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HERBAL SUNSCREENS IN THE ERA OF GREEN COSMECEUTICALS: REVIEWING THE ROLE OF POLYPHENOLS

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ABSTRACT

The rising consumer demand for environmentally friendly and skin-safe photoprotective products has catalysed research into plant-derived sunscreens. Polyphenols, a large class of plant secondary metabolites including flavonoids, phenolic acids, stilbenes, and tannins, possess UV-absorbing, antioxidant, anti-inflammatory, and DNA-protective activities that make them promising cosmeceutical ingredients. This review synthesizes current evidence on the mechanisms by which polyphenols confer photoprotection, evaluates formulation strategies and analytical approaches for herbal sunscreens, discusses safety and regulatory considerations, and identifies gaps and future directions for translating polyphenolic actives into effective, standardized, and scalable green sunscreens.

KEYWORDS: Herbal sunscreen, Polyphenols, Green cosmeceuticals, Photoprotection, Formulation, SPF, UV-A, UV-B.

1. INTRODUCTION

Sunlight exposure is the principal environmental risk factor for photoaging, immunosuppression, and photo-carcinogenesis.[24,33] Conventional sunscreens rely on synthetic organic filters (e.g., avobenzone, octocrylene) and inorganic filters (zinc oxide, titanium dioxide) to attenuate ultraviolet (UV) radiation. Concerns about systemic absorption, endocrine disruption, and environmental impacts of some synthetic filters, together with consumer preference for natural ingredients, have driven interest in herbal and plant-based alternatives.[34,39]

Polyphenols are ubiquitous plant secondary metabolites characterized by multiple phenolic hydroxyl groups attached to aromatic rings. They occur widely in fruits, vegetables, leaves, seeds, and bark. Their multifunctional bioactivity direct UV absorption, free radical scavenging, metal chelation, and modulation of cellular stress responses, makes them candidate actives for topical photoprotection.[1,2,8]

This review focuses on

1. The photoprotective mechanisms of polyphenols.
2. Representative polyphenolic scaffolds used or proposed for sunscreen applications.
3. Formulation approaches to maximize stability, skin delivery, and broad-spectrum protection.
4. Methods to evaluate photoprotective performance.
5. Safety, standardization, and regulatory considerations relevant to green cosmeceuticals.

2. Classification and sources of polyphenols relevant to sunscreens

Polyphenols are commonly grouped into several classes[1,7,13]

- Flavonoids (e.g., quercetin, kaempferol, rutin, catechins) are abundant in green tea, grape seed, citrus, and buckwheat.[12.36]
- Phenolic acids (e.g., ferulic acid, caffeic acid, gallic acid) are common in cereal brans, coffee, and fruits.[4,9]
- Stilbenes (e.g., resveratrol) are found in grapes and berries.[11,45]
- Tannins and hydrolysable polyphenols (e.g., tannic acid) are present in bark and certain seeds.[20,42]

Many agro-industrial by-products (grape pomace, olive pomace, tea residues) are rich, low-cost sources of polyphenols and are attractive for sustainable ingredient supply chains.[38]

3. Mechanisms of photoprotection by polyphenols

Polyphenols contribute to skin photoprotection through several, often overlapping mechanisms

1. Direct UV absorption: Many polyphenols have conjugated aromatic systems that absorb in the UV-B and, to a lesser extent, UV-A ranges, providing intrinsic filtering capacity.[7,9,37]

2. Antioxidant activity: Polyphenols neutralize UV-generated reactive oxygen species (ROS), interrupt lipid peroxidation, and regenerate other antioxidants within the skin milieu.[1,14,29]

3. Anti-inflammatory effects: By modulating NF-κB, MAPK, and COX pathways, polyphenols reduce UV-induced erythema and inflammatory mediator release.[17,40,41]

4. DNA protection and repair modulation: Some polyphenols decrease the formation of cyclo-butane pyrimidine dimers (CPDs) and may upregulate DNA repair pathways.[1,16]

5. Photo-immunoprotecting: By attenuating UV-induced immunosuppression, polyphenols can contribute to defense against photo-carcinogenesis.[19,30]

6. Synergy with conventional filters: Polyphenols can stabilize labile organic filters (e.g., by quenching triplet states) or act as boosters to achieve the same SPF with lower concentrations of synthetic filters.[4, 39]

4. Representative polyphenolic actives and evidence

- Green tea catechins (epigallocatechin gallate, EGCG): Demonstrated antioxidant and anti-inflammatory protection in epidermal models; used as extract additives to reduce UV-mediated damage.[3,6,36]
- Ferulic acid: Absorbs UV and stabilizes formulations; commonly used with vitamins C and E to enhance photoprotection and photostability.[4]
- Resvertrol: Potent antioxidant and modulator of cellular stress responses; shows photoprotective effects in keratinocyte models.[11,45]
- Quercetin and rutin: Flavanols that absorb UV and exert antioxidative and anti-inflammatory effects.[12,42]

- Tannic acid and condensed tannins: High molar absorptivity in the UVB range; used in combination with polymers to form topical films/hydrogels with UV-attenuating properties.
- Rosmarinic acid and caffeic acid exhibit antioxidant and UV-absorbing properties.[9,3]
- Proanthocyanidins demonstrate collagen protection and antioxidant synergy.[5,20]

Evidence base includes in vitro spectrophotometric SPF estimates, cell culture assays (ROS, CPDs, cytokine release), ex vivo skin models, and a smaller set of in vivo or human volunteer studies assessing erythema reduction and SPF contribution when formulated.

5. Formulation strategies

Challenges when using polyphenols include poor water solubility, chemical instability (oxidation, photodegradation), potential for color and Odor, and skin penetration limitations. Strategies to address these include:[25,26]

- Encapsulation: Liposomes, solid lipid nanoparticles, polymeric nanoparticles, nano-emulsions, and cyclodextrin complexes improve solubility, photostability, and controlled release.
- Chemical derivatization: Esterification or glycosylation can improve solubility and skin affinity, though changes in bioactivity must be validated.
- Blend design: Combining multiple polyphenols or blending with inorganic filters (zinc oxide or TiO2) or UV absorbers to achieve broad-spectrum protection.
- Antioxidant networks: Co-formulation with vitamins (C, E), niacinamide, and chelators (EDTA alternatives) to minimize oxidation and synergize photoprotective action.[4,15]
- pH control and oxygen exclusion: Formulation pH, antioxidant preservatives, chelators, and opaque/airless packaging reduce degradation.

6. Analytical evaluation and claims substantiation

Standardized testing is essential to substantiate sunscreen claims. Key methods include[39,48]

- In vitro SPF assays: Diffuse transmittance/absorbance methods (ISO 24443, Mansur method) provide preliminary SPF estimates for extracts and formulations.[21,46,47]
- In vivo SPF testing: Human volunteer erythema endpoint testing per international standards (ISO 24444) remains the regulatory gold standard for SPF labelling.[22]
- PUVA/UVA-PF methods: Persistent pigment darkening (PPD) and critical wavelength determinations for UVA protection evaluation.[23]

- Photostability testing: Measure retention of absorbance and filter performance after UV exposure.
- Cellular/biomarker assays: ROS, inflammatory cytokines, CPD quantification, and gene expression analyses for mechanistic substantiation.[16,42]
- Safety testing: Patch tests, irritation, sensitization panels, and percutaneous absorption studies to assess systemic exposure.

For herbal sunscreens, robust characterization of polyphenolic content (HPLC, LC-MS), batch-to-batch consistency, and stability are required to translate lab findings to marketable products.

7. Comprehensive Functional Classification of Plant-Derived Polyphenols for Photoprotection and Cosmeceutical Applications.

Table 1: Antioxidant / ROS-Scavenging Polyphenols.

S. No	Polyphenol	Chemical Class	Dermatological Role	Mechanistic Basis	Major Natural Source
1.	Apigenin	Flavone	Anti-inflammatory	ROS scavenging	*Matricaria chamomilla, Petroselinum crispum*
2.	Bisdemethoxycurcumin	Curcuminoid	Antioxidant	Radical scavenging	*Curcuma longa*
3.	Carnosic acid	Phenolic diterpene	Strong antioxidant	Lipid peroxidation inhibition	*Rosmarinus officinalis*
4.	Chlorogenic acid	Caffeoylquinic acid	Anti-photoaging	ROS suppression	*Coffea arabica*
5.	Chrysin	Flavone	Antioxidant	Free radical scavenging	*Apis mellifera* (propolis source)
6.	Cyanidin	Anthocyanidin	Antioxidant	ROS scavenging	*Vaccinium spp.*
7.	Dihydromyricetin	Flavanonol	Anti-inflammatory	ROS reduction	*Ampelopsis grossedentata*
8.	Embelin	Benzoquinone	Antioxidant	ROS scavenging	*Embelia ribes*
9	Gallic acid	Phenolic acid	Antioxidant	Radical scavenging	*Phyllanthus emblica*
10.	Glycitein	Isoflavone	Anti-photoaging	Antioxidant	*Glycine max*
11.	Myricetin	Flavonol	UV-ROS inhibition	Antioxidant	*Vaccinium myrtillus*
12.	Narirutin	Flavanone glycoside	Antioxidant	ROS inhibition	*Citrus sinensis*
13.	Protocatechuic acid	Phenolic acid	DNA protection	Antioxidant	*Hibiscus sabdariffa*
14.	Syringic acid	Phenolic acid	Antioxidant	ROS inhibition	*Vitis vinifera*
15.	Taxifolin	Flavanonol	Antioxidant	ROS inhibition	*Allium cepa*
16.	Vanillic acid	Phenolic acid	Antioxidant	Free radical scavenging	*Vanilla planifolia*

Fig. 1: Mechanism of Antioxidant / ROS-Scavenging of Polyphenols.

Table 2: Anti-Inflammatory (NF-κB / COX / Cytokine Modulation).

S. No.	Polyphenol	Chemical Class	Dermatological Role	Mechanistic Basis	Major Natural Source
1.	Apigenin	Flavone	Anti-inflammatory	NF-κB inhibition	*Matricaria chamomilla*
2.	Baicalein	Flavone	UVA protection	COX-2 suppression	*Scutellaria baicalensis*
3.	Curcumin	Diarylheptanoid	Anti-inflammatory	NF-κB inhibition	*Curcuma longa*
4.	Daphnetin	Coumarin derivative	Anti-inflammatory	Cytokine suppression	*Daphne odora*
5.	Esculetin	Coumarin derivative	Anti-inflammatory	COX inhibition	*Aesculus hippocastanum*
6.	Luteolin	Flavone	Anti-inflammatory	COX suppression	*Apium graveolens*
7.	Magnolol	Biphenol	Anti-inflammatory	NF-κB inhibition	*Magnolia officinalis*
8.	Oroxylin A	Flavone	Anti-inflammatory	NF-κB inhibition	*Scutellaria baicalensis*
9.	Rosmarinic acid	Phenolic ester	UV protection	Anti-inflammatory	*Rosmarinus officinalis*
10.	Scopoletin	Coumarin	Skin soothing	Anti-inflammatory	*Morinda citrifolia*
11.	Verbascoside	Phenylpropanoid glycoside	Anti-inflammatory	Cytokine inhibition	*Verbena officinalis*
12.	Trimethoxyflavone	Flavone	Anti-inflammatory	IκBα suppression	*Kaempferia galanga*

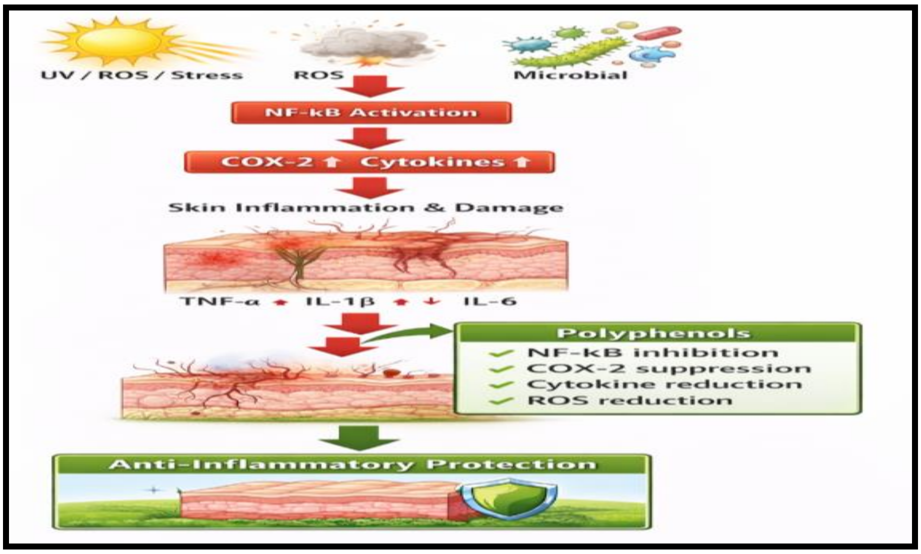

Fig. 2: Mechanism of Anti-Inflammatory (NF-κB / COX / Cytokine Modulation).

Table 3: UV-Absorbing / Photoprotective Chromophore Polyphenols.

1	Polyphenol	Chemical Class	Dermatological Role	Mechanistic Basis	Major Natural Source
1.	Caffeic acid	Hydroxycinnamic acid	UVB absorption	ROS inhibition	*Coffea arabica*
2.	Coumaric acid	Hydroxycinnamic acid	UV absorption	Chromophore	*Solanum lycopersicum*
3.	Coumarin	Benzopyrone	UV absorption	Aromatic chromophore	*Dipteryx odorata*
4.	Delphinidin	Anthocyanidin	UV absorption	Radical scavenging	*Vaccinium corymbosum*
5.	Isoliquiritigenin	Chalcone	UV absorption	Antioxidant	*Glycyrrhiza glabra*
6.	Isohamnetin	Flavonol	UVB absorption	ROS inhibition	*Hippophae rhamnoides*
7.	p-Hydroxybenzoic acid	Phenolic acid	UV absorption	Mild antioxidant	*Cocos nucifera*
8.	Pelargonidin	Anthocyanidin	UV absorption	ROS scavenging	*Fragaria × ananassa*
9.	Sinapic acid	Hydroxycinnamic acid	UV absorption	Chromophore	*Brassica nigra*
10.	Umbelliferone	Coumarin	Strong UVB absorber	UV chromophore	*Citrus aurantium*

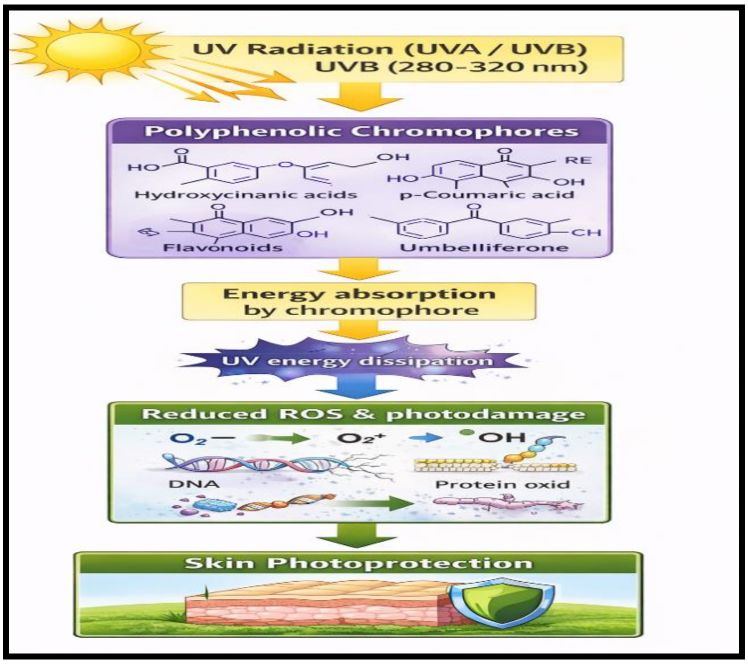

Fig. 3: Mechanism of UV-Absorbing / Photoprotective Chromophore Polyphenols.

Table 4: Anti-Photoaging (MMP / DNA / Collagen Protection).

S. No	Polyphenol	Chemical Class	Dermatological Role	Mechanistic Basis	Major Natural Source
1.	Catechin	Flavan-3-ol	Anti-photoaging	MMP inhibition	*Camellia sinensis*
2.	Curcuminoids	Polyphenolic pigments	Anti-photoaging	MMP suppression	*Curcuma longa*
3.	Epigallocatechin	Catechin	Anti-photoaging	Nrf2 activation	*Camellia sinensis*
4.	EGCG	Catechin gallate	Antioxidant	DNA protection	*Camellia sinensis*
5.	Fisetin	Flavonol	Anti-photoaging	MMP inhibition	*Fragaria vesca*
6.	Oleuropein	Secoiridoid phenol	Anti-photoaging	Antioxidant	*Olea europaea*
7.	Orientin	Flavone glycoside	DNA protection	Broad antioxidant	*Ocimum tenuiflorum*
8.	Procyanidins	Condensed tannins	Anti-photoaging	Collagen protection	*Vitis vinifera*
9.	Salvianolic acid B	Polyphenolic acid	Anti-photoaging	Antioxidant	*Salvia miltiorrhiza*
10.	Silymarin	Flavonolignan	UV-Immunoprotecting	Antioxidant	*Silybum marianum*

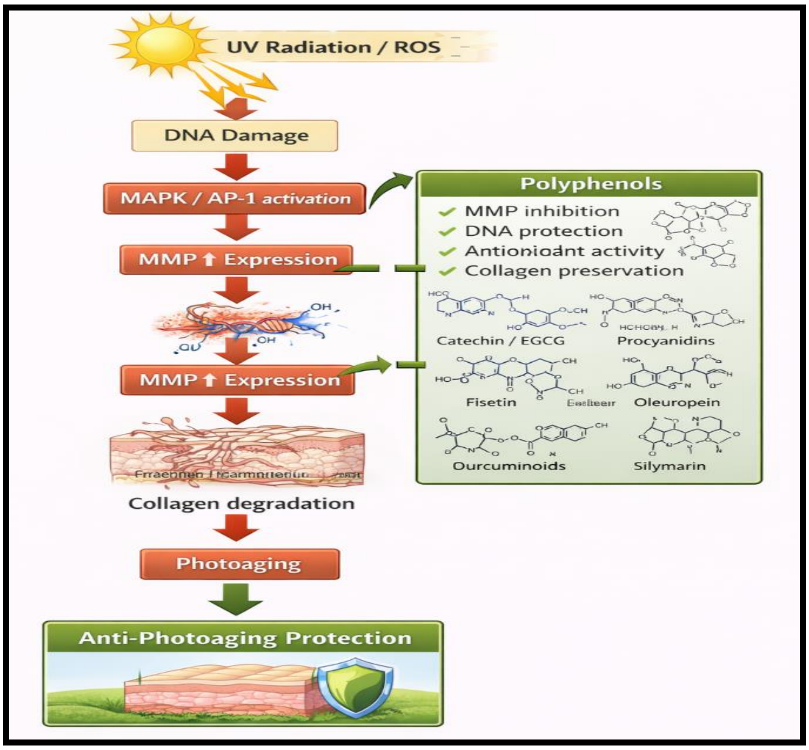

Fig. 4: Mechanism of Anti-Photoaging (MMP / DNA / Collagen Protection).

Table 5: SIRT1 / Anti-Aging Gene Modulators.

S. No	Polyphenol	Chemical Class	Mechanistic Basis	Major Natural Source
1.	Polydatin	Stilbene glycoside	SIRT1 activation	*Polygonum cuspidatum*
2.	Pterostilbene	Stilbene	SIRT1 activation	*Vaccinium angustifolium*
3.	Resveratrol	Stilbene	SIRT1 activation	*Vitis vinifera*

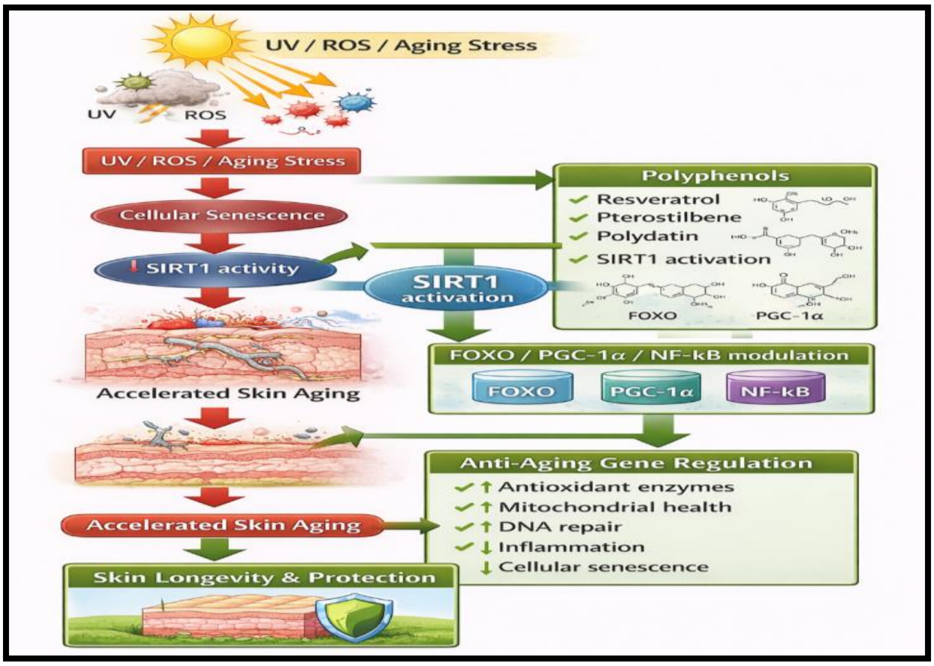

Fig. 5: Mechanism of SIRT1 / Anti-Aging Gene Modulators.

Table 6: Tyrosinase Inhibitors (Skin-Lightening).

S. No	Polyphenol	Chemical Class	Mechanistic Basis	Major Natural Source
1.	Arbutin	Hydroquinone glycoside	Tyrosinase inhibition	*Arctostaphylos uva*
2.	Ellagic acid	Ellagitannin derivative	Tyrosinase inhibition	*Punica granatum*
3.	Kojic acid	Fungal metabolite	Tyrosinase inhibition	*Aspergillus oryzae*

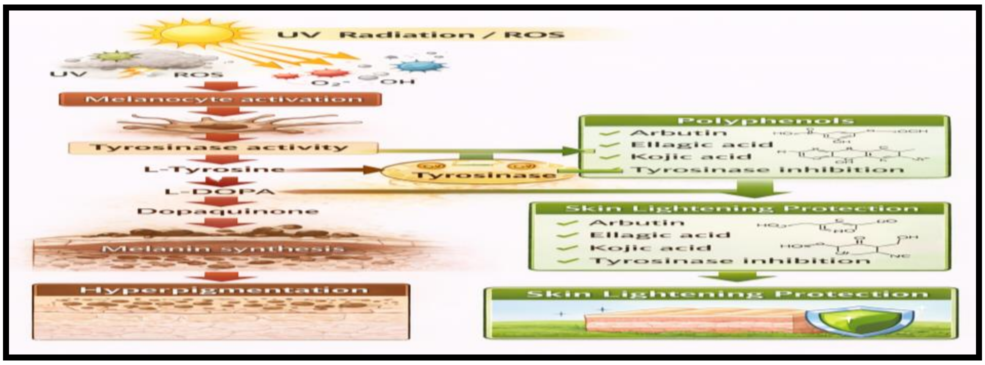

Fig. 6. Mechanism of Tyrosinase Inhibitors (Skin-Lightening).

Table 7: Hormonal / Phytoestrogenic Polyphenols.

S. No	Polyphenol	Chemical Class	Mechanistic Basis	Major Natural Source
1.	Daidzein	Isoflavone	Phytoestrogenic activity	*Glycine max*
2.	Genistein	Isoflavone	ER binding	*Glycine max*
3.	Secoisolariciresinol	Lignan	Phytoestrogenic	*Linum usitatissimum*

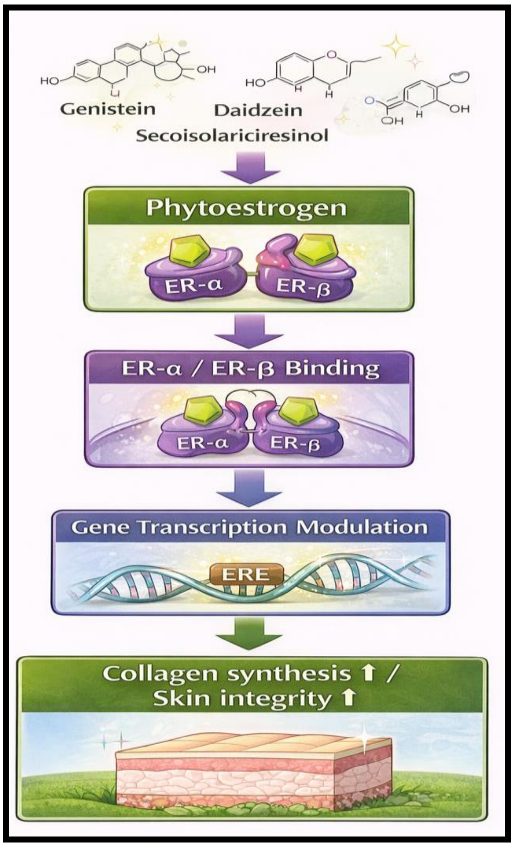

Fig. 7: Mechanism of Hormonal / Phytoestrogenic Polyphenols.

Table 8: Antimicrobial / Membrane-Active Phenolics.

S. No	Polyphenol	Chemical Class	Mechanistic Basis	Major Natural Source
1.	Eugenol	Phenylpropanoid	Membrane disruption	*Syzygium aromaticum*
2.	Hinokitiol	Tropolone	Chelation activity	*Chamaecyparis obtusa*
3.	Piperonylic acid	Phenolic acid	Membrane disruption	*Piper nigrum*
4.	Thymol	Monoterpene phenol	Membrane disruption	*Thymus vulgaris*
5.	Usnic acid	Dibenzofuran	Membrane disruption	*Usnea spp.*

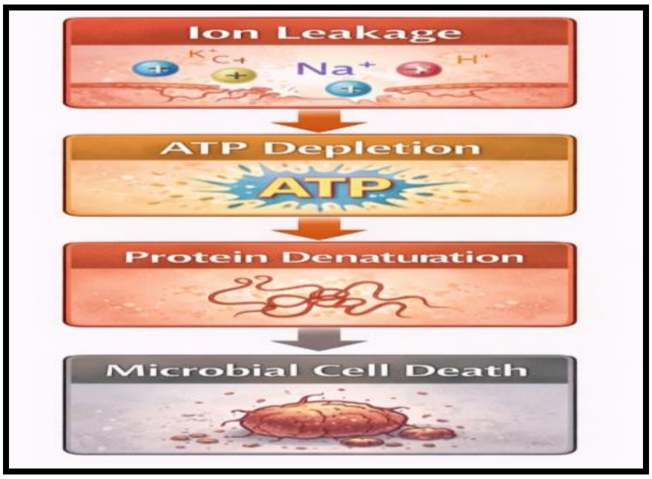

Fig. 8: Mechanism of Antimicrobial / Membrane-Active Phenolics.

Table 9: Miscellaneous / Supportive Dermatological Mechanisms.

S. No	Polyphenol	Key Mechanism
1	Ferulic acid	Photo-stabilization of vitamins C & E
2.	Bakuchiol	Retinol-like gene modulation
3.	Diosmetin / Diosmin / Hesperidin	Capillary stabilization (vascular dermo-protection)
4.	Hypericin	Photosensitizer (ROS generation)
5.	Phloridzin	SGLT inhibition (metabolic role)
6.	Schisandrin	Hepatoprotective antioxidant
7.	Sesamol	Lipid stabilization

8. Safety, toxicology, and environmental considerations

While many polyphenols have favourable safety profiles, potential issues include contact sensitization for certain botanical extracts, phototoxicity at high concentrations of some chromophores, and interactions with other actives. Regulatory frameworks for sunscreens vary by jurisdiction: in many countries, sunscreens are regulated as drugs/OTC products, while in others, they are cosmetics. This distinction affects claims, required clinical testing, and permissible activities. Environmental impact assessments (biodegradability, aquatic toxicity) are increasingly relevant, sourcing from Agro-waste streams and employing green extraction methods, which reduce the environmental footprint.[33,39,49]

9. Standardization and quality control

Key elements for reproducible herbal sunscreens:

- Phytochemical fingerprinting: HPLC/UPLC or spectrometric profiles to ensure consistent polyphenolic composition.[48]
- Functional assays: Routine in vitro SPF estimation, antioxidant capacity (DPPH, ORAC) as quality attributes.[43]
- Good manufacturing practices: Control of raw material origin, solvent residues, and microbial quality.

10. Gaps, challenges, and research opportunities

- Clinical evidence: There are relatively few randomized controlled human trials directly comparing herbal/polyphenol-based sunscreens to standard filters for SPF and long-term endpoints.[14,35]
- Standardized extract vs. isolated compound: Optimal approach, single purified polyphenolic actives or standardized multi-component extracts, remains unresolved.[1,8]
- Formulation optimization: Scalable encapsulation methods that maintain green chemistry principles are needed.
- Regulatory harmonization: Clear pathways for approval and labelling of plant-based sunscreens must be established to avoid misleading claims.
- Environmental fate: Systematic ecotoxicological profiling of botanical UV actives and their metabolites is limited.

11. Future perspectives

Integration of polyphenols as UV boosters (reducing required concentrations of synthetic filters), development of hybrid organic–polyphenolic actives, and circular-economy sourcing (valorisation of Agro-wastes) are promising directions. Advances in nanotechnology and polymer chemistry will help overcome delivery and stability barriers, but must be balanced with safety and sustainability criteria.[25,26]

12. CONCLUSIONS

Polyphenols represent a versatile, multifunctional class of compounds with real potential in green cosmeceutical sunscreens. They contribute direct UV attenuation, antioxidant buffering, and modulation of biological responses to UV. Translating this promise into effective, standardized products requires multidisciplinary effort, rigorous analytical standardization, robust formulation science, controlled clinical evaluation, and alignment with regulatory and environmental standards.

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