Comparison of Radiolytic Compounds from Saturated and Unsaturated Triglycerides and Fatty Acids

M. VAJDI, W.W. NAWAR, Department of Food Science and Nutrition, University of Massachusetts, Amherst, Massachusetts 01003 and
C. MERRITT, JR., Food Sciences Laboratory, U.S. Army Natick Research and Development Command, Natick, Massachusetts 01760

ABSTRACT

Formation of certain radiolysis products from palmitic acid, oleic acid, tripalmitin and triolein has provided a means for comparing the radiolytic effects in saturated and unsaturated triglycerides and fatty acids. These substances were chosen to represent the major constituents of fat found in beef. Fractionation and concentration of radiolytic compounds from the irradiated samples was accomplished by the means of size exclusion chromatography. Quantitative and qualitative analyses were performed using a combined GC/MS computer system. In addition to the primary radiolytic compounds, recombination products of relatively high molecular weight and various propanediol diesters from the corresponding glyceryl moities were identified. Quantitative analyses indicated a greater yield of various radiolytic compounds from free fatty acids than from the corresponding triglycerides. Similarly, radiolytic compounds were produced in greater quantities from the saturated fats than the unsaturated fats. Most of the radiolytic compounds identified in this study have not been previously reported.

INTRODUCTION

Studies of the effect of radiation on tributyrin and tricaproin (1,2,3) have helped us to elucidate the mechanism for the formation of radiolysis products. The concepts evolved have led to a further investigation of the formation of related compounds in larger triglycerides and in natural fats to establish that the behavior in irradiated natural fats is the same as predicted from the radiolysis of pure triglycerides and fatty acids. Therefore, the effect of radiation on tripalmitin, triolein, and corresponding fatty acids was studied to ascertain the formation of recombination products similar to those found in the low molecular weight triglycerides, to compare the formation of radiolytic compounds found in fatty acids and triglycerides, and to evaluate differences in radiolytic behavior in the saturated and unsaturated systems.

EXPERIMENTAL PROCEDURES

The compounds studied (tripalmitin, triolein, palmitic acid, and oleic acid) were purchased from ANALABS, Inc., North Haven, CT. Purity of each compound was established by GC on OV 17 and FFAP columns. Tripalmitin contained a trace amount of dipalmitin. The other compounds were chromatographically pure.

The compounds were irradiated in air with 50 Mrads at 25 C. The samples were held at 5 C after irradiation until analyzed.

Separation of the radiolytic products from the irradiated triglycerides and fatty acids was accomplished by size exclusion chromatography. The chromatograph was a Waters Associates, Inc., Model ALC202 equipped with UV and RI detectors and 2 ml loop injection port. The column system was comprised of 16 ft. of Poragel 60Å followed by 8 ft of Poragel 100Å in 3/8" o.d. tubes. The elution solvent was chloroform. Various fractions were collected and concentrated under nitrogen for the GC/MS analysis.

In the case of the irradiated fatty acids, an additional step was used to separate the radiolytic compounds from the substrate fatty acids. This was accomplished after the size exclusion separation by KOH-silicic acid chromatography of fractions II, III and IV. The ethyl ether eluate from the KOH/SiO_2 column was evaporated under nitrogen and introduced to the gas chromatograph for analysis. GC/MS analysis of the radiolysis products was performed as described previously (3).

RESULTS AND DISCUSSION

The gel permeation chromatograms of the four irradiated samples are presented in Figure 1. The formation of substances apparently of larger size than the triglyceride (the peak seen preceding the triglyceride) was more predominant in irradiated triolein than that of irradiated tripalmitin (Fig. 1) as indicated by the ratios of the corresponding peaks. A similar observation can be made in the case of the irradiated fatty acids since the peak preceding the fatty acid peak is larger for oleic than palmitic.

The radiolysis products found in Fractions III and IV from the triglycerides and II, III and IV from the fatty acids were determined by GC/MS and are listed in Table I. The radiolytic compounds found in triglycerides consisted of the n-alkane and n-alkene of one carbon atom less than

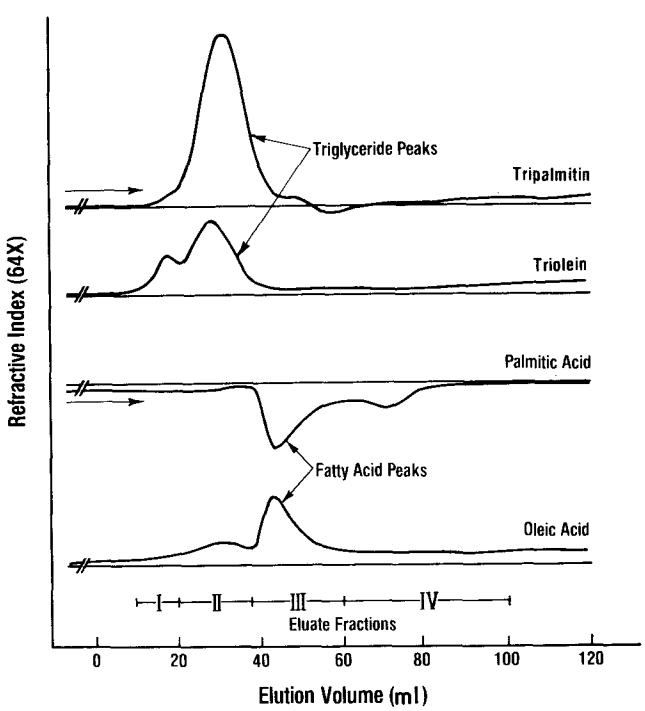

FIG. 1. Gel Permeation chromatography of irradiated triglycerides and fatty acids. Fraction numbers I - IV refer to eluates from chromatograms of all four substances.

TABLE I

Compounds Identified in the Irradiated Triglycerides and Fatty Acids[a]

Tripalmitin		Palmitic acid	
Compound	IDT	Compound	IDT
Pentadecane	A	Pentadecane	A
Palmitic acid	A	Gamma-palmitolactone	A
Gamma-palmitolactone	A	Delta-palmitolactone	H
Delta-palmitolactone	H	Nonacosane	H
Triacontane	A	Triacontane	A
Tetradecyl pentadecyl ketone	H	Dodecyl pentadecyl ketone	H
Dipentadecyl ketone	A	Tridecyl pentadecyl ketone	H
Pentadecyl palmitate	A	Tetradecyl pentadecyl ketone	H
1,2-hexadecanoyl propanediol diesters	A	Dipentadecyl ketone	A
1,3-hexadecanoyl propanediol diesters	A	Tridecyl palmitate	H
		Pentadecyl palmitate	A
Triolein		**Oleic Acid**	
Compound	IDT	Compound	IDT
Heptadecene	A	Heptadecene	A
Oleic acid	A	Gamma-oleolactone	H
Gamma-oleolactone	H	Tritriacontadiene	H
Tetratriacontadiene	H	Tetratriacontadiene	H
Hexadecadienyl, heptadecenyl ketone	H	Tetradecenyl, heptadecenyl ketone	H
Diheptadecenyl ketone	H	Pentadecenyl, heptadecenyl ketone	H
Hexadecadienyl oleate	H	Hexadecadienyl, heptadecenyl ketone	H
1,2-octadecenoyl propanediol diesters	A	Diheptadecenyl ketone	H
1,3-octadecenoyl propanediol diesters	A	Tetradecenyl oleate	H
		Hexadecadienyl oleate	H

[a]IDT: = Identification; A: = GC/MS identification based on authentic compounds; H: = GC/MS identification based on homolegous series and literature.

TABLE II

Quantitative Analysis of the Most Abundant Primary and Recombination Products Found in Irradiated Model Systems

Compound	Tripalmitin (mg/1gm)	Palmitic acid (mg/1gm)	Triolein (mg/1gm)	Oleic acid (mg/1gm)
Pentadecane	4.5	41.6		
Heptadecene			1.3	10.4
Palmitic acid	46.9	---		
Oleic acid			6.9	---
Dipentadecyl ketone	---	1.99		
Diheptadecenyl ketone			---	0.91

the constituent fatty acid, the free fatty acid, certain lactones, ketones and esters. As expected the free acids gave rise to similar radiolytic compounds with the exception of the diol diesters. The formation of these compounds is consistent with predictions based on mechanisms proposed earlier for the radiolysis of low molecular weight triglycerides (1,2,3).

Table II gives quantitative values for three of the major radiolytic products; i.e., the C_{n-1} hydrocarbon, the free fatty acid and the symmetric ketone. Irradiation of the free fatty acid produces more hydrocarbon and symmetric ketone than the corresponding triglyceride. A similar observation for the formation of the C_{n-1} hydrocarbon from various other acids and glycerides has been reported (4,5). If the radiolysis products from saturated and unsaturated compounds are compared, it can be seen that the major hydrocarbon, the free fatty acid and the symmetric ketone are produced in lesser quantities from the unsaturated compounds.

These results may be rationalized on the basis of the different localization of the electron loss upon irradiation. As previously explained, for the saturated compounds the charge density resides mainly on the carboxy oxygen enhancing cleavage near the carbonyl group which results in the production of the major primary radiolytic products (1). With the saturated compounds, on the other hand, the charge can also reside at double bond sites, thus reducing the probability of cleavage in the carbonyl region. Consequently, the amounts produced of radiolytic compound with carbon chains equal or nearly equal to that of the substrate fatty acid are considerably lessened.

ACKNOWLEDGMENT

The authors are indebted to Dr. J.H. Cornell who synthesized certain reference compounds, and to W.G. Yeomans, and R.A. Graham for their contributions to the acquisition and computer processing of mass spectral data.

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[Received June 8, 1978]