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Review

Apiaceae as an Important Source of Antioxidants and Their Applications

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Abstract: The excess level of reactive oxygen species (ROS) disturbs the oxidative balance leading to oxidative stress, which, in turn, causes diabetes mellites, cancer, and cardiovascular diseases. These effects of ROS and oxidative stress can be balanced by dietary antioxidants. In recent years, there has been an increasing trend in the use of herbal products for personal and beauty care. The Apiaceae (previously Umbelliferae) family is a good source of antioxidants, predominantly phenolic compounds, therefore, widely used in the pharmaceutical, cosmetic, cosmeceutical, flavor, and perfumery industries. These natural antioxidants include polyphenolic acids, flavonoids, carotenoids, tocopherols, and ascorbic acids, and exhibit a wide range of biological effects, including anti-inflammatory, anti-aging, anti-atherosclerosis, and anticancer. This review discusses the Apiaceae family plants as an important source of antioxidants their therapeutic value and the use in cosmetics.

Keywords: antioxidants; Apiaceae; phenolic compounds

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1. Introduction

The Apiaceae (previously Umbelliferae) is one of the best-known families of flowering plants (*Angiosperms*), which comprises of nearly 300–455 genera and 3000–3750 species distributed globally [1]. Apiaceae (Umbellifers) are nearly cosmopolitan whilethe Asia has the highest number of genera (289) of which most of them are endemics (177) followed by the Europe (126) and Africa (121) [2]. Celery (*Apium graveolens*), carrot (*Daucus carota*), Indian pennywort/Vallarai/Gotukola (*Centella asiatica* L. Urb), parsley (*Petroselinum crispum*), parsnip (*Pastinaca sativa*), wild celery (*Angelica archangelica*), coriander (*Coriandrum sativum*), cumin (*Cuminum cyminum*), fennel (*Foeniculum vulgare*), anise (*Pimpinella anisum*), dill (*Anethum graveolens*), and caraway (*Carum carvi*) are the economically important foods, herbs, and spice plants in the Apiaceae family [3–5]. Apiaceae plants have also been traditionally used for ethnomedicines; *Ferulago trachycarpa* [6], *Trachyspermum ammi* (Ajowain) [7], and *Capnophyllum peregrinum* [1,8]. Figure 1 shows some species from the Apiaceae family.

The comparison of global production statistics of Apiaceae crops is difficult as the data tracked by the Food and Agriculture Organization of the United Nations (FAO) is recorded under the crops belonging to other families. The only Apiaceae family crops recorded by FAO are grouped as "carrots and turnips" and "Anise, badian, fennel, coriander". Production of anise, badian, fennel, and coriander was recorded to be 1.97 million MT in

2019 with the highest quantity from Asia (87.6%) especially from India (1.4 MT). Other top five producers are Mexico, Syria, Iran, China, and Turkey. However, the production of carrots and turnips in 2019 was estimated to be 44.76 MT which is nearly 23-fold higher than that of carrots and turnips. The major production is again arising from the Asia (64.8%) especially in China while the other top five countries are Uzbekistan, the United States of America, Russia, Ukraine, and the United Kingdom [9].

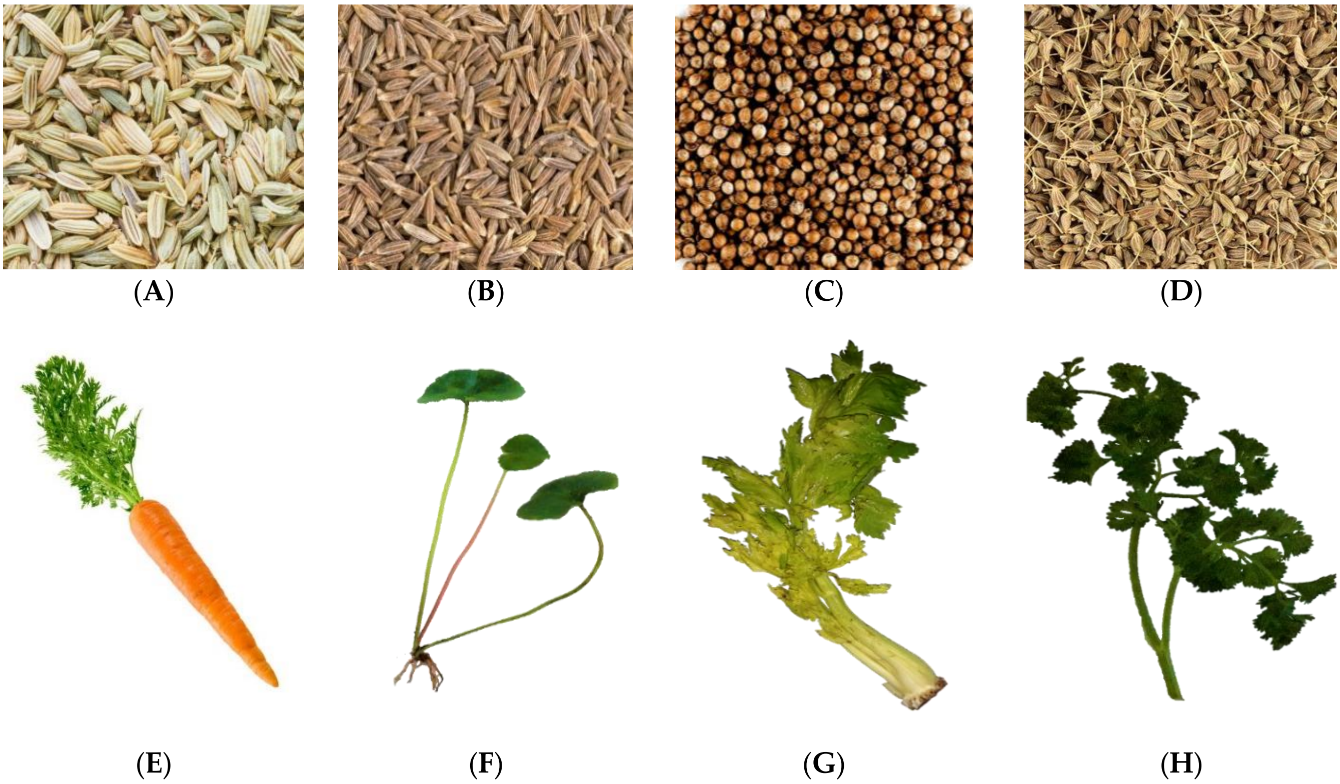

Figure 1. Different parts of selected Apiaceae family: (**A**) Fennel seeds; (**B**) Cumin seeds; (**C**) Coriander seeds; (**D**) Anise seeds; (**E**) Carrot; (**F**) Indian pennywort; (**G**) Celery plant; (**H**) Parsley (Photo courtesy of Thevin Randika).

Apiaceae family consists of economically important aromatic plants and are commonly used as food, flavors (spices, condiments), ornamental plants, for medical purposes and used in the food, perfume, pharmaceutical, cosmetic and cosmeceutical industries [5,10–12]. Some of the Apiaceae are spices, which have been used as a flavoring, seasoning, and coloring agent, and sometimes as preservatives throughout the world since ancient times, especially in India, China, and many other southeastern Asian countries [13]. Many species from Apiaceae have been used as a common household medicinal remedy for various health complications traditionally [14,15]. Many recent studies have also reported that several species in this Apiaceae family are good sources of bioactive phytochemicals with potent antioxidant, antibacterial, antibiotic or antimicrobial, and anti-inflammatory properties, antidiabetic, anticarcinogenic, cardioprotective, antihyperglycemic, hypolipidemic effects, and among others [7,15–17].

Due to health risks and toxicity, synthetic phenolic antioxidants are replaced with natural antioxidants [18–20]. The natural antioxidants from plant or spices and herbs extracts are vitamins, tocopherols, ascorbic acids, carotenoids, phenolic acid, flavonoids, tannins, stilbenes, lignans, terpenes, anthocyanins, alkaloids, components of essential oils, phospholipids, among others [13,19,21,22]. Apiaceae plants are rich source of these natural antioxidants of which phenolic compounds especially phenolic acids and flavonoids are found predominantly [7]. They are responsible for organoleptic characteristics such as bitterness, astringency, color, flavor, and odor [23].

Overproduction of the reactive oxygen species (ROS) results in oxidative stress that leads to several pathologies, such as hypertriglyceridemia, cancer, neurodegenerative diseases, diabetes, skin diseases, aging, wound healing, and cardiovascular diseases, because of its role in reducing inflammation, DNA damage changes to proteins and peroxidation of lipids [24–28]. These effects of reactive oxygen species (ROS) and oxidative stress can be balanced by antioxidant enzymes and natural dietary antioxidants [29]. Apiaceae rich in antioxidants, predominantly phenolic acids and flavonoids have many therapeutic benefits [7,30,31]. Table 1 shows the reported therapeutic effects of antioxidants from Apiaceae species.

Table 1. Therapeutic effects of antioxidants from Apiaceae species.

Apiaceae Family	Disease Condition
Anise (*Pimpinella anisum*)	Dementia [32], neurological disorder [33], Alzheimer's disease [34], depression [35], diabetes mellitus [36],
Caraway (*Carum carvi*)	Hypertriglyceridemia [30], reducing oxidative stress in diabetes mellitus [37], sepsis-induced organ failure [38], hypertension, eczema, and antiradical profile are the underlying mechanism for pharmacological properties such as antimicrobial, antidiabetic, anticarcinogenic/antimutagenic, antistress, antiulcerogenic agents [31,39]
Celery (*Apium graveolens*)	Hypertriglyceridemia [30], hyperlipidemia [40], pimples [41], antiproliferative and antiangiogenic effect on cancer [42]
Coriander (*Coriandrum sativum*)	Pimples/acne [41,43], breast cancer [43,44], hepatoprotective effect, gastric ulcers [45],
Cumin (*Cuminum cyminum*)	Antiradical profile are the underlying mechanism for pharmacological properties such as antimicrobial, antidiabetic, anticarcinogenic/antimutagenic, antistress, antiulcerogenic agents [31], neurodegeneration seen in Parkinson's disease [46]
Dill (*Anethum graveolens*)	Diabetes mellitus [15], hypertriglyceridemia [30],
Indian pennywort (*Centella asiatica* L. Urb)	Diabetes mellitus and its related complication [47], neuroprotective effect [48], skin aging, skin diseases, and damage [49], obesity [50], wound healing [51]

Furthermore, antioxidants such as vitamin A, vitamin C, vitamin E, thiols, flavonoids, and other polyphenolics have known applications in dermatology and cosmetology [49,52]. The application of these phenolic compounds in cosmetics has also proved for their anti-aging, photoprotective, antimicrobial, wound healing, and anti-inflammatory action [49,53].

Free radical scavenging and collagenase and elastase inhibitory activities of polyphenols can delay the aging process. The high antioxidant capacity of phytonutrients, especially flavonoids, and triterpenoids, involve in the stimulation of keratinocyte and fibroblast proliferation and play an important role in wound healing. Further polyphenols act as free-radical scavengers and can protect against ultraviolet (UV) damage [49,54–56]. Other than the active ingredients, antioxidants are added as protectors of other active ingredients of the cosmetics against oxidation [53,57].

Recently, natural antioxidants derived from plant sources such as spices, herbs, and the essential oil extracted from them have gained mounting interest in the application of cosmetic and pharmaceutical products [49,58]. Many studies revealed that plants from the Apiaceae family can be a good source of natural antioxidants and have the potential for pharmaceutical and cosmetic applications [1,59,60]. In this context, this review discusses the Apiaceae as an important source of antioxidants, its therapeutical benefit, anti-oxidant content, and anti-oxidant capacity of different species of Apiaceae, mechanism, and the application of antioxidants in cosmetics and cosmeceuticals.

2. Importance of Apiaceae as Food and Nutraceuticals

Different parts of the Apiaceae plants are generally consumed as vegetables or spices, such as leaves (carrot, fennel, dill, celery, parsley, and coriander), seeds (caraway, cumin, anise, dill, fennel, celery, angelica, and coriander), root (carrot, angelica), and leaf stalks (fennel) [23,61]. Aromatic spices have been traditionally used for the preparation of herbal teas, salads, and flavoring agents in stewed, boiled, grilled, or baked dishes, meat and fish dishes, and ice cream [62]. Some spices from Apiaceae are used as preservative agents in food due to the antioxidant components [13,23]. Apiaceae is largely produced for its application in foods, pharmaceuticals, perfumes, and cosmetic productions [63].

Furthermore, plants from the Apiaceae family are also a very important source of nutraceuticals and are well-known for their medicinal use since ancient times. Particularly in Asia and Africa, seeds and other plant parts of the Apiaceae have been used as a common household medicinal remedy for various health complications such as indigestion, constipation, hypertension, cardiovascular diseases, appendicitis, kidney stones, stomach ailments, abdominal pain, and acidity and to stimulates appetite, among others [14,15]. Many recent studies have reported that several species in the Apiaceae family are good sources of bioactive phytochemicals with potent antioxidant, antibacterial, antibiotic or antimicrobial, and anti-inflammatory properties, antidiabetic, anticarcinogenic, cardioprotective, antihyperglycemic, hypolipidemic effects, and among others [7,15–17].

Daucus carota Linn. (carrot) is reported to have anti-nociceptive, anti-inflammatory effects, hypoglycemic and antidiabetic activities [64]. Different parts of *Coriandrum sativum* Linn. (coriander) were reported to have antioxidant, antidiabetic, anticancer, antibacterial, antifungal, anti-inflammatory, antinociceptive, and anti-edema properties [65,66]. *Foeniculum vulgare* Mill. (fennel) has antimicrobial, antiviral, antiprotozoal, antioxidant, antitumor, anti-inflammatory, cytoprotective, hepatoprotective, hypoglycemic, and estrogenic effects [67]. Some studies showed that *Centella asiatica* (Indian pennywort) has antioxidant, antihyperglycemic, anti-inflammatory, analgesic effects, neuroprotective, memory enhancing, and skin protective activity [47,48,60,68]. In addition to that, *Centella asiatica* has also been used in treating all kinds of diseases such as gastrointestinal disease, gastric ulcer, asthma, wound healing, and eczema [60].

Essential oils of Apiaceous fruit such as cumin, caraway, and coriander have potent bactericidal activity against Gram-negative bacterial strains *E. coli* and *Bordetella bronchiseptica* [16]. Additionally, antioxidant and hepatoprotective effect has reported with essential oil extracted from caraway and coriander [69]. Essential oils extracted from plant source including Apiaceae has an effective antiviral agent that has potential to inhibit the viral spike protein and can be used as alternative therapies to manage diseases including SARS-CoV-2 [70]. Essential oil from *Coriandrum sativum* L. (coriander) has also shown antidiabetic, antioxidant, hypocholesterolemic, antihelmintic, antibacterial, hepatoprotective, anticancer, anti-inflammatory, antianxiety, and anxiolytic activities [45,58].

Angelica biserrata is a well-known medicinal plant in Chinese traditional medicine which has been broadly applied to treat inflammation, arthritis, and headache. They are also reported to have antitumor, anti-inflammatory, antioxidant, antibacterial, immunomodulatory, sedative, and analgesic effects and are being used in cosmetics [71,72]. *Ferulago* species have been used as a sedative, tonic, digestive, carminative, aphrodisiac and in the treatment of the intestinal worms and hemorrhoids [6]. Coumarin is the main phytochemical compound in *Ferulago* which has antibacterial, antifungal, anticoagulant, anti-inflammatory, anticancer, antihypertensive, antihyperglycemic, antioxidant, and anti-inflammatory [6].

3. Chemical Composition of Apiaceae Family and Their Antioxidant Activity

Antioxidants can be defined as substances that, when present at low concentrations, delay or prevent oxidation of a substrate mainly through their free radical scavenging activity [73]. The natural antioxidant capacity of plant or spices and herbs or their extract is mainly associated with the wide range of biologically active compounds that includes phenolic acid, flavonoids, alkaloids, carotenoids, vitamins, tocopherols, ascorbic acids, tannins, lignans, terpenes, components of essential oils, anthocyanins, phospholipids, among others [13,19,21,49]. Tables 2 and 3 summarize the primary antioxidant and other biologically active compounds present in the Apiaceae family.

Table 2. Chemical composition of some Apiaceae species.

Apiaceae	Plant Part Used	Uses [1]	Important Chemical Constituents	Reference
Anise (*Pimpinella anisum*)	S [2]	C [2]	Phenolic acids including anisic acid, chlorogenic acid isomers, caffeoylquinic acid, flavonoids including rutin, luteolin-7-glucoside, apigenin-7-glucoside, disorienting, other components trans-anethole, estragole, anise ketone caryophyllene, anisaldehyde, linalool, limonene, pinene, acetaldehyde, p-cresol, creosol, hydroquinine, farnasene, camphene, eugenol, acetanisole,	[21,74]
Caraway (*Carum carvi*)	R, L, S	C	Phenolic acids including chlorogenic, p-coumaric, caffeic, and ferulic acid, flavonoids including kaempferol, quercetin, 3-glucuronide, isoquercitrin, volatile compound including limonene, carvone, sesquiterpene, aromatic aldehydes, terpene esters, terpenol, terpenal, terpenon, safranal, tannins	[21,23]
Carrot (*Daucus carota*)	R, L	V	α- and β-Carotenes, ascorbic acid, tannin, phenolic acids including caffeic, chlorogenic, ferulic, 5-caffeolquinic acid, volatile terpinolene, β-caryophyllene, γ-terpinene, γ-bisabolene, myrcene, limonene, and α-pinene	[23,29,75]
Celery (*Apium graveolens*)	L, S	C, V	Phenolic acids including, p-coumaric, caffeic, ferulic, chlorogenic, and gallic acid, flavonoids included apigenin, luteolin, quercetin, rutin, and kaempferol, volatile compounds (limonene, myrcene, α-pinene, β-selinene) and other tannin, saponin, carotenoids, anthocyanins	[18,76,77]
Coriander (*Coriandrum sativum*)	L, S	C, V	Phenolic acids including p-coumaric, ferulic, vanillic, chlorogenic, caffeic, and gallic acid, flavonoids including quercetin, kaempferol, acacetin, rutin other linalool, borneol, geraniol, terpineol, cumene, pinene, γ-terpinene, limonene, myrcene, camphene, tocopherols, pyrogallol, p-cymol, n-decylaldehyde, acetic acid esters	[18,21,23]
Cumin (*Cuminum cyminum*)	S [3]	C, V [3]	Phenolic acids including quercetin, p-p-coumaric, rosmarinic, vanillic and cinnamic acids, and trans-2-dihydrocinnamic acid others cuminal, cuminaldehyde, linalool, cymene and γ-terpenoids, thymoquinone, 3-caren-10-al, γ-terpinene, p-cymene and β-pinene, pinocarveol, carotol, resorcinol, tannin	[23,78–81]
Dill (*Anethum graveolens*)	L, S	C, V	Phenolic acids: chlorogenic and benzoic acids, flavonoids: quercetin, kaempferol, myricetin, catechins, isorhamnetin, others carvone, limonene, geraniol, α-phellandrene, p-cymene	[21,23]
Fennel (*Foeniculum vulgare*)	L, S	C, V	Phenolic acids: p-coumaric acid, ferulic, quercetin, rosmarinic, tannic, caffeic, gallic, cinnamic, vanillic, ellagic, chlorogenic, and acid, flavonoids: rutin, quercetin, kaempferol, others vitamin C and E, oleoresins, β-carotene, β-sitosterol, campesterol, eugenol, carnosil, limonene, camphene, β-pinene, fenchyl alcohol, anisaldehyde, myristicin, dillapiole	[23,62,74,82]

Table 2. *Cont.*

Apiaceae	Plant Part Used	Uses [1]	Important Chemical Constituents	Reference
Indian pennywort (*Centella asiatica* L. Urb)	L	V	Flavonoids including quercetin, kaempferol, volatile pinene, terpene acetate, p-cyrnol, caryophyllene	[60]
Parsley (*Petroselinum crispum*)	L	C, V	Phenolic acids: chlorogenic acid, p-coumaric acid, caffeic acid, gallic acid, vanillic acid flavonoids: apigenin, luteolin, kaempferol, myricetin, rutin, quercetin	[18,21]
Wild celery (*Angelica archangelica*)	L, R, S [4]	C, V [4]	Phenolic acids: coumarin, other: terpenoids including α-pinene, δ-3-carene, β-phellandrene and limonene	[23]

[1] Christensen and Brandt, 2006 [61]; [2] Gülçın et al., 2003 [83]; [3] Embuscado, 2015 [78]; [4] Roslon et al., 2011 [84]; R: Root; L: Leaves; S: Seeds; C: Condiment or flavoring; V: Vegetable.

Table 3. Flavonoid content of some Apiaceae species.

Apiaceae Family	Mean Flavonoid Content (mg per 100 g)
Carrot (*Daucus carota*)	Kaempferol (0.24), Quercetin (0.21), Luteolin (0.11), Myricetin (0.04) (raw)
Celery (*Apium graveolens*)	Luteolin (762.4), apigenin (78.65) (seeds) Apigenin (19.10), Luteolin (3.50) (celery hearts, green) Apigenin (2.85), Luteolin (1.05), Quercetin (0.39), Kaempferol (0.22) (raw)
Coriander (*Coriandrum sativum*)	Quercetin (52.90) (leaves, raw)
Dill (*Anethum graveolens*)	Quercetin (55.15), isorhamnetin (43.50), kaempferol (13.33), myricetin (0.70) (fresh)
Fennel (*Foeniculum vulgare*)	Eriodictyo (1.08), Quercetin (0.23) (bulb) Quercetin (48.80), myricetin (19.80), isorhamnetin (9.30), kaempferol (6.50), luteolin (0.10) (leaves, raw)
Parsley (*Petroselinum crispum*)	Apigenin (4503.50), Isorhamnetin (331.24), Luteolin (19.75) (dried) Apigenin (215.46), Myricetin (14.84), Kaempferol (1.49), Luteolin (1.09), Quercetin (0.28) (fresh)
Parsnip (*Pastinaca sativa*)	Quercetin (0.99) (raw)

Source: USDA Database for flavonoid content [85].

Studies have shown that Apiaceae are excellent sources of antioxidants with a high content of phenolic compounds particularly phenolic acid and flavonoids [7]. A strong correlation between antioxidative activities and phenolic compounds was found [7,49,86]. Therefore, phenolic compounds are probably the major contributor to their antioxidant capacity.

Widely occurring phenolic compounds in plants includes flavonoids, flavanones, flavonols, and isoflavonoids, lignans, phenols, and phenolic acids, phenolic ketones, phenylpropanoids, quinonoids, stilbenoids, anthocyanins, anthochlors, benzofurans, chromones, coumarins, tannins, and xanthones [23].

4. Methods of Extraction and Identification of Antioxidant

Phenolics, flavanoids, anthocyanins stilbene, and lignan are hydro-soluble antioxidants while carotene, lycopene, lutein, and zeaxanthin are lipid-soluble antioxidants [87]. The effective extraction and proper assessment of antioxidants from food and medicinal plants are crucial to explore the potential antioxidant sources and promote the application as functional ingredients [87]. The antioxidative bioactive compounds can be extracted from fresh or dried (freeze-dried or air-dried) and treated (milling and homogenization) samples using conventional and unconventional methods [88].

Conventional methods or classical methods are generally based on the extractive potential of various solvents, using heating or mixing [54,89]. Solvents and their combination have been used for the extraction of plant phenolic compounds, often with different proportions of water [88]. Solvents are chosen based on the polarity of the compounds to be extracted [90]. Various common solvents in order of increasing polarity are hexane < ether < dichloromethane < chloroform < ethyl acetate < acetone < ethanol < methanol < water [89,90]. The combined use of water and organic solvent may facilitate the extraction of chemicals that are soluble in water and/or organic solvent [22]. Multiple solvents can be used sequentially to limit the number of analogous compounds in the desired yield [90]. Many other factors such as type and concentration of extraction solvent (sample to solvent ratio), extraction temperature, extraction time, and extraction pH, as well as the chemical composition and physical characteristics of the samples also influence the extraction efficiency [87,88].

Various classical methods include Soxhlet extraction, maceration, hydro-distillation, infusion, percolation, decoction, cold pressing or expression, and aqueous alcoholic extraction by fermentation [54]. In aqueous alcoholic extraction by fermentation, ethanol formed during fermentation enables the extraction of the active principles from the material and contributes to preserving the product's qualities [54]. These classical methods are time consuming, low efficient methods, require relatively large amounts of organic solvents, and may result in thermal degradation of compounds [87].

Non-conventional methods include ultrasound, microwave, and enzyme assisted extraction, high voltage electrical discharges, pulsed electric fields, and techniques based on the use of compressed fluids as extracting agents such as supercritical fluid extraction, subcritical water extraction, or pressurized fluid extraction [22,88,89]. These techniques are suitable to decrease volatility and thermal degradation during compounds extraction [19]. Some of them are considered to be "green techniques" [89].

The Folin–Ciocalteau method (F-C), has been widely used for the quantification of total phenolic compounds in plant material including Apiaceae [13,88,91,92]. Techniques such as gas chromatography (GC) and high performance liquid chromatography (HPLC) are used for chemical profiling and quantification of phenolic compounds [88]. Gas chromatographic (GC) techniques have been widely used especially for the separation and quantification of lipid peroxides, aldehydes, tocopherols, sterols, phenolic acids, and flavonoids [88,93]. Currently, HPLC is the most popular and reliable technique for the analysis of phenolic compounds [7,15,88,92], and several supports and mobile phases are available for the analysis of phenolics including anthocyanins, proanthocyanidins, hydrolysable tannins, flavonols, flavan-3-ols, flavanones, flavones, and phenolic acids in different plant extract and food samples [88].

5. Total Phenolic Content (TPC) and the Total Flavonoid Content (TFC) of Apiaceae

The total phenolic content (TPC) and the total flavonoid content (TFC) are varied within the Apiaceae family [7,91]. Table 4 shows the TPC and TFC content of some species of the Apiaceae family.

Other than these tabulated species, the TPC and TFC content of orange carrot in 80% methanolic extract is recorded as 179.3 mg GAE/100 g and 121.9 mg QE/100 g, respectively [96]. TPC and TFC content of aqueous extract of Indian pennywort (*Centella asiatica* (L.) Urb. was reported to be 2.86 g/100 g and 0.361 g/100 g [97].

However, the concentration of phenolic compounds in a particular species of plants varies significantly (Table 4) and depends on various factors such as variety or cultivar and its parts (seed, stem, root, etc.), geographical factors (characteristics of soil), environmental conditions such as temperature [23], climatic conditions [98], cultivation technology, and extraction parameters such as solvents used for extraction [23,99–102].

Table 4. The TPC and TFC of common plants of Apiaceae family.

Plant	**TPC (F–C Assay)**						**TFC**		
	[91] mg GAE/100 g DW (Seeds) [1]	**[92] mg GAE/100 g (Essential oil)**	**[13] g of GAE/100 g of DW (edible parts) [2]**	**[94] mg GAE/100 g DW (Seeds) [2]**	**[95] mg GAE/g DW (Aerial Parts) [2]**	**[7] mg GAE/g DW (Fruit) [3]**	**[94] mg CE/100 g DW (Seeds) [2]**	**[95] mg RE/g DW (Aerial Parts) [2]**	**[7] mg RE/g DW (Fruit) [3]**
Coriander (*Coriandrum sativum* L.)	160	28.48	0.88	17.04	13.72	38.83	11.10	10.24	45.26
Anise (*Pimpinella anisum* L.)	310	10.89		46.17			17.43		
Caraway (*Carum carvi* L.)		28.58	0.61	25.96		35.45	11.77		12.81
Dill (*Anethum graveolens*)	340		0.98	69.87		14.64	49.10		18.16
Parsley (*Petroselinum crispum*)		40.81	0.97		21.63			15.73	
Celery (*Apium graveolens*); Fresh	490	7.32			17.39	19.44		8.14	13.24
Fennel (*Foeniculum vulgare*)	320			115.96		21.71	68.10		15.85
Cumin (*Cuminum cyminum*)			0.23			25.29			38.36

F–C: Folin–Ciocalteu; GAE: Gallic acid equivalent; CE: Catechin equivalents; RE: Rutin equivalents; [1] 70% methanolic extract; [2] 80% methanolic extract; [3] methanolic extract.

6. Antioxidant Capacity of Apiaceae

So far, there is no single appropriate method to determine the total antioxidant capacity of a particular sample because lack of a validated assay that can reliably measure the antioxidant capacity of foods and biological samples [21,103]. Thus, various tests have been used and based on the chemical reactions involved, the methods are broadly categorized into two categories: single electron transfer (ET), and hydrogen atom transfer (HAT) assays. ET-based assays include 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2′-azinobis-3-ethylbenzothiazoline-6-sulfonate (ABTS) also known as Trolox equivalent antioxidant capacity (TEAC), and ferric reducing antioxidant power (FRAP), while HAT-based assays include oxygen radical absorbance capacity (ORAC) and total peroxyl radical-trapping antioxidant parameter (TRAP) [104,105].

These test assays can also be categorized as organic substrate-based assays such as DPPH and ABTS/TEAC, mineral substrate-based tests such as FRAP, and biological substrate-based ones such as and 2,2,-azobis(2-amidinopropane) dihydrochloride- (AAPH-) induced hemolysis assays [18].

Free-radical trapping capacity can be estimated using DPPH and TEAC/ABTS assays. The FRAP assay is a test that measures the antioxidant power based on the reduction of Ferric (Fe^{3+}) to Ferrous ions (Fe^{2+}) [18,87]. DPPH and TEAC/ABTS assays are broadly applied in assaying food samples [49,103]. Table 5 shows the antioxidant capacity of various plant materials from the Apiaceae family.

Table 5. Antioxidant capacity of Apiaceae species.

Plant of the Apiaceae Family	Total Antioxidant Capacity										
	[91] (Seeds) [1]		[92] (Essential Oil)			[13] (Edible Parts) [2]	[94] (Seeds) [2]	[95] (Aerial Parts) [2]			[7] (Fruit) [3]
	DPPH [a]	ABTS [a]	DPPH [b]	ABTS [c]	FRAP [c]	DPPH [d]	DPPH, IC50 [e]	DPPH IC50 [f]	ABTS [g]	FRAP [h]	DPPH, IC50 [i]
Anise (*Pimpinella anisum* L.)	260	187	5.21	798.8	654.8	-	39.4	-	-	-	-
Caraway (*Carum carvi* L.)	-	-	7.72	455.9	899.8	5.50	13.9	-	-	-	0.046
Celery (*Apium graveolens*); Fresh	480	1000	10.46	85.0	472.3	-	-	-	-	252.1	0.318
Coriander (*Coriandrum sativum* L.)	160	52	8.15	599.2	956.5	7.02	9.6	77.6	103.0	185.0	0.021
Cumin (*Cuminum cyminum*)	-	-	-	-	-	6.61	-	-	-	-	0.112
Dill (*Anethum graveolens*)	500	684	-	-	-	6.36	81.5	-	-	-	0.572
Fennel (*Foeniculum vulgare*)	170	180	-	-	-	-	113.2	-	-	-	0.146
Parsley (*Petroselinum crispum*)	-	-	13.3	788.4	2104.4	-	-	22.8	231.5	331.8	-

[1] 70% methanolic extract; [2] 80% methanolic extract; [3] methanolic extract; [a] mg TEAC/100 g DW; [b] mg AAE/100 g oil; [c] mM TE/100 g oil; [d] mmol of Trolox/100 g of DW; [e] mL/L; [f] µg/mL; [g] µmol TE/g); [h] µmol TE/g; [i] mg/mL.

Furthermore, methanolic and ethyl acetate extracts of aerial parts of carrot (*Daucus carota*) showed best antioxidant activity with IC_{50} of 86.89 µg/mL and 166.79 µg/mL, respectively [106]. Essential oil from wild carrot (*Daucus carota* L. ssp. Carota) contains phenylpropanoids, monoterpenes, sesquiterpenes, phenols, and flavonoids and showed an in vitro antioxidant activity with the good results of DPPH (2.1 mg/mL) and ABTS (164 mmol $FeSO_4$/g) assay [107]. The values for antioxidant capacity highly varied between the studies. Due to lack of a standard assay, it is difficult to compare the results reported by different research groups and the food and nutraceutical industry cannot perform strict quality control for antioxidant products [103].

7. Mechanisms of Antioxidant Activity

7.1. Free Radicals and Oxidative Stress

Oxidative stress is defined as an event where a transient or permanent disturbance in the ROS balance-state generates physiological consequences within the cell, and the precise outcome depends on ROS targets and concentrations [24]. An appropriate amount of ROS serves as signaling molecules to regulate biological and physiological processes including cell protection, in contrast, increased levels of ROS are shown to modify or degenerate biological macromolecules such as nucleic acid (DNA degeneration), lipids (lipid oxidation), and proteins (membrane protein degeneration), thus inducing cell dysfunction or death [28,108]. There are different types of ROS, such as superoxide (O_2^{-}), hydroxyl radicals ($HO^{\cdot}$), hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), peroxynitrite ($OONO^{\cdot -}$), nitric oxide ($NO^{\cdot}$), among others [24,109].

Normally, ROS are being constantly produced, and in the biological defense system, both enzymatic (superoxide dismutase, glutathione peroxidase, and catalase) and non-enzymatic (glutathione and ascorbic acid) antioxidants exist in the intracellular and extracellular environment to detoxify ROS and to maintain the oxidative balance [110]. In contrast, many factors such as diet, lifestyle, air pollution, exposure to UV radiation, chemicals, or inflammatory cytokines lead to increased intracellular ROS [28,49]. Excess ROS production, which exceeds the buffering capacity of antioxidant enzymes and antioxidants, shift the balance toward a more oxidative state [49].

7.2. Mechanisms of Antioxidant Activity

Antioxidants act as radical scavengers, hydrogen donors, electron donors, peroxide decomposers, singlet oxygen quenchers, metal-chelating agents, enzyme inhibitors, and synergists [110]. Phenolic compounds are classified as primary antioxidants and can protect from deleterious effects of oxidation in many ways, including free-radical quenching, chelating metal ions, preventing the accumulation of ROS, stimulation of in vivo antioxidative enzyme activities, and inhibiting lipid peroxidation [18,21].

Phenolic compounds are mainly free-radical scavengers which can delay or inhibit free-radical formation in the initiation step and/or interrupt the propagation step of autoxidation or lipid oxidation (Equations (1)–(7)), thus decreasing the formation of volatile decomposition products (e.g., aldehydes, ketones, alcohols, and epoxides) that cause rancidity [19,111].

Lipid autoxidation

Initiation:

$$RH \rightarrow R^\bullet + H^\bullet \text{ (by UV/singlet oxygen/metal catalysts/heat)} \quad (1)$$

Propagation:

$$R^\bullet + O_2 \rightarrow ROO^\bullet \quad (2)$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \quad (3)$$

$$ROOH \rightarrow RO^\bullet + HO^\bullet \quad (4)$$

Termination:

$$R^\bullet + R^\bullet \rightarrow RR \text{ (Nonradical products)} \quad (5)$$

$$R^\bullet + ROO^\bullet \rightarrow ROOR \text{ (Nonradical products)} \quad (6)$$

$$ROO^\bullet + ROO^\bullet \rightarrow ROOR + O_2 \text{ (Nonradical products)} \quad (7)$$

Phenolic antioxidants (AH) can donate hydrogen atoms to lipid radicals and produce lipid derivatives and antioxidant radicals (Equation (8)), which are more stable and less readily available to promote autoxidation [112]. The antioxidant free radical may further interfere with the chain-propagation reactions (Equations (9) and (10)) [19,103,111,112].

$$R^\bullet/RO^\bullet/ROO^\bullet + AH \rightarrow RH/ROH/ROOH + A^\bullet \quad (8)$$

$$A^\bullet + RO^\bullet/ROO^\bullet \rightarrow ROA/ROOA \quad (9)$$

$$RH + ROO^\bullet \rightarrow ROOH + R^\bullet \quad (10)$$

Other than the phenolic antioxidants, fat-soluble vitamin E (α-tocopherol) and water-soluble vitamin C (L-ascorbic acid) also scavenges free radicals [111]. α-Tocopherol has a free-radical-scavenging activity that prevents propagation of lipid peroxidation by scavenging lipid peroxyl radicals ($ROO^\bullet$) and plays a role as singlet oxygen quenchers and chemical scavengers [19]. Ascorbic acid is also able to chelate metal ions (Fe^{2+}), quenches O_2, and acts as a reducing agent [111]. Flavoring plant extracts often have strong H-donating activity thus making them extremely effective antioxidants mainly due to their phenolic acids (gallic, protocatechuic, caffeic, and rosmarinic acids), flavonoids (quercetin, catechin, naringenin, and kaempferol), phenolic diterpenes (carnosol, carnosic acid, rosmanol, and rosmadial), and volatile oils (eugenol, carvacrol, thymol, and menthol) content. Some plant pigments such as anthocyanin and anthocyanidin can chelate metals and donate H to oxygen radicals thus slowing oxidation via two mechanisms [111].

Phenolic acid can bind and precipitate macromolecules such as proteins, carbohydrates, and digestive enzymes imparting deleterious nutritional effects and influence functional properties [113].

8. Antioxidants in Skin Health

The aging process depends on various pathophysiological processes. Free radicals and ROS are the main factors inducing the skin aging process which causes many changes in the structure and chemical composition of skin cells; oxidative damage to DNA, lipids, and proteins, and degeneration of the tissues [26,49]. As a result of the activity of free radicals, structural proteins such as collagen and elastin are damaged because of the overexpression of the collagenase and elastase enzymes [49]. Therefore, inhibition of collagenase and elastase is one of the key factors that can prevent the loss of skin elasticity and therefore delay the aging process. Plants that are rich in biologically active polyphenols such as flavonoids, phenolic acids, tocopherols, tannins, among others, may have collagenase and elastase inhibitory activity [49]. Furthermore, free radicals may also cause the oxidation of lipids and proteins that build cell membranes leading to their damage. After a cell membrane damage, free radicals may cause DNA damage, which leads to cell death [49,56]. Therefore, the use of antioxidants is an effective approach to treat skin aging and related problems [114].

Many plants have been used in traditional medicine because of their beneficial effects on wound healing. Research also suggests that phytonutrients, especially flavonoids and triterpenoids, also play an important role in wound healing due to their anti-oxidant properties [51]. In the early stages of wound healing, fibroblasts play an extremely important role, which induces the synthesis of collagen or a new extracellular matrix and thick actin myofibroblasts. High anti-oxidant capacity and free radicals scavenging effect of antioxidants may involve in the stimulation of keratinocyte and fibroblast proliferation [49,51].

The topical applications of Indian pennywort (*Centella asiatica* L.) in cosmetic formulations containing phenolic compounds can reduce the effects of skin aging (specifically for wrinkles), skin diseases, damage, and protection against type B UV damage [49,55]. Indian pennywort (*C. asiatica* L.) has also a positive effect on wound healing because of various mechanisms including inhibition of inflammation, promotion of angiogenesis, induction of vasodilatation, and reduction of oxidative stress [49,51]. Dill (*Anethum graveolens*) and coriander (*Coriandrum sativum*) are used to treat pimples, the latex of *Ferula foetida* is used for wound healing and leaves of *Pleurospermum brunonis* are used to treat skin diseases in northern Pakistan [41]. Study of supplementation with antioxidant (carotene, lutein, lycopene, and tocopherol) resulted in reduced skin roughness and scaling [115]. Carrot (*Daucus carota*) and coriander (*Coriandrum sativum*) has sun-blocking, antioxidant, and anti-inflammatory properties [116]. Furthermore, carrot (*Daucus carota*), coriander (*Coriandrum sativum*), and fennel (*Foeniculum vulgare*) extract can be used in hyperpigmentation or skin brightening [115,116].

9. Cosmetic and Cosmeceutical Applications of Antioxidants from Apiaceae

Antioxidants are widely used in the pharmaceutical, food, and cosmetic industries [49]. Vitamin C (ascorbates), vitamin E (tocopherols), carotenoids, thiols, flavonoids, and other polyphenolics are some antioxidants with known application in dermatology and cosmetology [52]. Presently, natural antioxidants are preferred over synthetic antioxidants [3]. Permitted synthetic antioxidants, such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tertiary butylhydroquinone (TBHQ), and propyl gallate (PG) are frequently questioned for their safety because of their potential toxicity and health risk [18–20].

Recently, natural antioxidants derived from plant sources particularly spices and herbs, and their essential oil, have gained increasing interest in the application of cosmetic and pharmaceutical products [49,58]. Studies indicated that the plants from the Apiaceae family can be a good source of natural antioxidants (Table 2) and have the potential for pharmaceutical and cosmetic applications [19,49,92]. The application of phenolic compounds in cosmetics has also proved for their anti-aging, photoprotective, antimicrobial, wound healing, and anti-inflammatory action [53]. In cosmetic preparations, antioxidants have two functions: (1) as the active ingredients and (2) as protectors of other ingredients against oxidation or preservatives [57].

The cosmetic and dermatological importance of polyphenolic compounds is mainly based on antioxidant action [53]. Polyphenols reduce oxidative damage, prevent premature aging, provide photoprotective action, and helps in the treatment of sensitive or sun-stressed skin by anti-inflammatory activity. Antioxidants are also applied to prevent or reduce oxidative deterioration of active constituents of cosmetics and to avoid oxidation of oily content present in the formulation [53].

9.1. Apiaceae in Cosmetic Formulation

Furthermore, antioxidants can be added to cosmetic products because of their free-radical scavenging capacity which has a beneficial effect on the protection of human skin against the oxidative damage caused by ultraviolet radiation and by free radicals [54]. Apiaceae plant extract can be used as a natural sunscreen in pharmaceutics or cosmetic formulations and as a valuable source of natural antioxidants [1]. Carrot (*Daucus carota*) and coriander (*Coriandrum sativum*) from Apiaceae family are used in sunscreen as they contain a phenolic compound, 7-hydroxycoumarin that absorbs ultraviolet light strongly at several wavelengths (300, 305, 325 nm) [116]. β-carotene a predominant constituent in carrot (*Daucus carota*) and lycopene play a role in the protection against photooxidative damage by singlet oxygen and peroxyl radical scavenging activity and can interact synergistically with other antioxidants [117]. Other phytochemical compounds such as tocopherols, tocotrienols, ascorbate, polyphenols (flavonoids), selenium compounds, polyunsaturated fatty acids (PUFAs), also have photoprotective effect on skin [118].

Oils and extracts of Apiaceae seeds are widely used in pharmaceuticals as a flavoring agent in mouthwash and as fragrance component in toothpastes, soaps, lotions, and perfumes [63]. Coriander (*Coriandrum sativum*) oils are also used in cosmetic emulsions, and have beneficial effects in cellulites, relieving of facial neuralgia, fungal infection, arthritis, broken capillaries, dandruff, eczema, muscular aches and pains, rheumatism, spasms, stiffness, and sweaty feet [63].

Essential oils are used in skin cream, lotion, ointment, and other various cosmetic and personal care products. Essential oil from Apiaceae, anise (*Pimpinella anisum*), caraway (*Carum carvi*), coriander (*Coriandrum sativum*), cumin (*Cuminum cyminum*), and fennel (*Foeniculum vulgare*) is used in cosmetic industries as they are reported to have antimicrobial, anti-oxidant, anti-inflammatory, and anticancer activities [59,119]. Indian pennywort/Gotukola (*Centella asiatica*) is also used in the ointment, cream, among others [60]. Coriander (*Coriandrum sativum*) oil is also used in cosmetics, body care products and perfumes [45]. However, the cost of natural essential oils is higher than the synthetic oil source [59].

Essential oil of Apiaceae species such as coriander, caraway, carrot, cumin, fennel, and celery are used as fragrance component in cosmetic preparations including creams, lotions, perfumes, and oral care products [120] as they contain high volatile aromatic monoterpenes including cuminaldehyde, anethole, linalool, carvone, among others [121]. In addition, linalool (coriander, 30–80%), carvone (dill, 30–60%; caraway, 76.8–80.5%), cuminaldehyde (cumin, 27–50%), trans-anethole (anise, 77–94%; fennel, 69.7–78.3%), are the main component in essential oil from various Apiaceae shows potential anti-oxidant property [63,122].

Cuminaldehyde (4-isopropyl benzaldehyde) is an aromatic monoterpenoid volatile compound, a main constituent in essential oil of cumin (*Cuminum cyminum* L.), and found in caraway (*Carum carvi*) have been commercially used in perfumes and other cosmetics [123]. Linalool, a monoterpene alcohol, is predominantly present in coriander oil (30–80%) [63] and possess antioxidant, antibacterial and antifungal properties [124]. Linalool is widely used as a fragrance component in perfumes and cosmetics and can also be used as cosmetics preservatives [124,125]. D-carvone, a monoterpene, is the main component of the essential oil extracted from caraway (*Carum carvi*) (50–76%), and dill (*Anethum graveolens*) (30–60%) seeds extensively used in the perfumery, oral care, and cosmetic applications [126]. D-carvone in dill (*Anethum graveolens*) seed oil is a volatile compound that shows strong antioxidant activity than α-tocopherol and can be used as a natural preservative and anti-oxidant to prevent lipid oxidation and rancidity [127].

Fennel (*F. vulgare*) seed oils can be used in moisturizing cream formulas without altering their rheological properties (steady-flow, thixotropy and viscoelastic properties) and the low peroxide value indicated that it is rich in antioxidants which can react with radicals and thus prevent peroxide formation [128]. Cumin (*Cuminum cyminum*) seed extracts (oil) and their by-products can be used for functional food applications as well as for cosmetic, scented, and pharmaceutical applications [129].

Antioxidants from carrot (*Daucus carota*) (carotenoid and plant extracts) are used in moisturizer for their beneficial effect of breaking chain in lipid peroxidation, decreasing UV-induced erythema, and sunburn cell formation [130]. Spices and herbs, whole, or ground or essential oil extracts are proved to have the potential of inhibiting lipid oxidation and microbial growth. Therefore, they can delay the onset of lipid oxidation and development of rancidity and reduce the formation of harmful substances such as heterocyclic amines [78].

9.2. Limitation to Be Considered

The stability of antioxidants is one of the major problems as they are susceptible to hydrolysis and photodegradation in the presence of oxygen. Therefore, the selection of antioxidants and their concentrations in cosmetic formulations must be optimized [130]. The best current approach being to combine anti-aging natural antioxidants acting in synergy [131]. Generally, plant-derived antioxidants contain a mixture of compounds, which have synergetic effects [112]. The use of natural antioxidants including tocopherols, carotenoids can inhibit oxidative rancidity thus protect the oil-based food systems from their quality degradation. Some natural antioxidants (citric acid, ascorbic acid, lecithin) are often termed synergists because of their ability to promote the action of the primary antioxidant [112].

10. Safety

Sometimes the frequent use of *Centella asiatica*, *Coriandrum sativum*, and caraway are limited as they can cause allergic contact dermatitis [69,132]. Coriander essential oil intake resulted in elevated serum alanine transaminase and aspartate transaminase that correlated with the noted noxious effect on liver function [69]. Furthermore, autoxidation of linalool (a major component in coriander oil) on exposure to air forms linalool hydroperoxides which increase the allergenicity of linalool [125].

11. Conclusions

The imbalance between oxidative stress and the antioxidant defense caused by overproduction of ROS is considered to be the key factor in the development of several pathologies, including aging and skin-related diseases. The effect of ROS can be balanced by natural dietary antioxidants.

Recently, there has been a growing interest in the use of natural antioxidants from plant sources instead of synthetic compounds. Several data have been highlighted regarding the antioxidant capacity of various Apiaceae plants. They are excellent sources of antioxidants such as phenolic acids, flavonoids, tannins, stilbenes, coumarins, lignans, carotenoids, tocopherols, and ascorbates, of which phenolic compounds particularly phenolic acid and flavonoids are the major contributors. Many researchers have also studied several therapeutic benefits of Apiaceae.

The application of phenolic compounds in cosmetics has proved for their anti-aging-aging, photoprotective, antimicrobial, and anti-inflammatory action because of their free-radical quenching, chelating metal ions, inhibiting lipid peroxidation, and stimulation of in vivo antioxidative enzyme activities.

Many studies explored the potential of Apiaceae as a natural antioxidant source in pharmaceutical and cosmetic applications. Though, only a few studies mentioned the application of Apiaceae plants as a source of antioxidants in cosmetics and cosmeceuticals. Further investigations can be focused on the incorporation of Apiaceae plant-based antioxidants in cosmetics and personal care products and their stability, and toxicity.

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