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Natural antioxidants: A step forward to better health

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Abstract
Metabolic generation of free radicals has been of tremendous research study interest for health practitioners and scientists. These free radicals can go berserk to play havoc with homeostasis capacity of the body. According to the, United States Department of Agriculture (USDA) antioxidants remove free radicals from the body which can run rampant and actually damage cells, causing serious illness. Endogenous antioxidants of the body try to neutralise the oxidative stress caused by these radicals. As the natural capacity of body to counter these go down this needs to be supplemented by exogenous supply of health supplements & super-foods aflush with antioxidants. This review article majorly deals with the natural sources of antioxidants their classification, types, mechanism, potential sources and impacts on human physiology.

Keywords: antioxidants, free radicals, health supplements, reactive oxygen species

1. Introduction
Free radicals or reactive oxygen species are constantly being formed in our body due to various reasons causing oxidative stress[1]. High levels of free radicals are harmful. They can cause serious health issues like multiple illnesses, including diabetes, heart disease, and cancer. Antioxidants are molecules that fight with free radicals in our body. Our body has its own antioxidant defence to keep free radicals in check. Antioxidants can be defined as any substance that significantly delays or prevents the oxidation of a substrate in an organism. Without antioxidants, free radicals would cause serious harm very quickly, eventually resulting in death. However, free radicals also serve important functions that are essential for health for example; our immune cells use free radicals to fight infections. As a result, our body needs to maintain a proper balance of free radicals and antioxidants. When free radicals outnumber antioxidants and equilibrium is disturbed it leads to oxidative stress. It is a process that can trigger cell damage. Prolonged oxidative stress can damage our DNA and other important molecules in our body. Oxidative stress is thought to play a very important role in a variety of diseases. Several factors like lifestyle, stress, and environmental factors are known to promote excessive free radical formation and oxidative stress, including: air pollution, cigarette smoke, alcohol intake, toxins etc. Antioxidants are man-made or natural substances that may prevent or delay some types of cell damage. Diets high in vegetables and fruits, are good sources of antioxidants. Several vitamins, such as vitamins E and C, are effective antioxidants.

2. Classification of antioxidants
Antioxidants can be exogenous or endogenous depending upon their origin. Endogenous antioxidants are naturally produced inside the biological system whereas exogenous antioxidants are supplied from outside. They can be man made or natural. Natural antioxidants are classified[2] as given in following figure 1.

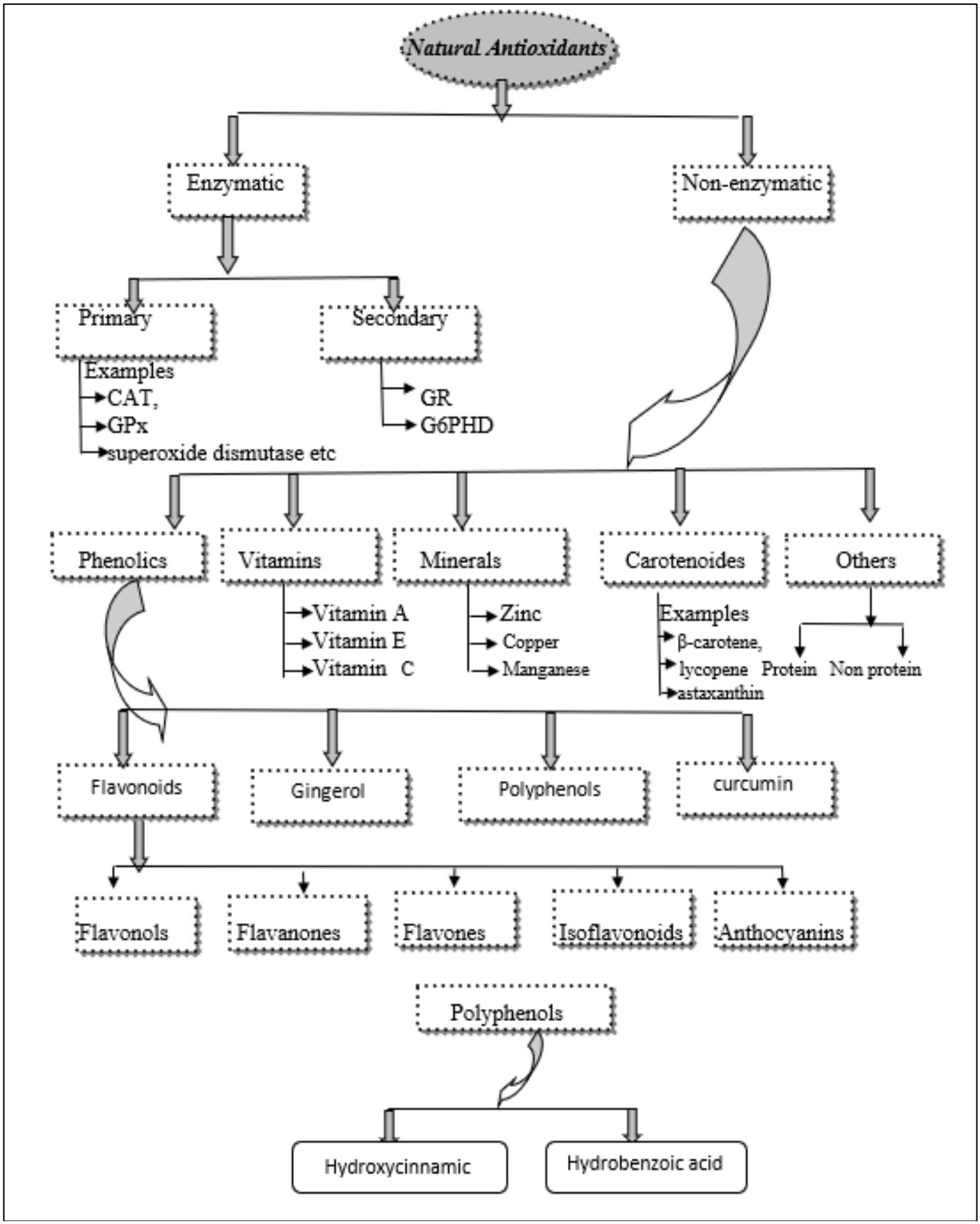

Fig 1: Classification of Natural Antioxidants

3. Types of Natural Antioxidants

Different types of antioxidants are all found in plant-based foods. Each antioxidant serves a different function and is not interchangeable with another. This is why it is important to have a varied diet. There are huge numbers of different substances that can act as antioxidants. Some of the main has been mentioned here.

3.1 Vitamins

Vitamins are essential trace substances to maintain normal physiological function of human body. The majority of vitamins cannot be synthesized by human body and can only be taken from foods. Vitamin C and vitamin E are the most well-known antioxidants and extensively studied. Vitamin C (ascorbic acid) is mainly found in fresh vegetables and fruits.

As a water-soluble vitamin, vitamin C plays its antioxidant role through circulation flow in blood, body fluid and cells, thus protecting cells and tissues from free radicals.
Vitamin E is a kind of fat-soluble vitamin, also known as tocopherol. Vitamin E has a very extensive function of protecting biological membrane in human body and nucleic acids in cells from the attacking of free radicals[3].
Vitamin D is a membrane antioxidant thus Vitamin D3 (cholecalciferol) and its active metabolite 1,25-dihydroxycholecalciferol and also Vitamin D2 (ergocalciferol) and 7-dehydrocholesterol (pro-Vitamin D3) all inhibited iron-dependent liposomal lipid peroxidation.

3.2 Carotenoids
Carotenoids are structurally and functionally a very diverse group of natural pigments of the polyene type [4]. Carotenoid is a fat-soluble natural pigment in dark green coloured and yellow fruits and vegetables, and is a general definition of polyunsaturated hydrocarbons containing 40 carbon atoms. They are efficient antioxidants scavenging singlet molecular oxygen and peroxyl radicals. In the human organism, carotenoids are part of the antioxidant defense system. Carotenoids contain many double bonds. Carotenoid antioxidants have protective functions for diabetes, and neurodegenerative, cardiovascular and inflammatory diseases. Oxidative stress and inflammation caused by free radicals are important factors for diabetes with the complication of eye problems.

3.3 Polyphenols
Polyphenols are natural organic compounds rich in fruits and vegetables, tea, red wine, honey and cocoa beans. Polyphenols are secondary metabolites that plants produce to protect themselves from other organisms. Dietary polyphenols have been shown to play important roles in human health. Polyphenols have been found to be strong antioxidants that can neutralize free radicals by donating an electron or hydrogen atom. High intake of fruits, vegetables and whole grains, which are rich in polyphenols, has been linked to lowered risks of many chronic diseases including cancer, cardiovascular disease, chronic inflammation and many degenerative diseases [5, 6].

3.4 Flavonoids
Flavonoids are an important class of natural products; particularly, they belong to a class of plant secondary metabolites having a polyphenolic structure, widely found in fruits, vegetables and certain beverages. They have miscellaneous favourable biochemical and antioxidant effects associated with various diseases such as cancer, Alzheimer's disease (AD), atherosclerosis [7-9], etc.
They are found in fruits, vegetables, grains, bark, roots, stems, flowers, tea and wine. It is well known that plants have many kinds of flavonoids. Common flavonoids compounds include flavones, isoflavones, anthocyanins and xanthonoids. Flavonoids execute the clearance of free radicals by trans-forming them into phenolic radicals (inert) after supplying the hydrogen to lipid compounds radicals.

4. Mechanism
Recently there has been an increased interest in research on reactive oxygen species (ROS) which have their specific role in the biological system. Increased levels of ROS have been shown to associated with many degenerative diseases such as cardiovascular diseases, cancers, type 2 diabetes, obesity, and hypertension. However, ROS may have dual roles. In a biological system, cells must sense their immediate surroundings and change their activity according to their microenvironment. For this there is a cell signalling pathway in which these ROS play an important role. To minimize the toxic effects of ROS and proper functioning of these cell signal pathway, nature has evolved a specific combination of antioxidants in different plants and organisms.
Based on various researches on the dual role of ROS and the large variety of ROS and mechanisms involved, it has been shown that it is beneficial to take combinations of antioxidants in their natural form which have been evolved naturally in plants according to their environment and needs instead of synthetic antioxidant supplements. Further, there may be variation in the antioxidant intake and their final activity in the cell which depends on the food processing, preparation and their absorption in the body.

4.1 Mechanism of action of some antioxidants on ROS
Vitamin C can reduce ROS responsible for its antioxidant property. It can be directly and rapidly reacted with superoxide ion O_2^- and singlet oxygen such as HOO^- or OH^- through dehydrogenation, and generate dehydroascorbate. As hydrogen donor, it can also play an indirect antioxidant effect through the reduction of oxidized vitamin E and thiol. The chemical equation [10] of reaction can be expressed as:

$$RO^{\bullet} + C_6H_7O_6^- \rightarrow RO^- + C_6H_7O_6^{\bullet} \rightarrow ROH + C_6H_6O_6^{\bullet}$$

Vitamin E can directly remove O_2^-, quench singlet oxygen and superoxide dismutase (SOD) and establish an antioxidant system in human body together with glutathione peroxidase (GSH-Px).

Carotenoids contain many double bonds. They can quench singlet oxygen in a physical way and can also react with oxygen free radicals in three ways such as electron transfer, hydrogen atom transfer and radical coupling. The reaction equations are $ROO^{\bullet} + Car \rightarrow ROO^- + Car^{\bullet+}$; $ROO^{\bullet} + Car \rightarrow ROOH + Car^{\bullet}$; and $ROO^{\bullet} + Car \rightarrow (ROO)Car^{\bullet}$, respectively. The most common carotenoids are β-carotene, γ-carotene and lycopene in plants, and astaxanthin in animals.

Polyphenols with multiple hydroxyl groups can effectively remove free radicals including O_2^- and singlet oxygen to execute healthcare functions. Phenolic compounds, as primary antioxidants, act according to two mechanisms[11]: hydrogen-atom transfer (HAT) or single-electron transfer (SET). The HAT mechanism occurs when an antioxidant compound quenches free radical species by donating hydrogen atoms:

$$nRO^{\bullet}{}_2 + ArOH \longrightarrow ROOH + ArO^{\bullet}$$

The free radical formed in this reaction is much more stable than $RO^{\bullet}{}_2$. The SET mechanism occurs in cases where an antioxidant transfers a single electron to aid in the reduction of potential target compounds:

$$nRO^{\bullet}{}_2 + ArOH \longrightarrow RO_{2-} + [ArOH]^{\bullet+}$$

The resultant radical-cationic antioxidant compound is then deprotonated by interacting with water:

$$[ArOH]^{\bullet+} + H_2O \rightleftharpoons ArO^{\bullet} + H_3O^+$$

$$RO_{2-} + H_3O^+ \rightleftharpoons ROOH + H_2O$$

Flavonoids execute the clearance of free radicals by transforming them into phenolic radicals (inert) after supplying the hydrogen to lipid compounds radicals.

5. Different Sources of Antioxidants

5.1 Fruits/Vegetables

Fruits and vegetable have been an integral part of our diets since ages. They have been known for their high nutritional value as a rich source of vitamins, minerals, catotenoides, polyphenols and other antioxidants. Polyphenols, present in fruits and vegetabables have been shown to have antioxidant properties that prevent lipid oxidation [12] Fruits and vegetables are also contain flavonoids including flavones, isoflavones, anthocyanins and xanthonoids which are known to scavenge free radicals by converting them into inert phenolic radicals. Isoflavone has shown to have a preventive effect on prostate cancer [13] Antioxidant contents of various fruits and vegetable have been summarized in the table-1 given below.

Table 1: Main Antioxidants present in common fruits/Vegetables

Name	Antioxidant contents
Apple	Proanthocyanidins, flavonoids (kaempferol, quercetin, and naringenin derivatives); phenolic acids (protocatechuic, caffeoylquinic, and hydroxycinnamic acid derivatives); hydroxychalcones (phloretin and 3-hydroxyphloretin derivatives); isoprenoid glycosides (vomifoliol derivatives) Flavanols, flavonols, dihydrochalcones, and hydroxycinnamates
Apricots	Beta carotene and vitamins A, C, and E
Asparagus	Vitamin E, vitamin C and glutathione
Avocados	lycopene and beta-carotene
Banana	Vitamin C, vitamin E, and β-carotene
Beet root	Betalains, vitamins C and E, carotenoids, flavonoids, and thiol (SH) compounds
Broccoli	Lutein and zeaxanthin
Cabbage	Beta-carotene, lutein
Carrot	Vitamins C and E, carotenoids, flavonoids, and thiol (SH) compounds
Cauliflower	Vitamins C and E, carotenoids, flavonoids, and thiol (SH) compounds
Cherries	Anthocyanins and cyanidin
Cranberries	Anthocyanins, proanthocyanidins, and quercetin
Grapes	Flavonoids catechin, epicatechin, quercetin, and anthocyanins
Guava	β-Carotene, lycopene, vitamin C, ellagic acid, anthocyanin
Lettuce	Phenolic acids, flavonoids, anthocyanins, and vitamins A and C
Mango	Beta-carotene
Oranges	Flavonoids (hesperetin and naringenin predominantly as glycosides), carotenoids (xanthophylls, cryptoxanthins, carotenes), and vitamin C
Papaya	Quercetin and β-sitostero
Pea	Vitamins C and E, carotenoids, flavonoids, and thiol(SH) compounds
Peach	Lutein, zeaxanthin and beta-cryptoxanthin.
Peanut	Coumaric acid and resveratrol
Pears	Ascorbic acid, flavonoids (quercetin, isorhamnetin, myricetin, kaempferol, and luteolin), betalains, taurine, total carotenoids and total phenolics
Plum	Proanthocyanidins, flavonoids kaempferol, quercetin, and naringenin derivatives); phenolic acids (protocatechuic, caffeoylquinic, and hydroxycinnamic acid derivatives); hydroxychalcones (phloretin and 3-hydroxyphloretin derivatives); and isoprenoid glycosides (vomifoliol derivatives)
Pomegranate	Vitamin C and polyphenols
Potatoes	Flavonoids, carotenoids
Pumpkin	phenolics, flavonoids, anthocyanins, and vitamins A and C,
Raspberries	Vitamin C, quercetin and ellagic acid
Spinach	Vitamins C and E, carotenoids, flavonoids, and thiol (SH) compounds
Strawberries	Vitamins C
Tomato	Vitamins C and E, carotenoids, flavonoids, and thiol (SH) compounds
Water melon	Lycopene, β-carotene, vitamin C
White cabbage	Vitamins C and E, carotenoids, flavonoids, and thiol (SH) compounds
White onion	Vitamins C and E, carotenoids, flavonoids, and thiol (SH) compounds

5.2 Fruits and vegetable wastes

The vegetables and fruit waste material like peels, left overs, shells, seeds, stems, and pulp residues that remained after extraction of juices and starch or sugar preparation have been shown to have more amounts of antioxidants than the fruits pulp itself without peel [14] Various Bioactive phytochemicals have been isolated from tomatoes and their processing by products which may be used to formulate functional foods or can be used as food additives [15]

Different antioxidants found in various fruits and vegetable wastes are summarized in the Table-2 given below.

Table 2: Antioxidants found in some fruits and vegetable wastes

Fruit	Residue	Antioxidant
Apple	Peel	Epicatechin, catechins, anthocyanins, quercetin glycosides, chlorogenic acid, hydroxycinnamates, phloretin glycosides, and procyanidins
Banana	Unripe (green) fruit and peel	Phenols and flavonoids
Carrot	Peel	Phenols, β-carotene
Coffee	Coffee ground and residue	Polyphenols, tannins, and gallic acids
Cucumber	Peel	Flavonoids and phenols pheophytin, phellandrene, caryophyllene
Grapes	Skin and seeds	Coumaric acid, caffeic acid, ferulic acid, chlorogenic acid, cinnamic acid, neochlorogenic acid, p-hydroxybenzoic acid, protocatechuic acid, vanillic acid, gallic acid, proanthocyanidins, quercetin 3-o-gluuronide, quercetin, and resveratrol
Guava	Skin and seeds	Catechin, cyanidin 3-glucoside, galangin, gallic acid, homogentisic acid, and kaempferol
Mango Peel	kernel	Gallic acid, ellagic acid, gallates, gallotannins, condensed tannins
Pomegranate	Peel and pericarp	Gallic acid, cyanidin-3,5-diglucoside, cyanidin-3-diglucoside, and delphinidin-3,5-diglucoside
Potato	Peel	Chlorogenic acid, caffeic acid, ferulic acid, gallic acid, vanillic acid, chlorogenic acid, ferulic acid, and phenols
Tomato	Skin and pomace	Carotenoids
Water melon	Peel, rinds	Citrulline, lycopene, flavonoids, and phenols

5.3 Herbs

Various herbs are being used as an ingredient of food all over the world are known to contain important antioxidants which are known to show varied biological activities against many diseases[16]. Some of their antioxidant content are summarized below in Table given below.

Table 3: Antioxidants found in Herbs

Name	Antioxidant contents
Allspice	Eugenol, quercetin, gallic acid, and ericifolin
Cinnamon	Polyphenol
Clove	Eugenol
Oregano	Thymol, carvacrol, limonene, terpinene, ocimene, and caryophyllene
Peppermint	Polyphenol
Rosemary	Diterpenes, carnosol and carnosic acid
Sage	160 distinct polyphenols
Thyme	Flavonoids (lutein, apigenin, naringenin, luteolin, and thymonin)

5.4 Mushrooms

Mushrooms belonging to the kingdom fungi have not been a part of ancient Indian cuisine but it finds its place in ancient Greek and Roman food. In modern world it has become an important source of supplements including carbohydrates, for example, β-glucans; lipids; B-vitamins, such as niacin, flavin, and pyridoxine; phenolics, like tocopherols; organic acids, for example, malate ascorbate, fumarate, and shikimate; monoterpenoid and diterpenoid; proteins, for example, hydrophobins; and trace components, for example, selenium [17-19]. Different antioxidant contents of various edible mushrooms are compiled it the Table givemn below.

Table 4: Antioxidant found in Mushrooms

Name	Antioxidant contents
Agaricus bisporus	Vitamin C, D, B12; folates; and polyphenols
Armillaria mellea	ascorbic acid and phenolic components
Auricularia auricula	phenolic substances
Boletus edulis	phenol contents polysaccharides
Ganoderma lucidum	polysaccharides, sterols, triterpenoids, nucleosides, and alkaloids
Grifola frondosa	phenols, ascorbic acid, α-tocopherol, and flavonoids
Hypsizigus marmoreus	Phenols and polysaccharides
Lentinus edodes	vitamin B, B1, B2, B5, B12, and pro vitamin D2
Pleurotus ostreatus	phenols, flavonoids, and carotenoids
Schizophyllum commune	polysaccharides and polyphenols

5.5 Medicinal Plants

Medicinal plants also contain several types of antioxidants like polyphenols, vitamins, carotenoids etc. Many of these medicinal plants are already an integral part of our diet and they have been traditionally used for different ailment from a long time. For example curcuma [20], capsicum [21] etc. Some medicinal plants with their antioxidant content are tabulated below.

Table 5: Antioxidant found in Medicinal plants

Name	Antioxidant contents
Allium sativum (garlic)	Vitamins phenolic compounds
Capsicum annuum (red pepper)	carotenoids, flavonoids, tocopherols, polyphenols and carotenoids
Curcuma longa	phenolic compounds
Eugenia caryophyllus (clove)	eugenol phenolic compounds
Leea indica	phenolic compounds
Moringa	Flavonoids, beta carotene
Murraya(Curry leaves)	Phenolic acids, tocopherol, beta carotene, lutein
Azadirachta indica (Neem)	Limonoids, flavonoids, ascorbic acid
P. lentiscus	alkaloid, sesquiterpenes
Polyalthia cerasoides	phenolic compound
Salvia officinalis (garden sage)	Polyphenol
Ocimum sanctum (Tulsi)	Eugenol, carvacrol, linalool, beta caryophyllene

6. Natural antioxidants in foods and their roles in prevention and treatment of diseases

Antioxidants are molecules that can safely react with free radicals to neutralize or terminate the chain reaction before vital molecules are damaged. They exert their defence mechanisms in a number of ways. Research studies suggest that antioxidants can prevent oxidative damage in those individuals who consume large amounts of fruits and vegetables seem to experience lower rates of diseases caused by oxidative damage. In human, oxidative damage and free radicals are associated with a number of diseases including atherosclerosis [22], Alzheimer's disease [23], cancer [24], ocular disease [25], diabetes [26], rheumatoid arthritis [27] and motor neuron disease [28]. Different antioxidants, their sources and target diseases are compiled in the table-6.

Table 6: Natural antioxidants[10] in foods and their roles in prevention and treatment of diseases.

Natural antioxidants	Foods rich in natural antioxidants	Target diseases
Anthocyanins	Black rice, purple sweet potato, blueberry, mulberry and other dark foods	Cardiovascular disease, neurodegenerative diseases, liver cancer
Astaxanthin	Shrimp shell, oysters and salmons	Aging, Alzheimer’s disease and inflammation
Carotene	Dark green or red and yellow fruits and vegetables	Eye diseases caused by diabetes
Cocoa polyphenol	Cocoa bean	Arteriosclerosis, coronary heart disease, and alcoholic liver
Flavonoids	Plants, berries, honey	Cardiovascular disease, arthritis, Alzheimer’s disease, stroke
Green tea polyphenols	Green tea	Aging, Alzheimer’s disease, diabetes, cardiovascular diseases, tumors and inflammation
Isoflavonoids	Soybean	Prostate, ovarian, cervical and breast cancers
Lycopene	Tomatoes	Parkinson’s and Alzheimer’s diseases
Red wine polyphenols	Red wine, grape seeds	Diabetes, cardiovascular diseases
Peach polyphenols	Peaches	Breast cancer
Vitamin C	Fresh fruits and vegetables	Cardiovascular disease, cancer, and cirrhosis
Vitamin E	Nuts, green fruits and vegetables	Lung, skin and prostate cancers
Xanthones	Mangosteen	Inflammation, nerve injury

7. Conclusion

Today researchers are showing much interest in antioxidants as they are important in maintaining the balance in body metabolism by trapping the free radicals generated in the body. It has been shown that a dietary intake of natural antioxidants in their usual natural form is beneficial instead of consuming synthetic supplements. However high doses of these antioxidant supplements have been shown to be associated with many health risks. For example supplementing of high doses of beta-carotene has shown to increase risk of lung cancer in smokers and vitamin E may increase prostrate cancer and one type of stroke. It is therefore necessary to maintain a balance of antioxidants in our body for better health benefits. This article emphasizes the role of natural sources of antioxidants in diet.

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