Thermal Decomposition of Tricaproin

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ABSTRACT

Tricaproin was used as model system to study thermal decomposition of simple triglycerides. The tricaproin samples were pyrolyzed under three different conditions: at 250 C for 1 hr, 270 C for 1 hr and 270 C for 15 hr. Hydrocarbons, acrolein, methyl hexanoate, hexanal, hexanoic acid, 6-undecanone, 2-oxoheptyl hexanoate, propanediol dicaproate, propenediol dicaproate, oxopropanediol dicaproate and dicaproin were identified. Mechanisms involving both free radical and nonfree radical reactions were proposed for the formation of these compounds.

INTRODUCTION

Thermal decomposition of triglycerides has not been thoroughly investigated. To our knowledge only two studies have been reported. In 1962, Crossley and coworkers (1) studied the effect of heat on tricaproin in the absence of moisture. After 4 hr of heating in nitrogen at 250 C the only decomposition product was capric acid. Under similar conditions but at 300 C, both acrolein and di-*n*-nonyl ketone and, to a lesser extent, the symmetrical ketones di-*n*-butyl, di-*n*-amyl and di-*n*-hexyl ketones were produced in addition to the major product, decanoic acid. In vacuum, the course of decomposition was similar to that observed under nitrogen. More recently, Kitamura (2) pyrolyzed trilaurin and tripalmitin at 300-700 C under nitrogen. He identified fatty acids, acrolein, ketones and olefins in the products of pyrolysis. Unsaturated glycol difatty acid esters and acid anhydrides were also detected as intermediates.

The present work was undertaken to study in some detail the thermal decomposition of tricaproin under nonoxidative conditions. The selection of a low molecular weight triglyceride as a substrate facilitates analysis of the higher-boiling decomposition products.

EXPERIMENTAL PROCEDURES

Tricaproin was purchased commercially and purified by cold-finger distillation as described previously (3). Purification was continued until no impurity could be detected by gas chromatography. One gram samples of the purified triglycerides were sealed under vacuum in glass ampoules and then heated under three different conditions: 250 C for 1 hr, 270 C for 1 hr and 270 C for 15 hr.

The methods used for the separation and identification of the decomposition products were the same as those reported previously (3,4). The compounds collected on the precolumn were separated on alumina for the analysis of hydrocarbons, on OV-1 and DEGS + H_3PO_4 for the analysis of acrolein, and on molecular sieve for the analysis of CO and CO_2. The higher-boiling compounds, collected by cold-finger distillation were separated on SE-30.

Whenever available, reference compounds were purchased commercially. Authentic samples of 2-oxopropyl hexanoate, 2-oxoheptyl hexanoate, 1,2-propanediol dicaproate, 1,3-propenediol dicaproate, 1,3-propanediol dicaproate, 2,3-propenediol dicaproate, and 2-oxo-1,3-propanediol dicaproate were obtained through P.R. LeTellier, University of Massachusetts, Amherst.

RESULTS AND DISCUSSION

The major components produced by heating tricaproin at 270 C for 15 hr, and their concentrations, are listed in Table I. Qualitatively, the same products were observed for the three different conditions of heating. The mass spectra of these compounds and their retention data on at least two different gas chromatographic columns were identical to those of authentic compounds.

It can be seen that a variety of compounds are produced by heat. First, the production of a series of *n*-alkanes and 1-alkenes is typical of thermal decomposition. Quantitatively, the *n*-alkanes were always higher than the corresponding alkenes of the same carbon number. Also typical is that pentane (the *n*-1 hydrocarbon) was the hydrocarbon produced in the largest quantity, while butene (the *n*-2) was the alkene formed in the largest quantity.

Using pyrolysis gas chromatography, other workers studied thermolytic dissociation patterns of methyl esters and found olefins and methyl esters to be the two major series of pyrolytic products (5,6). Contrary to our results, however, these workers observed the series of alkenes and not that of the alkanes, which were formed in our study in greater quantities. It may be possible that the heating conditions used in their work preclude the formation of saturated hydrocarbons. On the other hand Levy and Paul (5), in accord with our results, observed that the *n*-2 alkene was the major alkene produced.

The quantitative pattern of hydrocarbons observed in the present study is somewhat similar to that observed

TABLE I

Decomposition Products Identified in Tricaproin after Heating under Vacuum at 270 C for 15 hr

Compound	Concentration, µmol/100 g	Compound	Concentration, µmol/100 g
CO	a	Hexanal	8
CO_2	a	Methyl hexanoate	4
Methane	a	Hexanoic acid	4396
Ethane	3.0	2-Oxopropyl hexanoate	237
Ethene	1.4	6-Undecanone	449
Propane	10.4	2-Oxoheptyl hexanoate	60
Propene	7.2	1,2-Propanediol dicaproate	9
Butane	2.0	1,3-Propenediol dicaproate	44
1-Butene	62.7	1,3-Propanediol dicaproate	7
Pentane	100	2,3-Propenediol dicaproate	35
1-Pentene	4.5	2-Oxo-1,3-propanediol dicaproate	2
Acrolein	a	Dicaproin	2939

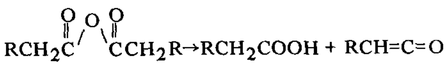
[a] Concentration was not determined due to extreme volatility or peak overlap.

when the triglyceride was exposed to gamma radiation (4). In the case of radiation a free radical mechanism was proposed, in which cleavage of the carbon-carbon bonds alpha and beta to the ester group are the preferential points of splitting along the hydrocarbon portion of the fatty acid moiety. The fact that the alkanes were produced in larger amounts than the alkenes indicated that hydrogen abstraction was the major route for the termination of these free radicals. On the other hand, the fact that the *n*-2 alkene is produced in larger amounts than the *n*-2 alkane was explained on the basis of the favored intramolecular process analogous to the McLafferty Rearrangement observed in the mass spectrometry of esters (7).

A theory explaining the formation of α-olefins in heated triglycerides was advanced by Kitamura (2), who suggests that acid anhydrides are formed which then give rise to acids and aldoketenes. The ketene further decomposes to produce CO and an alkene. This mechanism, however, would give rise to *n*-1 alkene as the major unsaturated hydrocarbon, which is contrary to the results presented here as well as those of other workers (5).

Quantitatively, hexanoic acid was the major compound produced from tricaproin by heating. The formation of the free fatty acid in the absence of water was also observed by Crossley et al. (1), and by Kitamura (2). Crossley and his coworkers explain the production of the free acid on the basis of a "six-atom-ring-closure" by way of a hydrogen bridge giving rise to the acid and a propenediol diester. This mechanism is now confirmed by the present study, since both 1,3-propenediol dicaproate and 2,3-propenediol dicaproate were positively identified. However the amounts produced of these propenediol diesters are too low to account for the relatively large amount of hexanoic acid produced. Perhaps the propenediol diesters undergo decomposition or polymerization. On the other hand, other pathways may also be involved in the formation of the free acid. A free radical mechanism resulting from homolytic cleavage at the acyloxy-methylene bond, similar to that occurring in radiolysis of triglycerides (4), may be taking place in the case of heating. This would also explain the formation of the saturated compounds, 1,2- and 1,3-propanediol dicaproate. It should be pointed out, however, that in the case of heating, the amounts of propanediol diesters produced are considerably lower than those of the unsaturated compounds (Table I). This is the reverse of the quantitative ratio observed in radiolysis.

Another route for the formation of the free acid may be via the decomposition of the anhydride (2):

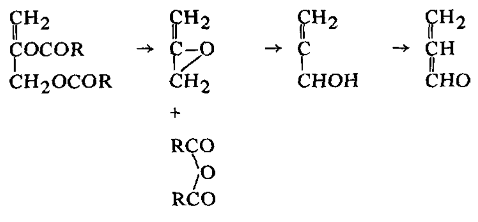


$$\mathrm{RCH_2\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}CH_2R \rightarrow RCH_2COOH + RCH{=}C{=}O}$$

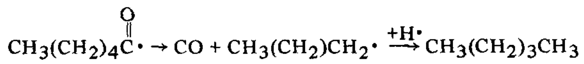
An additional pathway may be a reaction that simultaneously leads to the formation of acrolein as discussed by Crossley et al. (1):

Tricaproin → $\mathrm{OHC{-}CH_2{-}CH_2OCOR \rightarrow OHC{-}CH{=}CH_2 + RCOOH}$

Acrolein could also result from decomposition of the 2,3-propenediol diesters as suggested by Kitamura:



The formation of dicaproin, hexanal and oxo-propanediol dicaproate may be explained on the basis of homolytic splitting at the acyl-oxygen bond, also similar to radiolytic cleavage. The abstraction of hydrogen by the resulting free radical gives rise to diglycerides and hexanal. Loss of hydrogen from the dihexanoxyl propyl free radical produces oxo-propanediol dicaproate. However the quantitative data shown in Table I indicate that the amounts of hexanal and oxo-propanediol dicaproate are too small in comparison with the amount of dicaproin produced. The small amount of hexanal may be partly due to the ease of decomposition of the acyl radical giving rise to carbon monoxide and pentane:

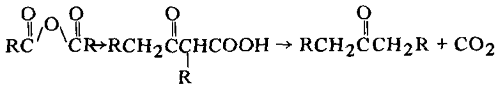


$$\mathrm{CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}\cdot \rightarrow CO + CH_3(CH_2)CH_2\cdot \xrightarrow{+H\cdot} CH_3(CH_2)_3CH_3}$$

The symmetric ketone, 6-undecanone, is one of the major components produced (Table I). This is in accord with the observation of Crossley et al. who proposed that the symmetric ketone results from decomposition of the anhydride, and that of Kitamura who argued that it results from two molecules of the free acid:

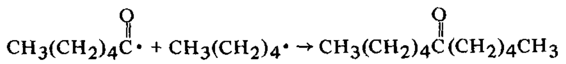
$$\mathrm{RCOOH + RCOOH \rightarrow RCOR + H_2O + CO_2}$$

However Koch and Leibnitz (8) presented evidence to support the hypothesis that ketones are formed from acids by way of anhydrides. This mechanism seems likely, because α-hydrogen atoms are more loosely held in anhydrides than in acids. Rearrangement of the anhydride to the β-keto acid would be followed by decarboxylation.



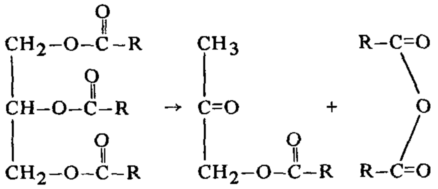
$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}R \rightarrow RCH_2\overset{O}{\overset{\|}{C}}\underset{R}{\underset{|}{C}}HCOOH \rightarrow RCH_2\overset{O}{\overset{\|}{C}}CH_2R + CO_2}$$

Postulation of the intermediate formation of β-keto acid is in accord with the observation that aliphatic acids without an α-hydrogen atom fail to give ketones. In addition, the symmetric ketone may be formed by combination of the acyl and the pentyl radicals:

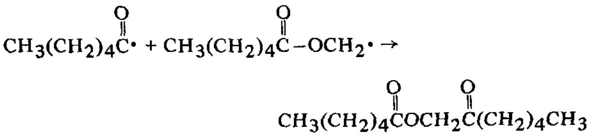


$$\mathrm{CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}\cdot + CH_3(CH_2)_4\cdot \rightarrow CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3}$$

The formation of 2-oxopropyl hexanoate, also in relatively large quantity, may be explained via a reaction which also yields the acid anhydride:

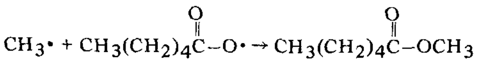


The compound, 2-oxoheptyl hexanoate, may result from combination of the acyl and the acyloxy-methylene radicals:



$$\mathrm{CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}\cdot + CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}{-}OCH_2\cdot \rightarrow CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}OCH_2\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3}$$

Similarly, methyl hexanoate may result from combination of a methyl radical with the acyloxy radical:



$$CH_3\cdot + CH_3(CH_2)_4\overset{\overset{O}{\|}}{C}-O\cdot \rightarrow CH_3(CH_2)_4\overset{\overset{O}{\|}}{C}-OCH_3$$

The compounds identified in this study are typical of thermal decomposition of saturated glycerides. It should be pointed out, however, that other decomposition products, e.g., dimeric or polymeric compounds of higher molecular weights, may also be produced but would escape detection under the experimental conditions used. In addition, various other reaction mechanisms would be expected if olefinic linkages are present. We are presently investigating thermal decomposition in an unsaturated model system.

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