

Lecture 12

Discipline: Bioorganic Chemistry

Lecturer: Associate Professor, Dr. Gulnaz Seitimova

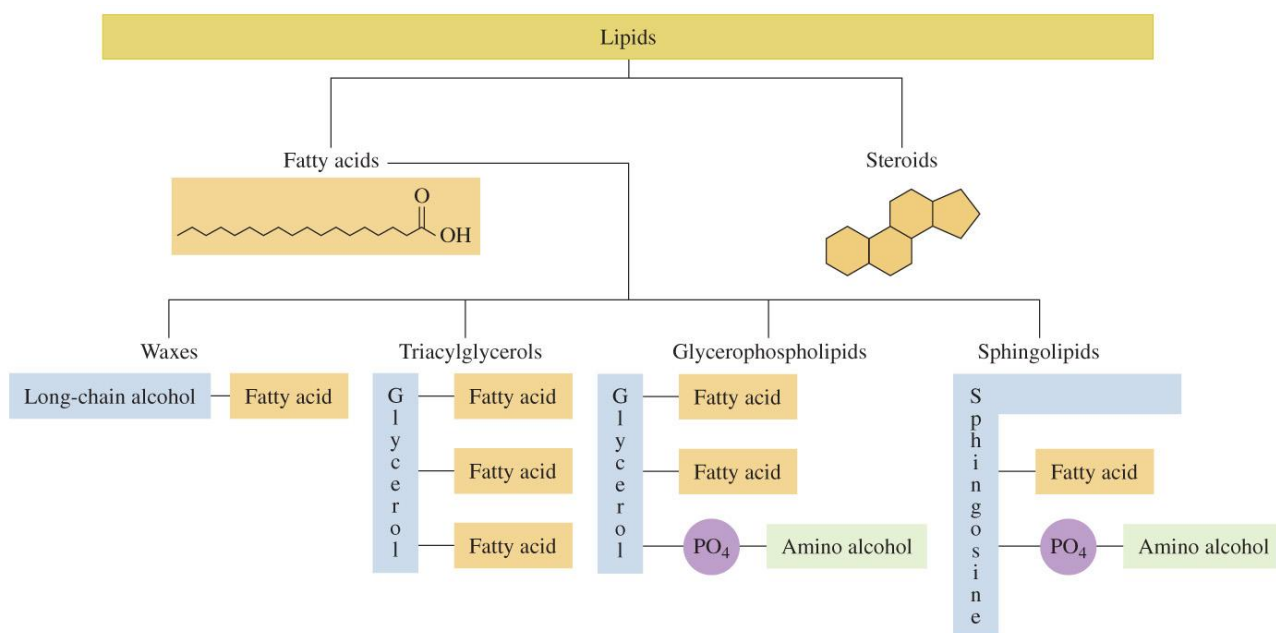
Title: Saponifiable and unsaponifiable lipids. Their classification. Features of the structure of neutral lipids (fats, oils), their structure and chemical properties.

Objective: The aim of this lecture is to introduce the structural and functional diversity of saponifiable and unsaponifiable lipids, classify them according to chemical features, and describe the structure, properties, and biological significance of neutral lipids including fats and oils.

Main Questions: Definition, general characteristics, and biological importance of lipids. Classification of saponifiable and unsaponifiable lipids. Structural features of neutral lipids (fats and oils). Chemical properties of fats and oils. Physiological functions of lipids in organisms. Applications in biochemistry, medicine, and industry.

Key Notes and Theses

Lipids are a large and diverse group of hydrophobic or amphipathic molecules that play essential roles in biological systems. They function as energy sources, structural components of membranes, signaling molecules, and precursors of hormones, vitamins, and metabolic intermediates. Lipids are broadly divided into saponifiable and unsaponifiable classes based on their ability to undergo alkaline hydrolysis.



© 2013 Pearson Education, Inc.

Saponifiable Lipids

Definition

Saponifiable lipids contain ester bonds that can be hydrolyzed by strong bases (NaOH or KOH) to produce glycerol and fatty acid salts (soaps).

Classification of Saponifiable Lipids

1. Simple lipids
 - Neutral lipids (acylglycerols: mono-, di-, and triacylglycerols)
 - Waxes (esters of fatty acids with long-chain alcohols)
2. Complex lipids
 - Phospholipids
 - Glycerophospholipids
 - Sphingophospholipids
 - Glycolipids
 - Cerebrosides
 - Gangliosides
 - Lipoproteins

Characteristics

- Derived from fatty acids
- Hydrolyzable by alkali
- Major structural components of cell membranes (phospholipids, glycolipids)
- Energy reserve molecules (triacylglycerols)

Unsaponifiable Lipids

Definition

Unsaponifiable lipids do not contain ester bonds and therefore cannot undergo saponification.

Classification

1. Isoprenoids (terpenoids)
 - Essential oils
 - Carotenoids
2. Steroids
 - Cholesterol
 - Sex hormones
 - Corticosteroids
3. Fat-soluble vitamins
 - Vitamins A, D, E, K
4. Prostaglandins and related signaling molecules

Characteristics

- Derived from isoprene units or sterol skeletons
- Play regulatory and signaling roles
- Do not yield fatty acids upon hydrolysis

Neutral Lipids (Fats and Oils)

Definition

Neutral lipids are nonpolar, uncharged molecules commonly found as storage lipids in plants and animals. The majority are triacylglycerols (TAGs) – esters of glycerol with three fatty acids.

Structure of Triacylglycerols

- Glycerol backbone (propane-1,2,3-triol)

- Three fatty acids attached via ester bonds
- Fatty acids may be:
 - Saturated (e.g., palmitic, stearic acids)
 - Unsaturated (e.g., oleic, linoleic acids)

Fats vs. Oils

- Fats: solid at room temperature; high in saturated fatty acids
- Oils: liquid at room temperature; high in unsaturated fatty acids

Melting point depends on:

- Degree of saturation
- Chain length
- Cis vs. trans configuration of double bonds

Chemical Properties of Neutral Lipids

1. Hydrolysis

- Acidic, enzymatic, or alkaline hydrolysis breaks ester bonds
- Alkaline hydrolysis → saponification
 - TAG + NaOH → glycerol + sodium fatty acid salt (soap)

2. Hydrogenation

- Conversion of unsaturated fatty acids into saturated ones
- Used in food industry (margarine production)
- May form trans fatty acids, which have adverse health effects

3. Oxidation

- Unsaturated lipids undergo oxidation leading to rancidity
- Initiated by oxygen, light, metals
- Generates aldehydes, peroxides, and volatile compounds

4. Esterification and Interestification

- Exchange of fatty acids between glycerol molecules
- Used to modify melting behavior of fats

5. Isomerization

- Cis double bonds can convert to trans configuration during cooking or processing

Physiological Functions of Lipids

1. Energy storage

- Triacylglycerols provide 9 kcal/g, more than twice carbohydrates
- Stored in adipose tissue

2. Structural role

- Phospholipids and glycolipids form membrane bilayers

3. Protective functions

- Thermal insulation
- Protection of internal organs

4. Regulation and signaling

- Steroids act as hormones
- Eicosanoids regulate inflammation and blood pressure

5. Transport

- Lipoproteins transport lipids in blood

- Fat-soluble vitamins require dietary lipids for absorption

Distribution in Nature

Neutral lipids occur in:

- Animals: adipose tissue, milk fat
- Plants: seeds, nuts, fruits (olive, sunflower, coconut oils)
- Marine organisms: fish oils (rich in polyunsaturated fatty acids)

Sterols and terpenoids are widespread across plants and animals.

Applications of Saponifiable and Unsaponifiable Lipids

Saponifiable lipids:

- Soap production
- Detergents
- Cosmetics
- Food industry
- Pharmaceutical formulations
- Nanocarriers for drug delivery

Unsaponifiable lipids:

- Hormone pharmaceuticals (estrogen, testosterone)
- Vitamin supplements (A, D, E, K)
- Steroid-based anti-inflammatory drugs
- Cosmetic antioxidants (tocopherols)

Questions for Knowledge Assessment

1. What are saponifiable lipids and what structural feature defines them?
2. Describe the main classes of unsaponifiable lipids.
3. What is the structural difference between fats and oils?
4. Explain the process and significance of saponification.
5. How do saturation and chain length affect the melting point of lipids?
6. What are the major biological functions of neutral lipids?
7. Why are trans fatty acids harmful to human health?
8. Give examples of physiologically important unsaponifiable lipids.

Recommended Literature

1. Nelson, D. L., Cox, M. M. (2017). *Lehninger Principles of Biochemistry* (7th ed.). New York: W.H. Freeman and Company.
2. Voet, D., Voet, J. G. (2011). *Biochemistry* (4th ed.). Hoboken, NJ: John Wiley & Sons.
3. Garrett, R. H., Grisham, C. M. (2016). *Biochemistry* (6th ed.). Boston, MA: Cengage Learning.
4. Stryer, L., Berg, J. M., Tymoczko, J. L., Gatto, G. J. (2015). *Biochemistry* (8th ed.). New York: W.H. Freeman and Company.
5. McMurry, J. (2010). *Organic Chemistry with Biological Applications* (2nd ed.). Belmont, CA: Brooks/Cole, Cengage Learning.

6. McMurry, J., Castellion, M. E. (2002). *Fundamentals of General, Organic, and Biological Chemistry* (4th ed.). Upper Saddle River, NJ: Prentice Hall.
7. Fromm, H. J., Hargrove, M. (2012). *Essentials of Biochemistry*. Berlin, Heidelberg: Springer-Verlag.
8. Hunter, G. K. (2000). *Vital Forces: The Discovery of the Molecular Basis of Life*. San Diego, CA: Academic Press.
9. Tyukavkina, N. A., Baukov, Y. I. (2014). *Bioorganic Chemistry* (in Russian). Moscow.
10. Ovchinnikov, Y. A. (1987). *Bioorganic Chemistry* (in Russian). Moscow.
11. Rouessac, F., Rouessac, A. (2007). *Chemical Analysis: Modern Instrumentation Methods and Techniques*. Hoboken, NJ: John Wiley & Sons.
12. Jeffery, G. H., Bassett, J., Mendham, J., Denney, R. C. (1989). *Vogel's Textbook of Quantitative Chemical Analysis* (5th ed.). London: Longman; John Wiley & Sons.