Chapter 1

Phenolic Compounds: Functional Properties, Impact of Processing and Bioavailability

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Abstract

In this chapter, we discuss the influence of the processing methods on the content of phenolic compounds in fruits and vegetables. The intake of fruits and vegetables based-foods are associated with delayed aging and a decreased risk of chronic disease development. Fruits and vegetables can be consumed *in natura*, but the highest amounts are ingested after some processing methods, such as cooking procedures or sanitizing methods. These methods are directly methods are directly related to alteration on the phenolic content. In addition, the postharvest conditions may modify several phytochemical substances. Phenolic compounds are referred to as phytochemicals found in a large number of foods and beverages. The relative high diversity of these molecules produced by plants must be taken into account when methods of preparation are employed to obtain industrial or homemade products. Phenolic compounds comprise one (phenolic acids) or more (polyphenols) aromatic rings with attached hydroxyl groups in their structures. Their antioxidant capacities are related to these hydroxyl groups and phenolic rings. Despite the antioxidant activity, they have many other beneficial effects on human health. However, before attributing health benefits to these compounds, absorption, distribution, and metabolism of each phenolic compound in the body are important points that should be considered.

Keywords: cooking procedures, sanitizing methods, postharvest, cultivating conditions, health benefits

1. Introduction

Most of the vegetables and some fruits are preferably consumed after some kind of processing, which can cause favorable or disadvantageous changes in the flavor and texture, increasing the food's palatability and affecting the quantity and quality of bioactive compounds, such as phenolics. The biological, physical, and chemical modifications that occur during some processing methods, as the cooking, are predominantly related with sensorial, nutritional, and textural alterations, which may be beneficial or harmful to the human health. A high temperature can inactivate microorganisms, decreases anti-nutritional factors, increases the digestibility of foods, and modifies the bioavailability of the phenolics. In contrast, the thermal processing may have negative effects on these bioactive compounds. Furthermore, other processing methods have been adopted for fruits and vegetables, whether for domestic consumption or in the food industry, for example, fresh-cut, drying, blanching, pasteurization, use of electric fields and membranes, among others. In this chapter, we will address the influence of some processing methods in plant-based food based on the phenolic content, as well as on their bioavailability.

2. Functional properties of phenolic compounds

Phenolic compounds are a main class of secondary metabolites in plants and are divided into phenolic acids and polyphenols. These compounds are found combined with mono- and polysaccharides, linked to one or more phenolic group, or can occur as derivatives, such as ester or methyl esters [1]. Among the several classes of phenolic compounds, the phenolic acids, flavonoids, and tannins are regarded as the main dietary phenolic compounds [2]. Many studies have shown a strong and positive correlation ($p \leq 0.05$) between the phenolic compound contents and the antioxidant potential of fruits and vegetables [3–5]. This antioxidant mechanism, present in the plants, has an important role in the reduction of lipid oxidation in (plant and animal) tissues, because when incorporated in the human diet, not only it conserves the quality of the food, but it also reduces the risk of developing some diseases. Studies have shown that a diet rich in fruits and vegetables contributes to the delay of the aging process and to the decrease of the inflammation and oxidative stress risk, related with chronic diseases (e.g., cardiovascular diseases, arteriosclerosis, cancer, diabetes, cataract, disorders of the cognitive function, and neurological diseases) [6–8].

The antioxidant activity of phenolic compounds is attributed to the capacity of scavenging free radicals, donating hydrogen atoms, electrons, or chelate metal cations [9]. Molecular structures, particularly the number and positions of the hydroxyl groups, and the nature of substitutions on the aromatic rings, confers to phenolic compounds the capacity of inactivating free radicals, which is referred to as structure-activity relationship (SAR). The hydrogen atoms of the adjacent hydroxyl groups (*o*-diphenol), located in various positions of the rings A, B and C, the double bonds of the benzene ring, and the double bond of the oxo functional group (-C=O) of some flavonoids, provide these compounds their high antioxidant activity (**Figure 1**). This characteristic can be observed in quercetin and catechin. Both compounds

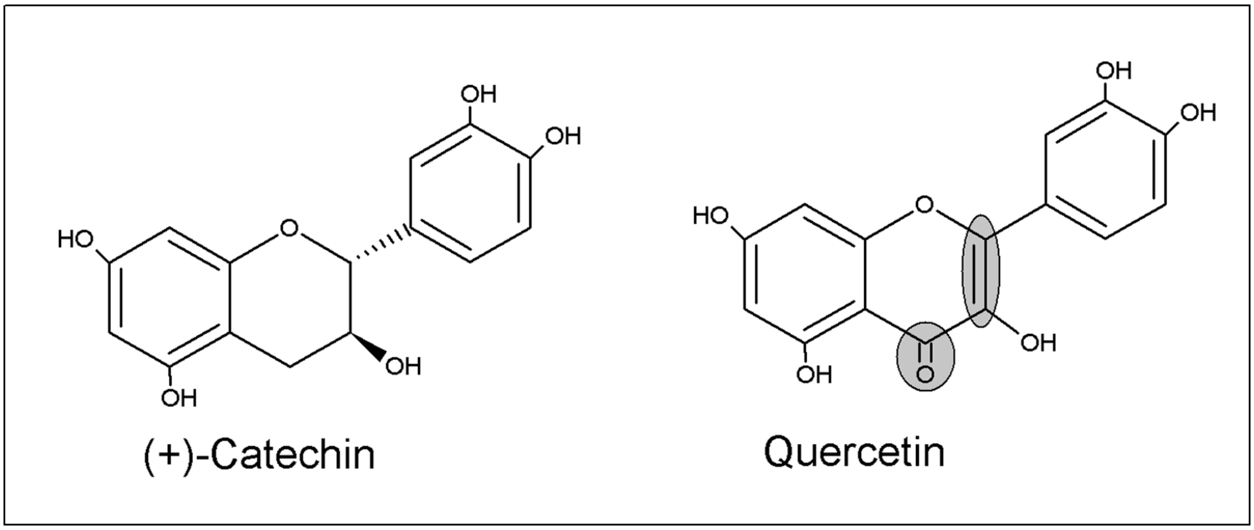

Figure 1. Double bonds of the benzene rings and the oxo function (gray background).

share a similar number of hydroxyl groups, at the same positions, however, quercetin also contains a 2,3-double bond in the C ring and the 4-oxo function [10]. The advantage of this structure is an enhancement of the TEAC (Trolox equivalent antioxidant capacity) value, when compared to the saturated heterocyclic ring of catechin with approximately half the antioxidant activity.

Even though there are innumerous studies comparing the biological actions and *in vitro* antioxidant activity of phenolics, and the function of its content in vegetables and consequently in human, there is no consensus about the best way of preparing/consuming fruits and vegetables intending preservation or to increase their antioxidant activity.

3. Processing methods and their impact on phenolic compounds

The functionality and stability of the phytochemical compounds in the human body depends, not only on the quantity, but also on the bond and/or interaction of these compounds with other molecules, on the location in the food matrix, and in the presence of other bioactive compounds. In plants, the phenolics can be found linked to the cell membranes/walls or can be free, and the food processing methods such as the use of high temperatures or freezing, can cause the release of these compounds, which is implied by an increase of its bioavailability in the human body. Some reports show that heating affects the content of some polyphenols, including flavonoids, due to the extractability alteration by the rupture of the cell wall. In this way, polyphenols linked to the wall could be released more easily on cooking than from the raw material [11]. Other authors confirm the release of these compounds by heat treatment, as described in sweet corn [12] and in citrus peel [13], due to breakdown of the matrix.

Domestic or industrial food preparation include a variety of processes, such as preparation (peeling, washing, and chopping), boiling, frying, and baking (traditional oven or microwave), among others [14]. Several research studies have shown increase in the phenolic compound levels, as well as in the antioxidant activity after cooking [15–17] or after other processes, while other studies related the thermal processing with the decrease of phenolic contents [18, 19]. Changes in the phenolic composition are of great complexity, because they vary according to their structure, to the analyzed food and, mainly, according to cooking method used in the preparation. There are indications that the retention of phytochemicals and the antioxidant properties after the cooking vary considerably between the different vegetables and methods used in their preparation [20–22]. Initially, it was believed that the thermal processing applied to several foods was prejudicial regarding the retention of the nutrients (e.g., antioxidants). However, the nutritional and bioavailability increased, and a higher antioxidant activity was observed in vegetables and/or fruits that went through thermal processing [22]. The heating may disrupt the cell membrane, leading to the release of membrane-bound phytochemicals, what may result in an increase in bioavailability Nevertheless, we will discuss forward that these compounds are not always increased. Many times, they are decreased and other times, the thermal processing does not affect the phenolic content.

Most of the studies show that the boiling may result in a decrease of the total phenolic compound content, while steam techniques and stir frying may promote an increase of these compounds. This may be explained by the fact that phenolics are highly soluble in water [23, 24] and, in the boiling process, they may be lost by leaching. However, heat treatment may soften the vegetal tissues and facilitate the extraction from the cellular matrix [25]. The rupture of the cell wall and of the other subcellular compartments, during the boiling, facilitates the migration of cellular components with the consequent release of these molecules into the boiling water.

Variations in the phenolic compounds may occur influenced by the food matrix used, as the verified reduction in the phenolic compounds content in broccoli (*Brassica oleraceae* L. cv. *gemmifera*) when submitted to thermal processing in water [26]. In tomatoes, the cooking by boiling, baking, and frying induced significant reductions ($p < 0.01$) in the total phenolic content [27]. Phenolic losses upon boiling or blanching were observed in several cruciferous vegetables, as kale (*Brassica oleracea* var. Acephala, cv. Winterbor), broccoli (*Brassica oleracea* var. botrytis italica, cv. Sebastian), brussels sprouts (*Brassica oleracea* L. var. gemmifera, cv. Maczuga), cauliflower (*Brassica oleracea* var. botrytis), white cauliflower (cv. Rober), green cauliflower (cv. Amphora) [28, 29], as well as spinach (*Amaranthus sp.*), cabbage (*Brassica oleraceae*), swamp cabbage (*Ipomoea reptans*), and shallots (*Allium cepa*) [30]. Broccoli (*Brassica oleraceae* L. cv. Lord) subjected to boiling, showed losses of flavonoids and phenolic acids by 72 and 52%, respectively, as compared with fresh broccoli [31].

In contrast to the described losses, some researchers relate an increase of the phenolic content in broccoli, green beans, and pepper when subjected to the boiling process [32]. The increase of phenolic content described in vegetables after cooking, has been attributed to the higher extractability of the cellular matrix compounds, as well as to the tissue dehydration [33, 34]. However, low correlation coefficients ($R = 0.5$) were observed between the increases in the content of total phenolic compounds in cooked peppers and the weight loss during cooking [35], suggesting that besides dehydration of peppers, others factors were involved in such increases.

In broccoli (*Brassica oleraceae* L. cv. Lord)) subjected to steaming, there was an increase of the total polyphenol content (1.6 times), flavonoids (1.5 times) and phenolic acids (1.3 times) in comparison to *in natura* broccoli [31]. This effect may be explained due to the rupture of complexes between the polyphenolic compounds and other compounds (e.g., proteins), resulting in a better availability by steaming extraction.

The steam-cooking process has proved to be effective in the maintenance or increase of the phenolic content in some vegetables. In study using kale (*Brassica oleraceae* L. var. acephala D.C) and red cabbage (*Brassica oleraceae* L. var. capitata), it was verified that steam cooking resulted in higher contents of bioactive compounds and higher antioxidant activity, which can be attributed to the absence of loss by leaching [21]. Corroborating with these results, studies realized on tubercles showed an increase in the total phenolic compounds contents (e.g., anthocyanin) after thermal treatments that do not use water in the process [36, 37]. The thermal treatment effect preserves or causes a little increase in the anthocyanin content in different potato "cultivar" (*Solanum tuberosum* L.) when cooked in microwave (9 min, 900 W), steamed (pressure cooker, 15 min), boiled (in water in a pressure cooker, 15 min), and baked (in a hot air oven, 40 min, 180°C) [38]. This increase may be attributed to the inactivation of the polyphenol oxidase (POD) due to the thermal treatment. Some cooking methods like microwave can destroy the potato cellular microstructure and induces a better extraction of the compounds from the cell matrix [39, 40].

Many studies on cooked potatoes showed that the total phenolic content may be maintained or even improved, based on the cooking method used [25, 40, 41]. In the study with different cultivations of potatoes cooked in microwave (2 min 30 s, 1100 w), baking (375°C, 30 min), and boiling (18 min), an increase in the quantity of chlorogenic acid, rutin, and kaempferol-rutinose was verified [25]. In opposition, another research on cooked potatoes by boiling (60 min), microwave (20 min) and baking (204°C, 60 min) showed reduction of 44, 55, and 53% for the total phenolic content, respectively [18]. In commercial processing, the pretreatment commonly used, such as blanching and dices processing, can also induce a significant loss of total phenolics [42]. Thus, cooking methods with lower temperatures should be preferred in order to maintain the phenolic compound contents in potatoes [43]. Steaming and microwaving are the cooking methods that retain the highest quantities of total phenolic compounds and antioxidant activity in cooked potatoes [44]. The stir-frying method induced the highest loss of these compounds (72.44%), followed by baking (40.51%), air frying (32.52%), and frying (14.08%).

Among the factors that affect the leaching of matrix compounds, we can include the polarity of medium used. Polar mediums, such as water, allow changes in the phenolic compound levels. In contrast, if the medium is nonpolar (use of oil for frying, in both deep frying and pan frying), the loss of compounds is lower due to the lack of diffusion or migration to the medium [19]. The use of extra virgin olive oil (EVOO) did not induce loss of the total phenolic compound content in fresh potato (*Solanum tuberosum*), pumpkin (*Cucurbita moschata*), tomato (*Licopersicum esculentum*), and eggplant (*Solanum melongena*). However, the retention of phenolic compounds was directly affected by the cooking technique used, deep frying > sautéing > boiling > boiling water/EVOO mixture [45]. Addition of oil during the cooking process may result in transference of some compounds present in the oil to the food. Comparing different oils (olive oil and sunflower oil) used to fry with grilling method, an increase in phenolic compounds can be observed [46]. This may be due to the thermal destruction of cell wall and other subcellular components, during the cooking process, stimulating the release of these compounds. At the same time, some mechanisms have been proposed to explain the variations found in the phenolic compounds in foods after thermal processing, such as the rupture of the phenol-sugar glycosidic bonds, leading to the formation of phenolic aglycons [47].

The phytochemical quantity retained in fruits and vegetables, after the processing, depends on the stability of these compounds during the different food preparations. Molecular modifications induced by processing and the transformations that occur before the consumption are mainly related to the sensibility of the compounds to oxidation and/or isomerization [17]. Reduction of phenolic amounts may occur due to isomerization of certain compounds caused by the high temperature. In catechin, the isomerization are clearly demonstrated [48], where epimerization changes the epistructured catechin to nonepistructured catechin and vice versa. Therefore, others methods of food processing that influence phenolic content, and not used in conventional domestic processing, should be considered.

3.1. Blanching

One of the first steps of vegetable and fruits processing, as well as before the extraction of juices, is the blanching process used mainly in order to inactivate enzymes and to remove undesirable microorganisms. Blanching is the treatment that can be used to inhibit the phenolic oxidation (browning). The browning reaction involves different compounds and follows chemical pathways that include reactions promoted by those enzymes not involved in catalytic processes, as the Maillard reaction that results in melanoidin formation [49]. Blanching may induce alterations in the content of some bioactive compounds in fruits and vegetables and is used to inactivate some enzymes, such as laccase, lipoxygenase, polyphenol oxidase, and peroxidase that affect the quality during storage. These enzymes can promote deterioration reactions and consequent undesirable changes in nutritional value, flavor, and color (including dark pigments).

Polyphenol oxidase (PPO, EC 1.14.18.1) and peroxidase (POD, EC 1.11.1.7) are involved in the phenolic compound oxidation and are very important in preserving the food quality. The phenolic compound oxidation induces the production of dark compounds (browning), that induces rejection by the consumers, and decreases the antioxidant capacity of foods [50]. The browning reactions have generally been assumed to be a direct consequence of phenolic compound oxidation by PPO action [51]. However, at least a partial role may be attributed to the action of peroxidase [52–54]. The mixing of phenolic compounds with polyphenol oxidase and peroxidase enzymes in the presence of oxygen produces colored pigments [55]. When there is disruption of the cell, some compounds such as phenolic acids suffer the action of the polyphenol oxidases that induces oxidation of phenolics and results in dark compound formation [56]. In addition, polyphenol oxidases catalyze two different reactions. The first is the *o*-hydroxylation of monophenols and diphenols (monophenol oxidase, cresolase activity) and the second reaction promotes the o-diphenol oxidation to *o*-quinone (diphenolase/

catecholase activity) [55]. This quinone formation suffers polymerization and causes yellow and brown coloring.

The peroxidase enzyme is one the most important enzymes responsible for polyphenol degradation. This enzyme is generally considered as the reference enzyme for blanching treatments, due to its high thermal resistance and high concentration in most vegetables. Residual POD activity could still be detected after a high-temperature blanching, and its inactivation in food product can indirectly indicate that other enzymes are likely to be inactivated [57]. In order to inhibit the polyphenol oxidases and peroxidases some treatments have been used, including the addition of ascorbic acid or chemical agents (sulfites), exclusion of oxygen, refrigeration, and nonthermal treatments. PPO is relatively thermolabile, temperatures above 50°C and proper time of treatment decreases its activity. At higher temperatures (above 80°C), these enzymes may be completely inactivated [58].

In blueberry fruits processed into juice, blanching induced an increase in the retention of anthocyanin levels (23% instead of 12%) and the total anthocyanin content of juice from blanched blueberry is twice the nonblanched one [59]. The blanching treatment thus demonstrated to be extremely effective in reducing the PPO activity and maximizing anthocyanin recovery. This effect should be a result of the complete inactivation of the PPO enzyme, or of the greater extraction yield linked to the increase of fruit skin permeability caused by the heat treatment [60]. In some eggplant genotypes, cooking processes as boiling and grilling induced a drastic decrease in PPO activity, with a little residual PPO activity [61]. Whereas, in wheat flour, the PPO showed the maximum decrease in its activity when processed in microwave (81.4%), compared to hydrothermal treatment (48.3%). The strong decrease of the PPO activity, after microwave, can be attributed to the higher heating uniformity and higher penetration power of the microwave.

The activity of the enzymes PPO and POD are closely related, acting in a combined form in the darkening of fruits and vegetables. The phenol oxidation by PPO produces hydrogen peroxide (H_2O_2), independently on the substrate used. The POD catalyzes the phenolic compound oxidation, since there is a high affinity between the H_2O_2, produced by the PPO, that acts as an electron acceptor and the vegetal phenolic compounds that work as electron donators (substrates: catechin, quercetin and its glycosides). This process promotes the oxidation of phenolic compounds and produces quinones that affect color, flavor, texture, and loss of the nutritional and functional quality [53, 62]. The PPO is more thermolabile when compared to the POD, however, variations may occur depending on the food matrix. In some cases, the inactivation can be obtained at 80ºC, which would explain, partially, the reason why the amount of phenolic compounds increases when the product is taken to high temperatures, as used during pasteurization or other procedures [62–65].

Generally, blanching is a thermal process used in combination with other methods and carried out by treating the fruits and vegetables with steam or hot water for 1–10 min at 75–95°C. Time/temperature combination may vary according to vegetable or fruit used [66]. Blanching performed on *Lagenaria siceraria* fruit before preparing the juice, using water at 90°C for 5 min, resulted in a total phenol content of 644 mg/100g, values similar to that found in unprocessed fruit (640 mg/100 g) [63]. However, when the combination of blanching and sonication was applied, there was an increase in the total phenolic compounds of 63% and there was also an alteration in the structure of the molecules after the process, indicating that the use of both methods increases the quantity of these compounds.

3.2. Processing methods applied to beverages

3.2.1. Clarification

This process is regularly used in beverage industries to remove phenolic constituents that give color, astringency, and bitterness to the juices. In addition, these compounds, high-molecular weight proteins, and pectins contained in juices may cause turbidity (haze formation) and, consequently, decrease the product acceptance by the consumer [50]. To remove all undesirable molecules, the clarification process consists of the addition of gelatin, bentonite, polyvinylpolypyrrolidone (PVPP), and kieselsol, among others. After that, the juice samples are subjected to ultrafiltration several times, a process used in beverages to remove high-molecular weight proteins and other compounds added during clarification process (gelatin, bentonite, PVPP, kieselsol). Employing this method helps to avoid the formation of cloudy appearance during processing and storage. However, besides the direct reduction of phenolic compounds induced by clarification, the ultrafiltration process can remove the phenolic compounds that are complexed with proteins [67].

3.2.2. Pasteurization process and emerging technologies

Beyond the clarification, many juices are submitted to the pasteurization process (heat process used to inactivate pathogenic microorganisms) that, not only eliminates microorganisms, but also affects the PPO activity, which indirectly degrades monomeric anthocyanin by forming *o*-quinones from polyphenols during enzymatic browning [68]. On the other hand, pasteurization is one of the methods used in industrial scale that causes the highest losses of bioactive compounds. According to Azofeifa, after the pasteurization of the blackberry (*Rubus adenotrichus* Schltdl) juice, many phenolics may be lost [69]. This study described a decrease from 191 to 181 mg of cyanidin-3 glucoside per gram of extract, when the temperature was increased from 75 to 92°C, even using the least time in the highest temperature. Another study showed that the increase of pasteurization temperatures promotes loss of phenolic compounds in orange juice [70].

New emerging technologies have been used in the beverage industry, such as high intensity pulsed electric field (HIPEF), high pressure, and ultrasound. All of these technologies are nonthermal processes that help stabilizing the beverages from microorganism-induced damages or enzymatic degradation, and have few or any negative effect on the phenolic compounds [71–74].

Another processing that affects the amount of phenolic compounds is the fermentative process. In wine, for example, the phenolic compounds not only have functional properties, but also have important functions for the product's sensorial quality, impacting the color, flavor, smell, and aging [75–77]. The different steps involved in the process, such as the wine-making technique used, the maceration characteristics (temperature, enzymes, and chemical reagents used), fermentation, presence of alcohol, and aging cause alterations in the phenol concentration, mainly in the anthocyanins, which are pigments responsible for the color and have great biological importance [75, 76].

3.3. Sanitizing methods

Currently, in the food processing, there is a great concern about the residues formed by the action of some compounds used during the sanitation. During harvest, transportation, or processing, the tissues may be mechanically injured that facilitates the food contamination [78]. In many countries, the use of chlorinated compounds, particularly the hypochlorite salts, is very common to minimize the pathogen infestation rate. Sodium hypochlorite is a potent sanitizer that has oxidant action and is used in domestic or industrial food processing. However, the use of chlorine or chlorine-based products, has some disadvantages, such as the formation of organochlorinated compounds, chloroform, trihalomethanes, and haloacetic acids, that have known or suspected carcinogenic or mutagenic effects, with proven toxicity to liver and kidneys [79]. Due to these effects, its use has been forbidden in organic foods. The relation between products containing chlorine and the phenolic compound content has been investigated and there is still no consensus about the results. In mushrooms, the use of sodium hypochlorite at room temperature induced the disappearance of phenolics and the formation of their oxidation products [80]. The losses of flavonols (23%) and anthocyanins (13%) due to leaching were detected after sanitation using sodium hypochlorite at 50°C in red onion slices [81]. In contrast, in carrots, washing in chlorinated water (100 mg/L) did not induce alterations in the phenolic compound content [82].

One of the alternatives for hypochlorite is ozone (O_3), used as an antimicrobial agent since the end of the nineteenth century to purify potable water. The use of O_3 has many advantages over other chemical oxidants, its precursors are numerous and economically profitable and can be used in gaseous or aqueous state, depending on the product [83, 84]. Beyond its antimicrobial activity against a wide range of microorganisms, O_3 can destroy chemical residues and convert nonbiodegradable organic materials into biodegradable materials [85]. At the same time, due to its fast decomposition into oxygen and to the fact that it does not form residues in the treated products, its use in the food processing is authorized by the organic certification [86]. Various research groups have studied the relation of the ozone action with the phenolic compounds, but contradictory results about its action have been described. Certainly, some fruits and vegetables may be more susceptible to the action of this gas and may show different responses, mainly regarding the stress caused by the oxidant action.

Both the time and ozone concentration may cause different responses. In pineapple, banana, and guava, the application of gaseous O_3 induced a significant increase in total phenolics, whereas in bananas and pineapples, the flavonoid content increased in response to up to 20 min of ozone treatment. For guava fruits, the flavonoid content increased and total phenolic decreased inversely when these fruits were exposed up to 10 min [87]. The authors attribute the increase of these compounds to the activation of the enzyme phenylalanine ammonia-lyase (PAL; EC 4.3.1.5), which may have increased due to the stress. The increase of the phenolic compounds and flavonoid contents in these fruits may be caused by other factors, such as the modification of the cell wall that occurs when a plant cell is exposed to ozone, increasing the extractability and release of the phenolics bonded to the cell wall. In kiwifruit stored in an enriched environment with ozone and under refrigeration for 30 days or for 3 months followed by 12 days of shelf life, there was an increase in the content of phenolic compounds [88]. In this study, the authors affirm that ozone acts as a potent elicitor to anti-free-radicals found in oxygen and nitrogen-reactive species.

The decrease in the content of some polyphenols caused by the treatment with ozone in grape juice has been described [89]. After the use of ozone at low concentration (1.6% w/v) for 10 min, there was a significant decrease of 78.0, 95.0, and 99.0% for cyanidin-3-O-glucoside (Cy3Gl), delphinidin-3-O-glucoside (Dy3Gl), and malvidin-3-O-glucoside (My3Gl), respectively. However, at higher ozone concentrations (7.8% w/w) only Cy3Gl and Dy3Gl were observed to be stable. The anthocyanin degradation influenced in the color of grape juice due to ozone processing can be attributed to the strong oxidizing potential of ozone [90].

Thus, ozone can induce increase or decrease of some phenolic content. In organic and conventional Palmer mangos, sanitized with ozonized water, no effect in phenolic content was observed [91]. The variations in the contents of these compounds were in function of the cultivation mode (organic or conventional) of the fruit. A similar result was described in organic or conventional cabbage treated with ozonized water. There were no variations in the total phenols or flavonoid contents due to sanitizing treatment [92].

Other chemical treatment used to inactivate pathogenic or spoilage microorganisms is the ultraviolet-C light (UV-C), a non-ionizing germicide radiation with wavelength range from 200 to 280 nm. Treatment with UV-C radiation has been widely studied as a fruits and vegetables disinfectant, and offers an alternative for chemical sterilization and preserves food quality [93]. UV-C radiation delays the maturation, decreases the senescence, maintains the quality of the products for a longer time, and reduces the postharvest deterioration of fruits and vegetables [94, 95]. The UV-C has been suggested as a suitable stress-promoting technology. This treatment may also accelerate the ethylene production and, consequently, activate the expression of ethylene response factor (ERF) genes. This response is consistent with the fact that UV-C is a stress agent in plants and generally increases the ethylene production under stress, probably by acting on system 2 autocatalytic ethylene [95, 96]. Even though the UV-C increases the ACC (1-aminocyclopropane-1-carboxylate) oxidase transcription and stimulates the ethylene production, the maturation evolution is still delayed [95].

The application of hermetic doses of UV-C not only is capable of improving the storage time, but can also increase the nutritional and functional properties of fruits and vegetables. The alteration of the ERF expression, through hormonal induction or abiotic stress, may induce secondary metabolic pathways, e.g., the phenolic compounds production [95, 97, 98]. Low UV-C doses may efficiently reduce the microbial population in fresh-cut products, which is one important sector of the food market. The UV-C treatment (0, 1, 3, 5, and 10 min) increased the total phenol and flavonoid contents in fresh-cut mangoes during storage for 15 days at 5°C, and this effect can be attributed to the increase of the phenylalanine ammonia-lyase activity. In addition, the irradiation improved the antioxidant capacity, which is probably related to the increase of the phenolic compound content [99]. The UV-C radiation (1.5 and 3.0 kJ/m^2), in minimally processed Satsuma mandarin, promoted an increase in the flavonoid content (22.20 and 21.34% for narirutin, 11.75 and 33.25% for hesperidin) and total phenolic compounds (5.73 and 8.13%), after 3 days of storage [100]. According to the authors, this flavonoid increase may be related to the citrus defense mechanism in reaction to the stress induced by the UV-C application.

Another type of radiation that has been widely used in the maintenance of the quality of fresh and dry foods is the ionizing radiation, which can be constituted by electrons of high energy, X-rays, or gamma rays (^{60}Co or ^{137}Ce) [101]. Among the gamma radiation effects, we can highlight the delay in the maturation, the reduction of the microorganisms in grains, cereals, fruits and spices, reduced storage losses, and extended shelf life. However, the irradiation may induce stress signals and stress responses in fruits and vegetables that increases the antioxidant compounds [102]. In juices of carrot (*Daucus carota* var. sativa) and kale (*Brassica oleraceae* var. acephala), treated with gamma-irradiation (10 kGy), there were an increase in the total phenol contents and antioxidant capacity, when compared to nonirradiated juice [103].

The alterations induced by the gamma-irradiation in dry herbs and spices are related with the radiation dose applied, and generally, result in an increase of the total phenolic compound contents [104], whereas by using gamma-irradiation at 10 kGy, in *Thymus vulgaris* L., no modification in the phenolic profile and bioactive properties, were observed [105]. On the other hand, the gamma-irradiation can either decrease or improve the bioactivity of irradiated samples, depending on the changes in the structure of different antioxidant molecules and/or breaking some chemical bonds [106]. The influence of different radiation doses (1, 5, and 8 kGy) were also verified on the color, organic acids, total phenolics, total flavonoids, and antioxidant activity of dwarf mallow (*Malva neglecta* Wallr.) [107]. Irradiation at 5 kGy increased the amounts of citric and succinic acids, and decreased the fumaric acid levels. In contrast, in the decoction prepared, the antioxidant properties and levels of total phenolics and flavonoids were decreased with the 8 kGy dose.

3.4. Drying methods

The traditional/conventional drying process is accomplished by heat, and in this process, two transport phenomena occur simultaneously. The first is a moisture movement and the second is a heat transfer [108]. In this method the increase in temperature may induce reduction of phenolic compounds, however, depending on the air velocity and on the heat exposure time, the antioxidant compounds content, as well as the antioxidant activity, can be affected [109, 110]. The effect of temperature (40, 60, and 80°C) and air velocity (0.5, 1.0, and 1.5 m/s) on the drying kinetics and quality attributes of apple (var. Granny Smith) slices during drying were studied [109]. The authors found that the total phenolics decreased with temperature, but a reduced thermal degradation was observed at high air velocity. On the other hand, there was the least destruction of phenolic content at 80°C and 1.5 m/s, probably due to short drying time and, therefore, less exposure of the phenolics to thermal effect. Even though the quantity of phenolic compounds decreased with the increasing temperature, the same effect was not observed for the antioxidant activity (DPPH). At 80°C, the antioxidant activity values did not differ from that measured at 40°C. This effect can be explained by the development of

Maillard browning reaction occurring concomitantly with other events, contributing to generation and accumulation of different antioxidants. Similar results were observed in quinoa, in which a moderate correlation between the phenolic compound content and the antioxidant activity DPPH, were observed at 40 and 80°C [109].

The scientific community has turned its attention to advances in the dehydration methods that preserve and retain the nutrients, stimulated by the increasing demand of dehydrated food products with higher quality, and resulting in more efficient methods and operations. New dehydration methods can retain the amount of nutrients in dry fruits and vegetables in a similar content to the fresh vegetables [111]. Total phenolic compounds were either unaffected or actually increased in concentration and/or extractability after high-pressure preservation treatments and microwave preservation. The results were similar, total phenolic contents either declined (4–91%) or increased (104–125%), depending on the particular food species. Nevertheless, at microwave vacuum preservation, total phenolics were retained at higher levels than in those fruits and vegetables that were air-dried; since the microwave power is less than 500 W. Interestingly, when total phenolic levels at microwave vacuum preservation is compared to freeze-drying, the results showed that freezing-drying is a better dehydration method than microwave vacuum drying.

4. Bioavailability of phenolic compounds

The major sources of phenolics are fruits, vegetables, and beverages, such as coffee, tea, wine, and fresh-fruit juices. Besides its potential effects in protecting against several chronic diseases, it is essential to understand the modifications occurred to these compounds after food processing, and its bioavailability. Better knowledge of the modifications induced by different processing methods in phenolic compounds are essential to evaluate appropriately the bioavailability of these compounds.

The bioavailability of bioactive compounds is the absorptive process of these molecules across the intestine into the circulatory system, after food ingestion. In a review study, reported values of several polyphenols ingested pure (isolated compound) or in foods, ranged from 0.072 to 5 μM, when reached the plasma. The total intake of polyphenols, in the studies grouped for this review, ranged from 6.4 to 1000 mg/day [112]. In elderly Japanese population, the consumption of polyphenols ranged from 183 to 4854 mg/day, with 665 to 1492 mg/day on an average. Beverages such as coffee and green tea were the largest source of these compounds [113].

Usually, from the total phenolics ingested, phenolic acids account for approximately one-third and flavonoids account for the two-thirds remaining. Phenolic and polyphenolic compounds, in isolate or associated to vitamins, such as carotenoids, vitamin E, and vitamin C, are reducing agents that protect human body's specific tissues against oxidative stress. However, polyphenols are the most abundant antioxidants in diets based on fruits and vegetables. The most abundant benzoic acids ingested in human diet are gallic, ellagic, protocatechuic, and 4-hydroxybenzoic acids. Therefore, cinnamic acids are mainly represented by caffeic, ferulic, sinapic, and p-coumaric acids. Diets based on plant foods are a

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rich source of polyphenols that have health benefits and avoid the development of chronic diseases. However, food processing, such as blanching and thermal treatments, may influence its levels and induce its conversion to secondary compounds. In addition to molecular modifications occurring in phenolics during food processing, the absorption and metabolism of these compounds are triggered by enzymatic and nonenzymatic reactions (**Figure 2**). These molecules can also suffer conjugation reactions that may increase or decrease their bioavailability.

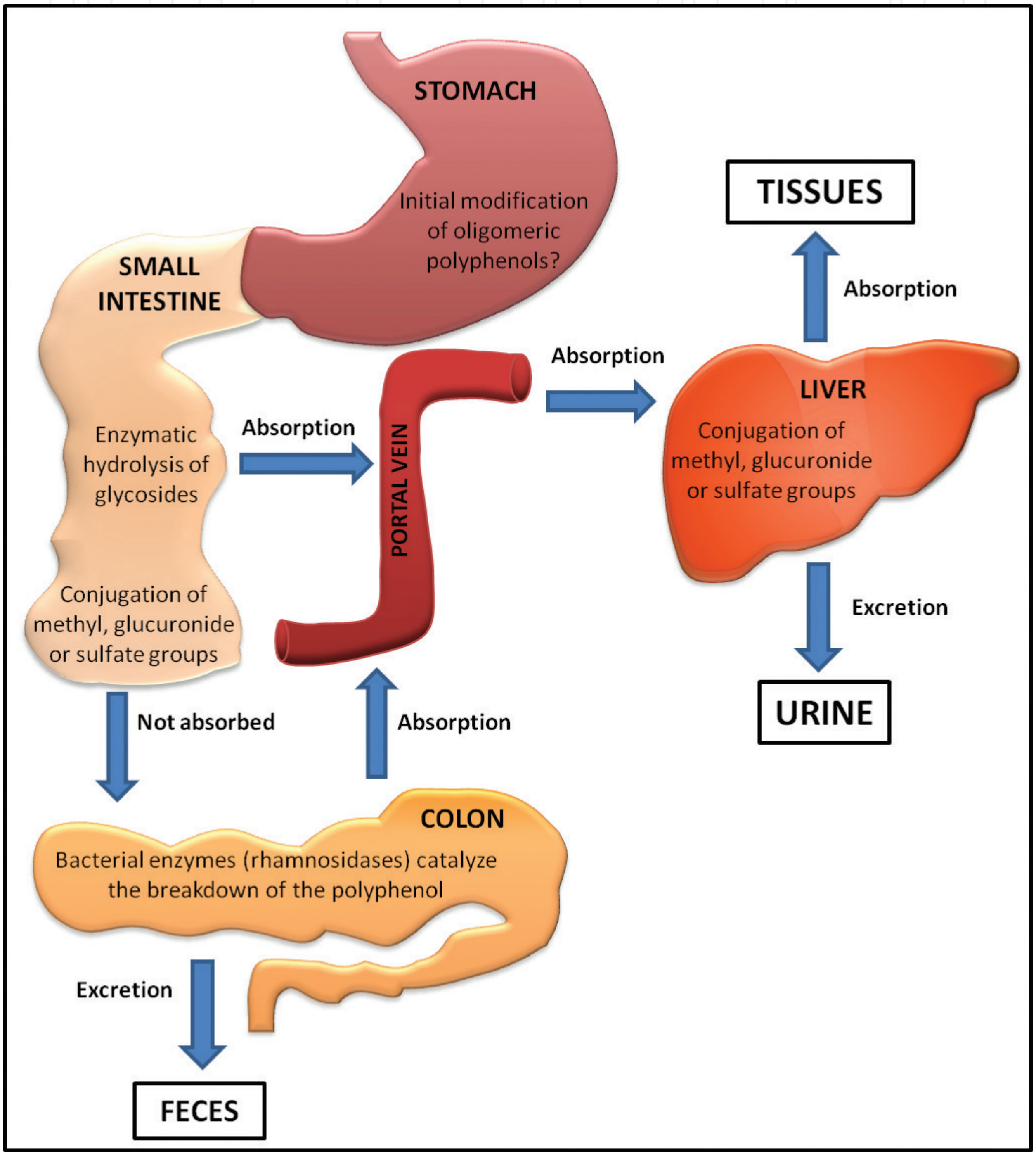

Figure 2. Predicted routes for absorption of dietary phenolics.

Oligomeric polyphenols may suffer initial modifications induced by gastric acid from stomach during the absorption process. In the small intestine, the glycosidic polyphenols are cleaved to release the glycoside radical before absorption. This process is mediated by enzymes, that have affinity for glucose, xylose, and galactose, such as lactase phlorizin hydrolase (LPH) and cytosolic β-glucosidase (β-CBG) [114]. However, the polyphenols resistant to the action of these enzymes are not absorbed in the small intestine and may be cleaved by intestinal bacteria to produce small molecules as phenolic acids. The structures of polyphenols can still pass by conjugation reactions with addition of methyl, glucuronide, or sulfate groups. Remaining polyphenols, mainly that attached to rhamnose, are modified for α-rhamnosidases produced by colonic microflora.

After these absorptive processes the phenolics follow to four possible pathways: 1—excreted through feces; 2—absorbed by intestine/colon mucosa, pass through portal vein and reach the liver; 3—are further conjugated in the liver with methyl, glucuronide or sulfate groups and released in blood stream for tissues absorption; 4—excreted in urine.

5. Conclusion

Processing methods has been associated with changes in the quantity and quality of (poly) phenols. The high diversity of these molecules produced by plants must be taken into account when processing methods of preparation are employed to obtain industrial or homemade products. There are innumerous studies comparing the biological actions and *in vitro* antioxidant activity of phenolic compounds in function of its content in plant-based foods and consequently, in humans. The phytochemical amount retained in fruits and vegetables after the processing, depends on the stability of these compounds during different food preparations. Molecular modifications induced by processing, and transformations that occur before the consumption, are mainly related to the sensibility of the compounds to oxidation and/or isomerization.

The physical and chemical transformations that occur during the thermal processing in each species and between different species can vary, depending on the processing method used, as well as on the temperature and time employed. In general, the thermal processing methods as the beverage pasteurization result in loss of the phenolic compound content, due to the high temperatures employed, as well as the cooking of vegetables in water, because it promotes the leaching of the phenolic compounds. Even though it is not possible to affirm that these effects are observed in all foods, the thermal processing methods such as microwave cooking, steam cooking, air frying, oil frying, and grilling induce alterations in the food matrix, promoting the extraction of these compounds and increasing its bioaccessibility.

Methods such as blanching can minimize the phenolic compounds oxidation by inactivating the enzymes (i.e., PPO and POD) responsible for the darkening of the vegetables and can be used as a preprocessing in order to avoid the loss of these compounds during the process of hot-air drying. The drying at microwave vacuum induces total phenolics retention at higher levels than in those fruits and vegetables that were air-dried. Regarding dehydration, the best method seems to be freeze-drying.

Beyond the thermal processing, the sanitizing methods such as the use of sodium hypochlorite and ozonization can also affect the amount of phenolic compounds, in a dependent manner of the food matrix, compound/method employed, concentration, and sanitation time. The use of ionizing and nonionizing radiation in the food sanitation, cause modifications in the profile of the phenolic compounds and the results vary according to the dose. However, the application of this technology usually induces the increase of the phenolic content, which may be related to the vegetable defense mechanism on reaction to the stress induced by the radiation application.

Better knowledge of the modifications induced by different processing methods in phenolic compounds is essential to properly evaluate the bioavailability of these compounds. The molecular modifications occurring in phenolics during food processing, the absorption and metabolism of these compounds are triggered by enzymatic and non-enzymatic reactions, and these molecules can suffer conjugation reactions that may increase or decrease their bioavailability and consequently, affect the beneficial effects to human health.

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