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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).