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FOOD TECHNOLOGY

Agro-industrial wastes as sources of bioactive compounds for food and fermentation industries

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ABSTRACT: *Agro-industrial wastes are of great interest because they are important natural sources of bioactive compounds and can generate value-added byproducts. Recent studies have shown that byproducts generated by the food processing industry are rich in bioactive compounds, such as phenolic compounds, organic acids, and carotenoids, among others. The growing interest in replacing synthetic antioxidant and antimicrobial compounds with natural ones has stimulated a search for these bioactive compounds from plant sources, especially from fruit-processing wastes. The study aims to project the agro-industrial wastes as potential natural sources of antioxidants and antimicrobials and the feasible technological applications in food and fermentation industries, especially the bioethanol industry.*
Key words: *phenolic compounds, antioxidant activity, antimicrobial activity, agro-industrial waste.*

Resíduos agroindustriais como fontes de compostos bioativos para as indústrias de alimentos e de fermentação

RESUMO: *Resíduos agroindustriais são de grande interesse por serem importantes fontes naturais de compostos bioativos e assim gerar subprodutos de valor agregado. Estudos recentes mostraram que o processamento de alimentos gera subprodutos ricos em compostos bioativos tais como compostos fenólicos, ácidos orgânicos e carotenóides, entre outros. O crescente interesse em substituir compostos antioxidantes e antimicrobianos sintéticos por naturais tem estimulado a procura por esses compostos bioativos a partir de fontes vegetais, especialmente de resíduos de processamento de frutas. O objetivo desta revisão é destacar os resíduos agroindustriais como potenciais fontes naturais de antioxidantes e antimicrobianos assim como as possíveis aplicações tecnológicas nas indústrias de alimentos e de fermentação, especialmente a indústria do bioetanol.*
Palavras-chave: *compostos fenólicos, atividade antioxidante, atividade antimicrobiana, resíduo agroindustrial.*

INTRODUCTION

The production of primary and secondary metabolites is a characteristic property of living organisms that could be utilized for pharmacological and technological purposes. These chemical compounds are called “natural products.” Besides their pharmaceutical actions on humans, they also possess biological activity. Natural antimicrobials are secondary metabolites, which possess antimicrobial activity, and are extracted from different sources such as plants, animals, and microorganisms. Besides this, these secondary metabolites also contain the property of antioxidants, and therefore, are considered a prospective option for food preservation in contrast to synthetic preservatives (ARSHAD & BATOOL, 2017).

The valuable sources of these natural products with antimicrobial and antioxidant properties are the residues resulting from the agro-industrial processes, which may contribute to a significant pollution problem in lack of proper management. With no viable alternatives, they are often discarded directly into the surrounding environment. Apart from a considerable loss of valuable materials, the large amount of wastes produced by agro-industries also raises serious management problems, both from economic and environmental points of view (MIRABELLA et al., 2014). Many of these wastes, however, can potentially be used in other production

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systems, such as the production of natural food additives. Research on the composition and characterization of the generated wastes has been carried out with the objective that the waste residues can be put to value-added applications with possible technology (VIEIRA et al., 2009). Sustainable applications of the waste products (as alternatively called "byproducts") include production of organic fertilizers, animal feeds, ethanol, enzymes, essential oils, and additives in various technological processes (FERRARI et al., 2004; KOBORI & JORGE, 2005; ALEXANDRINO et al., 2007; RODRIGUES et al., 2009; LIU et al., 2012). It is also observed that plant foods and their food processing byproducts are the potential source of phenolic bioactive compounds that have valuable health benefits (CAMARGO et al., 2018).

Initially, interest was focused on the study of substances possessing antioxidant and antimicrobial activities that emerged from the search for new additives, which could be used in place of the synthetic ones already being used in technological processes. Synthetic additives alter enzymes and lipids in humans and animals and have a potential carcinogenic effect (ROCHA et al., 2007). Thus, recent research has been conducted to replace chemical additives by non-synthetic ones that can be produced from agro-industrial wastes. The growing interest for natural antioxidant and antimicrobial compounds has led to research on plants as a source of such bioactive compounds (MOURE et al., 2001; SHAKER, 2006; CARPENTER et al., 2007; OLIVEIRA et al., 2009; SASSE et al., 2009; BREWER, 2011; SHIRAHIGUE et al.., 2011; BABBAR et al., 2011; LOPES et al., 2013; ARBOS et al., 2013; CAMARGO et al., 2014; SILVA & JORGE, 2014; CAMARGO et al., 2018; SERRANO-LEÓN et al., 2018).

In this review, we aimed to project the agro-industrial wastes as potential natural sources of antioxidants and antimicrobials and explored their possible technological applications in the food and fermentation industry.

Bioactive compounds: application as antioxidants and antimicrobials

Bioactive compounds are defined as substances with biological activity and are able to modulate metabolic processes resulting in the promotion of better health conditions. The benefits exhibited by these compounds include antioxidant activity, inhibition or induction of enzymes, inhibition of receptor activities, and induction and inhibition of gene expression (CORREIA et al., 2012). Fruits, vegetables, and whole grains are good sources of bioactive compounds, which include a heterogeneous class of compounds mainly phenolics, carotenoids, tocopherols, phytosterols, and organosulfur compounds (CARBONELL-CAPELLA et al., 2013; SERRANO-LEÓN et al., 2018) (Figure 1).

The secondary metabolites produced by plants such as flavonoids, thiosulfinates, glucosinolates, organic acids, and saponins are antimicrobial agents used against a great variety of microorganisms. The most important group of compounds with antimicrobial activity is phenolics, which include terpenes, aliphatic alcohols, aldehydes, ketones, acids, anthocyanins, and isoflavonoids (SPANOS & WROLSTAD, 1992; BURT, 2004; ARSHAD & BATOOL, 2017). Phenolic compounds are widely distributed in nature and are the most abundant secondary metabolites reported in plants (MAXCHEIX et al., 1990). The primary action of phenolics is related to the plant defense against biotic and abiotic stresses, pests, and pathogens (ATANASOVA-PENICHON et al., 2016; ZHANG & TSAO, 2016; CAMARGO et al., 2018).

Flavonoids are a large group of phenolic compounds reported in various fruits, vegetables, roots, etc. (MIDDLETON & KANDASWAMI, 1994; HOLLMAN & KATAN, 1997). The monomeric units of these compounds consist of two substituted benzene rings (A and B) and, in most cases, a heterocyclic ring (C) (HOLLMAN et al., 1996). More than 4,000 compounds of flavonoids have been identified (JAYAPRAKASHA et al., 2003). The different substitutions in rings A, B, and C, as well as the different ways in which ring B is bound to ring C, allow the formation of several types of flavonoids with different biological characteristics. Flavonoids consist of different subclasses as illustrated in Figure 1: flavanones, flavonols, flavones, flavanols (or flavan-3-ols), isoflavones and anthocyanidins (HE & GIUSTI, 2010; OLIVEIRA et al., 2014). They occur in various foods, such as anthocyanidins in grape, wine, cherries, and eggplant peel; flavonols in onion, broccoli, kale, apple peel, tea, and grape; flavones in sorghum, lemon, red pepper, and parsley; flavanols in apple skin, banana, berries, *Camelia sinensis* teas; isoflavonoids in soybean and soy products; and flavanones in citrus fruit and tomato skin, as some examples, many of them with antioxidant and antimicrobial activities (RICE-EVANS et al., 1996; HOLLMAN & KATAN, 1997; OLIVEIRA et al., 2014; XU et al., 2017). The highest activities are displayed by the class of flavanols, especially the procyanidin group and catechins, epicatechins, and their esterified derivatives.

Within the phenolics, non-flavonoids comprise phenolic acids, tannins, stilbenes and

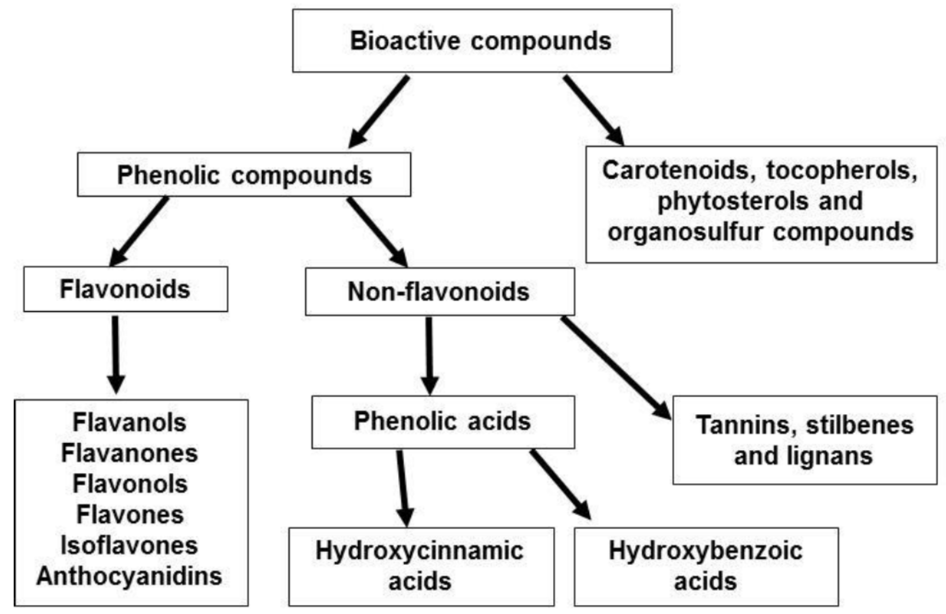

Figure 1 - The main classes of bioactive compounds.

lignans. Phenolic acids are widely spread throughout the plant kingdom and their effects have been ascribed to their antioxidant, antimutagenic, anticarcinogenic, antimicrobial, and other biological properties (XU et al., 2008). Substituted derivatives of hydroxybenzoic and hydroxycinnamic acids are the predominant phenolic acids. The most common hydroxycinnamic acids are caffeic, p-coumaric, and ferulic acids, which frequently occur in food as simple esters with quinic acid or glucose (SHAHIDI & AMBIGAIPALAN, 2015), while the most common benzoic acid is gallic acid, occurring in red fruits, onions and black radish (XU et al., 2017).

Tannins are water-soluble polyphenols commonly presented as hydrolysable tannins or condensed tannins, the latter are the most common, consisting of two or more monomeric (+)-catechin or (-)-epicatechin units. Tannins are able to bind and precipitate proteins and other macromolecules in aqueous solutions, to bind metals and form blue to black complexes with iron salts, with molecular weight ranging from 500 to 3,000 daltons (SALMINEN & KARONEN, 2011). The most known stilbene is resveratrol, which is reported in vine plant, peanut and berries, and extensively studied for its multiple bioactivities (XU et al., 2017). Lignans are present in seeds, vegetable oils, cereals, legumes, fruits and vegetables, displaying an enormous structural diversity. The most common lignans are lariciresinol, pinoresinol, secoisolariciresinol, syringaresinol, matairesinol, 7-hydroxymatairesinol, sesamin, sesamolin and sesamol (GERSTENMEYER et al., 2013).

The great diversity of bioactive compounds reported in plant processing residues encourages the search for natural antioxidants for application in food and drug industries. According to the FDA (*Food and Drug Administration*), antioxidants are substances used to preserve food by retarding deterioration through rancidity or discoloration that is caused by the oxidation process (DZIEZAK, 1986). These are compounds present in small amounts with a primary function of preserving or retarding oil and fat oxidations (POKORNY, 1991). These substances may have originated from commercial sources and naturally isolated compounds from foods (ADEGOKE et al., 1998). An essential requirement for the use of an antioxidant in food requires it to be efficient at low concentrations, compatible with the substrate, sensory acceptability, non-toxicity, and protection of the food from the deleterious effects of oxidation (SCHULER, 1990).

An antioxidant functions in various ways: competitively binding to oxygen, delaying the initiation step, and/or inhibiting the propagation step by destroying or binding free radicals or inhibiting the catalysts and stabilizing the hydroperoxides (ALLEN & HAMILTON, 1994). The antioxidant may act on the cell membranes to protect food by: (1) sequestering free radicals and not starting the oxidation process; (2) inactivating metallic ions; (3) removing oxygen reactive species; (4) sequestering single oxygen; (5) destroying peroxides and preventing formation of radicals; and (6) removing and/or decreasing the local oxygen concentration (DZIEZAK, 1986).

Due to the potential risks of synthetic antioxidants to human health, much interest has been developed in natural sources of these compounds to reduce or delay oxidation processes on food in recent years (AHN et al., 1998; JAYAPRAKASHA et al., 2001; MOURE et al. 2001; BREWER, 2011). Natural antioxidants are molecules present in plants, in small amounts, which inhibit the oxidation process that produces free radicals. Natural antioxidants have the ability to reduce the rate of oxidation of the lipid compounds present in certain dietary products. These antioxidant compounds include flavonoids, phenolic acids, carotenoids, and tocopherols (KHANDUJA & BHARDWAJ, 2003; OZSOY et al., 2009).

The antioxidant potential of the bioactive compounds depends on the number and arrangement of the hydroxyl groups. These compounds can donate hydrogen atoms to lipid radicals and produce lipid derivatives and antioxidant radicals, which are more stable and less readily available to promote autoxidation (SHAHIDI & AMBIGAIPALAN, 2015).

Plants are the main sources of natural antimicrobials, i.e., compounds capable of inhibiting the growth of microorganisms. They can be used along with older antibiotics to increase their potency to avoid the development of microbial resistance. The plant compounds that are extensively utilized for antimicrobial purposes comprise alkaloids, sulfur-containing compounds, terpenoids, and phenolic compounds (KHAMENEH et al., 2019). Thus far, more than 1,350 plants with antimicrobial activities and more than 30,000 antimicrobial substances extracted from plants have been reported (TAJKARIMI et al., 2010). Plants are a big bet as sources of natural antimicrobials, and in this sense, the utilization of plant parts normally discarded as wastes arises as a sustainable and safe option in the search for novel antimicrobial agents.

Agro-industrial wastes as sources of bioactive compounds

The agro-industrial products from food industries produce a large amount of vegetable and fruit wastes, which affect municipal landfills. Despite being highly biodegradable, these generate leachate and are responsible for methane emission (MISI & FORSTER, 2002). These wastes are generated by different processes and contain an appreciable amount of bark, seeds, and other types of plant components. These waste components serve as a source of proteins, enzymes, essential oils, and other compounds with biological activity that can be recovered and used. The processing of food from vegetable origin results in production of byproducts that are rich sources of bioactive compounds (SCHIEBER et al., 2001) (Figure 2). The availability of these compounds in the agroindustry residue will depend on the mode of extraction, type of solvent, and purification (SOQUETTA et al., 2018). A general scheme to obtain extracts from different parts of the plants is shown in figure 3.

Antioxidant and antimicrobial activities have been reported in several agricultural products (BALASUNDRAM et al., 2006). DENG et al. (2012) evaluated the potential of wastes from 50 fruits (peel and seed) as resources of bioactive compounds and demonstrated that the antioxidant potential was higher in residues than in pulps. A large group of bioactive compounds was identified such as catechin, cyanidin 3-glucoside, epicatechin, galangin, gallic acid, homogentisic acid, kaempferol, and chlorogenic acid.

Tables 1 to 4 list the studies that used agro-industrial residues as natural sources of antioxidants and antimicrobials and summarize the main results and technological applications.

Wastes from fruit processing: rich sources of bioactive compounds with technological applications

Grape

Grape (*Vitis vinifera*) seed extracts are obtained as the byproducts of wine-making or grape juice and are rich in proanthocyanidins (condensed tannins) and other phenolic compounds (RABABAH et al., 2004; MIELNIK et al., 2006; WEBER et al., 2007). Phenolic compounds in grape and grape products can be divided into two groups, non-flavonoids and flavonoids. The most common phenolic acids found in grape include cinnamic acids (coumaric acid, caffeic acid, ferulic acid, chlorogenic acid, and neochlorogenic acid) and benzoic acids (p-hydroxybenzoic acid, vanillic acid, and gallic acid). Flavonoids include flavan-3-ols (catechin, epicatechin polymer and ester with galactic acid or glucose), flavonols (quercetin) and red and blue anthocyanins (SHI et al., 2003; SHAHIDI & AMBIGAIPALAN, 2015). Studies have shown that grape seeds are rich sources of monomeric

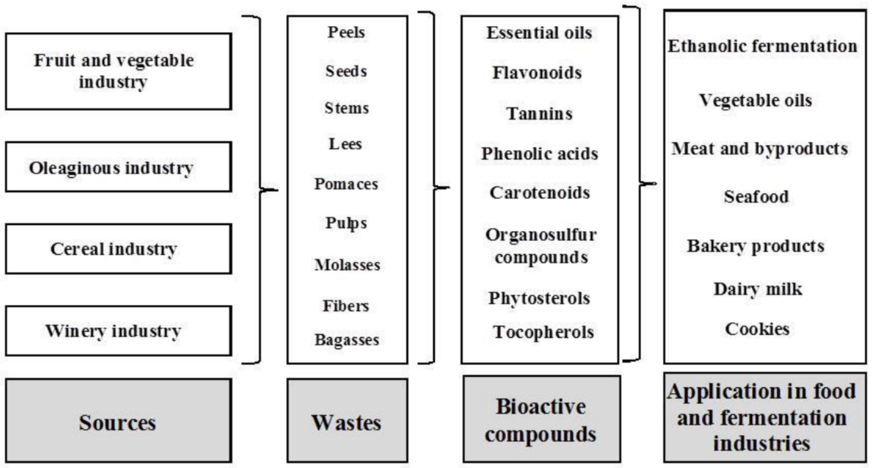

Figure 2 - Use of agro-industrial wastes as natural sources of bioactive compounds in food and fermentation industries.

phenolics such as (+)-catechins, (–)-epicatechin, (+)-gallocatechins, (–)-epigallocatechin, and their dimeric, trimeric, and tetrameric proanthocyanidins (SHAHIDI & AMBIGAIPALAN, 2015).

The utilization of wastes produced from the wine industry as natural antioxidants has been extensively studied in various types of raw material, such as beef, chicken, pork, and turkey, by means

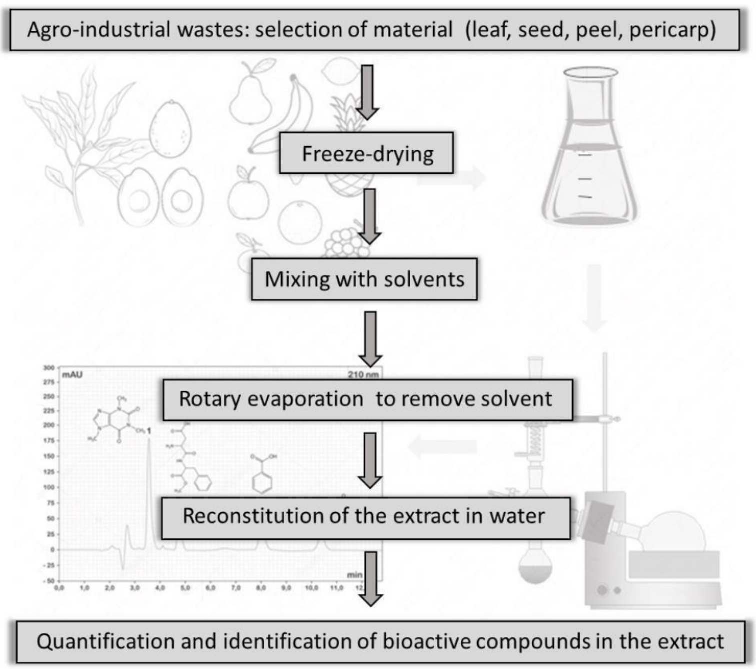

Figure 3 - A general scheme of the extraction method to obtain a bioactive compound-rich extract from agro-industrial wastes (stems, seeds, peels, leaves, etc.).

Table 1 - Agro-industrial residues as natural sources of antioxidants and antimicrobials, the main results of the study, and the technological applications of the wastes – PART I.

Sources	Main results and applications
Avocado peel, kernel, and pulp	Avocado byproducts presented a very distinct phenolic profile. Higher concentration in peels, mainly epicatechin derivates followed by chlorogenic derivates (MELGAR et al., 2018).
Avocado seed fatty acid derivatives	The study describes the antilisterial potential of an enriched acetogenin extract from avocado seeds. Seeds contained 1.6 times higher acetomigenin levels than pulp. Results strengthen the potential of avocado acetogenins, especially from avocado seed, as a source of natural antimicrobial food additives (SALINAS-SALAZAR et al., 2017).
Crude epicarp and seed extract from avocado fruits	The ethanolic extracts showed antimicrobial activity toward both Gram-positive and Gram-negative bacteria (except Escherichia coli), while inhibition of the water extracts was only observed for Listeria monocytogenes and Staphylococcus epidermidis. The crude extracts of the epicarp and seed of mature avocados contain antimicrobials and show the potential to be used as food additives (CHIA & DYKES, 2010).
Acerola peel	The acerola peel extract exhibited high total phenolic content. DPPH (2,2 –Diphenyl-1-picrylhydrazil) scavenging capacity of acerola waste was >70% and it can be considered as a promising source of natural antioxidants (CAETANO et al., 2009).
Acerola bagasse flour	In the extract, phenolic compounds were identified in the following order of increasing concentration: quercetin, p-coumaric acid, gallic acid, epigallocatechin gallate, catechin, syringic acid, and epicatechin. It showed antioxidant potential and bactericidal activity for both Gram-negative and Gram-positive strains, presenting the potential to be used in the food industry (MARQUES et al., 2017).
Mango, pineapple and passion fruit byproducts	The fruit byproducts have the potential to be used as functional ingredients, providing dietary fiber (for nutritional and technological purposes) and natural antioxidants to foods (SELANI et al., 2016).
Mango seed	Mango seed is a potential source of nutritional food ingredients due to the high quality of fat and proteins and the high content of compounds with antioxidant and antimicrobial activities (TORRES-LEON et al., 2016).
Mango peel and kernel	Phenolic compounds in the extracts ranged from 3,123 to 6,644 mg of catechin 100 g–1. The extracts showed good antimicrobial activity against E. coli, Salmonella sp., Pseudomonas aeruginosa, and Staphylococcus aureus. Mango residues are good sources of phenolic compounds, antimicrobial and antioxidant agents and should be exploited by the food industry (ARBOS et al., 2013).
Brazilian mango	A total of 12 flavonoids and xanthones were identified in the pulps, peels, and seed kernels with larger amounts of these compounds in the organically grown Ubá variety. The Ubá mango pulp presented higher antioxidant activity and the peel and seed kernel extracts showed higher antioxidant activity than the commercial standard (RIBEIRO et al., 2008).

of varied matrices such as hamburgers, meatballs, restructured, sausages, and marinated patties. The addition of grape seed and peel extracts (Isabel and Niagara varieties) as natural antioxidants delayed the lipid oxidation of chicken meat (processed, cooked and stored under refrigeration for 14 days), with results comparable to the synthetic antioxidant butylated hydroxytoluene (BHT). The addition of grape extracts combined with vacuum packaging proved to be a good technique to increase the lipid stability of cooked chicken meat (SHIRAHIGUE et al., 2010).

Grape seed and peel extracts (Isabel and Niagara varieties) were as effective as the synthetic antioxidants (BHT and a commercial mixture of sodium erythorbate, citric acid, and sugar) in the prevention of lipid oxidation in the processed products of both raw and cooked chicken, which were stored under frozen conditions for nine months (SELANI et al., 2011). They also improved the oxidative stability of cooked beef (AHN et al., 2002), cooked chicken meat (SHIRAHIGUE et al., 2011), and parts of turkey (LAU & KING, 2003).

The efficacy of grape polyphenols in delaying the lipid oxidation of fish-based products when stored under frozen conditions was also demonstrated. PAZOS et al. (2005a) verified the antioxidant activity of grape flavonoids obtained from the byproducts of the wine industry in systems containing fish oil and mackerel muscle (*Scomber scombrus*) and also observed that oligomeric flavonoids have a high potential in inhibiting oxidation in emulsions and in frozen fish muscle. Grape extract and its purified fractions were used in preserving fish

Table 2 - Agro-industrial residues as natural sources of antioxidants and antimicrobials, the main results of the study, and the technological applications of the wastes – PART II.

Sources	Main results and applications
Peanut skins	All extracts presented antioxidant and bacteriostatic activity against L. monocytogenes and bactericidal activity against S. aureus. Results indicated technological potential of the extracts as natural additives to improve food quality (CALOMENI et al., 2017).
Peanut skins	The addition of 2.5% peanut skins rendered an increase of up to 30% in the total polyphenols. Sensory evaluation tests demonstrated that peanut skin-fortified cookies were well-accepted and the positive effects in cookies were increased with the increasing polyphenols and potent antioxidant activity (CAMARGO et al., 2014).
Black tea processing waste	Black tea processing waste (BTPW) can be used as a source of antioxidant and antimicrobial phenolic compounds (catechins, theaflavins, and gallic acid). BTPW extracts exhibited antimicrobial activity against S. aureus, Shigella lexneri, and Bacillus cereus; however, the inhibition of Candida albicans was not observed. BTPW can be used for the development of value-added products with antioxidant and antimicrobial properties for the applications in food, pharmaceuticals, cosmetics, and agricultural sectors (ÜSTÜNDAG et al., 2016).
Oliva oil processing residue	These byproducts exhibited high levels of phenolic compounds such as hydroxytyrosol and oleuropein. Oliva oil processing residue showed potential in the improvement of sensorial quality in milk and antioxidant capacity in fatty food matrices (ARAÚJO et al., 2015).
Oils from the seeds of grape, guava, yellow melon, passion fruit, pumpkin, graviola, and tomato	These oils are predominantly unsaturated with a high percentage of linoleic essential fatty acid (38.8-79.4%), besides significant quantities of tocopherols, phytosterols, and phenolic compounds. Tomato and guava oils showed better results in the antioxidant tests and pumpkin oil had a higher induction period in the oxidative stability test. Results provide information that enables the use of new alternative sources of vegetable oils with biological activities, which can serve as ingredients in food and drugs (SILVA & JORGE, 2014).
Apricot pomace	Apricot by-products were enriched with phenolic compounds by solid-state bioprocessing using filamentous fungi. The antioxidant potential increased significantly and the fermentation process with filamentous fungal strains not only helped to increase lipid recovery from apricot kernels, but also resulted in oils with better quality attibutes, i.e., high linoleic acid content (DULF et al., 2017).
Plum pomace	Solid-state fermentation helped to achieve higher lipid recovery from plum pomaces and also resulted in oils with better quality attibutes (DULF et al., 2016).
Tomato wastes	The antimicrobial activity of tomato waste extracts against S. aureus exhibited moderate correlation with the isochlorogenic acid content of the samples; however, no correlation was reported between the antioxidant capacity and total phenolic content of the samples. The results suggested that tomato waste represent a reliable source of natural bioactive molecules and can serve as functional ingredients in new food formulation (SZABO et al., 2019).

meat among species that had high concentrations of polyunsaturated fatty acids (PAZOS et al., 2005b).

The addition of fruit residues (grape seed, orange peel, and tomato paste) was an alternative source of natural antioxidants in enriching rice-based extruded foods (YAGCI & GOGUS, 2009). Bread formulated with a grape seed extract showed increased antioxidant activity and a decreased amount of carboxymethyl-lysine, a compound formed by the potentially toxic Maillard reaction. The only attribute imparted by the use of grape extract was the color of the bread (PENG et al., 2010). Grape extracts also increased the oxidative stability of the lipid in cheddar cheese (SHAN et al., 2011) and the antioxidant activity in ice creams (HWANG et al., 2009).

The antimicrobial activity of grape extracts has been reported in the literature against a variety of microorganisms such as lactic acid bacteria, foodborne pathogens, and wine spoilage yeasts (JAYAPRAKASHA et al., 2003; BAYDAR et al., 2004; BROWN et al., 2009; KATALINIC et al., 2010; PERUMALLA & HETTIARACHCHY, 2011; PASTORKOVA et al., 2013). Growth of foodborne pathogens such as *Staphylococcus aureus, Salmonella* sp., *Escherichia coli, Listeria monocytogenes,* and *Campylobacter* sp. were inhibited by grape seed extracts (ROTAVA et al., 2009; SHAN et al., 2011; SILVÁN et al., 2013; FILOCAMO et al., 2015). A flavan-3-ol enriched grape seed extract inhibited the growth of lactic acid bacteria such as *Lactobacillus*

Table 3 - Agro-industrial residues as natural sources of antioxidants and antimicrobials, the main results of the study, and the technological applications of the wastes – PART III.

Sources	Main results and applications
Jabuticaba seeds	The gross jabuticaba seed extract was partially purified and exhibited high antimicrobial potential toward bacteria. Electrospray ionization coupled with tandem mass spectrometry data showed the presence of ellagitannins and ellagic acid in the extracts, which are probably responsible for the antimicrobial and antioxidant activities (HACKE et al., 2016).
Apple, pear, tomato, goldenrod and artichoke wastes	This study demonstrated the possibility of recovering high amounts of phenolics with antioxidant properties from fruit and vegetable residuals not only for food but also for cosmetic applications (PESCHEL et al., 2006).
Apple peels, carrot pulp, white and red grape peels and red beet peels and pulp	The thermally processed red grape waste had the highest antimicrobial effect and also antimutagenic activity toward S. typhimurium. Apple peel, carrot pulp, red and white grape peel and beetroot pulp can be exploited for their nutrients and antioxidant components and used to add value in food formulations (VODNAR et al., 2017).
Avocado, jackfruit, longan, mango, and tamarind seeds	The seeds showed a much higher antioxidant activity and phenolic content than the edible portions. The contribution of all fruit seed fractions to the total antioxidant activity and phenolic content was always >70% (SOONG & BARLOW, 2004).
Kinnow peel and seeds, litchi pericarp and seeds, grape seeds, and banana peel	Kinnow peel extract exhibited the highest reducing power and DPPH free radical scavenging activity, whereas the phenolic content (TPC) of 37.4 mg gallic acid equivalents (GAE) g–1 was highest for grape seed extract. Banana peel extract with a low TPC showed the lowest reducing power, as well as DPPH free radical scavenging activity among the fruit residues (BABBAR et al., 2011).
Chokeberry pomace	The extractable phenolics and total flavonoids increased during fermentation processes. A longer fermentation period resulted in a greater loss of anthocyanins. The HPLC-MS analysis of phenolic compounds showed that the amounts of flavonols and cinnamic acids increased while the concentrations of glycosylated anthocyanins decreased substantially. The present investigation demonstrated that the fermentation process enriched the chokeberry pomace with phenolic antioxidants and lipids with better nutritional quality characteristics (DULF et al., 2018).
Citrus residues	Linalol is the major component of the leaf essential oil and limonene in the fruit peel essential oil. The essential oil from leaves showed antimicrobial activities against bacteria but not against fungi. The essential oil from the fruit peel showed no antimicrobial activity (LOPES et al., 2013).
Citrus byproducts	In the agar diffusion assays, the essential oils inhibited all of the tested microorganisms and the major inhibition zones were detected on Candida utilis. As for the bacteria, the oils showed better inhibition of S. aureus than that of E. coli and P. aeruginosa. The inhibitory effect of the citrus oils was effective on Penicillium expansum fungus; except for Cravo-lemon oil, which showed a growth-stimulating effect (GERHARDT et al., 2012).

fermentum and *L. plantarum* (TABASCO et al., 2011), which are the common contaminants of the bioethanol industry process (BASSO et al., 2014). Grape extracts have been reported as more effective against bacteria than yeasts; and consequently, the results obtained with lactic acid bacteria are shown to be very promising for application in the ethanol fuel industry.

Citrus

Citrus fruits, chiefly, oranges, mandarins, limes, and lemons, are the most produced and consumed fruits in the world (OLIVEIRA et al., 2009). Different citrus fruits have a small edible portion and generate a large amount of residues such as peels and seeds during food processing (MIRABELLA et al., 2014). These residues are the sources of several compounds, mainly, water-soluble sugars, fibers, organic acids, amino acids and proteins, minerals, oils, and lipids. They also contain flavonoids and vitamins (FERNÁNDEZ-LOPEZ et al., 2004). Residues such as dry pulp and molasses, fiber, seeds, and bagasse are the sources of essential oils, pectin, ascorbic acid, and flavonoids (BRADDOCK, 1995; OZAKI et al., 2000; SCHIEBER et al., 2001).

Citrus peels are rich in various nutrients that act as functional and beneficial components, which have wide applications, depending on their composition. These byproducts have several secondary metabolites, such as terpenoids,

Table 4 - Agro-industrial residues as natural sources of antioxidants and antimicrobials, the main results of the study, and the technological applications of the wastes – PART IV.

Sources	Main results and applications
Winery grape residue	The grape extracts were effective in promoting oxidative stability when applied at concentrations of 40 or 60 mg of GAE kg–1 with results similar to the synthetic antioxidant BHT. The antioxidant effects of the extracts were highly dependent on the concentration. The addition of winery grape residue to raw and cooked chicken meat provided a satisfactory protective effect against lipid oxidation in cooked chicken meat stored under refrigeration (SHIRAHIGUE et al., 2011).
Winery grape residue	Winery grape residue extracts were effective in inhibiting the lipid oxidation of raw and cooked chicken meat with results comparable to synthetic antioxidants. The extracts caused alterations in color and sensory results of cooked samples. In the sensory evaluation of odor and flavor, the extracts produced satisfactory results, which did not differ from synthetic antioxidants. The addition of winery grape residue to frozen cooked chicken meat provided a satisfactory protective effect against lipid oxidation with results comparable to a synthetic antioxidant (SELANI et al., 2011).
Grape seeds	Grape seed extract showed potential inhibition of oxidative rancidity in cooked pork patties in comparison to current synthetic antioxidants (SASSE et al., 2009).
Grape seeds and bearberry	Grape seed extracts and bearberry decreased the lipid oxidation in raw pork patties after 9 and 12 days from storage. The antioxidant activity of extracts was observed in cooked pork patties demonstrating thermal stability. Results showed the potential use of health-promoting nutraceuticals in meat and meat products (CARPENTER et al., 2007).
Grape seeds	Monomeric procyanidin was reported to be the major compound at 48% and 40% abundance in acetone: water: acetic acid (90:9.5:0.5) and methanol: water: acetic acid (90:9.5:0.5) extracts, respectively. It was tested for antibacterial activity against B. cereus, Bacillus coagulans, Bacillus subtilis, S. aureus, E. coli, and P. aeruginosa. Gram-positive bacteria and Gram-negative bacteria were completely inhibited at 850–1,000 ppm and at 1,250–1,500 ppm, respectively (JAYAPRAKASHA et al., 2003).
Grape seeds	The supplementation of grape seed extract prior to cooking significantly improved the oxidative stability of minced turkey meat during heat treatment and storage. The ability of grape seed extract to prevent lipid oxidation was concentration-dependent. The grape seed extract was very effective in inhibiting lipid oxidation of cooked turkey meat during chill-storage (MIELNIK et al., 2006).
Grape seeds and peels	The phenolic content (200 mg kg–1) in grape extracts did not have any effect on the conjugated diene hydroperoxides. After six days, the high antioxidative effect was observed for the secondary oxidation products in conjugated sunflower oil for peel extract followed by seed extract (SHAKER, 2006).

carotenoids, coumarins, furanocoumarins, and flavonoids, especially flavonones and polyethoxylated flavones, which are rarely reported in other plants. These compounds protect plants against several biotic and abiotic stresses (AHMAD et al., 2006). They are present in the citrus extracts and citrus oils, and due to their antimicrobial and antioxidant activities, there is a growing interest in their application in several areas of food technology (CHOI et al., 2000; FRIEDMANN et al., 2004; PATIL et al., 2009; ASHOK KUMAR et al., 2011; LIU et al., 2012).

The term 'Essential Oil' is utilized to designate complex mixtures of natural compounds of polar and non-polar natures (MASANGO, 2005). It is a product obtained by the distillation of natural materials, consisting of liquid, volatile, limpid, and colored mixtures of aromatic compounds extracted from herbs, spices, and from food and vegetable wastes (WU et al., 2017). Essential oils originate from the secondary metabolism of plants and consist of a mixture of compounds, mainly monoterpenes, sesquiterpenes, and oxygenated derivatives (alcohols, aldehydes, ester, ethers, ketones, phenols, and oxides). They also contain other volatile compounds, such as phenylpropanoids and substances containing sulfur or nitrogen (BAJPAI et al., 2008; VALERIANO et al., 2012).

Studies have reported the application of natural antimicrobials obtained from citrus essential oils (FISHER & PHILLIPS, 2008). These products have reported their use in the development of several pharmaceutical preparations due to their antiseptic properties (BISIGNANO & SAIJA, 2002). GERHARDT et al. (2012) evaluated the varieties of bergamot-pokan (*Citrus reticulata* Blanco), grapefruit (*Citrus maxima* (Burm.) Merr.), and lemon-bergamot (or lemon-clove, *Citrus limonia* Osbeck) in the growth inhibition of certain microorganisms, such as *E. coli*, *Enterococcus faecalis*, *S. aureus*, *Salmonella enteritidis,* and *Pseudomonas aeruginosa*, and observed that all extracts from these different citrus varieties were able to inhibit the growth and/or inactivate the bacterial action.

The control of certain lactic acid-producing spoilage bacteria in apple and orange juices was effective when citrus essential oils were added in combination with mild heat treatment process (PEDROSA et al., 2019). The lemon essential oil showed a considerable inhibitory effect on food spoilage yeasts, such as *Geotrichum candidum, Pichia anomala, Saccharomyces cerevisiae,* and *Schizosaccharomyces pombe*, as an alternative to synthetic preservatives in fruit-or-milk-based acidic products (TSERENNADMID et al., 2011). As indicated for grape extracts, citrus essential oil would be a prospective antimicrobial to be used in the bioethanol industry to control the growth of lactic acid bacteria and spoilage yeasts.

The cytotoxic activity of essential oils is attributed to the presence of phenolic compounds like aldehydes, terpenes, aliphatic alcohols, ketones, acids, and isoflavonoids. The phenolic compounds are thought to be the main compound of these oils responsible for the antibacterial properties, but there are reports of non-phenolic compounds, such as allyl isothiocyanate, that are more effective against Gram-negative bacteria (TURINA et al., 2006). The main characteristic feature of the essential oils is the property of hydrophobicity, which gives them the ability to alter the permeability of the mitochondrial cell membrane, thereby making it more permeable with consequent losses of ions and molecules (CARSON et al., 2002).

Mango

Mango (*Mangifera indica* L.) is an important tropical fruit in the world, which is extensively marketed because of vast production, wide distribution, and owing to its health benefits to humans (TORRES-LEON et al., 2016). Besides the excellent texture and flavor, it has a high nutritional value, being a source of vitamin A and C and rich in phenolic compounds (THARANATHAN et al., 2006).

Mango wastes, such as the seed kernel and peel, have high functional and nutritional potential. It is estimated that 35-60% of the fruit is discarded as wastes after processing (O'SHEA et al., 2012). The mango seed has been reported as a biowaste with a high content of bioactive compounds such as phenolic compounds, carotenoids, and vitamin C (JAHURUL et al., 2015; TORRES-LEON et al., 2016). The major phenolic compounds present in mango are gallic acid, ellagic acid, gallates, gallotannins, condensed tannins, mangiferins, catechin, epicatechin, and benzoic acid. Such compounds present in the seed and bark show greater antioxidant activity than the fruit as such (SOONG & BARLOW, 2004; RIBEIRO et al., 2008). This antioxidant activity is mainly due to their reducing properties, which play an important role in the neutralization or sequestration of free radicals or chelation of transition metals acting both in the initiation stage as well as in propagation of the oxidative process (SOARES, 2002).

Mango seeds can also be used as a source of natural antimicrobials. Ethanolic extracts of mango seeds exhibited a spectrum of antimicrobial activities and were effective against Gram-negative bacteria (KABUKI et al., 2000). The structure of its active component confirmed it to be a phenolic compound. The antibacterial activity of different mango peel extracts against Gram-positive *S. aureus* and Gram-negative *Pseudomonas fluorescens* was investigated. Extracts showed varying degrees of antibacterial activities against both organisms. Generally, Gram-positive bacteria are susceptible to natural compounds, while Gram-negative organisms exhibit less sensitivity. The peel from Langra mango variety extracted with 70% ethanol and 80% acetone exhibited maximum zone of inhibition against both organisms. The difference in the antimicrobial effects between Gram-positive and Gram-negative bacteria is due to the presence of different cell wall structures. Compounds that can effectively diffuse the lipid bilayer and increase membrane fluidity may be considered as more effective antibacterial agents (KANATT & CHAWLA, 2017).

Avocado

Avocado (*Persea americana* Mill.) is a dicotyledonous plant belonging to the Lauraceae family, a native of Central America and Mexico, and cultivated in almost all tropical and subtropical regions worldwide. The fruits have high nutritional quality; contain high levels of vitamin, minerals, proteins, fibers, and unsaturated fatty acids, which are beneficial to health (TREMOCOLDI et al., 2018). Avocado peels and seeds have high contents of bioactive compounds, such as phenolic acids, condensed tannins, flavonoids (including procyanidins and flavonols), hydroxybenzoic and hydroxycinnamic acids (HURTADO-FERNÁNDEZ et al., 2011; DAIUTO et al., 2014; FIGUEROA et al., 2018a, b).

Industrial processing of avocado generates large quantities of agro-industrial byproducts (peel and seed), ranging from 18% to 23% of fruit dry weight (WANG et al. 2010). The individual phenolic profiles of hydroethanolic extracts of peels and kernels of avocado variety Hass showed correlation with their antioxidant, antimicrobial, and cytotoxic activities. Avocado byproducts presented a very distinct phenolic profile, with a higher concentration in peels (227.9 mg g^{-1} of total phenolic content), mainly of (epi)catechin derivatives (175 mg g^{-1}), followed by chlorogenic derivatives (42.9 mg g^{-1}) (MELGAR et al., 2018). The bioactive compounds can also be reported in seeds, such as catechin, protocatechin, epicatechin, and also p-coumaric, caffeic, ferulic, synaptic, p-hydroxybenzoic, vanillic, syringic, and gallic acids (RODRIGUEZ-CARPENA et al., 2011).

Studies have shown the antimicrobial effect of the compounds extracted from avocado seed extract on microorganisms. SALINAS-SALAZAR et al. (2017) have shown a biocidal effect of avocado seed extracts (7.8–15 mg L^{-1}) on *L. monocytogenes*, suggesting that the effect was due to the increase in permeability of cell membrane. The ethanolic extract of avocado seed had antimicrobial action against *L. monocytogenes* (375.0 µg L^{-1}), *Staphylococcus epidermidis* (354.2 µg L^{-1}) and *Zygosaccharomyces bailii* (500 µg L^{-1}) (CHIA & DIKES, 2010).

CONCLUSION

Several low-cost raw materials are available as agro-industrial wastes that are valuable sources of bioactive compounds. The huge variety of compounds produced by plants as secondary metabolites may act as antioxidants and antimicrobials with applications in the food and fermentation industries. Fruit wastes, in particular citrus, avocado, grape, and mango wastes, have been used for the extraction of compounds with biological activities similar to the synthetic compounds that are commonly used. These compounds offer a more natural and safer option to the food industry. The fermentation process involved in the bioethanol production deals with bacterial contaminants that could be combated with these natural antimicrobials; however, their utilization in the context of this industry has not received due attention. A promising field of application emerges from these investigative reports that could relieve the unsustainable use of hazardous chemicals in the bioethanol industry to fight bacterial contamination.

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DECLARATION OF CONFLICT OF INTERESTS

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

AUTHORS' CONTRIBUTIONS

All authors contributed equally to this research.

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