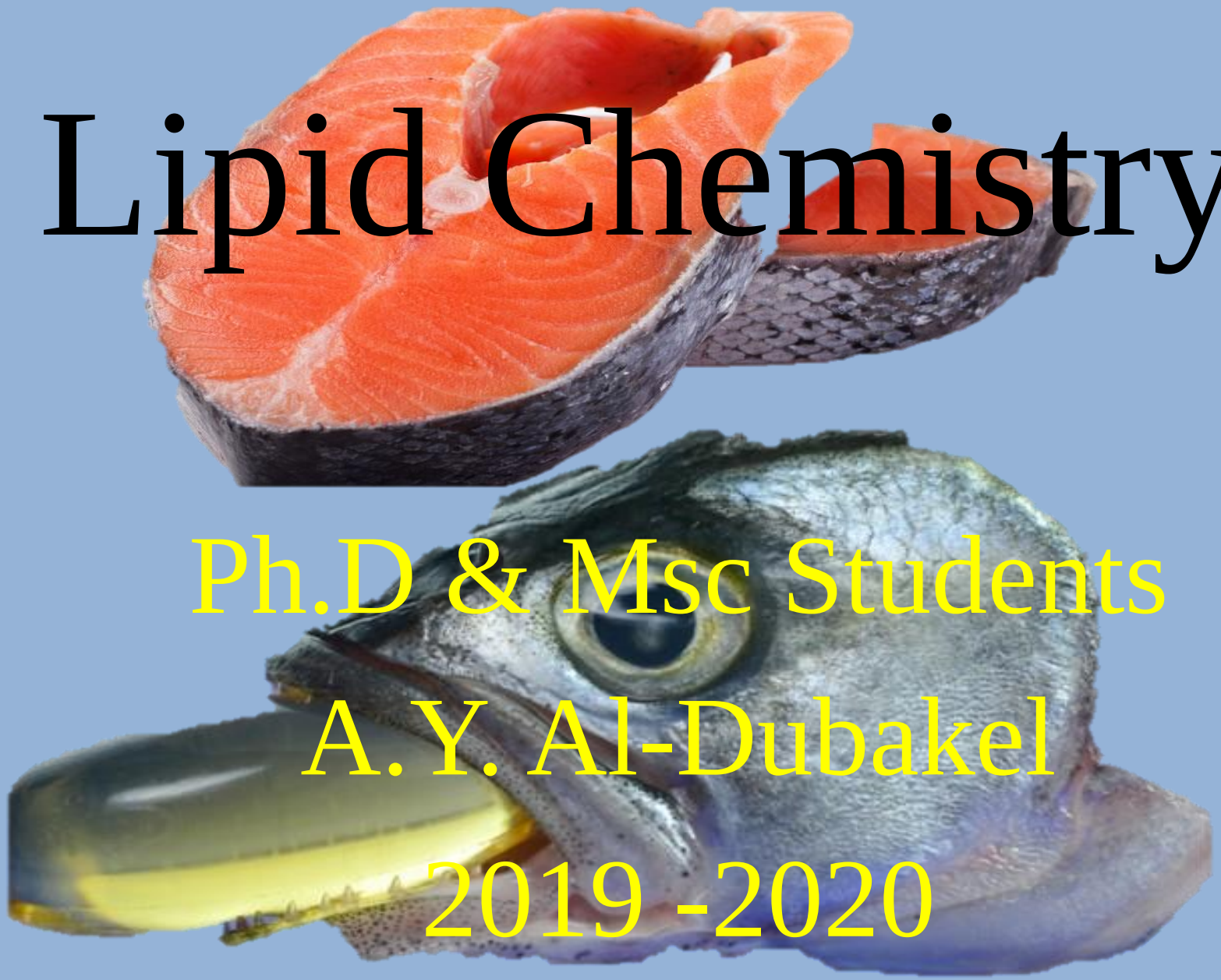
Lipid Chemistry



Ph.D & Msc Students

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Antioxidant

- An **antioxidant** is a molecule that can delay onset, or slow the rate of oxidation of oxidisable material. Oxidation reactions can produce free radical. In turn, these radicals can start chain reactions.

- Antioxidants terminate these chain reactions by removing free radical intermediates, and inhibit other oxidation reactions by acting as hydrogen donors or free radical acceptors.
- **ROO. + AH → ROOH + A.**

- Antioxidants are found in varying amounts in foods such as vegetables, fruits, grain cereals, eggs, meat, legumes and nuts.

- Antioxidants are widely used as preservatives in food and as ingredients in dietary supplements.

. **Natural antioxidants:** Ascorbic acid and tocopherols,

Synthetic antioxidants: Propyl gallate, isoamyl gallate, tertiary butylhydroquinone (TBHQ),butylated hydroxy anisole (BHA) and butylated hydroxy toluene (BHT).

Antioxidants can be directly added to vegetable oils or to melted animal fats after they are rendered.

Food products can also be dipped in or sprayed with solutions of antioxidants

Metabolism of fat

a) Metabolism of Triglycerides

Triglycerides are first converted to fatty acids and glycerol mostly in adipose tissue. The fatty acids are released into the plasma where they combine with serum albumin. Long chain fatty acids are oxidized in liver, heart, kidney, muscle, lung, brain and adipose tissue. Glycerol is utilized by liver, kidney, intestine.

b) Metabolism of fatty acids

The fatty acids components of the lipids entering the liver also have several different pathways

1. Oxidation to CO_2 with ATP production: Free fatty acids may be activated and oxidized to yield acetyl-CoA and ATP. The acetyl-CoA is oxidized via the citric acid cycle to yield ATP by oxidative phosphorylation. Fatty acids are the major oxidative fuel in the liver.

2. **Synthesis of fatty acids**: There are three types of fatty acid synthesis. (1) Elongation of existing short chain fatty acid in the mitochondria (2) Microsomal system of chain elongation and (3) The cytoplasmic synthesis of fatty acid from acetyl CoA.

3. Biosynthesis of cholesterol: Some of the acetyl-CoA derived from fatty acids (and from glucose) will be used as the major precursor for the biosynthesis of cholesterol, which in turn is the precursor of the bile acids and bile salts, which are essential for the digestion and absorption of lipids.

4. **Biosynthesis of lipids of plasma lipoproteins(Triglyceride and phospholipids):** Fatty acids are also used as precursors for the synthesis of the lipid portion (triglycerides and phospholipids) of the plasma lipoproteins, which carry lipids to adipose or fat tissue for storage as triglycerides.

5. Fomation of ketone bodies: Excess acetyl-CoA released on oxidation of fatty acids and not required by the liver is converted into the ketone bodies, acetoactate and D-β-hydroxy butyrate, which are circulated via the blood to peripheral tissues, to be used as fuel for the citric acid cycle. The ketone bodies may be regarded as a transport form of acetyl groups. They can supply significant fraction of the energy to some peripheral tissues, up to one-third in the case of the heart

Synthesis of fatty acid

There are three types of fatty acid synthesis. (a) Elongation of existing short chain fatty acid in the mitochondria (b) Microsomal system of chain elongation and (c) The cytoplasmic synthesis of fatty acid from acetyl CoA.

a. Elongation of smaller fatty acid mitochondrial System Mitochondria catalyses the incorporation of acetyl CoA into smaller chain fatty acids into longer chain fatty acids under anaerobic conditions.

The enzymes are mostly the same as those involved in β-oxidation except the α - β unsaturated acyl CoA reductase which converts α-β unsaturated acyl CoA to a saturated compound requiring NADPH+H+. Thiolase is not used in this pathway. Pyidoxal phosphate is required for the enzyme condensing acetyl CoA with acyl CoA.

b. Microsomal System of elongation of smaller fatty acid
This is the main pathway for the elongation of existing fatty acid molecules. Elongation of fatty acid chains occurs in the endoplasmic reticulum. This pathway the ("microsomal system") converts fatty acyl-CoA to higher fatty acids using malonyl CoA as acetyl donor and NADPH+H+as reducing agent catalyzed by the microsomal fatty acid elongase system of enzymes.
The acyl groups that may act as a primer molecule include the saturated series from C10-C16 upward, as well as unsaturated C18fatty acids.
Elongation of stearyl-CoA in brain increases rapidly during myelination in order to provide C22 and C24 fatty acids that are needed for the synthesis of sphingolipids.

c. Synthesis of fatty acids in cytoplasm

The main pathway for the synthesis of fatty acids from acetyl CoA occurs in the cytoplasm. This system is present in many tissues, including liver, kidney, brain, lactating mammary gland and adipose tissues. Its cofactor requirements include NADPH, ATP, Mn^{2+}, biotin, and HCO_3 (as a source of CO_2). Acetyl-CoA is the immediate substrate, and free palmitate is the end product.

Lipid Measurement General Methods

1) Soxhlet extraction

2) Folch's extraction

3) Liquid-solid extractions

4) Thin -layer chromatography

Lipid Measurement Specific Methods

a) Solvent Extraction

1) Batch Solvent Extraction

2) Semi-Continuous Solvent Extraction

3) Continuous Solvent Extraction

4) Accelerated Solvent Extraction

5) Supercritical Fluid Extraction