Production of Volatiles from Fatty Acids and Oils by Irradiation

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Summary and Implications

To understand the mechanisms of off-odor production in irradiated meat, the volatile compounds produced from individual fatty acids by irradiation were identified. Nonirradiated oil emulsions prepared with polyunsaturated fatty acids (PUFAs) produced many volatile compounds, but the amounts of volatiles generally decreased after irradiation. Although volatile profiles of fatty acid emulsions were changed by irradiation, the odor characteristics and intensity between irradiated and nonirradiated fatty acid emulsions were not different. Thiobarbituric acid-reactive substances (TBARS) values indicated that irradiation accelerated lipid oxidation during subsequent storage, but the volatiles produced by lipid oxidation were not the major contributors of off-odor in irradiated samples.

Introduction

Ionizing radiation is known to generate hydroxyl radicals in aqueous or oil emulsion systems. The hydroxyl radical is the most reactive oxygen species. It can initiate lipid oxidation by abstracting a hydrogen atom from a 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 after a series of secondary reactions. Aldehydes contributed the most to oxidation flavor and rancidity in cooked meat. Hexanal was the predominant aldehyde produced by lipid oxidation, and hexanal content correlated the best with TBARS of meat. This study was to determine the volatile compounds produced from individual fatty acids by irradiation as a step toward understanding the mechanisms of off-odor production in irradiated meat.

Materials and Methods

Selected fatty acids generally found in meat (palmitoleic, oleic, linoleic, linolenic, and arachidonic), corn oil (refined), and fish oil (refined) were used to determine their contribution to lipid oxidation-dependent production of volatiles by irradiation. An oil-in-water emulsion system was used in this study because it can increase the surface area of fatty acid or oil. Oil emulsion was prepared by blending 0.5 g of fatty acid or oil in 50 mL deionized distilled water. An aliquot of oil emulsion sample (15 mL) was transferred to a scintillation vial and irradiated at 0 or 5.0 kGy using a Linear Accelerator. Volatile profiles, TBARS, and odor characteristics of irradiated and nonirradiated oil emulsions were compared.

Results and Discussion

Many new volatiles were generated from oil emulsions of PUFAs by irradiation. The amounts of most of the volatiles in the oil emulsions of PUFAs, however, decreased after irradiation. Benzene and toluene were detected in irradiated fatty acids or oil emulsions. Sensory panelists described the odor characteristics of fatty acid emulsions as “fishy” and “metallic,” and the intensity and characteristics of odor from irradiated fatty acid emulsions were not different from those of nonirradiated emulsions. The volatile results of MUFA and PUFA emulsions indicated that irradiation newly produced or increased the amounts of 1-hexene, 1-heptene, 1-octene, and 1-pentene, which were known as the irradiation-dependent volatiles. The presence of large quantities of hydrocarbons, aldehydes and ketones in nonirradiated oil emulsions from PUFAs indicated that a significant degree of oxidative process had progressed in the oil emulsions before irradiation. The decrease of volatiles from the PUFA emulsions by irradiation suggested that the secondary products of lipid oxidation in the fatty acid emulsions could have reacted with the radiolytic products in the fatty acids to produce different volatiles or nonvolatile molecules. Consequently, the amounts of many volatiles were decreased by irradiation due to the secondary chemical reactions. In the MUFA emulsion, however, direct impact of electron energy should have broken acyl bonds, and produced short- chain hydrocarbons, and generated new volatiles.

Nonirradiated emulsion prepared with fish oil produced many volatiles, but the amounts changed after irradiation. The amounts of octane, pentane, heptane, and 2-propenal in emulsion prepared with fish oil increased significantly after irradiation, but the increased amounts were relatively small. The production of 2,5-octadiene and propanal in emulsion prepared with fish oil decreased, and 2-ethylfuran, 2-pentene, 1,2-dimethyl cyclopropane, and 2,4-octadiene disappeared after irradiation. Corn oil emulsion generated many new volatiles while fish oil emulsion decreased the number and amount of volatiles by irradiation as in MUFA and PUFA emulsions. The fatty acid compositions showed that corn oil had a much higher portion of MUFA than fish oil (Table 1) and corn oil had almost no lipid oxidation products before irradiation. The result of volatile analysis in corn and fish oils indicated that the volatile profiles of irradiated oils were influenced by the composition, the length of carbon chain, and the number of double bonds of fatty acids in oils.

Irradiation influenced the TBARS values of fatty acids emulsions (Figure 1). TBARS values of irradiated emulsion samples immediately after irradiation were lower than those of nonirradiated samples. After 5 d of storage at 4 °C, however, irradiated samples developed higher TBARS values than nonirradiated emulsions. Arachidonic acid, linolenic acid, and fish oil, which had a high proportion of multi-double-bonded fatty acids, had accelerated lipid oxidation after irradiation. Among the volatiles of emulsion prepared with arachidonic acid, linolenic acid, or fish oil, aldehydes including 2-propenal, propanal, butanal, pentanal, and hexanal increased the most during the storage (Table 2). Hexanal was produced only in emulsion prepared from arachidonic acid and propanal only from linolenic acid, indicating that n-3 PUFAs are the source of propanal and n-6 PUFAs of hexanal. Fish oil that contains both n-3 and n-6 PUFAs produced both propanal and hexanal. Longer storage time increased the amount of aldehydes and TBARS values in these oil emulsions, but irradiation had minimal effect on the increase of aldehydes and TBARS.

Conclusion

Irradiation produced a few new volatiles and increased the amount of 1-hexene, 1-heptene, 1-octene, and 1-pentene, which were known as the irradiation-dependent volatiles, in oil emulsion of MUFAs and PUFAs. These volatiles, however, had little effect on the sensory characteristics of oil emulsion. The amounts of aldehydes, the indicators of lipid oxidation, in oil emulsion did not increase by irradiation, and volatiles from lipids accounted for only a small part of the off-odor in irradiated meat.

Table 1. Fatty acid composition of corn oil and fish oil[1]

Fatty acid	Corn oil (%)	Fish oil (%)
C14:0	trace	7.25
C15:0	trace	0.56
C16:0	11.41	20.38
C16:1	trace	10.07
C17:0	trace	0.40
C18:0	1.87	3.50
C18:1	30.83	10.88
C18:2	55.89	1.75
C18:3	trace	3.29 1
C20:0	trace	0.53
C20:2	trace	1.56
C20:3	trace	2.04
C20:4	trace	0.57
C20:5	trace	11.62
C22:5	trace	2.20
C22:6	trace	11.47
Unidentified	trace	11.93

Table 2. Production of aldehydes and TBARS values in irradiated and nonirradiated emulsions prepared with arachidonic acid and linolenic acid, and fish oil during storage

	Arachidonic acid			Linolenic acid			Fish oil		
Volatiles	0 kGy	5 kGy	SEM	0					
kGy	5 kGy	SEM	0 kGy	5					
kGy	SEM								
Day 0	----------------------------- *total ion counts x 10^4* --------------------------------								
2-Propenal	0	0	-	0	0	-	179	287	67
Propanal	0	0	-	0[b]	1519[a]	32	0	0	-
Butanal	0	0	-	0	0	-	465[a]	175[b]	12
Pentanal	0	0	-	0	0	-	323[a]	81[b]	11
Total aldehydes (%)		0	0	-	0	0.5	-	5.3	7.8
TBARS (mg/kg)	2.58[a]	1.41[b]	0.17	4.51[a]	1.27[b]	0.03	2.27	2.38	0.13
Day 10									
2-Propenal	11435[b]	27531[a]	958						
4426[a]	3393[b]	280	7070[a]						
2775[b]	386								
Propanal	794[a]	0[b]	13	32297	30809	1083	24403a	10899[b]	744
Butanal	0[b]	223[a]	5						
117[a]	0[b]	10	1314[a]						
455[b]	21								
Pentanal	1180[b]	2494[a]	94	0	0	-	580[a]	248[b]	31
Hexanal	28864[b]	58702[a]	2302	0	0	-	0	0	-
Total aldehydes (%)		33.2	47.9	-	9.5	6.8	-	79.4	87.1
TBARS (mg/kg)	143.43	140.10	1.44						
	103.68[a]	76.37[b]	1.40	54.26[a]	26.86[b]	0.28			

Figure 1. TBARS of nonirradiated and irradiated oil emulsions prepared with fatty acids and oils during storage (different letters within a same storage time are differ significantly).