Journal of Berry Research 3 (2013) 1–14
DOI:10.3233/JBR-130047
IOS Press

Invited Review

UV-B and abscisic acid effects on grape berry maturation and quality

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Received 23 January 2013; accepted 30 January 2013

Abstract. This review provides an overview of existing literature on the effects of ultraviolet-B (UV-B) radiation and abscisic acid (ABA) on physiological and biochemical aspects affecting grape berry (*Vitis vinifera* L.) growth, maturation and their quality for winemaking. The UV-B (280–315 nm) comprises only a small fraction of sunlight that reaches the Earth's surface, but has enough energy to cause large photobiological effects on higher plants. The UV-B levels are greater in the tropics than in upper latitudes and also increase with altitude, hence some vineyards are exposed to high UV-B but photoprotection and repair mechanisms are usually sufficient to prevent the occurrence of damage in grapevine tissues. ABA is a phytohormone that, aside to control stomatal aperture, regulates acclimation to adverse environmental conditions, and controls grape berry maturation (non-climacteric). A promotive effect of UV-B on ABA biosynthesis has been found in grapevine leaves. Accumulation of phenols (namely phenolic acids, stilbenes and flavonoids) is an acclimation and protective response against UV-B, either directly by absorbing UV-B in epidermal tissues and/or by reducing its penetration through underlying tissues, or indirectly by scavenging free radicals so acting as antioxidants. High UV-B and ABA applications increase total phenols in grape berries, but those with higher antioxidant capacity (i.e. dihydroxylated anthocyanidins and flavonols like quercetin) are increased relatively more. These treatments also hasten berry sugar and phenol accumulation, but reduce berry growth and sugar per berry at harvest, and therefore decrease yield. The quality of grape berries for winemaking integrates various aspects, but for red wines, it has a high correlation with accumulation of phenolics stimulated by UV-B and ABA.

Keywords: UV-B radiation, abscisic acid, phenols, grapevines, berries, *Vitis vinifera* L.

Abbreviations

ABA	abscisic acid
CHS	chalcone synthase
FLS	flavonol synthase
F3′5′H	flavonoid 3′5′-hydroxylase
F3′H	flavonoid 3′-hydroxylase
IAA	indol-3-acetic acid
MDA	malondialdehyde

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MEP	methylerythrol phosphate
OMT	O-methyltransferase
ORAC	oxygen radical absorbance capacity
PAL	phenylalanine ammonia lyase
PAR	photosynthetically active radiation
PRD	partial rootzone drying
PSII	photosystem II
ROS	reactive oxygen species
UV	ultraviolet
UV-B	ultraviolet-B
$UV\text{-}B_{BE}$	biologically effective UV-B radiation

1. UV-B radiation

Ultraviolet (UV) radiation is a fraction of the solar electromagnetic spectrum with wavelengths between 200–400 nm, which are shorter than the photosynthetically active radiation (PAR; 400–700 nm) and it partially over imposes with that humans perceive as violet. Based on an international standardization (Commission Internationale de l'Éclairage), UV comprises UV-C, UV-B and UV-A. The UV-C (200–280 nm) is the fraction of shorter wavelengths and therefore of higher photon energy that is completely absorbed by ozone and atmospheric gases and do not reach the Earth's surface. The UV-B corresponds to 280–315 nm, which is mostly absorbed by ozone and atmospheric gases, although a certain proportion representing *ca.* 5% of UV and 0.5% of total electromagnetic energy received from the sun gets through the atmosphere [1]. The UV-A (315–400 nm) is the portion with longer wavelengths unaffected by atmospheric gases and represents the remaining 95% of the UV electromagnetic energy in the biosphere.

Although the UV-B represents only a small fraction of the sunlight [2], it has enough energy to cause large photobiological effects on higher plants, some related to the plant's response to the evoked damage, and others as an induced acclimation linked to the perception of UV-B [3–7]. The UV-B can damage macromolecules (nucleic acids, proteins and lipids are particularly sensitive), directly and/or indirectly through generation of free radicals (reactive oxygen species; ROS) so impairing cellular processes [8]. Importantly however, UV-B is not only a harmful agent but it has an important role as an informational environmental signal [6, 9–15].

2. Solar UV-B levels

Aside the capture of solar UV-B by the ozone layer in the stratosphere, there are a variety of factors that influence the UV-B levels to which plants are exposed. One of these factors, possible the most important, is the solar angle that determines the trajectory of light through the atmospheric barrier so defining the air mass thickness and interception by gases, which makes UV-B levels greater in the tropics than in higher latitudes [2, 12]. Another significant factor is the elevation of the sun over the zenith that changes during the day and with the seasons, and therefore UV-B levels are higher at midday and summer-time (in middle and high latitudes). The UV-B levels also increase with altitude, because of thinner air masses and higher atmospheric transparency to shorter wavelengths radiation, and weather conditions (cloud cover), surface reflection, atmospheric pollution and absorption by plant canopies greatly affect the amounts of UV-B [2, 16].

The UV-B levels can be assessed per area and time units as photon flux rates (μmol m^{-2} s^{-1}) or as irradiations (i.e. energy level; kJ m^{-2} h^{-1} or W m^{-2}), the latter being influenced by light wavelengths that determine the amount of energy per photon. Many authors frequently use and reports a measurement of UV-B relative to biological events, the so called biologically effective UV-B radiation ($UV\text{-}B_{BE}$), which incorporates an estimation of the biological effectiveness of UV-B based on the action spectrum for a selected response, such as redness of the skin by sunburn (erythema) in humans, or a well-known response in plants [17]. The different types of measurements are suitable for different purposes, i.e. for studies related to photoreception and signal transduction it seems to be more appropriate

to measure UV-B photon flux rates because those processes generally involve individual photons according to the photoreceptor absorption spectrum. However, if a particular response results in tissues oxidative damage, the energy of the radiation (irradiance measurements) appears to be more suitable [18].

3. Effects of UV-B on higher plants and grapevines

Several studies related to the impact of UV-B on various morphological, biochemical and molecular aspects have been published, but most of the responses that have been found are highly variable depending on species, experimental conditions and UV-B levels [6, 19]. Most studies are difficult to compare, mainly because some of them deal with plant's responses to UV-B as evoked damage, while others reports on induced acclimation to this environmental signal [3–7]. Differences in UV-B fluence rates, irradiances and time of exposure (doses) produce significant changes in the plant's responses [6, 11, 13]. Moreover, the effect of UV-B depends on the context in which UV-B treatment is given; that is, other environmental factors such as total radiation, temperatures, water and nutritional status can interact with UV-B effects [6, 17, 20]. In general, fewer effects are observed when plants are submitted to contrasting UV-B situations under field trials than in more strictly controlled environmental conditions [17]. It has been shown that under UV-B/PAR ratios higher than those found in natural conditions, generally in experiments performed in growth chambers with reduced PAR, UV-B effects can be exaggerated [21, 22], presumably because environmental PAR levels also induce protective and repairing mechanisms that reduce UV-B damages [23].

High UV-B levels may cause damages directly and/or indirectly, through overproduction of ROS, to a wide range of cellular constituents in different plant tissues. There are reports of impairment of nucleic acids, proteins and lipids that inhibit photosynthetic reactions and different cell membrane processes [3, 5, 6, 22, 24]. Plants have developed a complex antioxidant defensive system against increased ROS that involve both, enzymatic and non-enzymatic mechanisms. The former is represented by antioxidant enzymes such as superoxide dismutase (SOD), ascorbate peroxidase (APX), catalase (CAT) and glutathione reductase (GR), while the non-enzymatic antioxidants include carotenoids, tocopherols, ascorbate, glutathione and phenols [5]. The extent of the damage that occurs in plants grown with relatively high ambient UV-B levels is not clear and it is noticeable that plants in nature rarely exhibit visible damage. The harm is more likely to be evident when plants are exposed to UV-B without previous acclimatization, since if plants are acclimated to light in a particular environment, photoprotection and repair mechanisms are usually sufficient to prevent the occurrence of damage [18, 25].

In an field experiment with grapevines exposed to high UV-B levels (irradiances up to 0.40 W m^{-2} at noon hours) with high levels of PAR (and therefore reduced UV-B/PAR ratios) no damage was observed in cell membrane integrity [26], although there were increases in the contents of malondialdehyde (MDA) in leaves that reflected lipid peroxidation so indicating oxidative stress [27, 28]). It has been reported that high UV-B levels may cause structural damage to chloroplasts and photosynthetic pigments [29–32], limit gas exchange through reduction in stomatal conductance [33–35], and inhibit photosystem II (PSII) functionality [36]. However, the inhibition of PSII found in the experiments by Pfündel [36] was obtained in grapevine leaves acclimated to darkness before treatments with UV-B and therefore it does not seem to be a generalized UV-B effect. Photosynthetic pigments (chlorophylls and carotenoids) in grapevine leaves were reduced by UV-B [37], although it has been noticed that UV-B showed no effect when pigments are reported per leaf area basis and are reduced per leaf dry weight basis since UV-B also increase leaf thickness [26, 38]. Photosynthesis and stomatal conductance of grapevines were reduced by high UV-B levels through limitation of gas exchange of leaves, but UV-B was not effective in causing an impairment of the photochemical apparatus (measured as Fv/Fm; maximum potential quantum efficiency of PSII when all capable reaction centers are open, a direct measurement of PSII efficiency that excludes the indirect effect of UV-B reducing stomatal aperture) [38].

On the other hand UV-B has many photomorphogenic effects on plants, possibly as an acclimatization mechanism that reduces the interception of potentially harmful UV-B [39]. Even though results are variable, reductions in vegetative growth as shoot length, number of leaves and leaf expansion are generally found [40–42]. It has been also observed that UV-B increases leaf thickness, with the presence of more epidermal cells per leaf area [43, 44], augmentation of epicuticular waxes accumulation and of the number of trichomes [45]. Such mechanisms favor epidermal reflectance, reduce transmittance of UV-B, and increase the distance through the most sensitive internal

tissues [46, 47]. In grapevine, it was observed that exposition to high UV-B reduced shoot length and plant leaf area (smaller leaves and lower number of leaves) and augmented leaf thickness although epicuticular waxes content was not affected [38]. Many morphological effects may be due to alterations in the amount, distribution or sensitivity to phytohormones that promote cell elongation and growth, such as auxins. Ross and Tevini [48] demonstrated that indol-3-acetic acid (IAA) levels can be reduced by photooxidation in sunflower seedlings exposed to relatively high UV-B levels.

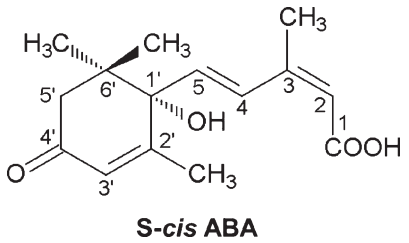
In addition to the above mentioned effects, a more general acclimation response to UV-B is the accumulation of phenolic compounds in epidermal cells [20, 49–51], also in grapevines [26, 38, 52]. Phenols absorb UV-B and reduce its penetration through underlying sensitive tissues [6, 53, 54], and likewise act as antioxidants [55–57]. In grapevine leaves a high correlation between phenol accumulation and oxygen radical absorbance capacity (ORAC) was found, and both were augmented by UV-B [38].

UV-B levels differentially regulate gene expression, and high UV-B levels activate a general stress signal transduction pathway which leads to a response similar to that that occurs after diverse biotic and abiotic stresses (i.e. induction of senescence genes and increase of pathogenesis-related proteins) [13]. Meanwhile, low UV-B levels, a stimulus probably perceived by an UV-B photoreceptor like the UV-B photoreceptor UVR8 [58] and transmitted downstream by several signaling pathways, induce the expression of a variety of genes involved in protective responses, e.g. biosynthesis of protective pigments, nucleic acids repair and antioxidant enzymes [59]. These differential expression of genes induced by UV-B was also observed in grapevines cultured *in vitro* and treated with high and low UV-B irradiances (0.33 W m^{-2} and 0.08 W m^{-2}, respectively) [60]. It has been also found that regulation by UV-B in the expression of many genes is tissue-specific, and that tissues not directly exposed to UV-B as roots showed alterations in gene expression, implying that the signal is transmitted from the illuminated tissues, although the nature of the signal remains obscure [61].

4. Abscisic acid

Abscisic acid (ABA) is a sesquiterpenic (C_{15}) phytohormone produced by degradation of C_{40} carotenoids biosynthesized in plastids through the methylerythrol phosphate (MEP) pathway [62]. The ABA first precursor is zeaxanthin (C_{40}), which is converted to xanthoxal (C_{15}) by a series of epoxidation, isomerization and dioxygenation reactions, then xanthoxal is transported to cytoplasm and subsequently oxidized to ABA. The orientation of carboxyl group at carbon 2 determines the *cis* (predominant in nature) and *trans* isomers, while an asymmetric carbon at position 1′ in the ring, results in the S and R (or + and −respectively) enantiomers (Fig. 1). The S enantiomer is the natural form and the commercially available synthetic ABA is a mixture of equal amounts of S and R forms.

ABA regulates plant responses to various (mostly stressful) abiotic and biotic factors, such as water restriction, high temperatures, frost and salinity. That is, ABA controls many physiological and biochemical processes, thus increases in ABA levels regulate acclimation to adverse environmental conditions [63–65]. ABA concentration in cytosol is highly regulated by biosynthesis, but also by catabolism, compartmentation, conjugation, and transport [66]. ABA can be deactivated by oxidation, but also by compartmentation in vacuoles and conjugation with other molecules like glucose [67].



S-*cis* ABA

Fig. 1. Chemical structure of S-*cis* abscisic acid (ABA), the naturally occurring active form.

ABA controls stomatal closure, including in grapevine [68], which is an important process that limits gas exchange and thereby affects indirectly the photosynthesis [69, 70]. It has been claimed that ABA is responsible for vegetative growth reduction in grapevine [71], although in *Ilex paraguariensis* shoot elongation was promoted by keeping a better tissue turgor via ABA application [72]. There is also evidence that ABA induce production of ROS that act as second messengers activating defensive responses [73]. As well, ABA signal induce expression of genes encoding both, antioxidants enzymes [74] and non-enzymatic defense systems [75]. That is, ABA increases the activities of antioxidant enzymes (CAT and APX) and the phenols and carotenoids contents in grapevine leaves as non-enzymatic defense mechanisms [26]. Carotenoids were also increased by ABA applications in *Ilex paraguariensis* [72] and wheat [76].

ABA levels greatly fluctuate during the plants ontogeny, and in grape berry skins increases markedly during veraison, which is the onset of berry ripening (when berries soften and start to accumulate sugars and color develops in red cultivars), and subsequently declined to be low at harvest [77–82]. Coincidently, the abundance of 9-cis-epoxycarotenoid dioxygenase (NCED1) transcripts, enzyme that catalyzes the first step of ABA biosynthesis, increases noticeably around veraison in grape berries [83]. This increase of ABA concentration at the tissue level may indicate a role of the hormone in controlling the berry development that triggers the beginning of ripening [77, 79, 80, 84]. Most of the knowledge about fruit maturation comes from climacteric fruits where the control of the process is predominantly carried out by the phytohormone ethylene. However, many fruits such as grape berries are considered non-climacteric and the mechanisms controlling the onset of ripening are still poorly understood [85]. The assumption that ABA regulates berry maturation in grapes has been justified by the fact that ABA applications hastened berry ripening [82], so increasing the accumulation of sugars [86] and phenols in the skins [81, 87–90].

5. ABA and UV-B

As mentioned previously, ABA regulates the plant responses to various stressful abiotic and biotic factors, controlling many physiological and biochemical acclimation processes. Therefore, it is feasible to assume that ABA regulates plant responses to UV-B, since many mechanisms of plants response are common for different stressful conditions. Few studies tried to address the interaction between UV-B and ABA in plants [91], but in some experiments it was found that ABA applications increase the tolerance of grapevines to UV-B [26, 82]. In these experiments grapevines were exposed to high ambient UV-B levels (irradiances that reach up to 0.40 W m^{-2}), and it was found that ABA levels increased in leaves, but not in berry skins, as compared with treatments in which UV-B have been filtered. A similar effect in leaves of Arabidopsis was found by Rakitin et al. [92], supporting a promotive effect of UV-B on ABA biosynthesis in tissues exposed to high ambient UV-B. Other studies reported the interaction between drought (condition that increases the endogenous ABA levels in xylem flow [68]) and UV-B, where water restriction treatments decreased the sensitivity to UV-B in different plant species [27, 93].

In experiments of our research group [26] it was found that ABA concentration in grapevine leaves increased 2.7-fold with high UV-B levels as compared with a minus UV-B treatment, so demonstrating that ABA is involved in the plant protection responses to UV-B. Such responses include the increase in the activity of antioxidant enzymes and enhancement of membrane sterols that participate in structural defense. These results [26] also suggested that the antioxidant defense system is initially activated by high UV-B levels and ABA acts downstream in the signaling pathways. In other experiments [82], the grape berry skins during different ontogenetic stages were analyzed, finding that solar UV-B in high altitude vineyards did not affected ABA levels. Therefore, it was proposed that berry skins are not as sensitive as leaves in the ABA responsive mechanism against UV-B. Of course, it should be as well considered that different responses among tissues may be because UV-B doses perceived by berry skins are probably lower than those received by leaves since berries have less sun exposure (they may be shadowed by the leaves). It is worst to mention that berry skins may be protected by accumulation of phenolic compounds in the epidermal cells that filter the UV-B [31]. It was also found that solar UV-B combined with weekly sprays of ABA (1 mM aqueous solutions) to the aerial part of the plant (i.e. including leaves and berries) increased sugar accumulation and total phenolic compounds in berries at veraison, advancing the onset of ripening, and subsequently decreasing berry growth and sugar content per berry, without affecting sugar concentration (°Brix) at harvest. In these berries, anthocyanins and polyphenols

in the skins increased by solar UV-B perception, with a further increase when combined with applications of ABA (interaction effect between UV-B and ABA) [82].

6. Phenolic compounds

A large variety of secondary metabolites that contain a phenol group are classified as phenolic compounds, and in plants nearly 10,000 have been chemically characterized. Phenols are chemically heterogeneous, some are soluble only in organic solvents, some are water-soluble carboxylic acids and glycosides, and others are large and insoluble polymers. According to their diversity, phenols have diverse biological functions in plants. Many compounds serve as attractants for pollinators and seed dispersers, others act as defense compounds against herbivores and pathogens, and others are protective compounds that respond to environmental stressful conditions, since they absorb UV and possess antioxidant capacity [94, 95], In addition to their biological function, phenols play a significant role in winemaking since they determine wine quality [96, 97]. Although they represent less than 5% of the total wine constituents, phenols significantly contribute to appearance (color), taste (bitterness), mouthfeel (astringency and body) and nutraceutical value (potential benefits to human health) [98]. Grapevines differ in phenolic composition and concentration based on varieties (genetic factors), growth and developmental stages (berry maturity), environmental conditions during its cultivation and management practices [99].

Phenolic compounds derived from the phenylpropanoid and flavonoids biosynthetic pathways, and are represented by phenolic acids (hydroxycinnamic and hydroxybenzoic acids), stilbenes like resveratrol, and flavonoids classified as anthocyanins, flavonols, flavanols and dihydroflavonols. Figure 2 shows the biosynthetic pathways of the major phenolic compounds of grape berries based on Castellarin et al. [100]).

Hydroxybenzoic acids (e.g. *p*-coumaric, caffeic and ferulic acids) are mostly present as glycosylated in the grape berries; while hydroxycinnamic acids (e.g. gallic, protocatechuic, vanillic and syringic acids) may be in free forms, although they are mainly esterified, in particular with tartaric acid, or glycosylated and acylated with anthocyanins. From an organoleptic point of view, phenolic acids are colorless and have no taste or smell. Stilbenes have two benzene rings, generally linked by an ethane or ethylene chain, and among these compounds the best known and studied in grapevines is resveratrol, which is produced by plants in response to fungal infections (that is, from a biological point of view is a phytoalexin) and other stressful biotic and abiotic factors [96].

Flavonoids are polyphenolic structures containing numerous double bonds and hydroxyl groups that can donate electrons through resonance to stabilize free radicals, and thus act as powerful antioxidants that protect living tissues against oxidative stress [101]. Anthocyanins are the most distributed flavonoid pigments responsible of red, pink, purple and blue colors observed in plants. In grapevine, anthocyanins are responsible for the red color in berries because they accumulate in vacuoles of skin epidermal cells [102, 103], and for red color in senescing leaves. They are classified according to the number and position of hydroxyl and methoxyl groups in the flavan nucleus, and in grapevines five anthocyanins have been identified: two dihydroxylated (cyanidin and peonidin) and three trihydroxylated (delphinidin, petunidin and malvidin). Anthocyanin color is influenced by many factors, including number of hydroxyl and methoxy groups, presence of esterified aromatic acids, and acidity of the cell vacuole. All grapevine varieties have the same basic anthocyanins, but there are variations in the anthocyanin profile. Among the five anthocyanidins, malvidin is more abundant and represents between 50 and 90% of total anthocyanins [82, 104]. Hydroxylation, glycosylation and methoxylation modulate anthocyanin antioxidant properties, and they are more stable in the glycoside forms (anthocyanins in general) or when they are methoxylated (as occurs with peonidin, petunidin and malvidin) that as aglycones (anthocyanidins). Trihydroxylated and methoxylated anthocyanins are more stable to oxidation and have less antioxidant capacity [105]. Wang et al. [106] analyzed the antioxidant capacity as ORAC of the different anthocyanins and found that cyanidin glycoside has the highest antioxidant capacity, while malvidin has the lowest. Also, predominance of trihydroxylated anthocyanins (oxidized forms) is associated with a higher ratio of flavonoid 3′5′-hydroxylase (F3′5′H) transcripts, as compared with those of flavonoid 3′-hydroxylase (F3′H), and there are increasing transcript levels of O-methyltransferase (OMT) on grape berries that accumulate predominantly methoxylated anthocyanins [100, 104]. Flavonols are flavonoids that represent yellow pigments in grape berry skins, while dihydroflavonols, their precursors, are pale colored compounds. Flavonols influence certain organoleptic characteristics important for wine quality such as bitterness and structure, but also stabilize and increase

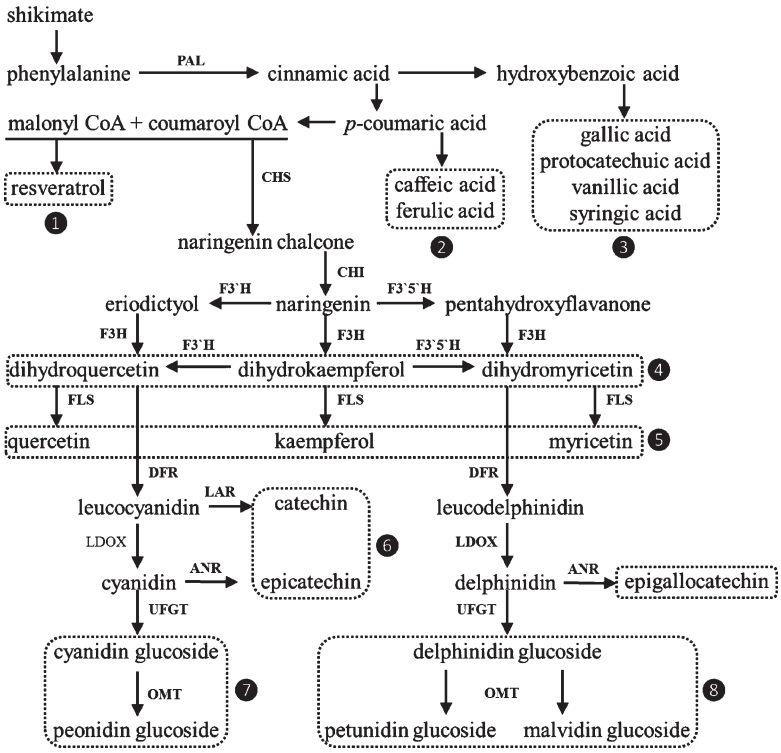


Fig. 2. Biosynthetic pathways of the major phenolic compounds of grape berries (based on Castellarin et al. [100]). Subgroup: 1, stilbenes; 2, hydroxycinnamic acids; 3, hydroxybenzoic acids; 4, dihydroflavonols; 5, flavonols; 6, flavanols; 7, dihydroxylated anthocyanins; 8, trihydroxylated anthocyanins. Abbreviations: ANR, anthocyanidin reductase; CHI, chalcone isomerase CHS, chalcone synthase; DFR, dihydroflavonol reductase; F3 H, flavanone 3-hydroxylase; F3′H, flavonoid 3′-hydroxylase; F3′5′H, flavonoid 3′5′-hydroxylase; FLS, flavonol synthase; LAR, leucoanthocyanidin reductase; LDOX, leucoanthocyanidin dioxygenase; OMT, *O*-methyltransferase; PAL, phenylalanine ammonia-lyase; UFGT, flavonoid 3-glucosyltransferase.

the color through co-pigmentation with anthocyanins [107–109]. They differ in the lateral nucleus substitution producing quercetin, myricetin and kaempferol, which in grape berry skins are mainly glycosylated [110]. Flavanols are flavonoids that in grape berries are found as monomers and oligomers, but the majority are polymers (proanthocyanidins or tannins) that protect the wine against oxidation, stabilize their color and increase the complexity of the flavor. Flavanols accumulate mainly before berry ripening and its contents decrease with the progress of maturation [111–113], because of polymerization and reduction in extractability [114, 115]. Their basic structural units are (+)-catechin and (−)-epicatechin and unlike anthocyanins and flavonols there are not flavanols glycosylated forms.

7. Phenolic compounds, ABA and UV-B

Accumulation of phenols (namely phenolic acids, stilbenes and flavonoids) is an acclimation and protective response against UV-B that may protect cell membranes, proteins and nucleic acids, either directly absorbing UV-B in epidermal tissues and/or reducing its penetration through underlying tissues [53, 54], or indirectly reacting with the ROS generated so acting as antioxidants [55–57, 116]. Phenols transform shortwave radiation with high energy that are potentially harmful to living tissues, in longer wavelength and less destructive radiation [117–119], and at the same time increase protection against oxidative stress because of their chemical structures capable of scavenging free radicals [120]. It has been demonstrated that the increase of phenolic compounds in leaves occurs because UV-B activates the expression of genes encoding some enzymes of the phenylpropanoids and flavonoids pathway, such as

phenylalanine ammonia lyase (PAL) and chalcone synthase (CHS), respectively [121, 122] also in grapevines [60]. Increases of phenolic compounds that absorb UV-B selective and passively in the epidermis probably represents the most cost-effective strategy, as in the case of adaptation to prolonged exposure to high ambient UV-B levels, situation that would be metabolically very expensive with continuous repairing processes [123, 124].

Higher phenolic compounds accumulations were observed in grapevine leaf epidermal cells [26, 38, 52] and berry skins [82], in response to UV-B. In grapevine leaves, quercetin, kaempferol and anthocyanins were specifically increased by UV-B, with a further increase when ABA was also applied, while the contents of caffeic and ferulic acids (hydroxybenzoic acids) were increased only by ABA [26]. An increase in the synthesis of quercetin and kaempferol, compounds with high antioxidant capacity, was also found by Kolb et al. [52] in grapevine leaves exposed to UV-B, and a high correlation between phenol accumulation and ORAC was also observed [38]. In grape berry skins the total anthocyanins were increased additively by high levels of ambient UV-B and ABA applications, but cyanidin, a dihydroxylated anthocyanidin with highest antioxidant capacity, was increased more with the combination of these treatments [82]. Bindon et al. [125] found an increase in delphinidin, cyanidin, peonidin and petunidin, and a reduction of the proportion of methoxylated anthocyanins (less antioxidant capacity) in response to partial rootzone drying (PRD), a management practice purported as maintaining high ABA levels in xylem flow [68]. The UV-B increased the total accumulation of flavonoids in grape berry skins [126] and in combination with ABA augmented the total non-anthocyanin phenols (phenolic acids, flavonols, dihydroflavonols and flavanols), increasing the relative abundance of flavonols like quercetin [82], one of the phenols with highest antioxidant capacity [127]. It is proposed that the relative abundance of flavonols is increased by UV-B and ABA applications, possibly because the enzyme flavonol synthase (FLS) is relatively more active than other enzymes of the flavonoid biosynthetic pathway [82].

8. Berry quality, ABA and UV-B

The quality for winemaking of grape berries integrates various aspects, but for red wines, especially those to be aged, it has a high correlation with accumulation of phenolics. Hence, wines with the highest concentrations of phenolic compounds are generally considered of excellence, although the best quality is highly depend on the phenolic profile. In viticulture, apart from the selection of the plant material (genetic factor), implantation site, plantation density and trellis system, there are different management practices often performed in implanted vineyards with the aim of increasing grape berry and wine qualities. For example, winter pruning and shoot removal determines the number of shoots and clusters per plant, and affects canopy density, photoassimilates source/sink ratio, and sunlight exposition of clusters. Also, through cluster thinning the photoassimilates sinks are reduced, with leaf removal the exposure of clusters to solar radiation is increased, and with water restriction the berry size is decreased (higher skin/pulp ratio).

It was found that exposure of grapevines to relatively high UV-B levels combined with applications of ABA increases the load of sugar in berries until the phenological stage of veraison [82], and that ABA applications increase monosaccharides (glucose and fructose) accumulation in berries and roots at veraison [128]. Also, UV-B and ABA effects at veraison, promoting the sugar accumulation in fruits, is different at harvest, where accumulation of sugar per berry decrease and sugar concentration is not affected because UV-B/ABA combined treatments also reduce berry size mainly after veraison [82]. Some studies have shown that ABA applications can increase sugar accumulation in berries [79, 84, 129] promoting berry growth [80, 130], because ABA stimulate acid invertase activities [86, 131], expression of hexose transporters [132–134] and enzymes that soften the cell wall [131]. There are other reports where grape berry maturation [135] or growth [81] were not affected by application of ABA. Differences between studies may be due to timing of applications relative to veraison, a critical factor in determining ABA effects, and also to the grapevine varieties used, since there may be genetic differences in sensitivity to phytohormone. Other factors such as ABA concentrations, number of applications, combined with the hydric situation of the vineyard (that may enhance ABA levels) and the phenological stage considered as veraison (e.g. 50, 80 or 100% colored berries), could also affect the results between different studies and their interpretation.

High ambient UV-B levels, combined with applications of ABA produce reductions in grape berry growth, mainly after veraison, and therefore reduce yield [82]. These effects may be associated with decreases in the cell wall elasticity of the berries, as it was found in grape berries cultured *in vitro* [85]. Also, it was reported that application of ABA may promote degradation of vacuolar invertases, which play a fundamental role in the accumulation of hexose

sugars in the grape berries [136]. The increments promoted by UV-B and ABA of berry skins phenols, including the flavonols quercetin and kaempferol, may be influencing auxin levels in berries since these phenols may act as inhibitors of auxin transport [137] so affecting the extensibility of cell walls [138] and therefore the berry growth.

The results obtained in the study from our laboratory [82] show a positive effect of the perception of relatively high UV-B levels and the application of ABA on the accumulation of anthocyanins in grape berry skins, increasing the amounts of anthocyanins at veraison and maintaining the differences with controls (UV-B filtration and no ABA application) until harvest. The effect of ABA was also obtained by many authors [79, 81, 84, 88, 89, 129, 135, 139, 140] and can be explained by the activation of enzymes of the phenylpropanoid and flavonoid pathways [87, 141], with a peak of enzyme activity during ripening [142]. It has been also found that applications of ABA increase the expression of genes involved in the acylation of anthocyanins and in the transport of anthocyanins to the vacuoles of the skins epidermal cells [131, 143]. It has also been demonstrated that UV-B increases the expression of CHS and PAL enzymes in grapevine leaves [60, 144]. Higher concentrations of total anthocyanins were obtained in berries of the cv. Syrah exposed to the sunshine as compared with shaded fruits, but these differences lasted for a short time and disappeared towards harvest [145]. The latter can be caused by the higher temperatures that occur due to sun exposure, which limit the accumulation of anthocyanin possibly by reduction of the biosynthesis and/or an increase in anthocyanin degradation [146, 147]. In an experiment where the temperature was kept similar in both, treated and control clusters, and the effect was restricted to UV-B differences, grape berry skin phenols were increased by UV-B and maintained until harvest [82].

Although the anthocyanin profile is mainly a genetic characteristic and the relative proportions of the five anthocyanidins seem to be specific to each variety [148], perception of high UV-B levels and the application of ABA additively reduced the proportion of trihydroxylated anthocyanins (more oxidized), and the application of ABA *per se* reduced the proportion of methoxylated anthocyanins [82]. It is suggested that F3′H is relatively more active than F3′5′H when grapevines perceived UV-B and ABA levels increased, while the activity of OMT is reduced by ABA. Adaptive changes in the composition of anthocyanins profiles was also found by many authors. As an example, fruit exposed to sunlight reduces the proportion of trihydroxylated anthocyanins when compared with the shaded fruit [146, 149–151]. Additionally, it was showed that the degree of hydroxylation and methoxylation of anthocyanins in grape berries may also be altered by changes in the water status of the plant [125].

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