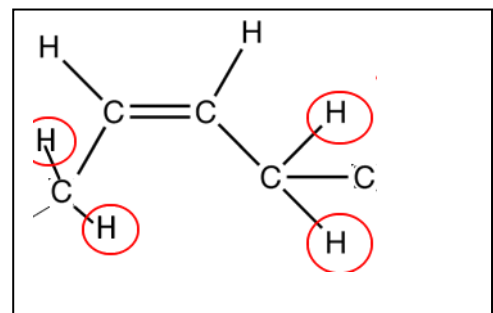


Lesson 3 Rancidity

Introduction

Because of their chemical structure, the presence of double bonds, unsaturated fats and oils are prone to chemical changes, via enzyme action, exposure to light or atmospheric oxygen. One of these chemical processes is known as **oxidative rancidity** and produces products with unpleasant smelling compounds. Oxidative rancidity occurs when an unsaturated triglyceride is exposed to oxygen. This causes the unsaturated triglyceride to form compounds such as short chain aldehydes, ketones and fatty acids with an unpleasant smell and taste. Butyric acid is one such short chain fatty acid that many may recognise as the distinct smell of parmesan cheeses or vomit. The higher the degree of unsaturation the more vulnerable the molecule becomes to oxidative rancidity. This reaction is a free radical chain reaction that involves the removal of a hydrogen radical (H•) from the fatty acid chain followed by a series of reactions with oxygen, rearrangements, and chain cleavage to produce foul smelling and tasting compounds.

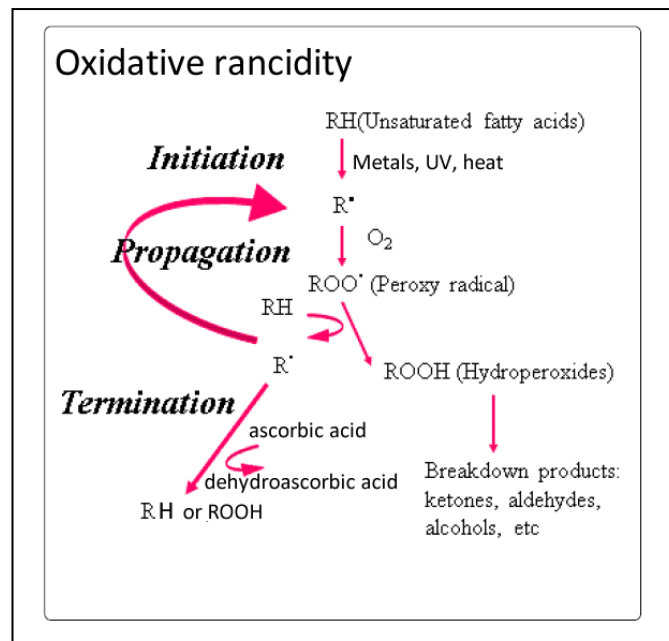
The methylene group, next to a double bond (-CH=CH-CH₂-CH=CH-) is particularly vulnerable to losing a hydrogen. The lipid radical (R•) formed rapidly reacts with oxygen to form a peroxy radical (ROO•) can receive a hydrogen atom to form a lipid hydroperoxide (ROOH) which is relatively stable and exists in significant quantities in many natural fats. The lipid hydroperoxide has no off-flavour but can rapidly break down (particularly in the presence of heat and a metal catalyst) to form malodorous short chain compounds..



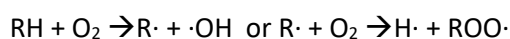
Lipid oxidation

Phases of lipid oxidation

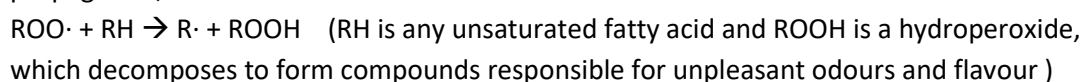
The overall mechanism of lipid oxidation consists of three phases listed below. R• represents a free radical formed by removing a hydrogen from a carbon atom adjacent to a double bond



- (1) initiation, the formation of free radicals;



- (2) propagation, the free-radical chain reactions



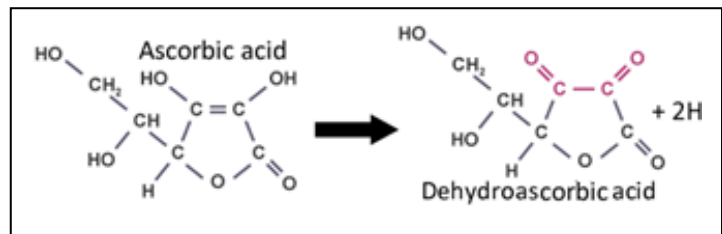
- (3) termination, the formation of non-radical products.



Anti-oxidants

The most common method of preventing oxidative rancidity, is by using compounds known as antioxidants. These compounds do not stop the formation of free radicals but they do prevent their propagation. Vitamin C is used as an antioxidant it is more readily oxidised than fats and oils. When a peroxide radical is formed (ROO·) vitamin C will donate hydrogen atoms to the radical thus preventing its reaction with nearby fat molecules.

Ascorbic acid is converted to the stable compound, dehydroascorbic acid, by losing two hydrogen atoms from the hydroxyl groups present on the ring structure of the molecule.



Apart for antioxidants, other factors that influence the rate of rancidity are:

Temperature: The rate of oxidative rancidity is highly dependent on temperature, the higher the temperature the greater the rate.

Oxygen: Exposure to atmospheric oxygen accelerates the rate of oxidative rancidity, especially in the presence of U.V. light.

Type of fat: The more unsaturated the fat molecule the greater the tendency for oxidative rancidity. Vegetable oils, although unsaturated, are generally more resistant to oxidative rancidity than animal fats because they contain natural antioxidants. Vitamin E is a common antioxidant found in vegetable oils. Fish oils, on the other hand, are highly unsaturated and hence more susceptible to oxidative rancidity.

Metals. Metals such as copper, iron, manganese, and chromium increase rate of fat oxidation.

Water. Enzymes such as lipases are present naturally in fats. These enzymes catalyse hydrolytic reactions that breakdown fats in the presence of water.

- 1) Explain how vitamin C acts as an antioxidant.
- 2) Fill the gaps below by choosing from the list of words. You may use any word more than once or not at all
Saturated fatty acids, aldehydes, triglyceride, ketones, oxygen, hydrogen
Oxidative rancidity occurs when a _____ is exposed to _____. This causes the _____ to form short chain compounds of _____, _____ and _____.
- 3) Ascorbic acid is an antioxidant. It is classified as a reducing agent. Explain why it is classified as a reducing agent and how this prevents oxidative rancidity.
- 4) The unpleasant smells and flavours associated with rancid foods are associated with which group/s of compounds?
a) Ketones, b) oxygen, c) alcohols, d) aldehydes, e) carboxylic acids, f) saturated fatty acids.

- 5) Animal fats are more likely to become rancid than plant oils even though plant oils have unsaturated fats. Explain why.
- 6) Explain why the softer the fat, the more susceptible it is to oxidative rancidity.
- 7) Hydrogenation, is a process where hydrogen atoms are added across a double bond. This process effectively hardens fat and decreases the molecules susceptibility to oxidative rancidity. Explain why hydrogenation hardens the fat and reduces its vulnerability to oxidative rancidity.
- 8) Rancidity can be prevented by covering the butter and storing it in a refrigerator.
- 9) When acting as an antioxidant Vit C is converted from ascorbic acid ($C_6H_8O_6$) to dehydroascorbic acid ($C_6H_6O_6$). What type of reaction is this? Explain.
- 10) It is found that storing meat in plastic containers in cool storage causes them to last longer. Explain why.
- 11) Meat is sometimes packed in containers filled with pressurised nitrogen gas. Explain why.

