Chapter 24

Lipids

Chapter 24 suggested problems: none

Class Notes

I. Classification of lipids

A. General

1. (Lehninger: 279) "Water-insoluble organic biomolecules that can be extracted from cells and tissues by nonpolar solvents, e.g., chloroform, ether, or benzene."

2. There are several families of lipids but all derive their unique properties from a substantial hydrocarbon aspect

3. Biological functions

a. Provide structure in membranes

b. Storage and transportation of metabolic fuel

c. Chemical messengers

4. Often combined with other classes of biomolecules to form glycolipids (contain both lipids and carbohydrates) and lipoproteins (contain both lipids and proteins)

5. Several ways of classifying lipids, but most commonly by backbone structure

B. Complex lipids (hydrolyzable or saponifiable)

1. Usually contain one or more fatty acids joined to backbone via ester linkage

2. Acylglycerols: glycerol backbone

3. Phosphoglycerides: glycerol-3-phosphate backbone

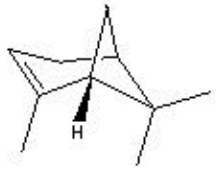
4. Sphingolipids: sphingosine backbone (amino alcohol)

5. Waxes: high MW esters of long-chain fatty acids and long-chain monohydroxyalcohols or sterols

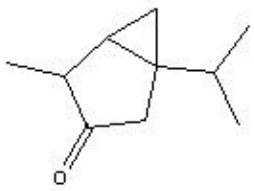
C. Simple lipids (nonhydrolyzable or non-saponifiable)

1. Do not contain fatty acids and are therefore not esters and not hydrolyzable

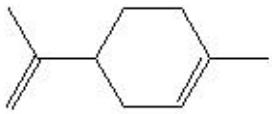
2. Terpenes
    a. Chains of multiple isoprene (2-methyl-1,3-butadiene) units
        i. Monoterpenes: 2 isoprene units
        ii. Sesquiterpenes: 3 isoprene units
        iii. Diterpenes: 4 isoprene units
        iv. Triterpenes: 6 isoprene units
        v. Tetraterpenes: 8 isoprene units
    b. Can have head to tail chains, tail to tail chains, or irregular chains
    c. Hundreds have been identified, esp. in plants
    d. Most have characteristic odors and flavors and are major components of essential oils
        i. Frankincense: "mainly monoterpene hydrocarbons, notably pinene, dipentene, limonene, thujone, phellandrene, cymene, myrcene, terpinene. . . ." (source: "The Illustrated Encyclopedia of Essential Oils" by Judith Lawless)
            1. Pinene: (1S)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene



            2. Thujone: 1-Isopropyl-4-methylbicyclo(3.1.0)hexan-3-one

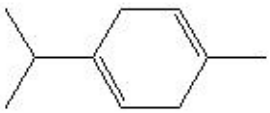


            3. Limonene: 1-methyl-4-(1-methylethenyl)cyclohexene

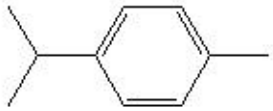


            4. Phellandrene: 1-Isopropyl-4-methyl-2,4-cyclohexadiene

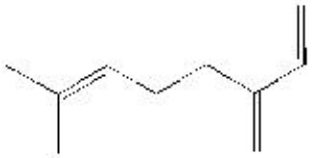
            5. Terpinene: 1-Isopropyl-4-methyl-1,4-cyclohexadiene



6. Cymene: 1-Methyl-4-isopropylbenzene

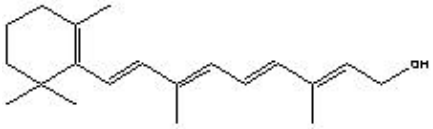


7. Myrcene: 7-Methyl-3-methylene-1,6-octadiene

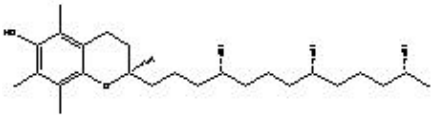


e. Vitamins A, E, and K are terpenes

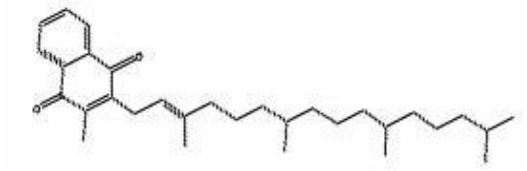
i. Vitamin A: 2,4,6,8-nonatetraen-1-ol,
3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-, (all-E)-;



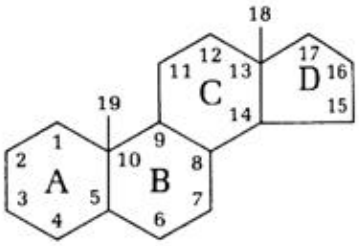
ii. Vitamin E: 2H-1-Benzopyran-6-ol,
3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-,[2R-[2R*(4R*,8R*)]]-



iii. Vitamin K:



3. Steroids: based on perhydrocyclopentanoanthracene structure



4. Prostaglandins (eicosanoids): based on arachidonic acid, a 20:4 fatty acid

II. Fatty acids

common name	systematic name	structure	symbol
saturated fatty acids			
lauric	n-dodecanoic	$CH_3(CH_2)_{10}COOH$	12:0
myristic	n-tetradecanoic	$CH_3(CH_2)_{12}COOH$	14:0
palmitic	n-hexadecanoic	$CH_3(CH_2)_{14}COOH$	16:0
stearic	n-octadecanoic	$CH_3(CH_2)_{16}COOH$	18:0
arachidic	n-eicosanoic	$CH_3(CH_2)_{18}COOH$	20:0
lignoceric	n-tetracosanoic	$CH_3(CH_2)_{22}COOH$	24:0
unsaturated fatty acids			
palmitoleic		$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	16:1
oleic		$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	18:1
linoleic		$CH_3(CH_2)_4(CH=CHCH_2)_2(CH_2)_6COOH$	18:2
linolenic		$CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COOH$	18:3
arachidonic		$CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2COOH$	20:4
eicosapentaenoic		$CH_3CH_2(CH=CHCH_2)_5(CH_2)_2COOH$	20:5

A. General

1. Saturated fatty acids - no double bonds
2. Unsaturated fatty acids - 1 or more double bonds, generally cis configuration
3. Monounsaturated and polyunsaturated fatty acids
4. Palmitic and stearic are the most abundant
5. Essential fatty acids: synthesized only by plants but required by animals: linoleic and linolenic
6. Nonessential fatty acids: synthesized by animals
7. w-nomenclature system: the carbon atom in the terminal methyl group is labeled the w-1 carbon and the w-number of the fatty acid is number of the first carbon of the first double bond
    a. Linolenic: w-3 fatty acid
    b. Linoleic: w-6 fatty acid

B. Physical properties - depend on the number of carbon atoms and double bonds

1. Low solubility in aqueous solution
2. cis-double bonds introduce "kinks" into hydrocarbon chains and affect the ability of the molecules to pack closely together
3. trans-double bonds do not introduce distortion to the same extent

III. Triacylglycerols (triglycerides)

A. General

1. Constitute up to 90% of our dietary intake of lipids

B. Structure

1. Formed by the esterification of a glycerol molecule with 3 fatty acid molecules (glycerol triesters)

2. Simple triacylglycerols: all the fatty acids are the same

3. Complex (mixed) triacylglycerols: the fatty acids are all different

C. Physical properties

1. Oils: liquid triacylglycerols at STP

2. Fats: solid triacylglycerols at STP

3. Any fat or oil is a mixture of various triacylglycerols

D. Chemical properties

1. Hydrolysis: deesterification to produce fatty acids and glycerol, can be acid or base catalyzed

2. Catalytic hydrogenation of carbon-carbon double bonds and conversion of unsaturated to saturated fats

3. Rancidity

a. Due to bacterial hydrolysis and fatty acid production, especially butyric and hexanoic acid production

b. Air oxidation of double bond results in C=C cleavage and formation of two carboxylic acid groups

IV. Waxes

A. High MW esters of long-chain fatty acids and long-chain monohydroxyalcohols or sterols

1. Soft and easily shaped when warm, hard when cold

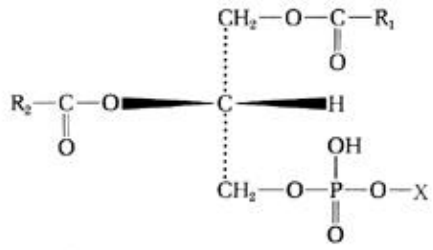
2. Provide protective coatings on skin, fur, feathers, leaves, fruits, and arthropod exoskeletons

3. Beeswax: palmitic acid esters with 24-36 carbon alcohols

V. Amphipathic hydrolyzable lipids

A. Amphipathic: both polar and nonpolar parts

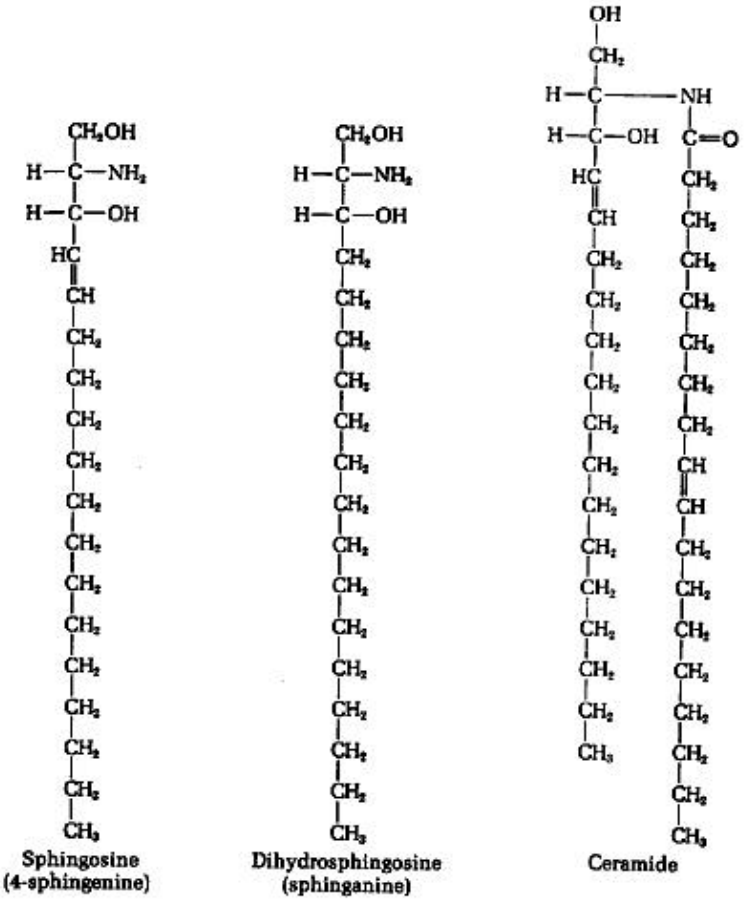
B. Phosphoglycerides: glycerol-3-phosphate backbone



General structure of phosphoglycerides.
The moiety X is contributed by an alcohol.

1. Also called glycerol phosphatides, phosphatides, and phospholipids
2. Not all phosphorus-containing lipids are correctly classed as phospholipids (e.g., sphingomyelin also contains phosphorus but is better classed as a sphingolipid)
3. Major components of cell membranes, seldom found elsewhere in cells
4. C-2 is chiral, can have D-glycerol-1-phosphate or L-glycerol-3-phosphate
5. "X" bonded to the phosphate group is generally an alcohol, often enthanolamine, choline, serine, inositol

C. Sphingolipids: sphingosine backbone (amino alcohol)



Sphingosine (4-sphingenine) | Dihydrosphingosine (sphinganine) | Ceramide

1. Sphingolipids are based on sphingosine rather than glycerol
2. Sphingophospholipids have a phosphodiester group attached to the sphingosine H-1 hydroxyl group

3. Sphingoglycolipids are bonded to a saccharide (may be mono or oligo) group at the sphingosine H-1 hydroxyl group via an acetal linkage

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[Chemistry 1120 Index Page]

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