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UNVEILING THE FUNCTIONAL IMPLICATIONS AND COMPLEX INTERPLAY BETWEEN BOUND PHENOLIC COMPOUNDS AND PHENOLICS IN FOOD: A COMPREHENSIVE REVIEW

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ABSTRACT

Bound phenolic compounds (BPs) are abundant in plant-based foods and have gained increasing attention due to their potential health benefits. However, the physiological implications of BPs and their interactions with food matrices remain relatively unexplored. This review aims to provide a comprehensive overview of the functional implications of BPs and the complex interplay between BPs and food components. The digestion process plays a crucial role in determining the bio-accessibility and bioavailability of BPs. Upon reaching the large intestine, BPs encounter the vast and diverse gut microbiota, leading to microbial transformation and the generation of bioactive metabolites. The catabolic activity of gut microbiota, termed colonic fermentation, involves various structural modifications of parent BPs, resulting in the production of microbial metabolites. The characteristics of the food matrix, the type of phenolic–food macromolecule interaction, and the chemical nature of the BPs significantly influence the amount of BPs reaching the colon and the rate of microbial transformation. Moreover, the release kinetics of BPs to the colonic lumen can be modulated through the addition of certain ingredients or technological processes during food processing. The functional implications of BPs on gut microbiota are extensive, including prebiotic effects, anti-microbial properties, and regulation of gut microbial metabolism. BPs can selectively stimulate the growth of beneficial gut bacteria, inhibit the growth of harmful microbes, and influence the production of short-chain fatty acids, which are essential for gut health. Additionally, the synergistic effects of BPs and dietary fiber on gut microbial ecology have been observed, further highlighting the intricate interactions between phenolics and food components. Understanding the functional implications of BPs and their interactions with food matrices is crucial for harnessing their potential health benefits and designing innovative food products with enhanced bioactivity. Further research in this area will shed light on the complex mechanisms underlying BPs' effects on gut microbiota and their overall impact on human health.

***Keywords*:** Functional food, Health benefits, Microbiota

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1. INTRODUCTION

Phenolic compounds, abundant secondary metabolites found in various plant tissues, have garnered significant attention for their diverse functional implications on human health. Among the vast array of phenolic compounds, bound phenolic compounds (BPs) stand out as a particular focus of research due to their unique interactions with dietary fibers and other food components. The interplay between BPs and the food matrix not only influences the bio-accessibility and digestion of phenolics but also exerts a profound impact on their health-promoting effects (Ferreira et al. 2017). Phenolic compounds have long been acknowledged for their pivotal roles in plant defense mechanisms and adaptation responses to environmental stressors. Moreover, they contribute to the sensory attributes of fruits, flowers, and vegetables, enhancing the flavor and color of various plant-based foods. Beyond their aesthetic and ecological functions, phenolic compounds have captured the interest of researchers due to their potential health benefits. Studies have revealed that these bioactive compounds possess antioxidant, anti-inflammatory, antitumor/anticancer, pharmacological, and antimicrobial properties, making them promising candidates for preventing chronic diseases and promoting overall well-being (Wong et al. 2013; Roleira et al. 2015; Lin et al. 2016; Alu'datt et al. 2018; Lyu et al. 2020; Zhai et al. 2021; Rahman et al. 2021; Ngo et al. 2022; Fu et al.

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2022). The chemical structure of phenolic compounds, consisting of an aromatic ring with one or more hydroxyl groups, plays a crucial role in determining their biological activities. Furthermore, the biochemical pathways involved in the production of phenolics, with shikimic acid as the main precursor, contribute to the extensive diversity of phenolic compounds, with over 8000 varieties identified to date. In the quest to comprehend the functional implications of phenolic compounds, researchers have classified them into two main groups: flavonoids and nonflavonoids. Nonflavonoids encompass phenolic acids, lignans, stilbenes, and other lower molecular weight compounds, each exerting distinct biological effects. Additionally, phenolic compounds can be categorized as free, conjugated, or insoluble bound phenolics (BPs). The covalent attachment of BPs to the structural components of the plant cell wall distinguishes them from their free and conjugated counterparts, giving rise to unique functional properties (Chawla et al. 2023). Understanding the interactions between BPs and the food matrix is crucial in comprehending their bioavailability and physiological impact. BPs may form complex associations with dietary fibers, proteins, lipids, and other food components, influencing their solubility, stability, and release during digestion. Such interactions can affect the liberation of phenolic compounds in the gastrointestinal tract, influencing their absorption and metabolism (Du and Myracle 2018; González et al. 2021; Wang et al. 2022).

In this review, we aim to provide a comprehensive analysis of the functional implications arising from the interaction of BPs and phenolics with dietary fibers and other food components. We explore their influence on phenolic bio-accessibility, transformation during digestion, and their role in modulating the composition and activity of the gut microbiota. By shedding light on the intricate relationships between BPs and the food matrix, this review seeks to elucidate how dietary choices and food processing methods can impact the health-promoting effects of phenolic compounds. A deeper understanding of these interactions could pave the way for optimizing dietary strategies to harness the full potential of phenolic compounds for human health and well-being.

1.1. Structural Diversity of Phenolic Compounds

The structural diversity of phenolic compounds (PCs) is vast, with a wide range of chemical configurations found in various plant tissues. PCs are secondary metabolites synthesized by plants that play essential roles in their defense mechanisms, environmental adaptation, and interaction with their surroundings. These compounds are not only beneficial for plants but also have significant implications for human health due to their bioactive properties. Understanding the diverse structural classes of PCs is crucial in exploring their biological activities and potential applications in medicine, nutrition, and other fields (Rocchetti et al. 2022).

***1.1.1. Phenolic Acids*:** Phenolic acids constitute a significant group of PCs and are commonly divided into two main categories: hydroxycinnamic acids and hydroxybenzoic acids. These compounds are widely distributed across different vegetal products, including fruits, vegetables, grains, and nuts. Phenolic acids participate in various biochemical processes within plants, influencing growth, development, and defense against pathogens and environmental stresses. Hydroxycinnamic acids contain a C6-C3 backbone (Rocchetti et al. 2022). Some well-known examples of hydroxycinnamic acids include p-coumaric acid, caffeic acid, and ferulic acid. These compounds are often found bound to other molecules or components of the plant cell wall, making them insoluble in water. Hydroxybenzoic acids, on the other hand, feature a C6-C1 backbone, with a phenyl group substituted by a carboxylic acid and at least one hydroxyl group. Common examples include salicylic acid, protocatechuic acid, vanillic acid, and gallic acid. Like hydroxycinnamic acids, hydroxybenzoic acids are also usually found as bound forms within the plant cell (Fig. 1)

***1.1.2. Flavonoids*:** Flavonoids are among the most abundant and diverse groups of phenolic compounds found in plants. They are characterized by a phenyl benzopyran skeleton formed by two phenyl rings (A, B) connected by a heterocyclic pyran ring (C). Flavonoids are usually water-soluble and often occur in glycoside-conjugated forms in fruits, vegetables, and derived products. The vast array of flavonoids exceeds 6000 identified varieties, each with unique chemical structures and potential biological activities. Flavonoids have been extensively studied for their health-promoting effects, particularly due to their antioxidant and anti-inflammatory properties (Vuolo et al. 2019). Different classifications of flavonoids have been proposed, and the six major families include:

i) Flavonols, such as kaempferol and quercetin.
ii) Flavones, including apigenin and luteolin.
iii) Flavanones, represented by hesperidin and naringenin.
iv) Flavan-3-ols, like catechin and epicatechin, which can polymerize to form condensed tannins.
v) Anthocyanidins are responsible for the vibrant colors of fruits and flowers, like pelargonidin and cyanidin.
vi) Isoflavones, known for their estrogenic properties, such as genistein and daidzein.
vii) Flavonoids can undergo various modifications in nature, including glycosylation, esterification, and polymerization reactions, resulting in different subclasses with unique properties.

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1.1.3. ***Stilbenes*****:** Stilbenes are another class of phenolic compounds characterized by two phenyl rings joined by a two-carbon bridge (C6-C2-C6). These compounds serve as phytoalexins, which are defense molecules produced by plants in response to pathogenic attacks or environmental stresses. One of the most well-known stilbenes is resveratrol, found in the skin of red grapes, wine, and other berries. Resveratrol has attracted significant attention for its potential health benefits, particularly its cardioprotective and anti-aging properties (Rocchetti et al. 2022).

1.1.4. **Coumarins:** Coumarins represent a distinct group of bioactive phenolic compounds, featuring a fused benzenic ring with an oxygen heterocycle. Coumarins are found in various vegetal tissues and are abundant in essential oils of plant families like Asteraceae, Apiaceae, and Rutaceae. This class of compounds is further divided into different subclasses, including simple coumarins, furocoumarins, pyranocoumarins, and substituted coumarins. Some examples of common coumarins found in plant foods include hydroxycoumarin, esculetin, bergamottin, deltoin, and khellactone (Ferreira et al. 2017).

1.1.5. **Lignans:** Lignans represent a group of PCs formed by two phenylpropanoid units (C6-C3-C3-C6). They are typically found in cereals, fruits, and vegetables, with flaxseeds being particularly rich in these compounds. Lignans, such as secoisolariciresinol, matairesinol, and sesamin, have been studied for their potential health benefits, including their role as antioxidants and their ability to mimic phytoestrogens (Luna-Guevara et al. 2018).

1.2. Interactions of Dietary Fibers: Covalent and Noncovalent Bonds

Covalent and noncovalent interactions with dietary fibers play a crucial role in shaping the bioavailability and bioactivity of phenolic compounds (PCs) in plant-based foods. These interactions occur within the complex food matrix and significantly influence the nutritional and health benefits derived from the consumption of such foods. Understanding the mechanisms and implications of these interactions is essential for optimizing the delivery and potential health-promoting effects of PCs (Jakobek et al. 2020).

1.2.1. ***Noncovalent Interactions*****:** Noncovalent interactions are reversible interactions between PCs and dietary fibers, driven by various forces, such as van der Waals forces, electrostatic attraction, hydrophobic contacts, and hydrogen bonding. Among these forces, hydrogen bonding plays a dominant role in determining the binding affinity between PCs and dietary fibers. Hydrogen bonding involves attractive interactions between the hydroxyl groups of PCs and the polar groups in dietary fibers, such as hydroxyl or carboxyl groups. These interactions are relatively weak and can be influenced by environmental factors such as pH, temperature, and ionic strength (Jakobek and Matić, 2019). One of the significant consequences of non-covalent interactions is the formation of inclusion complexes between PCs and dietary fibers. PCs can become entrapped within the porous structure of dietary fibers, leading to improved stability, protection against degradation, and controlled release of PCs during digestion. This inclusion of complex formation can enhance the bioavailability of PCs by shielding them from enzymatic degradation and promoting their absorption in the gastrointestinal tract (Zhu et al. 2018). Moreover, noncovalent interactions can modify the physicochemical properties of PCs, such as solubility and antioxidant activity. PCs bound to dietary fibers may exhibit altered water solubility, which can affect their release and distribution in the food matrix and during digestion. Additionally, the antioxidant activity of PCs can be influenced by their interaction with dietary fibers, as the accessibility of reactive sites and the reaction kinetics may be altered in the bound form (Jakobek and Matić, 2019).

1.2.2. ***Covalent Interactions*****:** Covalent interactions involve the formation of chemical bonds between PCs and components of dietary fibers, resulting in mostly irreversible binding. These interactions occur via covalent cross-linking, where PCs become covalently attached to the structural polysaccharides (e.g., cellulose, hemicellulose, pectin, and arabinoxylans) and rod-shaped proteins (e.g., lignin) present in dietary fibers (Rocchetti et al. 2022).

In plants, covalent bonding with dietary fibers is a natural defense mechanism against pathogens, insects, and environmental stresses. PCs, as part of the plant's defense system, can form covalent bonds with cell wall components, reinforcing the structural integrity of the plant and providing protection against external threats. The covalent attachment of PCs to dietary fibers can also contribute to the formation of complex macromolecular structures, such as lignin–phenolic acid and lignin–flavonoid complexes. These interactions can result in the formation of complex matrices within the cell walls, influencing the mechanical properties and physiological functions of plant tissues (Jakobek and Matić 2019).

1.3. Phenolics: Understanding their Bioaccessibility

The bioaccessibility of phenolics refers to the proportion of these compounds that are released from the food matrix during digestion and are potentially available for absorption in the gastrointestinal tract. It is a critical aspect

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of understanding the health-promoting effects of phenolics present in plant-based foods. The bioaccessibility of phenolics plays a key role in determining their bioavailability, which refers to the actual amount of phenolics that are absorbed into the bloodstream and are available for various physiological functions in the body (Jakobek and Matić 2019). During digestion, phenolics are embedded within the complex food matrix, bound to various components such as dietary fibers, proteins, and lipids. These interactions can affect the release of phenolics during digestion and their subsequent absorption in the intestine. Phenolics that are bound tightly to food components may have reduced bioaccessibility as they are less likely to be released and become available for absorption. On the other hand, phenolics that are loosely bound or remain in a soluble form have higher bioaccessibility as they are more readily released and absorbed (Tomas et al. 2020). The bioaccessibility of phenolics can vary widely depending on the food source and the processing methods used. For instance, phenolics in raw fruits and vegetables may have higher bioaccessibility compared to cooked or processed foods due to changes in their chemical structure caused by cooking or processing. Furthermore, the presence of dietary fibers can significantly influence the bioaccessibility of phenolics. Phenolics can form noncovalent interactions with dietary fibers, such as hydrogen bonding, which can reduce their release during digestion and lower their bioaccessibility. However, these interactions can also have beneficial effects, such as protecting phenolics from degradation by digestive enzymes and delivering them to the colon where they may undergo fermentation by gut microbiota (Jakobek and Matić 2019).

In vitro, digestion models are commonly used to simulate gastrointestinal conditions and assess the bioaccessibility of phenolics. These models involve a series of steps that mimic the oral, gastric, and intestinal phases of digestion, and they allow researchers to study the fate of phenolics during digestion and absorption. Various factors, such as pH, temperature, food particle size, and the presence of bile salts and digestive enzymes, are carefully controlled in these models to replicate physiological conditions as closely as possible (Rocchetti et al. 2020). In recent years, researchers have also started exploring dynamic digestion models that incorporate a colonic fermentation step to better understand the fate of phenolics in the lower parts of the digestive tract. This approach provides more comprehensive information about the bioaccessibility and potential health effects of phenolics. Understanding the bioaccessibility of phenolics is crucial for predicting their health benefits, as only bioaccessible phenolics can be absorbed and exert their potential antioxidant, anti-inflammatory, and other bioactive effects in the body. Research in this area continues to evolve, providing valuable insights into the factors that influence the bioaccessibility of phenolics and how food processing and preparation methods can impact their availability for human health (Rocchetti et al. 2022).

1.4. Presence of Bioactive Compounds (BPs) in Plant-Based Foods: Extracting and Profiling BPs

Extraction and profiling of Bound Phenolic Compounds (BPs) from plant foods are essential steps in understanding their occurrence, composition, and potential health benefits. BPs are phenolic compounds that are not easily soluble in aqueous or organic solvents due to their interactions with macromolecules like cellulose, protein, and lignin, as well as the presence of covalent bonds in the plant cell wall. Extracting and characterizing BPs requires specialized techniques to release them from their bound forms and analyze their chemical structures.

Extraction Methods

1.4.1. Chemical Methods: Chemical methods involve the use of various solvents or reagents to break the bonds between BPs and other plant components. Common solvents used include methanol, ethanol, and acetone. Acid hydrolysis is another chemical approach that uses acid (e.g., hydrochloric acid) to cleave the covalent bonds and release BPs. However, these methods can be harsh and may lead to the degradation of some phenolic compounds.

***1.4.2. Enzymatic Methods*:** Enzymatic methods utilize enzymes (e.g., cellulases, hemicellulases, and pectinases) to specifically target and break down the cell wall components, liberating BPs from their bound forms. Enzymatic methods are considered gentler and more specific compared to chemical methods, allowing for a more accurate profiling of BPs (Tomas et al. 2020).

***1.4.3. Physical Methods*:** Physical methods involve mechanical disruption of the plant cell walls using techniques such as grinding, homogenization, or ultrasonication. These methods help to release BPs by breaking the physical barriers that bind them to the cell wall components.

Profiling of BPs

Once BPs are extracted, various analytical techniques are used to profile and identify the individual phenolic compounds present:

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***1.4.4. High-Performance Liquid Chromatography (HPLC)*:** HPLC is a powerful analytical technique used to separate and quantify individual phenolic compounds in a mixture. It allows for the identification of specific phenolics present in the extract and the determination of their concentrations.

***1.4.5. Gas Chromatography-Mass Spectrometry (GC-MS)*:** GC-MS is commonly used to analyze volatile phenolic compounds. After extraction, the compounds are converted to volatile derivatives and analyzed using gas chromatography, followed by mass spectrometry for identification.

***1.4.6. Liquid Chromatography-Mass Spectrometry (LC-MS)*:** LC-MS is another widely used technique that combines liquid chromatography with mass spectrometry for the identification and quantification of phenolic compounds. It provides high sensitivity and selectivity for the analysis of complex phenolic mixtures (Rocchetti et al. 2022).

***1.4.7. Nuclear Magnetic Resonance (NMR) Spectroscopy*:** NMR spectroscopy is a non-destructive technique that provides structural information about phenolic compounds. It is particularly useful for determining the connectivity of atoms in the molecules.

***1.4.8. Total Phenolic Content (TPC) Assays*:** TPC assays, such as the Folin-Ciocalteu method, are colorimetric assays that provide a quick estimate of the total phenolic content in an extract. While they do not give specific information about individual phenolics, they offer a rapid assessment of the overall phenolic content. The combination of these extraction and profiling techniques allows researchers to gain insights into the composition and diversity of BPs present in different plant foods. Understanding the occurrence and bioavailability of BPs is crucial for evaluating their potential health benefits and contributes to the growing knowledge of the roles of phenolic compounds in human nutrition and wellness (Tomas et al. 2020).

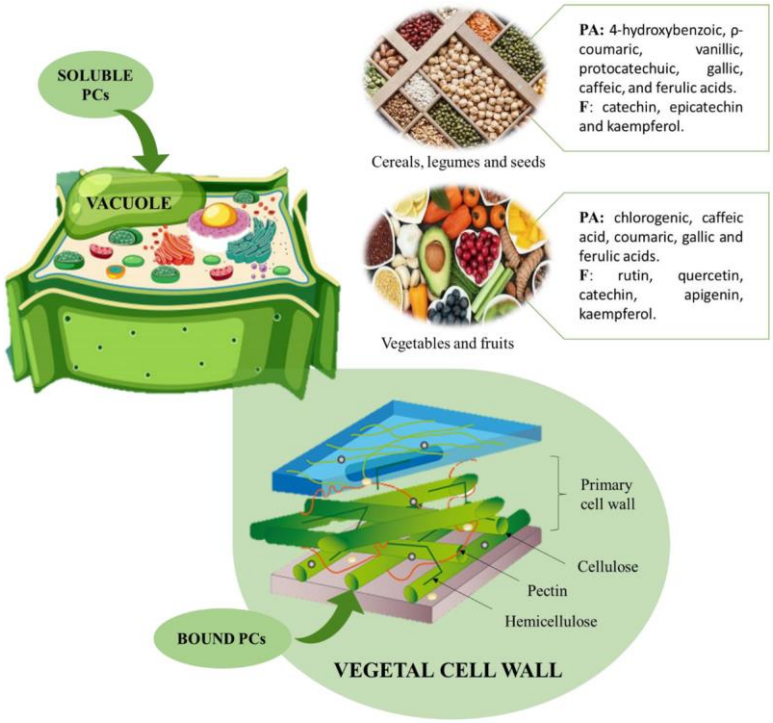

Fig. 1: Distribution of soluble and insoluble bound phenolic compounds (PCs) and several of the phenolic acids (PA) and flavonoids (F) present in different plant foods (Rocchetti et al. 2022).

1.5. Alkaline and Acidic Hydrolysis: Chemical Extraction Methods

Alkaline and acidic hydrolysis are chemical extraction methods used to release bound phenolic compounds (BPs) from plant materials. BPs are phenolic compounds that are tightly bound to macromolecules like cellulose, lignin, and proteins in the plant cell wall, making them insoluble in aqueous or organic solvents. Alkaline and acidic hydrolysis treatments are employed to break the ester and glycosidic bonds that link BPs to the cell wall components, thereby liberating the phenolic compounds for further analysis and characterization (Rocchetti et al. 2022).

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***1.5.1. Alkaline Hydrolysis*:** Alkaline hydrolysis involves treating the plant material with alkaline solutions, commonly using sodium hydroxide (NaOH) or potassium hydroxide (KOH). This method is particularly effective for releasing phenolic acids, which are prevalent BPs in plant tissues. The process of alkaline hydrolysis involves the following steps: a. Sample Preparation: The plant material is finely ground or homogenized to increase the surface area, facilitating the extraction process. b. Alkali Treatment: The plant material is mixed with an alkaline solution, such as NaOH or KOH, and the reaction is typically carried out in the dark under an inert gas atmosphere (argon or nitrogen) to prevent oxidation of the phenolic compounds. c. Ascorbic Acid or Chelators Addition: To minimize oxidation further, antioxidants like ascorbic acid or chelating agents may be added to the reaction mixture. d. Neutralization: After the hydrolysis reaction, the pH of the mixture is adjusted to neutral or slightly acidic values (around pH 3 or 4) using hydrochloric acid (HCl) or citric acid. This step prevents the formation of quinones, which can arise from the deprotonation of phenolic hydroxyl groups in a strong alkali environment. e. Filtration and Concentration: The mixture is then filtered to remove the insoluble residues, and the resulting extract is concentrated to obtain the liberated phenolic compounds (Rocchetti et al. 2022). Alkaline hydrolysis ensures the irreversible hydrolysis of ester bonds, effectively releasing BPs from their bound forms. However, this method may require longer extraction times and a more complicated sample pretreatment due to the need for strict conditions to prevent oxidation and quinone formation.

***1.5.2. Acidic Hydrolysis*:** In the acidic hydrolysis method, the plant material is treated with acidic solutions, often using hydrochloric acid (HCl) or sulfuric acid (H2SO4). This approach also breaks the ester and glycosidic bonds between BPs and the plant cell wall components, making the phenolic compounds accessible for further analysis. The process of acidic hydrolysis involves the following steps: a. Sample Preparation: Similar to alkaline hydrolysis, the plant material is ground or homogenized to increase the surface area for extraction. b. Acid Treatment: The plant material is mixed with an acidic solution, such as HCl or H2SO4, and the reaction is typically conducted at elevated temperatures to facilitate the hydrolysis process. c. Neutralization: After the hydrolysis, the pH of the mixture is adjusted to neutral or slightly alkaline values using a base like sodium hydroxide (NaOH) to neutralize the acidic solution. d. Filtration and Concentration: The extract is then filtered to remove any insoluble residues, and the liberated phenolic compounds are concentrated for further analysis. The acidic hydrolysis method may require higher processing temperatures, which can lead to the degradation of some phenolic compounds. However, like alkaline hydrolysis, it is an effective approach for releasing BPs from their bound forms (Rocchetti et al. 2022). Both alkaline and acidic hydrolysis methods have their advantages and drawbacks. Researchers should select the appropriate method based on the targeted compounds and the characteristics of the food matrix under investigation. These chemical extraction methods play a crucial role in understanding the occurrence and potential health benefits of BPs in plant foods, contributing to the broader knowledge of phenolic compounds' impact on human nutrition and health (Wang et al. 2020).

1.6. Enzymatic and Physical Extraction Methods for Bound Phenolic Compounds

Phenolic compounds in plant foods can exist in bound forms, tightly associated with macromolecules such as cellulose, hemicellulose, lignin, and proteins, making them difficult to extract using conventional methods. Enzymatic and physical extraction techniques offer alternative approaches to release these bound phenolic compounds (BPs) from the plant cell wall, providing valuable tools for researchers and food scientists to study and utilize the health-promoting properties of these bioactive compounds (Wang et al. 2020).

***1.6.1. Enzymatic Extraction Methods*:** Enzymatic extraction involves the use of specific carbohydrate-hydrolyzing enzymes to break down the complex structures of the plant cell wall and release BPs. Several types of enzymes are employed, each targeting different components of the cell wall, such as pectinase for pectin, cellulase for cellulose, hemicellulase for hemicellulose, amylase for starch, and β-glucosidase for glycosidic bonds (Wang et al. 2020). The process of enzymatic extraction typically includes the following steps:

i) **Enzyme Treatment:** The plant material is first treated with the appropriate enzymes, which are added to the extraction medium. The enzymes catalyze specific reactions, breaking the chemical bonds that link BPs to the cell wall components.
ii) **Hydrolysis:** The enzymes hydrolyze the ester and glycosidic bonds between the BPs and the macromolecules of the cell wall. This process liberates the phenolic compounds, making them available for further analysis.
iii) **Filtration and Concentration:** After enzymatic hydrolysis, the extract is filtered to separate the liberated BPs from the insoluble residues. The resulting extract, enriched with BPs, can then be concentrated for characterization and quantification (Wang et al. 2020).

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The efficiency of enzymatic extraction may vary depending on the complexity of the cell wall structure and the composition of phenolic compounds present in the plant material. Different plant sources and phenolic compounds may require specific enzymes and reaction conditions to achieve optimal extraction yields. Enzymatic extraction offers several advantages over conventional chemical methods. It is a milder and more specific approach, as it targets the bonds between BPs and the cell wall without the use of harsh chemicals. Additionally, enzymatic extraction can help preserve the integrity and bioactivity of the released phenolic compounds (Wang et al. 2020).

***1.6.2. Physical Extraction Methods*:** Physical extraction methods utilize non-conventional technologies, such as ultrasonication, microwaves, and ultrahigh pressure, to disrupt the plant cell wall and enhance the release of BPs. These techniques apply energy to the plant material, leading to mechanical or thermal effects that facilitate the solubilization of phenolic compounds. The process of physical extraction includes the following steps:

i) Application of Energy: Ultrasonication involves the application of high-frequency sound waves that create cavitation bubbles, leading to mechanical disruption of the cell wall. Microwave extraction uses electromagnetic waves to generate localized heating within the plant material, causing rapid expansion and contraction and breaking down the cell structure. Ultrahigh-pressure treatment involves subjecting the plant material to extreme pressure, leading to mechanical disruption of the cell wall.
ii) Increased Solubilization: The application of energy accelerates the solubilization of phenolic compounds, enabling them to be released into the extraction medium.
iii) Filtration and Concentration: After physical treatment, the extract is filtered to separate the liberated phenolic compounds from the solid residues. The resulting extract can then be concentrated for further analysis.

Physical extraction methods offer advantages such as reduced extraction time, improved efficiency, and preservation of thermolabile compounds compared to conventional techniques. They are particularly useful for processing large quantities of plant material and enhancing the extraction efficiency of BPs (Wang et al. 2020).

1.7. Profiling and Analysis of BPs by Targeted/Untargeted Metabolomics

Profiling and analyzing bound phenolic compounds (BPs) in complex food matrices often require advanced analytical techniques, and metabolomics approaches play a vital role in this endeavor. Metabolomics is a rapidly evolving field that aims to comprehensively study and identify small molecule metabolites present in biological systems, including foods. It can be categorized into two main strategies: targeted and untargeted metabolomics.

***1.7.1. Targeted Metabolomics*:** Targeted metabolomics involves the quantification and identification of specific known compounds of interest. Researchers select a set of target compounds based on prior knowledge or specific research questions. In the context of BPs, researchers may choose to target specific phenolic acids, flavonoids, lignans, or other phenolic compounds known to be present in the food matrix under investigation. Targeted metabolomics uses various analytical techniques, such as liquid chromatography (LC) or gas chromatography (GC) coupled with mass spectrometry (MS), to quantify and characterize the selected compounds accurately (Wu et al. 2018).

For example, in a study focused on BPs in blueberries, researchers might target specific anthocyanins, flavonols, and hydroxycinnamic acids known to be present in blueberries. LC-MS/MS can be utilized to precisely quantify and identify these targeted compounds, providing valuable information about their abundance and distribution in the food sample.

***1.7.2. Untargeted Metabolomics*:** In contrast, untargeted metabolomics aims to comprehensively analyze all metabolites present in a given sample without prior knowledge of their identities. This unbiased approach allows researchers to identify unexpected or novel compounds that may not have been previously characterized. Untargeted metabolomics relies on powerful analytical techniques, such as high-resolution mass spectrometry combined with advanced data processing and statistical analysis methods (Rocchetti et al. 2022). In the context of BPs, untargeted metabolomics can reveal the presence of lesser-known or unidentified phenolic compounds, providing insights into the complex chemical composition of the food matrix. By comparing the metabolite profiles of different food samples, researchers can identify characteristic metabolic fingerprints that distinguish one food from another.

***1.7.3. Challenges and Advantages*:** Both targeted and untargeted metabolomics approaches have their strengths and limitations. Targeted metabolomics is more focused and allows for accurate quantification and identification of specific compounds, making it suitable for hypothesis-driven research. On the other hand, untargeted metabolomics provides a more holistic view of the metabolome and allows for the discovery of novel compounds, but it may

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require more extensive data analysis and validation efforts (Rocchetti et al. 2022). Profiling and analyzing BPs using metabolomics approaches can significantly enhance our understanding of the chemical diversity and health-promoting properties of these compounds in various foods. This knowledge has implications for food quality, safety, and nutritional value, as well as the development of functional foods and dietary interventions targeting specific health benefits. However, due to the complexity of metabolomics data and the diversity of phenolic compounds, collaborations between food scientists, chemists, bioinformaticians, and nutritionists are crucial for the successful application and interpretation of metabolomics studies in the context of BPs.

1.8. Profile and Distribution in Cereals and Pseudocereals, Legumes, and Vegetables

Profile and distribution of bound BPs (Fig. 1) in cereals and pseudocereals, legumes, and vegetables are of great interest in the field of nutrition and food science. These compounds, which are covalently bound to the plant cell wall and are insoluble in water or organic solvents, play essential roles in the plant's defense against environmental stressors, such as UV radiation, pathogens, and herbivores. Additionally, BPs are recognized for their potential health benefits and contribute significantly to the nutritional value of various plant-based foods.

***1.8.1. Cereals and Pseudocereals*:** Cereals and pseudocereals, such as maize, rice, barley, oat, quinoa, and wheat, are staple foods in many regions. These grains contain varying levels of BPs, which are primarily found in protective tissues, including the bran, pericarp, and seed coat. The nutritional tissues of grains typically have lower amounts of BPs. Phenolic acids and flavonoids are among the major classes of BPs identified in these cereals. For example, p-coumaric acid, ferulic acid, vanillic acid, and caffeic acid are commonly found in cereals. The distribution of BPs in different grains can vary based on factors such as the genotype, environmental conditions, and processing methods (Wang et al. 2020).

***1.8.2. Legumes*:** Legumes, including lentils, chickpeas, kidney beans, black beans, and soybeans, are rich sources of protein, dietary fiber, and various bioactive compounds, including BPs. Similar to cereals, BPs in legumes are predominantly found in the outer protective layers, such as the seed coat. They contribute to the legumes' defense mechanisms and potential health benefits. BPs in legumes include phenolic acids like protocatechuic, gallic, p-coumaric, and ferulic acids, as well as flavonoids and their derivatives. The distribution and content of BPs can vary among different types of legumes and even within varieties of the same legume species (Shahidi and Yeo 2016).

***1.8.3. Vegetables*:** Vegetables are an essential part of a balanced diet and are rich sources of vitamins, minerals, and bioactive compounds, including BPs. However, the BP content in vegetables is generally lower compared to cereals and legumes. They are primarily present in the skin or outer layers of vegetables. Phenolic acids, such as chlorogenic, caffeic, coumaric, and ferulic acids, are commonly found in vegetables. Additionally, bound flavonoids and anthocyanins contribute to the BPs profile in some vegetables. Carrots, onions, potatoes, tomatoes, and leafy greens are examples of vegetables containing BPs. The specific BP content can vary based on the vegetable type, variety, and maturity stage (Ayoub et al. 2016). Analyzing the profile and distribution of BPs in cereals, pseudocereals, legumes, and vegetables is crucial for understanding the nutritional and functional properties of these foods. Different extraction and analytical techniques, such as alkaline or enzymatic hydrolysis followed by chromatography coupled with mass spectrometry, are used to identify, and quantify BPs in these plant-based foods. This knowledge can be utilized to develop strategies for enhancing the content of health-promoting BPs in foods, as well as in the development of functional foods with specific health benefits. Moreover, investigating the effects of processing and cooking methods on the retention and bioavailability of BPs will aid in optimizing dietary practices to maximize the intake of these beneficial compounds (Rocchetti et al. 2022).

1.9. Effect of Processing Bound Phenolic Compounds (BPs)

Bound phenolic compounds (BPs) are phenolic compounds that are chemically bound to other components in plant foods, such as cell wall materials like cellulose, hemicellulose, and lignin. These BPs are often associated with dietary fiber and are less bioaccessible than their free counterparts, meaning they are not easily released and absorbed during digestion. Food processing techniques have the potential to alter the structure of the plant matrix and the interactions between BPs and other components, thereby affecting their bioaccessibility and bioavailability. Understanding the impact of processing on BPs is crucial for optimizing the health-promoting properties of these bioactive compounds in various food products (Rocchetti et al. 2022).

***1.9.1. Thermal Processing*:** Cooking: Cooking is a common thermal processing method that involves the application of heat to food. Boiling, steaming, baking, and frying are typical cooking methods. Studies have shown that cooking can increase the bioaccessibility of BPs. For example, boiling or steaming vegetables can disrupt the

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plant cell walls, releasing BPs from their bound forms and making them more available for absorption in the gut (Khan et al. 2018).

***1.9.2. Pasteurization and Sterilization*:** Pasteurization and sterilization are thermal processing methods used to extend the shelf life of food products by eliminating or reducing microorganisms. While these processes can lead to some loss of free phenolic compounds due to thermal degradation, they can also disrupt the plant cell walls, releasing BPs and increasing their bioaccessibility.

***1.9.3. Nonthermal Processing*:** a. High-Pressure Processing (HPP): HPP is a nonthermal processing method that involves subjecting food products to high hydrostatic pressure. HPP can disrupt the plant cell structure and increase the release of BPs, leading to enhanced bioaccessibility.

1.9.4. High-Intensity Pulsed Electric Fields (PEF): PEF is another nonthermal processing technique that uses short bursts of high-voltage electricity to disrupt cell membranes. Studies have shown that PEF can increase the bioaccessibility of BPs by promoting the release of phenolic compounds from their bound forms.

***1.9.5. Ultrasound*:** Ultrasound processing involves the application of high-frequency sound waves to food. Ultrasound can disrupt the plant cell walls, leading to the release of BPs and increasing their bioaccessibility.

***1.9.6. Fermentation*:** Fermentation is a traditional food processing method that involves the use of microorganisms, such as bacteria or yeast, to convert sugars and other compounds into metabolites. Fermentation can lead to changes in the content and profile of BPs. For example, some bacteria can release enzymes that hydrolyze the chemical bonds between BPs and other components, making them more bioaccessible (Barba et al. 2017).

***1.9.7. Dietary Fiber Interactions*:** Dietary fiber, which is rich in BPs, can also influence the bioaccessibility of these compounds. Some processing methods may alter the structure of dietary fiber, leading to enhanced release of BPs. On the other hand, certain processing techniques may lead to interactions between BPs and dietary fiber, limiting their bioaccessibility (Khan et al. 2018).

1.10. Functional Implications of Phenolics–Food Interaction

Functional implications of phenolics-food interaction refer to the effects and consequences of the interactions between phenolic compounds (PCs) and other food components on human health and nutrition. PCs are a diverse group of bioactive compounds found in various plant-based foods, such as fruits, vegetables, whole grains, nuts, and beverages like tea and coffee. These compounds have gained considerable attention due to their potential health benefits, including antioxidant, anti-inflammatory, anticancer, and cardioprotective properties. However, the functional implications of PCs can be influenced by their interactions with other food components, such as proteins, carbohydrates, lipids, and enzymes during digestion and absorption (Rocchetti et al. 2022). Here, we will explore the key functional implications of phenolics-food interactions:

i) **Bioavailability and Absorption:** The bioavailability of PCs is crucial for their health effects. Interactions with food components can affect the solubility and stability of PCs during digestion, ultimately influencing their absorption in the gastrointestinal tract. For example, the presence of dietary fiber can reduce the bioavailability of certain PCs by forming complexes that are not easily absorbed.
ii) **Antioxidant Activity:** PCs are well-known for their antioxidant properties, but these activities can be modulated by their interactions with other food components. For instance, PCs can interact with proteins, affecting both the antioxidant potential of PCs and the functionality of the proteins. Such interactions may lead to the formation of protein-phenolic complexes, altering the overall antioxidant capacity of the food (Khan et al. 2018).
iii) **Modulation of Disease Risk:** PCs have been associated with the prevention of chronic diseases, including cardiovascular diseases, diabetes, and certain types of cancers. The interactions between PCs and other food components can influence the bioactivity of PCs, potentially impacting their protective effects against these diseases (Wang et al. 2022).
iv) **Impact on Gut Microbiota:** The gut microbiota plays a crucial role in the metabolism of PCs. Interactions with dietary components can affect the composition and activity of gut microbiota, potentially influencing the metabolism of PCs and their downstream effects on health.
v) **Influence on Flavor, Color, and Texture:** PCs can contribute to the flavor, color, and texture of foods. Their interactions with other food components may alter these sensory attributes, impacting overall food palatability and consumer acceptance.

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vi) **Nutrient-Nutrient Interactions:** PCs may interact with other nutrients present in the diet, affecting their absorption and utilization. For example, PCs can form complexes with certain minerals, potentially reducing their bioavailability.
vii) **Processing and Storage Stability:** During food processing and storage, PCs can undergo chemical reactions with other food components, leading to changes in their stability and bioactivity. Understanding these interactions is essential for preserving the health benefits of PCs in processed foods (Vuolo et al. 2019).
viii) **Formulation of Functional Foods:** Phenolics-food interactions can be leveraged to develop functional foods with enhanced health benefits. Formulating foods to optimize PCs' bioavailability and interactions with other bioactive compounds can create synergistic effects on health.
ix) **Individual Variability:** The response to phenolics-food interactions can vary among individuals due to genetic, physiological, and dietary differences. This variability needs to be considered when assessing the health implications of PCs in different populations.

1.11. Microbial transformation of phenolics in the large intestine

Microbial transformation of phenolics in the large intestine, also known as colonic fermentation, is a crucial process that occurs after the digestion of dietary phenolic compounds (PCs). The large intestine, specifically the colon, is home to a diverse and extensive population of microorganisms known as the gut microbiota. These microbes play a fundamental role in breaking down complex dietary components that have not been fully digested and absorbed in the small intestine.

The journey of PCs through the gastrointestinal tract begins in the stomach, where they may be partially degraded by acidic conditions and digestive enzymes (Vuolo et al. 2019). In the small intestine, some PCs may undergo further hydrolysis and enzymatic actions, leading to the release of phenolic aglycones from their bound forms, such as glycosides. However, not all PCs are fully broken down in the upper gastrointestinal tract. Instead, some reach the colon intact or as phenol-food macromolecule complexes, which are not easily absorbed due to their size or structure. Once in the colon, these intact PCs and phenol-food complexes become substrates for the colonic microbiota. The gut microbiota comprises a vast array of bacteria, archaea, viruses, and fungi that have coevolved with humans and play crucial roles in digestion, metabolism, and immune function (Zhu et al. 2018). The microbial communities in the colon are highly diverse and can vary greatly among individuals based on diet, genetics, age, and other factors. Colonic fermentation of PCs involves a series of microbial metabolic reactions aimed at breaking down these compounds further. The gut microbiota possesses a wide range of enzymes capable of metabolizing various PCs.

The fermentation process includes deglycosylation, dehydroxylation, α- and β-oxidation, dehydrogenation, demethylation, decarboxylation, C-ring fission, and C-ring cleavage. These reactions can result in significant structural modifications of the parent PCs, leading to the production of microbial metabolites (Jakobek and Matić, 2019). The metabolic fate of specific PCs depends on their chemical structure, the type of glycosidic linkages, and the nature of the substituent groups. Different classes of PCs, such as phenolic acids, flavonoids, and tannins, can undergo distinct transformations by the gut microbiota. For instance, phenolic acids like ferulic acid, caffeic acid, and gallic acid can be converted to various phenolic acid derivatives through microbial fermentation. Flavonoids, such as anthocyanins, undergo deglycosylation and ring-cleavage reactions to produce diverse phenolic acids and other metabolites (Tomas et al. 2020). One of the well-studied microbial transformations of PCs is the metabolism of ellagitannins, which are present in foods like pomegranates and some nuts and berries.

The gut microbiota can hydrolyze ellagitannins to release ellagic acid, which is subsequently transformed into urolithins through a series of reduction and dehydroxylation reactions. Urolithins, particularly urolithin A and urolithin B, are known to be bioactive and have potential health benefits (Wang et al. 2020). The microbial metabolites generated through colonic fermentation are often more bioavailable than the parent PCs. They can be absorbed into the bloodstream and distributed throughout the body, where they may exert various physiological effects. Some microbial metabolites may have antioxidant, anti-inflammatory, anti-cancer, and cardiovascular health benefits (Ferreira et al. 2017). The composition and activity of the gut microbiota play a critical role in determining the extent and nature of PC metabolism in the colon. Individual differences in gut microbiota composition can lead to variations in the production of specific microbial metabolites, which may explain why people respond differently to dietary PCs.

2. CONCLUSION

In conclusion, the functional implications of bound phenolic compounds (BPs) and their interactions with food components are complex and multifaceted. BPs, abundant in plant-based foods, hold immense potential for promoting human health and preventing non-communicable diseases. The digestion process plays a critical role in determining the bioaccessibility and bioavailability of BPs, and upon reaching the large intestine, BPs encounter the

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diverse gut microbiota, leading to microbial transformation and the generation of bioactive metabolites. The interaction between BPs and food matrices significantly influences their fate and bioactivity. The type of phenolic–food macromolecule interaction, the chemical nature of the BPs, and the characteristics of the food matrix all influence the amount of BPs reaching the colon and the rate of microbial transformation. Technological processes during food processing can also modulate the release kinetics of BPs to the colonic lumen, further impacting their functional implications. Studies have shown that BPs can have profound effects on gut microbiota, with various functional implications. BPs can act as prebiotics, selectively stimulating the growth of beneficial gut bacteria while inhibiting the growth of harmful microbes. The gut microbiota's fermentation of BPs results in the production of short-chain fatty acids, which play crucial roles in maintaining gut health and overall well-being. Additionally, the synergistic effects of BPs and dietary fiber on gut microbial ecology have been observed, underscoring the importance of considering the interactions between phenolics and food components for enhancing their health benefits. These interactions provide a promising avenue for designing innovative food products with enhanced bioactivity and improved gut health outcomes. Despite significant progress in this area, there is still much to explore and understand regarding the functional implications of BPs and phenolics–food interactions. Further research is needed to unravel the complex mechanisms underlying BPs' effects on gut microbiota and their overall impact on human health. Continued investigations in this field will offer valuable insights into harnessing the full potential of BPs as bioactive compounds, ultimately contributing to the development of personalized and functional foods that promote optimal health and well-being. Emphasizing the significance of the gut microbiota–phenolics interplay, this review underscores the importance of considering the entire food matrix to fully appreciate the functional implications of bound phenolic compounds and their interaction with other food components in the context of human health.

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