Eur Food Res Technol (2000) 211:247–251

ORIGINAL PAPER

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The influence of the pH value on the formation of Strecker aldehydes in low moisture model systems and in plant powders

Received: 2 November 1999

Abstract Strecker aldehydes are regularly found in the low boiling point fraction of volatile compounds of processed plant foods. They are produced via the Strecker degradation of amino acids. The formation of 3-methylbutanal (3-MB) in a glucose- and leucine-containing low moisture model system and the formation of acetaldehyde, 2-methylpropanal, 2-methylbutanal and 3-MB in plant powders showed a linear pH dependence. The formation of the Amadori rearrangement product (ARP) fructose-leucine (fru-leu) in the model system, in contrast to it's degradation, was not influenced by the pH. The formation of the 3-deoxyosone [3-deoxy-D-erythro-hexos-2-ulose (3-DH)] by degradation of fru-leu was slower at pH 7 than at pH 5 suggesting that it is either less stable at pH 7 or being formed to a lesser extent. Further experimental results suggested that enolisation and retro aldol reactions of reducing sugars also contribute to the production of Strecker aldehydes as the pH is increased, by creating α-dicarbonyl compounds. The appearance of fructose in the glucose-containing model systems indicates enolisation reactions in the course of a Maillard reaction.

Key words pH · Strecker aldehyde · Amadori rearrangement product · Deoxyosone · Maillard reaction

Introduction

The Maillard reaction is very significant for foods since it strongly affects their quality. In the course of the Maillard reaction Strecker aldehydes are produced by Strecker degradation of amino acids. The Strecker aldehydes acetaldehyde (AA), 2-methylpropanal (2-MP), 2-methylbutanal (2-MB) and 3-methylbutanal (3-MB) are regularly found in the low boiling point fraction of volatile compounds of processed plant foods [1–6]. It is generally accepted that the Maillard reaction proceeds faster when the pH is increased [7], since this reaction occurs between an uncharged amine and a carbonyl compound. The effect of the pH value on formation of brown pigments, on the degradation of amino acids as well as on the browning activities of different sugars and the formation of volatile compounds such as pyrazines has already been investigated [8–15]. Chan and Reineccius [16] were probably the first who investigated the influence of pH on the formation of the Strecker aldehydes 3-MB and phenylacetaldehyde in aqueous glucose/leucine and glucose/phenylalanine model systems, respectively. They found an increase in Strecker aldehyde formation when the pH was raised from 6 to 7 and a slight decrease between pH 7 and 8, which they explained by assuming that the loss of aldehydes through secondary reactions is greater at pH 8 than at pH 7.

Our investigations aim at interpreting the pH dependence of the Strecker reaction with respect to the pH dependence of the overall Maillard reaction. Pursuing this, we correlated the pH dependence of Strecker aldehyde formation to the pH-dependent rate of formation and decomposition of Amadori rearrangement products (ARPs) and deoxyosones [determining the 3-deoxyosone i.e. 3-deoxy-D-erythro-hexos-2-ulose (3-DH)], and investigated how the Lobry de Bruyn van Ekenstein rearrangement and retro aldol reactions, which both contribute to the formation of reactive α-dicarbonyl compounds, are influenced by the pH. In order to investigate this issue we used low moisture model systems as well as plant powders modified with respect to pH and composition. We chose spray dried tomato powder and ground spice paprika as examples of products of plant origin since they are the most popular vegetable products worldwide [17, 18].

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Materials and methods

Materials

Glucose, L-leucine, glyoxal (40% in water), methylglyoxal (40% in water), AA, 2-MP, 2-MB, 3-MB, diethylene glycol dimethyl ether, magnesium nitrate hexahydrate, sodium chloride, xylite, trehalose dihydrate, hydroxylammonium chloride, pyridine, *N*,*O*-bis(trimethylsilyl)-acetamide, 1,1,2-trichlortrifluorethane and trimethylchlorosilane were purchased from Fluka, Buchs, Switzerland; citric acid monohydrate, hydrochloric acid (0.1 M) and sodium hydroxide (0.1 and 1 M) from Grüssing, Filsum, Germany; microcrystalline cellulose 0.020 mm (Avicel) was purchased from Serva, Heidelberg, Germany. The ARP fructose-leucine (fru-leu) was prepared and its purity (99%) controlled by ion exchange chromatography applying the method described by Schräder and Eichner [19]. Headspace vials (22 ml) were obtained from Perkin Elmer, Ueberlingen, Germany.

Reagents

Citrate buffers (0.1 M) were prepared as follows. Solution A: 21.01 g citric acid monohydrate and 200 ml 1 M sodium hydroxide were dissolved in distilled water and the volume was brought to 1000 ml; solution B: 0.1 M hydrochloric acid; solution C: 0.1 M sodium hydroxide. Mixing of 40.3 ml A with 59.7 ml B, 96.4 ml A with 3.6 ml C, and 50.5 ml A with 49.5 ml C yielded buffer solutions of pH 3.0, 5.0 and 7.0 respectively. A 0.1 M leucine solution was prepared by dissolving L-leucine in water, using ultra sonication and adding as much hydrochloric acid as necessary for dissolution. An aqueous 1.0 M fru-leu solution was prepared, and 0.5 M solutions of methylglyoxal and glyoxal were prepared by diluting 7.50 and 5.70 ml of the stock solutions (40% in water) respectively with water to 100.0 ml.

Preparing the model systems and the plant powders of different pH values

Models G/L-3, G/L-5 and G/L-7. Glucose (1.80 g) and 5.0 ml of the 0.1 M leucine solution (containing 66 mg leucine), 20 ml buffer (containing $x = 0.28$, 0.56 and 0.33 g dry substance; pH 3, 5 and 7), 20 ml distilled water and (10.0–1.80–0.066–x) g microcrystalline cellulose were mixed and the pH adjusted to the correct value, using sodium hydroxide solution and/or hydrochloric acid. The mixtures were then deep frozen, freeze-dried and homogenised. The model systems contained 1.0 mol/kg glucose and 50 mmol/kg leucine.

Models G/L(1:1)-7, glx/L-7, meglx/L-7. These model systems contained 50 mmol/kg glucose, glyoxal and methylglyoxal respectively and an equimolar amount of leucine. They were prepared using the same procedure as described for the models above. The citrate buffer of pH 7.0 was used.

Models F-L-3, F-L-5, F-L-7. These model systems contained 50 mmol/kg of the ARP fru-leu and citrate buffers of pH 3, 5 and 7. They were prepared using the same procedure as described above.

pH-modified plant powders. Plant powder 5 g was suspended in 25 ml distilled water and the pH adjusted with hydrochloric acid or sodium hydroxide. The pH was monitored with a glass electrode. The adjusted pH values were 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 for paprika and 4.1, 5.0, 5.6, 6.4, 7.2 and 8.3 for tomato. The natural pH values (5 g powder/25 ml water) were 4.9 for paprika and 4.1 for tomato.

Adjusting the a_w value

After freeze-drying, aliquots of 200 mg of the model systems and of 500 mg of the plant powders were adjusted to a_w–values of 0.52 or 0.75 (only the models G/L(1:1)-7, glx/L-7, meglx/L-7) by storing them for 4 days in headspace vials placed in exsiccators over saturated magnesium nitrate hexahydrate ($a_w = 0.52$) or sodium chloride ($a_w = 0.75$) solutions at ambient temperature (20 °C).

Quantitative headspace-GC determination of Strecker aldehydes

A stock solution of the above mentioned aldehydes was prepared for headspace-GC by adding 100 mg of each volatile compound to 100 ml diethylene glycol dimethyl ether.

The quantitative determination of the Strecker aldehydes present in the model systems and in the plant powders was carried out according to the standard addition method. The aldehyde stock solution (10, 20 and 30 µl) was added to the aliquots of the model systems and the tomato and paprika powders put into the headspace vials. The vials were sealed immediately after filling and the sample mixed thoroughly with a reaction tube mixer. Original samples and standard addition samples were analysed by headspace-GC.

Analysis of Strecker aldehydes by headspace-GC analysis

The samples were heated in the headspace oven (90 °C) for different times (30–120 min). A Perkin Elmer Headspace-GC 8410 equipped with the autosampler system HS-101, a FID and a 60 m × 0.32 mm × 1.0 µm fused silica Stabilwax capillary column was used. The oven temperature was held at 40 °C for 5 min and then heated to 70 °C at 2 °C/min; this temperature was held for 5 min. The injector and detector temperatures were 130 °C and 230 °C respectively. The carrier gas (helium), hydrogen, air and make-up gas (nitrogen) pressures were 200, 140, 140 and 75 kPa, respectively. FID-sensitivity was high. Peak areas were integrated with a Merck-Hitachi D 2000 integrator. The autosampler parameters were: needle temperature, 120 °C; sample temperature, 90 °C; thermostatting time, variable; transfer line temperature, 130 °C; pressurisation time, 0.8 min; injection time, 0.06 min; injections per vial,1; and withdrawal time, 0.2 min.

Analysis of fru-leu, 3-deoxyosone, glucose and fructose

These sugars and sugar derivatives were analysed in the model systems G/L-3, G/L-5 and G/L-7. After heating the aliquots of the model systems (200 mg; a_w 0.52) for 10–120 min at 90 °C in a water bath, they were extracted with 2.0 ml of distilled water. After centrifugation, 500 µl of the supernatant was freeze dried, oximated, silylated and analysed by GC-FID according to the method described by Schräder and Eichner [19]. Xylit and α-trehalose were used as internal standards. Concentrations were calculated via the response factors obtained with the reference standard substances (glucose, fructose, fru-leu). The response factor of the 3-deoxyosone was estimated by using the response factors of glu and fru, which were equal. The 1-deoxy-2,3-D-erythro-hexodiulose (1-deoxyosone), a possible decomposition product of fru-Leu, could not be detected with this method.

Determination of the ASTA colour value

The colour value of spice paprika powder which depends on the carotenoid content was determined according to the AOAC method 971.26 which is used by the American Spice Trade Association (ASTA). The carotenoids of a defined sample quantity (50–100 mg) are extracted with acetone and the absorption of the extract is measured at 460 nm.

Results and discussion

Investigation of the Strecker aldehyde formation in model systems and in vegetable powders as a function of the pH value

In Fig. 1 the formation of 3-MB in the model systems G/L-3, G/L-5 and G/L-7 as well as the formation of the sum of aldehydes (AA, 2-MP, 2-MB and 3-MB) in the vegetable powders are presented, each of them showing almost identical characteristics of formation as a function of heating time at 90 °C. As can be seen in Fig. 1, the formation of 3-MB in the glucose/leucine model systems showed certain induction periods; this must be due to the fact that the α-dicarbonyl compounds required for Strecker aldehyde formation are formed in the consecutive steps of the Maillard reaction. After the induction period, aldehyde formation followed a straight line in the model systems as well as in the vegetable powders. The r^2 values ranged from 0.975 to 0.995 for the model systems and from 0.987 to 0.993 for paprika and tomato. The rate constants $(\Delta C/\Delta t)_{pH}$ of the aldehyde production in the model systems increased strongly with the increase in pH from 3.0 to 7.0.

A plot of the amount of Strecker aldehydes formed in the model systems as well as in the paprika and tomato powders after heating them for 60 min at 90 °C (60 min isochrones) versus pH yielded straight lines, as shown in Fig. 2. The data presented in Fig. 2 were normalised by fixing the maximum values of each data set at unity (maximum value = 1). The regression values r^2 for the linear pH dependence of the Strecker aldehyde formation as shown in Fig. 2 were 0.999 for the model systems, 0.969 for paprika and 0.986 for tomato powder. Moreover, it is striking that the influence of pH was highest in the model system and lowest in the tomato powder.

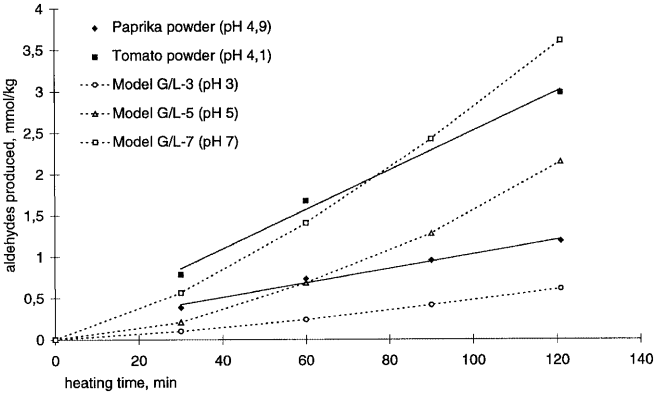

Fig. 1 Formation of 3-methylbutanal (3-MB) in glucose- and leucine-containing (molar ratio 20:1) low moisture model systems at different pH values and of the sum of the Strecker aldehydes acetaldehyde (AA), 2-methylpropanal (2-MP), 2-methylbutanal (2-MB) and 3-MB in commercially dried plant powders as a function of heating time. Reaction conditions: $a_w = 0.52$ (20 °C); T = 90 °C

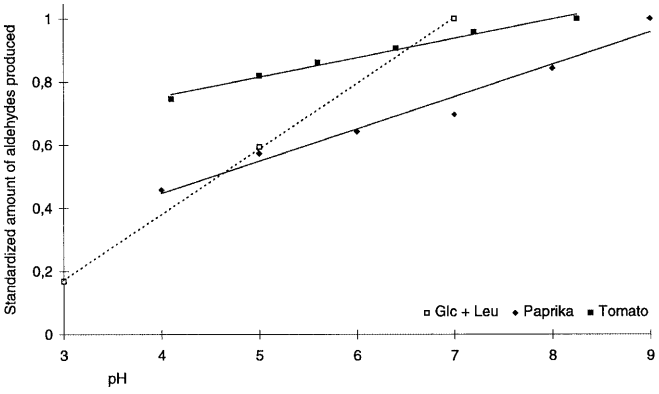

Fig. 2 Formation of 3-MB in low moisture model systems containing glucose and leucine (molar ratio 20:1) and of the sum of the Strecker aldehydes AA, 2-MP, 2-MB and 3-MB in plant powders as a function of pH. Reaction conditions: $a_w = 0.52$ (20 °C), T = 90 °C, 60 min

Interpreting the pH dependence of Strecker aldehyde formation with respect to overall Maillard reaction

Figure 3 shows the formation of fru-leu and it's decomposition product 3-DH at different pH values. It is important to note that the pH denoted in Fig. 3 refers to the pH value that had been adjusted in the aqueous suspensions of the model systems before they were freeze-dried. The concentration of the 1-deoxyosone which may be formed by decomposition of fru-leu, could not be determined by the analytical method applied. As shown in Fig. 3, during the first 20 min of heating at 90 °C the formation of fru-leu did not depend on the pH. After about 40 min a period of a constant concentration level of fru-leu was reached. It is worthwile noting that the fru-leu concentration almost reached a 90 mol% level, in relation to the molar concentration of the amino acid present in the system, proving that amino acid and glucose had reacted nearly completely. In the period of constant fru-leu concentration its formation and decomposition obviously have the same reaction rate. After this period the concentration of the Amadori compound decreased with increasing pH value indicating that the rate of decomposition of fru-leu increased with increasing pH value. In order to prove this observation the model systems F-L-3, F-L-5 and F-L-7 containing fru-leu at pH 3.0, 5.0 and 7.0 (pH values adjusted before freeze drying of the models) were heated for 30 min at 90 °C, and the decrease of fru-leu concentration as a function of pH was determined. As shown in Fig. 4, the rate of degradation of fru-leu did indeed increase with increasing pH, confirming the results shown in Fig. 3.

The formation of 3-DH presented in Fig. 3 showed an induction period because it is formed in a secondary reaction. At pH 5 and pH 7 the curves are almost identical during the first 30 min. In one particular time interval the concentrations of 3-DH remained almost constant, revealing that the rates of its formation and

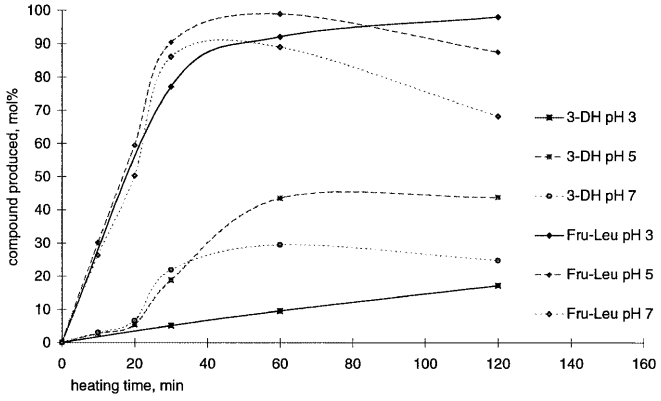

Fig. 3 Formation of fructose-leucine (fru-leu) and 3-deoxyosone (3-DH) in glucose- and leucine-containing (molar ratio 20:1) low moisture model systems at different pH values as a function of heating time. Reaction conditions: $a_w = 0.52$ (20 °C); T = 90 °C

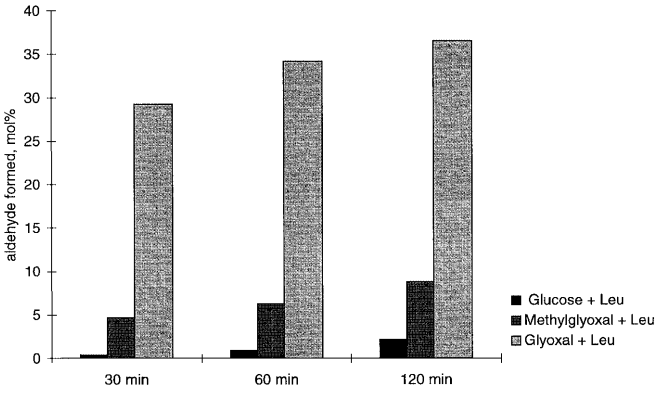

Fig. 5 Formation of 3-MB in low moisture model systems containing equimolar amounts of leucine and an α-dicarbonyl compound and glucose as a function of heating time. Reaction conditions: $a_w = 0.75$ (20 °C), pH = 7.0, T = 90 °C

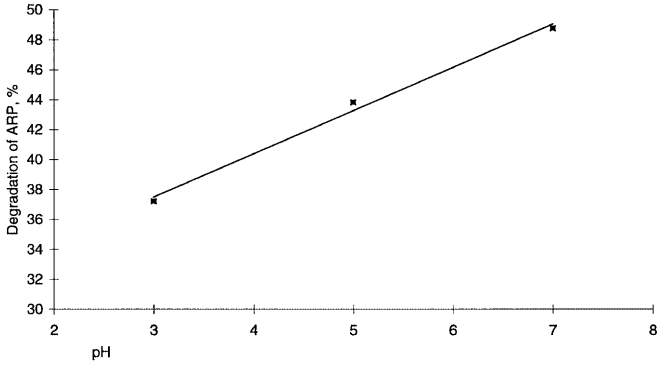

Fig. 4 Degradation of the Amadori rearrangement product (*ARP*) fru-leu in a low moisture model system as a function of pH. Reaction conditions: $a_w = 0.52$ (20 °C), T = 90 °C, 30 min

decomposition were equal for some time. As demonstrated in Fig. 3, the rate of decomposition of 3-DH was obviously highest at pH 7, because at this pH value the concentration of 3-DH reached much lower levels than at pH 5, whereas at pH 3 the rate of 3-DH formation was lower, showing a linear time dependence without perceptible decomposition. If we compare the characteristics of formation and decomposition of 3-DH to that of fru-leu within the first 30 min as shown in Fig. 3, it is surprising that the amount of Strecker aldehyde produced during that time at pH 7 exceeded the amount produced at pH 5 by more than twice. In order to explain the difference in the aldehyde formation between pH 5 and pH 7 one has to consider two additional reactions that influence the Strecker degradation. Firstly, increasing pH favours retro aldol reaction. Retro aldol fragmentation of reducing sugars or ARPs results in the formation of short chain α-dicarbonyl compounds such as glyoxal and methylglyoxal [20, 21] which both strongly accelerate the Strecker degradation of amino acids. Figure 5 shows the formation of 3-MB in low moisture model systems containing glucose, methylglyoxal and glyoxal as reaction partners of leucine, indicating the much higher reactivity of the α-dicarbonyl compounds compared with glucose. It is interesting to note that comparing glyoxal and methylglyoxal, the methyl group of the latter lowers the reactivity of the α-dicarbonyl structure. It was confirmed by Hayashi and Namiki [22] that in aqueous glucose/amino acid model systems, depending on the pH value, fragmentation of glucose yielded glyoxal and methylglyoxal within 30 min when heating the models at 80 °C. They observed that at a pH value of 6.4 this fragmentation occurred to a great extent.

Secondly, it is well known that the Lobry de Bruyn van Ekenstein rearrangement of reducing sugars is favoured when the pH is increased. Rearrangement of glucose yields, among other compounds, fructose. Thus, the production of fructose from glucose can be utilised to indicate the Lobry de Bruyn van Ekenstein rearrangement reaction. Figure 6 shows the characteristics of the formation of fructose from glucose in the model systems G/L-3, G/L-5 and G/L-7. As can be seen, fructose formation occurred readily after heating and could be described approximately as a zero order reaction within the limits of 10–120 min. The r^2 of the linear regression ranged from 0.963 to 0.999. Plotting the rates of fructose formation versus pH yielded a straight line ($r^2 = 0.998$; data not shown), revealing a linear pH dependence of fructose formation in the pertinent pH interval. Thus fructose production is a suitable and pH-sensitive parameter in order to investigate enolisation reactions in the course of Maillard reaction.

We propose that fructose production in the glucose- and leucine-containing model systems G/L-3, G/L-5 and G/L-7 is also correlated to the formation of α-dicarbonyl compounds via fragmentation reactions such as the above mentioned retro aldol reaction. Moreover, one has to consider that the Lobry de Bruyn van Ekenstein rearrangement reaction occurs via an endiol structure which in the presence of traces of heavy metal ions [23, 24] is easily oxidised to form an α-

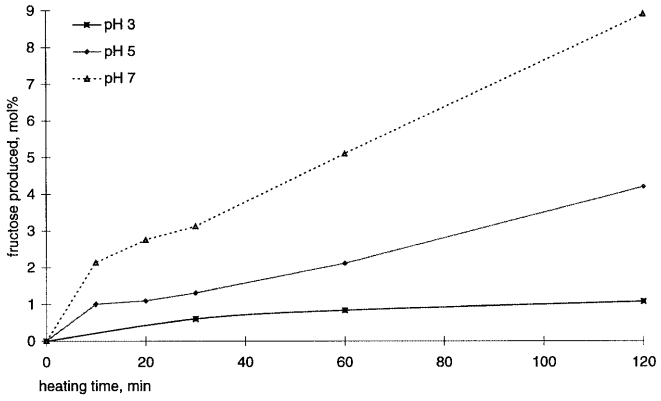

Fig. 6 Formation of fructose in glucose- and leucine-containing (molar ratio 20:1) low moisture model systems at different pH values as a function of heating time. Reaction conditions: $a_w = 0.52$ (20 °C); T = 90 °C

dicarbonyl structure capable of reacting with amino acids to form Strecker aldehydes. The model systems we investigated contained sufficient oxygen, and probably traces of heavy metals, making such oxidation reactions possible.

Elucidating the effect of freeze-drying on the texture and the chemical reactivity of plant powders

To investigate the influence of the pH value on chemical reactions in spice paprika and in tomato powders, they were suspended in water and freeze-dried after adjusting the desired pH value in the aqueous suspension (see Materials and methods). In order to estimate the effects of freeze-drying on texture and chemical reactivity of a vegetable powder (using paprika powder) separately, an original sample of spice paprika (a_w adjusted to 0.52) and a sample suspended in water and freeze-dried (a_w adjusted to 0.52 after freeze-drying) were heated for 60 min at 90 °C and analysed with respect to the formation of Strecker aldehydes and to the loss of colour (ASTA value).

This investigation revealed that freeze-drying resulted in a decrease in the density of the powder from 0.4 g/ml to 0.2 g/ml. The particle size increased and the surfaces of freeze-dried particles seemed to be more porous (macroscopic observations). After heating for 60 min at 90 °C the freeze-dried powder produced 15.0% more Strecker aldehydes than the original sample and showed a decrease in ASTA colour value, which is proportional to the concentration of carotenoids, of 10% while the original powder only lost 1% of its colour.

It turned out that freeze-drying obviously accelerated the Maillard reaction and the oxidative carotenoid degradation in paprika spice powder. We assume that sugars and amino acids are first extracted from cells when the powder is suspended in water and then concentrated on the surface of the particles during freeze-drying, resulting in an increased formation of Maillard reaction volatiles when heated. The decrease in the density probably indicates an increase in particle porosity accompanied by an air (oxygen) uptake into the particle structure which facilitates the oxidative degradation of paprika carotenoids.

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