

Thermal Degradation of Lipids. A Review

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Thermally induced reactions occurring in lipids under nonoxidative conditions are reviewed. Free fatty acids may be formed in both the absence and presence of moisture. In thermal hydrolysis of triglycerides, there is a preferential release of the

shorter-chain and the unsaturated fatty acids, but no positional specificity is observed. The mechanisms of formation of lactones, methyl ketones, hydrocarbons, and monocarboxylic and dicarboxylic methyl esters in heated fats are discussed.

Most studies involving the effect of heat on lipids can be categorized as follows:

Studies in which heat was applied under strictly nonoxidative conditions, with the objective of investigating the effect of heat alone.

Oxidation studies in which fats were oxidized under a flow of oxygen or air, and various degrees of heating applied to speed up the reaction or to produce greater quantities of products. The changes observed are in many cases explained on the basis of classic oxidative mechanisms such as the theory of Farmer *et al.* (1943), and modifications or extensions of such theory.

Thermal studies in which no particular effort was made to distinguish between oxidative and nonoxidative effects.

This report is devoted to the effect of heat alone. Reactions known to occur, during nonoxidative heating of fats, include dehydration, decarboxylation, hydrolysis of the ester bond, double bond conjugation, polymerization, dehydrocyclization, aromatization, dehydrogenation, and degradation by carbon-carbon cleavage.

Free fatty acids can be formed upon heating in both the presence and absence of water. In a moisture-free system, esters which possess a β -hydrogen in the alcoholic component may undergo a chelate type of "6-atom-ring-closure," by way of a hydrogen bridge (Hurd and Blunck, 1938). Readjustment of the electrons would give rise to an acid and an olefin (Figure 1). Methyl esters cannot form 6-atom rings and are thus more stable than ethyl esters. Triglycerides, however, contain a β -hydrogen and thus formation of the ring followed by cleavage is possible (Figure 2,A).

Crossley *et al.* (1962) studied the effects of heat on tri-caprin in the absence of moisture. After 4 hours of heating in nitrogen at 250° C. the only decomposition product was capric acid. Under similar conditions but at 300°, 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. Formation of acrolein and the anhydride followed by decarboxylation to form the saturated symmetrical ketone is shown in Figure 2,B.

If fats are heated in the presence of moisture, hydrolysis of the ester linkages takes place, and free fatty acids are released. Several years ago Lascaray (1945, 1949) es-

tablished that the reaction is essentially homogeneous and takes place within the oil phase rather than on the water-glyceride interface. Mills and McClain (1949) concluded that thermal hydrolysis proceeds in a stepwise manner through diglyceride to monoglyceride to glycerol. Little evidence has been available as to whether thermal hydrolysis involves any specificity, with regard to the nature of the acid (fatty acid specificity) or its location on the glyceride molecule (positional specificity). Noble *et al.* (1967) studied hydrolysis in samples of corn oil, cottonseed oil, and lard heated at 200° C. in the presence of moisture and noted a preference for the hydrolysis of the shorter chain and the unsaturated acids. More recently, Buziassy and Nawar (1968) reported on a study of thermal hydrolysis using simple model systems containing specific fatty acids in specific positions.

Table I shows the effect of the nature of the acid on the rate of its hydrolysis. Glyceride mixture A contained equimolar amounts of the C₄, C₈, and C₁₂ acids randomly distributed on the glyceride molecules. Mixture B contained equimolar amounts of C₁₂, C₁₆, and C_{18:1} randomly distributed. When these glycerides were heated at 200° C. for 3 hours, the shorter acids were released to a greater extent than the longer chain acids. Also, the unsaturation increases the rate of hydrolysis. The hydrolysis of the C₁₂ acid was higher when heated in the presence of shorter chain glycerides, than in the presence of the longer chains (Table I). Specificity of heat hydrolysis in favor of the shorter and the unsaturated acids is explained by their greater solubility in water. In addition, the presence of short chains in the molecule appears to contribute to a greater accessibility of water to the whole molecule.

In an experiment designed to study the effect of the position of a fatty acid on the rate of its thermal hydrolysis, trilaurin was synthesized with the fatty acid on the 2-position labeled with ¹⁴C. A portion of the labeled glyceride was treated with lipase until 10% of the glyceride was hy-

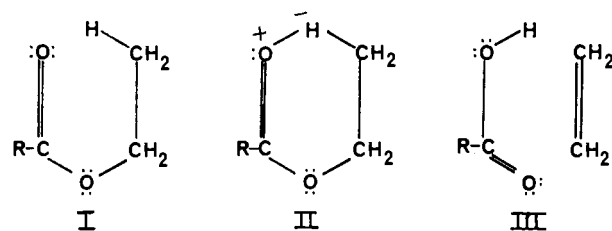


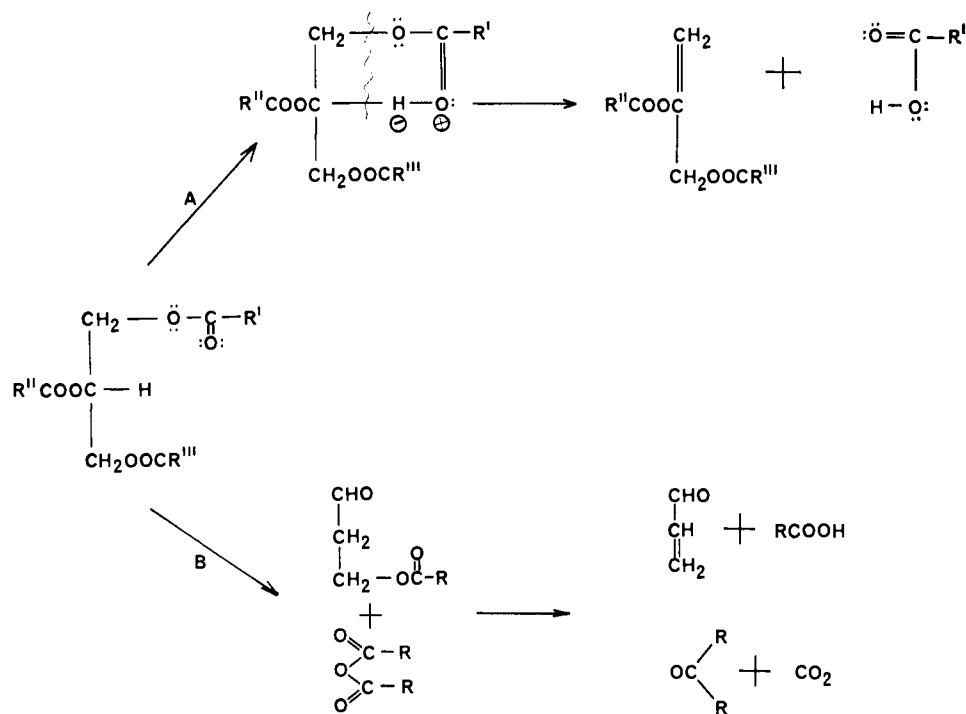
Figure 1. Formation of free fatty acids by heating in the absence of moisture

Hurd and Blunck, 1938

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Figure 2. Decomposition of triglycerides by heat in absence of moisture

Modification of scheme of Crossley *et al.*, 1962



dolyzed and the free acids analyzed in a combination "gas chromatography-flow counter," which permits simultaneous measurements of fatty acids and their radioactivity. As shown in Figure 3, only a trace of activity was detected in the free acids, confirming that the label was essentially in the 2-position. A second portion of the labeled glyceride was methylated in the conventional manner, and the total fatty acids were analyzed by the same technique, while the third portion was heated at 200° C. for 2.5 hours (resulting in approximately 10% hydrolysis) and the relative activity of the free acids determined. There is no significant difference between the relative activity of the acids released by heat and of total fatty acids before heating (Figure 3). Thus the variables related to water solubility in the fat outweigh any effect the position of the fatty acid may have on the rate of its heat hydrolysis.

If the esterified acids possess certain functional groups, their hydrolysis by heat may result in the formation of compounds of particular flavor significance. Among these are lactones and methyl ketones. Various investigators (Langler and Day, 1964; Nawar *et al.*, 1962; Patton and Tharp, 1959; Van der Ven *et al.*, 1963) have observed the formation of a series of C₃ to C₁₅ methyl ketones on heating milk fat in the absence of oxygen. Van der Ven *et al.* (1963) and Parks *et al.* (1964) presented evidence that

the methyl ketone precursors were β -keto esters. The latter workers isolated and identified the β -keto-acid-containing glycerides and estimated that they amounted to 0.05% of the milk fat.

A series of C₆-C₁₈ δ - and C₃-C₁₆ γ -lactones were shown to form by heating milk fat (Boldingh and Taylor, 1962; Forss *et al.*, 1966; Keeney and Patton, 1956; Muck *et al.*, 1963). These compounds possess a "coconut-like flavor" and may cause desirable or objectionable flavors, depending on the concentration and the type of food product. Jurriens and Oele (1965), Kinsella *et al.* (1967), Parliment *et al.* (1966), and Wyatt (1966), using thin-layer, column, and gas chromatography, confirmed that the lactone precursors are the corresponding δ - and γ -hydroxalkanoic acids esterified in glyceride molecules. The hydroxyfatty acids are liberated by heat and spontaneously lactonize to yield lactones. By treating the "hydroxy acid-containing glycerides" with pancreatic lipase, Kinsella

Table I. Hydrolysis of Random Triglycerides Heated^a at 200° C. for 3 Hours

Triglycerides A		Triglycerides B	
Acid	% hydrolysis	Acid	% hydrolysis
4:0	54.2	12:0	18.0
8:0	31.6 ^a	16:0	14.0 ^a
12:0	27.2	18:1	16.6

^a Difference significant at 1%.

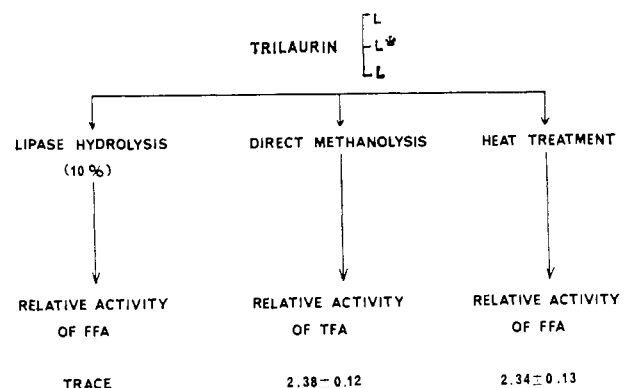


Figure 3. Scheme for studying the effect of position of lauric acid on its thermal hydrolysis

Relative activity = area of radioactivity peak/area of corresponding GC peak (Buziassy and Nawar, 1968)

et al. (1967) concluded that the δ - and γ -hydroxy acids were esterified to the primary positions of the glyceride molecules.

Characterization of large numbers of compounds resulting from thermal decomposition of natural fats is becoming more and more feasible because of continuing advances in methodology of fractionation and identification. However, because natural fats are complex, it is often difficult to determine or even to speculate on the mechanisms by which these compounds are formed. Work on simple model systems of glycerides, fatty acids, and methyl esters, although not always directly applicable to natural fats, can assist in understanding possible mechanisms. Although literature lists large numbers of identified compounds, surprisingly little attention has been given to determining the quantities in which these compounds are formed. Quantitative compositions are of great value not only from the standpoint of flavor but also in the interpretation of mechanisms.

In this connection, recent work conducted in Germany by Sen Gupta (1966) on methyl oleate is noteworthy. The ester was heated at 280° C. for 65 hours and a large number of compounds were isolated and identified. Only five compounds—i.e., 9-octadecene, decanoic acid methyl ester, 9,17-hexacosadiene, 9,17-hexacosadienoic acid methyl ester, and 9-octadecene-1,18-dioic acid dimethyl ester—were produced in relatively large quantities. To explain the formation of these compounds, the author postulates a preferential homolytic splitting at positions alpha to the double bond as shown in Figure 4. The formation of a significant quantity of 9-octadecene is attributed to addition of the octyl radical (I) to radical IV. Similarly addition of radical III to radical II results in the formation of 9-octadecene-1,18-dioic dimethyl ester. The author further concluded that radical II is capable of abstracting three hydrogen atoms from methyl oleate (Figure 5) and also from octadecene (Figure 6) to form the corresponding terminally unsaturated radical and methyl decanoate. Each of the resulting unsaturated radicals reacts with radicals I and III to give the compounds with 26 carbon chains.

More recently Nawar and Dubravcic (1968) criticized these mechanisms for two reasons. Splitting at positions alpha to the double bond is unlikely, since vinylic bonds are much stronger than allylic bonds (109 *vs.* 60 kcal. per mole, respectively). Secondly, the probability of a specific abstraction of three hydrogen atoms from the hydrocarbon end of long-chain molecules to form terminal ethylenic linkages must be extremely remote. Nawar and Dubravcic suggested an alternative mechanism in which homolysis at β -positions produces the radicals shown in Figure 7. Octadecene and octadecenedioic acid dimethyl ester result from reactions of radicals I and IV, and II and III, respectively. Methyl oleate may also decompose to produce CO₂, a methyl radical, and a 17-carbon alkenyl radical which may then form ethylene and a 15-carbon radical (V) (Figure 8). The shortening of alkyl radicals by two carbon atoms with the formation of ethylene has been shown to occur in thermal degradation (Markley, 1961). Radical V can react with IV to give 9,17-hexacosadiene or with II to give 9,17-hexacosadienoic acid methyl ester. The formation of decanoic acid methyl ester can occur via loss of ethylene from radicals I and III

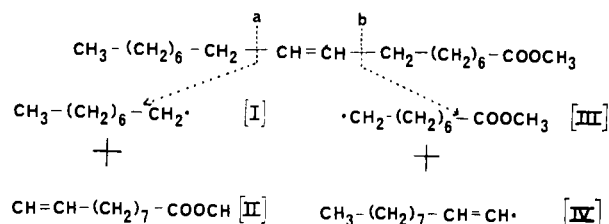


Figure 4. Formation of free radicals from methyl oleate by heating (Sen Gupta, 1967)

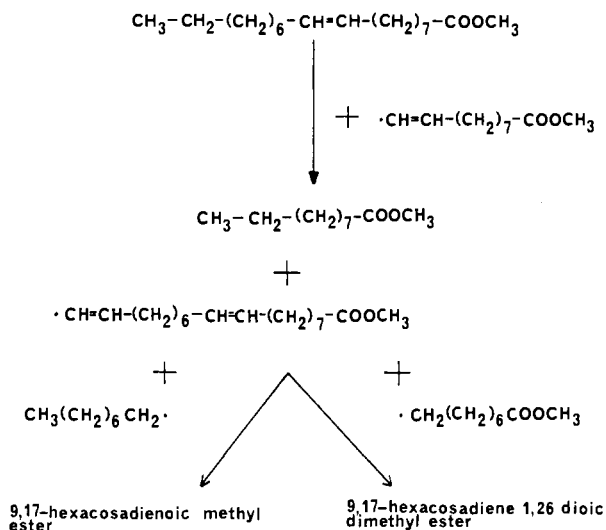


Figure 5. Abstraction of hydrogen from methyl oleate and formation of 26 carbon chains (Sen Gupta, 1967)

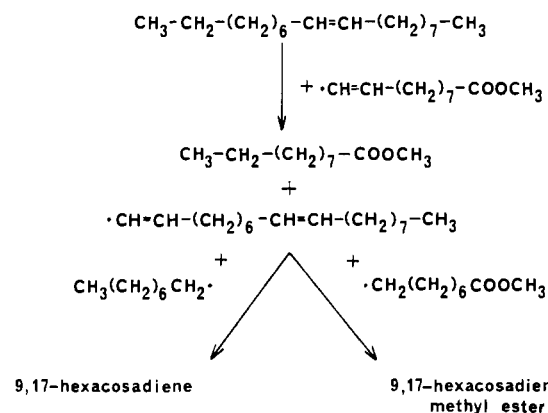


Figure 6. Abstraction of hydrogen from octadecene and formation of compounds of 26 carbon chains (Sen Gupta, 1967)

of Figure 8 and addition of the resulting two 5-carbon radicals.

Using pyrolysis gas chromatography, Levy and Paul (1967) studied thermolytic dissociation patterns of methyl esters. Pyrolysis products could be classified into two series, olefins and methyl esters. In case of saturated methyl esters major splitting beta to the carbonyl group was observed, while dissociation at positions beta to the double bond was more abundant in the case of unsaturated methyl esters. For methyl palmitate, for example:

