Available online at www.sciencedirect.com
SCIENCE DIRECT®
Food Chemistry 93 (2005) 273–278
Food Chemistry
www.elsevier.com/locate/foodchem

Antioxidant activity of water-soluble Maillard reaction products

Yusuf Yilmaz [a,*], Romeo Toledo [b]

[a] Department of Food Engineering, Pamukkale University, Çamlık 20017, Denizli, Turkey
[b] Department of Food Science and Technology, The University of Georgia, Athens, GA 30602-7610, USA

Received 10 May 2004; received in revised form 22 September 2004; accepted 22 September 2004

Abstract

Maillard reaction products (MRP) results from a condensation reaction between amino acids (or proteins) and reducing sugars or lipid oxidation products, and MRP exhibit in vitro antioxidant activities. The objective of this study was to determine antioxidant activities of water-soluble MRP from the reaction between histidine (His) and glucose (Glu) by using the oxygen radical absorbing capacity ($ORAC_{PE}$) assay with phycoerythrine. Heating His–Glu mixture at 100 °C up to 30 min did not generate MRP with antioxidant activity. However, significant formation of MRP with $ORAC_{PE}$ values of 0.25, 0.43, and 0.44 μmol Trolox equivalent/mg reaction mixture was observed when the mixture was heated at 120 °C for 10, 20, and 30 min, respectively. Heating the mixture at 120 °C over 30 min reduced the peroxyl radical scavenging activity of the MRP, possibly due to the degradation of antioxidant MRP formed in the earlier stages of the reaction. In conclusion, MRP obtained from His–Glu mixture possesses peroxyl radical scavenging activity, and this activity can be quantified by the $ORAC_{PE}$ assay.

Keywords: Maillard reaction; ORAC; Antioxidant activity; Peroxyl radical scavenging activity; Glucose; Histidine

1. Introduction

The Maillard reaction, a well-known non-enzymatic browning reaction involving a reducing sugar and an amino acid, may produce colored or colorless reaction products depending on the stage of the reaction as well as other factors such as pH, type of reactants, temperature, water activity, etc. Condensation reactions between amino acids and lipid oxidation products may also form MRP, and the role of lipids in the Maillard reaction is similar to the role of reducing sugars (see Hidalgo & Zamora, 2000). A group of compounds in the final products of the reaction includes high molecular weight melanoidins, which are furan ring and nitrogen containing brown compounds. Little is known about their physical, chemical and physiological properties because of their complex structures. This complexity in MRP structures limits the determination of antioxidant activity for each compound in the whole group of MRP. Therefore, the recently developed $ORAC_{PE}$ assay can be used to determine the total antioxidant capacity of MRP formed during thermal processing of foods.

The Maillard reaction plays an important role in the production of quality bakery products. Color of bread crust and pasta products is determined particularly by MRP. Dehydrated food, baked and grilled meat products, and thermally processed foods may contain various levels of MRP. Since various factors such as type

Abbreviations: AAPH, 2,2′-azobis(2-amidinopropane) dihydrochloride; DPPH, 2,2-diphenyl-1-picrylhydrazyl; Fru, fructose; Glu, glucose; Gly, glycine; His, histidine; HMF, 5-hydroxymethyl-2-furaldehyde; Lac, lactose; Lys, lysine; MRP, Maillard reaction products; $ORAC_{PE}$, oxygen radical absorbing capacity with β-phycoerythrine; β-PE,β-phycoerythrine.

* Corresponding author. Tel.: +90 258 212 5532; fax: +90 258 212 5538.
E-mail address: yusufy@pamukkale.edu.tr (Y. Yilmaz).

0308-8146/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.foodchem.2004.09.043

of reactants (Wijewickreme, Kitts, & Durance, 1997), temperature, pH (Monti, Bailey, & Ames, 1998), water activity, intermediate products (Vasiliauskaite & Wedzicha, 1997) and availability of oxygen can strongly affect the formation and properties of the final reaction products, model systems have been studied more often than the actual food.

MRP, especially melanoidins, have been reported to have antioxidant activity through scavenging oxygen radicals or chelating metals (Table 1). MRP from histidine had the highest antioxidant activity determined by conjugated diene formation from peroxidation of linoleic acid among MRP from either dipeptides of histidine–phenylalanine or lysine–alanine, amino acids histidine, lysine, or ascorbic acid when glucose was used as a reducing sugar (Reische, 1994). Compounds in the MRP with amino reductone structures may have both antioxidant and pro-oxidant activities (Pischetsrieder, Rinaldi, Gross, & Severin, 1998) depending on the reaction conditions. MRP obtained from heated histidine and glucose exhibit copper ion binding ability in oil/water mixtures (Bersuder, Hole, & Smith, 2001).

The oxygen radical absorbance capacity assay can be used to quantify the antioxidant capacity of foods by measuring peroxyl radical scavenging activity of the compounds present (Cao & Prior, 1999). This assay is based on the chemical damage to β-PE caused by a peroxyl radical producing compound (i.e. 2,2′-azobis(2-amidinopropane) dihydrochloride (AAPH) in this assay), reducing the fluorescence emission of β-PE. The presence of antioxidants in the medium prevents the damage and prolongs the fluorescence emission. Antioxidant capacity of foods can be quantified by measuring the area under the relative fluorescence intensity vs. time curves (Cao & Prior, 1999). Antioxidant activities of foods are calculated in terms of Trolox equivalents. This indication provides the means of comparison among the antioxidant activities of numerous foods.

The objective of this study was to determine the antioxidant activity of water-soluble MRP from glucose–histidine mixture by means of $ORAC_{PE}$ assay.

2. Materials and methods

2.1. Production of MRP

L-Histidine hydrochloride monohydrate and D-(+)-glucose were purchased from Sigma Chemical Co. (St. Louis, MO). Histidine and glucose were mixed (1:2 ratio), and approximately 30% (w/v) deionized water was added to the mixture in screw-capped tubes. The screw cap was kept loose to expose the reaction mixture to air while heating in a vegetable oil bath at either 100 °C for 10, 20, 30, and 60 min or 120 °C for 5, 10, 20, 30 and 60 min simulating conditions on baking. Then the screw cap was tightened, and tubes were kept at −18 °C until extraction. pH was not controlled during the production of MRP. Triplicates of the experiment were run.

2.2. Extraction of antioxidant MRP

Deionized water (40 ml/g mixture) was added to the mixture and vortexed until MRP dissolved. The mixture was centrifuged at 26,000*g* for 30 min at 4 °C. Supernatants were collected and subjected to $ORAC_{PE}$ assay. At least two $ORAC_{PE}$ assays were done on each replicate of the treatments.

Table 1
Antioxidative properties of Maillard reaction products obtained from model systems reported in the literature

Model system Sugar–amino acid	Mode of antioxidative property	Reference
Glu–His	Copper chelator	Bersuder et al. (2001)
	Oxygen radical scavenger	Lingnert et al. (1983)
	Peroxyl radical scavenger	Lingnert and Eriksson (1980a,b)
Glu–Lys	Copper chelator	Wijewickreme et al. (1997), Dittrich et al. (2003), Wijewickreme and Kitts (1998)
	DPPH radical scavenger	Morales and Jimenez-Perez (2001)
	Peroxyl radical scavenger	Bressa et al. (1996)
	Hydroxyl radical scavenger	Wijewickreme et al. (1999)
Glu–Gly	Copper chelator	Dittrich et al. (2003)
	Peroxyl radical scavenger	Wagner et al. (2002)
	Hydroxyl radical scavenger	Yoshimura et al. (1997)
	Fe^{2+} chelator	Yoshimura et al. (1997)
Fru–Lys	Copper chelator	Wijewickreme et al. (1997),Wijewickreme and Kitts (1998)
	Hydroxyl radical scavenger	Wijewickreme et al. (1999)
Lac–Lys	Peroxyl radical scavenger	Monti et al. (1999)