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Effect of food processing on antioxidants, their bioavailability and potential relevance to human health

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ABSTRACT

It has long been recognized that the antioxidants present in fresh plant materials may be very different to those we ingest *via* our foods. This is often due to the use of food processing strategies involving thermal/non-thermal treatments. Current research mostly focuses on determining what is present in vegetative starting materials; how this is altered during processing; how this influences activity in the gut and following uptake into bloodstream; and which *in vivo* physiological effects this may have on human body. Having a better understanding of these different steps and their importance in a health-and-nutrition-context will place us in a better position to breed for improved crop varieties and to advise the food industry on how to optimize processing strategies to enhance biochemical composition of processed foods. This review provides an overview of what is currently known about the influence which food processing treatments can have on antioxidants and gives some pointers as to their potential relevance.

Moldão-Martins, & Alves, 2019).

and hence, may influence the health-promoting properties of the final food products (Al-juhaimi et al., 2018; Khan et al., 2018; Lourenço,

A requirement for a specific processing step usually stems from a

variety of origins. For example, the need to prolong shelf-life; the desire

to have certain products available out of season; to optimize products

especially suited for home-consumption; to develop strategies to design

new or alternative food products with modified/supplemented flavor

and texture; to maintain or improve nutritional characteristics; and, to

increase quality and therefore value, to generate extra income for the

producer (Toledo, Singh, & Kong, 2018). Although the effect of processing on the fate of antioxidants has previously been reviewed, the

extent of their losses or even gains and the influence which processing

can have on bioavailability have been reported to differ considerably.

This relates to the exact nature and conditions of the processes applied,

the variety/origin of the food material used, and the biochemical

1. Introduction

The best sources of antioxidants are fruits and vegetables which are now regularly reported to promote health and quality of life, particularly by reducing the risk of chronic degenerative diseases, such as cardiovascular disease and certain types of cancer (Aune et al., 2017; Gürbüz, Uluişik, Frary, Frary, & Doğanlar, 2018). Their protective effects have mainly been attributed to the presence of bioactive antioxidant compounds (i.e. carotenoids, flavonoids, and other dietary antioxidants), as these likely prevent cell damage through synergistic interactions (Chugh & Kamal-Eldin, 2020; Mao et al., 2019). Although fruits and vegetables are commonly consumed as fresh produce, they are also often processed into a variety of food products including juices, pastes, canned foods, etc. (Gülçin, 2012, 2020). These products can also be valuable sources of antioxidants. However, various processing methods can have marked effects on fruit and vegetable antioxidants

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properties of the antioxidant itself (Arfaoui, 2021; Kamiloglu, Boyacioglu, & Capanoglu, 2013; Ribas-Agustí, Martín-Belloso, Soliva-Fortuny, & Elez-Martínez, 2018; Verghese, Willis, Boateng, Gomaa, & Kaur, 2021).

It is essential we gain a deep understanding of the consequences of processing on food composition in order to be able to design optimized strategies for the preservation and/or improvement of the antioxidant activity and bioavailability of these functional components in important key foodstuffs common to our daily diet (Barba et al., 2017; Ribas-Agustí et al., 2018; Verghese et al., 2021). To ascertain what the causality is behind various, contrasting (even apparently contradictory) results as reported in recent literature on the effect of industrial treatments, we need to perform an extensive evaluation as is detailed below. Thermal and non-thermal treatment effects on food composition as well as the bioavailability of different dietary antioxidants are both given particular emphasis as these are potentially the two most influential factors determining end-quality (Ahmed & Eun, 2018; Barba et al., 2017; Yuste et al., 2020).

2. Dietary antioxidants and their health effects

There is still growing interest in the new diet-health paradigm which places increasing emphasis on the positive aspects of our diet. This has led to nutritional studies in which our foods are being analyzed for their protective and disease prevention potential (Campbell, 2017; Corzo et al., 2020; Patel, Chandra, Alexander, Soble, & Williams, 2017). As a result of this research, fruits and vegetables have gained a more important status in the human diet as being potentially "functional foods". These are foods which are capable of providing additional physiological benefits, including preventing or delaying the onset of a range of chronic diseases, due to their potentially health-promoting antioxidant constituents (Corsetto et al., 2020; Grosso, 2018; Lammi & Arnoldi, 2021). This topic has already reached the recognition of the consumer and is becoming increasingly prominent in advertising campaigns.

Oxidative stress has been well-documented as the cause of a number of health disorders, including cardiovascular malfunction, certain types of cancer, type 2 diabetes, and many other auto-immune diseases as well as and often linked to, ageing (Apak et al., 2022; Cetin Cakmak & Gülçin, 2019). This stress results from the release of free oxygen radicals in the body (Al-juhaimi et al., 2018; Sarkate, Jambhorkar, & Sakhale, 2020; Warraich, Hussain, & Kayani, 2020). Antioxidants in fruits and vegetables are able to stabilize reactive oxygen species due to their free radical scavenging capacity (Warraich et al., 2020). Such a modulation of in vivo oxidative stress protects the cellular lipids, proteins, and DNA from molecular damage. Accordingly, the ingestion of these biologically active components either as fresh fruits and vegetables or their processed products has been correlated with the prevention and lower incidence of several degenerative diseases (Aune et al., 2017; Cömert & Gökmen, 2020; Huang, 2018; Kiokias, Proestos, & Oreopoulou, 2018; Patel et al., 2017).

The most thoroughly-studied groups of dietary antioxidants in fruits and vegetables include the carotenoids (i.e. α -carotene, β -carotene, lycopene, etc.) and phenolic compounds (i.e. flavonoids) (Table 1). Although any potential causal relationships are still controversial, epidemiological studies have provided useful data in evaluating the possible protective effects of foods or food components in disease prevention (Battino et al., 2019; Cömert & Gökmen, 2020). A high dietary intake of fruits and vegetables that are rich in carotenoids (particularly β -carotene and lycopene) has been associated with a decreased risk of developing cancer, which, in particular, is more consistent for forms of lung and stomach cancer (Rowles & Erdman, 2020; Saini, Keum, Daglia, & Rengasamy, 2020) and a decreased risk of developing cardiovascular problems (Jahns et al., 2018; Matsumoto et al., 2020). In addition, among the carotenoids, lutein and zeaxanthin have also been suggested to have a protective role against developing certain eye diseases (Johra, Table 1

		common foods.

Dietary antioxidants	Example compounds	Major food sources	References
Carotenoids	α-carotene, β-carotene, lutein, lycopene	tomato, carrot, spinach, chili (red), kale, lettuce	Bartali & Semba (2021); Chacón-Ordóñez et al. (2019); Rodrigo et al. (2015); Rowles & Erdman (2020)
Flavonoids			
Flavonols	quercetin,	onions, apples,	Guaadaoui et al. (2020);
	kaempferol	berries, tea, red	Maleki et al. (2019);
		wine	Rodríguez-García et al.
Flavones	apigenin, chrysin	parsley, thyme	(2019); Waheed Janabi
Flavanones	hesperidin, naringenin	citrus	et al. (2020)
Flavanols	catechin,	tea, apples	
	epicatechin		
Anthocyanins	cyanidin, pelargonidin	cherries, grapes	
Isoflavones	genistein,	soy beans,	
	daidzein	legumes	

Bepari, Bristy, & Reza, 2020). A dietary deficiency in carotenoids such as α -carotene, β -carotene, which are precursors of vitamin A, is a global health problem responsible for growth retardation in children and an increased susceptibility to infection, blindness, and death (Carazo et al., 2021; Hanson et al., 2018).

Flavonoids, which constitute the major subclass of polyphenols, are common in the daily diet (Table 1). These bioactive components have received considerable attention because of their health-promoting effects as antioxidants and have been identified as strong candidates in the prevention of human diseases such as cancer, cardiovascular diseases as well as some pathological disorders such as gastric and duodenal ulcers, allergies, vascular fragility, and viral and bacterial infection (Dabeek & Marra, 2019; Fusi et al., 2020). For instance, the intake of quercetin (one of the major plant flavonols) has been inversely associated with the levels of both total cholesterol and low-density-lipoprotein (LDL) cholesterol in human plasma (Dabeek & Marra, 2019). In addition, anthocyanin consumption has also recently been related to several health-promoting effects, including anti-obesity (Kim et al., 2020; Xie, Su, Sun, Zheng, & Chen, 2018) and the regulation of plasma cholesterol and lipid levels (Xu et al., 2021; Zhao et al., 2021). Results obtained from both in vitro and in vivo studies have revealed several other healthrelated effects of anthocyanins, including inhibition of tumor development (Lee et al., 2020; Paramanantham et al., 2020) and prevention of certain cardiovascular risk factors (Krga & Milenkovic, 2019; Xu et al., 2021).

3. Changes in antioxidant profile during food processing

It has been proposed that it is healthier to consume natural antioxidants through foods which are inherently rich in these bioactive compounds, rather than ingestion in the form of dietary supplements or pills (Burton-Freeman & Sesso, 2014). Furthermore, it has also been pointed out that food composition tables, which are tools used for epidemiological and nutritional studies, generally only include information on the consumption of raw-state foodstuffs whereas nutritional properties and biological activity are known to be significantly influenced by food processing (Tanemura, Machii, & Urushihara, 2020). Food processing is a broad concept as strategies can range from being simple to being considerably complicated depending on the desired end product. For example, fresh produce may require non-thermal pre/post operations, such as washing, selection, packaging, transportation and storage at the point of retail. In contrast, production of fully processed products generally includes multiple non-thermal as well as thermal treatments, like washing, selection, cutting, removal of the seed and skin, blanching, roasting, evaporation, pasteurization, canning, and prolonged storage. Such complex production strategies with many consecutive steps have a high potential to affect the nutritional status of the end product, and especially so if different heat treatments are involved (Knorr, Augustin, & Tiwari, 2020; Sá, Moreno, & Carciofi, 2020).

It has long been recognized that fruit and vegetable processing results in the loss of antioxidants with a concomitant reduction in bioactivity in processed products compared to the fresh equivalents (Boz & Koelsch Sand, 2020; Chen, Chaudhary, & Mathys, 2020). This is suggested as a result of oxidation, (non)enzymatic conversion, thermal degradation, leaching, etc. that occur during processing. However, it is now increasingly evidenced that food processing does not necessarily negatively affect the functional properties of food components (Lafarga, Viñas, Bobo, Simó, & Aguiló-Aguayo, 2018; Yuste et al., 2020). Several recent studies have reported that compounds possessing antioxidative effects, may occur in increased quantities and with enhanced bioavailability following food processing protocols which involve e.g. moderate heating or enzymatic disruption of cell walls (Al-juhaimi et al., 2018; Barba et al., 2017; Castro et al., 2020; Ribas-Agustí et al., 2018). Therefore, the exact effect may be managed by a combination of the processing strategies used, in association with the specific biochemical composition of the raw materials included.

3.1. Thermal treatments

Generally, industrial food processing strategies aimed at generating a range of end-products include one or more temperature treatment steps. These can include drying, blanching, boiling, pasteurizing, etc. These treatments are employed for specific reasons such as the inactivation of microorganisms or enzymes, to decrease the water content and thus concentrate the product, or for example, to soften the materials in order to facilitate the separation of fruit/vegetable flesh from the skin. During treatment, next to the desired goal, several additional changes may also occur, including the alteration of the biochemical composition and nutritional value of the food material as a result of quantitative/qualitative changes in the composition of different antioxidant groups. This has been an issue of particular interest in many recent studies and is therefore, the focus of this section (Table 2).

3.1.1. Carotenoids

Among the isoprene antioxidants, lycopene has long been recognized as being the most abundant in our food. It is also the most efficient carotenoid singlet oxygen quencher (free radical scavenger), with a capacity found to be more than twice that of β -carotene (Di Mascio, Kaiser, & Sies, 1989; Przybylska, 2020). Tomatoes and tomato products are the primary suppliers of lycopene to the human diet while other fruits such as apricots, pink grapefruit, watermelon, guava, and papaya are also recognized as (seasonal) dietary sources (Caseiro et al., 2020; Grabowska et al., 2019). As many tomato products are often processed in a variety of ways (as well as also often being cooked before eating), the effect of thermal treatments on carotenoids, and in particular lycopene, in tomato products has widely been studied (Badin, Quevedo-Leon, Ibarz, Ribotta, & Lespinard, 2021; Cámara et al., 2013; Cooperstone, Francis, & Schwartz, 2016; Graziani et al., 2003; Gupta, Balasubramaniam, Schwartz, & Francis, 2010; Hashemi et al., 2019; Mahieddine, Amina, Faouzi, Sana, & Wided, 2018; Makroo, Rastogi, & Srivastava, 2017; Mayeaux, Xu, King, & Prinyawiwatkul, 2006; Müller et al., 2011; Re, Bramley, & Rice-Evans, 2002; John Shi, Dai, Kakuda, Mittal, & Xue, 2008; Sramek, Schweiggert, van Kampen, Carle, & Kohlus, 2015). Various steps applied during the production of tomato products may cause the degradation of carotenoids, but they are also known to be necessary for enhanced carotenoid extraction, together which lead to conflicting results in different studies on carotenoid profiles (Schieber & Weber, 2016).

Lycopene and other carotenoid contents can be altered during

thermal treatment in a positive or negative direction depending on several factors, such as the degree of degradation, trans- to cis-form isomerization, effectiveness of extraction from the plant matrix, and the actual carotenoid itself (Hashemi et al., 2019; John Shi et al., 2008). Research on cis-lycopene isomers have gained increasing interest since these have been reported to exert higher antioxidant activity (Müller et al., 2011) and bioavailability (Cámara et al., 2013) than all-translycopene which is the major form in raw fruit produce. In a study, the thermal pre-treatment of dried tomato pulp at 120 or 150 °C for 1 h resulted in 10 % and 56.2 % increases in cis-lycopene contents, respectively, which were further shown to be more extractable in organic solvents (ethanol or ethyl acetate) and supercritical carbon dioxide (3 mL/min for 8 h) compared to all-trans-isomers (Honda, Watanabe et al., 2017). In another study performed by the same research group (Honda, Murakami et al., 2017), heating (at 120 °C for 30 min) different tomato products, including soup and sauce, in the presence of 5 % oil led to significant enhancement in cis-lycopene contents ranging from 39.2 % to 50.7 % increases. The effect of thermal processing on carotenoid isomerization and degradation was investigated in *tangerine* tomatoes, which, unlike red tomatoes, are rich in cis-lycopene (specifically tetra-cis-lycopene) instead of the all-trans isomer (Cooperstone et al., 2016). Heat treatment of tangerine tomato sauce (supplemented with 0, 1, 5, 15, and 30 % olive oil (w/w)) in a boiling water bath at 100 $^{\circ}$ C for 30, 60, 120, and 180 min led to significant decreases in the tetra-cis-lycopene content with each additional increase in heating time and overall ca. 80 %reduction was observed at the end of 180 min heating compared to the initial content measured in sauce. No significant influence of the oil content was observed. In contrast, increased heating times were determined to lead to significant increases in all-trans-lycopene and other-cislycopene levels of tangerine tomato sauce, while the total lycopene content decreased. All in all, these results were proposed to indicate the vulnerability of tetra-cis-lycopene to thermal degradation, in addition to its isomerization to other cis-forms and to all-trans-lycopene. Besides, among the individual carotenoids tested (all of which are considered to occur as cis-isomers), phytoene and phytofluene contents did not show significant changes during 180 min of boiling; while the levels of ζ-carotene and neurosporene significantly decreased (but relatively, to a lesser extent, compared to the decrease in tetra-cis-lycopene) after the same treatment (Cooperstone et al., 2016). This was different from the lycopene from red tomatoes which appeared to be relatively more stable to heat processing (Hackett, Lee, Francis, & Schwartz, 2004). In another study, Mayeaux et al. (2006) reported 10, 30, and 70 % degradation of pure lycopene after 10 min heating at temperatures of 100, 125, and 150 °C, respectively while these values increased to approximately 47, 79, and 95 %, respectively, after 60 min of heating. These results appear to indicate a poor stability for lycopene during long heating times and its rapid decomposition at temperatures above 150 °C. This study also determined significant differences in lycopene stability between heating a pure lycopene standard and cooking a tomato slurry. Less lycopene degradation was observed when baking tomato slurry at 218 °C for 15 min (\approx 48 % loss), 30 min (\approx 59 % loss) and 45 min (\approx 75 % loss). It was considered that the moisture in tomato slurry could help to slow down the heat transfer as well as to hydrolyze possible lycopene derivatives to release more free lycopene. Dramatic losses in lycopene content upon frying the tomato slurry for 2 min at 145 °C (approximately 70 % loss) and at 165 °C (approximately 75 % loss) were partly associated with rapid losses of moisture in the initial minutes of exposure to the frying temperatures. Additionally, microwave cooking (at 1000 W for 20, 30, 45, and 60 s), with a relatively lower processing temperature (max 100 °C) and shorter heating time, contributed to the highest degree of lycopene retention in tomato slurry. Here, the highest percentage loss was 35 % after 60 s of heating (Mayeaux et al., 2006). Isothermal heat treatment of crushed tomato at 70, 80, 90, and 100 °C for 120 min resulted in an increased rate of lycopene loss with increased temperature, leading to 23.94, 30.17, 45.05, and 55.24 % losses, respectively. This was linked to destruction by heat and oxidation (Badin et al., 2021).

Table 2

Food Product	Processing Conditions	Impact on carotenoids/phenolics	References
Tangerine tomato sauce (added with 0 %, 1 %, 5 %, 15 %, and 30 % olive oil (w/w))	Heating at 100 °C for 30, 60, 120, and 180 min	g at 100 °C for 30, 60, 120, and n ↓ Total lycopene (with each additional increase in heating time) ↓ Tetra- <i>cis</i> -lycopene (with each additional increase in heating time) ↑ Other- <i>cis</i> -lycopene (no change at 30 min of heating) ↑ All- <i>trans</i> -lycopene (120 min and 180 min) No change in phytoene and phytofluene contents ↓ ζ-Carotene and neurosporene	
Tomato slurry	Microwave cooking (1000 W for 20, 30, 45, and 60 s) Pan frying (145 °C and 165 °C for 1 and 2 min) Baking (177 °C and 218 °C for 15, 30, and	(with each additional increase in heating time) ↓ Lycopene (all treatments)	Mayeaux et al. (2006)
Crushed tomato	45 min) Isothermal heat treatment at 70, 80, 90, and 100 °C for 120 min	\downarrow Lycopene (with each additional increase in processing temperature)	Badin et al. (2021
Tomato paste	Vacuum drying (200 mbar; 50, 60, and 70 $^{\circ}\mathrm{C})$	↓ All- <i>trans</i> -lycopene (all treatments) ↑ <i>cis</i> -Lycopene isomers	Sramek et al. (2015)
Tomato juice (high lycopene)	Air drying (50, 60, and 70 °C) Freeze drying (-45 °C for 48 h) Pressure assisted thermal processing (600 MPa, 100 °C, 10 min)	 β-carotene (except for freeze drying (no change), vacuum drying (70 °C) (no change), and vacuum drying (50 °C) (increase)) ↑ All-<i>trans</i>-lycopene (pressure assisted thermal processing) No change in all-<i>trans</i>-lycopene during thermal sterilization 	Gupta et al. (2010)
Tomato juice	Thermal sterilization (100 °C, 35 min) Ohmic heat treatment (90 °C for 1 min) Conventional hot break treatment (90 °C	No change in <i>cis</i> -lycopene during all treatments ↑ Lycopene (all treatments)	Makroo et al. (2017)
Tomato	for 5 min) Microwave heating (1000 W, for 30 s and 300 s)	\uparrow Lycopene (with each additional increase in treatment time)	Mahieddine et al. (2018)
Sweet potato	Boiling (10 min) Steaming (97 ± 2 °C, 15 min) Microwaving (800 W, 5 min) Baking (200 °C, 15 min)	 ↑ Total polyphenols (all treatments) ↑ Total anthocyanins (all treatments) ↓ Chlorogenic acid(all treatments) ↓ Neochlorogenic acid (all treatments) 	(2010) Musilova et al. (2020)
Strawberry	Steam blanching (85 °C, 3 min) Pasteurization (85 °C, 3 min)	 ↓ <i>trans</i>-Ferulic acid (all treatments) ↓ Anthocyanins (steam blanching) ↑ Anthocyanins (pasteurization) 	Garzoli et al. (2020)
Purple skin eggplants	Boiling (5, 10, and 15 min) Steaming (5, 10, and 15 min) Microwaving (700 W; 5, 10, and 15 min)	↑ Total phenolic content (all treatments)	(2020) Chumyam et al. (2013)
Maqui fruit	Conventional canning (CC) (100 °C, 5 min in boiling water) Convective forced hot air drying (CFHAD) (60 °C, 72h), Osmotic drying (OD) (60 °C, 1h; pre- treatment with sucrose solution for 12h) Freeze-drying (FD) (-70 °C, 20h)	↓ Hydroxycinnamic acid and luteolin-7-O-glucoside (CFHAD, OD, and FD) ↑ Hydroxycinnamic acid and luteolin-7-O-glucoside (CC) ↑ Rutin and hyperoside (FD and CFHAD) ↓Rutin and hyperoside (CC and OD)	Concha-Meyer et al. (2021)
Apricots	Canning (121 °C, 30 min) Freezing (-18 °C) Drying (65 °C, RH 70%)	 ↑ Ellagic acid, gallic acid, ferulic acid, epicatechin, epigallocatechin, rutin (in canned samples as compared to frozen samples) ↓ Ellagic acid, gallic acid, ferulic acid, epicatechin, epigallocatechin, rutin (in dried samples as compared to frozen samples) 	Wani et al. (2020
Raspberry, boysenberry, redcurrants, and blackcurrants	Convective drying; 50 °C for 48h 65 °C for 20h 130 °C for 2h	 ↓ Total anthocyanins by HPLC and monomeric anthocyanins (all treatments; higher degradation rates at higher temperatures) ↑ Total polyphenol content (in methanolic extract) (all treatments) ↑ Total polyphenol content (in acetone extract) (65 °C for 20h) ↓ Total polyphenol content (in acetone extract) (50 °C for 48h and 130 °C for 2h) 	Bustos et al. (2018)
Grape juice	Hot press (maceration at 60 °C for 60 min)Hot break (preheating at 80 °C for 5 min, followed by maceration at 60 °C for 60 min)Cold press (at room temperature for 60 min) Artisanal steam extraction (85 °C)	In hot break, hot press, and steam extraction compared to cold press; ↑ Total phenolics ↑ Total monomeric anthocyanins ↑ Individual flavanols (included procyanidin B1, (-)-epicatechin, and (-)-epigallocatechin as the major ones) ↑ Individual flavonols (included quercetin 3-pyranoside as the major one) ↑ Individual anthocyanins (included malvidin 3-glucoside, cyanidin 3-glucoside, delphinidin 3- glucoside, malvidin 3,5-diglucoside, and cyanidin 3,5-diglucoside as the major ones) ↑ Individual phenolic acids (including chlorogenic acid, O-coumaric	Silva et al. (2019
Lychee juice	70 $^{\circ}\text{C}$ or 121 $^{\circ}\text{C}$ for 30 min	acid, and caffeic acid as the major ones) ↑ Total phenolics (all treatments; favoured by heating at 121 °C) ↑ Total flavonoids (121 °C) ↑ Gallic acid (121 °C) ↑ (-)-Gallocatechin (generated at 121 °C)	Su et al. (2019)

Accordingly, a conventional drying process, in which elevated temperatures are applied over a longer period of time, may be particularly harmful to carotenoids in tomato products (Schieber & Weber, 2016). Sramek et al., (2015) studied and compared the effects of drying tomato paste to a powder on the carotenoid content using three different drying methods: vacuum drying (200 mbar; 50, 60, and 70 °C), air drying (50, 60, and 70 $^{\circ}\text{C}$), and freeze drying (-45 $^{\circ}\text{C}$ for 48 h). The highest levels of lycopene (all-trans-isomer) retention were observed in freeze-dried and vacuum-dried (at 50 and 60 °C) powders with slight, but insignificant decreases in lycopene contents compared to the initial tomato paste. However, vacuum drying at higher temperatures (70 °C) resulted in a significant lycopene reduction (10 % loss). Maximum levels of lycopene loss occurred during air drying, ranging between 18 % (at 50 °C) and 33 % (at 70 °C), as compared to the initial levels in tomato paste. These observations also suggest that the detrimental effects of higher temperatures on carotenoids are greater in the presence of oxygen during processing.

In contrast to above detailed findings, increased carotenoid concentrations in processed products have also been reported in several other studies. Graziani et al. (2003) showed a significant increase (more than 30 %) in lycopene content when unpeeled tomatoes were heated in an oil bath at 100 °C for 2 h. Re et al. (2002) measured higher lycopene contents and antioxidant activities during processing of tomato pulp for paste production under different temperatures. The use of more recent technologies, such as combined pressure-heat treatments including high pressure processing (700 MPa, 45 °C, 10 min) and pressure-assisted thermal processing (600 MPa, 100 °C, 10 min) have also been shown to contribute to increased all-trans-lycopene contents (12 % and 7 %, respectively) in (high lycopene) tomato juice (Gupta et al., 2010). This has been explained by the ability of combined pressure-temperature treatments to affect cell membrane permeability (Shi & Le Maguer, 2000) and the plant matrix (i.e., proteins and carbohydrates as matrix macromolecules) (Butz & Tauscher, 2002), thus facilitating the release and extraction of lycopene, which also leads to its enhanced bioavailability (Gupta et al., 2010). Similarly, ohmic heat treatment (90 °C for 1 min) and conventional hot break treatment (90 °C for 5 min) of fresh juice from fully ripe tomatoes both led to increased release of phytochemicals from the fruit matrix, giving rise to significant increases in lycopene content (by 21.3 and 20.5 %, respectively) during the first 15 and 75 s of ohmic and conventional heat treatments, respectively, with no significant changes during further heating (Makroo et al., 2017). Moreover, microwave drying of tomato slices led to increased lycopene contents those ranged from \approx 5.8 mg/kg fw in the control sample to \approx 32 mg/kg fw and \approx 41 mg/kg fw in microwave-treated samples after 30 s and 300 s treatment times, respectively (Mahieddine et al., 2018).

3.1.2. Phenolics

Phenolic compounds are abundantly present in many fruits and vegetables which also undergo several industrial and domestic food preparation techniques before consumption. Many of these processing methods again involve thermal treatments which are reported in several studies to result in detrimental changes with regard to the retention of phenolics in these crops (Concha-Meyer, Sepúlveda, Pérez-Díaz, & Torres, 2021; Garzoli et al., 2020; Musilova et al., 2020). However, several other studies indicate the opposite, relating the thermal processing to an increase in phenolic content (Chumyam, Whangchai, Jungklang, Faiyue, & Saengnil, 2013; Concha-Meyer et al., 2021; Garzoli et al., 2020; Rossi et al., 2003; Silva et al., 2019; Su et al., 2019). The food matrix has been identified to be a more

important factor in determining the fate of polyphenolic compounds during food processing (Rothwell et al., 2015) although the chemical structure of the compound itself and the method used in preparation also have considerable influences (Arfaoui, 2021; Minatel et al., 2017). Heating ruptures cell walls and leads to the release, and hence, enhanced extractability of membrane-bound phenolics. However, at the same time, an increase in temperature results in thermal degradation and oxidation of the more susceptible compounds belonging to this group (Arfaoui, 2021; Minatel et al., 2017). All of these influencing factors may contribute individually or in combination to the reported contradictory results for the alterations in the profile of phenolic compounds under different thermal treatments applied to plant matrices.

In a recent study, total phenolic and total anthocyanin levels, as well as total antioxidant capacities of four different sweet potato varieties were all measured to be significantly increased as a result of four different heat treatments. These included boiling (10 min), steaming (97 \pm 2 °C, 15 min), microwaving (800 W, 5 min), and baking (200 °C, 15 min). Of these, baking and microwaving appeared to be more favorable in terms of having the highest total phenolic, anthocyanin and antioxidant capacity levels. On the contrary, each of these treatments, and specifically boiling, had a negative effect on the levels of individual phenolic acids. Considerable decreases were reported for chlorogenic acid (\geq 29 %), neochlorogenic acid (\geq 47 %), and *trans*-ferulic acid (\geq 29 %) after boiling of the analyzed sweet potato varieties (Musilova et al., 2020). Garzoli et al. (2020) reported a lower retention rate of anthocyanins in steam blanched (85 °C, 3 min) strawberry samples in comparison to the pasteurized (85 °C, 3 min) samples. While the anthocyanin levels were not significantly altered during the pasteurization process, the blanching process did lead to a 44 % decrease in the levels of anthocyanins compared to those were measured in the pasteurized samples (Garzoli et al., 2020). In another study, the total anthocyanin content of blueberry juice, produced using 3 min steamblanched fruits was determined to be two times higher than that in juice obtained from non-blanched fruits (Rossi et al., 2003). Furthermore, boiling, steaming, or microwaving of purple skin eggplants for 5, 10, and 15 min were all found to give rise to significant increases in the total phenolic content and antioxidant capacity; while the lowest level of increase was observed for the boiling treatment (Chumyam et al., 2013). All these contradictory observations from different studies could be linked to the two-sided effects of boiling/blanching (utilizing water as the treatment medium) on polyphenols which could contribute, on one hand, to the leakage (loss) of water-soluble phenolics into the surrounding medium (Arfaoui, 2021), while, on the other hand, to the protection of these compounds from oxidation through enzyme inactivation (Minatel et al., 2017).

Concha-Meyer et al. (2021) investigated the effects of conventional canning (100 °C, 5 min in boiling water), convective forced hot air drying (60 °C, 72 h), osmotic drying (60 °C, 1 h; a pre-treatment with sucrose solution for 12 h), and freeze-drying (-70 °C, 20 h) on the stability of non-anthocyanin phenolic compounds as well as the antioxidant capacity of a wild native berry, maqui. Convective forced hot air drying and osmotic drying led to significant decreases (by approximately 45 %) in hydroxycinnamic acid and luteolin-7-O-glucoside levels compared to those measured in the frozen control sample and these reductions were linked to the use of heat. On the other hand, sucrose addition during conventional canning was suggested to protect these compounds from thermal degradation. Fruit samples treated by freeze-drying or convective forced hot air drying had significantly higher (even higher than those of the control samples) rutin and hyperoside (quercetin-3-D-

galactoside) contents compared to samples treated with the other methods. Water-based thermal processing in osmotic drying was suggested to result in the leaching of rutin that led to decreased contents. On the other hand, antioxidant activity significantly increased after freezedrying, convective hot air drying and osmotic drying; while conventional canning resulted in significant decreases. This may be linked to the dissolution and degradation of anthocyanins (not studied in this work) in canning solution (Concha-Meyer et al., 2021). In another study, among three different processing techniques applied to apricots, canning (121 °C, 30 min) was reported to be the most efficient method for preserving the contents of various phenolic compounds, including ellagic acid, gallic acid, ferulic acid, epicatechin, epigallocatechin, and rutin. Freezing (-18 °C), and drying (65 °C, RH 70 %) methods were less effective. During canning, the heat used may contribute both by inactivating oxidative enzymes (i.e., polyphenol oxidase) and releasing bound phenolics through disruption of cellular structures. The exclusion of oxygen in canning may also help to prevent oxidative degradation. While in drying, a longer period of processing time and the presence of oxygen could result in a higher rate of loss of the analyzed bioactives (Wani, Masoodi, Haq, Ahmad, & Ganai, 2020).

In thermal treatments, optimizing the temperature, together with the processing time, may give better results in regard to bioactive retention. Bustos et al. (2018) studied different air-drying conditions on raspberry, boysenberry, redcurrant, and blackcurrant fruits to determine the best temperature-time parameters to preserve polyphenolic content and antioxidant activity. The application of an intermediate drying temperature of 65 °C for 20 h was measured to give significantly higher total polyphenol contents and antioxidant activities in comparison to drying at 50 °C for 48 h or at 130 °C for 2 h. These findings indicated the detrimental effects of long term or high temperature thermal treatments on the phenolic compounds present in berry fruits. On the other hand, anthocyanin levels in berries were suggested to alter in a more directly proportional manner to the drying temperature than to exposure time, and generally, higher losses were observed with increased temperature. In another study, the alterations in phenolic compositions and antioxidant activities of grape juices were determined and compared using a range of processing methods, including hot press (maceration at 60 °C for 60 min), hot break (preheating at 80 °C for 5 min, followed by maceration at 60 °C for 60 min), cold press (at room temperature for 60 min) and an artisanal steam extraction (at 85 °C). The juices processed using classical heating methods contained higher levels of total phenolics and total monomeric anthocyanins (determined by spectrophotometric methods), as well as total flavanols, flavonols, anthocyanins, and phenolic acids (determined through HPLC measurements of individual phenolics). Of these, the hot break method was found to be the most effective one. In parallel, the antioxidant activities of the juices produced with the classical methods were also found to be higher than the juice prepared by the cold press method. These results also support the notion that moderate heating contributes to a greater retention of antioxidant phenolics during juice extraction (Silva et al., 2019). Heat treatment of lychee juice at 121 °C (for 30 min) led to significant increases in total phenolic (up to 165.16 %) and total flavonoid (up to 121.82 %) contents, and in total antioxidant activity, in comparison to those values determined for untreated juice and the juice treated by heating at 70 °C for 30 min. Moreover, (-)-gallocatechin was determined to be generated after thermal processing at 121 °C, accounting for 89.5 % of the total phenolics present. It was suggested from these observations that a heat treatment at 121 °C could contribute to the release of phenolics from lychee juice, as well as promoting the formation of new flavonoid group bioactives (Su et al., 2019).

3.2. Non-thermal treatments

Non-thermal treatments that are applied in conventional food processing, such as cutting, homogenization, peeling, grinding, etc., all potentially influence the antioxidant properties of food products. In recent years, other "emerging" or "novel" non-thermal food processing technologies, including high pressure, pulsed electric field, ultrasound processing, etc. have widely been studied due to their ability to provide better consumer-targeted processed foods with the desired amounts of nutrients and other health-promoting components (Khan et al., 2018). In this section, the updated literature available on the effects of these novel non-thermal treatments are evaluated in the context of the main anti-oxidants (Table 3).

3.2.1. Carotenoids

Thermal treatments may help to extract higher levels of carotenoids from the plant matrix, but high temperatures may also lead to their degradation or isomerization which results in detrimental effects on these bioactives. Consequently, novel non-thermal processing technologies have been proposed as alternative methods to produce a better quality product (López-Gámez, Elez-Martínez, Martín-Belloso, & Soliva-Fortuny, 2021).

González-Casado et al. (2018) applied pulsed electric field (PEF) to whole tomatoes with different field strengths (0.4, 1.2, and 2 kV/cm) and numbers of pulses (5, 18, and 30 pulses) at 20 °C before their use in preparing tomato puree (with 5 % olive oil, w/w). Total carotenoid concentrations in purees prepared from PEF-treated tomatoes were found to be significantly higher (up to 52 % increase when 30 pulses of 2 kV/cm was applied) in comparison to the purees prepared from untreated fruits. The most intense PEF treatment (30 pulses at 2 kV/cm) also led to increased concentrations of individual carotenoids, including phytoene (178 % increase), phytofluene (131 % increase), lycopene (1.5-fold increase), and δ -carotene (104 % increase), in purees obtained from PEF-treated tomatoes in comparison to the product obtained from untreated fruits. In another study, moderate intensity PEF treatments (1 kV/cm for 4, 80, and 320 µs of treatment durations) provided higher levels of total lycopene, all-trans, and cis-lycopene in whole tomatoes with increasing treatment time (Jayathunge et al., 2017). These higher concentrations were suggested to indicate the enhanced extraction ability of these bioactives as a result of the electropermeabilization of cell membranes (Vallverdú-Queralt et al., 2013), as well as the activation of secondary metabolic pathways, as a stress response to PEF treatment (Galindo et al., 2009), that results in the biosynthesis of these carotenoids in tomato fruits to overcome stress conditions (Vallverdú-Queralt et al., 2012).

The stability of carotenoids was studied in tomato juice treated with either high pressure homogenization (HPH) at 200, 300, 400, and 500 bar (twice for 15 min; maximum temperature did not exceed 35 °C) and ultrasonic (US) power of 200, 400, 600, and 800 W (for 20 min) and compared to that in the untreated juice. Among the juice samples treated with HPH, the highest total lycopene content was measured in samples treated at 200 bar (significantly higher than the untreated juice), while considerable lycopene loss (48 %) occurred as the pressure increased to 500 bar. The same trend was also observed for all-trans lycopene as this was the dominant isomer, but the trend was reversed for *cis*-lycopene isomers. Ultrasound treatment gave rise to significant increases in total lycopene, as well as in all-trans lycopene, at 200 W and 400 W compared to levels in untreated juice. The highest values were measured after a US treatment of 400 W. These results suggest a facilitated release of lycopene from cells with the lowest to moderate levels of high pressure and ultrasonic power applications as tested in this study (Zhang et al., 2019). In another report, guava juice was treated with high-power US processing, performed at a power of 1000 W for 0 min (control sample), 3 min, 6 min, and 9 min, under a constant temperature of 25 $^\circ\text{C}.$ The lycopene content in US-treated samples gradually decreased as the treatment time increased (Campoli, Rojas, do Amaral, Canniatti-Brazaca, & Augusto, 2018). This lycopene degradation was suggested to be related to the effect of cavitation where high temperatures occur at the regions of bubble implosion (Rastogi, 2011) leading to possible reactions of lycopene with the free radicals that are formed during this phenomenon (Sun et al., 2017; Ulloa et al., 2015). In addition, oxidation

Food Product	Processing Conditions	Impact on carotenoids/phenolics	References	
Tomato puree (prepared from untreated or PEF-treated tomatoes)	PEF (0.02–2.31 kJ/kg; 0.4, 1.2, and 2 kV/ cm; 5, 18, and 30 pulses)	All treatments; the highest values at the most intense (2 kV/cm, 30 pulses) treatment; ↑ Total carotenoids	González-Casado et al. (2018)	
Whole tomatoes	PEF (1 kV/cm for 4, 80, and 320 $\mu s)$	↑ Phytoene, phytofluene, lycopene, δ-carotene, and lutein ↑ Total lycopene, all- <i>trans</i> - and <i>cis</i> lycopene (all treatments; with each additional increase in treatment time)	Jayathunge et al. (2017)	
Tomato juice	HPH (200, 300, 400, and 500 bar; twice for 15 min)	automain increase in treatment inner) Total lycopene and all-trans-lycopene (200 bar) [†] Total lycopene (200 and 300 bar) [†] 5-cis-lycopene (200 and 300 bar) [‡] 5-cis-lycopene (400 and 500 bar) [‡] 13-cis-lycopene (all pressures) [†] 13-cis-lycopene (200 and 400 bar) [‡] 13-cis-lycopene (200 and 500 bar) [‡] 13-cis-lycopene (200 and 500 bar) [‡] β-carotene (200 bar)	(2017) Zhang et al. (2019)	
Tomato juice	US (200, 400, 600, and 800 W for 20 min)	↑ Total lycopene and all- <i>trans</i> -lycopene (200 and 400 W) ↓ 5- <i>cis</i> -lycopene (all US powers) ↑ 9- <i>cis</i> -lycopene (200, 400, and 800 W) ↑ 13- <i>cis</i> -lycopene, ζ-carotene (all US powers)	Zhang et al. (2019)	
Guava juice	US (1000 W; 0, 3, 6, and 9 min)	\downarrow Lycopene (with each additional increase in the treatment time)	Campoli et al. (2018)	
Carrot juice	HPP (300 MPa (1 cycle and 3 cycles), 450 MPa (1 cycle), and 600 MPa (1 cycle) for 5 min)	\downarrow Total carotenoids, β-carotene, α-carotene, ζ-carotene, phytofluene, and phytoene (all treatments; highest loss at 300 MPa (3 cycles), lowest loss at 600 MPa)	Stinco et al. (2019)	
Cranberrybush puree	HPP (200, 400, and 600 MPa for 5 or 15 min) PEF (3 kV/cm, 5, 10, and 15 kJ/kg)	↑ Total phenolics, total flavonoids, total anthocyanins and chlorogenic acid	Ozkan et al. (2021)	
Fruit juice blend (orange, kiwi, pineapple, and mango) with water	PEF (35 kV/cm for 1800 μs)HPP (400 MPa for 5 min)	(generally with the trend of increase with increasing pressures and longer duration times in HPP, and with increasing energy input values in PEF) In both HPP and PEF: ↓ Total phenolics, chlorogenic acid, p-coumaric acid, p-hydroxybenzoic acid, hesperidin, quercetin, and rutin ↑ Caffeic acid and ferulic acid No change in naringenin	Rodríguez-Roque et al. (2015)	
Fruit juice blend (orange, kiwi, pineapple, and mango) with milk or soymilk	PEF (35 kV/cm for 1800 μs) HPP (400 MPa for 5 min)	<pre>In both HPP and PEF: ↑ Total phenolics (fruit juice-milk and fruit juice-soymilk) ↓ Ferulic acid and rutin (fruit juice-milk) ↓ Ferulic acid (fruit juice-soymilk) ↑ Rutin (fruit juice-soymilk) ↑ Caffeic acid, chlorogenic acid, p-coumaric acid, p-hydroxybenzoic acid, hesperidin, naringenin, and quercetin (fruit juice-milk and fruit juice- soymilk)</pre>	Rodríguez-Roque et al. (2015)	
Strawberry puree (with or without mixing protein-rich kale juice)	PEF (11.9 kV/cm, 120 kJ/kg) HPP (600 MPa for 1 min)	 trotal anthocyanins (during HPP and PEF treatment of strawberry-kale mixture) ↑ Total anthocyanins (PEF-treated strawberry) ↓ Total anthocyanins (HPP-treated strawberry) 	Stübler et al. (2020)	
Açaí juice	HPP (400, 450, 500, and 600 MPa for 5 min)	 ↓ Total monomeric anthocyanins, cyanidin 3-glucoside, and cyanidin 3-rutinoside (all treatments) ↑ 3,4-dihydroxybenzoic acid, 4-hydroxybenzoic acid, vanillic acid, caffeic acid, syringic acid, <i>p</i>-coumaric acid, isoorientin, orientin, and ferulic acid (450, 500 and 600 MPa; the highest increases at 500 MPa) No change in total phenolic content (all treatments) 	da Silveira et al. (2019)	
Açaí juice	US (0, 0.9, 1.8, 2.7, and 3.6 kJ/cm ³)	↓ Total monomeric anthocyanins (up to 1.8 kJ/cm ³) ↑ Total monomeric anthocyanins (2.7 and 3.6 kJ/cm ³) ↑ Total phenolic content (with increasing energy densities)	de Souza Carvalho et al. (2020)	
Apple-grape juice blend Blanching (in hot water at 100 °C for 4 min) High temperature-short time (HTST) (72 °C for 15 s) US (25 kHz for 5 and 10 min) Thermo-US (40 °C, for 5 min and 10 min; 50 °C for 5 min and 10 min)		 Total phenolics, total flavonoids, and total flavonols (all treatments except for blanching) ↑ Phenolic acids (chlorogenic acid, caffeic acid, <i>p</i>-coumaric acid, syringic acid, gallic acid, vanillic acid, caftaric acid) (HTST and US (10 min)) ↑ Flavanols (catechin, epicatechin, epigallocatechin gallate, procyanidin B1, procyanidin B2) (HTST and US (10 min)) ↑ Anthocyanins (petunidin 3-O-glucoside, peonidin 3-O-glucoside, malvidin 3-O-glucoside, cyanidin 3-O-glucoside, malvidin 3-O-glucoside, malvidin 3-O-glucoside, malvidin 3-5-diglucoside, malvidin 3,5-diglucoside, malvidin 3,5-diglucoside (HTST and US (10 min)) 	Aadil et al. (2020)	

PEF: Pulsed electric field; HPH: High pressure homogenization; US: Ultrasound; HPP: High pressure processing.

of lycopene can result from the release of oxygen due to the disruption of the juice microstructure (Aguilar, Garvín, Ibarz, & Augusto, 2017). (Stinco et al., 2019) investigated the effects of high pressure processing (HPP) treatments, applied at 300 MPa (1 cycle and 3 cycles), 450 MPa (1 cycle), and 600 MPa (1 cycle) for 5 min at room temperature (\approx 22 °C), on the carotenoid profile of cloudy carrot juice. Almost all HPP treatments led to significant reductions in the levels of total carotenoids, as well as in individual carotenoids (including β -carotene, α -carotene, ζ-carotene, phytofluene, phytoene, and lutein). The highest and lowest levels of carotenoid losses in HPP-treated carrot juices were observed for HPP at 300 MPa in three cycles (leading to 41 % carotenoid degradation) and HPP at 600 MPa (leading to 26 % carotenoid degradation), respectively. These results were proposed to represent a dual effect of HPP on carotenoids in carrot juice as a result of the disruption of the cellular structure; firstly, an induction of carotenoid degradation through increased exposure of these bioactives to enzymes, oxygen, etc., and secondly an improved extractability of carotenoids as a result of their facilitated release from the matrix particles that decrease in size. The highest pressure performed in this study (600 MPa) was found to lead to relatively lower levels of carotenoid degradation and/or higher levels of carotenoid extraction compared to the other treatments.

3.2.2. Phenolics

Nowadays, there is also growing interest for the use of non-thermal technologies on whole fruits and vegetables, as well as their products, in order to minimize the loss of phenolic compounds, which are known to be more vulnerable to high temperatures (Khan et al., 2018). Ozkan et al. (2021) studied the alterations in the total phenolic, total flavonoid, total anthocyanin, and chlorogenic acid contents, as well as antioxidant capacities of cranberry purees subjected to HPP (200, 400, and 600 MPa for 5 or 15 min) and PEF (3 kV/cm, 5, 10, and15 kJ/kg) treatments. Increased pressure levels and longer duration times in HPP, and increased specific energy input values in PEF treatment were determined to lead to higher total phenolic and total flavonoid levels. However, only the PEF treatment performed at 15 kJ/kg specific energy input level yielded significantly higher values than for the untreated puree. The trend for total anthocyanin contents of HPP and PEF-treated purees was a slight (but not statistically significant) increase. HPP and PEF treatments also gave rise to an increase in the content of chlorogenic acid, which is the major phenolic compound in cranberrybush fruit, by \approx 6–7 % and \approx 5.6–11 %, respectively. While HPP did not cause significant differences in antioxidant capacity, PEF treatment of 15 kJ/kg did give a significantly higher antioxidant capacity which may be due to higher levels of phenolics and flavonoids occurring in these samples. These slight increases observed in HPP and PEF-treated samples were proposed to be triggered by the enhanced extractability of phenolics as a result of improved cell permeability, as well as to the possible inactivation of the endogenous deteriorative enzymes.

In another study, Rodríguez-Roque et al. (2015) studied and compared the effects of high-intensity PEF (35 kV/cm for 1800 μ s) and HPP (400 MPa for 5 min) on phenolic compounds in three different fruit juice-based beverages obtained by mixing a fruit juice blend (orange, kiwi, pineapple, and mango juices) with milk, soymilk, or water. In the fruit juice-water mixture, both high-intensity PEF and HPP treatments resulted in significant decreases in the concentrations of individual phenolics, including chlorogenic acid, p-coumaric acid, p-hydroxybenzoic acid, hesperidin, quercetin, and rutin; while caffeic and ferulic acid showed significant increases, and naringenin did not show any significant change. Alterations in the contents of individual phenolics (except for rutin), after high-intensity PEF and HPP treatments, followed the same trend in fruit juice-milk and fruit juice-soymilk mixtures, which was different from the fruit juice-water mixture. Ferulic acid and rutin levels in fruit juice-milk mixtures and only ferulic acid level in fruit juice-soymilk mixtures decreased significantly in the high-intensity PEF and HPP-treated samples. Others, including caffeic acid, chlorogenic acid, p-coumaric acid, p-hydroxybenzoic acid, hesperidin, naringenin,

and quercetin, (and rutin in fruit juice-soymilk mixture) increased significantly. In parallel to the results obtained for individual phenolics, both high-intensity PEF and HPP treatments led to significant decreases in total phenolic content (measured by HPLC) of fruit juice-water mixtures, while significant increases were observed in total phenolics in the fruit juice-milk and fruit juice-soymilk mixtures following both treatments. These observations indicated the significant influence of the food matrix on the concentration of phenolic compounds which was in this case positively influenced by the addition of milk or soymilk to the blended fruit juices.

Stübler et al. (2020) investigated the stability of polyphenols in strawberry puree as influenced by different processing techniques (thermal (72 °C for 1 min), PEF (11.9 kV/cm, 120 kJ/kg; included preheating to 35 °C), and HPP (600 MPa for 1 min at room temperature) as well as by mixing with a protein-rich kale juice. These different treatments applied all led to significant increases in the antioxidant capacities of the individual strawberry (with water) and kale (with water) systems; while no significant alteration was observed for the strawberrykale mixture. Total anthocyanin levels in the mixture slightly increased during HPP and PEF treatments as compared to the untreated mixture. On the other hand, for the individual strawberry-water-system, thermal and PEF treatments yielded significantly higher total anthocyanin levels, while the HPP treatment did cause a decrease in the levels of anthocyanins than untreated strawberries. These opposing effects of HPP on the anthocyanin levels of the strawberry-water-system (leading to a decrease) and strawberry-kale mixture (leading to an increase) suggests that HPP may interfere with the complexation of anthocyanins with components of the kale matrix. Anthocyanin stability during processing should therefore better be evaluated by considering both the matrix involved (formulation) and the processing conditions.

High pressure processing of açaí juice at 400, 450, 500, and 600 MPa for 5 min at 20 °C led to significant reductions in total monomeric anthocyanin levels (except for 600 MPa, for which the decrease was not significant), as well as in individual anthocyanins (included cyanidin-3glucoside, and cyanidin-3-rutinoside) compared to the levels determined for untreated juice. This was attributed to the release of oxidative enzymes from damaged cells which were suggested to be only partially deactivated during HPP. Non-anthocyanin phenolic compounds, including 3,4-dihydroxybenzoic acid, 4-hydroxybenzoic acid, vanillic acid, caffeic acid, syringic acid, p-coumaric acid, isoorientin, orientin, and ferulic acid, were retained in HPP-treated juices and even showed significant increases at 500 MPa (28 % to 69 % increases were observed for isoorientin and caffeic acid as compared to control samples). Here this was linked to the enhanced extractability of phenolics as HPP promoted cell wall breakdown and facilitated release of these compounds from the food matrix. However, total phenolic levels in HPP-treated juice samples did not differ from untreated juice (da Silveira et al., 2019). This may be an overall result of the decrease in anthocyanin levels together with increases in non-anthocyanin phenolics. The treatment of açaí juice by US treatment, applied at five levels of energy density (0, 0.9, 1.8, 2.7, and 3.6 kJ/cm³), led to slight, but not significant, decreases in total monomeric anthocyanins up to the energy density of 1.8 kJ/cm³, as compared to untreated juice. Higher energy densities contributed to increased anthocyanin levels which were significant at a US treatment of 3.6 kJ/cm³. Again this may have arisen from the facilitated release of anthocyanins as a result of the rupture of cell walls that was promoted at the higher energy densities (de Souza Carvalho et al., 2020).

Aadil et al. (2020) compared the effects of blanching (in hot water at 100 °C for 4 min), high temperature-short time (HTST) (72 °C for 15 s), ultrasonication (25 kHz for 5 and 10 min), and thermo-ultrasound (40 °C, for 5 min and 10 min; 50 °C for 5 min and 10 min) treatments on the levels of total and individual phenolics of an apple-grape juice blend. The maximum levels of total phenolics, total flavonoids, and total flavonols were measured in juice samples treated with ultrasonication for 10 min and all were significantly higher compared to the levels in

untreated (fresh) juice and the juices subjected to the other thermal and ultrasound treatments. In parallel to what was observed for total contents of phenolics, the levels of individual phenolics, including phenolic acids (chlorogenic acid and caftaric acid being the most abundant), flavanols (epigallocatechin being the most abundant), stilbenes (resveratrol), and anthocyanins (malvidin 3,5-diglucoside and malvidin 3-O-glucoside as the most abundant) were all measured to be significantly higher in juice samples treated with ultrasonication for 10 min as compared to the untreated juice as well as to the other thermal-(blanching, HTST) and ultrasound-treated (40 °C, for 5 min and 50 °C, for 5 min) samples. This increased concentrations of phenolics during ultrasonication may be linked to the mass transfer effects of shock and shear waves generated during the cavitation process which may contribute to the elevated diffusion rates of these compounds (Zou & Hou, 2017).

4. Changes in antioxidant bioavailability during food processing

To exert their health-protective effects, in other words, to be biologically active, antioxidant compounds must first be released from the food matrix during digestion in the gastrointestinal tract and further chemically modified into absorbable units (become 'bioaccessible') (Heaney, 2001). After this, they can finally be absorbed into the bloodstream and transferred to the systemic circulation for utilization in metabolic functions (become 'bioavailable') (Wood, 2005). The term bioavailability, including all the actions that take place under the term bioaccessibility, further refers to the transport and distribution of bioactive compounds to their target tissues and cells where they can exert their bioactivities and hence, have a positive effect on human health (Carbonell-Capella, Buniowska, Barba, Esteve, & Frígola, 2014; Wood, 2005). However, since practical and ethical issues make it difficult to measure the bioactivity of food components, bioavailability is considered as the fraction of an ingested compound (or its active metabolite) that reaches systemic circulation (Holst & Williamson, 2008), and bioactivity often remains undetermined. In vitro digestion procedures, that simulate gastric and small intestinal digestion, and which are in some cases followed by the simulation of uptake by Caco-2 cells, are generally performed for evaluating bioaccessibility (Courraud, Berger, Cristol, & Avallone, 2013). On the other hand, bioavailability of a food compound can generally be determined using in vivo models to measure changes in plasma concentrations of that specific compound in humans or animals after its acute or chronic administration as a single compound or in a food matrix (Rein et al., 2013).

The primary factors that largely influence the bioaccessibility and bioavailability of dietary antioxidants are the concentration and complexing of these compounds within the plant matrix in combination with their chemical structure. It has been well-documented that food processing introduces many factors which can substantially influence, in a positive or negative manner, the bioaccessibility and bioavailability of antioxidant compounds from plant materials (Fig. 1). Postharvest processing plays a significant role in determining the composition of foods of plant origin and affects the levels of many bioactives in the related foodstuffs. This can result in altered amounts of ingested and potentially bioavailable antioxidant phytochemicals in processed foods. In addition, food processing can potentially change the chemical form of the compounds of interest which, in turn, may have a substantial positive or negative impact on bioavailability (Cermak et al., 2009). There is currently a general lack of information on the effect of food processing methods on antioxidant bioavailability. In this section, processing methods will be assessed in their relation to in vivo and in vitro bioavailability conditions of antioxidant bioactives (Table 4).

4.1. In vivo bioavailability

Although *in vivo* approaches are considered more realistic, the high expense and difficult implementations of these methods make them less preferred by researchers. Therefore, very few -and even old- data are available representing the processing effect on the bioavailability of phytochemicals *in vivo* (Ribas-Agustí et al., 2018).

Several studies support the concept that the disruption of the food matrix by heat, homogenization or both can have a positive effect on in *vivo* bioavailability of β -carotene and other plant carotenoids. A recent *in vivo* study investigated the human plasma bioavailability of β -carotene, lutein, and isothiocyanate after consumption of broccoli which was exposed to varying cooking procedures, including steam cooking (100 % RH, 99 °C, 13 min) and boiling (10 min). The lutein and β -carotene levels in the serum were not significantly altered through consumption of broccoli prepared by different cooking procedures; while steamcooking gave rise to a significant increase in plasma bioavailability of isothiocyanate (by 138 %) compared to the values obtained with the boiling procedure (Orlando et al., 2022). Edwards et al. (2002) tested and compared the *in vivo* bioavailability of carrot carotenoids (α - and β -carotene) supplied in a carrot puree (in a commercial baby food form), in boiled-mashed carrots, and raw chopped carrots. The absorption levels of α -carotene and β -carotene were determined to be approximately 2-fold higher in carrot puree than in boiled-mashed carrots

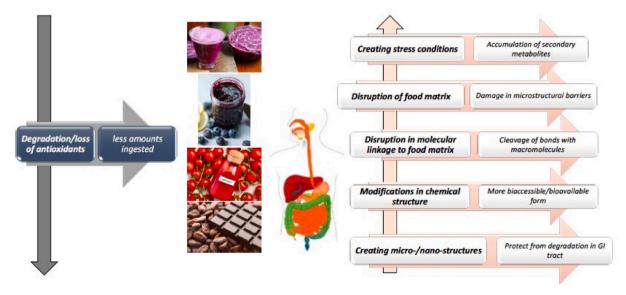


Fig. 1. Relationship between food processing strategies and bioavailability/bioaccessibility of antioxidant compounds.

Table 4

Processing effects on isomerization, in vivo and in vitro bioavailability of dietary antioxidants.

Food product	Processing conditions	Type of study	Impact on antioxidant bioavailability	References
Tomato	Moderate intensity PEF (4, 80, 320 μ s, 0.1 Hz, 1 kV/ cm), blanching (90 °C, 2 min), US (20 %, 7 min),	Isomerization	\uparrow Lycopene bioaccessibility (9.6 % with 4 μs PEF)	Jayathunge et al. (2017)
	high intensity PEF (1500 $\mu s,35$ kV/cm) combinations		↑ <i>trans</i> - and <i>cis</i> -lycopene (4.01 and 5.04 µg/g, respectively with blanching/PEF combination)	
Dried tomato pulp	HT (120, 150 °C, 1 h)	Isomerization	↑ Total lycopene bioaccessibility (15.6 %) ↑ <i>cis</i> -isomers (10 and 56.2 % for 120 and 150 °C HT)	Honda et al. (2017a)
Tomato paste with 5 % oil	HT (120 °C, 30 min)	Isomerization	\uparrow cis-isomerization ratio (in a range of 39.2–50.7 %)	Honda et al. (2017b)
Tomato puree with onion	HT (90 °C, 2 h)	Isomerization	↑ 5- <i>cis</i> -lycopene (20 % of total isomers, correlated with onion concentration)	Yu et al. (2019a)
Tomato puree with onion	Microwave heating (250 W, 20 min)	Isomerization	\uparrow cis-isomerization ratio (in a range of 66–99 %)	Yu et al. (2019b)
Purified lycopene	HT (50 °C, 24 h) Fluorescent light irradiation (4, 25 and 40 °C, 30 days)	Isomerization	↑ <i>cis</i> -isomers (56.01 % with HT) all- <i>trans</i> configuration with fluorescent light	Murakami et al. (2018)
Carrot	Cooked, pureed vs raw, chopped carrots	in vivo	\uparrow Plasma β-carotene levels (65 % vs 41 %)	Livny et al. (2003)
Cherry tomato	Domestic cooking (100 °C, 15 min)	in vivo	\uparrow in vivo absorption of naringenin and chlorogenic acid	Bugianesi et al. (2004)
Purple carrot	Cooking	in vivo	↑ Urinary recovery of nonacylated anthocyanins (36 %)	Kurilich et al. (2005)
Corn	Cooking (100 °C, 15 min)	in vitro	\uparrow <i>in vitro</i> bioavailability of carotenoids (0.9-fold for lutein and 1.2-fold for zeaxanthin).	Liu et al. (2004)
Fresh pastes of tomato, lettuce, zucchini, and green and red pepper	US (40 kHz, 250 W, 4 $^\circ \mathrm{C}$ for 20 min)	in vitro	\uparrow Bioaccessibility of phenolic compounds (for lettuce and green pepper, in a range of 11 to 150 %)	Lafarga et al. (2019)
Smoothies of fresh fruit juices	Mild and intense HT (90 $^\circ C$ and 120 $^\circ C,$ 20 s)US (bath, 60 $^\circ C,$ 20 min)	in vitro	↑ Bioaccessibility; β-Cryptoxanthin (10% with intense HT and US) α-carotene (30–70% with mild/intense HT) β-carotene (35–70% with mild/intense HT)	Buniowska et al. (2019)
Red-flesh apple	Thermal (hot air-drying-60 °C/80 min – 70 °C/40 min,	in vitro	Lutein (20% with mild HT) ↑ Polyphenol bioavailability (120, 70 and 40% with	Yuste et al. (2020)
	and purée pasteurization-94 °C 10 min) and non- thermal (freeze-drying) treated		pasteurization, hot air-drying and freeze drying, respectively).	
Camu-camu juice	Cold plasma processing (10–30 min 30 mL/min plasma flow rate	in vitro	\uparrow Bioavailability of ascorbic acid (in a range of 5–20%)	Castro et al. (2020)
Black plum fruit	Drying (40 $^\circ C)$ and juice processing (pasteurized at 90 $^\circ C,1$ min, further concentrated at 40 $^\circ C$ to 15 $^\circ brix)$	in vitro	\uparrow Bioaccessibility (330 and 250% with drying and 80 and 100% with juice processing for β-carotene and lycopene, respectively).	Kumari & Gunathilake (2020)
Carrot	PEF (5 pulses of 3.5 kV/cm) treatment	in vitro	 ↑ Bioaccessibility of total phenolic and carotenoid (20.8 and 11.9%, respectively). 	López- Gámez et al. (2021)

PEF: Pulsed electric field; HT: Heat treatment; HPH: High pressure homogenization; US: Ultrasound; HPP: High pressure processing,

which was linked to a reduced particle size (increased surface area), greater heat exposure or a combination of both in puree (Edwards et al., 2002). These results were also in accordance with those of Livny et al. (2003) who observed significantly higher plasma β -carotene levels following consumption of cooked, pureed carrots (\approx 65 %) as compared to raw, chopped carrots (\approx 41 %). In addition, Rock et al. (1998) also reported that continuous consumption of pureed, cooked carrots and spinach enhanced the plasma response of β -carotene (3-fold higher increase) in comparison to the consumption of these vegetables in their raw, unhomogenized form. In the case of pureed vegetables, smaller particle sizes and mechanical disruption of the plant cells are presumed to make the carotenoids more available for absorption in the intestinal lumen (Edwards et al., 2002). Processing of tomatoes into tomato paste, which includes both mechanical homogenization and heat treatments, was shown to lead to significant increases in lycopene bioavailability. Consumption of tomato paste resulted in a 22-380 % higher lycopene response in plasma or in triglyceride-rich lipoproteins compared to the levels following consumption of the same amount of lycopene in fresh tomatoes (Gärtner, Stahl, & Sies, 1997; Porrini, Riso, & Testolin, 1998). Similarly, serum lycopene levels were recorded to be greater in humans after consumption of heat-processed tomato juice but not after unprocessed juice. This improved bioavailability of lycopene from the processed food was again attributed to its release as a result of plant cell

disruption during mechanical and thermal processing, as well as to heatinduced *trans*- to *cis*-isomerization (Gärtner et al., 1997; Stahl & Sies, 1992). Mild heat treatment was also suggested to improve carotenoid bioavailability from plant foods through the weakening of carotenoidprotein complexes (de Oliveira et al., 2020) and solubilizing cell wall pectin with subsequent softening of the tissue, thus making compounds more accessible to absorption (Neves et al., 2021).

Bugianesi et al. (2004) investigated the effect of domestic cooking (100 °C, 15 min) on the subsequent absorption of naringenin and chlorogenic acid from cherry tomatoes. They found enhanced polyphenol bioavailability after the consumption of cooked cherry tomatoes in comparison to the consumption of their fresh counterparts. They concluded, as in the case of the carotenoids, that mechanical and heat treatments may provide the energy necessary to break the matrix interactions of polyphenols, thus, improving their bioaccessibility *in vivo*. Kurilich et al. (2005) also reported an improved urinary recovery of nonacylated anthocyanins (by about 36 % increase) after a cooking treatment was applied to purple carrots, but there was no significant effect of cooking on acylated anthocyanins.

The bioavailability of isoflavones from untreated, enzyme-treated and fermented soymilk was compared using human subjects. Although the total isoflavone content hardly differed between these three sources, the proportion of isoflavone aglycones was substantially higher in enzyme-treated and fermented soymilk (greater than90 %) than in untreated soymilk (<1%), which determined to give rise to significantly higher isoflavone bioavailability from the enzyme-treated and fermented products (Kano, Takayanagi, Harada, Sawada, & Ishikawa, 2006). The predominant presence of aglycone forms of isoflavones in enzyme-treated and fermented soymilk could be the reason for this higher isoflavone bioavailability in processed soy products in this study since it is known that the isoflavone glycosides are not directly bioavailable and need to be hydrolyzed to release the aglycones to be able to be absorbed (Setchell et al., 2002).

4.3. In vitro bioavailability

Although carefully-controlled investigations using human subjects are necessary for accurate determination of *in vivo* bioavailability of food components, *in vitro* models which are designed to simulate different phases of digestion, are also widely used. *In vitro* simulated digestion methods have the advantages of being cost-effective and, in general, rapid methods for predicting nutrient bioavailability (Van Buggenhout et al., 2010). Furthermore, they provide the opportunity of a higher rate of control of the system being examined.

In terms of carotenoid bioavailability, latest research focused on enhancing the bioavailability of lycopene, as the most abundant carotenoid in tomato, through its structural isomerisation from all-translycopene (that comprises around 80–97 % of total lycopene content in tomato) to *cis*-lycopene which is well-accepted to be more bioavailable than all-trans-isomers by the fact that serum and tissue lycopene is more than 50 % cis-lycopene (van Breemen et al., 2002). For this purpose, Jayathunge et al. (2017) investigated various thermal and non-thermal processing methods applied to tomato juice for their effects on lycopene isomerization and hence, on its bioavailability. As a result of the applied combinations of blanching (90 $^\circ$ C for 2 min), ultrasonication (20 % amplitude for 7 min) and high intensity pulsed electric field treatments (1500 μ s, 35 kV/cm) to tomato juice, these authors reported significant increases in trans- and cis-lycopene contents as a result of blanching/pulsed electric field combination which further contributed to a 15.6 % increase in total lycopene bioaccessibility (Jayathunge et al., 2017).

Liu et al. (2004) compared the carotenoid bioavailability in cooked and raw whole foods using an *in vitro* simulated gastrointestinal digestion coupled to an *in vitro* Caco-2 cell culture model and determined that cooking (100 °C water bath for 15 min) provided significant increases in the bioavailability of carotenoids, included lutein (0.9-fold increase) and zeaxanthin (1.2-fold increase). Similarly, using these coupled *in vitro* models, *all-trans-*, 13-*cis-* and 15-*cis-β*-carotene isomers sourced from cooked (boiled/pureed and boiled only) carrots were found to be taken up to a greater extent compared to those from raw carrots. Moreover, uptake of *all-trans-* and 13-*cis-β*-carotene was significantly (p< 0.05) higher from boiled-and-pureed carrots than from raw or boiled carrots (Aherne, Daly, Jiwan, O'Sullivan, & O'Brien, 2010).

In recent years, many in vitro bioavailability studies have also been conducted in order to assess and examine the effects of novel processing techniques on the bioavailability of antioxidative compounds. A study that investigated the effect of ultrasonication (40 kHz, 250 W, 4 °C for 20 min) on the bioaccessibility of antioxidant compounds in fresh pastes of tomato, lettuce, zucchini, and green and red pepper reported that the bioaccessibility of phenolic compounds in lettuce and green pepper was significantly increased by sonication by 11 % to 150 % higher values concerning the gastric and/or intestinal phases. However, this treatment had no influence on the in vitro bioavailability of phenolics in tomato, red pepper and zucchini (Lafarga, Rodríguez-Roque, Bobo, Villaró, & Aguiló-Aguayo, 2019). Stimulated acute intake of puree samples treated with pasteurization (94 $^{\circ}$ C for 10 min), hot air-drying (60 $^{\circ}$ C for 80 min or 70 °C for 40 min) (70 % increment) or freeze-drying processes determined to exert a higher in vitro bioavailability of polyphenols for each of the treatment with the values of 120 %, 70 %, and 40 %

increases, respectively, in comparison to the values observed for untreated purees, clearly emphasizing the impact of processing on phenolics absorption (Yuste et al., 2020). The in vitro bioavailability of ascorbic acid in camu-camu (Myrciaria dubia) juice treated with cold plasma processing for 10, 20, or 30 min was measured to be enhanced for all different processing times applied, with increases of 5, 8 and 20 %, respectively (Castro et al., 2020). Drying (at 40 °C to reach a constant weight) and juice processing (squeezing followed by pasteurization at 90 $^{\circ}$ C for 1 min, filtering, and further concentrating at 40 $^{\circ}$ C) of black plum (Syzygium caryophyllatum) fruit were both reported to result in a decrease in the bioaccessibility of total phenolics (around 80 %), and similarly, the bioaccessibility of total flavonoids was measured to be reduced by 57 and 35 % after drying and juice processing treatments, respectively. In contrast, significant increases in the bioaccessibility values of β -carotene and lycopene were recorded after drying (330 % and 250 %, respectively), and juice processing (80 % and 100 %, respectively) treatments. On the other hand, none of the treatments affected the bioaccessibility of monomeric anthocyanins (Kumari & Gunathilake, 2020). In another study, a significant increase (by 20.8 %) in the bioaccessibility of total phenolics was observed for fresh carrot treated with pulsed electric field (5 pulses of 3.5 kV/cm). An increase in carotenoid bioaccessibility was also recorded in the same study (López-Gámez, Elez-Martínez, Quiles-Chuliá, et al., 2021). Recently, a very clear overview has been presented by Thakur et al. (2020) where they highlighted that the bioaccessibility of polyphenols and carotenoids in fruits and vegetables increased mainly following thermal treatments such as cooking, frying and pasteurization. Freezing was evaluated to produce contradictory results; while among the non-thermal techniques, high pressure-processing was indicated as the most promising technology for enhancing bioaccessibility of bioactive compounds such as tocopherols.

5. Concluding remarks and recommendations for future research

From the above overview, it can be concluded that although many studies have been performed for the purpose of determining the changes in the content, profile, and bioavailability of dietary antioxidants resulting from different processing methods, the findings obtained may often not be comparable since different approaches, contrasting plant materials, and different methods and analyses are often used. The fates of bioactive components may differ in different foods/matrices, even when the same processing conditions have been used. It is therefore not easy to dissociate processing effects from food matrix effects. In addition, the degradation of antioxidants is not only a function of the processing conditions (i.e. temperature, degree of heating, etc.) applied, but also may depend on other specific parameters, including pH, chemical properties of the compound of interest and presence/absence of oxygen. Furthermore, there are many published techniques for assessing individual antioxidants or the total phenolic/flavonoid contents and antioxidant capacities in processed products. However, wide variations in analytical techniques make comparisons between different studies difficult and also raise the question whether conflicting results may be associated with non-standardized assay techniques. Especially, with regard to antioxidant capacity methods, it is not expected that a single protocol can determine all the antioxidant compounds and it is apparent that each method may have its own advantages and disadvantages. The principles of these methods, such as the radical that is generated, the end-point of detection, or the required reaction time, can vary to a great extent. The formation of radicals, and their solubility in different solvent systems, also might differentiate. Consequently, it is highly recommended to conduct several test procedures to obtain a full evaluation of antioxidants and their activity.

It has been clearly demonstrated that the physical state and processing history of a food item have a marked effect on the availability of dietary antioxidants for absorption by the human body. Although it is still difficult to make general statements regarding the effects of processing strategies on bioavailability, several studies have supported the concept that the disruption of the food matrix by heat, homogenization or both, has a positive effect by making compounds more accessible. These findings therefore, do not support the concept that heat-processed foods provide lower nutritional values than fresh products, but rather suggest that processing sometimes might be nutritionally beneficial for certain products. Moreover, any treatment that alters the glycosidic structure of flavonoids, i.e., leading to deglycosylation, is also prone to modulate their bioavailability.

It must be particularly considered that plants show a large variation in terms of the composition of their bioactive components linked to their specific variety, region of origin, climate, phytosanitary protocols, harvest history etc. This itself may already explain a large part of the variations observed. In addition, aspects like the food matrix, other components that were ingested simultaneously within the complex meals can be additional determinant factors. Finally, in terms of biological relevance, the high inter-individual variability of human metabolism with high levels of complexity makes general predictions regarding the bioavailability and bioefficiency of dietary antioxidants for individuals very challenging and require situation-specific approaches/evaluations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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