Volatile Production and Lipid Oxidation of Irradiated Cooked Sausage with Different Packaging

D. U. Ahn and D. G. Olson, professors,
C. Jo, graduate research assistant,
S. K. Jin, visiting scientist,
Department of Animal Science,
and J. Love, professor
Department of Food Science and Human Nutrition

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Summary and Implications

Irradiation dose had a significant effect on the production of volatiles in both vacuum- and aerobic-packaged cooked pork sausage, but its effect on the thiobarbituric acid reactive substances (TBARS) values was minor. Storage increased the production of volatiles and changed the composition of volatiles only in aerobic-packaged sausage. Among the volatile components, 1-heptene and 1-nonene were influenced most by irradiation dose, and aldehydes by packaging type. The TBARS values and volatiles of vacuum-packaged irradiated cooked sausage had very low correlation.The TBARS, however, had very high correlation with the amount of aldehydes and total volatiles, and ketones and alcohols with long retention times in aerobic-packaged pork sausage. Heptene and 1-nonene could be used as indicators for irradiation, and propanal, pentanal, and hexanal for the oxygen-dependent changes of cooked meat.

The results indicated that irradiation had some effect on lipid oxidation of cooked pork sausages, especially with aerobic packaging, but oxygen availability (packaging) to meat during storage had much stronger impact. The low correlations of irradiation-dependent volatiles (e.g., 1-heptene and 1-nonene) with TBARS values regardless of packaging and storage conditions indicated that volatile compounds responsible for irradiation odor were different from those of lipid oxidation odor in cooked pork sausages.

Introduction

Irradiation is one the best methods for microorganism control in raw meat and is permitted for use in both poultry and red meat. One of the major concerns in irradiating meat, however, is its effect on meat quality. Irradiation-induced oxidative chemical changes are dose dependent, and the presence of oxygen has a significant effect on the rate of oxidation[6]. Hashim et al.[5] showed that irradiating uncooked chicken breast and thigh produced a characteristic bloody and sweet aroma that remained after the thighs were cooked but was not detectable after the breasts were cooked. Schweigert et al.[13] reported that the precursors of the undesirable odor compounds in irradiated meat were water soluble and contained nitrogen or sulfur and that methyl mercaptan and sulfur dioxide formed from sulfur (S)-containing compounds (e.g., glutathione) contributed to the irradiation odor. Patterson and Stevenson[9] reported that dimethyltrisulfide is the most potent off-odor compound, and dietary tocopherol and ascorbic acid reduced the development of off-odor in irradiated raw chicken meat. Others reported that irradiation had no detrimental effect on the flavor of vacuum-packaged raw and cured meat, and electron beam treatment had little effect on the odor and flavor of reheated meat with sous-vide treatment[16].

Irradiated raw pork meat, regardless of packaging method, produced more volatiles than nonirradiated patties and developed a characteristic aroma shortly after irradiation[2]. Although lipid oxidation still may be responsible for part of the characteristic aroma in irradiated meat, other mechanisms, such as radiolysis of proteins, could play an important role in the production of the characteristic aroma in irradiated meat. The effects of irradiation on lipid oxidation in cooked meat would be different from those in raw meat. Cooked meat is highly susceptible to lipid oxidation because the cooking process denatures antioxidant enzymes, damages cell structure, and exposes membrane lipids to the external environment. Raw meat itself has very strong antioxidant capabilities unless it is heated, denatured, or contains added prooxidants. Cooked meat, however, is highly susceptible to lipid oxidation[1]. Currently, irradiation studies are mainly focused on the antimicrobial and certain quality aspects of raw meat and little information on lipid oxidation of irradiated cooked or further processed meat products is available.

The objective of this research was to determine the effects of irradiation dose on lipid oxidation and volatiles production in cooked sausages with different packaging and storage time.

Materials and Methods

Sample preparation. Lean pork (95%) was purchased from a local meat packing plant and ground twice through a 9-mm plate. Sausage was prepared from lean ground pork, pork backfat (10% of lean meat), salt (2%), ice (7.5%), and 1% soy protein concentrate (90% protein). No spices were added to avoid potential antioxidant effects and complication of volatile profiles. The sausage was cooked in a smokehouse with steam to an internal temperature of 75°C and chilled in ice water. Half of the cooked sausages were vacuum-packaged (-1.0 bar) using a Multi Vac vacuum packager in impermeable nylon/polyethylene bags, and the other half in oxygen-permeable bags. After packaging, they were irradiated using electrons from a Linear Accelerator (Circe

IIIR) to an absorbed dose of 0, 2.5, or 4.5 kGy (dose rate was 107 kGy/min). The temperatures of the sausage were 4°C during irradiation and stored for up to 8 days at 4°C. The degree of lipid oxidation and volatiles in cooked sausages was determined after 0, 4, and 8 days of storage. Lipid oxidation was determined by the thiobarbituric acid reactive substances (TBARS) method described in detail in Ahn et al.[3]. A purge-and-trap apparatus connected to a GC was used to trap and quantify the volatile compounds produced in cooked pork sausage during irradiation and subsequent storage.

Volatiles analysis. Precept II and Purge-and-Trap Concentrator 3000 (Tekmar-Dohrmann) were used to purge and trap the volatiles potentially responsible for off-odor in irradiated cooked pork sausage. A GC (Model 6890, Hewlett Packard Co.) equipped with a flame ionization detector was used to analyze volatiles after thermally desorbing the trapped volatiles. In preparation for volatiles analysis, sausage (2 g) was weighed into a sample vial (40 ml), an oxygen absorber (Ageless type ZPT-50) was added, and the vial was capped tightly with a Teflon-lined open-mouth cap and was placed in a refrigerated (3°C) sample tray. The sample was purged by using an auto sampling unit (Precept II) equipped with a robotic arm. The sample was heated to 32°C and then purged with helium gas (40 ml/min) for 11 min. Volatiles were trapped by using a Tenax/silica gel/charcoal column (Tekmar-Dohrmann) and desorbed for 1 min at 220°C. The temperature of transfer lines connecting Precept II and the Concentrator 3000, and the Concentrator 3000 and the GC inlet, was maintained at 135°C.

A split inlet (split ratio, 49:1) was used to inject volatiles into a DB-Wax capillary GC column (0.25 mm i.d., 60 m, and 0.25-mm film thickness, Hewlett Packard), and ramped oven temperature conditions (32°C for 2 min, increased to 40°C @2°C/min, increased to 50°C @5°C/min, increased to 70°C @10°C/min, increased to 140°C @20°C/min, increased to 200°C @30°C/min, and held for 4.5 min) were used. Inlet temperature was set at 180°C, and the detector temperature was 280°C. Helium was used as a carrier gas, and a constant column flow of 1.2 ml/min was used. Detector air, H_2, and make up gas (He) flow rates were 300 ml/min, 30 ml/min, and 28 ml/min, respectively. Individual peaks were identified by the retention time of volatile standards. The area of each peak was integrated and the total peak area (pA*sec) was reported as an indicator of volatiles generated from the meat samples.

Statistical analysis. The experiment was designed to determine the effect of irradiation dose, packaging, and storage time on the production of volatiles and lipid oxidation in cooked sausages. Analysis of variance was used to determine the effect of irradiation dose and storage time on volatiles and lipid oxidation of irradiated cooked pork sausage with different packaging conditions. The volatiles data of sausage from different packaging types were analyzed independently by SAS software[12]. Correlation coefficients between volatile components and TBARS also were calculated. The Student-Newman-Keuls multiple range test was used to compare differences among mean values. Mean values and standard errors of the mean (SEM) were reported.

Results and Discussion

Volatiles production. In vacuum-packaged cooked sausage, irradiation dose had a significant effect ($P<.05$) on the production of volatiles but the effects of storage time were minor (Table 1). At day 0, the amounts of 1-heptene, 2-propanone, and 1-nonene increased as irradiation dose increased. The production of hexanal, 1-pentanol, and 1-heptanol decreased ($P<.05$) with the increase of irradiation dose. Except for 1-pentene+hexane and nonanal, the amount and profile of volatiles in the sausages changed only slightly during storage. The ups and downs of 1-pentene+hexane and nonanal during storage were not consistent with storage time and could not be explained. The amounts of propanal and pentanal were influenced by irradiation at day 8 but the changes were not consistent with irradiation dose (Table 1). Irradiated sausages (2.5 or 4.5 kGy) produced more total volatiles than nonirradiated except for those irradiated at 4.5 kGy and stored for 8 days. The amounts of total volatiles during storage were mainly influenced by 1-pentene+hexane, 2-methylpentanal, and trimethylhexane whose changes were not consistent with storage time. Ahn et al.[2,4] reported that the amount of total volatiles was not consistently influenced by storage time but was increased ($P<.05$) by irradiation.

In aerobic-packaged irradiated cooked pork sausage, irradiation dose and storage time had significant effects ($P<.05$) on the production and composition of volatiles (Table 2). The amounts of 1-heptene and 1-nonene increased ($P<.05$) as irradiation dose increased as in vacuum-packaged sausages. Cooked pork sausage irradiated at 2.5 kGy produced higher amounts of 1-pentanol and 1-heptanol than those at 0 and 4.5 kGy at day 0 but the amount of 1-pentanol, 1-hexanol, and 1-heptanol showed decreasing trends as irradiation dose increased at day 4 and day 8. In day 0 samples, irradiation greatly increased ($P<.05$) the production of 1-pentene+hexane but had no effect on day 4 and day 8 samples. The amounts of propanal, pentanal, 2-methyl pentanal, and hexanal were not influenced by irradiation dose but increased ($P<.05$) during storage. After 4 days of storage in aerobic packaging these aldehydes became the major volatile compounds of irradiated cooked pork sausage, and the amounts were two- to fourfold higher than that of the day 0 samples. Other volatiles such as 1-pentene+hexane, 1-pentanol, 1-hexanol, and 1-heptanol also increased ($P<.05$) during storage in aerobic packaging (Table 2).

Among the volatile components, the amounts of 1-heptene and 1-nonene were the only two volatile compounds influenced ($P<.001$) by irradiation dose. Therefore, they could good indicators for irradiation treatment in cooked pork sausage. The production of 2-methylpentanal and trimethylhexane were influenced (P<.001) by storage (Table 3) but the changes were not consistent with storage time (Tables 1-2). The productions of 1-pentene+hexane, aldehydes (propanal, pentanal, hexanal, and nonanal), ketones, alcohols, and total volatiles were influenced (P<.05) by both storage time and packaging (Table 3).

To date over 1,000 flavor compounds have been identified as flavor and aroma compounds in cooked meat and these flavor compounds are produced by the thermal degradation of sugars, amino acids, and nucleotides as well as the Maillard reaction and lipid oxidation[15,17]. Many researchers[8,11,18] reported that lactones, aromatic and nonaromatic heterocyclic compounds, S-containing compounds, and furan compounds are important contributors to the meaty aroma notes of cooked meat. Merritt[7] suggested that the volatile compounds responsible for off-odors in irradiated meat are produced by changes in the protein and lipid molecules and are different from those of lipid oxidation. Schweigert[13] reported that the precursors of the undesirable odor compounds in irradiated meat were water soluble and contained nitrogen, sulfur or both, and that methyl mercaptan and sulfur dioxide, formed from the S-containing compounds (e.g., glutathione), contributed to the irradiation odor. The major volatile components, however, found in irradiated cooked pork sausage analyzed by the purge-and-trap/GC method used in this study were lipid oxidation-related compounds, most of which were aldehydes, alcohols, ketones, and alkenes with low carbon numbers.

The major reason samples in this study had relatively simple volatile composition compared with other studies was derived from the low temperature purge (40°C) used. Exhaustive distillation of meat at high temperature would not produce the kind of volatile compounds found in cooked sausages at the time of sensory analysis. Little if any S-containing compounds, pyrazines, and furans were detected in the irradiated cooked pork sausage when purged at 40°C. Although the flavor dilution factors of S-containing compounds, pyrazines, and furans are very high[9], their contributions to flavor of cooked sausages at 40°C should be negligible. As shown by Ramarathnam et al.[10], hexanal was the major lipid oxidation-related volatile in cooked meat, but the contribution of other aldehydes such as heptanal, octanal, and nonanal to off-flavor of cooked meat also would be significant because of their high flavor dilution factors[17].

TBARS (2-thiobarbituric acid reactive substances) values. The changes of TBARS values in irradiated cooked pork sausage with different packaging conditions and storage time indicated that storage time had no effect on the TBARS of vacuum-packaged sausage but had significant (P<.05) effects in aerobic-packaged sausage (Table 4). The TBARS values of the sausage in vacuum packaging remained constant during the 8-day storage periods, whereas values of sausage in aerobic packaging increased two- to fourfold from day 0 values. Irradiating cooked pork sausage had some effect on the TBARS values of vacuum-packaged sausages at day 0 and those of aerobic-packaged sausages at day 0 and day 4. Compared with storage time in aerobic packaging, however, irradiation effects on the TBARS values of cooked meat were minor (Table 4). Ahn et al.[2,4] also reported that preventing oxygen exposure after cooking was more important for TBARS values than antioxidant, irradiation, and storage conditions of raw meat.

Relationships of volatile compounds with TBARS. Table 5 indicates that there is little relationship between TBARS values and volatiles produced in irradiated cooked pork sausage with vacuum packaging. With aerobic packaging, however, TBARS values of irradiated cooked pork sausage had very high correlation (P<.0001) with the production of 1-pentene+hexane, propanal, pentanal, hexanal, 3-heptanone, 1-pentanol, cyclohexanone, 1-hexanol, 1-heptanol, and total volatiles. The relationships between TBARS values and the amount of 2-methylpentanal, trimethylhexane, and nonanal also were significant. The production of pentanal was the only volatile compound significantly (P<.01) correlated with TBARS in both vacuum and aerobic packaged cooked sausages. The production of 1-pentene+hexane, propanal, pentanal, hexanal, 3-heptanone, 1-pentanol, cyclohexanone, 1-hexanol, nonanal, 1-heptanol, and total volatiles had a very high correlation (P<.0001) with the TBARS values of irradiated cooked pork sausage when both vacuum- and aerobic-packaged sausages were combined. 2-Propanone was correlated (P<.0001) to TBARS when both aerobic and vacuum packaging were combined but not when packaging type was analyzed separately. This result indicates that the amount of aldehydes, total volatiles, and ketones and alcohols with longer retention times can be good indicators of oxidative changes in cooked irradiated meat.

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Table 1. Production of volatiles in vacuum-packaged cooked irradiated pork sausages influenced by irradiation dose and storage time (4°C).

	Day 0			Day 4			Day 8		
Volatile compound	0 kGy	2.5 kGy	4.5 kGy	0 kGy	2.5 kGy	4.5 kGy	0 kGy	2.5 kGy	4.5 kGy
	Peak area (pA*sec)								
1-Pentene, hexane	84.78	99.33	93.88	45.28c	67.35b	89.20a	118.13	132.63	120.73
1-Heptene	6.35c	38.03b	7 3.38a	8.25c	36.50b	73.05a	10.90c	40.80b	60.73a
Propanal	2.26	3.19	2.65	3.81	3.18	3.80	8.58b	9.55a	8.75b
2-Propanone	18.93c	22.80b	25.60a	20.55c	24.28b	28.75a	19.45c	22.78b	26.35a
1-Nonene	12.93c	30.43b	44.38a	11.55c	28.78b	41.88a	11.75c	30.05b	41.33a
Pentanal	20.75	26.13	25.45	21.53	24.23	21.15	26.15ab	28.58a	24.38b
2-Methylpentanal	104.80	133.15	134.23	99.00	115.53	98.00	155.20	163.70	143.85
2-Pentanone	12.85	16.95	19.05	13.10	12.30	10.63	20.10	20.00	20.13
Trimethylhexane	70.70	90.90	92.75	62.15	71.55	59.83	97.63	103.40	90.65
Hexanal	57.43a	48.65ab	37.30b	66.83a	55.25ab	47.58b	48.80a	48.58a	34.75b
3-Heptanone	2.30	1.95	1.90	2.23	2.30	1.90	2.20	2.03	2.00
1-Pentanol	13.35a	11.40b	9.23c	14.35a	11.23b	10.40b	12.33a	13.55a	8.83b
Nonanal	2.80	2.70	2.65	2.35b	2.65ab	2.93a	tr	tr	tr
1-Heptanol	3.55a	2.98ab	2.35b	3.55a	2.88b	2.60b	3.48a	3.20a	2.18b
Total volatiles	420.5b	534.6a	571.3a	381.3b	465.0a	499.2a	540.4b	625.0a	590.3ab

Samples (2 g) were purged at 32°C. n = 4. SEM = standard error of mean.
Different letters within a row of the same storage time are different (P<.05).

Table 2. Production of volatiles in aerobic-packaged cooked irradiated pork sausages influenced by irradiation dose and storage time (4°C).

	Day 0			Day 4			Day 8		
Volatile compound	0 kGy	2.5 kGy	4.5 kGy	0 kGy	2.5 kGy	4.5 kGy	0 kGy	2.5 kGy	4.5 kGy
	Peak area (pA*sec)								
1-Pentene, hexane	41.63b	91.10a	94.40a	131.28	137.78	154.05	182.48	183.18	185.00
1-Heptene	7.35c	48.13b	86.18a	16.18c	48.03b	89.58a	21.50a	64.10b	88.50c
Propanal	3.10	4.60	5.03	20.03	23.25	23.52	24.92	27.25	24.25
2-Propanone	21.73c	27.98b	31.60a	80.55a	61.40b	32.15c	55.20	30.45	33.78
1-Nonene	12.90c	30.78b	40.40a	15.30c	30.28b	40.38a	14.85c	31.83b	40.60a
Pentanal	15.13	14.65	14.28	37.43	40.53	42.40	36.60	38.80	37.43
2-Methylpentanal	57.13	43.40	42.65	182.98	168.58	166.98	110.28	114.30	115.58
2-Pentanone	8.15	5.83	7.10	20.85	19.03	21.75	11.35	11.50	11.58
Trimethyl hexane	44.80	34.54	33.48	122.03	112.05	110.78	70.18	73.45	74.35
Hexanal	44.18	68.20	56.48	287.68	283.18	270.90	333.70	338.30	291.25
3-Heptanone	2.15ab	2.38a	1.90b	4.13	4.00	3.70	5.08	4.63	3.83
1-Pentanol	11.78b	16.08a	12.13b	37.28a	34.18a	30.08b	44.33a	38.25b	31.70b
Cyclohexanone	tr	tr	tr	3.68	3.33	3.10	3.85	3.65	3.30
1-Hexanol	tr	tr	tr	2.80	2.80	2.60	3.43a	3.13a	2.63b
Nonanal	2.68	2.35	3.08	4.43	4.60	4.53	3.95	4.33	4.30
1-Heptanol	2.93b	4.08a	3.03b	10.00	9.28	8.48	10.93a	10.18a	8.05b
Total volatiles	281.9b	397.9a	435.5a	981.5	988.1	1010.5	941.0	986.7	964.2

Different letters within a row of the same storage time are different (P<.05).
Samples (2 g) were purged at 32°C. n = 4. SEM = standard error of mean.

Table 3. Effects of irradiation dose, storage time, and packaging on volatiles production from cooked pork sausages.

Volatile compound	Irradiation effect	Storage effect	Packaging effect
d.f.	2	2	1
	Probabilities		
1-Pentene, hexane	0.19	0.0001	0.0001
1-Heptene	0.0001	0.86	0.06
Propanal	0.95	0.0001	0.0001
2-Propanone	0.48	0.007	0.0001
1-Nonene	0.0001	0.98	0.88
Pentanal	0.67	0.0001	0.0035
2-Methylpentanal	0.89	0.0001	0.15
2-Pentanone	0.89	0.009	0.02
Trimethylhexane	0.89	0.002	0.33
Hexanal	0.86	0.0001	0.0001
3-Heptanone	0.30	0.0001	0.0001
1-Pentanol	0.30	0.0002	0.0001
Nonanal	0.76	0.007	0.0001
1-Heptanol	0.34	0.0003	0.0001
Total volatiles	0.45	0.0001	0.0001

n = 24 for irradiation effect and storage effect and n = 36 for packaging effect.

Table 4. Changes of TBARS values in cooked irradiated pork sausages with different packaging and storage.

	Vacuum packaging				Aerobic packaging			
Storage	0 kGy	2.5 kGy	4.5 kGy	SEM	0 kGy	2.5 kGy	4.5 kGy	SEM
(day))	TBARS values (mg MDA/kg meat)							
0	0.71by	1.08x	0.91xy	0.08	1.23cy	1.33cy	1.95bx	0.10
4	0.89a	0.92	0.87	0.03	4.57bxy	3.97by	5.16ax	0.24
8	0.83a	0.85	0.77	0.05	6.91a	5.94a	5.41a	0.44

Different letters within a row of the same packaging are different (P<.05). n = 4.
Values with different superscript letters within a column of the same irradiation dose are different (P<.05). SEM = standard error of mean.

Table 5. Correlation coefficient between volatile compounds and TBARS value.

Volatile compound	Vacuum packaging	Aerobic packaging	Vacuum+aerobic packaging
1-Pentene, hexane	0.02	0.77**	0.61**
1-Heptene	0.02	0.02	0.06
Propanal	0.04	0.81**	0.84**
2-Propanone	0.04	0.11	0.31**
1-Nonene	0.03	0.00	0.00
Pentanal	0.19*	0.65**	0.54**
2-Methylpentanal	0.05	0.30*	0.03
2-Pentanone	0.09	0.16	0.00
Trimethylhexane	0.01	0.23*	0.03
Hexanal	0.01	0.86**	0.93**
3-Heptanone	0.00	0.83**	0.88**
1-Pentanol	0.00	0.83**	0.90**
Cyclohexanone	0.00	0.69**	0.79**
1-Hexanol	0.00	0.82**	0.89**
Nonanal	0.00	0.60*	0.74**
1-Heptanol	0.02	0.80**	0.89**
Total volatiles	0.06	0.75**	0.74**

*Significant at P<.01 and **significant at P<.0001. n = 36 for vacuum-packaged and aerobic-packaged and n = 72 for vacuum+aerobic packaged.