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Plants and Phytoconstituents Having Sunscreen Activity

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ABSTRACT

Sunscreens are those preparations which are rubbed on to the skin surface for the purpose of protection from the harmful UV radiations from the sun. Exposure to those radiations can results in harmful effects such as cancer, edema, varied pigmentation and erythema as a result of DNA damage. Majority of organic chemicals used in sunscreen formulations have not been established as safe. Natural sunscreens gained importance over synthetic ones due to their less side effects, greater protection and easy availability. A wide range of natural products derived from plants, algae and propolis have shown potential photo protective effect. Natural compounds including flavonoids, cinnamates, polyphenols, carotenoids,anthocyanins,triterpenoid saponins have shown desired Sun Protection Factor (SPF) in addition to anti-inflammatory and anti-oxidant property.

Key words:
UV radiations,
anti- oxidant activity,
Herbal, SPF.

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INTRODUCTION

Skin is considered to be the largest integumentary system of human body. So intense care is needed to protect skin from the deleterious effect of nature; since it is widely exposed to nature. The concept of beauty has been started from ancient civilization. Sun is the source of light and energy. Besides that, sun is a mood enhancer, triggers the production of Vitamin D, increases serotonin production and various other benefits for humans. On the other hand, sun also has some deleterious effect on humans such that over exposure may result in sun burn, rashes, skinmelanoma, skin cancers etc. The various radiations are responsible for this harmful effect. Sunlight is composed of 40% visible, 50% infrared and remaining 10% ultraviolet rays. The ultraviolet radiation can be categorized in to UV A (315-400 nm), UVB (280-315 nm) and UV C (200-280 nm).

PROPERTIES OF UV RADIATION[1-5]

UV A radiation have longer wavelength and are less affected by altitude and atmospheric conditions. It is useful for the production of vitamin D3 by the irradiation of 7 dihydro cholesterol. These radiations reach deeper layers of epidermis and dermis and also result in immediate tanning or darkening of skin due to excess production of melanin in epidermis. They also damage elastic and collagen fibers of connective tissue of skin and also reported for premature aging, necrosis of endothelial cells and damage to dermal blood vessels. They also suppress immunological function.

UV B radiation are also known as burning rays because they are 1000 times more capable of causing sunburn than UVA.These are not completely filtered by ozone layer.It acts mainly on epidermal basal cell layer of skin and are more genotoxic than UVA. It also causes acute inflammation and intensifies photo aging.

UV C radiations possess highest energy and greatest potential to cause biological damage. Since they are filtered by the stratospheric ozone layer before reaching the earth, they are less effective and hazardous.

MECHANISM OF ACTION

UV rays mediated photooxidative damage reaches the dermal capillaries via epidermis and dermis and cause depletion of enzymatic and non-enzymatic antioxidants in Stratum corneum,epidermis and dermis. Photo oxidation of preexisting melanin and its precursors will occur which result in immediate and persistent pigment darkening. Solar irradiation also results in the upregulation of certain enzymes like hemooxygenase, ferritin, glutathione peroxidase, catalase etc.

UV rays initiate photo oxidative reactions and then activate protein kinase C and reactive oxygen species which in turn react with protein, lipids and DNA to produce cyclobutene pyrimidine dimmers which is responsible for causing edema, skin sunburn, cell apoptosis and erythema.UV irradiation also stimulate cell surface growth factor and cytokine receptors on keratinocytes and fibroblast in skin which alters the regulation of cell proliferation [1]. According to WHO, globally each year is reporting 132,000 melanoma skin cancers and 2-3 million non-melanomaskin cancers. The most predisposing factors to the above said one is the recreational exposure to sun and the history of sunburn[6].

IMPORTANCE OF SUNSCREEN

UV radiation is essential to human health such that it helps in the intestinal absorption of calcium, phosphorous and for the production of vitamin D3. On the other hand,these radiations also harm our health by directly interacting with DNA, RNA proteins, lipids and thereby causing potential carcinogenic effect. The most efficient way to protect skin from harmful UV radiation is the topical application of any active molecule which has UV absorbing or reflecting property[7]. This is why the sunscreen has gained importance in the current scenario.

The demand for sunscreen increases in the market trend since the people are aware about the utility it offers to them. The sunscreens are generally rated and marketed with a Sun Protection Factor (SPF) that measures the fraction of sunburn producing UV rays that reaches the skin. WHO recommends to apply a broad-spectrum sunscreen of SPF 15+ liberally and re-apply every two hours, or after working, swimming, playing or exercising outdoors[8].The goal of sunscreen formulation is to block UV rays and increase the protection from UV rays.

An ideal sunscreen should have the following property:

- Filtering activity against UVB and UVA radiation
- Anti-oxidant and reactive oxygen species scavenging property
- Anti-mutagenic property
- Anticancer property
- Booster effect
- Safety stability of active compound.

Sunscreens can be classified as follows:

I. Based on mode of action they can be classified as

1. Physical sunscreen: Reflect harmful rays away from skin.
   Eg: zinc oxide and titanium dioxide.
2. Chemical sunscreen: Absorbs UV rays.
   Eg: microfine titanium dioxide, avobenzone and oxybenzone.
   The combination of both physical and chemical active ingredients is considered to be a best sunblock. Physicalsun blocks are having scattering affect thereby results in whitening phenomenon while majority of organic chemicals used in sunscreen formulations have not been established as safe.

II. Based on application they can be classified as

1. Topical: They either absorb or reflect radiation to protect from harmful radiation.
   Eg: PABA derivatives, Benzophenone.
2. Oral: These are consumed orally to avoid skin damage.
   Eg: Carotenoids.

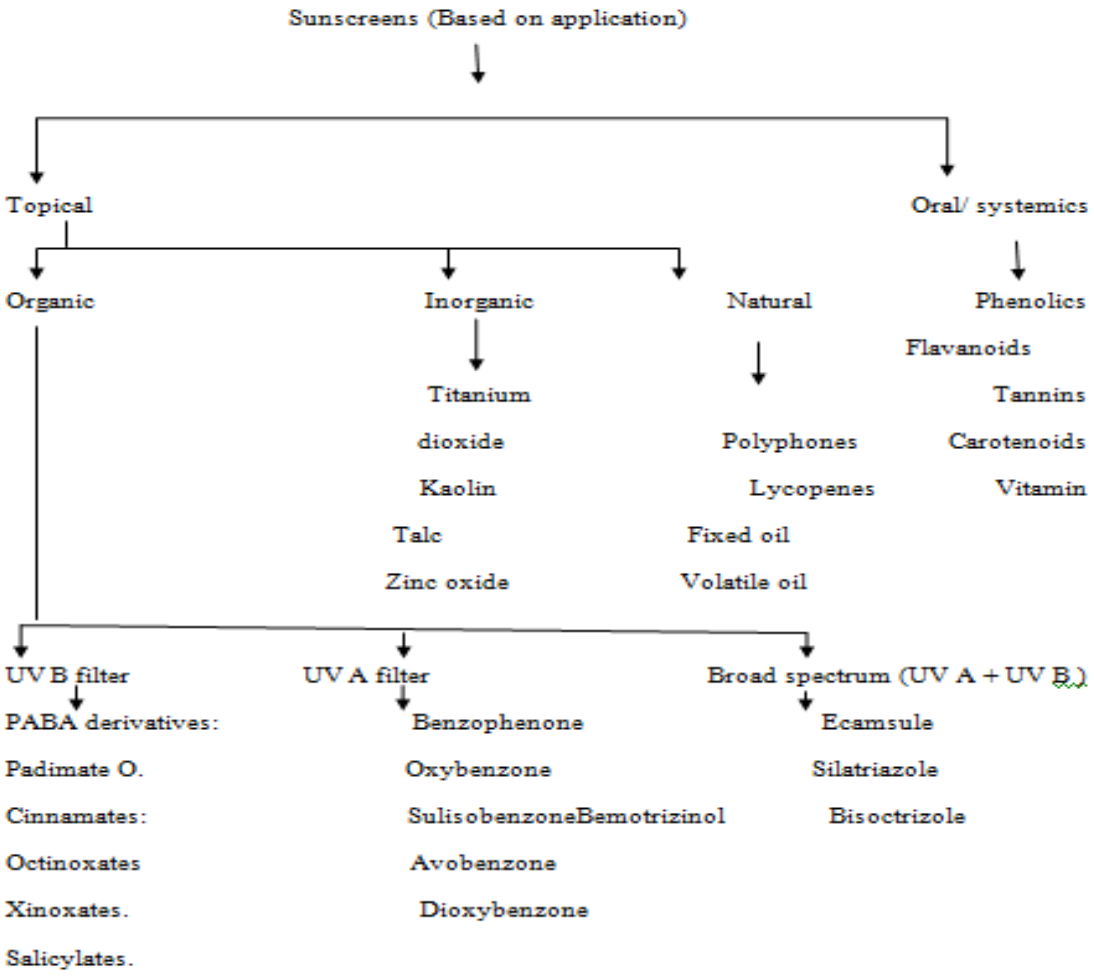

Figure 1: Classification of Sunscreens.

GUIDELINES FOR EVALUATION OF SUNSCREENS

Sunscreens are evaluated by some conditions including labeling requirements and standard according to countries. It includes:

a. US FDA Method
   FDA requires that sunscreen products have a critical wavelength of at least 370 nm (mean value must be equal to or greater than 370nm) to be labeled as providing "broad spectrum" UVA and UVB protection.
b. UK Method of boot star rating
   UV transmittance is measured through a sunscreen film and the ratio between the mean UVA and UVB absorbance measured before and after irradiation of the sunscreen products is calculated.
c. AUSTRALIAN standard method
   Percentage of UV radiation absorbed by product is measured using spectrophotometer and if the product transmits less than 10% of the incoming radiation between 320 – 360 nm is only considered as a long wave protector.
d. COLIPA guidelines of EUROPEAN countries
   It allows the *invitro* measurements of UVA protection factor valueswhich should co -relate well with in –vivo results,which is determined with PPD method.
   e.Bureau of INDIAN Standards
   They set relevant cosmetic product standards keeping key points on stability data. For sunscreens,there is no maximum SPF rating.
e. JAPAN Cosmetic Industry Association
   In Japan,in vivo testing is required for UVA and labeling according to protection grade of UVA.
f. CHINA
   According to Hygienic Standard for Cosmetics 2007, product name must be labelled in Chinese language and have a Chinese name and labeling should follow water resistance norms .

IMPORTANCE OF HERBAL SUNSCREEN

According to some regulatory agencies evidence has been submitted such that fast sun protective action has found from synthetic sunscreens accompanied with its potential risk. According to Centres for Disease Control and Prevention [CDC] held in 2007, mothers with high levels of oxybenzone in their body gave birth to underweight baby girls. Oxybenzone is an active ingredient in synthetic sunscreen which has result in the above said toxicity. According to Therapeutic Goods Administration [TGA] in Australia, a free radical formation was induced by zinc oxide and titanium dioxide (common components of synthetic sunscreens) in presence of light and this may damage the normal cells. Zinc oxide and titanium dioxide which has been used instead of PABA, an earliest ingredient in synthetic sunscreens was found to possess potential risk like dermatitis, discoloration of skin etc[9]. This is why herbal sunscreen gained importance during this era.

Demand for an herbal cream increased over a chemical based cream since the herbal cream is having less or no side effects. Herbal ingredients do not provoke allergic reactions, no negative side effects, no comedogenic effect. These are more effective and are rich with its stability, safety, purity, cost effective, easily available and found in large variety of plants since the nature has gifted us with everlasting treasure of herbal ingredient. Even today people in rural areas use natural remedies (plant extract)for traditional cosmetics since skin is the primary part exposed to nature[9-10].Recently, natural substances has been considered as potential sunscreen resources because of their absorption in UV rays[11].In addition to UV absorption property they were also found to act as anti oxidants, anti-inflammatory and immuno modulatory agents[7]. The role of natural compounds as photoprotective compounds has been widely studied and found that considerable number of commercially available sunscreens contain herbal extracts but not as sun filters. Despite numerous scientific reports no natural compound or vegetable extract has been approved by any country as UV filters for sunscreen and thereby till there is no officially approved commercial sun filter[12].

HERBS AND NATURAL COMPOUNDS AS SUNSCREENS

Nature has gifted with parity of herbs, plants and the answer for all our queries is lying itself in the nature. For the protection of skin. Ayurveda combined the knowledge of nature into many formulations by utilizing many herbs[13].The number of natural products derived from propolis, plants, algae and lichens that have shown potential photoprotective properties against UV radiation induced skin damage[7]. Epiphorelic acid I and II, salazinic acid, usnic acid, secalonic acid and calycine were found from lichens which possess antioxidant and broad-spectrum UV absorbing capacity[12].

Table 1: List of some plants and their Phytoconstituents having sunscreen activity.

PLANT NAME	PLANT PART	TYPE OF COMPOUND	MAJOR CONSTITUENTS	MAIN EFFECT
Calendula officinalis	Flower	Polyphenols Flavonoids	Rutin, Narcissin	Prevent UV radiation induced oxidative stress.
Fragaria anagassa	fruits	Anthocyanins Hydrolysable tannins	Pelargonidin	Antioxidant, Anti inflammatory
Vaccinium myrtillus	Fruits	Polyphenols	n.r	ROS formation stimulated by UV A is reduced
Punicagranatum	Fruits, peel	Anthocyanidins, Hydrolysable tannins	Delphinidin Cyanidin Pelargonidin	Synergistic photoprotective activity in nano structured lipid carrier
Phyllanthus emblica	Fruit	Polyphenols Flavonoid	Phyllembin Vitamin C Minerals Amino acids	Free radical scavenging action Action against UV radiation penetration
Luffa cylindrical	Fruit	Triterpenoid saponins Flavonoids	LucyosideA,B,C,D,E,F Ginsenoside Lucynin A	Antioxidant Nourishing action to skin Emollient
Solanum lycopersicum	Fruit	Carotene	Lycopene Vitamin A, C, E Anthocyanin	Protection against neuro degenerative disease Antioxidant
Citrus limonum	Fruit	Alpha pinene Camphene Beta pinene Linalool	Ascorbic acid	Potent antioxidant action Removing dead skin cells Emollient
Piper longum	Fruit	Alkaloids Amides Carbohydrates	Piperine Methyl piperine Piperinic acid	Antioxidant UV protectant
Culticum reflexum	Leaves	Phenolic compounds Flavanols	Rutin Kaemferol Quercitin	Antioxidant, Free radical scavenger
Pimenta psuedocaryophyllus	Leaves	Flavonoids Polyphenols	n.r	Inhibit UV radiation induced inflammation and oxidative stress
Portulaca oleracea	Leaves	Carotenoids Betaxanthins	Omega 3 fatty acid Eicosapentanoic acid	Anti-mutagenic Antioxidant
Aloe barbadensis	Leaves	Vitamins Aminoacids Polysaccharides	Oleic acid Caprylic acid Stearic acid	Moisturizer Immune enhancer
Glycine max	Seeds	Soy isoflavone	Genistein	Antioxidant,Reduces photodamage and transepidermal water loss
Moringa oleifera	seeds	Lipid fraction	n.r	UV absorber
Pongamia glabra	Seeds	n.r	Pongamol Karanjin	UV absorber
Silybummarianum	Seeds	Flavonolignans	Silymarin Silybin Silydianin	Inhibit UV induced damage Antioxidant
Vitis vinifera	Seeds	Polyphenols	Flavan 3-ol derivatives Catechin Oligomeric proanthocyanidins.	Free radical scavenging effect Reducing oxidative stress and apoptosis
Juglans regia	Seeds	Amino acids Carbohydrates Polyunsaturated fatty acid	Juglone Linoleic acid Linolenic acid	Keratin protection of skin Antioxidant

Coeffea genus	Green dry coffee bean	Lipid fraction	Linoleic acid Palmitic acid	UV-absorber, emollient
Pinus pinaster	Bark	Phenolic compounds Polyphenols	Catechin, epicatechin, taxifolin	Reduces UVB-induced skin erythema,free-radical-scavenging effect
Rubia codifolia	Root	Flavonoids Glycosides	Pseudopurpurin Manjistin Puroxanthin	Treat hyperpigmentation, Allergies, Sunburn
Curcuma longa	Rhizomes	Curcuminoids Volatile oils	Curcumin Demethoxy curcumin Turmerone Zingiberone	Hydroxyl radical scavenger UV protective action
Malus domestica	Peel	Phenolic phytochemicals Flavonoids	Quercetin Epicatechin Procyanidin b-2	Free radical scavenger Antioxidant
Camellia sinensis	n.r	Polyphenols	Epicatechin Epicatechin-3 gallate	Photostabilising capacity, anticarcinogenic, anti-inflammatory
Terminalia chebula	n.r	Polyphenols Flavanoids Tocopherols	Chebulinic acid Tannic acid Ellagic acid	Scavenger of DPPH radical, Lipid peroxidation
Daucus carota		Carotenoids	Beta carotene Oxyacetylene	Free radical scavenger Nourishes skin
Porphyra(algae)		Proteins	Mycoporine	UV absorbing action

The evaluation for sunscreen specificity include polyphenols of green tea extract of *Aloe barbadensis* aromatic compounds from lichens glycosides of aesculin and essential oil of *Murrayakoenigi* leaf. There was a strong evidence that DNA damaging UV light induces the accumulation of UV light absorbing flavonoids and other phenolics in dermal tissue of plant body[15].For the treatment and prevention of UV mediated diseases, a new possibility is offered by the anti-oxidants from natural resources. For example; considering the Iranian flora rich in medicinal plants, 4 plants were reported recently for its potential anti-oxidant activity. These include *Sambucus ebulus, Zea maize, Feijoasellowiana* and *Crataegus pentagy.*

NATURAL COMPOUNDS WITH PHOTOPROTECTIVE EFFECTS

I. FLAVANOIDS[1,2,3,16,17]

a. QUERCETIN

It is chemically 3,5,7,3'4'-pentahydroxy flavones. They are having antioxidant, anti-inflammatory effect which also provide protection against UV A and UV B radiations. A quercetin rich diet has been reported to inhibit the development of carcinogens induced rat mammary cancer, oral carcinogenesis. It is present in various common fruits and vegetables, beverages and herbs. The highest concentrations are found in onion. SPF of quercetin matches with a synthetic sunscreen agent called homosalate.

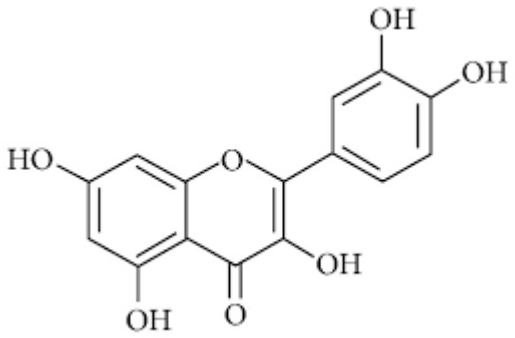

Fig 2: Quercetin

b. APIGENIN

It is chemically 5,7-dihydroxy flavones. They found to inhibit UV mediated induction of ornithine decarboxylase activity, and effective in UV A and UV B induced skin carcinogenesis. It is commonly found in *Calendula officinalis, Artemesia inculta* and *Cuminum cyminum*.

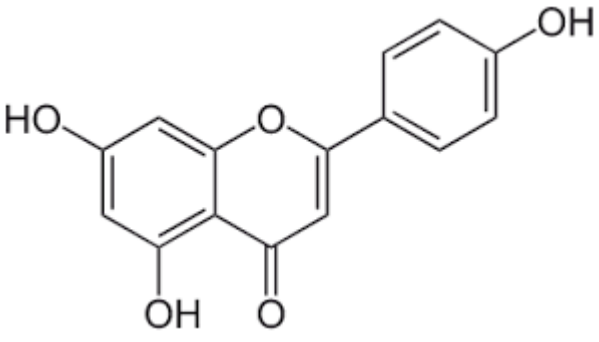

Fig 3: Apigenin

c.SILYMARIN

It is the standardized extract of flavonolignan in the ratio of 1:1 of diastereomer. Silibinin A and silibininB. Silymarin consist of silybin,silidianin and silicristin.They suppress immune system,anti-inflammatoryand prevent oxidative stress. It is commonly found in *Silybum marianum.*

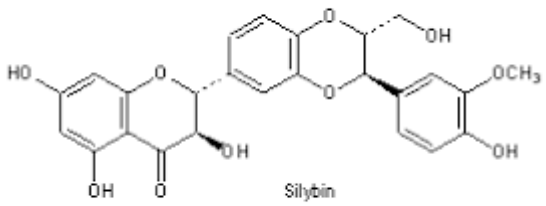

Fig 4: Silybin

II.POLYPHENOLS[1,2,3,16,17,18]

a. RESVERATROL

It is chemically trans 3'4'5' trihydroxystilbene.It is a fat soluble stilbene belongs to the class of polyphenolic compounds. They are having antioxidant, antimutagenic, and anti-inflammatory effect. On topical application, found to inhibit UV B induced tumor. They are commonly found in *Polygonum cuspidatum, Veratrum grandiflorum, Vitis vinifera* etc.

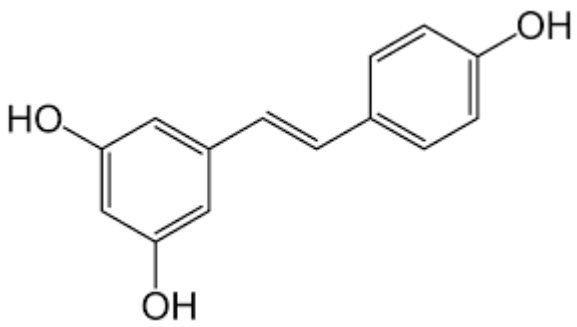

Fig 5: Resveratrol

b.TANNINS[1,16]

It consists of catechins including epicatechin, epicatechin 3 gallate,epigallocatechin, gallocatechin. They inactivate ROS and helps to reduce DNA damage and incidence of erythema.They are commonly found in green tea, pomegranate and amla.

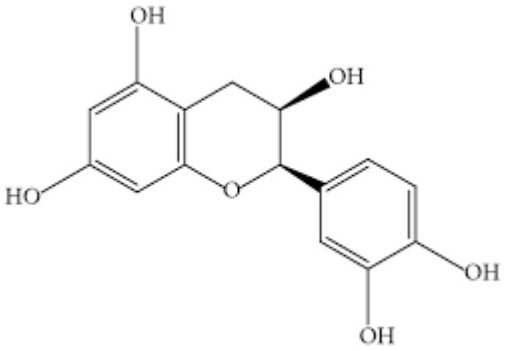

Fig 6: Epicatechin

c. CINNAMIC ACID DERIVATIVES[14]

One of the best candidates for UVB filters in the (310–325 nm) wavelength is cinnamic acid derivatives. A significant protection values in both UV A and UV B regions has been reported in a formulation containing a mixture of polyphenols including caffeic acid with caffeic acid phenylethyl ester or dimethyl caffeic acid, along with their photoprotective activity.Cinnamic acid derivatives are also considered to be best candidate for UVB filters which include Carnuaba wax obtained from *Copernicia cerifera* found to act as organic filters. A recent study which comprises of the encapsulation of titanium dioxide with carnauba wax produces significant increase in sun protection factor.

III.ANTHOCYANINS[1,16]

It includes cyanidin- 3 glycosides, pelargonidin, nasunin. They function as a potent antioxidant; protect cell membrane lipids from oxidation. Pelargonidin protect tyrosine from peroxynitrite. They also inhibit the adverse effects of UV B exposure. They are commonly found in Punicagranatum, cereal grains, yellow to purple colored fruits and berries.

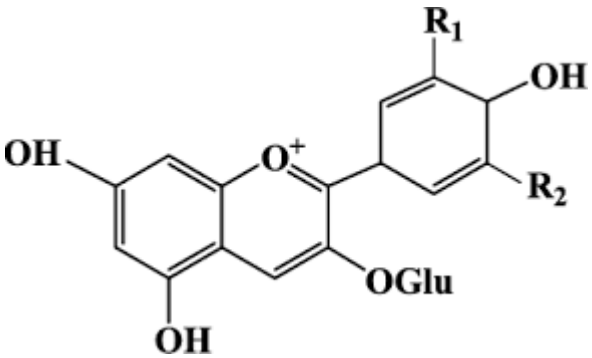

Fig 7: Anthocyanins

IV.CAROTENOIDS[2, 6, 19]

They are derivatives of phytoene and phytofluene. It includes beta carotene, lycopene.Carotenoids are potent singlet oxygen quenchers.They act as antioxidant, photooxidant,increase resistance to oxidative stress. It also gives protection against macular degeneration.They are commonly found in *Solanum lycopersicum* and *Daucus carola.*

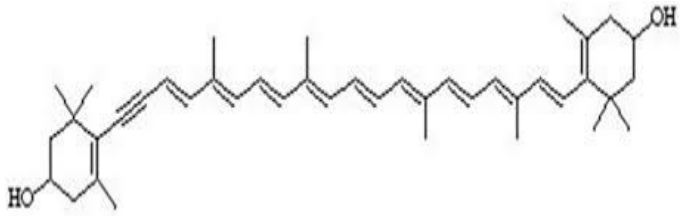

Fig 8: Carotenoids

CONCLUSION

Different category of compounds including flavonoids, cinnamic acid derivatives, carotenoids, polyphenols and anthocyanins have been incorporated in various herbal sunscreen preparations and were found to be effective. These compounds have essential characteristics for sunscreen since they possess potent photoprotection and antioxidant effects. Synergistic action was reported in the combination of different extracts with increased sun protection factor. Herbal sunscreens with combination of different plant extracts can

effectively replace synthetic sun screens in the near future due to their minimal side effects and greater potency.

FUTURE PERSPECTIVE

It is necessary to carry out future research to identify herbal photoprotective drugs and to increase its sun protection factor using synergistic combinations. In addition, it is important to find new methodologies to evaluate their efficacy.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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