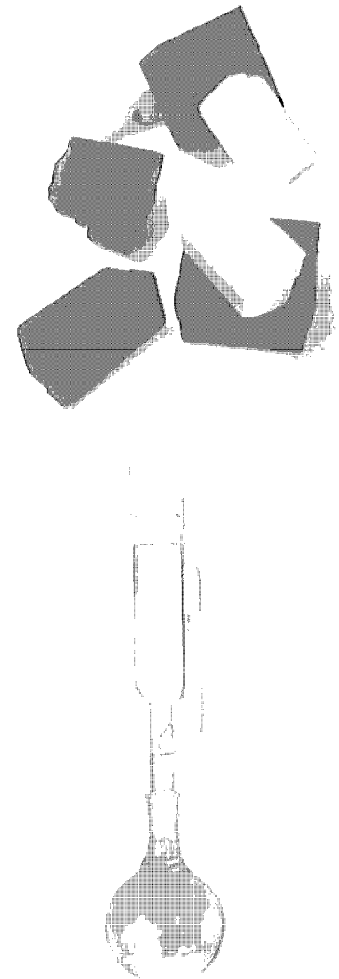
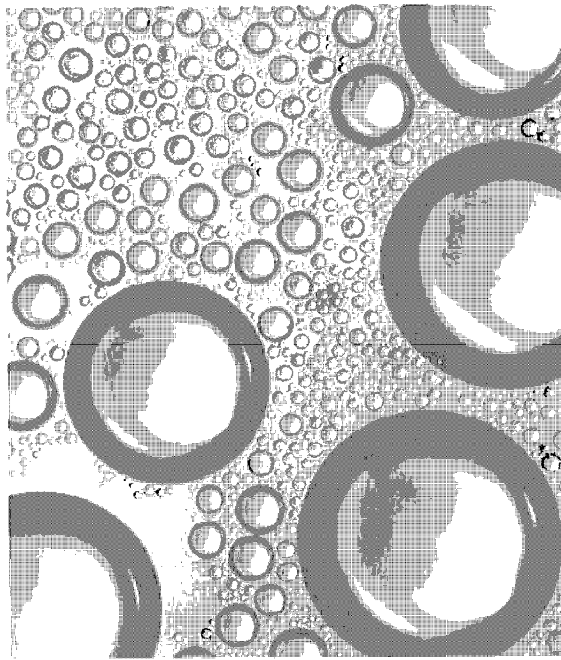
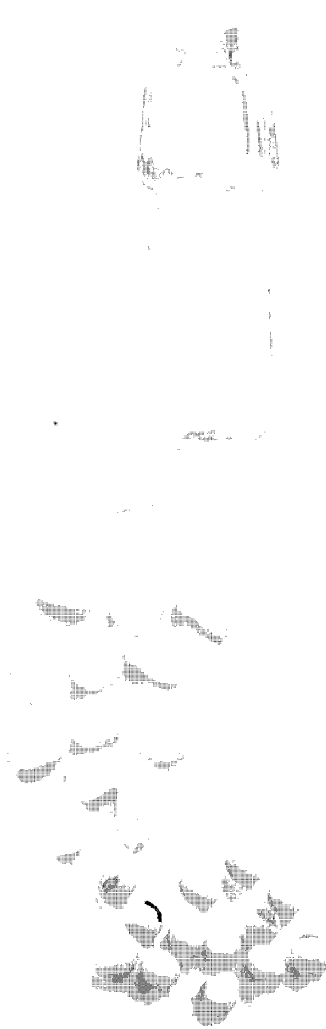


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PRACTICAL GUIDES FOR THE FOOD INDUSTRY

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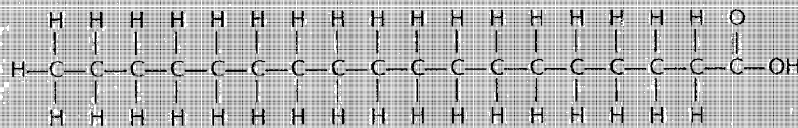
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nected with their conversion to a particular group of prostaglandins (see Chapter 9).

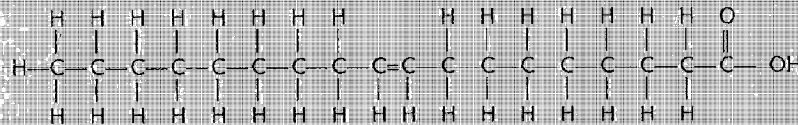
The chemical reactivity of unsaturated fatty acids is determined by the position as well as the number of the double bonds in the molecule. Reactivity increases markedly with an increase in the number of double bonds, provided they are *conjugated* (separated only by one single bond) or *methylene-interrupted* (separated by a $-\text{CH}_2-$ unit) (Box 1-5). If a fatty acid has two isolated double bonds (separated by two or more methylene units), its reactivity is only slightly greater than that of a fatty acid that has only one double bond. These differences are important when the fat is subjected to oxidation and also during the hydrogenation process.

In most naturally occurring unsaturated fatty acids, the double bonds are in the *cis* configuration. This means that the carbon chains on the

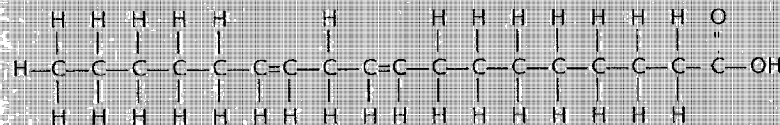
Box 1-3. Saturation



Stearic acid, C18:0 (saturated)



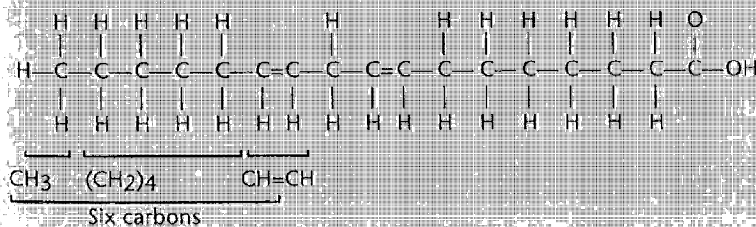
Oleic acid, C18:1 (monounsaturated)



Linoleic acid, C18:2 (polyunsaturated)

Box 1-4. An Omega Fatty Acid

There are six carbons between the terminal methyl group and the double bond, so linoleic acid is designated an $\omega 6$ fatty acid.



Carboxyl group—The chemical functional group on one end of a fatty acid. This is the same as a carboxylic acid (COOH), which can lose a proton and become COO^- , or combine with an alcohol group to form an ester.

Aliphatic—Describing a straight chain of carbons with no branching or ring structure.

Saturated—Describing a carbon chain in which the carbons are connected to each other by single bonds, drawn as C-C. It has no carbon-to-carbon double bonds.

Monounsaturated—Describing a fatty acid that has one double bond ($\text{C}=\text{C}$) in the carbon chain. Oleic acid is the most common of these.

Polyunsaturated—Describing a fatty acid that has more than one double bond ($\text{C}=\text{C}$) in the carbon chain. Linoleic acid is an example.

Omega fatty acids—A method of nomenclature that designates the number of carbons between the terminal $-\text{CH}_3$ group and the last double bond in the fatty acid. This is useful in discussing the physiological role of certain polyunsaturated fatty acids.

Conjugated—Describing a situation in which double bonds between carbon atoms occur in a series with one single bond in between ($\text{C}=\text{C}-\text{C}=\text{C}$).

Methylene-interrupted—Describing a situation in which double bonds between carbon atoms occur in a series with two single bonds in between ($\text{C}=\text{C}-\text{C}-\text{C}=\text{C}$).

CHEMICAL REACTIONS

Ester cleavage. The ester bonds in fat can undergo a variety of splitting reactions (Fig. 1-7). Some of these are important in food applications, while others have other industrial significance.

Hydrolysis. The addition of water yields a free fatty acid and a free hydroxyl group. This reaction, called *saponification*, is usually catalyzed with a base such as sodium hydroxide, and the fatty acid is neutralized to a sodium soap.

Glycerolysis. Glycerol can be the hydroxyl donor, forming a mono-glyceride with the fatty acid and leaving a mono- or diglyceride behind. This reaction is the basis for making monoglyceride emulsifiers for food use. In commercial production, a basic catalyst, usually potassium carbonate, is used.

Alcoholysis. The reaction of fat with alcohol is usually catalyzed with an acid such as HCl or a sulfonic acid resin. For example, reaction of fat with methanol yields the methyl esters of the fatty acids, which are used to analyze the composition of the fat by gas-phase chromatography.

Interesterification. A free fatty acid can displace another fatty acid from an ester, leaving a glyceride with somewhat changed properties because its fatty acid structure has changed. This reaction is used to change fat properties. Lard, for example, has a nonrandom fatty acid distribution in its triglycerides. All the palmitic acid (25% of the total) is found in the 2 position. As a result, lard crystallizes rather readily in the β form, which is not desirable for bakery purposes. Heating in the presence of sodium methoxide or metallic sodium causes the fatty acids to shuffle their positions in the triglycerides randomly. The resulting fat has a lower SFI profile and is stable in the β' crystal state, giving a more plastic shortening. Another application involves blending 20 parts fully hydrogenated soybean oil (which forms β crystals) with 80 parts refined soybean oil, then interesterifying. The product has the SFI profile appropriate for soft tub margarine, is β' stable, and has only a trace of *trans* double bonds.

Reduction. Fat ester bonds can also be split reductively, yielding glycerol and long-chain alcohols. The reductant is an amalgam of sodium and potassium metals. The resulting fatty alcohols are used to make various detergents and lubricants (waxes) and are of great economic importance.

Oxidation. *Autoxidation* of fats occurs with unsaturated fatty acid chains. The relative rates of oxidation of oleic, linoleic, linolenic, and arachidonic acids (which have one, two, three, and four double bonds, respectively) are 1, 12, 25, and 50. The double bonds in the polyunsaturated acids are separated by methylene groups and are *cis* in their configuration.

Autoxidation is a series of *free radical* reactions, initiated and propagated by free radicals reacting with methylene $-\text{CH}_2-$ groups that are adjacent to double bonds (Fig. 1-8). (A free radical is an unpaired electron, indicated as a heavy dot in chemical formulas. It is a very reactive species.) At the beginning of the autoxidation process, a

Hydrolysis—A chemical reaction in which a molecule splits into two parts. A molecule of water also splits into H and OH, which are added to the places where the original bond was broken. A fatty acid is removed from a glyceride by hydrolysis of the ester bond.

Saponification—A chemical reaction caused by addition of alkali in which the fatty acids attached to a glycerol are cleaved off to produce soap (fatty acid salts) and a glycerol molecule.

Glycerolysis—A chemical reaction in which glycerol is combined with one or more fatty acids to form a glyceride.

Alcoholysis—A chemical reaction in which fatty acids react with alcohol to form an ester.

Intesterification—Changing the positions of the fatty acids on triglycerides. This is a commercial processing step to change the physical properties of a fat.

Reduction—Changing an acid group on a fatty acid to an alcohol group. This is done with metal reducing agents to create fatty alcohols for industrial uses.

Autoxidation—A reaction in which fats undergo oxidative changes due to the double bonds in their structure. The reaction can initiate and proceed without outside influences.

Free radical—An unpaired electron that is an unstable intermediate in the development of lipid oxidation and rancidity.

Peroxy radical—An intermediate in lipid oxidation in which the fatty acid radical has added two oxygen atoms and is still a free radical. It is characterized by the structure $\text{COO}\cdot$.

Hydroperoxide—An intermediate in lipid oxidation in which the fatty acid has added two oxygen atoms and a hydrogen atom at the point of oxidation. It is no longer a free radical but eventually degrades to flavor compounds associated with rancidity.

Rancidity—An off flavor in a fat or oil caused either by oxidation or by the release of flavorful fatty acids from the triglyceride.

Stability—The resistance of a fat source to the formation of rancidity.

Antioxidants—Compounds that can inhibit the development of lipid oxidation.

hydrogen radical is extracted, and one of the double bonds shifts, moving the radical site to the outer carbon (reaction 1). Dissolved oxygen adds to this site, generating a *peroxy radical* (reaction 2); this abstracts a hydrogen from a donor—perhaps another methylene group—making a *hydroperoxide* (reaction 3). The hydroperoxide splits to generate two free radicals, a hydroxyl and an alkoxy radical (reaction 4). This cleavage is catalyzed by traces of metal ion such as copper or iron. The net result is three free radicals, each of which can initiate another chain of reactions. The rate of reaction is self-enhancing, i.e., it is an *autocatalytic* reaction.

The signs of *rancidity* (musty odors; bitter, disagreeable flavors) are due to breakdown products of the alkoxy radical structure. These products are a variety of aldehydes and ketones derived from breaking the fatty acid carbon chain at the point where it is oxidized. Common products are heptanal, ethyl hexyl ketone, and the ω -aldehyde of nonanoic acid.

The reactions described above can occur in the dark, as long as molecular oxygen and an initiating free radical species are present. If the oil is exposed to light, oxygen may be photoactivated to singlet oxygen, which can initiate the chain at the second step shown in Figure 1-8.

In summary, four main factors contribute to autocatalytic rancidity:

- Chain initiation by trace free radicals
- Chain propagation by molecular oxygen
- Hydroperoxide cleavage catalyzed by metal ions
- Chain initiation by photoactivated oxygen.

These factors can be minimized by good manufacturing practices. The trace free radicals arise from peroxides that are left behind from inadequate refining and deodorization. Molecular oxygen should be excluded by processing, transporting, and storing oil under a nitrogen atmosphere. Metal ions can be kept out of the oil by having properly designed and maintained equipment, and traces of metal in the oil can be inactivated by chelation with citric acid. Finally, the exposure of oil to light should be minimal. With these precautions, oil oxidative *stability* can be increased several fold.

Oxidative stability can also be increased with *antioxidants*. These react with the active free radicals, transferring the radical function to the antioxidant (Fig. 1-9). Because of the ring structure of the antioxidant, this radical has low reactivity and does not initiate new reaction chains. However, if free radicals continue to form, due to the presence of oxygen and trace metals, eventually all the antioxidant will react, and the autocatalytic sequence will develop without hindrance.

Several organic compounds are in use today as antioxidants. They all have in common the ring structure shown in Figure 1-9, but they vary somewhat in the structure of the side groups. The ones approved by the Food and Drug Administration (FDA) for use in foods are:

- BHA, butylated hydroxyanisole (shown in Fig. 1-9)
- BHT, butylated hydroxytoluene (as in Fig. 1-9, with $-\text{CH}_3$)

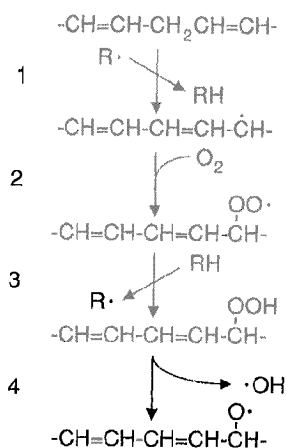


Fig. 1-8. Reactions occurring during autooxidation of fat.

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