Relative Reactivities of Amino Acids in the Formation of Pyridines, Pyrroles, and Oxazoles

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The contributions of ^{15}N-labeled glycine and tested amino acids (glutamine, glutamic acid, asparagine, aspartic acid, lysine, arginine, phenylalanine, and isoleucine) to pyridine, pyrrole, and oxazole formation were investigated. Ten pyridines, nine pyrroles, two oxazoles, three amines, and one benzonitrile were identified in the present study. The quantities of pyridines, pyrroles, and oxazoles in the reaction mixture of glycine and aspartic acid were the highest. Aspartic acid, lysine, and asparagine had the highest contribution in pyridine, pyrrole, and oxazole formation, respectively. In the presence of glycine, glutamic acid showed the least contribution, whereas asparagine had the highest contribution to the formation of all nitrogen-containing compounds among the tested amino acids. While lysine was able to increase the reactivity of glycine, arginine inhibited the capability of glycine to produce nitrogen-containing volatile compounds.

Keywords: *Model Maillard reaction; amino acid reactivities; heterocyclic flavor compounds*

INTRODUCTION

It is well-known that the Maillard or nonenzymatic browning reaction has a profound contribution to food flavors. The effect of different amino acids on the formation of Maillard types of flavor compounds has been widely studied (Koehler et al., 1969; Shigematsu et al., 1972). However, most of the studies have been focused on the reaction between a single amino acid and sugar (Piloty and Baltes, 1979; Fry and Stegink, 1982; Ashoor and Zent, 1984). Flavor formation involving the interaction of more than one amino acid in the Maillard reaction has not been investigated. In an earlier paper (Hwang et al., 1995), we reported the competition in flavor formation between different amino acids and ^{15}N-labeled glycine in a reaction system containing glucose by examining the relative reactivities of eight different amino acids (glutamine, glutamic acid, asparagine, aspartic acid, lysine, arginine, phenylalanine, and isoleucine) on the formation of pyrazines. In the present paper, we further report the relative reactivities of these eight different amino acids on the formation of pyridines, pyrroles, and oxazoles.

EXPERIMENTAL PROCEDURES

Materials. L-Glycine, L-glutamine, L-glutamic acid, L-asparagine, L-aspartic acid, L-lysine, L-arginine, L-phenylalanine, L-isoleucine, and wheat starch were purchased from Sigma Chemical Co. (St. Louis, MO). Glucose and deuterated toluene (toluene-d_8), the internal standard, were obtained from Aldrich Chemical Co. (Milwaukee, WI). Glycine-α-*amine-*^{15}N was purchased from Isotec, Inc. (Miamisburg, OH) with a stated purity of 99%. Tenax TA (2,6-diphenyl-*p*-phenylene oxide) adsorbent (60–80 mesh) was obtained from Alltech Associates (Deerfield, IL). Carbotrap (activated graphitized carbon) adsorbent (20–40 mesh), C_5–C_{25} *n*-paraffin standard, and silanized glass wool were purchased from Supelco Inc. (Bellefonte, PA).

Volatile Generation and Isolation. Twenty grams of wheat starch and an equal amount (2.66 μmol of each) of glucose, L-glycine-α-*amine-*^{15}N, and tested amino acid (L-glutamine, L-glutamic acid, L-asparagine, L-aspartic acid, L-lysine, L-arginine, L-phenylalanine, or L-isoleucine) were mixed with 150 mL of deionized water and adjusted to pH 7 by using hydrochloric acid or sodium hydroxide. After being freeze-dried, the solid mixture was placed in the upper level of a desiccator; a Pyrex dish containing 20 mL of deionized water was placed in the lower level to adjust the moisture content of the samples back to 12–14%. The samples were further transferred into a reaction vessel and heated at 180 °C for 1 h.

The heated samples (2 g of each) were packed in the center of glass tubes, and silanized glass wool was placed at the two ends of the tubes. One microliter of 1.001 mg/mL deuterated toluene was spiked into the tubes as the internal standard. The tubes were further sealed in a Scientific Instrument Services (SIS) solid sample purge-and-trap apparatus (Ringoes, NJ), and the volatiles were purged with nitrogen at a flow rate of 40 mL/min to silanized glass-lined stainless steel desorption tubes (4.0 mm i.d. × 10 cm length). The desorption tubes were also from SIS and consisted of a 3-cm bed volume of Tenax TA adsorbent and a 3-cm bed volume of Carbotrap adsorbent. This volatile isolation was carried out at 80 °C for 1 h.

Volatile Analysis by Gas Chromatography–Mass Spectrometry (GC–MS). The volatile analysis was conducted according to the same method as described by Hwang et al. (1993). Linear retention indices for the volatiles were determined through the use of a C_5–C_{25} *n*-paraffin standard, according to the method of Majlat et al. (1974). All mass spectra obtained were identified by utilizing an on-line computer library (NIST) or published literature.

Calculations for the Relative Contribution of ^{14}N Nitrogen and ^{15}N Nitrogen to Flavor Formation. The flavors monitored in this study were pyridines, pyrroles, oxazoles, amines, and benzonitrile. The molecular weights of those flavor compounds will increase 1 mass unit when ^{15}N atoms are incorporated, instead of ^{14}N atoms, in heterocyclic rings which only contain one nitrogen atom in each compound. Thus, each flavor compound may have two different molecular weights, denoted W_1 and W_2. W_1 represents one ^{14}N nitrogen atom in the ring, and W_2 has one ^{15}N nitrogen atom in the ring. The simultaneous equations below are used to solve the contribution of each component (W_1 and W_2) present in a mixture. This detailed explanation was previously reported by Hwang et al. (1993).

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$$M_{exp} = M_n W_1 + (M - 1)_n W_2 \quad (1)$$

$$(M + 1)_{exp} = (M + 1)_n W_1 + M_n W_2 \quad (2)$$

$(M - 1)_n$, M_n, and $(M + 1)_n$ are the experimental relative abundances of the ion peaks of the flavor compounds from the reaction of nonlabeled glycine, tested amino acid, and glucose. M_{exp} and $(M + 1)_{exp}$ are the experimental abundances of the ion peaks of the flavor compounds generated from the reaction of glycine-^{15}N, tested amino acid, and glucose.

After the relative contributions of the two different compounds (W_1 and W_2) were calculated, the percent of the contribution from a tested amino acid and labeled glycine could be determined by using eqs 3 and 4. As mentioned above, W_1 contains one ^{14}N nitrogen atom in the ring; therefore, the nitrogen of component W_1 is from tested amino acids. On the other hand, component W_2 contains one ^{15}N nitrogen atom from ^{15}N labeled glycine.

$$\% \text{ contribution of tested amino acid} = [W_1/(W_1 + W_2)] \times 100\% \quad (3)$$

$$\% \text{ contribution of labeled glycine} = [W_2/(W_1 + W_2)] \times 100\% \quad (4)$$

RESULTS AND DISCUSSION

In an earlier paper (Hwang et al., 1995), we reported a total of 56 pyrazines in the reaction systems containing ^{15}N labeled glycine and 8 other amino acids. In this paper, we further report another 25 nitrogen-containing reaction products (Table 1): 10 pyridines, 9 pyrroles, 2 oxazoles, 3 amines, and 1 benzonitrile. In comparison with pyrazine formation, these nitrogen-containing heterocyclic compounds represent a relatively small proportion. However, they possess some unique sensory properties which may contribute significantly to the flavor of processed foods.

The 10 identified pyridines included 7 alkylpyridines, 2 acylpyridines, and 1 phenylpyridine. These pyridines have been reported in coffee, barley, roasted lamb, and meat (Buttery et al., 1977; Mottram, 1991; Suyama and Adachi, 1980). Some pyridines possess pleasant odors; however, most pyridines have green, bitter, astringent, roasted, burnt, pungent vegetable, or phenolic properties (Maga, 1981a; Pittet and Hruza, 1974). In general, alkylpyridines possess a less desirable odor (Fors, 1983), whereas acylpyridines have more pleasant aromas; for example, 2-acetylpyridine has a cracker-type aroma (Buttery et al., 1971). The formation of pyridine may involve the condensation of aldehydes, ketones, or α,β-unsaturated carbonyl compounds with ammonia which is degraded from amino acids (Suyama and Adachi, 1980). Thus, various types of substituted pyridines can be produced from different combination of aldehydes, ketones, or carbonyl compounds (Table 1). The yields and relative contributions of tested amino acids to pyridine formation are shown in Figure 1. Aspartic acid had the highest contribution and isoleucine the lowest contribution in the formation of pyridines. Aspartic acid also generated the highest quantity of pyridines, while arginine had the lowest quantity of pyridine in the presence of glycine. Although it has been suggested that the availability of ammonia is the determining factor in generating pyridines (Baines and Moltkiewicz, 1984), this hypothesis is not supported in our study. If the availability of ammonia was the determining factor to form pyridine, the yields of the glutamine and asparagine reaction mixtures would be higher than those of the glutamic acid and aspartic acid reaction mixtures which have the labile amide side chains as the additional sources of ammonia. However, the yield of the glutamine reaction mixture was about the same as that of the glutamic acid reaction mixture, and the yield of the asparagine reaction mixture was even lower than that of aspartic acid reaction mixture. Therefore, these results might imply that the α-amino groups of amino acids prefer to condense with carbonyl compounds via a one-step reaction to form pyridines rather than to degrade to ammonia and later incorporate into a pyridine ring.

Pyrroles identified in this study included four alkylpyrroles, two acylpyrroles, two pyrrolealdehydes, and one furfurylpyrrole. These pyrroles tend to contribute baked cereal product notes or smoky notes (Ohloff and Flament, 1978) and have been reported in various heated foods, especially coffee (Flament, 1991; Fors, 1983). It was also found that acylpyrroles have sweet, smoky, and slightly medicine-like odors (Shigematsu et al., 1972, 1977). Pyrrolealdehydes seem to have an odor analogous to xylene, cinnamaldehyde, or benzaldehyde (Kato, 1967), while 1-furfurylpyrrole has a green hay-like aroma (Walradt et al., 1970). Alkylpyrroles may have undesirable intense petroleum-like odors; however, they give a sweet, slightly burnt-like aroma on extreme dilution (Fors, 1983). There are two pathways to form pyrroles. One results from the interaction between an amino acid and a 3-deoxyhexosone through the Strecker degradation followed by dehydration and ring closure (Kato and Fujimaki, 1968). The other pathway is the reaction of furans with amines or amino acids. This reaction requires a carbonyl function in position 2 of the furan derivative (Rizzi, 1974).

The yields and relative contributions of the tested amino acids to pyrrole formation are shown in Figure 2. The overall contributions of the tested amino acids were below 35% in generating pyrroles when they competed with glycine. This result is due to glycine, which, having no side chain, is more flexible than other amino acids for involvement in the formation of pyrroles. For a comparison of each system for the contribution of amino acids to the formation of pyrroles, phenylalanine and isoleucine had the least contribution, whereas asparagine, aspartic acid, and lysine had the highest contribution. The yield from the reaction mixture of aspartic acid and glycine was the highest.

If we further examine the relative contributions of the tested amino acids to the formation of 1-methylpyrrole and 1-methylpyrrole-2-carboxaldehyde, more than 90% of the nitrogen atoms were from glycine. Moreover, the yields of 1-methylpyrrole and 1-methylpyrrole-2-carboxaldehyde were the two highest in most of the reaction mixtures (Table 1). As mentioned above, glycine can produce 1-methyl-substituted pyrrole or pyrrolealdehyde by either reacting with 3-deoxyhexosone through the Strecker degradation or exchanging the oxygen atom of the corresponding furan. The other amino acids might require an extra cleavage step to form 1-methyl-substituted pyrrole or pyrrolealdehyde. These results indicate that glycine is superior to other amino acids in the production of pyrroles.

The yields and relative contributions of the tested amino acids to oxazole formation are shown in Figure 3. Unlike the other nitrogen-containing heterocyclic compounds, the quantities of oxazoles were very few in this study (Table 1). Oxazoles existing in cooked foods have also been reported, though in relatively small amounts (Baltes et al., 1989). There was no oxazole identified in the reaction mixture containing glycine

Table 1. Pyridines, Pyrroles, Oxazoles, and Other Nitrogen-Containing Compounds Identified in the Reaction of Glucose, Glycine-α-*amine*-^{15}N, and Tested Amino Acids

compound	yield (mg/g of glucose)								
	Ctrl[a]	Gln[a]	Lys[a]	Asn[a]	Phe[a]	Glu[a]	Asp[a]	Ile[a]	Arg[a]
pyridines									
pyridine	–[b]	–	–	6.3	–	–	8.5	–	–
4-methylpyridine	–	–	–	–	–	–	14.5	–	–
2-methylpyridine	–	–	–	–	–	–	4.6	–	–
2-ethylpyridine	–	–	–	–	–	–	8.3	2.2	–
2,5-dimethylpyridine	–	–	–	–	–	–	1.4	–	–
3-ethyl-2,6-dimethylpyridine	2.5	11.6	–	5.1	4.5	6.5	–	–	–
3-butylpyridine	1.7	4.3	–	–	–	9.6	1.7	–	–
2-acetylpyridine	23.3	31.5	33.3	14.3	10.2	32.2	18.0	5.5	6.0
2-propionylpyridine	–	1.6	–	0.8	–	–	6.5	–	–
2,6-diphenylpyridine	–	–	–	–	11.8	–	–	–	–
pyrroles									
pyrrole	–	–	–	9.3	–	6.1	10.0	5.0	4.8
1-methylpyrrole	9.4	30.2	4.6	26.7	58.9	59.0	131.5	26.8	11.8
2,5-dimethylpyrrole	1.2	–	–	4.4	–	3.9	4.0	4.7	1.8
tetramethylpyrrole	–	–	–	–	–	2.2	–	–	–
2-acetylpyrrole	3.8	17.0	42.1	9.2	–	15.8	8.7	–	16.8
1-methyl-2-acetylpyrrole	44.0	29.5	102.7	27.0	69.1	54.1	52.0	25.0	27.8
1-methylpyrrole-2-carboxaldehyde	–	6.4	–	–	10.0	–	–	7.5	6.0
1-ethylpyrrole-2-carboxaldehyde	–	20.1	49.0	6.1	14.2	14.5	9.6	18.6	8.3
1-(2-furanylmethyl)pyrrole	–	8.2	–	6.9	6.1	9.2	10.2	–	6.4
oxazoles									
4,5-dimethyloxazole	–	9.8	17.0	–	–	13.9	14.0	–	7.7
trimethyloxazole	–	–	–	–	–	–	9.0	–	–
2-acetyl-4,5-dimethyloxazole	–	–	–	–	–	–	10.1	–	–
other nitrogen-containing compounds									
benzonitrile	–	–	–	–	2.4	–	–	–	–
N-(2-methylbutylidene)-2-methylbutylamine	–	–	–	–	–	–	–	69.7	–
bis(2-methylbutyl)amine	–	–	–	–	–	–	–	65.9	–
tris(2-methylbutyl)amine	–	–	–	–	–	–	–	83.0	–
totals	85.9	170.2	248.57	116.1	187.2	227.0	322.4	313.9	97.4

[a] Ctrl, glycine only; Gln, labeled glycine and glutamine; Lys, labeled glycine and lysine; Asn, labeled glycine and asparagine; Phe, labeled glycine and phenylalanine; Glu, labeled glycine and glutamic acid; Asp, labeled glycine and aspartic acid; Ile, labeled glycine and isoleucine; Arg, labeled glycine and arginine. [b] Not observed.

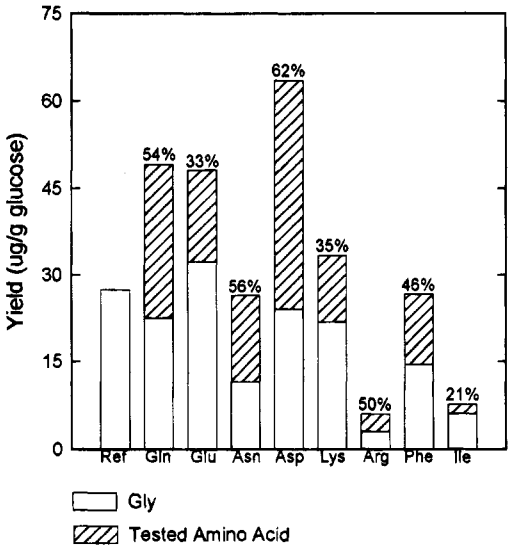


Figure 1. Total yields and relative contributions of pyridines generated from reaction systems containing tested amino acids and glycine. Ref, glycine only; Gln, labeled glycine and glutamine; Glu, labeled glycine and glutamic acid; Asn, labeled glycine and asparagine; Asp, labeled glycine and aspartic acid; Lys, labeled glycine and lysine; Arg, labeled glycine and arginine; Phe, labeled glycine and phenylalanine; Ile, labeled glycine and isoleucine. The numbers on the tops of the columns show the percent contributions of each tested amino acid.

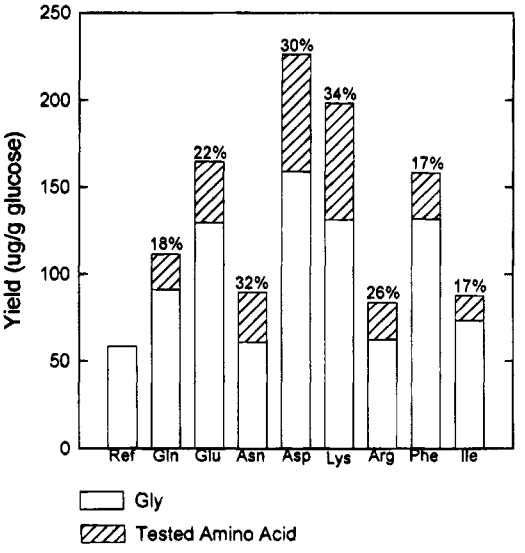


Figure 2. Total yields and relative contributions of pyrroles generated from reaction systems containing tested amino acids and glycine. Abbreviations and explanations are as in Figure 1.

only or in the reaction mixture containing glycine and phenylalanine. The yield of oxazoles in the reaction mixture of glycine and aspartic acid was the largest. Asparagine had the highest contribution in the generation of oxazoles. Although oxazoles are formed only from heat treatment (Flament, 1991), the exact mechanism of oxazole formation is not quite known. 4,5-Dimethyloxazole was the most abundant oxazole identified in this study. There are two possible pathways for the formation of 4,5-dimethyloxazole as shown in Scheme 1. The first is the reaction of glycine directly with diacetyl which originates from glucose to form an unstable Schiff base followed by decaboxylation, ring closure, and aromatization to produce 4,5-dimethyloxazole. In this case, the source of nitrogen atoms would

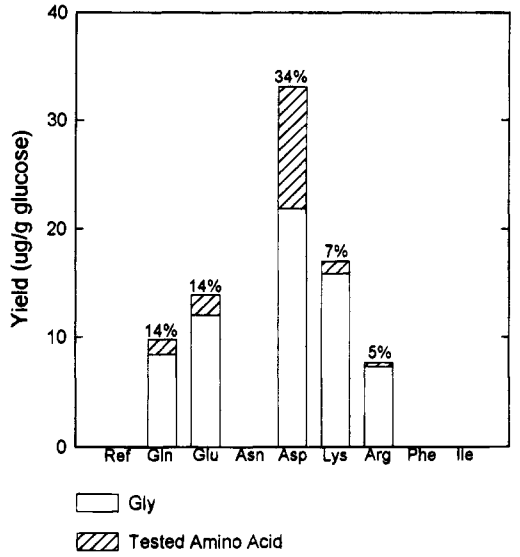


Figure 3. Total yields and relative contributions of oxazoles generated from reaction systems containing tested amino acids and glycine. Abbreviations and explanations are as in Figure 1.

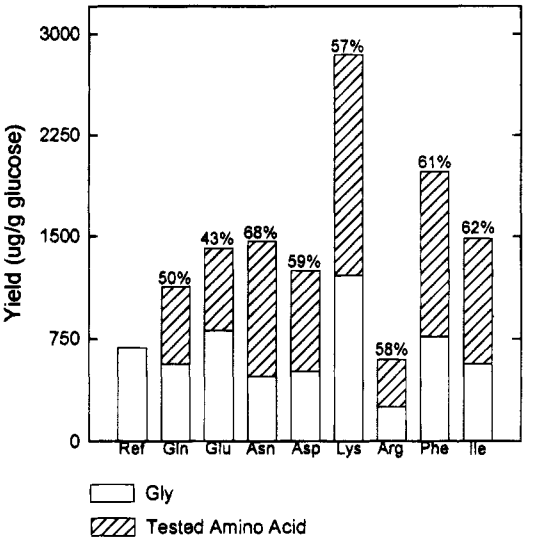
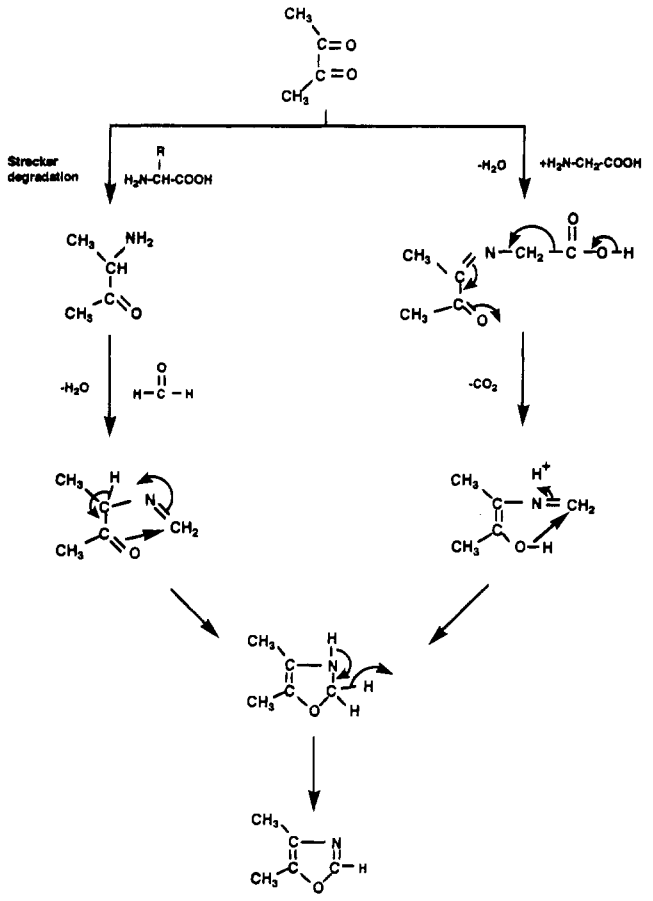


Figure 4. Total yields and relative contributions of all nitrogen-containing compounds generated from reaction systems containing tested amino acids and glycine. Abbreviations and explanations are as in Figure 1.

Scheme 1. Proposed Pathways for the Formation of 4,5-Dimethyloxazole



be solely from glycine. The other pathway is through Strecker degradation. Strecker degradation of amino acids and diacetyl yields 2-amino-3-butanone. 4,5-Dimethyloxazole is then produced by the condensation of 2-amino-3-butanone with formaldehyde. In this case, the source of nitrogen atoms would be either glycine or the other tested amino acids. In our study, it seemed that the former pathway was more favorable because more than 80% of the nitrogen atoms in the 4,5-dimethyloxazole ring come from glycine. 4,5-Dimethyloxazole and trimethyloxazole observed in the present study have been identified in various processed foods such as coffee, cocoa, roasted green tea, meat, and baked potato (Coleman et al., 1981; Flament, 1991; Maga, 1981b).

Besides those nitrogen-containing heterocyclics, we found three amines from the isoleucine mixture and one benzonitrile which were specific products of the phenylalanine mixture (Table 1). Since these amines were only identified from the reaction mixture containing isoleucine, they might be generated from the interaction of 2-methylbutanal with the amino group of isoleucine or glycine. About 96% of the nitrogen atoms in benzonitrile were contributed from phenylalanine. This implies that benzonitrile is mainly the direct degradation product of phenylalanine.

The yields and relative contributions of the tested amino acids to the formation of all nitrogen-containing compounds, including pyrazines, pyridines, pyrroles, oxazoles, amines, and benzonitrile, are summarized in Figure 4. Glutamic acid was the lowest contributor, while asparagine was the highest contributor, to flavor formation among the tested amino acids in the presence of labeled glycine. Figure 4 also shows that the yield of all nitrogen-containing flavors from labeled glycine in the lysine reaction mixture is the highest and more than that in the glycine reaction mixture alone. The yields of all nitrogen-containing flavors from labeled glycine in the arginine reaction mixture were the lowest and even less than that in the glycine reaction mixture alone. This suggests that the lysine acts as a synergist to increase the reactivity of other amino acids (glycine in this case); however, the arginine could depress specifically pyrroles, oxazoles, and pyridines at the expense of other products.

Another interesting phenomenon was that the yield of nitrogen-containing compounds in the asparagine reaction mixture was not the highest one even though asparagine had the highest contribution. Theoretically, those amino acids consisting of side-chain nitrogen could result in a higher quantity of nitrogen-containing flavors due to two nitrogen sources. The participation of side-chain nitrogen of glutamine and lysine in pyrazine formation has been proved by Hwang et al. (1993, 1994). Therefore, this result seems to reveal that amino acids

possessing side-chain nitrogen except lysine are not only involved in flavor generation but also reduce the reactivity of glycine. Unlike the amide side chains of asparagine and glutamine as well as the δ-guanidino group of arginine, the ε-amino group of lysine can participate in the Maillard reaction and catalyze the sugar fragmentation (Hwang et al., 1994). This unique property of lysine may be the reason that lysine is recognized as the most reactive amino acid in the Maillard reaction and why it produced the largest quantities of volatile compounds in the present study.

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