Effect of Irradiation on Meat Fats

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Studies on chemical changes in meats during irradiation were directed to meat fats. Off-odors produced during irradiation of certain meats at sterilization levels do not arise directly from chemical changes in the meat fats. Oxidative changes (peroxide, carbonyl, and free fatty acid formation) are not marked during irradiation or subsequent storage, if the presence of oxygen is minimized. Accelerated peroxide formation occurs during storage of irradiated fats as compared to nonirradiated controls when oxygen-permeable packages are used.

PRESERVATION OF FOOD by irradiation sterilization has recently attracted considerable interest. However, foods such as meat develop off-odors and off-flavors and become discolored upon exposure to sterilizing dosages of ionizing radiations (*9*). Studies in this laboratory have been directed to ascertaining the nature and magnitude of chemical changes that occur during irradiation of meat (*2, 4, 6*) including proteolytic enzyme activity, levels of certain sulfur constituents, and myoglobin stability. In the present study, chemical changes during irradiation and storage of beef and pork fat have been determined.

Hannan and associates (*7, 8*) studied the formation of peroxides in butterfat during irradiation and storage. Recent work by Mead (*10*) and Polister and Mead (*11*) indicates that irradiation causes the induction of autoxidation of methyl linoleate. In view of these findings, special attention was given in the present work to the determination of oxidative changes (formation of peroxides carbonyl compounds, and free fatty acids) which occurred when fats were irradiated with varying dosages of gamma rays and when these fats were stored after irradiation.

Experimental

Two radiation sources were used. A cobalt-60 source (refrigerated at 5° C.) with a dose rate of approximately 90,000 rep per hour was used for irradiation of small quantities of fat. Another gamma-ray source, located at the Materials Testing Reactor Site, Arco, Idaho, with a dose rate ranging from 1.0 to 16.4 $\times$ 10^6 rep per hour was used for irradiation of larger quantities of fat.

Approximately 80-gram samples of pork or beef fat (all lean removed) were packed either in saran casing (oxygen-impermeable) or in Visking casing (oxygen-permeable) with minimum air space, prior to irradiation in the cobalt-60 source. Approximately 400 grams of fat were ground and packed in No. 2 cans with about 0.5-inch air space and shipped in a container with dry ice for the irradiations conducted at Arco. Prior to irradiation, the contents of the cans were brought to the temperature of ice water, then irradiated and repacked in dry ice for the return shipment. Effects of irradiation on rendered beef fat, prepared in the laboratory, were also studied. In all studies controls were run simultaneously with irradiated samples. Peroxide values, per cent carbonyl oxygen, and per cent free fatty acids were determined on both control and irradiated samples.

Peroxide values and free fatty acids were determined by standard methods (*1*). Peroxide values are reported in milliequivalents per kilogram of fat, and free fatty acids in percentage of the fat (as oleic acid). Carbonyl measurements were made by the method of Drozdov and Materanskaya (*5*) using hydroxylamine hydrochloride and are expressed as percentage of carbonyl oxygen in the fat. Storage experiments were done at 5° and 24° C.

Results and Discussion

The major change observed during irradiation of the meat fats or subsequent storage of the irradiated samples was an increase in peroxide values. The carbonyl values ranged from 0.1 to 1.0% for individual samples. The change in carbonyl values during irradiation was small, and the significance of the small changes observed must be further studied before any definite conclusions can be made. The major attention in this paper, therefore, is given to changes in peroxide values and in some cases to changes in free fatty acids.

The results in Table I for representative tests with nonrendered beef fat irradiated in Visking casing showed a slight but consistent increase in peroxide value over that observed for the irradiation of samples in saran casing. These observations are consistent with the fact that oxygen is required for the peroxidation of fats. More oxygen would be available for the samples packed in Visk-

Table I. Effect of Irradiation and Subsequent Storage on Peroxide Values of Nonrendered Beef Fat

(2.1 $\times$ 10^6 rep. treatment, cobalt-60 source, University of Chicago. Storage tests conducted at 5° C. for 4 weeks. Peroxide values expressed as milliequivalents per kilogram of fat)

	Characteristics of Fat			Non-irradiated	Irradiated		Non-irradiated, Stored	Irradiated and Stored	
	Fat, %	H_2O, %	IV[a]		Saran casing	Visking casing		Saran casing	Visking casing
Sample A	82.3	8.5	48	0.1	0.3	1.9	...	...	...
				0.2	1.3	3.1			
				0.5	0.9	4.1			
Sample B	87.2	7.7	45.2	0.5	1.6	...	0.6	2.6	...
Sample C	86.0	8.1	46.8	0.5	1.6	...	0.5	2.0	...
Sample D	72.0	9.8	46.9	0.4	...	2.0	0.4	...	18.7
Sample E	90.0	5.8	46.4	0.6	...	2.1	0.3	...	21.3

[a] IV, iodine value.

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ing casing, which is freely permeable to oxygen. Samples which were irradiated in saran or Visking casing and then stored for 4 weeks at approximately 5° C. showed marked differences in peroxide value after storage. A much greater increase in peroxides occurred for the irradiated samples stored in Visking casing (Table I) than for nonirradiated samples stored in Visking or saran casings or for irradiated samples stored in saran casings.

This marked increase in oxidation of irradiated fats stored in the presence of oxygen—the so-called aftereffect of irradiation—has also been observed for purified methyl linoleate after irradiation and subsequent storage (*10, 11*). These findings clearly indicate that the presence of oxygen should be minimized, not only during irradiation, but also during storage, to avoid major oxidative changes in these fats. No marked differences were observed between pork fat and rendered or nonrendered beef fat in peroxide values after irradiation (Tables I and II). Storage of rendered beef fat in Visking casing showed a marked increase in peroxide values, although somewhat less than that observed for nonrendered beef fat. Stored pork fat, on the other hand, was fairly stable for the period of storage in both saran and Visking casing.

Irradiation of fat packed in cans at levels of 2×10^6 and 4×10^6 rep showed lower peroxide values and higher free fatty acid content for most of the samples when the higher dosage was used (Table III). Extensive studies with a considerable range of increasing dosages will be needed to determine the exact relation of irradiation dosage to peroxide content and the correlation with increased free fatty acid formation. The present results suggest that with high irradiation dosages some cleavage of fatty acid peroxides occurs with the resultant formation of fatty acids or fatty acid split products.

A consistent increase in free fatty acids and a decrease in peroxide values were observed during storage of the samples irradiated in cans at either 2×10^6 or 4×10^6 rep (Table III). The magnitude of these changes for peroxide values is much less than those observed when fats were irradiated and stored in Visking casings (Table I). Little change in the peroxide values of the nonirradiated controls but a considerable increase in free fatty acids occurred during storage. The latter is probably attributable to bacterial or enzymatic action during storage of these nonirradiated samples at 24° C.

Gross observations indicated no off-odors produced after irradiation or storage of the irradiated samples in cans where treatment at 2 to 4×10^6 rep was used. Thus, it appears that fat is not the constituent of meat responsible for the off-odors (and flavors) observed during irradiation. Fats may have a significant influence in indirect chemical reactions in a food during irradiation or subsequent storage (effect on heme pigments, other easily oxidized constituents by chain oxidations, etc.). In fact, preliminary findings indicate that with beef containing high levels of intramuscular fat, less glutathione is destroyed and less hydrogen sulfide is produced during irradiation than with beef containing low levels of intramuscular fat (*3*). Destruction of glutathione and production of hydrogen sulfide were observed previously during irradiation of fresh beef (*2*). These findings are also consistent with the observation that less objectionable off-odors and flavors are produced when pork is irradiated as compared to beef (pork muscle is higher in fat). It would appear worth while to study the chemical and organoleptic changes when graded levels of fat are added to beef and pork muscle samples prior to irradiation.

Table II. Effect of Irradiation and Subsequent Storage on Peroxide Values of Rendered Beef and Nonrendered Pork Fat

(2.0×10^6 rep treatment, cobalt-60 source, University of Chicago. Storage tests conducted at 5° C. for 4 weeks. Peroxide values expressed as milliequivalents per kilogram of fat)

	Characteristics of Fat			Non-irradiated	Irradiated		Non-irradiated, Stored	Irradiated and Stored	
	Fat, %	H_2O, %	IV		Saran casing	Visking casing		Saran casing	Visking casing
Rendered beef fat	...	...	48.7	0.4	3.4	...	0.5[a]	2.0	...
				0.4	2.6	...	0.3[a]	2.7	...
				0.4	...	3.0	0.3	...	11.0
				0.4	...	2.1	0.5	...	5.3
Pork fat	80.0	6.3	54.5	0.3	1.6	1.8	0.8[a]	2.5	...
				0.4	1.7	1.9	0.8	...	3.5

[a] Saran casing; for all others Visking casing was used.

Summary

Chemical changes in meat fats (rendered and nonrendered beef and pork fats) that occur during irradiation with gamma-rays and subsequent storage of the fats were investigated. On an overall basis, increases in peroxides, carbonyl compounds, or free fatty acids were small in beef and pork fat irradiated at 2 or 4×10^6 when the presence of oxygen was minimized.

A marked increase in peroxide values was observed when irradiated fats were stored at 5° C. in an oxygen-permeable casing as compared to nonirradiated fats stored in an oxygen-permeable casing, and irradiated and nonirradiated samples in an oxygen-impermeable casing or in sealed cans.

A lower peroxide value was observed when treatment at 4×10^6 rep was used as compared to 2×10^6 rep for nonrendered fats irradiated in cans. Per-

Table III. Effect of Different Levels of Irradiation and Subsequent Storage on Chemical Changes in Fat Packed in Cans

(Irradiated at Arco, Idaho. Storage tests conducted for 4 weeks at 24° C.)

	Characteristics of Fat				Control Non-irradiated	Irradiation Dosage, Rep		Non-irradiated, Stored	Irradiation Dosage, Rep	
	Fat, %	H_2O, %	IV	Analysis[a]		2×10^6	4×10^6		2×10^6 (stored)	4×10^6 (stored)
Nonrendered beef fat	89.0	5.0	48.3	P.V.	0.3	5.6	3.2	0.5	1.9	1.9
				F.F.A.	0.7	0.8	0.9	6.7	1.6	1.5
	89.4	6.3	48.0	P.V.	1.3	4.1	2.9	0.5	1.8	1.5
				F.F.A.	0.6	0.7	0.8	4.1	1.4	1.5
Nonrendered pork fat	80.0	6.3	54.5	P.V.	0.3	2.8	2.1	0.4	0.7	1.4
				F.F.A.	0.2	0.4	0.5	7.7	1.9	1.3
Rendered beef fat	...	...	48.7	P.V.	0.4	2.3	2.7	...	...	...
					0.3	3.9	3.8	...	...	...

[a] P.V., peroxide value, milliequivalents per kilogram of fat.
F.F.A., free fatty acids, per cent oleic acid per gram of fat.

oxide values for both dosage treatments decreased and the free fatty acids increased during storage of the samples in cans at 24° C.

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FRUIT JUICE CONSTITUENTS

Chromatographic Comparison of Nonvolatile Acids of Fresh and Stored Apple Juice Concentrate

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The nonvolatile acids of fresh and of storage-darkened apple juice concentrate were separated by the use of paper chromatography following silicic acid partition chromatography. No difference could be detected in the acids between the fresh and the darkened concentrate. The use of three different solvent mixtures and six spray reagents for paper chromatography, together with 41 reference acids, allowed tentative identification of galacturonic, quinic, phosphoric, citric, malic, chlorogenic, citramalic, caffeic, succinic, and lactic acids by their R_f values and colors produced with the spray reagents. Seven acids present in minor amounts were not identified.

APPLE JUICE can be concentrated at a low temperature to 70° Brix. The resulting product is much more stable to decomposition by microorganisms, and the reduced water content saves in shipping, packaging, and storage costs. Although the concentrate is more stable than fresh juice, it does darken upon storage. The rate of darkening is influenced by the varieties of apples from which the concentrate was produced, as well as by other factors.

There is evidence that this deterioration during storage is due to the Maillard or nonenzymatic browning reaction. In his recent review of browning reactions, Hodge (*10*) has pointed out that organic acids have been shown to be involved both directly in a reducing sugar–organic acid reaction and synergistically in a reducing sugar–amino acid–organic acid type of reaction. This study was undertaken to find out if there were any changes in the identity and amount of acids when apple juice was concentrated and allowed to darken. Qualitative and quantitative changes could be due either to participation of the acids in the browning reaction or to normal degradation of sugars and other compounds.

Materials and Methods

Preparation of Concentrate The apple juice was prepared from a blend of two parts of Jonathan and one part each of McIntosh, Northern Spy, and Stayman Winesap apples. Immediately after pressing, the juice was passed through an apparatus for essence recovery (*8*), depectinized, and filtered. The treatment of the juice is that used in the preparation of full-flavor apple juice concentrate. The treated juice (18.6° Brix) was frozen and stored for experimental work (*7*).

A sample of this juice was concentrated in a laboratory vacuum still to 69° Brix and stored in an incubator at 100° F. After several months the darkened sample was removed and diluted to 18.6° Brix.

Ion Exchange Treatment A column containing Zeo Rex cation exchange resin (Permutit Co.) was regenerated with 2*N* hydrochloric acid and washed until the effluent produced a negative chloride test as described by Porter, Buch, and Willits (*18*). A De Acidite (Permutit Co.) anion exchange column was regenerated with 1*N* sodium hydroxide and washed until the effluent was neutral to phenolphthalein (*18*). The juice or diluted darkened concentrate was mixed with an equal volume of water, run through the Zeo Rex resin, and then rinsed with four bed-volumes of water. The effluent (sugars plus acids) and rinse were then run through the De Acidite column, followed by a four-bed-volume rinse with water. De Acidite was chosen because it is a weakly basic resin and does not cause degradation of sugars, as was found to be the case with strongly basic resins (*13, 17*). The acids were eluted from the column with an excess of 0.1*N* sodium hydroxide. This eluate, containing the sodium salts of the acids plus sodium hydroxide, was run through a column of regenerated Zeo Rex. This normality of alkali was found to be sufficient for complete recovery and was much better than the stronger alkali usually employed (1*N* or 2*N*), because one pass through the cation column would free the acids. The stronger alkali required several passes with regenerations after each pass, or another larger column had to be set up. The effluent, containing only the free acids, was concentrated in vacuo to a definite volume and used for chromatographic analysis. In later work Dowex