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FOOD SCIENCE & TECHNOLOGY | REVIEW ARTICLE

Food processing and its impact on phenolic constituents in food

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Abstract: Most food processing techniques involve a sequence of operations bringing about the desired changes in the raw material, with each operation having its impact on the food constituents. For bioactive compounds (phenolics) to exert their positive health effect, they first have to withstand food processing conditions, be released from the food matrix and be bioaccessible in the gastrointestinal tract, undergo metabolism and reach the target tissue of interest. Because of their possible biological effects in humans, it is necessary that changes in phenolic compounds during processing should be evaluated to assess the dietary value of the processed products. Data on the effect of processing on phenolic compounds show that food processing plays a significant role in the bioaccessibility and bioavailability of polyphenols. Consequently, food processing research should be tailored towards optimisation of processing methods that have the potential of retaining, releasing or at best transforming these compounds into more bioavailable forms.

Subjects: Food Analysis; Fruit & Vegetables; Nutraceuticals & Functional Foods

Keywords: food processing; anthocyanins; phenolic acids; flavonoids; bioaccessibility; bioavailability

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Dr Lisa Marshall is a member of the Food Chemistry Research Group, School of Food Science and Nutrition, University of Leeds. Her research interest includes investigating the reactions and interactions of components of food using analytical techniques. Studies look at key components such as proteins, carbohydrates and lipids as well as small molecules, for example vitamins, minerals, food additives, flavours, colours, heat-induced and natural toxicants as well as bioactive compounds.

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PUBLIC INTEREST STATEMENT

The demand for functional foods and nutraceuticals worldwide has increased significantly as people come to terms with the ancient quote of Hippocrates, "let food be thy medicine and medicine thy food". One group of food compounds attracting interest in the scientific community is polyphenols, which are present in most fruit and vegetables as well as in some cereals and grains. These compounds have been shown to possess health beneficial effects beyond basic nutrition. However, during the food processing, the content as well as the nutritional benefit can be altered either positively or negatively depending on the processing method employed.

The aim of this review, therefore, was to examine the literature to evaluate the impact of different food processing techniques on these beneficial compounds. This kind of review is necessary to inform the best practices during processing at both industrial and domestic scale to achieve maximum health benefit for consumers.

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1. Introduction

Food processing can be defined as the methods and techniques employed to convert raw ingredients into food or to transform food into other forms fit for consumption by humans or animals either in the home or by the food industry.

The broad objectives of food processing are as follows: To extend the shelf life or the duration of time in which the food is deemed to be wholesome, free of biochemical and microbiological spoilage and nutritious to consumers; To make more bioaccessible nutrients required for health; To spice-up the diet by introducing variety to the organoleptic properties (colour, texture, aroma and flavour) of foods; To restore and/or raise nutrient levels in food; and To make a profit for food companies and provide employment. Most food processing techniques involve a sequence of operations to bring about the desired change in the raw material. Furthermore, each unit operation has its own particular effect on the food constituents (nutrients, phytochemicals and organoleptic properties), and the final product quality is determined by the combination of the effects from each operation (Fellows, 2009). Bioactive compounds have to endure the impact of food processing, become bioaccessible in the gastrointestinal tract, and be metabolised into different forms before being transported to the target tissue. Consequently, the role that food processing has on plant bioactives is important, as it represents the first step in the challenging journey of bioactive compounds reaching the target tissues. In addition, because of their possible biological effects in humans, it is necessary that the changes in phenolic compounds during processing should be evaluated to better assess the dietary value of the processed products (Skrede, Wrolstad, & Durst, 2000). In the light of the above-mentioned reasons, this review examines the existing data on the impact of different processing techniques on phenolic compounds and for emphasis food sources rich in these compounds are mentioned.

2. Phenolic compounds

Polyphenols constitute to one of the most common and widespread groups of substances in flowering plants, occurring in all vegetative organs, as well as in flowers and fruits. They are plant secondary metabolites engaged in the defence mechanism of plants against predators, UV radiation, pathogens, oxidative stress and harsh climatic conditions (Ferrazzano et al., 2011). They can be classified into the following groups, namely, hydroxybenzoic acids, hydroxycinnamic acids, anthocyanins, proanthocyanidins, flavonols, flavones, flavanols, flavanones, isoflavones, stilbenes and lignans (Manach et al., 2005) In the human body, polyphenols have been extensively reported as possessing several biological properties such as anti-diabetic, anti-inflammatory, antihypertensive and cardioprotective functions (Ganesan & Xu, 2017).

3. Effect of processing on phenolic compounds

3.1. Anthocyanins

3.1.1. Properties of anthocyanins

Anthocyanins are bioactive compounds that are present in fruits and vegetables. They differ with respect to their anthocyanidin skeleton, type of sugars and potential aliphatic and aromatic acyl moieties, and their substitution positions (Andersen & Jordheim, 2010). Although there are several anthocyanidins occurring in nature (Table 1), the six most prevalent occurring in fruits and vegetables are cyanidin 50%, pelargodinin 12%, peonidin 12%, delphinidin 12%, petunidin 12% and malvidin 7%. Anthocyanindin stability is affected by the ring B substituents (Figure 1) and additional methoxyl or hydroxyl groups attached to the B ring decreases its stability in neutral media; this makes pelargodinin the most stable anthocyanidin. Glucose, galactose, rhamnose and arabinose are the sugars mostly found, usually as 3-O-glycosides or 3,5-O-diglycosides. In addition, the presence of rutinosides (6-O-α-L-rhamnosyl-D-glucose), sambubiosides (β-D-xylosyl-(1→2)-β-D-glucose), 3–7-diglycosides and 3-triosides do appear. Many anthocyanins are seen to be acylated by aliphatic or aromatic acids, with the most frequent acyl groups being coumaric, caffeic, ferulic, benzoic, synapic, malonic, acetic, succinic, oxalic and malic acids (Clifford, 2000).

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Table 1. Structural identification of anthocyanidins (aglycones)

Name	Abbreviations	Colour	Substitution pattern							
			3	5	6	7	3'	4'	5'	
Apigeninidin	Ap	Orange	H	OH	H	OH	H	OH	H	
Aurantinidin	Au	Orange	OH	OH	OH	OH	H	OH	H	
Capensinidin	Cp	Bluish-red	OH	OMe	H	OH	OMe	OH	OMe	
Cyanidin	Cy	Orange-red	OH	OH	H	OH	OH	OH	H	
Delphinidin	Dp	Bluish-red	OH	OH	H	OH	OH	OH	OH	
Europinidin	Eu	Bluish-red	OH	OMe	H	OH	OMe	OH	OH	
Hirsutidin	Hs	Bluish-red	OH	OH	H	OMe	OMe	OH	OMe	
6-Hydroxycyanidin	6OHCy	Red	OH	OH	OH	OH	OH	OH	H	
Luteolinidin	Lt	Orange	H	OH	H	OH	OH	OH	H	
Malvidin	Mv	Bluish-red	OH	OH	H	OH	OMe	OH	OMe	
5-Methylcyanidin	5-MCy	Orange-red	OH	OMe	H	OH	OH	OH	H	
Pelargonidin	Pg	Orange	OH	OH	H	OH	H	OH	H	
Peonidin	Pn	Orange-red	OH	OH	H	OH	OMe	OH	H	
Petunidin	Pt	Bluish-red	OH	OH	H	OH	OMe	OH	OH	
Pulchellidin	Pl	Bluish-red	OH	OMe	H	OH	OH	OH	OH	
Rosinidin	Rs	Red	OH	OH	H	OMe	OMe	OH	H	
Tricetinidin	Tr	Red	H	OH	H	OH	OH	OH	OH	

Source: (Castañeda-Ovando et al., 2009)

Figure 1. Flavonoid skeletal carbon structure.
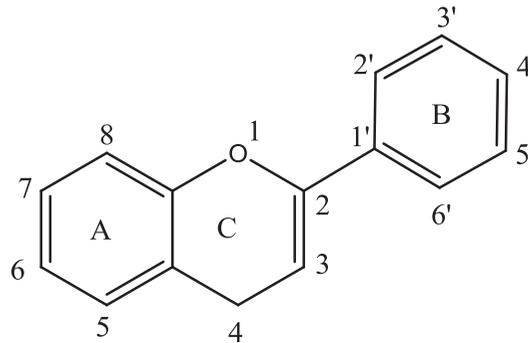
The most frequent acyl moiety occurring in about 25% of anthocyanins is malonic acid. The tertiary structure adopted by anthocyanins in intact plant tissues offers them protection from nucleophilic attack by water and produces the hyperchromic and bathochromic effects. However, once detached from their primary environment and protection offered by co-pigmentation they become unstable and breakdown easily.

3.1.2. Effect of processing on anthocyanins

The factors that influence its stability include the pH, oxygen, temperature, light, metal ions enzymes and sugars (Clifford, 2000). With respect to pH, anthocyanins exist in four different forms (Figure 2) depending on the pH. At pH 1, the flavylium cation (red colour) predominates and is responsible for the purple red colours. When the pH is between 2 and 4, the quinoidal blue species dominates. At pH 5 and 6, the colourless species which are the carbinolpseudo-base and a chalcone exist together and when the pH is above 7, the anthocyanins degrade depending on their substituent groups (Castañeda-Ovando, Pacheco-Hernández, Páez-Hernández, Rodríguez, & Galán-Vidal, 2009). During processing operations like juice extraction, cutting and dicing, disruption of the cell arrangement occurs allowing for substrate and the enzyme to mix together. In the process, enzyme hydrolysis occurs and the sugar at position C3 is cleaved off, thereby exposing the resulting chalcone, which being unstable breaks down to 2,4,6-trihydroxyphenylacetaldehyde and a benzoic acid. To slow down the rate of the breakdown of the pigment, the enzyme can be inactivated by applying a mild heating procedure known as blanching; this process has been shown to have a positive effect on anthocyanin retention and stability (Skrede et al., 2000).

Figure 2. Anthocyanins chemical form depending on pH and degradation reaction for anthocyanins. Where R1 = H or a saccharide, R2 and R3 = H or Methyl (Castañeda-Ovando et al., 2009).
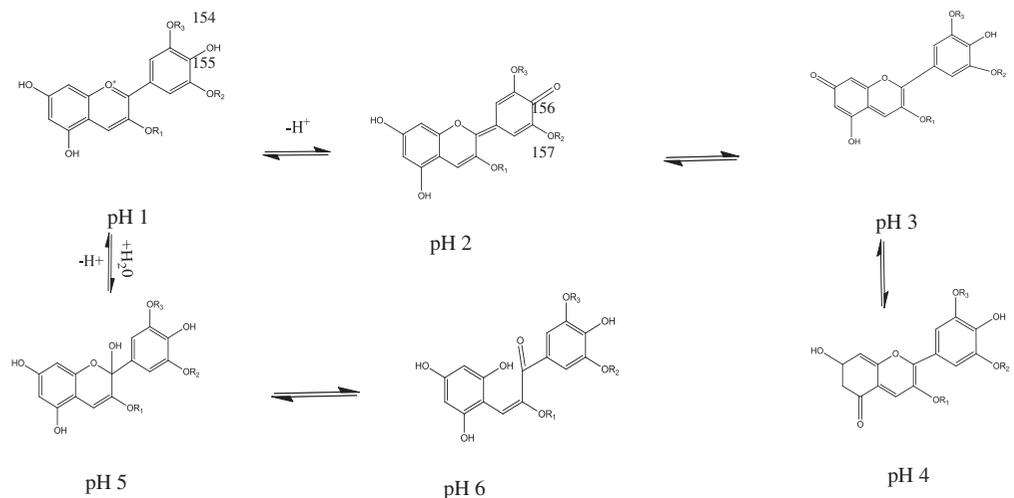
Another factor that plays a major role in anthocyanin degradation either through direct oxidative mechanism or through the action of polyphenol oxidases (PPO) is oxygen. Although the anthocyanins are not substrates for PPO, those possessing a dihydroxyl B-group react with the o-quinones derived from the oxidation of phenolic compounds by PPO to form brown condensation products. The anthocyanins not having the dihydroxyl B-group form adducts with such quinones (Clifford, 2000). The degradation products formed from these reactions are generally unstable and degrade further to form colourless compounds. To overcome this, the addition of sulphur dioxide as an antioxidant to fruits and vegetable is frequently employed as it has been reported to slow down anthocyanin degradation (Bakker & Bridle, 1992). Thermal degradation of anthocyanins during processing results in the production of different degradation products which vary according to the heating temperature (Figure 3). The opening of the pyrylium ring and chalcone formation has been suggested as the initial step for anthocyanin breakdown. In addition, the hydrolysis of the sugar moiety and the aglycone probably due to the formation of cyclic adducts has also been proposed as a possible initial mechanism for its degradation (Patras, Brunton, O'Donnell, & Tiwari, 2010). The terminal degradation products from the chalcone were identified to be phenolic acids and phloroglucinaldehyde. The stability of anthocyanins can be enhanced by co-pigmentation. Co-pigmentation is a phenomenon in which pigments and other non-coloured organic components form molecular associations or complexes resulting in a brighter and more stable colour (Boulton, 2001). This occurrence is critical because colour remains a major quality criteria influencing consumer acceptability of a product. Co-pigmentation and polymerisation reactions have been reported to be responsible for the stability of wine colour.

3.2. Phenolic acids

3.2.1. Properties of phenolic acids
Hydroxybenzoic and hydroxycinnamic acid derivatives are major phenolic acids present in bound form in plant cells where they play a vital role in plant defence, in the maturation processes and development of fruit flavour quality (Fallico, Lanza, Maccarone, Asmundo, & Rapisarda, 1996). The hydroxybenzoic acid derivatives are present as sugar derivatives and organic acids in plant foods as well as present in lignins and hydrolysable tannins, while the trans-4-hydroxycinnamic acids (ρ-coumaric, caffeic, ferulic and sinapic) occur in the form of esters and glycosides. Ellagic acid, ρ-hydroxybenzoic and gallic acids have been reported to be the main phenolic acids present in the

Figure 3. Proposed mechanism for thermal degradation of anthocyanins (modified from Sadilova et al., 2007). The figure shows the hydrolysis of sugar moiety and aglycone formation as initial degradation step possibly due to the formation of cyclic adducts which later decomposes upon heating into a chalcone structure, the latter being further transformed into a coumarin glucoside derivative with a loss of the B-ring.
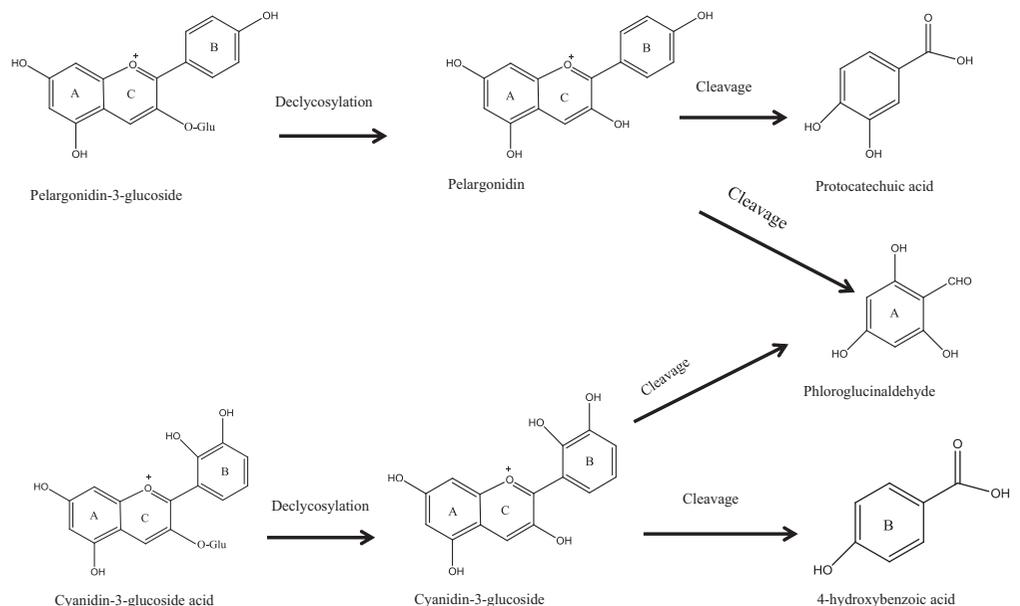
berry (strawberry, raspberry and cloudberry) family Rosaceae (Häkkinen, Kärenlampi, Mykkänen, Heinonen, & Törrönen, 2000; Veberic, Colaric, & Stampar, 2008). The main cinnamic compound found in apples, pears and potatoes is chlorogenic acid (3-O-caffeoylquinic acid). In grapes, caftaric acid (caffeoyltartaric) is most abundant, while ferulic acid esters are typical of citrus fruit. For cereals, the most abundant hydroxycinnamic acid is ferulic acid and its oxidative products, diferulic acids, while other hydroxycinnamic acids (sinapic acid, ρ-coumaric acid and caffeic acid) and benzoic acid derivatives also occur in small quantities in various grains and derived products (Dao & Friedman, 1992; Fallico et al., 1996; Gallardo, Jiménez, & García-Conesa, 2006; Nayak, Liu, & Tang, 2015).

3.2.2. Effect of processing on phenolic acids

The changes that occur in free and bound forms of phenolic acids during processing depends on the type of fruit, vegetable, plant food and the processing technique employed (Nayak et al., 2015). Furthermore, temperature, oxygen and enzymes are also major factors affecting the stability of phenolic acids (Dewanto, Wu, Adom, & Liu, 2002). For instance, an increase in ellagic acid content in strawberry fruit kept under modified atmosphere (5°C for 10 days) has been reported. The same effect was also seen when strawberries were processed into puree juice and stored at 4°C (Häkkinen et al., 2000; Oszmiański & Wojdyło, 2009). The increase in ellagic acid can be attributed to the hydrolysis of ellagitannins during processing and ageing. In the same way, pressure cooking of legumes resulted in improved bioaccessibility as the phenolic acids bound to the plant matrix were released (Chen et al., 2015). Likewise, when orange juice were processed by pulsed electric field and thermal pasteurisation, the contents of most of the phenolic acids in orange juice increased with the exception of neoeriocitrin and syringic acid. (Agcam, Akyıldız, & Evrendilek, 2014). In addition, Morales-De La Pena, Salvia-Trujillo, Rojas-Graü, and Martín-Belloso (2011) reported a similar trend and showed that after thermal processing or high intensity pulse electric field treatment, the concentration of most of the individual phenolic acids (caffeic, coumaric and ferulic) identified in the fruit juice-soya milk beverage increased except for sinapic and chlorogenic acids. On the contrary, processing of blue berries into jams produced a 20% reduction in ellagic acid levels, possibly due to the antioxidant activities of ellagic acid during the manufacturing process (Häkkinen et al., 2000). Similarly, food processing involving heat has been shown to decrease the chlorogenic acid content of potatoes. The decrease varied according to the type of the heat applied, with oven-baked potatoes having the greatest reduction and microwaved-treated retaining the highest amount (Dao & Friedman, 1992). The study also demonstrated that the nature of heating influences final levels of chlorogenic acid and controlling processing temperatures is critical in processing potato products. For ferulic acid esters, thermal processing and storage of orange juice result in the hydrolysis of the esters and release of the free acids, which may later undergo decarboxylation, leading to the formation of 4-vinyl guaiacol that imparts an unpleasant odour to the final product. Subsequently, 4-vinyl guaiacol may undergo thermal degradation to produce other phenolic compounds like vanillin, 4-ethyl or 4-methyl guaiacol (Lee & Nagy, 1990). Therefore, monitoring the levels of these compounds is important from the nutritional as well as organoleptic point of view.

In cereals, most of the phenolic acids occur in the bound form. However, during extrusion processing of wheat, barley oat and rye (temperatures between 120–200°C), an increase of 200 to 300% in free forms of vanillic, syringic and ferulic acids was observed indicating that hydro-thermal processing of cereal grains may release phenolic acids and their derivatives from the cell wall (Zielinski, Kozlowska, & Lewczuk, 2001). In another separate study, the ferulic content in bread supplemented with enzymatically treated bran was higher compared with native bran resulting in increased bioaccessibility (Amaya Villalva et al., 2018). Bryngelsson, Dimberg, and Kamal-Eldin (2002) demonstrated that autoclaving of oats increased the content of *p*-coumaric acid, vanillin and ferulic acid but had a negative impact on caffeic acid.

Similarly during the fermentation of rye and wheat, increased levels of ferulic acid and other phenolic acids were reported probably due to the activity of hydrolytic enzymes (Bhanja, Kumari, &

Banerjee, 2009; Katina et al., 2007). Overall, processing tends to have both positive and detrimental effects on phenolic acids in foods depending on the plant matrix and the processing method employed. Therefore, it is critical to determine not only optimal processing conditions that extend the shelf life of products but also in addition reduce the degradation of bioactive compounds present in them.

3.3. Flavonoids (flavonols flavan-3-ols, flavanone and isoflavones)

3.3.1. Properties of flavonols, flavan-3-ols, flavanone and isoflavones
Flavonols are flavones attached to a hydroxyl group at the 3-position (3-hydroxyflavones). They are very common in higher plants and are mostly present in the leaves and outer parts of the plant. Flavan-3-ols and their polymeric condensation products, the proanthocyanidins, are present as ingredients in the formulation of beverages, whole and processed foods, and herbal supplements. The food quality parameters most influenced by flavan-3-ols include the astringency and bitterness. With respect to the isoflavonoids, the phenylchroman B-ring is linked to position three instead of position two as in the other flavonoids (Corradini et al., 2011). Isoflavones are particularly abundant in plants especially in soy beans, Glycine max (L.). In particular, soy may play a role akin to phytoestrogens that bind to oestrogen receptors thereby interfering with the action of oestrogen, which is an established risk factor for hormone-dependent cancers such as prostrate and breast cancers (Ko et al., 2010).

3.3.2. Effect of processing on flavonols, flavanone, flavan-3-ols and isoflavones
There is growing evidence to support the cardioprotective effects of flavan-3-ols (present in tea and cocoa), flavonols (quercetin found in onion and most leafy vegetables) and isoflavones, present in soy (Curtis et al., 2012; Perez-Vizcaino & Duarte, 2010). However during processing, these phenolic compounds undergo significant changes in their structure that may impact on their biological activities. This is observed during black tea processing where catechins are acted upon by the oxidative enzymes, polyphenol oxidase and peroxidase, to form theaflavins and thearubigins during fermentation (Muthumani & Kumar, 2007). Furthermore, these oxidation products along with catechin are responsible for the taste and astringent character of black tea. Similarly, during the fermentation of cocoa beans, polyphenols undergo oxidation to condensed high molecular weight insoluble tannins which results in decrease in both catechin and epicatechin contents (Nazaruddin, Seng, Hassan, & Said, 2006; Wollgast & Anklam, 2000). The reverse occurs during the roasting of cocoa bean where (-)-catechin levels increase when bean temperature exceeds 70°C probably due to the epimerisation of (-)-epicatechin (Payne, Hurst, Miller, Rank, & Stuart, 2010). Flavonols constitute an integral part of the human diet with onions and asparagus being rich sources of quercetin 3, 4'-O-diglucoside and quercetin 4'-O-glucoside. The impact of domestic processing (blanching, chopping, maceration and boiling) on flavonol content in onions and asparagus was assessed: chopping caused a significant decrease in rutin content of asparagus but did not affect the levels of quercetin 3,4'-O-diglucoside and quercetin 4'-O-glucoside in onions (Makris & Rossiter, 2001). Boiling for 60 min produced the highest reduction in total flavonols, indicating that the impact of thermal heating on flavonols in these plant sources cannot be ignored. When broccoli was processed either by boiling or frying, the losses in quercetin derivatives were similar, while steaming retained higher amount of quercetin derivatives (Rothwell et al., 2015). The same authors also reported that with processed onions, irrespective of the processing technique (boiling, frying, microwaving or blanching), reduction in quercetin was similar. On the contrary, processing of tomatoes into juice and puree increased the levels of free quercetin in the tomato-based products; this may be attributed to the hydrolysis of rutin and other quercetin conjugates (Stewart et al., 2000). Similarly, there was no detrimental effect on the total flavanone content or individual flavanone glycosides after treatment of oranges with pulse electric field (Sánchez-Moreno et al., 2005). Furthermore, pasteurisation did not significantly affect the content of flavanone-7-O-glycosides in citrus juices (Sentandreu, Navarro, & Sendra, 2007). For soy products, for example, defatted soy (minimal heat during processing), the major isoflavone present is the malonylglucoside conjugates. When the processing temperature is increased to 100°C

(manufacture of soy milk, tofu and soy molasses), the isoflavone β-glucosides are mostly present. In the production of fermented soy foods (tempeh), the reduction of the malonylglucosides and the concomitant increase of the unconjugated aglycones (genistein and daizein) are observed as fermentation time increases (Barnes, Kirk, & Coward, 1994; Kwon, Daily Iii, Kim, & Park, 2010). In conclusion, while heat processing produces diverse effects on these phenolic compounds, fermentation does seem to have a positive effect in altering their structural composition, which in turn may have an impact on the bioavailability and bioefficacy of these compounds.

4. Effect of processing on the bioavailability of phenolic compounds

The biological effects or bioefficacy of phenolic compounds is dependent on their bioavailability once consumed (Rein et al., 2013; Scalbert & Williamson, 2000). The factors that play a major role in the bioavailability of phenolic compounds include the concentration within the cell wall, variations in cell wall structure, location of glycosides in cells, molecular structure and the binding of compounds within the food matrix (Parada & Aguilera, 2007). Most polyphenols present in food substances occur as glycosides, esters or polymers which cannot be easily absorbed. Before glycosylated polyphenols can be absorbed, it is necessary for the sugar moiety to be removed by enzymes present in the gastrointestinal mucosa, or in the colonic microflora, or through food processing (Scalbert & Williamson, 2000). The role food processing plays in altering the bioavailability of glycosylated polyphenols is demonstrated in the manufacture of tomato puree, where increased levels of free flavonols were reported due to hydrolysis and extraction from the food matrix (Stewart et al., 2000). It has also been shown that absorption of flavonols is affected by the attached sugars and the presence of fat, whereas epimerisation reactions occurring during processing could affect the absorption of flavanols such as catechins (Scholz & Williamson, 2007). Similarly, during fermentation of soy foods, the breakdown of glycosylated isoflavones by microorganisms into the aglycones may be beneficial, as it has been demonstrated that the isoflavone aglycones of soymilk absorb more efficiently and in greater amounts than their glucosides in humans (Kano, Takayanagi, Harada, Sawada, & Ishikawa, 2006). Furthermore, in cases where polyphenols occur as esters bound to hemicellulose or as large molecular weight compounds (proanthocyanidins or hydrolysable tannins), their bioavailability is reduced as these ester-linked substitutions or polymerisation chain reactions have a marked effect on the biological properties of the polyphenols (Scalbert & Williamson, 2000). Thermal processing might improve bioavailability as observed in the release of ferulic acid during extrusion processing of cereal grains (Zielinski et al., 2001), and in the breakdown of hydrolysable ellagitannins into ellagic acid during processing of jam from strawberry (Häkkinen et al., 2000). Regarding the effect of processing on phenolic compounds *in vivo*, there are a few authors who report this. For instance, the effect of the baking process on the bioavailability of blueberry phenolic compounds (anthocyanins, procyanidins and phenolic acids) was investigated after ingestion of a blueberry drink and a blueberry-baked product; they found no difference in the bioavailability of overall phenolic compounds between both products (Rodriguez-Mateos et al., 2014). In another separate study, cooking cherry tomato provoked an increase in bioavailability of naringenin and caffeoylquinic acid (Bugianesi et al., 2004). With respect to processing involving microorganism, the addition of α-amylase to extruded sorghum improved procyanidin bioavailability in pigs (Gu, House, Rooney, & Prior, 2008). Similarly, increased phenolic acids bioavailability and the production of 3-phenylpropionic acid, (end product of the ferulic acid colonic metabolism) were observed after fermentation with hemicellulase (xylanase), b-glucanase, a-amylase and ferulic acid esterase in wheat bran (Anson et al., 2011, 2009).

5. Future direction of food processing

Existing data on the effect of processing on phenolic compounds shows that food processing plays a significant role when it comes to bioaccessibility and bioavailability of polyphenols. High temperature processing which ensures food safety has both positive and detrimental effects on phenolic compounds. The reviewed literature also suggests that if food processing is judiciously applied, it can serve as a means of improving bioavailability of polyphenols through structural modification or breakdown of the parent compound. Therefore, food processing research should be

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tailored towards optimisation of both thermal and non-thermal methods that have the potential of retaining, releasing (bioaccessible) or at best transforming these compounds into more bioavailable forms.

Competing interest
The authors of this manuscript declare that they have no conflict of interest.

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