Chapter 6

Carotenoids in Raw Plant Materials

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Abstract

Carotenoids are rich sources of pro-vitamin A. These compounds are usually obtained from pumpkins (*Cucurbita maxima, C. pepo, and C. moschata*), as well as orange and yellow sweet potatoes. Carotenoids are C40 tetraterpenoids, which stand out for their antioxidant activity. Among them are carotenes (very apolar carbon and hydrogen molecules, like lycopene, β-carotene, α-carotene) and oxygenated derivatives and xanthophylls composed of oxygenated functions (less apolar molecules such as lutein, zeaxanthin, cryptoxanthin). β-Carotene is the most commonly found carotenoid, accounting for 25–30% of the total carotenoid content of plants. It is also the most active carotenoid, with the highest bioconversibility in the human body. β-Carotene is a suppressor of tumorigenesis in the skin, lung, liver, and colon, promoting the cessation of the cell multiplication cycle. Thermal processing can affect the sensory characteristics and the antioxidant compounds, altering the antioxidant potential of foods. Time, temperature, and style of cooking are determinant conditions for the increase or decrease of total antioxidant activity. The biological activity of carotenoids depends on their bioaccessibility and solubilization in the gastrointestinal tract. The purpose of this chapter is to offer information about some raw plant materials containing carotenoids.

Keywords: raw plant materials, yellow bitter and sweet cassava, sweet yellow and orange potato, pumpkin, carotenoids

1. Introduction

Some carotenoids are rich sources of pro-vitamin A and carrots (*Daucus carota* L.) were the first raw plant material source of carotenoids, which were isolated in 1831 [1], while the first separation and purification procedures were performed by Tswett [2]. Pumpkins

(*Cucurbita maxima, C. pepo,* and *C. moschata*), as well as orange and yellow sweet potatoes, are usually good sources of carotenoids including α and β-carotene. On the other hand, the yellow sweet and bitter cassava (*Manihot esculenta*) roots were studied by Oliveira et al. [3], which found lower contents of β-carotene. To improve these contents, many efforts have been made through the biofortification.

Carotenoids are chemically defined as C40 tetraterpenoids (naturally occurring hydrocarbons and their derivatives), obtained by the union of eight isoprenoid (C5) units of five carbon atoms [4].

The purpose of this chapter is to offer some information about some raw plant materials containing high and lower carotenoid contents.

2. Raw plant materials

2.1. Carotenoids

Due to their intense and striking colors, carotenoids have always been a subject of interest of scientists. The first report of isolation of these substances is from 1831, from the carrot (*Daucus carota* L.), which also gave rise to the name of the class, derived from the English "carrot" [1]. The first separation and purification processes of carotenoids are attributed to the Russian botanist Tswett [2], who invented the liquid chromatography for the separation of carotenoids from colored leaves [5]. Tswett also gave rise to the concept of a family composed of many compounds, carotenoids, among them carotenes (composed only of very apolar carbon and hydrogen molecules, like lycopene, β-carotene, α-carotene) and oxygenated derivatives and xanthophylls composed of oxygenated functions, such as ketones, ethers, hydroxides, epoxides, methoxides, or carboxylic acids (less apolar molecules such as lutein, zeaxanthin, cryptoxanthin).

Carotenoids have aliphatic or acyclic structures (open chain) and alicyclic or cyclic structures (closed chain). Cyclic or alicyclic carotenoids can be monocyclic (when there is a ring) or bicyclic (when there is more than one ring) [5]. β-Carotene is the most commonly found of these compounds, accounting for 25–30% of the total carotenoid content of plants [6] or even more in some of them.

Due to their double-bonded conjugate system, carotenoids exhibit ultraviolet and visible spectral absorption characteristics, and most have maximum absorption at three wavelengths, resulting in a spectrum consisting of three peaks. The greater the number of conjugated double bonds in the carotenoid, the greater the spectrum wavelength [7].

According to Krinsky et al. [8], at least seven conjugated double bonds are necessary for a carotenoid to have color, as in the case of ζ-carotene, which gives a yellow color to passion fruit. As the conjugate system is extended, the color also intensifies. Therefore, lycopene with 11 conjugated double bonds gives rise to the red color of tomatoes (*Solanum lycopersicum*). Cyclization places the double bonds within the rings, outside the plane of those of the polyene

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chain, decreasing their coloration. Thus, γ-carotene, with a double conjugated ring-located bond, is reddish orange, while β-carotene with two of these ring bonds is orange (carrot), although both have conjugated double bonds as does lycopene.

The detection of carotenoids, after separation by liquid chromatography methods, occurs in a characteristic absorption zone between 400 nm and 500 nm wavelength; the detection in cis- or *Z*- isomers usually occurs between 330 and 340 nm. The intensity of absorption is affected by the solvent or the composition of the mobile phase used in the analysis [7].

Carotenoids consist of a wide range of substances, with great structural diversity and varied functions, of which more than 600 have already been identified and had their chemical structures elucidated. They are probably the most occurring pigments in nature, and the many different colors we see are the result of the presence and combination of these different compounds [8].

The official nomenclature of carotenoids was established in 1974 by the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Biochemistry [9].

They stand out commercially in the production of rations for breeding sites (fish, crustaceans, and poultry) and are used as food dyes and in aromas. In addition to the food industry, carotenoids play an important role in the pharmaceutical industry due to their nutritional and functional properties, as precursors of vitamin A, antioxidant activity, among others [10].

They can be divided into two groups: carotenes and xanthophylls. Carotenes are pure hydrocarbons, which have an orange to red coloration. This group includes β-carotene, α-carotene, ζ-carotene, δ-carotene, and lycopene. β-Carotene is the most commonly found of carotenes, accounting for 25–30% of the total carotenoid content of plants and even more in some of them [6].

It is also the most active carotenoid, with the highest bioconversibility in the human body, covering 15–30% of all serum carotenoids. β-Carotene is described as a suppressor of tumorigenesis in the skin, lung, liver, and colon, promoting the cessation of the cycle of cell multiplication. It also shows a suppression activity superior to that promoted by α-carotene [11]. Lycopene does not have pro-vitamin A activity but is considered as the carotenoid with the highest singlet oxygen sequestration capacity, possibly due to the presence of two unconjugated double bonds, which make it more reactive [12, 13].

Thermal processing can lead to important changes in the sensory characteristics and the content of antioxidant compounds, altering the antioxidant potential of foods. Conditions such as time, temperature, and style of cooking are determinants for the increase or decrease of the total antioxidant activity [14].

The biological activity of carotenoids depends on their bioaccessibility and solubilization in the gastrointestinal tract. Due to their lipophilic nature, these compounds do not disperse well in the aqueous medium of the gastrointestinal tract. Therefore, it is important to analyze how food matrix and processing affect their bioaccessibility. Rodriguez-Roque et al. [15] formulated beverages with mixtures of fruit juices and water, milk, and soy applying three treatments: high intensity pulse electric fields, high pressure processing, and thermal treatment, to evaluate bioaccessibility of carotenoids and on lipophilic antioxidant activity. Bioaccessibility of carotenoids was reduced after all treatments, except for *cis*-violaxanthin and neoxanthin, which increased 79% in beverages treated with high intensity pulse electric fields and high pressure processing. The thermal treatment presented worst decreasement of the bioaccessibility in 63%. High-intensity pulse electric fields and high pressure processing can be considered as promising technologies to obtain nutritive and functional beverages.

2.2. Orange flesh sweet potato (*Ipomoea batatas*)

Sweet potato (*Ipomoea batatas* (L.) Lam.) is a typical vegetable of tropical and subtropical countries (Mozambique), being one of the most consumed in Brazil, mainly by low-income populations. It occupies the sixth position among the most cultivated vegetables in the country, being an excellent source of energy and protein for the families of small farmers in the Northeast and South regions. It presents no difficulties in its cultivation, besides being very resistant to the dry climate, having a great capacity of adaptation, and is one of the largest energy producers per unit of area and time. Another advantage is that it requires low financial investments, with high returns having great importance in animal feed, industrial production of flour and starch and can be cooked in different styles in boiling water [16, 17].

It is a herbaceous crop with extensive growth in tropical and subtropical regions of the world, being important in many developing countries. Archeological, linguistic, and historical evidences establish that sweet potatoes originated in the region of Central and South America. The ability of this crop to adapt to a wide variety of climatic conditions allowed for its development in tropical and temperate regions of Africa, Asia, and the Americas. Compared to other crops, sweet potatoes are able to grow at an accelerated rate under various environmental conditions and are highly adaptable under marginal growing conditions. It has a short production cycle, high nutritional value, and sensory versatility in terms of color, flavor, and texture [18].

In Brazil, sweet potato presents low average productivity due to the occurrence of pests and diseases, inadequate production technology, and the absence of selected cultivars. However, improved productivity can be easily achieved through the use of seedlings from disease-free matrices obtained from tissue culture laboratories [17].

Its forms of consumption are the same as those of other sweet potato cultivars, as well as having similar production techniques. Its planting can be carried out at any time of the year, provided that the minimum local temperature in the period is equal to or above 15°C [16].

In the form of flour, *Beauregard* sweet potato is a possible total or partial substitute of wheat flour in recipes, allowing its introduction in school meals and in basic baskets [16]. Its high content of β-carotene, on average 115 $\mu g.g^{-1}$ of root, gives intense orange coloration to its pulp [16]. Carvalho et al. [19] found 111.44 $\mu g\ g^{-1}$ of total carotenoids, 104.17 $\mu g\ g^{-1}$ of β-carotene, 13-*cis* isomer 3.38 $\mu g\ g^{-1}$ and 9-*cis* isomer 1.49, respectively, in the raw roots in the same variety, somewhat lower than was found before.

Many authors evaluated the β-carotene content in orange sweet potato cultivars and found variable contents: Hangenimana et al.—79.84 $\mu g\ g^{-1}$ [20], Takahata et al.—187.00 $\mu g\ g^{-1}$ [21], Lako et al.—150.0 $\mu g\ g^{-1}$ [22], Kidmose et al.—108.0 $\mu g\ g^{-1}$ [23], Teow et al.—226.00 $\mu g\ g^{-1}$ [24], Wu et al.—84.00 $\mu g\ g^{-1}$ [25], and Failla et al.—281.00 $\mu g\ g^{-1}$ [26].

The average found for the centesimal composition in orange flesh sweet potato was moisture—83.91 g 100 g^{-1}, ash—0.52 g 100 g^{-1}; protein—0.69 g 100 g^{-1}; lipids—0.10 g 100 g^{-1}; carbohydrates—13.42 g 100 g^{-1}, respectively, with a caloric value of 57.34 kcal 100 g^{-1} [19].

The orange sweet potato pulps have the potential to be used as food-based supplements to reduce vitamin A deficiency since β-carotene is one of the carotenoids with pro-vitamin A activity for human diet, exerting important functions in human physiology, acting as antioxidants, as protective pigments of the human retina, and as precursors of retinoids that influence gene expression [27].

Orange-fleshed sweet potato (OFSP) is a carotenoid-rich vegetable. Thermal treatment to process sweet potatoes can decrease the contents of these compounds in foods, reducing their bioactive properties. Raman spectroscopy can be employed as a fast tool in food analysis, especially to detect low concentrations of carotenoids and to monitor their degradation profile along time. Sebben et al. [28] evaluated two drying methods, hot air and microwave in a rotating drum, coupled to quantitative Raman spectroscopy. A 50% decrease in the carotenoid contents were found for both types of drying methods. The results were reproducible. The best linear correlations were R^2 = 0.90 for hot air and 0.88 for microwave dried samples, respectively.

Vitamin A deficiency (VAD) is a public health problem in some regions of Brazil. Enhancement of the use of orange-fleshed sweet potatoes as a pro-vitamin A source can be a strategy for prevention of this deficiency. Berni et al. [29] compared the pro-vitamin A contents, vitamin A equivalencies and β-carotene (βC) bioaccessibilities of two varieties (*Beauregard* and Amelia) of home-cooked orange sweet potatoes and two commercial ones. Pro-vitamin A carotenoid content in home cooked *Beauregard* variety was higher than in Amelia variety and in commercial products for babies. All-*trans*-βC was the most abundant carotenoid in all samples (raw, cooked, and commercial) as expected. Boiling and frying decreased total β-carotene. According to them, a portion of 100 g fresh weight of *Beauregard* contained over 100% of the estimated average requirement for children and women and up to 92% estimated average requirement for lactating women. The efficiency of micellarization of all-*trans*-βC after the in vitro digestion was relatively low (4–8%) and significantly less than for *cis*-isomers, the amounts of *trans*-βC captured into micelles from boiled *Beauregard* and fried Amelia varieties were higher than in micelles obtained from the digestion of commercial ones. Bioaccessibility of pro-vitamin A carotenoids in the micelle fraction of digested OFSP was confirmed in assays of Caco-2 human intestinal cells. They suggested that agricultural development of these two varieties: Amelia and *Beauregard* (biofortified), riches in *trans*-βC, and the improvement of home cooking styles can be strategies to increase the consumption of this food to reduce VAD in Brazil.

Islam [27] analyzed total carotenoids and *trans* and cis-β-carotene in different varieties of raw and cooked orange-fleshed sweet potato (OFSP) aiming to reduce VAD using plant-based foods. Intravarietal difference in carotenoids as well as in *trans* and *cis*-β-carotenes were found both in raw and boiled potatoes. Carotenoid content was higher in raw potatoes compared to boiled samples from the same variety, as expected by solids dissolution. Amongst the varieties, Kamalasundari (BARI SP-2) contained the highest amount of carotenoids both in raw and boiled samples. The β-carotene was significantly higher in Kamalsundari and BARI SP-5 varieties, while *trans*-β-carotene was found the major carotenoid in all of the raw potatoes. Boiling resulted in an increase in *cis*-β-carotene and a decrease in the *trans*-isomer contents. The use of Kamalsundari and BARI SP-5 orange-fleshed sweet potatoes was proposed as potential food-based supplements to reduce vitamin A deficiency.

Sweet potatoes have been the aim of research over the years due to their functional and nutritional properties. Carbohydrates, proteins, lipids, carotenoids, anthocyanins, phenolic acid conjugates, and minerals constitute versatile nutrients in different parts (tubers, leaves, stems, and stalks) of sweet potato. The unique composition of sweet potato provides various beneficial effects such as antioxidant, hepatoprotection, anti-inflammatory, anticancer, antidiabetic, antimicrobial, anti-obesity, and antiaging activities. Factors which affect the nutritional composition and bio-function of sweet potatoes include the varieties, parts of the plants, extraction time and solvents, post-harvest storage and processing. Differences between the *in vitro* and *in vivo* assays employed for bio-function evaluation also lead to variations in results from different studies, which makes direct comparisons inadequate or difficult. Leaves, stems, and stalks from sweet potatoes are still commercially underutilized. Results from several studies point out that sweet potato can be developed as a sustainable crop for different nutritionally enhanced and value-added food products aiming at the promotion of human health [30].

Sweet potato (*Ipomoea batatas* (L.) Lam) is one of the most popular and ancient roots in Brazil, which is consumed cooked, baked or as sweets, cooked in boiling water. Cooking can result in physicochemical transformations which modify its nutritional properties. Vizzotto et al. [31] evaluated physicochemical characteristics, bioactive compounds, and the antioxidant activity of 12 genotypes of raw and roasted sweet potato, with different pulp colors: cream pulp, orange pulp, and purple pulp. Total soluble solids, acidity, sugars, carotenoids, anthocyanins, phenolic compounds contents, and antioxidant activity show a wide variation of these parameters for both forms of preparation. Antioxidant activity varied considerably amongst the genotypes, from 210.29 to 7870.57 μg trolox equivalent.g^{-1} for pulps *in natura* and from 773.26 to 17,306.22 μg trolox equivalent g^{-1} for baked pulps. Contents of soluble solids, acidity, sugars, and bioactive compounds as well as total antioxidant activity were higher while the levels of carotenoids were lower in baked sweet potatoes than *in natura*. Genotype and color of sweet potatoes influenced their chemical composition. Cultivars Amelia and *Beauregard* stood out with respect to the amount of soluble solids and carotenoids, respectively. Selections of purple have to be recommended as sources of anthocyanins. Thermal processing influenced the concentration of antioxidant compounds and affected some of the physicochemical characteristics.

Yellow sweet potato is mostly produced in small scale by farmers. It is a source of energy and carotenoids in the human diet; however, it is a highly perishable crop. To increase its industrial use, yellow sweet potato flour was produced for use in bakery products. Nogueira et al. [32] evaluated the technological quality and the carotenoid content in sweet breads produced by replacing wheat flour with 0, 3, 6, and 9% yellow sweet potato flour. The increase in yellow sweet potato flour concentrations in bread resulted in a decrease of specific volume and firmness and an increase in water activity, moisture, orange coloring, and carotenoids. Storage led to the most significant changes after the 5th day, with a reduction in intensity of the orange color. The β-carotene content varied from 0.16 to 0.47 μg g^{-1} in breads with yellow sweet potato flour. The results suggest that the use of yellow sweet potato in breads can be beneficial for consumers' health and for the agricultural business as well.

2.3. Pumpkins (*Cucurbita moschata*)

A great number of pumpkin varieties, each of which contains a different amount of carotenoids, are cultivated worldwide [33]. In several Brazilian regions, *C. moschata* cultivars are known to contain a particularly high amount of α- and β-carotene. The β-carotene has 100% pro-vitamin A activity, and α-carotene has 53% pro-vitamin A activity [34–37].

Carotenoids have antioxidant activity, but few are converted in retinol (an active form of vitamin A) by the human body. Among more than 600 carotenoids which have pro-vitamin A activity, the most known are α- and β-carotene, and these are susceptible to degradation (isomerization and oxidation during the cooking process).

There are various studies about carotenoids from pumpkins, mainly β-carotene, and the large diversity of landraces and cultivars, among them the *Cucurbita maxima, Cucurbita moschata,* and *Cucurbita pepo.* The differences in carotenoids and β-carotene contents in these three species are important in order to choose the best one for cultivation and biofortification [19]. For instance, studies carried out by Carvalho et al. [19] revealed a large range of contents of carotenoids among samples of the same species of *Cucurbita moschata*. The total carotenoids content varied from 124.87 to 557.20 μg g^{-1} and others were above 60 μg.g^{-1}.

Priori et al. [38] evaluated the genetic variability for the synthesis of bioactive compounds, total phenolic compounds, carotenoids, antioxidant activity, and minerals of 10 accesses of pumpkin (*C. moschata*) landraces. They found a high genetic variability for the synthesis of phenolic compounds, carotenoids, antioxidant activity, and minerals, with the most promising C52 and C389 accessions, due to their high levels of total carotenoids.

2.4. Yellow sweet cassava (*Manihot esculenta*)

The manioc plant (*Manihot esculenta*, Crantz) belongs to the Euphorbiaceae family being native to South America, cultivated by the Indians responsible for its dissemination. The Portuguese spread it to other continents, especially Africa and Asia The plant is a bush of bulky roots, leaves petiolated and yellowish chalice flowers, arranged in panicles. Its tubercle is also known as cassava, aipim, castelinha, macacheira, cassava, sweet cassava, and cassava according to the regions where it is cultivated [13].

In Brazil, there are about 1200 varieties, classified as bitter or sweet according to its hydrocyanic acid content. Originated from South America, manioc (*Manihot esculenta*, Crantz), present in the indigenous culture and other ancient populations, has its historical importance because it has been the main energetic source for several generations of these peoples. It is still one of the main energy foods in the African, Latin American, and Asian continents, to about 500 million people, especially in developing countries [39].

Cassava is easily adapted to different types of soil and climate, usually grown on a small scale with little or no technology adoption, basically using family workers. In the case of Brazil, it is widespread throughout the region bounded by the geographic tropics. The world production has increased over the last decades, due to factors such as genetic improvement, use of technology in planting, and expansion of cultivated areas. However, the expansion of the areas remains centralized in the countries that have a tradition in the planting of this culture [3, 40].

The economies of African countries, the largest producer continent, and Latin America are based on the exploitation of the primary sector. Therefore, countries seek to increase production of crops that are strategic for maintaining the economy and serving the domestic market, raising production more than in other continents (Africa) or maintaining production (Latin America) in the last decades. On the other hand, Thailand, located on the second largest cassava (Asian) producer continent, is the largest cassava root exporting country.

The African continent, the world's largest producer of cassava roots, does not have countries that excel in the export trade of the product, prevailing the service in the domestic market, indicating that the crop is produced mainly by small producers, in precarious production systems, with little or no application of modern management and fertilization technology. Brazilian production stood out among the 80 cassava producing countries, reaching around 13% of world production [41], demonstrating that there is still room for growth of Brazilian production if modernization of plantation using technology and improvement is implemented. Ten states produced about 80% of the Brazilian production, with Pará and Bahia accounting for 36% of this total and Paraná, Rio Grande do Sul and Maranhão, 26%. The other five: Amazonas, Minas Gerais, Ceará, São Paulo and Mato Grosso do Sul contributed 18% of this production [41]. Overall, 62% of the national production comes from the North and Northeast regions. Brazil has encouraged the production and commercialization of agricultural products inside the country, through government financing programs such as the National Family Agriculture Program (PRONAF). This program is based on support for rural development, on the strengthening of family agriculture and its organizations, for example, cooperatives, as a segment that generates jobs, incomes, and increases the nutritional quality of these populations [42].

In the last 10 years, efforts were made to identify new varieties of able yellow cassava to improve the nutritional quality for the populations with malnutrition problems, situated in the tropics, particularly in the Brazilian northeast, where the cassava constitutes one of the main cultivations and almost the only source of nutrients. The cassava culture of yellow coloration can be an excellent source of carotenoids, precursors of vitamin A such as α and β-carotene.

The total and α and β-carotene in raw varieties of bitter and sweet yellow cassava as well as in cooked ones were evaluated by Oliveira et al. [40]. A total of 28 varieties were analyzed: 12 in bitter, 11 in sweet yellow cassava, and 5 other varieties of bitter yellow cassava. The variability among the varieties of bitter yellow cassava revealed higher total carotenoids content compared to sweet yellow ones. However, the proportion of β-carotene in relation to the total carotenoids content was larger in the varieties of sweet yellow cassava. The bitter yellow cassava roots presented a variation in the total carotenoid content from 1.97 to 16.33 $\mu g\ g^{-1}$ and β-carotene from 1.37 to 7.66 $\mu g\ g^{-1}$, respectively. The isomers 13, 9-Z and all-*trans*-β-carotene were found in all varieties, being all-E-β-carotene the most abundant one [43–45].

3. Conclusions

The evaluation of β and α-carotene and total carotenoids content in cultivars, accesses, biofortified, and landraces of sweet potatoes, pumpkins, and yellow sweet and bitter cassava is very important to obtain plant raw materials with high contents of carotenoids that can be used for cultivation and minimize hunger in the low-income populations of all ages around the world [46, 47].

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Conflict of interest

There is no interest conflicts.

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