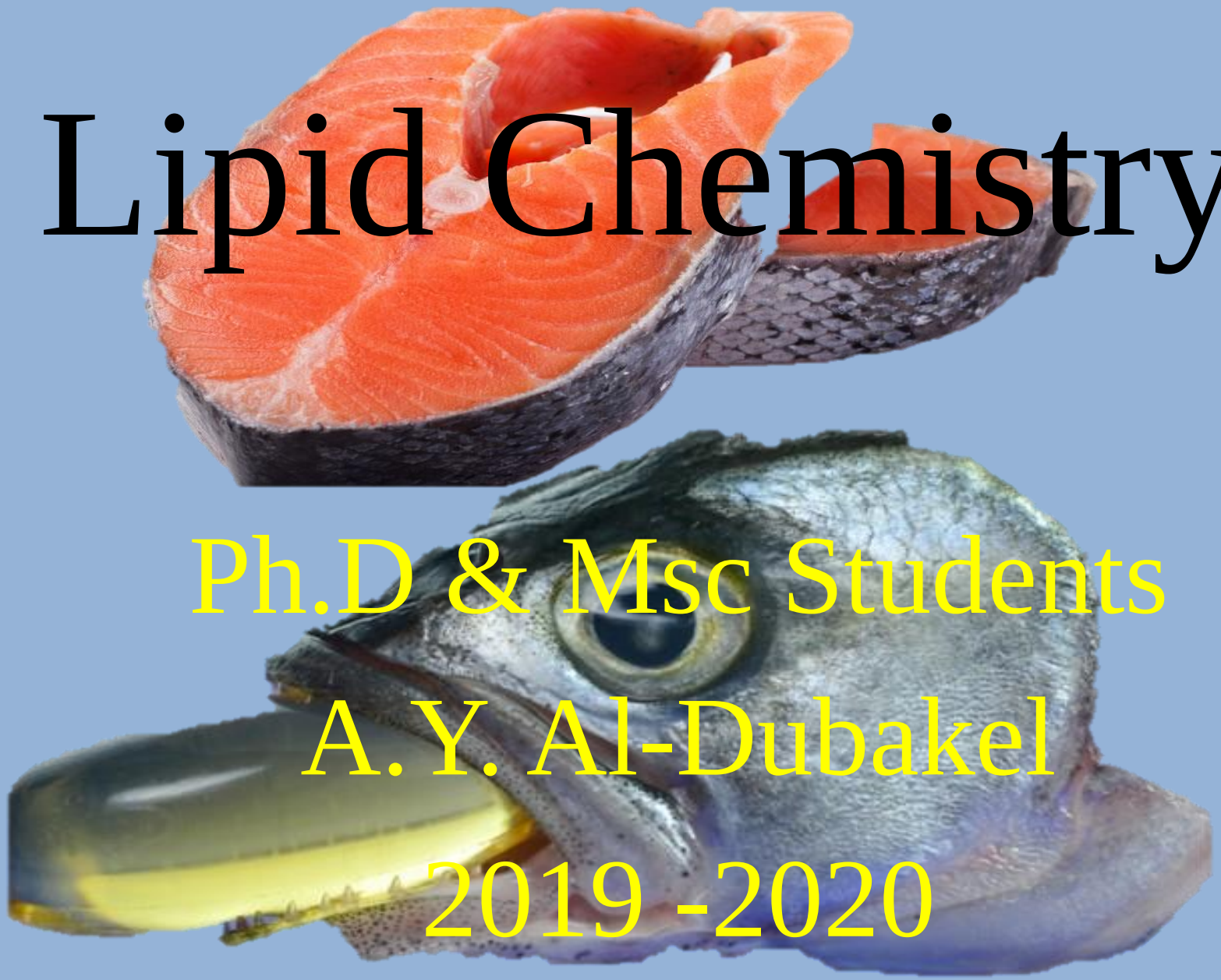
# Lipid Chemistry



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# Lecture 3

# Fish lipids

Lipid in fish generally carries natural flavour components. A certain amount of fat and fatty acid assists in providing smoothness of texture during eating of lean fish. In fatty fish the influence of fat on texture is even more important. The proximate composition of fish varies widely from species to species and even within the same species from one individual to another depending on age, sex, environment and season. The principal components of fish may be divided into five categories viz., water, protein, lipid, carbohydrate and ash.

# Proximate composition of fish

| Type of fish | Moisture % | Protein % | Fat % | Ash % | Carbohydrate % |
|---|---|---|---|---|---|
| Fatty fish | 68.8 | 20.0 | 10.0 | 1.2 | Negligible |
| Lean fish | 81.8 | 16.4 | 0.5 | 1.3 | < 0.5 |
| Crustaceans | 76.0 | 18.8 | 2.1 | 3.1 | < 0.5 |
| Mollusks | 81.0 | 12.0 | 1.5 | 2.6 | 2.9 |

**Notice the relation between Mois. & Fat**

# Variation of lipid content of dark and white meat of some fishes

| Fish species | Kind of meat | Moisture % | Crude protein % | Crude fat % |
|---|---|---|---|---|
| Tuna | D | 66.4 | 22.9 | 6.7 |
| | W | 68.5 | 22.9 | 4.5 |
| Sardine | D | 70.0 | 15.9 | 12.8 |
| | W | 72.0 | 23.1 | 2.9 |
| Mackerel | D | 54.2 | 14.9 | 29.7 |
| | W | 65.5 | 21.2 | 13.1 |
| Herring | D | 57.8 | 15.5 | 28.2 |
| | W | 74.0 | 22.0 | 13.0 |

# Distribution of Fat in Fish

The term lipid will be used for total fat component in fish. However, term fat is used for selected anatomical deposits, which are mostly triglyceride. In lean fish, the dark (red or lateral line) muscle has about twice the lipid of white muscle. The percentage of cellular lipid in the white muscle is normally altered by season. The lean muscle fish generally have more fat in livers (e.g. cod) which show seasonal variation. In the fatty fish species, the muscle shows fluctuating levels of seasonal variation in neutral fat

**a. Neutral fat (Triglycerids)**

Triglyceride or the neutral fat forms the major constituent of fish lipid. There are variations in the amount of neutral fat in muscle. The belly flap is a high fat section of many fishes. (E.g. In mackerel -29% lipid in belly flaps, 18.3% lipid in dark muscle and 7.6% in white muscle). In male mackerel the skin fat forms 40% of the total fat in the whole fish.

Triglyceride distributed through fish muscle tends to have a homogeneous fatty acid composition Most species of marine organisms try to obtain an optimal fat and fatty acid composition and their behavior and food preferences lead towards this objective. Their is usually a polyenoic fatty acid such as 20.5ω3 or 22:6ω3 in the 2 position, a saturated or monoenoic fatty acid in the 1 position and a monoenoic fatty acid in the 3 position.
The triglycerides of marine mammals are different, with the polyethylenic fatty acid concentrated at position 1 and 3.
Triglyceride

$^{1}CH_2O$ – COR - Saturated or monoenoic
|
2CHO – COR - 20.5ω3 or 22:6ω3
|
$3CH_2O$ – COR - Monoenoic

**b. Basic cellular lipids (Phospholipids)**

Lean white fish muscle contain a minimum of about 0.7% of basic cellular lipid, of which 85-95% is ‘polar’ lipids, mostly phosphatidyl ethanolamine and phosphatidyl choline. The balance of this type of basic lipid includes sterol ester and free sterol, free fatty acid and triglyceride.

This basic mixture represent the structural lipid of cell walls, and that any excess of triglyceride and/or certain other non-polar lipids such as wax esters or glyceryl ethers, provide the ‘fat’ of fatty fish.

# Fatty acids of fish lipid

The fatty acid s present in fish lipid is classified into three groups, saturated acids, monoenoic acids and polyenoic acids.

**1. Saturated Fatty Acid s**

The saturated fatty acids present in fish lipids are myristic or (14:0), palmitic or hexadecaenoic(16:0) and stearic or octadecaenoic(18:0). Palmitic (16:0) acid, is the principal saturated fatty acid (10-30% of the total), myristic (14:0) acid (5-10% of the total) and stearic (18:0) acid 1-3% of all fatty acid s. The 20:0, 22:0 and 24:0 fatty acid s are just detectable at levels of 0.01-0.1%. These fatty acid s can all be biosynthesized by the organisms, but they are also freely absorbed from dietary fats. Bacteria also contribute odd number straight-chain fatty acid s.

## 2. Monoenoic Fatty Acids

The monoenoic acids present in fish lipids are, oleic (C18:1ω7) , gadoleic (20:1 ω9) and cetoleic (22:1 ω11). The monoenoic fatty acids, palmitoleic acid (16:1) and oleic (18:1 ω9) of fish oils can be synthesized by fish and other marine organisms from acetate units. Palmitoleic acid forms 10-30% of the total 18:1 isomers. The origin of the 20:1 ω9 is by chain elongation of 18:1 ω9. The proportion of the minor isomers 20:1 ω11 and 20:1 ω7 relative to the major isomer 20:1 ω9 are similar in several fish oils. The dominant 22:1 isomer in marine fish oil is 22:1 ω11. In herring only the 22:1 ω9 isomer is biosynthesized.

## 3. Polyenoic Fatty Acids

The important polyenoic acid present in fish lipids are Eicosapentaenoic (EPA) (C20:5 ω3) and Docosahexaenoic (DHA) (C22:6 ω3). They give marine oils their most specific characteristics. The polyenoic fatty acid s (EPA) and (DHA) originate in unicellular phytoplankton or in some seaweed.

The average fatty acid composition of phytoplankton includes all the principal fatty acid found in the oils and lipids of the higher organisms. The $C_{18}$ fatty acid s 18:2 ω6 (linoleic acid) and 18:3 ω3 (linolenic acid) do not accumulate in most fish oils to the extent of more than 1% or 2% of fatty acid s. In many invertebrate lipids 20:5 ω3 is the dominant polyunsaturated fatty acid . This is possibly due to dietary algae.

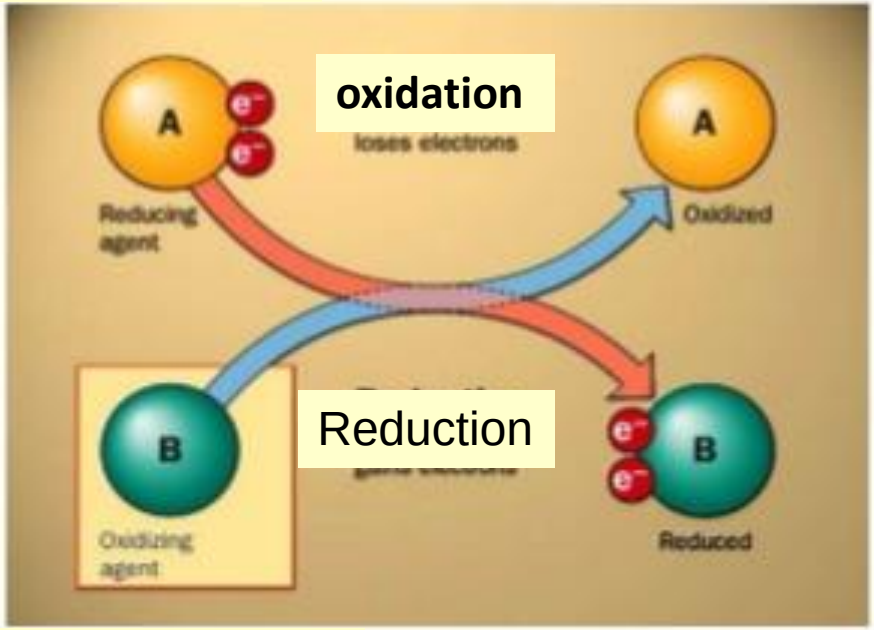
# Lipid oxidation

Lipid oxidation is one of the major causes of food spoilage. In edible oils and fat-containing foods, it leads to the development of various off flavors and off odors, generally known as oxidative rancidity, which renders the foods less acceptable. It may also be able to decrease the nutritional value of food and in some cases may produce potentially toxic products. It may be sometimes desirable as in the case of cheese.

# Oxidation

- Oxidation is any chemical reaction that involves the moving of electrons. Specifically, it means the substance that gives away electrons is oxidized.

Reducing agent




Oxidizing agent

# Types of Oxidation

Oxidaion is caused by a biochemical reaction between fats and oxygen called as autoxidation and it is the main reaction involved. The lipids of foods can be oxidized by both non- enzymic and enzymic mechanisms. Lipid oxidation generally occurs after a long induction period. Once started it is generally a very rapid reaction.