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Review Article

THE HEALTH BENEFITS OF NATURAL SKIN UVA PHOTOPROTECTIVE COMPOUNDS FOUND IN BOTANICAL SOURCES

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ABSTRACT

In recent years, botanicals have gained importance due to their dermal photoprotective effect against the harmful UV radiation. This radiation generates reactive oxygen species which attack proteins, lipids, and nucleic acids among others. This leads to the cellular oxidation, which is reflected as tanning, skin inflammation, erythema, immunosuppression, photoaging and skin cancer. The photoprotective activity of synthetic sunscreens is unsatisfactory due the proved incomplete spectral protection, toxicity, and allergenicity. The phytotherapy treatment with antioxidant compounds with potential UV absorbing capacity could offer a more effective photoprotection since they may impede, reverse or delay the process of formation of DNA adducts. The wide diversity of botanicals with photoprotective activity is attributed to several types of substances with phenolic chromophores. These compounds can be classified as flavonoids, phytoestrogens, carotenoids, xhantophylls, coumarins, proanthocyanidins, anthocyanins, catechins, phenolic acids, triterpenes, alkaloids, etc. The bioactivity of these compounds is not limited to the photoprotective action, but antioxidant, anti-inflammatory, antimutagenic and immunomodulatory properties. The regular intake of these botanicals not only prevents but also delays the deleterious effects of sun radiation onto the skin. Therefore, these botanicals have gained considerable attention and are now included in most vitamin and cosmetic products. This review gives an overview of photoprotective botanicals mainly focused on UVA chromophores that are able to inhibit or reverse the damaging effects of sun radiation. The search criterion was made essentially on UVA photoprotective botanicals and related works published in the last ten years. The literature search included mainly the Google scholar, Science direct, and ISI web of knowledge databases.

Keywords: Ultraviolet radiation, Photoprotective botanicals, Antioxidants, Phytotherapy.

INTRODUCTION

The solar radiation reaching the Earth is mainly in the wavelength ranging from 200 to 4000 nm. This radiation is composed of 50% visible light (VIS, 400-800 nm), 40% infrared radiation (IR, 1300-1700 nm), and 10% ultraviolet radiation (UV, 10-400 nm)[1]. In addition, ultraviolet radiation can be divided into three categories such as long wave UVA (320-400 nm), medium wave UVB (280-320 nm) and short wave UVC (200-280 nm) [2] (fig. 1). Since UVC is highly energetic, it is extremely dangerous to living beings. Fortunately, the ozone layer and atmospheric oxygen absorb this radiation and only a small portion reaches the earth surface [3]. The UVC radiation is efficiently absorbed by mitochondrial DNA in cells located to the level of spinous layers, but not in the basal layer. It causes DNA damage producing pyrimidine dimers, such as cyclobutane pyrimidine dimers (CPD) and pyrimidine (6-4) pyrimidone photoproducts (6-4PPs) [4].

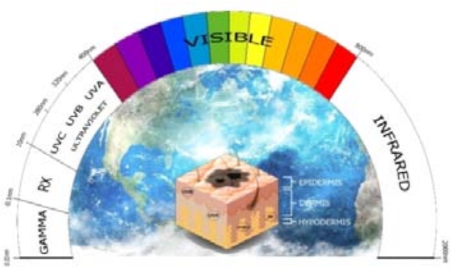

Fig. 1: The incident solar radiation on Earth

Effects of UVA radiation

The ratio of UVA to UVB reaching the earth surface is 20:1 and the incident UV radiation is strongest between 10 AM and 4 PM. Since UVA is of longer wavelength compared to UVB, it is less affected by altitude or atmospheric conditions. UVA rays are beneficial since they increase vitamin D3 production by irradiation of 7-dihydrocholesterol. UVA also intensifies darkening of the preformed melanin pigment favoring tanning [5]. The effectiveness of UV to induce erythema declines rapidly with longer wavelength. Therefore, 1000 times more UVA is needed to induce erythema as compared to UVB [6]. UVA can penetrate deeper than UVB through the skin, and is not filtered by window glass. Further, more than 90% of solar radiation that reaches the Earth is UVA. For this reason, even under the cloud shadow, ~50% of UVA is able to reach the ground [7].

Cellular defenses against UVA-induced damage include antioxidant molecules (i.e., glutathione, carotenoids, ascorbate, and α-tocopherol), and proteins (i.e., ferritin, heme oxygenase, glutathione peroxidase, superoxide dismutase, catalase, etc.) [8]. However, UVA could bypass these defenses reaching the dermis and affecting dendritic cells, fibroblasts, matrix metalloproteinases, T-lymphocytes, mast cells, and endothelial cells.

Moreover, UVA is about 1000 times more effective in producing an immediate tanning effect when compared to UVB. Long-term exposure to UVA damages the underlying structures in the dermis causing premature photoaging. Further, UVA causes skin sagging and suppress some immunological functions. For this reason, chronically transplant immunosuppressed patients living in regions of intense sun exposure experience a high rate of skin cancer. Moreover, UVA could trigger oxidative changes in exposed individuals generating singlet oxygen, hydrogen peroxide and hydroxyl free radicals. These cause damage to cellular proteins, lipids and saccharides leading to necrosis of endothelial cells, damaging the dermal blood vessels. Further, UVA produces structural changes in DNA (i.e., the formation of di-pyrimidine photoproducts) forming malignant melanoma in 67% of cases [2].

The time course for UVA-induced erythema and tanning are biphasic. Erythema is often evidenced immediately at the end of the irradiation period. It fades in several hours followed by a delayed erythema starting at 6 h and reaching its peak after 24 h of sun exposure [9]. Single UVA exposure does not increase epidermal thickness; only repeated exposures cause an increase in thickness [10]. The immediate pigment darkening, which occurs within seconds after UVA and visible light exposure disappears within 2 h, and is the result of photo-oxidation of pre-existing melanin or melanogenic precursors. On the other hand, the persistent darkening is a delayed tanning, which peaks 72 h after UV exposure. This darkening is caused by increased tyrosinase activity and hence, the formation of new melanin, increasing the number of melanocytes transferred to keratinocytes and melanosomes.

The acute response after UV exposure is an inflammatory reaction that is mediated by several possible mechanisms including: (i) The generation of reactive oxygen species (ROS) and free radicals such as superoxide anion ($^1O_2$), hydroxyl (*OH), or peroxy radicals (*OOH) which can induce mutations in the mitochondrial DNA, leading to the loss of enzymes involved in oxidative phosphorylation and hence, a deficient energy metabolism [11]. These ROS can attack DNA and activate matrix metalloproteinases implicated in collagen damage and photoaging. On enzymes, the effect of ROS results in: (i) catalytic capacity reduction, often determined by sulfhydryl oxidation and modification of amino groups by malonylation [12]. (ii) The generation of prostaglandins (PGD2, PGE2), histamines, leukotrienes, and other cytokines. (iii) A direct action of absorbed photons on DNA of viable nuclei of skin cells. This third factor is more unlikely to occur [13].

Effects of UVB radiation

In the last two decades, the UVB radiation has been pounding the Earth surface with a higher intensity due to the ozone layer depletion in the upper atmosphere. As a consequence, UVB radiation is able to damage the human skin causing erythema, edema, hyperplasia, hyperpigmentation, immunosuppression, cutaneous photoaging and induction of cancers (fig. 2). It should be noted that there is no pigment production after UVB exposure unless there is a preceding erythemal response. UVB radiation constitutes approximately 5% of the total solar UV radiation. UVB is more genotoxic than UVA and acts predominantly in the epidermal basal layer of the skin. After a single acute UVB exposure, there is an increase in the epidermal, and to a lesser extent the dermal, mitotic activity, which persists from days to weeks, leading to an approximate two-fold thickening of the epidermis and dermis [10].

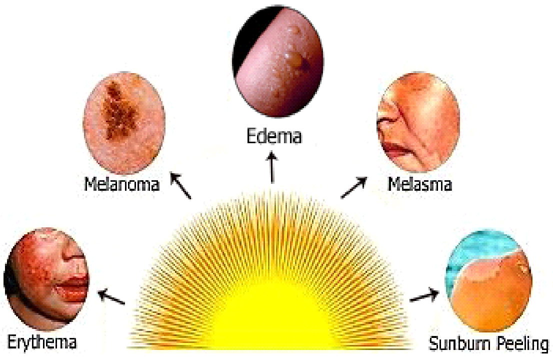

Fig. 2: Effects of UVB radiation onto the skin

UVB radiation also affects keratinocytes, Langerhans cells and melanocytes leading to isomerization of trans to cis-urocanic acid, stimulation of DNA synthesis, free radical production in the skin, and cell cycle growth arrest [2]. UVB-induced erythema occurs approximately 4 h after exposure and fades within 24h. In skinny and older individuals, UVB erythema may be persistent, sometimes lasting for weeks [5]. UVB radiation is directly absorbed by DNA, forming dimeric photoproducts between adjacent pyrimidine bases, and cyclobutane pyrimidine dimers [14]. Further, the release of ROS and inflammatory cytokines such as interleukin IL-1b, IL-6, IL-10 impair the antigen ability of Langerhans cells which may result in immune suppression [15]. UVB rays also cause lipid peroxidation in which free radicals receive electrons from the lipids in cell membranes resulting in cell damage. For instance, ROS degrade unsaturated lipids and form malondialdehyde which is considered a marker of lipid peroxidation [16].

On the other hand, UV also affects human hair and the effect of UV radiation on hair defer on their wavelength. Thus, UVB radiation is the main responsible for hair protein loss, whereas UVA promotes color changes. UVB is largely absorbed by the cuticle, whereas UVA penetrates the cuticle layers and promotes oxymelanin production, leading to bleaching and generates oxyradicals, such as superoxide and hydroxyl, which oxidize hair molecules modifying the color characteristics of hair [17]. Further, visible light promotes melanin granules degradation contributing to photobleaching.

The use of UV-protective compounds is important since an average American female is exposed to 2200 $mJcm^{-2}$), whereas males are exposed to 2800 $mJcm^{-2}$ each year, with an additional exposure of about 800 mJ cm^{-2} of solar UVB radiation during a vacation period [18]. In order to prevent or ameliorate the skin photodamage, synthetic sunscreens and botanical compounds can be used. These offer UV protection by either topical or oral applications.

The natural skin protection

The natural sun blockers of the skin are proteins, absorbing lipids, and nucleotides. The cellular chromophore for UVA radiation is the trans-urocanic acid [19], whereas the set of chromophores for UVB radiations are represented by a wider group composed by nucleic acids, amino acids, (i.e., tryptophan and tyrosine), quinines, flavins, porphyrins, and urocanic acid [20]. There are several processes that control the penetration of UV rays into the skin. The most important are: (i) reflexion and occurs at the level of the cornified layer; (ii) Diffusion occurs on the cornified layer, especially for melanin that mainly diffuses short wavelengths. Further, (iii) absorption occurs in the cornified layer where 70% of UVB is absorbed by the polar amino acids of keratin and urocanic acid, whereas melanin and carotenoids absorb UV rays and visible light, respectively [21]. Other UV protective secondary metabolites are squalane, which is the most important protective lipid of the skin. On the other hand, allantoin is a nucleotide that naturally occurs in the body and also absorbs the UV radiation. Allantoin also heals minor wounds and promotes skin healing [22].

Ultraviolet chromophores found in botanicals

In the last 10 y, a new trend towards naturally occurring compounds has emerged. The production of secondary metabolites in plants is often due to a specific response to their environmental conditions. Thus, several species, especially those exposed to intense radiation have evolved a variety of photoadaptive mechanisms including production of antioxidant and UV absorbing compounds [5]. The light-capturing property of these compounds is correlated to their antiradical activity and is restricted to chemical features such as aromatic rings, cyclic or conjugated double bonds, stereochemistry and typology of substituents [22].

These features have a p-electron system, which is one of the most effective UV radiation absorbers [6]. These compounds protect plants from photo-oxidative damage through their antioxidant, anti-inflammatory and immunomodulatory activities [26]. For this reason, the oral or topical administration of these compounds can partially inhibit or minimize the number of UV-mediated inflammatory and phototoxic skin reactions involving drug-induced photosensitization, epidermal edema, or vesicle formation [13]. Most of these antioxidants are polyphenols compounds that quench the excited state of the harmful ROS and control the multiple signaling pathways neutralizing targets involved in solar damage preventing photo-immunosuppression [27].

Polyphenols are ubiquitous compounds found in most fruits and vegetables and are associated with a wide number pharmacological activities including antiallergic, antimicrobial, antiviral, anti-inflammatory, hepatoprotective, vasoactive, antithrombotic, antiulcerogenic, antioxidant, free radical scavenging, antitumor, and antiprotozoal properties [28]. They act as reducing agents, hydrogen donors, single oxygen quenchers and potential metal chelators. The beneficial effects of polyphenols, are mainly attributed to their antioxidant or radical scavenging properties. The regular Consumption of plants rich in polyphenols is associated with the reduced the risk of acquiring cancer, cardiovascular diseases, atherosclerosis, diabetes and Alzheimer's disease [29]. Polyphenols also reduce the scavenging capacity of oxygen free radicals, reduce platelet aggregation and decrease arterial blood pressure. Radical reactions occur in many biological processes as a consequence of living in an oxidizing environment. Differences in the phenolic content of the same extract depend on the extraction procedure, solvent type source and stability in respect to UV radiation. The antimicrobial activity of some polyphenols is explained by the reaction of the bacterial cell with sulfhydryl groups of proteins causing protein precipitation and enzyme inhibition of microorganisms [30, 31].

The number of natural polyphenols has been estimated to be more than 5000 compounds including 2000 flavonoids, and new molecules are yet to be discovered. Phenolic compounds acting as UV blockers can be divided into phenolic acids, terpenoids, monoterpenes, tannins, flavonoids, and volatile oils. Tannins, in turn, include condensed polymers of catechins or epicatechin and hydrolysable polymers of gallic or ellagic acids. On the other hand, phenolic acids include hydroxycinnamic compounds such as caffeic, ferulic, *p*-coumaric and their acidic derivatives (e. g., rosmarinic and chlorogenic acids) [12, 32].

Soluble and insoluble polyphenols absorb radiation efficiently in the range of 304-350 nm and 352-385 nm, respectively. Although these compounds absorb UV light, they transmit visible and photosynthesis radiation into the mesophyll cells of plants [33].

Phenolic compounds are always present in the form of glycosides in plants and are barely present in the free form. Hence, several hydrolytic procedures like acid and alkaline hydrolyses have been used to convert glycosides to aglycones. Moreover, the antioxidant activity of phenolic glycosides is mainly due to the catechol structure in the aglycones [34].

Other examples of phenolic compounds comprise kinetin, pycnogenol, allantoin, hesperidin, diosmin, mangiferin, lycopene, and extracts from aloe, horse chestnut, chamomile, comfrey, soy, pomegranate, garlic, and ginger [12, 35]. A detailed description of the antioxidant properties of polyphenolic compounds is discussed in the following sections:

Flavonoids

Flavonoids are non-nutrient secondary metabolites ubiquitous in plants, fruits, and vegetables that serve multiple functions including protection from mutagenic UV rays, pollination, feeding deterrence and microbe defense [36]. In humans, they are associated with protection against various diseases, such as cardiovascular and cancer diseases due to their antimutagenic, antimicrobial, antiviral, antiplatelet, antiallergic, estrogenic, antioxidant, anti-inflammatory and sunscreen properties promoting the repair of DNA adducts. The beneficial properties of flavonoids are mostly attributed to their ability to scavenge free radicals, chelate metal ions, activate antioxidant enzymes or inhibit certain enzyme systems. The antioxidant properties of flavonoids are due to the presence of phenol groups. Dietary flavonoids are normally found as conjugated glycosides except for fermented foods [37, 38].

Many flavonoids are found to be better antioxidants than ascorbic acid, alpha-tocopherol, and beta-carotene (19). They are classified in: (i) flavones, such as catechin; (ii) flavonols, such as quercetin; (iii) flavones, such as diosmetin, and (iv) anthocyanidins [39]. In general, flavonoids show two UV absorption bands, one between 240-280 nm and the other one at 300-370 nm relative to simpler phenolics [40, 41]. For instance, quercetin, kaempferol, and isorhamnetin are flavonoids that show UV absorption maxima in the vicinities of 250-280 nm and 310-385 nm [42, 41]. Further Quercetin, cyanidin and kaempferol are found in flowers of *Hibiscus rosa-sinensis* and *Rosa damascena*. These compounds are also attributed refrigerant, emollient, demulcent, aphrodisiac; and emmenagogue properties [43].

On the other hand, flavanols from cocoa protect against UV radiation and increase microcirculation in human skin [44]. Further, daidzin and genistin are found in soybean; puerarin is found in kudzu, whereas formononetin and biochanin A are found in red clover and chickpea. Conversely, isoflavones are commonly found in passion fruit [45].

Quercetin is a flavonoid of widespread occurrence in nature. It is able to scavenge free radicals generated in the aqueous phase, increasing the resistance of lipids against peroxidation. Quercetin exhibits two UV absorption bands at 257 and 373 nm, which are attributed to conjugations in the B-ring and A-ring, respectively (fig. 3) [37]. However, it has been proved that the glycosylation of quercetin in rutin decreases its antioxidant and antimicrobial activities [46].

Trans-resveratrol is an antioxidant stilbenoid compound used in medical applications for lowering the risk of coronary heart disease and also has anticarcinogenic properties. It ameliorates the damage caused by UVB exposure to SKH-1 mice. The protective effects of resveratrol are mediated through its antioxidant potential and its ability to modulate cell cycle and apoptosis signaling pathways. Resveratrol can be found in grape skin, peanuts, soy, tea and other plants. In the human diet, it is regularly introduced mainly through the ingestion of wine, in which both trans and cis isomers are found [47].

Chrysin is a flavonoid found in honey and propolis which inhibits metastasis of cancer cells. Chrysin also has antioxidant, anti-inflammatory and antimicrobial activities [48].

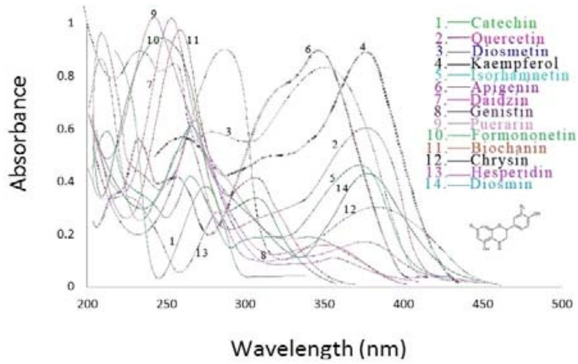

Fig. 3: Typical UV absorption bands of flavonoids

Another compound is silymarin, which is a flavonolignan extracted from the fruits and seeds of milk thistle (*Silybum marianum* L.). The seeds of milk thistle have been used to treat liver diseases. Silymarin is a mixture of mainly three flavonolignans, silybin (silybinin), silydianin and silychristin. Silybinin is the major (70-80%) and most active biological component [32]. Silymarin is a free radical scavenger and inhibits lipid peroxidation and has membrane stabilizing effects. The UV absorption maximum of silymarin occurs at 287 nm [49–51].

Hesperidin is found in citrus species and is the active constituent of tangerine peel. It has an anti-inflammatory effect by the inhibition of eicosanoids synthesis and has a blood cholesterol lowering effect. It also has antimicrobial, antioxidant and diuretic activities. It prevents poisoning caused by heavy metals. It is also used against diabetes and gastroesophageal reflux diseases. Hesperidin is converted to hesperetin by intestinal microflora and subsequently, absorbed from intestinal mucosa.

Diosmin is a synthetic or modified hesperidin of the flavonoid family. It is an oral phlebotropic drug used in the treatment of venous and hemorrhoidal diseases. It has anti-inflammatory and antiapoptotic activities. It also improves lymphatic drainage by increasing the frequency and intensity of lymphatic contraction and increases the total number of functional lymphatic capillaries [52]. The UV spectra of hesperidin and diosmin in 0.2N NaOH shows a peak at 268 and 285 nm, respectively [45]. Chalcones such as sakuranetin are lipophilic compounds found in trees belonging to *Prunus spp*. (bark and wood), *Eucalyptus spp*. and *Juglans spp*. (bark). It shows the typical peak of flavanones at 280 nm. The addition of sodium acetate, aluminum chloride or sodium hydroxide causes a bathochromic shift to 368 nm [53].

Naringin and rutin are among the most studied flavonoid glycosides. Naringin is a natural flavanone isolated mainly from citric fruit peels such as *Citrus paradisi* and *Citrus aurantium* peel. Naringin has anti-inflammatory, antioxidant, antimicrobial, antiviral, antiulcer, anticarcinogenic and hypolipidemic activities. Naringin may also protect vascular smooth muscle cells by increasing the strength and resistance of blood vessels, and thus has anti-atherogenic effects.

Phytoestrogens

Phytoestrogens are products having estrogenic effects. Soy isoflavones are the most frequently used phytoestrogens and has the potential to reduce the symptoms associated to menopause. Additionally, they prevent chronic pathologies such as osteoporosis, cardiovascular diseases, and hormone-related cancers. Daidzein, genistein and glycitein are the major isoflavones found in soy extracts. They also, occur naturally in soy as their glycosides, named daidzin, genistin and glycitin. When orally administered, isoflavones glycosides undergo enzymatic hydrolysis in the small intestine releasing the aglycones, which are responsible for their biological effects. Genistein is the most active compound exhibiting the highest affinity for estrogenic receptors, being approximately ten times more active *in-vivo* than daidzein. After forming a complex with $AlCl_3$, it shows an UV maximum at 382 nm (fig. 4) [54].

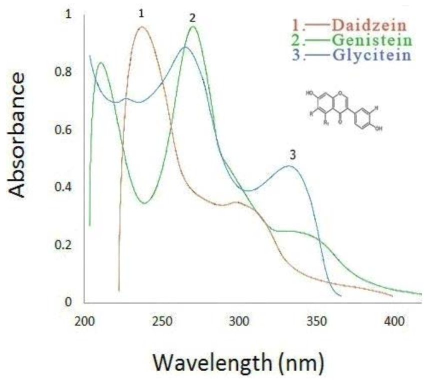

Fig. 4: Typical UV absorption bands of phytoestrogens

Carotenoids and xanthophylls

Carotenoids are tetraterpenes and hence contain 40 C-atoms in eight isoprene residues. They all have a center of symmetry. Carotenoids can be further classified into carotenes (pure carbohydrates without additional groups) and xanthophylls (carotenoids containing oxygen). Members of both groups are components of chloroplasts involved in light absorption and photon canalization of photosynthesis [55].

Carotenoids act as antioxidants due to the ability to quench ROS such as singlet molecular oxygen or superoxide, peroxide and hydroxyl radicals generated by exposure to UV radiation. These radicals damage cells by initiating a lipid peroxidation [56]. Carotenoids may be responsible for the decreased cancer incidence associated with the consumption of certain fruits and vegetables. Carotenoids such as alpha-carotene, beta-carotene, beta-cryptoxanthin and lycopene also contribute to UV protection (fig. 5).

Xanthophyll pigments are derived from carotenoids and also have photoprotective properties. For instance, lutein is derived from carotenes, violaxanthin is a derivative of alpha-carotene, and zeaxanthin is a beta-carotene derivative. The supplementation of a combination of β-carotene, lutein, and lycopene at a dose of 8 mg/day is sufficient to ameliorate the UV-induced erythema in humans [57].

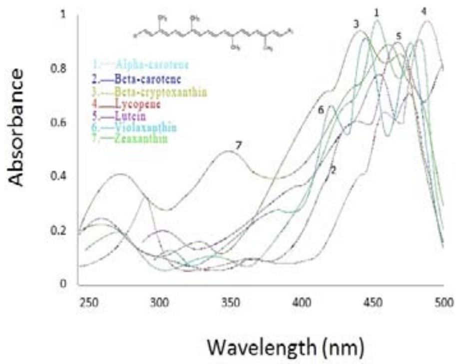

Fig. 5: Typical UV absorption bands of carotenoids

The red color of ripe pepper is caused by the presence of lycopene. Likewise, carotenoids precursors such as phytoene and phytofluene are found in tomatoes. Phytoene and phytofluene contribute up to 30% of total carotenoids in tomato [57]. After absorption in the intestine, carotenoids are transported through the bloodstream by lipoproteins to various target tissues. Since carotenoids are lipophilic, they accumulate in body sites high in total fat levels including the stratum corneum of human skin, the sole of the feet, forehead, the palm of the hands, and adipose tissue [58].

Some of these compounds have a specific function. For instance, zeaxanthin and lutein (isomeric dihydroxy carotenoid) are the major constituents of the retinal macular region and are essential for the visual functionality. The radical scavenging and photoprotective activities are determined by the number of conjugated double bonds and the presence of ionone rings. For instance, lycopene, β-carotene, and zeaxanthin, have a similar hydroxyl radical scavenging ability and contain 11 conjugated double bonds. Conversely, lutein containing only 10 conjugated double bonds, scavenges hydroxyl radicals less effectively. The mechanism of hydroxyl radical scavenging occurs via bond formation between the hydroxyl radical and the double bonds in the carotenoid [59].

Catechins

Catechins found in green tea (*Camelia sinensis*) have antifungal activity against *C. albicans*. The major component (epigallocatechin-3-gallate, EGCG) is responsible for its antifungal effects. EGCG and epicatechin-3-gallate are potent inhibitors of the dihydrofolate reductase (DHFR) activity, which is important for cell proliferation and cell growth [60].

Among all the naturally occurring catechins and (-)-epicatechins, when oligomerized exhibit an improved antiproliferative activity. The oligomerization leads to the appearance of a dark-red solution having a new broad absorption peak at 390 nm. These oligomers are water-soluble and stable for three months (fig. 6) [61].

Anthocyanins and proanthocyanidins

Anthocyanins are derived from anthocyanidins by adding sugar. Anthocyanins such as flavonoid glycosides, capensinidin, delphinidin, cyanidin, malvidin, pelargonidin, puchellidin, peonidin, petunidin, rosinidin and tricetinidin have photoprotective properties. They are used in the treatment of circulatory and eye disorders, have free radical scavenging properties and possess radioprotective, anti-inflammatory, anticancer and cardioprotective properties [62].

Proanthocyanidins show a catechin-like peak at 280 nm (fig. 7) [63].

They also have antioxidant activity. For instance, proanthocyanidins from cranberry scavenge ROS and lower the risk of urinary tract infection. In addition, proanthocyanidins have a strong inhibitory capability on pancreatic α-amylase, and thus can be used in the treatment for type II diabetes mellitus.

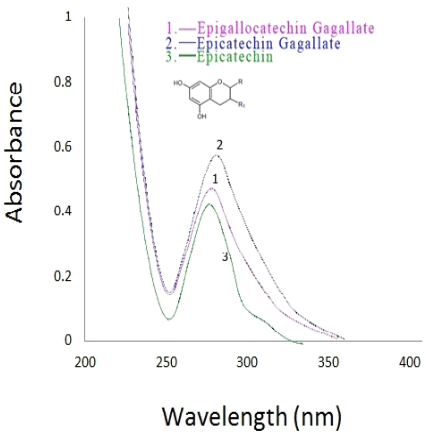

Fig. 6: Typical UV absorption bands of catechins

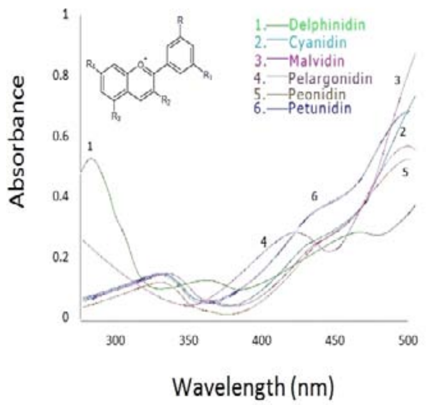

Fig. 7: Typical UV absorption bands of anthocyanins

Polymeric and oligomeric proanthocyanidins, also called condensed tannins consist of chains of flavan-3-ol units, (+)-catechin, and (-)-epicatechin linked through C4-C6 and C4-C8 inter flavan bonds. Two popular sources of oligomeric proanthocyanidins are grape seed and pine bark extracts. Cyanidin-3-O-glucoside and cyanidin-3-O-rutinoside are found in red copihue petals (61). Pelarnidin-3-glucoside is the major anthocyanin component in strawberry (77-95%). Proanthocyanidins are also found in Longan pericarps and in *Pinus radiata* bark [65].

Blueberries (*Vaccinium myrtillus*) have anthocyanin compounds such as cyanidin, delphinidin, malvidin, petunidin, and peonidin which are used to treat a coronary heart disease and urinary tract disorders. They also improve visual acuity. The total anthocyanin amount ranges from 300 to 700 mg/100 g [66].

Phenolic acids

This group of polyphenols includes caffeic, ferulic, *p*-coumaric, protocathechuic, *p*-hydroxybenzoic, vanillic and chlorogenic acids, both in free and bonded forms. Most of them are found in *Silphium perfoliatum L.* [67]. The most important phenolic acid is caffeic acid, which is one of the hydroxycinnamate and phenylpropanoid metabolites. It is widely distributed in blueberries, coffee drinks, cider and apples. It possesses antioxidant, antiviral, choleretic, cholekinetic, antibacterial and antineoplastic activity *in-vitro*. It combats skin infections such as acne and rosacea. Caffeic acid also shows the angiogenic activity of mononucleous blood leukocytes in healthy humans [68].

Caffeic acid can also be found in the ester form with sugars as a glycoside bonded with 3,4-dihydroxyphenylethylalcohol as occur in phenylpropanoids (i.e., echinacosides) found in the *Echinacea* genus.

On the other hand, ferulic and *p*-coumaric acids are found in corn, oat and wheat grains. Ferulic acid exhibits a maximum absorbance at 215 nm with additional peaks at 287 nm and 312 nm. In contrast, p-coumaric acid displays a maximum absorbance at 286 nm with additional peaks at 209 nm and 220 nm (fig. 8) [69].

In some cases, the antioxidant activity increases with the number of hydroxyl and methoxy groups. For instance, the catechol group has the ability to enhance the radical scavenging activity due to the o-Quinone formation. On the other hand, the antioxidant activity does not change in case of esterification of caffeic acid by quinic acid leading to the formation of chlorogenic acid [70].

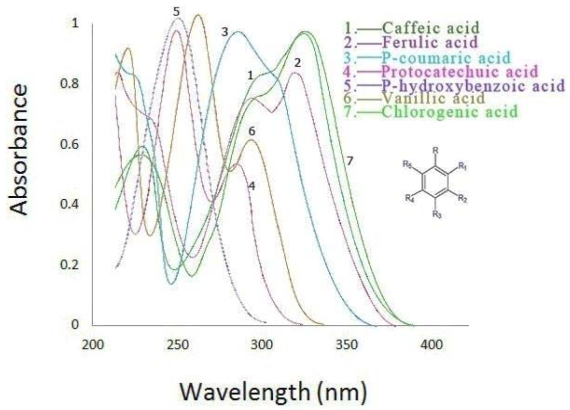

Fig. 8: Typical UV absorption bands of phenolic acids

Triterpenes

Triterpenes are a group of molecules that contain 30 C-atoms and are generated by the polymerization of six isoprene units forming pentacyclic triterpenes. Lupeol is a pentacyclic triterpene used to treat cardiovascular ailments, renal disorders, hepatic toxicity, arthritis, diabetes, microbial infections and cancer. Lupeol is also anti-inflammatory, antiangiogenic, antihypercholesterolemic and antioxidative. Lupeol is not toxic in animals at doses ranging from 30 to 2000 mg/kg [71].

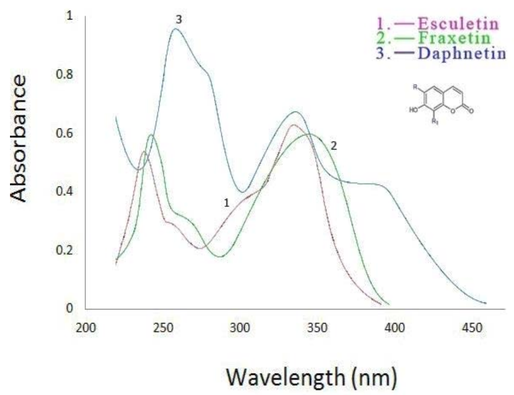

Fig. 9: Typical UV absorption bands of coumarin derivatives

Coumarin derivatives

Coumarin is a compound with a vanilla-like flavor mainly found in Tonka beans. It is also found in several plants such as lavender, licorice, strawberries, apricots, cherries, cinnamon, and sweet clover. Coumarin can occur either free, or combined with glucose (coumarin glycoside). Natural coumarin derivatives such as esculetin, fraxetin, and daphnetin are inhibitors of the lipooxygenase and cyclo-oxygenase enzymatic, and the neutrophil-dependent superoxide anion systems. For this reason, these coumarin derivatives possess anti-inflammatory, anticoagulant, and antioxidant activities [72] (fig. 9).

Alkaloids

Harmane and norharmane are representative members of the group of the β-carboline alkaloids such as natural indole alkaloids that possess a common tricyclic pyrido-indole ring structure. They are present in numerous plants including *Peganum harmala* and *Passiflora incarnata,* which have been used to treat gastrointestinal symptoms and malaria. These substances also exhibit antioxidant and neuroprotective effects against neurotoxins [73]. Piperlongumine and piperlonguminine are other alkaloids which have an absorption maximum in acidic ethanol at 328 nm, whereas in the presence of ethanolic alkali shows a peak at 304 nm [74].

Arbutin

Arbutin is an unstable phenolic compound that tends to change color due to oxidation at high temperatures. Upon absorption into the skin, it is transformed to hydroquinone *in-situ*. It inefficiently inhibits melanin production *in-vivo*. It is well known, that tyrosinase is the key and rate-limiting enzyme responsible for the conversion of tyrosine into melanin. The competitive inhibition of tyrosinase by arbutin results in decreased or absent melanin synthesis by melanocytes in human skin. Thus, it is used to decrease the levels of melanin in skin diseases including solar lentigines, melasma, and post-inflammatory hyperpigmentation. On the other hand, deoxyarbutin is a synthetic arbutin derivative created by the removal of hydroxyl groups from the glucose side-chain of arbutin, but it does not have the stability problems of arbutin [75].

Usnic acid

Usnic acid is a yellow pigment found in some lichens. Usnic acid is also called usnein or usniacin since it is not an organic carboxylic acid. Lichens are symbiotic organisms composed of a fungus that grows a photosynthesizing partner of algae or cyanobacteria. The fungus component provides shape while its partner produces food. Lichens are able to survive in a resting state for months with a slow metabolism, producing active compounds that give protection to the lichen. The lichen named *Usnea barbata* contains 1.5% of usnic acid.

Usnic acid has a keto-enol tautomerism. Both enantiomers possess antimicrobial and antimycotic properties. Usnic acid is poorly soluble in water and many organic solvents. The (-)-enantiomer is a selective herbicide due to its ability to inhibit carotenoid biosynthesis. It uncouples oxidative phosphorylation in mitochondria. It also, damages mitochondria of treated epimastigotes in parasites but exhibits some antioxidant properties. The UV spectrum of usnic acid has two maxima, one larger at 232 nm and another less intense band at 282 nm [76].

Oils as photoprotective substances

Essential oils are secreted by glandular trichomes, contain lipophilic pythocomplexes and are made up of terpenic and other phenolic molecules [22]. Vegetable oils from coconut, cotton, *Achillea millefolium, Hamamelis virginiana, Matricaria chamomilla, Mentha piperita* and *Salvia officinalis* have compounds which are structurally similar to synthetic sunscreens [37]**.** Plant seed oils possess antimicrobial and antioxidant compounds. Except those obtained from avocado and cocoa may be used as photoprotective agents. The primary compounds derived from the oxidation process show absorbance bands around 240 and 320 nm (conjugated dienes). Furthermore, secondary compounds (trienes, aldehydes, β-unsaturated, and conjugated α-ketones) have absorption peaks around 280 and 320 nm. Thermal oxidation of vegetable oils causes a band shift (bathochromic effect), but a decrease of the iodine index. Fatty acids can be classified in saturated (no double bonds between the carbon atoms) or unsaturated (one or more double bonds). Unsaturated forms are divided into three groups such as monounsaturated, polyunsaturated and long-chain polyunsaturated. Most of the properties of the oils are controlled by the fatty acid composition [74]. Saturated oils are more stable and do not become rancid as quickly as unsaturated oils. However, unsaturated oils are smoother, more precious, less greasy, and better absorbed by the skin [75]. The oxidative stability of a vegetable oil can be influenced by the amount of antioxidants naturally present.

Cocoa oil absorbs all visible light after 540 nm [76]. Further, grape seed [77], wheat germ [78], sesame seed [79] and almond [80] show an absorbance peak at 680 nm. Absorption of light is ranked from 45% to 5% from avocado [81], argania [82], carrot [83], jojoba [84], sesame, apricot to almond, respectively. Except for sesame seed, all oils absorb UVA radiation after 345 nm [85]. On the other hand, the sunflower UV spectrum shows absorption maxima from 260 to 285 nm [86, 87]. Further, butiri oil shows a high absorption in the spectral region between 280 and 360 nm, which increases upon thermal oxidation [53]. The presence of an absorption band at 410-476 nm is due to oxidative cleavage of carotenoids into apocarotenoids during the refining process [88]. Coconut oil can form a complex with silver showing a UV spectrum peak at 400 nm confirming the formation of silver and triglycerides compounds [89, 90].

Plant extracts with diverse photoprotective properties

Aglycones of basil have antioxidant capacity. Their ethanolic extract decreases lipid accumulation in macrophages. Basil and thyme methanolic extracts contain quinones and chlorophylls having UV absorption peaks in the regions of 400-417 nm and 600-660 nm, respectively (table 3).

Table 3: Absorption bands of extracts containing photoprotective compounds

Plant	Scientific name	Flavonoids and quinines (nm)	Carotenoids (nm)	Reference
Basil	*Ocimum basilicum*	417	598 652	[93]
Thyme	*Thymus vulgaris*	417	653 599	[94]
Clove	*Syzygium aromaticum*	398	-	[95]
Oregano	*Origanum vulgare L.*	330, 420	-	[96]
Rosemary	*Rosmarinus officinalis L.*	327, 398	-	[97]
Sage	*Salvia officinalis*	330, 398	-	[98]
Cinnamon	*Cinnamomum zeylanicum*	399	-	[99]
Comfrey	*Symphytum officinale L.*	325	-	[100]
Corn cob	*Zea mays L.*	-	-	[1]
Macambira de lajedo	*Encholirium spectabile*	325	-	[101]
Rose	*Rosa Kordesii*	325	-	[102]
Boldo	*Peumus boldus*	325	-	[103]
Elder	*Sambucus nigra*	330, 354	-	[104]
Caroá	*Neoglaziobia variegata*	340	-	[105]

Conversely, clove, cinnamon, rosemary and sage are characterized by absorption bands in the range of 330-420 nm, corresponding to phenolic acids and their derivatives (flavones, flavonols, phenylpropenes and quinones). Oregano shows the largest content of phenolic derivatives (280 nm) and flavonoids (330 nm). The UV spectrum of the extract shows a peak at 390-420 nm attributed to flavonoids and quinones oxidation, whereas chlorophylls show a peak at 600-660 nm [91]. Fruits of *Emblica officinalis* Gaertn contain flavones, alkaloids, tannins and gallic acid [92].

Aloe spp

The UV-protective components of aloe are mainly composed by anthraquinones and flavonoids. The main anthraquinones are aloe emodin, aloin, aloetic acid, anthranol, barbaloin, isobarbaloin, and emodin. The absorption band between 320 and 380 nm indicates the presence of phenolic compounds. It also shows a characteristic fluorescence emission maximum at 448 nm when excited at 365 nm. Aloe contains the highest concentration of fluorophore compounds such as flavonoids, flavonols, and anthraquinone moieties [106]. The gel and sap show a peak at 217-220 nm, 265-268 nm and 360-370 nm characteristics of anthraquinones [107].

Calendula officinalis

It has anti-inflammatory, skin healing, and antiseptic properties, and thus is used to treat various skin ulcerations, eczema, conjunctivitis, and stomach ulcers. *C. officinalis* also has antispasmodic, cholagogic, and vulnerary properties. It has flavonoids, phenolic acids, saponins, carotenoids and triterpenic alcohols, both in their free and esterified forms. *C. officinalis*-derived carotenoid pigments and polyunsaturated fatty acids such as calendic acid have anti-inflammatory properties.

Calotropis gigantea

Milkweed is used to control dermal fungal infections, microbial infections, and pain treatment. The latex has toxic effects following injection, oral administration or dermal contact. Fractionation of the latex into its rubber and rubber-free fractions makes it less toxic. The rubber-free fraction of the latex is rich in soluble proteins and is responsible for most of its medicinal properties due to its antimicrobial and wound healing properties [68].

Capparis spinosa

It has rutin and gallic, caffeic, coumaric, vanillic, syringic, ferulic, and chlorogenic acids. The leave extracts show a significant decrease in the level of serum glucose. It also has antifungal, antibacterial, antiamoebic, antiworm, antihyperlipidemic, antihypertensive, antileishmania, anti-hepatotoxic and antiallergic activities. Flavonoids present in this plant may be responsible for the observed activities [108].

Citrus sinensis

It contains flavonols (i.e., quercetin, dihydroquercetin, and isorhamnetin), flavanols (i.e., (-) catechin, (-)-epicatechin, and epigallocatechin), isoflavones (i.e., daizdein), flavanones (i.e., naringenin, and eriocitrin), stilbenes (i.e., resveratrol, trans-resveratrol, and 3,4,5,4'-Tetramethoxystilbene), hydroxycinnamic acid (i.e., sinapic acid, caffeic acid, chlorogenic acid, rosmarinic acid), isoflavonoids (i.e., biochanin A), lignans (i.e., Secisolariciresinol, and 7-hydroxymatairesinol) [49].

Curcuma longa

The rhizomes contain curcumin, which is a phenolic compound having antitumor, anti-inflammatory and antioxidant activities. Curcumin can coordinate with metallic ions through the acetylacetonate group. A palladium complex with curcumin induces cell growth inhibition and apoptosis of human prostate cancer cells (LnCaP, PC3, and DU145). The UV-Vis absorption spectrum of curcumin displays two bands at 261 and 417-480 nm. On the other hand, the spectrum of the complex shows four peaks at 262, 406, 430, and 454 nm) indicating metal complexation of a carbonyl group of curcumin [109].

Crocus sativus L.

Saffron contains crocetin esters, safranal, and picrocrocin showing absorption bands at 440 nm, 330 nm, and 257 nm. The coloring strength is representative of the crocetin ester content [110, 111].

Ginkgo biloba

It contains flavonoids such as quercetin, kaempferol, and isorhamnetin. The UV absorption spectrum of quercetin shows two absorption peaks between 250-260 nm and 370 nm, respectively [39].

Glycine max

Sunscreen pretreatment of swine skin with soy extracts, prior to UVB exposure reduces UVB-induced DNA and cellular damage. Further, soy extracts reduce UVB-induced COX-2 expression and hence, the inflammatory activity. In addition, soy extracts inhibit VEGF-induced endothelial tube formation in Matrigel®, which suggests a possible inhibitory effect on angiogenesis and tumor progression [112]. The reaction of soybean leaf extract with palladium ions forms a dark brown complex indicating the formation of palladium nanoparticles. These nanoparticles exhibit an absorption band at 420 nm due to Pd^{2+}ions [113, 114].

Glycyrrhiza glabra

Glabridin is the major component of licorice extract and has antimicrobial, anti-inflammatory, anticancer, antinephritic, neuroprotective and cardiovascular protective activities. Glabridin also inhibits lipid peroxidation of LDL, human cytochrome P450s, combat osteoporosis and inflammatory bone diseases [115].

Gossypium hirsutum L.

The oil of cotton seed contains gossypol, a polyphenolic compound which act for the self-defense against insect pests. The toxicity of gossypol is associated to the reaction of its phenolic groups with amino acids and minerals. Hydrogen bonding and oxidation of the carbonyl groups result in easily reactive quinones that bind proteins. Toxicity symptoms comprise loss of appetite, weight loss, liver damage, lung lesions, cardiac irregularity, and anemia due to iron complexation. It also blocks spermatogenesis and reduces sperm motility. In females, it disturbs menstrual cycle, pregnancy, and early embryo development. It has UV spectral maxima at 273 nm and 285 nm [116].

Indigofera heterantha

It contains triterpenes, steroids, alkaloids, and flavonoids. Minor compounds are saponins, tannins, quinines, caffeic acid, gallic acid, rutin, myricetin, quercetin and galangin. It is used against abscesses to treat dentifrice and mouth ulcers, dandruff, psoriasis, eczema, burns, syphilis and other skin infectious diseases. It acts as antimicrobial, antioxidant, anti-inflammatory, antidyslipidemic and hepatoprotective, and it also acts as a lipoxygenase inhibitor. The extract shows absorptions bands at 324 and 275 nm. However, a number of peaks are observed in the region of 250-275 nm [113].

Juglans nigra

The walnut extract contains many quinine pigments having a basic benzoquinone chromophore. The UV spectra show three peaks at 260 nm, 340 nm and 430 nm, ascribed to the naphthoquinone components [117].

Lapageria rosea

Copihue contains O-pelargonidin, with only one hydroxyl group giving an orange color; whereas cyanidin with two hydroxyl groups presents a red color, and delphinidin with three hydroxyls tends to a violet color. Successive acylations in the B-ring will produce petunidin and malvidin giving a deeper blue color. It has been used as skin tanner, insecticide, and repellent [61].

Luffa cylindrica

The fruit of sponge gourd which is popularly known as *Luffa cylindrica* (LC) belongs to the Cucurbitaceae family. Furthermore, nanocomposites with a Novolac resin have been produced by sonication. The UV absorption spectrum of the nanocomposite reveals two large peaks at 286 nm and 353 nm. The peaks reveal the presence of carbonyl groups in the nanocomposite [118].

Mangifera indica

It contains mangiferin, a xanthone glycoside which inhibits bowel carcinogenesis. It also has antioxidant, antitumor, immunomodulatory, antiviral, antipyretic, antidiabetic, anthelmintic, antimicrobial, and neuroprotective activities [119].

Phyllanthus emblica

Its fruit contains flavones, saponins, alkaloids, quinones, tannins, gallic, and ellagic acids. It prevents or retards the oxidation of vitamins. It is diuretic, aperient, laxative and antiscorbutic. It is also used to treat hemorrhages, diabetes, ulcers and dysentery [92].

Piper longum

It is a climbing plant used in the treatment of asthma and chronic bronchitis due to the presence of several alkaloids having a piperidine moiety. The roots contain piperlongumine, piperlonguminine, and piperine [71].

Pongamia pinnata

The seed oil of Karanja have anti-inflammatory, antidiarrheal, antiplasmodial, antifungal, and analgesic properties, and is used to treat leprosy, leucoderma, lumbago, rheumatism, fistulous sores, foul ulcers, gonorrhea, and urethritis. It contains bioflavonoids (flowers), and furanoflavonoids such as karanjin, ponga pin, kanjone, pongamol, and pongaglabrone along with other simple flavonoids and lipids like arachidonic acid. The aqueous and ethanol extracts show a maximum absorbance at ~232 nm and ~269 nm, respectively, and moderate absorbance from 335 to 400 nm. The methanolic extract shows absorbance at 338 nm, whereas the acetonic extract shows absorbance exclusively in the UVA region [120].

Terminalia catappa

It is rich in polyphenolic components such as punicalagin, punicalin, chebulagic acid, corialgin, vixetin, and rutin. It also contains triterpenoids such as ursolic acid. The leaves possess several pharmacological activities including antioxidative, hepatoprotective, analgesic, anti-inflammatory, antidiabetic, and anti-HIV reverse transcriptase activities.

Vaccinium spp

The most representative species are *Vaccinium myrtillus L.*, *Vaccinium vitisidaea L.*, and *Vaccinium uliginosum* L. UV spectra of methanol extracts of *V. myrtillus* and *V. uliginosum* show two peaks, one in the UVB region between 280 and 290 nm, and another in the UVA region at 330 nm.

Vernonia spp

Vernonia is used to treat inflammation, malaria, fever, worms, pain, diuresis, cancer, and several gastrointestinal problems. It also has hypotensive, phototoxic, antibacterial, immunomodulatory, hepatoprotective, antiulcerogenic and antihistaminic effects. These activities can be attributed to the presence of terpenes, steroids, catechins, proanthocyanidins, saponins, tannins, alkaloids, flavonoids, and specific compounds such as vernolepin, hesperidin, methyl hesperetin, homoesperetin-7-O-rutinoside, apigenin, luteolin sitosterol, and stigmasterol. The vernonioside B2 has contraceptive and anti-inflammatory effects [121].

Vitellaria paradoxa

Shea butter is a moisturizer, having exceptional healing properties in the skin and hence, it is used to treat skin allergies, insect bites, sunburns, frostbites, and other skin conditions. The absorption spectrum shows a wide peak between 200 and 300 nm, suggesting the presence of either ethylenic bonds with conjugation or carbonyl compounds. The visible region shows a maximum absorbance at 450 nm suggesting the presence of carotenoids compounds. Further, the peak at 700 nm suggests the presence of chlorophylls [122].

Vitis spp

Grapevine seeds are a rich source of polyphenols, which are characterized for having antibacterial and antioxidant activities. Each year, grape processing for wine production yields approximately 5 million tons of seeds residues. During red wine production, polyphenols are extracted from the grapevine seeds and passed to the wine. Grapevine seeds contain gallic acid, catechin, epicatechin, and a wide variety of procyanidins. These compounds are powerful scavengers of free radicals and effective inhibitors of LDL oxidation. The spectrum of the phenolic compounds derived from the acetonic and methanolic extracts of grapevine seeds reveals absorbance maxima at 280 nm, originated from tannins, catechins, and gallic acid derivatives. The extract from *V. riparia* seeds contains the highest levels of free catechins (2.3 mg/g) and ester-bound gallic acid (4.7 mg/g of extract). Grapevine seeds contain large amounts of tannins, and a much smaller amount of *p*-coumaric acid and flavan 3-ols, or catechins such as flavan-3-ol isomers, (+)-catechin and (−)-epicatechin. Their capacity for scavenging free radicals is 18-fold higher than that of ascorbic acid [123, 124].

CONCLUSION

High exposure to UV radiation increases the risk of developing skin aging and cancer. The regular consumption of vegetables and fruits rich in antioxidant polyphenolic compounds provides protection against the harmful effects of UV radiation such as oxidative stress, inflammation and cancer. However, the photoprotective and antioxidant capacity of those compounds depend on their dose and type. The photoprotective and anti-inflammatory actions could be related to the antioxidant activity, or to their ability to regulate cell signaling pathways. Botanicals with a photoprotective activity are gaining attention from researchers of cosmetic and pharmaceutical corporations due to the multiple health benefits and cost-effectiveness. However, a lot of research is yet to be conducted to determine their dose-effectiveness therapy, interactions, stability and their most suitable delivery systems.

CONFLICT OF INTERESTS

Declared none

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