Hydrocarbons in Irradiated Beef and Methyl Oleate

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Abstract

The presence of hydrocarbons among the volatile compounds in food products, particularly in irradiated meat, was first discovered by Merritt and his co-workers in 1959 (5,6). It is the purpose of this paper to focus wider attention on this significant discovery and to report briefly on new work which relates the formation of hydrocarbons in irradiated meat to lipids.

Experimental

THE PREPARATION of samples of irradiated ground beef and the isolation and collection of the volatile components were accomplished by procedures already described (4). The total condensate was separated by low temp-high vacuum distillation into a "water fraction" and a combined "carbon dioxide-center cut" fraction. The latter was then separated on a programmed, cryogenic temp gas chromatograph (7) employing a 6 ft x ¼ in. packed column and a Ra 226-argon ionization detector. The stationary phase was 5% (wt/wt) squalane on 80–100 mesh firebrick. The temp program was from −65C to 25C at ca. 2C/min. A typical chromatogram is shown in Figure 1. As each major peak of the chromatogram appeared on the recorder it was trapped (1) for mass spectrometric analysis.

Mass spectrometric analysis was also conducted of the volatile compounds collected under vacuum at −196C from irradiated methyl oleate. The procedures for direct fractionation described by Bazinet and Merritt (2) were used for this analysis.

Results and Discussion

The sterilization of beef and other meat products by means of electron or γ radiation is accompanied by chemical changes and a characteristic flavor change which is commonly called irradiation "off-odor." Several groups of investigators have identified some of the volatile compounds isolated from irradiated meats and have demonstrated a quantitative relationship between the presence of these compounds and irradiation dose. All the compounds have been found to be present in unirradiated meat and their presence in greater amt in the irradiated product may contribute to the overall off odor sensation; but their presence, from the viewpoint of chemical composition, is not peculiar to irradiated meat.

We have now shown that homologous series of *n*-alkanes and *n*-alk-1-enes are found in irradiated ground beef and that these hydrocarbons are not found in an unirradiated control sample. Data now available indicate contribution of these hydrocarbons to the off odor sensation. The volatile compounds identified from irradiated ground beef are summarized in Figure 1. The samples were irradiated at 2,4 and 6 megarads. All members of the homologous series of *n*-alkanes and *n*-alk-1-enes from C_2 to C_8 except ethane were found. Higher homologs were not found, however, because of the limit of volatility imposed by the method of separation employed, i.e., vacuum distillation at −80C. If present among irradiated beef volatile compounds, the higher homologs would be found in the "water fraction" which has not been analyzed in this study. In a subsequent investigation, however, Wick (12) has employed gas chromatographic separation and IR analysis of an extract of an aqueous distillate of the volatile compounds in an irradiated beef slurry. Her data suggest that C_9–C_{12} *n*-alkanes and *n*-alk-1-enes are present.

The carbonyl and sulfur compounds were easily identified among the volatile compounds isolated from unirradiated ground beef, but no hydrocarbons could be found. (Wick also reported that hydrocarbons were found only in irradiated samples.) Moreover, in the "carbon dioxide center-cut fraction," the relative abundance of hydrocarbons is much greater than that of other types of compounds (see Fig. 1). It is clearly evident that hydrocarbons are formed in beef by radiation and it seems that their formation in large amt also contributes to the off odor.

The hydrocarbons produced by irradiation of ground beef are believed to arise from the lipid. This hypothesis is supported by the fact that hydrocarbons have been shown to be present among the thermal decomposition products of soybean oil and methyl oleate and the oxidation products of safflower and olive oil (9–11). Traces of hydrocarbons were also found among the volatile compounds isolated from oxidized potato granules (3).

We have found that hydrocarbons are produced in abundance upon irradiation of methyl oleate. The mass spectrometric analysis of the volatile products isolated from a sample irradiated under vacuum with a dose of 8 megarads showed the presence of both the

Gas chromatogram of the "center cut" of the volatile components isolated from a sample of irradiated ground beef[a]

Hydrocarbons	Carbonyl Compounds
1. Ethene Propene, propane	2. Ethanal
6. *n*-But-1-ene, *n*-butane	7. But-3-en-2-one
11. *n*-Pent-1-ene	10. Propenal
13. *n*-Pentane	12. Propanone
16. Benzene	14. Butanone
18. *n*-Hex-1-ene	24. But-2-enal
19. *n*-Hexane	
25. *n*-Hept-1-ene	Sulfur Compounds
27. *n*-Heptane	Hydrogen sulfide[b]
28. *n*-Oct-1-ene	3. Methanethiol
29. *n*-Octane	4. Carbonyl sulfide
26. Toluene	8. 2-Thiapropane
Alcohols	15. Carbon disulfide
21. Methanol	20. 2,3-Dithiabutane
23. Ethanol	

[a] Peaks 5, 9, 17, 22 were not identified.
[b] Not detected on gas chromatograph, but identified by the mass spectrometer among the components trapped as peaks 1, 2 and 3.

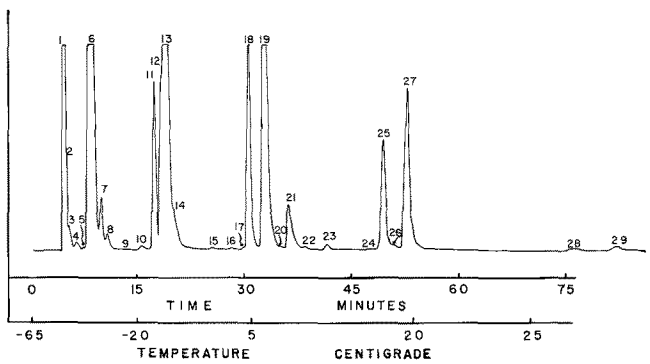

FIG. 1.

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C_{3-7} *n*-alkanes and *n*-alk-1-enes.

New techniques employing programmed cryogenic temp gas chromatography (7) with rapid scanning mass spectrometry (8) now permit easy separation and identification of the volatile compounds in complex mixtures. These techniques have already been used to verify and extend the analyses described in this paper. For example, methane, ethane and some branched chain hydrocarbons now have been identified. These methods are also currently being used to extent the investigations to meats other than beef and to several fundamental lipid substances related to meats. The discovery of the widespread occurrence of hydrocarbons in irradiated lipids as well as in oxidized and thermally decomposed lipids suggests that much further detailed investigation is required to understand the various mechanisms involved in the degradation of natural fats and oils.

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Lipid Metabolism in Germinating Flaxseed[1]

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Abstract

Flaxseed was germinated in the dark at 25C for 90 hr and the amt of triglycerides, free fatty acids (FFA) and phospholipids, as well as the fatty acid composition of each, were determined at 18-hr intervals. The amt of FFA increased greatly during germination. There was no preferential metabolism of any particular fatty acid in either the triglyceride or FFA fractions. The percentage of linolenic acid in the phospholipids increased as germination progressed. Behenic, lignoceric and cerotic acids were observed in the FFA fraction after 54 hr of germination. Odd-numbered saturated and unsaturated acids, indicative of an α-oxidation mechanism, were observed in the FFA fraction at 54 hr and in the triglyceride fraction at 72 hr.

Introduction

THE METABOLISM of storage lipid, primarily triglycerides, provides the main source of energy for the germination process in oil-bearing seeds. Although both the glycerol and fatty acid portions of the triglyceride molecule are utilized during germination, the metabolism of the fatty acids was of primary interest in this study. Many workers have studied the changes in the lipids of germinating flaxseed (*Linum usitatissimum* L.) (1). However, most of these reports have dealt with the gross changes in the lipids such as iodine value (I.V.), acid value and oil content. The most extensive study of the changes in germinating flax was made by Desveaux and Kogane-Charles in 1952 (2). They reported the fresh wt, dry wt, total lipid content, FFA content, the amt of reducing, nonreducing and easily hydrolyzable carbohydrates, I.V., neutralization equivalent, non-saponifiable content and the organic acids during 12 days of germination. Most recently, Huber and Zalik (3) reported the changes in oil content, fatty acid composition and amino acid composition in developing and germinating flaxseed. The latter work was the first to use gas chromatography to determine the fatty acid composition during germination.

Although much is known about the changes in lipid content during germination, little is known about the changes in the fatty acid composition of the individual lipid classes. In most of the previous studies, petroleum ether was used as an extraction solvent and consequently the polar lipids were not quantitatively extracted. In addition, observations were not made during the initial 5 days of germination, which Halvorsen has shown to be period of active lipid metabolism (4). Desveaux and Kogane-Charles (2) reported a 23% decrease in the I.V. of the oil while Ermakov and Ivanov (5) and Paatela (6) observed no significant change in the I.V. during germination.

In view of the inadequacies and conflicting results of previous studies on germinating flaxseed, it seemed advisable to reexamine the changes in lipids which occur during the initial germination period.

Experimental

General Comments. All solvents were distilled prior to use. All operations involving the total lipid extract were conducted under nitrogen to reduce the possibilities of oxidation. When not in use, the total lipid extract was stored under nitrogen in the dark at −17C. All of the spectrophotometric analyses were conducted with a Beckman DK-2 spectrophotometer using cells with a 1-cm light path.

Germination. Flaxseed, variety C.I. 1303, was surface sterilized with a 2.67% aqueous sodium hypo-

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[2] Crops Research Div., ARS, USDA.
[3] This paper is taken in part from the dissertation for the degree of Doctor of Philosophy of D.C.Z., 1964.