



## History and current state of Photoprotective :An Overview

Pragati Baghel\* and Neeraj Sharma

1. Research Scholar, Bhagwant University, Sikar Road, Ajmer, Rajasthan, India.

Email id: [pragatipharma20@gmail.com](mailto:pragatipharma20@gmail.com)

2. Principal, Bhagwant University, Sikar Road, Ajmer, Rajasthan, India.

Email id: [neerajsharma236@gmail.com](mailto:neerajsharma236@gmail.com)

\*Corresponding Author: Pragati Baghel

[pragatipharma20@gmail.com](mailto:pragatipharma20@gmail.com)

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### Abstract

Physicians that work in the field of skin care promote photoprotection as the most effective preventative health strategy. Although it is ideal to avoid the sun as much as possible, many people's jobs and lifestyles require them to do so. Acute impacts of sunlight on the skin include erythema and pigmentation, as well as long-term consequences including photoaging and photocarcinogenesis. The goal of photoprotection is to limit exposure to the sun and halt the progression of actinic damage. Topical, oral, and mechanical photoprotection, as well as photoprotection education, are all types of photoprotection. It is suggested that initiatives aimed at children, adolescents, adults, and outside employees be implemented. Advertising in the media is extremely significant and beneficial. Physical and chemical sunscreens are two types of topic sunscreens. Physical filters are inorganic, mineral-based filters that improve UV (ultraviolet) radiation reflection. By absorbing UV radiation, chemical or organic filters alter the molecular structure. All people so over age of six months are advised to wear sunscreen, and it is best to use broad-spectrum products with an SPF of at least 30. Combining oral photoprotection with mechanical sun protection techniques including clothes, hats, sunglasses, window covers, and shadows appears to provide significant benefit.

**Keywords:** Photoprotection; UV radiation; SPF; Photocarcinogenesis; Photoaging; Pigmentation.

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### Introduction

In order to defend themselves from the molecular harm that sunlight causes, organisms employ a biological mechanism called photoprotection. Plants and other oxygenic phototrophs have evolved a number of photoprotective systems to defend themselves against

photoinhibition and oxidative stress brought on by excessive or variable light. Animals and humans have created photoprotective systems to guard against DNA deterioration, skin damage from UV rays, and the aftereffects of oxidative stress. The necessity to protect oneself from the sun has long been known. Olive oil was employed as a sort of sunscreen by the ancient Greeks, but it was ineffective. In 1944, a pharmacist by the name of Benjamin Greene employed a sticky, crimson material known as red vet pet to protect soldiers from the sun's harmful rays (red veterinary petrolatum).By physically obstructing the sun's rays, it achieved this. Even while it wasn't as effective as contemporary sunscreens, it was a start. Sunscreens have advanced significantly since then [1, 2].

### **Ultraviolet Radiation (UVR)**

The strongest portion of the sun's spectrum that reaches Earth is UVR (400–100 nm). UV-C (280-100 nm) and UV-A (400-315 nm) are three of the different ultraviolet light wavelengths [2, 3, 4]. The stratospheric ozone layer absorbs nearly all UV-C and a sizable portion of UV-B rays. 5 percent of UV-B and 95% of UV-A make up the entire UVR that reaches the Earth's surface. The biosphere is affected by these energy components [5, 6]. Studies on how the human body reacts to UV radiation have revealed that there are many health advantages, including the production of vitamin D, which is crucial for the prevention of osteoporosis and skeletal disease [7], as well as the lessening of the illnesses of mental health conditions like seasonal affective disorders and schizophrenia [8]. But excess UVR exposure has been linked to a number of detrimental consequences, including DNA mutation, skin cancer, cataract formation, and skin ageing, according to previous research and reviews [2, 10, 11]. So it's crucial to strike a balance between UVR exposure and defense against UV-A and UV-B overexposure.

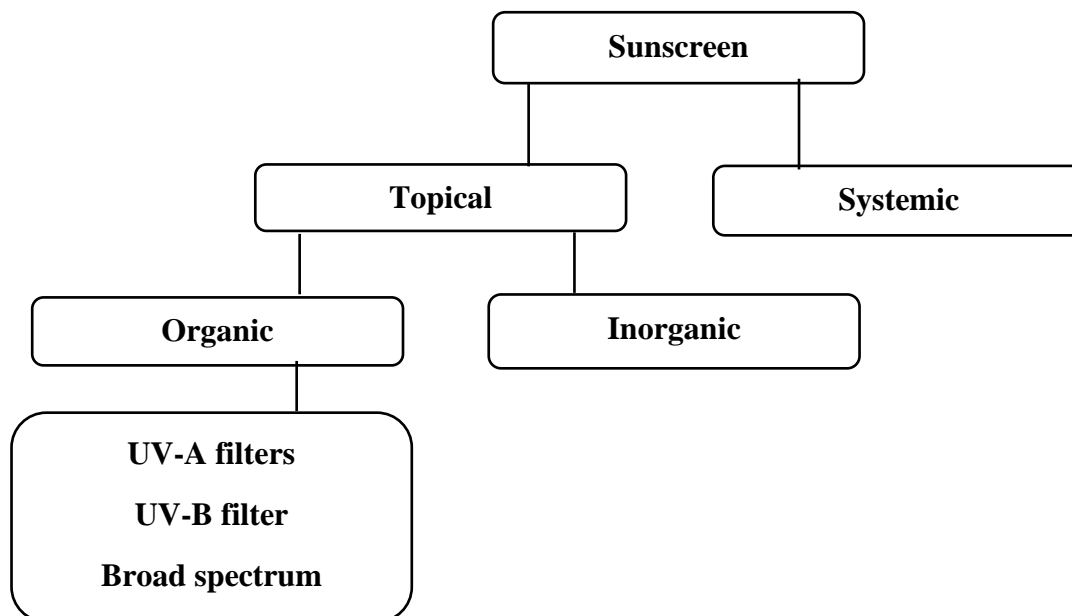
Skin pigmentation, which is made up of a class of UV-absorbing molecules called melanin, is one of many natural defense mechanisms the human body has to mitigate the consequences of UVR exposure. Despite the fact that melanin absorbs UVR before it damages DNA in exposed skin, it is insufficient to protect skin when UVR exposure is high [11]. Additionally, tanning causes an increase in melanin synthesis, which is a gradual process that can take three to five days before it provides any discernible photoprotection. Protecting against UVR and maintaining antioxidant homoeostasis are two methods for preventing or minimising photoaging. In order to uncover biological targets of UVR and the subsequent cascade of impaired cell functioning and tissue deterioration, recent research studied the

harmful consequences of UVR at the cellular and molecular levels. DNA damage has been reported to be brought on by UVA and UVB radiations, including mutations of important regulator genes. Despite endogenous DNA repair mechanisms, persistent DNA damage from prolonged UV exposure can result in photoaging and the development of skin cancer. Commercial UV filters that can instantly defend skin from photodamage are therefore essential [12].

### Sunscreens

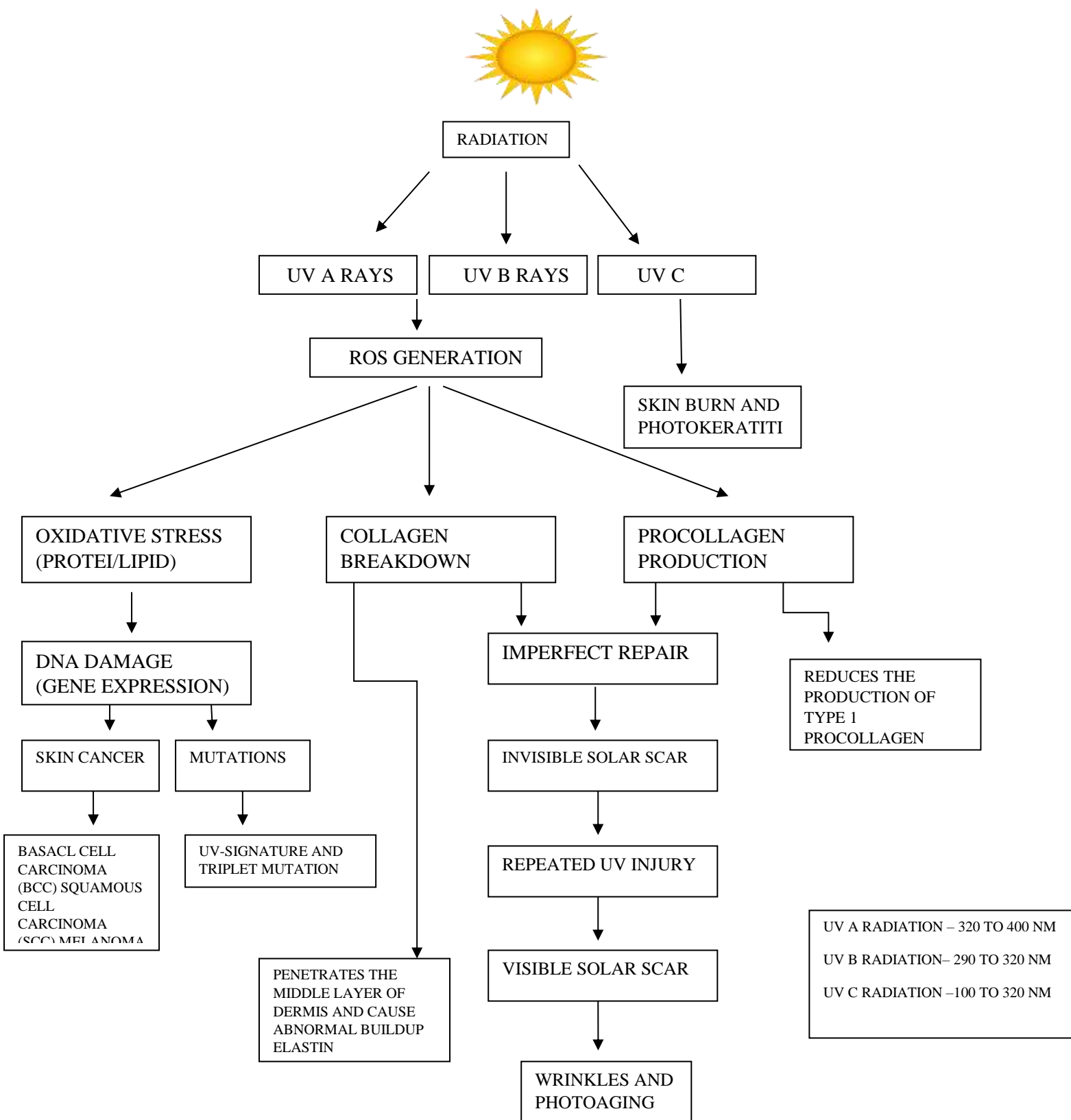
The visible light and infrared radiation that make up 98% of the solar irradiance are not protected by current sunscreen technologies (IR). Free radicals are produced in the skin as a result of interactions between photons in the visible and infrared regions and the skin. Surprisingly, visible light and an IR wavelength termed infrared A (IRA, 760-1440 nm) can reach the skin far deeper than UV rays. Therefore, even those wearing UV protection will experience the negative effects of visual and infrared radiation, which produce reactive oxidants and can overwhelm the skin's redox defenses. Through opsins, melanocytes in the skin detect UVA and blue light and begin the process of melanogenesis [13].

Since the sunscreens are categorized as either chemical absorbers or physical blockers based on how they work. Aromatic compounds with a carbonyl group are often the main component of chemical sunscreens. The molecule's basic structure allows it to absorb high-energy UV radiation and release the energy as lower-energy rays, protecting the skin from potentially dangerous UV rays. As a consequence, the majority of the ingredients (apart from avobenzene) do not significantly alter chemically when exposed to UV radiation. As a result, skin-damaging ultraviolet light cannot reach the skin and these compounds can maintain their UV-absorbing qualities without photodegradation. UVR is reflected or scattered by physical blocks or non-chemical sunscreens. They're made up of inert minerals like titanium dioxide and zinc oxide [14].



**Figure 1: Types of Sunscreen**

Table 1 lists the most common substances that can be found in sunscreens. These substances block UVR light at a certain wavelength. The absorbance may be relatively effective for UVB alone or for UVB + UVA, depending on the molecular structural characteristics of each molecule. The various varieties of sunscreen are shown in Figure 1.



**Figure 2: Effect of ros generation by uv rays on skin**

**Table 1: Compounds used in Sunscreens**

S. No.	Compounds Absorbs UVA	Compounds Absorbs UVB
1.	Oxybenzone	PABA
2.	Sulisobenzene	p-Amyl dimethyl PABA (padimate A)
3.	Dioxybenzone	2-Ethoxyethyl-p-methoxycinnamate
4.	Methyl anthranilate	Digalloyltriolate
5.	Avobenzone	Ethyl 4-bishydroxypropyl aminobenzoate
6.	Terephatylidenedicamphor sulfonic acid	2-Ethoxyethyl 2-cyano-3,3-diphenylacrylate
7.	Bisethylhexyloxyphenolmethoxyphenyltriazene	2-Ethylhexyl p-methoxycinnamate

### Ultraviolet B Blockers

#### Para-aminobenzoic acid

One of the first chemical sunscreens to be made widely available on the market was this one. An alcoholic vehicle, clothing discoloration, and a variety of unpleasant reactions are among the issues that limit its use. Two ester derivatives, padimate O and octyl dimethyl PABA, have been linked to improved compatibility with several different cosmetic vehicles as well as a reduced risk of discoloration and unpleasant reactions. Padimate O is the best UV-B absorber available. Due to a decline in its usage and a rise in the demand for products with a higher SPF, several active ingredients have been combined to create a solitary product that offers the appropriate SPF, and sunscreens have been substituted with single PABA esters.

#### Cinnamates

Cinnamates have almost completely surpassed PABA compounds as the next most effective UV-B absorbers. The most commonly used sunscreen component is octinoxate, also known as octylmethoxycinnamate. Padimate O is more powerful than octinoxate.

### **Octyl salicylate**

Octisalate, also known as octyl salicylate, is a chemical that is added to sunscreens to provide UV-B protection. Since salicylates absorb UV-B light at a modest rate, additional UV filters are often employed in addition to them. It is necessary to use other salicylates at higher concentrations. All of them are really safe.

### **Octocrylene**

To get higher SPF formulations, octocrylene can be combined with additional UV absorbers. Octocrylene may increase the overall stability of sunscreen chemicals in a solution when mixed with other sunscreen compounds, such as avobenzone.

### **Phenyl benzimidazole sulfonic acid**

As most chemical sunscreen components are oils soluble in the oil phase of emulsion systems, many of these products have the appearance of being thick and greasy. The water-soluble component ensulizole, also known as phenyl benzimidazole sulfonic acid, is used in cosmetic moisturising products to make them feel lighter and less greasy. It is a selective UV-B filter that nearly entirely lets UV-A through.

### **Ultraviolet- A Blockers**

#### **Benzophenone**

Nevertheless of the fact that benzophenones normally absorb UV-B radiation, oxybenzone also does so. A versatile broad-spectrum absorber, oxybenzone may be employed in many different contexts.

#### **Anthranilate**

Poor UV-B filters, anthranilates absorb mostly in the UV-A2 wavelength region. In this range, anthranilates are both less effective and less often used than benzophenones.

#### **Avobenzone**

It provides exceptional UV-A protection throughout the majority of the UV-A spectrum, including UV-A1. Regarding its photostability and propensity to deteriorate other sunscreen components, this potentially major addition to sunscreen compositions for real broad-spectrum UV protection has raised concerns.

**Mexoryl SX or terephthalylidenedicamphor sulfonic acid**

It offers UVA protection between 320 and 340 nm, although it is water soluble and less water-resistant.

**Methoxy phenyl triazenebisethylhexyloxyphenol**

Avobenzone-containing sunscreens benefit from this broad-spectrum sunscreen filter, which improves photostability [1].

**MethoxypropylaminoCyclohexenylideneEthoxyethylcyanoacetate (MCE)**

MCE a novel UVA1 filter with a peak of absorption at 385 nm, was recently certified for use in sunscreen products by the Scientific Committee on Consumer Safety.

**Earlier Attempts at Sun Protection**

According to studies [15], lupine lightens the complexion, jasmine helps repair DNA, and rice bran absorbs UV radiation. The attention in UV filters to shield the skin from photodamage, however, was inspired by Ritter's discovery of UVR in 1801 and Widmark's experimental work in 1889, which showed that UVR produces erythema solare (sunburn). Towards the close of the nineteenth century, the notion of creating and utilising chemical-based UV filters to stop photodamage began gaining popularity. In 1935, Schueller created "Ambre Solaire," the first commercial sunscreen using the UV filter benzyl salicylate. Following then, a slew of new sunscreen chemicals [16, 17] were discovered. UV filters, both natural and artificial, have been explored in recent years in a challenge to address photoprotection.

Physical (inorganic) blockers and chemical (absorptive) absorbers are the two main kinds of UV active substances used in sunscreen formulas today (organic). Zinc oxide and titanium dioxide (TiO<sub>2</sub>) make up the bulk of UV-A/UV-B radiation blockers that are physical (ZnO). Before UV-A/UV-B radiation reaches the skin, it is absorbed by chemical substances including oxybenzone, avobenzone, homosalate, octocrylene, and many others [18].

**Existing Sunscreens Have Issues**

Even though there are several commercial sunscreen solutions available for photoprotection, further research is required to address their drawbacks. Only a few downsides include the



insufficient supply of certified UV-A filters, photoinstability, environmental impacts, and dermatological effects [19, 20, 21].

Sunscreens must be photostable in order to protect against the harmful effects of UVR exposure (i.e., do not degrade after absorption of UVR). According to Kockler et al. [22], a number of commercial sunscreens become photounstable in the UV-A region after being exposed to the sun and UV radiation. Gonzalez et al. [23] found that certain widely marketed broadband sunscreen formulations are photounstable in a similar experiment. To provide a workable solution for the maximum level of photoprotection, industry and researchers are still working to produce photostable sunscreen formulations.

Because UV-B light is more intense than UV-A radiation, the development of UV-B filters has attracted a lot of attention over the years. Although UV-A radiation has a lower intensity, it is more common on Earth's surface and penetrates the skin considerably deeper than UV-B radiation, reaching the dermis [24, 25]. The effects of UV-A radiation on DNA mutation, acquired immune suppression, and reactive oxygen species (ROS) have all been linked to cancer development and skin ageing [26, 27]. Since the skin effects of UV-A radiation were recognised, the sunscreen business and regulatory organisations have suggested a need for a broad-spectrum sunscreen (i.e., sunscreens that span across both UV-B and UV-A). However, only a small number of UV-A filters have received FDA/EU approval, and the most widely used one (avobenzene) is not especially photostable [28, 29, 30, 31]. Therefore, more research is required to find efficient UV-A filters.

Several chemical UV filters have been advocated for to be banned throughout the years owing to their negative effects on the environment. The developmental and reproductive toxicity of certain commonly used organic UV filters (oxybenzone, avobenzene, and octocrylene) on fish and corals has been the subject of several research [31]. Organic UV filters have collected in soil, sediments, and aquatic biota such as clams, urchins, dolphins, and fish [32, 33]. Environmentally friendly sunscreens must be created in order to preserve both human photoprotection from UVR and a healthy ecosystem.

### **Nature-Inspired Sunscreens**

Research on UV filters that are inspired by nature has grown in popularity recently, with an emphasis on UV filters that are inspired by plants and microbes. Therefore, the objective of

this analysis is to examine the results and potential applications of UV filters with natural inspiration in order to create sunscreens that are more efficient and secure.

### **Plant Ultraviolet Filters**

It has been found that plant species have a disease load from UVR that is comparable to that reported in people. Although some UVR exposure is essential for photosynthesis in plants and hence necessary, too much UVR can be damaging [48]. Just as it does for humans, moderate UVR exposure has significant effects on plants. UV-B radiation in particular acts as a signal transducer for a number of mechanisms that initiate or control life-supporting gene responses in plants [34]. It has also been shown that UV-B radiation increases the expression of genes involved in UV defence and DNA repair, indicating that it actively promotes life under the sun [35, 36]. On the other hand, excessive UVR exposure can have a negative impact on growth as well as transpiration, photosynthesis, and other processes. It is possible for reactive oxygen species to interact with DNA nucleotides and harm DNA either directly through photodamage or indirectly through their production [35, 36]. There have also been other effects, including decreased pollen production in some plants and photomorphogenesis in plant leaves, which thickens the epidermal and makes a plant more susceptible to disease [35, 36]. On the other hand, inadequate UVR (UV-B) exposure may make a plant more susceptible to infections and diminish the UV-B signalling pathway, which promotes a variety of photophysical activities [35, 36].

### **Microbial Ultraviolet Filters**

Microorganisms, like plants and people, must protect themselves from the damaging DNA damage induced by UVR [37, 38]. Microorganisms like cyanobacteria, fungi, and micro- and macroalgae utilise a family of secondary metabolites called mycosporines and mycosporine-like amino acids to counteract this problem [39, 40]. Mycosporines are derived from cyclohexenone units, and various amino compounds are linked to the carbon three position (relative to the carbonyl). Due to their interchangeability in the literature, mycosporines and mycosporine-like amino acids are both referred to as MAAs in this introduction [41].

Although there is much debate over MAAs and their place in biological processes, they are thought to serve a variety of purposes, including osmotic control, oxidative stress defence, thermal stress protection, and acting as intracellular nitrogen stores [42]. Furthermore, MAAs offer their producing organisms photoprotection against damaging UVR [41, 43]. MAAs have

been shown to have photoprotective characteristics because of their effective electromagnetic spectrum absorption in the UV region and a link between MAA concentration and UVR exposure [43].

### **Side effects of Sunscreens**

Contact dermatitis and photosensitivity reactions have been linked to the use of sunscreens that include oxybenzone, cinnamates, and aminobenzoic acid and its esters (PABA) [44, 45]. These people should refrain from using sunscreen that includes aminobenzoic acid or one of its derivatives since they have chemical similarities with other medications that trigger photosensitivity responses, such as menthyl anthranilate, aminobenzoate, and padimate A or O. (aminobenzoate, menthyl anthranilate, or padimate A or O). For these individuals, oxybenzone- or cinoxate-containing sunscreen should be suggested [46]. Fragrances, lanolin, alcohol, and preservatives, among other substances, can irritate or sensitise the skin and eyes.

Several sunscreens that include padimate-O contain NPABAO, a brand-new nitrosamine [47]. It is unknown if sunscreens include nitrosamines at levels high enough to cause worry [47], despite the fact that they can cause cancer.

### **Controversies concerning sunscreens**

Children below six months of age might not have fully formed biological systems that can metabolise and excrete medications acquired via the skin, and their skin might absorb chemicals differently than that of adults. Therefore, it is advised to keep infants under the age of six months away from sunscreens that include aminobenzoic acid and to never apply sunscreen on infants under the age of six months.

Sunscreens decrease sunburn when used generously and often. Although there is inadequate data on humans to support a cancer-preventive benefit against basal cell carcinoma and cutaneous malignant melanoma, sunscreens also offer protection from other forms of harm [48].

Free radicals can harm cellular DNA when PABA, oxybenzone, and padimate O interact with the skin [49, 50, 51]. PABA has been shown to be mutagenic in certain studies, while it has also been reported to be neither mutagenic nor photomutagenic in others [52]. Despite the fact

that vitamin D levels have not been affected by several clinical studies, it has been hypothesised that frequent use of sunscreens may hinder vitamin D synthesis [53].

### **Sunscreen Application**

The perfect sunscreen should be efficient against UVA and UVB rays, well-tolerated, aesthetically pleasant, non-toxic, photostable, water-resistant, and reasonably priced.

Regrettably, such sunscreen is not yet available. To give the sunscreen time to penetrate the skin and form a protective barrier, apply it 20 to 30 minutes before going outside in the sun. PABA and therapies containing PABA-like substances may need to be administered up to two hours before exposure to the sun to have the best impact [53]. Contrary to popular belief, which maintains that sunscreen has to be reapplied every two to three hours, research has demonstrated that the best protection is provided by applying sunscreen 15 to 30 minutes before contact with the sun and reapplying 15 to 30 minutes afterwards. It is only necessary to reapply after engaging in activities like swimming, perspiring, or rubbing [1].

The majority of people do not use enough sunscreen to provide proper protection. Studies show that most people only apply 20 to 50 percent of the recommended quantity of sunscreen. A 1.73 m<sup>2</sup> adult need around 35 ml of sunscreen on average. The teaspoon recommendation for applying sunscreen is as follows: To each arm, face, and neck, apply a little more than a 12 teaspoon (or about 3ml). Apply a little more than a teaspoon (6ml) to each leg, chest, and back [1].

Better sun protection is provided by applying sunscreen in a suitable amount (2 mg/cm<sup>2</sup>) as opposed to using sunscreen with a higher SPF rating.

Patients should use broad-spectrum sunscreens with an SPF of 30 or higher to effectively prevent UVB and UVA radiation. A sunscreen with an SPF of 15 blocks approximately 94% of UVB radiation. An SPF of 30 in sunscreen blocks 97 percent of UV radiation. SPF is only effective against UVB sunlight. In terms of UVA protection, chemical sunscreens offer around 10% of the UVB rating [54].

UVB and UVA blockers include natural pigments similar titanium dioxide and zinc oxide. Certain compounds can now be added to sunscreen products to improve their ability to block

UVA rays. Avobenzone and Mexoryl SX are two examples of such compounds. Without sunscreen, foundation makeup products with pigment content may only provide an SPF of 4 or less. Most sunscreen-containing cosmetics, on the other hand, have SPF ratings ranging from 15 to 30.

## Conclusions

The best form of photoprotection is exposure avoidance, which includes avoiding midday sun, wearing protective clothes and eyewear, finding shade, and applying sunscreens as directed. Photoprotection is a crucial preventative health precaution since UVR exposure is a major contributor to the majority of skin cancers. The usage of photoprotective measures is still limited and sporadic in spite of this. Instead of a lack of effectiveness of current procedures or goods, current restrictions are caused by adherence to usage and misunderstandings or difficulties that encourage riskier behaviours.

Despite certain populations being more sensitive, everyone should apply sunscreen daily. It is envisaged that better usage would arise from adjusting guidance to specific instances and reducing compliance restrictions. Widespread cultural alterations appear to be in their early phases, notwithstanding certain apparent advances in understanding that have not yet been matched by the associated behaviours. To prevent skin ageing, persistent dermatoses, and, most importantly, skin cancer, initiatives to normalise sun-safe behaviour are necessary. The protection of vulnerable groups, as well as the empowerment and education of their patient populations, may be significantly aided by medical professionals. There are innumerable instances of governmental and educational initiatives that have been effective.

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