Effect of Cooking on Radiation-induced Chemical Markers in Beef and Pork during Storage

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Summary and Implications

Raw and cooked beef and pork loins were irradiated at 0 or 5 25 kGy. The radiation induced marker compounds, such as hydrocarbons, 2-alkylcyclobutanones and sulfur volatiles, were determined after 0 and 6 months of frozen storage. Two hydrocarbons [8-heptadecene (C17:1), 6,9-heptadecadiene (C17:2)] and two 2-alkylcyclobutanones [2-dodecylcyclobutanone (DCB), 2-tetradecylcyclobutanone (TCB)] were detected only in irradiated raw and cooked meats. Although pre-cooked irradiated meats produced more hydrocarbons and 2-alkylcyclobutanones than the irradiated cooked ones, the amounts of individual hydrocarbons and 2-alkylcyclobutanones, such as 8-heptadecene, 6,9-heptadecadiene, DCB, and TCB, were sufficient enough to detect whether the meat was irradiated or not. Dimethyl disulfide and dimethyl trisulfide were also detected only in irradiated meats, but dimethyl trisulfide disappeared after 6 months of frozen storage under oxygen-permeable packaging conditions. The results indicated that 8-heptadecene, 6,9-heptadecadiene, DCB, TCB and dimethyl disulfide, even though they were decreased with storage, could be used as marker compounds for the detection of irradiated beef and pork regardless of cooking under the frozen conditions for 6 months.

Introduction

The U.S. Food and Drug Administration (FDA) approved irradiation for poultry and red meats to control food borne pathogens and extend products' shelf-life. Many other countries also have approved irradiation to control pathogens and parasites, and extend shelf-life of various food items including red meats and poultry. Since mid-1980s, extensive research for developing detection methods for irradiated foods has been conducted. Some chemical changes in foods, which can be used as irradiation indicators or markers, occur during irradiation by free radical reactions. 2-Alkylcyclobutanones (2-ACB) such as 2-dodecylcyclobutanone (DCB) and 2-tetradecylcyclobutanone (TCB) are formed in irradiated fat or oil by the loss of an electron from acyl-oxygen bond in fatty acids, followed by arrangement process to produce 2-alkylcyclobutanones specific to their parent fatty acids. Because 2-dodecylcyclobutanone (DCB) and 2-tetradecylcyclobutanone (TCB) are not detected in nonirradiated foods, they were used as markers for detecting irradiated foods. These 2-ACBs are extracted using n-hexane or n-pentane along with fat, fractionated using adsorption chromatography prior to separation using a gas chromatography (GC) and detection using a mass spectrometer (MS). Other 2-ACBs such as 2- (tetradec-5'-enyl) cyclobutanone derived from oleic acid also have been identified in irradiated food stuffs.Hydrocarbons (HC) in fat-containing foods were generated by the primary and secondary reactions after the chemical bonds in fatty acids are broken by irradiation. The fatty acid moieties of triglycerides are mainly broken at alpha and beta positions of carbonyl groups and two types of hydrocarbons, which contain one (Cn-1) or two (Cn-2:1) less carbon atoms than its parent fatty acids, are formed.

Ionizing radiation generates hydroxyl radicals in aqueous or oil emulsion systems. Hydroxyl radical is the most reactive oxygen species and can initiate lipid oxidation by abstracting a hydrogen atom from fatty acyl chain of a polyunsaturated fatty acid (PUFA) and form a lipid radical. In the presence of oxygen, the lipid radical rapidly reacts with oxygen to form a peroxyl radical which, in turn, can extract a hydrogen atom from another fatty acyl chain, yielding a new free radical that can perpetuate the chain reaction, and a lipid hydroperoxide that can be degraded into various volatile compounds including aldehydes, ketones, hydrocarbons, and sulfur compounds, after a series of secondary reactions. Some gases such as carbon monoxide, carbon dioxide and methane are also produced by reactions between meat components and free radicals. However, little information on the chemical changes induced by free radicals in precooked irradiated or irradiated cooked meats is available.

The objective of this study was to identify the marker compounds that can be used for detecting irradiated raw as well as cooked ground beef and pork irradiated before or after cooking.

Materials and Methods

- Fresh meats (beef loin and pork loin) were purchased from local supermarkets, ground separately through a 5-mm plate, and vacuum-packaged in an oxygen-impermeable nylon/polyethylene bags (~100 g) (O2 permeability, 9.3 mL O2/m2107 /24 hr at 0°C) within 6 hr of purchase.
- Five treatments were prepared depending on cooking and irradiation conditions: 1) nonirradiated raw meat (uncooked-0 kGy), 2) irradiated raw meat (uncooked-5 kGy), 3) nonirradiated cooked meat (cooked-0 kGy), 4)

precooked irradiated meat (cooked-5 kGy), 5) irradiated cooked meat (5 kGy-cooked).

- Samples were analyzed at 0 day and after 6 months of storage at -40°C under oxygen permeable packaging conditions.
- Hydrocarbons and 2-alkylcyclobutanones were determined using the GC/MS method after separating from meat samples.
- Sulfur volatiles were determined using a dynamic headspace GC/MS method.

Results and Discussion

- The amounts of radiation-induced hydrocarbons in beef and pork increased in upon irradiation at 5 kGy.
- Cooking newly produced 1-hexadecene in pork but found in nonirradiated raw beef at 0 month storage which were significantly increased after cooking. Thus, 1-hexadecene cannot be used as an irradiation marker for beef.
- 8-Heptadecene (C17:1) and 6,9-heptadecadiene (C17:2), derived from oleic acid and linoleic acid, respectively, were found at high concentrations in irradiated meats, but not detected in both nonirradiated raw and cooked beef as well as pork. Therefore, 8-heptadecene and 6,9-heptadecadiene can be used as markers for irradiated raw and cooked beef and pork.
- 2-Dodecylcyclobutanone (2-DCB) and 2-tetradecylcyclobutanone (2-TCB) were detected only in irradiated beef and pork regardless cooking treatment. Among the 2-ACBs, 2-(5'-Teradecenyl) cyclobutanone (2-TeCB) was present at the highest level in both irradiated beef and pork, but was also detected in non-irradiated meats. 2-DCB was the best candidate for irradiation marker among the 2-ACB compounds because it was detected only in irradiated meats.
- During storage, the concentrations of 2-ACBs decreased drastically in all irradiated meats, but detectable level of them were still remained in the meat after 6 months of storage at -40°C.
- Sulfur volatiles (dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide) were detected in beef and pork, respectively.
- Dimethyl disulfide and dimethyl trisulfide were not found in non-irradiated meats, but present in irradiated ones.
- Irradiated pork produced more sulfur volatiles than irradiated beef. Most of the sulfur-containing compounds disappeared after 6 months of storage at -40°C. Nevertheless, dimethyl disulfide was still detectable in all meats after 6 months of frozen storage under oxygen permeable packaging conditions.

Conclusions

Two hydrocarbons, 8-heptadecene (C17:1) and 6,9-heptadecadiene (C17:2) and two 2-alkylcyclobutanones, 2-dodecylcyclobutanone (DCB) and 2-tetradecylcyclobutanone (TCB) were detected only in irradiated beef and pork regardless of cooking treatment. Although hydrocarbons and 2-alkylcyclobutanone levels were decreased during storage, detectable levels of 8-heptadecene, 6,9-heptadecadiene, 2-dodecylcyclobutanone, and 2-tetradecylcyclobutanone were still remaining and they could serve as indicators for irradiated raw and cooked beef and pork. Dimethyl disulfide was only detected in irradiated beef and pork samples regardless of cooking treatment and after frozen-stored for 6 months under oxygen permeable packaging conditions, indicating that it also could be used as an irradiation marker for raw and frozen cooked beef and pork.

Table 1-Effect of irradiation timing and subsequent storage at -40°C on the concentrations of radiation-induced hydrocarbons in cooked beef.

Hydrocarbons	Storage time (mo)	Raw meat 0 kGy	Raw meat 5 kGy	Cooked before IR 0 kGy	Cooked before IR 5 kGy	Cooked after IR 5 kGy
	-------------------- (Total ion counts × 104) -----------------------					
1-Tetradecene(C14:1)	0	-[k])	9.30bx	-	12.23ax	8.06cx
1-Tetradecene(C14:1)	6	-	6.37by	-	7.35ay	7.58ay
Pentadecane(C15:0)	0	1.61cx	7.12bx	1.35cx	14.39ax	7.86bx
Pentadecane(C15:0)	6	1.46dx	5.10cy	1.04ex	9.9ay	5.78by
1-Hexadecene(C16:1)	0	0.86dx	6.74cx	1.33dx	9.91bx	19.616ax
1-Hexadecene(C16:1)	6	-	4.47cy	0.56dx	5.97by	15.80ay
6,9-Heptadecadiene(C17:2) 0	-	2.51ax	-	2.54ax	1.73bx	
6,9-Heptadecadiene(C17:2) 6	-	1.82ax	-	1.98ay	1.49ax	
8-Heptadecene(C17:1)	0	-	7.00ax	-	6.94ax	4.53bx
8-Heptadecene(C17:1)	6	-	5.05by	-	5.75ay	3.07cy
n-Heptadecane(C17:0)	0	2.88bx	5.43ax	3.44bx	6.18ax	6.17ax
n-Heptadecane(C17:0)	6	0.37cy	3.83by	0.38cy	5.24ax	5.51ax

[a-d]Different superscript letters within a column of the same storage day are significantly different ($p < 0.05$); n = 3.
[x,y]Different superscript letters within a row are significantly different ($p < 0.05$).
[k]Not detected.

Table 2-Effect of irradiation timing and subsequent storage at -40°C on the concentrations of radiation-induced hydrocarbons in cooked pork.

Hydrocarbons	Storage time (mo)	Raw meat 0 kGy	Raw meat 5 kGy	Cooked before IR 0 kGy	Cooked before IR 5 kGy	Cooked after IR 5 kGy
	---------------------------- (Total ion counts × 104) ------------------------------					
1-Tetradecene(C14:1)	0	0.42bx	5.63ax	0.37bx	5.50ax	5.10ax
1-Tetradecene(C14:1)	6	-[k])	4.81ay	-	4.23cy	4.47bx
Pentadecane(C15:0)	0	0.59cx	6.13ax	1.41cx	4.50bx	5.15bx
Pentadecane(C15:0)	6	-	5.35ax	1.33dx	2.97cy	4.03by
1-Hexadecene(C16:1)	0	-	3.19ax	1.93bx	3.22ax	3.12ax
1-Hexadecene(C16:1)	6	-	2.89ax	1.80bx	3.25ax	1.06by
6,9-Heptadecadiene(C17:2)	0	-	3.37ax	-	3.51ax	3.09ax
6,9-Heptadecadiene(C17:2)	6	-	1.17cy	-	1.82ay	1.55by
8-Heptadecene(C17:1)	0	-	6.25ax	-	5.57ax	6.66ax
8-Heptadecene(C17:1)	6	-	4.57ay	-	4.11ax	4.20ay
n-Heptadecane(C17:0)	0	0.86cx	4.13ax	1.34cx	1.02cx	2.16bx
n-Heptadecane(C17:0)	6	0.20cy	4.12ax	0.37bcy	0.62[b]cx	0.70by

[a-d]Different superscript letters within a column of the same storage day are significantly different ($p < 0.05$); n = 3.
[x,y]Different superscript letters within a row are significantly different ($p < 0.05$).
[k]Not detected.

Table 3-Effect of irradiation timing and subsequent storage at -40°C on the concentrations of radiation-induced 2-alkylcyclobutanones in beef and pork.

Cooking treatment	IR dose (kGy)	2-DCB		2-TCB		2-TeCB	
		0 mo	6 mo	0 mo	6 mo	0 mo	6 mo
		---------------------------- (Total ion counts × 104) ------------------------------					
Beef							
Raw meat	0	-*k*)	-	-	-	1.28cx	0.55cy
Raw meat	5	1.93ax	0.96by	0.51ax	0.14ay	5.81ax	2.97ay
Cooked before IR	0	-	-	-	-	0.67cx	0.42cy
Cooked before IR	5	1.63ax	1.06ax	0.25bx	0.05bx	4.39bx	2.76ax
Cooked after IR	5	0.76bx	0.23cx	0.13bx	0.10abx	2.09cx	1.77bx
Pork							
Raw meat	0	-*k*)	-	-	-	0.25ax	0.22cx
Raw meat	5	0.41ax	0.08by	0.44ax	0.11ay	0.82ax	0.40cy
Cooked before IR	0	-	-	-	-	0.30ax	0.27cx
Cooked before IR	5	0.45ax	0.25ax	0.65ax	0.42ax	0.88ax	0.68bx
Cooked after IR	5	0.46ax	0.23ay	0.38ax	0.19ay	0.54ax	0.95ax

[a-c]Different superscript letters within a column of the same storage day are significantly different ($p < 0.05$); n = 3.
[x,y]Different superscript letters within a row are significantly different ($p < 0.05$).
[k]Not detected.

Table 4-Effect of irradiation timing and subsequent storage at -40°C on the concentrations of radiation-induced sulfur compounds in cooked beef and pork.

Cooking treatment	IR dose (kGy)	Dimethyl sulfide		Dimethyl disulfide		Dimethyl trisulfide	
		0 mo	6 mo	0 mo	6 mo	0 mo	6 mo
		-------------------------- (Total ion counts × 104) ----------------------------					
Cooked Beef							
Raw meat	0	721	0	0b	0c	0b	0
Raw meat	5	1064	0	2833ab	2054b	0b	0
Cooked before IR	0	790	0	0b	0c	0b	0
Cooked before IR	5	0	0	2872ab	2255b	0b	0
Cooked after IR	5	662	0	5933a	3835a	485a	0
Cooked Pork							
Raw meat	0	907	0	0b	0	0b	0
Raw meat	5	2135	0	3394ab	136	0b	0
Cooked before IR	0	573	0	0b	0	0b	0
Cooked before IR	5	249	0	4317a	44	489a	0
Cooked after IR	5	815	0	3405ab	690	535a	0

[a,b]Different superscript letters within a column of the same storage day are significantly different ($p < 0.05$); n = 3.