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Antioxidant Potential of Fruits and Vegetables

Kamlesh Prasad[1*], Ravneet Kaur[1] and Shubhra Shekhar[2]

[1]Department of Food Engineering and Technology, SLIET, Longowal, Punjab, India
[2]Department of Food Process Engineering, NIT, Raurkela, India

[*]**Corresponding author:** Kamlesh Prasad, Department of Food Engineering and Technology, SLIET, Longowal, Punjab, India, Tel: 9417741225; Email: profprasad@gmail.com

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Abstract

An antioxidant is of great interest among researchers, scientists, nutritionists, and the public because of its ability to prevent oxidative damage, as indicated by various studies. This chapter mainly focuses on the free radicals and their types; antioxidants and their mode of action against free radicals; fruits, vegetables, and their byproducts as a source of antioxidants; and various analytical methods employed for assessing antioxidant activity. Antioxidants discussed in this chapter are ascorbic acid, vitamin E, carotenoids and polyphenols, and their mechanism of action. Different antioxidant activity assay techniques have been reported. Fruits and vegetables are abundant sources of these secondary metabolites. The waste generated during processing has many bioactive materials, which possibly be used in value-added by-products.

Keywords: Antioxidant; Free radical; Oxidative stress; Secon dary metabolite; Ascorbic acid; Carotenoids; Polyphenol; Degenerative diseases

Introduction

The word antioxidant is commonly heard nowadays, especially whenever there comes a topic of health concern. People consume antioxidants as a symbol of a healthy lifestyle to fight against various health problems, better skin, and anti-aging benefits. What makes antioxidants so important? The trait responsible for such importance of antioxidants is their ability to stop free radical reactions that can have potentially deleterious effects [142]. This gives rise to various questions like- What are the free radicals? What are the sources of free radicals? What are their harmful effects? What are antioxidants? What are the common sources of antioxidants? How do they work against free radicals? Answers to these questions are discussed in the present chapter.

Free radicals

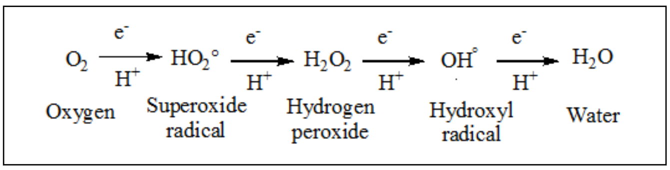
Free radicals are those atoms or molecules with an unpaired electron in their outer orbit [42]. Any electron present alone in an orbital is referred to as an unpaired electron, and it is accountable for the reactive and unstable state of the free radical. The vital class of free radicals generated in a living system is usually derived from Oxygen and Reactive Oxygen Species (ROS) [3]. Hydroperoxyl ($HO2^{O}$), alkoxy (RO^{O}), peroxyl ($RO2^{O}$), hydroxyl (OH^{O}), and superoxide radical ($HO2^{O}$) are common among Oxygen free radicals. Nitrosative stress is the condition that occurs due to the overproduction of Reactive Nitrogen Species (RNS) [67,121]. Nitric oxide (NO^{O}) and nitrogen dioxide ($NO2^{O}$), the nitrogen-free radicals can also be converted into other nonreactive species under the antioxidant-dependent reactions. Thus, ROS and RNS include radicals and non-radical species like hydrogen peroxide, singlet oxygen, ozone, organic peroxide, peroxynitrite, nitrosyl cation, nitroxyl cation, dinitrogen trioxide, and nitrous acid [35]. When Reactive Oxygen Species (ROS) reacts with thiols, they give rise to Reactive Sulfur Species (RSS) [84].

The most reactive hydroxyl free radical is formed by exposure to ionizing radiations. These radiations lead to the formation of Ho and OH^{O} by causing the fission of OH bonds in water

$$H_2O \rightarrow H^{o} + OH^{o}$$

Harmful effects are initiated when the hydroxyl radical reacts with macronutrients such as carbohydrates, protein, and lipids along with DNA, the genetic material [147].

Molecular Oxygen receives one electron and is converted to superoxide anion, a reduced form [52]. Superoxide anion is formed in the mitochondria during the initial step of the electron transport system [37]. Oxygen is reduced to water during the electron chain reaction. The electrons escape a chain reaction and react directly with Oxygen in its formation [52].



Many other reactive oxygen species are also formed in the living system by the formed superoxide anions. These include hydrogen peroxide, hydroxyl radicals or singlet oxygen [139].

Hydrogen peroxide ($H2O2$) is a nonradical that is formed by the super oxide radical when it undergoes nonenzymatic or enzyme-catalyzed (Superoxide Dismutase, SOD) dismutation reaction. It is very diffusible within and between the cells [21].

$$O_2 \xrightarrow[H^+]{e^-} HO_2^{\circ} \xrightarrow[H^+]{e^-} H_2O_2 \xrightarrow[H^+]{e^-} OH^{\circ} \xrightarrow[H^+]{e^-} H_2O$$

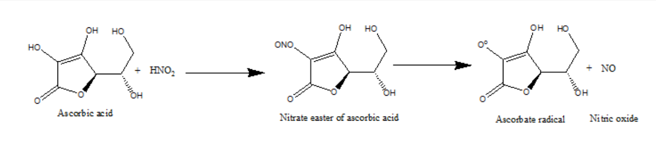
Oxygen — Superoxide radical — Hydrogen peroxide — Hydroxyl radical — Water

In the presence of metal ions and superoxide anion, hydrogen peroxide generates a hydroxyl radical.

$$HO_2^{\circ} + H_2O_2 \longrightarrow OH^{\circ} + OH^- + O_2$$

Superoxide radical + Hydrogen peroxide → Hydroxyl radical + Hydroxyl ion + Oxygen

Nitric oxide is formed during the metabolization of arginine to citrulline by the enzyme Nitric Oxide Synthase (NOSs) via five electron oxidative reactions [40]. Nitric oxide readily diffuses through cytoplasm and plasma membranes due to its solubility in both liquid and liquid media [23].



Sources of Free Radicals and Harmful Effects

Oxygen, an essential element of life, also has harmful effects on the human body by forming reactive oxygen species [83]. Free radicals are produced internally as well as due to external factors.

Internal factors

- Normal metabolism within mitochondria during electron transport reactions and another mechanism [17]
- Xanthine oxides
- Inflammation Processes by neutrophils and macrophages
- Phagocytosis
- Ischaemia
- Peroxisomes [83]

External factors

- Radiation
- UV rays, X rays, γ rays
- Environmental pollutants
- Certain drugs, pesticides, anesthetics
- Ozone
- Cigarette smoke [74]

Reactive oxygen species mediate damage to cells structures, including lipids and membrane protein and the nucleic acid under the presence of its higher concentration. This condition is termed oxidative stress [112]. These free radicals' processes are also associated with various food products. The rancidity of fatty foods like potato chips and butter is due to free radical chain oxidation. Oxidation of Polyunsaturated Fatty Acid (PUFA) is also associated with free-radical processes [114]. The importance of antioxidants is because of their property to stop the free radical chain reaction.

Antioxidants

An antioxidant is a chemical compound that has free radical scavenging properties, can delay or inhibit cellular damage and neutralize the effect of free radical by donating an electron [48]. Antioxidants thus counteract oxidative stress. A series of defense mechanisms have been developed to combat the exposure to free radicals from various sources [18]. Antioxidants further contribute to disease prevention and protect cells from the toxic effects of free radicals by neutralizing their excess. Antioxidants can be endogenous, generated in situ or exogenous, supplied through food [111].

To prevent the condition like oxidative stress, it is essential to maintain a balance between the production of free radicals and antioxidants defense [5]. Fruits and vegetables are consumed by people as a source of antioxidants, as they are rich in flavonoids and antioxidants. It contributes by protecting the human being from cancer and cardiovascular problems, the ill effects of free radicals [49].

Antioxidants remove free radical intermediates and prevent or slow down the oxidation of other molecules by being oxidized themselves and terminate the chain reactions [133].

Antioxidants can act as

- Scavenging the peroxidation initiating species
- Decomposition of lipid peroxide
- prevent the generation of reactive species by chelating metal ion
- Preventing the formation of peroxides by quenching activity
- Reducing localized O2 concentrations [99]

Antioxidants also play an essential role in food products by preventing oxidation reactions, browning in fruits and vegetables, and rancidity in fats and oil [49].

Antioxidants may be of natural or synthetic origin. Natural antioxidants are the important secondary metabolites of plant origins mainly explored in preparing some functional foods. In food systems, during storage, the use of nutritional antioxidants and the micro-nutrient such as vitamin E helps maintain the color, texture, and flavor of the food product by preventing or retarding lipid peroxidation and reducing lipid peroxidation protein oxidation [32].

Vitamin C

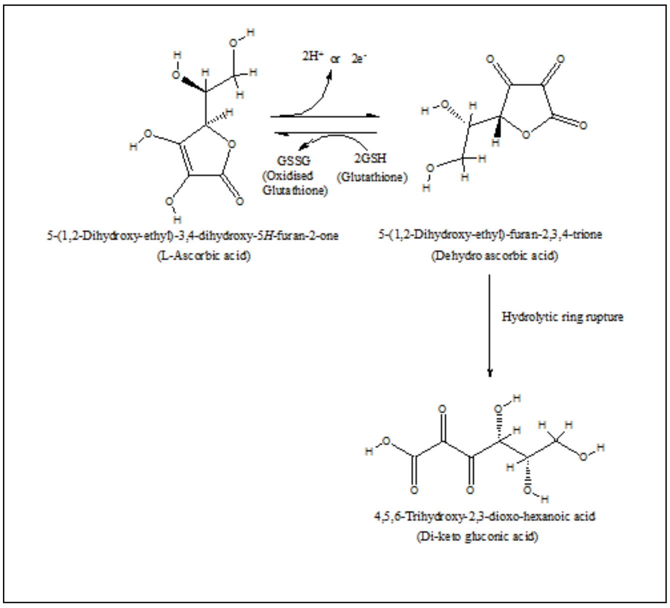
Ascorbic acid is a water-soluble vitamin commonly known as Vitamin C and was reckoned as L-ascorbic acid in 1965 by the IUPAC- IUB commission on biochemical nomenclature. Ascorbic acid has a 2,3-enediol group responsible for its antioxidant activity [81]. It is a 6-carbon lactone and cannot be synthesized in the human body, and is water-soluble; it must be regularly supplied through external means.

It plays an essential role in the biosynthesis of collagen, carnitine, and neurotransmitters [81]. The normal metabolic respiration process of the body produces potentially damaging free radicals. These free radicals can be efficiently quenched by ascorbic acid due to its reducing nature [2].

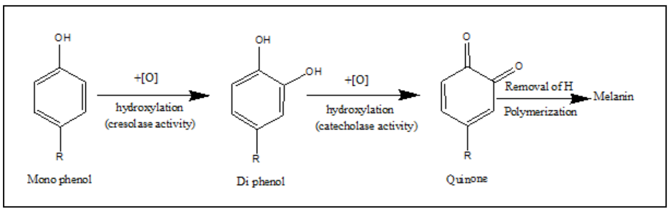
Ascorbic acid, after oxidation, leads to the formation of a dimer called Dehydroascorbic Acid (DHA). DHA is an oxidized form of ascorbic acid and can be reduced back to ascorbic acid by the action of glutathione (GSH) [1]. In aqueous solutions, Dehydroascorbic acid exists as hydrated hemiketal [126].

The formation of dehydroascorbic acid from ascorbic acid is a two-step reversible oxidation process, during which ascorbyl radical is formed as an intermediate [75]. Ascorbyl radical is involved in the termination of free radical reactions, due to the delocalized nature of unpaired electron present in it, it reacts with free radicals [126].

Dehydro-ascorbate is irreversibly converted to 2,3-diketo-L-gluconic acid with the hydrolysis of lactone ring [12,22]. Diketo-L-gluconic acid is unstable and does not have biological activity [26].



In fruits and vegetables with low levels of antioxidant (Vitamin C), on cutting, there is the exposure of the phenolic group to Oxygen, and the cresolase and catecholase activity act and form quinone, which converts further to dopachrome before its polymerization into brown melanin pigment. Ascorbic acid can reverse this reaction, which converts quinones back to phenolic form [82].



Termination of lipid peroxidation chain reaction is carried by ascorbic acid by donating an electron to lipid radical, which gets converted to ascorbate radical. These ascorbate radicals further react with each other to form ascorbate and dehydroascorbate molecules. Dehydroascorbate molecule on the addition of two electrons is converted back to ascorbate molecule because DHA does not have the antioxidant capacity, and this process is carried out by oxidoreductase [102].

Ascorbic acid prevents the formation of N- nitrosamines in nitrate-cured meats. It results in NO's formation, which is desirable for cured meats color [82]. L- ascorbic acid protects against oxidation of low-density lipoprotein implicated in the development of atherosclerosis by scavenging reactive oxygen species, which prevent oxidative stress [58].

Vitamin E

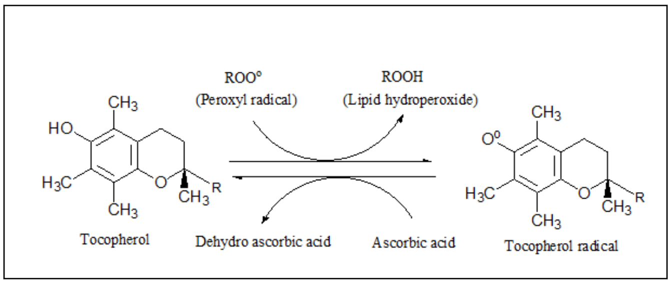
Vitamin E is a fat-soluble vitamin found in tocopherol and tocotrienol structures which exists in eight different isomeric forms equal configurations for both the forms [34]. All eight forms are lipophilic. Chromanol group is responsible for antioxidant activities, and its methylation differs among all the members of the vitamin E group [101].

Amount of methyl groups attached to phenol ring and pattern of methylation are responsible for reactive antioxidant activities for these isomers, which is found to be α>β>γ>δ. The highest activity of α - tocopherol is due to the presence of 3-methyl substituents [64]. The Food and Nutrition Board defines Vitamin E requirements in the human body are fulfilled only by α-tocopherol.

Vitamin E repairs the oxidizing radicals during lipid auto-oxidation and halts the propagation step, thus acting as a chain-breaking antioxidant [127].

ROO°	+	Toc-OH	⟶	ROOH	+	Toc-O°
Peroxyl radical		α - tocopherol		Lipid hydroperoxide		α - tocopherol radical

Ascorbic acid is responsible for the regeneration of α - tocopherol from α - tocopherol radical. Thus, there is a synergistic effect between α-tocopherol and ascorbic acid [150].



Vitamin E consumption plays an essential role in preventing the oxidation of low-density lipoprotein cholesterol and reduces the risk of heart diseases [54]. Otherwise, it may lead to atherosclerosis. Vitamin E intake is associated with preventing several diseases like cancer, cardiovascular diseases, eye disorders, neurological disorders, and aging [5].

Carotenoids

Carotenoids are yellowred pigments synthesized naturally by plants and some microorganisms [108]. They have an isoprenoid polyene structure [16]. These are a group of tetra terpenoids that they contain eight isoprene units with 40 carbon atoms.

Carotenoids can be categorized into two groups:

- Carotenoid hydrocarbons (carotenes) contains specific end group as in β-carotene or lycopene
- Oxygen carotenoids (xanthophylls) as zeaxanthin and lutein [108]

Consumption of foods that are a rich source of carotenoids is related to a decrease in age-related diseases. Coronary heart diseases associated with oxidation of LDL cholesterol can be prevented by lycopene and β carotene [149].

Antioxidant activities of carotenoids are due to their structure which contains conjugated double bond, and their ability to delocalize unpaired electrons [96]. Singlet molecular oxygen $^1O2$ and peroxyl radicals are among the two reactive oxygen species that are most likely to be scavenged by carotenoids [151]. At a low concentration of Oxygen, the antioxidant activity of carotenoids increases, and at higher concentrations, it acts as a pro-oxidant [29].

Scavenging of superoxide anions (•O2-) by β- carotene occurs as follows [30].

$$\underset{\text{Superoxide anion radical}}{^{\bullet}O_2^-} + \underset{\text{Carotenoid}}{CAR} + 2H^+ \rightleftharpoons \underset{\text{Carotenoid}}{CAR^+} + \underset{\text{Hydrogen peroxide}}{H_2O_2}$$

Carotenoids can hinder free radical chain reactions that occur during lipid peroxidation due to their antioxidant activity. Free radical reactions proceed in the following manner [69].

Initiation

$$\text{Initiator} + RH \rightarrow R^{o}$$

Propagation

$$R^{o} + O_2 \rightarrow ROO^{o}$$

Termination

$$ROO^{o} + ROO^{o} \rightarrow \text{Product}$$

This chain reaction can be inhibited by carotenoids in 3 ways [68].

- Electron transfer

$$ROO^{o} + CAR \rightarrow ROO^{-} + CAR^{o\,+}$$

- Hydrogen abstraction

$$ROO^{o} + CAR \rightarrow ROOH + CAR^{o}$$

- Addition of radical species

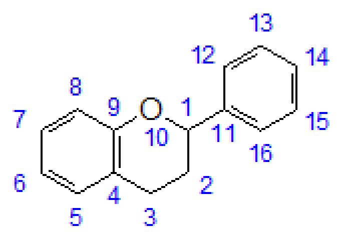
$$ROO^{o} + CAR \rightarrow (ROO - CAR)^{o}$$

The photooxidative process leads to eye and skin diseases on exposure to light. The light filtering effect and antioxidant activity of carotenoids can protect against the ill effects of these processes [138]. β carotene acts as a provitamin and precursor for the formation of vitamin A in the human body.

Polyphenols

Polyphenols are chemical compounds having phenolic structures and are obtained from plant sources [144]. These have several bioactive properties like they may act as attracting agents for pollinators, contribute to pigmentation of plants, as an antioxidant, and protection from UV light [98].

The chemical structure of these compounds comprises an aromatic ring with one or more hydroxyl groups. These can be simple phenolics or in polymeric form having high molecular mass [6]. The most important group of polyphenols is flavonoids (glycosides with benzopyrone nucleus). Flavonoids include flavones, flavonols, flavanone, flavonols, and anthocyanins [135]. Flavonoids consist of 15 carbon atoms having an arrangement as shown below in fig. These are compounds having a low molecular weight [90].



Flavonoids

The antioxidant activity of these compounds is due to their ability to donate hydrogen and metal ion chelation [15]. Phenolic radicals formed after presenting hydrogen atoms do not readily participate in other radical reactions, as they become resonance stabilized [79]. Flavonoids can form a complex with metals and thus prevents metal-initiated lipid oxidation [55].

The difference in structure and glycosylation patterns of these compounds is responsible for their different antioxidant activity. Glycosides of anthocyanidins are called anthocyanins. These are the most extensive water-soluble pigments, commonly present in flowers and fruits [15].

Tannins are an important group of polyphenolic compounds, having high molecular weight. These are categorized as hydrolyzable and condensed tannins [113]. Hydrolyzable tannins are derived from the esterification of gallic acid (3,4,5-trihydroxy

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benzoic acid). Galloyl group of core polyol (formed from esterification of gallic acid) is further esterified to obtain hydrolyzable tannins [46]. Condensed tannins are the polymeric compounds obtained from polyhydroxy flavan-3-ol. These are also known as pro-anthocyanidins [113]. Tannins have metal ion chelating properties, act as an agent for protein precipitation, and possess antioxidant activity [46].

Polyphenolic compounds act as antioxidants to inactivate free radicals by two mechanisms

- Hydrogen atom transfer mechanism
- Single electron transfer mechanism

It is supposed that an antioxidant ArOH transfers its hydrogen atom to react with free radical in the hydrogen atom transfer mechanism.

$$ArOH + R^{o} \longrightarrow ArO^{o} + RH$$

In the single electron transfer mechanism, it is supposed that an oxidant donates an electron to the antioxidant molecule [80]:

$$Ar\bar{O}H + R^{o} \longrightarrow ArOH^{+} + R^{-}$$

Methods for Antioxidant Assessment

Antioxidants play an essential role in problems related to oxidative stress, such as neurodegenerative and cardiovascular diseases. People nowadays are more focused on antioxidant-rich foods, so it is vital to assess these components' antioxidant activity or free radical scavenging capacity. There are various ways of measuring antioxidant activity (Figure 1). Different methods follow different reaction mechanisms. These can be classified according to the reaction mechanism as:

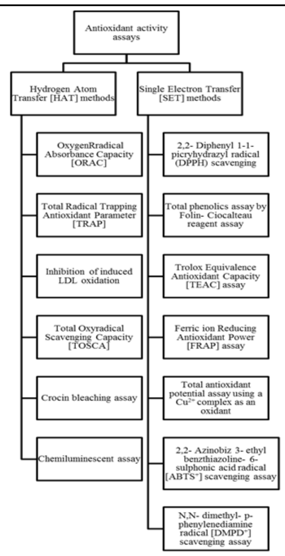


Figure 1: Antioxidant assay techniques

Hydrogen Atom Transfer (HAT) method is based on the determination of free radical scavenging activity of antioxidants by donating a hydrogen atom. These are rapid reactions and do not depend on pH and solvent but are affected by the existence of reducing agents [117]. In contrast, the Single Electron Transfer (SET) method is based on the ability of an antioxidant component to reduce the compounds such as carbonyls, radicals or metal ions by transferring a single electron [57]. The most commonly used method is the Oxygen Radical Absorbance Capacity (ORAC) assay. This method is based on the principle of decrease in intensity of fluorescent compounds like β-phycoerythrin or fluorescein due to the oxidative degradation by radicals (which leads to the formation of non- fluorescent compound) generated from thermal decomposition of AAPH (2, 2'- azobis (2- amidino propane) dihydrochloride) which is used as free radical generator. The antioxidant activity is measured as a decrease in the amount and rate of formation of non-fluorescent products [19,107]. This method provides an advantage that by altering the solvent and source of free radicals, it is possible to determine the hydrophilic and hydrophobic antioxidants. In this method, a controlled source of radicals is provided that simulates the reactions between lipids and antioxidants in food [106,116].

The Total Radical-trapping Antioxidant Parameter (TRAP) assay is based on the same principle as ORAC. The antioxidant activity is measured as the moles of peroxyl radicals that are trapped by one liter of antioxidant solution. Like the ORAC method, the loss of fluorescence is monitored. Trolox is used as a standard to compare the plasma-induced lag phase to that induced by antioxidant sample solution in the same plasma sample. It determines the activity of non-enzymatic antioxidants like ascorbic acid and glutathione, but this method is time-consuming and requires expertise [57].

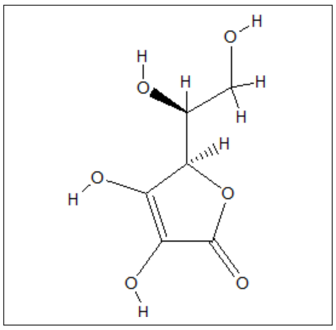
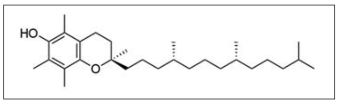
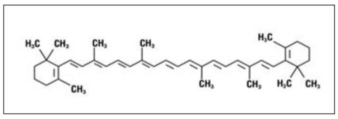
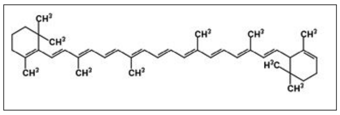
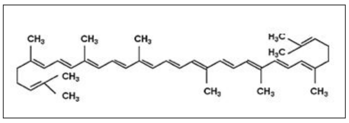
Ferric Reducing Antioxidant Power (FRAP) assay is based on the formation of the blue-colored ferrous complex by the antioxidants by reducing ferric 2,4,6- tripyridyl- s-triazine complex $[Fe3+\text{-}(TPTZ)2]^{3+}$ in an acidic medium [8]. Reactions carried out under acidic conditions (pH 3.6) to maintain the solubility of iron. Reducing 1M ferric ions to ferrous ions is known as one FRAP unit [85].

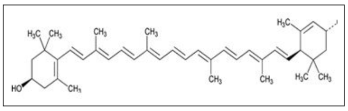
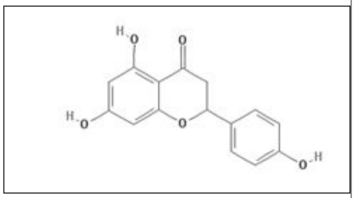
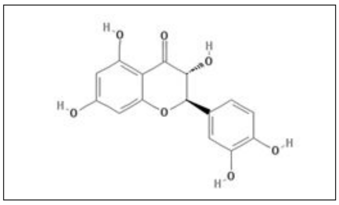
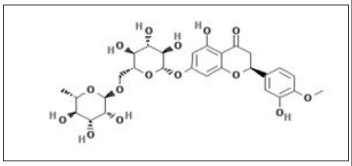
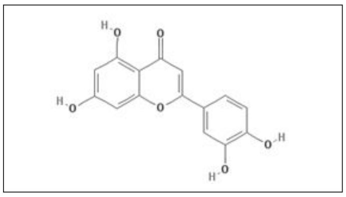
In the method of DPPH (2,2- Diphenyl- 1- picryl hydrazyl) assay, the ability of an antioxidant to scavenge DPPH radical (purple color) and reduce it to diphenyl picryl hydrazine (yellow color) is measured. Reaction carried out in an alcoholic solution [123]. Generally, the results are described as efficient concentration (EC 50). To bring about a 50% decrease in the concentration of DPPH, the amount of antioxidant required is reported as EC50 value [14].

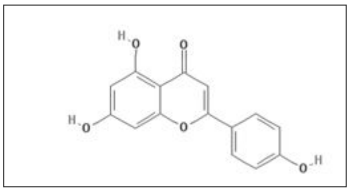
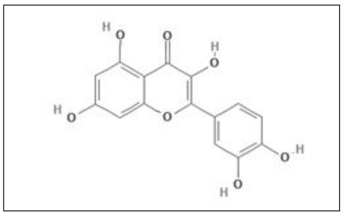
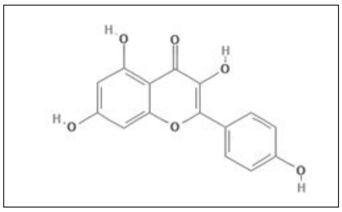
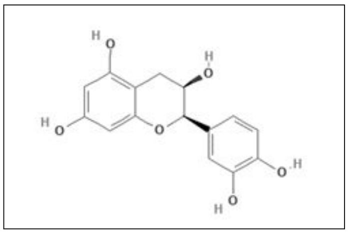
Sources of Antioxidants

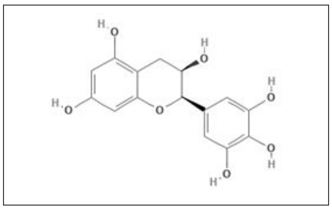
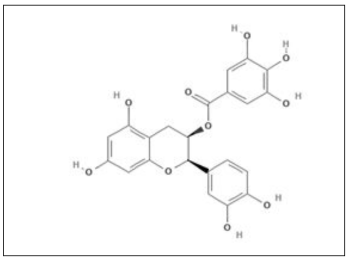
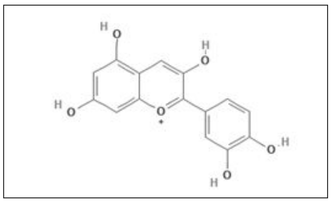
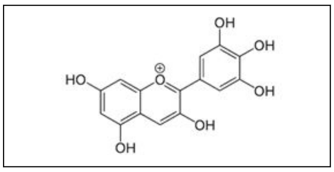
Besides providing essential nutrients, fruits and vegetables also contain substantial amounts of biologically active secondary metabolites [131]. The secondary metabolites of plants that provide numerous health benefits are covered elsewhere [51,134]. The principal dietary components found in the antioxidant properties of fruits and vegetables are polyphenols, flavonoids, carotenoids, vitamin C, vitamin E, glutathione, selenium indoles, and protease inhibitors (Table 1) [65].

Table 1: Antioxidant, chemical structure, antioxidant activity, and sources.

Antioxidant	Chemical structure	Antioxidant activity (mm)	Sources
Vitamins			
Vitamin C		1.0 ± 0.02	Citrus fruits, gooseberry, broccoli, spinach
Vitamin E		1.0 ± 0.03	Green leafy vegetables, nuts
Carotenoids			
β- Carotene		1.9 ± 0.1	Beetroot, apricots, carrots, tomatoes, mango, papaya, oranges
α- Carotene		1.3 ± 0.04	Carrots, leafy vegetables
Lycopene		2.9 ± 0.15	Apricots, grapefruit, guava, watermelon, papaya, carrots, tomato

Lutein		1.5 ± 0.1	Banana, satsuma peel, egg yolk, green vegetables
Flavonoids **Flavanones**			
Naringenin		1.5 ± 0.05	Citrus fruits
Taxifolin		1.9 ± 0.03	Citrus fruits
Hesperidin		1.0 ± 0.03	Orange
Flavones			
Luteolin		2.1 ± 0.05	Red pepper, celery, olive

Apigenin		1.5 ± 0.08	Celery, parsley
Flavonols			
Quercitin		4.7 ± 0.10	Onion, lettuce, broccoli, tomato, tea, red wine, apple
Kaempferol		1.3 ± 0.08	Leek, broccoli, grapefruit, tea
Flavanals			
Epicatechin		2.4 ± 0.02	Apricot, cherry, grape, peach, blackberry, apple, tea

Epigallocatechin		3.8 ± 0.06	tea
Epi catechin gallate		4.9 ± 0.02	tea
Anthocyanidins			
Cyanidin		4.4 ± 0.12	Cherry, raspberry, strawberry
Delphinidin		4.4 ± 0.11	Aubergine skin
Hydroxycinnamic acid			

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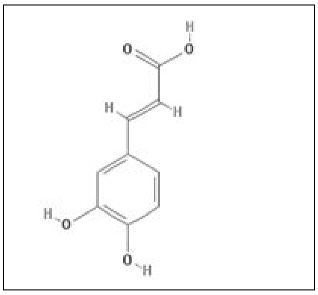
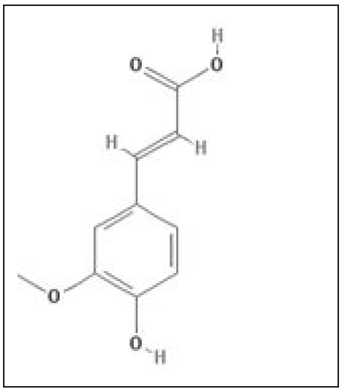
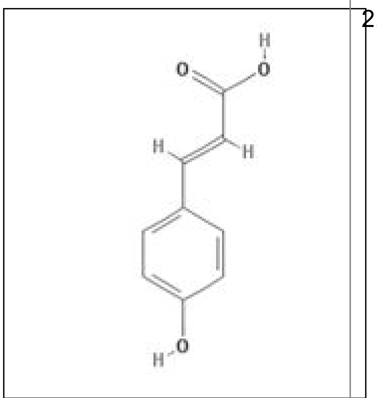
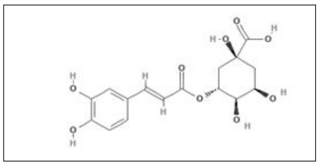
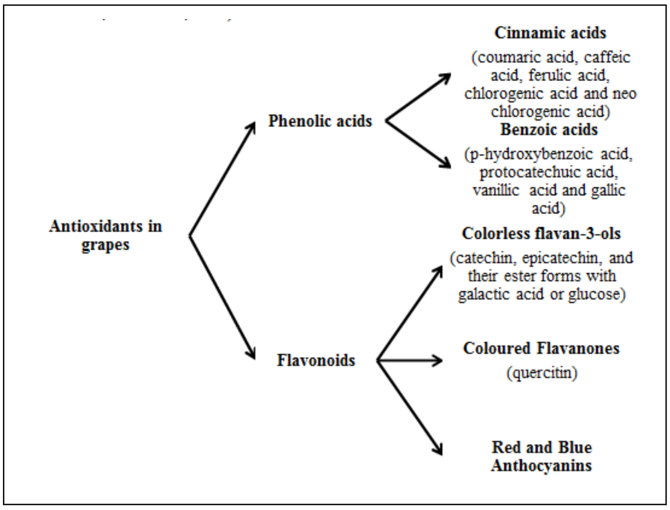
Caffeic acid		1.3 ± 0.01	White grapes, cabbage, asparagus, olive
Ferulic acid		1.9 ± 0.02	Cabbage, tomato, asparagus
p- coumaric acid		2.2 ± 0.06	White grapes, cabbage, asparagus, tomato
Chlorogenic acid		1.3 ± 0.02	Apple, peach, pear, cherry, tomato

The varying amounts of waste material are generated during the preparation of cut or processed fruits and vegetables [61]. Peels and seeds are the byproducts generated in large amounts during minimal processing of fruits and vegetables and comprise of large quantities of phytochemical components with antimicrobial and antioxidant properties [97,130,145]. All of these can be effectively utilized as a source of antioxidants. The fruits and vegetable tissues are rich in bioactive compounds like phenolics, vitamins, and carotenoids. These are even present in higher amounts in byproducts compared to the final product [4].

Grapes

Fresh grapes, grape juice, and grape wine are excellent sources of phenolic antioxidants (Figure 2). Flavonoids and other phenolic compounds present in grapes have anticarcinogenic, anti-allergic, anti-inflammatory, hepatotoxic, and antioxidative effects [24,92]. The majority of phenolics present in grapes are 60-70% in seeds and 28-35% in the skin, whereas pulp contains utmost to 10%. These phenolics can act as free radical scavengers and act as antioxidants. The grape seed oil also offers various health benefits like improving vision, protection of skin from sun damage, improved blood circulation, reduced oxidation of low-density lipoproteins, and reduced risk of coronary heart disease [129]. The antioxidant activity of grape juice is highest among the commercial juices, followed by grapefruit juice, tomato, orange, and apple [147]. Phenolic antioxidants obtained from grape pomace were found to exhibit the property to retard oxidation of human Low-Density Lipoprotein (LDL) cholesterol [93].



Apple

"An apple a day keeps the doctor away," can be attributed to the number of phytochemicals present in apples. Apple is a rich source of polyphenols, vitamins, and carotenoids that prevent free radical damage due to their high antioxidant activity. Antioxidant compounds in apples are quercitin-3-glucoside, quercitin-3-galactoside, catechin, epicatechin, procyanidin, cyanidin-3-galactoside, chlorogenic acid, coumaric acid, and gallic acid [13]. The amount of these compounds varies with the cultivars and between the flesh and peel of an apple. These phytochemicals are rice in peels as compared to flesh. Peels contain a high amount of quercetin conjugates whereas, chlorogenic acid is present in higher concentrations in the flesh [33]. Phloridzin, an antioxidant compound, mainly present in apple seeds [31], is a derivative of chalcone, also having anti-diabetic activity because of its ability to inhibit sodium-linked glucose transport, thus limiting the absorption of glucose in the intestine and kidney [28,87].

Berries

Berries are highly perishable, soft fruits, including strawberries, raspberries, blueberry, blackberry, blackcurrant, bilberry, and cranberry are rich source of bioactive compounds, mainly phenolics [141]. Blackcurrant, bilberry, and chokeberry contain a higher amount of phenolic content as compared to other berries [62]. Phenolic acids present in berry fruits include p-hydroxybenzoic acid, gallic acid, salicylic acid, ellagic acid (benzoic acid derivatives) and p- coumaric acid ferulic acid, caffeic acid (cinnamic acid derivatives) [47]. Hydrocinnamic acids can inhibit LDL oxidation [91]. There is a decrease in the phenolic content of strawberries during the development from the unripe to the ripened stage [120]. Strawberries have a similar total antioxidant capacity as that of blackberries and raspberries but are lower than blueberries [63].

Other than cut fruits, most of the berries are used as raw material for the preparation of various processed products like jams, jellies, and juices. During the processing, a large amount of waste is generated. This waste can be used to recover highly valuable bioactive compounds. Blackberry and raspberry seeds can be used for extraction of oil that is rich in antioxidant compounds such as phenols, carotenoids, and tocopherols along with linoleic acid (omega -6) and α- linoleic acid (omega-3) in 2 to 4:1 ratio [118]. Leaves and pomace from cranberry juice processing have more antioxidant activity and contain a higher amount of polyphenols than the juice [105].

Pomegranate

Pomegranate (*Punica granatum*) arils have high antioxidant activity [41] due to phenolic compounds such as anthocyanins (cyanidin, delphinidin, pelargonidin 3-glucoside and 3,5-diglucoside), punicalagin isomers and ellagic acid derivatives. These compounds inhibit lipid oxidation due to their free radical scavenging activity [103].

Pomegranate peels and seeds that are the byproducts of juice processing are wasted or used as animal feed. But, it has been found that the amount of bioactive compounds or the antioxidant activity of the extracts of peel is higher than that of juice [154]. Pomegranate seeds can be used for oil extraction that contains bioactive components. The oil extracted from pomegranate seeds has fatty acid called punicic acid (conjugated linoleic acid isomer) [66] that constitute about 70- 76% of the seed oil and has high phytosterol content [73]. There are various health benefits of this pomegranate seed oil due to its unique chemical composition. Some of these benefits include modifying blood lipid profile in people suffering from hyperlipidemia [60].

Orange

Orange segments are a rich source of carotenoids (a class of natural pigments), such as zeaxanthin, β- cryptoxanthin, antheraxanthin, violaxanthin, and mutatoxanthin. Consumption of carotenoids is linked with reducing the risk of degenerative diseases in the body [104]. Oranges are rich in various antioxidant compounds, mainly ascorbic acid and phenolic compounds [38].

During the processing of oranges for juice manufacturing, a large amount of waste comprises peels and seeds. These are an abundant source of phytochemicals that are associated with a reduction of free radical damages. Various flavonoids have been identified in the orange peel, including hydroxylated poly ethoxy flavones and methylated flavonoids. These bioactive compounds are found to have protective action against oxidative stress [86].

Banana

Banana is a global food that belongs to the genus Musa [76]. Major producers of bananas in the world are India, China, the Philippines, and Ecuador. The largest importer and exporter of bananas globally are the USA and Ecuador, respectively [36]. There is a distinctive arrangement of secondary metabolites in a banana that is responsible for its antioxidant properties. Dessert banana is a rich source of various polyphenolic compounds and flavonols. The major polyphenolic compounds present in the edible part are catechins, epicatechins, gallic acid, tannins and anthocyanins [89]. Bananas are also an abundant source of carotenoids, mainly present in peels. The major carotenoids include lutein, violaxanthin, neoxanthin, isoleucine, α- and β-carotene [140]. Seratonin is a biogenic amine found in banana that imparts the feeling of happiness and wellbeing. The antioxidant potential of banana peels is more potent than that of pulp, inhibits lipid peroxidation, and has high free radical scavenging activity [43].

Banana offers several health benefits, such as retardation of the aging process, reducing the risk of degenerative diseases like heart problems, atherosclerosis, brain dysfunction, and inflammation. It also provides resistance against oxidative changes in low-density lipoprotein and reduces oxidative stress due to bioactive compounds like dopamine and ascorbic acid. Serotonin stimulates the intestinal smooth muscles and thus inhibiting gastric secretion [72]. Banana peel can be utilized as a potential source of antioxidant compounds instead of discarding it.

Mango

Mango comes second, after the banana, regarding production. India is the largest producer of mango. The edible slices of mongo consist of significant amounts of antioxidant compounds. Xanthones are found in high concentrations comprising mainly of mangiferin (1,3,6,7-tetrahydroxyxanthone-2-glycopyranoside) and c-glucoside xanthone [10].

Mango by products, mainly peels, have shown high antioxidant activity. The phenolics and flavonoid content of mango peels is responsible for its anti-proliferative potential against cancer cells [94]. Mangiferin content of peels is about three times higher than that of pulp [124]. Gallo-tannins are found in higher amounts in mango kernels (15.5 mg/gm dry matter) followed by peel (1.4 mg/gm dry matter) and lowest in pulp (0.2 mg/gm) [9]. Mango peel extracts can scavenge singlet oxygen ($^1O2$), hydroxyl radical and superoxide anion due to the presence of compounds- ethyl gallate and Penta-o-galloyl glucoside [59].

Tomato

Tomato is an important and widely consumed vegetable [132]. It is considered beneficial for health as it provides carotenoids, flavonoids, and phenolic acids [137]. During the production of tomato juice, about 3-7% of raw material is wasted, which comprises skin and seed.

Tomatoes are a rich source of carotenoid, the lycopene responsible for their characteristic red color [128]. The lycopene content of tomato peel is five times higher than pulp [88]. Thus, the hot break method is preferred in tomato juice extraction to get the tomato product of intense redness due to higher lycopene concentration.

Carrot

Carrot is a significant and widely consumed root vegetable that is a rich source of dietary fiber and secondary metabolites, mainly carotenoids and phenolics [5 0,51,119]. Carrot provides substantial health benefits [45] due to compounds like tocopherol, ascorbic acid, and β- carotene and hence is also called vitaminized food [53].

Carotenoids acts as a precursor of vitamin A, especially the β-carotene, which are the major bioactive components present in carrots [100]. The most prevalent phenolic acid present in carrots is caffeic acid and thiamin, folic acid, riboflavin, and vitamin C, which are in considerable amounts of carrot roots [56]. Carrot peel, the by-product of the processing industry, accounts for about 11% of the fresh carrot and can provide 54.1% of the total phenolic content of carrot. Therefore, these peels can be utilized for the value addition of various food products [153].

Garlic

Garlic is widely consumed as a spice and flavoring agent. Because of its preventive and curative action against various ailments, it is widely utilized for dietary and medicinal values [115,122]. Garlic consists of the high content of γ-glutamylcysteine, which is believed to be responsible for various health benefits provided by garlic, along with other sulfur-containing compounds [7]. The chief bioactive component of garlic is allicin (diallyl this sulphonate). Raw garlic homogenate also consists of other significant sulfur-containing compounds, including allyl methyl sulphonate, γ- glutamyl cysteine, and 1-propenyl allyl thio sulphonate [78].

Garlic has been found to increase the resistance against LDL oxidation and thus is beneficial for heart and blood vessels because oxidative modification of LDL can lead to the formation of plaque in blood vessels by deposition of fatty streaks [77]. Garlic in the form of 10% homogenate in a salt solution and its supernatant fraction was found to be capable of reducing the free radicals generated from the Fenton reaction, and it was also effective in reducing the free radicals in cigarette smoke [143].

Garlic shows protective action against oxidative damage of tissues induced by nicotine. It was also found to be effective against carbon tetrachloride damage. Rats intoxicated with carbon tetrachloride were given an oral dosage of garlic oil, and it was found to prevent liver damage by peroxidation of lipids, alkaline phosphatase, and serum transaminase. These results are similar to that of vitamin E [3].

Onion

Onion consists of substantial bioactive compounds, mainly flavonoids [125]. Flavonols are the significant flavonoids present in onions, quercetin derivatives being the most important ones [136]. Quercitin 3,4'-diglucoside and quercitin 4'- glucoside accounts for around 80-95% of total flavonols [44].

Some varieties of red onions also consist of anthocyanins. Anthocyanins are mainly concentrated in the outer skin of the onion (63%), and flavonoids in the skin are present mainly in aglycone forms [39]. So, the onion skin, which is generated as a waste, can be used to extract bioactive components.

Potato

Potato is considered the king of vegetables. It is the most widely consumed vegetable and the significant raw material for processed products like chips, fingers, fries, etc., during the processing of potatoes; peels are a considerable waste. Potato waste consists of various antioxidant compounds: caffeic acid, chlorogenic acid, protocatechuic acid, gallic acid, and para-hydroxybenzoic acid [95]. The antioxidant capacity of polyphenolic extracts obtained from potato peels is found to be analogous to that of synthetic antioxidants [BHA (Butylated Hydroxy Anisole) and BHT (Butylated Hydroxy Toluene)]. It was found that soybean and sunflower oil thermal degradation was suppressed when potato peel extract was incorporated in these oils, which may be attributed to chlorogenic and gallic acid in the extract [152].

Beetroot

Beetroots are an abundant source of valuable bioactive components such as carotenoids [27], betacyanins [109], betanin, flavonoids, and polyphenols [146]. The antioxidant activity of beetroots is primarily attributed to the total phenolic content of about 50-60 µmol/gm of dry weight [20]. The entire phenolic content in different portions of beetroot is found to be in the following order: Flesh (13%) <crown (37%) <peel (50%) [71]. Beetroot peel's major phenolic compounds are p-coumaric acid, ferulic acid, and cyclodopa glucoside derivatives [70].

Betacyanins found in red beets have antioxidant activity and free-radical scavenging properties [110]. These are responsible for the inhibition of cervical and ovarian cancer cells [155]. Betalains improve the antioxidant profile of humans by reducing the oxidative degradation of lipids by scavenging the free radicals [25].

A large amount of horticultural waste is generated when preparing either cut fruits and vegetables or processed products. So, it can be a better option to utilize these wastes into valuable byproducts by extracting various phytochemicals to utilize in pharmaceuticals, cosmetics, and food products as functional ingredients. These bioactive compounds can be used in vegetable oils to prevent oxidation and edible coatings to increase shelf life.

Conclusion

Antioxidants prevent oxidative damage in food products and protect the human body from damage caused by reactive species such as ROS, RNS, RSS, and free radicals. Antioxidants prevent the damage induced by free radicals acting through different mechanisms like free radical scavenging, prevention of free radical formation, or decomposition of reactive species. Antioxidants such as ascorbic acid, vitamin E, carotenoids, and polyphenols can be obtained from plant sources, mainly fruits and vegetables fresh and processed products. The by-products obtained during the processing of fruits and vegetables can be utilized as a potential source for the extraction of antioxidants as these consist of high amounts of bioactive compounds. Secondary metabolites in peels and seeds of some fruits and vegetables like grapes, berries, pomegranate, garlic, onion, etc., can be higher than their pulp and juice. Such horticultural by-products can be utilized as a source of bioactive compounds in pharmaceutical, cosmetic and food products.

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