting these compounds, as prolonged skin contact enhances the diffusion of phenolic compounds into the wine [71].

Maceration refers to the process of allowing the crushed grape skins to remain in contact with the fermenting juice to extract phenolic compounds, including procyanidins. The technique and duration of maceration can significantly impact procyanidin levels [71].

The length of time that grape skins are in contact with the wine during fermentation or post-fermentation maceration directly influences the level of procyanidins in the wine. The longer the skin contact, the higher the procyanidin content, as more polyphenols are extracted from the skins.

After fermentation, maceration may continue for days or weeks to further extract phenolic compounds. This process increases the concentration of procyanidins, contributing to the wine's flavor profile, color, and antioxidant properties [72].

Aging plays a significant role in the polymerization and stabilization of procyanidins in wine. Both the method and environment of aging affect the final concentration and characteristics of procyanidins in the wine [73].

The use of oak barrels in wine aging is a common practice that impacts the phenolic composition of the wine. Oak can contribute additional phenolic compounds to the wine, influencing its color, flavor, and tannin structure. However, oak aging can also promote the polymerization of procyanidins, leading to the formation of larger molecules that may have different sensory attributes (e.g., reduced astringency) [63,64,73].

In addition to barrel aging, bottle aging allows for the gradual oxidation and polymerization of procyanidins. Over time, this oxidation can lead to a more stable and smoother wine, with softer tannins and less astringency. However, the aging process may reduce the concentration of free procyanidins as they polymerize into larger structures [64,74].

Techniques to enhance procyanidin content:

Several techniques can be employed to optimize the extraction and preservation of procyanidins in wine, ensuring their health benefits and enhancing sensory qualities.

- **Enzyme treatment**. The use of enzymes such as pectinase during fermentation can help break down cell walls and improve the extraction of procyanidins and other polyphenols from grape skins and seeds. This results in a higher concentration of procyanidins in the wine [75-79].
- **Microoxygenation**. This technique involves introducing small amounts of oxygen into the wine during aging. Microoxygenation can promote the polymerization of procyanidins, reducing their astringency while enhancing their antioxidant properties and stability [80,81].
- **Pre-fermentation treatments.** Techniques like cryomaceration (macerating grapes at low temperatures before fermentation) can increase procyanidin extraction, particularly for certain grape varieties known to have high phenolic content [82-87].

Winemaking technology has a significant influence on the accumulation of procyanidins in wines. The extraction of procyanidins is affected by a variety of factors including berry size, grape handling, fermentation conditions, maceration techniques, and aging processes. Understanding the effects of temperature, fermentation time, maceration duration, and aging methods can help winemakers optimize the levels of these important polyphenols in their wines. By utilizing specific winemaking practices, it is possible to enhance the sensory attributes and health benefits of wines, making them a more beneficial and enjoyable product for consumers [88-93].

6. Conclusions

In conclusion, proanthocyanidins, particularly procyanidins, play a crucial role in the sensory and health-related properties of wines, contributing to their color, astringency, and antioxidant potential. The physical, chemical, biochemical, and physiological characteristics of procyanidins have a significant impact on wine quality, with factors such as climate, soil, and grape variety influencing their accumulation in red wines.

The accumulation of procyanidins in red wines is strongly affected by climate, soil, and grape variety, each contributing to the wine's sensory characteristics and potential health benefits. Optimal conditions, such as moderate temperatures, adequate sunlight, and slightly acidic, well-drained soils, alongside the careful choice of grape varieties that naturally accumulate higher levels of procyanidins, are key to enhancing the polyphenol content and producing high-quality red wines.

Winemaking practices greatly influence the accumulation and characteristics of procyanidins in wine. By carefully managing factors such as grape handling, fermentation conditions, maceration, and aging, winemakers can optimize procyanidin levels, enhancing both the sensory experience and the health benefits of the final product.

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