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Esterases e seu potencial biotecnológico na indústria de alimentos: uma revisão

Esterases and their biotechnological potential in the food industry: a review

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Resumo: As enzimas são biocatalisadores eficientes que podem ajudar no processamento de alimentos de maneira mais segura e ecológica. Estas reações podem ser realizadas em condições mais amenas e com excelente seletividade do produto, por isso a importância de estudos de suas aplicações. Além disso, devido a menores demandas de energia e menor produção de resíduos, elas foram aplicadas com sucesso a uma variedade de indústrias, incluindo indústrias de alimentos, detergentes, farmacêuticas e de biocombustíveis. As mais utilizadas pelo setor alimentício são as hidrolases. A hidrólise e síntese de ligações éster são catalisadas por hidrolases de éster carboxílico. Este grupo de enzima é classificado em 122 classes, de acordo com os substratos e éster carboxílico que elas hidrolisam. Algumas carboidrato esterases, tanases, esterases lipolíticas e outras esterases têm mostrado propriedades interessantes para vários tipos de processamento de alimentos. Além de seu uso direto, como na síntese de flavorizantes, clarificação de bebidas, digestão de ração, biosensores, por exemplo, elas demonstraram ser úteis para a desintoxicação de alimentos e gerenciamento de resíduos. Apesar de sua considerável importância, há escassez de revisões sobre esterases na indústria de alimentos e este trabalho teve como objetivo compilar todas as informações relevantes sobre esses catalisadores.

Palavras-chave: Carboidrato esterases. Tanases. Esterases lipolíticas. Indústria de alimentos. Enzimas alimentícias

Abstract: Enzymes are efficient biocatalysts that can help food processing in a safer and more environmentally friendly manner. These reactions can be performed in milder conditions and with excellent product selectivity, hence the importance of studies about their applications. Furthermore, due to lower energy requirements, lower waste production, they have been successfully applied to a variety of industries, including food, detergent, pharmaceutical and biofuels industries. The most used by the food sector are hydrolases. The hydrolysis and synthesis of ester bonds are catalyzed by carboxylic ester hydrolases. This group of enzymes is classified in 122 classes, according to the substrates

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and carboxylic ester they hydrolase. Some carbohydrate esterases, tannases, lipolytic esterases and other esterases have shown interesting properties for various types of food processing. Apart from their direct use, such as in flavoring synthesis, beverage clarification, feed digestion, biosensors, for example, they have been shown to be useful for the detoxification of food and management of waste. In spite of their considerable importance, there is a scarcity of reviews about esterases in the food industry and this paper aimed at compiling all the relevant information about these catalysts.

Keywords: Carbohydrate esterases. Tannases. Lipolytic esterases. Food industry. Food enzymes

1 INTRODUCTION

Many reactions performed by the industries can happen in milder conditions, with lower energy requirements and higher product specificity by dint of enzymes. Since they are biocatalysts, the waste generation is also lower. Owing to these characteristics, enzymes have been successfully used by food, detergent, pharmaceutical and biofuels industries. Their market was calculated at $11.47 billion in 2021 and an increase of 6.5% in their compound annual growth rate is expected to happen between 2022 and 2030. These biocatalysts have been applied to food production since ancient times, for example, cheese, yogurt, beer, wine, vinegar and sourdough. Enzymes used by the food industries can be endogenous, when they are naturally found in cells and tissues of the food, and they may present desired or undesired properties, or exogenous, when they are purposedly added. The most used by the food sector today are hydrolases, namely, invertases, amylases, lactases, lipases, lysozymes, proteases and pectinases (Zhang *et al*., 2018; Maghraby *et al*., 2023; Motta *et al*., 2023).

Carboxylic ester hydrolases are a diverse group that catalyzes the hydrolysis and synthesis of ester bonds (EC 3.1.1.x), such as glucuronoyl esterases, feruloyl esterases and acetyl xylan esterases (Monrad *et al*., 2018; Adesioye *et al*., 2016; Nieter *et al*., 2016). They are classified into 122 classes, depending on their substrates and carboxylic ester they hydrolase, from EC 3.1.1.1 to 3.1.1.118, with four additional classes, namely, 3.1.1.B10, 3.1.1.B11, 3.1.1.B12, and 3.1.1.B13. This diversity equals to their ample usage. They can be used in the synthesis or hydrolysis of ester compounds with applications in the food, pharmaceutical, biochemical, and biotechnology industries (Dahiya and Nigam 2022; Ghodke and Punekar, 2022). Besides esters, esterases are able to hydrolase thioesters and

phosphoesters. In organic phase, however, the ester synthesis can be favored. Furthermore, they present broad specificity and regiospecificity, which partly explain their biotechnological potential (Dahiya and Nigam 2022; Rafeeq *et al*., 2022).

Some carboxylic ester hydrolases are already being used by the food industries, such as feruloyl esterases and lipases, and others have shown great potential, which justifies the importance of new studies that will unveil new applications and allow their ampler usage. They can be applied to biosensors for aspartame detection, for instance. First, a carboxyl esterase cleaves the aspartame molecule, releasing methanol, which is then oxidized by an alcohol oxidase. The oxygen consumption is measured by an oxygenmeter. Due to its extensive use, it is imperative to have efficient and cheap ways to detect and determine aspartame concentration in the food industry, since approximately 1 in 24,000 individuals in world suffer from phenylketonuria. Esterases can also be employed in the clarification of juices, food flavors synthesis, the reduction of insoluble precipitates and bitterness of beverages, inter alia (Odaci 2004; Radulescu *et al*., 2014; Kohli *et al*., 2015; Cai *et al*., 2020; Czarnecka *et al*., 2021; Lekmish, *et al*., 2021; Elhawary *et al*., 2022). However, in spite of their importance for the food industry, there is lack of reviews that pertain to this subject. Thus, in this work, we aim to cover the current and potential uses of esterases in the food industry, describe their major characteristics and try to draw their future in this realm.

2 STRUCTURE AND MECHANISMS

These enzymes can act on specific and general esters. They can catalyze the hydrolysis and formation of esters. The E.C 3.1.1.x enzyme commission number was given to the esterases, in which X depends on the substrate the esterase will act on. The main reaction catalyzed by them is the hydrolysis:

$$R1\text{-}COO\text{-}R2 + H_2O \rightarrow R1\text{-}COOH + R2\text{-}OH$$

Here, R represents a hydrocarbon moiety. Varying the conditions, it is possible to procure other reactions, namely, esterification, transesterification, acidolysis and alcoholysis, as follows:

R1-COOH + R2-OH → R1-COO-R2 + H_2O (esterification)

R1-COO-R2 + R3-COO-R4 → R1-COO-R4 + R3-COO-R2 (transesterification)

R1-COO-R2 + R3-COOH → R3-COO-R2 + R1-COOH (acidolysis)

R1-COO-R2 + R3-OH → R1-COO-R3 + R2-OH (alcoholysis)

Besides, they have broad specificity and regiospecificity, which add to their biotechnological appeal, and they generally follow the Michaelis-Menten kinetics, in which the velocity of the reaction increases as the substrate concentration also increases, until a plateau is achieved. However, true lipases, which are active against long-chain acylglycerols, do not follow Michaelis-Menten kinetics and present interfacial activation, due to a lid that covers their active sites. Not until the concentration of substrate is enough to form micelles and emulsions is the lid moved, allowing the substrate to reach the active site, thus increasing the velocity dramatically (Sandoval *et al*., 2018; Dahiya and Nigam, 2022).

Most carboxylic ester hydrolases have the Pfam PF00561 domain, i.e., they have α/β hydrolase fold (Figure 1).

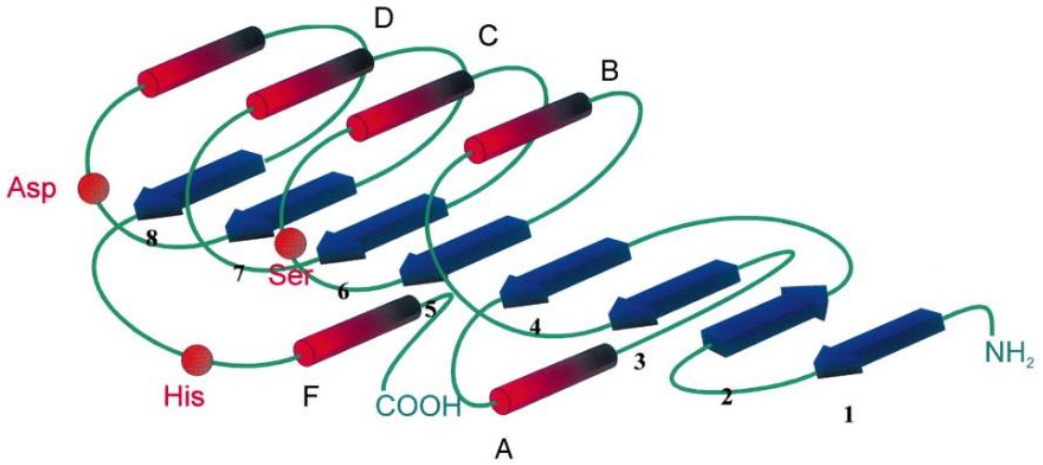

Figure 1. The α/β-hydrolase fold. The β-sheets are represented by blue arrows (1-8), while the α-helices are shown as red columns (A-F). The common catalytic triad Ser-Asp-His is represented by red circles (Adapted from Bornscheuer, 2002).

In addition, they usually have the catalytic triad Ser-Asp/Glu-His and the serine is frequently found in the consensus sequence Gly-X-Ser-X-Gly, also known as the "nucleophilic elbow", in which X represents any amino acid. Notwithstanding, new information that concerns the structure of esterases is in constant development. For example, it has been demonstrated that the serine can also be found in the Gly-Asp-Ser-Leu (GDSL) sequence, near the N-terminus (Bornscheuer, 2002; Sandoval *et al*., 2018). Moreover, Chen *et al*. (2016) attempted to classify the carboxylic ester hydrolases according to their primary, secondary, and tertiary structures available and were able to produce 91 families, 36 of them being grouped into five clans. One clan with standard α/β-hydrolase folds, two with similar folds but differing in the sequences of the β-strands, one with six-bladed β-propeller and one with three-α-helix bundle tertiary structures. The families that did not fit in any of those clans have a variety of structures or members with no resolved structures. Therefore, due to the great variety of family of esterases, the structures and mechanisms aforementioned are ascribed to the principal esterases, mainly "true" esterases and lipases, i.e., lipolytic esterases, with resolved structures, that have hitherto been studied. Hence, they cannot be considered a rule for all esterases, and it is probable that other structures and mechanisms will be revealed over time as new esterases are discovered.

3 POTENTIAL AND CURRENT USES IN THE FOOD INDUSTRY

The great variety of esterases justifies, at least in part, for their enormous biotechnological and economic potential. Lipolytic esterases account for 10% of the global market of enzymes (Meneses *et al*., 2021). Moreover, esterases present excellent chemo-, regio-, and/or enantioselectivity. Some esterases can also catalyze the reverse reaction in certain conditions, especially when water is removed from the medium. Therefore, these enzymes can be applied, for example, to the synthesis of pharmaceutical drugs, laundry detergents, oil chemistry, degradation of waste materials, synthesis of perfumes, and, in the food industry, they have been utilized, for instance, in the production of beverages, dairy and bakery products, modified acylglycerols, among others (Chandra *et al*., 2020; Bhardwaj *et al*., 2021; Zhang *et al*., 2023). Nonetheless, not all groups of esterases are

interesting for the food industry. Therefore, the objective of the following sessions is to summarize the state of the art of the esterases relevant to the this sector.

3.1 Carbohydrate esterases

Mono-, oligo- and polysaccharides often have -O or -N modifications, bonded by ester, and carbohydrate esterases remove them, facilitating the action of glycosyl hydrolases. Carbohydrate esterases are one class of five, namely, glycoside hydrolases, glycosyltransferases, polysaccharide lyases, and auxiliary activities. Information about these five classes is compiled in the Carbohydrate-Active Enzyme (CAZy) database. Carbohydrate esterases are further divided into 16 families (Sandoval *et al*., 2018).

3.1.1 Feruloyl esterases

The cell wall of plants is made of three main polysaccharides: cellulose, hemicellulose (xylan and its derivatives) and pectin. The rigidity of the cell wall depends, at least in part, on ferulic acids that bridge these polysaccharides (Thaker *et al*., 2021). Feruloyl esterases (EC 3.1.1.73) are carbohydrate esterases from family 1 that are able to hydrolase the ester bonds between ferulic acid, or other cinnamic acids, and cell wall polysaccharides of plants. Initially, there were four classes of feruloyl esterases, A-D, according to the artificial substrates they act on and primary sequences. The enzymes of class A are active against methyl ferulate (MFA), methyl p-coumarate (MpCA) and methyl sinapate (MSA), but does not accept methyl caffeate (MCA) as substrate, class B against MFA, MpCA and MCA, and class C and D against all substrates (Nieter *et al*., 2016). Currently, there are 13 families, which were obtained via 20 amino acid sequences of the enzymes studied so far and 247 available fungi genomes (Vega-Rodríguez *et al*., 2022).

These enzymes can be found in plants, bacteria and fungi. The discovery of the first feruloyl esterase was carried out in the bacterium *Streptomyces olivochromogenes*. Other bacterial sources are species from the genus *Lactobacillus*, such as *L. amylovorus*, *L. farciminis* and *L. plantarum*, *Streptomyces werraensis*, *Streptomyces* spp., *Clostridium thermocellum*, *Actinomyces* spp., *Dickeya dadantii*, *Geobacillus thermoglucosidasius*, and *Burkholderia pyrrocinia*. Fungi are the most studied producers, of which the principal

are *Aspergillus niger*, *A. oryzae* and *A. nidulans*, *Thielavia terrestris*, *Penicillium chrysgenum*, *Schizophyllum commune* and *Neurospora crassa*. For some phytopathogenic fungi, these enzymes are important to breach the cell wall of plants. A variety of plants has been shown to be producers, such as maize pollen, barley grain, malted finger millet, but, generally, the production is low (Thaker *et al*., 2021; Liu *et al*., 2022). However, microbial sources of enzymes are often preferred owing to their easier obtainment, better performance and genetic changes by recombinant DNA technology can be procured more easily (Singh *et al*., 2016; Raveendran *et al*., 2018).

The importance of feruloyl esterases for the food industries is based on the fact that these industries produce great quantities of agricultural waste, which are used as fertilizer, animal feed or burned. However, this material can be diverted to better use. For instance, the ferulic acid liberated by these catalysts is a useful food preservative, with antioxidant and antimicrobial properties. The ferulic acid can also be utilized in the obtainment of flavor compounds, such as vanillin, especially precious for the production of sweets such as ice creams, cakes and soft drinks, and 4-vinyl guaiacol, which is particularly valuable for wines, beers and soy sauce (Salgado *et al*., 2012; Banerjeeaand and Chattopadhyay, 2018; Vega-Rodríguez *et al*., 2022). Diverse studies have shown other possible applications of these esterases in the preparation of different food products. To name a few, lactic acid bacteria can be employed in the processing of plant biomass so as to produce ferulic acid to be then converted into vanillin, resulting in naturally flavored yoghurt and curd. The degradation of the xylan layer, which covers β-glucan, by feruloyl esterase has been reported to aid β-glucanase action, thus producing a clearer beer. Fruit juices industries may also benefit from them due to their clarification properties. In order to produce crispier bread for a longer time, these esterases might be applied to the improvement of the protein strength and reduction of the staling process. The phenolic flavor of black chocolate is the result, at least in part, of feruloyl esterase that liberates ferulic acid in the fermentation process of cocoa (Swamy and Govindaswamy, 2015).

Some enterprises already sell enzymatic cocktails containing feruloyl esterases, which represent their growing importance. For instance, the company Biocatalysts offers the Depol® products, which are taste modifiers and flavor enhancers, Prozomix has a cocktail, obtained from *Clostridium thermocellum* cultures, suitable for biomass conversion and

carbohydrate research, and Creative Enzymes® also has a food grade product. Nonetheless, in spite of all their potential, their ampler usage is still hindered by substrate or product inhibition, small substrate acceptance, limited stereo- and/or regioselectivity and inability to act under industrial conditions. Hence, more research is needed so as to improve these feruloyl esterases' characteristics so as to facilitate their usage by the food sector (Vega-Rodríguez, 2022).

3.1.2 p-coumaroyl esterase

The *p*-coumaroyl esterase is a not very studied enzyme, but with a potential that cannot be ignored. Its classification is EC 3.1.1.B10 and, according to BRENDA database, the first report of this enzyme was published in 1990, by Borneman *et al*., in anaerobic fungi found in cattle rumen. They are carbohydrate hydrolases from family 1. Bacteria and fungi are reported to be producers (Kim and Baik, 2015).

Since *p*-coumaric acid is an isomer of hydroxycinnamic acid, sometimes *p*-coumaroyl esterases are also considered a feruloyl esterase by researchers (Castanares *et al*., 1992). Notwithstanding, feruloyl esterases not always present activity against *p*-coumaric acid from complex cell walls. For example, feruloyl esterases from *Aspergillus* were demonstrated to have little activity against *p*-coumaric acid (Yu *et al*., 2004). Actually, the classification of *p*-coumaroyl esterases is very controversial. For example, other studies later showed that some feruloyl esterases have the ability to release *p*-coumaric acid from different materials (Liu *et al*., 2022).

And as controversial as *p*-coumaroyl esterase's classification is the classification of feruloyl esterases. According to Crepin's classification, feruloyl esterases can be distributed in A, B, C and D and putative E types. In a more recent classification, 13 subfamilies are suggested with an unclassified group, indicating that new classes may be created as new esterases are discovered (Oliveira *et al*., 2019). Indeed, Nieter *et al*. (2017) heterologously expressed a *Rhizoctonia solani* putative type B feruloyl esterase gene in *Pichia pastoris* and, due to its more pronounced activity against methyl *p*-coumarate, was considered to be a *p*-coumaroyl esterase, with little sequence similarity to any known feruloyl esterase, indicating that this may be a new type of enzyme. Therefore, as new esterases are described, the true classification of *p*-coumaroyl esterases will become

clearer. Anyhow, the *p*-coumaroyl esterase of *R. solani* was used to decrease the 5-O-caffeoylquinic acid concentration, which is related to low cup quality, of coffee powder, and might be stomach irritating, even though this acid is an antioxidant and may contribute to the prevention of several diseases. This same esterase was also successfully used in the chlorogenic acid degradation of apple juice, since it is associated with sour and bitter taste. Moreover, an increase in the concentration of caffeic acid was observed in both beverages, without altering the taste. Caffeic acid is more antioxidative than 5-O-caffeoylquinic acid; therefore, this enzymatic treatment can improve their antioxidant and anti-inflammatory properties. As chlorogenic acids are commonly found in higher dicotyledonous, other beverages may benefit from this enzyme, like tomato juice, for example (Siebert *et al*., 2018; Siebert *et al*., 2019; Wang *et al*., 2022). .

3.1.3 Acetylxylan esterases

Acetylxylan esterases (EC 3.1.1.72) belong to the carbohydrate esterase families 1 to 7, 12 and 16, which indicates their ample sequence variety and biochemical properties. They are responsible for removing acetic acid from acetylated hemicellulose, especially glucuronoarabinoxylan and xylooligosaccharides (Sandoval *et al*., 2018; Kato *et al*., 2021). Hemicellulose is a heteropolysaccharide xylan and its heterogeneity is important for its solubility, and consequent cell wall hydrodynamics, and for preventing microorganism invasion in plants (Puchart and Biely, 2023). The removal of these acetyl groups increases cellulase accessibility and, therefore, these enzymes are significant for lignocellulose degradation. Although some plant esterases are reported to have activity against acetylxylan, these esterases are mainly found in microorganisms from diverse environments, such as the bacteria from the genera *Fibrobacter*, *Bacillus*, *Thermobifida* and *Streptomyces*, and filamentous fungi from the genera *Trichoderma* and *Aspergillus*. Furthermore, they were first identified in the cellulolytic enzyme systems of the fungus *Schizophyllum commune* (Adesioye *et al*., 2016; Popa *et al*., 2020; Puchart and Biely, 2023).

Acetylxylan esterases have some importance for the food industry, particularly when used with other enzymes. For example, they aid feed digestion when applied to feedstock, since the lignocellulosic biomass is very viscous. Along with xylanases and cellulases, they

have been shown to be useful for improving milk production in goats and Murray buffaloes (Sista Kameshwar and Qin, 2018). They can also be utilized as prebiotics. The hydrolysis of xylan generates xylooligosaccharides, which cannot be hydrolyzed or absorbed in the upper gastrointestinal tract, hence, they can booster the growth or activity of bacteria in the colon and cause health benefits. In addition, together with pectinases, they can help to clarify juices. The cloudiness and high viscosity observed in these beverages are the result of pectic substances obtained from the fruits. Therefore, their enzymatic removal improves taste, texture and appearance of the product (Motta *et al*., 2013; Popa *et al*., 2020; Patel *et al*., 2022).

3.1.4 Cutinases

Belonging to the *α/β* hydrolase superfamily, the cutinases are serine hydrolases of small molecular weight and have the EC number 3.1.1.74. They are carbohydrate hydrolases from family 5. These enzymes show activity against cutin, an aliphatic polyester, and have characteristics of lipases and lipolytic esterases, such as the Ser-His-Asp catalytic triad. However, unlike lipases, these enzymes do not have a hydrophobic "cap" that covers its active site. New molecular structure studies have revealed a somewhat flexible active site and the presence of a "mini-cap" (Martínez and Maicas, 2021; Liang and Zou, 2022). The main producers are fungi, such as *Alternaria brassicicola*, species from the genus *Aspergillus*, *Colletotrichum*, *Fusarium*, among others, but plants and bacteria are also sources.

Owing to their diverse evolution, not only cutinases can be used in the degradation of cutin and synthetic plastic, which show large molecular weight, but also for small molecules, such as esters, short-chain and long-chain triacylglycerols. In addition, they can be applied to esterification and transesterification reactions (Liang and Zou, 2022). In regard to the food industry, cutinases have ample application. For instance, patents have been created for treating fruit, berry and vegetable materials, by dint of cutinases. They can be also be useful in the process of drying unmacerated fruit and vegetables, by increasing water permeability. This increased permeability can also be useful for delivering sweeteners, preservatives, flavor enhancers, and stabilizers. Besides, they have been successfully utilized in the production of lipolyzed milk fat and dairy flavors

(Nyyssölä, 2015). It has been also demonstrated the capability of cutinases to improve the efficiency of pesticides, thus increasing crop yields and reducing pesticide consumption. Other studies showed their ability to decolorize the molasses wastewater of sugar factories and degrade synthetic and polymers contaminations, which can help the food industry to deal more efficiently with its waste (Liang and Zou, 2022).

3.1.5 Pectin esterases

Thirty percent of the carbohydrates of dicots, monocot and gymnosperms cell walls are pectin, a heterogenous polysaccharide. Pectin interacts with hemicellulose and cellulose, holding the cell wall together. Its structural classes are homogalacturonan, rhamnogalacturonan I, rhamnogalacturonan II and substituted galacturonan like xylogalacturonan, and apiogalacturonan. Pectinases hydrolase pectin and are composed of de-esterifying and de-polymerizing enzymes. The de-esterifying enzymes are carbohydrate esterases, viz., pectin methyl esterase and pectin/rhamnogalacturonan acetyl esterase (Ahmed *et al*., 2021).

Pectin methyl esterases (EC 3.1.1.11) belong to the family 8 of the carbohydrate esterases and they carry out the demethylesterification of methyl ester residues at the C6 of galacturonic acid, thus releasing non-methyl esterified homogalacturonan, protons and methanol (Kontogiorgos *et al*., 2020). They are found in higher plants, phytopathogenic fungi, and bacteria, and perform a variety of functions. In plants, they are involved in the production of methanol, stem elongation, solid wood properties, and, in pathogens, play a key role in the plant-pathogen interactions. These enzymes have many applications, sometimes used in combinations with other pectinases, such as clarification of juices, firming of fruits and vegetables before processing, such as pasteurization, freezing and dehydration, modification of pectin, production of low sugar jam and jellies, oil extraction, peeling of delicate fruits, among others (Kohli *et al*., 2015).

Pectin acetyl esterase (EC 3.1.1.6) and rhamnogalacturonan acetyl esterase (3.1.1.86) carry out the removal of acetyl groups from homogalacturonan and rhamnogalacturonan regions, respectively. Pectin acetyl esterase from fungi and bacteria belong to the family 12 of carbohydrate hydrolases, while those from plants belong to family 13. There are also members from family 16, but they are solely from fungal origin. On the other hand,

rhamnogalacturonan acetyl esterases are part of family 12. Similar to pectin methyl esterases, these two esterases can be used with other pectinases and have been shown to be useful in the gelation process of the food industry, for example. In other fields, they have been applied to the obtainment of biofuel and other products from biomass, hydrogel beads for drug delivery, and substances with anti-cancer activity derived from pectin (Ma *et al*., 2018; Sandoval *et al*., 2018; Ahmed *et al*., 2021).

3.2 Other esterases

3.2.1 Tannases

Tannins are polyphenolic substances that can be found in vegetable parts, such as leaf, bark, fruit, root, wood and seeds. These compounds are part of the defense mechanism of plants, protecting them from bacterial, fungal and viral infections and, owing to their bitter taste, confer safeguard against insects and herbivores. Not only tannins are useful for plants, but also for humans. Plants extracts containing them have been used by China and Japan for centuries to treat inflammation, tonsillitis, hemorrhage, diarrhea, and even cancer. Furthermore, they can be applied to the treatment of heavy metal poisoning, HIV, and Hepatitis B. Nonetheless, due to its ability to precipitate proteins and digestive enzymes, they are considered anti-nutritional and the culprits of the bitterness of tea, fruit juices and wine. Tannin acyl hydrolase (E.C.3.1.1.20), with their esterase and depsidase activity, act on tannins and gallic acid esters, releasing glucose and gallic acid (Aharwar and Parihar, 2018; Biswas *et al*., 2022).

These enzymes' production is induced by tannic acid and microorganisms are the main producers, including filamentous fungi, such as *Penicillium* sp. and *Aspergillus*, a high number of bacteria, and a few yeasts such as *Aureobasidium* sp. and *Sporidiobolus* sp. However, fungi are the most efficient of them, and submerged solid state fermentation (SSF) is the most used method of production, by virtue of low-cost substrate, lack of feedback inhibition, higher enzyme yield and easier purification and production. Because of that, different companies have been utilizing fungi for their production (Biswas *et al*., 2020; Cavalcanti *et al*., 2020; Biswas *et al*., 2022).

These catalysts present wide application and, with respect to food industries, they can be used, for example, as a clarifying agent for coffee flavored beverages, the reduction of insoluble precipitates and bitterness of beverages, better quality animal feed and black tea infusion, the production of gallic acid, a protector for crops and food storage, whose worldwide demand is some 8000 t. On account of their catalytic potential and commercial applications, different companies now commercialize tannases, like Kikkoman (Japan), Novo Nordisk (Denmark), ASA special enzyme GmbH (Germany), Amano (Japan), Biocon (India), Julich (Germany), Wako Pure Chemical Industries, Ltd. (Japan), and Sigma–Aldrich Co. (USA) (Dhiman *et al*., 2018; de Las Rivas *et al*., 2019; Lekmish, *et al*., 2021).

3.2.2 Lipolytic esterases

Lipolytic esterases comprise lipases, from the triacylglycerol ester hydrolase family (EC 3.1.1.3), and "true" esterases, which belong to the carboxyl ester hydrolases (EC 3.1.1.1). Lipases, with a hydrophobic domain around the active site, catalyze the hydrolysis of long-chain triacylglycerols (C ≥10) into glycerol and fatty acids, whereas the "true" esterases, with an acyl binding pocket, present activity against short-chain triglycerides. In addition, both show the characteristic α/β hydrolase fold, and their catalytic domain has a Ser at the active site, found in the consensus sequence G-X-S-X-G. The Ser is part, together with a His and Asp or Glu, of a very conserved catalytic triad (Castro *et al*., 2018; Barzkar *et al*., 2021; Rafeeq *et al*., 2022;).

Lipases have enormous biotechnological potential and are the third most used enzyme in the world, after proteases and amylases, due to, at least in part, its high stability in non-aqueous environments, because they do not require cofactors, and their immobilization is relatively easy. Furthermore, in water-restricted environments, they can catalyze esterification, interesterification and transesterification reactions. They are ubiquitous and produced by plants, animals and microorganisms (Melani *et al*., 2020; Barzkar *et al*., 2021). The food industry is one of largest consumers of lipases, employing them in dairy products, fruit juices, baked products and the synthesis of modified acylglycerols. They are very useful in the synthesis of food aromas. For example, lipases of the fungus *Penicillium roquefortii* can produce methyl ketones and improve blue cheese production,

and furfuryl acetate, a flavoring agent for food and bakery products, can be obtained with lipase from *Burkholderia cepacia*. Human-like milk and cocoa butter equivalents can be obtained by the special treatment of fats by lipases. What is more, they have been successfully used to speed up the ripening of cheese, in tea processing, as biosensors for the food industry, vitamin C ester production, an antioxidant for fat-rich foods, in wine manufacturing, among others, besides their indirect application in the treatment of wastes (Chandra *et al*., 2020; Melani *et al*., 2020).

"True" esterases can also be very interesting for biotechnological applications, since they present high enantioselectivity, stability in organic solvents and broad substrate specificity. Additionally, they can catalyze ester synthesis in non-aqueous environments. Nonetheless, these catalysts are not as common as lipases in the industries, mainly because of a lack of availability, despite their wide distribution in animal, plants and microorganisms (Rafeeq *et al*., 2022; Sharma *et al*., 2022). Despite this, these esterases have been shown to have great potential for the food industry. For instance, free all-*trans*-astaxanthin improves immune response and memory, has antioxidant and antitumor activity, *inter alia*, and have extensively been used in food, aquaculture and poultry production. This compound has been synthesized by a "true" esterase, which was isolated from marine genomic DNA libraries, using *Haematococcus pluvialis* microalgae oil (Lu *et al*., 2018). Along with an alcohol oxidase, an esterase from porcine liver was applied to the development of an aspartame biosensor (Odacı, 2004). Moreover, they have already been employed for food flavors synthesis and shown to intensify flavor production during cheese making (de Luca *et al*., 2018; Cai *et al*., 2020; Dong *et al*., 2020).

3.2.3 Miscellaneous esterases

Some groups of esterases are not yet of great importance for the food industry directly, but show promise for the productive chain as a whole. For example, pyrethroid hydrolases (EC 3.1.1.88) are esterases found in animals, microorganisms and plants. They play a key role in degrading pyrethroid insecticides, which are vastly used in food production. It is hoped that they will be used in bioremediation and removal of these pesticides in the future (Bhatt *et al*., 2020). On the other hand, there are esterases that do not belong to any very important group for the food industry individually, but present interesting features

when used with other esterases, as is the case with aromatic carboxylesterases. Phthalate esters are used in the synthesis of polyester resins, plastic bottles, polyester fibers and plasticizers. Aromatic carboxylesterases, which are composed by members of various classes of esterases, such as cocaine esterase (EC 3.1.1.84) and mycophenolic acid acylglucuronide esterase (3.1.1.93), have evolved, and have been evolving, to degrade these new substrates, rare before human activity. Fifty per cent of all plastic generated is made of packaging. Therefore, these esterases will certainly help the industries cope with this growing problem (Ncube *et al*., 2021; Ghodke and Punekar, 2022).

Still, there are esterases which researchers were not able to determine their proper classification; however, they present features that may benefit the food industry eventually. For instance, strains of *Lactobacillus plantarum* with high esterase activity have shown the ability to detoxify the mycotoxin zearalenone, which may be helpful to treat contaminated feed (Chen *et al*., 2018). By using an esterase, Jayshree and Vasudevan (2019) were able to develop an easier way to determine phthalate esters spectrophotometrically in drinking water stored in PET bottles. Hence, as esterases are more profoundly understood, it is expected that new classes with attractive applications in the food industry will be unveiled. All groups of esterases relevant to the food industries are summarized in Table 1, below.

Table 1 - Esterases relevant to the food industries.

Group of esterases	Reaction catalyzed	Applications in the food industry	References
Feruloyl esterases	Hydrolysis of ester bonds between ferulic acid and cell wall polysaccharides of plants.	Flavor synthesis; clarification of beverages; bakery; dairy products.	Salgado *et al*., 2012; Swamy and Govindaswamy, 2015; Banerjeeaand and Chattopadhyay, 2018; Vega-Rodríguez *et al*., 2022.
p-coumaroyl esterase	Hydrolysis of *p*-coumaric acid from complex cell walls.	Decrease of chlorogenic acids in plant-based beverages, such as coffee and apple juice.	Siebert *et al*., 2018; Siebert *et al*., 2019; Wang *et al*., 2022.
Acetylxylan esterases	Removal of acetic acid from acetylated hemicellulose, especially glucuronoarabinoxylan and xylooligosaccharides.	Feed digestion; Prebiotics synthesis; Juice clarification.	Motta et al., 2013; Adesioye *et al*., 2016; Popa et al., 2020; Puchart and Biely, 2023.
Cutinases	Hydrolysis of cutin.	Fruit, berry and vegetable treatment; dairy products;	Nyyssölä, 2015; Liang and Zou, 2022.

		Pesticide enhancer; Waste treatment.	
Pectin esterases	Demethylesterification of methyl ester residues and removal of acetyl groups of pectin.	Juice clarification; Fruit and vegetable treatment; Jams and jellies; Oil extraction; Gelation.	Kohli *et al.*, 2015; Sandoval *et al.*, 2018; Ahmed *et al.*, 2021.
Tannases	Hydrolysis of ester and depside linkages in hydrolyzable tannins.	Beverage clarification; animal feed; Black tea; Production of gallic acid.	Dhiman *et al.*, 2018; de Las Rivas *et al.*, 2019; Lekmish, *et al.*, 2021
Lipolytic esterases	Hydrolysis of long-chain triacylglycerols.	Dairy products; fruit juices; bakery; synthesis of modified acylglycerols; synthesis of food aromas; tea; biosensors; wine; waste treatment.	Odacı, 2004; de Luca *et al.*, 2018; Lu *et al.*, 2018; Cai *et al.*, 2020; Chandra *et al.*, 2020; Dong *et al.*, 2020; Melani *et al.*, 2020.
Miscellaneous esterases	Hydrolysis of different esters.	Waste management: degradation of pyrethroid insecticides and plastics; Mycotoxin detoxification; phthalate esters determination in drinking water.	Chen *et al.*, 2018; Jayshree and Vasudevan, 2019; Bhatt *et al.*, 2020. Ncube *et al.*, 2021; Ghodke and Punekar, 2022.

3.3 New technologies and future perspectives for esterases in the food industry

As with other enzymes, most applications of esterases in the food industry will depend on new technologies that will circumvent their intrinsic drawbacks. Enzymes often do not exhibit the characteristics that fit the harsh conditions demanded by various industries, such as non-natural substances, extreme pH and temperature and low water activity. In order to improve their performances, immobilization can be an option, where an insoluble, reusable enzymatic platform is generated, with high catalytic activity and stability. Immobilization involves the incarceration of enzymes to a matrix, which must provide regenerability and inertness, by different methods. Esterases can be immobilized by covalent binding, adsorption, entrapment, cross-linking and encapsulation. In adsorption, weak forces are formed when enzymes and the support are mixed in the right conditions. Covalent binding immobilization can occur due to the presence of side chain amino acids that react to activated functional groups, such as epoxy and vinyl groups activated with bromide. Covalent or non-covalent bonds mediate the interaction between esterases and fibers or gels in the entrapment, in which the catalysts have freedom to move within constrained spaces. Similarly, in encapsulation the enzymes are packaged in

semi-permeable membranes and can move freely within delimited spaces. Finally, in cross-linking, the immobilization depends on exclusively the enzymes, which are chemically or physically fused together (Berna *et al*., 2018; Sharma *et al*., 2022).

Another alternative to meet industrial demands is protein engineering. This technique aims at developing random or targeted genetic diversity, in order to obtain better versions of the original enzymes for certain conditions. Most commonly, directed evolution or rational design are used. The former emulates natural evolution, in which a cycle of mutagenesis and selection of the best phenotypes is performed. Then, the selected mutants undergo other rounds of mutagenesis and selection until an interesting variant is obtained. On the other hand, rational design takes advantage of available functional and structural information to generate specific mutants that may present better features, greatly diminishing the number of mutagenesis and selection experiments. What is more, the integration of both protein engineering and immobilization may help facilitate the use of esterases in the food industry in the future, and other enzymes as well (Berna *et al*., 2018).

4 CONCLUSIONS

In summary, esterases catalyze the hydrolysis and synthesis of ester bonds, with broad specificity and regiospecificity, that are crucial for the maintenance of life. Of the multifarious classes of esterases, a few have been shown to be relevant to the food industry and were compiled in this review, viz., some carbohydrate esterases, tannases, lipolytic esterases and miscellaneous esterases that can be applied to food production directly, waste management or detoxification. Yet, the future of these enzymes in the food sector will be determined by the discovery of new enzymes, and technologies, such as immobilization and protein engineering, which will adapt the attributes necessary for the industries.

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