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Review

Dairy products and the Maillard reaction: A promising future for extensive food characterization by integrated proteomics studies

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Methylglyoxal (CID 880)
Lactulosyl-L-lysine (CID 3082392)
N^{ε}-carboxymethyl-L-lysine (CID 123800)
Furosine (CID 123889)
Pentosidine (CID 119593)
N^{ε}-carboxyethyl-L-lysine (CID 11241427)
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A B S T R A C T

Heating of milk and dairy products is done using various technological processes with the aim of preserving microbiological safety and extending shelf-life. These treatments result in chemical modifications in milk proteins, mainly generated as a result of the Maillard reaction. Recently, different bottom-up proteomic methods have been applied to characterize the nature of these structural changes and the modified amino acids in model protein systems and/or isolated components from thermally-treated milk samples. On the other hand, different gel-based and shotgun proteomic methods have been utilized to assign glycation, oxidation and glycoxidation protein targets in diverse heated milks. These data are essential to rationalize eventual, different nutritional, antimicrobial, cell stimulative and antigenic properties of milk products, because humans ingest large quantities of corresponding thermally modified proteins on a daily basis and these molecules also occur in pharmaceuticals and cosmetics. This review provides an updated picture of the procedures developed for the proteomic characterization of variably-heated milk products, highlighting their limits as result of concomitant factors, such as the multiplicity and the different concentration of the compounds to be detected.

Contents

Abbreviations: Hex, the Amadori product with D-glucose or D-galactose; G, glyoxal; MG, methylglyoxal; 3-DP, 3-deoxypentosone; 1-DG, 1-deoxyglucosone; 3-DG, 3-deoxyglucosone; 3-DGal, 3-deoxygalactosone; 3-DLact, 3-deoxylactosone; GONE, glucosone; Trios, triosone; -DH, -derived-dihydroxyimidazoline; -H, -derived hydroimidazolone; -He, -derived hemiaminal; GOLD, G-derived Lys dimer; MOLD, MG-derived Lys dimer; DOLD, DG-derived Lys dimer; GODIC, G-derived imidazolium cross-link product; MODIC, MG-derived imidazolium cross-link product; DOGDIC, 3-DG-derived imidazolium cross-link product; NL, neutral loss; MRM, multiple reaction monitoring.

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1. Introduction

Cow's milk and other bovine dairy products play a major role in human nutrition. To promote microbiological safety and extend shelf life, most milk is not consumed raw, but undergoes thermal treatments before retail and intake. These actions induce variable physicochemical modifications in milk molecules, depending on the duration/harshness of heating. Pasteurization (15–20 s at 72–75 °C), and gradually, UHT treatment (2–3 s at 135–150 °C), sterilization (10–30 min at >110 °C), concentration *in vacuo*, and formation of milk caramel affect the nutritional quality and alter the sensory attributes of the final products. These treatments generate chemicals not present in the raw material, including those due to non-enzymatic processes that occur during heating of combinations of proteins and reducing sugars, in what is known as the Maillard reaction (van Boekel, 1998). This yields a multitude of products depending on: *a*) the different reactions occurring in series and in parallel; *b*) the many proteins present in cow's milk (about 2500 of them); *c*) the reactivity of protein amino acids; and *d*) the most abundant sugars present in the raw material, *i.e.* lactose, D-glucose and D-galactose, which are in part transformed during heating into lactulose, epilactose and D-tagatose. The effect of thermal treatment plays a central role also in infant formulas, where milk molecules (whey proteins, caseins, lactose, D-glucose, D-galactose and fatty acids) are mixed with additional ingredients, including vegetable oils and other additives, to meet babies' diet requirements (Pischetsrieder & Henle, 2012).

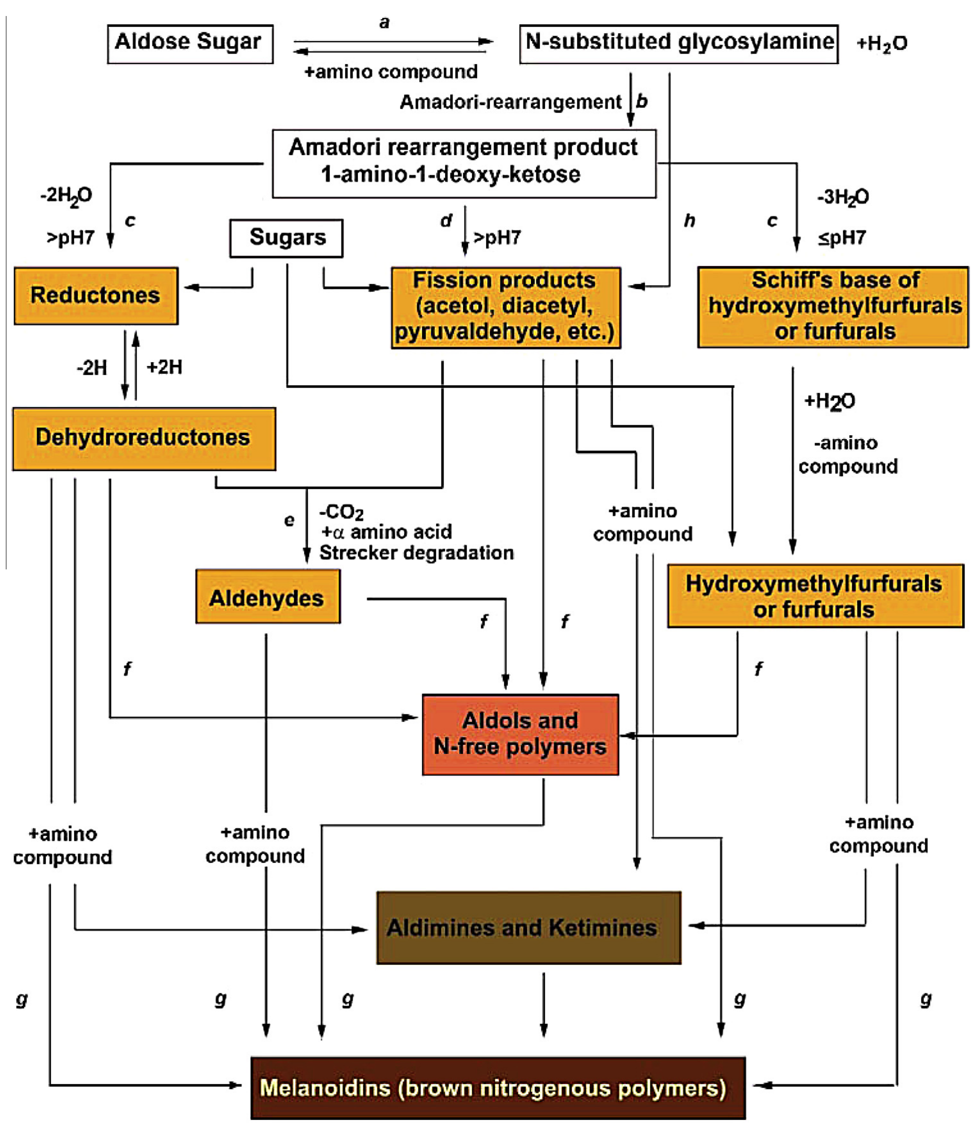

Fig. 1. The Hodge Diagram. The initial reaction between a reducing sugar and a protein –NH_2 group forms the unstable Schiff base (reaction *a*), which then slowly rearranges to form the corresponding Amadori product (reaction *b*). Degradation of the Amadori product (reaction *c*). Formation of reactive carbonyl and α-dicarbonyl compounds (reaction *d*). Formation of Strecker aldehydes of amino acids and aminoketones (reaction *e*). Aldol condensation of furfurals, reductones, and aldehydes produced in reaction *c*, *d* and *e* without the intervention of NH_2-containing compounds (reaction *f*). Reaction of furfurals, reductones, and aldehydes produced in reaction *c*, *d* and *e* with NH_2-containing derivatives to form melanoidins (reaction *g*). Free radical-mediated formation of carbonyl fission products from the reducing sugar (Namiki pathway) (reaction *h*).