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

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HIGHLIGHTS

- Radiolysis of amino acid side chains were the major cause of volatile production.
- The Strecker degradation were involved in the production from sulfur amino acids.
- Odor of the irradiated sulfur amino acids were similar to that of irradiated meat.
- Methionine was the major amino acid in the production of irradiation off-odor.

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ABSTRACT

Sulfur-containing amino acids were used to study the mechanisms of off-odor production in meat by irradiation. Irradiation not only increased the amounts of volatiles but also produced many new volatiles from sulfur-containing amino acid monomers. We speculate that the majority of the volatiles were the direct radiolytic products of the side chains, but Strecker degradation as well as deamination and decarboxylation of radiolytic products were also involved in the production of volatile compounds from sulfur amino acids. The volatile compounds produced in amino acids were not only the primary products of irradiation, but also the products of secondary chemical reactions after the primary compounds were produced. Cysteine and methionine produced odor characteristics similar to that of the irradiated meat, but the amounts of sulfur volatiles from methionine were far greater than that of cysteine. Although the present study was carried out using an amino acid model system, the information can be applied to the quality indexes of irradiated meats as well as other food products.

1. Introduction

Previous studies indicated that many volatile compounds such as 2-methyl butanal, 3-methyl butanal, 1-hexene, 1-heptene, 1-octene, 1-nonene, hydrogen sulfide, sulfur dioxide, mercaptomethane, dimethyl sulfide, methyl thioacetate, dimethyl disulfide, cis-3- and trans-6-nonenals, oct-1-en-3-one and bis(methylthio-) methane and trimethyl sulfide were greatly increased or newly produced from meat by irradiation (Patterson and Stevenson, 1995; Ahn, 2002; Fan et al., 2002). Among the volatiles, sulfur compounds played the most important roles in irradiation off-odor of meat, and the production of sulfur compounds and the intensity of sulfury odor was irradiation dose-dependent (Ahn et al., 2000; Ahn and Lee, 2002). However, the amounts of aldehydes, the indicators of lipid oxidation, were not influenced by irradiation (Jo and Ahn, 2000), and the volatiles produced from lipids accounted for only a small part of the off-odor in irradiated meat (Ahn et al., 1998, 1999). These studies also indicated that irradiation off-odor was different from warmed-over flavor in oxidized meat, and the mechanisms and the volatiles involved in irradiation odor were different those of oxidation odor (Ahn et al., 2000; Jo and Ahn, 2000).

We hypothesize that sulfur amino acids will be the major components involved in the production of off-odor in irradiated

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meat. This is the second part of the model system study that uses amino acid monomers to determine the mechanisms of volatiles production from irradiated meat. Only the volatile generation mechanisms from sulfur amino acids by irradiation were discussed here. The objectives of this study were to (1) determine the volatile compounds produced from sulfur amino acids by irradiation, (2) elucidate the production mechanisms of volatiles from sulfur amino acids by irradiation, and (3) characterize the odor and evaluate the contribution of volatiles from sulfur amino acids to the overall odor of irradiated meat systems.

2. Materials and methods

2.1. Sample preparation

Three sulfur-containing amino acid monomers that include methionine, cysteine, and cystine (Sigma-Aldrich, St. MO, USA) were tested. 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). 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 nonirradiated 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 (Ahn et al., 2000). 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 four hours 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.

A 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 2.50 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^*sx10^4) 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 were tested. All the treatments were presented to each panelist, and the order of presentation was randomized. Panelists characterized overall odor characteristics.

Table 1
Production of volatile compounds from sulfur-containing amino acid monomers solution by irradiation.

Amino acid	Volatiles	0 kGy	5 kGy	SEM
		——————Total ion counts × 10^4——————		
Cysteine	Mercaptomethane	0[b]	4684[a]	661
	Carbon disulfide	0[b]	17841[a]	1108
	Dimethyl disulfide	0[b]	3555[a]	656
Cystine	Acetaldehyde	0[b]	62647[a]	7742
	2-propanone	0[b]	4723[a]	284
	Carbon disulfide	102[b]	472[a]	43
	3-methyl pentane	796[a]	89[b]	125
	Hexane	35484[a]	4087[b]	4795
	Methyl cyclopentane	6671[a]	2110[b]	879
Methionine	Mercaptomethane	0[b]	5198[a]	1335
	2-Propenal	0[b]	3757[a]	846
	2-Propanone	0[b]	655[a]	38
	Dimethyl sulfide	0[b]	120056[a]	899
	Hexane	222[b]	689[a]	39
	Butanal	0[b]	164[a]	13
	(methylthio)-ethane	0[b]	1510[a]	67
	Thiophene	0[b]	74[a]	3
	3-(methylthio)-1-propene	0[b]	230[a]	8
	Dimethyl disulfide	131[b]	208770[a]	990
	Methyl ethyl disulfide	0[b]	417[a]	22

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