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Mechanisms of volatile production from non-sulfur amino acids by irradiation

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HIGHLIGHTS

- Irradiation increased the amounts of volatiles and produced new volatiles from amino acid monomers.
- Radiolysis of side chain was mainly involved in the production of volatiles from amino acids.
- The odor characteristics of the irradiated non-sulfur amino acids were different from irradiated meat.
- The contribution of volatiles from non-sulfur amino acids can be minor.

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ABSTRACT

Non-sulfur amino acid monomers were used to study the mechanisms of volatile production in meat by irradiation. Irradiation not only produced many volatiles but also increased the amounts of volatiles from non-sulfur amino acid monomers. The major reaction mechanisms involved in volatile production from each group of the amino acids by irradiation differ significantly. However, we speculate that the radiolysis of amino acid side chains were the major mechanism. In addition, Strecker degradation, especially the production of aldehydes from aliphatic group amino acids, and deamination, isomerization, decarboxylation, cyclic reaction and dehydrogenation of the initial radiolytic products were also contributed to the production of volatile compounds. Each amino acid monomers produced different odor characteristics, but the intensities of odor from all non-sulfur amino acid groups were very weak. This indicated that the contribution of volatiles produced from non-sulfur amino acids was minor. If the volatile compounds from non-sulfur amino acids, especially aldehydes, interact with other volatiles compounds such as sulfur compounds, however, they can contribute to the off-odor of irradiated meat significantly.

1. Introduction

Irradiation is known as the most effective technology for inactivating foodborne pathogens and improving the safety of meats. However, the use of irradiation in meat is limited because of its effects on meat quality and the health concerns of some compounds produced by irradiation. Irradiation produces various volatile compounds that can contribute to the characteristic irradiation aroma, and changes color that significantly affect the consumer acceptance of meat (Lee and Ahn, 2003; Ahn et al., 2012).

Irradiation of meats not only produced many volatile compounds, but also increased the amounts of volatiles already present in non-irradiated meat (Ahn et al., 1998; Fan et al., 2002). Several sensory works characterized the odor of irradiated meat as a “hot fat”, “burned oil”, “burned feathers”, or “bloody and sweet”. However, irradiation odor disappeared in chicken breast while remained in thigh meat after cooking (Heath and Pharm, 1978; Hashim et al., 1995; Ahn et al., 2000). Patterson and Stevenson (1995) reported dimethyl trisulfide, cis-3- and trans-6-nonenals, oct-1-en-3-one and bis(methylthio-)methane as the main off-odor compound in irradiated chicken meat.

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Zhu et al. (2004) reported that irradiation produced a metallic-like flavor in ready-to-eat turkey hams due to increased production of acetaldehyde. Aldehydes were commonly used as indicators for lipid oxidation (Ahn et al., 2012), but irradiation had little effects on the production of aldehydes in an oil emulsion system and lipids were responsible for only a small part of the off-odor produced (Ahn et al., 1998; Lee and Ahn, 2002). These studies also indicated that the mechanisms and the volatiles involved in irradiation odor were different from the warmed-over flavor in oxidized meat (Jo and Ahn, 2000; Lee and Ahn, 2002; Zhu et al., 2004). So, we hypothesize that proteins and amino acids are the major meat components responsible for the off-odor production in irradiated meat. However, little is known about the production mechanisms of volatiles from proteins. This is a part of the follow up studies of our previous works that determined volatiles production mechanisms of meat components by irradiation (Jo and Ahn, 1999; Lee and Ahn, 2002; Ahn and Lee, 2002). Although a few studies on the radiolysis of single or few specific amino acids or peptides have been published (Tajima et al., 1969; Neta et al., 1970; Akira, 1966; Ahn, 2002), little work has been done to elucidate the basic mechanisms involved in the generation of volatile from all amino acids. Because the production mechanisms of off-odor volatiles from sulfur amino acids are reported elsewhere, only non-sulfur amino acids will be discussed here. The objectives of this study were to (1) determine the volatile compounds produced from aqueous solution of non-sulfur amino acids by irradiation, (2) elucidate the production mechanisms of volatiles from non-sulfur amino acids by irradiation, and (3) characterize the odor and evaluate the contribution of volatiles from non-sulfur amino acids to the odor of irradiated meat systems.

2. Materials and methods

2.1. Sample preparation

Eighteen amino acid monomers which include alanine, proline, arginine, glutamic acid, tyrosine, leucine, serine, lysine, isoleucine, threonine, aspartic acid, phenylalanine, glutamine, glycine, valine, histidine, asparagine and tryptophan (Sigma, St. Louis, MO, USA) were used to make the model system of aqueous amino acid solutions. Each amino acid monomer (50 mg/10 mL) was dissolved in a citrate–phosphate buffer (100 mM, pH 6.0) and irradiated at 0 or 5.0 kGy absorbed dose using an Electron Beam irradiator (Circe IIIR Thomson CSF Linac, St. Aubin, France). Some of the amino acid monomers (aliphatic and hydrophobic) were not soluble but used as was. Four replications were prepared for each amino acid. Immediately after irradiation, 2-mL portions of the amino acid solution (4 portions) were transferred to sample vials, flushed with helium gas (99.999% purity) for 5 s at 40 psi, and then capped. One of them was used to analyze volatile profiles, and the other three were used to determine odor characteristics. Volatile profiles and odor characteristics of irradiated and non-irradiated amino acid monomers were compared. A purge-and-trap dynamic headspace/GC–MS was used to quantify and identify volatile components, and trained sensory panel evaluated the overall odor characteristics of the samples.

2.2. Volatile compounds analysis

A purge-and-trap apparatus (Precept II and Purge & Trap Concentrator 3100, Tekmar–Dohrmann, Cincinnati, OH, USA) connected to a gas chromatography/mass spectrometry (GC/MS, Hewlett-Packard Co., Wilmington, DE, USA) was used to analyze volatiles produced (Jo and Ahn, 1999). Sample solution (2 mL) was placed in a 40-mL sample vial, and the vials were flushed with helium gas (40 psi) for 5 s. The maximum waiting time of a sample in a refrigerated (4 °C) holding tray was less than 2 h to minimize oxidative changes before analysis. The sample was purged with helium gas (40 mL/min) for 12 min at 40 °C. Volatiles were trapped using a Tenax column (Tekmar–Dohrmann) and desorbed for 2 min at 225 °C, focused in a cryofocusing module (–90 °C), and then thermally desorbed into a column for 30 s at 225 °C.

An HP-624 column (7.5 m × 0.25 mm i.d., 1.4 mm nominal), an HP-1 column (52.5 m × 0.25 mm i.d., 0.25 mm nominal; Hewlett-Packard Co.), and an HP-Wax column (7.5 m × 0.25 mm i.d., 0.25 mm nominal) were connected using zero dead-volume column connectors (J &W Scientific, Folsom, CA). Ramped oven temperature was used to improve volatile separation. The initial oven temperature of 0 °C was held for 2.5 min. After that, the oven temperature was increased to 15 °C at 2.5 °C/min, increased to 45 °C at 5 °C/min, increased to 110 °C at 20 °C/min, increased to 210 °C at 10 °C/min, and then was held for 2.5 min at the temperature. Constant column pressure at 20.5 psi was maintained. The ionization potential of the mass selective detector (Model 5973; Hewlett-Packard Co.) was 70 eV, and the scan range was 18.1–250 m/z. Identification of volatiles was achieved by comparing mass spectral data of samples with those of the Wiley library (Hewlett-Packard Co.). The area of each peak was integrated using the ChemStation (Hewlett-Packard Co.), and the total peak area ($pA^*s \times 10^4$) was reported as an indicator of volatiles generated from the sample.

2.3. Odor characteristics

Ten trained sensory panelists characterized the odor of samples. Panelists were selected based on interest, availability, and performance in screening tests conducted with samples similar to those to be tested. During training, a lexicon of aroma terms to be used on the ballot was developed, and references that can be used to anchor the rating scale were identified. Samples were placed in glass vials, and the sample temperature was brought to 25 °C before samples are tested. All the treatments were presented to each panelist, and the order of presentation was randomized. Panelists characterized overall odor characteristics.

2.4. Statistical analysis

Data were analyzed using the generalized linear model procedure of SAS software (version 9.1, NC, USA); the Student's *t*-test was used to compare differences between irradiated and non-irradiated means. Mean values and standard error of the means (SEM) were reported. Significance was defined at $p < 0.05$.

3. Results and discussion

3.1. Acidic group amino acid monomers

From the acidic amino acid group (aspartic and glutamic acids), three different aldehydes (acetaldehyde, propanal, and butanal), 2-propanone and methyl cyclopentane were produced by irradiation (Table 1). However, the production of acetaldehyde (CH_3CHO) and 2-propanone from the aspartic acid was the most prominent.

It is well documented that irradiation (IR) of water at 25 °C produces many reactive species as shown below (Garrison, 1987): Among the irradiation products of water, aqueous electron (e_{aq}^-), hydroxyl radical (.OH), and hydrogen atom (H^+) are the most actively involved in various reactions with meat components such as amino acids, proteins, lipids, vitamins, and carbohydrates (Simic, 1983).

Table 1
Production of volatile compounds from acidic and amide group amino acid monomers solution by irradiation.

Amino acid	Volatiles	0 kGy	5 kGy	SEM
		Total ion counts × 10^4		
Acidic group amino acids				
Aspartic acid	Acetaldehyde	0[b]	10,229[a]	146
	Propanal	0[b]	191[a]	4
	2-propanone	0[b]	7230[a]	363
	Hexane	1817[a]	1026[b]	78
	Methyl cyclopentane	627[a]	232[b]	53
Glutamic acid	Acetaldehyde	0[b]	498[a]	91
	Butanal	0[b]	229[a]	50
	Hexane	215[b]	1790[a]	361
	Methyl cyclopentane	0[b]	267[a]	51
Amide group amino acids				
Asparagine	Acetaldehyde	0[b]	586[a]	81
	2-propanone	460	666	137
	Hexane	501	500	20
	Methyl cyclopentane	246[a]	77[b]	20
Glutamine	Pentane	69[a]	0[b]	8
	1,3-pentadiene	1967[a]	0[b]	117
	Hexane	1278[b]	3633[a]	368

[a] Means within a row with no common superscript differ significantly ($P<0.05$), $n=4$.
[b] Means within a row with no common superscript differ significantly ($P<0.05$), $n=4$.

H_2O (IR) → e_{aq}^- (2.8) + H_3O^+ (2.8) + .OH (2.8) + H^+ (0.5) + H_2 (0.4) + H_2O_2 (0.8) (Reaction 1)

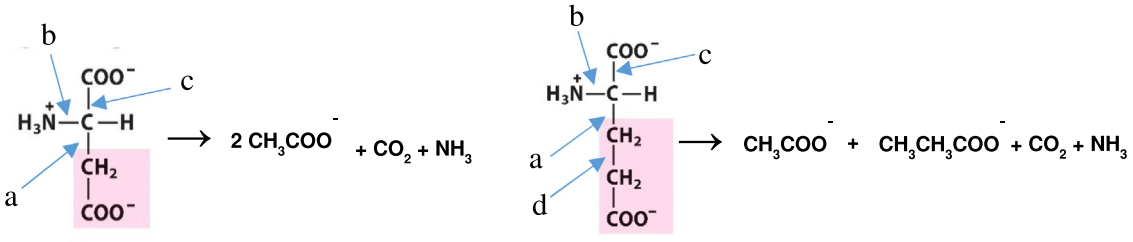
(The numbers in parenthesis are the relative amounts of the species, G-value, produced per 100 eV absorbed).

It is assumed that acetaldehyde (CH_3CHO) was formed from aspartic acid and glutamic acid by irradiation through the following reactions: (1) the side chain (arrow 'a' in Reaction 2) and amino group ($-NH_2^-$, arrow 'b' in Reaction 2) were cleaved from the α-carbon, which generates two acetic acids (CH_3COOH) from one aspartic acid, and one acetic acid and one propionic acid (CH_3CH_2COOH) from glutamic acid (Reaction 2); (2) Acetic acid can also be formed when the bond between $-CH_2-CH_2-$ of glutamic acid side chain (arrow 'd' in Reaction 2) is cleaved. The acetic acids formed can be converted to acetaldehyde through the oxidation–reduction reactions (Fujisawa et al., 1983). Considering the amount of acetaldehyde (CH_3CHO) in irradiated aspartic acid was much greater (20 ×) than that in glutamic acid, cleavage between α-carbon and side chain was much easier than that at $-CH_2-CH_2-$ of glutamic acid (Table 1). We speculate that the production of acetic acid from the α-carbon moiety of aspartic acid and glutamic acid is not the main pathway in producing acetaldehyde.

ozone produced from oxygen by irradiation, forms propionic acid from aspartic acid and butanoic acid (CH_3CH_2 CH_2COOH) from glutamic acid (Reaction 3) (Cederstav and Novak'vt, 1994). However, the amounts of propanal and butanal formed were small, indicating that this is not a major reaction pathway.

$RCH(NH_2)COOH + O_3 + O_2 + H_2O \rightarrow$
$RCHO + CO_2 + NH_3 + H_2O_2 + O_2$ (Reaction 3)

Theoretically, acetaldehyde can also be formed from the α-carbon moiety of aspartic acid and glutamic acid (Reaction 2) via a different pathway: the acetic acid formed can react with hydroxyl radical (.OH), a main product of irradiation (Reaction 1), and generate an ethen-1-ol (CH_2CHOH). However, the majority of the end product is acetaldehyde instead of ethen-1-ol because the equilibrium constant between acetaldehyde and ethen-1-ol is in favor of acetaldehyde ($K=3\times10^{-7}$ at 25 °C, Reaction 4) (Schonberg and Moubacher, 1952). However, this pathway may not be involved in the production aldehydes from aspartic acid and glutamic acid (also from other amino acids) considering no propanal is produced from glutamic acid (Table 1).



Aspartic acid Glutamic acid (Reaction 2)

It is assumed that the Strecker degradation was involved in the production of propanal from aspartic acid and butanal from glutamic acid (through the bond breakage at arrows 'a', 'b', and 'c' in Reaction 2). The Strecker degradation, through the actions of

2-Propanone [$(CH_3)_2CO$], a major volatile formed from aspartic acid by irradiation, should have been formed from acetic acid through the ketonic decarboxylation of two acetic acids (Reaction 5) (Swendseid et al., 1942). However, most of the acetic acid may

$CH_2{=}CHOH \rightleftharpoons CH_3CHO$ (Reaction 4)

be from the side chain group because the production of acetic acid from α-carbon moiety is not the main reaction pathway as discussed above (Reaction 2).

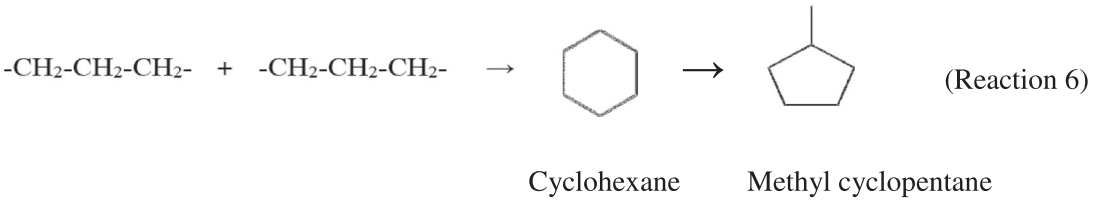
$CH_3COO \rightarrow CO_2 + (CH_3)_2CO$ (Reaction 5)

Very high levels of acetaldehyde and 2-propanone formed from aspartic acid by irradiation indicate that the production of acetic acid is via the radiolytic degradation of the side chain is the major pathways involved. However, irradiation of glutamic acid did not produce 2-pentanone. One of the main reasons for that could be high boiling point of 2-pentanone (101 °C) compared with 2-propanone (56 °C), even if it is formed through the ketonic decarboxylation of propionic acid, which made it difficult to volatilize and to be detected. Another possibility is that it took a two-step pathway to form a cyclohexane: (1) butanoic acid was formed by decarboxylation and deamination of α-carbon moiety (Reaction 4), and (2) then the decarboxylation of the side chain and cyclic reaction. The cyclohexane can be easily converted to methyl cyclopentane as shown in Reaction 6 (Itoh et al., 2000). The amount of hexane (C_6H_{14}) also increased significantly.

irradiation products (e_{aq}^-, .OH, and H^+) as well as oxygen in the solution. The aldehydes such as propanal and butanal are intermediates between the alcohols and acids, and are more reactive than the alcohols because of their double-bond linkage with oxygen. However, it seems that decarboxylation at α-carbon was not a highly favorable reaction, considering only small amounts of propanal, butanal, and methyl cyclopentane were formed from the acidic amino acid monomers (Table 1).

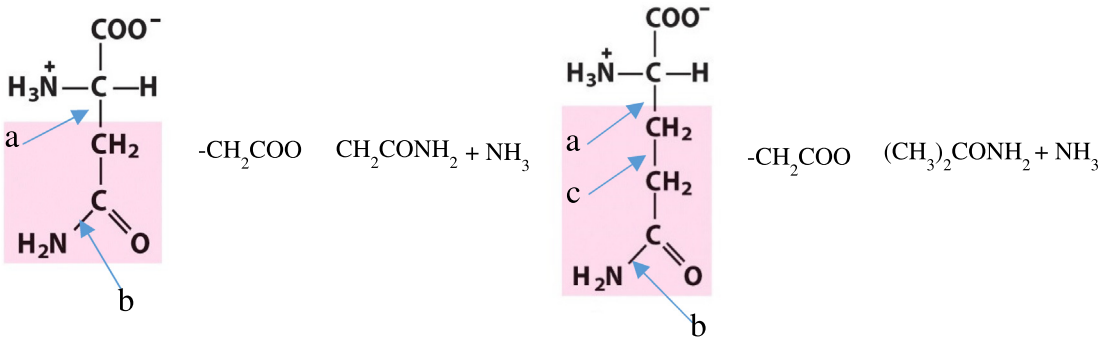
3.2. Amide group amino acid monomers

The changes of volatile compounds in amide group amino acids by irradiation were small compared with those in aspartic acid although acetaldehyde was produced from asparagine (Table 1). The acetaldehyde formed from asparagine by irradiation could be through the oxidation–reduction reaction of the acetic acid formed through the following pathway: cleavage of side chain and then the removal of $-NH_2$ group from the side chain (arrows 'a' and 'b' in Reaction 7).



(Reaction 6)

Cyclohexane Methyl cyclopentane



Asparagine Glutamine (Reaction 7)

Dogbevi et al. (1999) reported that deamination during irradiation was one of the main steps involved in the mechanisms of radiolytic degradation of amino acids. The formation of propionic acid from aspartic acid and butanoic acid from glutamic acid indicated that the decarboxylation is from the α-carbon site, and the oxidation–reduction reactions of acids and aldehydes require

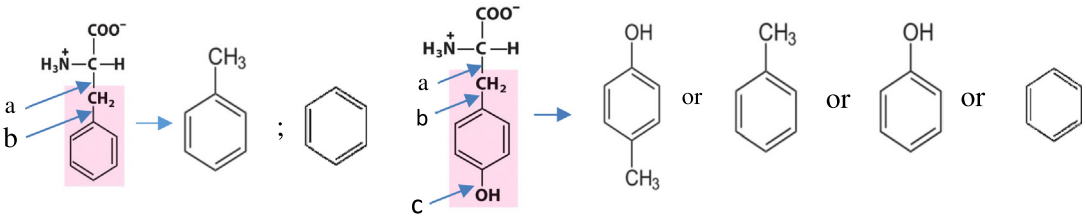
From the side chain of glutamine, propanal (CH_3CH_2CHO) should be formed (arrows 'a' and 'b' in Reaction 7). However, propanal was not detected in irradiated glutamine. Also, acetaldehyde was not formed from glutamine, indicating that a cleavage at $-CH_2-CH-$ of the side chain (arrows 'c' in Reaction 7) did not take place. Instead, the amount of hexane increased

significantly from glutamine after irradiation. This indicated that cyclic reaction could be involved (Reaction 6). However, it is assumed that the Strecker degradation was not involved in the production of aldehydes or ketones from amide group amino acids. Other major changes of volatiles in glutamine were the disappearance of pentane and 1,3-pentadiene, suggesting that various other chemical reactions are also taking place during and after irradiation.

3.3. Aromatic group amino acid monomers

As in amide group amino acids, irradiation did not increase the amounts of total volatile much from the aromatic and basic group amino acids although a few volatile compounds were produced or disappeared after irradiation (Table 2). Phenylalanine showed greater changes in volatile composition than tryptophan or tyrosine, but the amounts of volatiles in those amino acids after irradiation were relatively small. Irradiation of phenylalanine produced two volatile compounds (benzene and toluene) and significantly increased the amounts of methyl cyclopentane. Benzene and toluene are the products of direct cleavage of the side chain between $-CH_2$ and benzene ring (arrow 'b' in Reaction 8) and between the α-carbon and $-CH_2$ of phenylalanine (arrow 'a' in Reaction 8).

Tyrosine can produce methyl phenol, methyl benzene, phenol, or benzene depending upon the sites of cleavages (arrows 'a, b, or c' in Reaction 8). However, none of these four compounds were detected from tyrosine. Instead, a generation of acetaldehyde was observed (Table 2).



Phenylalanine Tyrosine (Reaction 8)

The formation of methyl cyclopentane could be through the production of benzene and the rearrangement of benzene. Benzene is known to go through rearrangement at high temperature to produce methyl cyclopentane. Hydrogenation reaction of benzene in the presence of metal catalysts is also well known and can

Table 2
Production of volatile compounds from aromatic and basic group amino acid monomers solution by irradiation.

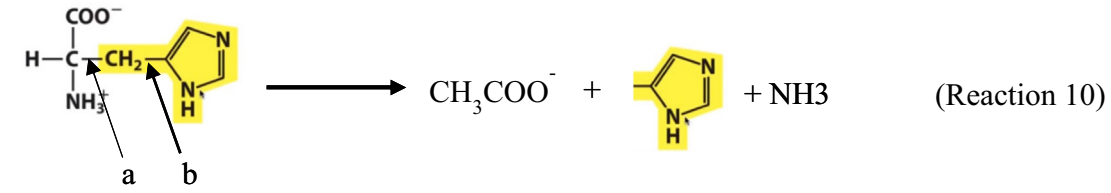
Amino acid	Volatiles	0 kGy	5 kGy	SEM
		Total ion counts × 10^4		
Aromatic group amino acid				
Phenylalanine	1,3-pentadiene	1057[a]	0[b]	35
	2-propanone	1212[a]	0[b]	281
	Hexane	5978	4887	998
	Methyl cyclopentane	1589[b]	2564[a]	244
	Benzene	0[b]	318[a]	6
	Toluene	0[b]	788[a]	42
Tryptophan	Hexane	95[b]	591[a]	47
	Methyl cyclopentane	0[b]	134[a]	16
Tyrosine	Acetaldehyde	0[b]	1092[a]	96
	Hexane	85[b]	434[a]	43
	Methyl cyclopentane	0[b]	89[a]	11
	Cyclohexane	85[a]	0[b]	2
Basic group amino acid				
Arginine	Hexane	310[b]	1386[a]	136
	Methyl cyclopentane	0[b]	156[a]	13
	Cyclohexane	207[a]	0[b]	15
Histidine	1,3-pentadiene	2349[a]	0[b]	95
	2-propanone	0[b]	8175[a]	1576
	3-methyle pentane	267[a]	0[b]	15
	Hexane	14,199[a]	4457[b]	635
	Methyl cyclopentane	3142[a]	2636[b]	154
Lysine	3-methyl pentane	0[b]	103[a]	2
	Hexane	887[b]	5087[a]	161
	Methyl cyclopentane	160[b]	3004[a]	78

[a] Means with no common superscript differ significantly ($P<0.05$), $n=4$.
[b] Means with no common superscript differ significantly ($P<0.05$), $n=4$.

produce cyclohexane, which can be converted to methyl cyclopentane (Reaction 6). However, the production of acetaldehyde from tyrosine cannot be explained at this point, even though the Strecker degradation of tyrosine or the ozonolysis of benzene was reported to produce glyoxal (William et al., 1969; Hazen et al., 1996; Adameic et al., 2001).

3.4. BASIC group amino acid monomers

The changes of volatile compounds in basic group amino acids by irradiation were also small although irradiation significantly increased the production of hexane and produced methyl cyclopentane from arginine (Table 2). The production of methyl cyclopentane from arginine should be through the breakage of the side chain at arrow 'a' and 'b' positions of the side chain, which generate $(-CH_2)_3$ (Reaction 9), and then going through the cyclic reaction to form methyl cyclopentane as shown in Reaction 6.



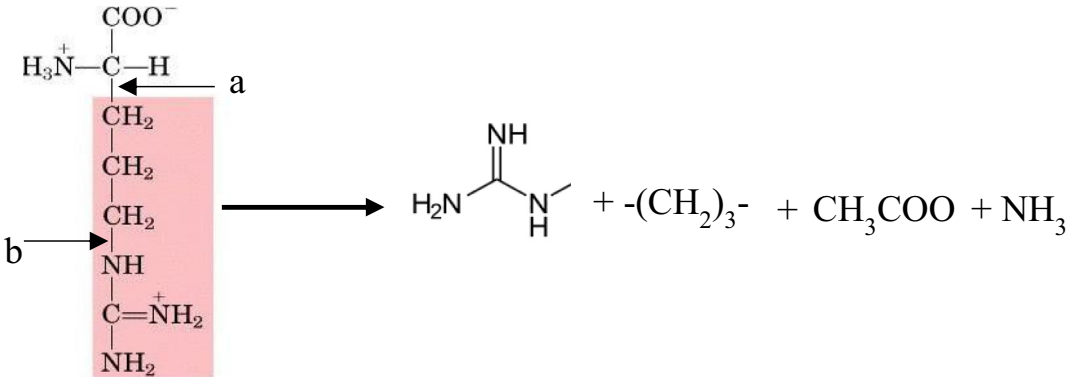
Histidine

(Reaction 10)

Irradiation of lysine produced a volatile compound, 3-methyl pentane and significantly increased hexane and methyl cyclopentane through the similar mechanisms shown in Arginine. As in other amino acids containing nitrogen atom in their side chains (asparagine, glutamine, and tryptophan), the amounts of volatiles produced from the basic group amino acids were small because of the low volatilities of N-containing compounds (Table 2).

3.5. Aliphatic group amino acid monomers

Among the aliphatic group amino acids, isoleucine, leucine, and valine were influenced the most by irradiation. However, the side chains of aliphatic group amino acids are very stable to radiolytic degradation due to their structural (non-polar) characteristics.

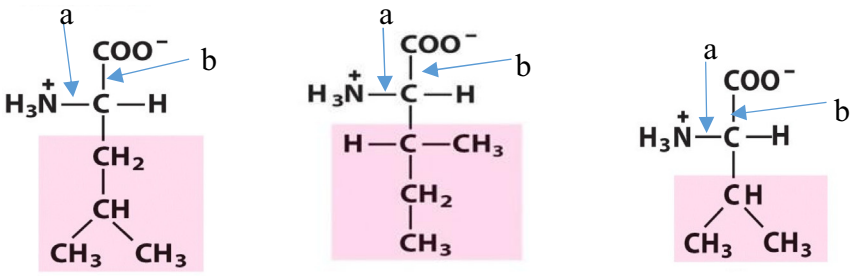


Arginine

(Reaction 9)

A large amount of 2-propanone was produced, but 1,3-pentadiene and 3-methyle pentane disappeared in histidine after irradiation. The production of 2-propanone from histidine is through the ketonic decarboxylation of two acetate ions (CH_3COO^-) formed from the side chain cleavage between the imidazole ring and the $-CH_2$ (arrow 'b' in Reaction 10) and deamination from the α-carbon site. However, cleavage of the side chain at arrow 'a' (Reaction 10) does not generate volatile compounds due to low volatilities of N-containing compounds.

Among the volatile compounds, the production of 2-methyl butanal from isoleucine, 3-methyl butanal from leucine, and 2-methyl propanal from valine by irradiation were the most prominent (Table 3). The formation of 2-methyl butanal from isoleucine, 3-methyl butanal from leucine, and 2-methyl propanal from valine by irradiation was through the Strecker degradation as explained previously in the propanal and butanal production from aspartic acid and glutamic acid, respectively (Reaction 4). From the aliphatic group amino acids, the bonds between H_3N and α-carbon



(Reaction 11)

(arrows 'a' in Reaction 11) and –COO and α-carbon (arrows 'b' in Reaction 11) are the primary point for the radiolytic degradation (deamination and decarboxylation) because those are the weakest points. However, the production of the three major aldehydes (2-methyl butanal, 3-methyl butanal, and 2-methyl propanal) from isoleucine, leucine and valine in protein or peptides through the Strecker degradation is less likely because the production of those aldehydes involves the breakage of two peptide bonds.

Mottram et al. (2002) reported that the branched chain of aldehydes was produced by the degradation of amino acids via the Strecker degradation during irradiation. This indicated that Strecker degradation could be the main pathway for producing volatile compounds from aliphatic group amino acids by irradiation. Jo and Ahn (2000) also recognized 2-methyl butanal and 3-methyl butanal as the marker volatile of isoleucine and leucine, respectively, by irradiation. Other important volatile compounds produced by irradiation include 2-methyl propanopropanal in leucine, and 2-methylprop-2-enal and 2-propanone in valine, but their amounts were less than 1/10 of the key volatile compound from the three amino acids (2-methyl butanal, 3-methyl butanal, and 2-methyl propanal).

Irradiation of glycine, alanine, and proline, however, did not produce any aldehydes. Instead, 3-methyl pentane and methyl cyclopentane were produced from alanine, and methyl cyclopentane was produced from glycine. Also, the amount of hexane significantly increased from the three amino acids. The production of alkane and branched alkane from glycine, alanine, and proline indicated that these three amino acids did not go through the Strecker degradation. Instead, they went through the deamination process by hydroxyl radical (.OH) and aqueous electron (e_{aq}^-) to produce carboxylic acids (Neta et al., 1970; Garrison, 1987). Garrison (1987) explained that the attack of .OH radical in alanine and glycine occurs almost exclusively at the α-carbon position. The decarboxylation process of carboxylic acid produces alkanes with one less carbon (Reactions 12 and 13) (Kraeutler and Bard, 1978). The cyclic reaction of alkanes produces cyclohexane and methyl cyclopentane as shown in Reaction 6. The changes in volatile compounds in the rest of the aliphatic amino acids (alanine, glycine, and proline), however, were much smaller than those of the isoleucine, leucine and valine (Table 3).

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad \text{(Reaction 12)}$$

$$CH_3COOH \rightarrow CH_3CH_3 + 2\ CO_2 + H_2 \quad \text{(Reaction 13)}$$

3.6. Aliphatic hydroxyl group amino acid monomers

A very large amount of acetaldehyde as well as several other aldehydes including 2-propenal, propanal, butanal, and 2-butenal were produced from serine while acetaldehyde and propanal were produced from threonine by irradiation (Table 3). Also, the results indicated that aliphatic and aliphatic hydroxyl group amino acids were highly susceptible to irradiation (Table 3). The formation of acetaldehyde from serine by irradiation follows a two-step reaction: first, amino and carboxyl residues are cleaved from the α-carbon to generate ethen-1-ol, and then forms acetaldehyde (Reaction 3).

A vast increase of 2-propanone was also observed in threonine after irradiation. Some acetaldehydes were also formed from threonine. However, it is not formed through the same reaction mechanisms as in serine but through the production of (CH_3CHOH^-) from the side chain. 2-Propanone should also have been produced from threonine by the ketonic decarboxylation of the side chain moiety (2 CH_3COO^-) (Reaction 5). Yaylayan and Wnorowski (2001) reported that pyrolysis of serine and threonine produced around 70 different products: the retro-aldol cleavage produces formaldehyde and glycine from serine, and acetaldehyde and glycine from threonine. A decarboxylation produces 1-amino ethanol from serine and 1-amino-2-propanol from threonine. Subsequent deamination produces acetaldehyde or 2-propanone. Deamination and isomerisation can lead to the formation of pyruvic acid from serine and 2-ketobutanoic acid from threonine (Metzler and Snell, 1952). These two acids can decarboxylate and form acetaldehyde and propanal, respectively. As indicated, the initial degradation reactions of serine and threonine produce aldehydes and ketones. In this experiment, irradiation of serine and threonine produced acetaldehyde, 2-propanal, and 2-propanone (Table 3).

Some of the volatile compounds are common to most of the non-sulfur amino acids: hexane was found in all amino acids and methyl cyclopentane was found in all amino acids but glutamine and isoleucine. Cyclohexane was detected only in non-irradiated aliphatic group amino acids (alanine, glycine, isoleucine, leucine and proline) and arginine but disappeared after irradiation (Tables 1–3), indicating that this compound is highly susceptible to radiolytic degradation.

Each amino acid can produce unique volatile compounds because the side chain of each amino acid is different. These results indicated that the side chains of most of the amino acids are highly susceptible to radiolytic degradation, and some side chain groups are more susceptible than others. In general, larger side chains are more susceptible to radiolytic attack and produce more volatile compounds than smaller ones. The Strecker degradation also played an important role in producing aldehydes by irradiation, especially from aliphatic amino acids. Maillard reaction and Strecker degradation are two important reactions that provide attractive flavor and color in foods (Jing and Kitts, 2002). The Strecker degradation is considered as a "sub-reaction" category of the Maillard reaction scheme, and the importance of the Strecker degradation of amino acids in the development of flavor in food has been discussed since 1950s (Shankaranarayana et al., 1974;

Table 3
Production of volatile compounds from aliphatic and aliphatic hydroxyl group amino acid monomers solution by irradiation.

Amino acids	Volatiles	0 kGy	5 kGy	SEM
		Total ion counts × 10^4		
Aliphatic group amino acids				
Alanine	3-methyl pentane	0[b]	121[a]	9
	Hexane	224[b]	2049[a]	631
	Methyl cyclopentane	0[b]	803[a]	155
	Cyclohexane	90[a]	0[b]	2
Glycine	Hexane	130[b]	3824[a]	289
	Methyl cyclopentane	0[b]	2055[a]	168
	Cyclohexane	72[a]	0[b]	1
Isoleucine	2-butene	0[b]	57[a]	3
	Butane	0[b]	445[a]	21
	Acetaldehyde	0[b]	359[a]	12
	1-butene	0[b]	422[a]	21
	2-methyl butane	0[b]	260[a]	4
	2-pentene	0[b]	1120[a]	24
	2-methyl-1-butene	0[b]	194[a]	3
	2-methyl-2-butene	0[b]	119[a]	3
	3-methyl pentane	0[b]	140[a]	3
	Hexane	230	829	195
	2-butanone	0[b]	859[a]	66
	Cyclohexane	94[a]	0[b]	2
	2-methyl butanal	0[b]	41,360[a]	661
Leucine	2-methyl-1-propene	0[b]	333[a]	16
	Propane	0[b]	192[a]	19
	2-methyl-2-butene	0[b]	376[a]	4
	2-methyl butane	0[b]	212[a]	2
	2-propanone	0[b]	578[a]	72
	2-methyl propanopropanal	0[b]	4084[a]	121
	Hexane	210[b]	590[a]	74
	Methyl cyclopentane	0[b]	74[a]	9
	Cyclohexane	101[b]	0	4
	3-methyl butanal	0[b]	36101[a]	937
	2-methyl butanal	0[b]	441[a]	15
Proline Valine	Hexane	282[b]	1098[a]	79
	Cyclohexane	203[a]	0[b]	9
	2-propanone	0[b]	5828[a]	882
	2-propanol	0[b]	444[a]	41
	2-methyl propanal	162[b]	57,538[a]	1416
	2-methylprop-2-enal	0[b]	1758[a]	126
	Hexane	1285[a]	625[b]	71
	Butanal	0[b]	94[a]	7
	Methyl cyclopentane	579[b]	116[a]	51
	2-methyl propanenitrile	0[b]	111[a]	10
	3-methyl butanal	0[b]	500[a]	31
Aliphatic hydroxyl group amino acids				
Serine	Acetaldehyde	0[b]	145,373[a]	463
	2-propenal	0[b]	561[a]	50
	Propanal	0[b]	196[a]	3
	2-propanone	0[b]	9861[a]	446
	Guanidine	0[b]	91[a]	8
	Pentanal	78[b]	157[a]	8
	Hexane	2446[a]	1805[b]	184
	Butanal	0[b]	149[a]	16
	Methyl cyclopentane	780	674	70
	Acetic acid ethyl ester	0[b]	563[a]	21
	2-butenal	0[b]	181[a]	13
Threonine	acetaldehyde	0[b]	2660[a]	364
	Propanal	0[b]	2659[a]	215
	2-propanone	0[b]	28,986[a]	10,714
	Hexane	924	1543	460
	Methyl cyclopentane	255	714	215
	2,5-dimethyl furan	0[b]	81[a]	30
	1-(1-propynyl)cyclopropanol	0[b]	1166[a]	62

[a] Means with no common superscript differ significantly ($P < 0.05$), $n = 4$.
[b] Means with no common superscript differ significantly ($P < 0.05$), $n = 4$.

Yaylayan, 2003). However, the involvement of the Strecker degradation in volatile production in proteins, peptides, or foods may not be as extensive as in some amino acid monomers as shown in this study. Except the Strecker degradation discussed here, other Maillard-type reactions were not involved in the volatile production of irradiated amino acids probably because no reducing sugars were included in the model system (Yaylayan, 2003).

Although the amounts of acetaldehyde and propanal are smaller than that of 2-propanone (e.g., threonine), their contribution to irradiation off-odor will be greater because their odor

Table 4
The major volatiles and the odor characteristics of irradiated amino acid monomers.

Amino acid	Major volatiles	Odor characteristics
Acidic group amino acids		
Aspartic acid	Acetaldehyde, 2-propanone	No odor
Glutamic acid	Hexane, acetaldehyde	Honey, sweet
Amide group amino acids		
Asparagine	Acetaldehyde	No odor
Glutamine	Hexane	Hospital odor
Aromatic group amino acids		
Phenylalanine	Benzene, toluene	Solvent odor
Tryptophan	Methyl cyclopentane	Farm odor, fowl odor
Tyrosine	Acetaldehyde, hexane	Alcohol, mild solvent
Basic group amino acids		
Arginine	Hexane	Bean sprouts, sperm, detergent
Histidine	2-Propanone	No odor
Lysine	Hexane, methyl cyclopentane	Sour
Aliphatic group amino acids		
Alanine	Hexane, methyl cyclopentane	Sour, yoghurt, cheesy, aftershave
Glycine	Hexane, methyl cyclopentane	Fresh bread, sweet
Isoleucine	2-Methyl butanal	Licorice, roasted nuts
Leucine	3-Methyl butanal, 2-methyl propanopanal	Roasted nuts, grease, wax, gasoline
Proline	Hexane	Sweet and nutty
Valine	2-Methyl propanal	Roasted nuts
Aliphatic hydroxyl group amino acids		
Serine	Acetaldehyde, 2-propanone	Coleslaw, sweet
Threonine	2-Propanone, acetaldehyde, propanal	Hospital odor

threshold are much lower than that of the 2-propanone (Leonardos et al., 1969; Brewer and Vega, 1995) Aldehydes are intermediates between the alcohols and the acids. Aldehydes of lower molecular weight are characterized by their unpleasant, sharply pungent, and irritating odors. As the molecular weight of aldehydes increases, the odor profile gradually leads a more pleasant sweet character, especially those with C_8 to C_{10} have a very attractive odor (Heath et al., 1990). In this study, aldehydes with lower molecular weight (C_3 to C_5) were mainly detected by irradiation. Therefore, it is assumed that these low-molecular-weight aldehydes may have contributed to the irradiation off-odor.

3.7. Major volatiles and odor characteristics

Table 4 showed the major volatiles from amino acids and their odor characteristics after irradiation. The volatiles (most of them are major) produced from amino acids by irradiation differ significantly depending upon their side chain groups: acetaldehyde from acidic and amide group amino acids; methyl cyclopentane from some aromatic and aliphatic group amino acids; branched aldehydes (e.g., 2-methyl butanal, 3-methyl butanal, 2-mehtyl propanopanal and 2-methyl propanal) from aliphatic group amino acids; acetaldehyde and 2-propanone from aliphatic hydroxyl group amino acids; 2-propanone from histidine, a basic group amino acid (Table 4). The reactions involved in the production of volatile from amino acids by irradiation is summarized in Fig. 1. The odor characteristics of the irradiated amino acids were different, even though the major volatile compounds of some amino acids were the same (Table 4). Glutamic acid, glycine, proline and serine produced sweet notes; glutamine, phenylalanine, tyrosine, and threonine generated solvent or alcohol-like odor; tryptophane produced fowl odor; lysine and alanine produced sour odor; arginine produced beany odor; and isoleucine, leucine, and valine produced nutty odor. Although each of the irradiated non-sulfur amino acid monomers produced characteristic odors, their odor intensities were low.

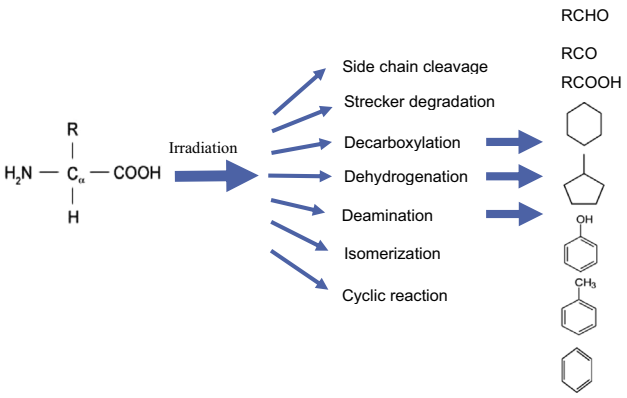


Fig. 1. Reactions involved in the production of volatiles from amino acids by irradiation.

4. Conclusions

Although speculative, we concluded the majority of the volatiles generated from non-sulfur amino acid monomers were from the side chains of amino acids. However, Strecker degradation was the major mechanism involved in the production of aldehydes from aliphatic group amino acids. The volatile compounds produced from non-sulfur amino acids were not only the primary products of radiolytic degradation, but also the products of extensive chemical reactions after they were produced by irradiation. Each amino acid monomers group produced different odor characteristics, but the intensities of odor from all amino acid

groups were weak. The present study was carried out in a given reaction medium using amino acid monomers. Therefore, some of the volatiles and their production mechanisms shown here cannot be directly applied to the peptides and proteins in food products. However, this study can help understanding the mechanisms behind the production of volatiles from foods containing proteins and amino acids by irradiation.

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