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Past and Present in Photoprotectives: An Overview

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Abstract: ***Physicians working in the field of skin care promote photoprotection as the most effective preventive health strategy. Although it is ideal to avoid the sun as much as possible, many people's jobs and lifestyles necessitate exposure to it. 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 recommended that initiatives targeting children, adolescents, adults, and external employees be implemented. Advertising in the media is highly significant and beneficial. Physical and chemical sunscreens are two types of topical 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 of the material. All individuals over the 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, such as clothing, hats, sunglasses, window covers, and shade, appears to provide a significant benefit.***

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

I. INTRODUCTION

To defend themselves against the molecular harm caused by sunlight, organisms employ a biological mechanism known as photoprotection. Plants and other oxygenic phototrophs have evolved various photoprotective systems to defend themselves against photoinhibition and oxidative stress induced by excessive or variable light. Animals and humans have evolved photoprotective systems to protect against DNA deterioration, skin damage from UV rays, and the effects of oxidative stress. The necessity of protecting oneself from the sun has long been recognised. The ancient Greeks used olive oil as a form of sunscreen, but it proved ineffective. In 1944, a pharmacist named 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].

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A. Ultraviolet Radiation (UVR)

The most substantial portion of the sun's spectrum that reaches Earth is UVR (400–100 nm). UV-C (280-100 nm) and UV-A (315-400 nm) are two distinct ultraviolet light wavelengths [2, 3, 4]. The stratospheric ozone layer absorbs nearly all UV-C and a sizable portion of UV-B rays. Five per cent 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 illnesses related to mental health conditions like seasonal affective disorders and schizophrenia [8]. But excess UVR exposure has been linked to several detrimental consequences, including DNA mutation, skin cancer, cataract formation, and skin ageing, according to previous research and reviews [9, 10, 11]. Therefore, it's crucial to strike a balance between UVR exposure and defence against overexposure to UV-A and UV-B.

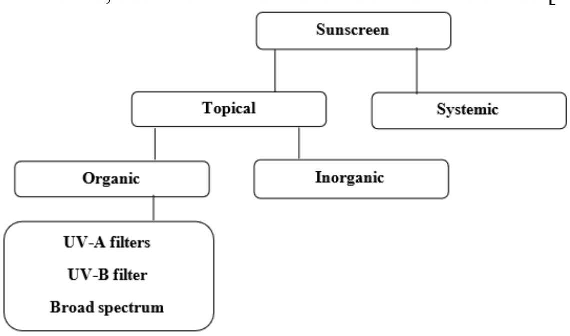
Skin pigmentation, which is made up of a class of UV-absorbing molecules called melanin, is one of many natural defence mechanisms the human body has to mitigate the consequences.

Of UVR exposure. Although melanin absorbs UVR before it damages DNA in exposed skin, it is insufficient to protect the skin when UVR exposure is high [11]. Additionally, tanning causes an increase in melanin synthesis, a gradual process that can take three to five days to provide any discernible photoprotection. Protecting against UVR and maintaining antioxidant homeostasis are two methods for preventing or minimising photoaging. To uncover the biological targets of UVR and the subsequent cascade of impaired cell functioning and tissue deterioration, recent research has studied the harmful consequences of UVR at the cellular and molecular levels. DNA damage has been reported to be caused by UVA and UVB radiation, including mutations of critical regulatory genes. Despite endogenous DNA repair mechanisms, persistent DNA damage resulting from prolonged UV exposure can lead to photoaging and an increased risk of skin cancer development. Commercial UV filters that can instantly defend skin from photodamage are therefore essential [12].

II. SUNSCREENS

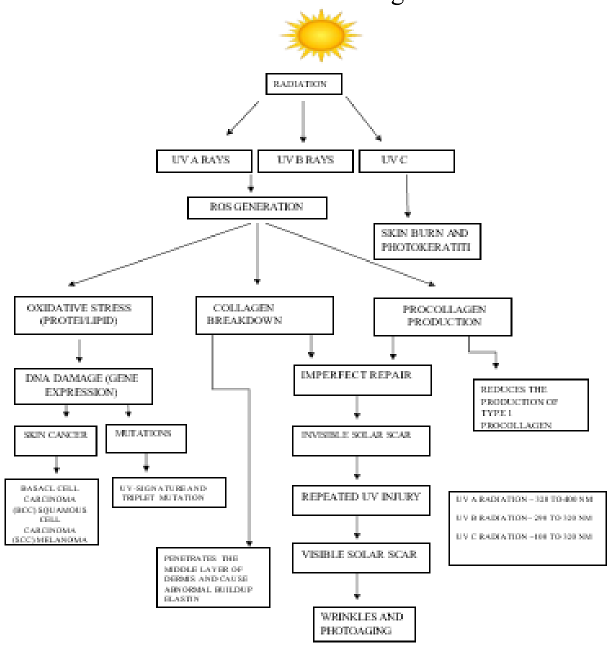
The visible light and infrared radiation that make up 98% of the solar irradiance are not protected by current sunscreen technologies (IR). Free radicals are produced in the skin as a result of interactions between photons in the visible and infrared regions and the skin. Surprisingly, visible light 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 still experience the adverse effects of visual and infrared radiation, which produce reactive oxidants and can overwhelm the skin's antioxidant defences. Through opsins, melanocytes in the skin detect UVA and blue light, initiating the process of melanogenesis [13].

Sunscreens are categorised as either chemical absorbers or physical blockers based on their mode of action. Aromatic compounds with a carbonyl group are often the main component of chemical sunscreens. The molecule's basic structure enables it to absorb high-energy UV radiation and release the energy as lower-energy rays, thereby protecting the skin from potentially dangerous UV rays. As a consequence, the majority of the ingredients (apart from avobenzone) do not undergo significant chemical changes 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 composed of inert minerals, such as titanium dioxide and zinc oxide [14].



[Fig.1: Types of Sunscreens]

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



[Fig.2: Effect of ROS Generation by UV Rays on Skin]

Table-I: Compounds used in Sunscreens

S. No.	Compounds Absorb UVA	Compounds Absorb UVB
1.	Oxybenzone	PABA
2.	Sulisobenzone	p-Amyl dimethyl PABA (Padimate A)
3.	Dioxybenzone	2-Ethoxyethyl-p-methoxycinnamate
4.	Methyl anthranilate	Digalloyltrioleate
5.	Avobenzone	Ethyl 4-bishydroxypropyl aminobenzoate
6.	Terephthylidenedicamphor sulfonic acid	2-Ethoxyethyl 2-cyano-3,3-diphenylacrylate
7.	Bisethylhexyloxyphenolmethoxyphenyltriazene	2-Ethylthexyl p-methoxycinnamate

III. 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 discolouration, 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 various cosmetic vehicles, as well as a reduced risk of discolouration and unpleasant reactions. Padimate O is the best UV-B absorber available. Due to a decline in usage and a rise in demand for products with a higher SPF, several active ingredients have been combined to create a single product that offers the appropriate SPF, and sunscreens have been replaced with single PABA esters.

A. 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.

B. 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 used in conjunction with them. It is necessary to use other salicylates at higher concentrations. All of them are safe.

C. 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.

D. Phenyl Benzimidazole Sulfonic Acid

As most chemical sunscreen components are oil-soluble in the oil phase of emulsion systems, many of these products have a thick and greasy appearance. 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.

E. Ultraviolet- A Blockers Benzophenone

Nevertheless, the fact that benzophenones typically

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absorb UV-B radiation also applies to oxybenzone. A versatile, broad-spectrum absorber, oxybenzone can be employed in various contexts.

F. 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.

G. 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 significant addition to sunscreen compositions for broad-spectrum UV protection has raised concerns.

i. Mexoryl SX or terephthalylidenedicamphor sulfonic acid

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

ii. Methoxy phenyl triazenebisethylhexyloxyphenol

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

iii. MethoxypropylaminoCyclohexenylideneEthyoxyethylcyanoacetate (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.

H. 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 prevent photodamage began gaining popularity. In 1935, Schueller created "Ambre Solaire," the first commercial sunscreen using the UV filter benzyl salicylate. Following that, a slew of new sunscreen chemicals [16, 17] were discovered. UV filters, both natural and artificial, have been explored in recent years as a challenge to address photoprotection.

Physical (inorganic) blockers and chemical (absorptive) absorbers are the two main types of UV-active substances used in sunscreen formulas today (organic). Zinc oxide and titanium dioxide (TiO_2) 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].

IV. EXISTING SUNSCREENS HAVE ISSUES

Although several commercial sunscreen solutions are available for photoprotection, further research is needed 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 to protect against the harmful effects of UVR exposure (i.e., do not degrade after absorption of UVR). According to Kockler et al. [22], several commercial sunscreens become photounstable in the UV-A region after exposure to sunlight and UV radiation. Gonzalez et al. [23] found that specific widely marketed broadband sunscreen formulations are photounstable in a similar experiment. To provide a workable solution for maximum photoprotection, industry and researchers continue to work on producing photostable sunscreen formulations.

Due to the greater intensity of UV-B light compared to UV-A radiation, the development of UV-B filters has garnered considerable 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, 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 industry and regulatory organisations have suggested a need for broad-spectrum sunscreens (i.e., sunscreens that span 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 (avobenzone) 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 banning over the years due to their adverse environmental effects. The developmental and reproductive toxicity of specific commonly used organic UV filters (oxybenzone, avobenzone, and octocrylene) on fish and corals has been the subject of several studies [31]. Organic UV filters have accumulated in soil, sediments, and aquatic biota, including clams, urchins, dolphins, and fish [32, 33]. Environmentally friendly sunscreens must be developed to preserve both human photoprotection from UVR and a healthy ecosystem.

A. Nature-Inspired Sunscreens

Research on UV filters inspired by nature has gained popularity recently, with a particular emphasis on those derived from plants and microbes. Therefore, the objective of This analysis aims to examine the results and potential applications of UV filters inspired by natural sources, to create more efficient and secure sunscreens.

B. 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 several 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 hurt growth, as well as transpiration, photosynthesis, and other physiological processes. Reactive oxygen species can interact with DNA nucleotides, harming 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 layer and makes a plant more susceptible to disease [35, 36]. On the other hand, inadequate UVR (UV-B) exposure may render a plant more susceptible to infections and diminish the UV-B signalling pathway, which promotes various photophysical activities [35, 36].

C. Microbial Ultraviolet Filters

Microorganisms, like plants and people, must protect themselves from the damaging DNA damage induced by UVR [37,38]. Microorganisms, such as 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 due to their effective absorption of the electromagnetic spectrum in the UV region and a correlation between MAA concentration and UVR exposure [43].

D. 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 individuals should avoid using sunscreen that contains aminobenzoic acid or one of its derivatives, as they share chemical similarities with other medications that can trigger photosensitivity responses, such as menthyl anthranilate, aminobenzoate, and padimate A.

O. (aminobenzoate, menthyl anthranilate, or padimate A or O). For these individuals, sunscreen containing oxybenzone or cinoxate should be recommended [46]. Fragrances, lanolin, alcohol, and preservatives, among other substances, can irritate or sensitise the skin and eyes.

Several sunscreens that contain padimate-O include NPABAO, a newly identified nitrosamine [47]. It is unknown whether sunscreens contain nitrosamines at levels high enough to cause concern [47], despite their association with cancer.

E. Controversies Concerning Sunscreens

Children below six months of age may not have fully developed biological systems that can metabolise and excrete medications acquired through the skin, and their skin may absorb chemicals differently than that of adults. Therefore, it is advisable to keep infants under the age of six months away from sunscreens that contain aminobenzoic acid and to refrain from applying sunscreen to 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 is mutagenic in certain studies, while it has also been reported to be neither mutagenic nor photomutagenic in others [52]. Despite the fact Although 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].

F. 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 suggests that sunscreen must be reapplied every two to three hours, research has shown that the best protection is achieved by applying sunscreen 15 to 30 minutes before exposure to 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 apply only 20 to 50 per cent of the recommended quantity of sunscreen. A 1.73 m^2 adult needs around 35 ml of sunscreen on average. The teaspoon recommendation for applying sunscreen is as follows: Apply a little more than 12 teaspoons (or approximately 3 mL) to each arm, face, and neck. 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 2) 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 protect against both UVB and UVA radiation. A sunscreen with an SPF of 15 blocks approximately 94% of UVB radiation. An SPF of 30 in sunscreen blocks approximately 97% 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, such as 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.

V. CONCLUSIONS

The most effective form of photoprotection is exposure avoidance, which involves avoiding midday sun, wearing protective clothing and eyewear, seeking shade, and applying sunscreen as directed. Photoprotection is a crucial preventive health precaution, as UVR exposure is a major contributor to the majority of skin cancers. The use of photoprotective measures is still limited and sporadic, despite 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.

Although specific populations may be more sensitive, everyone should apply sunscreen daily. It is envisaged that better usage would arise from adjusting guidance to particular instances and reducing compliance restrictions. Widespread cultural alterations appear to be in their early phases, notwithstanding certain apparent advances in understanding, which the associated behaviours have not yet matched. 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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After aggregating input from all authors, I must verify the accuracy of the following information as the article's author.

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