Potential Chemical Markers for the Identification of Irradiated Sausages

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Joong Ho Kwon, Visiting Scientist;
Ki Chang Nam, Postdoc;
Byungrok Min, Postdoc;
Eun Joo Lee, Assistant Scientist;
Dong U. Ahn, Professor,
Department of Animal Science

Summary and Implications

Hydrocarbons, gas compounds, and off-odor volatiles were determined for irradiated (0 or 5 kGy) commercial sausages with different fat contents (16% and 29%) during a 60-d storage period at 4 ◦C. Total of 4 hydrocarbons (C14:1, C15:0, C16:2, and C17:1) were detected only in irradiated sausages: the amount of C16:2 was the highest, followed by C17:1, C14:1, and C15:0. The concentrations of hydrocarbons decreased significantly ($P < 0.05$) with storage, but were still detectable at the end of 60-d storage. Irradiated sausages produced significantly higher amounts of CO than the nonirradiated ones. CH4 was detected only in irradiated sausages. Dimethyl disulfide was detected only in irradiated sausages and its concentration decreased significantly ($P < 0.05$) with storage. Fat content of sausages showed a significant effect on the production and retention of hydrocarbons, gas compounds, and sulfur volatiles in irradiated sausages during storage. Some hydrocarbons (C16:2, C17:1, C14:1, and C15:0), CH4, and dimethyl disulfide were only found in irradiated sausages indicating that these compounds can be used as potential markers for irradiated sausages.

Introduction

As foods travel around the globe, control of pathogens in foods becomes even more important than before. Extensive research for many decades indicated that food irradiation is a safe and effective technology to control food borne pathogens as well as to increase the shelf life of many food products. However, informative labeling is needed to enhance consumer understandings on the beneficial effects of irradiated foods and to facilitate its quarantine requirements. All available methods to detect irradiated foods have certain advantages with some inherent limitations. Therefore, none of a particular existing detection method can be used to authenticate all irradiated food products.

Ionizing radiation is known to generate hydroxyl radicals in aqueous or oil emulsion systems. These radicals can break acyl oxygen bond in food components and form aldehydes, Cn-1 alkanes, short-chain hydrocarbons, CO, free fatty acids, and alcohols. Hydrocarbons are the major radiolytic products in fat and the hydrocarbons produced are related to the fatty acid composition of fat. Many scientists tested the possibility of using hydrocarbons and 2-alkylcyclobutanones as markers for radiation-induced changes in fat-containing irradiated foods. The determination of evolved gases such as carbon monoxide, hydrogen, hydrogen sulfide, and ammonia from irradiated foods has also been explored. The off-flavor in irradiated raw meat is considered as the combined effect of radiolytic S-volatiles and lipid oxidation products. Irradiation may induce off-flavors by enhancing lipid oxidation in different meat products. However, irradiation off-odor was mainly produced by the sulfur-volatiles such as dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide rather than aldehydes from lipid oxidation. Sulfur-volatiles are highly volatile and detected less in aerobically packaged than vacuum packaged meats as they escape from packaging bags with time.

This study was aimed at monitoring the radiation-induced chemical changes, such as production of fat-derived hydrocarbons, gas compounds, and off-odor volatiles in commercial sausages with different fat contents during storage at 4 ◦C, and at evaluating the potential of using these chemical compounds as radiation markers for the sausages.

Materials and Methods

Frankfurter sausages with 2 different fat contents (16% and 29%) were individually vacuum-packaged in oxygen-impermeable nylon/polyethylene bags (9.3 mL O2/m2/24 h at 0 ◦C), and irradiated at 0 or 5 kGy using a Linear accelerator (Circe IIIR, Thomson CSF Linac, France).

The hydrocarbons produced by irradiation was identified by comparing the retention time and mass spectral data of samples with those of an authentic hydrocarbons standard based on the Wiley library.

Gas compounds were analyzed using a GC.

Off-odor volatiles were determined using the dynamic headspace GC/MS method.

Results and Discussion

- Two types of hydrocarbons were predominantly produced from fatty acids by irradiation: one is the hydrocarbons with 1 carbon less than the parent fatty acids (Cn-1) and the other is the one with 1 carbons less and an additional double bond at position 1 (Cn-2, 1-ene). Therefore, 8-heptadecene (C17:1) and 1,7-hexadecadiene (C16:2) from oleic acid, n-pentadecane (C15:0) and 1-tetradecene (C14:1) from palmitic acid, n-heptadecane (C17:0), and 1-hexadecene (C16:1) from stearic acid were detected in irradiated sausages.

- Total of 4 hydrocarbons (C14:1, C15:0, C16:2, and C17:1) were found in both types of irradiated sausages, but not in nonirradiated ones. Detection levels of these 4 hydrocarbons were in the order of C16:2, C17:1, C14:1, and C15:0 from the highest to the lowest. The detected amounts of C17:1 and C16:2 generated from oleic acid were higher than any other pair of hydrocarbons from a fatty acid in all samples. C17:0 was found in both nonirradiated and irradiated sausages with 16% fat, but was found only in irradiated sausages with 29% fat. Hydrocarbon C16:1 was found in all samples, but irradiation significantly increased its concentration in both sausages (16% and 29% fat), mainly due to the radiation induced cleavage of stearic acid. Despite the fact that the concentrations of hydrocarbons decreased during storage, radiation-induced hydrocarbons remained detectable after 60-d storage at 4 ◦C. C17:1 was detected only in irradiated sausages after 60 d of storage regardless the fat content of sausages.
- Carbon monoxide was present in both nonirradiated and irradiated sausages but its concentration increased significantly after irradiation. CH4 was absent in nonirradiated but was found in irradiated sausages. CO2 was also detected in both irradiated and nonirradiated sausages, but greater amount was found in sausages with 29% fat than 16% fat after irradiation. Concentrations of all 3 gases in all samples increased significantly ($P \leq 0.05$) during the 60-d storage at 4 ◦C in vacuum packaged sausages.
- Dimethyl disulfide was produced only in irradiated sausages. A significant decrease in dimethyl disulfide concentration was observed after 60 d of storage at 4 ◦C. Carbon disulfide, another sulfur-containing volatile compound, was found in irradiated and nonirradiated sausages with 29% fat after 60-d storage at 4 ◦C, where its concentration was significantly higher in irradiated than nonirradiated samples.

Conclusions

Presence and pattern of 4 hydrocarbons (C16:2, C17:1, C14:1, and C15:0), and production of CH4 and dimethyl disulfide could be used as potential markers to detect irradiated sausages with different fat contents. The concentrations of radiation-induced detection markers significantly ($P \leq 0.05$) decreased during storage, but were still detectable after 60 d of storage at 4 ◦C.

Table 1–Hydrocarbons (μg/g fat) of nonirradiated and irradiated sausages with different fat contents during 60-d storage at 4 ◦C.

		C14:1		C15:0		C16:2		C16:1		C17:1		C17:0	
Fat content	Irradiation dose	Storage day		Storage day		Storage day		Storage day		Storage day		Storage day	
(%)	(kGy)	0	60	0	60	0	60	0	60	0	60	0	60
16	0	0	0	0	0	0	0	$_{ax}$2.16	$_{ax}$0.90	0	0	$_{ax}$1.08	$_{bx}$0.95
	5	$_{ax}$1.08	$_{bx}$0.43	$_{ax}$1.03	$_{bx}$0.20	$_{ax}$2.77	$_{bx}$1.22	$_{ax}$1.92	$_{bx}$1.03	$_{ax}$2.30	$_{bx}$0.87	$_{ax}$1.17	$_{bx}$0.95
29	0	0	0	0	0	0	0	$_{ax}$0.87	$_{ay}$0.76	0	0	0	0
	5	$_{ax}$0.99	$_{bx}$0.24	$_{ax}$0.87	$_{bx}$0.16	$_{ax}$2.20	$_{bx}$0.67	$_{ax}$1.25	$_{bx}$0.98	$_{ax}$2.40	$_{bx}$0.84	$_{ax}$1.17	$_{bx}$0.82

$_{xy}$Means with different superscripts within a column of same fat content are significantly different ($P < 0.05$). n=3.
$_{ab}$Means with different superscripts in a row of the same compound are significantly different ($P < 0.05$).

Table 2–Gas production (ppm) of nonirradiated and irradiated sausages with different fat contents during 60-d storage at 4 ◦C.

	Irradiation	CO		CH_4		CO_2	
Fat (%)	dose (kGy)	0	60	0	60	0	60
16	0	$_{by}$3.6	$_{ay}$52.3	0	0	$_{bx}$320	$_{ay}$5154
	5	$_{bx}$4.8	$_{ax}$83.0	$_{bx}$1.4	$_{ax}$20.3	$_{bx}$289	$_{ax}$8133
29	0	$_{by}$3.6	$_{ay}$75.3	0	0	$_{by}$242	$_{ax}$35770
	5	$_{bx}$14.9	$_{ax}$232.3	$_{bx}$2.8	$_{ax}$39.7	$_{bx}$613	$_{ay}$26682

$_{xy}$Means with different superscripts within a column of same fat content are significantly different ($P < 0.05$). n=3.
$_{ab}$Means with different superscripts in a row of the same compound are significantly different ($P < 0.05$).

Table 3–Off-odor volatiles (total ion counts ×10^4) of nonirradiated and irradiated sausages with different fat contents during 60-d storage at 4 ◦C.

	Irradiation	Dimethyl disulfide		Hexanal		Carbon disulfide	
Fat (%)	dose (kGy)	0	60	0	60	0	60
16	0	0	0	$_{by}$1692	$_{ax}$2483	0	0
	5	$_{ax}$2487	$_{bx}$117	$_{ax}$3001	$_{bx}$2227	0	0
29	0	0	0	$_{ay}$1974	$_{by}$1336	0	$_{ay}$10748
	5	$_{ax}$1144	$_{bx}$170	$_{ax}$2988	$_{ax}$2978	0	$_{ax}$18368

$_{xy}$Means with different superscripts within a column of same fat content are significantly different ($P < 0.05$). n=3.
$_{ab}$Means with different superscripts in a row of the same compound are significantly different ($P < 0.05$).