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RADIATION EFFECTS ON BEEF

An Investigation of Some Volatile Components of Irradiated Beef

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The volatile components produced by concurrent radiation-distillation at 5 megarads of raw ground beef have been studied in an effort to identify the substances responsible for the characteristic unpleasant odor of beef preserved by radiation. It has been proved that 3-(methylthio)-propionaldehyde (methional) is a major component of the mixture of at least 12 substances detected, and that it makes a major contribution to the unpleasant odor of irradiated beef. The synthesis of methylthioacetaldehyde, ethylthioacetaldehyde, and 2-(methylthio)-propionaldehyde is reported.

A PROBLEM associated with radiation-sterilization of beef is the production of an unpleasant flavor and odor. This investigation has been carried out in an effort to characterize and identify the substances responsible for the characteristic unpleasant odor of irradiated beef.

Prior to this work Burks (9) had studied the amines produced by irradiation of beef and found ammonia and at least six other amines, the two major components being methylamine and ethylamine. He concluded that volatile bases are partial contributors to the odor of irradiated beef. Merritt (21) studied the volatile components of irradiated beef by means of low-temperature, high-vacuum distillation techniques, gas chromatography, and mass spectrometry. Of the 10 compounds thus identified in a "center cut," methyl disulfide and isobutyl mercaptan alone were present in irradiated beef and absent in nonirradiated beef. The relation of these compounds to the odor of irradiated beef was not directly determined, although it was believed that they probably contribute in part. Odorous compounds were known to be present in the "water fraction."

Batzer and Doty (3) found unusually large amounts of volatile sulfur compounds in irradiated beef. Sribney, Lewis, and Schweigert (28) found carbonyl compounds and peroxides.

In the current study, the isolation of volatile compounds has been accomplished by means of concurrent radiation-distillation of raw, ground beef. This procedure was originally developed for milk (30). Its advantage is that it makes possible, in theory, the isolation of volatile substances very soon after their production by radiation.

Experimental Procedure and Results

Production of Volatile Components of Irradiated Beef. An aqueous slurry of 10 pounds of ground, raw beef was circulated in the usual manner (31) through an irradiation chamber beneath the electron beam of a 1-m.e.v. (General Electric) resonant transformer, to a flash evaporator for the removal of volatile components, and back through the irradiation chamber. The condensate thus obtained was found (31) to possess the typical odor of irradiated beef. The conditions of a typical concurrent radiation-distillation of a ground beef slurry are given in Table I.

Investigation of Irradiated Beef Distillates. Carbonyl Compounds. The distillate (approximately 7 liters) was

Table I. Experimental Conditions of a Typical Concurrent Radiation-Distillation of a Slurry of Ground Beef

Conditions	Quantities
Quantity of ground beef	10 lb.
Volume of beef slurry	8 l.
Dose	5 megarad
Av. pressure at pump	23 mm. Hg
Av. temperature	32-36° C.
Evaporation rate	6 l./hr.
Total distillate collected	6.5 l.

treated with a solution of 2,4-dinitrophenylhydrazine reagent (2 grams per liter of 2*N* hydrochloric acid). A small portion of the neutral, hexane-soluble fraction of the 2,4-dinitrophenylhydrazones obtained was separated by partition chromatography on Celite columns with nitromethane as the stationary phase and hexane the mobile phase. Initial examination of the total mixture indicated, on the basis of its ultraviolet spectrum in chloroform (λ_{\max} . 354 $m\mu$), that dinitrophenylhydrazones of simple aliphatic aldehydes were present (17). Further examination of the fractions showed, by magnesium carbonate fusion, that a number contained sulfur, thus indicating that sulfur-containing aldehydes were present.

Paper chromatographic examination

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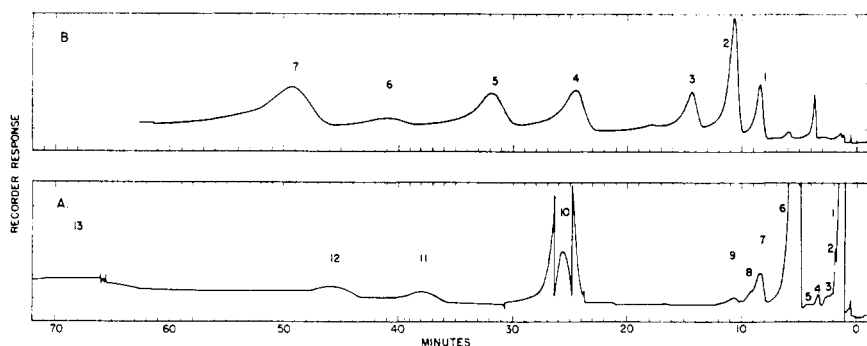


Figure 1. Gas chromatograms

A. Irradiated meat isolate, 5 μ l.

B. Mixture, 10 μ l. of the 7 sulfur-containing reference compounds

Conditions: Column, Perkin-Elmer B; temperature, 105° C.; pressure, 20 p.s.i.; flow, 190 ml. per min.; carrier gas, helium

Table II. Relative Retention Times of Volatile Components of Irradiated and Nonirradiated Beef

[Relative to 3-(methylthio)-propionaldehyde]

Peak	Column				Pluronics ^c irradiated
	Perkin-Elmer B ^a		Silicone-Stearate ^b		
	Irradiated	Non-irradiated	Irradiated	Non-irradiated	
Ether					
1	0.05	0.05	0.06	0.06	...
2	0.07	0.08
3	0.10
4	0.13	0.14
5	0.17	0.15	...
6	0.21	0.20	0.22	0.21	0.20
7	0.33	0.33
8	0.36	0.38	...
9	0.42	0.42	0.46
Irradiation odor					
10	1.00	...	1.00	...	1.00
11	1.48	...	1.42
12	1.79
Irradiation odor, 13	2.49-2.77	...	2.3-2.7	...	1.00

^a Temperature, 105° C.; helium flow rate, 190 ml./min.; sample (1 hr. old) vol. 2 to 5 μ l.

^b Temperature, 125° C.; flow rate, 100 ml./min.; sample (24 hr. old) vol. 2 to 3.5 μ l.

^c Temperature, 105° C.; flow rate, 350 ml./min.; sample (>24 hr. old) vol. 1 μ l.

of sulfur-containing fractions and of authentic 2,4-dinitrophenylhydrazones of 3-(methylthio)-propionaldehyde, and of 3-(methylthio)-butyraldehyde, using solvent systems known (12) to be capable of separating a homologous series of saturated aliphatic aldehyde-2,4-dinitrophenylhydrazones, showed that these sulfur-containing compounds or isomers of these compounds might indeed be present.

Attempts to separate further and isolate the unknown sulfur-containing dinitrophenylhydrazones on a larger scale by partition chromatography on Celite columns in the manner mentioned above were unsuccessful. It was found that the fractions thus obtained decomposed somewhat upon exposure to light and air and thus did not accurately represent the substances present in the beef distillate. Direct evidence that this behavior was typical of dinitrophenylhydrazones of δ -alkyl aldehydes was obtained by observing similar in-

stability in the case of the corresponding derivatives of 3-(methylthio)-propionaldehyde, 3-(methylthio)-butyraldehyde, and 3-(ethylthio)-propionaldehyde.

Since partial decomposition of the derivatives was observed, it appeared that continued use of column chromatography would be complicated by the presence of artifacts. It was decided to drop further separation of dinitrophenylhydrazones until it was determined whether gas chromatography could be applied more profitably to the study of meat volatiles.

Solvent Extraction and Gas Chromatography. Isolation of the volatile components of the beef distillate was carried out by means of solvent extraction of the sodium chloride saturated distillate followed by separation of the extracted residue by gas chromatography. It was recognized that this procedure offered possibility for decomposition of the substances present, but it offered an advantage in that the odor of the isolates

obtained could be compared with the typical unpleasant odor of irradiated beef.

Ether extraction of distillates obtained from concurrent radiation-distillation at 5 megarads of an aqueous slurry of 10 pounds of raw, ground beef yielded, after careful removal of the solvent by distillation, approximately 50 to 90 mg. of a yellow oil which strongly exhibited the irradiated beef odor. The oil was found by sodium fusion to contain sulfur.

Extraction of distillates obtained from 10 pounds of nonirradiated beef in an exactly similar manner yielded approximately 20 to 50 mg. of an oil which also contained sulfur, but which was not at all similar in odor to the characteristic irradiated beef odor.

Gas chromatographic separation of irradiated and nonirradiated beef isolates has been carried out by means of three columns: Perkin-Elmer B (di-2-ethylhexyl sebacate); 1 part of DC 550 Silicone-stearic acid (75) (9 to 1) to 2 parts of Chromosorb (30- to 60-mesh), weight of the stationary phase was 20.5 grams; and 1 part of Pluronics F-68 (Wyandotte Chemical Corp.) to 5.7 parts of firebrick (30- to 60-mesh), weight of the stationary phase was 20.0 grams. All columns were 2 meters long and 1/4 inch in outside diameter stainless steel. Helium was the carrier gas. A Perkin-Elmer Model 154-C Vapor Fractometer with a thermistor-type conductivity cell was used. The recorder sensitivity was 2 or 4 mv. full scale.

Relative retention times—relative to 3-(methylthio)-propionaldehyde—of components of the irradiated and nonirradiated beef isolates are shown in Table II. In each case, the isolates were separated on the Perkin-Elmer B column as soon as solvent removal had been accomplished. Separation on the silicone-stearate column was carried out approximately 24 hours later, while separation on the Pluronics column was carried out at least 30 hours after solvent removal. Thus the diminished number of components detected with the latter two columns was probably as much a result of the age of the isolates as of any inability of these columns to bring about separation.

As shown in Table II, at least 12 components are present in irradiated beef isolates immediately after isolation. The chromatogram of these substances is shown in Figure 1, curve A. Of these 12 components, five have been found in nonirradiated beef (Table II). Observation of the odor of the effluent carrier gas in all chromatographic separations resulted in the determination that two peaks were generally responsible for the characteristic irradiation odor. Neither of these peaks nor any irradiation odor

was found in the separation of nonirradiated beef isolates.

Direct evidence of the chemical nature of the substance represented by peak 10, the major component exhibiting irradiation odor, was obtained by trapping it in 2,4-dinitrophenylhydrazine reagent. The dinitrophenylhydrazone thus obtained melted at 120–121° C. The presence of sulfur in component 10 was proved by modification of Granatelli's (13) method for sulfur determination by Raney nickel desulfurization. Paper chromatography of the derivative (relative R_f value 0.95) and of the 2,4-dinitrophenylhydrazone of 3-(methylthio)-propionaldehyde (relative R_f value 1) in the solvents of Gaddis and Ellis (12) showed these compounds to be very similar. The ultraviolet spectrum (λ_{max} , 359 $m\mu$ in ethyl alcohol) of the unknown derivative was typical (7, 17) of saturated aliphatic dinitrophenylhydrazones and similar to the spectrum of 3-(methylthio)-propionaldehyde 2,4-dinitrophenylhydrazone.

Similar investigation of component 13, which also exhibited irradiation odor, indicated that no sulfur was present, but a very small quantity of a 2,4-dinitrophenylhydrazone derivative was isolated. Paper chromatography of the derivative according to the methods of Gaddis and Ellis (12) indicated that it contained a carbonyl compound having 8 or 9 carbon atoms. The ultraviolet spectrum of the derivative in chloroform had a maximum at 355 $m\mu$, typical of saturated aliphatic aldehydes.

Investigation of component 6, a major constituent of nonirradiated as well as irradiated beef isolates, by the same means indicated that neither sulfur nor a carbonyl compound was present.

Preparation of S-Alkyl Aldehydes as Reference Compounds. In order to determine the identity of the sulfur-containing aldehyde responsible for irradiation odor and present in component 10, a number of authentic samples of such compounds and of their 2,4-dinitrophenylhydrazone derivatives have been synthesized. Physical properties and structural formulas of these compounds are given in Table III. Three of these substances, ethylthioacetaldehyde, 2-(methylthio)-propionaldehyde, and 3-(methylthio)-propionaldehyde, are isomeric and therefore could not necessarily be expected to be separated by paper chromatography of their dinitrophenylhydrazones.

The synthesis of 3-(methylthio)-propionaldehyde (2, 24, 26, 34), 3-(methylthio)-butyraldehyde (8, 32), 3-(ethylthio)-propionaldehyde (10, 27, 33), and 3-(ethylthio)-butyraldehyde (14, 29) had been previously reported in the literature. The synthesis of methylthioacetaldehyde (18, 29), ethylthioacetaldehyde (6), and 2-(ethylthio)-propionaldehyde (27) had been attempted,

Table III. Physical Properties and Structural Formulas of Substances Synthesized as Reference Compounds

Compound	Structure	Refractive Index, n_D^{25}	Melting Point, ° C. of 2,4-Dinitrophenylhydrazone
1. Methylthioacetaldehyde	$\text{CH}_3\text{SCH}_2\text{C}(=\text{O})\text{H}$	1.4780	131.0–131.5
2. Ethylthioacetaldehyde	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{C}(=\text{O})\text{H}$	1.4732	125.5–126.0
3. 2-(Methylthio)-propionaldehyde	$\text{CH}_3\text{CH}(\text{SCH}_3)\text{C}(=\text{O})\text{H}$	1.4723	151.0–151.5
4. 3-(Methylthio)-propionaldehyde	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{C}(=\text{O})\text{H}$	1.4798	119.0–120.5
5. 3-(Methylthio)-butyraldehyde	$\text{CH}_3\text{CH}(\text{SCH}_3)\text{CH}_2\text{C}(=\text{O})\text{H}$	1.4734	81.0–82.0
6. 3-(Ethylthio)-propionaldehyde	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{C}(=\text{O})\text{H}$	1.4778	97.0–97.5
7. 3-(Ethylthio)-butyraldehyde	$\text{CH}_3\text{CH}(\text{SCH}_2\text{CH}_3)\text{CH}_2\text{C}(=\text{O})\text{H}$	1.4710	134.0–135.0 ^a

^a Melting point of semicarbazone derivative; 2,4-dinitrophenylhydrazone was unstable.

but only ethylthioacetaldehyde had been obtained (6) in a form which approached purity. 2-(Methylthio)-propionaldehyde has not been reported in the literature.

Bromoacetaldehyde Dimethylacetal. This compound was prepared from vinyl acetate and bromine, according to the method of Bedoukian (4) in 70.8% yield, boiling point 38.2° C. (8 mm.), n_D^{25} 1.4425. Calculated for $\text{C}_4\text{H}_8\text{O}_2\text{Br}$: C, 28.42; H, 5.37; Br, 47.28. Found: C, 28.08; H, 5.15; Br, 47.09.

Methylthioacetaldehyde Dimethylacetal. Bromoacetaldehyde dimethylacetal (21.5 grams, 0.13 mole) was added dropwise to a solution (chilled in a dry ice bath) of sodium mercaptide which had been prepared from 5.5 grams of sodium in 60 ml. of anhydrous ethyl alcohol and 12.6 grams (0.26 mole) of methyl mercaptan. The resulting reaction mixture was allowed to come to room temperature, was warmed at 50° to 60° C. for 1 hour, and allowed to stand overnight at room temperature. Sodium bromide was removed by filtration and the filtrate diluted with water to approximately twice its volume. This solution was extracted with ethyl ether and the ether extract was dried over anhydrous sodium sulfate. After removal of the ether by distillation at atmospheric pressure, the residue was purified by vacuum distillation in a semimicro column. The product was

obtained in 60.8% yield (10.8 grams), boiling point 55° C. (10 mm.), n_D^{25} 1.4508. Calculated for $\text{C}_5\text{H}_{12}\text{O}_2\text{S}$: C, 44.09; H, 8.88; S, 23.54. Found: C, 43.58; H, 8.91; S, 23.49.

Ethylthioacetaldehyde Dimethylacetal. This compound was prepared in the same manner as the acetal of methylthioacetaldehyde, from 25 grams (0.15 mole) of bromoacetaldehyde dimethylacetal and sodium ethyl mercaptide which had been made from 7 grams of sodium in 100 ml. of anhydrous ethyl alcohol and 19 grams (0.31 mole) of ethyl mercaptan. It was obtained in 62.0% yield (13.9 grams), boiling point 63–64° C. (11 mm.), n_D^{25} 1.4504. Calculated for $\text{C}_6\text{H}_{14}\text{O}_2\text{S}$: C, 47.97; H, 9.39; S, 21.34. Found: C, 48.11; H, 9.54; S, 21.35.

Methylthioacetaldehyde. Compound 1, Table III, was prepared from 4.0 grams (0.029 mole) of the dimethylacetal by hydrolysis in the presence of 8.2 ml. of a 1% solution of aqueous hydrochloric acid. The reaction mixture was heated under reflux for one-half hour, allowed to cool to room temperature, and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the product was purified by vacuum distillation. Compound 1 was obtained in 21.4% yield (0.56 gram), boiling point 35° C. (10 mm.), n_D^{25} 1.4780. Calculated for

Table IV. Relative Retention Times of Authentic Reference Compounds

[Relative to 3-(methylthio)-propionaldehyde]

Compound	Column		
	Perkin-Elmer B	Silicone- searate	Pluronics
1. Methylthioacetaldehyde	0.34	0.41	0.36
2. 2-(Ethylthio)-acetaldehyde	0.59	0.66	0.54
3. 2-(Methylthio)-propionaldehyde	0.44	0.54	0.34
4. 3-(Methylthio)-propionaldehyde	1.00	1.00	1.00
5. 3-(Methylthio)-butyraldehyde	1.33	1.22	1.00
6. 3-(Ethylthio)-propionaldehyde	1.69	1.50	1.42
7. 3-(Ethylthio)-butyraldehyde	2.02	1.79	1.28
Column efficiency ^a for 3-(methylthio)-propionaldehyde	797	432	637

^a Given in number of theoretical plates for 1- μ l. sample calculated by the formula, $n = 16D^2/W^2$ where D = distance from air peak to peak maximum and W = width of peak at the base measured between tangents to the peak inflection points (16).

C_3H_6OS : C, 39.97; H, 6.71; S, 35.57. Found: C, 40.06; H, 6.77; S, 35.62.

The 2,4-dinitrophenylhydrazone derivative was prepared from the dimethylacetal according to the method of Bedoukian (5). The derivative, after recrystallization from 95% ethyl alcohol, melted at 131.0–131.5° C. Calculated for $C_9H_{10}N_4SO_4$: C, 40.00; H, 3.73; N, 20.73; S, 11.86. Found: C, 40.12; H, 3.71; N, 20.71; S, 11.78.

The semicarbazone of methylthioacetaldehyde was prepared from the free aldehyde, melting point 133.5–134° C. Calculated for $C_4H_9N_3SO$: C, 32.64; H, 6.16; N, 28.55; S, 21.78. Found: C, 32.81; H, 6.18; N, 28.69; S, 21.66.

Ethylthioacetaldehyde. Compound 2, Table III, was prepared from 4.8 grams (0.032 mole) of the corresponding dimethylacetal in the manner described above. The product was obtained in 46.9% yield (1.57 grams), boiling point 46.5° C. (10 mm.), n_D^{25} 1.4732. Calculated for C_4H_8OS : C, 46.12; H, 7.74; S, 30.78. Found: C, 46.12; H, 7.80; S, 30.88.

The 2,4-dinitrophenylhydrazone derivative was prepared from the dimethylacetal. The derivative after recrystallization from 95% ethyl alcohol melted at 125.5–126° C. Arens *et al.* (7) give a melting point of 124–125° C. Calculated for $C_{10}H_{12}N_4SO_4$: C, 42.25; H, 4.25; N, 19.71; S, 11.28. Found: C, 42.01; H, 4.24; N, 19.86; S, 11.42.

The semicarbazone of ethylthioacetaldehyde was prepared from the free aldehyde, melting point 93–93.5° C. Calculated for $C_5H_{11}N_3SO$: C, 37.25; H, 6.88; N, 26.06; S, 19.89. Found: C, 37.28; H, 6.79; N, 26.16; S, 19.98.

2-Bromopropionaldehyde Diethylacetal. It was prepared from 101.8 grams (1.75 mole) of propionaldehyde (redistilled) and 80 ml. of bromine according to the method of Kuhn and Grundmann (19). The crude product was purified by distillation in a packed column and was obtained in 64.0% yield (235.8 grams), boiling point 69° C.

(10 mm.), n_D^{25} 1.4368, Marvell and Joncich (20) give n_D^{20} 1.4371. Calculated for $C_7H_{15}O_2Br$: C, 39.83; H, 7.16; Br, 37.85. Found: C, 39.99; H, 7.19; Br, 38.02.

2-(Methylthio)-propionaldehyde Diethylacetal. Bromopropionaldehyde diethylacetal (10 grams, 0.047 mole) was added dropwise to a solution, at 0° C., of sodium methyl mercaptide which had been prepared from 5.5 grams of sodium in 100 ml. of anhydrous ethyl alcohol and 12.5 grams (0.26 mole) of methyl mercaptan. The resulting reaction mixture was brought to room temperature, heated under reflux on a steam bath for 7 hours, and allowed to stand overnight at room temperature. Sodium bromide was removed by filtration. The filtrate was treated with 20 ml. of alcoholic sodium methyl mercaptide, heated under reflux for 8 hours, and left overnight at room temperature. Sodium bromide was again removed by filtration. The filtrate was diluted with water to twice its volume and was extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the crude product was purified by distillation. The product was obtained in 31.9% yield (2.75 grams), boiling point, 76° C. (10 mm.), n_D^{25} 1.4448. Calculated for $C_8H_{18}SO_2$: C, 53.89; H, 10.18; S, 17.98. Found: C, 53.01; H, 9.97; S, 16.45. Gas chromatography of the product on a Perkin-Elmer B column under the conditions given in Table II, showed it to be almost pure. The impurity was 2-bromopropionaldehyde diethylacetal.

2 - (Methylthio) - propionaldehyde. Compound 3, Table III, was prepared, in the usual manner, from 30.0 grams (0.17 mole) of the slightly impure corresponding diethylacetal by hydrolysis in the presence of 30 ml. of 1% aqueous hydrochloric acid. The product obtained was purified by distillation. The distillate thus obtained (3.94 grams, 22.4% yield) was redistilled and the center fraction was found

to be pure, 0.2418 grams, boiling point 40° to 42° C. (27 mm.), n_D^{25} 1.4723. Calculated for C_4H_8OS : C, 46.12; H, 7.74; S, 30.78. Found: C, 46.10; H, 7.76; S, 30.75.

The 2,4-dinitrophenylhydrazone derivative was prepared in 53% yield from the diethylacetal. After recrystallization from 95% ethyl alcohol it melted at 151.0–151.8° C. Calculated for $C_{10}H_{12}N_4O_4S$: C, 42.25; H, 4.25; N, 19.71; S, 11.28. Found: C, 42.37; H, 4.27; N, 19.58; S, 11.00.

The semicarbazone of 2-(methylthio)-propionaldehyde was prepared from the free aldehyde, melting point, 118–118.5° C. Calculated for $C_5H_{11}N_3SO$: C, 37.25; H, 6.88; N, 26.06; S, 19.89. Found: C, 37.16; H, 6.91; N, 26.04; S, 19.91.

3 - (Methylthio) - propionaldehyde. Compound 4, Table III, has been prepared (32) in 50.0% yield from acrolein and methyl mercaptan in the presence of cupric acetate, boiling point, 64° C. (17 mm.), n_D^{20} 1.4789. Bedoukian (5) gives n_D^{20} 1.4790. Its 2,4-dinitrophenylhydrazone was prepared, melting point, 121–122° C. Bedoukian (4) gives a melting point of 120.5° C.

3-(Methylthio)-butyraldehyde. Compound 5, Table III, has been prepared in 76.2% yield from crotonaldehyde and methyl mercaptan in the presence of triethylamine according to the method of Brown, Jones, and Pinder (8), boiling point 65° C. (12 mm.). Brown, Jones, and Pinder (8) give a boiling point of 40° C. (2.5 mm.), n_D^{25} 1.4734. The 2,4-dinitrophenylhydrazone was prepared, melting point 81.0–82.0° C., Brown *et al.* (8) give a melting point of 85–86° C.

3-(Ethylthio)-propionaldehyde. Compound 6, Table III, was prepared (8) from acrolein and ethyl mercaptan in the presence of triethylamine. The yield obtained after purification by vacuum distillation was 17.0%, boiling point 73–74° C. (15 mm.). Parham, Heberling, and Wynberg (23) give a boiling point of 58° to 63° C. (11 mm.), n_D^{25} 1.4778. The 2,4-dinitrophenylhydrazone was prepared, melting point 97.0–97.5° C. Yamada (33) gives a melting point of 105–106° C.

3-(Ethylthio)-butyraldehyde. Compound 7, Table III, has been prepared (14, 29) in 70.0% yield from crotonaldehyde and ethyl mercaptan in the presence of triethylamine, boiling point 81° C. (17 mm.), n_D^{25} 1.4710. Hall and Howe (14) give a boiling point of 92–93° C. (24 mm.) and n_D^{20} as 1.4720. The semicarbazone derivative melted at 134–135° C. Hall and Howe (14) give a melting point of 137.5° C. The 2,4-dinitrophenylhydrazone could not be prepared because of its instability.

Gas Chromatographic Separation of S-Alkyl Aldehyde Reference Compounds. Relative retention times—

relative to 3-(methylthio)-propionaldehyde—were determined for each of the seven synthetic reference compounds on the three columns previously described. These retention times are given in Table IV. The separation obtained by analysis of a mixture of the seven reference compounds on the Perkin-Elmer B column is shown in Figure 1, curve B. It is clear on the basis of this chromatogram and the data given in Tables III and IV that 3-(methylthio)-propionaldehyde is the only compound which is similar in behavior to the substance which produced the typical irradiation odor in component 10.

Identification of Component 10 as 3-(Methylthio)-propionaldehyde. Presumptive evidence that component 10 was 3-(methylthio)-propionaldehyde was provided by its retention time on three gas chromatographic columns, by the presence of sulfur in it, by the ultraviolet spectrum and melting point of its 2,4-dinitrophenylhydrazone, and by its *R_f* value during paper chromatography.

Evidence that component 10 was indeed 3-(methylthio)-propionaldehyde was the similarity of its infrared spectrum with that published by Patton and Barnes (26), and the fact that a mixed melting point of the 2,4-dinitrophenylhydrazone of component 10 (melting point 120–121.0° C.) and of an authentic sample of the 2,4-dinitrophenylhydrazone of 3-(methylthio)-propionaldehyde (melting point 120–120.5° C.) was not depressed (melting point 120–121° C.).

Discussion

On the basis of the evidence presented above, it is believed that 3-(methylthio)-propionaldehyde (methional) has been proved to be present in the volatile components of irradiated beef, and to make a major contribution to the characteristic unpleasant odor of irradiated beef. This had been postulated previously by Witting and Batzer (32) who suggested that this compound, as well as 3-(methylthio)-butyraldehyde, might be present in irradiated beef. No evidence for the presence of the latter compound has been found in the current work. The proposal of Witting and Batzer (32) that 3-(methylthio)-propionaldehyde is an odorless compound is not supported by this work. The observations of Zlatkis (22) on the odor of

methional purified by gas chromatography are supported.

3 - (Methylthio) - propionaldehyde (methional) has been identified in the volatile carbonyl compounds from cheddar cheese (17). It has been suggested by Patton (24) to be an odorous component of processed foods which results from Strecker degradation of methionine. It has been said to be the cause of the sunlight flavor in milk (25). Although neither of these products resembles irradiated beef in odor, it is reasonable to believe that the strong unpleasant odor of pure methional has been dampened by other volatile components present.

The current investigation has been confined to the aqueous distillate obtained by concurrent radiation-distillation of slurries of raw, ground beef. This limitation was imposed because the distillates exhibited the typical irradiated beef odor. It is probable that investigation of components too volatile to remain in the distillate would have resulted in identification of the substances identified by Merritt (27).

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