


REVIEW

Natural products and extracts from plants as natural UV filters for sunscreens: A review

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Abstract

Although solar exposure is necessary for human health, phototoxicology induced by excessive UVB and UVA radiation, which involves sunburns, skin aging and even tumorigenesis, has been widely researched. Sunscreen is one of the most important ways to protect skin from UV phototoxic damage. As well as inorganic and organic UV filters, some natural products or plant extracts with aromatic rings in their structures, such as flavonoids or polyphenols, can absorb UV to reduce sunburn, acting as a natural UV filter; they also show antioxidant or/and anti-inflammatory activity. This could explain why, although there are no official approval natural commercial sun-filters, more and more commercial sunscreen products containing plant extracts are available on the market. Here we summarize articles focusing on natural UV filters from plant published in the last 6 years, selecting the most significant data in order to better understand the photoprotective activity of natural products and extracts from plants, including their major constituents and main biological effects, methods for evaluating UV radiation resistance, anti-UV radiation experimental models and anti-UV radiation mechanisms.

KEYWORDS

antioxidants, evaluation method, natural products and extracts from plants, natural UV filters, SPF value

1 | INTRODUCTION

The sun is the energy source for living organisms and the earth. Regarding human health, solar radiation exerts most of its positive effects by activating 7-dehydrocholesterol to synthesize Vitamin D₃ in human skin epidermis to prevent osteomalacia. In addition, nitric oxide (NO) production induced by ultraviolet (UV) helps to reduce blood pressure and is anti-bacterial. Exposure to UV rays can improve one's mood by inducing the release of endorphins.

Solar UV radiation is divided into three categories based on wavelength, namely UVA (400–315 nm), UVB (315–280 nm) and UVC (280–100 nm).¹ UVC rays are dispersed and reduced by the ozone layer and do not reach the ground. About 90%–99% of UVA and 1%–10% of UVB rays reach the earth's surface. The epidermis of the skin serves as a barrier to protect the body from the external environment.² Nonetheless, chronic exposure or intermittent over-exposure of human skin to UV rays leads to various skin diseases, including immunosuppression, irreversible skin photoaging and dermal pathologies, including tumorigenesis. Sunscreen is the

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most effective way, apart from sun avoidance, to prevent phototoxic damage, including sunburn, skin aging, collagen degradation, wrinkle formation, and pigmentation, to the skin,^{3,4} and is thus the best way to protect skin against damage from UV rays.

Recently, researchers into skin protection have shown considerable interest in the use of botanicals. Research suggests that natural products are reasonably likely to be the future of cosmetics, and this trend necessarily involves UV filters.⁵ Many components are reported to have great potential for use as sunscreen additives in the cosmetics industry. This review presents an overall profile of the botanical extracts or components with anti-UV radiation identified in the last 6 years, including classification of the components, their main biological effects, methods of evaluation and experimental models of UV radiation resistance, and the mechanisms of anti-UV activity involved.

2 | METHODS

The present review is based on searches of the following electronic databases: Pubmed, Google Scholar, Web of Science, Elsevier and Wiley. The databases were systematically searched for articles published in the last 6 years. Selection criteria were that retrieved articles should include only natural herbal extracts, or pure molecules available from plant sources. The following keywords were used: sunscreen, SPF or Sun Protection Factor, UV filter, natural UV filter. All key words were searched individually and in combination. Only articles written in English were selected.

3 | SUNSCREENS—TYPES OF SUN FILTERS

Sun filters are classified as inorganic UV filters, organic UV filters, and plant compounds agent. Inorganic UV filters are classified as physical filters, because their active components are minerals, namely TiO₂ and ZnO. They protect skin from solar radiation by scattering and reflecting UV rays.^{6–9} They tend to be opaque and therefore appear white on the skin, which makes them cosmetically less acceptable as sunscreens, and they also have numerous safety challenges that need to be overcome.^{10–12}

Currently, more than 60 kinds of organic sunscreens have been researched and developed internationally, but there are strict restrictions on their use. There are 14 organic sunscreens approved by the FDA in United States, 20 in the European Union, 27 in Japan, and 25 in China. P-Aminobenzoic acid (PABA) was the first UVB absorber, patented in 1943 and used by US military during Second World War and then marketed, but was found to be a strong irritant and carcinogenic to the skin. Subsequent research developments include, among others, PABA derivatives, cinnamates, salicylates, benzophenones, benzimidazoles, and camphor derivatives as UVB absorbers, and dibenzoymethanes (such as Parsol 1789) as UVA absorbers. Chemical sunscreens may exhibit phototoxicity and photosensitization, and interactions between UV absorbers and solvents

and matrices can cause cross-sensitization and therefore the amounts used in sunscreens are strictly limited. Since UVB causes immediate and serious sunburn mainly by acting on epidermis layer, and is more genotoxic and about 1000 times more capable of causing sunburn than UVA,¹³ most organic UV filter research is focused on the UVB range.

Plant compounds with aromatic rings usually show a broader absorption spectrum covering a wavelength range of 200–400 nm. Botanical ingredients used as UV filters also usually exhibit strong antioxidant properties. Therefore, these natural products are more advantageous as UV filters and are likely to be the future of sunscreens. Based on these properties, the addition of botanical ingredients to skin-care cosmetics has been a predictable trend.¹⁴

4 | PLANT COMPONENTS ACTING AGAINST UV RADIATION

In order to better understand the important role that plant extracts can play in photoprotection, we identified through extensive searches and rigorous screening the most significant data for plant extracts and natural products with photoprotective ability published between 2016 and 2021, which are summarized in Tables 1 and 2.^{15–53} The tables include the plant parts used, extraction methods, types of compound, major constituents and main effects. Our work refers to and follows the review by Matteo Radice et al., who summarized research papers published from 2000 to 2015 on herbal extracts and biomolecules as natural photo-protection alternatives to synthetic UV filters.⁵⁴

4.1 | Flavonoid and total polyphenolic compounds

As shown in Table 1, total flavonoids and total polyphenolics are the most studied components with photoprotective properties. In the strict sense, flavonoids are a category of polyphenolic compounds synthesized via the phenylpropanoid metabolic pathway in plants and have attracted considerable attention recently in scientific and therapeutic fields. The presence of double bonds or aromatic rings in the molecular structure of flavonoids gives them UV absorption properties in range of 200–400 nm, which makes them suitable for use as sunscreens agents. The flavonoids most often reported to possess photoprotective ability are rutin and quercetin, which have been identified separately or together in *Campomanesia*,²⁵ *Hylocereus polyrhizus*,³³ *Moringa oleifera*,³⁹ *Dalbergia ecastaphyllum*,²⁸ *Disterigma alaternoides*,²¹ *Drimys granadensis*,²¹ *Ginkgo biloba* L.,²⁹ *Ruta graveolens* L.,²⁹ *Moringa oleifera*³⁹ and *Vitis vinifera* L.^{29,53} These flavinoids showed a significant antioxidant ability, but, interestingly, low SPF values, with the exception of the extract from *Hylocereus polyrhizus*, which is rich in rutin and phenolic acids (gallic acid and sinapic acid), and showed UVA/UVB absorption, antioxidant and photoprotective effects and an SPF value reaching 35.02.³³

TABLE 1 List of plant extracts with photo protective properties

Plant name	Plant part(s) used	Plant extract	Type of compounds	Ref.
<i>Achillea biebersteinii</i> Afan.	Flower	Hydroglycolic Extracts	Phenolic acids, coumaroylquinic acid isomers and flavonoids	[15]
<i>Achillea millefolium</i> yarrow	Flower	Hydroglycolic Extracts	Polyphenols,	[15]
<i>Aloe vera</i>	Leave	Aloe vera gel was dried	n.r.	[16]
<i>Amaranthus viridis</i>	Fabrics	Methanolic and aqueous	Phenolics and flavonoids	[17]
<i>Angelica pubescens</i>	Root	Steam distillation	Oils	[18]
<i>Aporosa lindleyana</i>	Leaves	70% methanol	n.r.	[19]
<i>Argyrea populifolia</i>	Leaves	70% methanol	n.r.	[19]
<i>Atalantia ceylanica</i>	Leaves	70% methanol	n.r.	[19]
<i>Baccharis antioquiensis</i>	Aerial parts	Acidulated acetone	Total anthocyanins, total phenols	[20,21]
Blackberry, raspberry	Fruits	Ethanol	Anthocyanins, flavonoids	[22]
<i>Calamagrostis effusa</i>	Rhizome	Acidulated acetone	Total anthocyanins, total phenols	[20]
<i>Calea fruticosa</i>	Aerial parts	Extracted successively with n-hexane, ethyl acetate, and ethanol	Flavonoids and terpenoids, sesquiterpenic lactone, flavonol, glucosylated coumarin	[23]
<i>Castilleja fissifolia</i>	n.r.	Acidulated acetone	Total anthocyanins, total phenols	[20]
<i>Charthamus tinctorius</i> L.	Seed Oil	Commercial products	Oil	[24]
<i>Campomanesia</i>	Leaves	Hydroalcoholic extract	Total of flavonoids, phenolic compounds	[25]
<i>Coffea arabica</i>	Coffee	80% acetone, or hydroalcoholic	Total phenolics	[26,27]
<i>Dalbergia ecastaphyllum</i>	Leaves	Hydroethanol	Carotenoids, chlorophylls, total phenolic and flavonoids	[28]
<i>Dirmophandra mollis</i> Benth	Beans	Ethanol	Flavonoid	[29]
<i>Disterigma alaternoides</i>	Leaves	Acidulated acetone	Total phenolic; Total monomeric anthocyanin pigment, Total anthocyanins	[21]
<i>Drimys granadensis</i>	Leaves	Acidulated acetone	Total phenolic; Total monomeric anthocyanin pigment, Total anthocyanins	[21]
<i>Elaeagnus angustifolia</i>	Leaves	70%MeOH	Flavonoids, Phenols	[30]
<i>Erlangea tomentosa</i>	Leaves	Dichloromethane + MeOH, water	n.r.	[31]
<i>Ginkgo biloba</i> L.	Purchased extract	Ethanol	Flavonoid	[29]
<i>Helianthus annuus</i> L. cv	Leave	Methanolic extract	Hydroxycinnamic acids, cell wall-bound phenolics	[32]
<i>Hibiscus furcatus</i>	Leaves	Methanol	n.r.	[19]
<i>Hibiscus roseus</i>	Leaves, flowers	Acidulated ethonal	Phenolic compounds	[14]
<i>Hesperomeles ferruginea</i>	n.r.	Acidulated acetone	Total anthocyanins, total phenols	[21]
<i>Hylocereus polyrhizus</i>	Peels	Ethanol	Flavonoid, phenolic acids (gallic acid and sinapic acid) and one vitamin B2	[33]
<i>Hypericum juniperinum</i>	n.r.	Acidulated acetone	Total anthocyanins, total phenols	[20]
<i>Ipomoea mauritiana</i>	Leaves	Methanol	n.r.	[19]
<i>Juglans regia</i> L.	Male flower	Methanolic	Antioxidant fatty acids, flavonoids and other secondary metabolites	[34]
Larch	Bark	Ethanol	Larch bark tannin	[35]
<i>Lasia spinosa</i>	Leaves	Methanol	n.r.	[19]
<i>Leucas zeylanica</i>	Leaves	Methanol	n.r.	[19]
<i>Litchi chinensis</i>	Leaves	Ethanol	n.r.	[36]

(Continues)

TABLE 1 (Continued)

Plant name	Plant part(s) used	Plant extract	Type of compounds	Ref.
<i>Lycopodiella alopecuroides</i>	Aerial parts	Acidulated acetone	Total phenolic; Total monomeric anthocyanin pigment; Total anthocyanins	[20,21]
<i>Mentha × villosa</i>	Aerial parts	Ethanol	Polyphenols, flavonoids, and rosmarinic acid	[37]
<i>Miscanthus-sacchariflorus-</i>		Aqueous-dioxane	Lignin	[38]
<i>Mollugo cerviana</i>	Leaves	Methanol	n.r.	[19]
<i>Morella parvifolia</i>		Acidulated acetone	Total phenolic, monomeric anthocyanin pigment	[20]
<i>Moringa oleifera</i>	Leaves	Hydroalcoholic, methanolic, and water extract.	Total phenol	[39]
<i>Nephelium lappaceum</i> L.	Peel	Ethanol	Tannins and flavonoids	[40]
<i>Ola x zeylanica</i>	Leaves	Methanol	n.r.	[19]
<i>Ophiorrhiza mungos</i>	Leaves	Methanol	n.r.	[19]
<i>Pentacalia pulchella</i>	n.r.	Acidulated acetone	Total anthocyanins, total phenols	[20]
<i>Perilla, Perilla frutescens</i>	Seed	Cold pressing and filtering	Cold-pressed perilla oil	[41]
<i>peromeles ferruginea</i>	n.r.	Acidulated acetone	Total phenolic, monomeric anthocyanin pigment	[20]
<i>Plectranthus amboinicus</i>	Aerial parts	Ethanol	Polyphenols, flavonoids, and rosmarinic acid	[37]
<i>Plectranthus caespitosus</i>	Leaves	Dichloromethane + MeOH, or water	n.r.	[31]
<i>Plectranthus ecklonii</i> Benth	Aerial parts	Aqueous and ethanol extract		[42]
<i>Plectranthus zeylanicus</i>	Leaves	Methanol	n.r.	[19]
<i>Pnus-densiflora</i>	n.r.	Aqueous-dioxane	Lignin	[38]
<i>Polypodium leucotomos</i>	Leaves	Hydrophilic extract		[43,44]
<i>Prasiola calophylla</i>	Leaves	Methanol		[45]
<i>Psidium guajava</i> L.	Fruit	Hydroalcoholic extract	Flavonoids, tannins	[46]
<i>Psorospermum febrifugum</i>	Stem bark	Dichloromethane+MeOH, or water	n.r.	[31]
<i>Radix Scutellariae</i>	Root	Ethanol	Flavonoid glycosides	[47]
<i>Ruta graveolens</i> L.	Leaves	Ethanol	Flavonoid	[29]
<i>Sargassum cristafolium</i>	Leaves	Ethanol	n.r.	[48]
<i>Scutellaria radix</i>	Root	Aqueous ethanol	Flavonoids	[49]
<i>Silybum marianum</i> L.	Seeds	n.r.	Silymarin, Flavonolignans	[50]
<i>Solanum nigrum</i>	Fabrics	Methanolic and aqueous	Phenolics and flavonoids	[17]
<i>Sophora japonica</i> L.	Flower	Water	Polysaccharide	[51]
<i>Spermacoce princeae</i>	Leaves	Dichloromethane + MeOH, or water	n.r.	[31]
<i>theaflavin</i>	Purchased purified product	n.r.	Polyphenlic	[52]
<i>Vitis vinifera</i> L.	Peel or fruits	Hydroalcoholic	Flavonoid enriched extract (FE)	[29,53]

Monomeric anthocyanin pigment,^{14,20,21} ellagitannins³⁹ and catechin^{14,29} are also considered to be potent antioxidants that attenuate UV-induced free radical damage. These botanical compounds, including for example, extracts from rambutan,⁴⁰ *Pinus densiflora*,³⁸ *Psidium guajava* L.,⁴⁶ and *Scutellaria radix*,⁴⁹ may strengthen radiation resistance by stabilizing or reconstituting

their chemical structures during UV radiation, but do not show direct photoprotective activity.

Soto ML et al. have also reported that grape extracts rich in flavonoids and phenolic acids are critical therapeutic components of new after-sun cosmetics that act by reducing oxidative stress, inflammation and immunosuppression in sunburned skin.⁵⁵

TABLE 2 List of plant: species with major constituent and main biological effects

plant name	Major constituent(s)	Main effect(s)	Ref.
<i>Achillea biebersteinii</i>	Chlorogenic acids, caffeic acid, cynarin, quinic acid, kaempferol, jaceidin, axillarin, kaempferol	Antioxidant, Tyrosinase Inhibitory Activity, SPF (5%, 11.67)	[15]
<i>Achillea millefolium</i> yarrow	Quinic acid, 5-caffeoylquinic acid (CQA), 3-CQA, 4-CQA, axillarin, jacedin, kaempferol and cynarin	Antioxidant activity, Tyrosinase Inhibitory Activity, SPF (5%, 14.04)	[15]
<i>Aloe vera</i>	Aloe gel nanoparticles–chitosan	UV-protection factor (UPF) on coated fabrics (52.1, 57.2)	[16]
<i>Amaranthus viridis</i>	n.r.	UPF (ultraviolet protection factor)†	[17]
<i>Angelica pubescens</i>	Osthole, eugenol, α -bisabolol	Anti-inflammatory, anti-UV-B radiation, skin lesions↓, epidermal hyperplasia↓	[18]
<i>Aporosa lindleyana</i>	n.r.	Antioxidant activity, UV absorber, SPF (21.4)	[19]
<i>Argyrea populifolia</i>	n.r.	Antioxidant activity, UV absorber, SPF (12.5)	[19]
<i>Atalantia ceylanica</i>	n.r.	Antioxidant activity, UV absorber, SPF (26.8)	[19]
<i>Baccharis antioquiensis</i>	Total phenolic, monomeric anthocyanin pigment	UV absorber, Antioxidant activity, SPF (4.73), Photostability, UVA–UVB absorption coefficient	[20,21]
Blackberry, raspberry	n.r.	Antioxidant activity, SPF (54.57 to blackberry and 37.32 to raspberry)	[22]
<i>Calamagrostis effusa</i>	Total phenolic, monomeric anthocyanin pigment	UV absorber, Antioxidant activity; UVA–UVB absorption coefficient	[20]
<i>Calea fruticosa</i>	Apigenin-4',7-dimethyl ether, budlein A, quercetin, and cichoriin	Antiproliferative and photoprotective activities; SPF (13.79)	[23]
<i>Castilleja fissifolia</i>	Total phenolic, monomeric anthocyanin pigment	UV absorber, Antioxidant activity; UVA–UVB absorption coefficient	[20]
<i>Charthamus tinctorius</i> L.	Acacetin	Inhibit UVB-induced MMP-1 protein expression	[24]
<i>Campomanesia</i>	Myritrine, myricetin, cardamonin, stictane-3,22-diol valonic acid, gallic acid, myricitrin, rutin, quercetin pentose, quercetin deoxyhexoside, quinic acid	UV absorber, SPF (5.58), photoprotective	[25]
<i>Coffea arabica</i>	Total phenolics	Against UV-B, MMP-1, MMP-3, MMP-9, ROS, photo-protective activity, Xanthine oxidase inhibition activity, antioxidant, SPF (liposome/PHB) particles, 15.13)	[26,27]
<i>Dalbergia ecastaphyllum</i>	Caffeic acid, catechin, epicatechin, naringenin, naringin, protocatechuic acid, quercetin, rutin, sinapic acid, vanillic acid, β -resorcylic acid	Antioxidant, Tyrosinase inhibitory activity, SPF (~45)	[28]
<i>Dirmophandra mollis</i> Benth	Caffeic acid, catechin, epicatechin, naringenin, naringin, protocatechuic acid, quercetin, rutin, sinapic acid, vanillic acid, β -resorcylic acid	Antioxidant, SPF (4.96)	[29]
<i>Disterigma alaternoides</i>	Quercetin, rutin	Antiradical capacity; Antioxidant activity; UVA–UVB absorption coefficient	[21]
<i>Drimys granadensis</i>	Quercetin, rutin	Antiradical capacity, Antioxidant activity, UVA–UVB absorption coefficient	[21]
<i>Elaeagnus angustifolia</i>	n.r.	8%SPF 21.05	[30]
<i>Erlangea tomentosa</i>	n.r.	Antioxidant, SPF (16.64)	[31]
<i>Ginkgo biloba</i> L.	Quercetin;rutin	SPF (7.06), Antioxidant	[29]
<i>Helianthus annuus</i> L. cv	n.r.	Anti-UVA	[32]

(Continues)

TABLE 2 (Continued)

plant name	Major constituent(s)	Main effect(s)	Ref.
<i>Hesperomeles ferruginea</i>	Total phenolic, monomeric anthocyanin pigment	UV absorber, Radical scavenging capability, antioxidant activity, UVA–UVB absorption coefficient	[20]
<i>Hibiscus furcatus</i>	n.r.	Anti-UVA, SPF (29.4), antioxidant	[19]
<i>Hibiscus roseus</i>	Hydroxycinnamic acid derivatives; flavonoids, Catechin derivatives, dihydrochalcones; anthocyanins, phenolics	SPF (2.6), Collagenase Inhibition Activity, antioxidant	[14]
<i>Hylocereus polyrhizus</i>	Rutin, phenolic acids (gallic acid and sinapic acid) and vitamin B ₂	UVA/UVB absorber, Antioxidant; photoprotective, SPF (35.02)	[33]
<i>Hypericum juniperinum</i>	Phenolic acids	UV absorber, antioxidant, photoprotective	[20]
<i>Ipomoea mauritiana</i>	(gallic acid and sinapic acid) and one vitamin B ₂	Antioxidant, SPF (11.3)	[19]
<i>Juglans regia</i> L.	3,7-Dimethyl-1,6-octadiene, pentadecanoic acid, 14-methyl, methyl ester, 2-(2,6-dimethoxy-benzoylamino)-propionic acid, ethyl ester, hexadecanoic acid, ethyl ester (palmitic acid), 10-octadecenoic acid, methyl ester, erucic acid; 1,2,3-benzothiadiazole; estra-1,3,5(10),6-tetraene-3,17-diol, (17 β); 17-acetate, 2,2,4-trimethyl-3-(3,8,12,16-tetramethyl-heptadeca-3,7,11,15-tetraenyl)-cyclohexanol and oleic acid, trimethylsilyl ester	Antioxidant; anti-inflammatory, photoprotective, SPF (8.8), UVB absorber	[34]
Larch	Tannin	Antioxidant, LBT/PVA composite membranes demonstrated excellent UV protection ability	[35]
<i>Lasia spinosa</i>	n.r.	Antioxidant, anti-inflammatory, anti-UVB, SPF (8.9)	[19]
<i>Leucas zeylanica</i>	n.r.	SPF (39.8); Radical scavenging capability; antioxidant activity	[19]
<i>Litchi chinensis</i>	n.r.	The sunscreen formulation with LC showed a photoprotection of 32.9%	[36]
<i>Lycopodiella alopecuroides</i>	Total phenolic, Total monomeric anthocyanin pigment, Total anthocyanins	UV absorber, antioxidant, photoprotection	[20,21]
<i>Mentha × villosa</i>	Rosmarinic Acid, total Flavonoids	SPF (13.73); antioxidant, UVA–UVB absorption coefficient	[37]
<i>Miscanthus-sacchariflorus</i>	Lignin	UV blocking activity, SPF (1%, enhanced SPF value of commercial sunscreen 31.6)	[38]
<i>Mollugo cerviana</i>	n.r.	Antioxidant, photostability, SPF (29.5)	[19]
<i>Morella parvifolia</i>	n.r.	Antioxidant activity; photoprotective	[20]
<i>Moringa oleifera</i>	Rutin, Quercetin, Ellagic acid, Chlorogenic acid, Ferulic acid	Antioxidant activity, SPF (4%water extract, 2.01), UVAPF ₀ (1.44), UVA–UVB absorber	[39]
<i>Nephelium lappaceum</i> L	Flavonoids, tannins	UVB absorber, SPF (1% extract increased 7.5% EPMC SPF value from 11.2 to 26.3)	[40]
<i>Olax zeylanica</i>	n.r.	SPF (24.5), Radical scavenging capability, antioxidant activity	[19]
<i>Ophiorrhiza mungos</i>	n.r.	SPF (39.2); Radical scavenging capability; antioxidant activity	[19]
<i>Pentacalia pulchella</i>	n.r.	Antioxidant activity; photoprotective, SPF-(10%P. pulchella, 4.36)	[20]
<i>Perilla</i> , <i>Perilla frutescens</i>	Linolenic acid, Oleic Acid, Linoleic Acid	Antioxidant, MMP-1 \downarrow , skin wrinkle scores \downarrow , skin aging \downarrow galactosidase and MMP-3 mRNA \downarrow	[41]
<i>Plectranthus amboinicus</i>	Rosmarinic Acid, total Flavonoids	SPF (14.79), antioxidant	[37]

TABLE 2 (Continued)

plant name	Major constituent(s)	Main effect(s)	Ref.
<i>Plectranthus caespitosus</i>	n.r.	Antioxidant, SPF (37.84)	[31]
<i>Plectranthus ecklonii</i> Benth	Rosmarinic acid and parvifloron D	Antioxidant activity; photoprotective ability, The extract association with benzophenone-4 provided an SPF augmentation of 19.49%	[42]
<i>Plectranthus zeylanicus</i>	n.r.	SPF (11.5), Radical scavenging capability, antioxidant activity	[19]
<i>Pinus-densiflora</i>	lignin	UV blocking activity, SPF (1%, enhanced SPF value of commercial sunscreen 11.6)	[38]
<i>Polypodium leucotomos</i>	n.r.	The UV Barrier-Function and Immune Protection- Capability	[43,44]
<i>Prasiola calophylla</i>	Prasiolin, mycosporine-like amino-acid (MAA)	A new UV-sunscreen compound, UVA absorber	[45]
<i>Psidium guajava</i> L	n.r.	Photoprotective activity, SPF (1.0, improve SPF value of 7.5% 2-ethyl-hexyl methoxycinnamate formulation to 8.1)	[46]
<i>Psorospermum febrifugum</i>		Antioxidant, SPF (16.67)	[31]
<i>Radix Scutellariae</i>	Baicalin, wogonoside	Antioxidant (ABTS), IL-6↓, MMP-1↓, p-c-fos, p-c-jun↓ p-ERK /p-JNK/ p--p-38↓TGF-β1, p-Smad2/3↓Nrf2 (in nuclear), HO-1, and NQO-1↑	[47]
<i>Ruta graveolens</i> L.	Quercetin; rutin	SPF (5.34), Antioxidant	[29]
<i>Sargassum cristafolium</i>	n.r.	Anti-UVA; photoprotective;Histological analyze	[48]
<i>Scutellaria radix</i>	Baicalin and balcalein	SPF22.7 (sunscreen 5% SR extract BuOH fraction), scavenge Free radical	[49]
<i>Silybum marianum</i> L.	Silymarin, flavonolignans	UVA protection factor (PF-UVA), UVB-protective	[50]
<i>Solanum nigrum</i>	n.r.	Improve UPF (ultraviolet protection factor) value	[17]
<i>Sophora japonica</i> L.	Polysaccharide	ROS↓, p-JNK/ p--p-38↓	[51]
<i>Spermacoce princeae</i>	n.r.	Antioxidant, SPF (17.05)	[31]
<i>theaflavin</i>	Theaflavin	Antityrosinase activity, antioxidation, UV filter, SPF	[52]
<i>Vitis vinifera</i> L.	Quercetin; rutin	SPF (3.17); antioxidant activity	[29,53]

4.2 | Polysaccharides

Few polysaccharides have been reported to possess anti-UV ability. The polysaccharide from the flower bud of *Sophora japonica* L. has shown significant UV-protectant ability through decreases in UVB radiation-induced ROS and MAPK signal protein p-JNK/ phospho p-38.⁵¹ The superoxide anion radical was initially generated by exposure to UVA, while the generation of the hydroxyl free radical was related to UVB irradiation. The ability of the polysaccharide in the flower bud of *S.japonica* L to scavenge hydroxyl free radicals and superoxide anion radicals has been confirmed.⁵⁶ Fructan from white garlic has also been reported to have a protective effect on UVB-induced keratinocyte damage.⁵⁷

4.3 | Lignin

Lignin is a kind of aromatic polymer abundant in plants. It is a natural UV screening agent, but, as reported in a few studies recently, its unfavorable dark color hinders its application as a high value addition

to sunscreens.³⁸ Lee S.C. documented an improved method for separating and purifying lignin to prevent it from darkening during the process of delignification, allowing the purified lignin to be used as a natural sunscreen component for the first time.³⁸

4.4 | Phenylpropionic acids

Phenylpropionic acids are naturally occurring organic acids found in plants. They can combine with sugar or polyols and exist in plants in the form of glycosides or esters, showing strong physiological activity. A lot of phenylpropionic acids such as chlorogenic acids, caffeic acid, quinic acid and cynarin from *Achillea biebersteinii*¹⁵ and *Achillea millefolium* (yarrow), caffeic acid, catechin, epicatechin, naringenin, naringin, and protocatechuic acid from *Dalbergia ecastaphyllum*²⁸ and *Dirmophandra mollis* Benth,²⁹ rosmarinic acid from *Plectranthus amboinicus*³⁷ and *Plectranthus ecklonii* Benth⁴² have been reported to show anti-UV ability through antioxidant and tyrosinase inhibitory activity. This suggests that phenylpropionic acids show anti-UV property indirectly.

4.5 | Other compounds

Besides the compounds mentioned above, some research has shown that osthole—a natural coumarin,¹⁸ α -bisabolol—a sesquiterpene,¹⁸ carotenoids,²⁸ and herbal oils,^{24,41} have also shown significant UV-protectant abilities.

5 | EVALUATION MODELS AND MECHANISMS FOR UV RADIATION RESISTANCE

5.1 | Anti-UV evaluation model in vitro

Skin cell models in vitro are mostly derived from human cell cultures, thereby avoiding the complication of interspecific differences, and have the advantages of short test periods and being easy to operate. HaCaT cells are a non-tumor-origin immortalized human normal skin keratinocyte strain that has similar differentiation characteristics to normal in vivo keratinocytes, and has the advantage of being easy to culture and passage multiple times. Therefore, they are widely used in anti-UV radiation drug screening and mechanism research.

5.2 | Cell viability

MTT is coloring agent usually employed to evaluate the viability of epidermal cells. After incubating with a drug, the culture medium needs is removed from the cell plate, and a new culture medium mixed with 5% of MTT is added and incubated for 4 h, followed by addition of DMSO to dissolve formazan crystals. Finally, the absorbance value at 490nm is detected.⁵⁸ Due to a certain level of carcinogenicity and consequent safety risks for operators, MTT has gradually been replaced by CCK-8 recently. For the CCK-8 coloring agent assay, the cells are incubated with new culture medium mixed with 10% CCK-8 for 0.5–1 h, and absorbance is detected at OD₄₅₀. The easier operation and lack of toxic side effects make CCK-8 method more acceptable for operators.

5.3 | Ultraviolet scanning

UV transmission measurements are performed using a spectrophotometer equipped with an integrating sphere.⁵⁹ The ϵ_{λ} value—the absorption characteristics of 1 mole of sunscreen at a thickness of 1 cm at a wavelength of λ —is used to determine the ability of filter to absorb UV in the range of 280–400 nm.

5.4 | Determination of the SPF value

In 1934, Friedrich Ellinger first put forward the concept of a minimal erythema dose (MED).⁶⁰ MED was defined as the minimal dose or period of UV radiation sufficient needed to produce a minimal

perceptible erythema on unprotected skin. F. Creiter introduced the term sun protection factor (SPF) in 1974.⁶¹ The SPF was defined as the UV energy required to generate a MED on protected skin divided by the UV energy required to generate a MED on unprotected skin. It is usually used to evaluate how well a sunscreen protects skin from UVB rays.

Studies have shown that extracts from natural plants enhance the SPF of sunscreen formulations (Table 2). G.B. Katarzyna et al. reported that a water: polyethylene glycol (4:1) extract of *Achillea millefolium* (yarrow) provided a maximum SPF value of 14.04 ± 0.17 , while a 5% hydroglycolic extract of *Achillea biebersteinii* provided a maximum SPF value of 11.67; the extracts also showed cytotoxicity for A375 melanoma and human keratinocyte HaCaT cells.¹⁵ T.N. Mayuri and co-researchers reported that 1 mg/ml methanol extracts of *Hibiscus furcatus*, *Atalantia ceylanica*, *Mollugo cerviana*, *Leucas zeylanica*, *Ophiorrhiza mungos* and *Olax zeylanica* leaves displayed SPF values ≥ 25 , with the value for *Atalantia ceylanica* extract being 26.8, while a 1% methanol extract of *Miscanthus sacchariflorus* showed good UV blocking activity and anti-UVB ability, and enhanced the SPF value of commercial sunscreen to 31.6.¹⁹ Milleno Dantas Mota and co-researchers reported that a 1% ethanol extract of *Nephelium lappaceum* L. peel improved the SPF value of a sunscreen formulation containing 7.5% of ethylhexyl methoxycinnamate (EHMC) from 11.2 to 26.3.⁴⁰ *Nephelium lappaceum* L. also displayed a higher total phenolic content (151 mg/g), which could explain the reported SPF values. Another study by Jane Namukobe et al. reported the photoprotective effect of plants in Uganda; 2 mg/mL of aqueous extracts from *Spermacoce princeae* and *Plectranthus caespitosus* provided SPF values of 37.84 and 17.05, respectively, and 2 mg/ml of organic extracts from *Erlangea tomentosa* and *Psorospermum febrifugum* provided SPF values of 16.46 and 16.67, respectively.³¹ *Pinus densiflora* extract also showed good UV blocking activity, with a 1% extract increasing the SPF value of commercial sunscreen by 11.6.³⁸ *Plectranthus ecklonii* Benth extract combined with benzophenone-4 provided an SPF augmentation of 19.49%.⁴²

5.5 | UVA-protection factor (PF)

UVA (320–400 nm) does not primarily lead to reddening or pain, but could cause invisible skin damage and skin photoaging. The COLIPA in vitro UVA method, a standard and reproducible measure of sunscreen UVA protection, was published in 2010.⁶² The L'Oréal company reported a revised COLIPA in vitro UVA method in 2013⁶³ and this is currently the most authoritative method for determination of UVA protection in the world.

5.6 | Photoprotective efficacy in vitro

Photoprotective efficacy in vitro is calculated according to the following formulas:

$$\% \text{SPF}_{\text{eff}} = \text{SPF}_{\text{in vitro}} \text{ after irradiation} / \text{SPF}_{\text{in vitro}} \text{ before irradiation} \times 100$$

$$\%UVA - PF_{\text{eff}} = \frac{UVA - PF_{\text{in vitro}} \text{ after irradiation}}{UVA - PF_{\text{in vitro}} \text{ before irradiation}} \times 100$$

UVB efficacy is estimated by SPF after and before UV radiation; UVA efficacy is estimated by UVA-PF after and before UV radiation.²⁰ Six parallel tests are performed for each sample.

5.7 | SI value

The selectivity index (SI) is defined as the value of the toxic concentration divided by bioactive concentration for a drug or sample.⁶⁴ An effective drug should have a relatively high toxicity concentration but a low active concentration. For any study of a botanical drug and/or isolated plant component, estimation of the SI value is crucially important to determine whether to continue the study. The index has also been used by researchers in Japan to evaluate anti-UV activity, defined as the value of the concentration that reduces the viable cell number by 50% divided by the concentration that increases the viability of UV-irradiated cells to 50% (Table 3).⁶⁵⁻⁶⁸

6 | ANTI-UV EVALUATION MODEL IN VIVO

HR-1 hairless mice and C57BL/6 mice are the current strains used to establish animal models in vivo to evaluate the anti-UV ability of plant extracts. Choi Sun-Il et al. used HR-1 hairless mice to investigate the anti-photoaging properties of soybean cake, sesame seed cake and fermented rice bran induced by UVB irradiation.⁶⁹ Nan et al used C57BL/6 mice to evaluate the anti-UV ability of quercetin-loaded chitosan nanoparticles.⁷⁰

For animal models in vivo, the HE and Masson methods are used to evaluate pathological and histological changes.

7 | ANTI-UV MECHANISMS OF NATURAL PLANT SUBSTANCES USED AS SUNSCREEN FILTERS

7.1 | UVA and UVB absorption

A perfect botanical UV filter can absorb UV rays, convert the electrons to an excited state, and then convert them back to the original state through ultra-fast photoisomerization, effectively transferring the UV energy to the environment to avoid DNA damage. Therefore, evaluation of whether botanical extracts exhibit photo-protection after UV irradiation is crucial for their application as UV filters in sunscreen formulas.

UVA can be subdivided into UVA-2 (320–340nm) and UVA-1 (340–400nm). UVA-1 has the strongest penetrating power and can reach the dermis layer of the skin and tan the skin. It is radiation most damaging to the skin, but it is also the easiest to ignore. Although the

TABLE 3 Selectivity index (SI) value of herbal constituents

Category	Cell line	SI value	References
Shosokoto	HaCaT	34	[62]
Hangesyashinto	HaCaT	>28	[62]
Uniseiin	HaCaT	>23	[62]
Saireito	HaCaT	>19	[62]
Ninjinyotiyō	HaCaT	23	[62]
Scurellaria root	HaCaT	38	[62]
Polyporus sclerotium	HaCaT	>26	[62]
Gardenia fruit	HaCaT	>23	[62]
Japanese Gentian	HaCaT	>20	[62]
Saposhnikovia root	HaCaT	>20	[62]
Glycyrrhizin	HaCaT	36	[62]
Vitamin C (Positive control)	HaCaT	200	[62]
Luteolin 6-C-β-D-glucoside in leaves of <i>Sasa senanensis</i> Rehder	HSC-2	>2	[63]
Luteolin 7-O-β-D-glucoside in leaves of <i>Sasa senanensis</i> Rehder	HSC-2	7	[63]
Luteolin 6-C-α-L-arabinoside in leaves of <i>Sasa senanensis</i> Rehder	HSC-2	>7	[63]
Tricin in leaves of <i>Sasa senanensis</i> Rehder	HSC-2	27	[63]
Alkaline extracts in leaves of <i>Sasa senanensis</i> Rehder	HSC-2	40	[63]
Lentinus edodes mycelia extract (LEM)	HSC-2	13.9	[64]
lignin-carbohydrate complex (LCC) from pine cones and seed shells	HSC-2	7.6–38	[64]
Vanillin		63.8	[64]
Gallic acid		5.4	[64]
EGCG		>2.6	[64]
EGCG	HSC-2	7.7	[65]
Gallic acid	HSC-2	17.1	[65]
sodium ascorbate (Vc)	HSC-2	42.4	[65]
Lentinus edodes Mycelia Extract (LEM)		41.9	[65]

intensity of UVA-1 is weak, especially in the non-summer seasons, it still causes skin damage due to long-term accumulation of the radiation dose. UVA-2 can reach the epidermis, like UVB, and can cause sunburn, redness and pain, solar keratosis, and loss of transparency.

Botanicals rich in flavonoids and total phenolic compounds, such as ellagic acid, corilagin, geraniin, apigenin, quercetin, catechin, and anthocyanins in rambutan extract, always show a maximum absorption range of 280–400nm.⁴⁰ All of the botanical components have conjugated bonds and chemical groups responsible for absorbing UV radiation at different wavelengths. Quercetin and anthocyanins directly absorb UV radiation to inhibit UVB-induced skin damage. Thus we find that the substances from plants showing

photoprotective activities almost always belong to total phenolic and flavonoid groups, as summarized in Table 2.

On the other hand, most of chemical sunscreen filters, such as PEG-25 PABA, ethylhexyl salicylate, octocrylene, and 4-oxy-methylcinnamate-2-ethylhexyl, are focused on UVB absorption. Parsol 1789 is one of the most effective UVA absorbers in chemical sunscreen filters, but is difficult to synthesize, and has poor photostability and high sensitization. Therefore, natural substances from plants have unique advantages in developing sunscreen filters compared to chemical sunscreen filters.

7.2 | Anti-oxidant activity

Most of the herbal extracts with anti-UV ability have shown anti-oxidant activity, as shown in Table 2. Antioxidant activity is a crucial mechanism by which botanical extracts exert photo-protective activity.

7.2.1 | Anti-oxidant activity in vitro

Up to now, a number of analytical methods for evaluating the antioxidant activity of plant extracts have been developed, including evaluation of the ability to eliminate radicals, ABTS,^{71,72} DPPH,⁷³ oxygen radical absorbance capacity (ORAC),⁷⁴ photochemiluminescence (PCL) or reduction potentials of compounds (ferric reducing antioxidant potential, FRAP). Among these, evaluation of the eliminating ability of ABTS and DPPH ability is efficient and has been adopted in most cases for primary determination of antioxidant activity in vitro of herbal extracts; see Table 2 for details. Using these methods, many researchers have reported significant antioxidant activity of various plant extracts.^{15,19–21,26,28,29,31,35–41,43,47,48,52–54}

7.2.2 | ROS assay

Reactive oxygen species (ROS) are highly reactive chemicals derived from O₂, including hydroxyl radicals, singlet oxygen molecules, peroxides, superoxides and alpha-oxygen. ROS are the normal metabolism byproducts of oxygen at low levels in organisms and play an important role in cell signaling and homeostasis.^{3,4} When organisms are under environmental stress (e.g. UV or heat exposure), ROS levels can increase dramatically. If the excessive ROS are not eliminated quickly, significant damage to cell structure may result. Excessive UV radiation-induced ROS in skin cells further lead to DNA damage, membrane lipid-peroxidation, skin aging and tissue damage.

The antioxidant properties of natural products and extracts from plants may provide new possibilities to treat and prevent skin from UV-induced damage. Polyphenolic and flavonoid compounds are important sources of natural antioxidant extracts. Furthermore, ROS play a central role in initiating and driving various signaling pathways that lead to a cellular response to UVA and UVB irradiation. Therefore

ROS detection has been used to evaluate the antioxidant activity of natural products or extracts. CGA isolated from beans of *Coffea arabica* dose-dependently inhibited intracellular ROS production in CCRF cells stimulated by UV radiation.²⁶ Pretreatment of HaCaT cells with a methanol extract of the male flower of *Juglans regia* L. for 0.5 h before UVB-irradiation inhibited ROS generation and lipid peroxidation, and restored antioxidant activity in cells.³⁴ Cold-pressed perilla oil extracted from *Perilla frutescens* reduced UV-induced ROS production in NHDF cells,⁴¹ and 1.0 mg/ml of polysaccharide from the flower bud of *Sophora japonica* L. significantly decreased the level of ROS induced by UVB (120 mJ/cm² and 240 mJ/cm²).⁵¹

7.3 | MMPs

Matrix metalloproteinases (MMPs), a family of zinc-containing proteinases, are responsible for degradation of extracellular matrix (ECM) proteins.⁶ Previous studies have revealed that UV radiation promoted the expression level of interstitial collagenase (MMP-1), stromelysin-1 (MMP-3), and gelatinase (MMP-9) in human skin in vivo.⁷ Via this mechanism, UV irradiation can rapidly induce and activate transcription factor AP-1, and the latter could strongly regulate the expressions of MMP-1, MMP-3 and MMP-9 in human skin in vivo. On the other hand, UV directly induces an increase in ROS, which provokes secretion of inflammatory cytokines and enhances levels of MMPs in dermal fibroblasts, furthermore reducing the synthesis of procollagen, collagen, elastin fibers, fibronectin, and laminin, and thus having adverse effects on skin elasticity resulting in wrinkle formation.⁷⁵ Therefore, MMPs are thought to be responsible for dermal photoaging in human skin.

Evaluation of MMP-1 expression along with collagen synthesis is therefore a preliminary screening process for anti-aging agents due to its significant ability to initiate collagen cleavage.⁷⁶ Safflower seed oil and its purified compound acacetin significantly inhibited UVB-induced MMP-1 protein expression in HaCaT cells and human dermal fibroblasts (HDF).²⁴ Chlorogenic acid isolated from beans of *Coffea arabica* effectively suppressed the expression of the MMP-1, 3, and 9 and increased synthesis of type-I procollagen in UVB-stimulated CCRF cells.²⁶ Cold-pressed perilla oil (CPO) from *Perilla frutescens*, mainly consisting of linolenic acid and oleic acid, markedly suppressed UV-induced MMP-1 protein levels in NHDF cells.⁴¹ Wogonin, baicalin and baicalein isolated from *Radix Scutellariae* diminished the increase in MMP-1 mRNA levels caused by UVB radiation, and 100 µg/ml of enzyme-treated *Radix Scutellariae* reduced UVB-induced MMP-1 expression by 68.35%.⁴⁷ MMP-1 expression is also related to the activation of mitogen-activated protein kinase (MAPK)/AP-1 pathway.⁹

7.4 | MAPK signaling pathways

MAPKs are a large family of protein kinases that phosphorylate and sequentially activate one another in a series of distinct cascades

in response to extraordinarily diverse sets of stimuli involved in the regulation of development, growth, differentiation, inflammation and cell death. The family includes Jun-N-terminal kinase (JNK), extracellular-regulated protein kinase (ERK), and p38 kinase. The MAPK pathway is a well-known ROS-sensitive signaling pathway.^{77,78} Activation of MAPKs by UV radiation is one of the early cellular responses and depends strictly on time, dosage and wavelength.⁷⁹ Wang et al verified that enzyme-treated *Radix Scutellariae* significantly inhibited the excessive UVB-induced expressions of MMP-1 and IL-6 by inactivating the MAPK/AP-1 and NF- κ B/I κ B- α signaling pathways, and their compounds baicalin and wogonoside significantly decreased p-ERK, p-JNK, and p-p-38 levels.⁴⁷ Our research reported that polysaccharide from the flower bud of *Sophora japonica* L. decreased ROS generation, and down-regulated the expression of phosphor-JNK and phosphor-p38 MAPK proteins significantly in UVB-irradiated cells.⁵² Evidently therefore, the MAPK signaling pathways form a core unit of UV-induced stress responses in human keratinocytes, which had been summarized by Zerihun Assefa et al.⁸⁰

8 | CONCLUSION

More and more commercial sunscreen products with natural products or extracts from plants are available on the market due to the many benefits they provide that traditional sunscreens do not have. Here we have summarized the articles on anti-UV activity published in the last 6 years and selected the most significant data to better understand the photoprotective activity of natural products and extracts from plants, including their major constituents and main biological effects, methods for evaluating UV radiation resistance, anti-UV radiation experimental models, and anti-UV radiation mechanisms. This review will provide a strong foundation for evaluating the status and potential use of natural UV filters.

AUTHOR CONTRIBUTIONS

Liyan Li and Hui Ding designed and supervised the manuscript. Liyan Li, Chong Lan wrote the manuscript. Tao Huang, Yunge Ma and Yingyan Li revised the manuscript. All authors read and approved the final manuscript.

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CONFLICT OF INTEREST

The authors declared no conflict of interest for this article.

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