Primary Radiolytic Fragmentation in Tricaproin

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A highly purified triglyceride, tricaproin, was exposed to γ radiation at 6 Mrads and its breakdown products were analyzed by gas chromatography, mass spectrometry, and infrared spectrophotometry. The use of such a low molecular weight substrate, as a model system, permitted the identification of not only the short chain fragments reported earlier, but also a number of the corresponding glyceryl residues. The latter group included an ethanediol diester, propanediol diesters, propenediol diesters, diglycerides, and triglycerides. Reaction mechanisms are proposed to explain the formation of these compounds.

Merritt and coworkers (1965, 1966, 1967) identified a homologous series of *n*-alkanes and 1-alkenes in irradiated fats. More recently, Dubravcic and Nawar (1968) examined the effect of γ radiation on the decomposition of seven simple triglycerides containing the C_{12} to C_{18} fatty acids and concluded that while random splitting of carbon–carbon bonds along the fatty acid chains may account for the production of small amounts of hydrocarbons, the principal cleavages occurred in the vicinity of the carbonyl group, giving rise to certain "major" radiolytic products. They speculated that the major hydrocarbons resulted from cleavage of the bonds between C_1 and C_2 and between C_2 and C_3 of the fatty acid chain. The formation of aldehydes was explained by cleavage of the acyl–oxygen linkage, and that of methyl and ethyl esters by cleavage in the glycerol moiety. No information could be obtained on the identity of any radiolytic products of higher molecular weight than the ethyl esters.

The present work was undertaken to study the irradiation of a low molecular weight triglyceride, *i.e.*, tricaproin, in order to allow the examination of the higher molecular weight radiolytic products.

EXPERIMENTAL

Materials. Tricaproin (99% purity) was purchased from the Hormel Institute, Austin, Minn., and further purified by high vacuum–cold finger distillation. The triglyceride was distilled, using the same conditions employed to recover the radiolytic products, until no peaks other than tricaproin were obtained upon gas chromatographic analysis of the distillate.

Reagents and, when possible, reference standards of the highest purity were obtained commercially. Several compounds were synthesized in the laboratory.

Irradiation. Five-gram samples of tricaproin were sealed under vacuum in glass ampoules and irradiated with γ rays from a Cobalt-60 source at the Marine Products Development Irradiator, Gloucester, Mass. A dose of 6 Mrads was administered at 17° C, at a rate of 6915 rads/min.

Distillation. The methods used for the recovery of the radiolytic products are the same as those described by Nawar *et al.* (1969).

Gas Chromatographic Analysis (gc). The higher-boiling radiolytic products obtained from the cold-finger distillation were separated on two 6-ft × 1/8 in. columns, one packed with 10% silicone SE-30 and the other with 10% diethylene glycol succinate (DEGS) + 2% H_3PO_4. Also used was a 250-ft × 0.02-in. capillary column coated with SE-30. The lower boiling hydrocarbons obtained from the precolumn distillation were separated on a 12-ft × 1/8-in. alumina column.

Three gas chromatographic instruments were used in this study; an F&M model 810, and a Varian Aerograph model 1200, both equipped with flame ionization detectors, and an F&M model 720 preparative unit equipped with a thermal conductivity detector. The F&M 720 was used to trap compounds for ir and nmr analysis. This was accomplished with the use of two 8-ft × 0.5-in. columns, one packed with 10% SE-30 and the other with 10% DEGS + 2% H_3PO_4.

Quantitative determinations were made as described previously (Nawar *et al.*, 1969) except those for the higher boiling radiolytic products. These were quantitated by placing three internal standards in the irradiated triglyceride and then injecting a 1-μl aliquot of the triglyceride directly into the gc. Methyl heptanoate was used as the internal standard for hexanal, 2-ethylcyclobutanone and methyl hexanoate, heptanoic acid for hexanoic acid, and ethyl laurate for the remaining products.

Identification. Unless otherwise stated, identification of the radiolytic products was accomplished by comparing their gc retention and mass spectral fragmentation with those of authentic compounds. Whenever feasible, infrared analysis was carried out.

Mass Spectrometry (ms). A combination gas chromatograph (Varian Aerograph model 1200)–mass spectrometer system was used in which 50% of the column effluent was admitted *via* a heated line to a Biemann helium separator and then to the ion source of an Hitachi–Perkin-Elmer RMU-6A mass spectrometer. The source was operated at 80 eV and the ionization chamber held at 250° C. The accelerating voltage was set at 2500 V and the electron multiplier was also operated at 2500 V.

Infrared Spectrophotometry (ir). Components eluting from gc columns were each collected in a capillary tube and rinsed into a 0.1-mm sodium chloride cavity cell with carbon tetrachloride or with anhydrous diethyl ether for the preparation of KBr pellets. Infrared analysis was conducted on a Perkin-Elmer model 337 grating infrared spectrophotometer fitted with a 4× beam condenser.

Synthesis of Reference Compounds. The isomeric diglycerides, 1,2- and 1,3-dicaproin, were prepared by the acid-catalyzed reaction of hexanoic acid with glycerol. The re-

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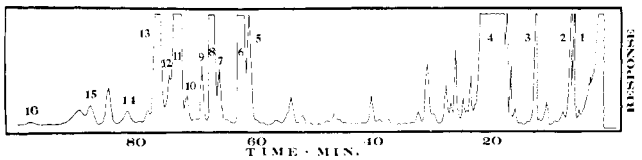


Figure 1. Gas chromatogram of the higher boiling compounds in irradiated tricaproin (6-ft × 1/8-in. SE-30, prog. 50–200° C at 2°/min), peak numbers correspond to listing in Table I

Table I. The Higher-Boiling Compounds by Irradiation of Tricaproin at 6 Mrads and 17° C

Compound	Peak no. in Fig. 1	Concentration μM/100 g	Identification gc	Identification ms
Hexanal	1	172	++, *d*	+
2-Ethyl cyclobutanone	2	96	++	+, *b*
Methyl hexanoate	3	39	++	+
Hexanoic acid	4	1220	++	+
1,2-Ethanediol dicaproate	5	12	++	+, *b*
1,2-Propanediol dicaproate	6	324	++	+, *b*
1,3-Propenediol dicaproate	7	45	++	+, *b*
1,3-Propanediol dicaproate	8	221	++	+, *b*
2,3-Propenediol dicaproate	9	32	+	+, *b*
1-Oxo-2,3-propanediol dicaproate	9	*a*		*c*
2-Oxo-1,3-propanediol dicaproate	10	*a*	+	+, *b*
1,2- and 1,3-dicaproin	11	295	++	+, *b*
1-Formyldicaproin	11	*a*	+	+
2-Formyldicaproin	12	*a*	+	+
1- and 2-acetyldicaproin	13	79	++	+
Propanoyldicaproin	14	*a*	+	+
Butanoyldicaproin	15	*a*	+	+
Pentanoyldicaproin	16	*a*	+	+

[a] No quantitation made due to overlapping or low concentration. [b] Confirmed by ir also. [c] By ms interpretation only, no authentic sample. [d] ++ Gc retention agreed with authentic compound on two columns.

action was monitored by gas chromatography and continued until maximum diglyceride production was reached. The resulting mixture was separated by preparative thin-layer chromatography on plates coated with a 0.4-mm layer of Silica Gel G impregnated with H_3BO_3 (80 ml of 0.5 *M* H_3BO_3 per 40 g of Silica Gel G). The chromatograms were developed in chloroform–acetone 95:5 (v/v). The diglyceride bands were separately scraped from the plates and extracted with methylene chloride. The purity of the 1,3- and 1,2-dicaproin was verified by reacting an aliquot of each of these with bis-(trimethylsilyl)trifluoroacetamide to form the silyl ether derivatives. The silyl ethers were then subjected to gas chromatographic analysis using a 6-ft × 1/8-in. column packed with 10% DEGS with 2% H_3PO_4. The silyl ethers of the 1,3- and 1,2-dicaproin were separable by programming this column from 100 to 200° C at 4° C/min. If one isomer was found to be contaminated by the other, the isomer was rechromatographed on the borate impregnated Silica Gel G and the purity rechecked by gas chromatography until only one isomer was found to be present.

All the triglycerides except the 1- and 2-formyl dicaproin were synthesized by reacting the appropriate acid chloride with the pure isomeric diglycerides, 1,2- and 1,3-dicaproin, according to Mattson and Volpenhein (1962).

1- and 2-formyl dicaproin were synthesized, according to Buzas *et al.* (1962), by separately reacting 1,2- and 1,3-dicaproin with equimolar amounts of formic acid, pyridine, and dicyclohexylcarbodiimide in diethyl ether at 0° C.

1,2-Propanediol dicaproate, 1,3-propanediol dicaproate, 1,2-ethanediol dicaproate, and 2-oxo-1,3-propanediol dicaproate were synthesized, according to Mattson and Volpenhein (1962), by reacting hexanoyl chloride with 1,2-propanediol, 1,3-propanediol, 1,2-ethanediol, and 1,3-dihydroxy-2-propanone, respectively.

2-Ethyl cyclobutanone was synthesized from 2-hexynyl *m*-nitrobenzenesulfonate, according to Hanack and Herterich (1966). The 3-hexynyl *m*-nitrobenzenesulfonate was made by reacting 3-hexyn-1-ol with NaH in benzene for 4 hr. The reaction mixture was allowed to react with *m*-nitrobenzenesulfonyl chloride overnight at ambient temperature and washed with 20% aqueous Na_2CO_3 at 0° C. The benzene solution was then dried over Na_2SO_4, the solvent removed under vacuum, and the product checked by ir analysis.

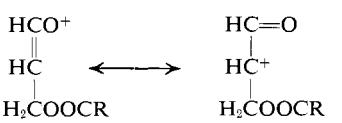
RESULTS

The low boiling compounds identified in irradiated tricaproin, by gc and ms, were the C_{1-5} *n*-alkanes and the C_{2-5} 1-alkenes. At 6 Mrads and 17° C, these compounds were produced in the following quantities: methane 15; ethane 20; ethene 14; propane 12; propene 4; butane 10; 1-butene 39; pentane 181; and 1-pentene 14 μM/100 g.

A chromatogram showing the separation of the higher-boiling compounds on SE-30 is shown in Figure 1. The identified compounds are listed in Table I, together with the criteria used in their identification. The remaining compounds, which are considered to result from the combination of various radiolytic fragments, will be discussed in a separate publication.

The spectral properties of the aldehyde, methyl ester, free fatty acid, diglycerides, and triglycerides identified are typical of their classes and are available in the literature.

The mass spectra of long chain esters of diols have been published by Baumann *et al.* (1969). A study of the mass spectral fragmentation of ethane- and propanediol diesters of short chain fatty acids has recently been completed in our laboratory and will be reported separately. To our knowledge, however, the mass spectra of propenediol diesters have not been reported and therefore will be discussed here. In the present work, 1,3-propenediol dicaproate has been positively identified whereas 2,3-propenediol dicaproate has been tentatively identified among the radiolytic products. The mass and ir spectra of peak 7, identified as 1,3-propenediol dicaproate, are shown in Figure 2. In the mass spectrum, a molecular ion can be observed at *m/e* 270. The base peak at *m/e* 99 and the ion at *m/e* 117 are characteristic of hexanoate esters and represent the fragments $[CH_3(CH_2)_4CO]^+$ and $[CH_3(CH_2)_4COO + 2H]^+$, respectively. While the peak corresponding to $[M-RCOO]^+$ is very prominent in the spectra of glycerides (Sun and Holman, 1968) and of propanediol diesters, the ion is extremely small in the spectrum of propenediol dicaproate (*m/e* 155 in Figure 2). On the other hand, the ion $[M-RCO]^+$, usually insignificant in case of the glycerides and propanediol diesters, is the second most intense peak (*m/e* 171) in the spectrum of the propenediol diester, if the hydrocarbon peaks are excluded. This is probably due to resonance stabilization of this ion, which is only possible in case of the unsaturated compounds



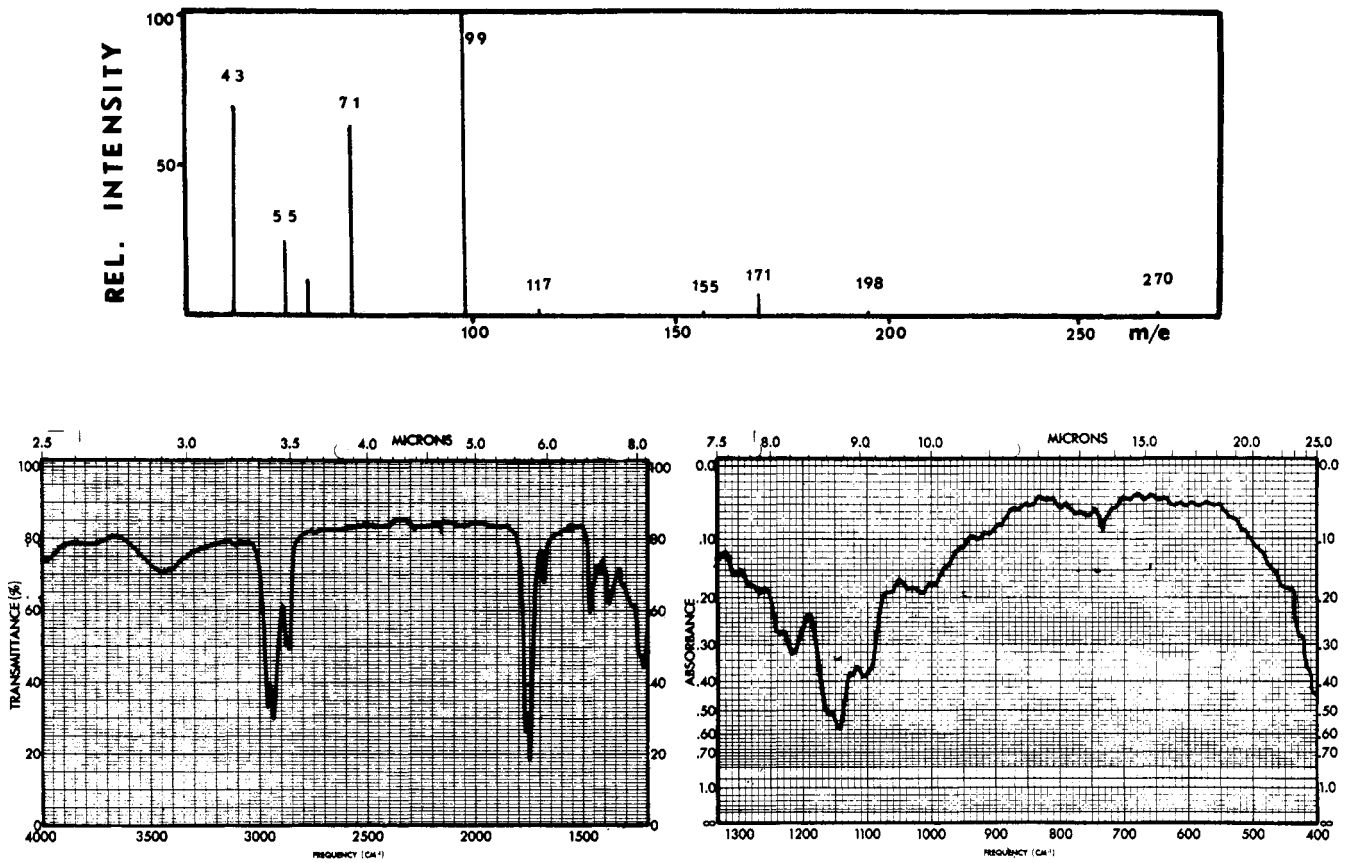


Figure 2. Mass (top) and infrared (bottom) spectra of 1,3-propenediol dicaproate

As in the mass spectra of propanediol dicaproates, a metastable peak is observed in the spectra of propenediol diesters at *m/e* 50.9 corresponding to the transition $99^+ \rightarrow 71^+ + 28$ (Beynon *et al.*, 1965). The remainder of the low mass ions are derived from the alkyl portion of the fatty acid chain. The ir spectrum of peak 7 contains absorption bands characteristic of the structure of a propenediol diester. The absorption at 1680 cm^{-1} is indicative of a –C=C– stretch, that at 1750 cm^{-1} represents the carbonyl stretch of an ester group while the band at 1770 cm^{-1} is likely to result from the carbonyl strength of the vinyl ester. The bands in the region 1108 cm^{-1} to 1240 cm^{-1} are similar to those reported by Baumann and Ulshofer (1968) in the spectra of long-chain saturated diol diesters. When the component represented by peak 7 was hydrogenated (Lustre and Issenberg, 1969), a compound having identical gc retention and ms properties to those of 1,3-propanediol dicaproate (peak 8) was obtained, confirming that peak 7 was 1,3-propenediol dicaproate. This conclusion was further verified by nuclear magnetic resonance (conducted by Varian applications laboratory on an HA-100 spectrometer equipped with a Spectro-System 100 for multiscan averaging). The mass and infrared spectra for peak 9 were similar to those of 1,3-propenediol dicaproate.

An attempt was made to synthesize 1,3- and 2,3-propenediol dicaproate by reacting phosphorus pentoxide with 1- and 2-dicaproin in chloroform at room temperature. When the reaction mixture was chromatographed on SE-30, two peaks had retention times and mass spectral characteristics identical to peaks 7 and 9 in Figure 1. However, these compounds could not be synthesized in sufficient quantities to permit further verification. Nevertheless, based on the data acquired, it was concluded that peaks 7 and 9 represent 1,3- and 2,3-propenediol dicaproate, respectively.

The mass spectrum of 2-oxo-1,3-propanediol dicaproate (peak 10) is shown in Figure 3. No molecular ion is present. The ion at *m/e* 230 results from the loss of butene *via* a McLafferty rearrangement as typical of esters (Ryhage and Stenhagen, 1963). This ion may undergo a second McLafferty rearrangement, on the remaining acyl moiety, to produce the peak at *m/e* 174. The fragments at *m/e*, 171, 157, 129, and 99 represent the ions $[M–CH_3(CH_2)_4CO_2]^+$, $[M–CH_3(CH_2)_4CO_2CH_2]^+$, $[CH_3(CH_2)_4CO_2CH_2]^+$, and $[CH_3(CH_2)_4CO]^+$, respectively. Five metastable ions are present in this spectrum. These are in agreement with calculated values tabulated by Beynon *et al.* (1965) for the following transitions: m* 50.9 ($99^+ \rightarrow 71^+$), m* 62.4 ($157^+ \rightarrow 99^+$), m* 76.0 ($171^+ \rightarrow 114^+$), m* 106.0 ($157^+ \rightarrow 129^+$) and m* 107.2 ($230^+ \rightarrow 157^+$). The ir spectrum of this compound (Figure 3) displays a carbonyl stretching band at 1750 cm^{-1} and also absorption bands in the range 1090 cm^{-1}–1240 cm^{-1} similar to those reported by Baumann and Ulshofer (1968) for propanediol diesters. The sharp band at 1420 cm^{-1} is characteristic of the bending frequency of active methylene groups (Nakanishi, 1964).

The isomeric diglycerides, 1,2- and 1,3-dicaproin, could not be separated as such by gas chromatography. Also, on SE-30 they eluted together with 1-formyl dicaproin (Peak 11 in Figure 1). However, they could be isolated from the remainder of the radiolytic mixture by trapping from a 10% DEGS + 2% H_3PO_4 column. They were then converted into their trimethylsilyl ether derivatives, which are readily separable by gas chromatography. The gc retention time and the mass spectral fragmentation pattern of the silylated and unsilylated diglycerides as compared to the silylated and unsilylated synthetic isomeric diglycerides served to confirm their identification.

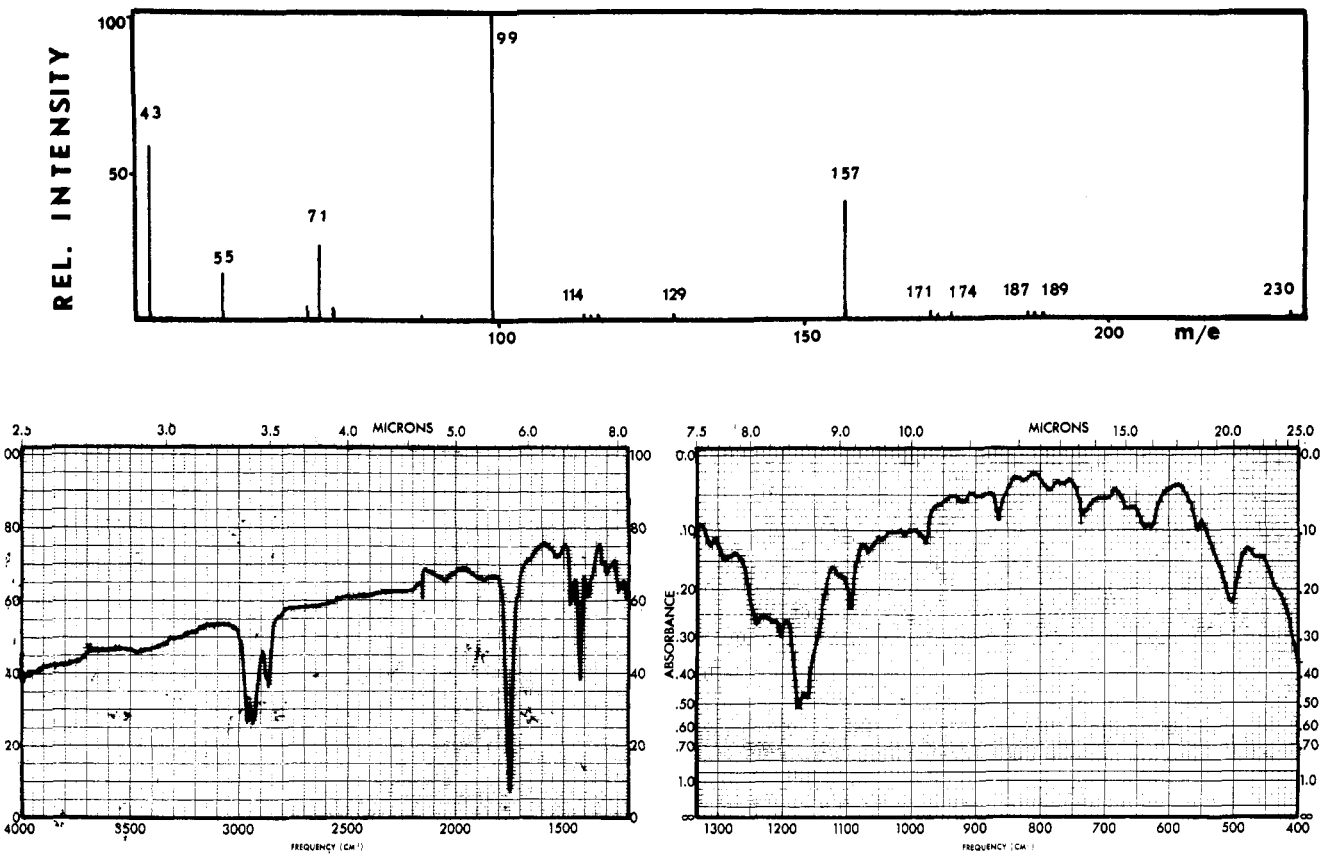


Figure 3. Mass (top) and infrared (bottom) spectra of 2-oxo-1,3-propanediol dicaproate

Five triglycerides have been identified. The isomers of only two of these, formyldicaproin and acetyldicaproin, could be separated by gas chromatography. 1-Formyldicaproin was separated from 2-formyldicaproin on the SE-30 column. For identification purposes, the diglycerides were separated from 1- and 2-formyldicaproin by trapping the formyldicaproin from the DEGS column as described above. 1- and 2-acetyldicaproin could only be separated on an SE-30 capillary column.

The 1 and 2 isomers of propanoyldicaproin, butanoyldicaproin, and Pentanoyldicaproin were not separable by gas chromatography. The presence of the 1 isomer of each of these three triglycerides was ascertained by mass spectrometric fragmentation (Barber and Merren, 1964), but no experimental evidence was obtained to prove the formation of their 2 isomers.

DISCUSSION

The presence of hydrocarbons, hexanal, and methyl hexanoate in irradiated tricaproin appears to follow the general pattern described by Dubravcic and Nawar (1968) for the higher molecular weight triglycerides. In the present study, however, the free fatty acid, ethyl cyclobutanone, and several glyceryl residues were identified.

It can be seen from Table I that the major primary radiolytic product formed is hexanoic acid. The most abundant radiolytic glyceryl residues produced are the propanediol dicaproates. The mechanism shown in Figure 4 accounts for the formation of these compounds. As shown by Williams (1962), the first step in radiation-induced reactions of organic oxygen compounds is ionization *via* loss of a nonbonding electron, with the result that the unpaired electron is highly localized on the oxygen atom. Scission of an acyloxy–methylene bond in the tricaproin molecule ion, as in Figure 4, would produce an acyloxy free radical and a carbonium ion. The formation of an acyloxonium ion and a dihexanoxyl propyl free radical may be possible, but since the fragment $[M-RCOO]^+$ is relatively abundant in the mass spectra of triglycerides whereas the fragment $[RCOO]^+$ is very small

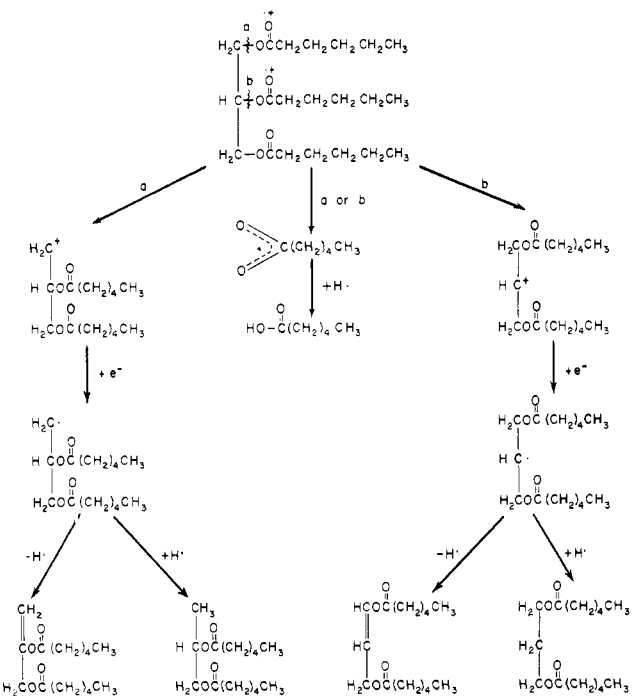


Figure 4. Splitting at the acyloxy–methylene bond

(Sun and Holman, 1968), it has been assumed that in radiolysis the charge is also retained by the glyceryl residue. The acyloxy free radical may then abstract a hydrogen atom to produce hexanoic acid and the carbonium ion could be neutralized by electron capture (Williams, 1963) with the formation of a free radical. The dihexanoxyl propyl radical may abstract hydrogen to form 1,2- or 1,3-propanediol dicaproate, depending on whether scission occurred on the primary or secondary position of the triglyceride. The loss of hydrogen from the 1,3- and 2,3-dihexanoxyl propyl free radicals, probably by disproportionation, would lead to the formation of 1,3- and 2,3-propenediol dicaproate. However, the saturated diol diesters are present in much larger amounts than the unsaturated diol diesters (Table I) so that hydrogen abstraction must be the preferential route for the termination of these free radicals. Another possible route for the formation of the free acid and the propenediol diesters is *via* a six-membered ring intermediate analogous to that previously proposed for thermal degradation (Crossley *et al.*, 1962; Nawar, 1969). Such radiation-induced intramolecular reactions involving six-membered ring intermediates have been shown by Williams (1962) to be exothermic.

The radiolytic products hexanal, 1,2-, and 1,3-dicaproin may arise from cleavage of the acyloxy bond in either the 1 or 2 position of tricaproin (Figure 5). Also, 1-oxo-2,3- and 2-oxo-1,3-propanediol dicaproate can be formed by scission at these bonds. All that is required is the loss of a hydrogen atom from the intermediate free radicals with the formation of a π bond between the carbon and oxygen atoms. Cyclization and scission at acyloxy bonds may also account for the formation of 2-ethyl cyclobutanone.

The hydrocarbons and the triglycerides appear to arise from cleavage of carbon–carbon bonds of the fatty acid chains. Again, as in the previous cases, hydrogen abstraction appears to be the preferential route for the termination of these free radicals. However, the fact that butene is present in a larger amount than butane may be due to the production of the former *via* an intramolecular process analogous to the "McLafferty Rearrangement" observed in the mass spectrometry of triglycerides (Lauer *et al.*, 1970). Hydorgen transfer from the fourth carbon with a simultaneous 2,3 cleavage leads to the formation of the neutral 1-olefin. As previously mentioned, this type of reaction is energetically favorable. Direct homolytic scission of this β carbon–carbon bond probably occurs to a lesser extent, since a smaller amount of butane is also produced.

As indicated above, pentane is the major hydrocarbon formed, followed by butene, and these two are present in a larger quantity than the other hydrocarbons. Likewise, it is obvious that among the triglycerides identified 1- and 2-acetyl dicaproin are produced in the largest quantity, followed by 1- and 2-formyl dicaproin. Therefore, cleavage of the carbon–carbon bonds α and β to the ester group in either the 1 or 2 position of tricaproin is the preferential points of cleavage along the hydrocarbon portion of the fatty acid moiety. This is in agreement with the findings of Dubravcic and Nawar (1968). However, the quantitative relationship between the corresponding residues was inconsistent. The triglycerides, 1- and 2-formyl dicaproin, corresponding to the major hydrocarbon pentane, are present in a much smaller amount than 1- and 2-acetyl dicaproin, the triglycerides corresponding to the second most abundant hydrocarbon butene. A likely explanation is that, in addition to the mechanism shown in Figure 6, pentane may be also formed by dissociation of either the hexanoyl or the hexanoxyl

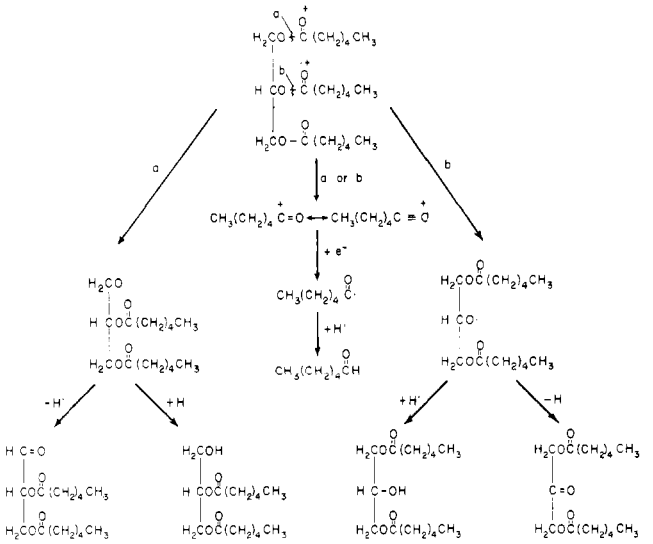


Figure 5. Splitting at the acyl–oxygen bond

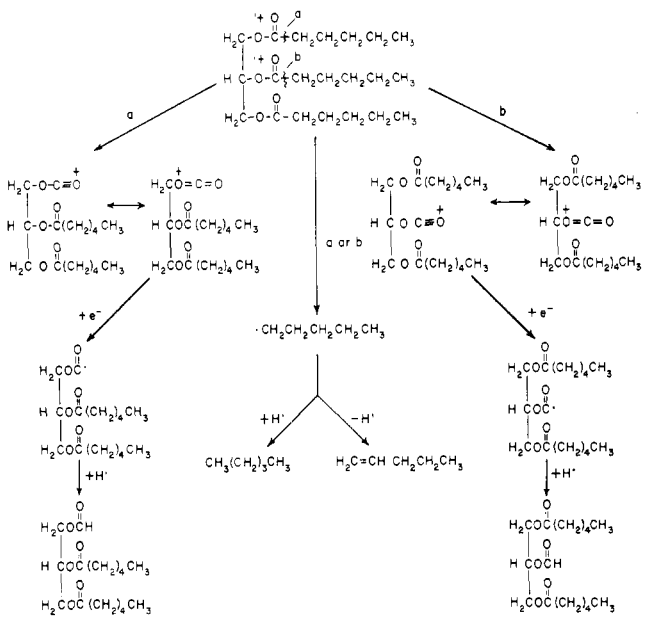
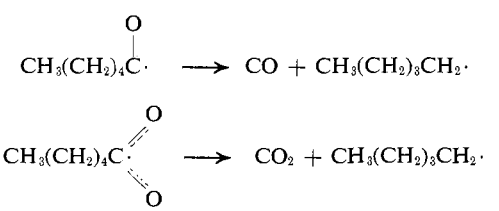
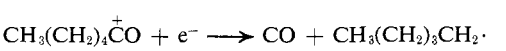


Figure 6. Splitting at the α bond of the fatty acid moiety

radicals (both of which should be abundant radiolytic intermediates as shown in Figures 4 and 5)



or through dissociative recombination as shown by Williams (1962)



The formation of CO and CO_2 in the radiolysis of carboxylic acid esters has been previously reported (Hall *et al.*, 1963).

On the other hand, the relatively small amount of formyl

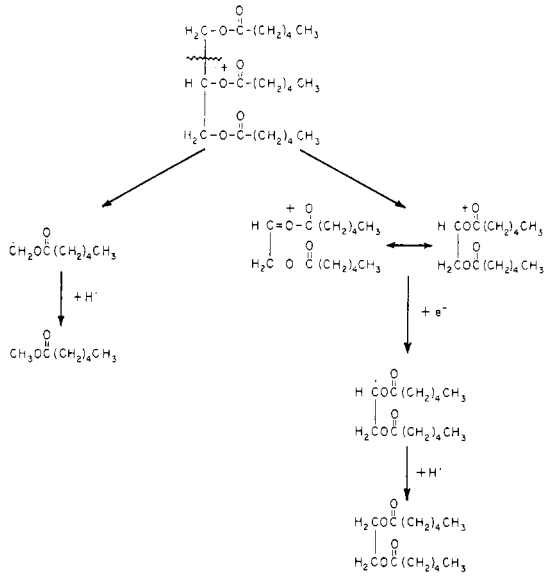


Figure 7. Splitting in the glyceryl moiety

dicaproin formed may be due to the instability of its intermediate which could decompose as follows

$$ROC\equiv\overset{+}{O} \longleftrightarrow R\overset{+}{O}=C=O \xrightarrow{+e^-} R\cdot + CO_2$$

where R is the remainder of the triglyceride. In contrast, the transition states in the formation of acetyl dicaproin would be stabilized by the six-membered ring in one case and by the resonance stabilization of the remaining free radical in the other

$$R\text{-}CH_2O\overset{O}{\overset{\|}{C}}\text{-}\dot{C}H_2$$

where R is the remainder of the glyceryl moiety plus two acyl groups.

The remainder of the hydrocarbons and triglycerides identified were present in a smaller amount. They most probably resulted from the random homolytic cleavage of carbon–carbon bonds along the fatty acid chain. The quantitative values given above indicate that the shorter chain hydrocarbons may also arise *via* secondary processes. This is further supported by the fact that these hydrocarbons are produced in much greater quantities than their corresponding glyceryl residues.

The formation of methyl hexanoate and ethanediol dicaproate may be explained by the scission of the carbon–carbon bond between carbons 1 and 2 of the glycerol moiety as shown in Figure 7.

While the quantitative data obtained are in agreement with the general concept presented here, more information would be necessary before an exact balance of the products of radiolysis can be made on a molar basis. Furthermore, the possibility that mechanisms other than those discussed here may also be involved cannot be ruled out.

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