

BIOACCESSIBILITY AND STABILITY OF PHYTOCHEMICAL COMPOUNDS, ESSENTIAL FEATURES IN THE DESIGN OF FUNCTIONAL FOODS: A REVIEW

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Abstract

Epidemiological and observational studies and research on the impact of diet on health have contributed to increasing demand for foods that have high nutritional value or that are specific to certain target groups of consumers. The study aims to review information regarding the stability of phytochemical compounds in food matrices subjected to heat treatment.

Research on the relationship between the nutritional quality of the diet and the values of inflammatory biomarkers measured in chronic non-transmissible diseases has highlighted the protective role of phytochemical compounds that are naturally present in foods. The development of functional foods based on phytochemical compounds must be supported by understanding the mechanisms of action of phytochemicals, strategies to ensure the maximization of their bioaccessibility and bioavailability, and the establishment of the reference dietary intake. Most studies have focused on quantifying the phytochemical response to processing and identifying the main factors of phytochemical compound stability, for example: type of process, food matrix structure and environment, and storage conditions. The development of functional foods based on phytochemical compounds requires a detailed understanding of the stability of these compounds and the uptake of phytochemicals transported by the food matrix.

The strategies for maximizing the bioavailability of phytochemical compounds require *in vivo* evaluation of the mechanisms of action observed within *in vitro*

studies and establishing reference dietary intake limits by identifying and assessing biological responses.

Key words: *Phytochemical compounds, Stability, Bioavailability, Functional foods.*

1. Introduction

Trends in research and innovation in the food system are reflected in European project funding. Functional foods are an area targeted by funded European projects, with the priority "nutrition for sustainable and healthy diets" accumulating 23% of total funding [1].

The population's food consumption patterns show significant differences that can be correlated with the particularities of available natural resources, gastronomic culture, and lifestyle. These patterns influence the health status of populations differently. The results of epidemiological and etiological studies on the impact of diet on health influence the design of food diets, the development of dietary guidelines for the general population, and the development of the production of functional foods. The demand for foods with high nutritional value or specific to certain target groups of consumers leads the actors of the food chain to the development and diversification of foods. Diet can influence inflammatory biomarkers. Some of the phytochemical compounds naturally present in food have an anti-inflammatory role and can reduce the risk of non-transmissible chronic diseases. This is one of the reasons why the dietary guidelines recommend regular consumption of fruits, vegetables, legumes, whole grains, nuts, fish, and low-fat dairy products [2, 3].

Reducing energy intake, and consumption of red meat, processed meat, salt, and sugar can reduce the level of inflammatory mediators and the risk of developing chronic non-transmissible diseases [4]. For example, the increased and diversified intake of phytochemicals from the Mediterranean diet (MedDiet) can correct the abnormalities associated with metabolic syndrome (e.g., dyslipidemia, hypertension, hyperglycemia, central adiposity, insulin resistance, low-grade inflammation [5 - 9]. Lopez *et al.*, [10], reported that MedDiet promotes a favorable microbial environment for the production of microbial phenolic metabolites that have beneficial effects on cardiovascular health. Phytochemical compounds resulting from the metabolism of dietary plants have, at least *in vivo*, antioxidant and anti-inflammatory potential [11 - 14], antitumor [15], anti-obesogenic [16], cardioprotective [17 - 20], antiviral and antibacterial [21, 22]. The molecular mechanisms that can explain these effects [23, 24], depending on the dose of polyphenolic compounds, absorption level, and metabolizing phenotype [25]. These aspects have been used for the development of nutraceuticals and functional foods [26 - 28]. Regular consumption of functional foods, as part of a diversified diet, has potentially positive effects on health. However, the development of functional foods containing phytochemical compounds requires knowledge of their bioaccessibility. The effects of food structure, matrix environment, and preparation/processing treatments are correlated with the bioaccessibility and bioavailability of phytochemical compounds in the food product. In a review published by Sabaghi *et al.*, [29], the need to study the complex effects (beneficial and adverse) of phytochemical compounds in food systems on human health is highlighted.

The purpose of this paper is to review information on the effects of heat treatments during processing/cooking on phytochemical compounds in foods. These data are useful for the design of functional foods, including the choice of preparation/processing methods to reduce losses of phytochemical compounds from ingredients.

Scientific research results were collected using the ScienceDirect Freedom Collection Elsevier, Springer Link, Wiley Online Library, Hindawi, Ed. Taylor and Francis e-Library platforms. The search was performed using keywords: phytochemical compounds, sources, solubility, stability, bioaccessibility, and bioavailability. Published data were analyzed, selected, and summarized on the stability of phytonutrients in to heat treatment of foods.

2. Phytochemical compounds present in the general diet

Dietary phytochemicals have been classified by Tiwari *et al.*, [30], according to the basic chemical formula,

in 12 major classes (Figure 1), or to the physiological effects exerted on the target tissues [31].

Polyphenols > 8.000 structures	Carotenoids > 600 structures (xanthophylls and carotenes)	Glucosinolates > 100 structures
Polysaccharides	Alkaloids > 21.000 structures	Polyacetylenes > 2.000 structures
Allium compounds	Terpenes > 55.000 compounds	Lectins > 500 structures characterized
Capsaicinoids	Chlorophyll	Betalains

Figure 1. Classification of phytochemicals according to the basic chemical formula [30]

Most phytochemical compounds have been studied individually, predominantly *in vitro*, to assess their bioavailability and stability. The low bioavailability has led the plant-based pharmaceutical industry to identify solutions to increase the extraction efficiency and stability of these compounds. The results obtained in the production of nutraceuticals can be used to develop functional foods, through the selection of the food matrix that ensures/increases the bioaccessibility and bioavailability of phytochemical compounds.

About 600 phytochemical compounds are found in the human diet. They come from the consumption of food products that resulted from minimal processing and/or that were obtained by transforming raw materials into different compositional formulations, subject to cooking and processing. Granato [24], investigated the main classes of phytochemical compounds (i.e., daily intake of flavonoids - 433 mg, phenolic acids - 303 mg, and stilbenes - 1.21 mg) identified in the diet of a group of Spaniards in whom the incidence of cardiovascular diseases was significantly reduced. It also brings to attention the fact that food matrices used as delivery systems of phytochemical compounds should be redesigned to increase their bioavailability and maintain their chemical stability.

2.1 Identified factors affecting the stability of phytochemical compounds in food matrices

The validation of the effects of phytochemical compounds carried by food regarding their biological action in promoting health is becoming a growing challenge for the food industry oriented towards increasing the nutritional value of food. It was found that the technological processes as well as the compositional structure of the food matrix can modify

the structure of the phytochemical compounds and their biological activity. In food production, heat treatment, fermentation, dehydration, enzymatic ripening, texturing, microwave heating, high-pressure preservation, etc., are the most common food cooking/processing methods. Tiwari *et al.*, [30], published a reference manual on phytochemical compounds: sources, health benefits, stability, factors and impact of food preparation processes on phytochemical compounds, and analytical methods for determining phytochemical compounds. The factors identified by the authors affecting the stability of phytochemical compounds in food matrices are summarized in Figure 2.

The authors focused their analysis on three major groups of phytochemical compounds: nitrogen-containing compounds, terpenoids, and phenolic compounds, selecting five groups of phytochemicals: polyphenols and anthocyanins, carotenoids, glucosinolates/isothiocyanates, polyacetylenes, and ascorbic acid, considered to be in major amounts in the human diet.

Alkaloids represent the major class of nitrogen-containing compounds, synthesized from aspartic acid, arginine, tryptophan, and tyrosine; terpenoids are compounds derived from acetyl-CoA, grouped into a unique class despite being chemically different, and phenolic compounds are divided into several subclasses. These nutrients may act individually or synergistically (additively or multiplicatively) with other compositional nutrients [32], and influence, through direct or indirect mechanisms, metabolic reactions [33, 34], or other nutritional compounds [35, 36].

The physiological response to the action of phytochemical compounds is considered a multifactorial character, which presents significant inter-individual differences. The observed differences are influenced by the metabolizing phenotype (which is determined by existing polymorphisms in genes encoding enzymes involved in the metabolism of phytochemical compounds), microbiome characteristics, and nutrient bioavailability [37 - 39]. The predisposition for the vast majority of multifactorial characters depends on the complex interactions that are established between different categories of risk or protective factors. Such interactions have also been identified in response to phytochemical compounds. It has been observed that polyphenols (e.g., flavonoids and their metabolites) can increase the production of short-chain fatty acids (SCFA) and reduce the level of tumor necrosis factor-alpha (TNF- α) induced by lipopolysaccharide (LPS) and thus influence the gut microbiota [37]. Achour *et al.*, [40], found that humans can partially absorb polyphenols from rosemary tea. The colonic microbiota plays a key role in the biotransformation of these polyphenols and the formation of bioavailable metabolites. The authors suggest that the bioavailability of phytochemical compounds should be correlated with the characteristics of the gut microbiota and with those of circulating and excreted metabolites. Recent studies have indicated that poor absorption of polyphenols can have complex effects: it alters the gut microbial community, causes reduced systemic inflammation, and improves metabolic outcomes. Terao *et al.*, [41], highlighted that nutraceutical use of flavonoids in functional foods is safe, low bioavailability, and target specificity can avoid harmful side effects.

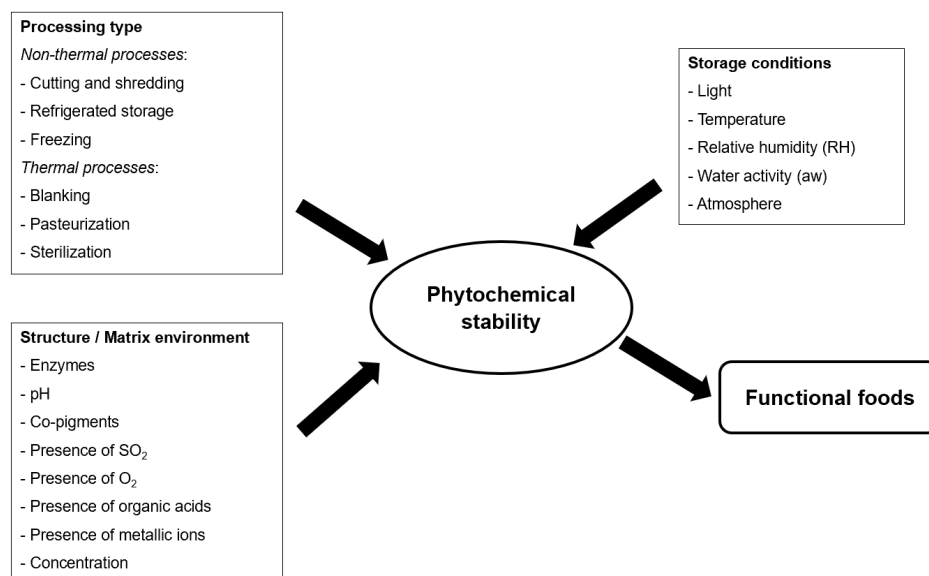


Figure 2. Factors affecting phytochemical stability [30]

Recent research suggests that the human nutritional phenotype is influenced by compounds resulting from the bioconversion of dietary flavonoids by gut microbiota.

Food preparation techniques can increase or decrease the content of phytochemical compounds in the food product. Thermal treatments are the most used method for food preparation in households and at the industrial level. The stability of phytochemical compounds in food matrices has been intensively studied. The results obtained were influenced by their concentration in food, their antioxidant activity (depending on the class of phytochemicals), the food matrix, and the treatments applied to the preparation [42 - 44]. Future studies should contribute to understanding the effects of dietary intake, the impact of bioavailability of phytochemicals, degradation pathways, and ways to protect phytochemicals from processed foods.

2.2 The influence of thermal processes on the general stability of the major classes of phytochemical compounds

The physical and chemical characteristics of phytochemicals provide clues to the bioaccessibility of major classes of dietary phytochemicals and the development of functional foods. Several factors (e.g., chemical characteristics, molecular symmetry and size, temperature, and pH of the food matrix) allow estimation of the stability and solubility of phytochemical compounds in intestinal juice. These characteristics can be modified during thermal treatments applied to foods (e.g., the severity of the thermal process, the exposure time, the thermal stability of the phytochemical compounds, their solubility in the matrix environment, the constituents of the matrix to which the phytochemical compound is linked, oxidative stability).

2.3 Polyphenols

Polyphenols are widely distributed in plant foods and play an important role in human nutrition. Polyphenols are classified into flavonoids and non-flavonoids and into subclasses defined according to the number of phenolic units they contain in their molecular structure, the groups of substituents, and/or the type of linkage between the phenolic units [45, 46].

The total concentration of phenols in plant tissues differs with the type of polyphenol, the plant, and the method of determination. The range in which these values are found is 1-25% of the dry mass. Anekplhakij *et al.*, [47], analyzed ten nut species that are more commonly used in human consumption and identified the different polyphenolic compounds (e.g. phenols and phenolic acid derivatives, flavonoids, and

stilbenoids, both subgroups of tannins, lignans, and coumarins).

Polyphenols are very sensitive to heat and light, have different solubility in water, a high rate of metabolism, and rapid elimination from the body. Ioannou *et al.*, [48], reviewed studies quantifying the effect of heat treatment and storage in the presence of light on the structure and antioxidant activity of six flavonoid model solutions. The results indicated that the particularities of exposure to light and the characteristics of thermal processes can induce structural changes (consequently also changes in antioxidant properties) that are also correlated with the characteristics of flavonoids. Gunathilake *et al.*, [49], showed that cooking by steaming, boiling, and roasting significantly alters the polyphenol and carotenoid content of 6 vegetables with green leaves. Roasting reduces the content of polyphenols, flavonoids, and carotenoids as well as antioxidant activity. Boiling and steaming have different effects on the number of polyphenols, carotenoids, and antioxidant capacity depending on the type of leaf. Antony and Farid [50], reviewed data describing the complex relationship between thermal degradation and decreased phenolic extraction yield at temperatures above 90°C. The conclusion of the study highlights that the thermal degradation of different types of phenols is dependent on the type of treatment applied, the source and how the polyphenols are bound in the matrix, the pretreatment of the material, the type and concentration of the solvent used and the pH of the extraction medium. Maghsoudlou *et al.*, [51], determined the content of phenolic compounds in fresh, boiled, and roasted quince fruit. The content of all polyphenols decreased under the action of temperature, and the antioxidant activity increased significantly in the roasted sample. The result was explained by the breaking of chemical bonds of high molecular weight polyphenols (which are partially soluble) and the appearance of lower molecular weight, soluble polyphenols. Zang *et al.*, [52], studied the effect of pretreatments performed for dehydration of *Dryopteris erythrosora* leaves on flavonoids and antioxidant capacity. The total flavonoid content of the samples initially dried in the shade and then oven-dried at 75°C was higher (7.6%) compared to 2.17% determined in samples dried at 75°C. The leaf pre-treatment method ensures the best stability of antioxidant activity. Water and natural light were found to influence the total flavonoid content of leaf samples the most.

2.3.1 Subclasses of polyphenols

2.3.1.1 Flavonoids

They are pigments present in plant tissue with strong antioxidant activity *in vivo*. They are soluble in water.

Flavonoids are classified according to the degree of oxidation of the C ring [53], where the main subclasses are: flavonols, flavones, isoflavones, flavan-3-ols, flavanones, and anthocyanidins.

Most flavonoids show little stability. The double bond in positions 2 and 3 of flavones and flavonoids produce changes towards a dense structure that affects bioavailability. Hydroxyl groups, ketones, and unsaturated double bonds of flavonoids make them sensitive to various physical (temperature, light) and physiological (enzymes, pH) factors that lead to biodegradation or biotransformation, limiting their effectiveness in the protection of inflammatory systems.

2.3.1.2 Flavan-3-ols

These compounds are a group of isomers of flavan-3-ols present in a variety of foods (e.g., fruits, wine, tea, cocoa, and chocolate). Solubility in water is dependent on low molecular weight. Flavan-3-ols have high stability at increasing temperatures and slightly acidic pH (4.9). Similarly, their isomers have good thermal stability. At neutral or alkaline pH, degradation and isomerization occur during heating and sterilization and cause significant losses of catechins. Black tea can bind iron by forming the iron-polyphenol complex. Dasedmir *et al.*, [35], obtained results of inhibition (97%) of the formation of the iron-polyphenol complex by adding lyophilized blueberries (50%) to the preparation of black tea.

2.3.1.3 Anthocyanidins

They are flavonoids (vacuolar pigments) responsible for the color of vegetables, fruits, and grains. The richest sources of anthocyanidins are berries and chokeberry (with a content between 100 - 700 mg/100 g of fresh product), and vegetables (with a content of up to 200 - 300 mg/100 g of fresh product). They are soluble in water, methanol, and ethanol. The food matrix environment, type of processing, storage conditions, and duration are factors that affect the stability of anthocyanidins. Studies suggest that these molecules are unstable and highly susceptible to degradation. Anthocyanidins act as chelators of metal ions (e.g., Fe, Cu, Al, and Sn) with a color-changing effect.

The stability of anthocyanins is significantly influenced by temperature. Heat treatments with temperatures higher than 100 °C (for example: extrusion, fat frying, spray drying, and sterilization) have been studied for anthocyanin-rich products. Studies for this purpose have been carried out by Bertelli *et al.*, [46], on extruded cornmeal with added blueberry and grape anthocyanins, in breakfast cereals, in sterilized grape

pomace, in vacuum-fried blue potatoes, and spray-dried acai pulp. Pigment loss was 32% at 77 °C, 53% at 99 °C, and 87% at 121 °C. Studies on anthocyanins have highlighted their low bioavailability: in fact, only 1 - 2% of dietary anthocyanins retain their original molecular structure. Among the factors that can explain these observations are: the pH of the gastrointestinal tract, enzymatic activity in the small intestine, phase II metabolism processes in the intestine and liver, and the enzymatic and catabolic action of the intestinal microbiota.

Ryu and Koh [54], demonstrate, in the study carried out on the stability of black soybean anthocyanins (all anthocyanins glycosylated with monosaccharides); grapes (glycosylated disaccharide anthocyanins (23%); acylated anthocyanins linked with two sugars (77%) and purple sweet potato (all acylated anthocyanins linked with three sugars), in the digestive tract, that the degree of glycosylation and acylation of anthocyanins affects their stability under simulated gastrointestinal conditions. The results of the study provide detailed information on anthocyanin structure to estimate their bioaccessibility as well as functional potential from consumption of anthocyanin-rich foods. Bakowska and Kolodziejczyk [55], studied the extension of the shelf life of five varieties of black currants by freezing (-20 °C, for 9 months). They found that the effects of freezing anthocyanins varied between cultivars. In some varieties, there were no changes in anthocyanins, in other crop varieties significant changes were recorded (- 20%, - 25%). Non-acylated anthocyanins were responsible for the decrease in total anthocyanin concentration. Similar results were observed in other studies on frozen berries.

2.3.1.4 Isoflavones

They can be found in a variety of plants: alfalfa, chickpeas, spice seeds, and legumes (soy being the predominant food source). Isoflavones as well as non-flavonoid lignans are classified as phytoestrogens due to their structural similarity to estrogen. Non-flavonoid lignans are present in high concentrations, primarily in cereal grains [31]. They have low solubility in aqueous medium and medium in lipids. Isoflavone aglycones show a higher solubility in a lipid medium. The most studied isoflavones come from soybeans and soy products. They are stable to heat treatments, even above 100 °C. At temperatures lower than 50 °C, they can undergo structural changes through conversions into different forms. Conjugates of malonylgénistin, malonyldaidzin, and malonyglycitrine are heat labile. The degradation of isoflavones during processing and storage remains an unsolved problem, mainly due to the complexity of conversions between different forms in separate or simultaneous steps [56]. Kuligowski *et*

al., [57], found that all forms of isoflavones analyzed decreased significantly after heat treatment. The decrease was found for daidzin (75%), genistin, daidzein, and genistein (76%), and glycitin (93%). Qu *et al.*, [58], studied the changes in isoflavones that occur in mature and immature soybeans during food processing. Water content is of decisive importance regarding the influence of temperature on the profile and content of isoflavones. After heat processing, total isoflavone content tended to decrease regardless of seed maturity and processing method. Moist heating tended to convert or degrade malonylglycosides to other isoflavone derivatives instead of acetylglycosides, while decarboxylation of malonyl isoflavones occurred simultaneously.

2.4 Stilbene

Stilbenes occur in a limited but heterogeneous group of plant families because stilbene synthase (STS), the key biosynthetic enzyme for stilbenes, is not ubiquitously distributed [59]. More than a thousand natural stilbenes are mentioned in the specialized literature. A limited number of plants, such as *Cyperaceae*, *Polygonaceae*, *Pinaceae*, or *Vitaceae*, synthesize these metabolites with a wide chemical diversity [60]. They have low solubility in aqueous medium.

Stilbenes (the most studied compound being resveratrol) have limited chemical stability, poor intestinal absorption (< 1%), and short-term tissue storage. The isomerization of trans-stilbene (E) to cis-stilbene (Z) occurs under the influence of light, while the reverse pathway is induced by heat or light. Z - stilbene has a melting point of 6 °C, while E - stilbene has a melting point of 125 °C [59].

2.5 Lectins

Lectins are ubiquitous proteins in nature in microorganisms, plants, and animals. In plants, they are present in all tissues with an estimated size ranging from 60 to 400 kDa [61]. They are soluble in water. Prasanna and Venkatesh [62], evaluated the stability of onion lectin at different pH and temperature values by measuring the biological activity (hemagglutination). They found that onion lectin exhibits stability in the pH range of 6 to 10, decreasing by more than 50% at pH 4 and pH 12. Hemagglutination activity was not lost up to 40 °C; this characteristic gradually decreases at temperatures above 40 °C and becomes undetectable at 80 °C. Clement and Venkatesh [63], studied the stability of two garlic lectins, mannose-binding *Allium sativum* agglutinin (ASA I) and *Allium sativum* agglutinin (ASA II), under different conditions of pH, temperature, and denaturants in relation to their biological activity. The hemagglutination capacity of the two lectins changes differently depending on pH (ASA I retains 80 - 100%

activity at all pH values, ASA II retains 100% activity at pH 6 and 8, 40% at pH 10 and 12, and 25% at pH 2 and 4). The hemagglutination activity of both lectins is maintained for 30 minutes at 60 °C but is canceled after incubation at 100 °C. Processes involving temperatures ≥ 100 °C have led to the complete inactivation of the alfalfa lectins. All heat processing treatments improved the bioactive compounds, antioxidant activity, and mineral profile of alfalfa seeds [64].

2.6 Carotenoids

Carotenoids are tetraterpenic pigments, being the most widespread in nature. They are present in some species of fungi, algae, plants (components of chloroplasts), and animals [65]. They are soluble in lipid medium. Carotenoids break down under attack by free radicals, such as singlet molecular oxygen and other reactive oxygen species. Light, enzymes, prooxidant metals, and co-oxidation with unsaturated lipids induce oxidation. The preservation process was found to result in the greatest carotenoid destruction, followed by UHT (high temperature/short exposure) treatment and acidification. Thermal treatment, light, and acids favor the isomerization of carotenoids in food, from trans- to cis-isomeric forms, and the degree of isomerization is directly correlated with the intensity and duration of thermal processing. Domestic cooking methods (microwave, steam, or boiling) do not significantly change the content of carotenoids in vegetables. Hydrocarbons (β -carotene, lycopene) and hydroxylated carotenoids (lutein) are less destroyed than epoxides [66]. The experiment carried out by Se Souza *et al.*, [67], demonstrated losses of carotenoids from a pumpkin-based product to be influenced by temperature and light exposure. Degradation kinetics were correlated with oxidative reactions. They depend on the content of dissolved oxygen in the product which is reduced in the presence of antioxidants (e.g., ascorbic acid). Degradation of carotenoids influences the color of foods as well as their nutritional value.

2.7 Alkaloids

Alkaloids are a large group of metabolites produced by a wide variety of organisms (for example: bacteria, fungi, plants, and animals) and are characterized by the presence of at least one nitrogen atom (amino or amido) enclosed in a heterocyclic system [68]. The alkaloids more frequently present in the human diet come from coffee, cocoa, tea, and plants from the *Solanaceae* family (potatoes, tomatoes, and eggplants). In general, alkaloids are soluble in acidic water and insoluble in neutral water as free forms. Their salts dissolve in neutral water.

The effect of thermal treatments (boiling, baking, and frying) does not quantitatively reduce the

glycoalkaloids, which show great stability at temperatures below 260 - 270 °C. Similar to solanine from potatoes, tomatine from ripe tomatoes has high stability, with greater losses during prolonged storage for tomatine from green tomatoes and losses of more than 90% in the case of lyophilization and freezing (-20 °C) [69].

2.8 Terpenes

Most dietary terpenes are present in seeds and herbs as part of essential oils. Biologically important tetraterpenoids include acyclic lycopene, monocyclic gamma-carotene, and bicyclic alpha- and beta-carotene. Terpenes are soluble in lipid medium. These linear and cyclized hydrocarbons are generally non-polar or mono-hydroxylated (non-polar: L-limonene, 5-epi-aristolochene, squalene, phytoene; partially polar: (-) menthone, capsidiol, β -sitosterol, gibberellin A4; with the highest polarity: (+)-neomenthyl- β -D-glucosides, β -sitosteryl linoleate, lutein), and their volatility decreases with increasing molecular weight. The characteristics (e.g., size, polarity, nature of the terpene molecule) of these terpene scaffolds are modified by hydroxylation, glycosylation, and acylation reactions [70]. In the study conducted by Martin *et al.*, [71], it is demonstrated that the solubility of terpenes in water shows a linear increase with temperature, the solubilities of the molar fractions being of the order of 10^{-4} , confirming the hydrophobic property of this class of phytochemical compounds. Low molecular weight terpenes are usually heat labile and susceptible to volatilization and degradation, mainly by oxidation and isomerization. De Matos *et al.*, [72], evaluated the strategies by which the stability of terpenes can be preserved under different environmental conditions. Encapsulation in micro or nanometric systems improves the bioavailability and bioefficacy of formulations and the controlled release of bioactive compounds.

2.9 Glucosinolates

Glucosinolates are secondary metabolites present in all *Brassica* families such as canola, cabbage, cauliflower, Brussels sprouts, turnips, broccoli, Chinese cabbage, radishes, mustard seeds, horseradish, etc. They are soluble in aqueous medium. Glucosinolates are hydrolyzed by the enzyme myrosinase to isothiocyanates, thiocyanates, nitriles, epithionitriles, hydroxynitriles, and oxazolidin-2-thiones. These reactions are influenced by the characteristics of the hydrolysis medium (e.g., ascorbic acid, epithio-specific protein (ESP), ferrous ions, pH, and temperature). The order of thermostability of individual glucosinolates at 80 °C changes at 120 °C due to differences in activation energies. During heat processing of *Brassica* vegetables, the glucosinolate content is reduced by enzymatic or thermal breakdown and

diffusion into the heating medium [65]. An example is the study conducted by Renz *et al.*, [73], in which they demonstrated that glucosinolates degrade into nitriles upon heat treatment, the heat stability is dependent on the concentration of the plant matrix, the abundance of H_2S , and the redox potential of the plant matrix. Side-chain oxidation and nitrile formation of glucosinolates compete during boiling. Some of the hydrolysis products can affect the smell and taste of food, the bitter taste can be caused by gluconapine, sinigrin, and 5-vinylloxazolidin-2-thione. In the review carried out by Barba *et al.*, [74], when studying *Brassica* vegetables during different thermal treatments (steaming, boiling, under vacuum, baking, frying, and microwaves) recorded a decrease in the content of glucosinolates in the range of 20 - 90%, with the steaming treatment registering the lowest loss of glucosinolate content.

2.10 Polyacetylenes

Acetylenic natural products are widely distributed, and present in plants, fungi, seaweeds, and sponges. Falcarinol, falcarindiol, falcarindiol-3-acetate, and panaxadiol type polyacetylenes are naturally found in plants from the *Apiaceae* and *Araliaceae* families, the most studied being in carrots and parsnips, parsley, celery, fennel [75]. Polyacetylenes show hydrophobicity, their reactivity being explained by their ability to stabilize the carbocation formed in the C-3 position by the conjugated triple bonds that favor nucleophilic substitution in this position [75]. Polyacetylenes are unstable in an oxidative, photolytic, or in thermal environment or in the case of pH changes. The concentration of polyacetylenes in carrots decreases by 25 - 50% after exposure to 90 °C for 2 minutes and by 70% after boiling for 12 minutes. Roasting fennel bulb slices (160 °C for 15 min) resulted in a significant decrease of falcarindiol, falcarindiol-3-acetate, and falcarinol by 81%, 78%, and 66%). Experiments confirm the heat sensitivity of falcarinol-type polyacetylenes [75]. Aguiló-Aguayo *et al.*, [76], found that the levels of falcarindiol-3-acetate and falcarinol in carrot juices acidified with ascorbic acid increased in parallel with increasing processing temperature. The highest levels were obtained by treating at 90 °C for 1 minute. An explanation would be the solubilization of intercellular cementing pectin facilitating the release of unbound polyacetylenes. Temperatures below 60 °C can activate the enzyme systems involved in the breakdown of pectins in the cells.

2.11 Capsaicinoids

The source of capsaicinoids are the pigments of pepper fruits: the most common are capsaicin (46% of total capsaicins), dihydrocapsaicin (~41%), nordihydrocapsaicin (7%), homocapsaicin (3%),

homodihydrocapsaicin (2%). The red color of ripe pepper fruits is due to the pigments capsanthin, its isomer capsorubin, and β -cryptoxanthin present as fatty acid esters. The pigments are present exclusively in peppers, they are not found in any other plant or animal species. The intensity of the red color of a pepper depends on the amount of these pigments [77]. Fat-soluble compounds formed from homovanillic acid that is insoluble in water, with an amphiphilic character that can favor their solubilization in emulsion. The matrix with the highest stability of capsaicinoids are oleoresins, which do not degrade at high temperatures and long-term storage. Reducing the water content of the fruit by drying affects the stability of the capsaicinoids. Drying ripe fruit at 60 °C to 8% moisture content decreases capsaicin content by 10%, losing 1-2%/month in cold storage and even more in ambient storage [77]. Studies on the stability of capsaicinoids to thermal processing demonstrate that it is dependent on genotype, stage of ripening, and processing conditions. In the study published by Campos *et al.*, [78], it was demonstrated that the intensity of thermal processing affects the digestive stability of capsaicinoids in green pepper (compared to fresh pepper the stability is reduced by 55% by boiling and by 72% by baking). Hamed *et al.*, [79], found that roasting significantly changes the levels of capsaicinoids correlated with the degree of maturity in different pepper varieties. Zhang *et al.*, [80], studied the thermal treatment stability of carotenoids and capsaicinoids in two chili juice food matrices (water system, CJ and oil system, HPB). Significant decreases instability were observed in CJ when the temperature increased from 60 to 100 °C (the contents of capsorubin, capsanthin, zeaxanthin, β -cryptoxanthin and β -carotene decreased by 30.25%, 25.82%, 31.00%, 23.85%, respectively 27.03% compared to the control). At temperatures below 60 °C, the stability did not change. The release and exposure to oxygen, and the isomerization of carotenoids can be accentuated by their increased diffusivity, which occurs naturally at high temperatures. No changes in carotenoid content were recorded in HPB at different heat treatment temperatures. The hypothesis is that the lipophilic system acts as an effective antioxidant, the carotenoids being easily encapsulated by hydrophobic fats that block contact with oxygen, reducing heat damage. The effective antioxidant action of capsaicin is also assumed. The conclusion of the study indicates that the oil can improve the stability of carotenoids and capsaicinoids to heat treatment.

2.12 Polysaccharides

Polysaccharides are macromolecules made up of monoglycoside units, covalently linked by α - and/or β -glycosidic bonds. Cellulose, pectin, and starch are some of the natural polysaccharides widely found in

plants, present in their primary cell wall. Numerous studies have been carried out on polysaccharides belonging to the Amaryllidaceae family (especially onions and garlic) due to their pharmacological properties and high dietary intake. They are both soluble and insoluble in water depending on the structure and monoglycoside unit. Li and Liu [81], studied the influence of temperature on the activity of 4 cold-water-soluble polysaccharides from the mushroom *G. frondosa* and the relationship between their structures and inhibitory activities on human lung tumor cells after heating at different temperature gradients. Heat treatment led to different levels of degradation, and their degrees of branching were reduced, resulting in lower antitumor effects.

2.13 Allium compounds

The most studied edible sources of *Allium* phytochemical compounds are onions, garlic, chives, and shallots, in a wide variety of varieties, distributed globally. *Allium* species contain significant amounts of flavonoids, phytosterols, steroidal saponins, organosulfur compounds, and other biologically active metabolites. The most representative bioactive sulfur compounds from *Allium* vegetables are alk(en)yl cysteine sulfoxides, S-allyl cysteine, thiosulfonates, diallyl, mono-di-, and tri-sulfides, vinylthiols. In garlic, more than 70% of thiosulfonates are formed from alliin which is degraded into di- and tri-sulfides. Garlic is the best source of thiosulfonates, with an average of 15 - 53 $\mu\text{mol/g}$, followed by onions with concentrations < 0.35 $\mu\text{mol/g}$ [82].

Organosulfur compounds (OSC) are known to be thermally labile and capable of undergoing heat-induced non-enzymatic transformations. Putnika *et al.*, [83], reviewed the chemical composition, and effects of processing on the nutritional and bioactive composition of *Allium* species and their extracts. Decomposition of alliin in a first-order reaction was observed at 60, 80, and 89 °C leading to the formation of S-Allylcysteine, allyl alanine sulfide, and dialanine sulfide ethers, compounds responsible for increasing the antioxidant properties of heat-treated alliin extract. Thermal degradation products of alliin and methionine (obtained in closed model systems), could non-enzymatically contribute to the typical flavor of processed *Allium* vegetables. The presence of flavones in solutions can mitigate the decomposition of OSC or volatile compounds by inhibiting their thermal degradation, and the presence of glucose can affect the level of volatile compounds. Purified alliinase has optimal enzyme activity between 35 and 40 °C. At 60 °C alliinase loses 50% of its activity after 15 minutes. Thiosulfonates are relatively unstable and able to decompose into polysulfides, thiosulfonates, and other OSCs with reaction rates influenced by temperature

and pH. Other studies, mentioned by the authors, determined the stability of allicin at pH = 5 - 6, and the presence of flavones slightly promoted the stability of allicin at room temperature. Blanching white leek stem was found to increase isoaline and methionine content while boiling degraded these compounds. Alliinase inactivation time they strongly depended on the heating method, temperature, and heat transfer rate. Locatelli *et al.*, [84], determined the antioxidant capacity of OSC from garlic paste cooked by boiling methods (in water, steam, and frying) compared to untreated garlic paste. The antioxidant capacity is present in all samples, although it is diminished compared to the raw paste. The mechanism of action characterizing the antioxidant activity of the raw garlic samples was the scavenging of free radicals versus the reduction of iron ions in the case of the cooked samples. For the roasted samples, the mechanism of action was found to be mainly pro-oxidant enzyme inhibitory activity as well as the ability to break radical chain propagation reactions. Ko and Nile [85], conducted a study to determine the effect of thermal treatments (boiling, frying, steaming) on OSC from onion bulbs. Onion OSCs include trans-S-1-propenyl-L-cysteine sulfoxide (> 70%), S-methyl-L-cysteine sulfoxide (20 - 25%), S-propyl-L-cysteine sulfoxide (< 10%) and smaller amounts of thiophene derives. Frying and steaming treatments retained the highest content of total OSC. When boiling in water, the content was significantly reduced (by 46.8%) due to losses in the cooking water, while no losses were observed by other cooking methods (microwaves).

2.14 Betalains

Betalains are a class of nitrogen pigments, present in beetroot, cactus fruits, and *Amaranthaceae* plants. They are soluble in water and polar solvents. Betalains stability is influenced by several factors: concentration, structure, matrix constituents, temperature, light, and storage conditions. It is documented that the stability of betalains in technological processes involving high temperatures is limited. The studies carried out recorded a degradation of betalains of the first order during the thermal treatment. The degradation kinetics is constant and increases proportionally with the increase in temperature, at high temperatures the degradation is accentuated. In various reports, a reduction of pH below 7 increased the degradation of these pigments at different temperatures [86]. During heat processing, betanin can be decomposed through a series of reactions such as isomerization, decarboxylation, and hydrolytic cleavage, leading to a gradual reduction of the red color and finally to the production of a light brown color. The stability of betaine has been shown to decrease dramatically in the temperature range of 50 - 80 °C [87].

3. Conclusions

- Foods rich in phytochemicals, such as fruits, vegetables, legumes, whole grains, nuts, and seeds, act as a natural medicine to improve health and longevity. The deficiency of phytochemical compounds contributes to the increase in the incidence of chronic non-communicable diseases. The detailed knowledge of the characteristics of phytochemical compounds helps the industry to design foods that, through the composition of the matrix and preparation methods, ensure the improvement of their bioaccessibility from the food matrix.
- Knowing the factors that can affect the stability of phytochemical compounds and understanding the chemical and enzymatic degradation pathways opens up a process of analysis where the phytochemical content can be severely affected by the food preparation method.
- The stability of phytochemical compounds in food matrices, subjected to heat treatment, differs a lot, as this review shows. The development of functional foods based on phytochemical compounds requires strategies to maximize their bioavailability by: *in vivo* evaluation of the findings of the mechanisms of action of phytochemicals *in vitro*; establishing dietary reference intakes for a wider range of micronutrients; development of foods with phytochemical compounds for an optimal micronutrients content and identifying individual biological responses to functional foods.

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