

C5720

Biochemie

01c-Aminokyseliny

Obsah

- Aminokyseliny jako stavební kameny bílkovin
- Obecná struktura, popis
- Významné vlastnosti
 - Chiralita
 - Acidobazicitá
 - Polarita
 - Reaktivita

Obecná struktura aminokyselin

- α -aminokyseliny (2-aminokyseliny)

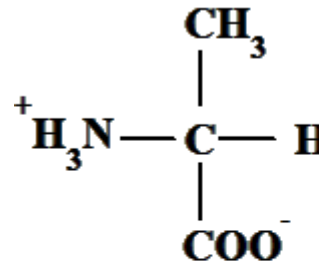
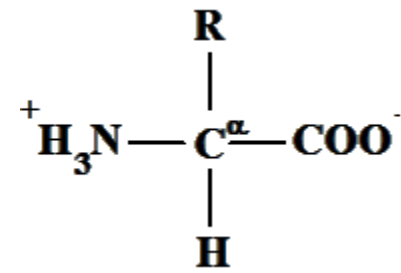
- R – specifický zbytek jednotlivých AK – dělení
- Výjimky – Pro

- Chiralita

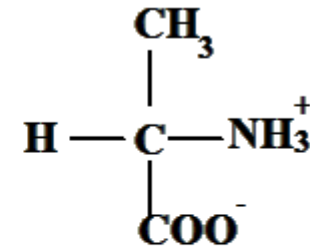
- Relativní – absolutní
- Význam pro strukturu a vlastnosti – bílkoviny aj. (thalidomid, toxiny, terpeny)

- L-aminokyseliny

- typické pro většinu biomolekul (D-vzácně)



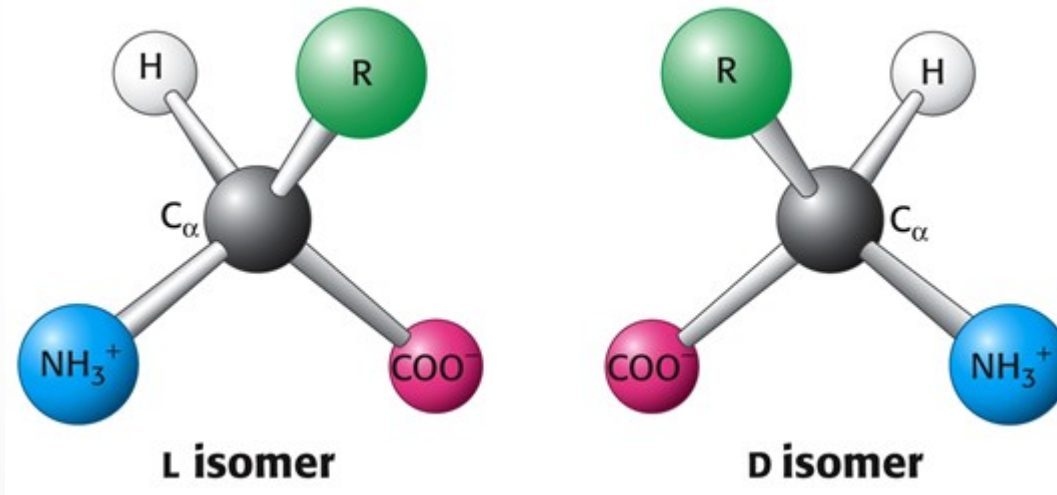
D-alanin



L-alanin

Chiralita aminokyselin

- Nejméně 1 asymetrický C (mimo Gly)



Chiralita aminokyselin

Absolutní konfigurace

Gly (G) není chirální

Cys (C) je v absolutní konfiguraci *R*

Ile (I) a Thr (T) mají dvě chirální centra.

L-Ile ($2S,3S$) a L-Thr ($2S,3R$)

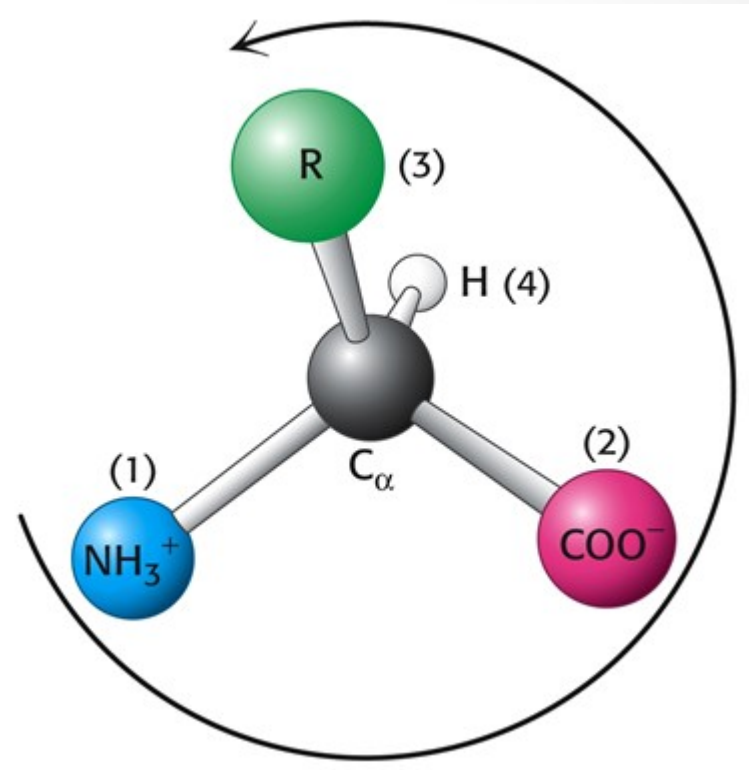
mají dva enantiomery

diastereoizomerní

k alloisoleucinu ($2R,3S$)

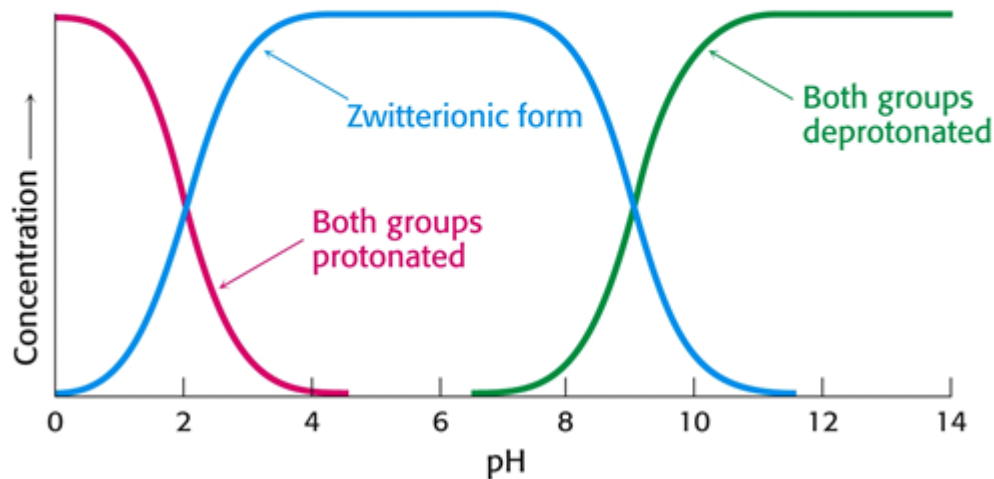
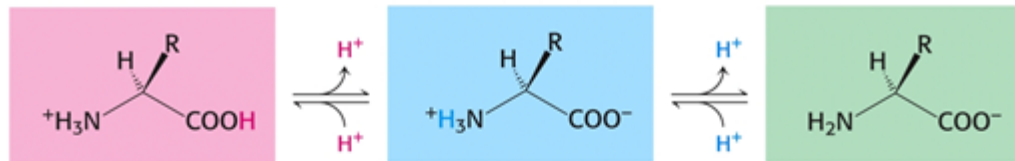
resp. k allothreoninu ($2R,3R$).

Všechny ostatní L-aminokyseliny jsou *S* !!



Acidobazické vlastnosti

- Obojetné ionty x zjednodušené vzorce
- Rozpustnost = $f(Q)$, soli x neutrální



Acidobazické vlastnosti

- Disociace AK
- Jednoduchá struktura
- Více disociabilních skupin – složitější křivka
- Pojem pI

$$pI = \frac{pK_{COOH} + pK_{NH_2}}{2}$$

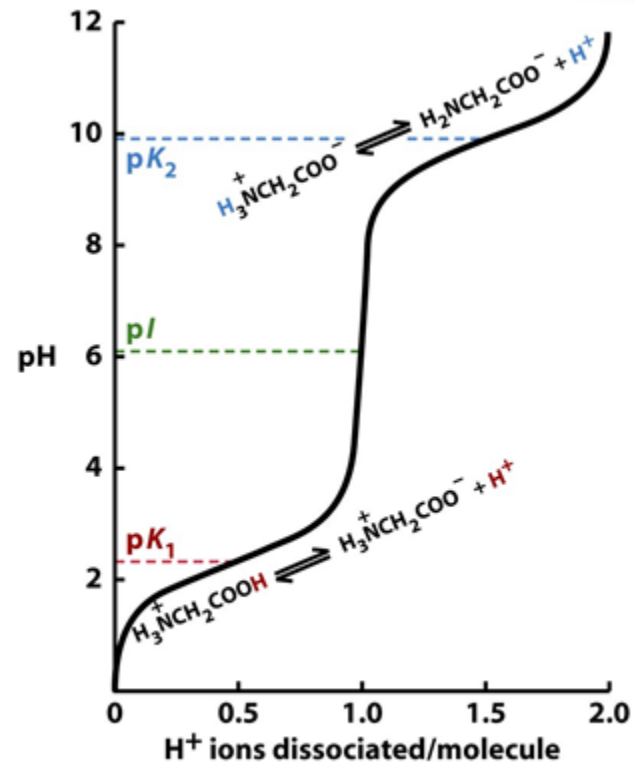


Figure 4-8 Fundamentals of Biochemistry, 2/e
© 2006 John Wiley & Sons

Acidobazické vlastnosti

TABLE 3.1 Typical pK_a values of ionizable groups in proteins

Group	Acid	⇌	Base	Typical pK _a *
Terminal α-carboxyl group				3.1
Aspartic acid Glutamic acid				4.1
Histidine				6.0
Terminal α-amino group				8.0
Cysteine				8.3
Tyrosine				10.9
Lysine				10.8
Arginine				12.5

*pK_a values depend on temperature, ionic strength, and the microenvironment of the ionizable group.

Více disociabilních skupin

$$pI = (pK_m + pK_n)/2$$

kde pK_m a pK_n ohraničují neutrální formu

Výpočet je informativní (vliv molekuly na disociaci)

Platí i pro jiné amfoionty

Skupina	pK	Skupina	pK	Skupina	pK
α COOH	1.8 - 2.5	β COOH	3.9	γ COOH	4.1
α NH ₂	9 - 10	ε NH ₂	10.8	guanidin	12.5
imidazol	6.0	SH	8.3	OH	10.1

Polarita

- Asymetrie elektronových hustot – nábojů
- Závisí na R
- Hydropatický index
 - ΔG transportu z o do i fáze
 - Oktanol – voda
 - Jiná vyjádření

TABLE 3.1 Hydropathy scale for amino acid residues

Amino acid	Free-energy change for transfer (kJ mol^{-1})
Isoleucine	3.1
Phenylalanine	2.5
Valine	2.3
Leucine	2.2
Methionine	1.1
Tryptophan	1.5 ^b
Alanine	1.0
Glycine	0.67
Cysteine	0.17
Tyrosine	0.08
Proline	-0.29
Threonine	-0.75
Serine	-1.1
Histidine	-1.7
Glutamate	-2.6
Asparagine	-2.7
Glutamine	-2.9
Aspartate	-3.0
Lysine	-4.6
Arginine	-7.5

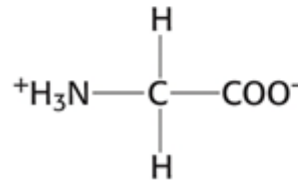
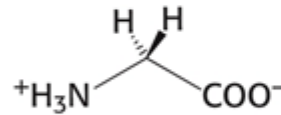
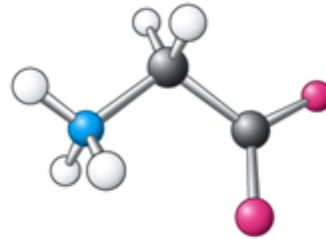
Přehled aminokyselin

- 20 + 1 + v bílkovinách, proteinogenní, kódované
 - Derivatizované – posttranslační modifikace
- Volné AK a deriváty, složky jiných biomolekul
- Dělení podle struktury – významných vlastností
 - Nepolární – neutrální – alifatické
 - Polární nedisociované (zbytky R)
 - Disociované (zbytky R)
 - Kyselé
 - Bazické
- Jiné dělení, prolínání skupin
 - Aromatické
 - Sírné
 - Heterocyklické apod.

Nepolární

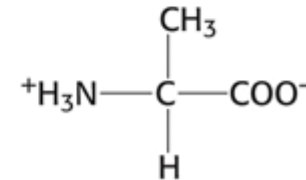
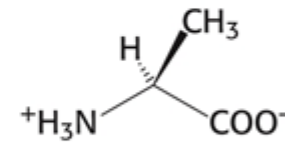
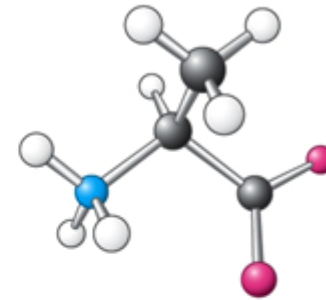
- Alifatické

Glycine
(Gly, G)



Glycine
(Gly, G)

Alanine
(Ala, A)

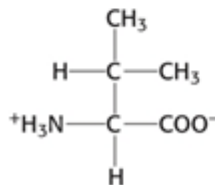
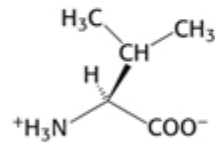
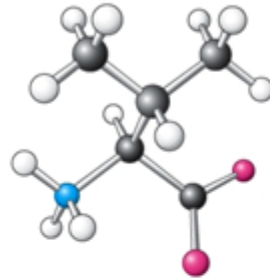


Alanine
(Ala, A)

Nepolární

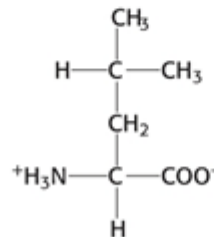
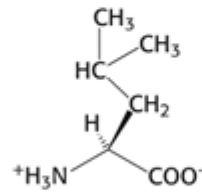
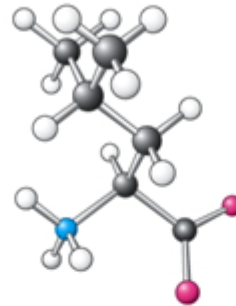
- Alifatické větvené Met sirná

**Valine
(Val, V)**



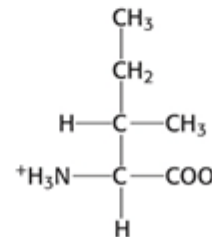
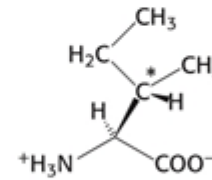
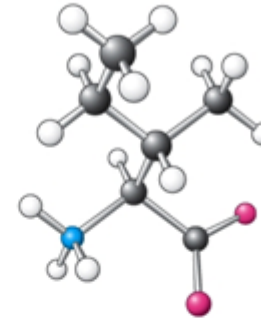
**Valine
(Val, V)**

**Leucine
(Leu, L)**



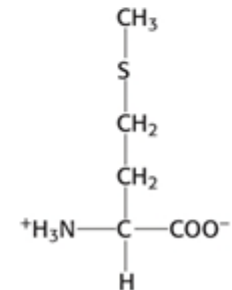
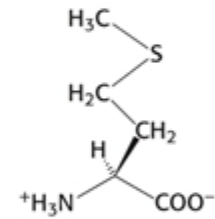
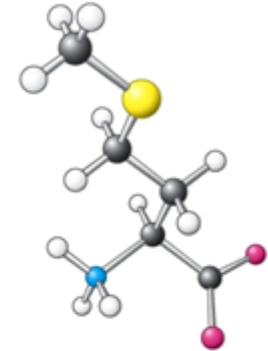
**Leucine
(Leu, L)**

**Isoleucine
(Ile, I)**



**Isoleucine
(Ile, I)**

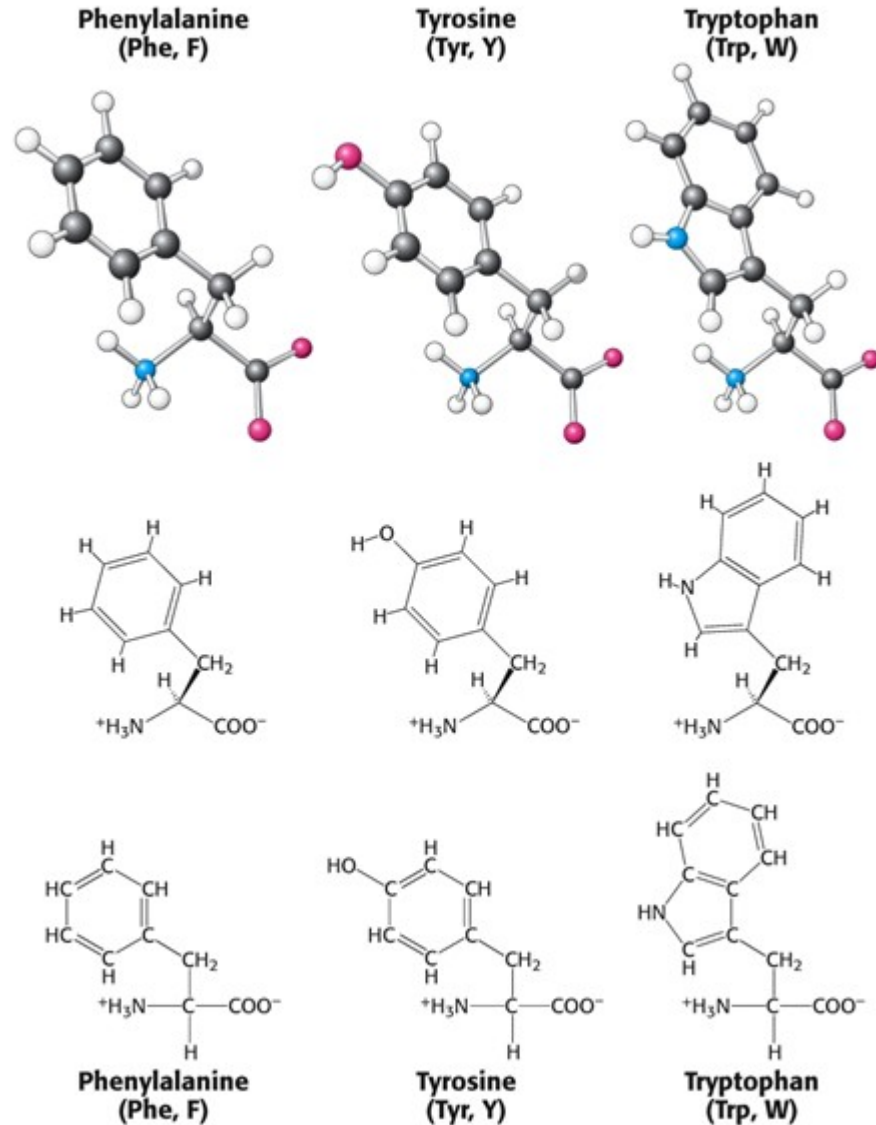
**Methionine
(Met, M)**



**Methionine
(Met, M)**

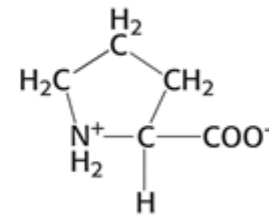
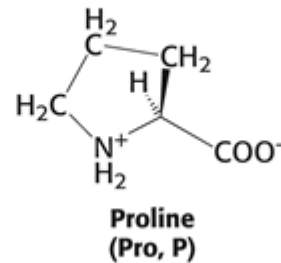
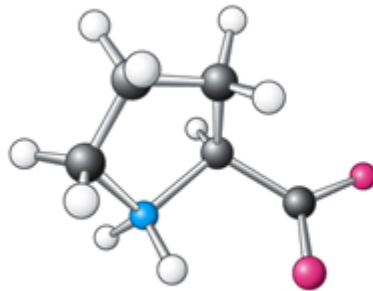
Nepolární

- Aromatické



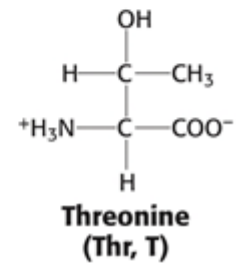
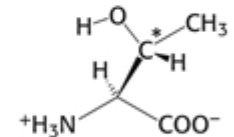
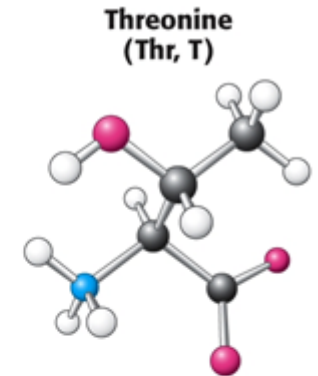
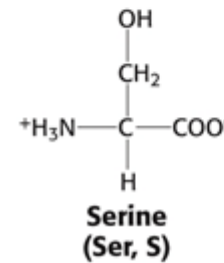
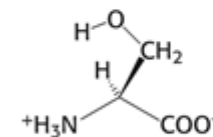
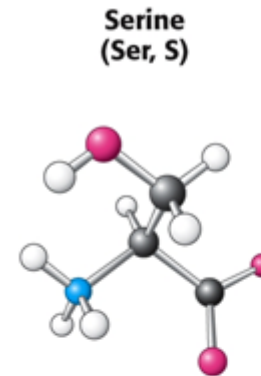
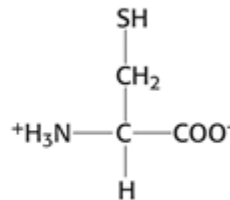
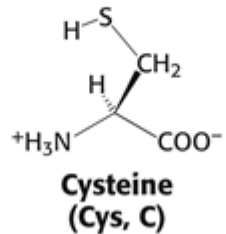
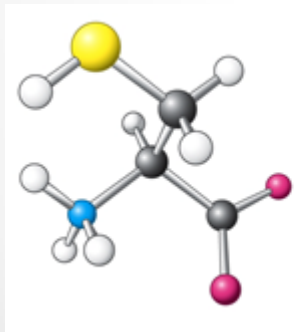
Nepolární

- Výjimečná struktura
 - Zvláštní dopad na strukturu polymeru – bílkoviny
- Heterocyklická



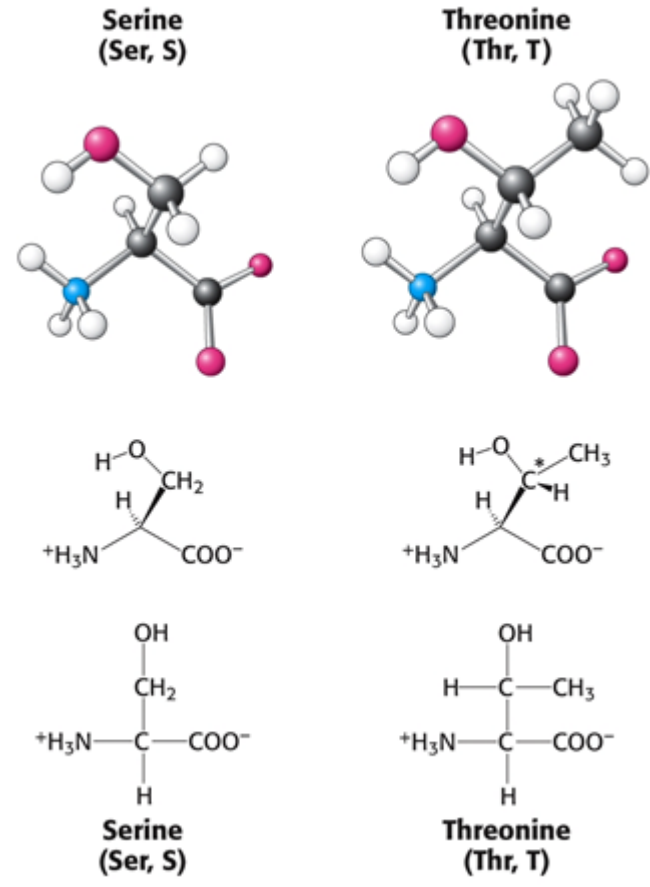
Polární nedisociované

- Hydroxy AK
- Sirná – Cys
(sl. kyselá)

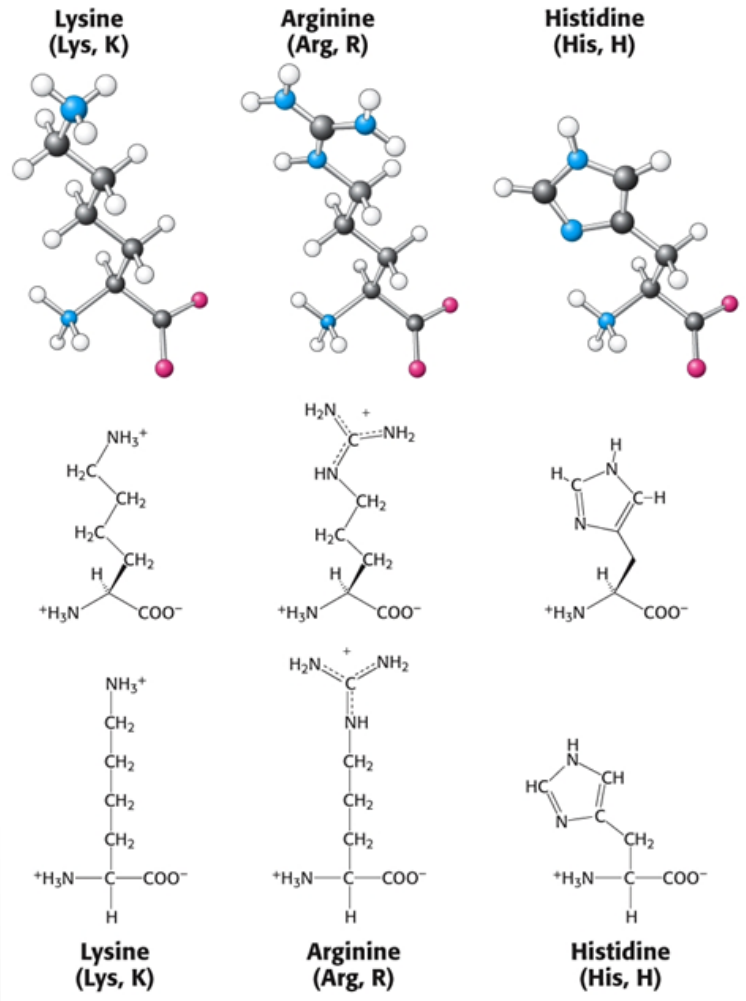


Polární nedisociované

- Hydroxy AK

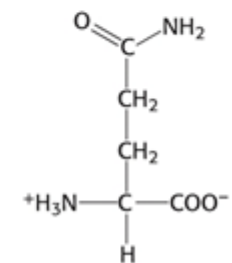
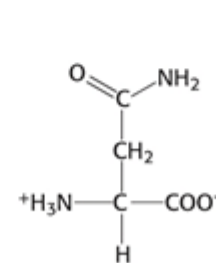
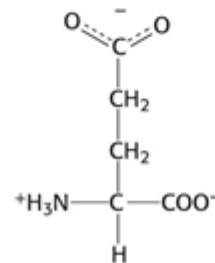
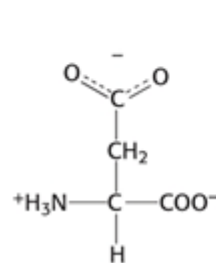
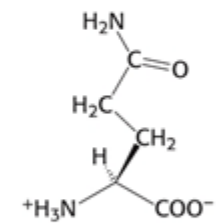
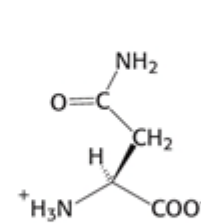
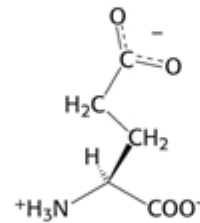
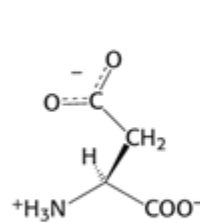
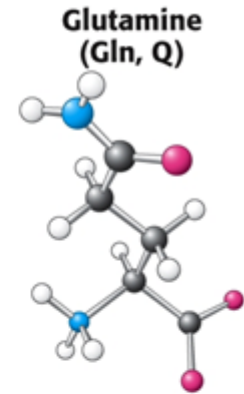
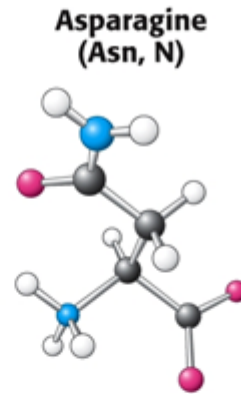
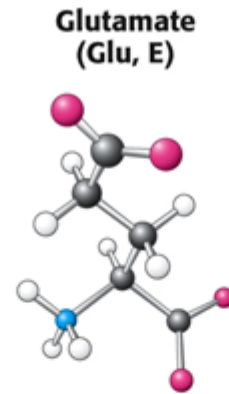
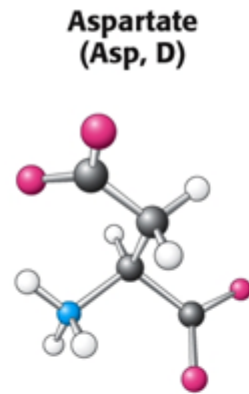


Disociované - bazické



Disociované - kyselé

- Asn a Gln nedisociované, nejsou aminy!



Aspartate (Asp, D)

Glutamate (Glu, E)

Asparagine (Asn, N)

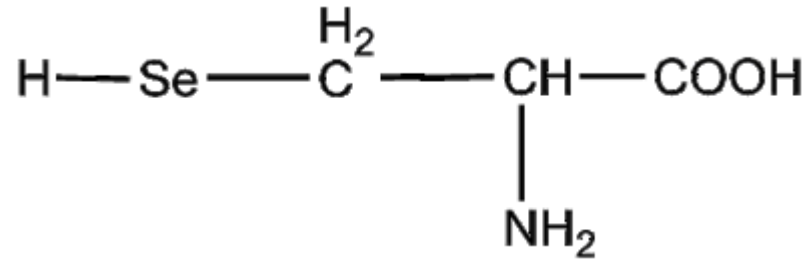
Glutamine (Gln, Q)

Speciální

- Výskyt omezen na několik bílkovin či mikroorganismů

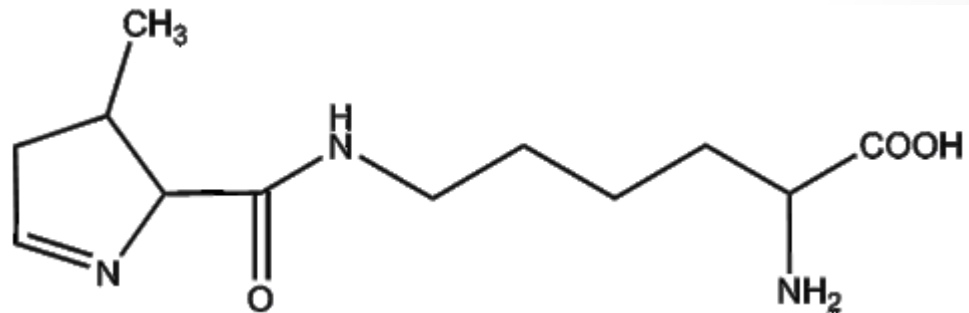
- Selenocystein

- GSH peroxidáza aj.
- Antioxidační



- Pyrolyzin

- Archea



Názvy a zkratky

- Troj- a jednopísmenkové

TABLE 3.2 Abbreviations for amino acids

Amino acid	Three-letter abbreviation	One-letter abbreviation	Amino acid	Three-letter abbreviation	One-letter abbreviation
Alanine	Ala	A	Methionine	Met	M
Arginine	Arg	R	Phenylalanine	Phe	F
Asparagine	Asn	N	Proline	Pro	P
Aspartic Acid	Asp	D	Serine	Ser	S
Cysteine	Cys	C	Threonine	Thr	T
Glutamine	Gln	Q	Tryptophan	Trp	W
Glutamic Acid	Glu	E	Tyrosine	Tyr	Y
Glycine	Gly	G	Valine	Val	V
Histidine	His	H	Asparagine or aspartic acid	Asx	B
Isoleucine	Ile	I	Glutamine or glutamic acid	Glx	Z
Leucine	Leu	L			
Lysine	Lys	K			

- Se-Cys = U

Rozšiřující informace

- <http://www.galenus.cz/clanky/biochemie/biochemie-proteiny-zakladni-aminokyseliny>

Názvy a zkratky

- Troj- a jednopísmenkové

AMK	Symboly		AMK	Symboly	
glycin	Gly	G	methionin	Met	M
alanin	Ala	A	glutamová k.	Glu	E
valin	Val	V	asparagin	Asn	N
leucin	Leu	L	glutamin	Gln	Q
izoleucin	Ile	I	lysin	Lys	K
serin	Ser	S	arginin	Arg	R
threonin	Thr	T	tyrosin	Tyr	Y
cystein	Cys	C	fenylalanin	Phe	F
histidin	His	H	tryptofan	Trp	W
prolin	Pro	P	asparagová k.	Asp	D

- Se-Cys = U

Chemická reaktivita

- Reakce karboxylu
 - Tvorba solí (disociace – viz výše)
 - Tvorba esterů
 - Tvorba anhydridů
 - **Tvorba amidů – vazba –CO-NH-**
- Reakce aminoskupin
 - Tvorba solí (disociace – viz výše)
 - **Acylace – vazba –CO-NH-**
 - Diazotace – $R-CH(NH_2).COOH + HNO_2 = R-CH(OH).COOH + N_2$ – van Slyke
- Reakce skupin bočního řetězce
 - Speciální, podle druhu AK
 - Význam metabolický – struktura, funkce (oxidace –SH aj.)
 - Analytické využití

Volné aminokyseliny a deriváty

- Součásti jiných biomolekul – β -alanin

- Funkce v metabolismu

– výše uvedené + další

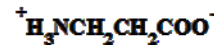
- ornitin a citrulin + Asp a Arg

- Nervové mediátory a hormony

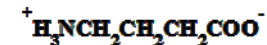
- γ aminomáselná
- DOPA, dopamin, adrenalin
- thyroxin, trijodthyronin

- Antibiotika

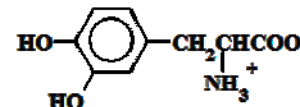
- azaserin, cykloserin, chloramfenikol



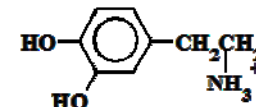
β alanin



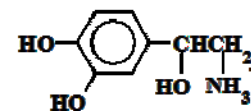
γ aminomáselná kyselina



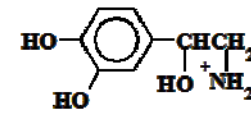
DOPA



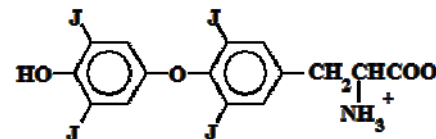
dopamin



noradrenalin



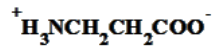
adrenalin



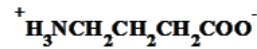
thyroxin

(3,5,3',5'-tetrajodthyronin)

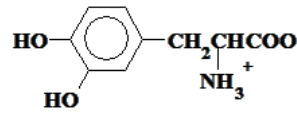
Volné aminokyseliny a deriváty



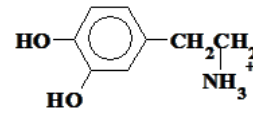
β alanin



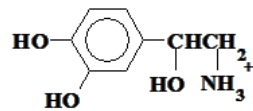
γ aminomáselná kyselina



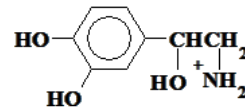
DOPA



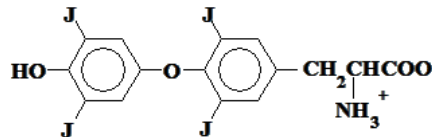
dopamin



noradrenalin



adrenalin



tyroxin

(3,5,3',5'-tetrajodthyronin)