Chem 431A-L24-F'07

admin:

Last time: We finished Chapt 7, started Chapt 10

FA's and TG's FA=fatty acid, TG=triglycerides or *triacylglycerols*

Today: Continue Chapt 10; more intro

Diglycerides (DG) and phospholipids (PL).

Wednesday, Nov. 21 deadline Chapt7 onlineQuiz

(0) REVIEW: FA's are very reduced molecs. redox energy
TG's neutral(charge) molecs; 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
(0a) 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.

(1) Hydrolysis of TGs under alkali conditions: *saponification*. The metal salt of a FA is "soap". 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^{2+}, Ca^{2+} 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).

(2) 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.

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

(5) Most common phospholipids 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 : FAs, the headgroups. Typically, PL's have a sat'd fa in the C_1 position and an unsat'd fa in the C_2 position. E.g. 1-stearoyl-2-oleoyl-phosphatidylcholine.
PC = phosphatidylcholine ("lecithin")
PE = phosphatidylethanolamine
($-O-(PO_2)-O-CH_2CH_2-NH_3^+$),

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-$CH_2CHOH-CH_2OH$)

Related to PG in structure is diphosphatidylglycerol (cardiolipin):
PG with a phosphoacylglycerol phosphoesterified in the C_3 position.
(so 4 FA tails)

Draw the general structure of a phospholipid both in a

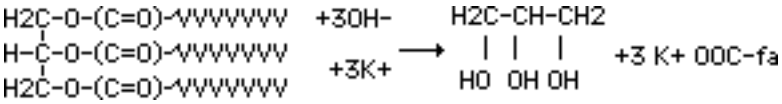
a) sphingolipids & glycosphingolipids
(consider the structures in the book)
-backbone is sphingosine
-general structure of ceramide
sphingomyelin
-sphingolipids: role in recognition sites of cell membranes
(recall the blood types)

Know role of phospholipases A_1, A_2 ,C D

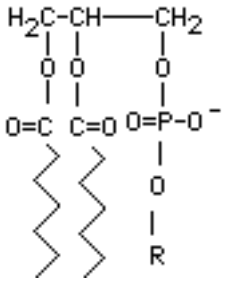
Example: Some bee and snake venoms (Eastern diamondback rattlesnake and the Indian cobra), are rich in phospholipase A_2 which when injected can hydrolyze FA's from the C_2 position leaving *lyzolecithin* from phospholipids in cell membranes, and cause detergent effect (dissolving red blood c membrans)

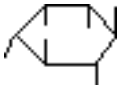
cholesterol
Know the structure

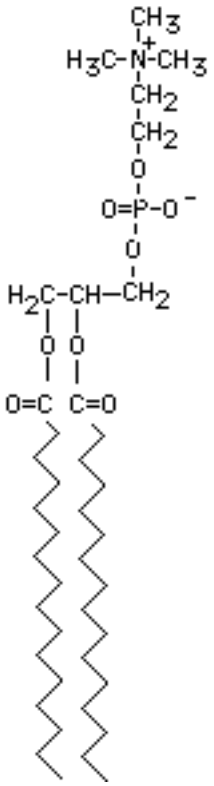
Some reactions and structures:
Saponification:



Phosphoglycerides (Glycerophosphates) PG:
1,2 diacylglycerol phosphate has a PO4 group at the C3 position.
- a member of the larger group of lipids called phospholipids.
If R = H, then, it's called <u>phosphatidic</u> <u>acid</u>. (parent compound for many PGs). other compounds are phosphatidyl -X



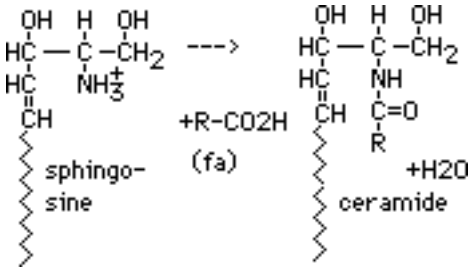
Diff. R's attach to the phosphate:
eg. R = $-CH_2CH_2-N^+(-CH_3)_3$ (choline) so Phosphatidylcholine
R=$-CH_2CH_2-NH_3^+$ (ethanolamine) so PE
R = $-CH_2CH(-NH_3^+)CO_2^-$(serine) so PS
R =  (inositol) so PI
R= glycerol so PG



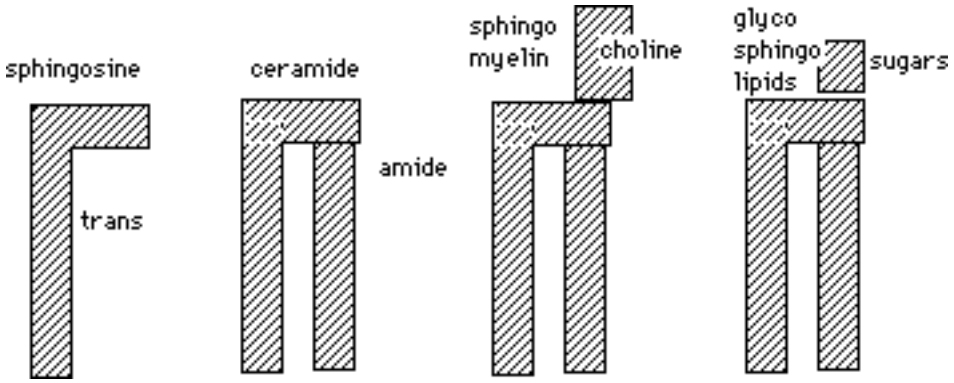
Note struc of PC. It is a general molec with the polar headgroup (ionized with - and + charges. there are 2 hydrophobic tails.

PC is commonly known as lecithin.
PS, PE and PI are of the same general shape and property.
Other phosphoglycerides:
diphosphatidyl glycerol (cardiolipin)
DG- PO_4- CH_2 - CH(-OH)-CH_2-PO_4-DG

suppose in PC, C1 linked to stearic acid, and C2 is linked to oleic acid, we say:
1-stearoyl-2-oleoyl-phosphatidylcholine.
Sphingolipids:
-another class of lipids frequ found in biomembranes
backbone is a 18 C amino alcohol (sphingosine)
formation of amide linkage bet fa and sphingosine
-contains a trans double bond within the alcohol
produces a ceramide. (looks from afar like a DG)

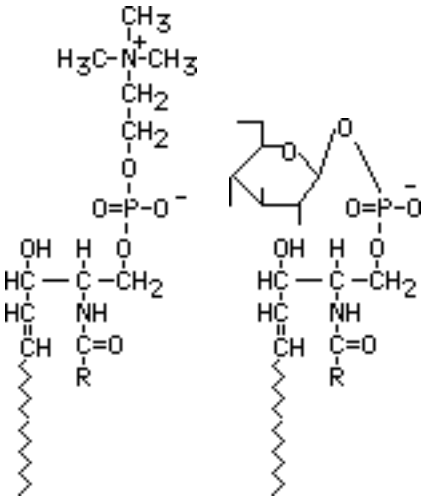


sphingomyelins = phosphorus containing subclass of sphingolipids, very impt in nervous tissue of higher animals.
sphingomyelins are formed by esterification of phosphorylcholine or p-ethanolamine to the 1-hydroxy group of a ceramide



Another class of ceramide based lipids are impt components of muscle and nerve membranes is animals: glycosphingolipids: ceramide + one or more sugar residues in a β-glycosidic linkage at the 1-hydroxy moeity. these are neutral (uncharged) sugar residues.

If only one glucose or galactose is attached, it is called a cerebroside.
when 3 or 4 sugars esterified one of which is a sialic acid, then it is a ganglioside.



sphinglmyelin cerebroside

Waxes are esters of a fatty acid and a long chain alcohol. Very hydrophobic (weakly hydrophillic head). wwater repellent coating of leaves and feathers for instance. beeswax, it is structural. hardness of waxes depends on chain length and degree of unsaturation. paraffin, highly saturated and long chain.

wax

Structure and properties of biomembranes:

-many varied functions.
-consider fatty acids: form micelles.
but phospholipids have very bulky Hϕ chains but very ionic polar headgroups. so it forms bilayers. (2 molecules thick).
-bilayers spontaneously form when mixed with water and dispersed with a sonicator for instance. the bilayers eventually close up and form compartments. "bilayer

vesicles". Many basic properties of membranes can be viewed from the lipid bilayer model.

for instance, water can pass thru the memb with some difficulty. In fact it is nearly impossible for anything else to pass thru.. nothing can really easily pass thru.
2 kinds of diffusion are possible in the membrane: flip-flop and 2-d diffusion.
-melting transition of the membranes
-membrane asymmetry
-characteristics of membrane proteins.