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Impact of Maillard type glycation on properties of beta-lactoglobulin

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Abstract

The Maillard reaction occurs during many thermal treatments of foods. It is used because of its role in creating colors, flavors, textures and other functional properties in foods. Glycated beta-lactoglobulin (BLG) can improve techno-functional properties as heat stability, emulsifying and foaming properties. Among the six common sugars used, arabinose and ribose induce the highest degree of modification of proteins. Glycation induced also the oligomerization of BLG monomers. Depending on the reactivity of the sugar, the population of oligomers produced showed smaller or larger heterogeneity in molecular masses. Antiradical properties of glycated BLG were estimated using a radical scavenging activity test. Glycation induced a radical scavenging activity; the intensity depended on the sugar used for modification.

Keywords: Glycation; Maillard reaction; Beta-lactoglobulin; Techno-functional properties

The non-enzymatic browning or Maillard reaction is of major importance in food preparation. This glycation reaction, which was first described by the French biochemist Louis Camille Maillard at the beginning of the 20th century (Maillard, 1912) is still extensively studied because of the high number and complexity of the products formed during its three different reaction stages (Ames, 1990). The early stage consists of condensation of a reducing sugar with an amino group and leads, via the formation of Schiff base and the Amadori rearrangement, to the so-called Amadori product. The second stage involves the formation of Advanced Maillard reaction Products (AMP), including numerous essential fission sugar–amino compounds (Friedman, 1996). The third stage results in the final Maillard reaction products containing condensation and polymerization products of proteins, inducing appearance of brown pigments called melanoidins.

Study and characterization of the Maillard reaction products could allow control of the formation of AMP, responsible in part for noxious effects in diabetes and in age-related cardiovascular diseases. This knowledge could lead to a better control of these reactions in order to modify food proteins and their functions. Maillard reactions are one of the simplest ways to modify food proteins as they take place when a protein and a sugar are just heated together. These non-enzymatic reactions are responsible for numerous changes on food properties and may impair food safety. Although these reactions are of a great importance in production of aroma, taste and color, they are often accompanied by a reduction of the nutritive value of different foods and by the formation of toxic compounds harmful for human health.

β-lactoglobulin (BLG) is the major whey protein. It is present in the milk of various ruminant species. This protein constitutes a major waste product of the cheese industry. Only recently, its use increased as a food additive thanks to its good nutritional properties. Consequently,

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the improvement of BLG functional properties may be of considerable interest to industry.

To improve their functional and physicochemical properties, dairy proteins have been modified by several methods (Haertlé and Chobert, 1999), such as phosphorylation, esterification, alkylation, and reductive amidation. BLG showed better emulsifying properties after glycation with glucose-6-P and better heat stability and solubility after glycation with glucose, mannose or galactose (Nacka et al., 1988). Study of the Maillard reactions between BLG and lactose revealed the presence of α-lactulosyllysine, a unique lactosylation site in the early step of the reaction (Fogliano et al., 1998) and heterogeneity of protein glycoforms.

1. Reaction conditions. Glycation in the presence of different sugars

Protein polymerization and glycation site specificity have been investigated according to the nature of sugar used for modification of BLG (Chevalier et al., 2001b). Among the six common sugars used, arabinose and ribose induced the highest degree of modification. (Fig. 1). Glucose, galactose and rhamnose were less reactive and lactose generated the lowest degree of modification. Proteins substituted with ribose or arabinose formed polymers stabilized by sugar-induced covalent bonds. When other sugars were used, parts of the aggregated proteins were stabilized only by hydrophobic interaction and disulfide bonds.

2. Changes of beta-lactoglobulin structure

Heating of BLG for 3 d at 60 °C did not induce major conformational changes, as observed by peptic hydrolysis. Nevertheless, when BLG was heated in the presence of sugars, larger structural modifications were observed depending on the sugar used (Chevalier et al., 2002). The

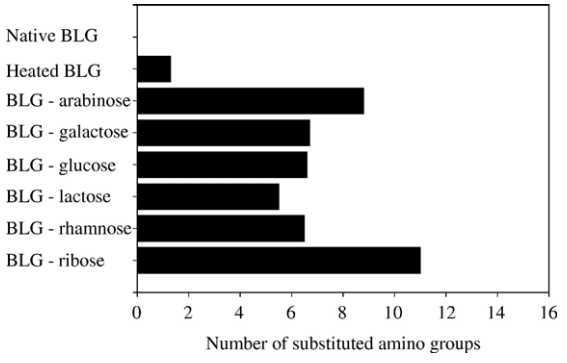

Fig. 1. Degree of modification of BLG as determined by the OPA method.

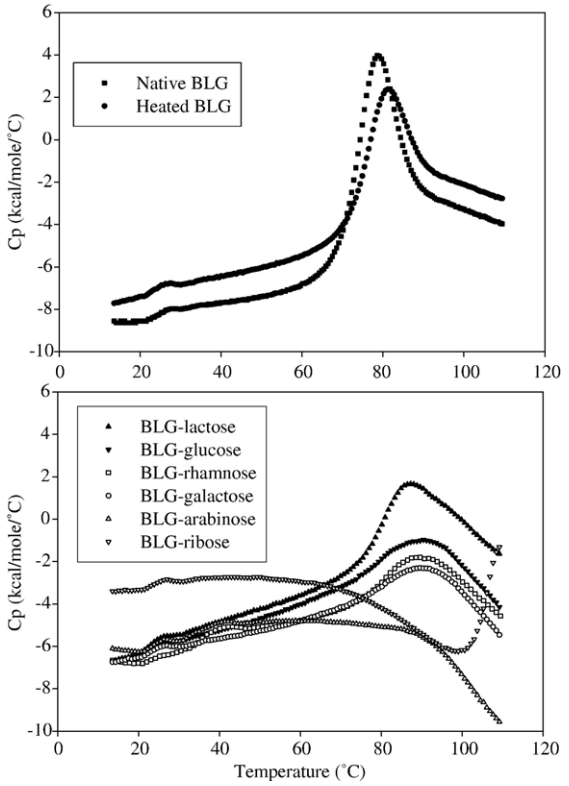

Fig. 2. Thermograms of denaturation of native, heated and glycated BLG.

degree of structural changes of BLG was related to the degree of glycation. A higher reactivity of the sugar (and hence a higher degree of modification) resulted in more denaturation of the glycated protein. According to work of Chevalier et al., 2001b, glycation of BLG induced polymerization. Maillard glycation increased also the temperature of denaturation of proteins glycated with galactose, glucose, lactose or rhamnose (Fig. 2). These results correlated well with those obtained in a previous study of glycated BLG (Chevalier et al., 2001b; see below), which demonstrated the importance of the sugar used on the improvement of emulsifying and foaming properties of the derivatives.

3. Change of techno-functional properties

Numerous attempts were made to improve the functional properties of whey proteins through physical, chemical and/or enzymatic treatments (e.g. Haertlé and Chobert, 1999).

The functional properties (solubility, heat stability, emulsifying and foaming properties) of BLG after glycation of the protein with several sugars were studied (Chevalier et al., 2001b). Protein samples were heated in