

PHOTOPROTECTIVE ANTIOXIDANT PHYTOCHEMICALS

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Abstract

Many ayurvedic natural products have properties to rejuvenate and protect the skin from environmental pollution, chemicals, atmospheric temperature fluctuation, UVA and UVB radiation, wrinkling, hyperpigmentation (excessive tanning) and inflammation. The present review focuses on properties and mechanism of action of photoprotective antioxidant phytoconstituents obtained from ayurvedic plants such as flavonoids, carotenoids, phenolics which can be useful in development of effective photoprotective herbal cosmetic formulation.

Keywords: UV rays, ROS, SPF, antioxidant

1. Introduction

Cosmetics products are formulated for application on the body for the purpose of cleansing, beautifying or altering appearance and enhancing the beauty.¹ These products have become an essential part of our lives. Phytoconstituents present in herbs are gaining popularity as ingredients in cosmetic formulations to protect the skin against exogenous and endogenous harmful agents and thus cure many skin conditions.² Exposure of skin to sunlight and other atmospheric condition causes production of reactive oxygen species, which can react with DNA, Protein and Fatty acids causing oxidative damage and impairment of antioxidant system.³

Ayurvedic herbs or herbal extracts act on these areas and produce healing, softening, rejuvenating and sunscreen effect. "The herbal cosmetics are products which are formulated using various permissible cosmetic ingredients to form the base in which one or more herbal ingredients are used to provide defined cosmetic benefits".³ The photoprotective phytoconstituents such as curcumin, resveratrol, tea polyphenols, silymarin, quercetin and ascorbic acid are very popular in the development of herbal cosmetic formulations.⁴

1.2 UV rays and skin: Ultraviolet (UV) radiation is defined as that portion of the electromagnetic spectrum between x rays and visible light, i.e., between 40 and 400 nm (30–3 eV)(5). Solar ultraviolet radiation (UV-R) comprises 3 categories depending on wavelength.

1. UV-A Radiation (320-400nm): When UV radiations reach to skin and which is known as ageing rays. As they penetrate deep into epidermis and dermis of skin. UV-A radiations produce immediate tanning effect-Darkening of the skin due to excess production of melanin in the epidermis. They causes premature photo ageing, suppress immunologic functions, and causes necrosis of endothelial cells, thus damaging the dermal blood vessels.

2. UV-B Radiation (280-320nm): UV-B radiations are known as burning rays as they are 1000 times more capable of causing sunburn than UV-A .UV-B rays act mainly on the epidermal basal cell layer of the skin but more genotoxic than UV-A radiations. Ultraviolet B (UVB) rays vary with time and season are major cause of sunburn. Sunburned skin is a leading risk factor for melanoma and non-melanoma skin cancer.

3. UV-C Radiation (200-280nm): UV-C radiations are filtered by stratospheric ozone layers.

Exposure of skin to UV rays (especially UVA rays from 320 to 400 nm) causes generation of reactive oxygen species (ROS) due to oxidative stress, collagen breakdown or procollagen production. Oxidative stress leads to DNA damage and thus cancerous skin. While repeated exposure of UV rays and collagen breakdown or procollagen production gives rise to wrinkles and photo ageing.⁵

1.3 Mechanism of photoreactions: Photo-oxidative mechanism depending on light-driven ROS formation now is accepted to cause skin photoaging and photocarcinogenesis.⁶ UVA rays mediated

photooxidative damage effectively reaches through the upper layers of skin into the human dermis and dermal capillary system. Substantial protein and lipid oxidation occurs in human skin epidermis and dermis together with a significant depletion of enzymatic and non-enzymatic antioxidants in the stratum corneum, epidermis and dermis.

The immediate as well as persistent pigment darkening responses of human skin are due to photooxidation of preexisting melanins (IPD) and its precursors (PPD), respectively. Also upregulation of hemeoxygenase-1 (HO-1), ferritin, glutathione peroxidase, Cu-Zn-dependent superoxide dismutase (SOD1), manganese-dependent superoxide dismutase (SOD2), and catalase occurs after solar irradiation.

UV rays contact initiates photo oxidative reactions to activate protein kinase C enzyme and reactive oxygen species which further reacts with protein lipids and DNA to form cyclobutane pyridine dimers. This leads to erythema, edema, skin sunburn and cell apoptosis. UV irradiation activates cell surface growth factor and cytokine receptors on keratinocytes and fibroblasts in human skin, critical in the regulation of cell proliferation and survival.³⁷ UV-driven formation of H₂O₂ regulates the tyrosine kinase activity of the epidermal growth factor receptor (EGF-R) and emerging evidence suggests the inhibition of protein tyrosine phosphatases as a consequence of UV-induced ROS formation.

1.4 Photoprotective herbal drugs⁷: As we know that it is impossible to avoid sun exposure and so everyone needs sun protection. But a regular application of chemical sunscreens (zinc oxide, titanium dioxide, avobenzene, p-Aminobenzoic acid etc.) is very harmful due to their side effects like melanoma, dermatitis, skin cancers. Even many times chemical sunscreens are unable to protect skin from UV rays. Hence people are demanding natural alternatives to this problem. There are many herbal sunscreen formulations are available in market however, no one is completely satisfying consumer's demand. Herbal extracts contains many constituents with different uses and hence it is must for researchers to study phytochemical properties while developing a good sunscreen. Mechanism of action of photoreactions is directing that antioxidant properties of herbal extracts are useful in sun protective effects.

1.5 Why antioxidants?⁸: As we know that, UV-R absorbed by skin surface which can produce harmful compounds called free radicals or reactive oxygen species (ROS), which can cause skin cancer and premature ageing and hence to reduce ROS generation and damage, researchers recommend using sunscreen to protect skin from harmful UV-R.

The possibilities in photo protection may include development of sunscreen which remain at the surface of skin for a longer time and may incorporate antioxidant that can neutralize ROS. Thus, naturally occurring herbal compounds such as phenolic acid, flavonoids and high molecular weight polyphenols are very useful for prevention of adverse effects of UV-R on the skin and also these herbal compounds which having its ability to stimulate the circulation of blood in skin and remove dead skin cells to giving fresher and younger appearance to the skin. In table 1 various photo protective herbal drugs and their mode of actions are explained in detail.

1.6 Sun Protection Factor⁹⁻¹²: The efficacy of sunscreen is usually express by sun protection factor which is defined as "UV energy required producing minimal erythema dose (MED) in protected skin divided by UV energy required to produce MED in unprotected skin." The minimal erythema dose (MED) is defined as "The lowest time interval or dosage of UV light radiation sufficient to produce a minimal, perceptible erythema on unprotected skin.

$$\text{SPF} = \frac{\text{Minimal erythema dose in non sunscreen protected}}{\text{Minimal erythema dose in sunscreen protected skin}}$$

In-vitro methods to determine sun protection factor are of two types which are as follows:

1. Otometric Model SPF-290 analysis: This method involves measurement of absorption or transmission of UV radiation through sunscreen product films in quartz plates or biomembrane over a wavelength range from 290nm-400nm. This study can be performed by transmittance measurement of sunscreen cream. Approximately 100 mg of sample has to apply and spared on 56 cm² areas of transport tape to obtain a sample film thickness of 2μl/cm². The sample thus prepared has to expose to Xenon arc lamp for determining the SPF and Boots Star Rating.
2. Spectrophotometric analysis: This method determines absorption characteristics of sunscreen agent's dilute solution.¹³⁻¹⁶ The observed absorbance values at 5nm interval (290 nm-320nm) has

to be calculated by using given formula. In this method (solvent method) different concentrations of test sample have to prepare in methanol.¹⁷

$$\text{SPF} = \text{CF} \times \frac{\sum_{290}^{320} \text{EE}(\lambda) \times 1(\lambda) \text{Abs}(\lambda)^{(29)}}{\sum_{290}^{320} \text{Abs}(\lambda)}$$

Where CF= correction Factor, EE= Erythrogenic effect of radiation with wavelength λ , Abs (λ)=Spectrophotometric absorbance values at wavelength λ

Conclusion

Herbal cosmeceuticals are natural products having ingredients with properties to rejuvenate and protect the skin from environmental pollution, chemicals, atmospheric temperature fluctuation, UVA and UVB radiations, wrinkling, hyperpigmentation (excessive tanning) and inflammation. The present review focused on photoprotective phytoconstituents¹⁸ such as flavonoids, carotenoids and phenolics compounds. The addition of herbal extracts for therapeutic use requires better understanding of phytochemicals possessing this potential. Only single ingredient formulation cannot satisfy consumer's demand of long lasting sunscreens with more than one benefit like moisturizer, whitening, refreshing. Due to potent antioxidant properties of these phytochemicals effective, stable and long lasting photoprotective polyherbal cosmetic formulation can be developed. This review will help to researchers in selection of appropriate photoprotective phytochemical/s combination.

Table 1: Antioxidant phytoconstituents with sun protection mechanism

| Sr.No | Crude drug | Biological source | Components | Mechanism of action |
|-------|------------------|--|---|--|
| 1 | Tea phenolics | <i>Thea sinensis</i> Theaceae | Catechin, gallocatechin, gallic acid, kaempferol, myricitin | Reduced production of cyclobutane-pyrimidine dimers. Protect UV-B induced cutaneous edema and erythema ¹⁹ . Reduced myeloperoxidase activity, H ₂ O ₂ & NO production & lipid peroxidation in human skin ²⁰ . |
| 2 | Curcumin | Roots of <i>Curcuma longa</i> Zingiberaceae | Curcumin (diferuloylmethane) | Scavenge ROS, by interrupting the activation of protein kinase C ²¹ . Enhance glutathione content & GST activity. ²² Inhibit lipid peroxidation & arachidonic acid. ²³ Inhibit Ornithin decarboxylase (ODC) activity |
| 3 | Silymarin | Milk thistle (<i>Silybum marianum</i>) | Silybin, silibinin, silibidianin, Silychristin, isosilybin | Inhibit skin edema, skin sunburn & cell apoptosis. Inhibit catalase activity. Inhibit induction of ODC and COX-2 activities. ²⁴ |
| 4 | Genistein | Soya (<i>Glycine max</i>) redclover, ginkgo biloba, greek oregano & greek sage) | Genistein | Inhibit UV-B induced H ₂ O ₂ production. Inhibit contact hypersensitivity. Reduced edema. ²⁵ |
| 5 | Garlic compounds | <i>Allium sativum</i> Liliaceae | Garlic sulphur compounds | Scavenging reactivity oxygen species (ROS) inhibiting LDL oxidation & lipid peroxide formation. ²⁶⁻²⁷ |
| 6 | Apigenin | Vascular plants (Parsley, celery, chamomile, thyme) | 5,7,4'- trihydroxystilbine | In cancer chemotherapy & counteract ROS & reduced oxidative stress with enzymatic antioxidant ²⁶⁻²⁷ |

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|----|--------------------------|---|---|---|
| 7 | Caffeic and Ferulic acid | Vegetables, Olive oils (<i>Olea europaea</i>) Oleaceae | Caffeic and Ferulic acid | Caffeic acid inhibited formation of hydroxyl radicals. Caffeic acid scavenged both hydroxyl and superoxide radicals. ²⁶⁻²⁷ |
| 8 | Ginkgo flavonoids | <i>Ginkgo Biloba</i> ginkgoaceae | Quercetin, epicatechin, rutin, apigenin | Free radical scavenging properties include inhibition of lipid peroxidation helping to maintain integrity and permeability of cell wall. ²⁶⁻²⁷ |
| 9 | Carotenoids | Tomatoes (<i>Solanum Lycopersicum</i>) Carrots (<i>Daucus carota</i>) | β -carotene, lycopenes | As a chain breaking antioxidant in a lipid peroxidation. ²⁶⁻²⁷ |
| 10 | α -tocopherol | Plant oils (Wheatgerm oil, sunflower) | α -tocopherol | A-tocopherol is lipid soluble antioxidant. It performs function as antioxidants by glutathione peroxides pathway and it protects cell membrane from oxidation by reacting with lipid radicals produced in lipid peroxidation chain reaction. ²⁶⁻²⁷ |
| 11 | Resveratrol | Grape (<i>Vitis vinifera</i>) Nuts, fruits | Trans-3'4'5'-trihydroxystilbene | Inhibit ODC and COX-2 activity. Inhibit increased level of lipid peroxidation. ²⁸ |
| 12 | Ascorbic acid | Most fruits and vegetables (Papaya, orange, Lemon, Grapes, Tomatoes, Mango) | L-ascorbic acid | Inhibit solar radiation induced p53 powerful antioxidant enhancer. ²⁹ |
| 13 | Quercetin | Apple (<i>Malus domestica</i>), Ginkgo biloba | Quercetin | Protect the antioxidant system. Protect activities of glutathione peroxides, reductase, and Catalase dismutase. ³⁰ |

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