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Research article

Functional roles of flavonoids in photoprotection: New evidence, lessons from the past

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ABSTRACT

We discuss on the relative significance of different functional roles potentially served by flavonoids in photoprotection, with special emphasis to their ability to scavenge reactive oxygen species (ROS) and control the development of individual organs and whole plant. We propose a model in which chloroplast-located flavonoids scavenge H_2O_2 and singlet oxygen generated under excess light-stress, thus avoiding programmed cell death. We also draw a picture in which vacuolar flavonoids in conjunction with peroxidases and ascorbic acid constitute a secondary antioxidant system aimed at detoxifying H_2O_2, which may diffuse out of the chloroplast at considerable rates and enter the vacuole following excess light stress-induced depletion of ascorbate peroxidase. We hypothesize for flavonols key roles as developmental regulators in early and current-day land-plants, based on their ability to modulate auxin movement and auxin catabolism. We show that antioxidant flavonoids display the greatest capacity to regulate key steps of cell growth and differentiation in eukaryotes. These regulatory functions of flavonoids, which are shared by plants and animals, are fully accomplished in the nM concentration range, as likely occurred in early land plants. We therefore conclude that functions of flavonoids as antioxidants and/or developmental regulators flavonoids are of great value in photoprotection. We also suggest that UV-B screening was just one of the multiple functions served by flavonoids when early land-plants faced an abrupt increase in sunlight irradiance.

1. Introduction

Flavonoids have long been suggested as serving multiple functions in photoprotection [1]. This is consistent with the location of flavonoids in a wide-range of plant organs as well as in different cells and cellular compartments [2]. A wide array of effective mechanisms for the transport of flavonoids within and out the cell has indeed been reported [3–6]. Early views that flavonoids are mostly located in the wall and the vacuole of epidermal cells [7–9], and in external surface organs (such as trichomes) [10], and hence primarily devoted to screen out the most energetic solar wavelengths reaching the leaf [11–13] needs to be considered with caution [14–16]. Indeed, flavonoids are also located in the leaf interior, both in the palisade and spongy mesophyll cells, depending on sunlight irradiance plants face with [16–20]. Flavonoids also occur in various compartments in mesophyll cells, including the nucleus [2,21], the chloroplast [22,23] and the vacuole [24,25]. It is worth noting that high light irradiance up-regulates the biosynthesis of dihydroxy B-ring-substituted flavonoids (such as luteolin 7-*O*- and quercetin 3-*O*-glycosides) whereas does not affect the biosynthesis of monohydroxy B-ring-substituted flavonoids (such as apigenin 7-*O*- and kaempferol 3-*O*-glycosides) [2,24–28]. Monohydroxy flavonoids, which have very similar UV-spectral features of their dihydroxy counterparts (Fig. 1), predominate in plants growing under deep or partial shading [16,20,29]. It is conceivable that dihydroxy flavonoids in addition to effectively attenuate UV-B radiation have to play additional roles in photoprotection [1,26,30].

Old and recent evidence suggests that flavonoids served important roles during the establishment of plants on the land that may go beyond their UV-B screening capacities [15,24,25,31–34]. Actually, carbon-based flavonoids replaced mycosporyne-like aminoacids (nitrogen-rich MAAs, usually detected in algae) as

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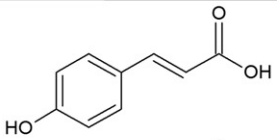
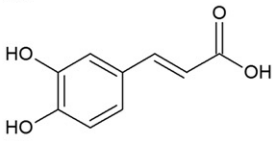
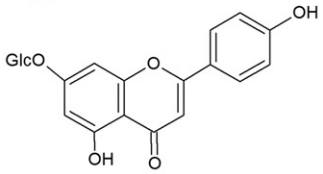
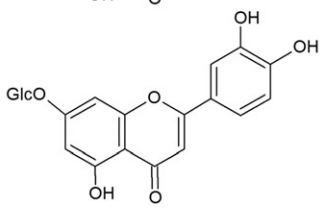
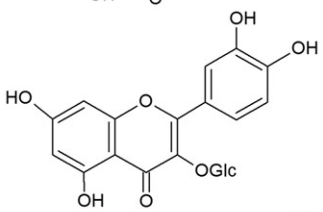
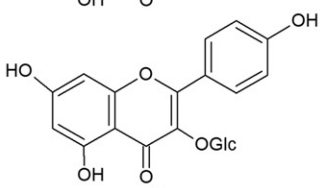
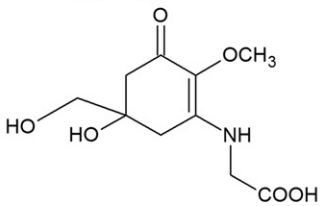
Metabolite	Molecular structure	λmax (± 2nm) over UV-B/UV-A	$\int_{290}^{320} \varepsilon$	$\int_{321}^{390} \varepsilon$
p-Coumaric acid		312	4.5E+05	0.048E+06
Caffeic acid		327	4.6E+05	0.66E+06
Apigenin-7-O-Glc		337	3.9E+05	0.92E+06
Luteolin-7-O-Glc		348	2.5E+05	0.81E+06
Quercetin-3-O-Glc		355	3.5E+05	1.0E+06
Kaempferol-3-O-Glc		351	3.9E+05	1.3E+06
Mycosporine-glycine		310	7.2E+05	0.97E+06

Fig. 1. Chemical structures of mono- and dihydroxy cinnamic acid derivatives and flavonoid glycosides together with their UV-spectral properties. Data for mycosporyne–glycine, as an example of mycosporyne like aminoacid (MAA) present in algae are reported. Molar extinction coefficients have been integrated over 290–320 (UV-B) and 321–390 nm (UV-A) spectral regions.

UV-B screening pigments [15,32] when plants moved from water. This shift in the metabolism of UV-B screening compounds conforms to early land plants having established in soils at low nutrient availability [35,36]. Flavonoids, particularly flavonols have been detected in liverworts and mosses, and have much lesser ability than MAAs to absorb wavelengths over the 290–320 nm – UV-B – solar spectrum region (Fig. 1). Flavonols, such as the UV-B responsive quercetin derivatives, have molar extinction coefficients (ε) maxima at around 350 nm and ε minima at approx. 300 nm [19]. This clear discrepancy between the induction spectrum, i.e. the UV-B spectral band, for flavonoid biosynthesis and the flavonoid absorption spectra still poses some concerns on their primary functions as UV-B screeners [2,15,37,38].

Light-responsive dihydroxy flavonoids have much greater ability than their monohydroxy counterparts to inhibit the generation of ROS, and then quench ROS once they are formed [39–41]. In healthy leaf cells flavonoids occurs as glycosides, so that the ROS-scavenger capacity of flavonoids depends on the presence of the catechol group in the B-ring of the flavonoid skeleton [39] (at least within the concentration range reported for leaf flavonoids up to date, e.g., 200 μM in the vacuole of mesophyll cells in *Catharanthus roseus*) [42]. Apigenin and kaempferol glycosides do not appreciably reduce superoxide anion (O_2^-) or the synthetic free radical DPPH at concentrations as high as 500 μM [19].

Therefore, flavonoids have been hypothesized to counter high light-induced oxidative damage by scavenging ROS rather than

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