

Journal of Pharmaceutical and Scientific Innovation

www.jpsionline.com (ISSN: 2277-4572)

Review Article

AN OVERVIEW ON HERBAL SUNSCREEN FORMULATION AND SUN PROTECTION FACTOR VALUE

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DOI: 10.7897/2277-4572.084141

Received on: 10/04/19 Revised on: 12/05/19 Accepted on: 30/06/19

ABSTRACT

The sunlight consists of harmful radiations which affects the skin. The Ultraviolet radiations are of 3 types Ultraviolet A, Ultraviolet B and Ultraviolet C. This article gives a detailed review on different types of Ultraviolet radiation. To protect our skin from Ultraviolet radiation sunscreen formulations are used which either absorbs scatters or reflects the radiation. The harmful effects on skin like photo aging, skin cancer, DNA damage are explained. The present review explains the various types of sunscreen formulations and the agents used for the purpose of sun screening. The agents are of two type's physical and chemical sun screening agents. The physical agents which block the sun light and the chemical agents which absorb the sunlight are listed and explained. To know the efficacy of the formulation sun protection factor calculation is done. The equation used to calculate the Sun Protection Factor value is explained in detail. The ultraviolet spectroscopic method is employed to calculate the Sun Protection Factor. The proposed method is found to be easy and rapid for the calculation of Sun Protection Factor values in the in vitro studies. The herbal formulation is more advantageous than the chemical formulation because of its fewer side effects. Few herbal sun screen agents are listed and explained its activity.

KEYWORDS: UV radiations, Sunscreen agents, Sun Protection Factor, Herbal sunscreens

INTRODUCTION

Studies have shown that more people are diagnosed with skin cancer each year in US than all the other cancers combined. One in every five Americans ends up with skin cancer before they reach the age of 70. ¹ Around 8 billion dollars spent to treat skin cancer every year. One statistics say that between 1994 and 2014 the people who got treated for skin cancer have increased to shocking 77%. Around 90% non-melanoma skin cancer are reason of UV radiation. The sad part is every hour a person dies because of skin cancer that is caused because of exposure to sun's UV radiation. ²

A survey shows for more than 20 years remarkable advance have been done in the studies of clinical effects and biologic effects of UV radiation including photo immunosuppression, erythemia, delayed tanning, photocarcinogensis and photo aging. Having knowledge on both ultraviolet radiation effects and advanced treatments this study has been done. Since 1920 people use sunscreen. Nowadays new formulations which has broad spectrum photo stable over ultraviolet radiation has been formulated. ³

In this study we have deeply discussed about:

- UV radiation
- Various harmful effects of UVR
- Need of sunscreen
- Currently available Sun screening agents
- Calculation of SPF factor
- Herbal sunscreen formulations
- Currently available sunscreen formulations

SKIN

Human skin is the largest organ. It is a unique organ which regulates heat& water loss from body and prevents the body from microorganism & chemicals. The skin covers about $1.7m^2$ of our body. The therapeutic agent administered to the skin acts both locally and systematically. The membrane of the skin is regarded as a physical barrier. The drug transport mainly takes place through the pores in the skin tissues. Some drug may prove to be optimal in *invitro* studies, but it should be prevented in case of any immunological response alteration.⁴

Structure of skin:

Human skin is the organ through which transdermal drug delivery is done; through it is more complex organ. The skin is mainly categorized to four layers,

- 1. Subcutaneous fat layer or hypodermis
- 2. Overlying dermis
- 3. Viable epidermis
- 4. Stratum corneum (non-viable epidermis)

EFFECTS OF UV ON SKIN

Sun light is mainly of wavelength from UV to visible light. UV is the ultraviolet radiation which is of three divisions such as UVA is of 320-400 nm, UVB is of 290-320nm and UVC is of 100-290nm. Solar radiation exposure has negative effect over the human skin. UV is most harmful radiation which may cause sunburns and skin cancers.⁵

Higher exposure of UV radiation may also cause photo irritation, photo aging and carcinogenesis. The UV radiations in human skin are shown in figure 1.

- UVA has long wavelength which penetrate and reach the bottom layer of the skin which causes tanning and aging of skin. It is lethal which increase the dermal inflammatory cells and destroy the epidermal antigen activity which is present in the epidermal Langerhans cells. It also accelerates reactive oxygen species (ROS) which causes damage to cell and produces immunosuppressive cytokines.⁶
- UVB has a short wavelength and enter to the epidermis and small amount into the dermis. It generates pyrimidine dimmers in DNA and damage the structure of DNA. As like UVA it also produces ROS which damages the skin cell and produces immunosuppressive cytokines.⁷
- UVC does not reach the surface of skin. It is blocked completely by the layer of ozone.⁸

THE VARIOUS EFFECTS OF UVR TO THE HUMAN SKIN ARE LISTED

PHOTO AGING

The skin aging process is complex and of two types: intrinsic and extrinsic aging. The intrinsic is mainly caused due to the genetic factors. Extrinsic aging is caused mainly due to the external factors like UVB and cause wrinkling and degeneration of elasticity of skin.⁹

The UVB radiation exposure, by including the oxidative stress causes skin aging. It also leads to the production of extracellular matrix (ECM), and activates the nitrogen-activated protein kinase (MAPK) pathway. Thus, the UVB induced photo aging can be prevented by inhibition of MAPK pathway.¹⁰

SKIN CANCER

UV radiation's unprotected exposure is the most harmful for skin cancer. Skin cancer can be developed by long term exposure of sun's UV radiation. Skin cancer is off two types: Melanoma skin cancer and non-melanoma skin cancer.

Melanoma skin cancer is the most serious form of skin cancer. UV exposure and sunburns are not only the cause for this type of skin cancer. It can also be caused due to other disorders including immune system deficiency and genetic factors.¹¹

Non-Melanoma skin cancer is not more deadly as melanoma, but it would spread if not treated and cause more serious health problem. The two main forms of non-melanoma skin cancer are basal cell carcinoma (BCC) and squamous cell carcinoma (SCC) is shown in figure 2. BCC grows very slowly and rarely spread to other part of the body. It appears as small fleshy bumps or like nodules on the neck and heads. It also can penetrate into bones and cause damage. SCC appears as red scaly patches or like nodules. This type can be developed to large masses and spread to all part of the body.¹¹

DNA DAMAGE

Clairine V. Khoe et al., (2018) attempted a study on "The sequence specificity of UV-induced DNA damage in a systemically altered DNA Sequence". He expresses that the exposure of UV radiation is the main reason for the mutation induction, and it causes skin carcinogenesis. These effects are due to formation of dimeric photoproducts within the adjacent pyrimidine bases on the DNA strand. There are two main UV-induced DNA lesions namely pyrimidine (6-4) pyrimidone photoproducts (6-4PPs) and cyclobutane pyrimidine dimers (CPDs). Here CPD is most important UV-induced lesion which relatively has high abundance, slow repairing and it is also called as mutogenicity. The CPDs are stable than 6-4PPs. The 6-4PPs

are heat liable and alkali have high temperature and pH treatment produces a single-strand break in the pyrimidine nucleotide 3' into dimer. DNA Damage due to effects of UV radiations is shown in figure $3.^{12}$

SUNSCREEN

To overcome the effects caused by the UV exposure, sunscreen products are used which protects the skin from those harmful effects. The main function of sunscreen product is protecting the skin from solar UV radiation's damaging effects.

The active ingredients in the sunscreen mainly scatter, reflect or absorb the UV radiation, before it is penetrated into the skin and prevents the components of skin from damage.¹³

A sunscreen product is more or less like an umbrella which protects from the harmful effects of rain. The sunscreen protects the skin from the harmful effects of UVR. The coasting of sunscreen formulation on the skin should be uniform. The layer of sunscreen applied should be very thin. The thickness should be less than 0.001 inches.¹⁴

Klein K (1997) reviewed on the Sunscreen products: formulation and regulatory considerations. He explained that formulation of the sunscreen is mainly based on the ingredient's polarity. The ingredients used can be separated according to its polarity. With the combination of viscosity and polarity of the ingredients, many types of sunscreen formulation can be prepared. Range of sunscreen product formulation types by overall formula polarity and product viscosity is shown in figure 4.

This selection of formulation is mainly done for the uniform coasting of sunscreen formulation in both valley and peaks of the skin. Sunscreen product applied to the skin surface with poor film formation and ideal film formation on the skin is shown in figure $5.^{15}$

SUN SCREENING AGENTS

The sun screening agents are divided into two types: physical and chemical based upon their mechanism.

Physical sun screening agents has the action of blocking the UVR entering the skin. It is also known as non-chemical agents which scatters or reflects the UV radiation. This agent mainly consists of inert minerals.

Chemical agent has the action of absorption. These agents are basically aromatic compounds with carbonyl group conjugates. This structure of molecules absorbs the big-energy UVR and gives low-energy UVR, where preventing the skin from UV rays damages. The chemical agents used in the sunscreen, depending upon the molecular structure shows the effectiveness for both UVA and UVB (or) only for the UVB radiation.¹⁶

The few physical and chemical sun screening agent used in cosmetics are given in table 1.

PHYSICAL BLOCKER

Titanium dioxide:

Titanium dioxide is a mineral based insoluble compound. It is a physical UV Radiation filter mostly used in cosmetic as sun screening agent. It scatters and reflects the UV radiation more efficiently at 60-120mm of size range. TiO₂ based sunscreen formulations are transparent and clear when applied to skin. Mostly used form of TiO₂ is rutile crystalline form. The basic application of TiO₂ is the photo-activity deactivation process. It has the antimicrobial and skin penetration property.

TiO₂ blocks both UVA and UVB radiations. Usually ultrafine form of titanium dioxide fives a broad spectrum of protection over the harmful effects of UV Radiation. TiO₂ is chemically stable and has less side effects. They prevent the skin from contact dermatitis and photo-allergic and also, they do not cause skin irritation.¹⁷

CHEMICAL ABSORBER

UVB Absorber:

PABA:

The Para-aminobenzonic acid was the first sun screening agent used. The ester derivatives like octyl dimethyl PABA (or) padimate O (its chemical structures are shown in figures 6 A and 6 B) have good compatibility profile with the vehicles used in cosmetics but it has few adverse effects over the skin. The padimate-0 derivative in the PABA is more potent towards the dangerous radiation from UVB. But PABA provides a very less SPF value. Thus, this is not mostly used in sunscreen formulations. Sill it can be used along with other active ingredients in the multi ingredient formulation.¹⁷

Benzophenone-3

Serpne, N et al (2007) attempted a study on Inorganic and organic UV filters: their role and efficacy in sunscreens and sun care products using Benzophenone-3 as sun screening agent (Chemical structure of Benzophenone-3 is shown in figure 7). In order to disperse the UV radiation benzopenone-3 uses transfer of excited state intramolecular proton to a hydroxyl group. It also changes the photons absorbed to a heat energy in order to disperse the absorbed UVR in a harmless form whereas it prevents skin from chemical damages. And he concluded that Benzophenone-3 strongly absorbs the ultraviolet radiation of range 280-340nm. Thus, it is basically a UVB absorber, but it also absorbs UV A2 at some extent.¹⁸

The few other UVB absorbers are:

- Cinnamates: It was a potent UVB absorber which replaced the p-Aminobenzoic acid
- Octyl Salicylate: Also called as ocisalate. It mainly provides augment action to protect against UVB> it is a poor UVB absorber, so it is combined with other UV agents, but these salicylates have better safety profile
- Octocrylene: This is also used when combined with some other sun screening agent for achieving good SPF value. Mostly it is used with avobenzone and provides a good stability¹⁷

UVA absorbers:

Some of the UVA absorbers used in cosmetics are Anthranilate, Avobenzone, Terephthalylidene dicamphor sulfonic acid, Bis ethyl hexyl oxy phenol methoxy phenyl triazene.

These agents absorb UVA along with UVB radiation. They absorbers the UV radiation of range 320-340nm. They are more effective when used in combination with another agent, but they provide good photo stability.¹⁷

SUN PROTECTION FACTOR

The sunscreen formulation's efficacy can be identified by calculating the sun protection factor (SPF). It is also known as the amount of UV energy necessary for the production of minimal erythema dose (MED) on the sunscreen applied human skin divided by amount of UV energy necessary for the production of MED of unprotected skin.

SPF= <u>minimal erythema dose in sunscreen-protected skin</u> <u>minimal erythema dose in nonsunscreen-protected skin</u>

The minimal erythema dose (MED) can be given as dose of ultraviolet irradiation required for the production of minimum erythema on the unprotected layer of skin.¹⁹

The most effective product which can protect the skin from sunburn should have high SPF value. In other ways the photoprotection provided by the sunscreen formulation over the UV Radiation is determined by in vitro or in vivo, and it is mainly determined by human volunteer phototesting. For many years this way of determination has been followed which is more precise and useful; but it was more expensive, time consuming and complex process. For developing in vitro required in the determination of photoprotection of sunscreen formulation needs lots of efforts.²⁰

There are two general methods of in vitro technique. The first type is measuring the transmission or absorption of UV radiation passing through a thin film of sunscreen product in a biomembrane or quartz plates. The second type is the method of sunscreen agent's absorption properties are determined by spectrophotometric analysis.

Research of Mansur et al. (1986) explains a mathematical equation as a replacement for in vitro method explained by Sayre et al., (1979), using UV spectrophotometry.

The equation proposed by Mansur et al., is given below;²¹

SPF = CF ×
$$\sum_{290}^{320} \text{EE}(\lambda) \times I(\lambda) \times \text{Abs}(\lambda)$$

where:

- I (I) Solar intensity spectrum
- EE (I) –Erythemal effect spectrum
- Abs (I) Absorbance of sunscreen product
- CF Correction factor (=10)
- The EE x I value is a constant value.

These values were developed by Sayre et al. (1979) and given in the table 2. $^{\rm 22}$

The values of the term: EE X I is a constant. The SPF value depends upon the absorbance of UV B rays ranging from 290 to 320 nm. Juchou et, al proved that the light will be transmitted through the skin if it's not absorbed. When the sunscreen substances absorb more UV, B rays it minimizes the UV rays that is transmitted through the skin. It is observed that SPF 15 can filter out 72% of UV B Rays while SPF 30 can block 90% of UVB rays. 97% of UVB rays are filtered by SPF 50 and only 3% of UVB rays are transmitted through the sunscreen.²³

Elizangel Abieu Dutra et al (2004) analysed the SPF values of various products available in the market. It was observed that some products labeled SPF were as same as that of the experimental value and some others varied. They stated that the differences may be due to different vehicle components such as emulsifiers, ethers and the dissolving agents.²⁴

Bernard P Buks et al (2017) analyzed that the sunscreen films protect us from harmful effects of solar UV radiation. The active ingredients absorb, scatter and reflect the light. They conducted on experiment of far UV filters and two solvents. They conducted that the solar irradiation is one of the main factors which damages the sunscreen in use.²⁵

Physical Blocker	Chemical absorber		
	UVA	UVB	
Titanium dioxide	Oxybenzone	PABA	
Zinc oxide	Arthranilate	Benzophenone-3	
Red petrolatum	Avovenzone	Cinnamates	
	Terephthalylidene dicamphor sulfonic acid	Octylsalicylate	
		Octocrylene	
	Bis ethyl hexyl oxyphenol methoxyphenyl		
	triazene	Phenyl benzimidazole sulfonic acid	

Table 1: List of physical and chemical sun screening agents.

Table 2 - Normalized product function used in calculating the SPF value

Wavelength (λ nm)	EE x I (normalized)
290	0.0150
295	0.0817
300	0.2874
305	0.3278
310	0.1864
315	0.0839
320	0.0180
Total	1

Table 3 - Currently available herbal sunscreen products

Branded sunscreen products	Manufacturer	Herbal constituent
Tomato sun Cream SPF36 PA++	Skinfood Cosmetics	Tomato
Natural Sun SPF25	Aubrey Organics	Green Tea, Aloe vera
Power light intensive fairness moisturizer SPF 15	Garnier	Lemon, Long dan
SPF30 natural mineral sunscreen	John Masters	Shea butter, Jojoba
Aroma sun tanning gel SPF10	Declore	Roman chamomile, Geranium Jasmine, Saffron,
		Bearbery
Saffron and bearberry fairness cream	Jovees	Saffron, Bearbery
Body lotion	Cosmetic Bakery	Sunflower oil
Hydra Light moisture-infusing lotion	Paula's choice	Pomegranate, Oats, Cranberry
Bio-pro carrot protective cream SPF15	Biotique Botanical Herbal	Carrot oil
Even out face cream SPF20	Oriflamme Cosmetics Inc	Liquorice
Ant wrinkle Moisturizing lotion SPF30	S B Cosmetics Inc,	Emblica
Super Resist antioxidant concentrate serum	Paula Choice	Turmeric
Biovera SPF75	Biotique Botanical Herbal extracts	Aloe vera
Save face & body sunscreen	Arbonne cosmetics	Bitter Orange



Figure 1: UV radiation in Human skin



Basal cell carcinoma and Sqamous cell carnoma Figure 2: Two main forms of Non-Melanoma skin cancer



Figure 3: DNA Damage due to effects of UV radiation.



Figure 4: Range of sunscreen product formulation types by overall formula polarity and product viscosity.



Figure 5: Sunscreen product applied to the skin surface (A) Poor film formation. (B) Ideal film formation on the skin.



Figure 6 A: Chemical structure of Para-Aminobenzoic acid



Figure 6 B: Chemical structure of Padimate-O



Figure 7: Chemical structure of Benzophenone - 3

Couteau et al (2012) clearly stated that the efficient protection from UV radiation is by using clothes. For uncovered areas, it is necessary to apply a sun product. Twenty products with various labeled SPF values were taken for study. They concluded that efficiency of the sunscreen is usually good with value of more than 30. 26

C. Malsawmtluangiet al (2013) found the SPF values of various herbal extracts from the kitchen with the spectrophotometer method. The SPF values were cancelled by Mansur mathematical equation. It was found that coconut had the high SPF value of 7.38 and watermelon had the lowest value of 0.97. they also stated that botanical and herbal agents play a safer role and are widely

accepted by the consumers. The botanical herbal extracts are good, cheap and are easily available in markets. $^{\rm 27}$

J.Hojerova et al (2011) studied the photostability and photoprotective efficacy of a few sunscreen products with the same label SPF value when subjected to sunlight. The main objective of his study was to show the difference in photoprotection of sunscreen product with different SPF values given on the package. This author used another formula for calculating SPF value,

In vitro SPF = $\frac{\int_{290}^{400} \text{EX IX dX}}{\int_{290}^{400} \text{EX IX TX dX}}$

where,

- E λ =Erythemal spectral effectiveness
- I λ =solar spectral irradiance
- T λ =spectral transmittance of the sample

And the UVA protection factor is calculated using the formula,

$$UVA - PF = \frac{\int_{320}^{400} P\lambda I\lambda d\lambda}{\int_{320}^{400} P\lambda I\lambda T\lambda d\lambda}$$

where,

- P λ =PPD action spectrum PPD (persistent pigment darkening) is the spectrum at 2-4 hours after the UVA exposure)
- I λ =solar spectral irradiance
- T λ =spectral transmittance of sunscreen layer at wavelength

In this study they concluded that the efficacy of sunscreen product depends on the photoprotectivity.²⁸

HERBAL SUNSCREENS

The people of early civilization used variety of products made from plants as sun protecting agents. Olive oil was used by Greek people. Rice, Jasmine, Lupine plants were used by the Egyptians. It is obvious that the modern trend of the world to search again for herbal products in all the fields. The consumers are more fond of herbal sunscreens which are known to be safe.

BENEFITS OF HERBAL SUNSCREEN

Numbers of people suffering from sunburn and skin sensitivity are very keen to use the products made from herbs, they do not want to use chemical sunscreens due to chemicals, its concentration and side effects on the skin. The people nowadays pay more interest for the herbal products.

The herbal sunscreens can easily be prepared without any special equipment. They are easily available and made from renewable resources in which the ingredients are readily available. They cause no side effects and they are less expensive.

HERBAL SUN SCREENING AGENTS

Luffa cylindrica: (vegetable sponge gourd)

It is a very fast-growing climber. The flowers are bright yellow. Hydrophobic antioxidant constitutes are present in fruit and they prevent free radicals. Thus, it is used as an effective sunscreen agent.²⁹

Portulaca oleracea: (pursalane)

Sanja et al (2009) in his study attempted on Characterization and evaluation of antioxidants activity of Portulaca oleracea. It is a warm climate herbaceous succulent plant. It has a high source of omega 3 fatty acids & antioxidant properties. It has many chemical constituents like flavonoids, alkaloids, vitamins, proteins and minerals. It is used in the treatment of sunburns.³⁰

Terminalia chebula:

This is commonly known as black or chebula myrobalan which is a species of terminates. It contains glycosides triterpenes, coumarin in conjugation with chepulin and other phenolic compounds. It also consists of ascorbic acid, gallic acid, ellagic acid which has got effective free radical scavenging properties.³¹

Piper longum:

This plant is called as Indian long pepper or pipili which is a flowering wine of the family Piperacea. The chemical constituents have insecticidal and anti-fungal properties. Pipperine which is the main constituent has antioxidant property, therefore it is used in skin care sun burn creams.³²

Aloe vera:

The aloevera is a treasure of valuable nutrition. It contains 240 nutritional and medicinal constituents including vitamins, minerals, sugars, lignins, anthra quinones, salicylic acids, sterols, etc.. the alovera contains proteolytic enzymes which repair the dead skin on the scalp. This aloevera gel is a magic wand to skin care.³³

Emblica officinalis:

This is also called as Amla. It is a deciduous tree on the family phyllanthacea where the edible fruit is used for medical purposes. The fruit contains high amounts of ascorbic acid which slows down the aging process. The high source of vitamin C acts as a scavenger for oxygen free radicals and the vitamin E, prevents the preoxidation of lipids.³⁴

Crocus sativus:

Abdullaev Fl (1993) reviewed on the Biological effects of saffron. The Crocus sativos is commonly called as saffron crocus which is a species of flowering plant in the Iridaceae family. It contains a lot of antioxidants flavanoids, anthocyanines which make it a good anti-inflammatory product.³⁵

Peumus boldus molina:

Hidalgo et al (1998) studied the action of Boldine as a sunscreen and its photo protector capacity against UVB radiation. It is a perennial tree basically from arid zones which belongs to the Monimiaceae family. The main chemical compound is boldine with the chemical formula $C_{19}H_{22}NO_4$ is an antioxidant which protects against the free radical formulation.³⁶

Turmeric:

It is derived from the plant Curcuma longa, belonging to the Zingiberacae family, a yellow spice commonly used in India. It is used in the preservation of food which has a yellow dye. This yellow color is given by the compound Curcumin. It contains many polyphenolic compounds and active ingredients in skin healing.

Curcumin is a wound healing compound because of its various antioxidant and anti-inflammatory activates. It stimulates the necessary cytokines. Curcumin as a potential remedy for acne induced by sebum. It lowers the oil level on the skin and removes free radical molecules. The anti-bacterial properties of curcumin help to kill the microbes on the skin which are the key responsible for the infection.³⁷

Alpinia galanga:

Jirawan et al (2005) experimented on Antimicrobial properties and action of galangal. It is a herb which belongs to the ginger family. It has been used as a medicine for long ages. The chemical constituents include sterols flavonoids & volatile oils. It has high anti- inflammatory properties. It has more than 40 antioxidants that fight against skin aging. $^{\rm 38}$

HERBAL SUNSCREEN PRODUCTS

The few currently available sunscreens products since 1920 in India are given in the table 3.3^{39}

CONCLUSION

Recent study in JAMA has showed that the chemicals present in the sunscreen enter the bloodstream more rapidly. Few chemical sun screening agents such as avobenzone, octocrylene, oxybenzone and ecamsule enter the bloodstream within an hour after application on skin. These chemicals may cause various harmful effects in human.⁴⁰ Thus it was concluded that herbal sun screening agent is more advantageous than chemicals because of its lesser side effects.

ACKNOWLEDGEMENT

The author would like to thank Department of Science and Technology – Fund to improvement of Science and Technology Infrastructure in Universities and Higher Educational Institutions (DST-FIST), New Delhi for their Infrastructure support to our department.

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How to cite this article:

Ashitha Saffrin M and Raman Sureshkumar. An overview on herbal sunscreen formulation and sun protection factor value. J Pharm Sci Innov. 2019;8(4):127-135. http://dx.doi.org/10.7897/2277-4572.084141

Source of support: Nil, Conflict of interest: None Declared

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