



Natural Antioxidants, Phenolics Compounds and their Effects on the Health

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Abstract – Antioxidants are of growing interest in recent years. More and more research is focusing on natural food antioxidants as the public is becoming aware of the importance antioxidants play in a healthy diet. Tocopherols are the best known and most widely used antioxidants, Phenolic compounds are a key source of antioxidant activity in fruits. Flavonoids, Antioxidants are frequently added to industrial products. A common use as stabilizers in fuels and lubricants to prevent oxidation, and in gasolines to prevent the polymerization that leads to the formation of engine-fouling residues. In 2007, the worldwide market for industrial antioxidants had a total volume of around 0.88 million tons.

Keywords – Antioxidant, Phenolics, Tocopherol, Tannins, Stability, The Effect in Health.

I. INTRODUCTION

Antioxidants are of growing interest in recent years. More and more research is focusing on natural food antioxidants as the public is becoming aware of the importance antioxidants play in a healthy diet. Tocopherols are also used as antioxidants for food. Reports revealing that BHA and BHT could be toxic, and the higher manufacturing costs and lower efficiency of natural antioxidants such as tocopherols, together with the increasing consciousness of consumers with regard to food additive safety, created a need for identifying alternative natural and probably safer sources of food antioxidants (Sherwin, 1990; Wanasundara and Shahidi, F. 1998). The replacement of synthetic antioxidants by natural ones may have benefits due to health implications and functionality such as solubility in both oil and water, of interest for emulsions, in food systems. However, some of them such as those from spices and herbs (oregano, thyme, marjoram, lavender, rosemary) have limited applications in spite of their high antioxidant activity, as they impart a characteristic herb flavor to the food, and deodorization steps are required (Reglero, Tabera, Ibañez, López-Sebastia Ramos, Ballester, & Bueno, 1999). Historically, antioxidants have been broadly described as “all substances that inhibited oxidation reactions, regardless of the mechanism, and narrowly as “those compounds that interrupt the free-radical chain reaction involved in lipid oxidation and those that scavenge singlet oxygen (Lindsay, 1996). It is important to note that “an antioxidant is a

reductant, but a reductant is not necessarily an antioxidant (Prior and Cao, 1999). There should, however, be a distinction between the chemical terms of reductant and oxidant as compared to the biological terms of antioxidant and pro-oxidant (Prior and Cao, 1999). The biological term antioxidant refers to any substance that when present at low concentrations compared with those of an oxidizable substrate significantly delays or prevents oxidation of that substrate (Halliwell, 1995). Reactive species known as pro-oxidants can be defined as a toxic substance that can cause oxidative damage to lipids, proteins and nucleic acids, resulting in various pathologic events and/or diseases (Prior and Cao, 1999).

These definitions emphasize that the value of an antioxidant is in its ability to inhibit the free radical chain reaction.

This is essential for stability in food systems and for health promotion *in vivo*.

During the last decade, the use of natural antioxidants and natural products has been widely studied by several researchers, in view of the concerns generated by the use of synthetic antioxidants (Kowalski, 2007; Azizkhani and Zandi, 2009).

The term natural antioxidants alludes to substances which occur in and can be extracted from plant or animal tissues and those which may be formed as a consequence of cooking or processing plant or animal components for food (Simic, 1981).

Natural antioxidants are found in almost all plants, microorganisms, fungi, and even in animal tissues (Pokorny, 1999).

As foods are extremely complex systems it is very difficult to determine the impact of each antioxidant compound individually. So there are many assays available to measure the antioxidant capacity of a food system.

For example used of these is the (DPPH) 2,2-diphenyl-1-picrylhydrazyl, β -Carotene bleaching assay (BCB) and reducing power.

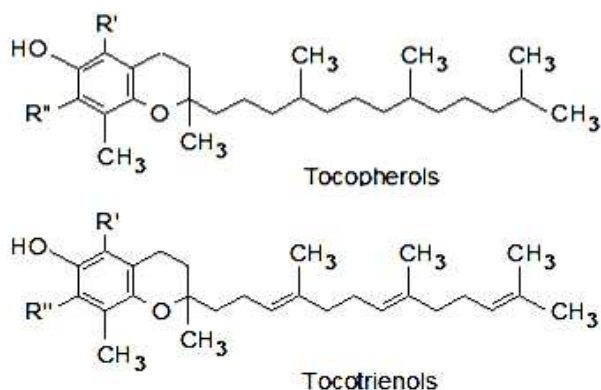


Table 1. Foods highest in antioxidants

Rank	Food	Serving Size	Total Antioxidant Capacity per serving size
1	Small Red Bean	1/2 cup dried beans	13727
2	Wild blueberry	1 cup	13427
3	Red kidney bean	1/2 cup dried beans	13259
4	Pinto bean	1/2 cup	11864
5	Blueberry	1 cup cultivated berries	9019
6	Cranberry	1 cup whole berries	8983
7	Artichoke hearts	1 cup cooked	7904
8	Blackberry	1 cup	7701
9	Prune	1/2 cup	7291
10	Raspberry	1 cup	6058
11	Strawberry	1 cup	5938
12	Red Delicious apple	1	5900
13	Granny Smith	1	5381
14	Pecan	1 ounce	5095
15	Sweet cherry	1 cup	4873
16	Black plum	1	4844
17	Russet potato	1 cooked	4649
18	Black bean	1/2 cup dried beans	4181
19	Plum	1	4118
20	Gala apple	1	3903

II. TOCOPHEROL AND THEIR ANTIOXIDANT ACTIVITY

Tocopherols are the best known and most widely used antioxidants. Tocopherols (Vitamin E) are lipid soluble, colorless to light yellow and thick textured oils. Tocopherols are rich in most vegetable oil, but fish oils and other animal fats contain much lower amounts of tocopherol than vegetable oil (Rossell, 2009). They can be classified as tocopherols (Toc) and tocotrienols (Toc-3) and within each of these two classes there are four isomers (α , β , γ and δ) making a total of eight tocopherol isomers (Cosgrove, Church, and Pryor 1987). Tocopherols are present at least in traces, in nearly all food materials and α -tocopherol is the most important antioxidant of the group (Figure 1).

III. PHENOLICS COMPOUNDS

Phenolic compounds are a key source of antioxidant activity in fruits. Flavonoids, the fraction of phenolics comprised of such compounds as flavones, isoflavones, flavonones and anthocyanins are known to be potent antioxidants in vitro (Moyer, Hummer, Finn, Frei and Wrolstad, 2002).

Polyphenols are able to act as reducing agents hydrogen donating antioxidants, as well as singlet oxygen quenchers (Dubost, Ou and Beelman, 2007). Phenolic compounds are known to terminate oxidation by participating in the reactions through resonance stabilized free radical forms, as well as acting as free radical scavengers (Lindsay, 1996). As suggested by (Dubost, Ou and Beelman, 2007), hydrogen donation may be a key mechanism of action of the antioxidant activity of phenolic compounds.

Polyphenols compounds are an essential part of the defense mechanism in plants. These compounds protect plants against the attack of environmental stresses such as ultraviolet light, microorganisms and insects (Craig, 1999).

Simple phenolic acids and flavonoids are the most common phenolic compounds and they generally occur as soluble conjugated (glycosides) and insoluble forms (Nardini and Ghiselli, 2004). In nature, phenolic acids occur mostly in the insoluble or bound forms, whereas flavonoids present as glycosides with a single or multiple sugar moieties linked through an OH group (O-glycosides) or through carbon-carbon bonds (C-glycosides).

Polyphenols are extensively studied and around 8000 are characterized, although it is possible that over one million molecules possessing protective functions may occur naturally in food plants (Sakakibara, Honda, Nakagawa, Ashida, and Kanazawa, 2003; Halvorsen, Carlsen, Phillips, Bohn, Holte, Jacobs and Blomhoff, 2006).

In the early 1980, an accurate procedure for the estimation of free, soluble conjugated and insoluble bound phenolics was developed and proved in different foods (Sosulski, Krygier, and Hogge, 1982). The insoluble bound phenolics have demonstrated a significantly higher antioxidant capacity compared to free and soluble conjugated phenolics (Chandrasekara, and Shahidi, 2010).

Nutritionally important bioactive compounds can be divided into more than ten different classes, including: phenolic acids, benzoquinones, hydroxycinnamic acids, phenylpropenes, coumarins, chromones, naphthoquinones, xanthenes, stilbenes, flavonoids, and lignans (Bravo, 1998). In fruits, polyphenols are commonly observed as flavonoids, phenolic acids, and tannins.

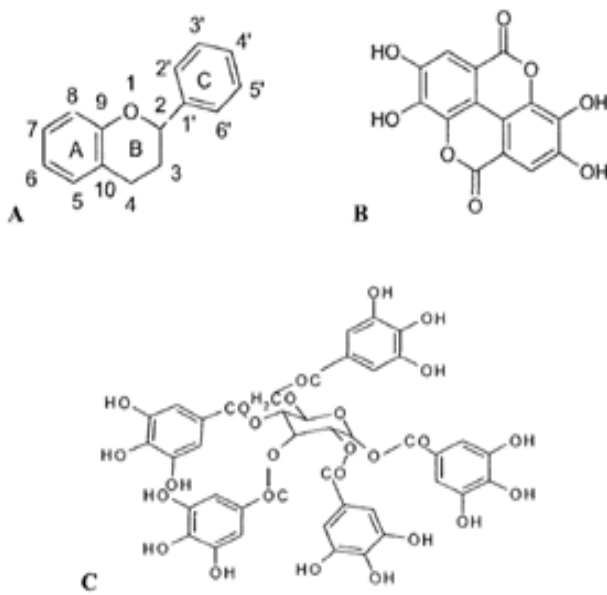


Fig. 2. Common polyphenols in fruits

IV. FLAVONOIDS

Flavonoids are the most abundant polyphenols in our diets. The basic flavonoid structure is the flavan nucleus, containing 15 carbon atoms arranged in three rings (C6–C3–C6). Flavonoids are themselves divided into six subgroups: flavones, flavonols, flavanols, flavanones, isoflavones, and anthocyanins, according to the degree of oxidation (oxidation state) of the oxygen heterocycle, central third ring. Their structural variation in each subgroup is partly due to the degree and pattern of hydroxylation, methoxylation, or glycosylation (Dai and Mumper, 2010). Flavonoids are the most abundant phenolic compounds in fruits and vegetables with more than 5000 compounds identified to date (Crespy, Morand, Besson, Cotelle, Vezin, Demigne. and Remesy, 2003). The most abundant flavonoids in fruits are the flavonols (quercetin, kaempferol and myricetin), flavones (apigenin and luteolin), flavanones (naringin, naringenin, hesperetin, hesperidin), flavan-3-ols (i. e. catechin, catechingallate, proanthocyanidins), and anthocyanidins (i. e. cyanidin, dephinidin, pelargonidin, and glucosidesanthocyanins) (Fig. 3) (Scalbert, Manach, Morand, Remesy and Jimenez, 2005).

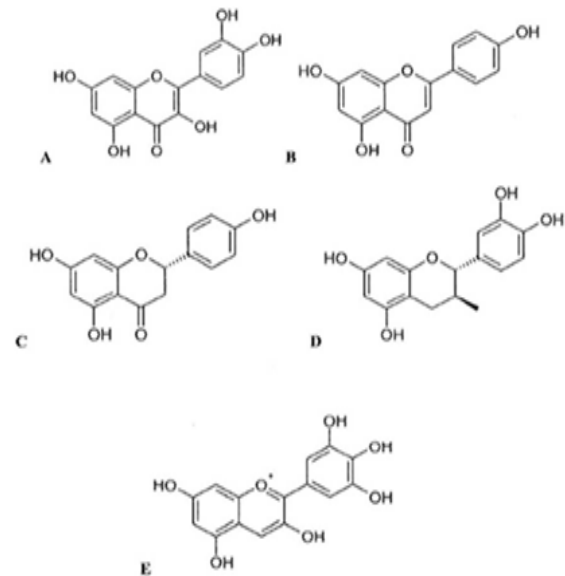


Fig. 3. The most Abundant Flavonoids in Fruits. (A) quercetin(flavonol), (B) apigenin (flavone), (C) naringenin (flavanone), (D) (+)- catechin (flavan – 3 – ol), (E) cyanidin (anthocyanidins).

Flavonols are the most widely distributed of the flavonoid compounds in fruits and are mainly in the glycosidic form with a hydroxyl group conjugated most commonly at position 3 of the C ring and with possible substitutions at 5, 7, 4', 3' and 5' positions. (Kris-Etherton, Hecker, Bonanome Coval, Binkoski Hilpert, Griel, and Etherton, 2002; Nichenametla, Taruscio, Barney, and Exon, 2006). Quercetin, kaempferol and myricetin, the most common flavonols, are quantified in apples, berries, plums, tomatoes, peaches and grapefruit (Harnly, Doherty, Beecher, Holden, Haytowitz, Bhagwat and Gebhardt, 2006).

Flavonoids have been associated with many physiological properties, including antioxidant, anti-inflammatory, antimicrobial, anti-hyperlipidemic, anticancer, anti-viral, and anti-allergenic, all of which are thought to play a role in reducing the risk of degenerative diseases

V. TANNINS

Tannins are polyphenols, with high molecular weight, which can bind to both proteins and carbohydrates. Tannins are one of the most wide spread polyphenolics in fruits, and are divided into two main classes: hydrolysable tannins and condensed tannins or proanthocyanidins (Singh, Bhat and Singh, 2003).

Condensed tannins are high molecular weight compounds formed from monomeric units of flavanols or flavan-3-ol, including (+) -catechin, (-) -epicatehin, (+) -gallocatechin, and (-) -epigallocatechin. Oxidative condensation occurs between the heterocyclic carbon C-4 of monomeric units of flavanols and the adjacent positions of carbons C-6 or C-8 of flavanols to create oligomers and polymers proanthocyanidins(Crozier, Clifford and Ashihara, 2006). Condensed tannins are responsible for



the astringency of many tannin-rich foods such as red wine and tea, resulting mainly from the precipitation of tannins with salivary proteins. Tannins exist in a wide variety of plant species. In a survey by (Bete - Smith and Metcalf, 1957), approximately 80% of woody perennial dicots and 15% of annual and herbaceous perennial dicots contained tannins.

VI. ANTHOCYANIN

Anthocyanin is responsible for the red and blue coloration of certain fruits, flowers and leaves (McDougall, Dobson, Smith, Blake and Stewart, 2005). and are present in high concentrations in blueberries, raspberries, strawberries and red grapes. The popularity of anthocyanin containing foods is increasing tremendously due to recent interest of multiple health promoting features including antioxidant, anti-inflammatory, and anti-cancer activities and more recently due to chemoprotective, vasoprotective and antineoplastic properties (Bae and Hyung, 2007).

Anthocyanins are commonly identified as an anthocyanidin-sugar conjugate in Fruits. Forms include conjugates with hydroxycinnamate and other organic acids, mostly malic and acetic acids such as in red wines [30]. Six different anthocyanidins aglycones, including pelargonidin, cyanidin, delphinidin, peonidin, petunidin, and malvidin are the most common constituents (Figure 4). Anthocyanidins are usually conjugated at carbons 3, 5, and 7 of C-ring and, 3' and 5' of B-ring with sugar conjugated at positions 3 and/or 5 of C-ring.

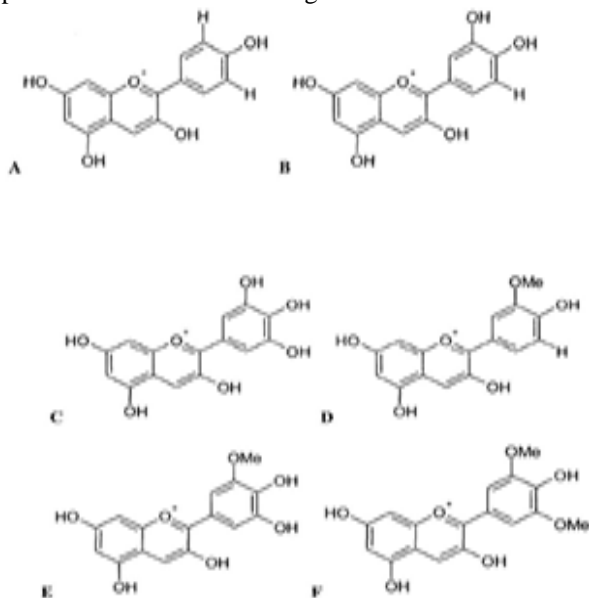


Fig. Anthocyanidins in fruit, (A) Pelargonidin, (B) Cyanidin, (C) Delphinidin, (D) Peonidin, (E) Petunidin, (F) Malvidin. Me, methyl.

VII. CONCLUSION

Antioxidants come up frequently in discussions about good health and preventing diseases. Antioxidants benefit the body by neutralizing and removing the free radicals

from the bloodstream. Antioxidant intake can help provide added protection for the body against Heart problems, Eye problems, Memory problems, Mood disorders and Immune system problems, finally Antioxidants have many industrial uses, such as preservatives in food and cosmetics and to prevent the degradation of rubber and gasoline.

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