International Journal of Agricultural Technology 2019 Vol. 15(4): 539-556
Available online http://www.ijat-aatsea.com
ISSN 2630-0192 (Online)

Effects of temperature on the main intermediates and products of the Maillard reaction in a chicken breast meat model system

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Chansataporn, W., Nopharatana, M., Samuhasaneetoo, S., Siriwattanayotin, S. and Tangduangdee, C. (2019). Effects of temperature on the main intermediates and products of the Maillard reaction in a chicken breast meat model system. International Journal of Agricultural Technology 15(4): 539-556.

Abstract The types and concentration of main intermediates and products of the Maillard reaction to understand the reaction in chicken meat during the roasting process were studied. Chicken extract of a pH and water activity similar to chicken breast was used as a model system. Samples were heated at various temperatures (100, 120, 140, 150 and 160 ^{o}C) and the changes in the intermediates (total acids, 3-deoxyglucosone (3-DG), methylglyoxal (MG), glyoxal, hydroxymethylfurfural (HMF), furfural and volatile compounds) and products (melanoidins; as ascertained via A_{420}) were investigated. The results showed that 3-DG, glyoxal and HMF were not detected, while MG was detected α-dicarbonyl compound detected. Furfural was found in the presence of ribose in chicken meat. Pyrroles, pyrazines, pyridines, aldehydes and furans were found to be the main volatile compounds in this system. A pH dropped and acid formation were observed during heating. The concentration of intermediates (MG, acids, furfural and volatile compounds) and products (melanoidins) increased with heating temperature and time. The formation of volatile compounds was predominant at a high temperature (140–160 ^{o}C). Based on the main types of intermediates and products found in chicken extract, the Maillard reaction pathway for chicken extract during heating was summarized. Reducing sugars reacted via the two main pathways of degradation to organic acids and reaction with amino acids. The reaction between reducing sugars and amino acids formed the important α-dicarbonyl MG, which was the central intermediate and might act as a substrate for the formation of furfural, volatile compounds and melanoidins.

Keywords: Chicken breast; Maillard reaction; Model system; Temperature

Introduction

The Maillard reaction is an important chemical reaction responsible for the brown color and flavor in roasted food. This reaction is a complex reaction of amino components (proteins, peptides, amino acids or amines) and reducing sugars in which no single reaction pathway but rather a whole network of

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various reactions take place (Martins *et al*., 2001; Belitz *et al*., 2009). However, up until now, knowledge of the Maillard reaction in a system with many types of amino acids and reducing sugars is not clearly understood.

Previous research into the Maillard reaction in model systems has reported that the types of intermediates and products depended on the type of reactants. For a simple system comprised of one pair of amino acids and a reducing sugar, the Maillard reaction mechanism in a glucose-glycine system produced 3-deoxyglucosone (3-DG) and 1-deoxyglucosone (1-DG) as the main α-dicarbonyl compounds, with organic acids and melanoidins as the stable end products of this system (Martins *et al*., 2003). Identification and quantification of the α-dicarbonyl compounds formed in the simple fructose-glycine, fructose-lysine, glucose-glycine, glucose-lysine, ribose-glycine and ribose-lysine systems revealed that the type of sugar was the most important factor affecting the type and quantity of α-dicarbonyl compounds, and that glucosone and 3-DG were generated in hexose model systems, while pentosone and 3-deoxypentosone were the major α-dicarbonyl compounds in systems with pentose (Chen and Kitts, 2011).

In contrast to the glucose-glycine system, the Maillard reaction in a more complex system of glutamine- and arginine-dextrinomaltose gave hydroxymethylfurfural (HMF), furfural, glucosylisomaltol and fluorescence as the main intermediates (Pastoriza *et al*., 2016). Recently, the formation and degradation of α-dicarbonyl compounds in a heated glucose-wheat flour system was reported, where α-dicarbonyl compounds [glucosone, 1-DG, 3-DG, 3,4-dideoxyglucosone, glyoxal and methylglyoxal (MG)] and heterocyclic compounds (5-hydroxymethyl-2-furfural) were detected (Kocadagli and Gokmen, 2016). Even though the Maillard reaction has been studied in various types of model systems, very little is known about the main intermediates formed in a complex system that has multiple types of reducing sugars and amino acids at concentrations close to those of real foods.

Roasted chicken is a popular cooked chicken product in the world markets because of its attractive attributes, including its unique flavor and brown color at the product surface. During the roasting process, heat and mass transfer occur simultaneously. When the surface temperature and water activity (a_w) of chicken meat reach certain values, the brown color at the product surface develops simultaneously. Previous research has revealed that the roasting condition, especially the roasting temperature and time, are the main factors affecting the surface temperature and a_w and hence affect the brown color development from the Maillard reaction. However, there is lack of knowledge on the Maillard reaction in a system composed of many types of amino acids and reducing sugars, similar to those of real chicken meat.

This research aimed to study the main intermediates and products from the Maillard reaction in roasted chicken with the alteration of temperature and time. Chicken extract was used as a model system. This study could provide an enhanced knowledge and understanding of the Maillard reaction in cooking chickens, which would help predict and optimize the industrial scale roasting of chickens in order to improve their quality.

Materials and methods

Sample preparation

Fresh chicken breast was purchased from a local supermarket. Visible fat was trimmed off. The samples were sliced and minced using a food processor.

Extraction procedure of chicken breast meat

The extraction procedure was adapted from that of Aliani and Farmer (2002). Twenty g of raw minced chicken meat was mixed with 50 ml of absolute ethanol and separated by centrifugation. The extraction and centrifugation were repeated two times with 50 ml of 80% (v/v) aqueous ethanol and the supernatants were combined and then extracted at a 1:2 (v/v) ratio of supernatant: chloroform. After phase separation for 40 min, it was a separating funnel, the aqueous phase was harvested and the organic phase was discarded. The aqueous extract was then filtered through Whatman No. 1 filter paper to yield the chicken extract, which had a pH of 6.53 ± 0.07 and an a_w of 0.95 ± 0.03.

Heating process

Chicken extract was filled into hermetically sealed stainless-steel tubes and heated at 100 ^{o}C in an oil bath (Soxtec, Model 1046, Höganäs, Sweden). After the chicken extract temperature reached 100 ^{o}C, changed in the reducing sugars, α-dicarbonyl compounds, furfural compounds, volatile compounds, total acids, pH and brown color formation were measured at time intervals. The experiment was performed in duplicate.

Determination of reducing sugar concentration

Total reducing sugars were analyzed following the method of Somogyi-Nelson (1945), based on the absorbance at 520 nm (A_{520}) of a colored complex

between the copper oxidized sugar and arsenomolybdate. The amount of carbohydrate was determined by comparison with a calibration curve using a colorimeter.

Determination of amino acids

The identification and quantification of amino acids by HPLC followed the method of Waters AccQ-Tag (1993). To 110 µl of chicken extract was added 50 µl of 1.5 M $NaHCO_3$ (pH 8.3), followed by 100 µl of 2 mg/ml dabsyl chloride in acetone. The mixture was heated at 70 ^oC in a hot-air oven (Memmert Model ULM 500, Germany) and then evaporated to remove the acetone in a rotary evaporator (Buchi Model R-215, Japan) for 5–10 minutes at 55 ^oC. Then, 1 ml of 70% (v/v) ethanol was added, mixed and filtered with a 0.2-µm syringe filter and analyzed by HPLC (Waters, Milford, MA, USA) with a reversed phase Symmetry Shield RP18 column (size 3.9 × 150 mm, 5 µm particle size, Water, Ireland) and Symmetry Shield guard column (size 3.9 × 20 mm, 5 µm particle size, Water, Ireland). The temperature was controlled at 30 ^oC. Mobile phase A consisted of a 70:20:10 (v/v/v) ratio of 25 mM sodium acetate (pH 6.5): acetonitrile (ACN): methanol, while mobile phase B consisted of a 10:45:45 (v/v/v) ratio of 25 mM sodium acetate (pH 6.5): ACN: methanol. The elution was performed with a linear gradient from 0–50% B (0–20 min), 50–100% B (20–27 min) and 100% B (27–32 min) at a constant flow-rate of 1 ml/min. The UV-visible detector was set at 456 nm. The concentration of amino acids was converted to and reported as mM/kg of chicken breast.

Determination of α-dicarbonyl compounds

α-Dicarbonyl compounds were quantified after derivatization to quinoxaline using an X-Select column. A mixture of ACN: 20 mM ammonium acetate buffer (pH 3.5) was used as the mobile phase (Martins and van Boekel, 2005) at a flow rate of 0.4 ml/minute at 37 ^oC. The sample injection volume was 10 µl.

Determination of heterocyclic compounds

Furfural and HMF contents were measured by the method of Andrade *et al*. (2010). Samples were filtered with a 0.2-µm syringe filter and analyzed by HPLC with an Atlantis C_{18} column. A 1:9 (v/v) ratio of ACN: HPLC grade water was used as the mobile phase at a flow rate of 1 ml/minute at 30 ^oC with a sample injection volume of 10 µl.

Determination of volatile compounds

Volatile compounds were analyzed using gas chromatography-mass spectrometry (GC-MS) following the method adapted from Kaewdit *et al*. (2012) using an HP 6890 (Hewlet Packard, USA) instrument equipped with an HP 5973 (Hewlet Packard, USA) mass detector. Two ml of sample was placed in a 20-ml vial and sealed tightly with a crimp cap and PTFE/silicone septum. The internal standard, propyl butyrate was added to calculate the amount of volatile compounds. For the solid phase microextraction (SPME), carboxen/polydimethylsiloxane (CAR/PDMS-85 μm)] fiber coatings were used with an extraction time of 40 minutes and extraction temperature of 40 ^{o}C. The SPME coating, which adsorbed volatile compounds from the sample vial, was then introduced into the GC injection port at 250 ℃ and kept for 4 minutes for desorption. An HP-5 MS column was used. Helium was used as the carrier gas at a constant flow with a linear velocity of 24.7 cm/s. The GC oven temperature was programmed at 35 ^{o}C for 2 minutes, then increased to 90 ℃ at 3 ℃/minute and then to 240 ℃ at 6 ℃/minute and held for 2 minute (Kaewdit *et al*., 2012).

Determination of total acids

Total acid concentration was analyzed by titration, adapted from that of Brands and van Boekel (2003). Samples were titrated with 0.1 N NaOH to pH 8.3 and the total amount of acid was calculated.

Measurement of pH value

The pH value was determined by using pH meter (CG840B, Schott, Germany).

Measurement of brown color formation

Brown pigment formation was measured via the absorbance at 420 nm (A_{420}) according to the method of Ajandouz *et al*. (2001), measuring the absorbance in a UV-2102 spectrophotometer (Shimadzu, Model UV-2101 PC, Kyoto, Japan).

Statistical analysis

The significance of differences in means was evaluated using one-way analysis of variance (ANOVA), followed by Tukey multiple range test, where

significance was accepted at the $p < 0.05$ level. Each experiment was performed in duplicate.

Results

Chemical composition in chicken extract

The reducing sugars glucose and ribose were both found in the chicken extract at concentrations of 8.50 ± 0.13 and 0.01 ± 0.00 mM/kg of chicken breast, respectively, (Table 1), but fructose was not detected.

Seventeen free amino acids (aspartic acid, glutamic acid, serine, threonine, glycine, alanine, arginine, proline, valine, methionine, isoleucine, leucine, phenylalanine, cysteine, lysine, histidine and tyrosine) were detected in the chicken extract. Arginine and proline were the main free amino acids in the chicken extract, followed by valine, lysine and threonine with concentrations of 0.341, 0.330, 0.130, 0.128 and 0.113 mM/kg of chicken breast meat, respectively, (Table 1).

Table 1. Chemical composition of the raw chicken extract used in this study

Chemical composition	Concentration (mM/kg chicken breast)
Reducing sugars	
Glucose	8.50 ± 0.13
Fructose	ND
Ribose	0.01 ± 0.00
Free amino acids	
Aspartic acid	0.041 ± 0.003
Glutamic acid	0.104 ± 0.001
Serine	0.062 ± 0.007
Threonine	0.113 ± 0.040
Glycine	0.014 ±0.000
Alanine	0.093 ± 0.003
Arginine	0.341 ± 0.002
Proline	0.330 ± 0.010
Valine	0.130 ± 0.001
Methionine	0.112 ± 0.008
Isoleucine	0.024 ± 0.001
Leucine	0.041 ± 0.005
Phenylalanine	0.056 ± 0.003
Cysteine	0.014 ± 0.001
Lysine	0.128 ± 0.003
Histidine	0.092 ± 0.002
Tyrosine	0.076 ± 0.002

ND: Not detected.

Changes in the MG, 3-DG and glyoxal concentrations

Changes in the α-dicarbonyl compounds, MG, 3-DG and glyoxal were investigated during heating. At the beginning of heating process, the MG concentration rapidly increased with heating time and then the rate declined (Figure 1). As the heating temperature increased, the rate of MG accumulation increased, reaching a final concentration of 0.3-1.8 mM. Glyoxal and 3-DG were not detected in the chicken extract during heating.

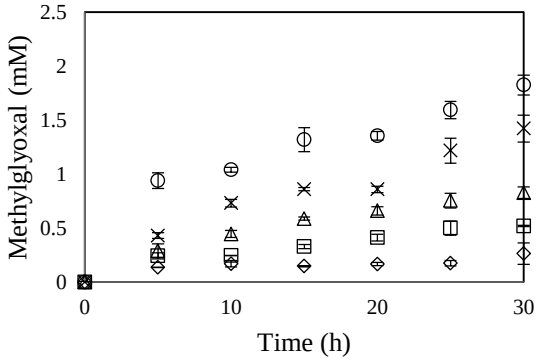

Figure 1. Effect of the temperature on methylglyoxal in chicken extract during heating at 100 (◊),120, ( ), 140 (Δ), 150 (x) and 160 (o)^{o}C. Data are shown as the mean ± SD from two experiments

Changes in the total acids concentration and pH value

Effect of the temperature on the total acids and pH of the chicken extract during heating are presented in Figure 2. At 100 and 120 ^{o}C, the total acids concentration and pH were almost constant. During heating at 140 and 150 ^{o}C, the total acids concentration in the heated chicken extract increased during the first 15 h and then remained almost constant, while at 160 ^{o}C it continually increased throughout the heating process (Figure 2a).

The change in the pH of the heated chicken extract (Figure 2b) was in line with those of the total acid formation (Figure 2a), where the pH in the chicken extract heated at 100 and 120 ^{o}C was nearly constant, while at 140, 150 and 160 ^{o}C it decreased from 6.5 to 5, 4.5 and 4.4, respectively.

Changes in the concentration of heterocyclic compounds

Furfural and HMF concentrations were analyzed in the chicken extract during heating. However, only furfural was detected, and its concentration increased with heating time and temperature (Figure 3). The presence of HMF was not detected in the heated chicken extract at all studied temperatures.

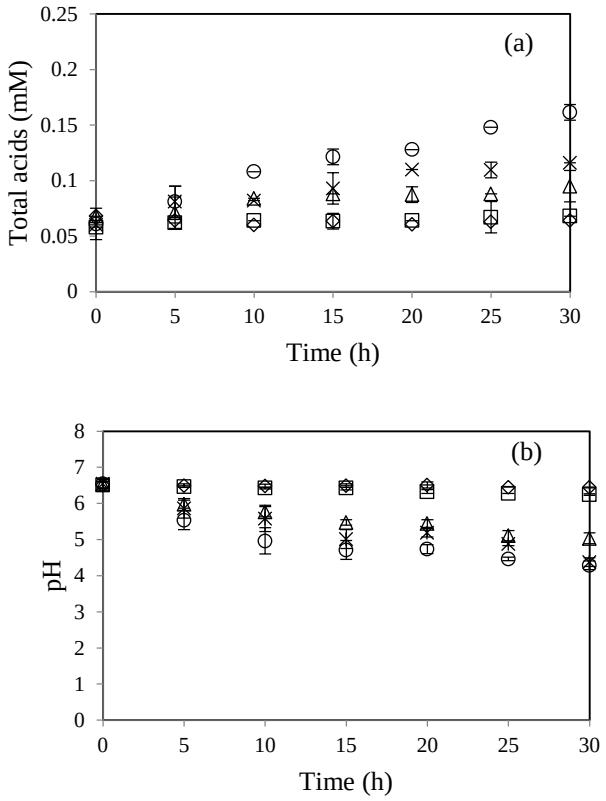

Figure 2. Effect of the temperature on the (a) total acids concentration and (b) pH in chicken extract during heating at 100 (◇), 120, ( ), 140 (Δ), 150 (x) and 160 (o) ^{o}C. Data are shown as the mean ± SD from two experiments

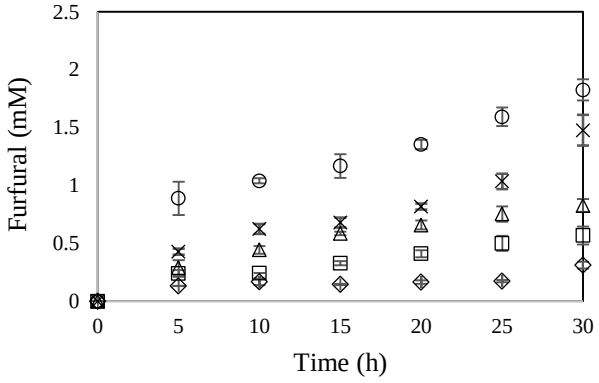

Figure 3. Effect of the temperature on furfural concentration in chicken extract during heating at 100 (◇), 120, ( ), 140 (Δ), 150 (x) and 160 (o) ^{o}C. Data are shown as the mean ± SD from two experiments

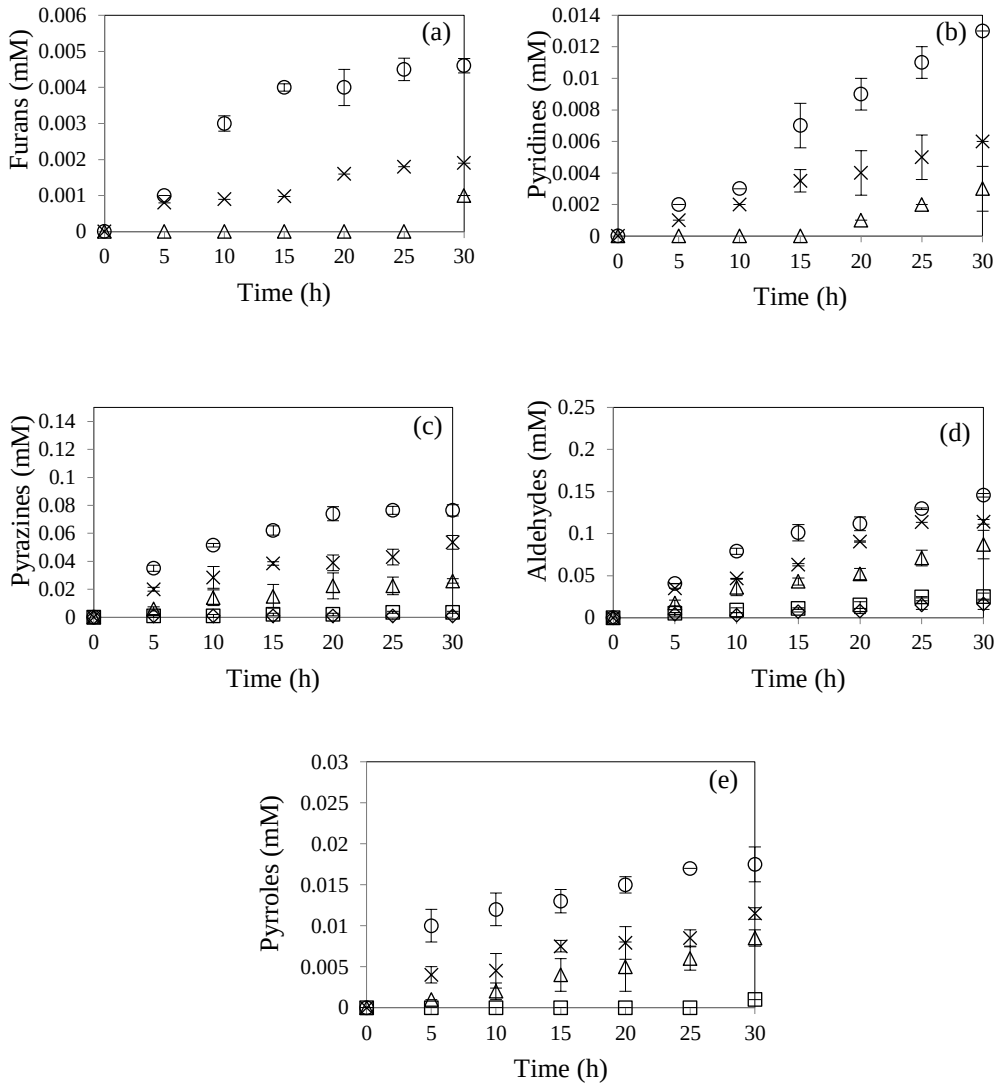

Figure 4. Effect of the temperature on the formation of volatile compounds in the chicken extract during heating at 100 (◊), 120, ( ), 140 (Δ), 150 (x) and 160 (o) ^{o}C. Data are shown as the mean ± SD from two experiments

Changes in the concentration of volatile compounds

Pyrroles, pyrazines, pyridines, aldehydes and furans were found as the major classes of volatile compounds in the chicken extract during heating (Figure 4). In the chicken extract, the formation of volatile compounds were

favored at a high temperature, while at a lower temperature the rate of formation of volatile compounds was very low.

Furans and pyridines were detected in the chicken extract after heating at a high temperature (Figure 4a and 4b). At 150 ^{o}C, the level of furans slightly increased with time while at 160 ^{o}C they rapidly increased until 25 h and then remained constant. Changes in the pyridines content were detected at 140, 150 and 160 ^{o}C. At 140 and 150 ^{o}C, the level of pyridines slightly increased during heating, while at 160 ^{o}C they rapidly increased throughout the heating process.

At a low temperature of 100 and 120 ^{o}C, the level of pyrazines and aldehydes (Figure 4c and 4d) were almost constant throughout the heating process, whereas at 140, 150 and 160 ^{o}C the formation of aldehydes, pyrazines and pyrroles increased with heating time (Figure 4e).

Browning formation (A_{420})

Browning formation in the chicken extract during heating is shown in Figure 5. The A_{420}, which represents the formation of melanoidins when the Maillard reaction had taken place, increased with the heating time and temperature.

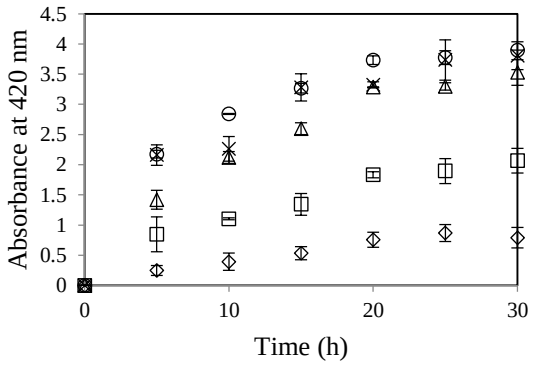

Figure 5. Effect of the temperature on the browning formation in chicken extract during heating at 100 (◇), 120, ( ), 140 (Δ), 150 (x) and 160 (o) ^{o}C. Data are shown as the mean ± SD from two experiments

Discussion

Chemical composition in chicken extract

Concentration of sugars in this chicken extract were different from those of other studies, which probably resulted from the different chicken breed. The amount of reducing sugars and phosphorylated reducing sugars from 24

chicken meats from five commercial brands had an average glucose and ribose concentration of 2.24 and 0.16 mM/kg of chicken breast, respectively, (Aliani and Farmer, 2002). In contrast, a study of heterocyclic amine formation in chicken breast muscle revealed that the concentration of glucose and ribose was over 10-fold higher at 22.9 and 1.65 mM/kg of chicken breast, respectively, (Gasperlin *et al*., 2009). This variation in the concentration of sugars resulted from the storage time after slaughter. During rigor mortis, enzymes in meat will digest the muscle and degrade glycogen to glucose, where the concentration of ribose in freshly killed breast and leg muscle were 0.20 and 0.07 mM/kg (dry weight), respectively, and increased to 0.37 and 0.27 mM/kg, respectively, after 24 h storage at 1 ℃ and to 0.93 and 0.60 mM/kg, respectively, after 6 d storage at 1 ℃ (Lilyblade and Peterson, 1962). In addition, the variation in the concentration of sugars resulted from differences in the maturity of chickens (Lilyblade and Peterson, 1962).

The variation in free amino acid concentrations found in different studies was due to the difference in feed, age and storage time of the chickens. For example, Gasperlin *et al*. (2009) reported that glutamine was the main free amino acid in chicken meat followed by leucine, glutamic acid, lysine, threonine and serine at concentrations of 2.29, 2.28, 2.10, 2.07 and 2.03 mM/kg of chicken breast, respectively. Aliani and Farmer (2002) revealed that glutamic acid was the main free amino acid in chicken muscle followed by alanine, glutamine, serine and lysine at 1.35, 2.00, 0.96, 1.16 and 0.77 mM/kg of chicken breast, respectively. Fujimura and co-workers (1997) reported that aspartic acid was the main free amino acid, followed by lysine, leucine, arginine and histidine at 0.18, 0.12, 0.14, 0.07 and 0.07 mM/kg in chicken breast, respectively.

Changes in the MG, 3-DG and glyoxal concentrations

An increasing MG concentration with heating has also been reported previously in other studies, including in a fructose-asparagine model system heated at 120-200 ^{o}C with an initial pH of 5.5 (Knol *et al*., 2010) and in 1:1 molar ratio fructose-glycine, fructose-lysine, glucose-glycine, glucose-lysine, ribose-glycine and ribose-lysine systems (0.8 M) heated at 121 ℃ for 5-90 minutes (Chen and Kitts, 2011). This was because the rate of reactions between the reducing sugars and amino acids increased with temperature (Martins *et al*., 2001).

Apart from the temperature, the type and concentration of reducing sugar also affected the MG concentration because α-dicarbonyl compounds are mainly produced from sugars in the Maillard reaction (Chen and Kitts, 2011).

In agreement with our results, the MG concentration was reported to be mainly influenced by the type of sugar and reaction time in a glucose-lysine model system and reached a maximum MG concentration of 80.3 μg/g dry matter (DM) after heating for 60 minutes or 90.0 μg/g DM within only 5 minutes in the ribose-lysine model system (Chen and Kitts, 2011). There was a relatively larger amount of MG generated in the fructose-glycine and fructose-lysine model systems compared to the glucose-glycine and glucose-lysine model systems, respectively, when the reaction time was less than 60 minutes. The authors concluded that the interaction between the type of sugar and time were the main contributors to MG production, whereas the heating duration was the most influential factor affecting the concentration of MG produced (Chen and Kitts, 2011).

Moreover, it compared to the type of sugar, the effect of the type of amino acid was much lower. This was because α-dicarbonyl compounds are mainly produced from the sugars in the Maillard reaction (Chen and Kitts, 2011). However, further investigation is needed to understand why the MG content was influenced more by the reaction time than by the type of sugar, and why there was a high contribution of interaction between the sugar and reaction time for this particular α-dicarbonyl compound. At this point, in the case of heated chicken extract that is composed of two types of reducing sugars, the roles of each type of reducing sugar on the MG concentration is still not clear.

Glyoxal and 3-DG were not detected in the chicken extract because of two main reasons. Both α-dicarbonyl compounds are very reactive (Martins *et al*., 2001) and might be formed and rapidly degraded to other intermediates or products. In the glucose-wheat flour (Kocadagli and Gokman, 2016) and glucose-glycine (Martins and van Boekel, 2003) systems, 3-DG was rapidly formed at the beginning of the heating process and then degraded. Moreover, the initial reducing sugar concentration played an important role in the formation of α-dicarbonyl compounds in the Maillard reaction, as previously pointed out. Since the α-dicarbonyl compounds (3-DG, 1-DG, MG and glyoxal) are degradation products of sugars (Martins *et al*., 2001; Chen and Kitts, 2011), the type and concentration of reducing sugar in the system significantly affected the concentration or formation of α-dicarbonyl compounds. Chen and Kitts (2011) studied all the detectable α-dicarbonyl compounds in model systems with sugars (fructose, glucose and ribose) at a concentration of 0.8 M (1,000-fold higher than in the chicken extract) and reported that 3-DG and glyoxal were detected. However, reducing sugars were present at a very low concentration (8.5 mM) in the chicken extract, and so 3-DG and/or glyoxal might be formed at a low concentration and quickly degraded to other compounds.

Changes in the total acids concentration and pH value

Total acids concentration and pH were almost constant at 100 and 120 ^{o}C, which indicated that the amount of acids formed during heating was dependent on the temperature, with less being formed at a lower temperature (Brands and van Boekel, 2002; Martins *et al*., 2003; Martins and van Boekel, 2005).

Increase of acids concentration with time at higher temperature agreed with Knol *et al*. (2010) who studied the Maillard reaction in a heated fructose-asparagine model system and found that acid concentration increased very little at 120 ^{o}C with time but increased with increasing temperature at 140 and 160 ^{o}C. This was because the increased temperature led to an increased reactivity between the reducing sugars and amino groups (Martins *et al*., 2001).

The type and concentration of sugars also affected the total acid concentration because the acids were formed by the degradation of sugars and Amadori compound with the released amino acids (Martins and van Boekel, 2005). At the same heating temperature (120 ^{o}C) the acid formation in the heated 0.2 mM equimolar glucose-glycine system at pH 6.8 (which was 10-fold higher than the sugar concentration in the heated chicken extract) reached a maximum concentration of 8 mM (100-fold higher than in the chicken extract). Multiresponse modelling has been applied to understand the complicated reaction pathways, like the Maillard reaction in the glucose-glycine model system. It was concluded that the acid content was identified as the main end product from the degradation of the α-dicarbonyl 1-DG, which was formed at a maximum concentration of 0.06 mM, while this compound was not detected in the heated chicken extract. Thus, a study of the Maillard reaction pathway is needed to further clarify the acid formation in the heated chicken extract.

Changes in the concentration of heterocyclic compounds

Formation of furfural mainly depends on the type of sugar (Martins *et al*., 2001) and heating time and temperature (Martins *et al*., 2001; Ummay *et al.*, 2018). Furfural is known to be formed when pentoses are presented in the system (Martins *et al*., 2001), and its presence in the chicken extract was consistent with the existence of ribose in the chicken extract (Table 1). Moreover, furfural was also found and used as a heating indicator in foods that contain pentoses, such as milk products, cereal, orange juice and jams (Ummay *et al.*, 2018).

The formation of HMF is mainly influenced by the pH (Martins *et al*., 2001), temperature and heating time (Perez Locas and Yaylayan, 2008; Belitz *et al*., 2009). This compound is a major degradation product of carbohydrates

and is generated through cyclization of 3-DG formed from the open-ring form of glucose (Perez Locas and Yaylayan, 2008; Belitz *et al*., 2009). In addition, HMF could also form by isomerization and degradation of reducing sugars (Ferrer *et al*., 2002; Giroux *et al*., 2010). Thus, the type and concentration of sugar also affected the HMF formation. In the same pH range, HMF was found at very low amount (0–20 μM) in the glucose-glycine model system at pH of 6.8, which had a 23-fold higher sugar concentration than in the chicken extract. Thus, as the HMF's precursor (glucose) in the chicken extract was present at a low concentration, then the HMF formation was potentially too low to be detected.

Changes in the concentration of volatile compounds

In the chicken extract, pyrazines, pyridines, pyrroles, aldehydes and furans were formed. Formation of pyrazines, pyridines and pyrroles has been reported previously in roasted chicken (Jayasena *et al*., 2013). The results also indicated that the formation of volatile compounds in chicken extract were favored at a high temperature. These results were in accordance with those reported in the xylose-chicken peptide system, where the formation of pyridines and furans were favored after 60 minutes at 140 and 120 ^{o}C (Liu *et al*., 2015). Formation of some volatile compounds at a high temperature was also in line with a previous study (Shi and Ho, 1994), which suggested that the formation of heterocyclic compounds, mainly pyrazines, pyridines, pyrroles and furans, required a high temperature.

In the chicken extract, the volatile compounds were generated in the Maillard reaction since other precursors, such as thiamine and lipids, were not present (Aliani and Farmer, 2005; Kerler *et al*., 2010). The types of volatile compounds formed in the Maillard reaction mainly depends on the type of amino acids and reducing sugars (Mottram, 1998; Martins *et al*., 2001; Aliani and Farmer, 2005; Berlitz *et al*., 2009; Kerler *et al*., 2010). The formation of volatile compounds in the xylose-chicken peptide model system at the same pH as the chicken extract (6.5) and heated at the same temperature (140 ^{o}C) gave similar types of volatile compounds, including aldehydes, pyrazines, pyridines, pyrroles and furans (Liu *et al*., 2015). In addition, the analysis of the flavor chemistry of chicken meat revealed the same types of volatile compounds as found in the chicken extract (Jayasena *et al*., 2013), but the types of amino acids and sugars were not mentioned in their study.

Browning formation (A_{420})

An increase in the A_{420} with heating time and temperature has been

reported previously (Brands and van Boekel, 2002, 2003; Martins *et al*., 2003; Martins and van Boekel, 2005; Knol *et al*., 2010). It is known that α-dicarbonyl compounds are important precursors of the browning formation (Chen and Kitts, 2011). Thus, it is plausible that MG was the key browning precursor in the heated chicken extract, and this is supported by Hofmann (1999), who stated that as the temperature increased the MG had a greater role in the browning formation in the glucose-alanine system.

Conclusion

This research demonstrated the types and concentration of the main intermediates and products of the Maillard reaction in chicken breast. Chicken extract with a similar pH and a_w as chicken meat was used as the model system and heated at a temperature of 100, 120, 140, 150 and 160 ^oC. The change in the concentration of intermediates (total acids, 3-DG, MG, glyoxal, HMF, furfural and volatile compounds) and products (melanoidins, via A_{420}) were investigated. 3-Deoxyglucosone could not be detected in this system, while its secondary products (furfural, pyrroles, pyrazines, pyridines and aldehydes) were formed. Thus, 3-DG may be formed but further rapidly reacted to form other products. Pyrroles, pyrazines, pyridines, aldehydes and furans were the main volatile compounds found in this system, and their formation was predominant at high temperatures (140–160 ^oC). A pH drop and formation of acidswere observed during heating, and the results indicated that the concentration of MG, total acids, furfural, volatile compounds and A_{420} increased with heating time and temperature.

Based on the main intermediates and products found in the heated chicken extract, the reaction pathway was summarized as follows. For the chicken extract, the sugars reacted through two main pathways. The first pathway was the thermodegradation of glucose during heating with the formation of organic acids, the stable Maillard reaction products (Martins and van Boekel, 2005). The second pathway was the Maillard reaction with amino acids (Martins and van Boekel, 2005). In the early stage of the Maillard reaction, condensation reactions between reducing sugars and amino acids followed by dehydration and rearrangement resulted in the formation of Amadori compounds (Yaylayan and Huyghues-Despointes, 1994). However, the relative unstable Amadori compounds easily degraded to 3-DG (Martins and van Boekel, 2003, 2005), which then transformed to MG through retro-aldolization (O'Brien *et al.*, 1989). Moreover, 3-DG could react through ring opening, enolization and water elimination to form 3,4-dideoxyosone, which then reacted to form furfural via water elimination (Martins and van Boekel,

2005).

Volatile compounds are important products of the Maillard reaction as it progresses via three possible pathways, which are the (i) formation through deoxyosone to form heterocyclic compounds, (ii) fragmentation of sugar chains through retro-aldolization or cleavage to form heterocyclic and alicyclic compounds and (iii) Strecker degradation to form aldehydes (Berlitz *et al*., 2009; Kerler *et al*., 2010; Jayasena *et al*., 2013). Melanoidins, also known as the Maillard reaction end products, are responsible for the color formation (Martins and van Boekel, 2005; Knol *et al*., 2010). Melanoidin formation results from various reactions of reactive compounds, including cyclizations, dehydrations, retro-aldolizations, rearrangements, isomerizations and further condensations. However, the mechanism of formation and structure of melanoidins (low and high molecular weight, brown, nitrogenous chromophores) are not clearly understood (Martins and van Boekel, 2005; Knol *et al*., 2010). It is known that α-dicarbonyl compounds are important precursors of the browning formation (Chen and Kitts, 2011). Therefore, MG could be a key precursor for the browning formation in heated chicken extract. This was supported by Hofmann (1999), who stated that as the temperature increased the MG had more participation in the browning formation in the glucose-alanine system.

Acknowledgement

The author would like to offer particular thanks to the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0125/2551). National Science and Technology Development Agency (NSTDA) is also acknowledged for supporting the research.

References

Ajandouz, E. H., Tchiakpe, L. S., Ore, F. D., Benajiba, A. and Puigserver, A. (2001). Effects of pH on caramelization and Maillard reaction kinetics in fructose-lysine model systems. Journal of Food Science, 66:926-931.

Aliani, M. and Farmer, J. L. (2002). Postcolumn derivatization method for determination of reducing and phosphorylated sugars in chicken by high performance liquid chromatography. Journal of Agricultural and Food Chemistry, 50:2760-2766.

Aliani, M. and Farmer, J. L. (2005). Precursors of chicken flavor. I. Determination of some flavor precursors in chicken muscle. Journal of Agricultural and Food Chemistry, 53:6067-6072.

Andrade, C. D., Seiquer, I., Haro, A., Castellano, R. and Navarro, M. P. (2010). Development of the Maillard reaction in foods cooked by different techniques. Intake of Maillard-derived compounds. Food Chemistry, 122:145-153.

Berlitz, H. D., Grosch, W. and Schieberle P. (2009). Food Chemistry, Germany, Springer, pp. 1070.

Brands, C. M. and van Boekel, M. A. (2002). Kinetic modelling of reactions in heated monosaccharide-casein systems. Journal of Agricultural and Food Chemistry, 50:6725-6739.
Brands, C. M. and van Boekel, M. A. (2003). Kinetic modelling of reactions in heated disaccharide–casein systems. Food Chemistry, 83:13-26.
Chen, X. M. and Kitts, D. D. (2011). Identification and quantification of α-dicarbonyl compounds produced in different sugar-amino acid Maillard reaction model systems. Food Research International, 44:2775-2782.
Ferrer, E., Alegrı´a, A., Farre´, R., Abella´n, P. and Romero, F. (2002). High-performance liquid chromatographic determination of furfural compounds in infant formulas. Changes during heat treatment and storage. Journal of Chromatography A, 947:85-95.
Fujimura, S., Muramoto, T., Do-Ura, I., Koga, H., Itou, H., Tone, N., Kadowaki, M. and Ishibashi, T. (1997). Effect of feeding area and feed intake on meat compositions and taste relating components of broiler chickens. Japanese Poultry Science, 34:373-381.
Gasperlin, L., Lukan, B., Zlender, B. and Polak, T. (2009). Effects of skin and grilling method on formation of heterocyclic amines in chicken pectoralis superficialis muscle. Journal of Food Science and Technology, 42:1313-1319.
Giroux, H. J., Houde, J. and Britten, M. (2010). Use of heated milk protein–sugar blends as antioxidant in dairy beverages enriched with linseed oil. LWT - Food Science and Technology, 43:1373-1378.
Hofmann, T. (1999). Quantitative studies on the role of browning precursors in the Maillard reaction of pentoses and hexoses with L-alanine. European Food Research and Technology, 209:113-121.
Jayasena, D. D., Ahn, D. U., Nam, K. C. and Jo, C. (2013). Factors affecting cooked chicken meat flavor: A review. Worlds Poultry Science Journal, 69:515-526.
Kaewdit, S., Oonjitti, S., Samuhasaneetoo, S., Penroja, P. and Leejeerajumneun, A. (2012). HS-SPME optimization of extraction condition for volatile compound analysis of Thai aromatic coconut juice. Silpakorn University International Conference on Academic Research and Creative Arts, Nakhon Prathom, Thailand, pp. 51-58.
Kerler, J., Winkel, C., Davidek, T. and Blank, I. (2010). Basic chemistry and process conditions for reaction flavours with particular focus on Maillard-type reactions. In: Food Flavor Technology, Wiley-Blackwell, Chichester, pp. 51-88.
Knol, J. J., Linssen, L. P. H. and Boekel, M. A. J. S. (2010). Unravelling the kinetics of the formation of acrylamide in the Maillard reaction of fructose and asparagines by multiresponse modelling. Journal of Food Chemistry, 120:1047-1057.
Kocadagli, T. and Gokmen, V. (2016). Multiresponse kinetic modelling of Maillard reaction and caramelization in a heated glucose-wheat flour system. Food Chemistry, 211:892-902.
Lilyblade, A. L. and Peterson, D. W. (1962). Inositol and free sugars in chicken muscle post-mortem. Journal of Food Science, 27:245-249.
Liu, J., Liu, M., He, C., Song, H. and Chen, F. (2015). Effect of thermal treatment on the flavor generation from Maillard reaction of xylose and chicken peptide. LWT-Food Science Technology, 64:316-325.
Martins, S. I., Jongen, W. M. F. and van Boekel, M. A. (2001). A review of Maillard reaction in food and implications to kinetic modelling. Trends in Food Science and Technology, 11: 364-373.
Martins, S. I., Marcelis, A. T. and van Boekel, M. A. (2003). Kinetic modelling of Amadori N-(1-deoxy-D-fructos-1-yl)-glycine degradation pathways. Part I-Reaction mechanism. Carbohydrate Research, 338:1651-1663.

Martins, S. I. and van Boekel, M. A. (2003). Kinetic modelling of Amadori N-(1-deoxy-d-fructos-1-yl)-glycine degradation pathways. Part II-Kinetic analysis. Carbohydrate Research, 338:1665-1678.
Martins, S. I. and van Boekel, M. A. (2005). A kinetic model for the glucose-glycine Maillard reaction pathways. Food Chemistry, 90:257-269.
Mottram, D. S. (1998). Flavour formation in meat and meat products: a review. Food Chemistry, 62:415-424.
O'Brien, J., Morrissey, P. A. and Ames, J. M. (1989). Nutritional and toxicological aspects of the Maillard browning reaction in foods. Critical Reviews in Food Science and Nutrition, 28:211-248.
Pastoriza, S., Rufián-Henares, J. Á., García-Villanova, B. and Guerra-Hernández, E. (2016). Evolution of the maillard reaction in glutamine or arginine-dextrinomaltose model systems. Foods, 5:86.
Perez Locas, C. and Yaylayan, V. A. (2008). Isotope labeling studies on the formation of 5-(hydroxymethyl)-2-furaldehyde (HMF) from sucrose by pyrolysis-GC/MS. Journal of Agricultural and Food Chemistry, 56:6717-6723.
Shi, H. and Ho, C. T. (1994). The flavour of poultry meat. In: Shahidi F, ed. Flavour of Meat and Meat Products, Blackie Academic and Professional. Glasgow, pp.52-69.
Somogyi, M. (1945). A new reagent for the determination of sugars. Journal of Biological Chemistry, 160:61-68.
Shapla, U. M., Solayman, M., Alam, N., Khalil, M. I. and Gan, S. H. (2018). 5-Hydroxymethylfurfural (HMF) levels in honey and other food products: Effects on bees and human health. Chemistry Central Journal, 12:1-18.
Waters AccQ-Tag chemistry package (1993). Instruction manual. In: Manual no. WAT 052874. Waters Corp., Milford, Mass.
Yaylayan, V. A. and Huyghues-Despointes A. (1994). Chemistry of Amadori rearrangement products: analysis, synthesis, kinetics, reactions, and spectroscopic properties. Critical Review in Food Science and Nutrition, 34:321-69.

(Received: 23 March 2019, accepted: 28 June 2019)