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Review

Plant Extracts as Natural Inhibitors of Non-Enzymatic Browning: A Case of Fruits and Fruit-Based Products

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Abstract

Heat processing in fruit and fruit-based food products is aimed at producing nutritious, shelf-stable, and consumer- appealing food products. However, the processing and prolonged storage conditions employed favour non-enzymatic browning (NEB) reactions. Recent research is aimed at finding natural products to inhibit deleterious food reactions, with NEB being one of them. This review discusses the role of plant extracts in inhibiting NEB reactions during the processing and storage of fruit and fruit-based products. The review follows a traditional narrative approach, where approximately 100 articles were reviewed by summarising the role of vegetables, fruits, and fruit-based products in the diet, followed by the chemical reactions taking place during processing and storage, with emphasis on the pathways of three types of NEB reactions. We evaluate the prevention of NEB reactions using plant and plant extracts with a focus on the inhibitory mechanisms, as well as limitations, thereof. Encapsulation was also discussed as a possible intervention for the limitations posed by plant extracts.

Keywords: non-enzymatic browning; heat processing; Maillard reaction; ascorbic acid; plant extracts; polyphenols; encapsulation

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Academic Editor: Antony C. Calokerinos

Received: 23 September 2025
Revised: 12 November 2025
Accepted: 4 December 2025
Published: 11 December 2025

Citation: Vhangani, L.N.; Van Wyk, J. Plant Extracts as Natural Inhibitors of Non-Enzymatic Browning: A Case of Fruits and Fruit-Based Products. *AppliedChem* **2025**, *5*, 39. https://doi.org/10.3390/appliedchem5040039

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1. Introduction

During the processing and storage of fruit and fruit-based products, non-enzymatic browning (NEB) reactions are responsible for the formation of undesirable brown colour and producing undesirable toxic compounds [1]. In light of this information, the prevention of NEB reactions is of utmost importance. Some mitigation strategies are possible, such as a reduction in processing temperatures and time and substituting highly reactive ingredients with less-reactive ingredients to inhibit NEB reactions during processing and storage. However, these interventions are not applicable to all product types and pose the risk of producing products of inferior quality in terms of attributes such as taste, colour, and flavour. Therefore, alternative inhibition methods must be pursued [2].

Chemical inhibitors are the most preferred choice due to their low cost and high performance. Amongst them, sulphites have proven to be superior in inhibiting NEB reactions, especially in blocking the initial condensation step of the Maillard reaction (MR) by attaching to the carbonyl of sugars or stabilising the intermediate hydroxymethyl furfural (HMF) to prevent further reaction [3]. Aminoguanidine (AG) is another well-known NEB inhibitor [4]. However, both of these inhibitors have been investigated with regards to safety concerns [3,4]. Due to the critical role that glycation plays in various

diseases, there is a need to find natural anti-glycation agents, which could be delivered through the diet. Therefore, the best alternatives are the utilisation of plant extracts [5].

Plant extracts are good candidates due to their versatile activities, having bioactive constituents, such as flavonoids, phenolic acids, curcumin, vitamin E, and C. Crude plant extract bioactives have been assessed for their ability to inhibit NEB/glycation markers such as HMF, furfural, glyoxal (GO), methyl glyoxal (MGO), and the development of advanced glycation end-products [4,6,7]. Using model systems, authors such as Favre et al. (2020) [8,9] showed that plant extracts exhibited an inhibitory effect against the formation of NEB product markers. Moreover, the inhibitory capacity was widely attributed to the presence of polyphenolic compounds [9,10]. The anti-glycation properties of polyphenols have been linked to their antioxidant activity [10–12].

Therefore, the aim of this study was to highlight the NEB taking place in fruit and fruit-based products during processing and storage, and to elucidate the effect of plant extracts in inhibiting the formation of NEB markers such as brown colour development, HMF, furfural, and other compounds.

2. Material and Methods

This review was conducted using a traditional narrative approach to provide a broad and critical synthesis of the scientific literature on non-enzymatic browning (NEB) reactions during food processing, with particular emphasis on their occurrence in fruit and fruit-based food products. The discussion includes the Maillard reaction (MR), sugar and ascorbic acid degradation and their mechanisms, as well as the anti-glycation potentials and mechanisms of plant polyphenols. Special consideration was given to research highlighting fruit processing practices such as canning, pasteurisation, and sterilisation, and to studies addressing the role of fruits and fruit-derived products in the human diet.

Academic publications were identified primarily through the Scopus database, with full-text access obtained from the Elsevier, Wiley, and MDPI journals. These sources were selected for their strong representation of research on NEB in food science and technology, and especially for their coverage of fruit chemistry and processing studies. The review considered literature published between 2000 and 2024, with the inclusion of a few earlier studies that remain relevant in shaping the field. Search terms combined key phrases and thematic concepts, including “non-enzymatic browning,” “polyphenols and NEB,” “anti-glycation,” “Maillard reaction,” “Maillard reaction mechanisms,” and “ascorbic acid degradation.”

Only publications written in English were initially screened, by reviewing titles and abstracts to identify their relevance to the themes. Articles meeting preliminary relevance criteria were then examined in full to confirm their contribution to the review’s objectives. Final inclusion was guided not only by predefined criteria such as relevance to food processing and chemistry, but also by the scholarly significance of the work, particularly its contribution to understanding NEB reactions in fruit systems and the implications for processed fruits and fruit-based products. Approximately 90 articles were studied; these provided a balanced overview of both early conceptual developments and recent research progress, allowing for a critical discussion of evolving knowledge, persistent challenges, and future directions in fruit-focused food chemistry, processing, and sustainable technology.

3. The Role of Vegetables, Fruits, and Fruit-Based Products in the Diet

The food-based dietary guidelines of the Food and Agriculture Organisation (FAO) of the United Nations recommend the consumption of plenty of fruits and vegetables. Nutritionists and dieticians have always highlighted the important role of the human

diet with reference to health. Food consumption is more than just satisfying hunger and nutritional requirements [13]. In addition, foods have recently been recognised as protective agents as well. Research has proven that a high intake of fruit and vegetables is linked to reduced risks of a number of chronic diseases [14]. This is attributed to their provision of an optimal mix of phytochemicals, natural antioxidants, fibres, and other bioactive compounds. Amongst them, antioxidants and vitamins present in fruit and vegetables are of utmost interest [15]. Although food composition tables rely mostly on food products consumed raw, they also take into consideration the fact that the concentration of nutrients and their biological activity may change due to environmental variables and processing. This aspect is of great importance, considering that fruit and vegetables are consumed in their raw state and are also processed for safety, quality, and economic reasons. Fruits and vegetables are subjected to blanching, freezing, drying, or canning, and these preservation methods are generally but often erroneously believed to be responsible for a depletion of naturally occurring nutrients in food [16].

However, while thermal processing preserves these food commodities against microorganisms, it may indeed also result in chemical reactions that also reduce their shelf-life [17,18]. During the preparation of white-fleshed fruits for canning, enzymatic browning takes place, and this is due to the contact of plant enzymes with phenols in the presence of oxygen, leading to the production of melanin [19]. However, pre-processing measures are undertaken to prevent this reaction. In addition, this reaction is completely inhibited once the contents are heat-processed, resulting in the deactivation of all enzymes. Hence, although enzymatic browning might not be a problem in this context, non-enzymatic browning reactions (NEB) may also take place [20]. Non-enzymatic browning control is more complex since there are three possible reactions, which are all favoured by key components as well as the processing and storage conditions of canned fruits.

3.1. Non-Enzymatic Browning Reactions

Non-enzymatic browning can be categorised into the Maillard reaction, ascorbic acid degradation, acid-catalysed sugar degradation, also commonly known as caramelisation, and to a large extent, lipid oxidation [17,21]. The most important aspect of these reactions is that a compound formed via one mechanism serves as a key reactant in the other. Thus, all these reactions might take place in the same food product [13,22]. Although non-enzymatic browning reactions produce desirable flavours, aromas, and colour, and, in some instances, enhance the antioxidant properties of certain food products, they also produce toxic compounds which results in reduced nutritional values of the food product they are formed in [13,23].

This is of great significance, considering that food safety is a major concern for food manufacturers, consumers, and health authorities. In recent years, the International Agency for Research on Cancer, the Food and Drug Administration, and the Joint FAO/World Health Organisation have identified some compounds that are generated in food as potentially toxic, mutagenic, or even carcinogenic. Such compounds may be formed through multiple pathways in which lipids, carbohydrates, amino acids or ascorbic acid are thermally degraded [24]. Some of these undesirable compounds include furfural (hydroxymethylfurfural, methyl furfural, and dimethyl hydroxyl furanone), acrylamide, and heterocyclic compounds (furans, pyrroles, and pyridines), whose concentration depends on the severity of the heat treatment and storage time and conditions [25]. Those compounds have been identified in a wide range of foods containing carbohydrates, such as processed fruits, honey, juices [26], milk, extruded cereals (e.g., breakfast and infant cereals), crackers, and bread [12,27].

Although the taste of food is one of the most important sensorial properties of food, colour is considered as the deciding factor as to whether a consumer will buy a certain food product or not. Since NEB has a significant influence on product quality, monitoring the extent of this reaction can be a valuable tool in food manufacturing processes. Thus, preventing browning in canned fruits is of vital significance [18]. Possible interventions the include lowering of processing temperatures and time and substituting sugar syrup with juice [2]. Most canned fruits lie in the high-acid food range; thus minimal processing is required since the pH acts as a preservative. However, with ascorbic acid browning, pH in the acidic range is a pre-requisite, and this reaction is accelerated at this pH [26]. Moreover, the canning industry recently moved from canning fruits in syrup to fruit juices, jellies, and nectars, as a means of reducing the sugar content of canned fruits, consequently reducing the chances of non-enzymatic browning via caramelisation. However, commonly used juices include apple and pineapple juice, and these contain substantial amounts of vitamin C, which, when present in higher quantities, can undergo browning [28,29]. Another intervention is that the industry has moved from the use of cans to plastic cups. The oxygen ingress rate is much higher in the latter packaging, which results in the oxidative degradation of ascorbic acid [28]. Hence, the inhibition of NEB seems to be a difficult task. The following sections will focus on NEB reactions and products formed in fruit and fruit-based products during processing and storage. The type of browning reaction taking place depends on the physicochemical properties of the food in question. At times, all of these NEB reactions might take place in one product; however, one pathway may dominate depending on intrinsic and extrinsic factors [1]. These chemical reactions are known to be a contributing factor to food quality, consequently affecting consumer acceptability. Another lesser-known consequence of NEB is the loss of nutrition and formation of toxic compounds [30]. To maintain the quality aspects of food, NEB reactions should be strictly monitored. As a result, product composition, observed changes, and formed compounds are used as quality markers. The ingredient type and concentration before and after, already point us in the direction of which reaction to look out for. The most pronounced change in this case is browning, measured by colour change [28,31]. The last category relates to chemical compounds that form due to the type of ingredient and processing conditions. By following these three markers, the NEB pathway can be elucidated [21].

3.2. Ascorbic Acid Degradation

Ascorbic acid, also known as vitamin C, is a water-soluble vitamin found abundantly in fruits and vegetables. The main physiological function of vitamin C is to form and maintain bones, blood vessels and collagen. Fruits and vegetables are known to be the main source of vitamin C; thus it is one of the indices used to measure the nutritional quality of fruits [32]. It also possesses health-promoting qualities such as its capacity to be used in the prevention of colds and flu and its association with the prevention of scurvy.

In food formulation, vitamin C is known for its role as an acidulant, a flour improver in baking, and a processing aid in preventing enzymatic browning [33]. Chemically, its lactone structure contributes to its reducing ability. Common processing and storage conditions of oxygen, heat, and the presence of enzymes and metals render vitamin C unstable [32]. Therefore, it is crucial to fully describe and understand the underlying mechanism of vitamin C degradation.

In fruit and fruit-based products, the degradation of AA during processing and storage has been found to occur via aerobic and anaerobic pathways, depending on factors such as temperatures, the presence or absence of oxygen, pH, light, and water activity and content [34]. Based on these factors, oxidative degradation is more pronounced during processing due to constant aeration, whilst non-oxidative degradation occurs mainly

during storage. Thus, at high oxygen concentrations, aerobic degradation preceded the anaerobic pathway.

3.3. Aerobic and Anaerobic Degradation of Ascorbic Acid

Figure 1 depicts the initiation of the oxidative degradation pathway of AA, where it is oxidised to form dehydroascorbic acid (DHA). The oxidation step is reversible in the presence of a reducing agent. The presence of water results in the hydrolysis of DHA to form 2,3-diketogulonic acid, which does not exhibit vitamin C activity. Decarboxylation of 2,3-diketo-gulonic acid leads to the formation of xylosone, which is further dehydrated to form reactive carbonyl compounds such as 2-furoic acid, 3-hydroxy-2-pyrone, and furfural, amongst many others [1]. Due to their high reactivity, carbonyl compounds may participate in the MR via condensation with amino acids or proteins to form brown polymers.

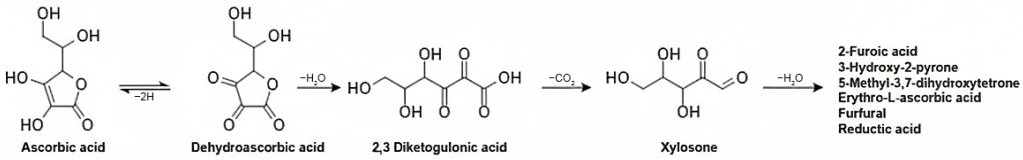

Figure 1. Schematic representation of the aerobic pathway of ascorbic acid degradation, adapted and recreated by the authors from Buve et al. (2021) [1].

3.3.1. Anaerobic Degradation of AA

The initial step of the anaerobic pathway involves the direct cleavage of the lactone ring of AA via hydrolysis to form 2,3-enegulonic acid, which is further decarboxylated to xylose (Figure 2). The formed xylose undergoes intramolecular rearrangement and dehydrations to form furfural [1].

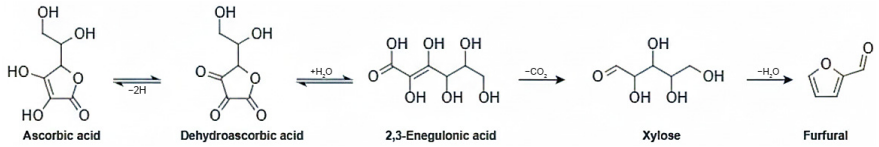

Figure 2. Schematic representation of the anaerobic pathway of ascorbic acid degradation, adapted and recreated by the authors from Buve et al. (2021) [1].

3.3.2. Ascorbic Acid Degradation in Fruit and Fruit-Based Products

Oxygen is present in food products via incorporation during preparation and processing, especially aeration during mixing. This is then transferred into the packaged food, present as dissolved and headspace oxygen. In addition, depending on the barrier properties of packaging, oxygen can diffuse through the package from the environment [31]. Pham et al. (2019) [35] observed a continuous diffusion of oxygen in orange juice packed in high-oxygen-permeable polyethylene terephthalate bottles during storage. On the other hand, Valero (2017) [18] found that residual oxygen dissolved in the syrup and trapped in the headspace was found in canned peaches, although preheating and exhausting was performed. Various authors reported on the aerobic degradation of AA taking precedence over the anaerobic pathway, especially in the presence of high oxygen concentrations. These authors observed that as the O_2 concentration depleted to lower levels, anaerobic AA degradation takes over. Therefore, aerobic AA degradation takes place during processing and a few days or weeks of storage, after which, anaerobic AA degradation takes place during the latter stage of storage. This is usually observed via imbalances in faster and greater depletion in AA, and smaller increases in DHA formation. Low oxygen levels also indicate a lower conversion of AA to DHA. For instance, Wibowo et al. (2015b) [36] re-

ported on a 75% loss of AA in orange juice after 8 and 32 weeks of storage at 42 and 20 °C, respectively, which was attributed to the drastic loss of the dissolved and headspace oxygen observed in the first two weeks of storage. Consequently, furfural was detected at week 2 for samples stored at 42 °C, which then continued to increase throughout 32 weeks of storage due to the anaerobic degradation pathway taking over when the oxygen concentration was low. The oxygen concentration of orange juice supplemented with AA and citric acid (CA) reached extremely low levels after 2 to 4 weeks of storage, with samples with the highest AA content exhibiting a faster consumption rate of oxygen [28]. Similarly, furfural was also reported after 2 weeks storage for juice + CA + AA and 6 weeks for juice + AA. Therefore, this implies that furfural formation via AA degradation is favoured at lower pH values. Lyu et al. (2018) [37] also observed a decrease in AA in peach juice of approximately 29, 40, and 47% after 40-day storage at 4, 25, and 37 °C, respectively. However, instead of furfural, they reported HMF as a product of aerobic degradation. Burdurlu et al. (2006) [22] also reported HMF as the main degradation product of AA degradation in citrus juice concentrates (orange, tangerine, lemon, and grapefruit), although they found that sugar degradation also took place, although it was preceded by the former reaction. Using precursor-based studies, Agcam (2022) [24] proved that AA-enriched fruit-based medium was superior in inducing furfural formation compared to sugar and amino acid-enriched samples. Furthermore, they found that no HMF formation was detected in the fruit juice-based medium enriched with AA only. Louarme and Billaud (2012) [13] investigated AA degradation during conventional and ohmic heating treatments of a chunky peach apple dessert. They confirmed that the oxidative thermal degradation of AA preceded sugar degradation during the three-step production process involving apple puree, peach dice, and the apple puree–peach dessert. They reported an approximately 33% loss in AA (supplemented in the puree), resulting in the formation of 3-hydroxy-2-pyrone ($3H_2P$) (2 mg 100 g^{-1}) at six and four times the levels of furoic acid and furfural. This was attributed to the wide pH range of the dessert, which favoured the formation of $3H_2P$, meanwhile the formation of furoic acid and furfural are known to be favoured by the high-acid medium of pH ($\leq$2).

3.4. Acid-Catalysed Sugar Degradation

Fruit and fruit-based products are classified according to acidity levels, including low-, medium-, and high-pH levels of pH > 4.5, 3.7–4.5, and <3.7, respectively [24]. Under these acidic conditions and other factors such as high processing temperatures and low a_w, sugar content, and prolonged storage, sugars decompose to form reactive intermediates that take part in browning formation [38]. Acid-catalysed degradation of sugars starts with the hydrolysis of a disaccharide (sucrose) or complex carbohydrate (starch) to its reducing forms (fructose and glucose) (Figure 3). Glucose and fructose undergo enolisation to form a 1,2-enediol intermediate. However, fructose can directly dehydrate, resulting in losing three molecules of water to form HMF [24]. The enediol is dehydrated and oxidised to form 3-deoxyglucosone (3-DG) and glucosone, respectively. The 3-DG compound degrades further via dehydration by losing two molecules of water to form HMF or undergoes retro-aldolisation to form methylglyoxal (MGO). On the other hand, in the presence of metals, the retro-aldolisation of glucosone yields threosone and glyoxal [26]. At this point of the reaction, the formed intermediate compounds are highly reactive and might polymerise with each other or react with amino acids to form brown polymers [29].

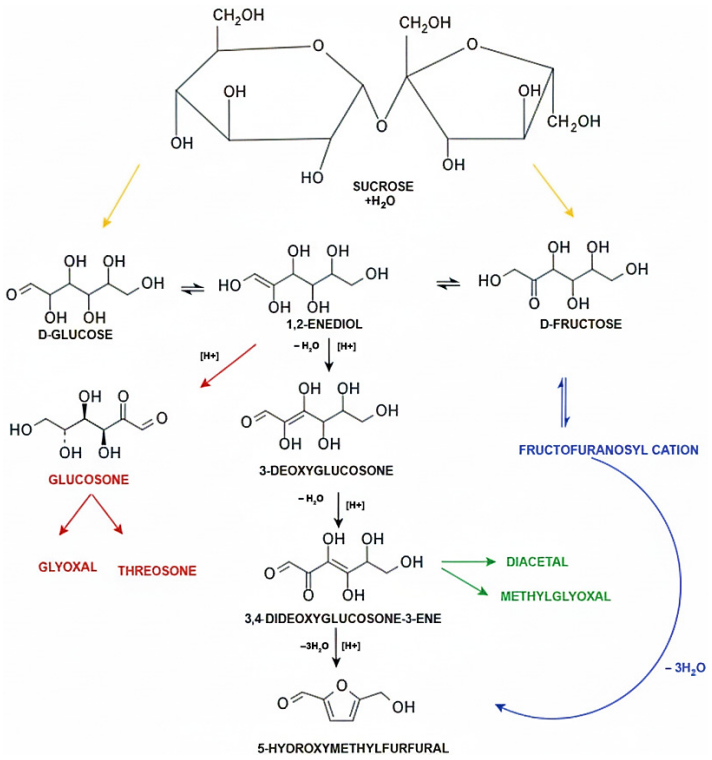

Figure 3. Schematic representation of the acid-catalysed degradation of sugars' pathway, adapted and recreated by the authors from Buve et al. (2021) [1].

Acid-Catalysed Sugar Degradation in Fruits and Fruit-Based Products

Fruits and fruit-based products, like apple and pear purees and orange juice, contain mainly three sugars: namely, glucose, sucrose, and fructose, with other complex carbohydrates like pectin, hemicellulose, and oligosaccharides, etc. [26,39]. In the food science literature, the concept of sugar concentration is commonly referred to as total sugar content, total soluble solids, or total dissolved solids, expressed as °Brix (°B) [31]. Alternatively, the reducing sugar content can be measured; however, the limitation in this is that the contribution of sucrose is overlooked. Therefore, reducing sugars must be determined in conjunction with total sugar content, as determined by Liao et al. (2020) [40] and Aktag and Gokmen [41]. The acid-catalysed degradation of sugars can be monitored by tracking sugar consumption via changes in the °B, total, or reducing sugar content of the product. However, to obtain an accurate measure of NEB, changes in sugar content must be examined in conjunction with the identification of specific intermediate or end-products.

Garza et al. (1999; 2000) [39,42] reported variations in sucrose, fructose, and glucose in peach and apple puree heated at 80–98 °C for 8 h. An initial increase in fructose and glucose occurred due to sucrose hydrolysis, which was counteracted as the two participated in acid-catalysed dehydration to form HMF. Pham et al. (2019) [43] also highlighted the process of sucrose hydrolysis as a step required prior to acid degradation of sugars to form HMF during the storage of orange juice. Contrary to the findings of Garza et al. (1999, 2000) [39,42], Pham et al. (2019) [43] observed that sucrose reduction did not coincide with an increase in fructose and glucose, alluding to the fact that complex carbohydrates such as pectin and hemicellulose were also hydrolysed to yield fructose and glucose. Based on the anomalies stated above, Buve et al. (2021) [1] cautioned against making conclusions about sugar degradation solely based on changes in the total and reducing sugar contents.

Other crucial aspects in sugar degradation relating to sugar are the concentration, type, and, most importantly, the pH of the food product. Concentration has a direct effect on the contents of the NEB reaction products formed. An increase in sugar has been proven to

have a positive correlation with HMF, furfural, and other dicarbonyl compounds. The HMF content of red and white grape juice concentrates increased as the total sugar increased from 15 to 45, and then to 65 °B. Hydroxymethyl furfural was more pronounced in white than in red grape concentrates [44]. Although red grape juice contained 3% more sugar, its pH averaged around 3.7, while that of white grape juice was lower at 3.3. In this case, pH was the rate-determining factor. The effect of low pH on HMF formation via sugar degradation was reported by Burdurlu et al. (2006) [22] on fruit juice concentrates of pHs ranging from 1.82 to 3.23, and the lowest activation energy (Ea) of 43 kcal·mol^{-1} for HMF formation was reported for lemon juice at pH 1.82, increasing to 80.02 kcal·mol^{-1} for orange juice at pH 3.2. In addition to sugar degradation, Burdurlu et al. (2006) [22] attributed HMF formation to both AA and acid-catalysed degradation. Pham et al. (2020) [26] noticed negligible changes in the sugars of control samples at pHs of 3.8 and 4.5 of pasteurised orange juice, while drastic hydrolysis of sucrose was observed for samples adjusted to pH 1.5 and 2.5. It is worthy of mentioning that sucrose hydrolysis was complete after 1 day and 2 weeks of storage for the pH 1.5 and 2.5 samples, respectively. Furthermore, these authors concluded that lowering the pH from 3.8 to 1.5 increased the degradation rate constant of AA, sucrose inversion, and the formation rates of furfural and HMF. Regarding sugar type, it has been established that monosaccharides react faster than disaccharides, since the latter requires the step of hydrolysis. In addition, the ketohexoses react faster than aldohexoses [24]. For instance, HMF can be formed via the direct dehydration of fructose, meanwhile, glucose requires the steps of enolisation to 1,2-enediol, dehydration to 3-deoxyglucosone, and then further dehydration to form HMF [24]. Hence, as expected, Gürsul Aktağ and Gokmen (2020) [38] found that HMF formation via dehydration of the fructofuranosyl cation was two, four, and seven times higher in peach nectar, apple juice, and orange juice compared to the 3-deoxyglucosone pathway due to a high fructose content. The fast reactivity of fructose is due to it being available as an open chain in aqueous media, thus making it more readily available to react as compared to glucose's reactivity, which is limited by its ring-opening step [45].

3.5. The Maillard Reaction (MR)

The MR is the most common type of NEB reaction occurring in food during the processing and storage of food products but is not common in fruits and fruit-based products. This is mainly due to the acidic nature of these products. However, when it does take place, it is usually preceded by ascorbic acid (AA) degradation. The MR occurs when a carbonyl-containing compound, namely, reducing sugars, aldehydes, or ketones, condenses with a free amino group of amino acids, peptides, or proteins during processing and prolonged storage of food products. The reaction is divided into early, intermediate, and advanced stages, with each resulting in a myriad of reaction products termed Maillard reaction products (MRPs) [46]. Processes such as roasting, baking, or frying result in the formation of colour and flavour which are amongst the favourable effects of the MR, while on the other hand, during drying, pasteurisation, sterilisation, and storage, the occurrence of the MR is unfavourable due to discolouration, off-flavour formation, as well as a reduction in nutritional value. Owing to this, it is essential to better understand the MR progression in order to control the formation of desirable attributes, while preventing or minimising undesirable effects [46].

As depicted in Figure 3, the first step of the MR involves the condensation of the carbonyl group of a reducing sugar and a free amino group of an amino acid [21]. This forms a reversible Schiff base adduct *N*-substituted glycosylamine, which, due to its instability, further rearranges to form a stable 1-amino-1-deoxy-2-ketose or 2-amino-2-deoxy-1-aldose, also known as Amadori or Heyns products, respectively (Figure 4). Depending on which

reducing sugar participated in the Maillard reaction, the rearrangement is either called an Amadori rearrangement, if an aldose sugar like glucose participated, or a Heyns rearrangement, if a ketose like fructose participated in the reaction [47]. These products are colourless or slightly yellow compounds and are known as intermediate Maillard reaction products, referred to as pre-melanoidins or low-molecular-weight fractions. As the reaction proceeds, more complex dark brown and fluorescent products are formed. The colour changes and intermediate products formed are used as an indicator of the progression of the reaction and to identify the stages of the MR [21].

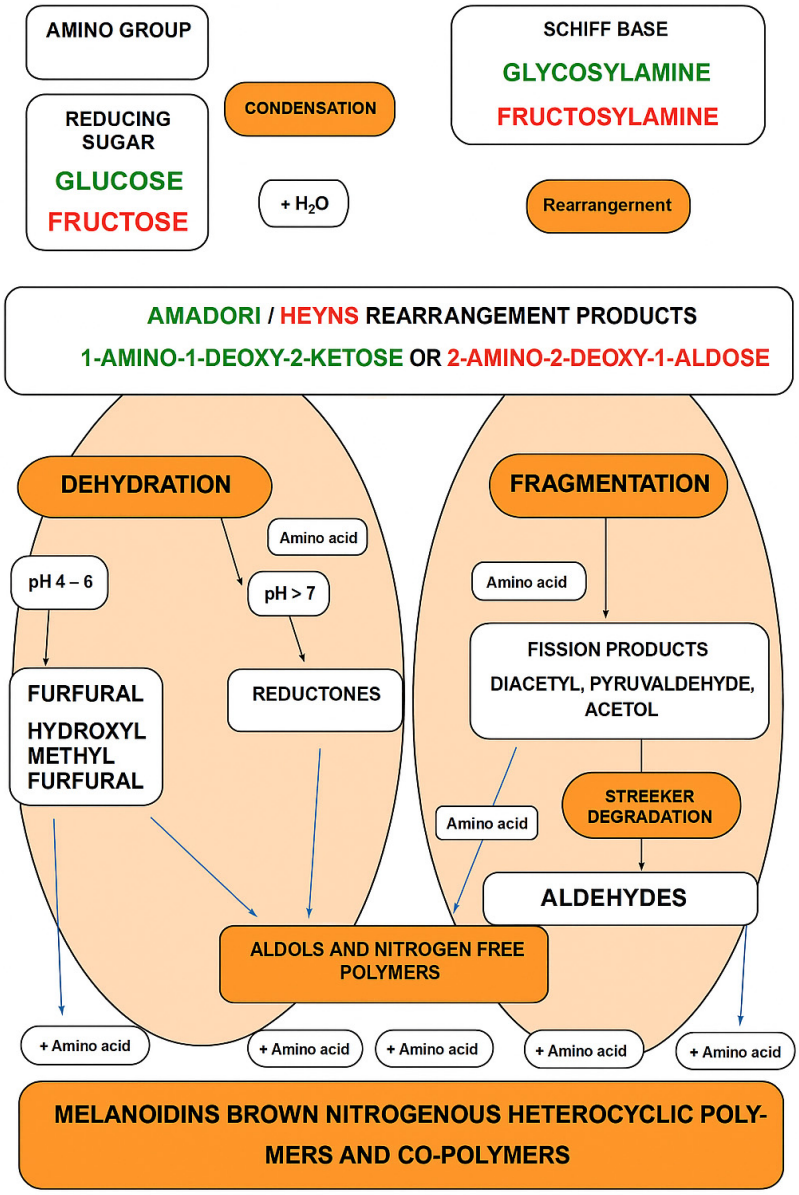

Figure 4. Schematic representation of the Maillard reaction pathway, adapted and recreated by the authors from Rufian–Henares and Pastoriza (2016) [21].

The intermediate stage begins when Amadori and Heyns products degrade, resulting in the formation of new molecules via dehydration, fission, and Strecker degradation. The newly formed compounds contribute to the flavour and aroma and vary in their characteristics depending on the conditions employed. At this stage, pH and reactant type are the important rate-determining factors (Figure 4). The sugar moiety of the Amadori/Heyns products is degraded into deoxyosones and various carbonyl compounds such as methylglyoxal and glyoxal, resulting in the release of the amino group. The subsequent pathways

of deoxyosones are mainly governed by the pH. At a pH below 5, their fragmentation leads to the formation of 3-deoxyosone, but if the pH is above 7, the pathway involving the 1- and 4-deoxyosones prevails. However, most food products are in the pH range of 4–6, where the 3-deoxyosones route predominates. Furthermore, the dehydration of 1-deoxyosone and 3-deoxyosones leads to the formation of reductones and furfurals, respectively. Specifically, 3-deoxyosones forms furfural when a pentose sugar is involved or hydroxyl methyl furfural (HMF) when a hexose sugar is involved. The Amadori rearrangement products have been reported to be less reactive than reductones and methylglyoxal, but 10–100 times more reactive than the parent reducing sugars. During the intermediate stage, amino acids act only as catalysts, but in the final stage they participate in the Strecker degradation reaction. In this reaction, the amino acids are degraded by pre-formed dicarbonyl compounds leading to the oxidative deamination and decarboxylation of amino acids to form aldehydes with one carbon atom less than the original amino acid. Furthermore, Strecker aldehydes are major contributors to the aroma of thermally processed food. Some examples include 3-methyl butanal, methional, and phenylacetaldehyde, which have been identified in yeast extracts, boiled chicken and beef, roasted coffee, chocolate, and various other food products. These are potent aroma components with extremely low odour thresholds [21].

In the final stage of the reaction, aldehydes, reductones, and other dicarbonyls polymerise in the absence of amino acids to give aldols and high-molecular-weight nitrogen-free polymers, while in the presence of amino acids, brown-coloured nitrogen polymers and co-polymers, called melanoidins, are formed. Although the structure of melanoidins is not well understood, it is known that it is the main contributor of colour in food [48].

Maillard Reaction in Fruit and Fruit-Based Products

The high sugar content and low-pH conditions of fruits juice concentrates are usually synonymous with AA degradation and sugar degradation (caramelisation), however, Wang et al. (2006) [49] and Ye et al. (2023) [34] solely attributed the browning and HMF development in carrot juice concentrates and a composite puree of *Choerospondias axillaris*, snow pear, and apple during storage to the MR. Zhu et al. (2009) [20] reported the formation of HMF in pasteurised apple juice (95 °C: 30 and 60 min) via the dehydration of sugars. However, a sudden decrease after 6 days of storage at 20 °C was observed due to condensation between HMF with available amino acids taking place via the MR. In another study, the HMF of orange juice heated at 90, 105, and 120 °C was lower for the latter two temperatures. They found that HMF quickly decomposed in fruit juice-based medium containing amino acids via the MR. Moreover, they concluded that fructose had remarkably higher potential to induce HMF. Canned peaches in syrup with a final pH of 3.7 were found to have simultaneously undergone AA and acid-catalysed sugar degradation during the initial stages of storage, followed by the MR in the later stages of the 365 days of storage at 30 °C. The reason for this is that, during the initial storage days, the acidic pH 2.7 favoured the former reactions. Although it is common knowledge that the classical MR via the condensation of sugar and amino acid is not favoured by pH < 4.0, it is the reactive carbonyl species (RCS) originating from AA and sugar degradation that condense with amino acids, and these are termed Maillard-associated reactions [26]. Attesting to this, Gursul Aktag and Gokmen (2021) [41] reported a decrease in free amino acids of apple concentrate at 33, 58, and 77% and pomegranate concentrate at 37, 67, and 87% as the sugar increased from 30 to 50, and then to 65 °B. In addition, the same study also reported a 71, 83, and 76% decrease in free amino acids of blueberry, raisins, and dates stored at 20 °C for 6 months. The changes observed in free amino acid content were presumed to be because of the MR. A negative correlation of 0.861 between the total free amino acid and the 3-DG contents of dates during storage led to the MR. Considering that the MR is favoured at a neutral pH, it is important

to mention that the initial pH of dates was the highest at 6.61, compared to the 3.79 and 2.64 pHs of raisin and blueberry, respectively. Furthermore, the mass spectra of Schiff base and adducts between amino acid asparagine and RCS (HMF and 3-DG) proved the occurrence of the MR during the storage of apple concentrate and raisins. Their highly acidic intrinsic nature notwithstanding, the MR could take place in dried fruits and juice concentrates due to a favourable a_w of 0.6–0.8. Contrary to the above findings, the earlier work of Aktag and Gokmen (2020) [38] observed no significant changes in the free amino acids of peach, apple, and orange juice stored at similar conditions as concentrates. The most probable explanation could be that the a_w of 0.9 of the juice was a rate-limiting factor for the MR. The effect of the MR on the browning of fruit juice has been long underestimated. This might be due to all the NEB reactions taking place simultaneously in a product and the possibility of the MR being ruled out erroneously based on the conditions of pH and a_w composition. As a result, reactant isotope labelling was sought and suggested as an ideal approach to track the precursors and intermediate compounds of NEB, in particular the MR [24,35]. With isotope labelling, Paravisini and Peterson (2019) [29] estimated that the MR generated up to 70%, with AA generating 30%, of the total browning of orange juice, with fructose being the main precursor of 3-DG (62%), MGO (75), glyoxal (GO) (78%), and acetol (26%).

3.6. The Multidimensions of NEB Reactions

Numerous authors have reported on the contribution of AA, acid-catalysed sugar degradation, and the MR on NEB reactions in fruit and fruit-based products [34,50]. To a large extent, NEB-related research focuses on the quantitative changes in the initial reactants (reducing sugars, amino acids, or ascorbic acid), changes in browning indices, as well as the formation of chemical markers (intermediate RCS). Unfortunately, these NEB reactions rely on a pool of similar reactants, environmental conditions, and may form the same intermediate compounds. In complex food systems, these reactions may take place simultaneously. For instance, Liao et al. (2020) [40] observed that the browning rate as measured by 420 nm was faster than HMF formation, which revealed that more than one NEB reaction was taking place. The interdependency of various NEB factors, as well as the transient nature of intermediate compounds, may lead to under- and overestimating the effect of one variable or pathway over another. Hence, the application of kinetics in conjunction with isotope labelling can solve the problem relating to the effect of the precursor on the identification of specific compound formation [34].

NEB-related reactions in fruits and fruit-based products and compounds formed, as a result, have been successfully defined using kinetic modelling. Garza et al. (2000) [39] established that sucrose reduction in apple puree followed first-order kinetics, whilst HMF formation was characterised by both first- and second-order kinetics. Similarly, first-order kinetic modelling was established for browning and HMF development in carrot juice concentrate during storage [49], ascorbic acid degradation in citrus juice concentrates [22], orange juice, and pasteurised mango juice [36]. However, in the same study, Wibowo et al. (2015b) [36] classified colour and HMF formation as best described by zero-order models. This happens to contradict the aforementioned results in terms of the modelling using kinetics. This is a common occurrence in NEB-related research and is usually due to the complexity of the reactions as well as the composition of the food system [34].

4. The Role of Plant Extracts in Inhibiting NEB Reactions

Recent trends in alleviating thermally induced toxic compounds focus on the utilisation of plant extracts [9,47,51]. This follows the current trend of using natural ingredients as an alternative to synthetic additives, and the optimisation of production processes for

improving the safety of processed and stored foods. Chemical inhibitors are the most preferred choice due to their low cost and high performance. Amongst them, sulphites have proven to be superior in inhibiting NEB reactions, in particular the MR. Sulphites are known to exhibit their mode of action via blocking the initial condensation step by attaching to the carbonyl of sugars, as well as stabilising the intermediate HMF, which prevents it from reacting further [17]. Another synthetic additive, the advanced glycation end-product (AGE) inhibitor aminoguanidine (AG) is known as an excellent trapper of MGO [4]. However, both of these have been investigated in terms of safety concerns when incorporated in food products. Sulphites have been subjected to increased regulatory scrutiny due to their association with initiating reactions in asthmatic individuals [3] and the suggestion that it reduces the uptake of the B vitamin thiamine. On the other hand, AG raises safety concerns due to possible side effects [51] related to weakened liver, anaemia, vomiting, gastrointestinal disorders, diarrhoea, dizziness, headache, and flu [4,11].

Due to the critical role that NEB reaction end-products play in food quality and glycation, there is a need to find natural additives which exhibit both anti-browning and anti-glycation properties to be delivered through the diet. Therefore, the best alternative is the utilisation of plant extracts [5] Many plants extracts, particularly medicinal types, have been studied for their antioxidant capacity due to their versatile bioactive constituents, such as vitamins, minerals, and polyphenols. The intake of foods with antioxidants has beneficial effects on human health, showing strong evidence that regular dietary intake of inherent antioxidants is associated with lowering risks of degenerative diseases, particularly cardiovascular diseases and cancer [52].

The indigenous South African plant species *Aspalathus linearis*, better known as rooibos, is native to the Cederberg of the Western Cape (South Africa) [53]. *Aspalathus linearis* is known for its commercial use as rooibos tea, where it is commercialised in two different forms: unfermented (green) and fermented (red) rooibos. *Aspalathus linearis* infusions have received great attention in recent years due to their bio-functional properties, with numerous studies having been conducted on the health-promoting properties associated with rooibos. These include antioxidant [54], anti-inflammatory [55], anti-carcinogenic [56], antimicrobial, anti-obesity, and hypoglycaemic [57] activities. These authors reported the presence of polyphenols as the responsible compounds for the above-mentioned properties [53].

4.1. Polyphenols as Major Bioactive Compounds in Plant Extracts

Polyphenols are secondary plant metabolites involved in defence against ultraviolet radiation or attack by pathogens [52]. They are found largely in fruits, vegetables, cereals, and beverages [15]. In food products, polyphenols may impart sensory attributes such as bitterness, astringency, colour, flavour, odour, and, in terms of functionality, stability against spoilage related to microbes and oxidation [58]. Of the prior mentioned varieties, green rooibos extracts and infusions have been proven to exhibit significantly higher antioxidant content compared to their red counterpart. This is mainly due to the decrease in the chief polyphenols aspalathin and nothofagin during fermentation. Evincing this were the findings of Joubert et al. (2005) [59], who reported a reduction in aspalathin content in ethyl acetate-soluble fractions of green rooibos extracts from 547 to 36.4 $mg \cdot g^{-1}$ after fermentation. Aspalathin and nothofagin are the major contributors to the total polyphenolic content, which in turn contributes the most towards bio-functional properties [54,60–62]. These two polyphenols fall under flavonoids, which is one of the four major classes of polyphenols, with the other three being phenolic acids, stilbenes, and lignans. In addition to flavonoids, phenolic acids are also of interest in the present study, since they have been

proven to exhibit anti-glycation activity in vitro (model and real food systems) as well as in vivo [5].

Many studies have been conducted and confirmed that different polyphenolic substances possess anti-glycation activities in vivo and in vitro, and that they could also prevent RCS production during food processing and storage [4,5,11]. The structure and type of polyphenols is greatly associated with the extent of the anti-glycation activities [63]. For instance, the higher the number of hydroxyl groups, the better the activity. Phenolic acids with three or more hydroxyl (OH) groups exhibited higher MGO-trapping abilities [5].

4.2. Plant Extract Mechanisms of Inhibition for NEB Reactions Using Plants Extracts

Several mechanisms of inhibition have been confirmed and elaborated based on the different stages of glycation. During the initial stages of the MR, polyphenols block the carbonyl or dicarbonyl groups of sugars, preventing the production of Schiff bases [11], and consequently the Amadori products [63]. When Schiff bases are formed, they become prone to oxidation and produce free radicals and RCS, with epigallocatechin gallate (EGCG) having been found to scavenge these free radicals [11], and significantly reduced browning in a glucose–glycine model system and apple sauce and bread roll formulation, compared to the control sample [46]. Furthermore, of special interest to the present study in relation to the possible anti-glycative properties of green rooibos based on the above finding, is that Joubert and DeBeer (2014) [64] found that aspalathin's antioxidant capacity compares to that of EGCG. Moreover, most of these polyphenols whose anti-glycation activities are noted are constituents of green rooibos, and it is reasonable to project that they would exhibit these properties in canned apples and in fruit juice in the current study. Moreover, the oxidation described is usually catalysed by metals. In addition, quercetin was found to inhibit AGE production through the trapping and blocking of MGO and GO, as well scavenging free radicals [5]. Ferulic acid has been found to inhibit dicarbonyl [5,51], formation and prevent Carboxymethyllysine and Carboxyethyllysine developments in model systems; however, its efficacy gravitates more toward the prevention of late-stage glycation. The anti-glycation action was credited to the antioxidant property of FA.

In addition, authors who studied the anti-glycative effect of plant extracts proved that these plant extracts exhibited considerably better anti-glycation activity than the identified individual polyphenols contained in the described extracts [46]. A case in point, the aforementioned study of Wu et al. (2009) [51] also reported that guava leaves and fruit extracts exhibited excellent metal-chelating (MTC) activities as well as activities inhibiting the progression of the early, intermediate, and final stages of the MR. Amongst the extracts, Shi Ji Ba, Ta Ba guava leaves, and whole-fruit extracts at 100 $\mu g \cdot mL^{-1}$ exhibited 7, 14, and 19% inhibitory activity against Amadori rearrangement products, and 28, 36, and 14% against the formation of bovine serum albumin BSA-glucose α-dicarbonyl, respectively. In addition, these guava extracts were compared to commercial AG, which exhibited 39% inhibition against glucose-BSA α-dicarbonyl. The inhibitory potency of guava extracts was due to the presence of four main polyphenols, phenolic acids (ferulic and gallic acid), and flavonoids (catechin and quercetin). Zhao et al. (2022) [65] made comparisons between a plant extract and their individual primary polyphenols. They revealed that chokeberry extracts exhibited the lowest 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) radical-scavenging, Ferric-reducing antioxidant power, and MTC compared to cyanidin-3-galactoside (Cy-3-gal), chlorogenic acid (CA), epigallocatechin gallate (EGCG), and quercetin (QC), which, nonetheless, exhibited better DPPH radical-scavenging activity than CA. However, chokeberry extracts exhibited the highest inhibition against BSA-glucose α-dicarbonyl at 48%, with the primary polyphenols' inhibition ranging between 15 and 44%.

4.3. Limitations of Plant Extracts

Although the above-mentioned plant extracts (Section 4.2) have been proven to exhibit excellent anti-browning activities in vitro, the final intended use is application in food formulation, and they must thus withstand processing and storage conditions. As a result, crude plant extracts or purified individual polyphenols have been reported to affect colour changes when incorporated in food or model systems [27]. This might be influenced by either natural pigmentation, or the reaction of polyphenols with food components resulting in colour augmentation. These changes are also accelerated by the high temperatures employed during common food preservation methods such as drying, pasteurisation, and sterilisation, leading to reduced bioactive function [66].

Concerning pure polyphenols, at concentrations of 1–1.5%, EGCG successfully reduced the browning rate of bread rolls. However, at increased concentrations of 3%, it exhibited pro-oxidative activity [46]. Qi et al. (2018) [67] also reported the efficacy of 0.01–0.1 $mg \cdot L^{-1}$ flavan-3-ols against the MR, however at 0.3–1 $mg \cdot L^{-1}$, darkening occurred due to autoxidation at high temperatures.

4.4. Encapsulation of Plant Extracts

The aforementioned instabilities (Section 4.3) of polyphenols during heat processing and storage may pose a challenge to using native plant extracts [68]. Consequently, the development of encapsulation methods and delivery systems containing specific compounds can improve some physicochemical properties of these extracts in food products. The encapsulation of sensitive compounds provides improved stability during processing, and in the final product by preventing reaction with other components in food products such as oxygen or water [69]. The release of microparticle content at controlled rates can be triggered by shearing, solubilisation, heating, pH, or the enzyme activity of these agents naturally present in certain plants, ensuring their stability. Common encapsulation materials include carbohydrates, protein and lipid polymers such as maltodextrin, inulin [70], soy protein isolates, sodium alginate, and cyclodextrins, to mention a few. The choice of polymer is crucial as it affects how the active compound is released. For instance, Hidalgo et al. (2018) [27] reported on elevated furosine levels in soy protein isolates applied to encapsulate beetroot pomace due to thermal treatments. Similarly, maltodextrin reacts with glycine to form browning compounds [71]. Lavelli and Sri Harsha (2019) [10] reported that sodium alginate-encapsulated grape skin extracts exhibited reduced potential to inhibit glycation of fructose-BSA and MGO-BSA model systems, which was due to some phenolics interacting with alginate, resulting in a decreased release. Therefore, the encapsulating polymer should not participate in any chemical reaction during processing or storage. Cyclodextrins have been proven not to participate in NEB reactions [71]. Moreover, unlike other potential encapsulants, β-CD is also known to aid in the extraction of these polyphenols from their sources, hence the term "β-CD assisted extracts" [8,72].

Many techniques applied to recover antioxidants from plants, such as Soxhlet extraction, are coupled with maceration, and are also dependent on the extracting solvent used for extraction. Water is the safest solvent that may be used for the extraction of bioactive compounds from plant materials; however, its capability is limited to polar compounds, and also results in lower extraction efficiency [73]. Polar organic solvents, on the other hand, are frequently applied for the recovery of polyphenols from plant materials. Solvents frequently used contain an aqueous mixture of ethanol, methanol, acetone, or ethyl acetate. Although these solvents are effective in increasing the extraction yield, enormous volumes are used, and they are not environmentally friendly, contributing to pollution. Hence "greener" extraction procedures are sought to reduce the environmental impact caused by these solvents [74,75].

4.5. Beta-Cyclodextrin- Assisted Extraction of Plant Extracts

Alternative green extraction methods, such as supercritical fluid and water extraction, ultrasound, and pulsed electric field-assisted extraction, are considered to reduce the use of organic solvents [68]. However, the cost associated with the procurement of these alternative technologies might prohibit their implementation. It is in light of this information that the present study focused on exploring the combination of water and beta-cyclodextrin (β-CD).

Cyclodextrins are made up of cyclic oligosaccharides consisting of a number of α (1 → 4)-linked D-glucose subunits with a truncated cone spatial geometry. The most common forms, alpha (α), beta (β), and lambda (γ-CDs), are composed of six, seven, and eight glucose units, respectively [74]. These molecules are widely used in the food, pharmaceutical, and chemical industries for their ability to form host–guest inclusion complexes with a wide range of bioactive compounds [74,76]. This results in the modification of the physicochemical properties of the encapsulated compound, leading to improved rheological and structural properties such gelling, viscosity, solubility, and stability [77]. Maraulo et al. (2021) [72] proved that β-CD enhanced the physical properties of olive pomace extracts via improved heat stability and reduced hydroscopicity, in addition to increased antioxidant activity. Numerous studies have been conducted where the ability of CDs to improve the extraction of polyphenols from plant matrices was investigated. In these studies, extraction parameters, such as the type of CD and its concentration, temperature, and time are likely to influence the process, having possible interactions among the variables [74,78–80]. For instance, the extraction of some phenolic compounds from plants with different aqueous CD solutions has been demonstrated to be an efficient and eco-friendly extraction process [81]. In another study, Rajha et al. (2015) [82] compared the efficacy of solvents, namely, water, methanol, and hydro-ethanol with that of a β-CD-water solution (37.7 $mg \cdot mL^{-1}$) to extract polyphenols from vine shoots. Results showed that it took ten hours of extraction time to attain the same polyphenolic yield with pure water, compared to five hours using the β-CD solution. In addition, β-CD-assisted extraction also resulted in a higher content of polyphenols than hydro-ethanol. The encapsulation role of β-CD-extracted polyphenols played a role in increasing stability against degradation by oxidation compared to methanolic extracts. Diamanti et al. (2017) [83] reported similar results, where β-CD enhanced the total phenolic content and the radical-scavenging activity of whole-pomegranate extracts.

Cyclodextrins have been proven to effectively enhance the extraction of polyphenolic compounds from plant material. Numerous authors who investigated the application of β-CD to enhance the extraction and encapsulation of polyphenols from plant materials used the response surface methodology to select optimal extraction parameters that resulted in high yields and improved functional properties [76]. Response surface methodology is a collection of statistical and mathematical techniques useful for the development, improvement, and optimisation of products and processes [8,73], in this case the yield of bioactive compounds. This technique is applied particularly when several input variables can potentially influence some performance measures or quality characteristics of the product/process. In studies conducted by the above-mentioned authors, some of the parameters that were optimised include β-CD concentration, solvent-to-plant material/polyphenol ratio [84], and extraction temperature and time [75,80]. In instances where extraction was used in conjunction with a technology such as ultrasound, parameters associated with the specific technology were also optimised [8,68].

In terms of h β-CD-encapsulated plant extracts' inhibition of NEB reaction products, Favre et al. (2018, 2020) [8,9] proved that β-CD-assisted extracts of thyme and green pepper were effective in retarding browning development (A_{420nm}) and HMF formation in

glucose-BSA model systems, correspondingly. Furthermore, the inhibition of browning development and HMF formation was correlated with antioxidant activity. Moreover, Vhangani and Van Wyk (2023) [85] proved that beta-cyclodextrin-assisted extracts of green rooibos at 0.25 and 0.5% inhibited the formation of HMF at 59–67% in heat-processed apples stored at 23 °C for 24 weeks.

5. Conclusions and Recommendations

The preservation of quality in fruits and fruit-based products is driven primarily by the co-current degradation of ascorbic acid (AA) and acid-catalysed sugar degradation. Our findings confirm that processing conditions, specifically high heat and low pH, are critical determinants of product integrity. We established that AA degradation frequently precedes sugar decomposition and produces markers, including 3-hydroxy-2-pyrone (3H2P), furfural, and, most notably, hydroxymethyl furfural (HMF). The presence of fructose has been shown to drastically accelerate HMF formation compared to glucose due to its higher reactivity. Furthermore, while these pathways contribute to browning independently, HMF itself can be consumed in the Maillard reaction (MR) in the presence of amino acids, further complicating the chemical profile of the stored or processed fruit products. Given the inherent difficulty of avoiding thermal and acidic conditions in fruit processing, the application of plant extracts emerges as an environmentally friendly solution. This paper highlighted the increasing trend towards using these natural ingredients, which are rich in polyphenols. Future investigations should focus on elucidating the exact molecular mechanisms by which specific polyphenols stabilise AA and combat reactive intermediates like HMF and furfural. Ultimately, the integration of natural plant extracts provides a vital pathway to mitigating the formation of thermally induced toxic compounds, thereby enhancing the safety, quality, and consumer appeal of processed fruit-based foods.

Author Contributions: Conceptualisation, L.N.V.; methodology/literature search, L.N.V.; validation (literature selection/interpretation), L.N.V.; writing—original draft preparation, L.N.V.; writing—review and editing, L.N.V. and J.V.W.; supervision, J.V.W.; project administration, L.N.V.; funding acquisition, L.N.V. All authors have read and agreed to the published version of the manuscript.

Funding: This project was supported by the national research funding (NRF) black academic advancement programme (BAAP) PhD track 2020–2022, grant no. 120639.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviation

Common Abbreviations Used in the Study

Abbreviation	Full Term
AA	Ascorbic Acid
AG	Aminoguanidine
AGE	Advanced Glycation End-Product
ARP	Amadori Rearrangement Products
β-CD	Beta Cyclodextrin
BSA	Bovine Serum Albumin
CA	Chlorogenic Acid
CA	Citric Acid

CD	Cyclodextrin There are no sources in the current document.
DHA	Dehydroascorbic Acid
EGCG	Epigallocatechin Gallate
FA	Furoic Acid
FAO	Food and Agriculture Organisation
HMF	Hydroxymethyl Furfural
MGO	Methylglyoxal
MR	Maillard Reaction
MTC	Metal Chelating
NEB	Non-Enzymatic Browning
RCS	Reactive Carbonyl Species

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