

Chem 431A lecture 9A
admin: quiz on Wednesday ; HW due tomorrow

Last lecture:
1) melting expts of DNA
2) sequencing of DNA

Today (**Chapter 10 - LIPIDS**)

Lipids: Review

1) Intro: lipids are last of the classes of biomolec
we'll cover in biochem.

they are nonpolar molecules (oily),

2) Storage lipids

Consider storage lipids

-composed of carboxyl group (C_1),

even number of C's (usually)

-saturated and unsaturated (mono, poly). double
bonds are typically cis.

- palmitic acid (16:0), octahexanoic acid



-highly reduced, has lots of energy stored for
oxidation.

-nonpolar character

-unbranched hydrocarbon tail.

are essential components of biomembranes, are
-fats

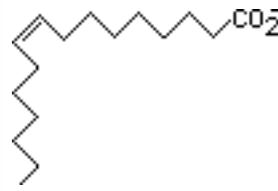
-fatty acids exist in great abundance not in free
form but in complexed form

-HC tail flexible but straight chain is favored.

palmitoleic acid: (16:1⁹) or (16:1(9)) or (16:1Δ⁹)..

-monounsaturated fa with double bond between C9
& C10.

-cis configuration causes a "kink" and bend with
struc consequences.



Kinds of fatty acids (fa's) (you need to know list) *** refer to table 10-1

Common name	Systematic name	Abbrev.	Structure	melting point
Lauric	n-dodecanoic acid	12:0	$CH_3(CH_2)_{10}COOH$	44.2
Myristic	n-tetradecanoic a.	14:0	$CH_3(CH_2)_{12}COOH$	53.9
Palmitic	n-hexadecanoic	16:0	$CH_3(CH_2)_{14}COOH$	63.1
Stearic	n-octadecanoic	18:0	$CH_3(CH_2)_{16}COOH$	69.6
Arachidic	n-eicosanoic	20:0	$CH_3(CH_2)_{18}COOH$	76.5
Palmitoleic	cis-9-hexadecenoic	16:1cΔ ⁹	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0°C
Oleic	cis-9-octadecenoic	18:1cΔ ⁹	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16
Linoleic	cis,cis-9,12-octadecadienoic	18:2cΔ ^{9,12}		5
α-Linolenic	all cis-9,12,15	18:3xΔ ^{9,12,15}		-11
γ-Linolenic	all cis-6,9,12	18:3xΔ ^{6,9,12}		

Know especially saturated: lauric, myristic,
palmitic, stearic arachidic; and unsat'd: palmitoleic,
oleic, linoleic, α-linolenic, γ-linolenic

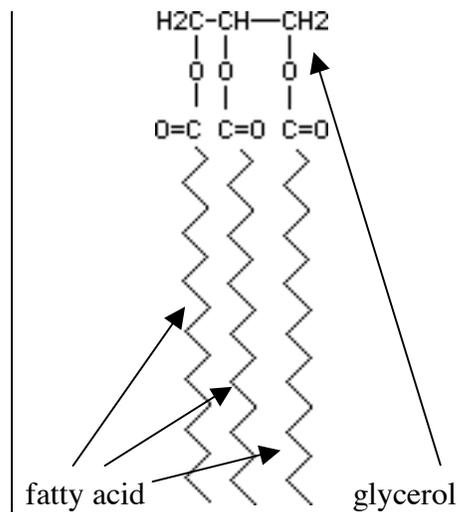
essential fa's can't be synthesized by body but need
to be in diet. (*essential* refers to dietary need)
linoleic & γ-linolenic acids are *essential* fatty acids.

triacylglycerols (triglycerides, TG) are the main neutral derivatives and is the form by which fatty acids are stored.
-breakdown releases CO_2 & H_2O

useful for energy storage in adipose tissue (oil depots)-
note: get 38 kJ/g TG vs 17 kJ/g CHO (and proteins). It doesn't

need to be heavy, no water of hydration needed unlike CHO).
Doesn't disturb *osmolarity* of the aqueous environment in cell.

simple TG : all three fa's are the same. example *tripalmitin*.
Note: if only 2 fa's, diglycerides, if only 1, monoglycerides.



(2) Recap: FA's are very reduced molescs. redox energy
TG's neutral(charge) molescs; no hydrn; 38kJ/g; compared to CHO's&prot's 17kj/g. 21%men,26%women's wt. Survive2-3mos starvation. Glycogen<day.

Insulation aquatic animals
(2a) We saw how TGs are synthesized from 3 FAs esterified onto a glycerol backbone. Simple TGs: tripalmitin = TG with 3 identical palmitic acid FA's.

(3) Hydrolysis of TGs under alkali conditions: *saponification*. (sapon=soap) soap is the metal salt of a FA. It acts as a detergent. Ie. It is able to emulsify by forming *micelles* around greasy particles and lift them off in water.
(some tie advance of civilization to the invention of *saponification*: the use of

wood ashes to get KOH and then using that to boil animal fat to get soap. Problem of such soap is that it forms scum when using hard water (Mg, Ca salts). Hard water comes from water in our faucets which are often from wells. So, other modern detergents are used. Eg. SDS sodium dodecyl sulfate (the sulfate in place of carboxylate).

(4) Our body utilizes the FA's by first hydrolyzing them from TG's using enzymes called *phospholipases*. The FA's are carried to the cells in association with *serum albumins* which allows the FA's to travel without deleterious (detergent) effects on the cells. Very bad for the cells otherwise.

(5) Diacylglycerols (DGs) or diglycerides: -contain only 2 FA's. in 1 & 2 positions. The 3rd position may be *esterified* to something else. Eg. If have a phosphoester at 3 position:*diacylglycerol phosphate* ("*phosphatidic acid*"). This is parent compnd for *glycerophospholipids*. Which are very impt in membranes.

(6) Most common phospholipids (PL) are:
 PC = *phosphatidyl choline (lecithin)*. Here the FAs are usually palmitic acid. The headgroup region has the (-) phosphate group and in addition, a (+) choline group. $-O-(PO_2)-O-CH_2CH_2-N(CH_3)_3^+$
 Note that the variables are : FA's, the

PS = phosphatidylserine:
 $(-O-(PO_2)-O-CH_2CH(CO_2^-)(NH_3^+),$
 PI = phosphatidylinositol.
 $(-O-(PO_2)-O-C_6H_6OH_5)$
 PG = phosphatidylglycerol
 $((-O-(PO_2)-O-CH_2CHOH-CH_2OH)$

Draw the general structure of a phospholipid

a) sphingolipids & glycosphingolipids
 (consider the structures in the book)
 -backbone is sphingosine
 -general structure of ceramide
 sphingomyelin
 -sphingolipids: role in recognition sites of cell membranes
 (recall the blood types)

headgroups. Typically, PL's have a sat'd FA in the C₁ position and an unsat'd FA in the C₂ position. E.g. 1-stearoyl-2-oleoyl-phosphatidylcholine.

PC = phosphatidylcholine ("lecithin")
 PE = phosphatidylethanolamine
 $(-O-(PO_2)-O-CH_2CH_2-NH_3^+),$

Related to PG in structure is diphosphatidylglycerol (cardiolipin):
 PG with a phosphoacylglycerol phosphoesterified in the C₃ position.
 (so 4 FA tails)

Know role of phospholipases A₁, A₂, C, D

Example: Some bee and snake venoms (Eastern diamondback rattlesnake and the Indian cobra), are rich in phospholipase A₂ which when injected can hydrolyze FA's from the C₂ position leaving *lyzolecithin* from phospholipids in cell membranes, and cause detergent effect (dissolving red blood c membrans)