Effect of Climate Change on Polyphenols Accumulation in Grapevine

Monis Hussain Shah, Rizwan Rafique, Tanzila Rafique, Mehwish Naseer, Uzman Khalil and Rehan Rafique

Abstract

Phenolics compounds in grapes contribute to berry and must color, organoleptic properties, nutritional value, antioxidant properties and provide protection against environmental challenges. Climate change has place mammoth challenges for the viticulture industry in different viticulture regions. Environmental variables determine to the greater extent, suitable grapes varieties for fresh as well as premium quality wine production. Grape berry composition is particularly affected by heat, drought, and intensity of solar irradiation. It is expected that climatic extremes will have an adverse effect on berry quality traits such as phenolic compounds in different grape cultivars. Polyphenols particularly anthocyanins decrease at elevated temperature, similarly flavanols levels increase with better exposure to solar radiation. Water availability is crucial for better vine growth and good production, however modest water stress particularly near veraison, upregulates the activity of key enzymes of the phenylpropanoid and flavonoid pathways. Therefore, it is important to know that how and when phenolic substance accumulate in berries and how various cultivars respond. This review elaborates the effect of weather conditions on biosynthesis of different phenolic compounds in grapes. Berry phenolic substances e.g., total phenolic compounds (TPC), total anthocyanins (TAC) and total flavonoid contents (TFC) synthesis is strongly regulated under the influence of environmental conditions during growing season. In this chapter we, shall focus on accumulation of phenolic compounds in grapevine in relation to climatic variations.

Keywords: Grapevine, berry phenolics, anthocyanins, temperature, CO\textsubscript{2}, radiations, water

1. Introduction

1.1 Global climate change

Climate changes are the mammoth challenges that human race will face in coming decades as described by Intergovernmental Panel on Climate Change. The increase in release of greenhouse gases, particularly CO\textsubscript{2} is considered as the main cause of global warming. The concentration of CO\textsubscript{2} has increased from 280 ppm to 400 ppm subsequently of 0.5–1°C rise in an average temperature. It is expected that mean global temperature will rise by 0.2–0.3°C per decade hence rise of 1.2 to 5.8°C
by the end of the twenty-first century. The increase in mean temperature in key viticulture regions was 1.6–1.8°C in Europe and 1.2–1.4°C across the globe during the growing seasons from 1950 to 2000 [1–4]. Similarly, a decrease in precipitation has been recorded in over southern Europe [5]. In addition to rising temperature, corresponding heat waves are becoming more common and frequent. Climate change is no doubt an inevitable challenge that must be dealt with serious policies in the upcoming decades. It is a major challenge that viticulture industry has to face in coming decades.

1.2 Climate a key determinant for viticulture

Climate is a limiting factor determining phenology, vegetative growth, physiological development, fruit production and consequently wine quality [6–8]. Geographical distribution of vineyards is determined by climatic factors. Weather parameters: temperatures, solar radiation, precipitation, and the inter-annual seasonal variability leads to annual changes in vine productivity [9–11]. Extreme weather events: hailstorms, excessive rainfall, late frost spells have been recognized as factors having detrimental impacts on grapevine productivity and quality [12].

1.3 Climate change impacts on viticulture

It is evident that climate change will have a negative impact on viticulture industry. Higher temperature during the active growing season will strongly affect grapevines because it is a major driver of development stages of grapevine [13]. Extreme heat stress during ripening period will abruptly reduce grapevine metabolism. It may result in higher sugar levels and lower acidity with potential increase in chances of wine spoilage [14] thereby lower production and quality. Furthermore, extreme heat and water stress, under future climates, may threaten final yields and productivity [15].

2. Grapevine phenolic compounds

Phenolic Compounds in grapes account for only a trivial proportion of the berry weight but contribute significantly to fresh fruit. All phenolic compounds have some common features as; an “aromatic ring” comprising of six carbon atoms having one or more hydroxyl (OH) groups or their derivatives as indicated in Table 1. They play an important role in color development, astringency, flavor and aroma to grapes. These compounds are the main substrates for grape juice and wine oxidation [16–18]. Their susceptibility to oxidation due to unsaturated double bonds and hydroxyl groups make phenolic compounds valuable antioxidants [19, 20]. Flavonoids and non-flavonoids phenolics are produced inside grape berries through biochemical pathway (Figure 1). Flavonoids accumulate mainly in the skin, seeds, and stem while neoflavonoids mostly accumulate in the mesocarp of the berry.

Phenolic profile of grapevines depends on, region, prevailing weather conditions, and site-specific viticultural practices [21–27]. Higher the total phenolic content more is antioxidant activity and it is a genotypic character [28–31]. Skin color (yellow, pink, red, blue-black and full black) is due to presence of anthocyanins. Anthocyanins are synthesized to protect the berries from the negative effect of adverse environmental conditions particularly ultraviolet radiation. Accumulation and degradation of already synthesized anthocyanins was noticed due to elevated temperatures during the ripening period [32, 33]. Therefore, in hotter regions the
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| Polyphenolic Compounds | Basic Chemical Structure | Examples |
|------------------------|-------------------------|----------|
| Anthocyanin            | ![Anthocyanin](image)    | Cyanidin-3-GLUa  
R1=OH, R2=H  
Delphinidin-3-GLU  
R1=OH, R2=OH  
Peonidin-3-GLU  
R1=OCH3, R2=H  
Malvidin-3-GLU  
R1=OCH3, R2=OCH3  
Petunidin-3-GLU  
R1=OCH3, R2=OH  
|                        |                         |          |
| Flavonols              | ![Flavonols](image)     | Isorhamnetin-3-GLU  
R1=OCH3, R2=H  
Kampferol-3-GLU  
R1=H, R2=H  
Laricitrin-3-GLU  
R1=OCH3, R2=OH  
Myricetin-3-GLU  
R1=OH, R2=OH  
Quercetin-3-GLU  
R1=OH, R2=H  
Syringetin-3-GLU  
R1=OCH3, R2=OCH3  
|                        |                         |          |
| Flavan-3-ols           | ![Flavan-3-ols](image)  | Catechin (Left)  
Epicatechin (Right)  
|                        |                         |          |
| Tannins                | ![Tannins](image)       | Proanthocyanidin tetramer having  
(from top to bottom) epigallocatechin,  
epicatechin, catechin, and epicatechin gallate  
|                        |                         |          |
| Hydroxycinnamic acid   | ![Hydroxycinnamic acid](image) | Caffeic Acid  
R1=OH, R2=OH  
Cinnamic Acid  
R1=H, R2=H  
Coumaric Acid  
R1=H, R2=OH  
Ferulic Acid  
R1=OCH3, R2=OH  
|                        |                         |          |
Phenolic Compounds

| Polyphenolic Compounds | Basic Chemical Structure | Examples |
|------------------------|--------------------------|----------|
| Hydroxybenzoic acid    | ![Chemical Structure](image1) | Gallic acid  
R1=OH, R2=OH  
Protocatechuic Acid  
R1=H, R2=OH  
Syringic acid  
R1=OCH3, R2=OCH3 |
| Stilbenes              | ![Chemical Structure](image2) | Piceid  
R1=OH, R2=GLU  
Pterostilbene  
R1=OCH3, R2=OCH3  
Resveratrol  
R1=OH, R2=OH  
Viniferins  
resveratrol polymers |

Table 1. Different classes of polyphenolic compounds and their basic structures along with examples are given.

Figure 1. Shikimate pathway for the biosynthesis of anthocyanins, Flavonols and flavonoids. (reproduced from the idea of Velasco et al. [146] with few modifications).

Anthocyanin in red and black grapes skin is affected more, while climatic conditions in colder growing regions favor their biosynthesis. Grapevine varieties (var.) have particular anthocyanin fingerprints e.g., malvidin-3-O-glycoside is most abundant in var. ‘Hasansky Sladky’ while in var. ‘Zilga’ it is delphinidin-3-O-glycoside. Moreover, their biosynthesis varies from year to year due to annual seasonal climatic variability [34].
2.1 Phenolic compounds biosynthesis in grapevine

Production of phenolic compounds is regulated by transcription factors which regulate the activity of genes involved in phenolic biosynthetic pathways. Moreover, location, timing, and extent of the production of phenolic compounds is also dependent on these transcription factors [35, 36]. In addition to grape berries, some flavonoids are produced in leaves and are imported via the phloem [37, 38]. Shikimate and malonate pathways are the two main “assembly lines”. The shikimate pathway (Figure 1) is the part of the biosynthesis chain of most plant phenolics, whereas the malonate pathway (Figure 2) is less important compared with Shikimate pathway in plants, but the malonate pathway is essential in fungi and bacteria.

3. Key climatic variables affecting grapes polyphenolic compounds

Secondary metabolites such polyphenols play significant ecological functions within the defense and signaling mechanisms in plants [39]. Different climatic variables such as air temperature, radiation, rainfall, relative humidity, wind, altitude, and topographic features play vital role in the polyphenol biosynthesis pathway in grapes. In this section, we shall review research studies focusing on key environmental variables.

3.1 Temperature

Temperature plays a significant role in vine phenology whereas increase in mean temperature prolonged the vegetative and reproductive cycle of grapevine and hence berry developmental and maturity stages are shifted in warmer months of the growing plant reproductive cycles [40]. Available historical records of harvest timings from different grape growing regions indicate an advance of 1–2 weeks during last few decades [41–46]. Although, some management practices may be the
one reason for the advancement of ripening [47]. The conjugated effects of progressive phenology along with rise in temperatures during berry ripening with higher sugar contents, lesser organic acids concentration and altered berry composition of metabolites, such as phenolic compounds [40]. Research studies have encompassed the effect of wide ranging of temperature intensities; from moderate to high heat stress i.e., up to 35–45°C during day or night period at key berry development stages. The genotype, plant material and experimental constraints may affect the response of berry metabolism to temperature variations [48]. Although, difficult to fully relate with field conditions, controlled climate chamber experiments are also conducted to understand the influence of environmental variations [49–51].

3.1.1 Temperature impact on phenolic compounds

Effects of temperature on polyphenols are not always consistent as recently highlighted [48, 52]. However, there are unequivocal scientific evidence which indicate the deleterious effects of elevated temperature on the biosynthesis of anthocyanins in the grape berry. Studies of the impact of elevated temperature were validated at physiological and molecular studies [53–62]. It was noticed that heat stress repressed chief anthocyanin biosynthesis regulators, such as VviMYBA1 and downstream regulating genes such as VviCHI, VviUFGT, VviDFR, VviF3H2, and VviLDOX. However, not all of these research studies indicated unambiguous suppression or a strong correlation with lower anthocyanin accumulation. Various aspects of viticulture e.g., vines, cultivars, berry development stages, treatment intensities and sampling strategy take part in accumulation and production of anthocyanin. The effect of temperature on anthocyanin biosynthesis varies highly between different genotypes. For instance, when maximum temperature exceeds 35°C during berry ripening, it inhibits the color formation prominently e.g., in cv. Grenache than in cv. Carignan [63].

Previously, it has also been established that timings of temperature variations during day-night period have a strong influence on berry metabolites and lower temperature near berry ripening time particularly at night was related with improved coloration of grapes [54]. It was recently confirmed through experiments at molecular level that lower night temperatures increased anthocyanin accumulation and expression of related genes e.g., VviF3H1, VviUFGT, VviCHS3, and VviMYBA1 [64]. More pronouncing effects of lower night temperature were noticed near veraison stage in Corvina grapes. In a related study on Kyoho grapes, 3°C rise in temperature (27 to 30°C) during berry ripening caused less berry coloration and induced a significant decrease in transcript levels of anthocyanin regulating genes [65]. Similarly, in cv. Merlot, increase in day’s temperature from 20 to 25°C during ripening caused decrease in anthocyanin levels by 37% [62]. In addition to repressing of anthocyanin regulating genes, high temperature may stimulate anthocyanin degradation due to the augmented activity of peroxidases [32]. It has been established that a peroxidase coding gene; VviPrx3 is up regulated, in berries when exposed to high temperature [66], and similar effects have been noticed in other plant species, such as Brunfelsia, litchi and strawberry [67–69].

A related increase in quantity of acylated and tri-hydroxylated anthocyanins has been observed in cvs. Merlot, Cabernet Sauvignon, Sangiovese and Malbec under higher temperature conditions [51, 60, 62, 70, 71], alongside overexpression of the acyltransferase gene Vvi3AT activity. Similarly for anthocyanins, elevated temperature impeded flavanol buildup while significantly augmented methoxylated (isorhamnetin & syringetin) and 3′, 4′, 5′-substituted (myricetin & syringetin) flavonols in cv. Merlot. More interestingly, rise in temperature may cause a disconnection of sugar-anthocyanin accumulation and biosynthesis, hence leading to a
lower anthocyanin-sugar ratio which might be due to delayed anthocyanin biosynthesis or lesser anthocyanin accumulation during ripening phases. The extent of this thermal decoupling is highly cultivar dependent as indicated for cv. Grenache and cv. Carignan and can vary even among the clones of same cultivar as discussed for cv. Tempranillo [62, 63, 71–74].

The effect of temperature on tannins biosynthesis is yet not fully understood. However, it may be pointed that elevated temperature can enhance the production of tannin monomers, flavan-3-ols as highlighted by [75]. However, some other studies report non-significant effects on tannin production as tannins were not much affected by heat stress in cv. Sangiovese at veraison stage. More recently, scientists came up with similar results indicating no effect on flavan-3-ol or tannin levels. Although, significantly higher galloylation of flavan-3-ols levels were noticed in consistent with earlier findings. It was further indicated that an overexpression of UDP glucose-gallic acid-glucosyltransferase genes under elevated temperature. Moreover, heat stress also reserved the expression levels of members of STS biosynthetic pathway. However, lower temperature upregulated STS transcripts hence accelerated stilbene biosynthesis [48, 60, 75–78].

3.2 Radiation

Berry exposure to sunlight is generally associated with better berry quality attributes due to more total soluble solids (TSS), anthocyanins, and phenolics. On the other hand, it also lowers acidity and pH along with lower disease incidence due to favorable improved microclimate [48, 79–81].

3.2.1 Effect of radiation on phenolic compounds

Increased levels of phenolic compounds have been noticed in cvs. Pinot Noir, Riesling, Summer Black and Cabernet Sauvignon owing to better exposure to sunlight [82–85]. It also augmented the expression level of regulatory and structural phenylpropanoid genes as highlighted by recent studies [86–89]. Flavonoids particularly flavonol glucosides are the most light-responsive phenolic compounds ones whose levels increased with better exposure to sunlight. This positive effect was in consistent with their UV radiation-screening activity and their capability to reduce oxidative damage. Flavonoids were produced upon exposure to UV-B radiation as adaptive traits to reduce the radiation damage, as there exists a strong correlation between physiology and quercetin-3-O-glucoside & kaempferol-3-O-glucoside levels in UV-B radiation stressed vines [90–96]. Recently, a more comprehensive study elucidated that shoot removal and leaf thinning in cvs. Cabernet Sauvignon & Petit Verdot improved light exposure, hence it significantly augmented the flavonols kaempferol, quercetin and myricetin levels. However, little or no change was noticed for other flavonoid compounds. Similarly, higher levels of hydroxycinnamic acids and flavonol were noticed due to increased sun light exposure in cv. Cabernet Sauvignon [89, 97].

Several transcriptomic studies indicated that flavonol genes such as VviGT5, VviGT6 and VviFLS1 were induced more than other phenylpropanoids genes when exposed to UV radiation as observed in cv. Tempranillo berry skin. In return, lower expression level of VviFLS4 gene and its transcriptional regulator i.e., MYB12 was noticed under shade [91]. However, it has not yet been established that to what level UV light contributed to stimulate the synthesis of phenolic compounds. It can be deduced from literature that UV-B radiations are responsible for overexpression of key flavonoid genes [39, 98–103]. Recently, VviHY5 and VviHYH; the two bZIP TFs elongated hypocotyl 5 protein (HY5) orthologs were identified as the key
components of UV-B reaction pathway along with mediated flavonol accumulation owing to high radiation exposure in grapevines [99, 104].

Anthocyanin accumulation increased significantly when grapes clusters were exposed to increased light, whereas shading decreased them. Recently, it was indicated that the UV-B radiation might prompted up-regulation of miR3627/4376 which facilitated anthocyanin accumulation [105, 106]. In a related in vitro study in which effect of berry exposure to light and temperature was studied it was inferred that elevated light increased anthocyanin levels in grapes [58]. The augmented anthocyanin levels found associated with the up regulation of correlated genes of anthocyanin biosynthesis pathway. Some other studies also endorse the stimulation of key anthocyanin genes e.g., TF VviMYBAa and VviUFGT under higher sun light exposure [65, 98]. Interestingly, UV-B radiation prompted the expression of VviMYBA1 gene while delaying the down regulation of VviMYBA6 and VviMYBA7 genes at later berry developmental stages [104]. Less light exposure modulated the quantity of di- to tri-hydroxylated anthocyanins more toward tri-hydroxylated anthocyanins as demonstrated through the down regulation of VviF3′5′Hs, somewhat similar but inconstant trends have been reported in cvs. Cabernet Sauvignon and Petite Verdot under warm climatic conditions [58, 89, 97, 98, 105]. However, low light conditions may increase non-acylated anthocyanins concentration as highlighted by [91, 106]. There is still need for further research to develop a better understanding.

3.3 Water

Water is an important constituent of plant structure and performs variety of functions in addition to transport of mineral nutrients from soil. It is a key component of photosynthetic pathway in plants. Moreover, water balance is necessary for quality table and wine grape production. Similarly, primary and secondary metabolite production is regulated by balanced water availability.

3.3.1 Impact of vine water status on phenolic compounds

Different primary and secondary metabolites are significantly influenced by drought stress in grapevines. Recent research has focused on probing the effects of water on berry physiology and quality attributes [39, 107, 108] and it has been noticed that drought stress may increase primary metabolites and polyphenols up to 85% and 60% respectively under different stress treatments. The impact of water deficit varies with intensity and duration of the stress conditions as well as berry developmental stage. Water deficit during the initial growth phases has more negative impact on final volume and yield at harvest as it reduces cell expansion, however rate of cell expansion is not affected much [109] while ripening phase, and it has little impact on berry size. Primary metabolites such as citric acid and glyceric acid synthesis was affected by both short and prolonged stress whereas polyphenols biosynthesis was accelerated only by the prolonged drought stress treatment.

Selective water deficit applications increased anthocyanin accumulation in grape skin along with the activation of genes of corresponding anthocyanin biosynthesis pathway [110]. For instance, in grape cv. Chardonnay, water stress increased the content of flavonols and decreases the expression of genes involved in biosynthesis of stilbene precursors [39].

It has been observed that modest water deficit i.e., predawn leaf water potential of 0.3 to −0.5 MPa is useful for better wine quality especially for red cultivars [111, 112] These positive effects may partially be attributed to increased solute concentration owing reduced berry volume under water deficit conditions. However, a higher buildup
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of secondary metabolites independent of change in berry volume has been reported [113]. More elaborative research findings at molecular level highlighted an upregulation of key enzymes of the phenylpropanoid and flavonoid pathways in response to water stress [39, 114–119]. But these beneficial effects were more noticeable when water deficit occurred throughout berry ripening phase [48].

In addition to an increase in the accumulation of phenylpropanoids and flavonoids due to water stress, an altered composition of anthocyanins has also been noticed owing to increased levels of tri-hydroxylated anthocyanins i.e., petunidin, delphinidin and malvidin [110, 120–123]. However, these observed changes in the anthocyanin profile of grapes due to water stress appear to be highly varietal dependent [124, 125] due to varying genotypic response associated to environmental variables. Similarly, an increase in proanthocyanidin concentration and proanthocyanidin polymerization along with higher catechin levels in grape berry skins have also been indicated by [126–128]. The increase in phenolic levels when water deficit occurred before veraison may be due to concentration effects [129, 130] however, several other scientists discussed increase in anthocyanin content at berry level [110, 113, 122, 131]. More focused research is needed to validate ribose, glyceric acid, citric acid, kaempferol-3-O-glucoside and quercetin-3-O-glucoside interactions as indicators of drought stress [132].

3.4 Impacts of elevated CO₂ concentration

Elevated atmospheric CO₂ is usually favorable for plant growth as it causes an increased photosynthetic carbon fixation hence more biomass and yield. Free Air Carbon enrichment (FACE) experiments on agronomic crops such as wheat, rice and soybean have outlined 12–14% increase in harvestable yield owing to elevated carbon dioxide (eCO₂) [133–135]. Although, there are limited studies on horticultural crops however, it has been indicated that eCO₂ increased total antioxidant capacity of fruits and vegetables, along with higher concentration of glucose, fructose, total soluble sugars, polyphenols compounds, flavonoids, ascorbic acid, and calcium [89]. Research studies on grapevine related to eCO₂ mainly focused on vegetative growth and photosynthetic responses while records on berry metabolism at physiological and molecular level are relatively scarce. However, most of the available records suggest an increase in photosynthetic activity hence better yield and biomass accumulation [93, 136–140]. Recently dependence of berry ripening rates on the carbon fixation was investigated however, only few quality attributes were found to be affected due to eCO₂ and that particularly; sugars, acids, and berry size [137, 142, 143]. Recently, it has been inferred in FACE experiment that eCO₂ did not negatively affected juice and wines quality [141]. Similarly, it had already been established that anthocyanins and proanthocyanidins were not affected by eCO₂ [136, 137, 142–144]. Moreover, in multi stress experiments on cv. Temperanillo cuttings where elevated temperature condition i.e., +4°C and CO₂ i.e., 700 ppm were simulated it was deduced that high CO₂ in combination with elevated temperature hastened berry ripening and decreased high temperature tempted anthocyanin–sugar decoupling in berries [145].

4. Conclusions

Polyphenols are the key secondary metabolite of grapes and have ample amounts of antioxidants. The production and biosynthesis of phenols is regulated by varying climatic conditions in addition to genotypic traits. Elevated temperature impairs phenolic biosynthesis pathways hence lesser accumulation, while lowers
temperatures favor their production. On the other hand, excessive radiation may cause degradation of these compounds. Optimum sunlight penetration is necessary for the activation of genes of phenolic biosynthesis pathways. Water balance is also important as modest water deficit near veraison can also promote their activity. For elevated carbon dioxide levels (eCO$_2$) despite limited studies, no major negative effects have been reported. However, there is need to study grapes phenolic compounds in relation to global climate change.

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