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Redox protective potential of fruits and vegetables: A review

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ABSTRACT

Although oxidation reactions are crucial for life, they can also be damaging to cells and tissues, causing variety of chronic ailments like, aging, cancer, autoimmune problems, cardiovascular and neurodegenerative disorders *etc.* Redox protective systems are present in body for general immunization against free radicals, which can be supported by antioxidants that we take in our daily diet. Natural antioxidants such as flavonoids, hydrolysable tannins, coumarins, xanthenes, phenolics, terpenoids, ascorbic acid, carotenoids and proanthocyanins are found in various plant products, including fruits, leaves, seeds oils, and juices. This review gives a brief account of research reports on fruits and vegetables which provide free radical scavenging compounds to the body.

1. Introduction

Free radicals adversely alter lipids, proteins, and DNA and trigger a number of human diseases. This radical formation occurs continuously in the cells as a consequence of both enzymatic and non-enzymatic oxidation reactions[1]. Currently, there is global interest in finding new and safe antioxidants from natural sources, to minimise oxidative injury of living cells through free radicals. Antioxidants may act as chemical traps/sinks that “absorb” energy and electrons, quenching reactive oxygen species (ROS) (carotenoids, anthocyanidins); catalytic systems that neutralize or divert ROS (antioxidant enzymes superoxide dismutase, catalase, and glutathione peroxidase); binding/inactivation of metal ions to prevent generation of ROS (ferritin, ceruloplasmin, catechins); and chain-breaking antioxidants which scavenge and destroy ROS (ascorbic acid, tocopherols, uric acid, glutathione, flavonoids)[2,3].

Natural antioxidants such as flavonoids, hydrolysable tannins, coumarins, xanthenes, phenolics, terpenoids, ascorbic acid, carotenoids and proanthocyanins are found in various plant products, including fruits, leaves, seeds, oils, and juices[4-7]. So regular consumption of fruits and vegetables has been consistently shown to be associated with reduced risk of developing chronic diseases such as cancer and cardiovascular disease[8,9]. This review discusses how fruits and vegetables that we eat are playing a positive role in sustaining our health through supply of natural antioxidants

on daily basis.

2. Fruits as natural antioxidants

Fruits are the most common ingredient in our food prescribed by nutritionists. Among all fruits, apples are commonly consumed and are the major contributors of phytochemicals in human diets[10]. Epidemiological studies have linked the consumption of apples with reduced risk of some cancers, cardiovascular disease, asthma, and diabetes[11]. In the laboratory, apples have been found to have very strong antioxidant activity. Apples contain a variety of phytochemicals, including quercetin, catechin, phloridzin and chlorogenic acid, all of which are strong antioxidants[12]. Apple peels have high concentration of phenolic content. The antioxidant activities of 4 varieties of apples (Golden Delicious, Rome Beauty, Idared and Cortland) were investigated. The total phenolic and flavonoid contents were higher in the peels than flesh[13]. Further observation showed quercetin glycosides in peels. Unripe apples with apple peels constitute valuable source of polyphenols[14-17]. In a study, indigenous fruits such as wood apple and Jambul were analyzed for total phenolic contents, total flavonoid content and ascorbic acid contents. Their antioxidant potential was in the order: Jambul > wood apple > ambadi > ambat chukka[18].

A variety of antioxidant entities, such as phenolics, anthocyanins and proanthocyanidins are present in grapes. They suppress platelet aggregation, lower cholesterol level in blood and are also anti-carcinogenic in action[19]. Similarly, in guava, antioxidant nutrients include ellagic acid derivatives, myricetin and apigenin[20].

Papaya pulps are rich in antioxidant agents which protect against colon cancer and heart diseases. These antioxidant components

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include carotene, vitamin C, vitamin B, flavonoids, folate, pantothenic acids, minerals such as potassium and magnesium[21]. A significant correlation was observed between antioxidant capacity and total phenolics, indicating that phenolics contribute to the antioxidant activity[22]. The *Carica papaya* extract also found to have hepatoprotective effect against carbon tetrachloride intoxicated rats and it was hypothesized that it might be mediating its protective effects either by decreasing the metabolic activation of carbon tetrachloride, or by acting as a chain breaking antioxidant for scavenging free radicals or by a combination of these effects[23].

Pineapple fruits being rich in phenolics provide a good source of antioxidant[24]. Pineapples contain flavonoids phenolic compounds, namely, the quercetin, flavones-3-ol, flavones, *p*-coumaric acid and ferulic. Vitamin C is also present in it[25,26]. Studies showed that the highest antioxidant activity through β -carotene bleaching assay was observed in unripe fruit (90.67 ± 0.29)% followed by young leave, ripe fruit and the seed[27]. The protective effect of pineapple peel extract against alcohol-induced oxidative stress was observed when applied to rats in experimental conditions[28].

Commercial pomegranate juices showed an antioxidant activity (18–20 trolox equivalent antioxidant capacity) three times higher than those of red wine and green tea (6–8 trolox equivalent antioxidant capacity)[29]. Pomegranate juice is an important source of anthocyanins, 3-glucosides, 3,5-diglucosides of delphinidin, cyanidin, and pelargonidin[30]. It also contains 1 g/L citric acid and 7 mg/L ascorbic acid[31]. It was reported that pomegranate peel extract had markedly higher radical scavenging capacity of superoxide anion, hydroxyl and peroxy radicals as well as it inhibited CuSO_4 -induced low-density lipoprotein oxidation. The total phenolics, flavonoids and proanthocyanidins were found to be higher in peel extract than in pulp extract. The large amount of phenolics contained in peel extract may cause its strong antioxidant ability[32].

Both total polyphenols and flavonoids are major contributors to the total antioxidant ability in mango fruit[33]. Various studies were conducted in this regard on different varieties of mangoes. A study reported that the content of phenolic compounds ranged from 48.40 to 208.70 mg/100 g, total carotenoid from 1.91 to 2.63 mg/100 g, beta-carotene from 661.27 to 2220 $\mu\text{g}/100$ g and total ascorbic acid ranged from 9.79 to 77.71 mg/100 g[34].

Five species of wild edible fruits e.g., *Gmelina arborea*, *Oroxylum indicum*, *Bauhinia racemosa*, *Caryota urens* and *Zanthoxylum rhetsa* were investigated for their antioxidant activities. The total phenol content varied from 0.061 ± 0.29 (*Zanthoxylum rhetsa*) to 0.500 ± 0.012 g/100 g fresh weight (*Caryota urens*). The result indicated that they could be used as potential source of natural antioxidant in the fodder or in pharmaceutical industry[35]. The total phenol content varied from 3.31 ± 0.10 to 27.67 ± 0.16 mg/g. Flavonoids and flavonols, anthocyanins, ascorbic acid, total phenolics and flavonoid levels were also recorded from these fruits[36,37].

Majority of fruits are rich in vitamin C, carotenoids and polyphenolic compounds, especially berry fruits are rich in this regard. Among berry fruits, the content of particular substances with antioxidant activity is rather diverse, some are rich source of vitamin C, the other contain huge amount of phenolic compounds[38]. Bagchi *et al.* studied antioxidant properties of a novel anthocyanin rich berry extract[39]. Its fruits and their seeds found to be rich sources of vitamins C, E and beta-carotene, proanthocyanidins, anthocyanins[40,41].

Antioxidant agents in plums were reported as neochlorogenic acid and the anthocyanins components were cyanidin-3-O-glucoside or -rutinoside[42]. While in strawberries, flavonoids and phenolic acids, such as hydroxycinnamic acids, ellagic acids, ellagitannins, Xavan-3-ols, Xavonols, and anthocyanins were reported[43-46]. Black berries contain phenolic compounds, such as ellagic acid,

tannins, ellagitannins, quercetin, gallic acid, anthocyanins, and cyanidins[47]. Blue berries' redox protective ability is due to presence of anthocyanin pigments[48,49].

The almond shell's extracts were investigated for their antioxidant activity and total phenolic contents. The shell extracts possessed considerable amount of gallic acid ranging from 1.36 to 7.21 mg/100 g of dry matter of total phenolics[50]. The total antioxidant activity varied from 94.38% to 95.49% and total phenolic content was found to be 4.455 mg/g in almond shell extract[51]. Quercetin, catechin, protocatechuic acid, vanillic acid, *p*-hydroxybenzoic acid containing phenolic compounds were also isolated from almond skins[52]. Different selected raw dry fruits almond (*Prunus amygdales*), walnut (*Juglans regia*), cashew nut (*Anacardium occidentale* L.), raisins (*Couma macrocarpa*), chironji (*Buchanania lanzan*) were analyzed for their antioxidant capacity[53]. Almond whole seed had (8 ± 1) mg of quercetin equivalents/g of ethanolic extract, brown skin had 88 ± 2 , and green shell cover had 71 ± 2 . Flavonoids are polyphenolic compounds containing multiple aromatic rings. Quercetin, quercitrin, kaempferol, isorhamnetin 3-o-glucoside and morin were determined to be the major flavonoids in almond skins[54].

Citrus contains a well-balanced fatty acid and antioxidant profile that provide protection against harmful substances especially free radicals. Limonene, a major component in many citrus essential oils, exhibited chemopreventive and therapeutic effects. Citrus fruits (grape fruits, oranges, lemons) are rich in antioxidants due to high content of vitamin C (40–50 mg/100 g) and phenolic compounds among which flavanones (naringenin, eriodictyol, hesperitin) dominate. Pink grape fruits reveal high content of lycopene[55,56]. Ascorbic acid, the most important antioxidant in citrus fruit juices protects from oxidative stress[57].

3. Vegetables as natural antioxidants

The best sources of antioxidants among vegetables are red pepper, tomatoes, onion, garlic, red beet and *Brassica* vegetables. Tomato antioxidants include carotenoids such as β -carotene and mainly lycopene, which is largely responsible for the scarlet color of the fruit and most of its physicochemical properties. Vitamins such as ascorbic acid and tocopherols, and phenolic compounds such as flavonoids, hydroxycinnamic acid derivatives, α -, β -, γ -, δ -carotene, zeaxanthin and lutein, neurosporene, phytoene, and phytofluene are also present[58-63]. Particularly, carotenoids presence in fruit peel and pulp reduce the risk of certain types of cancer, cardiovascular and xerophthalmia diseases[64,65].

Red pepper contains high content of vitamin C (144 mg/100 g) and cryptoxanthin[66]. About 100 g of fresh, red pepper has 240 mg of vitamin C and 0.7 mg of vitamin E[67]. In bell pepper, 63 compounds were identified including alcohols, aldehydes, ketones, acids, esters and sulphur and nitrogen containing compounds[68]. Bell pepper is good source of vitamin C and E, provitamin a, ascorbic acid and carotenoids (5.8 $\mu\text{g}/\text{g}$ of fresh green weight)[69].

Vegetables belonging to the Brassicaceae family are rich in polyphenols, flavonoids and glucosinolates, and their hydrolysis products may have antibacterial, antioxidant and anticancer properties[70]. The juice of some *Brassica* species has been proved to protect human hepatoma cells from the genotoxic effects of carcinogens[71]. Brassicaceae vegetables are recognized as a rich source of nutrients such as vitamins (carotenoids, tocopherol, ascorbic acid, folic acid), minerals (Cu, Zn, P, Mg, among others), carbohydrates (sucrose and glucose), amino acids (for example, L-alanine, L-aspartic acid, L-glutamic acid, L-glutamine, L-histidine, L-methionine, L-phenylalanine, L-threonine, L-tryptophan, and L-valine), and different groups of phytochemicals such as indole phytoalexins (brassinin, spirobrassinin, brassilexin,

camalexin, 1-methoxyspirobrassinin, 1-methoxyspirobrassinol, and methoxyspirobrassinol methyl ether), phenolics (such as feruloyl and isoferuloylcholine, hydroxybenzoic, neochlorogenic, chlorogenic, caffeic, *p*-coumaric, ferulic, and sinapic acids, anthocyanins, quercetin, and kaempferol), and glucosinolates (mainly glucoiberin, glucoraphanin, glucoalyssin, gluconapin, glucobrassicinapin, glucobrassicin, gluconasturtiin, and neoglucobrassicin). All of these phytochemicals contribute to the reported antioxidant, anticarcinogenic, and cardiovascular protective activities of *Brassica* vegetables. However, not all members of this family are equal from a nutritional viewpoint[72]. *Brassica* vegetables like kale, white cabbage, Chinese cabbage, broccoli sprouts and cauliflower are known for their vigorous properties which are due to the high amount of antioxidant compounds. Kale is a good source of carotenoids (17–34 mg/100 g)[73,74]. Plants of cabbage vegetables family also contain phenolic compounds, where rich sources are broccoli, kale and brussel sprout. Broccoli and asparagus antioxidant evaluation showed that they both contain flavonoids and both showed no significant difference in phenolic content, however the antioxidant activity of broccoli was ranked second in 10 common vegetables and sixth in 22 vegetables [75-77]. Amongst the three different cultivated forms of cabbage, red cabbage had higher vitamin C (24.38 mg/100 g), dl- α -tocopherol (0.261 mg/100 g) and phenolic content (101.30 mg/100 g) as compared to the white cabbage and savoy cabbage[78].

Spinach is known for its iron content, however, natural antioxidant mixture of spinach leaves has been shown to have antioxidative, antiproliferative and anti-inflammatory properties in biological systems[79]. Its antioxidant properties are due to presence of glucuronic acid derivatives of flavonoids, trans and cis isomers of *p*-coumaric acid and meso-tartrate derivatives of *p*-coumaric acid which were detected in aqueous extract of spinach[80]. Lutein is the most important component present. The concentration of lutein belonging to carotenoids is lower than polyphenolic acids but higher than flavonoids. Nevertheless, the presence of lutein in spinach and kale extracts has an insignificant influence on the total antioxidant activity of extracts obtained from these green vegetables[81].

Potato is the most used vegetable all over the world. The most present polyphenolic compound in potato tubers is amino acid tyrosine (770–3900 mg/kg), followed by caffeic acid (280 mg/kg), scopolin (98 mg/kg), chlorogenic acid (22–71 mg/kg), ferulic acid (28 mg/kg) and cryptochlorogenic acid (11 mg/kg) [82]. The carotenoids in potato are primarily lutein, zexanthin, and violaxanthin, all of which are xanthophylls. Phenolic compounds include chlorogenic acid, which constitutes about 80% of the total phenolic acids. The predominant flavonoids are catechin and epicatechin. Red-fleshed potatoes have acylated glucosides of pelargonidin while purple potatoes have, in addition, acylated glucosides of malvidin, petunidin, peonidin, and delphinidin[83,84].

Agaricus bisporus commonly known as table mushroom contains high content of several vitamins[85]. Aletor reported mushrooms as rich source of vitamins and minerals[86]. The total phenol contents of 3 species of wild mushroom (*Cantharellus friessi*, *Cantharellus subcibarius* and *Cantharellus cinerius*) were analyzed in addition to some bioactive compounds. The analysis revealed that the total phenol contents showed major antioxidant components ranging from 9.55 to 16.8 mg/g in different mushroom[87]. Total phenolic and flavonoid contents occurring in eight types of edible mushrooms (*Agaricus bisporus*, *Boletus edulis*, *Calocybe gambosa*, *Cantharellus cibarius*, *Craterellus cornucopioides*, *Hygrophorus marzuolus*, *Lactarius deliciosus* and *Pleurotus ostreatus*). Flavonoids, such as myricetin and catechin were also detected in the mushrooms studied. The antioxidant activity of *Sarcoscypha coccinea*, *Cantharellus cibarius*, *Bovista plumbea*, *Coprinus comatus* and *Coprinus atramentarius* was determined. In case of *Sarcoscypha coccinea*,

it varied from 89.90% to 38.72% in different concentrations of mushroom extract whereas in *Cantharellus cibarius* the antioxidant activity varied from 86.27% to 51.65% in different concentrations of extract. In case of *Bovista atramentarius*, the antioxidant activity varied from 82.50% to 48.35% and in *Colletotrichum atramentarium*, the antioxidant activity varied from 82.45% to 21.45% in different concentrations of extract respectively. Likewise, the antioxidant activity in different concentrations of *Coprinus comatus* the antioxidant activity varied from 58.50% to 10.75% respectively[88]. It was also suggested that mushroom rich in antioxidant activity have been shown to play an important role in prevention of cancer[89,90]. Mushroom comprises simple phenols such as phenolic acid and derivatives as well as complex structures such as flavones, flavonoids or anthocyanin[91].

Garlic and red onion are used as most common ingredients. These both are *Allium* species and are believed to have medicinal properties including antioxidants. Total phenolic content was higher in red onion as compared to garlic. In red onion, it is (53.43 \pm 1.72) mg gallic acid equivalent/100 g and in garlic it is (37.60 \pm 2.31) mg/100 g. Nuutila *et al.* compared the antioxidant activity of onion and garlic correlated positively with phenolics in extracts; onion was found to be better antioxidant than garlic[92].

Eggplant showed antioxidant activity. Studies showed the presence of delphinidin-3-rutinoside, nasunin, phenolic contents as major phytochemicals in it[93-95]. Quercetin glucoside [quercetrin; quercetin 3-O-xylosyl (1'' --> 2'') glucoside, quercetin 3-O-glucosyl (1'' --> 6'') glucoside, quercetin 3-O-glucoside and quercetin 3-O-(6''-O-malonyl)-glucoside] are antioxidant compounds found in lady finger (okra)[96,97]. Bitter gourd contains gallic acid, followed by caffeic acid and catechin[98]. Turnip showed radical scavenging activity due to presence of glucosinolates, phenylpropanoids, flavonoids, phenolics and organic acids[99]. Fibers, carotenoids, vitamins C and E, and phenolics such as *p*-coumaric, chlorogenic, and caffeic acids were reported in carrot[100]. Celery has caffeic acid, *p*-coumaric acid, and ferulic acid in major proportions, while the identified flavonoids were apigenin, luteolin, and kaempferol (Table 1)[101].

Table 1
Antioxidant component of fruits and vegetables.

Fruits/vegetables	Antioxidant component
Apple peel	Phenolic contents, flavonoid, anthocyanins
Wild edible fruits	Phenolic content
Berry fruits	Vitamin C, carotenoids, polyphenolic compounds
Blackcurrant	Vitamin C, carotenoids, phenolic compounds
Strawberry fruits	Vitamin C, phenolic compounds, anthocyanins, ellagic acid, polyphenols
Bilberries	Vitamin C, carotenoids, phenolic compounds
Almond shell	Phenolic contents
Tomatoes	Lycopene, polyphenol compounds, flavonoids, quercetin
Red pepper	Vitamin C, cryptoxanthin
<i>Brassica</i> vegetables	Vitamin C, carotenoids, phenolic compounds, hydroxycinnamic acid, ferulic, chlorogenic and flavonols
Garlic and red onion	Phenolic contents
Red beet juices	Betalain
Cranberries	Phenolic compounds, flavanones, anthocyanins, flavanols, procyanidin, quercetin, myricetin
Crowberry fruits	Vitamin C, phenolic compounds, beta carotene, flavanols, procyanidin, cinnamic acid
Citrus fruits	Vitamin C, phenolic compounds, flavanones, lycopene
Rosemary	Phenolics, carnosol, carnosic acid, rosmarinic acid, tocopherol, citric acid, ascorbic acid
Sage oregano	Rosmarinic acid, carvacrol, thymol

4. Condiments and spices

Spices are an integral part of cuisine in various parts of the world[102]. Herbs have been added to foods since ancient times, not only as flavoring agents, but also as folk medicines and food preservatives[103]. Many spices have been shown to impart an antioxidative effect in food. The antioxidant properties of a number of spices (clove, sage, oregano, rosemary and thyme) are being studied from fifties[104]. Spices are potential sources of phenolic compounds, flavones, ascorbic acid and carotenes[105]. Celery belonging to Umbelliferae plant family is rich in coumarins, flavonoids and linoleic acid[106]. Extracts of ten edible spices: including cumin, chilli, pepper, nutmeg, garlic, clove, ginger, coriander were evaluated. Methanol extract of cloves showed the highest total phenolic content (171.8 mg gallic acid equivalent/100 g dry weight clove powder)[107]. Five Indian spices solvent extracts were examined for their antioxidant and antimicrobial activity. The antioxidant activity was found to be different for different assays. By using DPPH method the antioxidant activity was cumin > garlic > cinnamon > turmeric > ginger; by ferric reducing antioxidant power method was garlic > cumin > turmeric > ginger > cinnamon; and by total phenolic content method was turmeric > cinnamon > garlic > cumin > ginger[108].

Some medicinal plants and dietary constituents having functional attributes are spices such as mustard, turmeric, cinnamon, saffron, curry leaf, fenugreek, and ginger. Some herbs as *Bixa orellana* and vegetables like amla, wheat grass, soyabean, and *Garcinia cambogia* have antitumor effects[109]. Phenolic substances have been reported for most of the Indian spices. Phenolics reported in basil are rosmarinic acid and other phenolic acids[110]. Parsley has apigenin glycosides[111]. Main phenolics are quercetin and kaempferol glycosides in cumin and fennel, whereas in aniseed quercetin, luteolin and apigenin glycosides were found[112]. Cardamom contains mainly phenolic acids, such as caffeic acid, *p*-coumaric acid, and protocatechuic acid[113]. No polyphenols have been reported in ginger, yet the main constituents, gingerol and zingerone, possess a monophenolic moiety and may therefore be Folin-Ciocalteu-reactive[114].

5. Conclusion

An imbalance between oxygen free radical (ROS) and antioxidant defence system may lead to the oxidative burden. In turn, it may lead to the damage of macromolecules such as carbohydrates, DNA and proteins. Fruits and vegetables may contain vitamin C, flavones, flavanones, carotenoids, anthocyanins and catechins etc as antioxidant components. All fruits and vegetables discussed in this review possess marked therapeutic properties and antioxidant activities with low side effects.

Conflict of interest statement

We declare that we have no conflict of interest.

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