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Received for review October 16, 1973. Accepted February 14, 1974. Mention of a trademark of a proprietary product does not constitute a guarantee or warranty of the product by the U. S. Department of Agriculture, and does not imply its approval to the exclusion of other products that may also be suitable.

Secondary Products from the Radiolysis of Tricaproin

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Tricaproin has been used as a model system to study the radiolysis of simple triglycerides. In addition to the primary radiolytic fragments and the recombination products reported earlier, certain compounds believed to result from more than one cleavage in the same parent molecule,

or from the decomposition of some primary intermediates, were classified as "secondary radiolytic products." In the present report, the identification and mode of formation of these compounds are discussed.

In our studies on the effects of high-energy radiation on fats, we selected tricaproin as a model system to investigate the mechanisms of radiolysis in saturated simple triglycerides. The use of this low molecular weight substrate permitted the separation and detection of both the short-chain radiolytic fragments and the higher molecular weight products. Among the radiolytic products 29 compounds, classified as "primary fragments," were found to result from scission of only one bond in the parent molecule. This group included hydrocarbons, aldehydes, methyl esters, ethanediol diesters, propane and propenediol diesters, diglycerides, and triglycerides (LeTellier and Nawar, 1972a). Quantitative analysis of these components indicated that cleavage of the ester bond (acyloxy-methylene) is the most predominant point of cleavage, while the acyl-oxy bond was the second most radiolabile linkage. More recently, we reported on the identification of 22 additional compounds which were classified as "recombination products," and believed to be produced by the combination of primary radicals, *i.e.* radicals formed by the cleavage of one bond in the parent molecule (LeTellier and Nawar, 1972b). These compounds consisted of longer chain hydrocarbons, ketones, esters, alkanediol diesters, and glyceryl ether diesters. In the present paper, the identification of certain other radiolytic products which could not be classified in the above two categories is discussed. Since these compounds are believed to result from more than one cleavage in the same molecule or from the decomposition of some primary intermediates, they are classified as "secondary products."

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EXPERIMENTAL SECTION

Five-gram samples of purified tricaproin were irradiated under vacuum (10^{-2} Torr) at 6 megarads and 17° . The methods used for irradiation of the samples and for the isolation and identification of the radiolytic products were described in detail previously (Nawar *et al.*, 1969; LeTellier and Nawar, 1972a). The compounds identified as secondary products are listed in Table I. With the exception of acetylene and hexanol, reference standards were synthesized in the laboratory and their structure verified by gc-mass spectrometry and infrared analysis.

Isopropyl and heptyl hexanoate were prepared by the reaction of hexanoyl chloride with the appropriate alcohol according to Mattson and Volpenhein (1962).

2-Oxopropyl hexanoate was synthesized by the reaction of the sodium salt of hexanoic acid with chloro-2-propanone according to Hann *et al.* (1930). The sodium salt of the acid was prepared by reacting equimolar amounts of sodium hydroxide and hexanoic acid in water. The water was then removed under vacuum, the anhydrous salt placed in *N,N'*-dimethylformamide, and an equimolar amount of chloro-2-propanone added. The reaction was allowed to proceed for 2 hr at 80° . A few milliliters of a saturated solution of NaHCO_3 was added and chloroform was used to extract the ester from this solution. The ester was then purified by gas chromatography on a 10% Se-30 column. The mass and ir spectra of 2-oxopropyl hexanoate are shown in Figure 1. The molecular ion is of very low intensity (0.6%). The spectrum exhibits many ions which are characteristic of the fragmentation pattern of straight-chain aliphatic esters (Sharkey *et al.*, 1959)—an alkyl ion derived from the acid moiety (m/e 71), an intense acylium ion (m/e

Table I. Secondary Products Isolated from Tricaprin Irradiated at 6 Megarads

Compound	Identification	
	Gc	Mass spectra
Acetylene	+	
Hexanol	+	+
Isopropyl hexanoate	+	+
2-Oxoethyl hexanoate	+	+, a
2-Hexanoyloxypropenal	+	+, a, b
2-Oxopropyl hexanoate	+	+, a
Heptyl hexanoate	+	+

^a Also confirmed by ir. ^b Also confirmed by analysis of its hydrogenation products.

99), a McLafferty rearrangement ion (m/e 116), and an ion resulting from 3,4-cleavage of the acid moiety (m/e 129). There also is a very intense peak at m/e 43 which probably results from cleavage of the bond α to the keto group ($[\text{CH}_3\text{CO}]^+$) and a characteristic ion at m/e 142 which appears to arise from the expulsion of formaldehyde from the molecular ion. This latter mode of decomposition is similar to that observed in the mass spectra of α -glycol diesters (Sasaki *et al.*, 1967). In addition, there are two ions of interest at m/e 74 and 87, long known to be characteristic of methyl esters. It is believed that these two fragments could also arise in the mass spectrum of 2-oxopropyl hexanoate by the scission between C_1 and C_2 of the alcohol moiety of the McLafferty (m/e 116) and

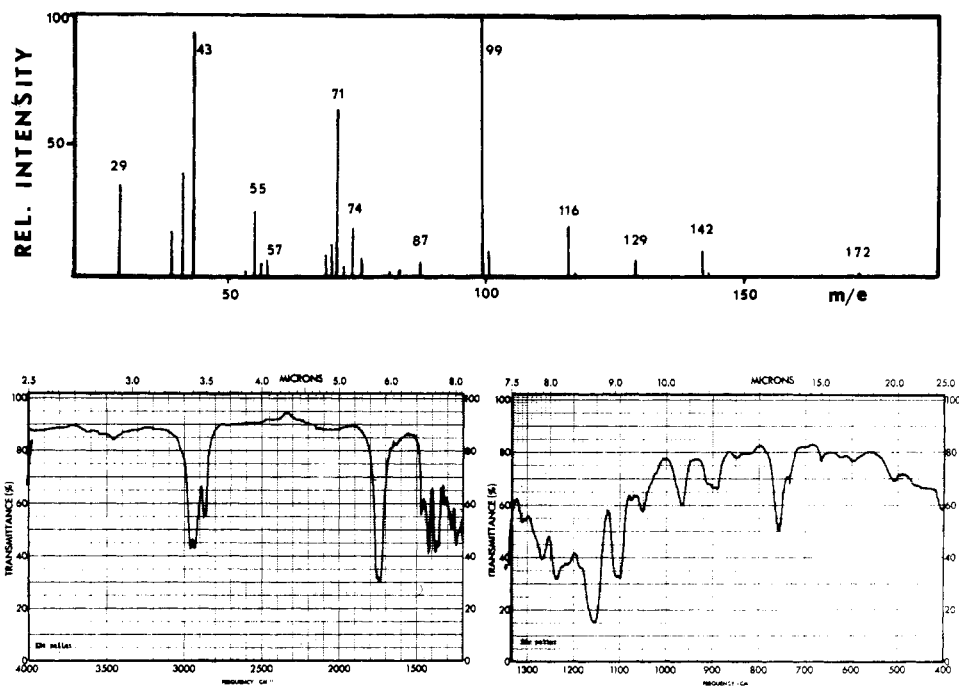


Figure 1. Mass and infrared spectra of 2-oxopropyl hexanoate.

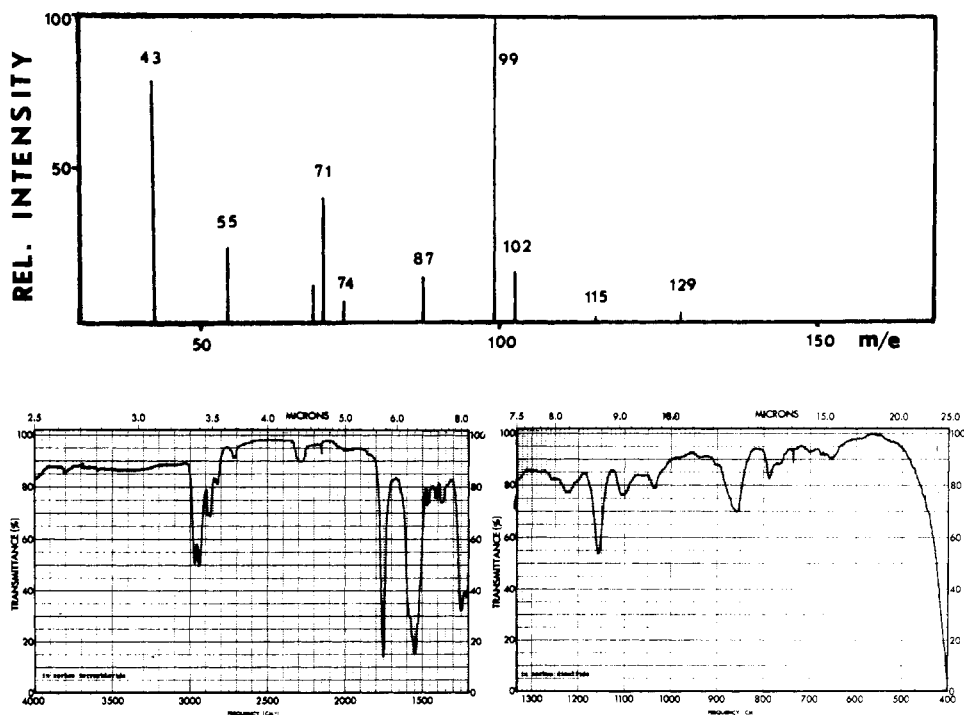


Figure 2. Mass and infrared spectra of 2-oxoethyl hexanoate.

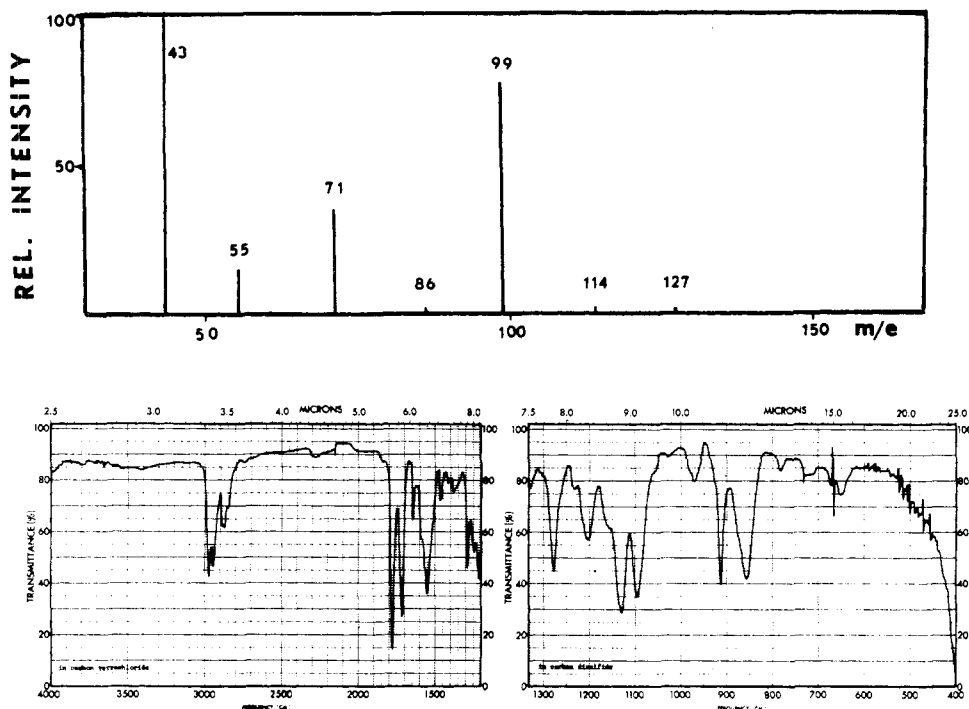


Figure 3. Mass and infrared spectra of 2-hexanoyloxypropenal.

3,4-cleavage (m/e 129) ions, respectively, with the rearrangement of a proton. A metastable ion observed at m/e 47.2 supports the decomposition of m/e 116 to 74 (Beynon *et al.*, 1965). The ir spectrum (Figure 1) exhibits two incompletely resolved carbonyl stretching bands; one at 1740 cm^{-1} for the ketonic carbonyl and the other at approximately 1760 cm^{-1} for the ester carbonyl. In addition, the ester C-O-C symmetric and asymmetric vibrations are present near 1100 and 1255 cm^{-1} , respectively. An intense peak at 1425 cm^{-1} accounts for the presence of the active methylene group (Nakanishi, 1964).

For the synthesis of 2-oxoethyl hexanoate a 5% aqueous HCl solution of dimethyl chloroacetal was refluxed for 15 min to cleave the acetal. The aldehyde was extracted with ether, the ether evaporated, and the aldehyde placed in *N,N'*-dimethylformamide. The sodium salt of hexanoic acid was added to this solution and the reaction allowed to proceed for 2 hr at 80° . The resulting ester was extracted with ether, washed with a 20% solution of NaHCO_3 , and dried. The mass and ir spectra of 2-oxoethyl hexanoate are given in Figure 2. The mass spectrum contains neither a molecular ion nor an expulsion ion. The ion of highest mass (m/e 129) probably originates by loss of the aldehyde group from the molecule-ion ($[\text{M} - \text{CHO}]^+$). Cleavage of the acyloxy-methylene bond resulting in the ion $[\text{CH}_2\text{CHO}]^+$ most likely accounts for the intense peak at m/e 43. The fragment at m/e 87 may be formed by loss of the alkyl group from the acid moiety of the molecule-ion ($[\text{M} - 71]^+$). The absence of the protonated acid ion (m/e 117) in the mass spectra of the 2-oxoalkyl hexanoates serves as a facile means of differentiating between their spectra and those of the alkyl hexanoates of the same molecular weight. The ir spectrum of 2-oxoethyl hexanoate contains only one carbonyl band (1750 cm^{-1}). However, the doublet at 2720 and 2825 cm^{-1} (Saier *et al.*, 1962) arises from the aldehyde group while the bands at approximately 1105 and 1158 cm^{-1} originate from the ester function.

The compound 2-hexanoyloxypropenal was characterized by comparison with a standard prepared from glycer-aldehyde by dissolving the latter in *N,N'*-dimethylformamide at 80° and adding hexanoyl chloride in excess amount. The mass and ir spectra of 2-hexanoyloxypropenal are shown in Figure 3. The mass spectrum exhibits a

fragmentation pattern very similar to that of 2-oxoethyl hexanoate. While a molecular ion is absent, an alkyl ion (m/e 71), an acylium ion (m/e 99), a McLafferty rearrangement ion (m/e 114), an ion resulting from 3,4-cleavage (m/e 127), and an ion (m/e 86) which appears to result from the loss of CO from the McLafferty ion (equivalent to m/e 74 in 2-oxoethyl hexanoate) are all present in this spectrum. The reason why the fragment m/e 43 is so intense is unknown. In the ir spectrum the C=C stretch is observed at 1650 cm^{-1} . The vinyl ester results in the carbonyl stretching band at 1780 cm^{-1} and in the C-O-C bands at 1094 and 1130 cm^{-1} . The aldehyde C-H doublet is seen at 2740 and 2850 cm^{-1} and the aldehyde carbonyl at 1715 cm^{-1} . The aldehyde group in this molecule is conjugated with the double bond and this is obvious from the comparison of this spectrum with that of 2-oxoethyl hexanoate. In the latter, the aldehyde carbonyl is present at 1750 cm^{-1} (unresolved from the ester carbonyl) but, in the spectrum of 2-hexanoyloxypropenal, the aldehyde carbonyl frequency is shifted down 35 cm^{-1} . Further evidence for the structure of the compound identified as 2-hexanoyloxypropenal was obtained from analysis of its hydrogenation products.

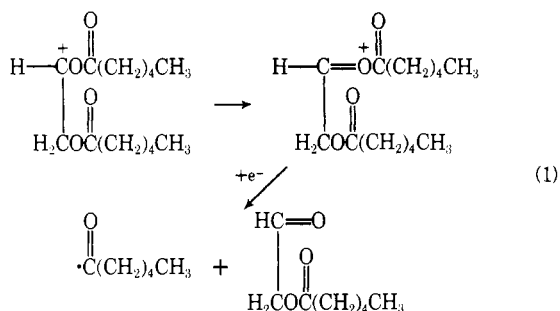
DISCUSSION

Unlike the radiolytic primary or recombination products identified earlier, the compounds we classified as secondary products appear to arise either from the occurrence of more than a single cleavage in the same molecule or from the decomposition of some primary intermediates.

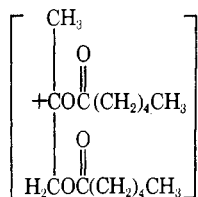
We have previously demonstrated that, in the radiolysis of simple triglycerides, cleavage at the acyloxy-methylene bond is the most abundant and results in the formation of relatively large quantities of propanediol diesters. An additional such cleavage in these primary products would produce the propyl and isopropyl esters. Thus, propyl hexanoate may result by the cleavage of the acyloxy-methylene bond in 1,3-propanediol dicaproate and the acyloxy-methine bond in 1,2-propanediol dicaproate. Iso-propyl hexanoate may originate solely by the scission of the acyloxy-methylene bond in 1,2-propanediol dicaproate. It should be pointed out that propyl hexanoate was also among the products considered to form by combination of primary radicals (LeTellier and Nawar,

1972b). However, this ester was produced in greater amounts than butyl and pentyl hexanoate and therefore must have also originated by means of a secondary reaction.

A likely pathway for the formation of 2-oxoethyl hexanoate is the dissociative electron recombination of the carbonium ion intermediate which was previously proposed in the formation of 1,2-ethanediol dicaproate (LeTellier and Nawar, 1972a) (eq 1). Dissociative recombina-

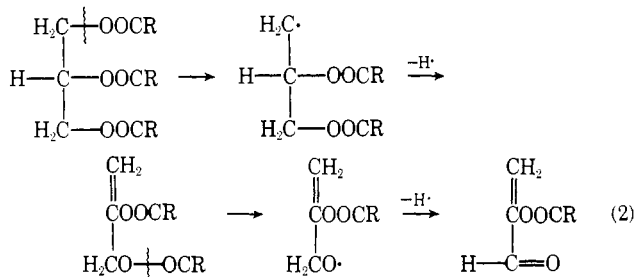


tion has been suggested by Williams (1963) as a possible means for neutralization of even-electron ions. Similarly, 2-oxopropyl hexanoate would arise from the intermediate



involved in the formation of 1,2-propanediol dicaproate.

The compound 2-hexanoyloxypropenal appears to arise from the primary radiolytic product 2,3-propanediol dicaproate (eq 2). Scission of an acyloxy-methylene bond in

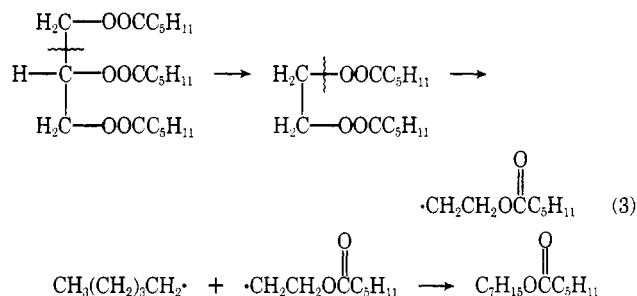


the tricaproin molecule-ion produces the dihexanoxyl propyl free radical which may lose a hydrogen atom to form 2,3-propanediol dicaproate. The latter may undergo additional cleavage at the acyl-oxygen bond, a site shown to be also preferential for radiolytic rupture, and the resulting free radical yields 2-hexanoyloxypropenal upon loss of hydrogen.

The source of acetylene is probably the primary radiolytic product ethene. Williams (1963) has reported that acetylene is the main gaseous product recovered from irradiated ethene. The mechanism by which hexanol is produced has not as yet been determined.

Heptyl hexanoate could not have been formed by the recombination of primary radicals as was the case for most of the other esters (LeTellier and Nawar, 1972b) since the radicals required for such a process are not formed by the scission of any bond in tricaproin. A possible mechanism for the formation of this compound is *via* the reaction of a pentyl radical (the major alkyl radical)

with an acyloxyethylene radical (which may arise from splitting at the acyloxy-methylene bond of the primary radiolytic product ethanediol dicaproate) (eq 3). Further



evidence for the availability of the acyloxyethylene radical is provided by the observation that ethyl hexanoate was present in a much larger amount than the remaining esters and therefore was produced in a larger amount than would be expected if this ester were formed solely by recombination of primary radicals.

It should be pointed out that ethyl esters were also identified in irradiated trioctanoin and tridecanoin. But, in tridecanoin, the amount of ethyl ester formed on irradiation was much greater than that isolated from either trihexanoin or trioctanoin and was present in a much larger concentration than the methyl ester. The only difference between these three triglycerides is that tridecanoin is solid while the other two are liquids at the irradiation temperature used. Ethyl esters were also recovered in large amounts in irradiated trilaurin, trimyristin, tripalmitin, and tristearin (Dubravcic and Nawar, 1968), but were not observed in irradiated tripalmitolein, triolein, and trilinolein. Aside from the difference in saturation, the only other difference between these triglycerides is that the unsaturated triglycerides are liquids. It therefore appears that the physical state of the triglyceride affects the formation of the ethyl ester.

ACKNOWLEDGMENT

The authors are grateful to John Kaylor, Marine Products Development Irradiator, Gloucester, Mass., for assistance with the irradiation of samples.

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Received for review January 24, 1974. Accepted April 2, 1974. This work was supported in part by U. S. Public Health Service Research Grant FD-00053.