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Review

Glycation a promising method for food protein modification: Physicochemical properties and structure, a review

Jianhua Liu, Qiaomei Ru, Yuting Ding *

Department of Food Science and Engineering, College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310014, PR China

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ABSTRACT

Glycation, otherwise known as Maillard reaction, endows food proteins with improved functional properties, such as solubility, water retention capacity, gelling capacity, and emulsifying properties, and it occurs under mild and safe conditions and requires no extraneous chemicals. These make the glycation a promising method for protein modification in food industry. Recent years have seen an increasing interest in physicochemical properties and structure of glycoconjugates, for a better understanding of the relationship between the structure and functional properties. Thus exploring the systematic research methods and information of physicochemical properties and structure will be very helpful. The aim of the present review is to summarize the state-of-the-art about research methods and results of physicochemical properties and structure of glycoconjugates of food proteins. Physicochemical properties include glycation extent, isoelectric point, surface hydrophobicity, and rheology. Structure analysis consists of microstructure of glycoconjugates, primary, secondary, and tertiary/quaternary conformation of proteins influenced by glycation. Finally, a way for a better understanding of the structure–function relationship is proposed. This review provides approaches to study the structure–function relationship of glycated proteins and can also be considered as a basis for further research.

Contents

Abbreviations: α-La, alpha-lactalbumin; ANS, 1-anilino-8-naphthalenesulfonate; AO, alginate oligosaccharide; ATR-FTIR, attenuated total reflectance-Fourier transform infrared; a_w, water activity; AGE, advanced glycation end product; ARP, Amadori rearrangement product; β-Lg, beta-lactoglobulin; CD, circular dichroism; CFG, corn fiber gum; CLSM, confocal laser scanning microscopy; D_{Avg}, average diffusion constant; DSC, differential scanning calorimetry; DSP, degree of substitution per protein molecule; E_0, elastic modulus of Hookean body; EW, egg white; ESI, electrospray ionization; FOS, fructooligosaccharides; FTIR, Fourier transform infrared; G', the storage modulus; GFC, gel filtration chromatography; GOD, glucose oxidase; GOS, galactooligosaccharides; GPC, gel permeation chromatography; ΔH, enthalpy change of the endotherm; HMF, hydroxymethylfurfural; HMW, high molecular weight; ^{1}H-NMR, hydrogen-1 nuclear magnetic resonance; HPGPC, high performance gel permeation chromatography; HPSEC, high performance size exclusion chromatography; IEF, isoelectric focusing; MALDI, matrix-assisted laser desorption; Mf, myofibrillar; MRP, Maillard reaction product; MS, mass spectrometry; η_N, Newtonian viscosity; OPA, o-phthaldialdehyde; OVA, ovalbumin; PCA, principal component analysis; PGWP, partially glycosylated whey protein; pI, isoelectric point; PPP, porcine plasma protein; RH, relative humidity; RP, rice endosperm protein; RP-HPLC, reverse-phase high-performance liquid chromatography; SAPP, acid-precipitated soy protein; SDS-PAGE, sodium dodecyl sulfate polyacrylamide gel electrophoresis; SEC, size exclusion chromatography; SE-HPLC, size exclusion high-performance liquid chromatography; SEM, scanning electron microscopy; SIMCA, soft independent modelling of class analogy; sIWP, soluble isolated wheat protein fraction; SPI, soy protein isolates; $\Delta T_{1/2}$, the width at half peak height of the endotherm; T_d, the maximal deflection temperature or peak transition temperature; TEM, transmission electron microscopy; T_m, high thermal transition midpoint; TNBS, trinitrobenzenesulfonic acid; T_0, the onset temperature of denaturation; TOF, time-of-flight; UPLC, ultra-performance liquid chromatography; UV, ultraviolet; WGP, wheat germ protein; WPI, whey protein isolate.

* Corresponding author. Tel./fax: +86 571 88320237.
E-mail address: dingyt@mail.hz.zj.cn (Y. Ding).

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1. Introduction

Food proteins are an essential component of the diet needed for survival of animals and humans. Their basic value in nutrition is to supply adequate amounts of needed amino acids (Friedman, 1996a). Apart from nutritional value, food proteins would provide unique functional properties, which affect their behavior in food systems during preparation, processing, storage, and consumption, and contribute to the quality and sensory attributes of food system. These functional properties of vital importance for proteins in food applications are solubility, swelling, water retention capacity, foaming properties, gelling capacity, emulsifying and fat binding properties (Zayas, 1997). These diverse properties are attributed to both intrinsic (molecular structure, composition) and extrinsic (temperature, pH, environmental chemicals) factors (Damodaran, 1996). When these factors are changed, food proteins' functional properties vary easily. Especially during food processing, proteins' functional properties are destroyed upon exposed to extrinsic factors.

Glycation is an effective method for improving the functional properties of food proteins and even endows them with novel functionality (Oliver, Stanley, & Melton, 2006). Although various techniques are available to prepare synthetic glycoproteins (Caer, Baniel, Subirade, Gueguen, & Colas, 1990; Christopher, Stowell, & Lee, 1980; Colas, Caer, & Fournier, 1993; Hattori, Aiba, Nagasawa, & Takahashi, 1996; Kitabatake, Cuq, & Cheftel, 1985), the glycoconjugates between proteins and polysaccharides using the Maillard reaction has received much attention in recent years. The Maillard reaction, which was first observed by the French chemist, Louis-Camille Maillard (1912), is a complex form of non-enzymatic browning resulting from a chemical reaction between an available amino group and a carbonyl-containing moiety (usually a reducing sugar). Glycation is based on the Amadori rearrangement steps in the Maillard reaction. Several reaction factors, such as temperature, time, pH, water activity (a_w), intrinsic properties of protein and sugar, and the amino group:reducing suger ratio influence the yields and types of Maillard reaction products (MRPs) (Labuza & Baisier, 1992; Van Boekel, 2001), and consequently physicochemical properties, structure and functional properties of modified food proteins. Owing to proceeding under mild and safe conditions requiring no extraneous chemicals, this reaction is superior to other types of chemical modification for food proteins, and poses a promising application for proteins modification in food industry.

It has been widely documented that glycation via the Maillard reaction can improve many important functional properties of food proteins, as reviewed by Oliver et al. (2006). Many of these studies, however, focus mainly on the improvement of functional properties, and pay less attention on physicochemical properties and structure of glycoconjugates. Due to lack of systematic research methods and information of physicochemical properties and structure, there is poor understanding of the relationship between the structure and functional properties of the glycoconjugates. The aim of the present review is to summarize the state-of-the-art about research methods and results of physicochemical properties and structure of glycoconjugates derived from the Maillard reaction. This review will provide the systematic methods to get insight into the information about the physicochemical properties and structure of glycoconjugates, and practically supplies approaches to study the structure–function relationship. Therefore, this review can also be considered as a basis for further research.

2. Maillard reaction and food protein glycation

2.1. Maillard reaction

The MRPs provide tastes, smells and colors that are much desired and lend their characteristics to a variety of foods. Since Louis-Camille Maillard first discovered the reaction in 1912, the first coherent Maillard reaction scheme was not put forward until 1953 by Hodge (1953) (Fig. 1).

Actually, the Maillard reaction can be divided into three stages: early, advanced, and final stages. In an early stage, a reducing sugar, such as glucose, condenses with a specific compound possessing a free amino group (of an amino acid or in proteins mainly the ε-amino group of lysine, but also the α-amino groups of terminal amino acids) to form a Schiff base with the release of water. The Schiff base subsequently cyclizes to the corresponding *N*-substituted glycosilamine, which then undergoes an irreversible Amadori rearrangement to form the Amadori rearrangement product (ARP), 1-amino-1-deoxy-2-ketose (Ames, 1992). The subsequent degradation of the Amadori product is dependent on the pH of the system. At pH = 7 or pH < 7, it undergoes 1,2-enolization mainly with the formation of furfural (when pentoses are involved) or hydroxymethylfurfural (HMF) (when hexoses are involved). At pH > 7, the degradation of the Amadori compound is thought to involve mainly 2,3-enolization, where reductones, such as 4-hydroxy-5-methyl-2,3-dihydrofuran-3-one (HMF_{one}), and a variety of fission products, including acetol, pyruvaldehyde, and diacetyl are formed. All these compounds are highly reactive and take part in further reactions. Carbonyl groups can condense with free amino groups, which results in the incorporation of nitrogen into the reaction products. Dicarbonyl compounds will react with amino acids with the formation of aldehydes and α-aminoketones. This reaction is known as the Strecker degradation. In an advanced stage, a range of reactions involving various divergent pathways occur, including cyclizations, dehydrations, retroaldolizations, enolizations, oxidations, fragmentations, acid hydrolysis, isomerizations, rearrangements, free radical reactions, and further condensations, leading to the formation of a large multiplicity of poorly characterized compounds (Friedman, 1996b; Ledl & Schleicher, 1990; Martins, Jongen, & Van Boekel, 2001). Most of the color is not presented until the final stage when highly colored, water-insoluble, nitrogen-containing polymeric compounds known as "melanoidins" are produced (Friedman, 1996b; Martins et al., 2001; Zhang & Zhang, 2007).

Although Hodge's work is very important and his findings are still useful today, it remains a controversial issue regarding the mechanism of the Maillard reaction. Firstly, the chemical structures and corresponding formation mechanism of advanced glycation end products (AGEs) have drawn wide attention (Ahmed, Frye, Degenhardt, Thorpe, & Baynes, 1997; Aoki et al., 2000; Dyer, Blackledge, Thorpe, & Baynes, 1991; Grandhee & Monnier, 1991; Machado et al., 2006; Méndez & Leal, 2004; Miyata & Monnier, 1992; Nagaraj & Monnier, 1992; Nagaraj, Portero-Otin, & Monnier, 1996; Obayashi et al., 1996; Tessier, Obrenovich, & Monnier, 1999). Secondly, only partial structures of melanoidins have been elucidated. Several review articles have summarized the researches