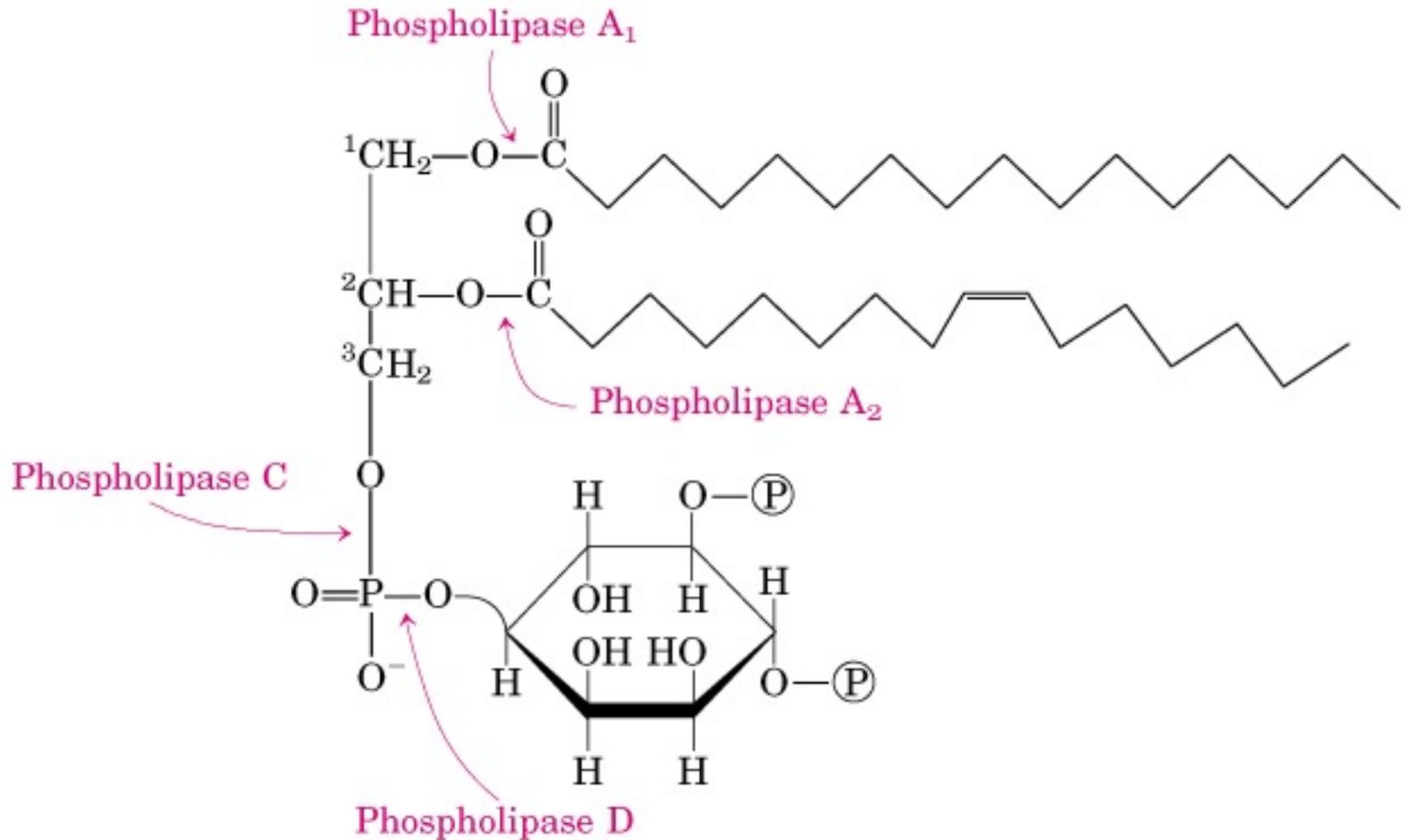
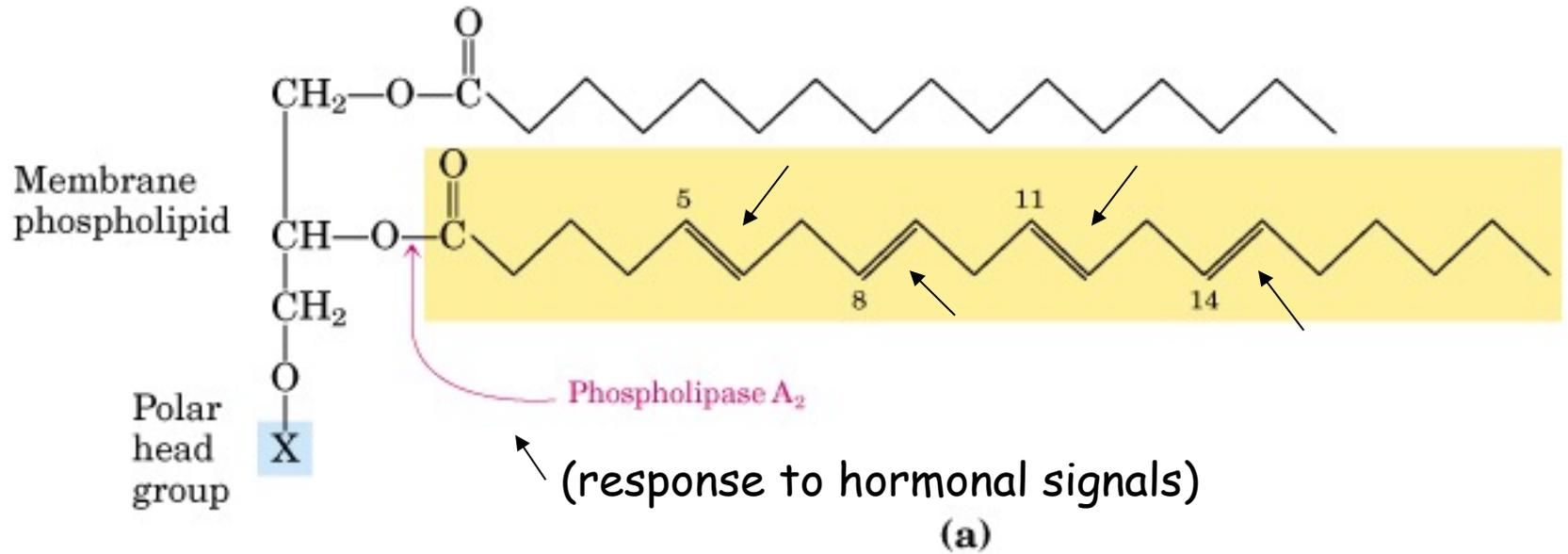


As especificidades das fosfolipases

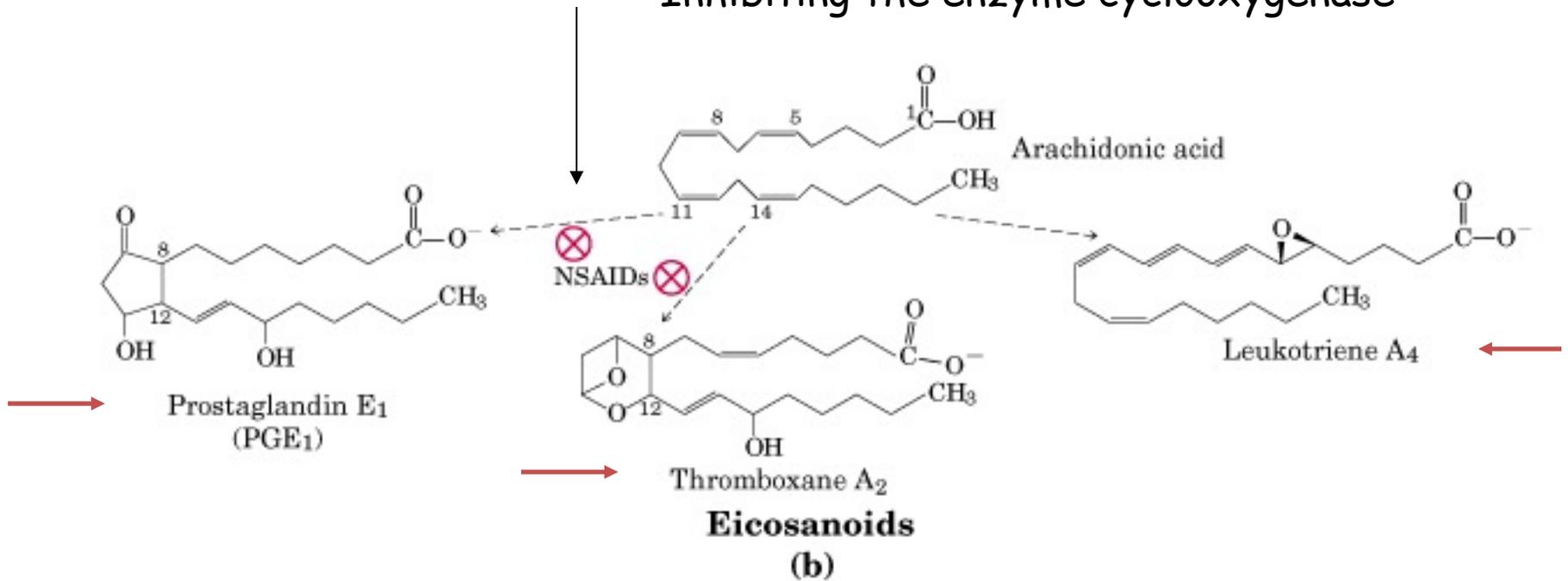


Arachidonic acid and some eicosanoid derivatives



Aspirin, acetaminophen, ...

Inhibiting the enzyme cyclooxygenase



Lipídios: Funções Principais

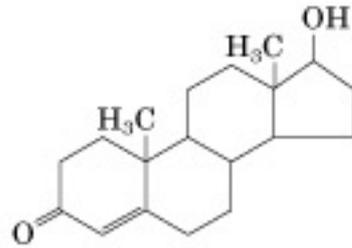
Ácidos Graxos → Unidades que compõe os triacilgliceróis e fosfolipídios
→ Produção de energia
→ Precursores de eicosanóides

Triacilgliceróis → Estoque de energia

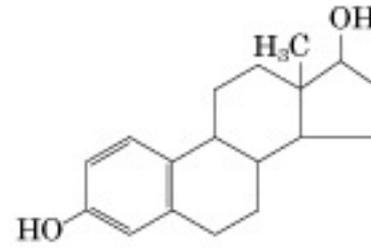
Fosfolipídios → Principal componente das membranas celulares

Esteróis
(Colesterol/
Esteres de Colesterol) → Componente de membrana celular
→ Precursor de ácidos biliares, vitamina D
→ Precursores de hormônios esteroidais

Steroid Hormones carry messages between tissues

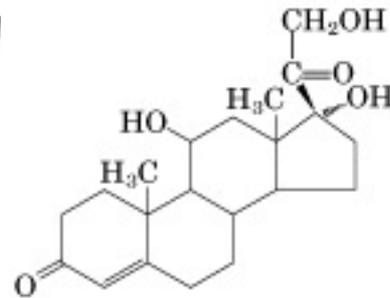


Testosterone

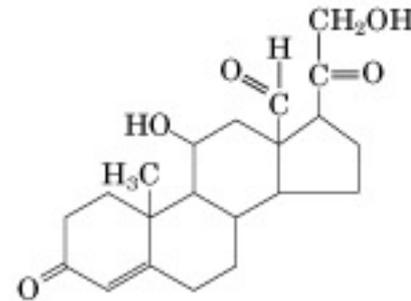


Estradiol

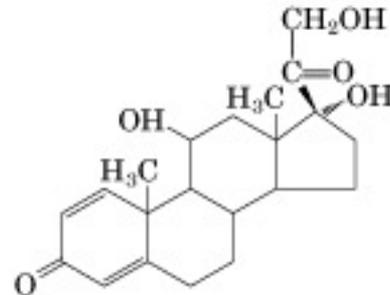
Steroids derived from cholesterol



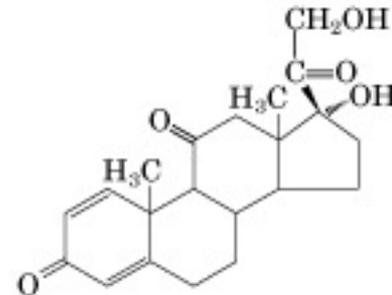
Cortisol



Aldosterone

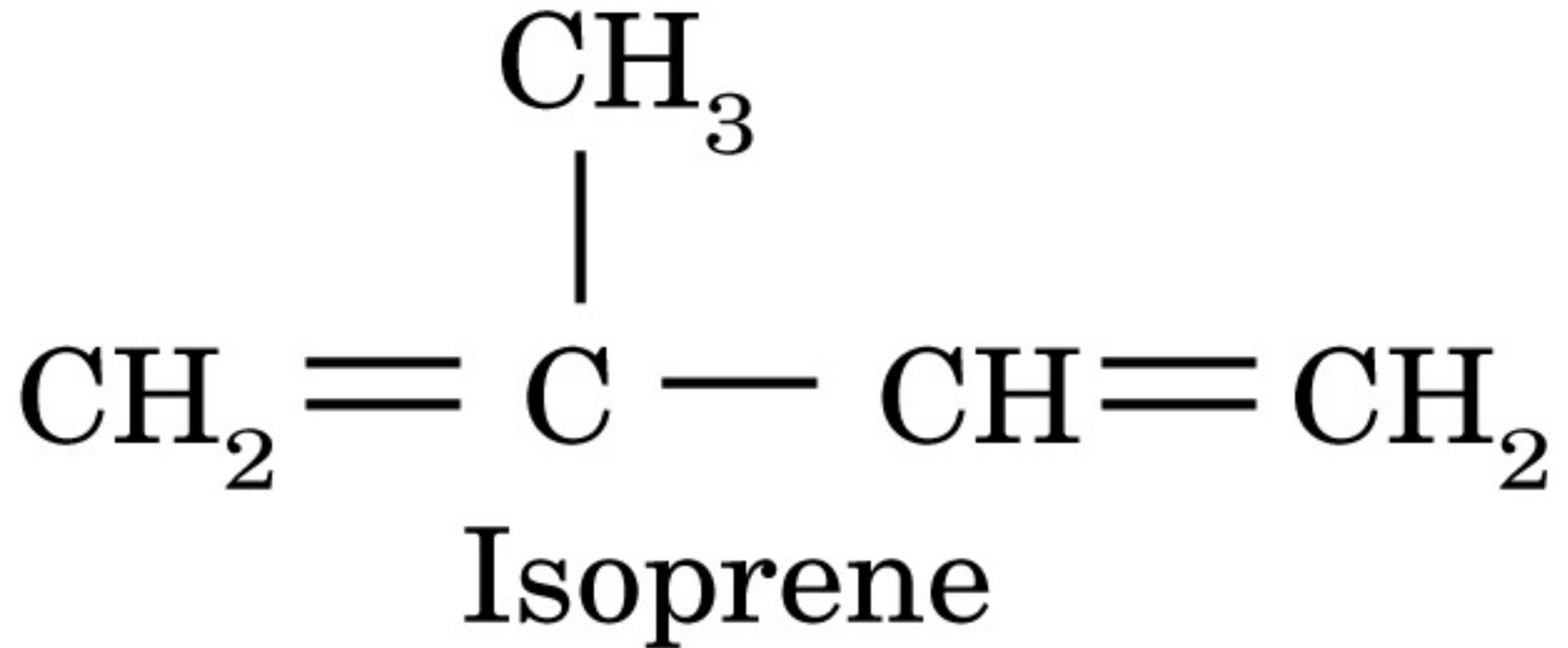


Prednisolone

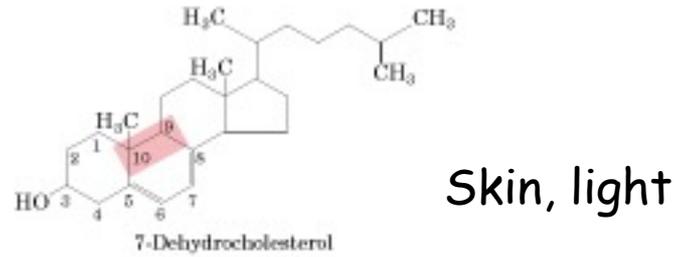


Prednisone

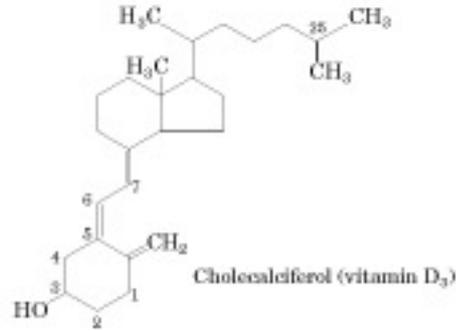
Vitamins D and A are hormone precursors



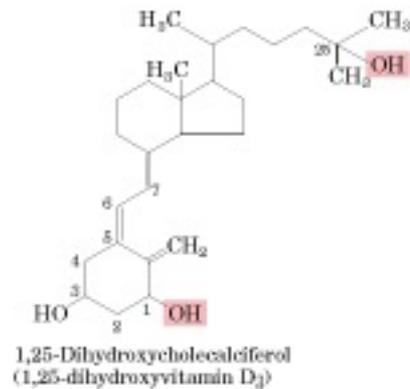
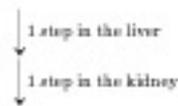
Vitamin D₃ production and metabolism



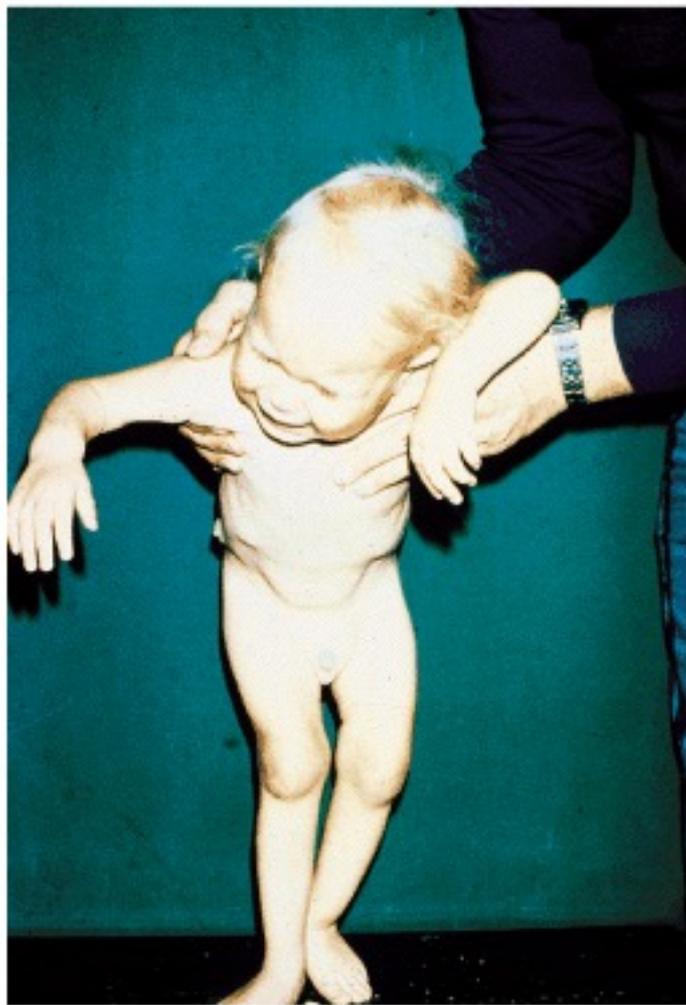
Skin, light



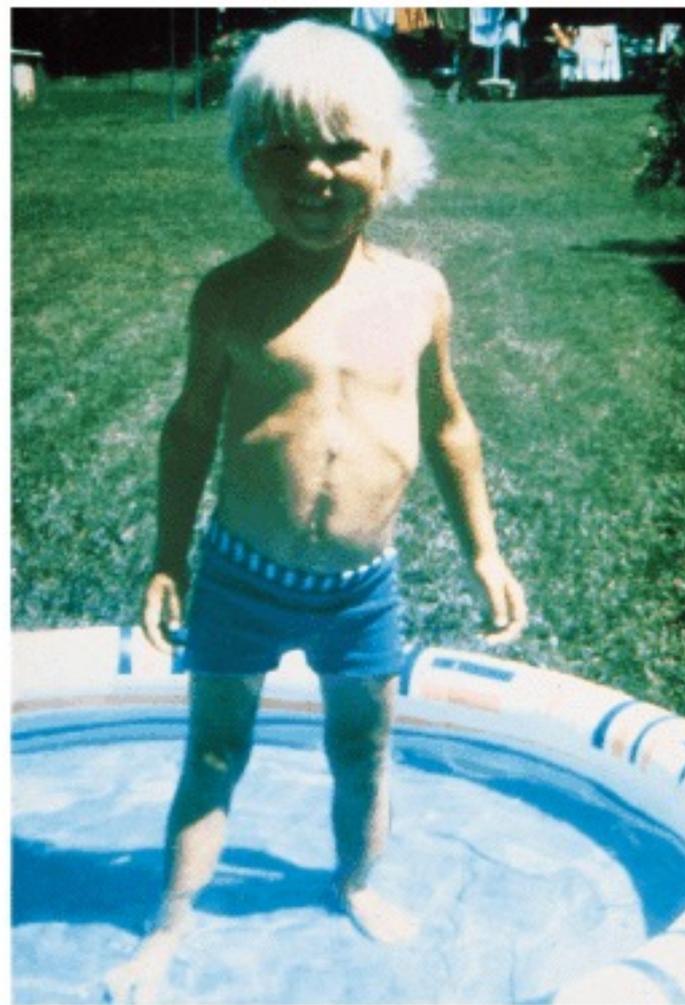
Liver, kidney



(a)



Before vitamin D treatment



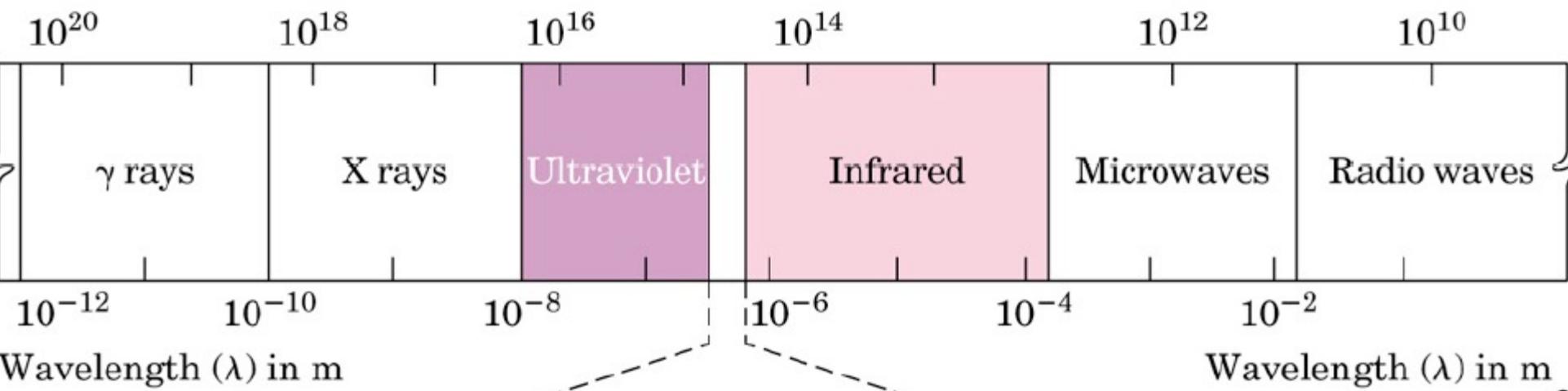
After 14 months of vitamin D treatment

(b)

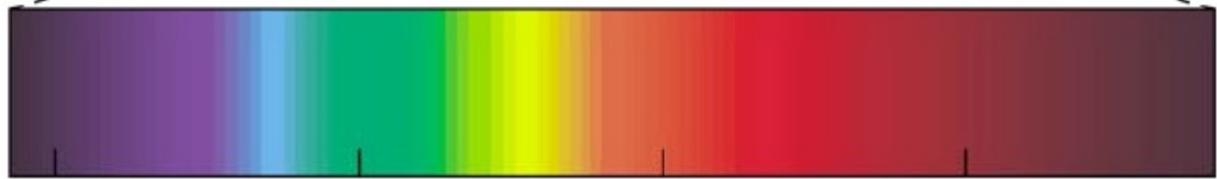




Frequency (ν) in Hz



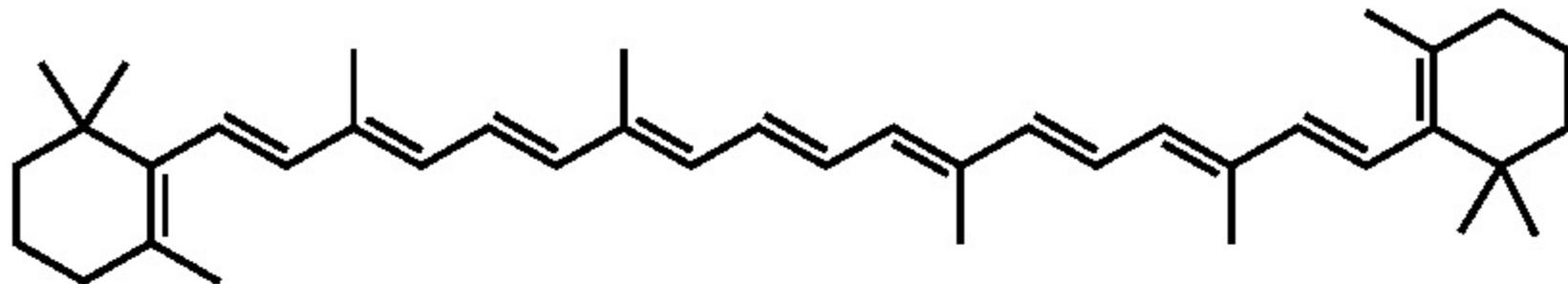
Visible



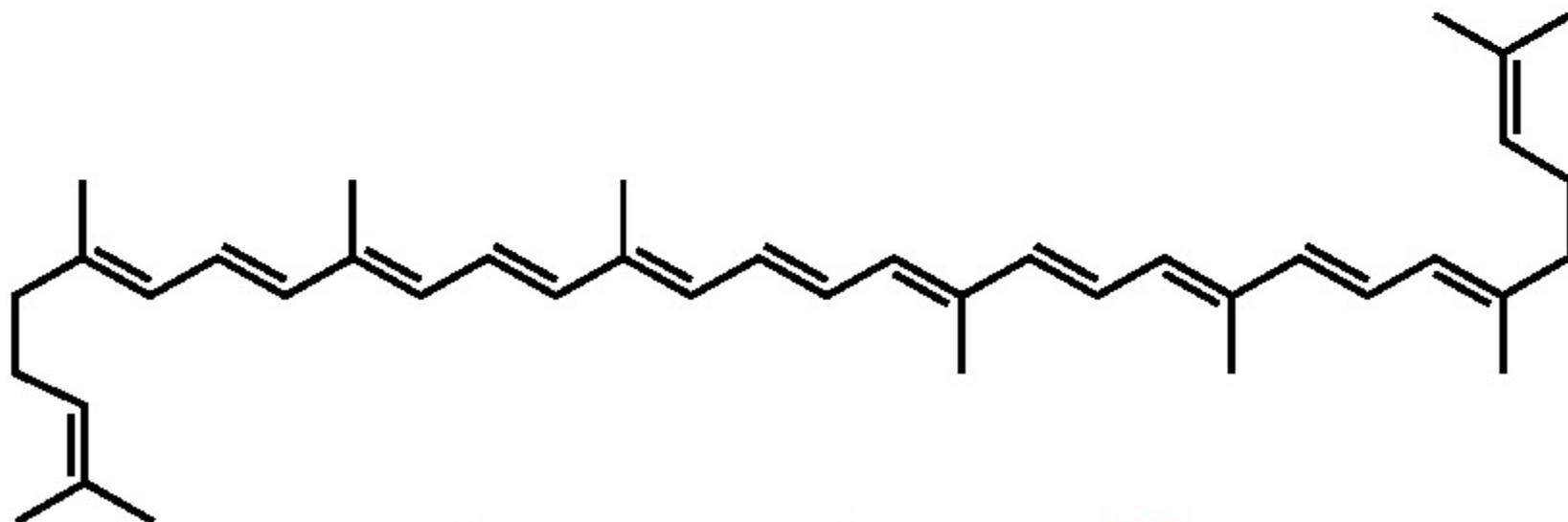
380 nm 500 nm 600 nm 700 nm 780 nm

3.8×10^{-7} m

7.8×10^{-7} m



β -carotene, $\lambda_{\max} = 455 \text{ nm}$



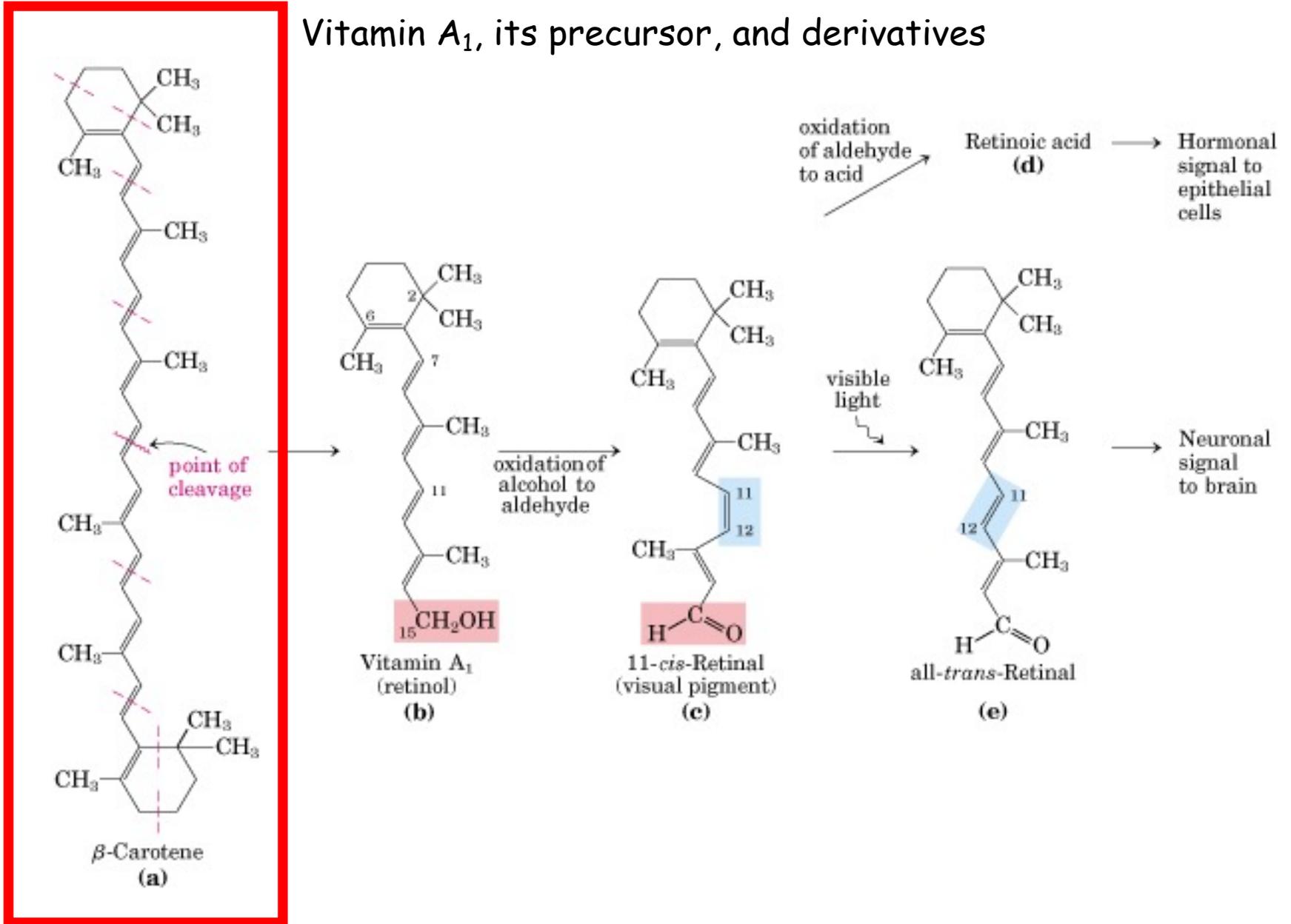
lycopene, $\lambda_{\max} = 474 \text{ nm}$







Vitamin A₁, its precursor, and derivatives

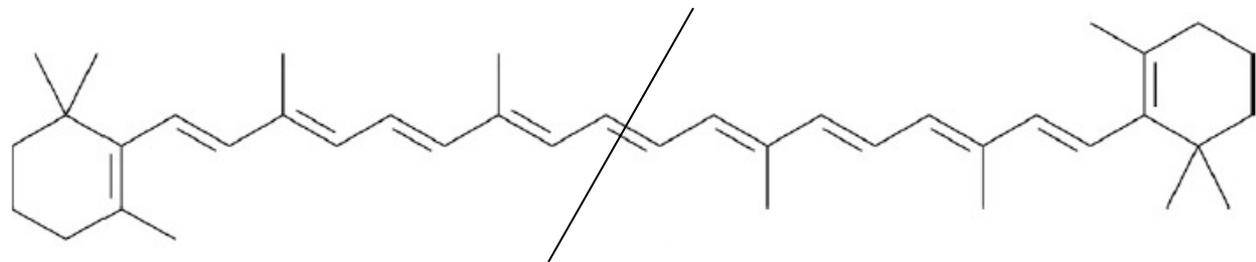




It is estimated 124 million children worldwide lack vitamin A, putting them at risk of permanent blindness and other serious ailments.



Golden promise: The yellow rice has the beta-carotene

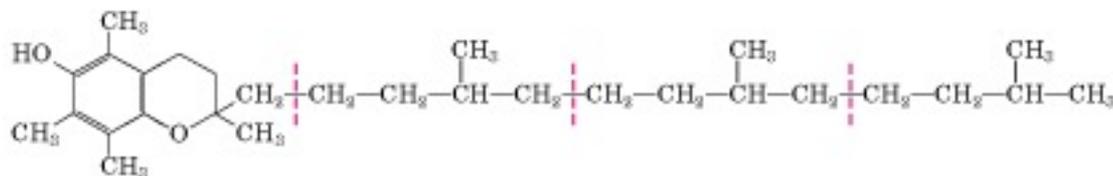




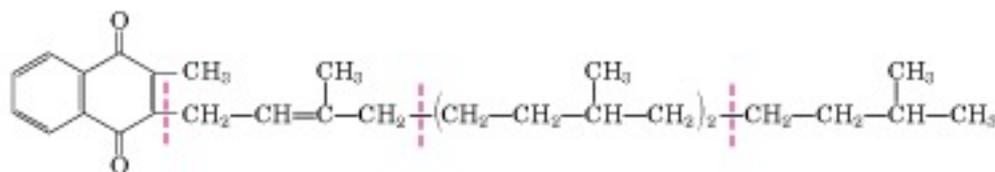


Vitamins E and K and the lipid Quinones are oxidation-reduction cofactors

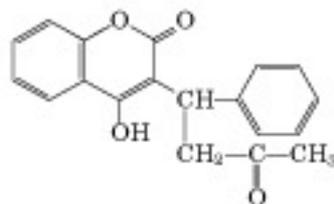
(a)
Vitamin E: an antioxidant



(b)
Vitamin K₁: a blood-clotting cofactor (phylloquinone)

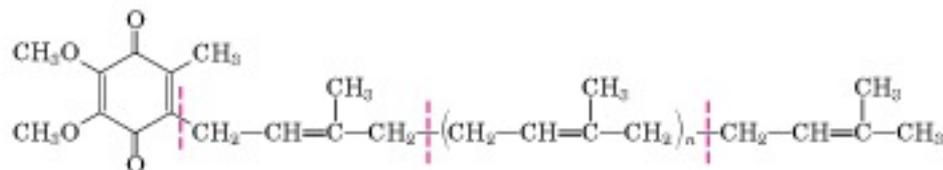


(c)
Warfarin: a blood anticoagulant

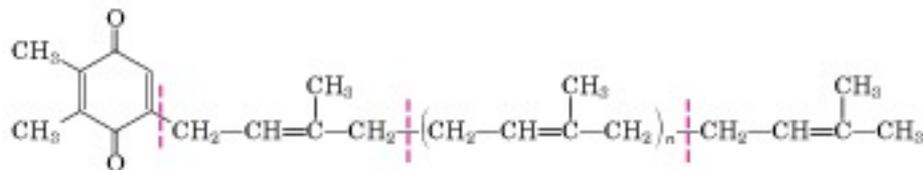


Some other biologically active
Isoprenoid compounds or derivatives

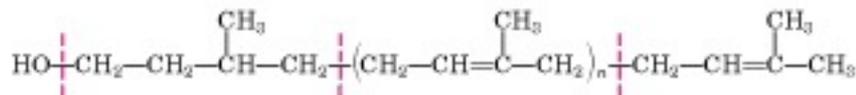
(d)
Ubiquinone: a mitochondrial electron carrier (coenzyme Q)
($n = 4-8$)



(e)
Plastoquinone: a chloroplast electron carrier ($n = 4-8$)



(f)
Dolichol: a sugar carrier
($n = 9-22$)

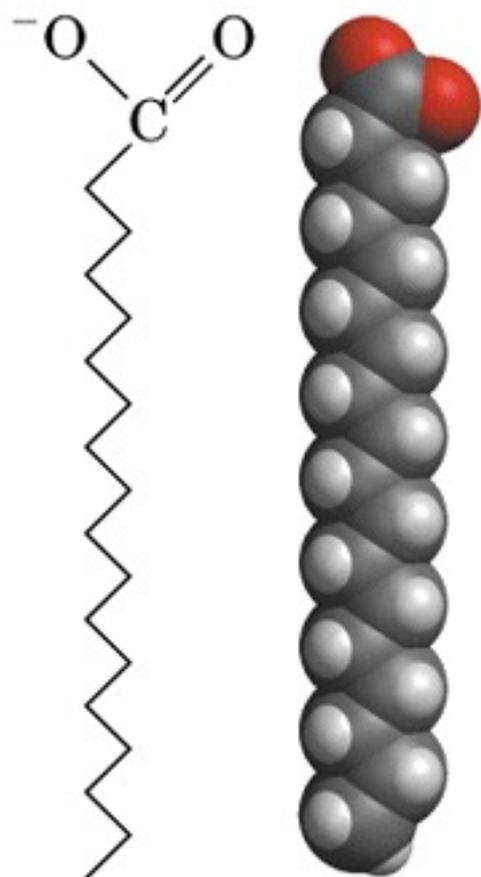


Por que estudar os lipídios?

Fontes de Ácidos Graxos

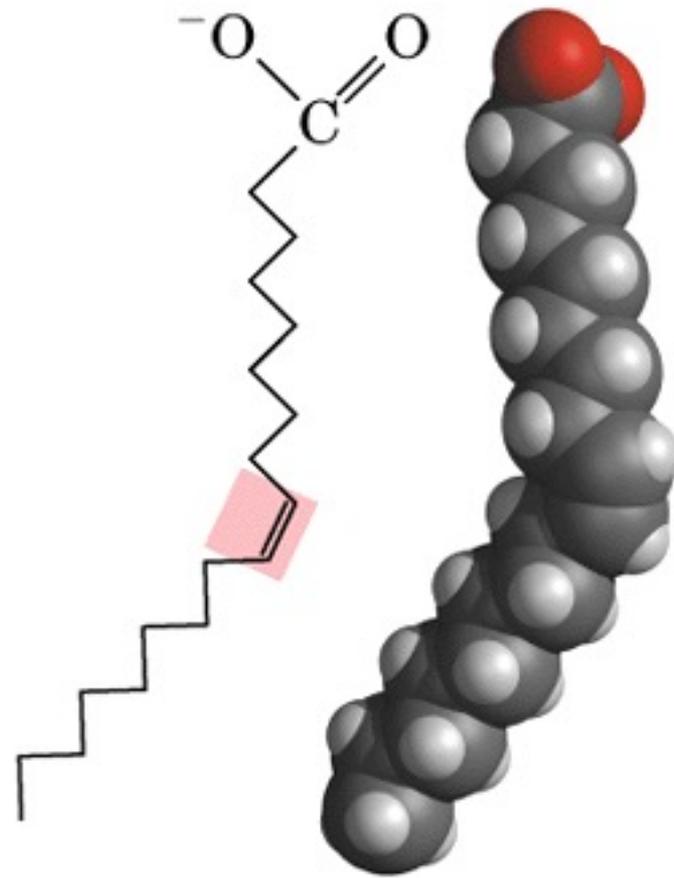
- Dieta
- Estoque de gorduras
- Síntese de outras fontes

Carboxyl
group

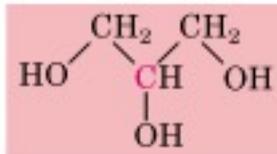


Hydrocarbon
chain

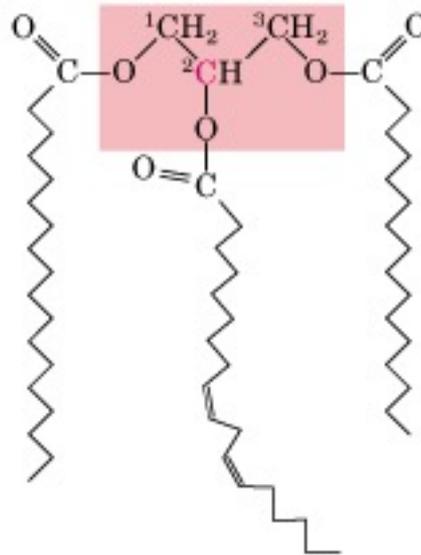
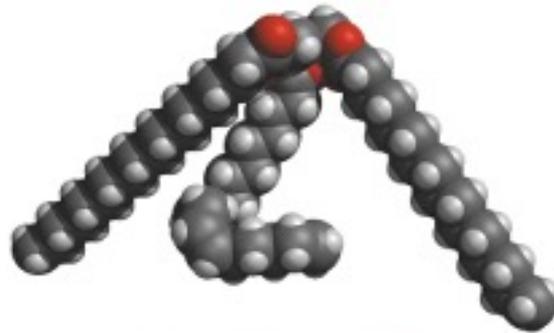
(a)



(b)



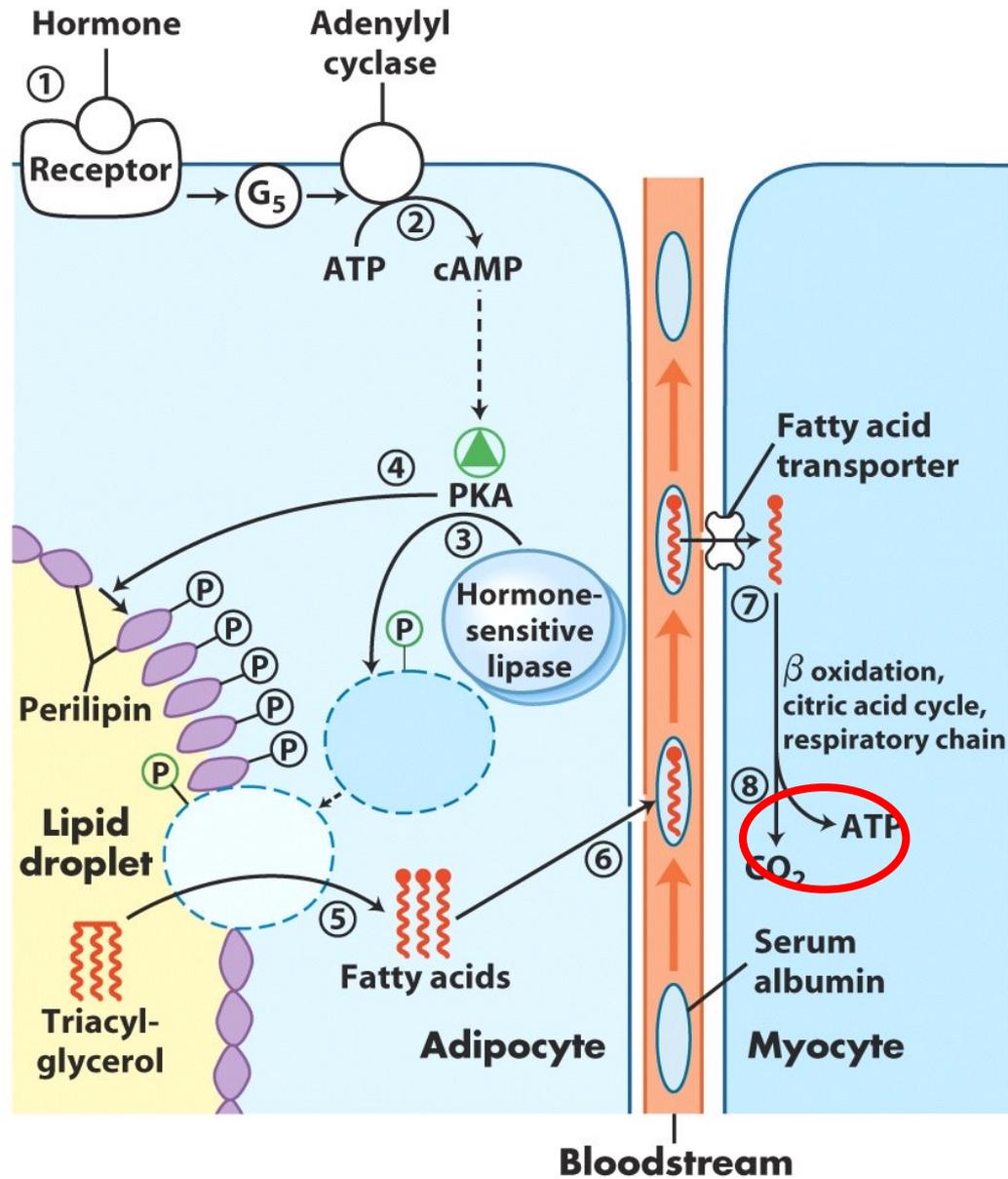
Glycerol



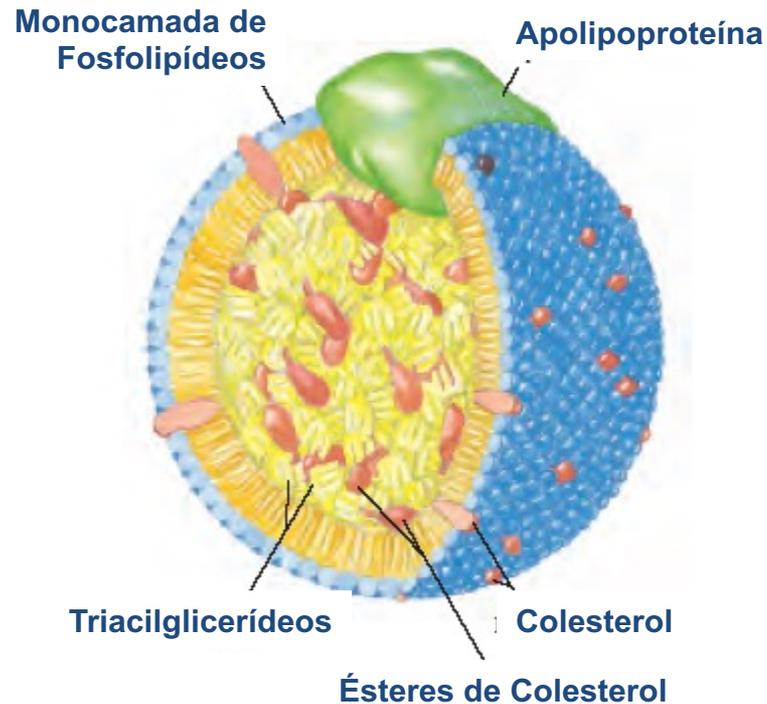
1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol,
a mixed triacylglycerol

Como ocorre o transporte de Lipídeos
na Circulação Sanguínea ?

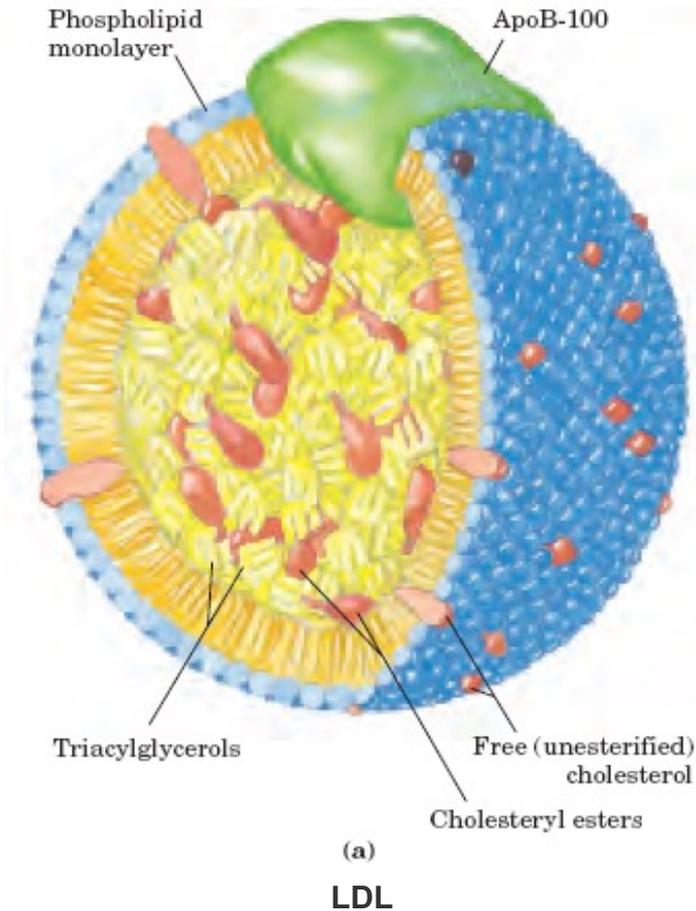
Ácidos graxos livres são transportados no sangue associados a **albumina**



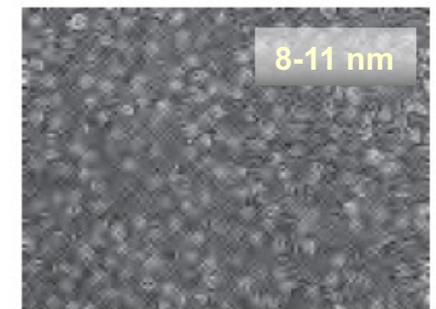
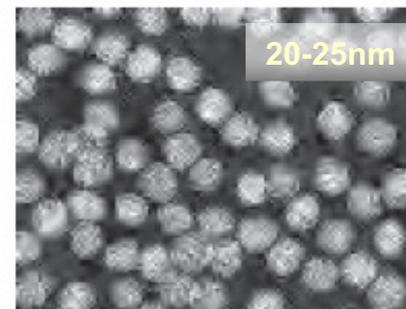
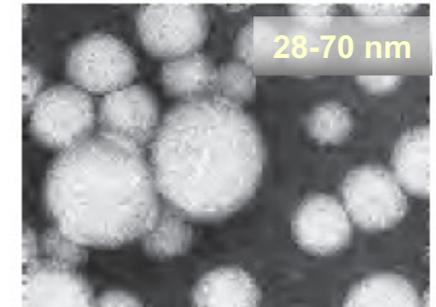
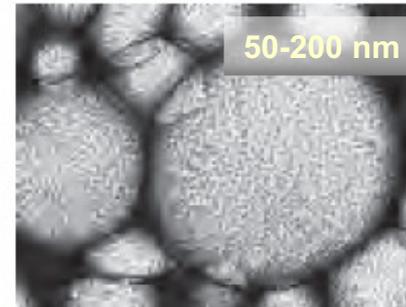
Triacilglicerol, Fosfolipídeos e Colesterol e Ésteres de Colesterol são transportados no sangue incorporados a **lipoproteínas**



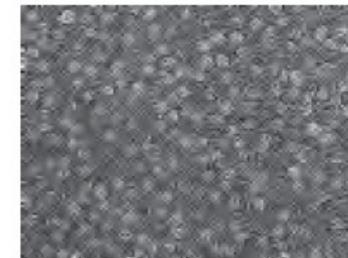
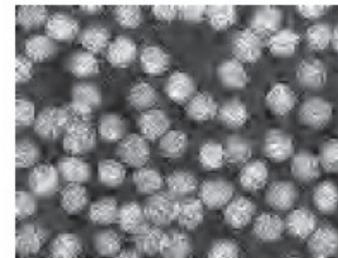
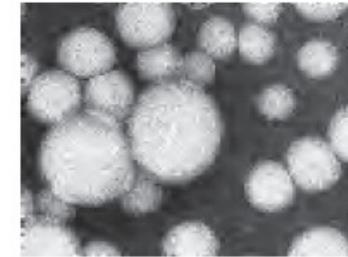
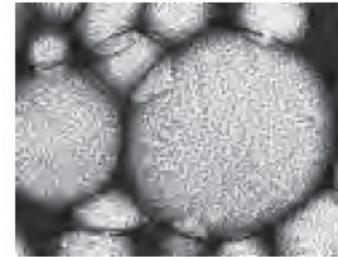
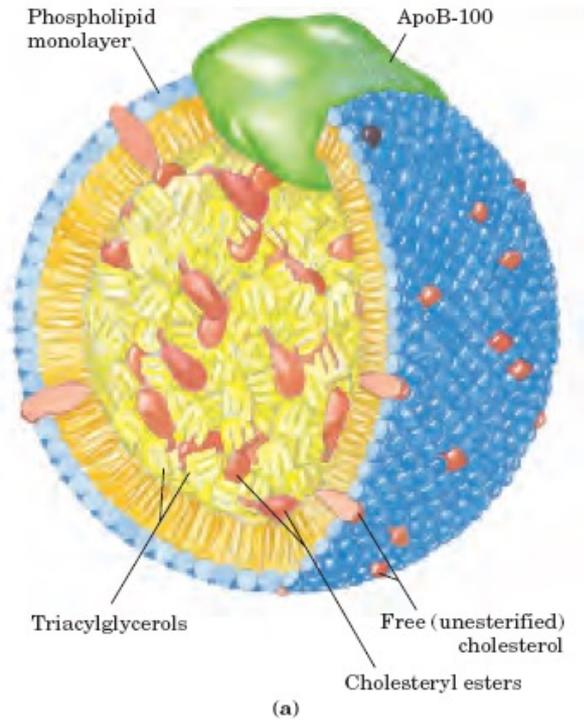
Lipoproteínas



4 tipos principais



Lipoproteínas



(b)

TABLE 21-2 Major Classes of Human Plasma Lipoproteins: Some Properties

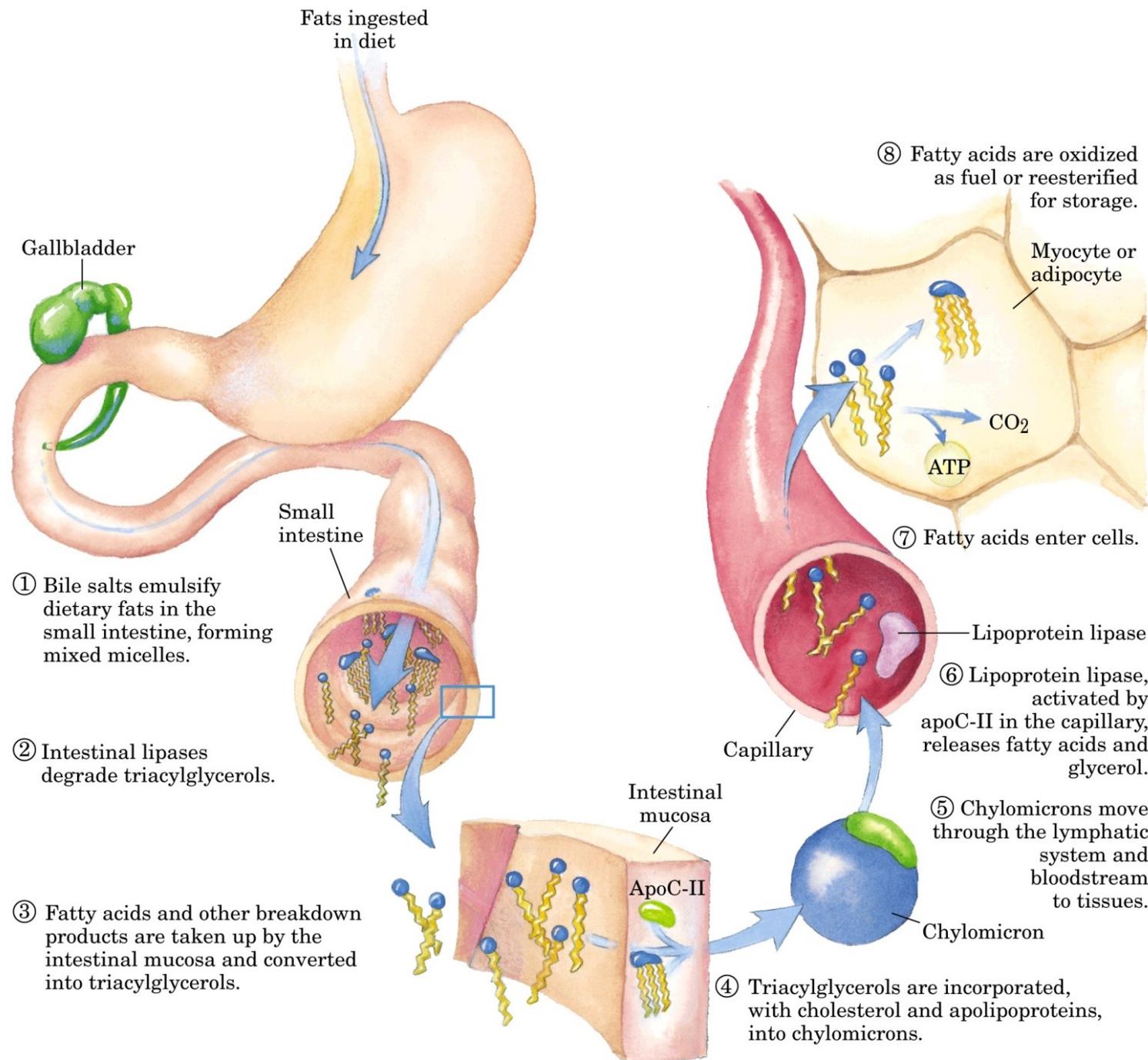
Lipoprotein	Density (g/mL)	Composition (wt %)				
		Protein	Phospholipids	Free cholesterol	Cholesteryl esters	Triacylglycerols
Chylomicrons	<1.006	2	9	1	3	85
VLDL	0.95-1.006	10	18	7	12	50
LDL	1.006-1.063	23	20	8	37	10
HDL	1.063-1.210	55	24	2	15	4

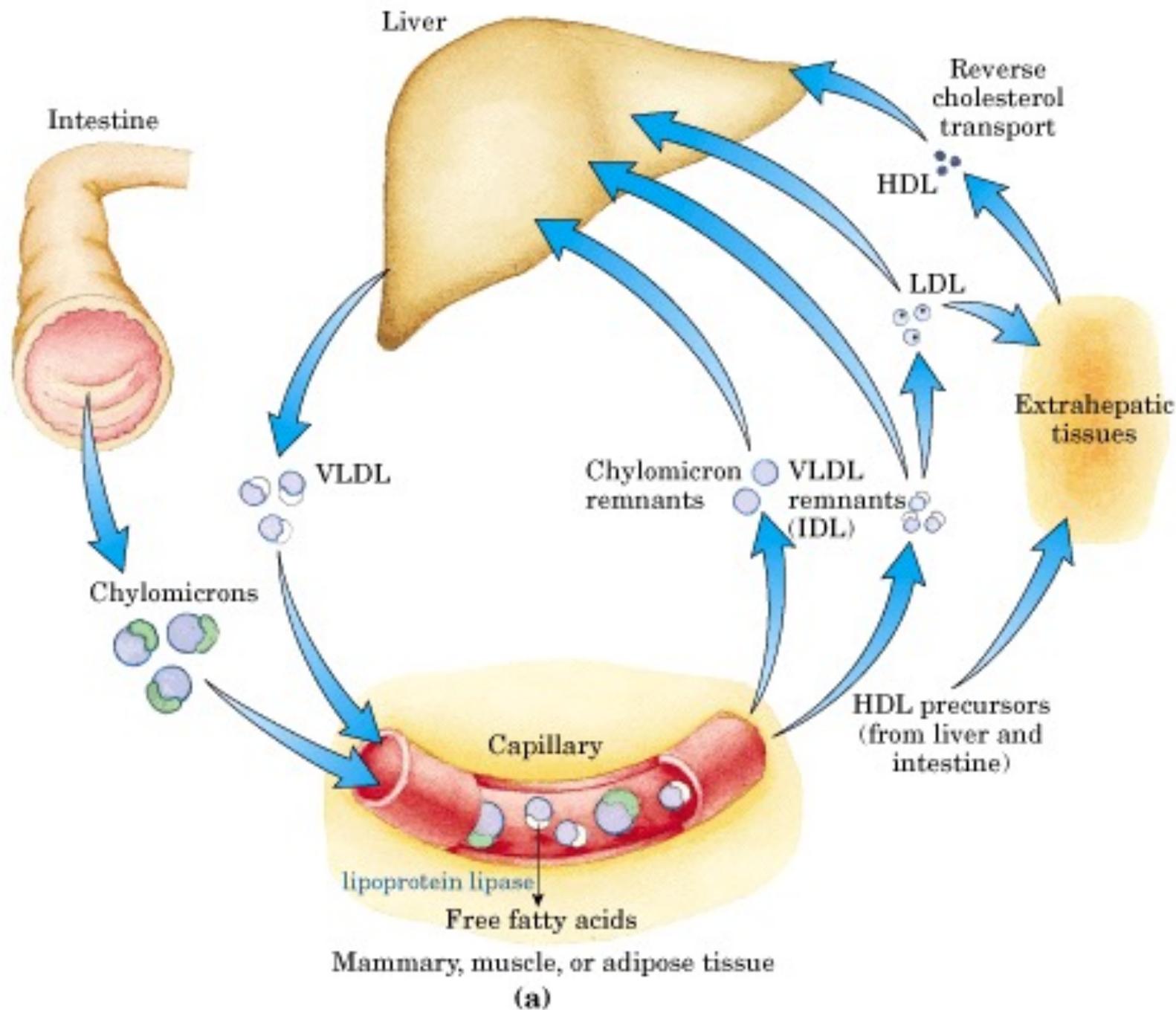
Source: Modified from Kritchevsky, D. (1986) Atherosclerosis and nutrition. *Nutr. Int.* 2, 290-297.

Menos denso
↓
Mais denso

Lipoproteínas

- Quilomícrons** → Sintetizados na mucosa intestinal. Transporta lipídeos da dieta do intestino para outros tecidos. TG são hidrolisados fornecendo ácidos graxos para os tecidos.
- VLDL** → Sintetizados no fígado. Transporta TG e colesterol do fígado para outros tecidos. Origina IDL e LDL.
- LDL(mau)** → Formado a partir da VLDL. Ricas em colesterol. Transporta colesterol para os tecidos extra-hepáticos.
- HDL(bom)** → Sintetizado no fígado e intestino. Sequestra o colesterol de tecidos extra-hepáticos sob a forma de ésteres de colesterol e leva até o fígado.







Blood plasma
after fast

Blood plasma
after meal

(b)

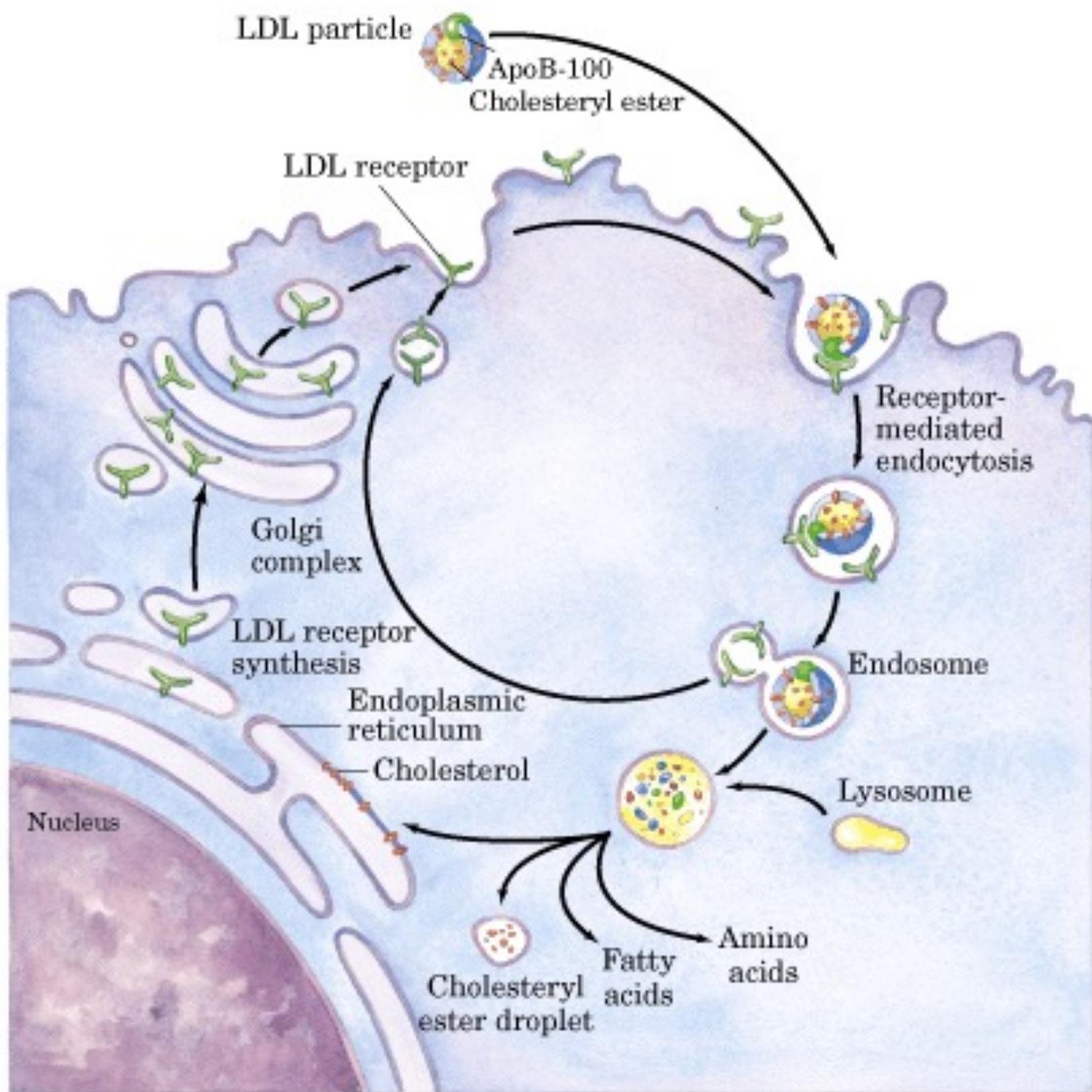
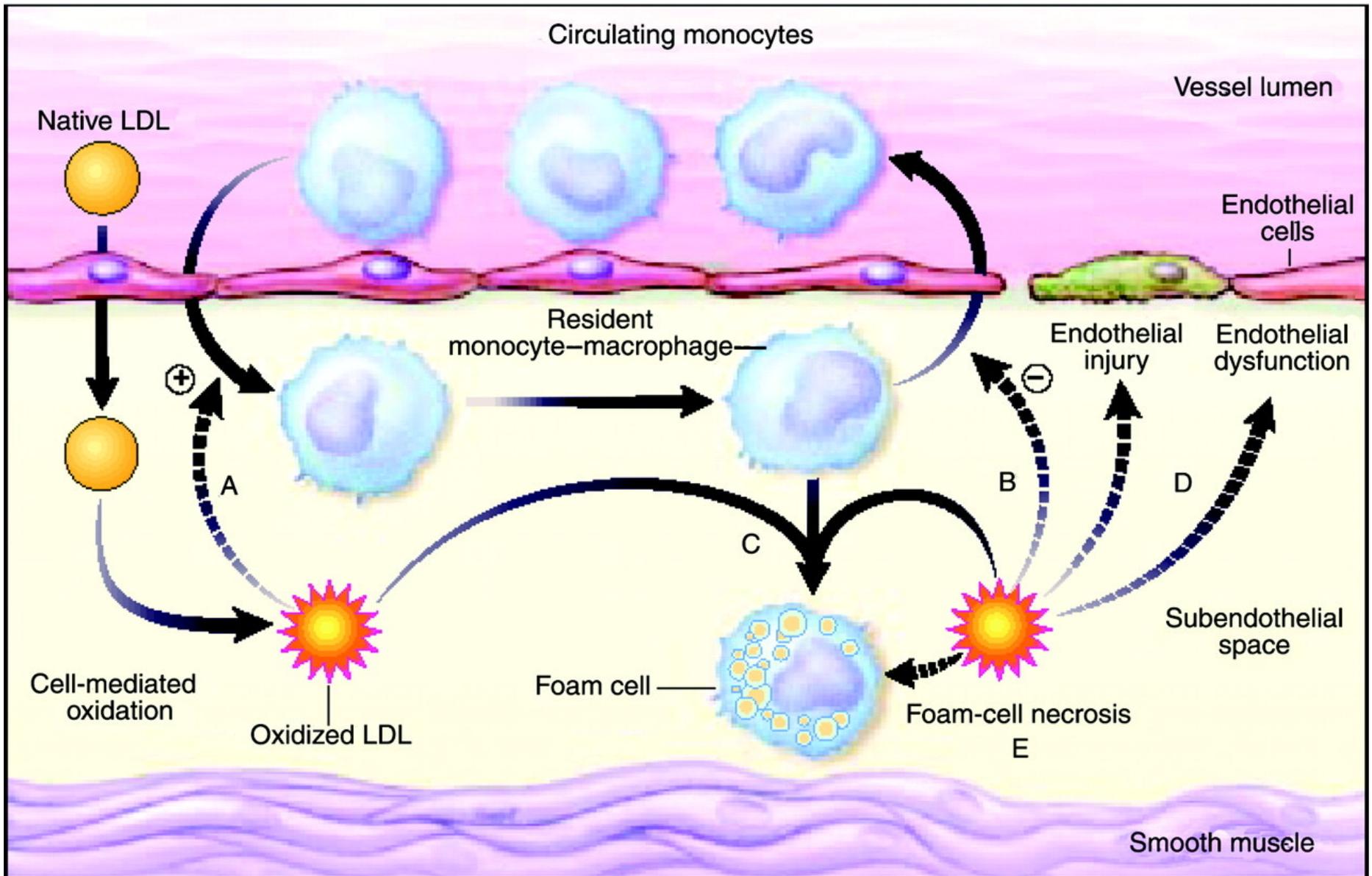
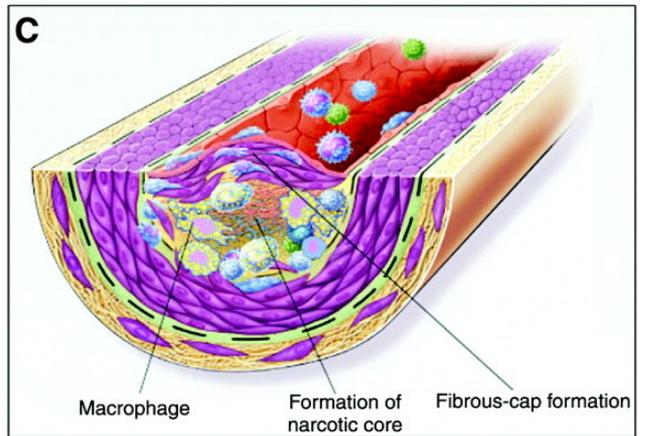
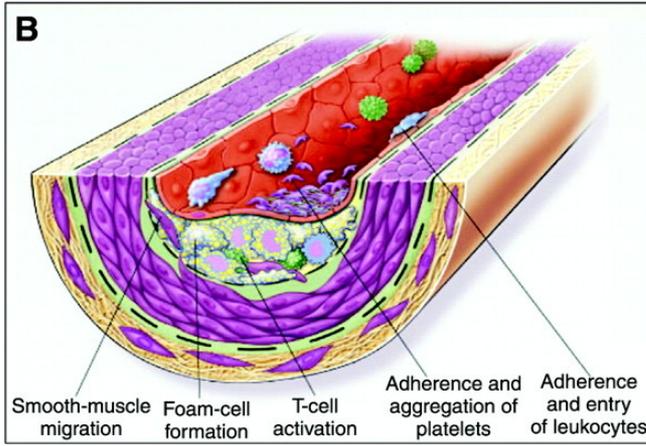
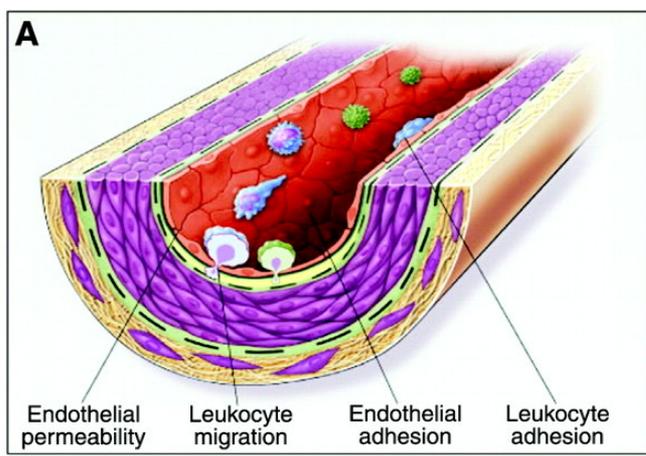


FIG. 5. Oxidative modification hypothesis of atherosclerosis



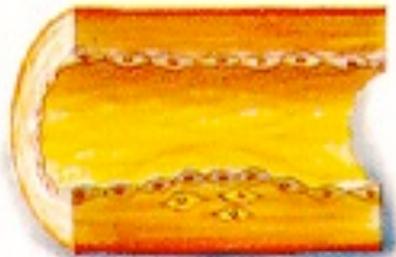
Stocker, R. et al. *Physiol. Rev.* 84: 1381-1478 2004;
doi:10.1152/physrev.00047.2003



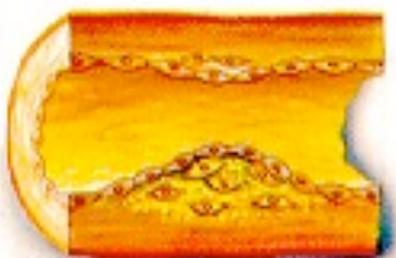
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Normal Artery



Fatty Streak



Fibrous plaque



**Calcified lesion
complications
Hemorrhage
Ulceration
Thrombosis**



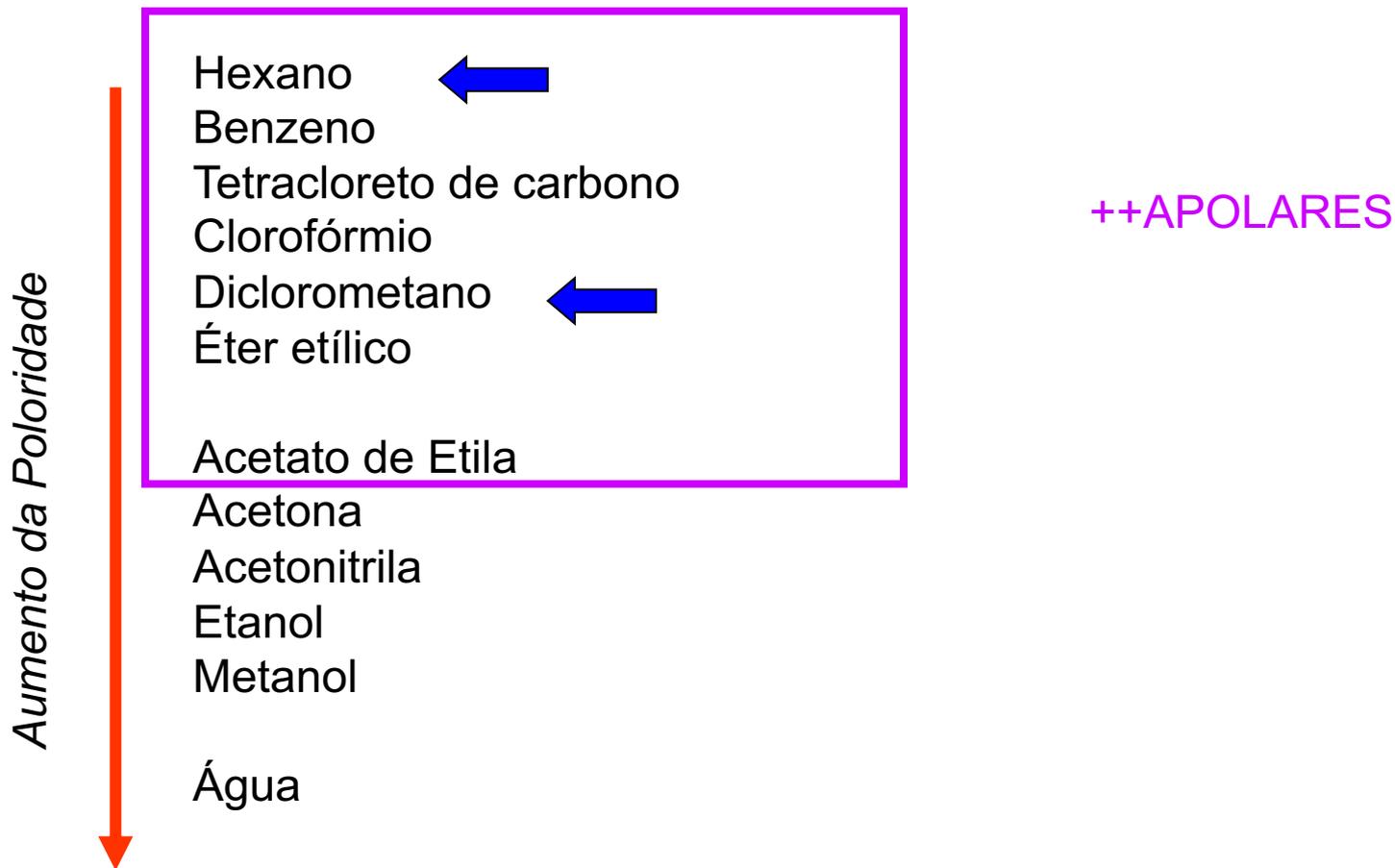
Análise de Lipídios

- Extração com solventes orgânicos
- Separação dos tipos de lipídios
- Detecção e análise

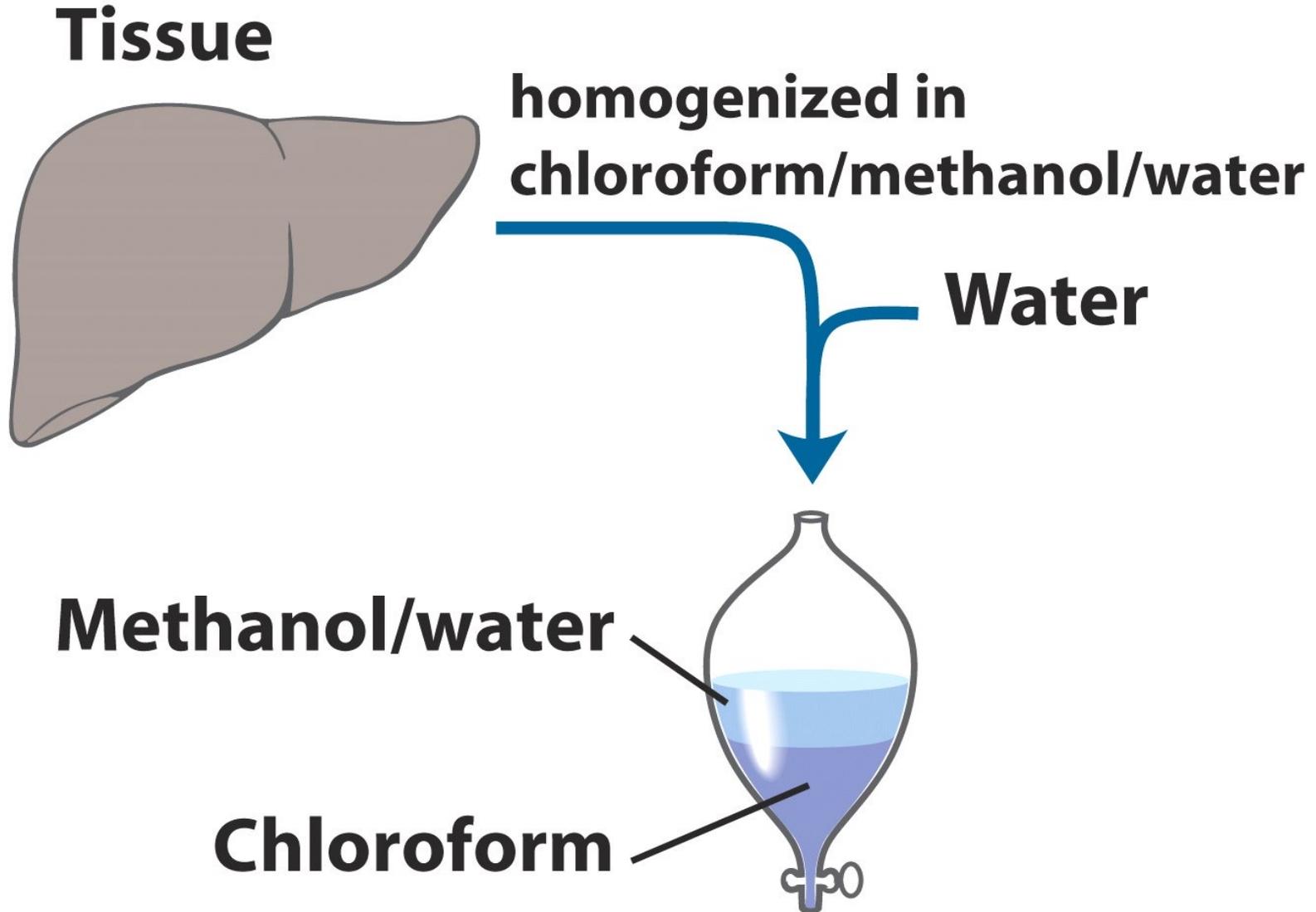
Análise de Lipídios

- Extração com solventes orgânicos
- Separação dos tipos de lipídios
- Detecção e análise

Solventes Orgânicos



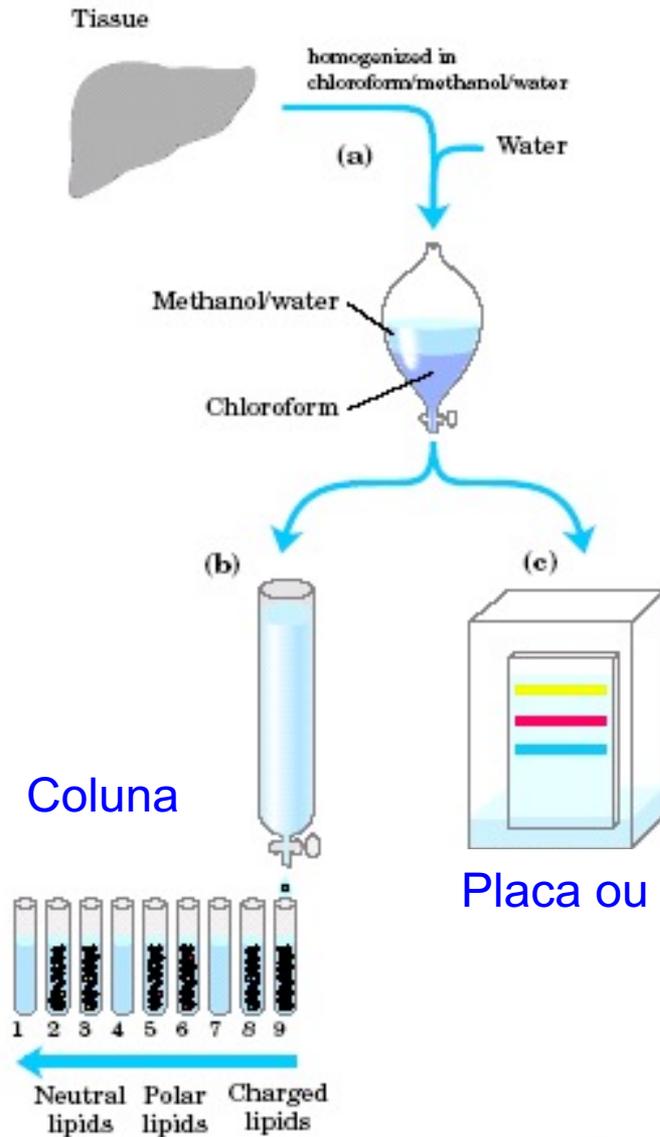
Extração de Lipídios



Análise de Lipídios

- Extração com solventes orgânicos
- Separação dos tipos de lipídios
- Detecção e análise

Separação dos Tipos de Lipídios



Cromatografia de Adsorção

Placa ou TLC (*Thin Layer Chromatography*)

Cromatografia de Adsorção

Princípio: Separação de mistura de compostos baseado nas diferenças de afinidade dos vários componentes de uma mistura entre o solvente utilizado (fase móvel) e a substância suporte (fase estacionária)

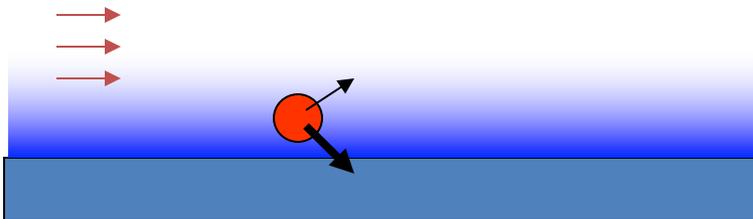
Cromatografia de Adsorção

Princípio: Separação de mistura de compostos baseado nas diferenças de afinidade dos vários componentes de uma mistura entre o solvente utilizado (fase móvel) e a substância suporte (fase estacionária)

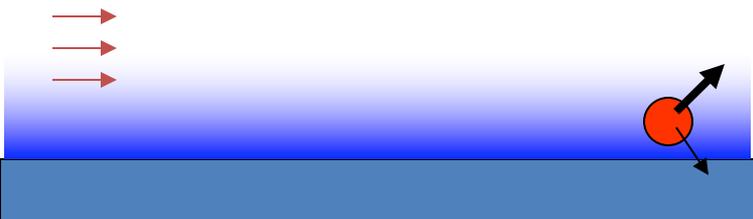


Fase Móvel

Fase Estacionária



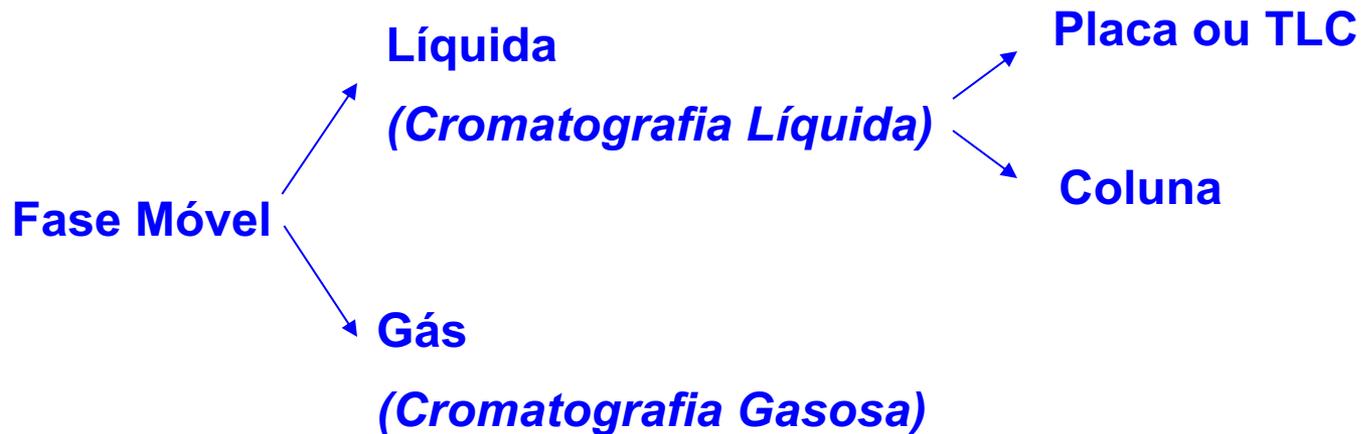
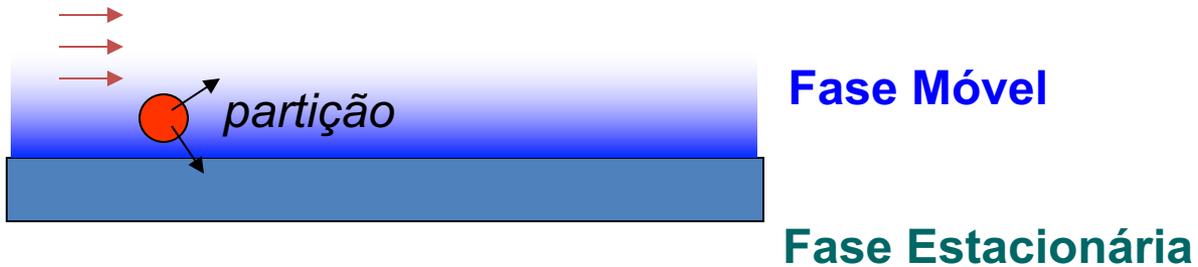
> interação com a fase estacionária



> interação com a fase móvel

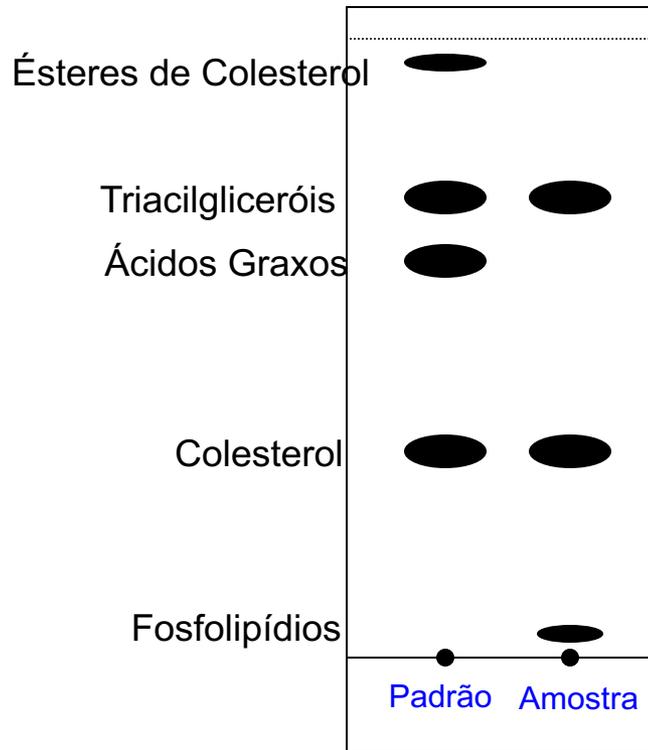
Cromatografia de Adsorção

Tipos de cromatografia



Cromatografia em Placa ou TLC

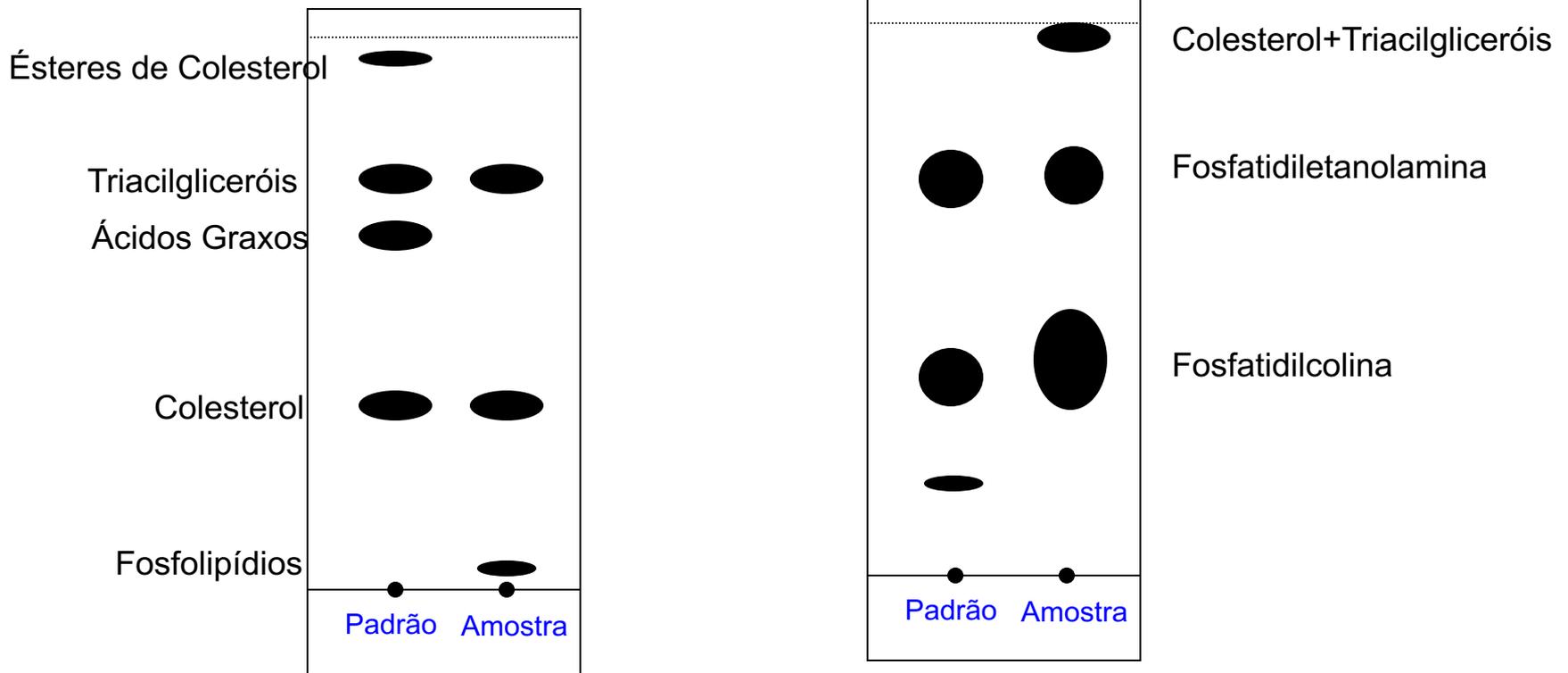
Amostra: Gema de ovo



Hexano/Isopropanol/Ácido Acético (90/10/1)

Cromatografia em Placa ou TLC

Amostra: Gema de ovo

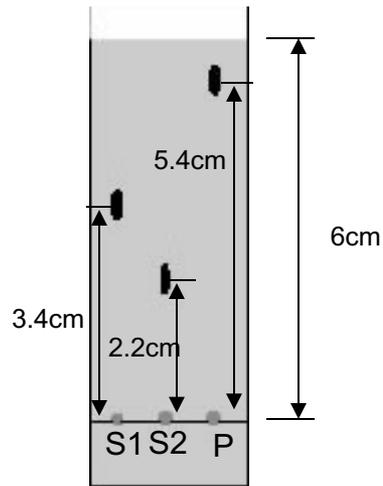


↑
Hexano/Isopropanol/Ácido Acético (90/10/1) Clorofórmio/Metanol/Água (65/35/5)

Análise de Lipídios

- Extração com solventes orgânicos
- Separação dos tipos de lipídios
- **Detecção e análise**

Medida do Rf



$$R_f = \frac{\text{Distância Amostra}}{\text{Distância Total}}$$

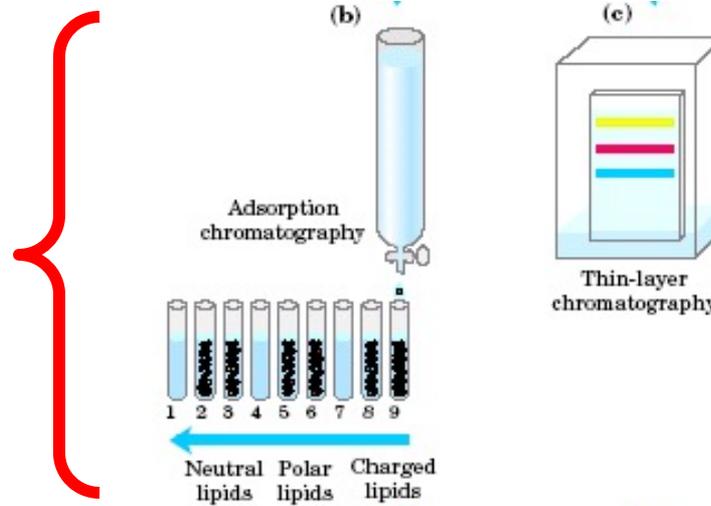
$$S1 \quad R_f = \frac{2.2 \text{ cm}}{6 \text{ cm}} = 0.37$$

$$S2 \quad R_f = \frac{3.4 \text{ cm}}{6 \text{ cm}} = 0.57$$

$$P \quad R_f = \frac{5.4 \text{ cm}}{6 \text{ cm}} = 0.90$$

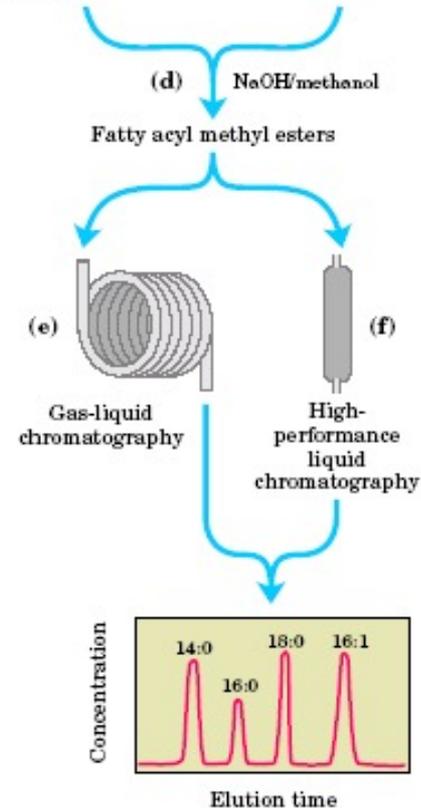
Separação dos Tipos de Lipídios

(TG, Colesterol, Fosfolipídio)

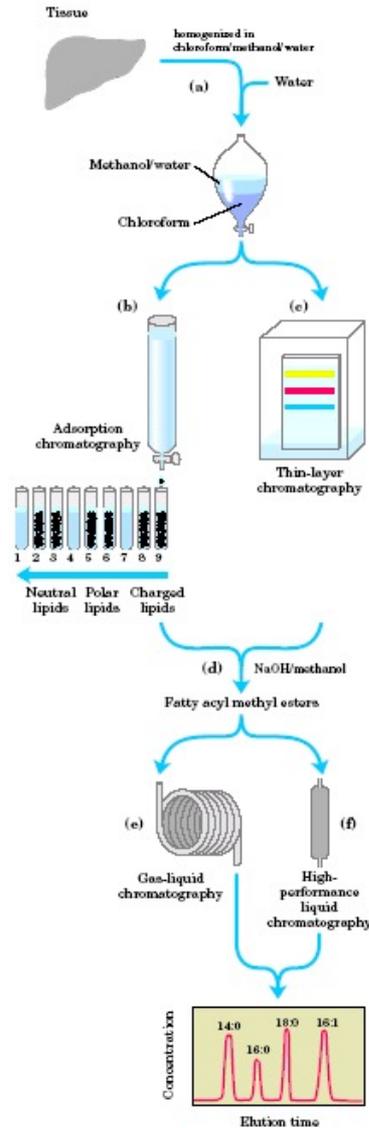


Análise de Ácidos Graxos

(saturados, monoinsaturados, poliinsaturados)



Análise de Lipídios - Resumo



Extração

Separação dos tipos de lipídios

Hidrólise

Separação e análise dos ácidos graxos