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Adaucto B. Pereira-Netto

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REVIEW



Tropical Fruits as Natural, Exceptionally Rich, Sources of Bioactive Compounds

Adaucto B. Pereira-Netto

Department of Botany-SCB, Paraná Federal University, Curitiba, PR, Brazil

ABSTRACT

Fruits are pointed out as natural sources of antioxidants, playing protective roles against aging, and chronic and degenerative pathologies. In this review it is shown that virtually unknown edible tropical fruits present significantly higher antioxidant activity when compared to temperate fruits considered to be good sources of antioxidants. For example, the pulp of fruits native to the Brazilian savanna, consumed widely by local populations, like araticum (*Annona crassiflora*) and pequi (*Caryocar brasiliense*), have shown an antioxidant capacity of 148 (IC₅₀ µg/mL DPPH) and 9.4 µg/mL, respectively. These antioxidant activities are much higher when compared to the antioxidant activity of 672 g/g DPPH reported for blackberries (*Rubus fruticosus*), temperate fruits thought to be good sources of antioxidants. These remarkably higher antioxidant activities found for some tropical fruits is related to the presence of exceptionally high levels of compounds known for their elevated antioxidant activity. Data provided in this review support recommendation for a broader use of antioxidant-rich tropical fruits for the enrichment of human diet with remarkable amounts of natural antioxidants beneficial to health.

KEYWORDS

Ascorbic acid; flavonoids; phenols; polyphenols

Introduction

During the past few decades, increased interest in nutrition, fitness and beauty have helped to raise concerns over human diet and health. Consequently, diets emphasizing the positive aspects of diet are increasingly popular. Fruits have been consistently reported in epidemiological surveys as naturally rich sources of antioxidants, helping to reduce the incidence of degenerative diseases, such as aging, arteriosclerosis, arthritis, brain dysfunction, cancer, heart disease and inflammation (Ellong et al., 2015), besides reducing the mortality risks with an average of 6% for each daily additional serving (Wang et al., 2014). In fact, mounting evidences point out that the potent antioxidant activity of fruit extracts is due to the additive and synergistic effects of combined phytochemicals present in the fruits, which might help to explain why no single synthetic antioxidant is able to replace the combination of natural phytochemicals found in fruits in achieving the desired health benefits.

Although there is an evident lack of updated statistics on the global demand for tropical fruits, tropical fruit consumption is clearly increasingly gaining importance due to their sensorial attractiveness and growing recognition of their nutritional and therapeutic values (Bicas et al., 2011). Regardless the fact that tropical fruit consumption is rapidly increasing, various tropical edible fruits presenting exceptionally high levels of antioxidants remain virtually unknown, not being mentioned even in nowadays scientific reports (for examples, please see Ellong et al., 2015; Oboh et al., 2015). Thus, this review is aimed at providing information on tropical edible fruits presenting exceptionally high levels of antioxidant activity. This information is focused on compounds contributing to this high antioxidant activity, especially phenolic and polyphenolic compounds, flavonoids included, and ascorbic acid.

Antioxidant activity of tropical fruits

Oxidation is a metabolic process that generates energy required for essential cell activities. However, oxygen metabolism in living cells also results in the unavoidable generation of oxygen-derived free radicals, the so called reactive oxygen species (ROS). The propagation of these potentially harmful free radicals can initiate radical cascade reactions that can result in attack against lipids in cell membranes, proteins in tissues, and DNA, inducing oxidations, which cause cell damage through a variety of mechanisms. In the case of DNA, this kind of oxidative damage has been shown to be highly correlated to the physiological conditions, such as mutagenesis, carcinogenesis, and aging. Antioxidants are compounds capable of scavenge ROS through the inhibition of the initiation or propagation of oxidative chain reactions, or suppression of the formation of free radicals which might have deleterious effects on human health. These ROS include reactive free radicals, such as alkoxyl (R-O), the highly reactive hydroxyl (OH), singlet oxygen ($^1\text{O}_2$), peroxy (R-O-O), superoxide (O_2^-), and non-radicals, such as hydrogen peroxide (H_2O_2), among others. Antioxidants provide protection against a variety of diseases, including arthritis, asthma, atherosclerosis, autoimmune diseases, bronchopulmonary dyspepsia, cancer, cataract, cerebral ischemia, diabetes mellitus, eczema, gastrointestinal inflammatory diseases, heart disease, besides genetic disorders (reviewed in Nimse and Pal, 2015). It has been hypothesized that one mechanism that animals might have evolved for coping with the oxidative damage is the consumption of dietary antioxidants (Bolser et al., 2013). In fact, several reports have demonstrated a negative relationship between fruit-rich diets and cancer incidence, while positive relationships have been shown for amount of fruit intake and cardiovascular and anti-hypertensive health-protective effects. The beneficial effect of fruit-rich diet has been increasingly attributed to the presence of various compounds known for their antioxidant activity like phenolic compounds, flavonoids included (Nimse and Pal, 2015). Furthermore, concerns about health safety have led to

restrictions on the use of synthetic antioxidants by the food industry, which significantly helped to raise interest in natural antioxidants. These restrictions, along with increased awareness about the benefits of antioxidants for health has also helped to fuel interest in fruits as natural sources of antioxidants among both people and the food industry. Several tropical fruits, especially the so called “super fruits”, like açai and acerola, have been attracting attention among people and the food industry because of their broad variety of unique shapes, size, flavour, taste, color, texture, but especially for their high content of health-promoting substances, like antioxidants. In fact, some of these fruits are already being used as natural sources of bioactive phytochemicals for application in health-promoting foods. Nevertheless, a large number of tropical fruits demonstrated to have exceptionally high levels of antioxidant compounds remain virtually unknown to the general public.

Surveys carried out on various tropical countries have shown that several of their native fruits present very high antioxidant activity. For example, fresh fruits of puça-preto (*Mouriri pusa*) and camu-camu (*Myrciaria dubia*), fruits native to Brazil, have shown antioxidant activity (EC_{50}) equal to 414 g/g DPPH and 478 g/g DPPH, respectively (Rufino et al., 2010). These antioxidant activities are considerably higher when compared to the antioxidant activities presented by temperate fruits thought to be good sources of antioxidants like blackberries (*Rubus fruticosus*, 672 g/g DPPH, Jakobek et al., 2009). However, even higher antioxidant activities have been reported for other less known tropical fruits, when compared to the antioxidant activity found for puça-preto and camu-camu. For example, Tan and co-workers (2011) have reported a value of 4,538 $\mu\text{mol Fe}^{+2}/\text{g DW}$ (Ferric ion Reducing Antioxidant Power, FRAP, assay) for kakadu plum (*Terminalia ferdinandiana*), a tropical fruit native to Australia, while Rufino and co-workers (2010) reported a value of 909 $\mu\text{mol Fe}^{+2}/\text{g DW}$ for puça-preto and 2,502 $\mu\text{mol Fe}^{+2}/\text{g DW}$ for camu-camu. Noteworthy, fruits native to the Brazilian savanna, consumed widely by local populations, present one of the highest antioxidant activities reported so far. For example, pulp of the araticum (*Annona crassiflora*) and pequi (*Caryocar brasiliense*) have shown an antioxidant capacity of 148 (IC_{50} $\mu\text{g}/\text{mL}$ DPPH) (Roesler et al., 2007) and 9.4 $\mu\text{g}/\text{mL}$ (Roesler et al., 2008), respectively. These antioxidant activities are much higher when compared to the antioxidant activities reported for more popular tropical fruits, considered to have high antioxidant activities, like seeded guava (*Psidium guajava*, 1,700 $\mu\text{g}/\text{mL}$) or papaya (*Carica papaya*, 3,500 $\mu\text{g}/\text{mL}$) (Lim et al., 2007).

Tropical fruits as sources of phenols

Phenolic compounds are classified as simple phenols or polyphenols based on the number of phenol units in the molecule. Modern analytical techniques, such as HPLC coupled to diode array detector with mass spectrometry, have significantly contributed to the separation of a growing number of

identified phenolic compounds in several food commodities (Spínola et al., 2015). Phenolic compounds consist one of the major classes of plant secondary metabolites, with several thousand (among them over 8,000 flavonoids) different compounds identified. These compounds present a large range of structures, including monomeric, dimeric and polymeric phenols (Soto et al., 2015), which determine their antioxidant capacity. Phenolic compounds are by far the most abundant dietary antioxidant in common human diets, being considered to be able to protect mammalian systems when eaten as fruit. Phenolics are able to scavenge free radicals, chelate metal catalysts, activate antioxidant enzymes, reduce α -tocopherol radicals, besides inhibiting oxidases, while their potent antioxidant activity has been attributed to the redox properties of their hydroxyl groups (reviewed in Oboh et al., 2015). A significant amount of evidences indicate that the role of phenolics in the prevention of several human diseases is likely related to their antioxidant activity, radical scavenging properties, and chelating activities.

Tropical fruits usually grow under high oxidative stress conditions, due to the high solar radiation and high temperature, which characterize the tropics. Phenolic compounds are important for plants, especially for the tropical ones, because these compounds are able to inhibit lipid peroxidation and deleterious effects of ultraviolet radiation in plant tissues. Temperate climate fruits like blueberry, with a total phenolic content (TPC) of 208 mg GAE/100 g (Table 1), are still considered to be good sources of phenolics. However, exceptionally high TPC has been reported for the also temperate climate fruits black chokeberry (*Photinia melanocarpa*, formerly *Aronia melanocarpa*, Table 1). Nevertheless, black chokeberry is a very rare example, or likely the only known example, of a temperate fruit presenting TPC over 1,000 mg GAE/100 g. Conversely, several studies have reported TPC over 1,000 mg GAE/100 g for various tropical fruits, including the increasingly known banana passion fruit and camu-camu (Table 1). Analysis of TPC for 58 non-traditional fresh Malaysian fruits demonstrated that 14 of them presented TPC over 1,000 mg GAE/100 g, one over 2,000 mg GAE/100 g and another one with TPC over 3,000 mg GAE/100 g (Table 1). Another survey, carried out in Africa, revealed four different fruits with amount of total phenolics ranging from 2,086 mg GAE/100 g to 5,978 mg GAE/100 g (Table 1). Cashew apple (*Anacardium occidentale*), Surinam cherry (*Eugenia uniflora*) and acerola, all from the tropical America, have been reported to present TPC of 3,957, 5,286, and 29,093 mg GAE/100 g, in a dry weight basis, respectively (Ribeiro Da Silva et al., 2014). Finally, a recent reassessment of the TPC for selected fresh kakadu plums (Table 1) demonstrated that those fruits likely presented the highest TPC reported so far for a natural phenolic source.

Analysis of Pearson's correlation coefficients for antioxidant activity capacity and antioxidant compounds in tropical fruits have shown a higher correlation for antioxidant activity capacity and TPC when compared to

Table 1. Total phenolic content of phenolic-rich temperate and tropical fruits.

Common name	Scientific name	Origin	Total phenolic content (mg GAE/100 g)	References
<i>Temperate fruits</i>				
Blueberry	<i>Vaccinium corymbosum</i>	North America	208	Rock et al., 2015
Black chokeberry	<i>Photinia melanocarpa</i> (formerly <i>Aronia melanocarpa</i>)	North America	1,079–1,921	Wangensteena et al., 2014
<i>Tropical fruits</i>				
Banana passion fruit	<i>Passiflora tarminiana</i>	Colombia	1018	Contreras-Calderón, 2011
Camu-camu	<i>Myrciaria dubia</i>	Amazon basin	1,161	Akter et al., 2011
	<i>Ximenia americana</i>	West Africa	2,086	Lamien-Meda et al., 2008
Buah Melaka	<i>Phyllanthus emblica</i>	Malaysia	2,664	Ikram et al., 2009
Sentol tempatan	<i>Sandoricum macropodium</i>	Malaysia	3,185	Ikram et al., 2009
	<i>Ziziphus mauritiana</i>	West Africa	3,240	Lamien-Meda et al., 2008
Mangosteen	<i>Garcinia mangostana</i>	South-East Asia	3,404	Chaovanalikit et al., 2012
	<i>Adansonia digitata</i>	West Africa	4,072	Lamien-Meda et al., 2008
	<i>Detarium microcarpum</i>	West Africa	5,978	Lamien-Meda et al., 2008
Kakadu plums	<i>Terminalia ferdinandiana</i>	Australia	2,560–8,270	Konczak et al., 2014

antioxidant activity capacity and compounds traditionally considered to present high antioxidant activity, such as ascorbic acid (Contreras-Calderón et al., 2011). When seen together, data presented in this review demonstrate that several tropical fruits, especially the ones presenting TPC over 1,000 mg GAE/100 g, might be used to replace, with broad advantages, temperate fruits in human diet as a source of high antioxidant capacity, health promoting, natural phenols.

Tropical fruits as sources of polyphenols

Polyphenols, a large and diverse group of secondary metabolites ubiquitously distributed in all higher plants (Mikulic-Petkovsek et al., 2015), are considered to be the most important dietary antioxidants due to their high antioxidant capacity and presence in plant foods (Kardum et al., 2014). The strong antioxidant activities of these compounds has been associated with their ability to scavenge free radicals, break radical chain reactions, and chelate metals (Kaisoon et al., 2011). Search on the phenol explorer-database on polyphenol content in foods (<http://phenol-explorer.eu/>, accessed on Dec., 9th, 2015) showed a polyphenol content (PPC) ranging from 154 to 820 mg GAE/100 g for temperate climate fruits considered to be good sources of polyphenols (Table 2). Nonetheless, very high PPC is reported on the phenol explorer database for black elderberry (*Sambucus nigra*, 1950 mg/100 g) and black chokeberry (1752 mg/100 g), two temperate climate fruit, though these PPC are the only ones above 1,000 mg GAE/100 g reported for temperate fruits. Conversely, survey on the literature shows that several fruits native to the tropics are richer sources of natural polyphenols, compared to temperate fruits considered to be good sources of these health-promoting compounds. In fact, various of these fruits present PPC

Table 2. Total polyphenolic content of polyphenolic-rich temperate and tropical fruits.

Common name	Scientific name	Total polyphenolics content (mg GAE/100 g)	References
Temperate fruits			
Raspberry	<i>Rubus idaeus</i>	154	Phenol-explorer, 2015 ²
Blueberry	<i>Vaccinium corymbosum</i>	223	Phenol-explorer, 2015 ²
Blackberry	<i>Rubus fruticosus</i>	569	Phenol-explorer, 2015 ²
Black currant	<i>Ribes nigrum</i>	820	Phenol-explorer, 2015 ²
Black chokeberry	<i>Photinia melanocarpa</i> (formerly <i>Aronia melanocarpa</i>)	1752	Phenol-explorer, 2015 ²
Tropical fruits			
Acerola	<i>Malpighia emarginata</i>	1,063	Rufino et al., 2010
Camu-camu	<i>Myrciaria dubia</i>	1,176–1320	De Rosso, 2013
Gabiroba	<i>Campomanesia xanthocarpa</i>	1,222	Alves et al., 2013
Yellow guava	<i>Psidium cattleianum</i>	3,713	Pereira et al., 2012
Yellow plum	<i>Ximenia americana</i>	3,002–4,025	Sarmiento et al., 2015

²<http://phenol-explorer.eu/>, accessed on Dec., 9th, 2015.

well over 1,000 mg GAE/100 g, with some species exceeding 3,000 mg GAE/100 g. Thus, several tropical fruits, especially the ones presenting PPCs over 1,000 mg GAE/100 g, can replace, with clear advantages, temperate fruits in human diet as a source of natural polyphenols.

Tropical fruits as a source of flavonoids

Flavonoids constitute the largest single class of polyphenols. These compounds present a common structure of diphenylpropanes (C6-C3-C6), consisting of two aromatic rings linked through three carbons (Chaovanalikit et al., 2012). The entire class of flavonoid structures, which incorporates over 8,000 secondary metabolite compounds, is found ubiquitously across plants and plant tissues (Kennedy, 2014). Major dietary flavonoids can be grouped into six major subclasses, flavanols, flavanones, flavonols, flavones, isoflavones, and anthocyanidins, essentially according to differences in the basic flavonoid structures of the compounds, i.e., the presence or absence of a ketone function at C4, a double bond at C2-C3 and a hydroxyl moiety at C3 (Johnston, 2015). Flavonoids are known for a quite long time to exhibit strong antioxidant capacity. The mechanism of antioxidant activity of these polyphenols involves the direct scavenging or quenching of oxygen free radicals or excited oxygen species, as well as the inhibition of oxidative enzymes that generate these ROS (reviewed in Kang et al., 2011). In addition to the reported antioxidant activity, flavonoids have also been shown to present important anti-inflammatory, antiallergic, anticancer, and antiviral properties, being used as drugs and/or dietary supplements for quite some time. Distinct structure–function relationships at various stages in cancer progression reflect diverse functional capabilities of flavonoids, like the control of cancer cells growth, besides displaying potent antioxidant and anti-inflammatory activities, ability to stabilize DNA triple helical complexes and affect tubulin polymerization (Mitrasinovic, 2015). Similarly to other phenolic compounds, the antioxidant activity of flavonoids is essentially determined by their chemical structure. More specifically, the precise activity of flavonoids primarily depends on the arrangement of functional groups on the core aromatic structure. Consequently, the spatial arrangement of functional groups is more relevant than the scaffold itself for the functional properties of the flavonoids (Mitrasinovic, 2015).

Various surveys carried out on tropical fruits have demonstrated that the presence of high total flavonoids (TF) content is not a rare event in those fruits. For example, a survey carried out using the pulp of eight different Brazilian fruits revealed that all of the eight fruits presented high TF content, including 217, 252 and 672 mg of epicatechin equivalents/100 g DW, respectively, for guava, soursop (*Annona muricata*), and açai (*Euterpe oleraceae*) (Paz et al., 2015). These amounts of TF are significantly higher when

compared to the amount of TF (quercetin, kaempferol, isorhamnetin, apigenin, and luteolin) reported for temperate fruits like pear (*Pyrus communis* Linn., 0.3 mg/100 g FW), strawberry (*Fragaria × ananassa*, 1.0 mg/100 g FW), and red fuji apple (*Malus pumila* Mill., 13 mg/100 g FW) (Cao et al., 2010). TF reported for açai is high even when compared to the TF found for red delicious apple (34 mg/100 g FW, Cao et al., 2010), a variety of apple considered to be a fruit presenting high TF content. Thus, the high amount of flavonoids found for several tropical fruits demonstrate that these fruits can be used to enrich human diet, acting as functional food. Furthermore, increased awareness about the high flavonoid content of several tropical fruits is expected to stimulate their use by the general population and food industry, in the last case especially as a value-added ingredient in new human health-oriented products, for both nutritional purposes and preservation.

Tropical fruits as sources of ascorbic acid

Vitamin C is defined as L-ascorbic acid (L-AA), the main biologically active form of vitamin C, and its oxidation product dehydroascorbate (Jain, 2015). L-AA is a ubiquitous molecule in eukaryotes (Wang et al., 2013), however, humans are not able to synthesize L-AA and their best natural source of this vitamin is dietary fruits and vegetables (Jain, 2015). Compelling evidence are now linking dietary L-AA to protective effects against various oxidative stress-related diseases, such as various types of cancers, cardiac disease, and cataract formation (Jain, 2015). The biological significance of the antioxidant activity of L-AA is that differently from other low-molecular-weight antioxidants like flavonoids, L-AA is able to terminate radical chain reactions through disproportionation to non-toxic, non-radical products.

Acerola is one of the very few food sources known to have L-AA content over 1,000 mg/100 g. Acerola's L-AA content (AAC) of 1,677 mg/100 g (<http://ndb.nal.usda.gov/ndb/foods/show/2120?fg=&manu=&lfacet=&format=&count=&max=35&offset=&sort=&qlookup=acerola>, accessed on November, 20th, 2015) is 31-fold higher when compared to the AAC reported for oranges (53 mg/100 g, <http://ndb.nal.usda.gov/ndb/foods/show/2330?manu=&fgcd=>, accessed on June, 26th, 2015). AAC of acerola is also considerably higher, when compared to the AAC found for other tropical fruits traditionally considered to present very high AAC, like papaya (39 mg/100 g, Ellong et al., 2015), cashew apple (228 mg/100 g, Contreras-Calderón et al., 2011), and guava (491 mg/100 g, Ellong et al., 2015). As the daily recommended intake of L-AA by the U.S. Food and Nutrition Board of the Institute of Medicine for non-smoken men, age 19 and older, is 90 mg/day (<http://www.nlm.nih.gov/medlineplus/ency/article/002404.htm>, accessed on June, 26th, 2015), a single fruit of acerola, which often is reported to weight around 8 g each, is more than enough to fulfill today's L-AA recommended daily intake.

Camu-camu is another of a few fruits with an extraordinarily high AAC, ranging from 2,280 mg/100 g fresh weight, at fully green stage, to 2,010 mg/100 g fresh weight, at fully ripe (red) stage (Chirinos et al., 2010). The AAC reported for camu-camu is much higher when compared to the AAC reported by Rufino and co-workers (2010) for other 17 tropical fruits, acerola included. Finally, kakadu plums are tropical fruits native to Australia used as a food source by northern Australian Aborigines for thousands of years. Even though kakadu plum-derived products are already world-wide available, the kakadu plum itself remains virtually unknown outside Australia. However, this broadly unknown fruit is becoming recognized as the richest food-source of L-AA on Earth. In fact, a recent reassessment of ACC in 45 accessions of kakadu plums showed an average value of 2,700 mg of ascorbic acid per 100 g of fresh weight of edible fruit, while values up to 5,300 mg/100 g were also found (Konczak et al., 2014). When compared to AAC found for commercial oranges, the highest reported value for AAC of kakadu plums is 100-fold higher. Thus, except probably for rose hips, all of the known edible fruits presenting AAC over 1,000 mg/100 g are native to the tropics.

Although citrus fruits were considered to be the best sources of L-AA for decades, the above presented data clearly demonstrate that exotic, edible tropical fruits, are by far the richest known natural sources of L-AA. Thus, L-AA-rich tropical fruits should be considered as an alternative source of vitamin C, or substitutes, for the traditional citrus fruits in the diet.

Regular consumption of high oxalate foods presents various threats to human health, including interference with calcium absorption and occasionally the development of calcium oxalate kidney stones in susceptible people (Nouvenne et al., 2008). As oxalate is the end-product of ascorbic acid metabolism, susceptible people should refrain from consumption of high amounts of fruit with heightened ascorbic acid content, like kakadu fruits, to reduce the risk of developing kidney stone (Williams et al., 2016). Although intake of fruits like kakadu should not be advised for the whole population, L-AA-rich tropical fruits are still a very valuable alternative, natural source of vitamin C.

Conclusions

Data presented in this review demonstrate that several tropical fruits are richer sources of antioxidants, like phenolic and polyphenolic compounds, flavonoids included, and ascorbic acid, when compared to temperate climate fruits. This feature demonstrates the great potential of several tropical fruits to enrich human diet with a large amount of natural antioxidants beneficial to health, helping to avoid both the use of synthetic and expensive antioxidants, and the possible risks, like toxicity, associated

with the use of dietary synthetic supplements. Thus, programs to further stimulate the consumption of antioxidant-rich tropical fruits should be created worldwide. Moreover, as developing countries account for about 98% of total tropical fruits production (<http://www.fao.org/docrep/006/y5143e/y5143e1a.htm>, accessed on June 23rd, 2015), such programs, besides being beneficial for the public health, would also be socially and economically important, especially for the tropical-fruit-producing countries. A wider recognition of the antioxidant properties of tropical fruits is also expected to significantly increase the marketing appeal of these fruits and consequently to stimulate their use by the food industry to improve the properties of foods, as a value-added ingredient, especially in new human health-oriented products.

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