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Chemical Changes Associated with Flavor in Irradiated Meat

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Chemical changes in meat that have been treated with ionizing radiations have been well documented. The recent development of new improved analytical methods employing combined gas chromatography and mass spectrometry systems with digital outputs permits computer processing of both qualitative and quantitative data. Precise determination of the variation in the amounts of components with various treatment conditions such as dose and temperature has now been made and correlated with sensory observations. The irradiation flavor increased and overall acceptance decreased with an increase in dose and/or irradiation temperature. Correspondingly, analyses of volatile compounds show increases of amount with increases in dose or irradiation temperature. When the proper conditions of dose and temperature are employed, however, wholly acceptable products that are both safe and savory can be produced.

Irradiated foods are not yet commodities of the market place. Their development, however, has progressed so successfully that it is currently expected that they shall become commercial items. It is appropriate, therefore, that a paper dealing with the flavor of irradiated meat be included in this symposium.

In the early days of the development of irradiated meat products there were changes induced that were frequently described as "off" odors and flavors (Batzer and Doty, 1955; Batzer et al., 1957). It has been generally acknowledged that these changes are primarily due to the formation of volatile compounds from lipid (Merritt et al., 1966; Dubravcic and Nawar, 1968; Champagne and Nawar, 1969) and protein precursors (Merritt, 1966; Merritt et al., 1967a) and there has been a continuing study of these changes for several years (Josephson and Merritt, 1972), so that the nature of the chemical changes which occur due to irradiation processing is now very well known. The understanding of the basic chemistry has been achieved mainly by qualitative analysis of the trace volatile components by combined GC–MS techniques (Merritt, 1970, 1972). Recent developments employing a digital computer system to GC–MS output now provide accurate quantitative data as well (Merritt et al., 1974). The precise determination of the variation in the amounts of components with various processing conditions such as dose or temperature now permits the correlation of chemical changes with sensory observations.

The results of these studies have led to developments in processing techniques so that contemporary meat products have very little so called irradiation flavor and are wholly acceptable consumer items.

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EXPERIMENTAL SECTION

The techniques by which the chemical analyses are carried out have been described previously in detail in a number of publications (Angelini et al., 1967; Merritt et al., 1959, 1966, 1967a,b, 1970, 1972, 1974). The analytical scheme used in the current study may be summarized as follows. The trace volatile compounds are separated from the meat by a high vacuum distillation at room temperature into a receiver at liquid nitrogen temperature. The total condensate thus collected is further fractionated by high vacuum distillation at −80° into so called water and carbon dioxide fractions. Each of these fractions is then analyzed by combined GC–MS techniques. The output of the GC–MS system operating in a repetitive scan mode is digitized directly by a minicomputer to provide mass spectra for each successive scan. These data are transferred to a laboratory automation computer which performs component identifications, produces reconstructed chromatograms, computes component amounts, and carries out correlations or any other data processing that may be required. (The current system has been upgraded from that described by Merritt et al. (1974) and now utilizes a Digital Equipment Corp. PDP 15/76 system as the main processor.) The current results to be described later have been achieved largely through the use of this computer system.

RESULTS AND DISCUSSION

The knowledge and understanding of the chemical changes which occur in meat as a result of irradiation have been acquired through a large number of studies by many workers extending over several years (Merritt, 1966, 1970;

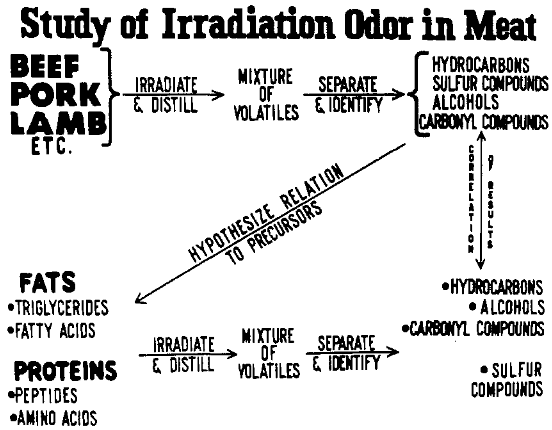


Figure 1. Schematic representation of studies performed to elucidate chemical changes produced in irradiated meat.

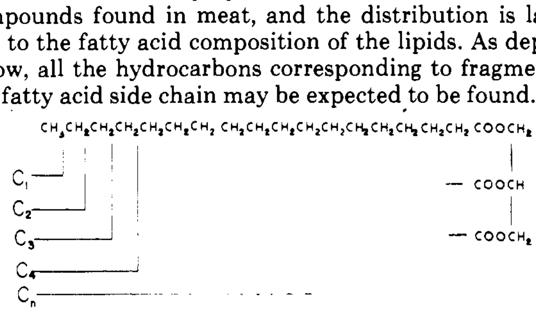
Table I. Compounds Found among Volatile Components from Irradiated Beef

Alkanes	C_1–C_{20}	Alkanols	C_2–C_6
Alkenes	C_2–C_{20}	Alkanals	C_2–C_6
Alkynes	C_2–C_{20}	Alkanones	C_2–C_6
Alkadienes	C_4–C_{20}	Esters	C_3–C_{18}
Thioalkanes	C_3–C_6	Thiols	C_1–C_4

Merritt et al., 1966, 1967a,b). The bulk of this work has been recently reviewed (Josephson and Merritt, 1972). The general approach used in this laboratory to elucidate radiation effects is summarized in Figure 1.

Initially, the various trace volatile compounds produced by irradiation in several kinds of meat were determined. These were found to be predominantly hydrocarbons, sulfur compounds, and certain alcohol and carbonyl compounds. The origins of these components were then established by carrying out analyses of the trace volatile components produced by irradiation in meat constituents such as the fat or protein fractions, and in model systems of triglycerides, fatty acid esters, peptides, and amino acids. It seems to be now well established that the hydrocarbons and oxygen compounds are formed predominantly from lipid, and the sulfur compounds, of course, from protein.

A summary of the many compounds found is seen in Table I. The many hydrocarbons present range in compound type from alkanes to alkadienes and in carbon number up to C_{20}. The alcohols and carbonyl compounds, as well as sulfides and disulfides, are usually found up to about C_6. Abundance varies greatly as seen in Table II. Hydrocarbons are usually by far the most abundant radiolysis compounds found in meat, and the distribution is largely due to the fatty acid composition of the lipids. As depicted below, all the hydrocarbons corresponding to fragments of the fatty acid side chain may be expected to be found.

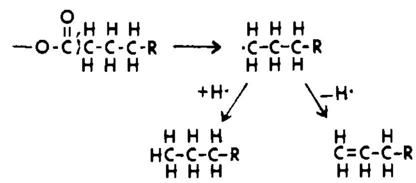


Although the direct cleavage mechanism for the formation of the various hydrocarbons in fats was proposed several years ago (Merritt et al., 1966) detailed studies of this mechanism by Nawar and his colleagues (Dubravcic and Nawar, 1968; LeTellier and Nawar, 1972) have shown that bond rupture in a triglyceride occurs preferentially at the

Table II. Relative Abundance of Volatile Compounds in Irradiated Beef

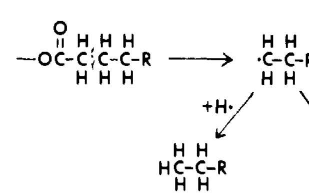
Volatile compd	ppm	Volatile compd	ppm
Alkanes	12	Alcohols	1.0
Alkenes	14	Alkanones	<0.5
Alkanals	1.5	Alkylbenzenes	<0.1
Sulfur compounds	1.0	Esters	<0.1

bonds adjacent, or near to, the ester linkages. If rupture occurs at the carbon α to the carboxyl group, the predominant components would be expected to be the alkanes and alkenes having one less carbon atom than the corresponding fatty acid:



Thus, tristearin yields predominantly heptadecane and heptadecene.

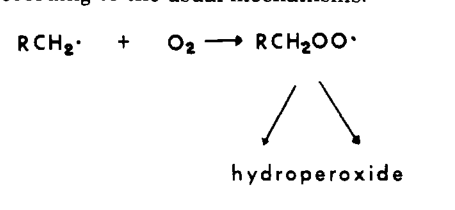
This mechanism is supported by a comparison of the radiolysis products obtained from several other triglycerides such as tripalmitin, trimyristin, trilaurin (Dubravcic and Nawar, 1968), and tricaproin (LeTellier and Nawar, 1972). The most abundant hydrocarbon in every case is the C − 1 alkane where C is the number of carbon atoms in the fatty acid. Correspondingly, in the alkene series the C − 1 alkene is most abundant. The next most preferred cleavage is at the carbon β to the carboxyl:



This cleavage leads to relatively abundant C − 2 alkanes and alkenes. Other cleavages of the alkyl side chain are random and lead to hydrocarbon fragments of lesser abundance.

The oxygenated components are formed from other cleavages about the carbons of the glyceryl moiety adjacent to the ester linkage.

The hydrocarbon and oxygen compounds resulting from cleavage may all be found in fats irradiated under high vacuum. In earlier studies (Batzer et al., 1957; Monty et al., 1961; Wick et al., 1967) carbonyl compounds were found in greater numbers and amount when oxygen was present during irradiation. At that time, irradiation odor tended to be associated with the carbonyl components, and various measures such as TBA value, peroxide number, etc., were used to try to evaluate the off flavors. These effects are now regarded as secondary and are thought to arise from a combination of the free radical induced by irradiation with oxygen to produce a hydroperoxide which in turn decomposes according to the usual mechanisms.



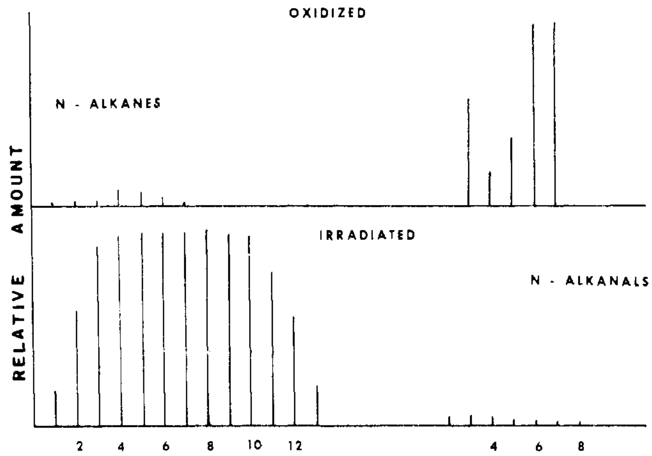


Figure 2. Comparison of the relative abundance of alkanes and alkanals among the volatile components produced by irradiation and oxidation of butterfat.

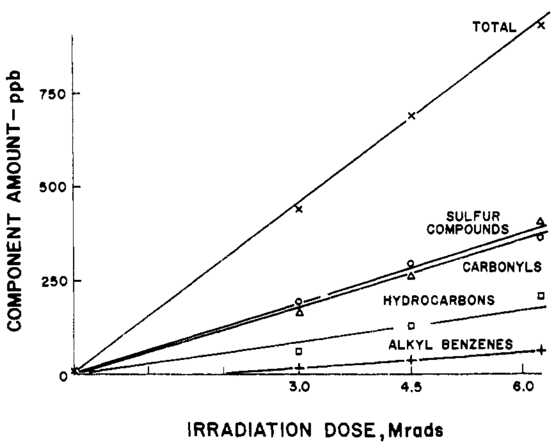


Figure 3. Graph showing relative amounts of component produced in beef irradiated as a function of dose at −185°.

A comparison of the relative abundance of hydrocarbons vs. carbonyls in radiolysis viz-a-viz oxidation was made several years ago in a study of butterfat (Forss et al., 1967; Merritt et al., 1967b). From the data shown in Figure 2 the evidence is preponderant that hydrocarbons contribute significantly more in the radiolysis situation. In modern processing technology, the meat is irradiated under vacuum and very few oxidative effects can be observed.

It has been clearly demonstrated that the sulfur compounds originated from the radiolysis of proteins as shown by a study (Merritt et al., 1967a) of amino acids, peptides, isolated beef protein, and fat-free fish, such as haddock. In white fish such as haddock or cod, very few hydrocarbons are found and those are short chain corresponding to cleavage of the alkyl side chains of certain amino acids. It is interesting to observe, however, as Dubravcic and Nawar (1969) have found that the hydrocarbon composition of irradiated mackerel oil is very similar to that of irradiated meat fats. It is likewise significant that an irradiation off odor is much more prevalent and harder to suppress in irradiated fatty fish than in fish which have essentially fat-free tissue.

The amount of component produced has long been known to be a function of radiation dose (Merritt et al., 1959) and temperature. With the sophisticated techniques now available to us, it is a relatively simple procedure to study these quantitatively. Moreover, in the development of processing methods, the technologists have accumulated large residues of sensory evaluation data relating to both consumer acceptance and expert evaluation (Shults and Wierbicki, 1974). It is now propitious to attempt to correlate some of these data.

Table III. Effect of Irradiation Dose[c]

Irradiation dose (min), Mrad	Off odor	Irrad flavor	Preference
0	1.0[a]	1.77[a]	7.64[a]
3.0	2.05	2.62	6.40[b]
4.5	2.20	3.18	6.18
6.0	2.41	3.36	5.54

[a] Significantly different from other samples. [b] Significantly different from 6.0-Mrads sample. $N = 23$, significance at the 5% level. [c] U.S. choice beef roast irradiated at −185°.

There are two parameters which primarily concern the technologist in developing an irradiation process—dose and the temperature at which the product is irradiated. Both of these are known to effect the flavor quality of the product. Although the dependence of component formation with dose and temperature has long been known, these factors have been reexamined employing modern instrumental analytical techniques (Merritt et al., 1974) in order to have data available for correlation with sensory data.

Figure 3 shows a graph which summarizes the amounts of all the individual components which were identified and determined and grouped according to functional group type. The linear dependence of component amount with dose is again clearly demonstrated. It is also significant that the amounts of the individual components are additive at all dose levels to give a linear plot for the total amount of volatile components produced.

An interesting observation with respect to these data is the fact that the hydrocarbons are less abundant than the carbonyls and sulfur compounds. This is not surprising, however, when considered in view of the fact that the fat content of this beef sample was only about 2 to 3%.

Table III shows the effect of irradiation dose upon the sensory evaluation of the product and may be compared with the data in Figure 3. (The sensory evaluation scale used by all panel members in all tests was a 9 point scale. Ratings for the sensory characteristics were made using an intensity scale of 1 to 9, with 1 denoting "none" and 9 being "extreme". Preference ratings were made on a hedonic scale of 1 to 9 with 1 being "dislike extremely", 5 being "neither like nor dislike", and 9 being "like extremely".) The off odor and irradiation flavor were evaluated by expert panel. They had no difficulty in establishing the increase in irradiation associated flavor and odor with dose. The consumer preference panel was able to detect the difference between the control and the irradiated samples, and also to distinguish a lower from a higher dose.

The process criterion for dose is the microbiological safety level. This has been established for sterilized beef at about 4.5 Mrads (i.e., at an appropriate temperature). It is important, therefore, to know also the effect of temperature upon the production of radiolysis components. Figure 4 shows data comparable to that shown previously (in Figure 3) for the dose effect. The amounts of the individual components are grouped according to compound type, and the total is likewise shown. (Similar graphs can be prepared, of course, for any individual component, if desired.) Although the relationship is not linear, there is an increase in the amount of component produced for a given dose (in this case 4.5 Mrads) as the temperature of irradiation is increased. The lower the temperature the less likely is an irradiation flavor to be detected.

To verify this precept a typical commercial beef loin irradiated at various temperatures was evaluated by an expert flavor panel. These data are seen in Table IV. It is no prob-

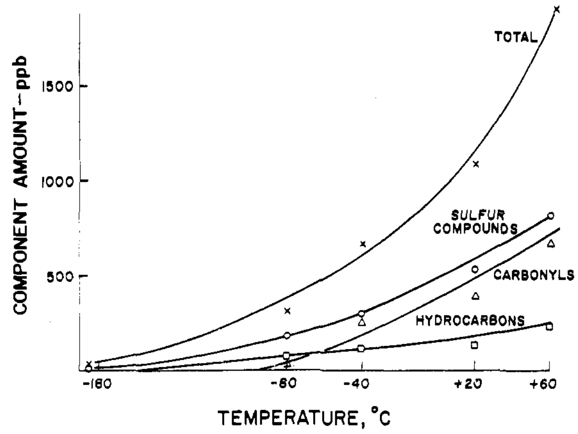


Figure 4. Graph showing relative amounts of component produced in beef irradiated with 4.5 Mrads as a function of temperature.

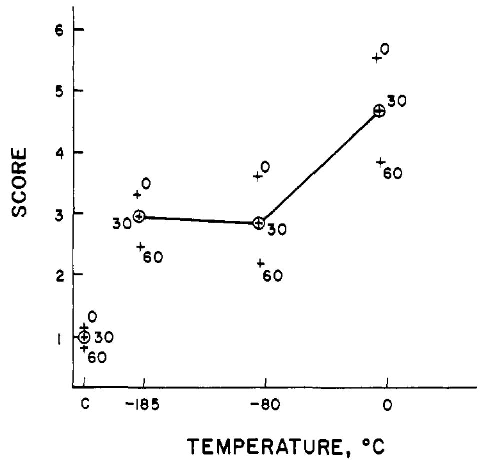


Figure 6. Graph showing average scores given by expert panelists for the irradiation flavor characteristic of beef irradiated at 5.6 Mrads as a function of temperature. Mean values for the variation in storage time are shown as circles. Values for the control samples are shown at "C".

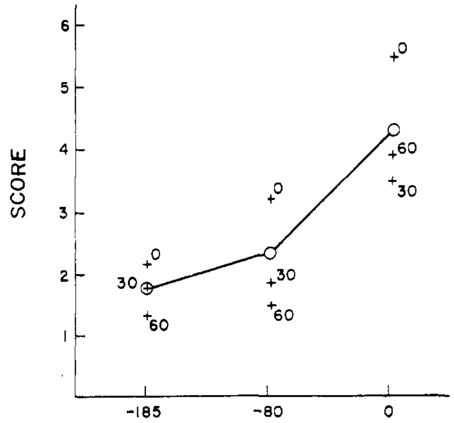


Figure 5. Graph showing average scores given by expert panelists for the off odor characteristic of beef irradiated at 5.6 Mrads as a function of temperature. Mean values for the variation in storage time are shown as circles.

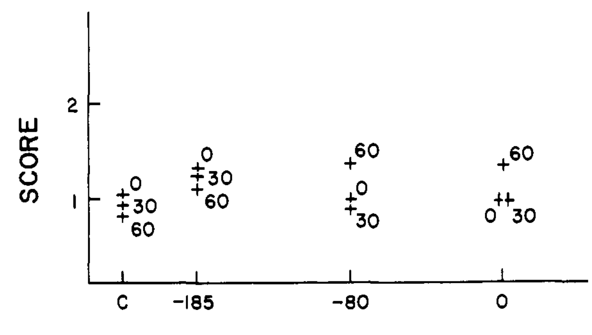


Figure 7. Graph showing average scores given by expert panelists for the off flavor characteristic of beef irradiated at 5.6 Mrads as a function of temperature. Legend as in Figures 5 and 6.

lem for the panelist to pick out the increased flavor development at the higher temperatures.

Shults and Wierbicki (1974) have carried out extensive studies of flavor evaluation on a wide variety of irradiated commercial meat products. They have studied choice cuts of roast, loin, top round, bottom round, and chuck, as well as commercial cuts of loin. Their data are too voluminous to describe in detail in this paper. However, since the results are nearly identical for all cuts of meat that were studied, the data from a survey of the effect of temperature on choice beef loin can be considered as typical. These data are seen in Figures 5–7. The average scores from 1 to 9 are given for quality evaluated as a function of irradiation temperature. The irradiation dose was in the range of 5.6 Mrads, and there were eight expert panelists. The evaluation of off odor is shown in Figure 5. Mean values for samples rated after 0, 30, and 60 days of storage are also shown. There appears to be a diminution of the off odor during storage, as the 60-day values are consistently less than the 0- or 30-day values. The values for the control are not shown, but they are all closely grouped about 1. All the values differed significantly from the control at the 5% level, and 0° samples likewise differed significantly from the −80 and −185° values.

Data for the panel evaluation of irradiation flavor are shown in Figure 6. The off odor and irradiation flavor factors are evaluated separately by the flavor panels. The irradiation flavor scores correlate extremely well with the off odor scores and differ significantly over the temperature range from −80 to −185° from the 0° samples. All the irradiated samples differ significantly from the controls. The trend toward diminution of irradiation flavor upon storage is also confirmed.

Table IV. Effect of Irradiation Temperature[a]

Irrad. temp, °C	Irrad. flavor
+60	4.1
+21	3.3
−40	2.9
−80	2.1
−185	1.5

[a] U.S. commercial beef loin. $N = 16$; 1–3 month storage; dose, 4.5–5.6 Mrads.

The panel was also asked to evaluate off flavors other than that characteristic of, or attributable to, irradiation. As can be seen in Figure 7 there were none.

Since off odor and irradiation flavor are both seen to increase with temperature of irradiation, and component amount is seen to do likewise, it seems desirable to try to correlate these parameters. In previous studies (Angelini and Walts, 1966) of lipid oxidation and the deterioration of quality of stored freeze dried eggs a linear relationship was established between the amount of total component and the flavor score. In this study a correlation coefficient has been calculated to see if a correlation exists. Since a graphical representation of the data (see Figure 8) suggests that

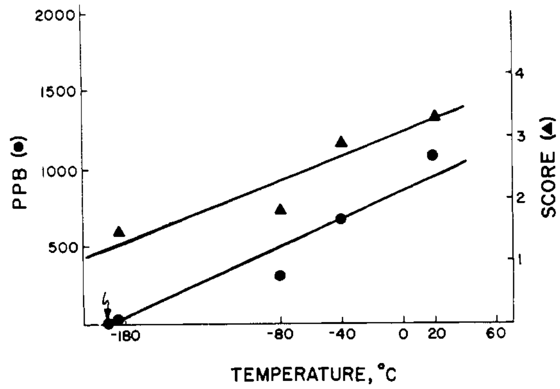


Figure 8. Graph showing a comparison of the relationship of component amount and flavor score of beef irradiated at 5.6 Mrads as a function of temperature. Arrow denotes value for unirradiated control.

Table V. Consumer Panel Ratings for Irradiated Beef Loins[a]

Irrad. temp, °C	Storage time, months	U.S. choice	U.S. commercial
−40	0	5.9	6.1
	3	5.9	5.7
−80	0	6.1	6.4
	3	5.9	5.8
−120	0	6.3	6.5
	3	5.9	5.7
−185	0	6.4	6.4
	3	5.8	5.5
Frozen control	0	6.8	6.4
	3	6.9	6.2

[a] $N = 36$; dose, 4.5–5.6 Mrads; 21° storage.

the relationships of flavor score and component amount may both be linear with temperature, a linear coefficient has been used to test the relationship. In this case:

$$r = \frac{N\Sigma xy - \Sigma x \Sigma y}{(N\Sigma x^2 - (\Sigma x)^2)^{1/2}(N\Sigma y^2 - (\Sigma y)^2)^{1/2}}$$

where x and y are the corresponding values of flavor score and component amount, respectively, and N is the number of values. A value of r close to unity indicates a high degree of correlation. When the calculation is performed using the data from Figure 3 and Table IV, r is 0.98.

The choice of parameters for a commercial process is obviously a series of compromises. The dose is determined by what is required for microbiological safety. The temperature should be as low as possible to ensure retention of natural flavor, but if it is too low, higher doses are required for sterilization. Moreover, it is difficult to achieve very low temperatures (e.g., −185°) in the commercial practice. The compromise seems to be set at about 4.5–5.6 Mrads for dose and −40° for temperature. The rating of such a product by a consumer panel is seen in Table V.

The data are presented for two cuts of meat irradiated at various cryogenic temperatures and stored for 0 and 3 months. The irradiated samples are seen to differ statistically from the control, but not from one another.

When the proper conditions of dose and temperature are employed, a wholly acceptable irradiated meat product can be produced that is both safe and savory.

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