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Maillard conjugate-based delivery systems for the encapsulation, protection, and controlled release of nutraceuticals and food bioactive ingredients: A review

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ABSTRACT

Bioactive compounds are mostly prone to decomposition during the production process, storage, and severe gastrointestinal conditions. Therefore, their potential application as functional ingredients in many food products has opened a new horizon in designing novel food-grade delivery systems. Protein-based delivery vehicles have been extensively applied for this purpose. The stability of such systems is substantially affected by destabilizing conditions such as pH change and high ionic strength, thereby affecting bioavailability and stability of the encapsulated bioactive compound. Protein-polysaccharide Maillard-type conjugates are one of the latest food-applicable carriers and promising attractive methods of delivering nutraceuticals. Recently, these types of carriers have been introduced to improve the bioavailability and stability of nutraceuticals and nutrients and to create novel functional foods. The present paper reviews the most recent potential applications of Maillard conjugates for designing delivery systems; i.e., oil-in-water (O/W) emulsion, nanoemulsion, double emulsions, nanoparticles, nanogels, and microencapsulation. It also highlights the structures/compositions of Maillard conjugates used for delivery in food. Moreover, the gastrointestinal fate of Maillard conjugate-based bioactive-loaded delivery systems has been discussed.

1. Introduction

In recent years, in the light of the significant advances in food science, novel approaches have been designed in the area of food-grade delivery systems in order to boost bioavailability, stability, and controlled release of bioactive drugs or nutrients (Augustin, Sanguansri, & Bode, 2006; Feng, Wu, Wang, & Liu, 2016; Lesmes & McClements, 2012; Li & Gu, 2014). These delivery systems include emulsions, hydrogels (nanogels and microgels), nanoparticles, and liposomes, which have manifold advantages and disadvantages related to the stability, bioavailability, biodegradability, biocompatibility, and cost (Fan, Yi, Zhang, & Yokoyama, 2018).

Among biopolymers, proteins are major materials that have been extensively used for delivery systems. However, these carriers have several drawbacks due to the impacts of pH value and ionic strength on protein structures, which can lead to precipitation (at isoelectric point, *pI*) and aggregation. In addition, protein in the protein-based delivery system can be readily hydrolyzed to lower molecular weight peptides and amino acids by digestive enzymes in the gastrointestinal tract (GIT), which in turn leads to burst release of biologically active compound followed by degradation and poor absorption (Li & Gu, 2014). On the other hand, the use of some methods, e.g., coacervation, anti-solvent precipitation, and emulsifying-cross-linking to design protein-based nanoparticles, has increased. However, the use of chemical cross-linkers residues such as glutaraldehyde and organic solvents in the above-mentioned methods causes health concerns and may reduce the application of these carriers in the targeted release of nutraceuticals (Fan et al., 2018).

Recently, protein-polysaccharide conjugates based on the Maillard reaction have received a great deal of attention for the encapsulation of volatile oils, flavors, and other bioactive compounds in food and pharmaceutical sectors owing to their unique characteristics including excellent solubility and emulsifying capacity (higher surface activity and emulsion stabilization), antioxidant properties, stability over a wide range of pH values, temperature and ionic strength, and providing a thicker, continuous, viscoelastic, and shear-resistant layer around oil particles and other oil-soluble bioactive components (Lesmes & McClements, 2012; Nooshkam & Madadlou, 2016a; Nooshkam & Madadlou, 2016b; Vhangani & Van Wyk, 2013; Vhangani & Van Wyk, 2016). All these characteristics make the Maillard conjugates good

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candidates for the development of a new class of encapsulants and drug delivery systems (Livney, 2008). In protein-polysaccharide conjugates, the polysaccharide moiety renders strong steric and sometimes electrostatic repulsion, and the protein in the conjugate can be attached to hydrophobic surfaces (Feng et al., 2016). However, it is necessary to control the Maillard reaction, and stop it in its early stages to prevent the formation of brown melanoidin polymers and undesired advanced glycation products, such as acrylamide (Spivey, 2010).

This review paper highlights the potential applications of Maillard-based conjugates in designing food-grade delivery systems to tailor their efficiencies in the case of encapsulation, protection, and delivery of biologically active compounds. It also highlights the structures/compositions of Maillard conjugates used for delivery in food along with the gastrointestinal fate of nutraceutical-loaded Maillard conjugate-based delivery systems.

2. A brief overview of the Maillard reaction

The Maillard reaction happens between free amino group of amino acids/peptides/proteins and carbonyl group of reducing sugars during heating/storage of many food products (Vhangani & Van Wyk, 2013). It comprises three main stages (Fig. 1), which are briefly summarized hereunder.

2.1. Early stage

The early stage of the reaction begins with the formation of covalent bond between the carbonyl group of a reducing sugar and the free amino group of an amino acid, peptide or protein to produce a Schiff base along with the release of one water molecule. Afterwards, the Schiff base undergoes the cyclization process to form a low stable condensation product N-substituted glycosylamine (O'Brien, Morrissey, & Ames, 1989). The reaction is followed by the rearrangement of glycosylamine to more stable 1-amino-1-deoxy-2-ketose from aldose sugars or 2-amino-2-deoxyaldose from ketose sugars as Amadori (ARPs) or Heyns (HRPs) rearrangement products, respectively (Troise & Fogliano, 2013). This step increases the reducing capacity and decreases the proteins' biological value. It is worth noting that the flavor, color, metal chelation, and toxicity of the obtained products are not changed at the early stage (Nursten, 2005). Moreover, the instability at high temperatures and the presence of oxidation and nucleophilic agents, are the main drawbacks regarding ARPs quantification; ARPs with high hydrophilic nature poorly absorb in the ultraviolet and visible regions, and the modification procedures to form easily active derivatives are not always effective nor practicable (Troise, 2018).

2.2. Intermediate stage

The intermediate stage is characterized by the degradation of ARPs and probably HRPs to the intermediate compounds through 1, 2-enolization and 2, 3-enolization routes based on the initial pH value. At pHs ≤7.0, the early compounds mainly undergo the 1,2-enolization pathway and form hydroxymethylfurfural from hexoses or furfural from pentoses. The 2,3-enolization route is mainly dominant at pH > 7.0 and leads to the formation of reductones, such as 4-hydroxy-5-methyl-2,3-dihydrofuran-3-one and fission products like acetol, diacetyl, and pyruvaldehyde from ARPs. These dicarbonyl compounds can react with amino acids and form aldehydes and aminoketones through Strecker degradation pathway (de Oliveira, Coimbra, de Oliveira, Zuñiga, & Rojas, 2016). Some documented characteristics of this stage are the production of yellow color, strong absorption in the near-ultraviolet region, reducing activity, and the generation of flavor or off-flavor and carbon dioxide (Nursten, 2005; Wu et al., 2014).

2.3. Final stage

At the final stage, reductones and fission products as well as Strecker degradation products undergo aldol and aldehyde-amine

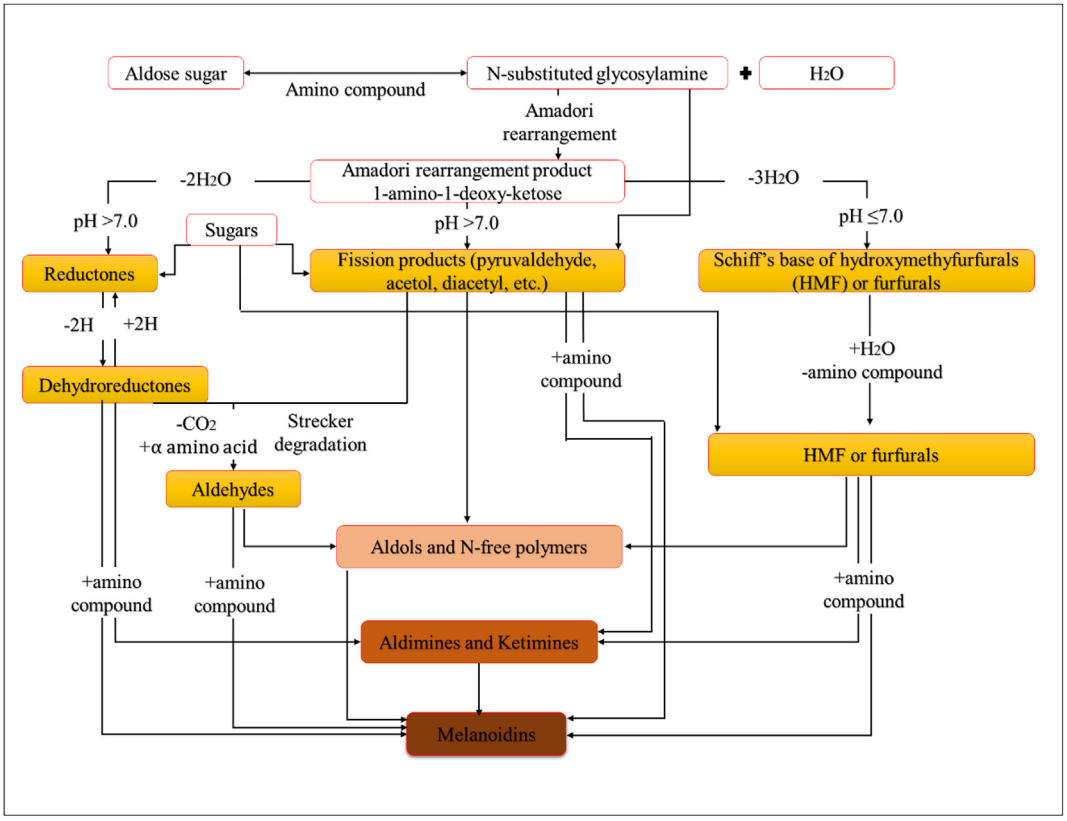

Fig. 1. The Maillard reaction pathways; designed with respect to Arena, Renzone, D'Ambrosio, Salzano, and Scaloni (2017).