

LIPIDI

Osnove biokemije
Boris Mildner

OSNOVNE KARAKTERISTIKE LIPIDA

- **Lipidi su raznolika grupa spojeva kojima je jedino zajedničko svojstvo da su netopljivi u vodi a topljivi su u organskim otapalima.**
- **Masti i ulja su spojevi u kojima organizam pohranjuje energiju (energetske rezerve).**
- **Fosfolipidi, glikolipidi i steroli su glavni strukturni elementi bioloških membrana.**

OSNOVNE KARAKTERISTIKE LIPIDA

- Druge vrste lipida iako prisutne u malim količinama imaju uloge kao: kofaktori, prijenosnici elektrona, spojevi koji vežu (“sidre”) proteine za staničnu membranu, pigmenti koji apsorbiraju svjetlost, emulgatori u probavnom traktu, hormoni i stanični glasnici...
- Lipidi ne stvaraju kovalentne polimere.

Masne kiseline

Gotovo sve masne kiseline u stanicama imaju parni broj ugljikovih atoma (obično 12 – 24). Mogu biti zasićene i nezasićene, a dvostruka veza je gotovo uvijek u *cis*-položaju.

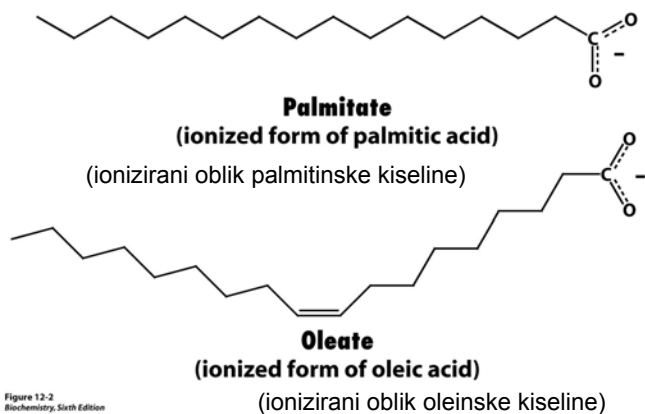
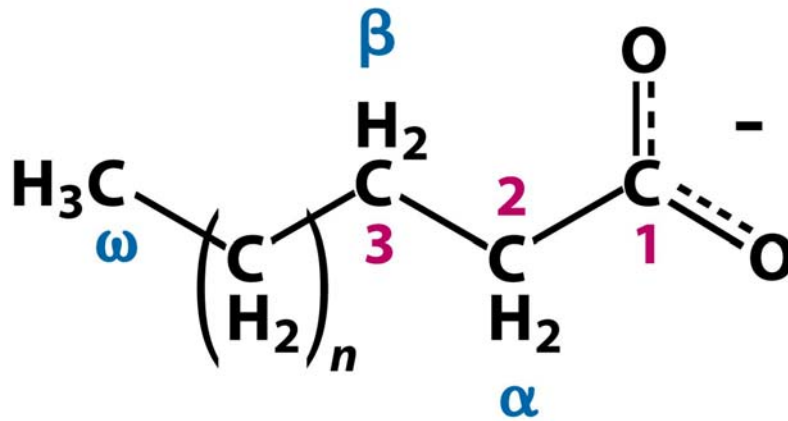


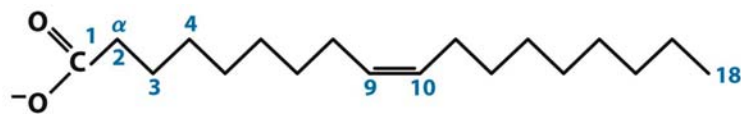
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Nomenklatura

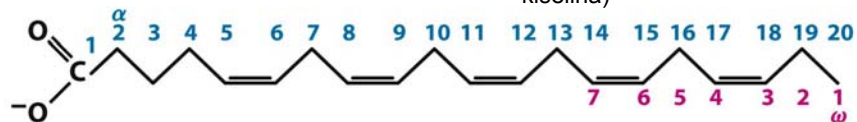


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Masne kiseline



(a) 18:1(Δ^9) cis-9-Octadecenoic acid (oktadekaenoična kiselina) (oleinska kiselina)



(b) 20:5($\Delta^{5,8,11,14,17}$) Eicosapentaenoic acid (EPA), an omega-3 fatty acid (eikozapentaenoična kiselina (EPA) – omega-3 masna kiselina)

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Neke prirodne masne kiseline

Ugljikova okosnica	Struktura* *pri pH = 7,0 karboksilne skupine su ionizirane	Sistematsko ime	Uobičajeno ime	Talište (°C)
12 : 0	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	<i>n</i> -dodekanoična kiselina	laurinska kiselina	44,2
14 : 0	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	<i>n</i> -tetradekanoična kiselina	miristinska kiselina	53,9
16 : 0	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	<i>n</i> -heksadekanoična kiselina	palmitinska kiselina	63,1
18 : 0	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	<i>n</i> -oktadekanoična kiselina	stearinska kiselina	69,6
20 : 0	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	<i>n</i> -eikozanoična kiselina	arahidična kiselina	76,5
24 : 0	$\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$	<i>n</i> -tetrakozanoična kiselina	lignocerinska kiselina	86,0
16 : 1 (Δ^9)	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_9\text{COOH}$	<i>cis</i> -9-heksadekanoična kiselina	palmitolenska kiselina	1,0 do - 0,5
18 : 1 (Δ^9)	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_9\text{COOH}$	<i>cis</i> -9-oktadekanoična kiselina	oleinska kiselina	13,4
18 : 2 ($\Delta^9,12$)	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	<i>cis</i> -, <i>cis</i> -9,12-oktadekanoična kiselina	linoleična kiselina	1,0 - 5,0
18 : 3 ($\Delta^9,12,15$)	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_5\text{COOH}$	<i>cis</i> -, <i>cis</i> -, <i>cis</i> -9,12,15-oktadekanoična kiselina	α -linolenska kiselina	-11,0
20 : 4 ($\Delta^5,8,11,14$)	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{COOH}$	<i>cis</i> -, <i>cis</i> -, <i>cis</i> -, <i>cis</i> -5,8,11,14-ikozatetraenoična kiselina	arahidonska kiselina	-49,5

Masne kiseline, zasićene i nezasićene

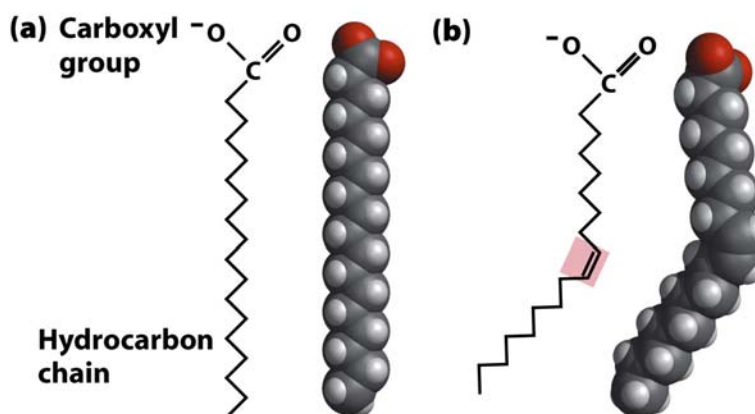


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Struktura zasićenih i nezasićenih masnih kiselina

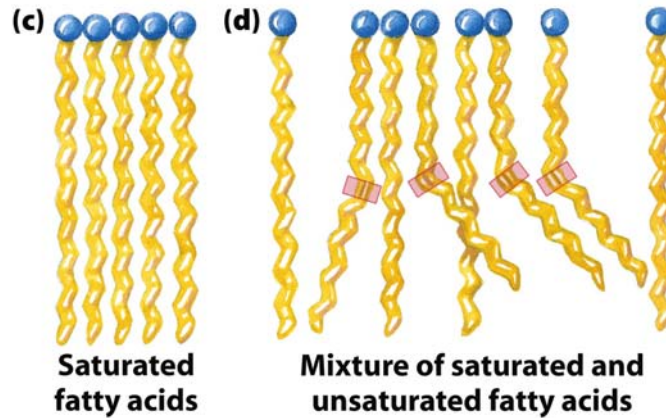
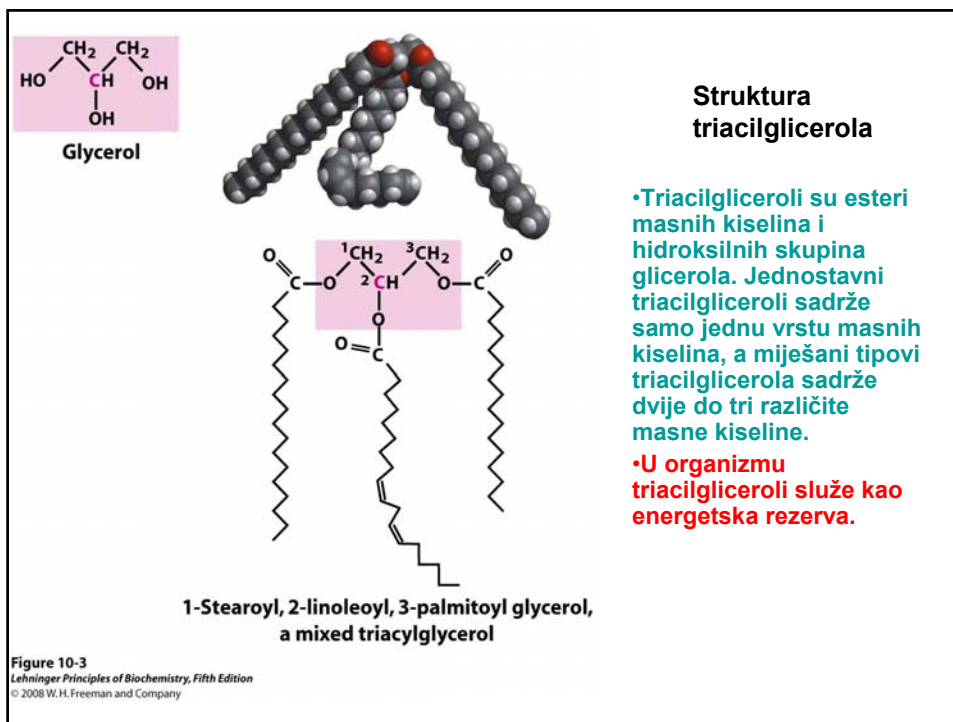


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Triacilgliceroli (masti i ulja)

- Esteri masnih kiselina i glicerola su **triacilgliceroli**.
Triacilglicerole dijelimo na masti i ulja.
- Triacilgliceroli su nepolarni hidrofobni spojevi netopljivi u vodi.
- Imaju manju specifičnu gustoću od vode, pa se miješanjem vode i triacilglicerola dobivaju dvije faze.



Presjek sjemenke *Arabidopsis*

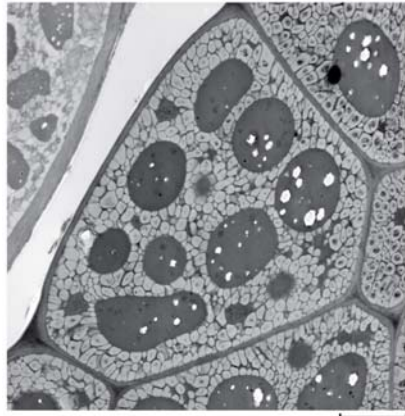


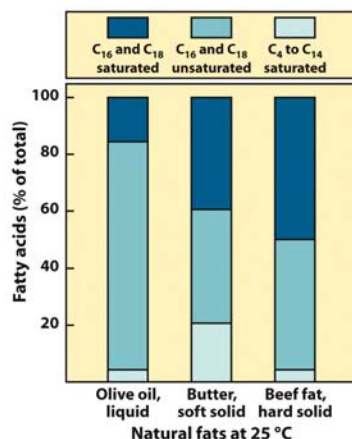
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Biljke pohranjuju triacilglicerole u svojim sjemenkama.

Triacilgliceroli

- Dva su razloga zašto je prednost da se triacilgliceroli čuvaju kao energetska rezerva a ne polisaharidi:
 - 1) Ugljikov atom masnih kiselina je reduciraniji nego ugljikov atom ugljikohidrata, pa oksidacijom triacilgliceroli oslobađaju više energije nego što se dobiva oksidacijom ugljikohidrata.
 - 2) Triacilgliceroli su hidrofobni pa ne vežu vodu, dok npr. 2 g polisaharida (glikogena) veže 1 g vode.

RASPODJELA MASNIH KISELINA U ULJU, MASLACU I LOJU



Triacilglicerole susrećemo u raznim namirnicama.

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“TRANS” MASNE KISELINE U HRANI

	Trans fatty acid content	
	In a typical serving (g)	As % of total fatty acids
French fries	4.7–6.1	28–36
Breaded fish burger	5.6	28
Breaded chicken nuggets	5.0	25
Pizza	1.1	9
Corn tortilla chips	1.6	22
Doughnut	2.7	25
Muffin	0.7	14
Chocolate bar	0.2	2

Source: Adapted from Table 1 in Mozaffarian, D., Katan, M.B., Ascherio, P.H., Stampfer, M.J., & Willet, W.C. (2006) Trans fatty acids and cardiovascular disease. *N. Engl. J. Med.* 354, 1604–1605.
Note: All data for foods prepared with partially hydrogenated vegetable oil in the United States in 2002.

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Djelomičnom hidrogenacijom jestivih ulja tijekom pripreve hrane dolazi do promjena *cis* položaja dvostrukih veza u *trans* položaj. U prehrani *trans* masne kiseline su rizičan faktor za različite bolesti srca.

STANIČNE MEMBRANE

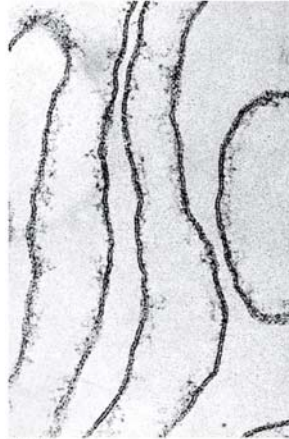


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PODJELA MEMBRANSKIH LIPIDA

Membranske lipide možemo podijeliti:

Fosfolipide:

- glicerofosfolipide (fosfatidilkolin, fosfatidiletanolamin, fosfatidilserin, fosfatidilinozitol, kardiolipin)
- sfingolipide (sfingomijelin)

Glikolipide:

- Cerebrozide (mosaharid (glukoza ili galaktoza) vezan za ceramid)
- Globozide (linearni di, tri ili tetra oligosaharidi vezani za ceramid)
- Gangliozide (razgranati oligosaharidi vezani za ceramid)

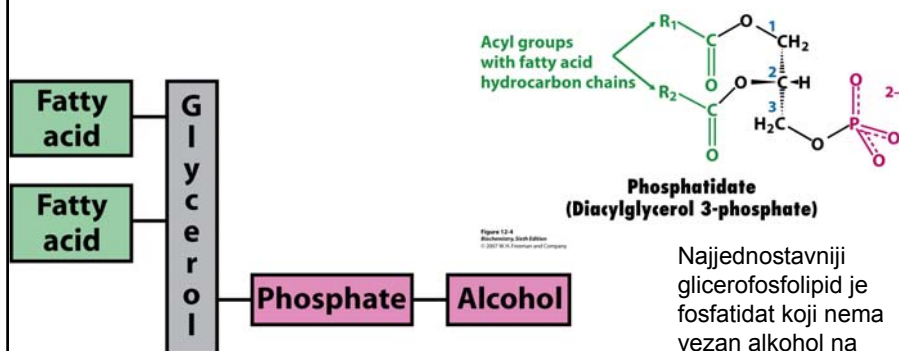
Sterole:

- Kolesterol (sisavci)
- Ergosterol (niži eukarioti)
- Bakterije nemaju sterole u plazmatskim membranama.

Membranski lipidi

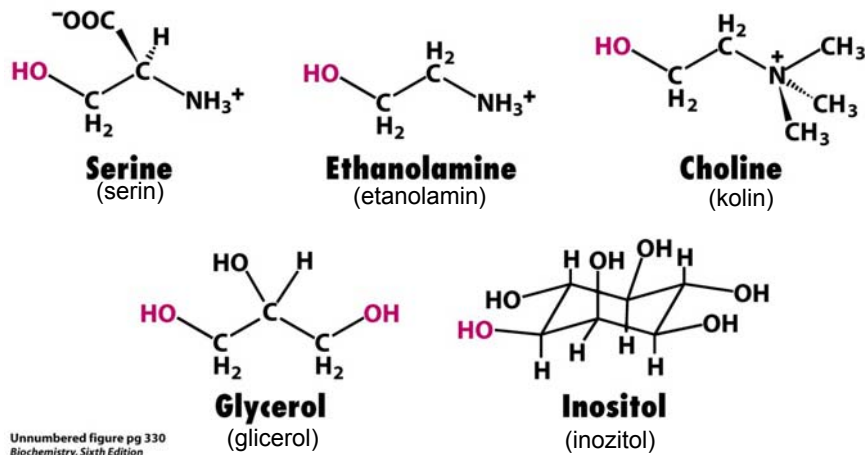
- **Lipidi s polarnim čeonim skupinama i nepolarnim “repovima” sastojci su staničnih membrana.**
- Najčešći sastojci u membranama su glicerofosfolipidi, kojima su na dvije hidroksilne skupine glicerola esterski vezane dvije masne kiseline, a na čeonu skupinu (treću hidroksilnu skupinu glicerola) putem fosfodieterske veze vezan je alkohol.
- Čeone skupine glicerofosfolipida se razlikuju. Najčešće glicerofosfolipidi kao čeonu skupinu imaju ili fosfatidiletanolamin ili fosfatidilkolin. Kod neutralnog pH, čeone skupine su nabijene.

GLICEROFOSFOLIPIDI



Najjednostavniji glicerofosfolipid je fosfatidat koji nema vezan alkohol na fosfatnu (“čeonu skupinu”). Zastupljenost fosfatidata u membranama je mala iako je to preteča ostalih glicerofosfolipida.

SPOJEVI KOJI SE VEŽU NA FOSFATNU SKUPINU FOSFATIDATA



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STRUKTURE GLICEROFOSFOLIPIDA

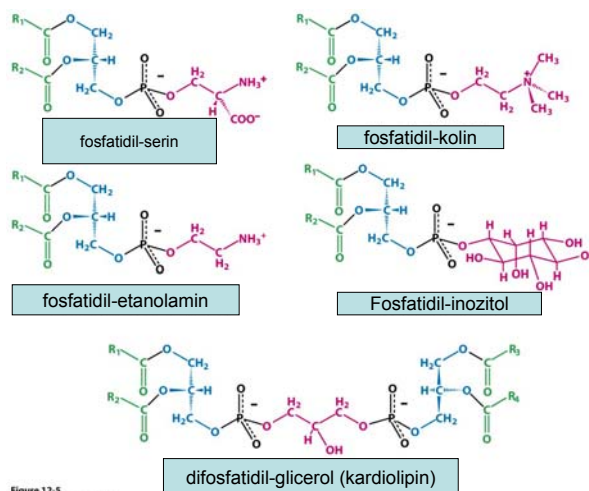


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NEUOBIČAJENI GLICEROFOSFOLIPIDI EUKARIOTA

eterskom vezom vezani alken

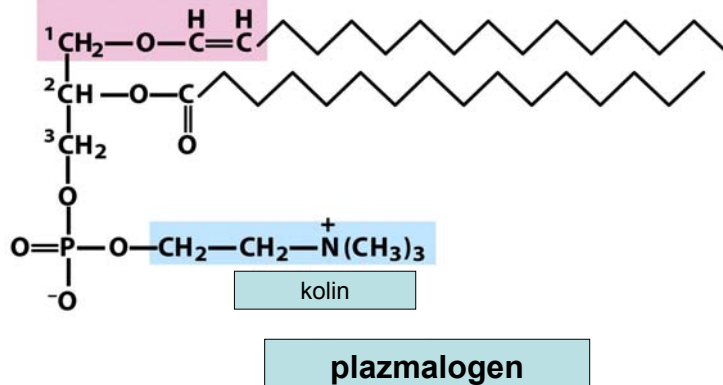


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NEUOBIČAJENI GLICEROFOSFOLIPIDI EUKARIOTA

eterskom vezom vezani alkan

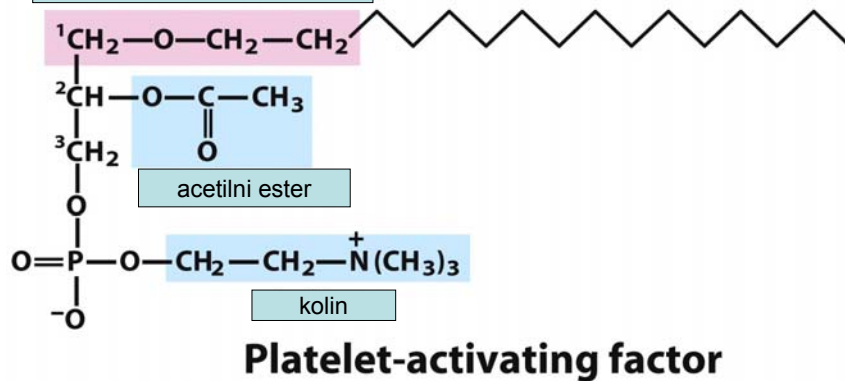
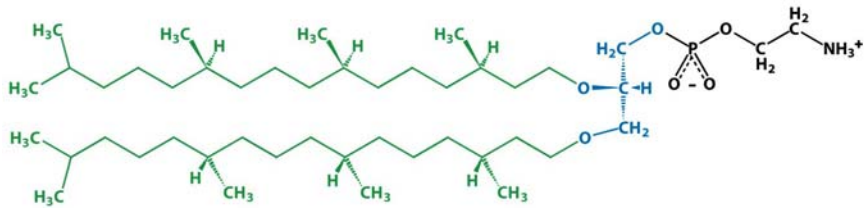


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GLICEROFOSFOLIPIDI ARHEJA

•Arheje imaju jedinstvene membranske lipide koji su eterskim vezama povezani s glicerolom. Ovi lipidi su stabilni u okolišu u kojem žive arheje.



Membrane lipid from the archaeon *Methanococcus jannaschii*

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SFINGOLIPIDI

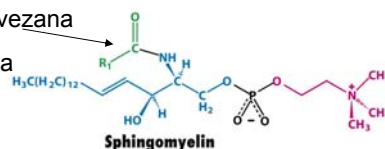
•Sfingolipidi umjesto glicerola imaju sfingozin. Sfingozin je dugolančani alifatski amino-alkohol.
•Sfingomijelin osim fosfatne kiseline i kolina ima dva dugolančana ugljikova lanca, od kojih jedan potječe od masne kiseline, a drugi od sfingozina.

(sfingozin)



Sphingosine

Masna kiselina je vezana
amidnom vezom za
sfingozin



Sphingomyelin

(sfingomijelin)

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Strukture fosfatidilkolina i sfingomijelina

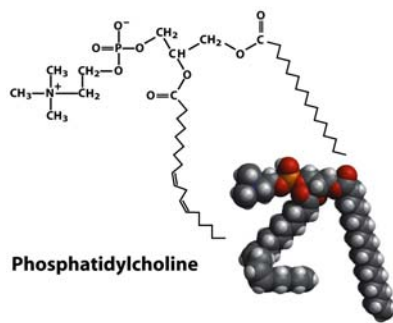


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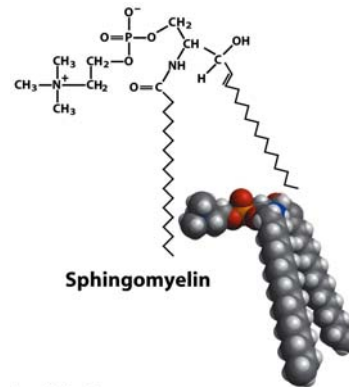


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PRIMJERI GLIKO(SFINGO)LIPIDA

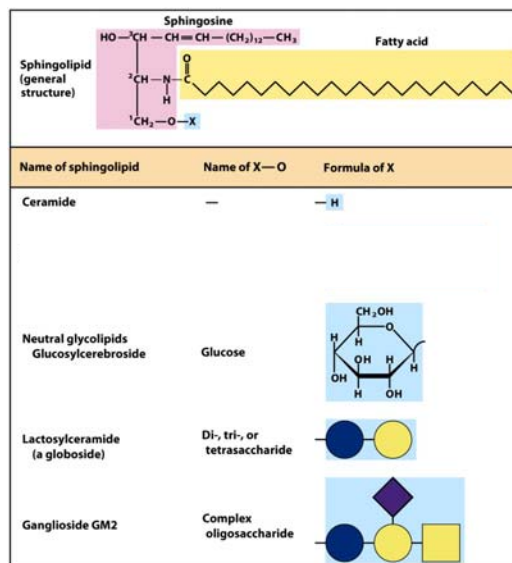
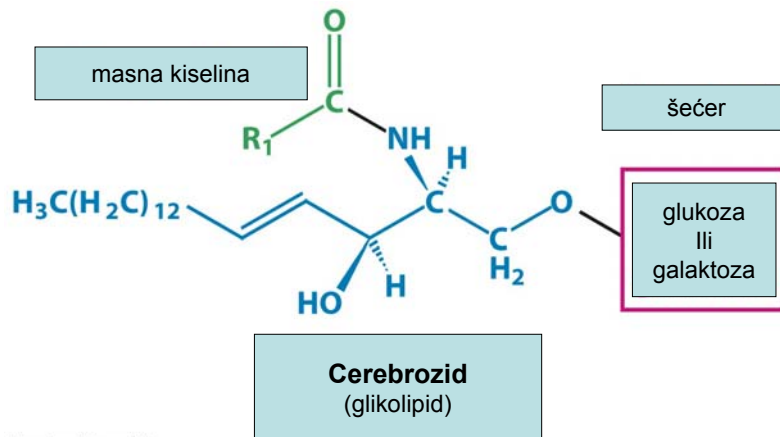


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GLIKOLIPIDI CEREBROZID (GLIKOSFINGOLIPID)



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Šećeri su direktno vezani za ceramid, odnosno za hidroksilnu skupinu sfingozina (nema fosfata!)

ANTIGENI KRVNIH GRUPA

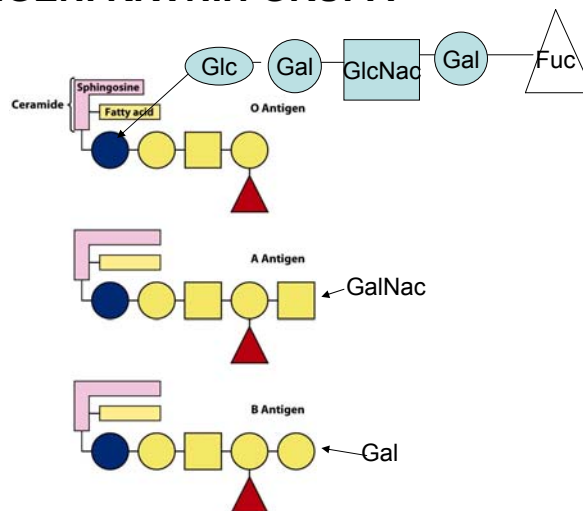
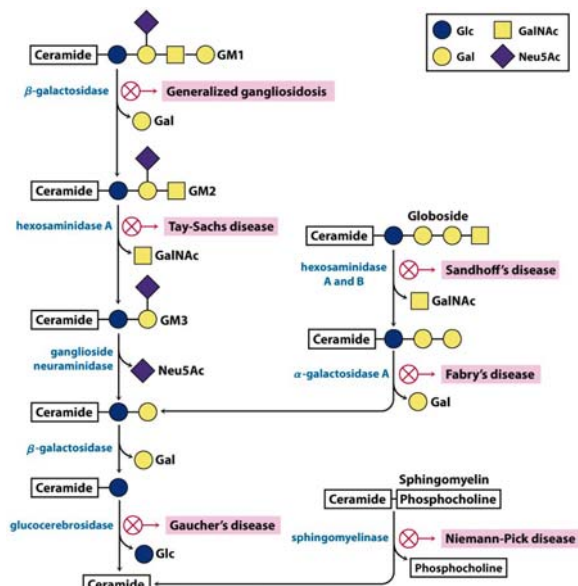


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Neke nasljedne bolesti (ganglioziidoze)



Box 10-2 figure 1
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Tri osnovne vrste lipida izgrađuju membranu Steroli

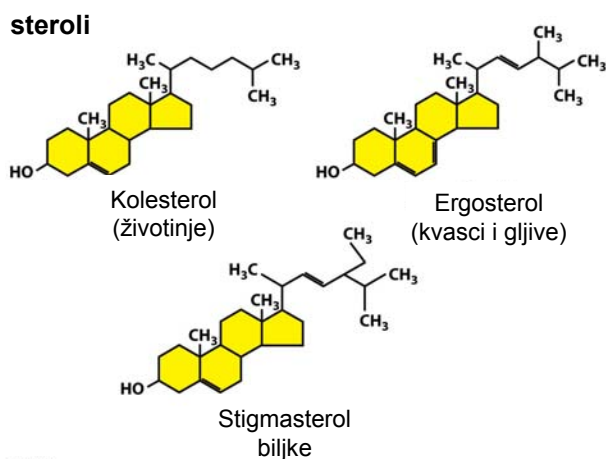
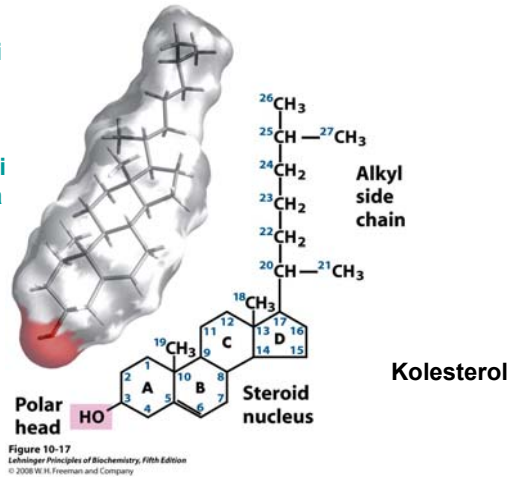


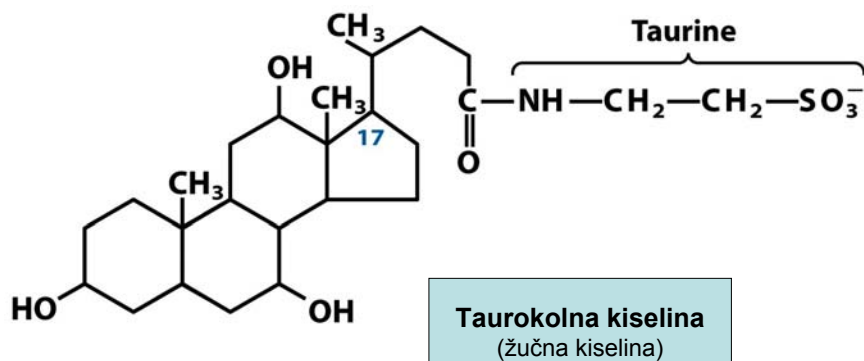
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Steroli

•Steroli su izgrađeni od četiri povezana prstena i jedan prsten ima hidroksilnu skupinu.
Kolesterol je glavni sterol u životinja, a ujedno je i preteča različitih steroida.



Osim u membranama, derivati kolesterola su važni u metabolizmu



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Steroidni hormoni (derivati kolesterola)

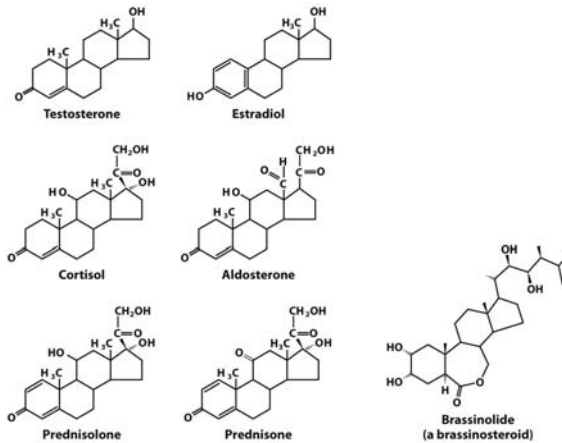
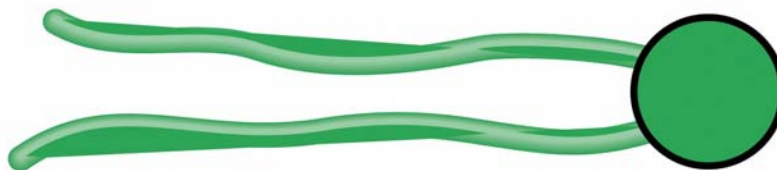


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Shematski prikaz membranskih lipida



Zajedničko svojstvo membranskih lipida je da su to amfipatske molekule koje imaju jedan hidrofilni kraj a suprotni kraj je hidrofoban.

Strukture (modeli) membranskih lipida

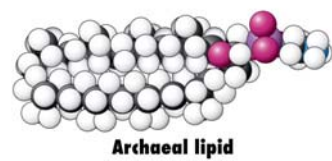
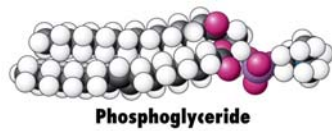


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Biološke membrane Sastav lipida u nekim membranama

TABLE 10-1 Major Lipid Components of Selected Biomembranes				
SOURCE/LOCATION	COMPOSITION (MOL %)			
	PC	PE + PS	SM	CHOLESTEROL
Plasma membrane (human erythrocytes)	21	29	21	26
Myelin membrane (human neurons)	16	37	13	34
Plasma membrane (<i>E. coli</i>)	0	85	0	0
Endoplasmic reticulum membrane (rat)	54	26	5	7
Golgi membrane (rat)	45	20	13	13
Inner mitochondrial membrane (rat)	45	45	2	7
Outer mitochondrial membrane (rat)	34	46	2	11
Primary leaflet location	Exoplasmic	Cytosolic	Exoplasmic	Both

PC = phosphatidylcholine; PE = phosphatidylethanolamine; PS = phosphatidylserine; SM = sphingomyelin.
SOURCE: W. Dowhan and M. Bogdanov, 2002, in D. E. Vance and J. E. Vance, eds., *Biochemistry of Lipids, Lipoproteins, and Membranes*, Elsevier.

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Različiti lipidi

Osim za potrebe čuvanja energije i za potrebe stvaranja membrana, u prirodi postoje različiti spojevi koje ubrajamo u lipide.

VOSAK

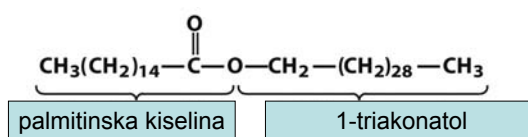


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Razgradnjom membranskih lipida stanica dobiva različite signale

Lipidi koji se koriste u signalizaciji (komunikaciji) stanica.

Fosfolipaze kidaju specifične veze glicerofosfolipida.

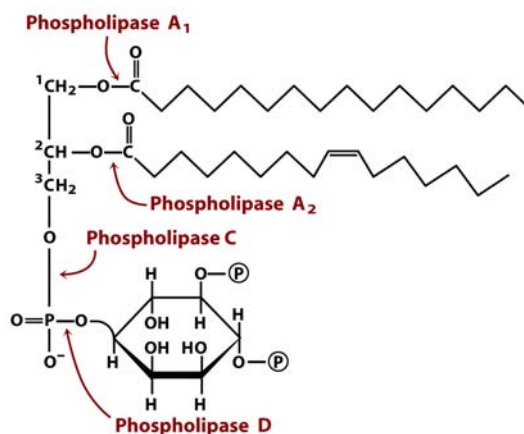


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Eikozanoidi

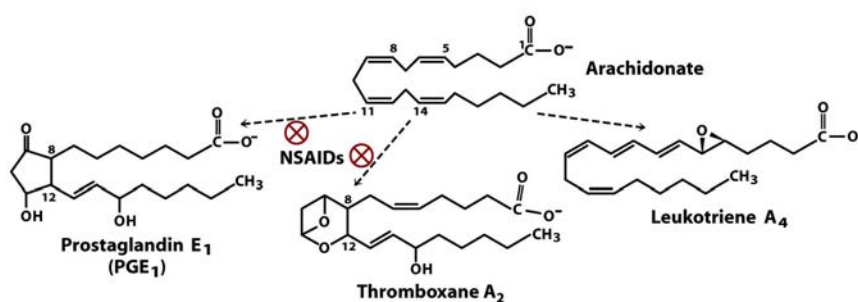
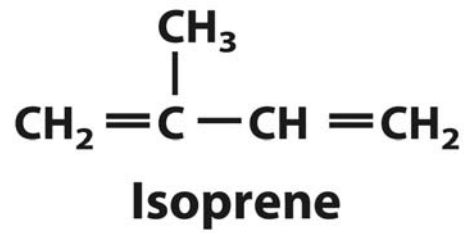


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Pretvorbom arahidonata nastaju tkivni hormoni prostaglandini, tromboksani i leukotrieni.

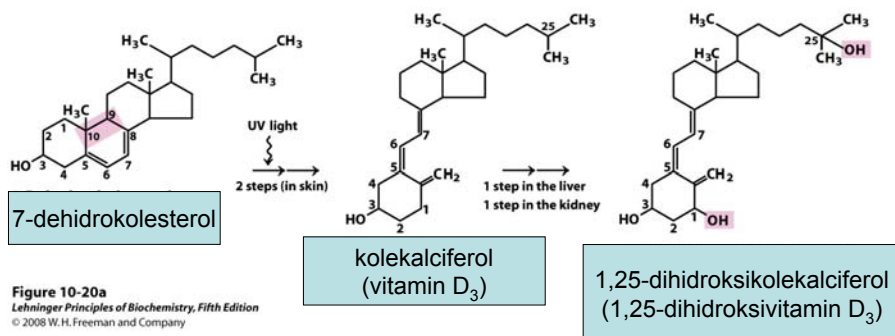
Izopren

Različiti lipidi su derivati izoprena.



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Primjeri prenola



Primjeri prenola

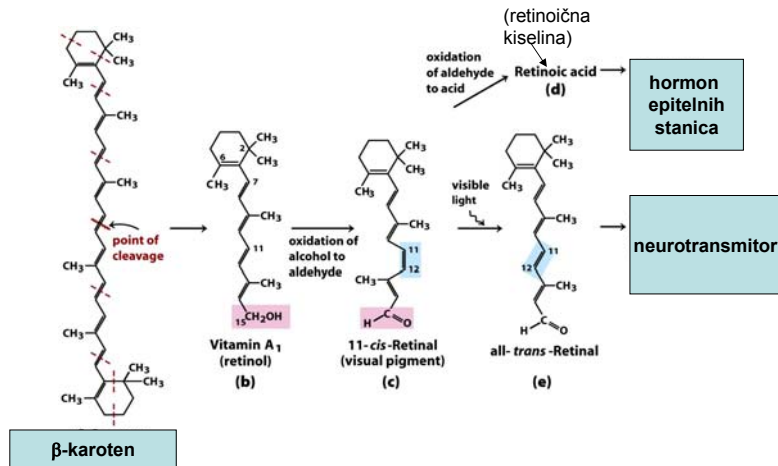


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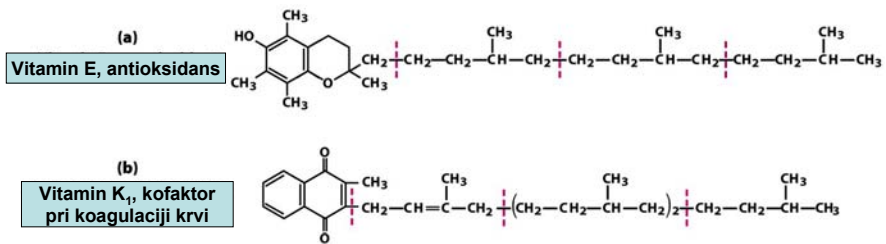
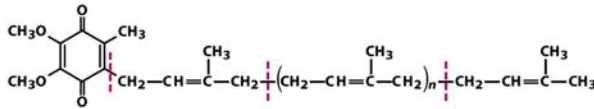


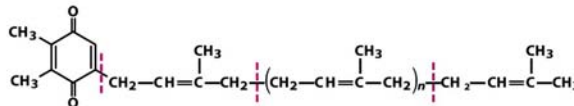
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Primjeri prenola

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



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



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

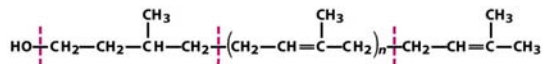


Figure 10-22d-f
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Primjeri prenola

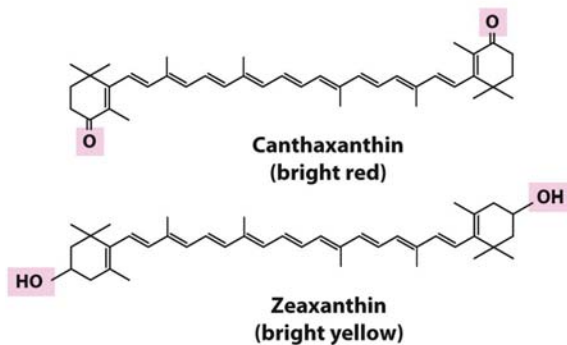


Figure 10-23
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Izolacija i karakterizacija lipida

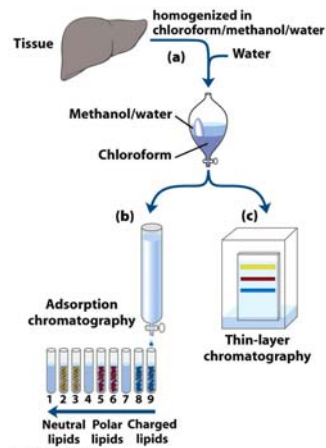


Figure 10-24 part 1
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Razdvajanje i identifikacija lipida

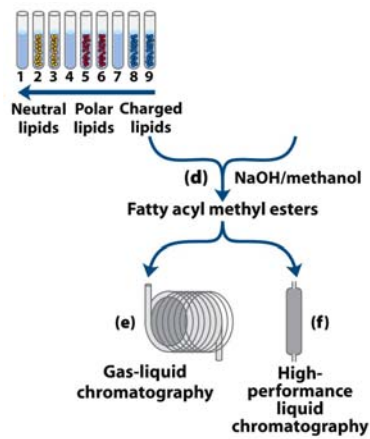


Figure 10-24 part 2
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Identifikacija lipida

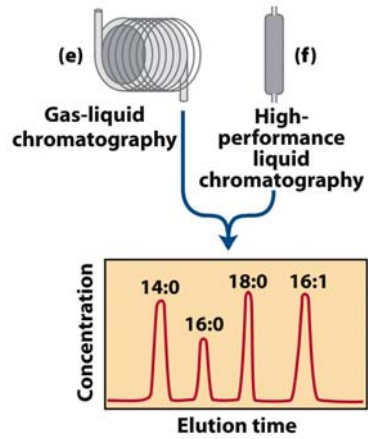


Figure 10-24 part 3
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Identifikacija lipida

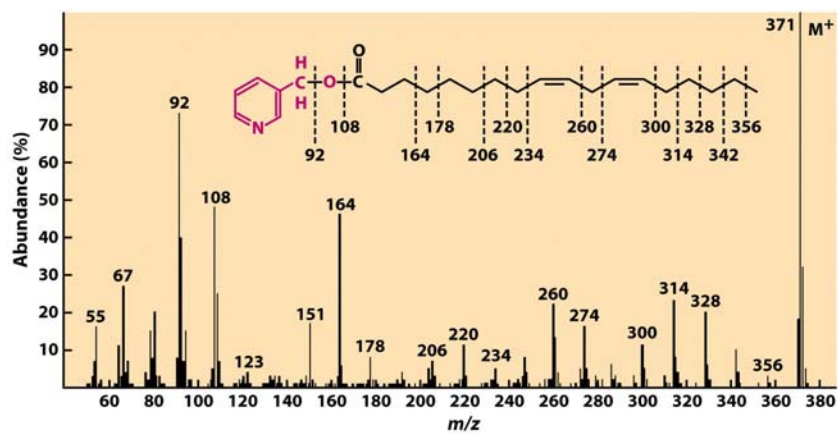


Figure 10-25
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