JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

Effects of Cationic Species on Visual Color Formation in Model Maillard Reactions of Pentose Sugars and Amino Acids

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Effects of cationic species on Maillard browning were examined after heating (ca. 100 °C) aqueous pH 7.2 buffered solutions of amino acids and pentose sugars. Metallic ions of Group I metals (Li, Na, K, Rb and Cs) produced a small increase in browning (A_{420}), but somewhat greater effects were observed with ions of Group II metals Ca and Mg. Browning was suppressed by triethylammonium ion, but unaffected by a salt of the stronger base, guanidine. The quaternary amine salt choline chloride produced enhanced browning and served as a model for phospholipid involvement in Maillard reactions. With α,ω-diamino acids increases in browning were observed which related to lowered pK_2 values resulting from positively charged ω-substituents in these molecules.

KEYWORDS: Maillard; browning; cations; metal ions; diamino acids

INTRODUCTION

Food color can be a crucial determinant of consumer acceptance of food products in the marketplace, and for many processed foods the desired colors are the result of thermally induced Maillard reactions. The rate and quality of color development during Maillard reactions are in general a function of many factors including choice of reactants, reactant concentrations, reaction time, temperature and ambient pH. However, in the practical world of food processing an independent control of color is often limited by process restrictions demanded by other aspects of flavor and product definition. The ultimate goal of this ongoing study is to identify catalytic species capable of altering the nature of color development during food-related Maillard reactions preferably without affecting other aspects of flavor.

The Maillard reaction involving amino acids and reducing sugars in aqueous media near neutral pH is believed to proceed via an ionic mechanism (*1, 2*) and is therefore potentially susceptible to catalysis by various ionic species. Indeed the addition of anionic or cationic species to Maillard systems is well-known to affect the nature of visual browning. Negatively charged ions like hydroxide and phosphate have been well recognized to accelerate Maillard browning (*3*) and recently the enhancing effects of polyatomic anions including phosphate, sulfite, carboxylates (*4*) and borates (*5*) were examined in greater detail for their browning potential in model Maillard systems. Polyatomic anions in general appear to accelerate browning by catalyzing carbohydrate reactions per se prior to the Maillard (amine/carbonyl) interactions which ultimately lead to the formation of colored melanoidins.

Maillard browning is also known to be affected by cationic species apart from hydrogen ions. Most frequently mentioned are metal ions, especially polyvalent transition metal cations. In a detailed early study Kato et al. (*6*) reported that iron(II) and iron(III) ions were most effective to promote browning in a glucose/ovalbumin system, while in contrast Fallico and Ames (*7*) later observed reduction of color by adding iron(II) to a glucose/phenylalanine model. More recently Kwak and Lim (*8*) reported color altering effects caused by six metal ions including nontransition metal ions sodium (I), magnesium (II), calcium (II) and zinc (II) in buffered (pH 6.5) aqueous systems involving combinations of five sugars and twelve amino acids.

The present work was designed to investigate the intrinsic catalytic effects of cationic species on Maillard browning.

MATERIALS AND METHODS

Chemicals and Reagents. All inorganic compounds were highest purity commercial materials, all of >99% purity. D-Arabinose 99%, glycine, D-xylose, L-histidine hydrochloride were from Sigma-Aldrich Inc., St. Louis, MO. D-Ribose, D-arginine hydrochloride, norvaline, 2,4-diaminobutyric acid dihydrochloride 98%, L-ornithine 99+%, DL-norleucine 98%, DL-2,3-diaminopropionic acid hydrochloride 99%, L(+) 2-aminobutyric acid 98% and triethylamine hydrochloride 99+% were from ACROS Organics, NJ, USA. 2,2-Bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol [bis/tris] 99%, L-lysine hydrochloride 98.5−101%, choline chloride and L-alanine were from Fisher Chemical Co. Guanidine hydrochloride was from MP Biochemicals LLC, Solon, OH. Bis/tris buffer solutions were prepared by adding conc HCl to 0.10 or 0.30 M bis/tris base in deionized water.

Experimental Procedures. Generally, solid reactants were dissolved in buffer solutions (60.0 mL) to provide initial concentrations of reducing sugars (0.10 M), amino acids (0.035 − 0.040 M) and optional

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10.1021/jf801197n CCC: $40.75 © 2008 American Chemical Society
Published on Web 07/09/2008

Table 1. Effects of Metal Ions on Maillard Browning in pH 7.2 Bis/Tris Buffer at 100 °C

model system[a]	metal ion	A_{420}	final pH	reaction color[d]
ribose/gly	none	0.277[b]	7.10	d. grn
	Na^+	0.319	7.24	d. grn
	Li^+	0.325	7.16	d. grn
	K^+	0.318	7.33	d. grn
	Rb^+	0.304	7.31	d. grn
	Cs^+	0.343	7.33	d. grn
	none	0.335[c]	7.04	d. grn
	Mg^{2+}	0.424[c]	7.02	d. yel
	Ca^{2+}	0.519[c]	6.91	d. yel
	Sr^{2+}	0.397[c]	6.94	d. yel
	Ba^{2+}	0.429[c]	7.04	d. yel
xylose/gly	none	0.249[c]	7.22	yel - grn
	Mg^{2+}	0.467[c]	7.09	red - brn
	Ca^{2+}	0.278[c]	7.01	d. yel
	Sr^{2+}	0.311[c]	7.17	d. yel

[a] Initial concentrations: sugars, 0.10 M; amino acids, 0.040 M; metal chloride salts, 0.040 M. Reaction time 80 min and 1:3 dilution for measurment of A_{420}. [b] Measurement error ca. ± 2%. [c] Initial concs: glycine, 0.035 M; metal chlorides, 0.016 M; reaction time 160 min and 1:4 dilution for A_{420} measurement. [d] Abbreviations: d = dark, grn = green, yel = yellow, brn = brown.

Table 2. Ribose/Amino Acid Reactions[a] in 0.10 M pH 7.26 Bis/Tris Buffer at 100 °C

$R(CH_2)_nCH(NH_2)CO_2H$ (**1**)				
amino acid	R [*n*]	pK_2/pK_3 (25 °C)[b]	A_{420}	final pH
glycine	H [0]	9.60/...	0.277[c]	7.10
alanine	H [1]	9.69/...	0.066	7.20
2,3-diamino-propionic acid	NH_2 [1]	6.67/9.62	3.74	6.46
histidine	$C_3H_3N_2$[1]	5.97/8.97[d]	0.132	6.75
2-amino-butanoic acid	H [2]	9.85/...	0.183	7.18
2,4-diamino-butanoic acid	NH_2 [2]	8.17/10.4	0.438	6.87
norvaline	H [3]	9.72/...	0.100	7.14
ornithine	NH_2 [3]	8.65/10.8	0.674	6.89
			0.871[e]	7.10[e]
arginine	CH_5N_3 [3]	9.09/13.2	0.183	7.07
norleucine	H [4]	9.76/...	0.109	7.14
lysine	NH_2 [4]	8.9/10.3	0.738	6.98
			0.846[e]	7.03[e]

[a] Initial conc: ribose, 0.10 M; amino acids, 0.040 M. Reaction time 80 min. [b] Data from refs *15* and *18*. [c] Absorbance after 1:3 aqueous dilution. [d] 5.97 and 8.97 represent p*K* values for dissociation of protonated imidazole and amino acid zwitterion repectively. [e] 0.30 M bis/tris buffer at pH 7.22.

additives (0.016 − 040 M) and rapidly (ca. 5 min) heated to and maintained at reflux temperature, ca. 100 °C. All α,ω-diamino acids were added in the form of their monohydrochloride salts. Beginning at the start of reflux ($t = 0$ min) 1.00 mL samples were withdrawn at $t = 10$, 20, 40, 80 and sometimes 160 min with precooled hypodermic syringes and immediately each was added to 2.00 or 3.00 mL of water for spectrophotometric analysis in 1 cm cuvettes at 420 nm vs pure water. Following removal of the last aliquot the residual reaction mixtures were rapidly cooled in ice to ca. 23 °C for an end point pH determination. Reactions performed at single reaction times, generally 80 or 200 min, employed 30.0 mL of buffers. At the prescribed time these reactions were rapidly cooled to ca. 23 °C before final pH determination and removal of a single 1.00 mL aliquot for aqueous dilution (1:3) and absorbance measurement at 420 nm. Overall precision of absorbance measurements was estimated by observing variations in absorbance (A) values in ribose/glycine control reactions at 10 − 80 min time intervals. For replicate experiments ($n = 3$) the precision ranged from ± 6.7% at $A = 0.015$ at 10 min to ± 1.7% at $A = 0.277$ at 80 min. Test results shown in **Tables 1** and **2** are data obtained from single experiments unless otherwise noted and their accuracy is assumed to lie within ±10% of the stated values.

Instrumental Analysis. UV−vis data were obtained with a computer interfaced Perkin-Elmer Lambda 35 spectrophotometer using a slit width of 1 nm. pH measurements were made at ca. 23 °C with a single glass electrode using a Fisher Accumet model 955 mini pH meter calibrated at pH 7.00 with standard buffer. Precision of pH measurement was nominally ±0.02 pH unit.

RESULTS AND DISCUSSION

The ionic nature of most Maillard reactions implies that positively charged species can be influential in Maillard browning. To test this hypothesis Group I and Group II metal chlorides and cationic organic chlorides were added to model Maillard systems consisting of pentose sugars and α-amino acids in a relatively inert (bis/tris) buffer near pH 7. In addition, reactions of sugars with α,ω-diamino acids (**1**) were examined to evaluate the intramolecular effect of an ammonium ion on browning. A search of the food literature failed to reveal any deliberate attempts to correlate the effects of added cationic species other than hydrogen ions on flavor aspects of the Maillard reaction. The present study was limited only to observations of visual color development.

Effects of Metal Ions. Previous studies (*6–8*) showed that Maillard browning is enhanced in the presence of added metallic salts; however, most of these studies employed polyvalent transition metals suggesting an unspecified contribution of redox processes in the observed browning. In this work Group I and Group II metals were employed to eliminate the redox complication and to isolate intrinsic effects of added cations.

Effects of metal ions were evaluated in a model systems usually containing pentose sugars (0.10 M), glycine (0.035 or 0.040 M) in the relatively unreactive tertiary amine buffer bis/tris at pH 7.2. Pentose sugars and glycine were chosen because of their high browning propensity (*4*). Reactant concentrations were adjusted to provide statistically significant absorbance values (A_{420}) at convenient reaction times. Metal ion concentrations (0.016 M or 0.040 M) were chosen at levels where it was assumed they could compete with protonated buffer (ca. 0.015 M) available from bis/tris (pK_a 6.5) at pH 7.2.

Group I metal ions (Li^+, Na^+, K^+, Rb^+ and Cs^+) at 0.040 M produced a modest, but reproducible increase in browning in the ribose/glycine system (**Table 1**). Addition of these ions led to A_{420} values ranging from 0.304−0.343, all slightly above the control A_{420} of 0.277 ± 0.005 ($n = 3$). There were no apparent differences in effect among the Group I ions. All reactions (including the control) gradually developed a pale blue-green color that became a deep green after 80 min. The peculiar green hue is an optical effect caused by small amounts of an intensely colored blue pigment formed in addition to the usual yellow → brown colored melanoidins. The blue pigment, known in the literature as "Blue M1" (*5, 9*), has been well characterized chemically and has a maximum absorbance at 625 nm. The compound's longer wavelength absorption produces minimal contribution to our absorbance measurements at 420 nm. The mechanism for formation of Blue M1 is as yet unclear, but glycine and pentose sugars seem to be uniquely involved.

Group II metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) at 0.016 M with exception of Ca^{2+} led to a small intensification of browning (**Table 1**). In a ribose/glycine system addition of Group II ions led to A_{420} of 0.397−0.513 versus a control value of 0.335. With exception of Ca^{2+} (A_{420} 0.513) there appeared to no significant differences in absorbance values among the various Group II ions. All Group II ions had little effect on reaction pH, but interestingly all reactions containing these ions gradually developed a more conventional deep yellow hue with no evidence of Blue M1 formation. Group II ions exhibited somewhat different effects in a xylose/glycine system under conditions identical to the ribose/glycine system (**Table 1**).

Under these conditions only magnesium ion caused a significant increase in browning (A_{420} 0.467 versus control value of 0.249). However, the presence of Mg^{2+}, Ca^{2+} and Sr^{2+} all appeared to suppress the Blue M1 formation observed in the control experiment.

The effects produced by calcium and magnesium ions were examined more closely in a ribose (0.10 M)/alanine (0.040 M) system designed to completely avoid the complication of Blue M1 formation. Replicate experiments performed for 200 min at 100 °C with $[Ca^{2+}]$ at 0.040 M led to deep yellow/orange coloration, a final pH of 6.80 and an average increase of 0.108 A_{420} units vs controls. A similar experiment using magnesium ion at 0.040 M produced a deep orange reaction mixture, an increase in browning versus control of 0.100 A_{420} units and a final pH of 7.02. Under these conditions a control reaction without metal ions added developed a pale yellow color and final pH of 7.11. Also, the addition of Ca^{2+} or Mg^{2+} at 0.040 M to the 0.10 M bis/tris buffer (pH 7.26) at 24 °C produced no significant pH change.

Mechanisms for the effects of metal ions on Maillard browning are still unclear. Control experiments run without amino acids or without sugars gave little or no browning suggesting metal ion involvement takes place at a stage following amine/carbonyl reactions. Some possibilities might be a "super acid" effect which has been predicted for polyvalent cations during general acid/base catalysis (*10*) or a metal ion/Schiff-base complexation as observed in vitamin B6 chemistry (*11*). More experiments are needed to establish these possibilities.

Effects of External Organic Cations. In view of the enhancing effects on Maillard browning observed with metal ions it seemed appropriate to investigate the behavior of some pertinent organic cations related to foodstuffs. Certain diamino acids arginine, lysine and ornithine possess in their sidechains basic guanidino and amino groups respectively that were presumed to be highly protonated, i.e., cationic at neutral pH. To investigate the possible *intermolecular* effects of these protonated amine functions during Maillard reactions, guanidine hydrochloride and triethylamine hydrochloride were added at 0.040 M to the ribose/monoamino acid reactions described in **Table 2**. Addition of the guanidine salt (pK_a ca. 12.5) produced no significant changes in degree of browning or final pH in reactions with glycine (A_{420} 0.302) or with norleucine (A_{420} 0.129) compared to control values shown in **Table 2**. Also, a ribose control reaction run with 0.040 M guanidine hydrochloride without glycine remained essentially colorless under the same conditions. In marked contrast to the guanidine salt the addition of triethylamine hydrochloride (pK_a 11.0) led to reduced browning versus controls, namely with glycine (A_{420} 0.116) and norleucine (A_{420} 0.042). Evidently the *intermolecular* effects of ambient amine salts on browning can differ depending upon the basic stength of the amine involved. A salt of the very strong nitrogen base guanidine was significantly ineffective for reduction of Maillard browning under our experimental conditions. The intermolecular effects of amine salts on browning are interpreted along with related *intramolecular* effects in a subsequent sections on α, ω-diamino acids and temperature effects on reaction mechanisms.

Certain lipid classes, i.e., the phosphatides which can contain cationic sites are also known to participate in Maillard reactions. Cephalins, i.e., phosphatidylethanolamines bearing free amino groups are known to be glycated via Schiff base formation, but corresponding protonated phosphatides are not mentioned as catalysts to control browning (*12*). Lecithin (phosphatidylcholine) is an ester/inner-salt derivative of choline, a quaternary ammonium compound [2-hydroxy-N,N,N-trimethylethanaminium]. This particular phosphatide is known to influence the course of ribose/cysteine Maillard reactions by altering the formation of volatile reaction products (*13*), but again the effect of a cationic phosphatide on color formation has apparently not been described. Choline chloride was selected as a model additive to simulate Lecithin and to test the effect of a relatively stable quaternary ammonium cation in our model 0.10 M ribose/0.040 M glycine system in pH 7.26 bis/tris buffer at 100 °C. Addition of choline chloride at 0.045 M to the standard ribose/glycine system led to a noticeable increase in browning rate measured at 420 nm (**Figure 1**). And, the effect was somewhat enhanced by increasing choline concentration to 0.090 M. Addition of 0.045 M choline to ribose alone in buffer gave zero color formation under the same conditions and buffer pH remained essentially unchanged after all choline chloride reactions. Therefore the effect of choline on browning probably occurs after the initial amine/carbonyl step in the Maillard reaction sequence. Choline chloride and Lecithin itself are known to act as methylating agents in the presence of ambient nucleophiles (*14*) suggesting that methylation of the ribose/glycine Schiff base could contribute to browning by providing an extra reaction pathway and additional reaction intermediates involved in color formation (**Figure 2**).

Effects of Internal Organic Cations: α,ω-Diamino Acids. At near neutral pH all α, ω-diamino acids possess ω-situated nitrogen functions which being basic are almost 100% protonated ($pK_3 \gg 9$ at 25 °C) [**Table 2**] (*15*) and as such may provide intramolecular cationic sites to affect Maillard browning. To evaluate this cationic effect a series of α,ω-diamino acids, including protein amino acids ornithine, lysine, arginine and histidine were reacted with ribose in 0.10 M bis/tris buffer at 100 °C (**Table 2**). And, in addition each of these amino acids was compared with a corresponding α-alkylamino acid lacking the ω-amine functionality. In Maillard reactions amino acids are believed to react in their amino carboxylate form ($H_2NCHRCO_2^-$) with reducing sugars (*16*). And, at any given pH the amount of available amino carboxylate is said to be governed by the familiar Henderson–Hasselbalch equation (eq 1) in which pK_2 represents the deprotonation equilibrium constants for individual amino acid zwitterions ($H_3N^+CHRCO_2^-$) and where (H_3N^+) and (H_2N) represent concentrations of zwitterion and deprotonated zwitterion respectively. Therefore at constant pH a lower pK_2 value will result in a higher concentration of reactive amino carboxylate.

$$\mathrm{pH} = \mathrm{p}K_2 - \log[(H_3N^+)/(NH_2)] \quad (1)$$

It is therefore predictable that amino acids with lower pK_2 values should produce more Maillard browning at a given pH. A similar effect of pK_2 on monoamino acid reactivity has already been proven for the Strecker degradation whose initial reaction steps are identical with those of the Maillard reaction (*17*). In the present study all α,ω-diamino acids (**1**, R = NH_2) have lower pK_2 values compared to related monoamino acids (**1**, R = H) and in each case with exception of histidine the diamino acids led to significantly more browning, i.e., higher A_{420} values than their monoamine counterparts (**Table 2**). For diamino acids (**1**) with R = NH_2 the reduced pK_2 values and subsequent effects on browning are explained by the presence of ω-situated NH_3^+ groups in the molecules. At near neutral pH the electrostatic effect of the extra NH_3^+ on zwitterion dissociation in diamino acids is known to fall off with increasing distance from the distal cationic center (*16*). This explains the more extensive browning

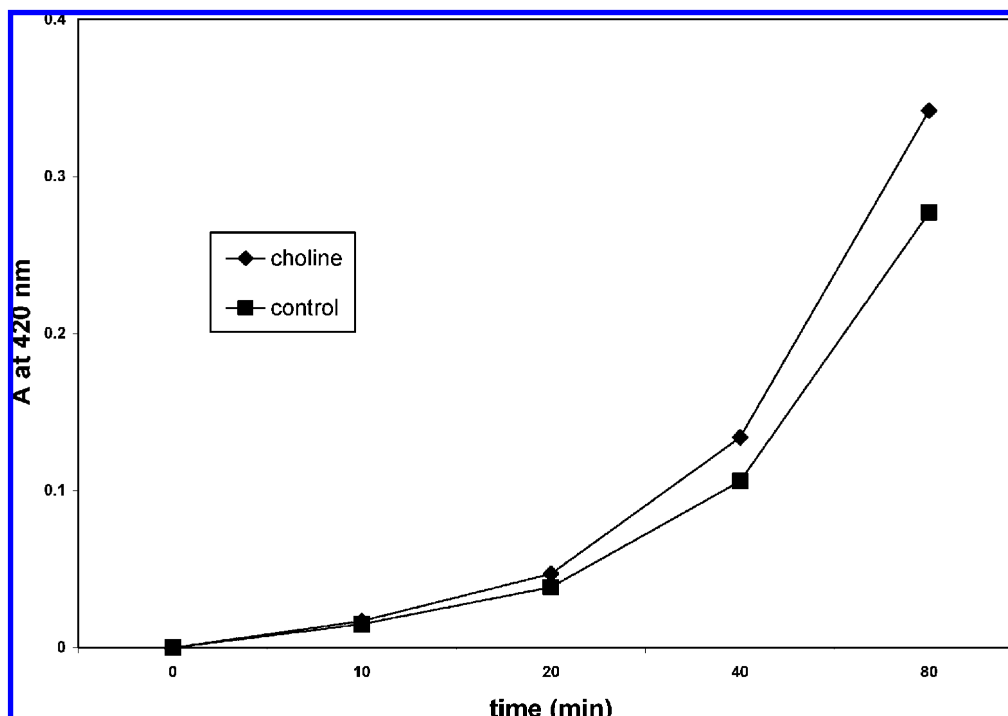


Figure 1. Effect of 0.040 M choline chloride in reaction of D-ribose 0.10 M plus glycine 0.040 M in 0.10 M bis/tris buffer (pH 7.26) at 100 °C.

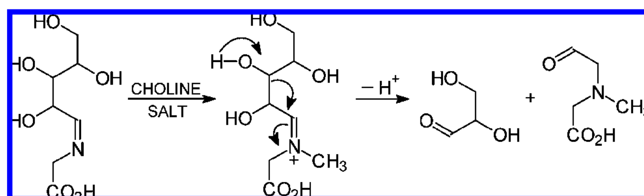


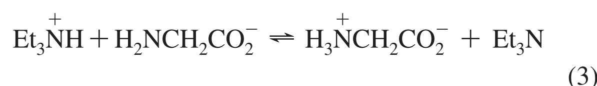
Figure 2. Reaction of a choline salt with the ribose/glycine Schiff base.

observed with 2,3-diaminopropionic acid (**1**, R = NH_2, $n = 1$, pK_2 6.67) [A_{420} 3.74] compared to lysine (**1**, R = NH_2, $n = 4$, pK_2 8.9) [A_{420} = 0.798]. Similar effects were observed with 2,4-diaminobutanoic acid (**1**, $n = 2$) and ornithine (**1**, $n = 3$) which have intermediate NH_3^+ to zwitterion distances. In the case of lysine a larger than expected effect on browning (A_{420} 0.738 to 0.846) was observed in spite of a relatively high pK_2 value 8.9. These results suggest the possibility of an additional effect on browning apart from the intramolecular electrostatic effect already mentioned. In arginine at neutral pH its guanidine moiety is completely protonated (pK_3 13.2), but its relatively large distance from the amino acid zwitterion (**1**, $n = 3$) leads to practically no effect on NH_3^+ ionization (pK_2 9.09 versus norvaline pK_2 9.72). And, the relatively low browning potential observed (A_{420} of 0.183 for arginine versus 0.100 for norvaline) precludes any secondary effect as was observed with lysine. Regarding histidine, according to the literature (*15*) its lower pK value of 5.97 represents deprotonation of the weakly basic imidazole moiety rather than the usual (pK_2) symbolic designation for ionization of an amino acid zwitterion. And, at the reaction pH of ca. 7 the unprotonated neutral heterocycle offers little electrostatic effect in the molecule. As a result the histidine zwitterion remains relatively highly protonated at neutral pH (pK 8.97) **Table 2** leading to predictable low browning (A_{420} 0.132).

Effects of Temperature on Reaction Mechanisms. Some of our experimental observations can be explained by considering the fact that the magnitude of equilibrium constants can vary with temperature. Given the well-known relationships $\Delta G_a = -2.303\,RT \log K_a$ and p$K_a = -\log K_a$ where K_a represents the equilibrium constant for dissociation of a protonic acid, ΔG_a is the Gibb's free energy change for dissociation, R is a universal gas constant and T is the absolute temperature, it follows that pK_a can also vary with temperature according to (eq 2) (*18*).

$$pK_a = \Delta G_a / 2.303RT \quad (2)$$

From (eq 2) it is clear that pK_a decreases with increasing temperature and that all pK values including those given for 25 °C in **Table 2** and the buffer pK will have lower effective values at a reaction temperature of 100 °C (373 K). For the present time it is assumed that sufficient differences exist between pK_2 and pK_3 of α,ω-diamino acids at 100 °C to support our hypothesis governing relative degrees of Maillard browning produced by these compounds. As mentioned previously, the addition of a triethylamine salt led to significant reduction of browning in ribose/glycine reactions. At 100 °C a reduced pK_a for triethylamine, i.e., less than pK_a 11.0 at 25 °C could make its salts sufficiently more acidic and able to compete with zwitterion deprotonation according to (eq 3). In this way a reduction in glycinate ion concentration can result in reduced Maillard browning.



$$Et_3\overset{+}{N}H + H_2NCH_2CO_2^- \rightleftharpoons H_3\overset{+}{N}CH_2CO_2^- + Et_3N \quad (3)$$

Ribose/glycine browning at 100 °C was not affected by addition of guanidine hydrochloride, a salt of a much stronger base (pK_a ca. 12.5). Apparently even at 100 °C an external guanidine salt is not sufficiently acidic to affect the concentration of glycinate ion. The effect of temperature on mechanism may also be involved in the intramolecular effects observed in some α, ω-diamino acids. In arginine the presence of a substituted guanidinium ion in the molecule may have contibuted to low browning potential by suppressing zwitterion deprotonation. And, for lysine, its unusually highly browning capacity may in part be due to a temperature dependent deprotonation of its ω-NH_3^+ group.

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Received for review April 15, 2008. Revised manuscript received June 5, 2008. Accepted June 7, 2008.

JF801197N