Effect of Free Fatty Acids on the Radiolysis of Triglycerides

Quantitative data are provided on some of the major radiolytic products of triglycerides, free fatty acids, and mixtures of both. A free fatty acid gives rise to a much greater amount of the "principal hydrocarbon" (i.e., the alkane with one carbon atom less than the parent fatty acid) than does the corresponding simple triglyceride. Thus, the amount of tridecane from myristic acid was 34 times greater than that from trimyristin and that of pentadecane from palmitic acid was 25 times greater than that from tripalmitin. Furthermore, the presence of free carboxylic acids appeared to accelerate the formation of the major hydrocarbon from the triglyceride. Some speculations on this behavior are proposed.

In previous publications, we provided quantitative data concerning radiolysis of a number of natural fats and simple triglycerides (Dubravcic and Nawar, 1968; Champagne and Nawar, 1969; LeTellier and Nawar, 1972). The radiolytic breakdown of triglycerides yields a series of saturated and unsaturated hydrocarbons, the type and quantity of which depend on the glyceride fatty acid composition. Of the hydrocarbons produced from each fatty acid, two were formed in relatively large quantities. One had one carbon atom less than the parent fatty acid and the other had two carbons less than the acid and an extra double bond. An aldehyde of the same chain length as the fatty acid was also formed in relatively large amounts. Based on the observation that the production of the "major" hydrocarbons increased linearly with an increase in radiation temperature or dose, a method was described to detect irradiation treatment in foods of known fatty acid composition (Balboni and Nawar, 1970). Neither the presence of air or moisture during the irradiation treatment nor mild heating had any significant effect on the amounts of the major hydrocarbon formed. In the course of additional work, however, we found that the presence of even small amounts of free fatty acids in natural fats or triglycerides resulted in remarkable increases in the formation of the principal hydrocarbon.

An experiment was therefore designed to investigate the effect of irradiation on free fatty acids and their mixtures with pure triglycerides. Samples of trimyristin (TM), tripalmitin (TP), myristic acid (MA), palmitic acid (PA), a mixture of 90% TM and 10% PA, and a mixture of 90% TP and 10% PA were irradiated at 6 megarads and 25 °C and in each case the principal alkane (the C_{n-1}), the principal alkene (the C_{n-2}), and the major aldehyde were measured. The irradiation treatment and the analyses were carried out as described previously (Dubravcic and Nawar, 1968).

The results given in Table I show that the quantity of tridecane in irradiated myristic acid was 34 times larger than that in irradiated trimyristin, and the amount of pentadecane from palmitic acid was 25 times greater than that from tripalmitin. Similar results were reported by Beke et al. (1974) who found that the free fatty acids liberate about 20 times more C_{n-1} alkane than the triglyceride.

The data in Table I further demonstrate that the free acid not only produces much greater quantities of the principal hydrocarbon, but also accelerates its formation from the triglyceride. Thus, irradiation of a mixture of PA and TP produced more pentadecane (394 μg/100 g) than would be expected (300 μg) based on the percentage of each of the individual substrates in the mixture. Similarly, the presence of 10% PA in trimyristin resulted in the formation of 164 μg of tridecane as compared to the amount of 95 μg/100 g expected from the mixture.

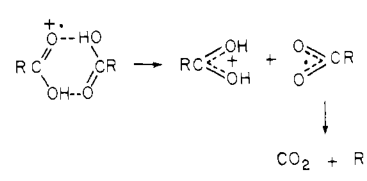
The amounts of the major alkenes produced from the free acids are only about 3 times larger than those resulting from the irradiation of their respective triglycerides. This may indicate that only one of the three component acyl groups per triglyceride molecule is involved in the production of the major alkene, since if calculated on the basis of micrograms of alkene/mole of substrate the amounts produced from free acids would be the same as those from triglycerides. The free acids produced approximately 7 times more of the major aldehyde than their respective simple triglycerides. Unlike the major alkane, the alkene and the aldehyde resulting from TP–PA mixtures were produced in about the same amounts expected from simple additive contribution of each substrate in the mixture with no catalytic effect exhibited by the free acid.

Table I. Quantitative Analysis[a] of the Major Hydrocarbons and Aldehydes Formed in Fatty Acids and Triglyceride–Acid Mixtures by Irradiation at 6 M and 25 °C (μg/100 g)

	Triglycerides		Free acids		Mixtures, 90/10	
	TM	TP	MA	PA	TM/PA	TP/PA
Alkanes						
13[b]	106		3560		164	
15		88		2210		394
1-Alkenes						
12	11		32		14	
14		13		46		16
Alkanals						
14	38		254		46	
16		21		158		32

[a] Averages from duplicate determinations. [b] Carbon number; TM = trimyristin; TP = tripalmitin; MA = myristic acid; PA = palmitic acid.

In the case of both the triglyceride and the free fatty acid, the major alkane can arise via homolytic cleavage at the α carbon–carbon bond of the fatty acid moiety followed by abstraction of a hydrogen atom by the alkyl radical, cleavage at the acyl–oxygen bond followed by loss of CO from the acyl radical, or formation of the acyloxy radical $RC(O_2)\cdot$ followed by loss of CO_2 (LeTellier and Nawar, 1972). On the other hand, the free acid can also undergo decarboxylation readily giving rise to the formation of relatively large quantities of the C_{n-1} hydrocarbon. Radiolytic decarboxylation in the case of free fatty acids may be enhanced by the carboxyl–carboxyl associative dimeric condition in the condensed state which facilitates intermolecular hydrogen atom transfer to the electron-deficient oxygen atom as proposed by Howton and Wu (1967):



In view of the above, it is possible to speculate on the catalytic effect of free acids on the formation of the C_{n-1}

alkane from triglycerides. The $RC(O_2)\cdot$ radical is a major intermediate in the radiolysis of triglycerides resulting from preferential scission at the glyceryl carbon–oxygen bond. This radical may suffer one of two possible fates. It can abstract a hydrogen atom to produce the free fatty acid, a major radiolytic product of all triglycerides. Or, it may lose CO_2 as shown above to yield the principal alkane. It can be seen that the second reaction would be favored perhaps at the expense of the first, by the presence of free carboxylic acids or the relatively great amounts of $RC(O_2)\cdot$ radicals produced from such acids and competing for termination by hydrogen abstraction.

It is evident from the results of this study that the free fatty acid (FFA) content must be carefully considered if quantitative analysis of the "major" hydrocarbons is to be used as a tool for evaluating the severity of irradiation in fat-containing foods. It is equally clear that radiolytic decomposition may be reduced by keeping the level of FFA in such foods to a minimum.

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CORRECTIONS

CHANGES IN CONCENTRATIONS AND INTERRELATIONSHIPS OF PHYTATE, PHOSPHORUS, MAGNESIUM, CALCIUM, AND ZINC IN WHEAT DURING MATURATION

In this article by Aratoonnaz Nahapetian and Abdollah Bassiri [*J. Agric. Food Chem.* **23**(6), 1179 (1975)], some of the data in Table III, p 1181, were not accurate. The correct information appears in the following table.

Table III. Average Changes in Concentrations of Mg, Ca, and Zn in Wheat (*Triticum aestivum* L.) Heads during Maturation

Days after anthesis	Concentration in dry matter[a]		
	Mg, ppm	Ca, ppm	Zn, ppm
0	751 ± 170	1331 ± 206	30 ± 3
7	728 ± 103	1226 ± 267	31 ± 4
14	794 ± 177	1236 ± 373	36 ± 4
21	874 ± 167	885 ± 159	32 ± 4
26	809 ± 215	731 ± 159	36 ± 6
48	1132 ± 659	1261 ± 562	36 ± 7

[a] Mean plus or minus standard deviation.

DETERMINATION OF MALATHION, MALAOXON, AND MONO- AND DICARBOXYLIC ACIDS OF MALATHION IN FISH, OYSTER, AND SHRIMP TISSUE

In this article by Gary H. Cook and James C. Moore [*J. Agric. Food Chem.* **24**(3), 631 (1976)] in Table III, p 634, the value for MCA in the gut should read 31.4 $\mu g/g$ instead of 1.4 $\mu g/g$.