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Mechanism and Examples of Maillard Reaction

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Abstract

The Maillard reaction, also known as the carbonyl-ammonia reaction, refers to the reaction between a compound containing an amino group and a compound containing a carbonyl group to produce melanoidins through condensation and polymerization. The Maillard reaction was originally discovered by the French chemist Maillard in 1912 while mixing glycine with glucose in a co-heating process, hence the name Maillard reaction. It is also known as the Maillard reaction because of the brown color of the product. Carbonyl compounds found in the reaction products include aldehydes, ketones, and reducing sugars. Amino compounds consist of amino acids, proteins, amines, and peptides. The result of the reaction enhances the color of the food and imparts a distinct flavor, such as the golden-brown hue of bread crust, the rich brown color of braised meat, and their intense aroma. However, the reaction process can also lead to a significant loss of protein and amino acids in the food, potentially generating toxic and harmful substances if not adequately controlled. This paper aims to elucidate the mechanism and influencing factors of the Maillard reaction and to list the common applications of the Maillard reaction in food.

Keywords

Maillard reaction, influencing factors, research, application

1. Reaction mechanism

The mechanism of the Maillard reaction has long been poorly studied. Hodge, a food chemist, made a preliminary explanation in the early years and thought that the Maillard reaction could be divided into three reaction stages [1]. At present, the mechanism of the primary and intermediate stages of the Maillard reaction has been basically clarified, but the mechanism of the final stage is still not very clear. In the following, the reaction between glucose and amine is used to illustrate the whole process of the Maillard reaction.

1.1 Primary stage

The reaction of reducing sugars with amino compounds undergoes carbonyl-ammonia condensation and molecular rearrangement. Firstly, the free amino group in the system condenses with the free carbonyl group to form an unstable imine derivative, Schiff base, which is unstable and then cyclises to N-glucosylamine, which undergoes an acid-catalysed molecular rearrangement by amidrine to form fructosylamine (1-amino-1-deoxy-2-keto sugar). The primary reaction products do not cause changes in food colour and flavour, but the products are precursor components of non-volatile flavour substances.

1.2 Intermediate level

This phase of the reaction can take place through 3 pathways.

The first pathway: under acidic conditions, fructosylamine undergoes 1,2-enolysis, then dehydration, deamination and finally hydroxymethylfurfural. The accumulation of hydroxymethylfurfural is closely related to the browning rate, and the browning reaction can occur soon after the accumulation of hydroxymethylfurfural, so the accumulation of hydroxymethylfurfural can be measured by spectrophotometer as an indicator to predict the browning rate.

Pathway 2: Under alkaline conditions, fructosylamines undergo 2,3-enolysis and are deaminated to produce reduced ketones and dicarbonyl compounds. Reduced ketones are chemically active and can be further dehydrated and then condensed with amines, or cleaved into smaller molecules such as diacetyl, acetic acid and pyruvic aldehyde.

Pathway 3: Maillard reaction Flavouring substances are produced in this pathway. In the presence of dicarbonyl compounds, amino acids are decarboxylated and deaminated, becoming aldehydes with one less carbon, and the amino group is transferred to the dicarbonyl compound, a reaction known as the Strecker degradation reaction. The carbonylamino compounds produced by this reaction are condensed to produce pyrazines.

1.3 Final stage

This stage consists of two types of reactions. That is alcohol-aldehyde condensation: two molecules of aldehydes self-condensation, further dehydration to generate higher unsaturated aldehydes; polymerisation reaction to generate black essence-like: intermediate stage to generate products [glucose ketonaldehyde, 3-deoxy Osulose (3-DG), 3,4-dideoxy Osulose (3,4-2DG), HMF, reduced ketones, and unsaturated imides, etc. after further condensation, polymerisation to form complex Polymer pigments [2].

2. Factors influencing the response [1]

2.1 Sugar

In terms of the speed of the occurrence of the Maillard reaction, the different structures and types of sugars lead to different speeds of the reaction. Generally speaking, the reaction speed of aldehyde is greater than that of ketone, especially the reaction of α and β unsaturated aldehyde and α-bicarbonyl compounds; the reaction speed of five-carbon sugar is greater than that of six-carbon sugar; the reaction speed of monosaccharides is greater than that of disaccharides; and the content of reducing sugar and the speed of browning are directly proportional to each other.

2.2 Amino compounds

Among the common amino compounds that cause the Maillard reaction, the order of the reaction speed is amine>amino acid>protein. Among them, amino acids are often used in the Maillard reaction, and the different types and structures of amino acids will lead to a great difference in the reaction rate, for example: amino acids with amino acids in the ε-position or the last position will react faster than the α-position, and basic amino acids will react faster than acidic amino acids.

2.3 Temperature

When the temperature difference is 10℃, the browning speed can be 3 to 5 times different. When the temperature is greater than 30℃, the browning speed is faster; less than 20℃, the browning speed is slower.

2.4 pH

In the range of pH 3 to 9, the rate of browning reaction increased with the rise of pH; at pH ≤ 3, the degree of browning reaction was slight. In the acidic environment, the reaction rate decreased. This is because N-glucosamine, which is a precursor substance for the formation of Maillard's characteristic flavour, is easily hydrolysed under acidic conditions.

2.5 Moisture content

With 10% to 15% moisture content, browning is easy to occur; with complete dryness, browning is difficult to carry out.2.6 Metal ions Copper and iron can promote browning reactions, with trivalent iron having a greater catalytic ability than divalent iron.

3. Status of research on the Merad reaction

3.1 Research on the control of the various factors influencing the Maillard reaction

Browning in the early stage of the Maillard reaction is necessary for the production of flavour intermediates during food processing, but it is detrimental to the preservation and quality of food, and this is what researchers in the food industry must study to curb. The following methods can be used to prevent browning.

(1) Oxygen isolation method, to prevent the oxidation reaction occurring due to contact with oxygen; (2) reduce the temperature, Maillard reaction is a heat-absorbing reaction, with the increase in temperature, the reaction rate is also

accelerated. Generally, the reaction rate increases 3~5 times for every 10℃ increase in temperature. Some studies have shown that the colour of glycine and glucose obtained at 100 ℃ requires a reaction of 250hr at 56 ℃ to achieve this colour. Therefore, food refrigeration or low temperature storage is conducive to inhibit browning of food. (3) Lowering pH value and regulating water activity, under acidic conditions (pH<3.0), the carbonyl-ammonia condensation in the Maillard reaction is a reversible process, because the free amino acid is closed in the process of carbonyl-ammonia condensation, and the pH of the reaction system decreases, so the alkaline condition is favourable for the reaction. (4) Add enzyme or chemical substance, in the dry protein powder storage process due to the lysine and glucose browning caused by the finished product loss of colour, if you add glucose oxidase in protein powder in advance, glucose oxidation into acid can prevent browning.

3.2 Study of antioxidant properties

The antioxidant property of the Maillard reaction was first discovered by Franzke and Iwainsky in 1954, who reported the oxidative stability of margarine with glycine-glucose reaction products, and then the antioxidant property of the Maillard reaction products attracted people's attention in the 80's, and became a hot spot of research. Research shows that the Maillard reaction is a gradual process, in addition to the final generation of black essence, in the reaction process there are volatile nitrogen-containing or sulfur-containing heterocyclic compounds and reduced aldehydes and ketones and other substances generated, and the antioxidant activity of some substances can be comparable to commonly used food antioxidants. (1) Studies have shown that different MRPs have different antioxidant properties, Kan Jianquan et al. showed that different amounts of non-dialysis black essence of black beans have very obvious antioxidant effects on lard, of which the antioxidant effect is more obvious when the additional amount is 0.5%, 1.0%, 1.0% of the addition amount is comparable to the effect of 0.2% of di-tert-butylhydroxytoluene (BHT); Yan Wu et al. showed that the antioxidant activity of the smoke prepared at a certain concentration is comparable to the effect of commonly used food antioxidants. Yan Wu et al. showed that the free radical scavenging ability of tobacco black essence prepared at a certain concentration was better than that of ascorbic acid, and its reducing ability and antioxidant value were close to that of ascorbic acid. (2) Studies over the years have shown that MRPs with different substrates have different oxidative properties, and the nature and structure of MRPs are highly dependent on the type, nature, and concentration of the reacting substrate, which has a certain antioxidant capacity, Bedinghaus et al. Different Maillard reaction products of amino acids and sugars were prepared and their inhibitory effects on the oxidation of processed steak lipids in cold storage were investigated. The results showed that different sources of melamine products had good inhibitory effects on lipid oxidation, and most of the lipid oxidation occurred in the first 5 d of refrigeration. xylose + lysine, xylose + tryptophan, dihydroxyacetone + histidine, and dihydroxyacetone + tryptophan melamine products had good inhibitory effects on lipid oxidation. K. Jayath Ila Kan et al. showed that under the same conditions, the antioxidant strengths of the products of the melamine reaction with glucose of different amino acids were as follows: lysine>glycine>tryptophan>methionine>aspartic acid. Benjakul found that the antioxidant properties of MRPs produced by protein-sugar reaction were poorer than those of MRPs produced by amino acid-sugar reaction. For the same amino compounds, the antioxidant capacity of MRPs produced by different sugars is also different, and galactose is larger than fructose and glucose.

3.3 Resistance to mutation

Anti-mutagenicity refers to resistance to the mutagenic effects of one or more chemical mutagens, thereby signalling a possible resistance to the carcinogenic effects of mutagens. Recent studies have shown that in addition to macronutrients and micronutrients, as well as a number of mutagenic carcinogens, human foods contain a large number of antimutagens, including MRPs, which have been implicated in a number of studies as having the potential to be antimutagenic. Some studies have suggested that the antimutagenic ability of MRPs may be related to the reducing polymers in nigrospermum parkii, which are reducing colloids with strong antimutagenic activity, eliminating free radicals, blunting enzyme inhibition, and reducing their mutagenic toxicity by binding to mutagenic chemicals. Moreover, MRPs have a strong adsorption and transport function and also play an important role in human cell tissues and metabolism. After the activation of enzymes in the human body, these black substances may have strong adsorption of viruses, bacteria, and metabolites in the human body, so as to regulate the disorders of the body's internal environment. According to Yang Ronghua et al. on soy sauce, soy sauce brown pigment physiological function of the review shows that the black essence is a class of polymerization degree of polymer mixtures, mostly in the form of short peptides or protein complexes, hydrophilic and very strong, with a function similar to dietary fibre, can reduce postprandial glucose, inhibition of pancreatic protease and ACE activity, blocking carcinogenic nitrosamine synthesis, anti-heterocyclic amine mutation, combined with the closure of the metal ions, with strong antioxidant activity and free radicals. It has strong antioxidant activity and free radical scavenging ability. In addition, Hayase et al. studied the capture of free radicals by melanoidin, and they thought that there should be reduced ketone, enamine, or pyrrole structure in melanoidin; Homma et al. studied the difference in the properties of melanoidin and the properties of melanoidin after redox, and they found that the intensity of the colour of melanoidin was reduced after redox and the molecular weight of the melanoidin increased after oxidation or reduction, and it could be thought that oxidation or reduction was the breakage of chromophore, but new polymerization took place. It can be assumed that the oxidation or reduction is the breakage of chromophore, but new polymerisation occurs.

4. Application of the Maillard reaction to foodstuffs

4.1 Maillard reactions in home cooking

The ingredients used in home cooking contain more or less the precursors needed to produce the food flavour needed for the Maillard reaction, which occurs when the conditions are right for the composition of the substances that have the ability to undergo the Maillard reaction. During storage and cooking, the ingredients produce their characteristic aromas and flavours, which are accompanied by a change in colour and a change in their physical properties. For example, the Maillard reaction occurs when the raw dough is baked into bread or fried into Chinese fries and other foods when raw steak is grilled into mature steak, when raw meat is made into braised meat or roasted meat, and when potatoes are fried into French fries.

4.2 Maillard Reactions and Food Colours

Maillard reaction gives food a certain dark colour, such as bread, coffee, black tea, beer, pastry, and soy sauce, for which the production of colour is what we expect. But sometimes the occurrence of the Maillard reaction is not what we expect, such as dairy processing, if the sterilisation temperature is not controlled well, the lactose and casein in the milk Maillard reaction will make the milk appear brown, affecting the quality of dairy products. The processing temperature should be controlled during the production of soy sauce to prevent the colour from being too dark. As well as the control of the golden colour of the bread crust, the amount of reducing sugar and amino acid added and the baking temperature should be controlled in the process of mixing to prevent the final reaction from over-generating burnt black colour.

4.3 Maillard Reactions and Food Flavours

By controlling raw materials, temperature, and processing methods, a variety of different flavours and aromas can be prepared, for example ribose reacts with cysteine and glutathione to produce roast pork flavour and roast beef flavour respectively. The same reactants react at different temperatures to produce different flavours, for example: glucose and valine at 100~150 ℃ and 180 ℃ temperature conditions, respectively, will produce toast flavor and chocolate flavor [3]; xylose and yeast hydrolysis protein at 90 ℃ and 160 ℃ respectively, will produce biscuit flavor and sauce meat flavor. Maillard reactions also contribute significantly to the flavour of soy sauce-type white wine [4].

4.4 Maillard Reactions and Food Nutrition

The effects of the Maillard reaction on the nutrition of foods include reduction of the nutritional quality of proteins, protein modification, and inhibition of trypsin-making activity For grain products, the Maillard reaction results in a lower biomass value of the proteins [5]. Amino acids in milk and dairy products are lost through the formation of pigment complexes and destruction in the Strecker degradation reaction. The pigment complexes as well as casein bound to sugars are not easily broken down by enzymes, thus reducing nitrogen utilisation. In addition, the end product of the Maillard reaction, melanoidin, has a strong inhibitory effect on trypsin [6], and the addition of melanoidin to the trypsin solution was found to have a hindering effect even at a concentration of 1ug/mL of melanoidin. It is now known that trypsin is produced in the pancreas, and if this enzyme is inhibited, it will cause angstroms in pancreatic function and promote insulin secretion. Soya paste containing melanoidins can be used as an insulin-promoting food, to be used in the prevention and improvement of diabetes mellitus.

5. Conclusion

Maillard reaction plays a very important role in the formation of colour, aroma, taste, and other flavour characteristics of food. In the food industry, the reasonable application of MRPs can not only improve the organoleptic quality of food but also enrich the variety of food and develop more new varieties. At present, some progress has been made in the study of small molecule compounds in MRPs, but the formation mechanism of intermediates and final products, as well as their structures and properties, are still unclear. Therefore, it is still necessary to carry out more in-depth research on how to quantitatively and qualitatively determine the composition, molecular structure, and antioxidant mechanism of the intermediates and end-products of MRPs at. Moreover, due to the complexity of the reaction process and the large number of products, that are affected by external factors, some of them are carcinogenic, mutagenic, and have toxic effects on human beings, such as acrylamide, furan and 5-hydroxymethylfurfural. Some of these products are carcinogenic, mutagenic, cardiovascular and renal damaging to humans, such as acrylamide, furan and 5-hydroxymethylfurfural, etc. It is important to study the formation mechanism and conditions of these MRPs in order to control the formation of these products so that the formation of these products can be promoted and the formation of hazardous products suppressed during food processing.

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