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Chapter

Natural Antioxidants: An Update

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Abstract

Antioxidants are the body's defensive mechanism against reactive oxygen species damage, which is typically caused by the different physiological activities that take place within the body. These antioxidants can be obtained from a variety of sources, including the body's own endogenous antioxidants and exogenous dietary sources. Generally, food items and several types of medicinal plants are considered as the sources of natural antioxidants. Natural antioxidants possess wide variety of bioassay properties like anti-cancer, anti-aging, anti-inflammatory etc. The substitution of artificial dietary antioxidants with natural ones in recent decades has increased interest in low-cost raw materials, particularly agricultural-based products, for the discovery of new antioxidants. For both natural and synthetic antioxidants, reports of biological features such as anti-allergic, anti-mutation, anti-cancer and anti-aging activity have been reported. The most significant natural antioxidants come from regularly eating fruits and vegetables, although other plant materials and agricultural waste are also major sources of antioxidants.

Keywords: antioxidants, vegetables, plants, fruits, herbs

1. Introduction

Reactive nitrogen and oxygen species (RNS and ROS), including nitric oxide radicals, hydroxyl, and superoxide, can harm DNA in biological systems and cause oxidation of proteins and lipids in cells [1]. Free radicals can typically be scavenged by the body's antioxidant system, which helps to keep oxidation and anti-oxidation in the right proportion. But when the body produces too many ROS and RNS due to exposure to toxins from the environment, radiation, alcohol, or cigarette smoke, the body's natural balance of oxidation and anti-oxidation is disturbed, which can result in a number of chronic and degenerative illnesses [2, 3]. Intake of exogenous antioxidants could be increased to minimize the consequences of oxidative stress by scavenging free radicals, quenching singlet oxygen, and acting as reducing agents. These antioxidants also operate as scavengers of free radicals and quenchers of singlet oxygen [4].

Plants are the ultimate sources of natural antioxidants that are consumed or used medicinally. Antioxidants are obtained from vegetables, mushrooms, fruits, spices, cereals, flowers and herbs [5]. Additionally, antioxidants can also be obtained from businesses that deal with agricultural byproducts [6]. Flavonoids, lignans, stilbenes, anthocyanins and several other polyphenolic compounds, vitamins and carotenoids

like carotenes and xanthophylls are obtained and derived from plants [7]. The natural antioxidants possess many pharmacological properties such as anti-cancer, anti-viral, anti-inflammatory and anti-bacterial [2, 7, 8].

Antioxidants can be divided into two major classes Antioxidants can be divided into two primary categories: Natural antioxidants and synthetic antioxidants. Free radical damage predominantly affects the cellular level of the body, and antioxidants protect against it there. As a result, enzymatic and nonenzymatic types of these antioxidants are also possible. The three primary enzyme-based antioxidants are glutathione peroxidase, catalase, and superoxide dismutase. The serum reflects the body's overall capacity for antioxidants, which is influenced by additional enzymes in the body [9]. The non-enzymatic class of antioxidants can be classified in several classes. Vitamins like vitamins C, E, A, peptides, enzyme co-factors (Q10) and a few minerals (selenium and zinc) usually serve as building blocks of the natural antioxidants [10]. The classification of natural antioxidants has been shown in **Figure 1**.

Some of the unfavourable or detrimental effects of synthetic antioxidant use have been uncovered by recent toxicological study. Researchers are now focusing their efforts on locating natural sources with sufficient antioxidant activity as a result of these studies. Furthermore, substantial concerns are raised regarding the cost and availability of these natural antioxidants. It is possible to define the numerous subcategories of natural antioxidants. Antioxidants, however, fall into two main categories: those that are present in frequently utilized or regular food items (such as

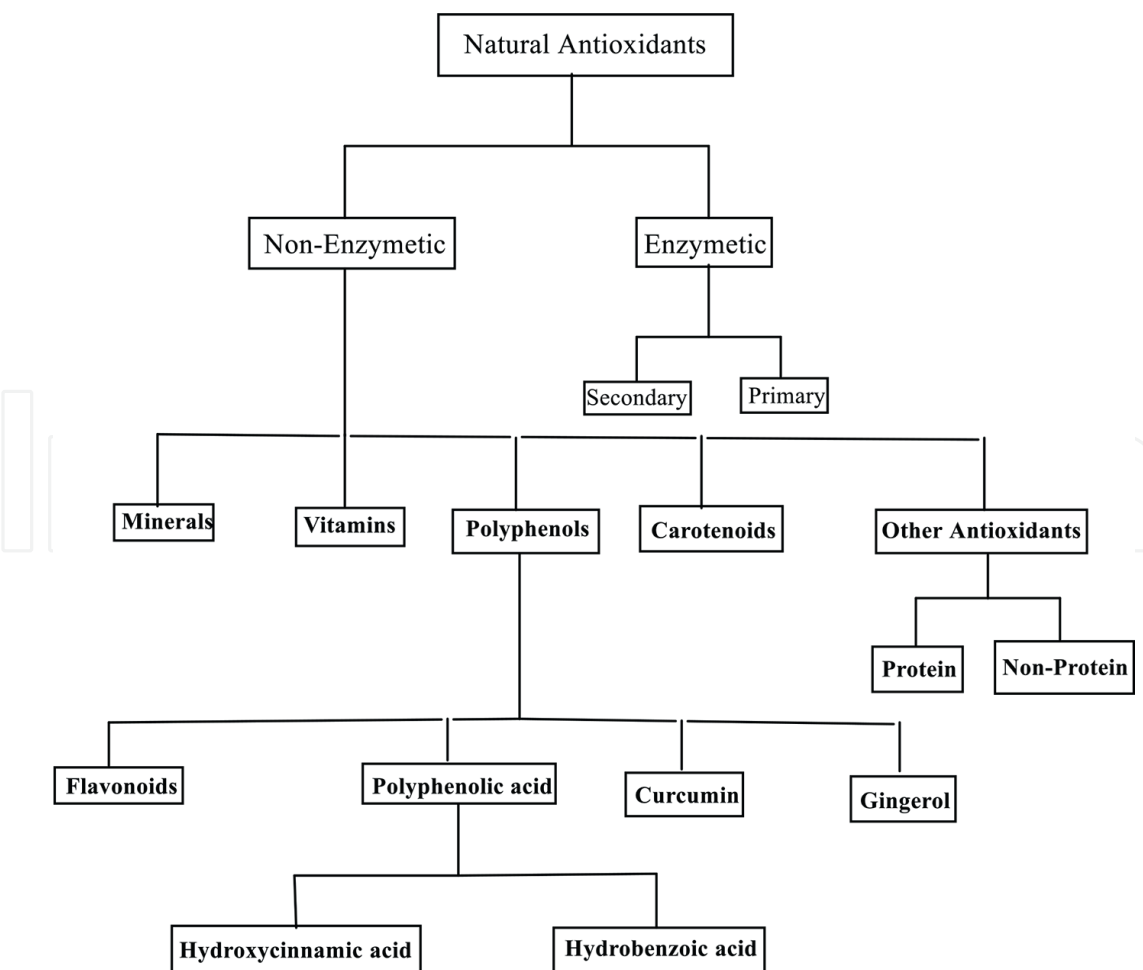


Figure 1. Classifications of Antioxidants obtained from natural sources [11].

beans, fruits, vegetables and cereals) and those that are present in plants or herbs that have some antioxidant potential but are not frequently consumed (such as medicinal plants and wild herbs) [12, 13]. Until now, researchers from all around the world have concentrated on discovering inexpensive, more natural sources of antioxidants. These findings will be utilised by the food, pharmaceutical, and beauty industries as an improved option for produced supplements. Despite the fact that synthetic supplements have not yet been proven to have substantial detrimental effects, supplementing should generally emphasise getting back to nature. In the next ten years, natural products-based items are going to get more and more important, and research in the area of naturally occurring antioxidants will be more and more emphasized and pursued [14, 15].

The current chapter's major goal is to provide an overview and summary of the natural sources having antioxidant potential.

2. Oxidative stress

Oxygen, which is essential for sustaining cell viability and metabolism and is associated with aerobic living conditions, is also dangerous due to its paramagnetism. The paramagnetic nature of oxygen results in creation of very reactive intermediates chemicals. These chemicals are referred to as "reactive oxygen species" (ROS). These ROS are free radicals (FRs) in nature. Maximum natural stability refers to the coupling of the electrons in the corresponding molecular orbitals of stable neutral compounds. Because of this, when an orbital is having un-paired electrons, extremely reactive chemical entities are formed. The chemicals have the natural inclination to obtain an electron from neighboring molecules to account for their electron deficiency [16]. The main free radical is the triplet state of oxygen which possess two unpaired electrons. The rate of the reaction of triplet state is usually slow, however, due to metabolic transformation into one or more very reactive species it can dangerously interact with biological systems. This kind of metabolic activation is generally preferred in biological systems due to conversion of O_2 to H_2O during the phenomena of electron transport chain. During electron transport chain ROS and FRs are produced due to transfer of electrons [17]. External stimuli like sun radiation can induce free radicals to develop in biological systems since UV light exists. UV rays causes the homolytic bonds between molecules to disintegrate. As a disease worsens, FR can also manifest. For example, during heart attack, many FRs are produced when supply of glucose and oxygen are interrupted to cardiac muscles. Another outside factor which enhances the rate of formation of FR is known as chemical intoxication. The organism promotes FR release because it needs to convert toxic substances into less toxic ones. The toxicity of numerous numbers of drugs is due to their inclination to produce FRs and interference with processes for the formation of FR. Similarly, food contamination with herbicides and chemicals may also act a source of FR formation [18].

Inflammations are induced due to endogenous components which ultimately results in the promotion of FR. The FR occur in immune system's cleaning cells and are responsible for removing dangerous microbes. Tissue damage comes from excessive FR during this phase. Superoxide ions ($O_2^{\bullet-}$) are generated NADPH oxidase in the phagocytic cells. $O_2^{\bullet-}$ which is thought of as the main ROS. It may produce secondary ROS after interacting with other molecules through enzymatic processes. The protonation of $O_2^{\bullet-}$ may result in the formation of H_2O^{\bullet} and H_2O_2 . When water is exposed to UV light,

molecular oxygen is exposed to cellular free radicals produced inside living cells, and water is photolyzed, $O_2^{\bullet-}$ is produced. as demonstrated by hemoproteins, NAD^{\bullet} , FpH^{\bullet} , semiquinone radicals, pyridinium cation radicals, etc. The phagocytic cells, during the process of respiration and oxygen ingestion, also produce $O_2^{\bullet-}$. The superoxide radical does not undergo rapid reaction with nucleic acids, polypeptides or carbohydrates [18].

Cells create $\bullet NO$ as a defense mechanism when nitric oxide synthase interacts with intracellular arginine. Lipid peroxidation in lipoproteins results from the creation of ONOO, which is created when O_2 and $\bullet NO$ mix. Autoimmune disorders which clearly demonstrate this phenomenon include vitiligo, Graves' disease, biliary cirrhosis, systemic lupus erythematosus, Hashimoto's disease, Rheumatoid arthritis, type 1 diabetes, inflammatory bowel syndrome, celiac disease, scleroderma, multiple sclerosis and psoriasis.

These chemical species are necessary for many of the chemical reactions that occur throughout metabolic activities, hence FR is required at all times. For instance, FR plays a role in the polymerization of glucose and amino acids to make glycogen and proteins. FR catalytically activates a variety of intermediary metabolic enzymes such as lipoxygenase, cyclooxygenase, and monoamine oxidase etc [18]. Antioxidant enzymes often successfully regulate these free radicals. Irreversible structural changes in essential macromolecules such as lipids, DNA and proteins also act as sources of ROS. Malonaldehyde and hydroperoxide, two substances that cause oxidative damage, are produced by these mechanisms. Neutral species like N_2O_3 and ONOOH as well as NO^{\bullet} , $ONOOCO^{2-}$ and NO_2^{\bullet} ONOO⁻ are all RNS. RNS are produced in small amounts during cellular growth, production of cellular energy, signaling, blood pressure modulation, relaxation of muscles, aggregation of platelets, neurotransmission and phagocytosis etc. [19, 20].

3. Importance of antioxidants

Both biochemical and biological defense systems have been developed by biological systems. in oxygenated circumstances. A microvascular system regulates the tissues' oxygen levels as far as physiological level is concerned, while at biochemical level, an enzymatic or non-enzymatic antioxidant defense system operates for the repair of the molecules.

3.1 Primary enzymatic type systems

Aerobic species have produced antioxidant enzymes such catalase, glutathione peroxidase, superoxide dismutase, and DT-diaphorase. SOD is responsible for the dismutation reaction that converts oxygen into hydrogen oxide, which is then converted back into oxygen and water in subsequent reactions that are catalyzed by catalase or GPx. The detoxification of a cell is performed by SOD. Because SOD requires a metal as a co-factor to detoxify a cell. Depending on the kind of metal ion required by SOD as a co-factor, different forms of the enzyme exist [21, 22]. CAT completes the detoxification process that SOD began by catalyzing the reduction of H_2O_2 . Iron or manganese act as co-factor during the reduction of H_2O_2 and results in the production of water and oxygen molecules [23]. CAT is so efficient that a very large number of H_2O_2 molecules can be destroyed in a single second. Its main function is to eliminate the H_2O_2 created when fatty acids are oxidised. Peroxisomes are where CAT is mainly found. A vital intracellular enzyme called GPx breaks down lipid peroxides to corresponding alcohols

and H₂O₂ in water; this predominantly occurs in the mitochondria and occasionally in the cytoplasm [24]. Selenium is necessary for the function of GPx. At least eight GPx enzymes (GPx1 to GPx8) are found in human beings [25].

Almost all cells contain GPx1, the most common selenoperoxidase among glutathione peroxidases. The enzyme is necessary to stop the oxidation of lipids, resulting in protecting the cells from oxidative stress [26]. When GPx activity is low, the functioning proteins and fatty acids in the cell membrane experience oxidative damage. The production and prevention of GPx, particularly GPx1, have been associated to a variety of diseases [27]. DT-diaphorase participates in the reduction of compounds with a quinone structure and catalyzes the conversion of quinone to quinol. Cells manufacture these enzymes under the direction of DNA [28].

3.2 Non-enzymatic type system

The antioxidants which capture FR, they constitute non-enzymatic type systems. They catch FR in order to prevent the radical initiation reaction. However, they are not as much reactive as that of the original FR. Antioxidants become free radicals in the process of neutralizing or trapping the radicals by donating electrons. The FR from antioxidants can be immediately and effectively neutralized by other antioxidants of this family. The cells utilize antioxidants and FR like α -tocopherol (vit E), ferritin, selenium, GSH, co-enzyme Q, zinc, bilirubin, cysteine, ascorbic acid (vit C), ubiquinone, melatonin and flavonoids. In some foods, the extracted flavonoids work with the ROS directly to form non-reactive or less reactive complexes, but in other foods, the flavonoids take part in the specific enzymatic catalysis as co-substrates [29].

4. Fruits and vegetables as sources of natural anti-oxidants

A class of chemicals with low and high molecular weights known as polyphenols is found in fruits and vegetables and has the ability to inhibit lipid oxidation. In addition to being functional derivatives like esters and methyl esters, most of them are the conjugates either mono or polysaccharides with one or more phenol linkages. This important class of natural antioxidants can be found in fruits like grapes, green and red teas, and other teas, especially those that are caffeine-free [30].

Yet, the polyphenols in teas are more important than those in fruits because of higher blood bioavailability. 15% to 20% of consumed polyphenols are absorbed by the human circulation (**Table 1**). This absorption is enhanced when no sugar molecules are present. Teas absorb polyphenols at a rate that is higher than that of fruits since fruits have a high sugar content [41, 42].

Flavonoids are also very rich sources of antioxidants. Food items like peaches, potatoes, berries, wheat and almonds are the richest sources of flavonoids [43, 44]. A subgroup of flavonoids called anthocyanin is found in berries and red wine. It is a potent antioxidant and has a lesser bioavailability than other flavonoids. Polyphenols can display their antioxidant properties and prevent the growth of plaque through low-density lipoprotein (LDL) oxidation [45]. Furthermore, it has been revealed that particular types of polyphenols can stop some important enzymes from oxidising, keeping their proper function. The family of carotenoids comes in second place to polyphenols as a significant class of phytochemical antioxidants present in fruits and vegetables. Veggies including potatoes, carrots, papayas, and apricots are the main sources of them [11].

S. no.	Common name	Antioxidant present	ORAC value (mmolTE/g)	Reference
1	Plum	Flavonoids, Phenolic Acids, Proanthocyanidins, Hydroxychalcones, isoprenoid glycosides.	94.8	[31]
2	Pomegranate	Polyphenols and Vitamin C and	1250	
3	Guava	Carotenoids, Lycophene, Vit C, anthocynin		[32]
4	Pears	Vit C, betalains, taurine, total carotenoids, flavonoids and total phenolics	140	[33]
5	Beet root	Carotenoids, Flavonoids Vit C and Vit E,	4100 (dry extract)	[34]
6	Apple	Flavonoids, Proanthocyanidins, , Phenolic acids, Isoprenoid-glycosides, Flavanols, Hydroxychalcones etc.	17.0	[31]
7	Papaya	β -sitosterol, Quercetin	300	[35]
8	Pea	Carotenoids, Flavonoids, Vit C, Vit E, Thio compounds	0.019	[34]
9	Spinach	Carotenoids, Flavonoids, Vit C α -tocopherol,	0.152	[34]
10	Carrot	Carotenoids, Flavonoids, Vit C and E, Thio compounds	0.060	[34]
11	White onion	Carotenoids, Flavonoids, Vit C and E, Thio compounds	0.085	[34]
12	White cabbage	Carotenoids, Flavonoids, Vit C and E, Thio compounds	0.061	[34]
14	Tomato	Carotenoids, Flavonoids, Vit C and E, Thio compounds	0.067	[34]
15	Cauliflower	Carotenoids, Flavonoids, Vit C and E, Thio compounds	0.102	[34]
16	Grape juice	Anthocyanins	255.6–460	[36]
17	Coriander	Monoterpenoid,		[37]
18	Ginger	Phenols	1870.1	[38]
19	Nigella sativa	4-terpineol Thymoquinone, Carvacrol	1.0	[39]
20	Walnut	Phenolics	1320.6	[40]

Table 1. Antioxidants obtained from various fruits, vegetables and natural sources.

The water-soluble antioxidant vitamin C, commonly referred to as ascorbic acid, is typically found in citrus fruits and vegetables including oranges, lemons, and tomatoes. It is a vitamin that is obtained from fruits and vegetables and serves as an antioxidant. It is advisable to consume vitamin C-containing fruits and vegetables in tiny, spaced-out portions rather than all at once because it demonstrates poor absorption when consumed in larger doses [46].

Vitamin E is reported to possess excellent antioxidant properties. It is a naturally occurring, nonpolar, fat-soluble vitamin that is present in lipid-rich foods including olives, almonds, and sunflower seeds. Vitamin E has a higher bioavailability than vitamin C because of its solubility in fat and potential for improvement when ingested with fatty meals [47].

5. Fruits and vegetable wastes as source of natural antioxidants

Producing, managing industrially, processing, preserving, and distributing fruits and vegetables all result in the generation of waste products. Over the past few decades, researchers have been experimenting with techniques to reuse these wastes in order to obtain medicinal benefits [48]. Vegetable and fruit wastes consists of the peelings, trimmings, seeds, shells, stems and pulp leftovers from juice extraction and starch or sugar processing. Between 25 to 30% of it is trash. These discarded scraps apparently contain more phenols and ascorbic acids than their pulp [49] likewise preferable in their unripe form than that of ripeness. Frequently, fruit peels have 2–27 times as much antioxidants as fruit pulp [50].

Only 25% as much phenolic compounds are present in banana pulp (232 mg/100 g) as there are in banana peels [51]. *Cucumis sativus* peel has been discovered to be an excellent source of flavonoids, which are regarded to have antioxidant potential. These wastes include a variety of bioactive components that can be gathered and used to create both culinary preparations and pharmaceutical preparations. The bioactive phytochemicals carotenes, tocopherols, terpenes, sterols, and polyphenols, all of which have strong antioxidant properties, are abundant in the tomato wastes. These natural antioxidants, which were derived from food waste, can be used to enhance food or make useful foods [52]. The mango peel is rich in dietary fibre, vitamin C, phenolic compounds, and carotenoids, among other antioxidants. These compounds have been proven to affect a variety of degenerative conditions, including cancer, Parkinson's disease, cataracts, and Alzheimer's disease [53]. Among the waste materials generated by the wine industry are degradable solids. These substances contain high levels of antioxidants, which have been shown to slow down a number of degenerative processes and have other advantageous impacts on health. Polyphenols make up around 6% of the waste produced by the coffee industry, whereas tannins make up about 4% [54, 55].

6. Important characteristics of antioxidants

A chemical or antioxidant system's main job is to stabilize the generated radical in order to prevent or detect a chain of oxidative propagation, which minimizes the body's exposure to oxidative damage [56]. Gordon categorized antioxidants according to that characteristic. Primary antioxidants (which halt a chain reaction and scavenge free radicals) and secondary, or preventive, antioxidants fall into two fundamental groups. A few examples of secondary antioxidant mechanisms include the deactivation of metals, stopping the formation of unfavorable volatiles, inhibiting lipid hydroperoxides, regenerating primary antioxidants, and removing singlet oxygen. Antioxidants are therefore "those substances that, in low quantities, act by preventing or greatly retarding the oxidation of easily oxidizable materials such as fats" [57].

7. Conclusion

Over the previous ten years, there has been an increase in interest in studying natural ingredients for usage in food and food products. Because natural sources are more useful and secure to use as dietary supplements than manufactured ones,

researchers from all over the world are concentrating on them. Despite the fact that there have never been any cases of harm associated with the use of synthetic antioxidants, there is still a considerable desire from consumers for products that are close to nature. Natural antioxidants and preservatives may also result in peroxidation of lipids and thus deterioration of quality and flavor of the food items.

Since ancient times, natural herbs, spices, and plant-based ingredients have been employed in traditional food preparation as flavorings, fragrances, and preservatives. A general overview of the possible benefits of several natural sources with respectable antioxidant capacity is what this chapter aims to deliver. The literature research gathered here will be useful to establish the relevance, active components, antioxidant potential and availability of various sources. This work will help the people to prioritize their daily requirements of natural antioxidants keeping in mind the cost-effectiveness and availability of natural sources because 70–80% of the world's population cannot afford current supplements and pharmaceuticals.

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