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Maillard Reaction and Lactose Structural Changes during Milk Processing

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Abstract Heat treatments often generate chemicals which are not present in the raw materials. Such is the Maillard reaction which, while heating combinations of protein and reducing sugars, produces substances known as melanoidins (aldehydes and ketones) that improve health, help the body expel harmful material and act as anti-aging compounds. During heating of milk, lactose undergoes reactions that have important consequencesfor the milk: changes in flavor, colour, nutritive value, and pH may result. For more severetreatments, lactose isomerization or reaction withproteins is more suitable and specific indicators such aslactulose or furosine, and hydroxymethylfurfural, correlated witheach other, have been related to the intensity of milk heattreatment. Although Maillard reaction in milk usually manifests undesired side effects, at the same time some reactions serve as indicators of the extent of the heat treatments used during production, since their concentrations increase with the heat treatment.

Keywords Maillard reaction, lactose, reducing sugar, melanoidins

Introduction

Health benefits of Maillard reaction products present in the diet have been highlighted by many authors. It is most important to characterize and quantify these products in order to achieve the best possible balance between benefits and potential risks and to establish guidelines for food health [1].

Milk as a raw material has a relatively short shelf life but it can be prolonged by heat treatment. To prevent microbiological hazards prior toconsumption, thedairy industry has accepted the pasteurization, sterilization, UHT and high-temperature processing as essential phases for extending the dairy products shelf life [2]. Heat treatment of milk during commercial processing operations not only inactivates the microorganisms but also results in a number of physico-chemical changes in the milk constituents [3].

According to ARENA et al., [4] pasteurization, and gradually, UHT treatment, sterilization, concentration in vacuo, and formationof milk caramel affect the nutritional quality and alter thesensory attributes of the final products. These treatments generatechemicals not present in the raw material, including those due tonon-enzymatic processes that occur during heating of combinations of proteins and reducing sugars, in what is known as the Maillard reaction. It is important to mention that the Maillard reaction occurs in milk for all types of heat treatment.

Maillard Reaction

Maillard reaction between areducing sugar (pentoses and hexoses) and aliphaticprimary or secondary amines of amino acids is thestarting point for the formation of the mixture ofinsoluble dark-brown polymeric pigments calledmelanoidins, i.e. the dark pigments of the browningreaction when toasting, etc [5]. In an early stage, a reducing sugar, like glucose,condenses with a compound possessing a freeamino group (of an amino acid or in proteins mainly the*ε*-amino group of lysine, but also the *α*-amino groups ofterminal amino acids) to give a condensation product N-substituted glycosilamine (Figure 1), which rearranges to formthe Amadori rearrangement product [6].

Many authors [7-9] reported dehydration and fragmentation in the sugar molecules, which occur at the intermediate stage. Amino acids are also degraded in this stage. Hydroxymethylfurfural (HMF) fission products such as pyruvaldehyde and diacetyl are formed in this intermediate stage.

This stage can be slightly yellow or colourless. α-Dicarbonyl compounds, e.g., butanedione, glyoxal, methylglyoxal are able to react with amino acids via the Strecker degradation (named after the German chemist Adolph Strecker) to give Strecker aldehydes of the amino acids and aminoketones; the latter subsequently condense to form pyrazines. Strecker aldehydes and pyrazines contribute to the aroma in heated foods [10].

All these products react further with amino acids in the third phase to form the brown nitrogenous polymers andcopolymers called melanoidins. These can be off flavours (bitter), off aromas (burnt, onion, solvent, rancid,sweaty, cabbage) or positive aromas (malty, bread crust-like, caramel, coffee, roasted). Also, a direct route to fission products from N-substituted glycosylamines, without the formation of an Amadorirearrangement product is possible. Through this process hundreds of compounds with different flavors are generated. Decay mechanism causes these to form more new aromatic compounds and the process continues on. Each type of food has a specific set of aromatic compounds formed during the Maillard reaction [11].

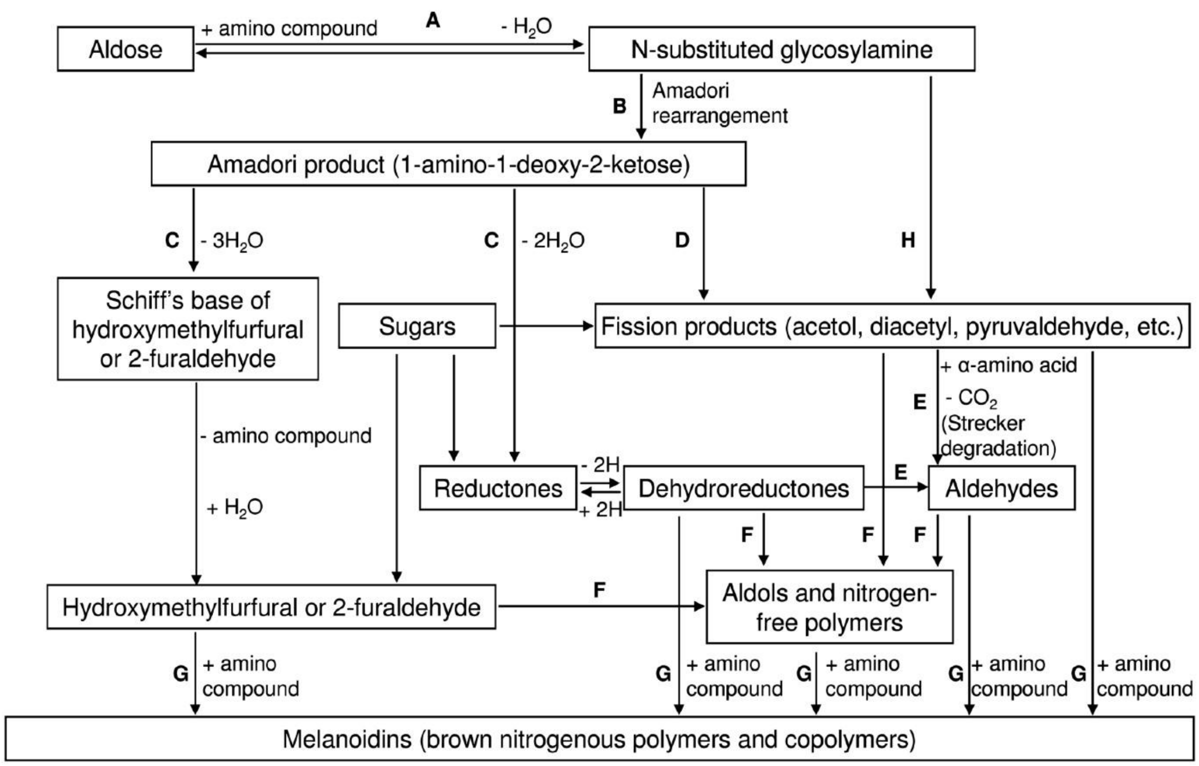

Figure 1: The Hodge diagram

Labuza [12], Davies et al., [13] as well as Rufian-Henares et al., [14], in their research report thatMaillard reaction is strongly influenced by the factors which affect different chemical reactions constituting it. Temperature, heating time duration, pH, presence of weak acids and bases, Aw,reactants type, amino acids, and sugar ratio and oxygen are reported to be the critical factors that influence the final product quality and its nutritional value [15].

This is also supported by Newton et al., [16] who stated that next to the pH (which is important when protonation of the amine group will slow the initial reaction and can determine which pathway the reaction predominantly follows after the formation of the Amadori compound), temperature (above 100 °C), sugar type and identity (aldose sugars react differently to ketose sugars) etc., the influence of metal (dairy products contain calcium and traces of other metals whichcan complex with the amino acids and influence the reaction) and the impact of emulsion structure are also significant as a factors influencing the Maillard reaction.

Lactose – reducing sugar in milk

Lactose is the main carbohydrate of milk and it is formed by the union of one molecule of D-galactose (engaged by its semi-acetyl function) and one molecule of D-glucose (committed by its hydroxyl 4 position). It has a β-galactoside 1,4 bond (which is hydrolyzed by a β-galactosidase) and is a 4-D-glucopyranosyl-β-D-galactopyranose [17].

According to Nelson and Cox [18], lactoseconsists of two monosaccharides joined covalently by an*O*-glycosidic bond, which is formed when a hydroxylgroup of one sugar molecule, typically cyclic, reacts withthe anomeric carbon of the other. The oxidation of a sugar by cupric ion (the reactionthat defines a reducing sugar) occurs only with the linearform, which exists in equilibrium with the cyclic form(s). The anomeric carbon of the glucose residueis available for oxidation, and thus lactose is areducing disaccharide (Figure 2).

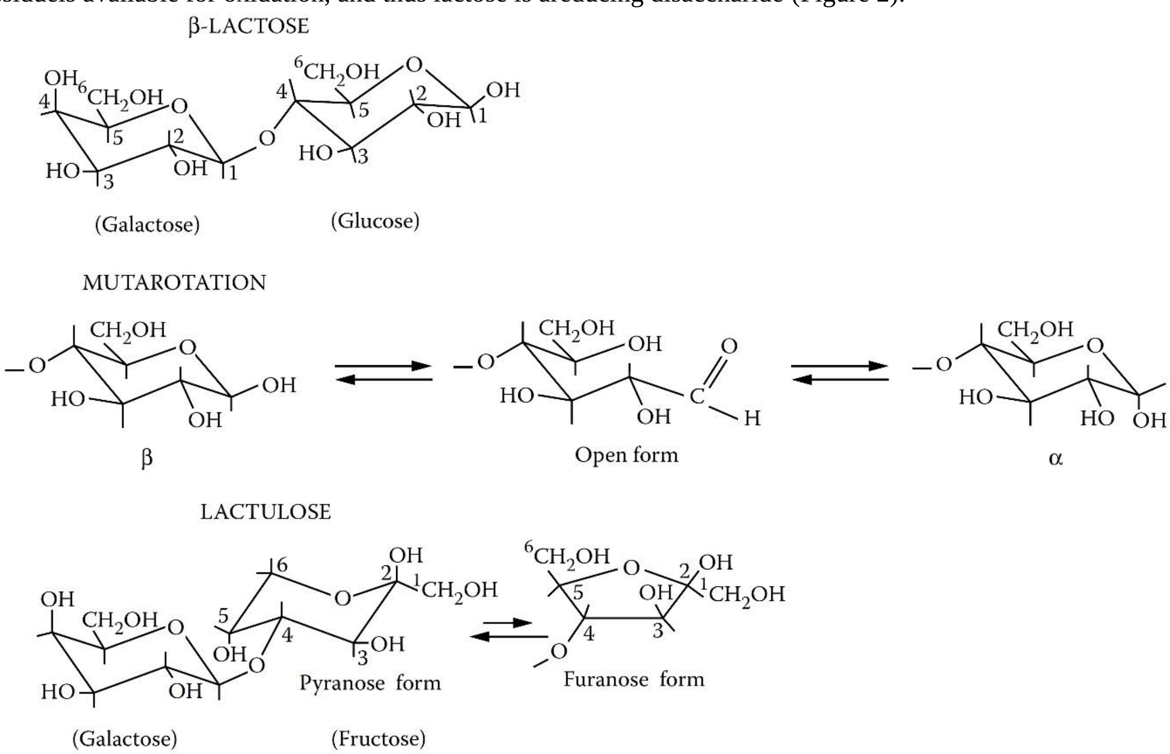

Figure 2: Chemical structure of β-lactose and lactulose and mutarotation process

Maillard reactions and lactose changes

During heating of milk, lactose undergoes reactions that have important consequencesfor the milk: changes in flavor, colour, nutritive value, and pH may result.Lactose is a reducing sugar that reacts withamino groups (in milk, supplied mainly by lysine residues) in the Maillardreaction. Besides, lactose may isomerize into other sugars; it may also degradeinto galactose and degradation products of glucose, including various organicacids [19].

Heating lactose causes several chemical modifications, the natureand extent of which depend on environmental conditionsand the severity of heating; changes include degradation to acids(with a concomitant decrease in pH), isomerisation (e.g., to lactulose),production of compounds such as furfural and interactionswith amino groups of proteins [20].

Many chemical heat-induced indices have been proposed for assessment ofheat treatment in milk, milk products, and model systems.Some of these parameters are related to an earlystage of the Maillard reaction evaluated by analysis of Amadori productsand loss of essential amino acids as lysine and carboxymethyllysine. Heat-induced parameters relatedto the advanced Maillard reaction are total 5-hydroxymethylfurfural(HMF), thebrowning index s-lysylpyrroleand galactosylisomaltol [21].

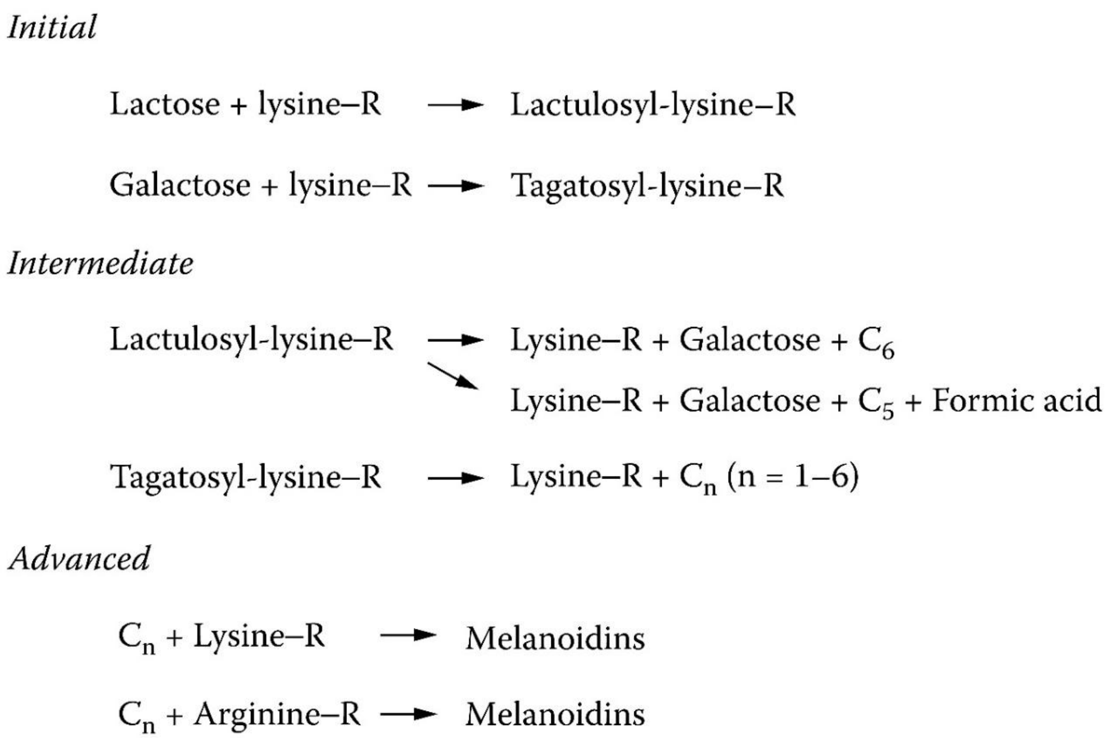

Figure 3: Maillard reactions – lactose

According to O'Brien [22], lactose may isomerize via the Lobrey de Bruyn-Alberda van Ekenstein transformation, followed by degradation to acids and other sugars. Alternatively, lactose may react with caseins and whey proteins of milk systems via the Maillard or non-enzymatic browning reaction (also referred to as glycation of proteins, e.g. in the case of lactose, lactosylation). Birloues-Aragon et al., [23], stated that for more severetreatments, lactose isomerization or reaction withproteins is more suitable and specific indicators such aslactulose or furosine, and hydroxymethylfurfural, correlated witheach other, have been related to the intensity of milk heattreatment. Metha and Deeth [24] go a step further and explain that besidesthe most remarkable reaction with lysine, lactose can also react with arginine, methionine, tryptophan, and histidine from proteins and peptides. Same authors' statement was confirmed by Jansson [25] with the explanation that while lactulosyl-lysine (Figure 3) is the major Amadori product formedin most milk products, certain dairy products such as lactosehydrolyzedmilk contain the more reactive monosaccharides glucoseand galactose, which form fructosyl- and tagatosyl-lysine, respectively.

Stanciuc et al., [26] compared the kinetics of colour development during the heat treatment under different conditions, in order to define suitable markers to sensitively assess the degree of reactions taking place in milk model systems accounting for the time-temperature effects. They suggest that the kinetics of lactose reactions, including theMaillard reaction, revealed that; lactose isomerization is quantitatively more important thanthe Maillard reaction at sterilization temperature (for instance 80% isomerization versus 20%Maillard at 1200 °C); andlactose isomerization is more strongly temperature dependent than theMaillard reaction.

Shimamura and Ukeda [27] examined Maillard reaction of milk in different model systems utilizing the XTT assay method (tetrazolium salt – XTT), taking into consideration its economic view and rapidity. The tetrazolium saltis reduced to water-soluble formazan which is suitable for thespectrophotometric measurement. After conducting this research, they concluded that: lactose and ε-amino groups of lysine residue in milk proteinsreact non-enzymatically to form the Amadori product by the heating process; aminoreductone structure is formed on the milk proteins after elimination of galactosemoiety from lactose through 4-deoxyosone pathway; and aminoreductone is oxidized byXTT, whereas XTT is simultaneously reduced to the corresponding water-solubleformazan (Figure 4).

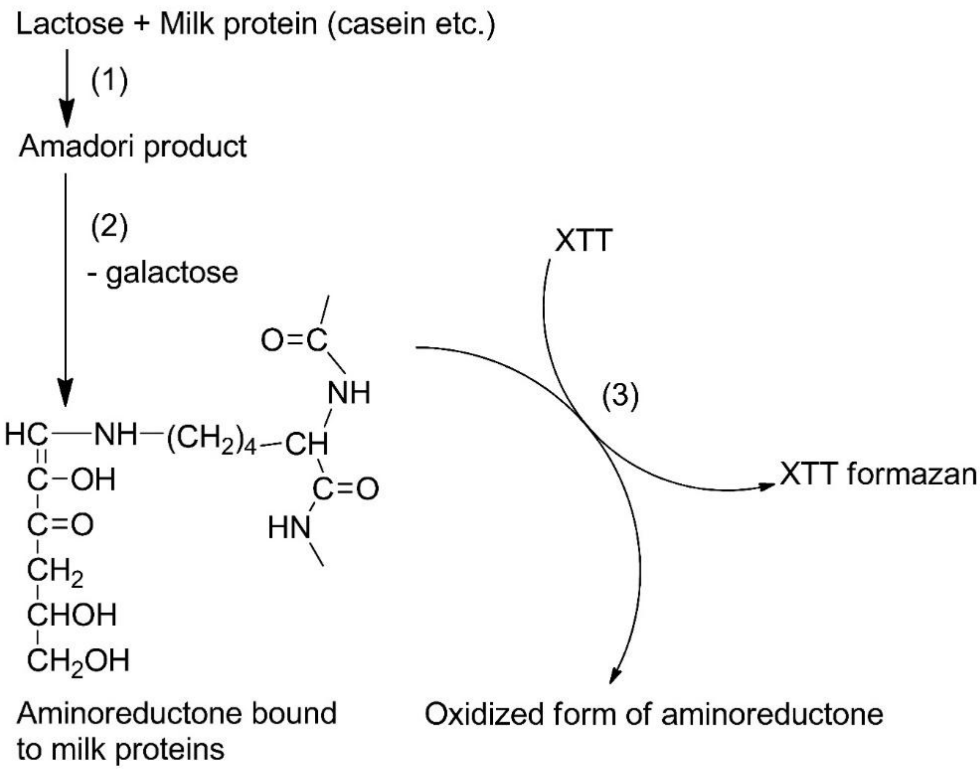

Figure 4: Principle of XTT assay

The final stage, as stated by Van Boekel [28], in which melanoidins (brown pigments) are formed and protein polymerization occurs, is largely unknown from a chemical point of view, let alone quantitatively. The outcome can only be that not all-important compounds are yet identified.

Conclusion

Maillard reaction still presents an attractive research topic and an opportunity to influence the qualitative value of processed food. Reactions which occur during the food processing exhibit different effects on the properties that are determining its acceptability by consumers. Although Maillard reaction in milk usually manifests undesired side effects, at the same time some reactions serve as indicators of the extent of the heat treatments used during production (e.g. lactulose, furosine, and hydroxymethylfurfural) since their concentrations increase with the heat treatment.

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