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Review

Plant-Derived bioactive compounds as skin photo protection agents

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Abstract

Exposure to the sun is unavoidable in daily life. Ultra-violet radiations are the major component of sunlight and play a significant role in damaging the skin. They induce many skin problems like erythema, sun burn, rashes as well as skin cancer. Although, the protective layer of earth, ozone layer, filters most of the damaging radiations from sun, but with the dramatic rise in pollution, global warming is reaching at its peak point. These pollutants deteriorate the protective ozone layer of earth, resulting in its thinning which in turn allows the passage of hazardous solar radiations to the earth. These radiations act as the most potent irritant for the skin cells. In order to avoid these hazardous effects of UV radiations, there is an emerging demand for the use of photo protectants. Manufacturers of various cosmetic and skin care companies are focusing on natural compounds to deal with skin problems caused by UV radiations. It includes phytochemicals and bioactive compounds from the plants. As these are natural and economic, they don't leave any damaging effect on body and are best photo protectants against UV radiations. There are several plants with their chemical compounds derived and studied for their photoprotective role. Most of them are proven best for cosmetic remedies. This review will provide a look over the plant derived bioactive compounds of Southeast Asia with their photo protectant effect.

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Introduction

Skin is a very important organ of human that covers the whole-body surface and performs numerous functions like defense and protection against the physical and chemical agents. It acts as a physical barrier between body and harsh environmental conditions. It keeps the water and electrolyte balance in check, performs a secretory function like production of sweat that helps in regulating the temperature of the body and in eliminating waste products. Sebaceous glands are also located on skin which produces sebum that creates a skin barrier against attacking microorganisms. Many sensory receptors are located over skin therefore it also acts as a sensory organ to sensitize the presence of touch, pain, and temperature. Any damage or disease to this precious organ can lead to serious threat to the health of the patient [1].

Nature has provided skin cells with inborn capacity of protecting itself by synthesizing melanin pigment in melanocytes. This pigment has an ability to absorb damaging solar radiations and prevent them from producing any skin changes. It performs its photoprotecting effect by absorbing UV radiations and shielding the epidermal cells of skin from DNA damage [2]. Human skin cells are constantly replaced by the new healthy skin cells in order to maintain its function and stability. With age the number of mitotic divisions in skin cells is reduced and they are countered by several genetic changes as a result of mutations thus bringing the skin toward unavoidable phenomenon named as skin aging [3]. Skin aging is a physiological procedure that occurs as a result of physical and chemical processes taking place inside the body. This natural procedure occurs with time and it cannot be stopped but can be delayed [4]. Several factors are involved that cause aging. They include intrinsic as well as extrinsic factors. Intrinsic factors include genetic changes like mutations while extrinsic factors include photoaging, which is the damaging effect of environmental radiations over skin. These include damaging radiations from sun, air pollution, inflammatory processes taking place in body etc. Both intrinsic and extrinsic mechanisms result in the excessive production of free radicals, reduction in the skin elasticity, breakage in the collagen fibers of skin that in turn enhance the process of aging [5].

Our skin is constantly exposed to several environmental, biological and a-biological factors that contribute in damaging the skin and lowering its protective action. If this damage continues at the same rate, then population have to face lot of problems regarding skin health. People of Southeast Asia are highly getting exposed to the intense levels of environmental pollution. They are increasingly getting affected by the skin diseases like sun burns, rashes, erythema, skin cancers, and allergic reactions to ultraviolet radiations coming from sun [6]. Solar radiation consists of visible light, infra-red radiation, and ultraviolet radiations. Out of these only the blue light (part of visible light), ultraviolet A and B (types of UV radiations) are potentially harmful for human skin. Although the naturally occurring ozone layer filter most of the damaging radiations from sun but with rise in population and increase in pollution global warming is reaching at the peak levels. These pollutants deteriorate the protective ozone layer of earth, resulting in its thinning which in turn allows the passage of hazardous solar radiations to the earth. These radiations act as the most potent irritant for the skin cells. They are majorly contributing to developing skin cancers and immunosuppression in the people of southeast Asia. They also cause photosensitivity thus increasing the sensitivity of skin to different hazardous chemicals and pollutants leading to allergic and oncogenic reactions [7].

There are two types of photoprotecting agents. One is chemical and other one is physical. Chemical photoprotective are applied over the skin for the purpose of absorbing damaging radiations from sun. chemical photoprotective provide a limited wavelength range of protection against ultraviolet radiation therefore the photoprotective that are chemical in nature are composed of different chemical compounds with different ranges of absorbing UV radiations. Physical photoprotective agents reflect the harmful radiations from the surface and don't allow them to reach up to the skin and produce their damaging effects [8].

Due to all these damaging effects of UV radiations, photoprotecting products should be consumed to reduce the effects of radiations on skin. There is a need for manufacturing therapeutic photoprotective that protect the skin and boost its defending efficiency. Manufacturers of various cosmetic and skin care companies are focusing on natural compounds to deal with all these problems and to treat skin diseases with the use of bioactive plant derived compounds. Medicinal plants are the natural compounds which contain both primary and secondary metabolites that play their photoprotective role against skin ailments caused by UV radiations [9]. The current study is the review of literature regarding the antioxidant, photoprotecting and antiaging properties of plant derived chemical compounds.

Ultraviolet radiations

Radiations coming from sun are electromagnetic waves that range from infrared (IR) radiations to ultraviolet (UV) radiations. It also contains visible light. All radiations coming from the sun are not harmful to the body, there are also beneficial sun rays that contain the molecules required for the activation of Vitamin D in the human skin. Vitamin D is essential for the absorption of calcium in the body. Yellow and red light (part of visible light) play their protective role on skin by reducing inflammation and strengthening the skin [10]. But along with these beneficial effects most of the radiations from the sun are very much damaging for the human skin these include Ultraviolet radiations A and B. Usually these radiations are filtered from the protective ozone layer of the earth but with the increase in global warming and rising pollution the ozone layer is getting thin day by day thus allowing the harmful radiations to reach the earth. UV radiations are classified into UVA, UVB and UVC. The wavelength of UVA is from 320nm to 400nm. The wavelength of UVB is from 290nm to 320nm and the wavelength of UVC radiation ranges from 200nm to 290nm (Table 1). UV radiations are considered as the most potent irritant and stimulant to damaging the skin cells. UV radiations that reach to the earth are UVA and UVB and their extent is affected by the altitude, area

locality, season and weather of the part of earth. As in the summer the composition of UV radiation is 96.5% UVA and 3.5% UVB. These radiations are highly potent during the time between 10am in the morning and 4pm in evening [11].

UVC radiation is the most energetic radiation out of all UV radiations, and it possesses high threat for human skin damage, but one beneficial effect of this radiation is that it doesn't reaches up to the earth as it is filtered by ozone layer.

Effects of UV radiation on skin

UV radiations coming from sun are very much damaging to the human skin and contribute to producing several skin diseases that are getting very much common day by day among the people of southeast Asia. UV Radiation contribute to producing skin changes by two ways. First is the direct absorption of mutagenic radiations from the skin that cause DNA damage leading to carcinogenesis and the other way is these radiations stimulate the production of free radicals that are itself damaging to the skin [12]. UVA radiation is popular in causing immune-suppression, aging of skin cells and most lethally skin cancer. UVB has both acute and chronic responses to skin. In acute reactions it includes skin problems like erythema, edema, skin burns, hardening and darkening of skin. Chronic responses of skin to the exposure of UVB include immune-suppression, photosensitivity, aging and carcinogenesis (Fig 1) All these changes may be persistent or can stay only for few days or hours [13].

Along with negative effects of these radiations on skin UVA also possesses beneficial effect on skin as it enhances vitamin D production on skin. It also causes tanning of skin by over production of melanin pigment.

Skin damaging agents

Free radicals

Free radicals are the actual skin damaging agents that contain oxygenated molecules in free state which are highly reactive. On one side oxygen is very much necessary for a living being for respiration on the same side reactive oxygen species (ROS) are very lethal and toxic even carcinogenic in nature. The ROS species consist of superoxide, H_2O_2 and hydroxyl radical. The damage caused by the free radicals or (ROS) is generally termed as oxidative stress [21]. (Fig 3) Several mechanisms are involved through which free oxygen radicals cause oxidative stress. These radicals accelerate many underlying signaling pathways that are directly involved in causing inflammation and cellular damage. Production of free radicals occur routinely in the body as a result of metabolic processes, but their overproduction can lead to serious consequences that may include inflammation, immunological problems, aging as well as cancer. Despite the changes on the skin, they also cause systemic problems like cardiovascular problems, eye problems like cataract, autoimmune diseases, Alzheimer disease [22] and metabolic disorders like diabetes. These changes occur at the cellular level affecting cell structure, DNA, their structural and functional components like lipids, carbohydrates and proteins [23].

Photoprotection

Radiations coming from sun damage the human body systems especially skin. Although the skin is gifted with the natural photoprotective mechanisms like endogenous melanin pigment [2] and epidermal cell renewing capability but, the direct exposure to the sun without any photoprotection can prove highly damaging to the skin because the amount of melanin in all people is not sufficient to perform the function of hundred percent protection against radiations. Along with this human being also have to face the unavoidable process of aging which weaken the integrity and elasticity of skin. The environment in which the human lives is full of oxidative stress generated by the free radicals affect the human skin. Human skin can tolerate about 105 hits of oxidative stress daily without any damage to the organ. The DNA and other metabolic processes remain stable and working with such a level of oxidative stress. Our body has a mechanism of developing antioxidants that protect the body and skin from skin damaging agents [24]. Working and production of these antioxidants gradually decline with age making skin more prone to the damaging effects of free radicals. So, in order to regain the antioxidant and self-protecting capability of human body there is a continuous need of substances that guard the skin on daily basis from the hits of oxidative stress. The use of these substances for defending oneself from the damaging effects of radiation is called photoprotection. (Fig 2) There are several photoprotecting compounds available that can be used for their beneficial effects. These include cosmetics, as well as compounds from the natural sources [25].

Photoprotection is also known as sun screening. Sunscreens are extensively being used throughout the world. They provide a shielding effect over skin and provide protection against the damaging effects of all types of lethal solar radiation. There are different photoprotecting mechanisms that can be utilized in manufacturing of sunscreen products. These are broadly classified into 3 types. First is stimulation and activation of natural photoprotective in skin which are melanin pigments. This can be achieved by enhancing the enzymatic activity of tyrosinase enzyme which is responsible for the synthesis of melanin pigment. Second is application of the shield over the skin that will act as a physical barrier between the radiations and skin like the physical and chemical photoprotective described above. The third mechanism is by potentiating the antioxidant, anti-inflammatory, and anti-aging potential of the body tissues. Maintenance of the integrity and collagen component of skin that will itself protect the skin from harmful effects of radiations [26].

Natural photoprotecting agents

The use of plants is gaining inspiration with time because they belong to nature and possess lesser side effects than synthetic compounds. Plants are used for medication, in diet as well as for beautification in cosmetics from a long time. As ultraviolet radiations are continuously coming from the sun and have a strong action in damaging the skin and causing sun burns, rashes, skin diseases, skin cancer there is a constant need of protection against these radiations. Medicinal plants have a great potential in protecting the skin against the lethal effects of these radiations due to their antioxidant and skin protecting effects. Antioxidants like vitamin C and vitamin E phenolic compounds perform their protective role for fighting with the reactive oxygen species generated by

the UV radiations. Now a days manufacturers of different cosmetic companies are greatly focusing on the use of these natural compounds from the plant origin that have the potential of protecting against UV radiations and promote the healthy skin in a better way. These chemicals absorb the radiations and prevent the damage. The most common UV absorbents are squalane, apigenin, flavonoids from plant origin. Squalane is extensively found in olive oil, it plays its role in protecting skin's lipid. Squalane is itself a protecting lipid of skin. Allantoin is present in comfrey plant. It belongs to nucleotide group; it is also naturally found in body for absorbing the definite range of UV radiations from sun that damage the body's DNA. It acts as emollient, antiallergic and soothing compound in preparations like antiacne, sun blocks, lotions etc. according to some research allantoin has also confirmed skin repairing activity [27].

Bioactive compounds from plants acting as photoprotective agent

Bioactive compounds from plants involve both primary metabolites as well as secondary metabolites. These are ascorbate, tocopherol, carotenoids, polyphenols, flavonoids etc. they have their common as well as distinct mechanism of action in preventing skin damage and cancers mentioned in Table 2. Ascorbate is well known for its antioxidant activity by reducing the oxidative stress generated by ROS. Tocopherol also possesses antioxidant property due to its capability to prevent lipid membrane peroxidation thus strengthening the skin against environmental insults. Carotenoids absorb UV radiations from sun in turn protecting the skin from their harmful effects. These metabolites play most of the roles in plants either they are in defense of plant, metabolism, nutrition, photosynthesis etc. there are distinct metabolites engaged in gifting the plants with capability for protecting against oxidative stress. Primary metabolites include vitamins, proteins, and lipids. [28]

Primary metabolites

Vitamin A: Vitamin A is a fat-soluble vitamin. It exists as a primary metabolite in many plants like carrots, spinach, pumpkin, potato. vitamin A possesses remarkable effect over skin health. It can be applied in both systemic and local ways. In both ways it shows anti-photo carcinogenic activity by several mechanisms that include inhibition of excessive cell proliferation, that is a key factor leading to cancer. It also absorbs UV radiation from sun thus protecting the skin from its lethal effects. Erythema caused by the severe exposure to the UVB radiations is also prevented by the retinyl palmitate which is a derivative of Vitamin A [29].

Vitamin C: It is a water-soluble vitamin found in many plants specially in citrus plants like lemon peel and orange. Use of Vitamin C has proved its antioxidant and photo protectant ability [30]. Vitamin C performs its antioxidant activity by enhancing the expression and regulation of genes that are involved in the synthesis of antioxidant enzymes [31]. These antioxidant enzymes initiate and manage the mechanisms to combat oxidative stress caused by free radicals generated from the UV radiations. Vitamin C is famous against protecting damage caused by UVA induced oxidative stress. It also inhibits enhanced apoptosis and regularize the cell cycle, involved in DNA repair and maintain the health and stability of skin. [32]

Vitamin E:

It is a fat-soluble compound that consist of four tocopherols [32]. Canola oil is the richest source of vitamin E [33]. The antioxidant and sun screening effect of vitamin C is potentiated by combining it with Vitamin E [34]. Vitamin E is found to be a strong photoprotective. It also enhances the hydration, elasticity and softness of skin and stabilizes the skin by strengthening of collagen fibers [35]. After topical administration of Vitamin E, it gets incorporated in the intracellular lipid structure of cellular membranes of skin thus increasing its integrity and protecting it from the irritants. It is used to treat several skin conditions like atopic dermatitis, skin cancer [36] acne, scleroderma [37].

Fatty acids

Essential fatty acids as their name indicate are not synthesized inside the body so they must be taken from outside in the form of supplements, diet or medication. These fatty acids have several beneficial effects in the without which the normal functioning of the body systems will become impossible. They can be obtained from the natural sources like seeds, fruits, nuts in the form of oil. Fatty acids are potent antioxidants [38]. Lenoleic acid (LA) and gamma lenoleic acid (GLA) are among the most important fatty acids required in the body. LA can be easily obtained from the plants like wheat, soybean sesame and sunflower seed oil etc. on the other hand oils of borage is a richest source of GLA. these fatty acids play their significant role in protecting the skin by enhancing the skin hydration, increasing the proliferative activity of epidermal cells to replace worn out old dead skin cells. Thus, in this way they regulate the skin balance and defend the skin from the harmful effects of harsh environmental physical and chemical condition thus providing a screening to the skin and potentiating photoprotection. Eicosa-pentaenoic acid (EPA) is another essential fatty acid that's have shown a remarkable reduction in erythemal skin changes caused by chronic exposure to UVB [47]. In one study results have shown the potential of EPA in filtering the UV radiations from sun thus protecting the skin from its lethal effects. So, it was concluded from the study that the use of EPA for prolonged duration can result in preventing against development of skin cancer.

Secondary metabolites

Anthocyanidins and proanthocyanins

These are the polyphenolic compounds found in many plants like blackberry, honey berry and bilberry. They have a potential in repairing damaged DNA and reverse mutations, normalize the nucleotide derangements. Berry juices rich in anthocyanins have proved to be effective in skin cell renewal. There antioxidant activity is four times more potent than Vitamin E. Nasunin, a type of anthocyanidin is seemed to interfere with the reactive oxygen species generating mechanisms in body [48]. Cyanidins inactivates the enzymes which are involved in the breakage of connective tissue of skin thus promoting the skin integrity and stability. Proanthocyanins are the potent inhibitors of carcinogenic mutations caused by UV radiations and other carcinogenic factors. Proanthocyanins are richly found in grape seeds.

Extensive studies have been conducted on the application of grape seed proanthocyanins as antioxidants and anticarcinogens. They also act as an immunomodulators in supporting the immune system against oxidative stress induced by free radicals. Tumor cells when treated with these proanthocyanins show a significant rise in deaths of cancer cells [49].

Resveratol

It is a plant derived chemical compound found in grapes, peanuts, crane berry etc. Theses herbs are extensively used for the purpose of medication in cancers and other disorders. The anti skin cancer activity of resveratol is documented in many researches. It has shown to suppress the cancer proliferation in mouse skin treated with cancer inducing chemicals. Resveratol also reduces oxidative stress and skin changes like edema induced by UVB when applied topically. Resveratol not only slows down the process of tumor formation but also inhibits the underlying mechanism of tumor formation. This property has been checked both pre and post treatment of the Resveratol [40].

Quercetin

Quercetin belongs to the class of flavonoids that possess strong antioxidant and anti-inflammatory properties. It is also popular for its immunomodulatory action, enhance the immunity against free radicals thus protecting the body against oxidative stress. There are more than 100 herbal plants that contain Quercetin. Remarkable concentrations are known to found in onion and other fruits and vegetables. Research conducted on mice induced with skin carcinogens have proved the antimutagenic effect of Quercetin when applied locally. Quercetin modulates many underlying signaling pathways in prevention of carcinogenesis. It induces apoptosis and regulate the generation of tumor necrosis factor [43]. It is also popular due to its sun screening effect against UVA and UVB radiations.

Silymarin

It is a plant derived bioactive compound found in *Silybummarianum* commonly known as milk thistle. Topical application of silymarin possesses anticarcinogenic activity. A research study conducted on hairless mice treated with UVB induced cancer has shown the reduction in numbers of tumors by 92%. It also reduces apoptosis thus preventing the cells from premature death thus improving the health of skin cells. In vivo studies also confirm the potential of silymarin in reducing UVB induced oxidative stress [50]

Apigenin

It is plant derived metabolite present in many herbs like carrot, citrus fruit, yarrow etc. it has reported anticarcinogenic activities induced by both UVA and UVB radiations. It inhibits the excessive cell growth and induce apoptosis [51]. Apigenin has proved its chemo preventive function against skin cancer. It stimulates the expression of gene that code for antiangiogenic protein. Antiangiogenic protein in turn inhibits cancer formation as a result of exposure to UV radiation. Cancer is usually associated with the generation of several inflammatory mediators that weaken the immune system. Apigenin is found to reduce the levels of inflammatory mediators specially cytokines, interleukin 6 and 12 [45].

Curcumin

It is plant derived pigment obtained from the rhizomes of *Curcuma longa,* commonly named as haldi and turmeric. It is yellow odorless compound that has anti-inflammatory, anti-cancer and as well as antioxidant potential. It is documented that the topical application of this pigment results in inhibition of generation of reactive oxygen species from UVA radiations coming from sun. it has proven to halt the apoptotic changes caused by UV irradiation in human epidermoid carcinoma [46].

Conclusion

With increasing population, the rate of pollution is also increasing, and it is increasing global warming thus damaging the ozone layer. So, the hazardous radiations from sun directly come on skin and cause several biological changes in the body that lead to different skin problems like erythema, redness, irritation, and cancer. Use of sunscreen products is becoming mandatory now a days specially in summer. Use of natural products becoming common and it is not unusual to use natural products in sunscreen products. Bioactive compounds from plants have a potential to protect the skin from UV radiation through different mechanism. So, the use of these compounds like polyphenols, flavonoids, lipids alone or in combination with other compounds can prove very much beneficial in enhancing sun screening. More research and studies on these bio active compounds individually are still required to further elaborate their role in skin protection so that it can aid in manufacturing a product totally based on plant derived bio-active compounds with ideal outcome.

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Table 1: Types of radiations coming from sun and their effect on human skin

Type of radiation	Further types	Wavelength	Effects on skin	References
Infra-red radiation	Short IR radiations	750-1000nm	Skin burns	[14]
	Medium IR radiations	1000-1500nm		
	Long IR radiations	>1500nm		
Visible radiation	Complete spectrum of light	400-750nm	---	[15]
	Yellow light	560-590	Photoprotective	[10]
	Red light	620-750	Healing, Reduce inflammation, Reduce skin fibrosis	[16]
	Blue light	400-500nm	DNA damage, Carcinogenic	[17]
Ultraviolet radiation	UVA	320-400	Photoaging DNA damage Immunosuppression Cancer	[18]
	UVB	290-320	Erythema Edema Darkening of skin	[19]
	UVC	22-290	No effect	[20]

Table 2: Plant derived bio-active compounds and their mechanism of action

Bioactive compound	Plant source	Action	Mechanism	Reference
Primary metabolites				
Vitamin A (Retinoids, retinyl palmitate)	sweet potatoes, spinach, carrots, pumpkin, and tomatoes	Anti-photocarcinogenic	Inhibit cell division, absorb UV radiation, prevent DNA damage	[29]
Vitamin C	Orange, lemon	Antioxidant, photoprotective	Promote the expression of genes involved in synthesis of antioxidant enzymes Cause DNA repair	[31]
Vitamin E	Canola oil, Wheat germ, Rapeseed, soya	Antiaging	incorporated in the intracellular lipid structure of cellular membranes of skin	[33]
Fatty acids	Wheat, Soybean Sesame and Sunflower	Antiaging, Antioxidant	Promotes Skin hydration, Eicosapentaenoic acid filter UV radiation	[38]
Secondary metabolites				
Anthocyanidins and proanthocyanins	blackberry, honey berry and bilberry	Photoprotective	potent inhibitors of carcinogenic mutations by UV radiations	[39]

Resveratol	Grapes, African myrrh	Skin anti-cancer	Suppress the proliferation of cancerous cells	[40]
Quercetin	Onion	Immunomodulatory and anti-mutagenic	Induce apoptosis and modulate several underlying cells signaling pathways	[41], [42], [43]
Silymarin	Milk thistle	Anticarcinogenic	Regulate apoptosis, reduce oxidative stress	[44]
Apigenin	Carrot, Citrus Fruit, Yarrow	Photoprotective, Anti-cancer	stimulate expression of gene that code for antiangiogenic protein.	[45]
Curcumin	Turmeric	Anti-oxidant and anti-cancer	inhibition of generation of reactive oxygen species from UVA radiations, cause apoptosis in epidermoid cancer cells	[46]

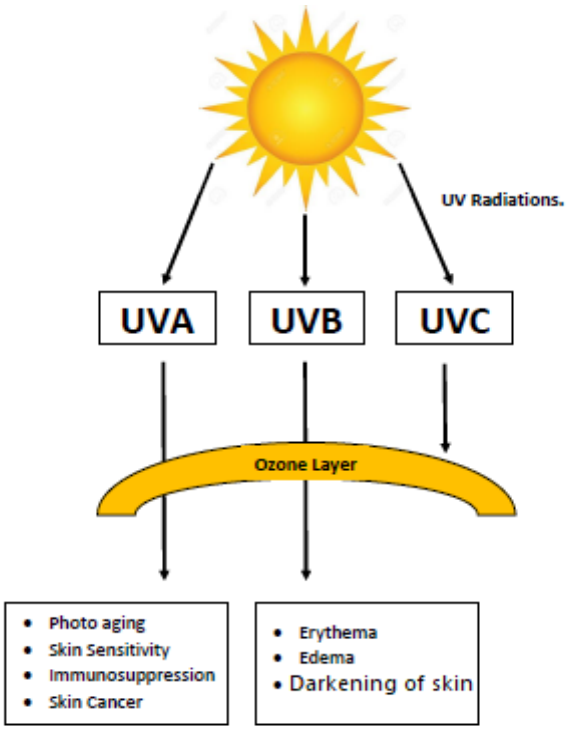

Fig: 1. Ultra Violet radiations from sun and their Effects on skin

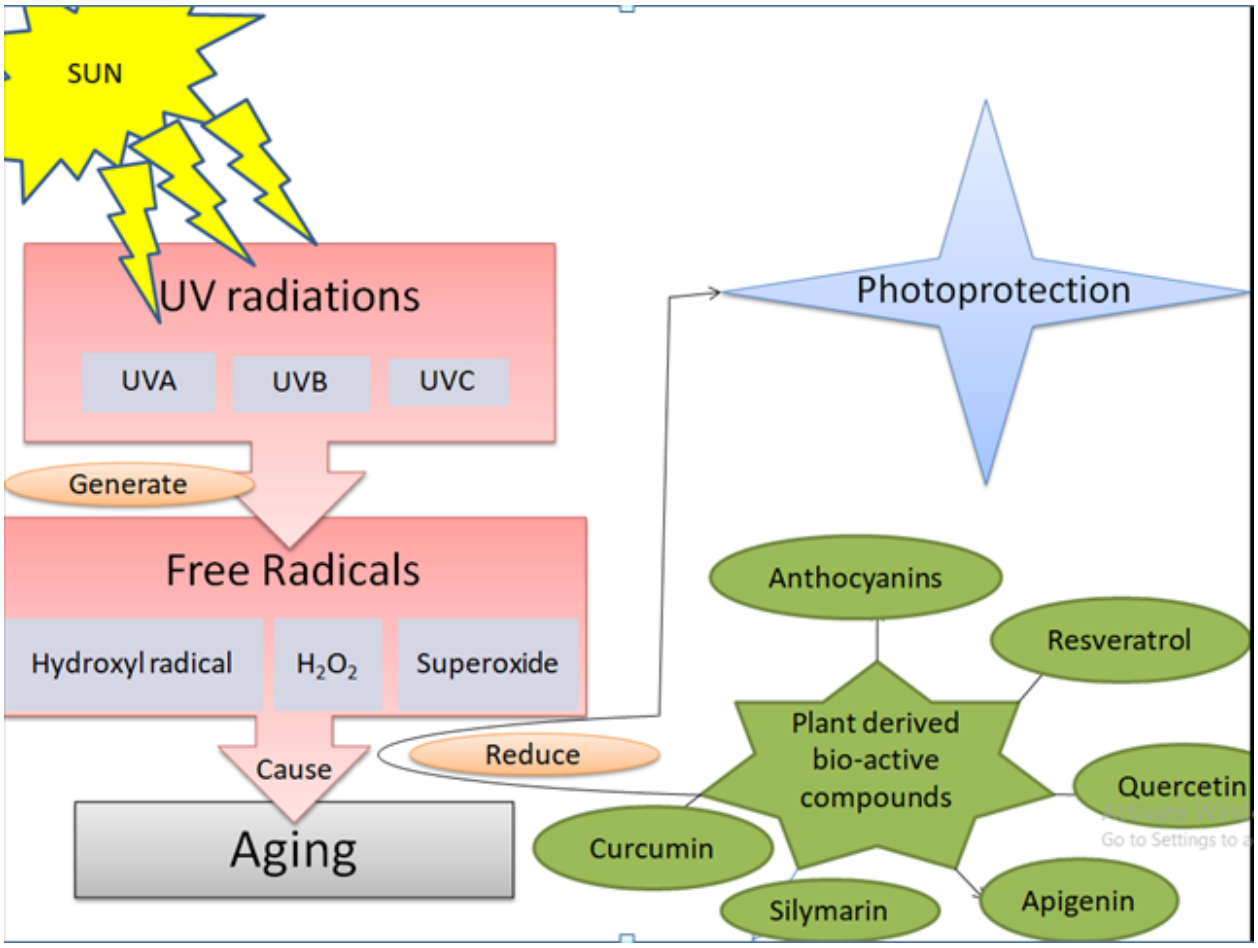

Fig: 2. Generation of free radicals from UV radiation and photoprotection through Plant derived bio-active compounds.