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REVIEWS

New developments in sunscreens

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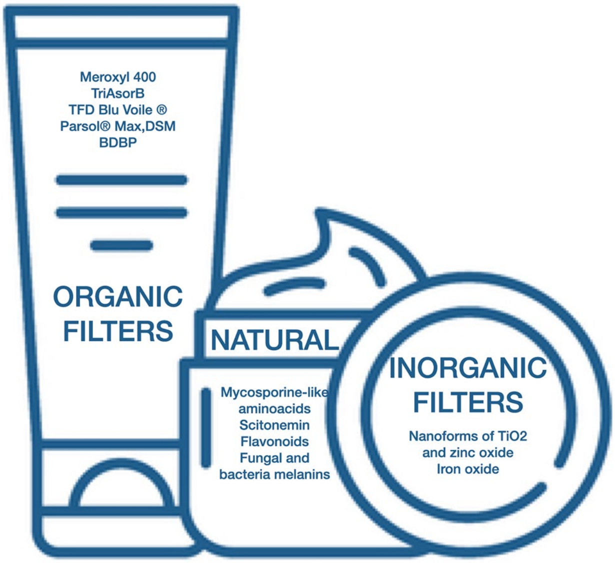
Abstract

Topical sunscreen application is one of the most important photoprotection tool to prevent sun damaging effects in human skin at the short and long term. Although its efficacy and cosmeticity have significantly improved in recent years, a better understanding of the biological and clinical effects of longer wavelength radiation, such as long ultraviolet A (UVA I) and blue light, has driven scientists and companies to search for effective and safe filters and substances to protect against these newly identified forms of radiation. New technologies have sought to imbue sunscreen with novel properties, such as the reduction of calorific radiation. Cutaneous penetration by sunscreens can also be reduced using hydrogels or nanocrystals that envelop the filters, or by binding filters to nanocarriers such as alginate microparticles, cyclodextrins, and methacrylate polymers. Finally, researchers have looked to nature as a source of healthier products, such as plant products (e.g., mycosporines, scytonemin, and various flavonoids) and even fungal and bacterial melanin, which could potentially be used as substitutes or enhancers of current filters.

Graphical abstract



Keywords Sunscreen · Sun protection factor · Photoprotection

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1 Introduction

Primary prevention strategies for avoiding sun damaging effects include different photoprotection measures as a good knowledge of solar UV incidence at earth surface for acquiring behavior of sun avoidance during the peak UV radiation hours (a practical clue is when shadows are shorter than those casting them) and the use of photoprotective clothing, wide-brimmed hats, and sunglasses, and finally, for non-covered skin, the use of broad-spectrum sunscreens is highly extended in general population [1–3]. Recent years have seen improvements in both the efficacy and cosmeticity of sunscreens. The main objective of sunscreens is to protect against sunburn, which they achieve thanks to the presence of filters that primarily block ultraviolet B (UVB) radiation. Research published in the 1990s highlighted the potential harmful effects of UVA radiation, prompting the addition of UVA filters to sunscreen and the establishment of regulations requiring measurement of the UVA protection factor [4]. Studies conducted in the 2000s documented the harmful effects of near-infrared radiation on the skin and certain substances, mainly antioxidants, that were added to sunscreen to protect against this type of radiation, although to date there is no validated method to measure the efficacy of this form of protection [5]. Finally, the harmful effects of visible light (VL), especially blue light and long UVA (380–400 nm), have been demonstrated in recent years, and include hyperpigmentation and photoaging [6–9].

In addition to new filters and antioxidants to prevent cutaneous damage caused by sunlight, repair products, especially DNA repair products, have also been included in sunscreen formulas [10]. Together, these discoveries have led to notable changes in sunscreen formulas, improving their capacity to protect against cutaneous photodamage.

Finally, some filters appear to have deleterious environmental effects, especially in marine environments, and some have been found in the plasma and urine of human users, although no serious effects on human health have been demonstrated to date [11].

This article reviews the most recent developments in new filters and innovative substances that neutralize sun damage and also repair DNA. We discuss molecules that are currently being investigated and may be marketed in the near future. Furthermore, we describe advances in the development of vehicles that make sunscreens more comfortable to use and increase their adherence.

2 Past, present, and future tasks in the development of sunscreen filters

It is almost 100 years since the first topical formulations for photoprotection were introduced into the market for primary prevention purposes. However, the earliest records of the use of substances, mainly extracted from plants such as rice, jasmine, and lupine, date back to almost 4000 BC in Ancient Egypt, [12] and the use of minerals such as zinc oxide is described in Indian writings from around 500 BC. [13] However, it was not until the inter-war period in the twentieth century, when sun and exposure for both tanning and as a healthy habit became widespread, that products to prevent skin damage in the short term, became available. Almost in parallel, pioneers in the fields of chemistry and pharmacy searched for molecules with the ability to absorb wavelengths that caused sunburn, which had already been linked to skin exposure to UVB radiation by Haussner and Vahle in 1922 [14]. These same authors developed the first commercial formulations based on the UVB-absorbing filters benzyl salicylate and benzyl cinnamate. Other filters developed at the time that enjoyed great commercial success include PABA, which was developed by Eugene Schueller's team and has survived to the present day, and red petrolatum, which was developed by Benjamin Green during the second World War and marketed as Coppertone: both were formulas designed to curb skin erythema and promote healthy skin tanning [12]. It was not until 1969 that the first negative effects of UVA (premature skin aging) were described, and formulas containing organic UVA-absorbing molecules such as butyl methoxydibenzoyl methane, patented in 1973 by Roche and approved in Europe in 1978 and by FDA finally in 1996, respectively, were subsequently developed [15, 16]. Since then, commercial photoprotection formulations have included combinations of different filter families.

The ideal sunscreen should contain a combination of filters against UVB (e.g., PABA derivatives or cinnamates), filters with UVA2 absorption (e.g., avobenzone) as well as filters that protect against UVA1 wavelengths, which have only recently started to be added to sunscreens in Europe [17–19]. Octocrylene is commonly used for its double properties, as an UVB-absorbing filter and second by its stabilization properties for the other filters contained in the formula as octinoxate and avobenzone, which are widely used but has poor photostability [20, 21]. Other groups of filters are approved in EU for two main reasons: filter size, which minimizes the risk of cutaneous penetration; and a low level of associated photosensitivity. These include molecules with maximum UVB absorption such as ethylexyl triazone, isoamyl methoxycinnamate, and 4 methyl benzylidene camphor, UVA absorption such as Mexoryl SX, and broad-band filters such as dometrizole trisiloxane (Mexoryl XL), bemotrizinol (Tinosorb S), and bisoctrizole (Tinosorb M) [22].

The combination of UVB and UVA filters has become commonplace over the last 30 years. The objective of these so-called "broad spectrum" sunscreens is actually to protect the skin against almost the entire spectrum of solar UV radiation to different skin biological effects as erythema or persistent pigment darkening. Solar protection factor, or the protection level of a sunscreen based on human UV erythemal action spectrum [23] was defined in 1974 by Franz Greiter, the creator of the Piz Buin company. UVA PF was later developed to assess psoralen-induced phototoxicity, and finally it was finally stablished by Chardon in 1997 for using persistent pigment darkening as an assessment method. [24, 25] The criterion for broad-spectrum formulations was established finally by the European Commission in 2006 in which the UVA protection factor (the potential to prevent persistent pigment darkening) must be at least 1/3 of the SPF (solar protection factor) [26]. In the US, the 2019 proposed rule is changing requirements for designation of broad-spectrum coverage, "A UVA I/UV ratio of 0.7 or higher, indicating that the product provides a minimum measure of UVA I radiation absorbance relative to total UV radiation (i.e., UVB + UVA) absorbance, in addition satisfying to the 370 nm critical wavelength requirement". Requiring a UVA I/UV ratio of 0.7 or higher for broad-spectrum products would mean that these products would have a more uniform amount of radiation protection across the UVA I, UVA II, and UVB ranges. [27]

3 New organic filters for new wavelengths photoprotection

It has taken more than 10 years to introduce new organic molecules to the list of approved sunscreens in the EU. These new filters have been designed to complement the previous combination of UVB and UVA filters by providing enhanced UVA photoprotection, specifically by protecting against wavelengths around and above 400 nm. Their development is the result of recent research into the effects of high energy visible radiation (HEVR), which causes skin hyperpigmentation as well as oxidative stress, immunomodulation, altered hydration levels, and even damage to cellular DNA. [6, 28–32] HEVR corresponds to wavelengths above 380 nm, including blue light wavelengths up to 450 nm. In 2021, a UVA1-type filter called methoxypropylamino cyclohexenylidene ethoxyethylcyanoacetate (MCE) appeared on the list of EU-approved sunscreens. This filter is designed to cover the lack of efficacy of classical sunscreens above 370 nm. The molecule has an absorption maximum at 385 nm with a molar extinction coefficient of 63.052 (L mol-1 cm-1), and a critical wavelength in the 290–400 nm range of 389 nm. It has good solubility in 50% water/ethanol and is highly thermostable in different media and photostable even in the presence of high O_2 concentrations [19]. Its efficacy has been demonstrated in combination with other filters both in vitro and in vivo: [19, 33] it can protect against damage caused by UVA1 radiation with a maximum of 380 nm in fibroblasts, inhibiting the production of metalloproteinases and the production of IL-6 and IL-8; and it reduces hyperpigmentation, immunosuppression, and photoaging in humans [19].

The sun filter most recently added (2021) to the EU-approved list is phenylene bis-diphenyltriazine (TriAsorB), a low-molecular-weight molecule (540.6 gmol-1) which, owing to its insolubility in hydrophilic and lipophilic media, gives rise to aggregates in dispersion above 100 nm, meaning that its penetration of the skin is very low. It has a high molar extinction coefficient of 329 nm (52.492 L mol-1 cm-1), and although capable of absorbing from UV to infrared radiation (IR) has maximum absorption around 370 nm, a critical wavelength around 390 nm, and its absorption spectrum reaches a limit of significant efficiency up to 450 nm [34]. Its efficacy against high energy visible radiation (HEVR) has been demonstrated by its inhibition of the formation of 8-deoxyguanosine in reconstructed skin after exposure to 80 J.cm-2 of blue light (max, 412 nm) [35]. It also shows efficacy against oxidative DNA damage and the generation of dark cyclobutane pyrimidine dimers (CPDs) when combined in a commercial formulation with other classical UVB and UVB/UVA sunscreens [35].

New organic sunscreen candidates for inclusion on approved sunscreen lists are still in development, and seek to provide new safe, stable, and even environmentally friendly molecules. Francois-Newton et al. [36] described a new sunscreen with a potential protective effect against blue light (TFD Blu Voile sunscreen) containing zinc oxide, titanium dioxide, and a trimethylol hexyllactone crosspolymer that acts as a blue light blocking ingredient itself. In vivo, this formulation reduces immediate and persistent hyperpigmentation induced by 415 nm blue light.

Methylene bis-benzotriazolyl tetramethylbutylphenol (Parsol® Max, DSM) [37] is a broad-spectrum photostable filter that has also been shown to provide protection in the blue light range.

Bis-(diethylaminohydroxybenzoyl)piperazine (BDBP) is another modern organic candidate blue light filter with an absorption band of 350–425 nm, and combined with classical filters has been shown to improve in vivo photoprotection of human volunteers against pigmentation [38].

4 Inorganic filters

Inorganic filters appear much less frequently than organic filters on the approved sunscreen lists of various international institutions, and until now have been based mainly on two elements used cosmetically since ancient times: titanium dioxide and zinc oxide [39]. Due to their low cosmeticity, their use had been relegated to a secondary role, i.e., to accompany other combinations of organic filters or for use alone for infant photoprotection or in patients with photosensitivity to organic filters. However, these mineral filters have recently got an important new status for their incorporation alone or combined with other organic filters. FDA (in its 2019 document) [27] recognized 22 UVF compounds in use in sunscreen products and classified them as Generally Recognized As Safe and Effective (GRASE) (Category I), those that are Non-GRASE (Category II), and those that require further evaluation (Category III). Titanium dioxide and zinc oxide were designated as GRASE-Category I (Federal Register 84FR6204-6275, 2019-03019). Regarding the ecological aspects of sunscreens, in spite of not really safe UV filter for the nature at all, both TiO2 and ZnO in the non-nano forms (over 100 nm) are mainly recommended and they are extensively included as part of "ocean safe" and "reef safe" sunscreens. [40–42]. Since the 1990s, they have been used in nano form and recent EU regulations [43] establish a minimum particle size (nano forms) and prohibit their use in aerosols. Their use is widespread and they will undoubtedly constitute fundamental components of future sunscreen formulations. Their broad absorption spectrum is another feature that makes mineral filters candidates for extensive use: their combination with classical organic filters can achieve an absorption spectrum that includes both visible and UV light. While the nano and micro forms of titanium dioxide offer reduced photoprotection in the UVA1 and visible light spectra, nano forms of zinc oxide are not affected in this way [44].

As mentioned above, photoprotection against light in the visible spectrum is a current goal of new sunscreens, as a large sector of the population is particularly affected by photoaging and unaesthetic hyperpigmentation, and these issues are exacerbated by HEVR, which has led to an increase in the use of tinted sunscreens [45]. These formulations consist of a blend of iron oxides (Fe_2O_3) and TiO_2, molecules that function as VL and UV filters, and different skin colors are mimicked using a combination of different oxidation states of iron oxide, which range from yellow to red or even very dark brown. Currently, tinted SPF 50 + photoprotective formulations can achieve sun protection factors for visible light above 10, based on their wavelength absorption potential against hyperpigmentation in the visible range [46]. There are very few reports of skin photosensitivity caused by iron oxide, [47] and tinted formulations have become popular not only as outdoor sunscreens but also as indoor sunscreens to protect against blue light from different electronic devices and artificial light. However, the real effect of these artificial light sources on the skin is minimal compared to sun exposure, [48] and photoprotection is only justified in cases of indoor exposure combined with sun exposure.

5 New technologies applied to sunscreens to improve efficacy and safety

Organic and inorganic filters are used not only to protect against UV and visible light, but also the effects of IR radiation. The photoaging effect of near-infrared radiation (NIR) on skin has been known for years. [49, 50]Tinted sunscreens are very effective against UV and visible radiation: their absorption spectrum reaches wavelengths up to 1300 nm, decreasing by 40–50% the average transmittance of radiation in the 760–1300 nm range (in measurements carried out by our research group following ISO protocols for measuring the UVA protection factor in vitro) [51]. However, growing alarm around the effects of climate change and increases in mean summer temperatures has increased interest in photoprotection against wavelengths with higher calorific value (e.g., IRB). Thus, new filters called cooling filters have been developed [52]. These consist of hydrogels with a three-dimensional network structure and high water content, containing hyaluronic acid and tannic acid with a broad-UV spectrum protection (280–360 nm). Adding polyols such as xylitol (2.0 wt%) decreases skin temperature by 6.6 ℃ after 5 min, an effect maintained for a long duration. In addition, these hydrogels have a high moisture content and show excellent adhesion to the skin, antioxidant activity, and a cooling effect.

One of the most important challenges in developing sunscreens is human safety, avoiding penetration through the skin. Thus, the development of appropriate vehicles has major implications for stability, as well as reducing skin permeability and ensuring homogeneous UV filter distribution to ensure optimal performance. The use of polysaccharide structures to form hydrogels increases filter safety by preventing crossing of the skin barrier. Another approach is the use of nanotechnology to generate hydrogels derived from benzofuroazepine to envelop molecules [53]. The use of cellulose nanocrystals has been shown to increase the efficacy of filters by minimizing their penetration [54]. Alginate microparticles are effective in increasing the photostability of 2-ethylhexyl 4-methoxycinnamate [55]. Cyclodextrins are polysaccharides used as inclusion complexes to increase sunscreen efficiency and safety [56]. These encapsulation techniques are providing novel, safe, and more eco-friendly sunscreens, and can be added to the encapsulation techniques used in many formulations that already are on the market, such as methacrylate polymers (PMMA) [57, 58]. Another technique used to prevent filter penetration is the creation of new crystalline structures through the melting and emulsification of filter agglomerates [59]. Technologies based on semi-crystalline polymers, such as the combination of alkyl acrylate/hydroxyethylacrylate copolymer (netlock technology), can stabilize filters in the formulation, ensuring prolonged permanence on the skin [60].

6 Natural sources of sunscreens against solar UV and visible light

"Green" approaches to the development topical photoprotectants have produced promising findings in recent years, with researchers and cosmetic developers recognizing the potential of photoprotective products based on natural products. No natural organic sunscreens are currently included in the lists of approved sunscreen filters of the different international regulatory agencies. Most of these substances are considered additives, and act as boosters in the formula, although several such compounds are potential sunscreen candidates owing to their high photoprotective efficacy [61]. Mycosporine-like amino acids (MAAs) are currently considered promising sunscreen candidates, given the large body of data generated over the last 20 years demonstrating a high degree of photoprotective efficacy [62]. MAAs are a family of low-molecular-weight molecules isolated from fungi and a variety of marine organisms, and are soluble in aqueous media, showing varying degrees of hydrophobicity. There are different types of MAAs with absorption maxima ranging from 310 nm (MAA-glycine) to 362 nm (usurijene). They have a high molar extinction coefficient, very similar to that of octinoxate and avobenzone, are thermally stable under different conditions, and are photostable at very high UV radiation doses. MAAs cause neither phototoxic nor photoallergy reactions. In addition, some have high antioxidant activity [63, 64], and therefore have been incorporated into various photoprotective formulas on the market as extracts or in combination with classic filters [65]. The main limitation to the use of natural MAAs is the amount of purified substance necessary: several grams are required in each formulation. To overcome this limitation, analogs have been synthesized in the laboratory. Following a simple process, Losantos et al. [65] developed a group of MAAs similar to natural MAAs, with different maximum wavelengths, very high molar extinction coefficients, and very high photostability. Genetic engineering approaches have also been applied to shinorin, which has been incorporated into the genome of the cyanobacterium *Fischerela* sp. for mass production [66].

Scytonemin, a very abundant pigment in Cyanobacteria, is a dimeric compound composed of indolic and phenolic subunits linked with an olefinic carbon atom, and has a maximum absorption spectrum of 386 nm. It is currently being studied for potential use as a UV filter to protect against very long UVA wavelengths and HEVR [67]. Scytonemin-3a-imine, derived from *Scytonema hoffmani* after exposure to high doses of solar radiation, shows absorption maxima at 366 and 437 nm [68]. Currently, its biotechnological production for commercial use is booming. [69].

Flavonoids are a second group of polyphenol molecules that are promising natural sunscreen candidates. Their molecular structure features aromatic rings and double bonds, conferring absorption across the entire UV spectrum. Among the ideal candidates, quercetin and especially rutin offer both high antioxidant activity and, crucially, high UV absorption potential, reaching SPFs above 35, [70] although total polyphenols extracted from some leaves and plants can achieve SPF values above 20 [71]. The traditional herbal formulation, Ubtan, based on different plant seeds (mainly flavonoids), can reach SPF values above 30 [72].

Lignin, the most abundant flavonoid in nature, is another candidate green sunscreen owing to its high UV absorption capacity (maximum absorption, 283 nm) and its antioxidant activity and biocompatibility. [73]. The low solubility and dark color of lignin are the main factors limiting its cosmetic use [74] . However, this limitation has been resolved by self-assembly of the native polymer into highly ordered lignin nanoparticles (LNPs) [75] and the development of a method to prevent darkening of lignin during the process of delignification for use in sunscreen [76].

Silymarin, a polyphenol obtained from the milk thistle plant *Silybum marianum,* is composed of different flavonoids such as silybin, silydianin, and silychristin. This molecule is well known for its antioxidant activity, and has been shown to absorb UVR, with a SPF up to 9 when formulated at 10%, [77] increasing further when combined with titanium dioxide and zinc oxides [78]. Again, its transformation into nanoparticles, which increase its solubility, makes it a strong candidate as a UV blocker [79].

One of the natural substances with potential as a booster, for both oral and topical applications, is the extract of the fern *Polypodium leucotomos*, which is rich in non-flavonoid catecholic compounds (benzoates and cinnamates such as caffeic acid and its derivative ferulic acid). This phenolic extract has been extensively studied for multiple properties that protect the skin against damage caused by UV and visible solar radiation, mainly due to its high antioxidant activity [80, 81]. It also protects against immunosuppression and hyperpigmentation caused by HEVR [82].

Finally, other natural products include fungal or bacterial melanins, which are potential biocompatible broad-spectrum sunscreens with high antioxidant activity. The addition of melanin derived from *Amorphotheca resinae* (5%) to sunscreen was shown to increase the SPF from 1 to 2.5, resulting in a critical wavelength of 388 nm and a UVA:UVB ratio of more than 0.81. Moreover, this compound showed antioxidant activity similar to that of ascorbic acid but greater than that of reduced glutathione [83]. Bacterial melanins such as

Table 1 Summary of innovations on sunscreens

- Organic filters
  - Methoxypropylamino Cyclohexenylidene Ethoxyethylcyanoacetate (Meroxyl 400)
  - Phenylene Bis-Diphenyltriazine (TriAsorB)
  - TFD Blu Voile ® (zinc oxide, titanium dioxide and a trimethylol hexylactone crosspolymer)
  - Methylene bis-benzotriazolyl tetramethylbutylphenol (Parsol® Max,DSM)
  - Diethylaminohydroxybenzoyl)piperazine (BDBP)
- Inorganic filters
  - Nanoforms of TiO2 and zinc oxide
  - Iron oxide
- Natural photoprotectors
  - Mycosporine-like aminoacids
  - Scitonemin
  - Flavonoids: quercetin, rutin, Ubtan, lignin, silymarin, Polypodiun leucotomus
  - Fungal and bacteria melanins
- New technologies to increase effacy and safety of sunscreens
  - Protection against calorific radiation (long infrared radiation)
    - Hydrogels with a three-dimensional network structure of hyaluronic acid and tannic acid withpolyols such as xylitol
  - Prevention to penetration in the skin
    - Polysaccharide structures to form hydrogels
    - Hydrogel to envelop molecules
    - Cellulose nanocrystals to envelope UV filters
    - Alginate microparticles as UV filter carriers
    - Cyclodextrin
    - Methacrylate polymers (PMMA)

DHICA from *Pseudomonas* sp. contains 5,6-dihydroxy indole 2-carboxyc acid (DHICA), which possesses typical eumelanin properties, exerting a photoprotective effect against UVB radiation in mouse fibroblast cells [84]. In their in vitro study, Kurian et al. demonstrated an increase in the SPF of a commercially available sunscreen following addition of bacterial melanin [85].

7 Conclusion

The sunscreen field is constantly evolving, with the development of novel compounds and formulations to increase both safety and efficacy. The last year alone has seen many innovations, with many promising molecules still under investigation (summarized in Table 1). New filters that provide balanced photoprotection against all forms of harmful solar radiations are already included in available sunscreens, improving their protection against hyperpigmentation, immunosuppression, and photoaging, while new vehicles provide greater protection against filter penetration of the skin. Finally, natural products, mainly derived from marine and terrestrial plants, hold great promise for future methods of skin damage prevention, and have produced a range of promising photoprotective molecules that can be used either alone or combined with sunscreens of mineral origin.

Author contributions JA, TG, and YG: contributed to the preparation of manuscript and critically modified. JA and TG: contributed in the preparation of figures. All authors contributed to the article and approved the submitted version.

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Declarations

Conflict of interest JA has served as advisor and speaker for La Roche-Posay, Cantabrialabs, Pierre Fabre, L'Oréal Paris and Rilastil. YG JA has served as advisor and speaker for, ISDIN, La Roche-Posay, Cantabria labs, Pierre Fabre, and Rilastil.

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