

Chemical Changes in Lipids Produced by Thermal Processing

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Since prehistoric times, people have been using heat in the preparation of their food to modify its flavor or texture and to improve its ability to be stored. Most of the food we consume today has been subjected to varied degrees of heat treatment at one stage or another, through, for example, cooking, baking, broiling, toasting, roasting, canning, concentrating, pasteurizing, drying, or frying. Depending on the nature of the food and the conditions of the treatment, heat will effect various chemical and physical changes in all of the food constituents. Not only do the different nutrients undergo decomposition reactions, but they also interact among themselves in extremely complex ways and form a large number of new compounds. Indeed, some of these changes are the very goal of the treatment. Other changes, however, are not so desirable, and may cause problems in both quality and wholesomeness. Obviously food scientists and technologists are concerned with these reactions and interactions in order to allow proper control of product quality and to insure nutritional value and safety.

Because of the obvious difficulties inherent in the study of a system as complicated as food, most of our basic knowledge in this area has been gained by investigating the effects of heat on the major food components organized in separate systems. The purpose of this article is to describe heat effects on the lipids.

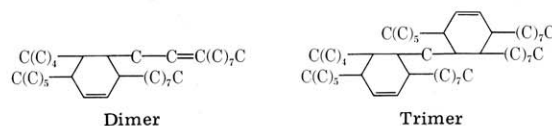
The chemical and physical changes that occur depend on the composition of the lipid and the conditions of treatment. If oxygen is scarce, thermolytic reactions will take place. In the presence of air, both oxidative and nonoxidative reactions will occur simultaneously. In addition, heat will accelerate the oxidative process and influence the course of oxidation both qualitatively and quantitatively.

Thermolytic Reactions

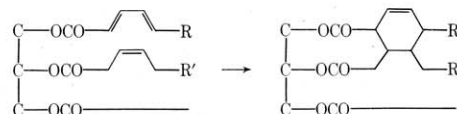
In general, very high temperatures are required to produce substantial nonoxidative decomposition of saturated fatty acids. However, using very sensitive measurement techniques, thermolytic products can be detected in simple triacylglycerols after they are heated in vacuum for only 1 h at 180°C. These products consist mainly of series of normal alkanes and 1-alkenes, fatty acids, symmetric ketones, oxopropyl esters, propene and propane diesters, and diacylglycerols. Acrolein, CO, and CO₂ are also formed (1).

In the case of unsaturated fatty acids the formation of dimeric compounds appears to be the predominant reaction. These compounds include dehydrodimers, believed to arise via the combination of allyl or pentadienyl radicals (e.g., Types I and II, Fig. 1), saturated dimers with cyclopentane structures (e.g., Type III, Fig. 1), and polycyclic compounds resulting from intramolecular addition to C-C double bonds (Types IV and V, Fig. 1).

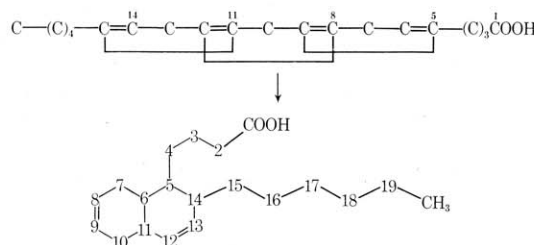
Dimerization and polymerization of unsaturated fatty acids can also occur via Diels-Alder type reactions. Thus, the conjugated diene from linoleate may react with oleate (or one of the unsaturated linkages in a polyene) to produce a tetra-substituted cyclohexene



In the case of glycerides such dimerization can take place between acyl groups in the same molecule.



Also typical of the reactions of unsaturated fatty acids is the addition of a free radical to a double bond in the same molecule giving rise to cyclic monomers. Cyclization occurs more readily in case of the longer chain polyunsaturated acids as shown for arachidonic acid



Oxidative Reactions

It is generally established that the reaction of unsaturated fatty acids with molecular oxygen proceeds via typical free radical mechanisms. Since direct reaction of unsaturated linkages with oxygen is thermodynamically difficult, production of the first few radicals necessary to start the propagation reaction must occur by some other means. It has been proposed that the initiation step may take place by decomposition of preformed hydroperoxides (via metal catalysis or heat), by exposure to light, by direct reaction of metals with oxidizable substrates, or by mechanisms where singlet oxygen is the active species involved.

Upon the formation of sufficient free radicals, the chain reaction is propagated by the abstraction of hydrogen atoms at positions alpha to double bonds, followed by oxygen attack at these locations, and resulting in the production of peroxy radicals, ROO·, which in turn abstract hydrogen from alpha methylenic groups of other molecules, RH, to form hydroperoxides, ROOH, and yield R· groups which react with oxygen, and so on (Fig. 2). Due to resonance stabilization of the R· species, the reaction is usually accompanied by shifting in the position of double bonds resulting in the formation of isomeric hydroperoxides often containing conjugated diene groups.

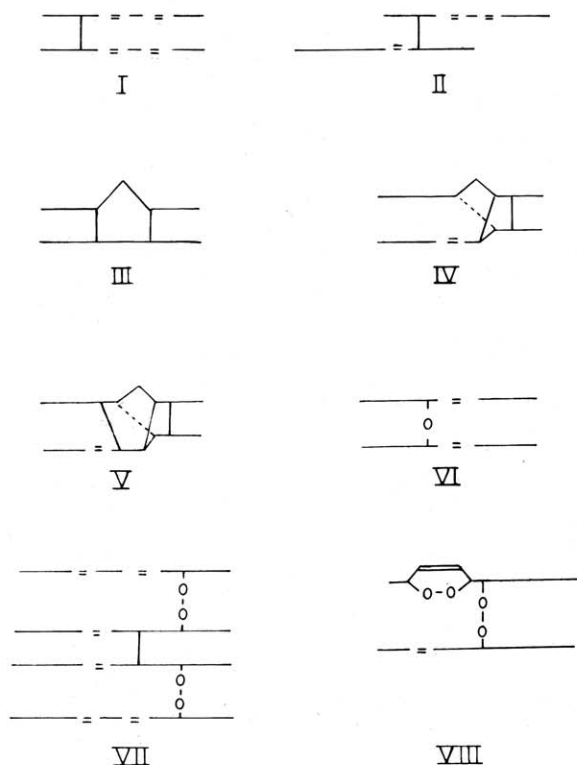


Figure 1. Dimeric and polymeric products.

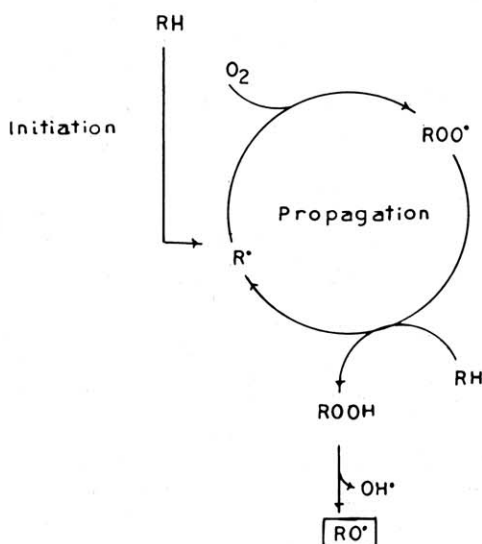


Figure 2. Scheme for the free radical autoxidation mechanism.

Peroxide Values (Meq/kg) for Ethyl Linolenate after Different Time-Temperature Treatments (6)

70°C		180°C		250°C	
Time (hr)	PV	Time (min)	PV	Time (min)	PV
6	1777	5	237	3	44
24.5	1058	10	251	5	77
45	505	20	119	10	198
69	283	30	80	20	67
		60	44	30	0

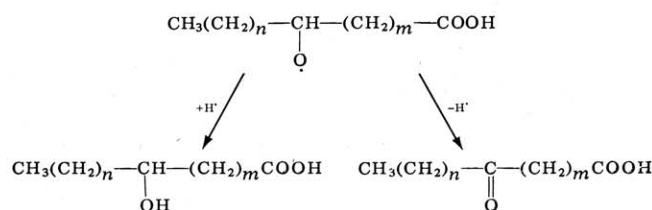
Detailed qualitative and quantitative analyses of the isomeric hydroperoxides produced from oleate, linoleate, and linolenate oxidized at different temperatures were recently made possible through the use of modern analytical tools (2-5). Oleate produces a mixture of *cis* and *trans* 8-, 9-, 10- and 11-allylic hydroperoxides. At 25°C and 40°C oxygen attack at carbons 8 and 11 is greater than at carbons 9 and 10. The difference between the two pairs of isomers becomes smaller at higher oxidation temperatures. At 25°C the proportions of *cis* and *trans* 8- and 11-hydroperoxides are similar, but the 9- and 10-isomers are mainly *trans*. At higher temperatures the amount of the *cis* 9- and 10-hydroperoxides approaches that of the *trans* isomers.

The 1,4-pentadiene structure in linoleates makes them much more susceptible to oxidation than is the propene system of oleates. Two hydroperoxides, the 9- and 13-isomers, are thus formed, in equal amounts, from linoleates. These are found in both the *cis,trans* and the *trans,trans* forms. Similarly, the hydroperoxides of linolenates consist of a mixture of 9-, 12-, 13-, and 16-conjugated hydroperoxides, with the 9- and 16-isomers being produced in higher proportions than the 12- and 13-hydroperoxides.

We have recently studied the effect of heating temperature and time on the oxidative decomposition of linolenate (6). Three temperatures were chosen: 70°C, a temperature within the range in which the isomeric hydroperoxide intermediates had been characterized and their ratios determined (3-5); 180°C, typical of frying operations; and 250°C, representing severe heating. Peroxide values for samples of linolenate heated at each of these temperatures for various periods of time are given in the table. The data indicate that hydroperoxides are formed at all three temperatures. At the higher temperatures, however, hydroperoxide decomposition occurs very rapidly, thus resulting in a net peroxide value of zero after heating for only 30 min at 250°C (see table).

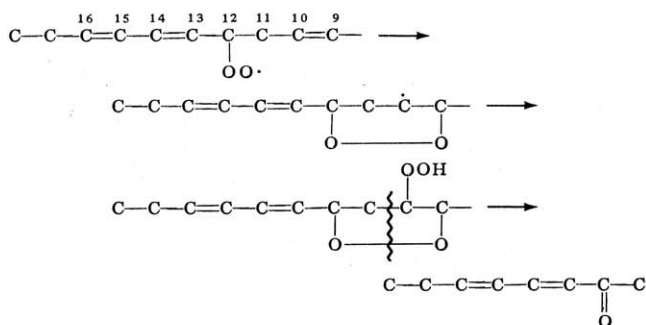
The hydroperoxides, formed as the primary products in lipid autoxidation, enter into numerous and complex breakdown and interaction mechanisms and produce a myriad of compounds with significant variation in molecular weight, flavor threshold, and biological significance.

Scission of the O—O bond in the hydroperoxide molecule yields the alkoxy radical, which may gain or lose a hydrogen atom to form the hydroxy or keto derivatives, respectively.

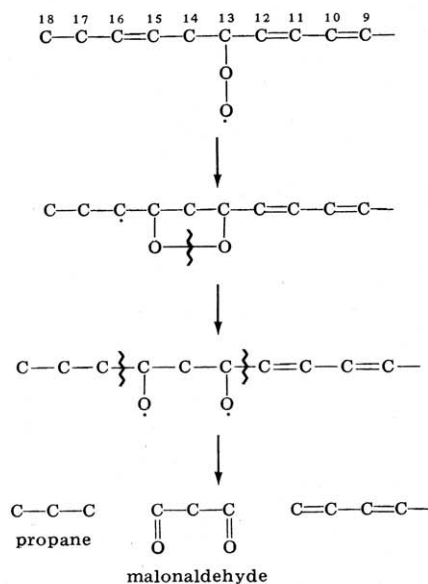


Alternatively, the alkoxy radical may decompose by carbon-carbon cleavage on either side of the alkoxy group to form aldehydes, hydrocarbons, semi-aldehydes, and acids. Thus, 2,4-decadienal, methyl octanoate, methyl 9-oxononanoate, and 3-nonenal arise from the 9-hydroperoxide of linoleate, while hexanal is the major aldehyde produced by decomposition of the 13-hydroperoxide isomer (Fig. 3).

In addition to the classic hydroperoxides mentioned above, a variety of cyclic and hydroperoxy cyclic peroxides are commonly formed in the oxidation of polyunsaturated fatty acids. Decomposition of such intermediates gives rise to specific volatile compounds, for example, 3,5-octadiene-2-one from the 12-hydroperoxide of linolenate



or malonaldehyde from the 13-hydroperoxide isomer



It can be seen that the major decomposition products from thermal oxidation of different fats can be predicted on the basis of their fatty acid composition. However, the number of volatile compounds that have been identified so far in thermally oxidized fats is literally in the hundreds (7-13). Undoubtedly, as the oxidative process continues, various other mechanisms come into play.

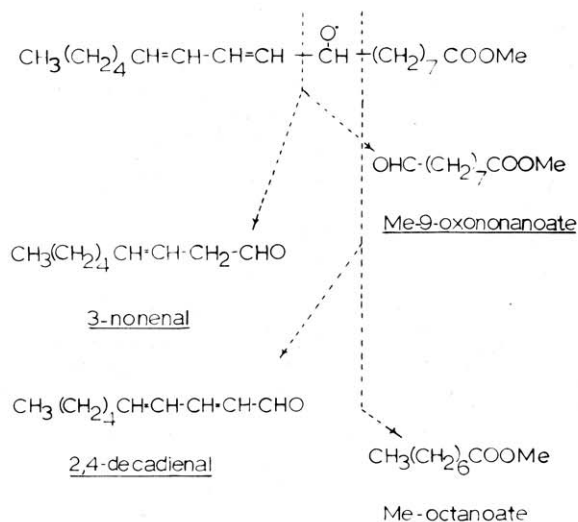


Figure 3. Decomposition of 9-hydroperoxy methyl linoleate.

At elevated temperatures, hydroperoxide decomposition and secondary oxidations occur at extremely rapid rates. The amount of a given decomposition product at a given time during the autoxidation process is determined by the net balance between the complex effects of many factors. Hydroperoxide structure, temperature, the degree of autoxidation, and the stability of the decomposition products themselves undoubtedly exert major influences on the final quantitative pattern. The picture is further complicated since these factors influence not only C—C bond scission, but also a large number of other possible decomposition reactions that occur simultaneously and in competition with C—C cleavage. The latter reactions include C—O scission, which may lead to positional isomerization of hydroperoxides (14), epoxidation, formation of dihydroperoxides, inter- and intramolecular cyclization, dimerization, and polymerization. Selected examples of such reactions are given below.

Aldehydes, the major oxidative products of fat oxidation, may further oxidize to their corresponding fatty acids. In addition, they may undergo autoxidation via the free radical chain reaction mechanism outlined above, giving rise to shorter-chain aldehydes, dialdehydes, hydrocarbons, etc., or epoxidation and cleavage as shown in Figure 4 for 2,4-decadienal (15), or condensation to form trioxanes and dioxolanes (16).

In the presence of a plentiful supply of oxygen, combinations between alkyl, alkoxy, and peroxy free radicals may result in a variety of dimeric and polymeric acids and glycerides with carbon-oxygen-carbon or carbon-oxygen-oxygen-carbon crosslinks (Type VI and VII, Fig. 1), as well as oxygen-containing dimers, trimers, or cyclic monomers (e.g., VIII, Fig. 1).

Saturated fatty acids and their esters are considerably more stable than their unsaturated analogs. However, when heated in air at temperatures higher than 150°C, they undergo oxidation, giving rise to a complex decomposition pattern. The major oxidative products consist of a homologous series of carboxylic acids, 2-alkanones, *n*-alkanals, lactones, *n*-alkanes, and 1-alkenes.

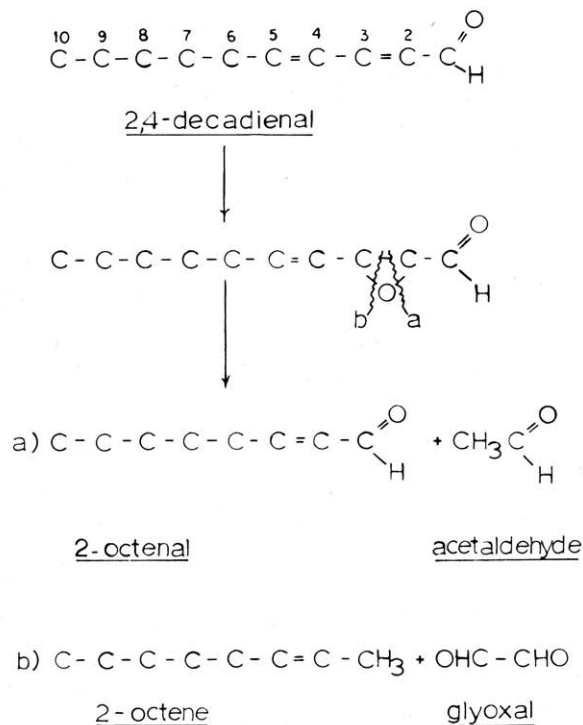
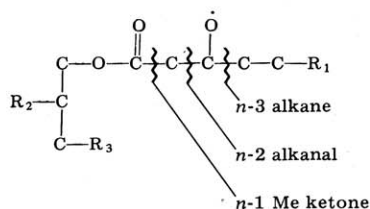


Figure 4. Further oxidation of 2,4-decadienal.

It is generally accepted that thermal oxidation of saturated fatty acids involves the formation of monohydroperoxides as a principle mechanism, and that oxygen attack can occur at all the methylene groups of the fatty acid. However, since the dominant oxidative products of saturated fatty acids are those with chain lengths near or equal to the parent fatty acids, it is likely that oxidation occurs preferentially at the positions near the ester carbonyl group. Oxidative attack at the β -carbon of the fatty acid, for example, results in the formation of β -keto acids which in turn yield C_{n-1} methyl ketones upon decarboxylation. Cleavage between the α - and β -carbons of the alkoxy radical intermediate gives rise to C_{n-2} alkanal while scission between the β - and γ -carbons produces C_{n-3} hydrocarbons



Gamma and delta lactones may result from oxygen attack at carbons 4 and 5, respectively.

Thermal and Oxidative Interaction of Lipids with Other Food Components

As in all biological systems the lipid molecules in food are often closely associated with neighboring nonlipid material such as proteins, carbohydrates, water, enzymes, salts, vitamins, and pro- and antioxidants. When food is subjected to heat in the presence of air, reactions of the lipids, or their decomposition products, with such compounds will influence the oxidative reaction pathways and thus the final outcome of the treatment. For example, some products of nonenzymatic browning are known to act as antioxidants. The basic groups in proteins may catalyze aldol condensation of carbonyls produced from lipid oxidation, resulting in the formation of brown pigments. Lipid hydroperoxides may induce oxidative changes in sulfur-containing proteins (17) causing significant nutritional losses, and secondary oxidation products from lipids can initiate free radical reactions in proteins or form Schiff-base addition products with the epsilon amino groups of lysine.

A number of volatile compounds resulting from thermal interaction of amino acids with fatty acid esters or triacylglycerols have been identified. These include amides, acid nitriles, alkyl pyridines, and pyrroles (18–20).

Chemistry of Frying

Deep-fat fried foods are becoming more and more significant as contributors to the total caloric intake in an average U.S. diet because of current trends in the eating habits of the American consumer. In the course of frying, food is placed in hot oil (about 180°C) in the presence of air for various periods of time. The finished product usually contains 5–40% absorbed oil.

As expected, thermal, oxidative, and hydrolytic reactions will take place in the oil producing a variety of physical and chemical changes. Among these are: production of volatiles; increase in viscosity, polarity, and free acid content; development of dark color; decrease in iodine value, changes in refractive index; decrease in surface tension; and an increased

tendency of the oil to foam. In addition, the particular food that is being fried plays an important role. It may produce volatiles of its own, it may interact with the frying oil, and it may contribute to the darkening of color.

Methods of Measurement

Several methods have been devised for assessing the extent of thermal or oxidative decomposition. No single test, however, can possibly measure all changes at once, or can be applicable to all conditions. Therefore, a combination of methods is often necessary to obtain reliable information.

The thiobarbituric acid (TBA) test is widely used for evaluating the extent of lipid oxidation. Oxidation products of unsaturated systems produce a color reaction with TBA. It is believed that the chromagen results from condensation of two molecules of TBA with one molecule of malonaldehyde. However, malonaldehyde is not always found in all oxidized systems, and various other compounds have been found to interfere with the TBA test by producing the characteristic pigment upon reaction with the reagents.

As discussed above, carbonyl compounds are major decomposition products of both oxidative and thermal decomposition. Methods for the determination of total carbonyl compounds are usually based on measurement of the hydrazones arising from reaction of aldehydes and ketones with 2,4-dinitrophenylhydrazine. The volatile carbonyl compounds may be analyzed by distillation of the fat, followed by reaction of the distillate with appropriate reagents. The anisidine and the Kreis tests are also designed to measure carbonyls.

Techniques to measure viscosity, free fatty acids, smoke point, foaming, changes in dielectric constants, polymer formation, and specific degradation products have been applied to monitor thermal and oxidative decomposition of oils during the frying process.

The ultimate judgment regarding the development of oxidized flavor in foods will always require sensory testing. Therefore, the value of any objective chemical or physical method depends largely on how well it correlates with organoleptic evaluation. Correlations of various chemical values (e.g., peroxide values, volatile compounds, etc.) with flavor panel scores have been used with varying degrees of success (21). In view of the practical implications involved, numerous laboratories are actively engaged in this area of investigation.

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