AMINOÁCIDOS

Carla Bittar

Bioquímica e Metabolismo Animal

AMINOÁCIDOS

- Compostos orgânicos
- Unidades formadoras de PROTEÍNAS
  - Ligações covalentes com perda de água
- Moléculas pequenas
  - PM de aproximadamente 130

FUNÇÕES BIOLÓGICAS

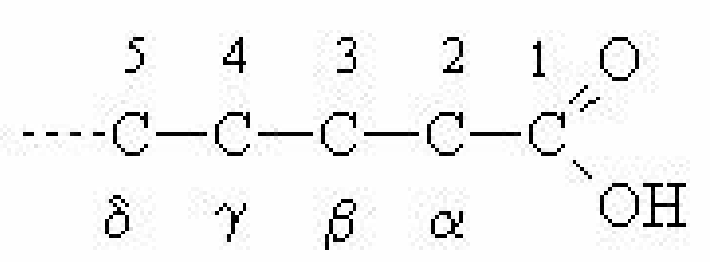
- Estrutura da célula
- Hormônios
- Receptores de proteínas
- Transporte de metabólitos e íons
- Enzimas
- Imunidade
- Gluconeogenese

Aminoácidos

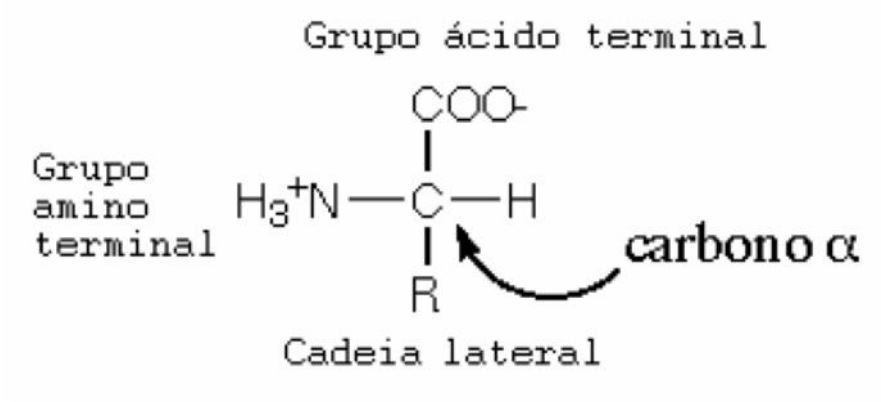
- Descobertos como resultado da hidrólise de proteínas
  - Asparagina (1806)
  - Treonina (1938)

  - Nomes relacionados a fonte da qual foram isolados pela primeira vez
    - Glutamato: glúten de trigo
    - Tirosina: tyros (queijo em grego)
    - Asparagina: aspargo

α-Aminoácidos

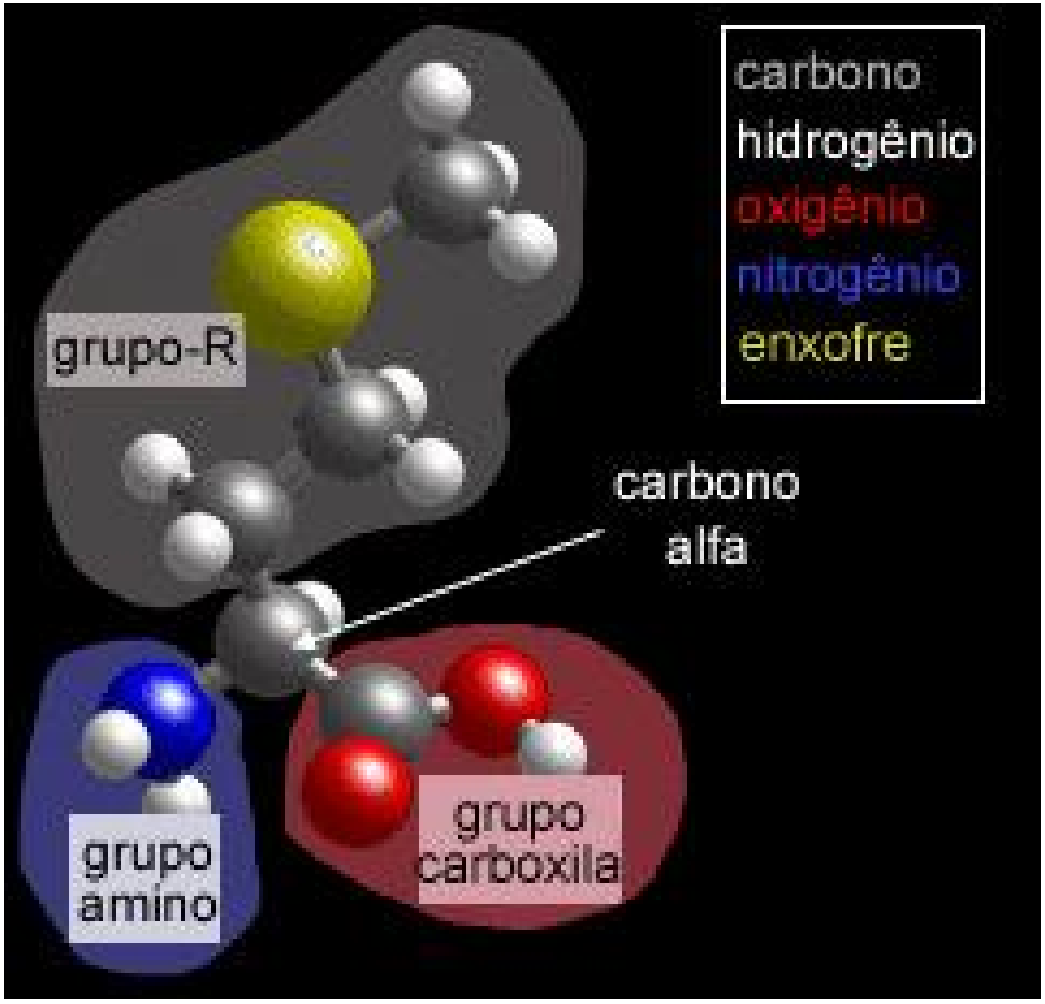


- Grupo amino e grupo carboxílico



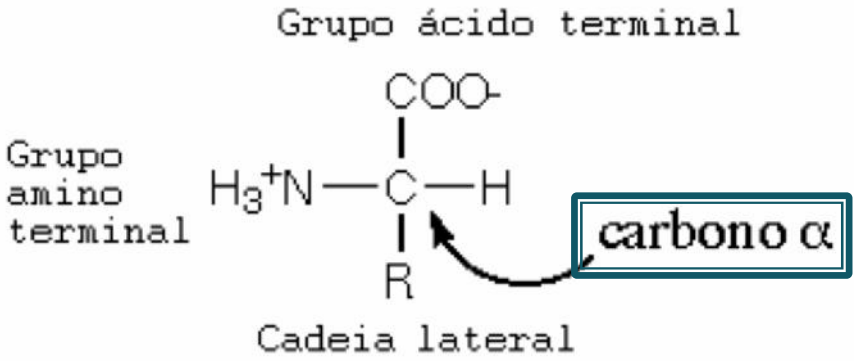
Estrutura
Tamanho
Carga elétrica

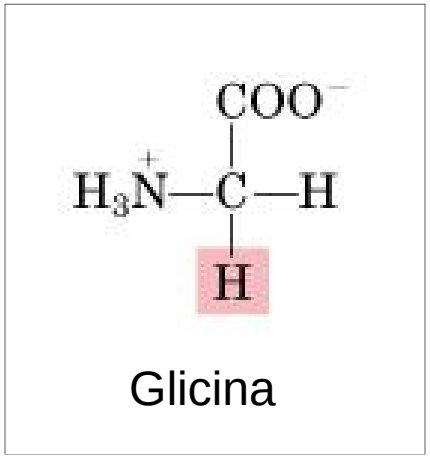
Metionina


carbono
hidrogênio
oxigênio
nitrogênio
enxofre
grupo-R
carbono
alfa
grupo
amino
grupo
carboxila

Propriedades gerais

- Solúveis em água, insolúveis em solventes orgânicos
- Elevado ponto de fusão
- Formam sólidos cristalinos



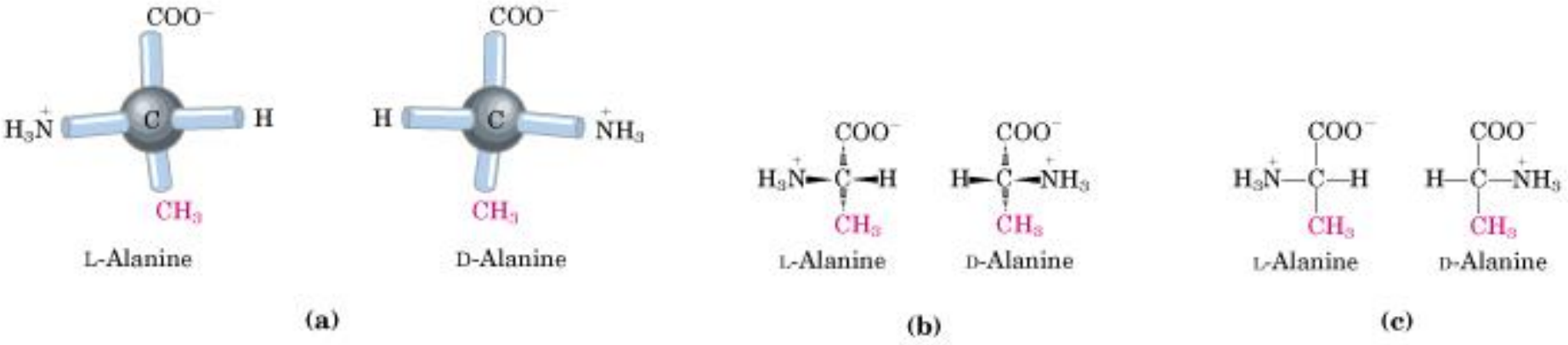


Glicina

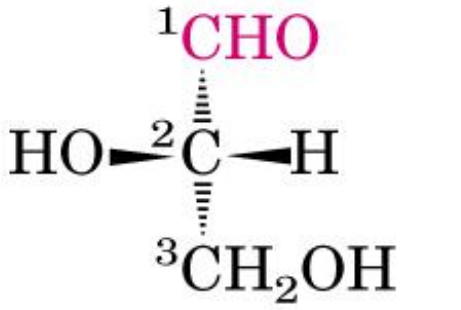
Propriedades gerais

- Opticamente ativos: Gira plano de luz polarizada para esquerda ou direita

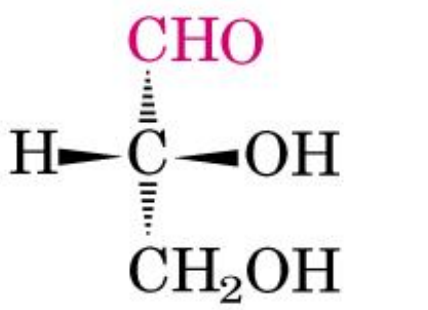
- Enatiômeros



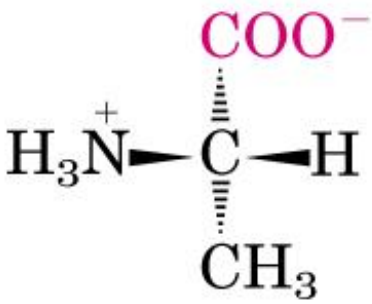
Estereoisomeria



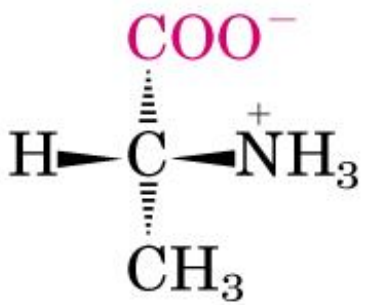
L-Glyceraldehyde



D-Glyceraldehyde



L-Alanine



D-Alanine

Estereoisomeria

- Os aminoácidos nas moléculas protéicas são sempre L-estereisômeros

- D aminoácidos
  - pequenos peptídeos de parede celular bacteriana
  - peptídeos com função antibiótica

Classificação de acordo com grupo R

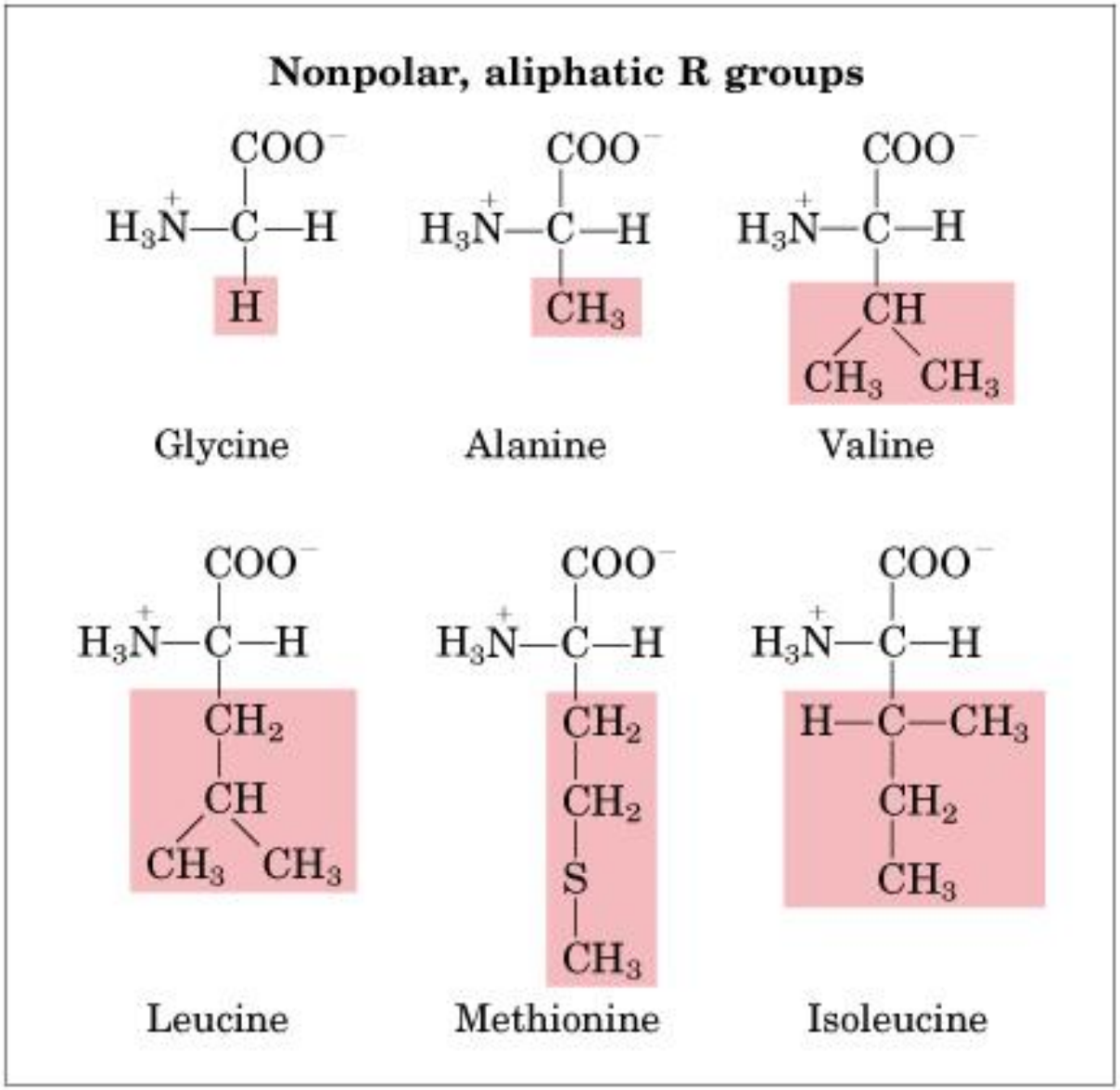
Properties and Conventions Associated with the Standard Amino Acids

Amino acid	Abbreviated names		M_r	pK_a values: pK_1 (—COOH)	pK_2 ($—NH_3^+$)	pK_R (R group)	pI	Hydropathy index*	Occurrence in proteins (%)†
Nonpolar, aliphatic R groups									
Glycine	Gly	G	75	2.34	9.60		5.97	−0.4	7.2
Alanine	Ala	A	89	2.34	9.69		6.01	1.8	7.8
Valine	Val	V	117	2.32	9.62		5.97	4.2	6.6
Leucine	Leu	L	131	2.36	9.60		5.98	3.8	9.1
Isoleucine	Ile	I	131	2.36	9.68		6.02	4.5	5.3
Methionine	Met	M	149	2.28	9.21		5.74	1.9	2.3
Aromatic R groups									
Phenylalanine	Phe	F	165	1.83	9.13		5.48	2.8	3.9
Tyrosine	Tyr	Y	181	2.20	9.11	10.07	5.66	−1.3	3.2
Tryptophan	Trp	W	204	2.38	9.39		5.89	−0.9	1.4
Polar, uncharged R groups									
Serine	Ser	S	105	2.21	9.15		5.68	−0.8	6.8
Proline	Pro	P	115	1.99	10.96		6.48	1.6	5.2
Threonine	Thr	T	119	2.11	9.62		5.87	−0.7	5.9
Cysteine	Cys	C	121	1.96	10.28	8.18	5.07	2.5	1.9
Asparagine	Asn	N	132	2.02	8.80		5.41	−3.5	4.3
Glutamine	Gln	Q	146	2.17	9.13		5.65	−3.5	4.2
Positively charged R groups									
Lysine	Lys	K	146	2.18	8.95	10.53	9.74	−3.9	5.9
Histidine	His	H	155	1.82	9.17	6.00	7.59	−3.2	2.3
Arginine	Arg	R	174	2.17	9.04	12.48	10.76	−4.5	5.1
Negatively charged R groups									
Aspartate	Asp	D	133	1.88	9.60	3.65	2.77	−3.5	5.3
Glutamate	Glu	E	147	2.19	9.67	4.25	3.22	−3.5	6.3

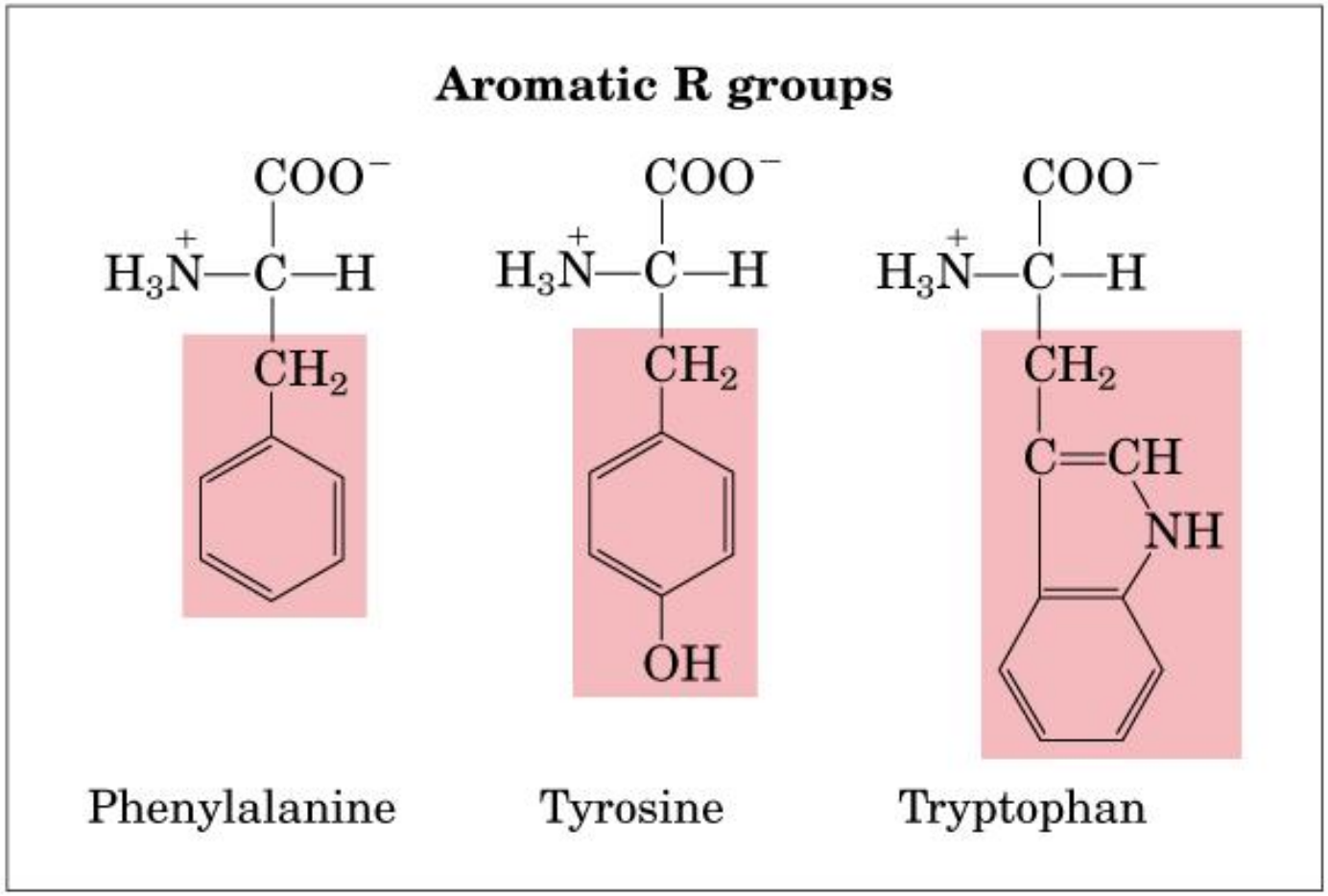
*A scale combining hydrophobicity and hydrophilicity of R groups; it can be used to measure the tendency of an amino acid to seek an aqueous environment (− values) or a hydrophobic environment (+ values). See Chapter 12. From Kyte, J. & Doolittle, R.F. (1982) *J. Mol. Biol.* **157**, 105 – 132.

†Average occurrence in over 1150 proteins. From Doolittle, R.F. (1989) Redundancies in protein sequences. In *Prediction of Protein Structure and the Principles of Protein Conformation* (Fasman, G.D., ed) Plenum Press, NY, pp. 599–623.

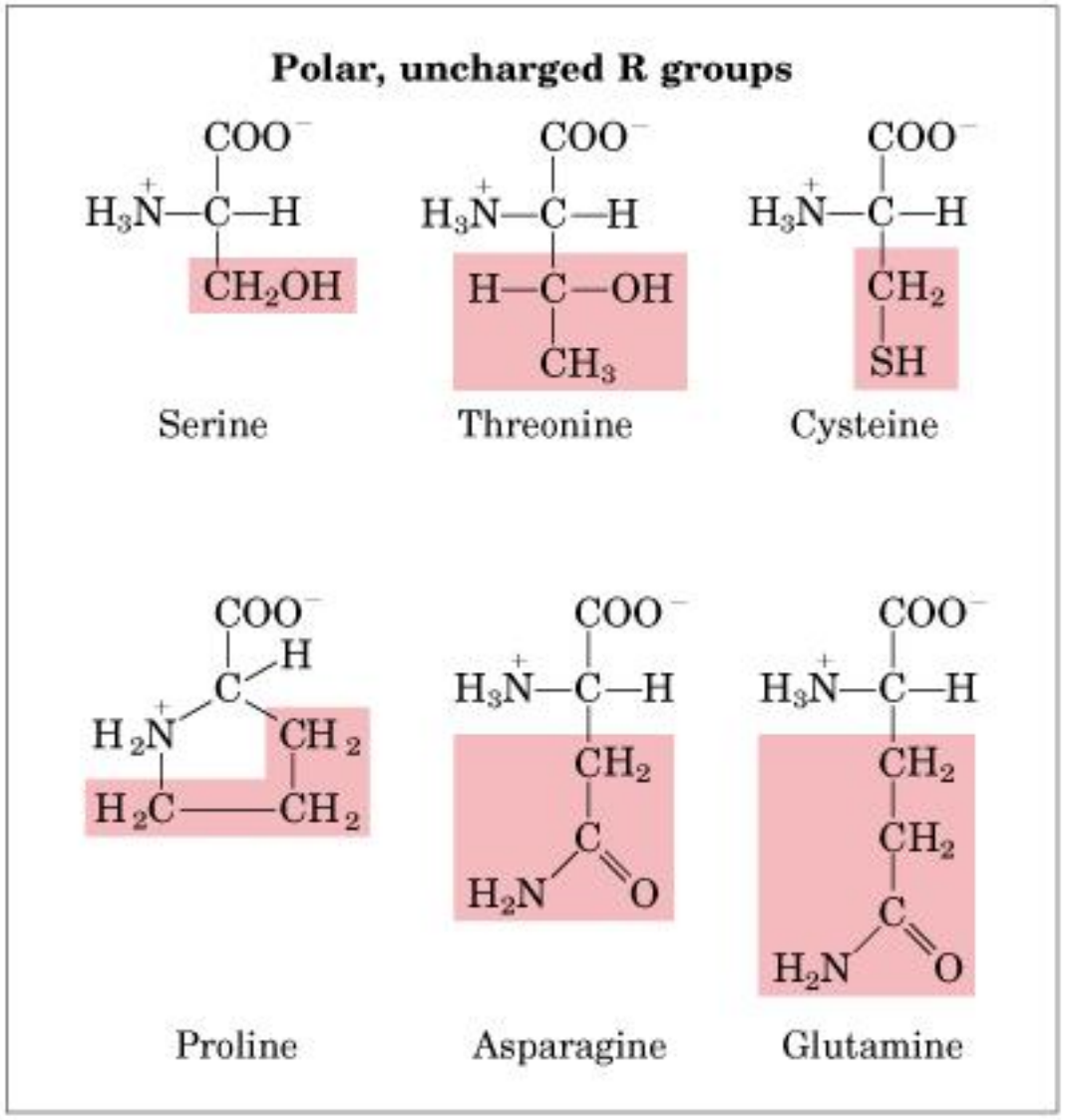
Aminoácidos não-polares alifáticos

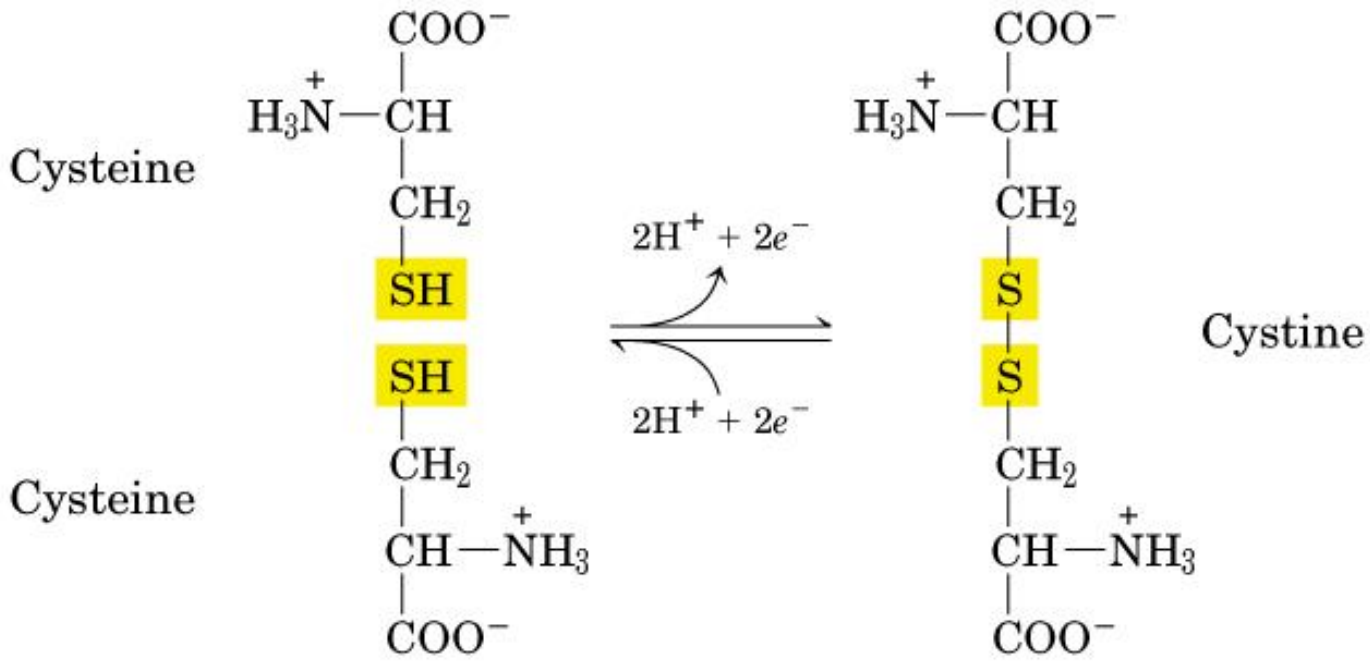


Aminoácidos com cadeias laterais aromáticas

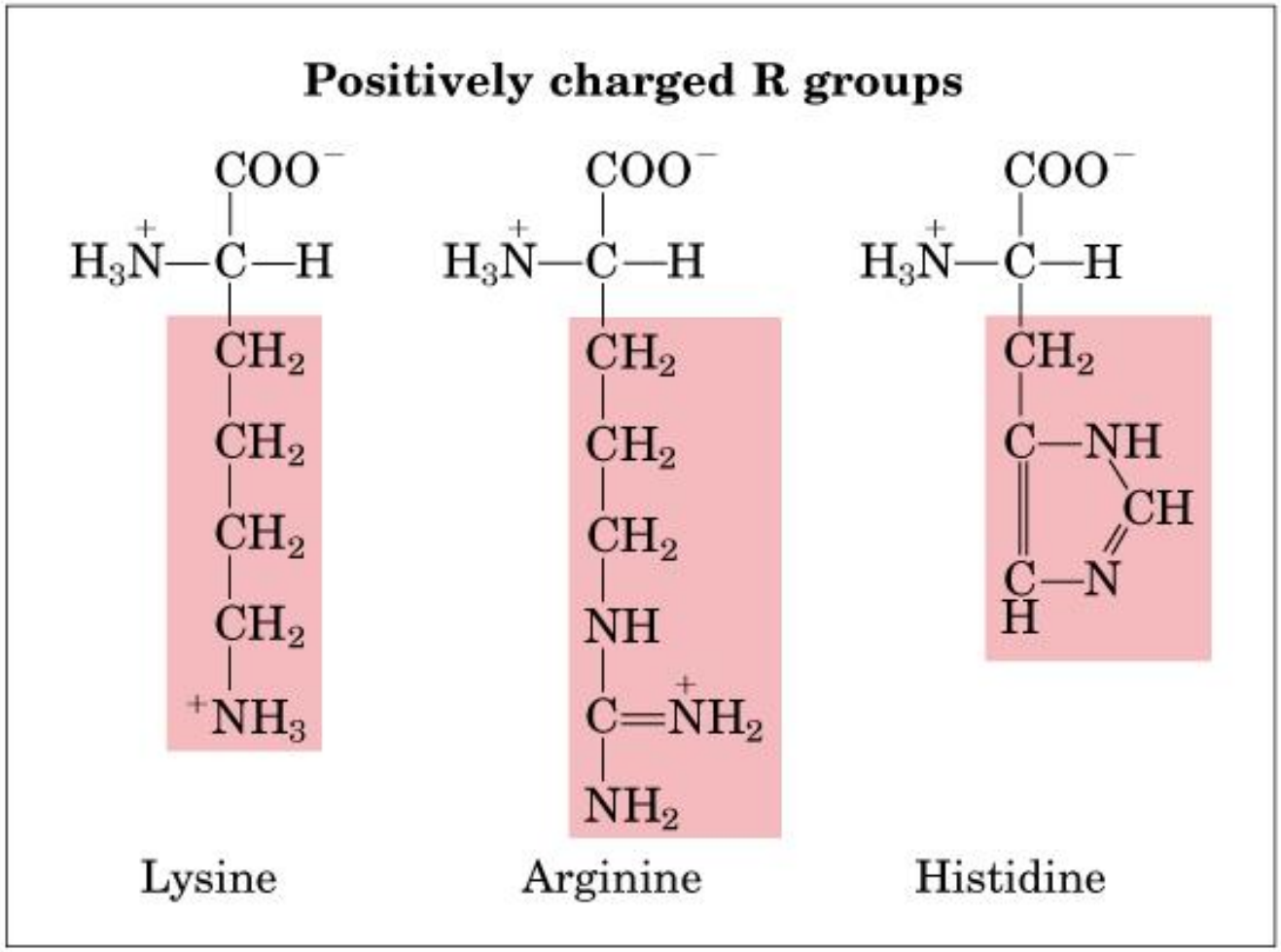


Aminoácidos com cadeias polares não-carregadas

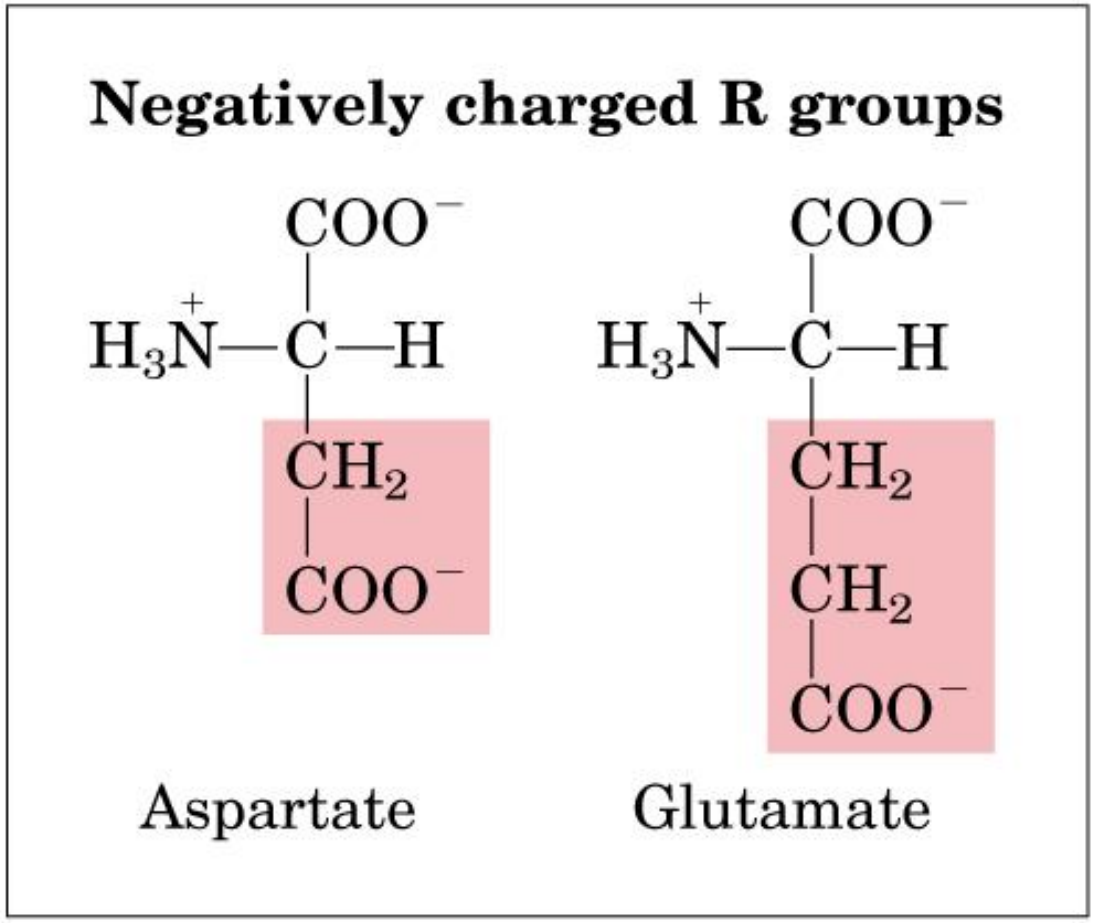



Cysteine
Cysteine
2H+ + 2e−
2H+ + 2e−
Cystine

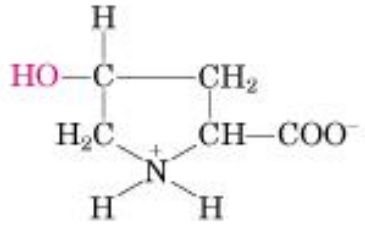
Aminoácidos com cadeias carregadas positivamente (básicos)



Aminoácidos com cadeias carregadas negativamente (ácidos)

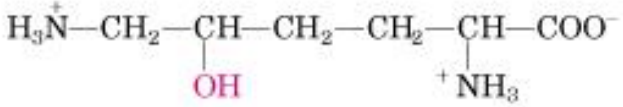


Aminoácidos "incomuns"

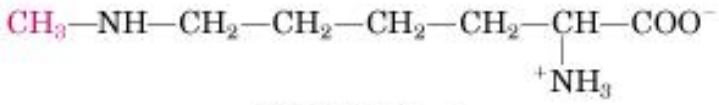


4-Hydroxyproline

Colágeno

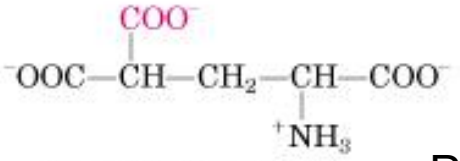


5-Hydroxylysine



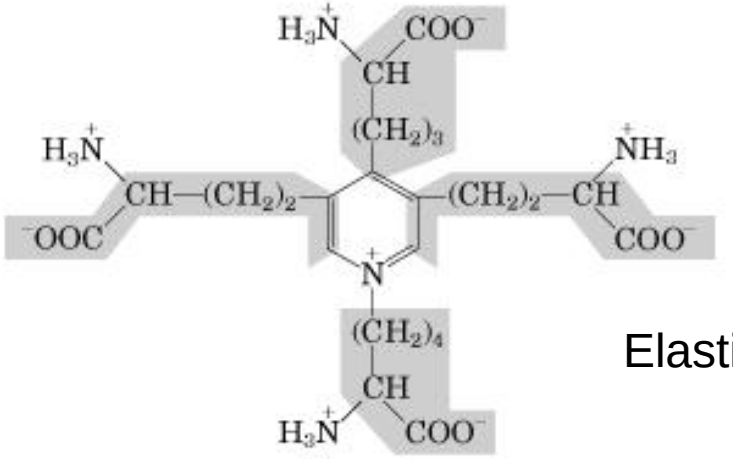
6-*N*-Methyllysine

Miosina



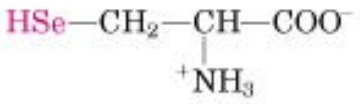
γ-Carboxyglutamate

Protrombina



Desmosine

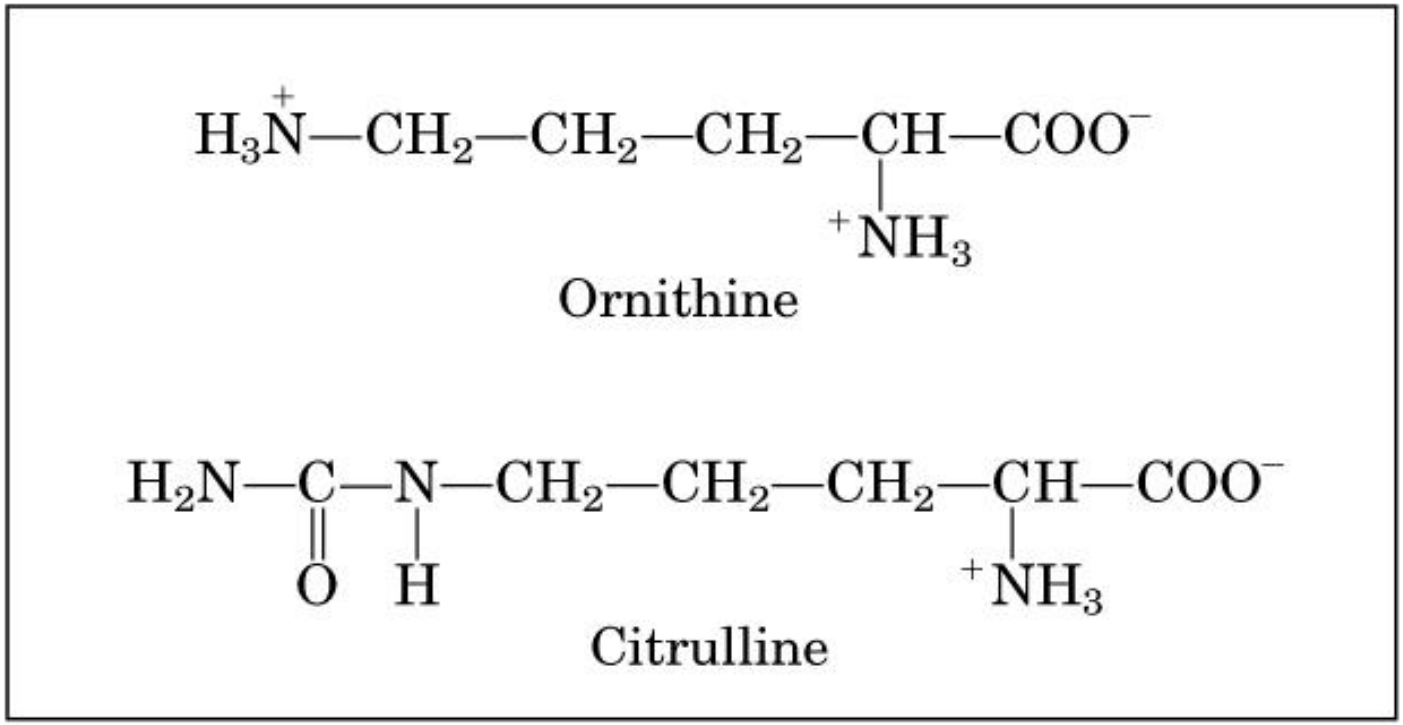
Elastina



Selenocysteine

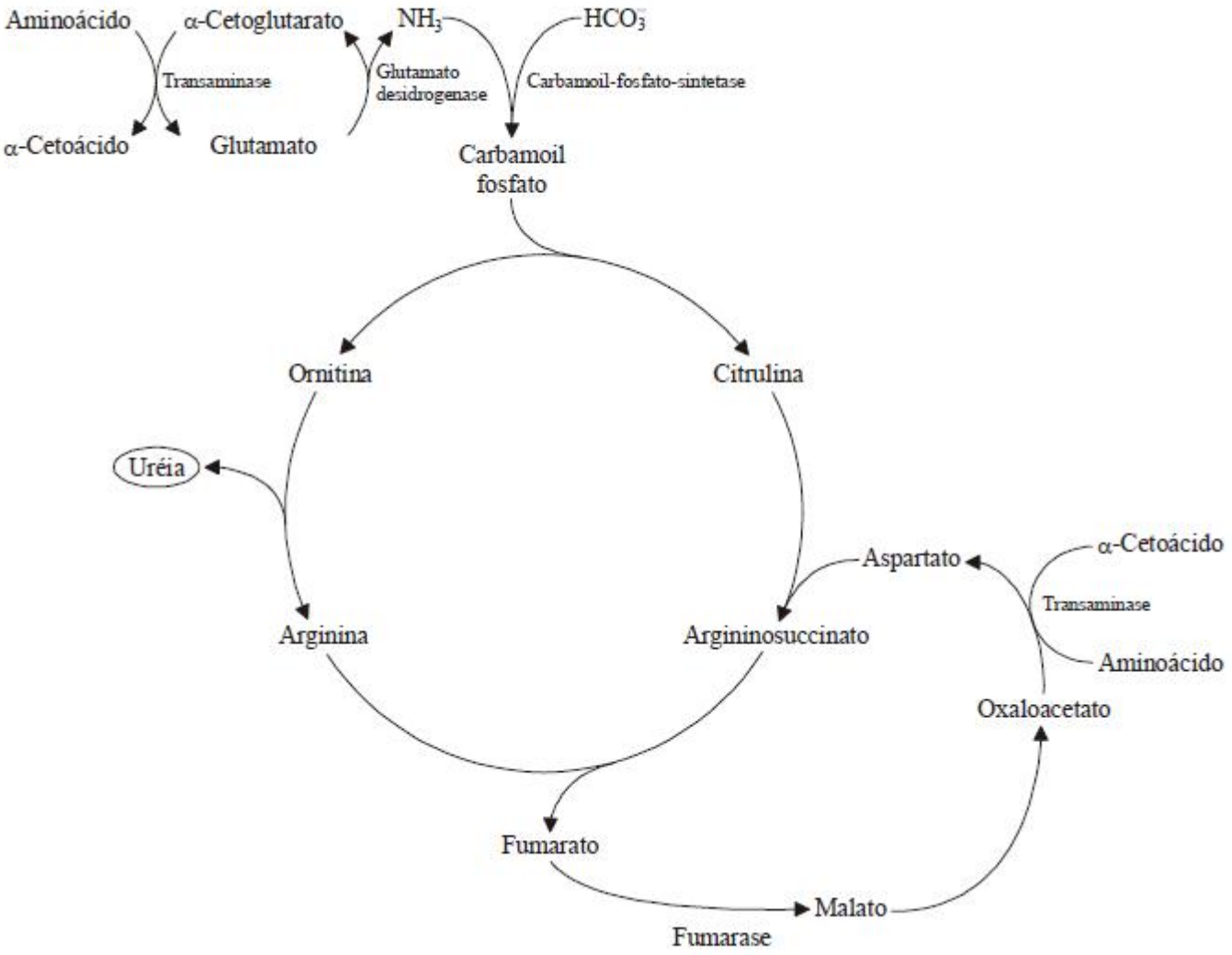
(a)

Aminoácidos "incomuns"



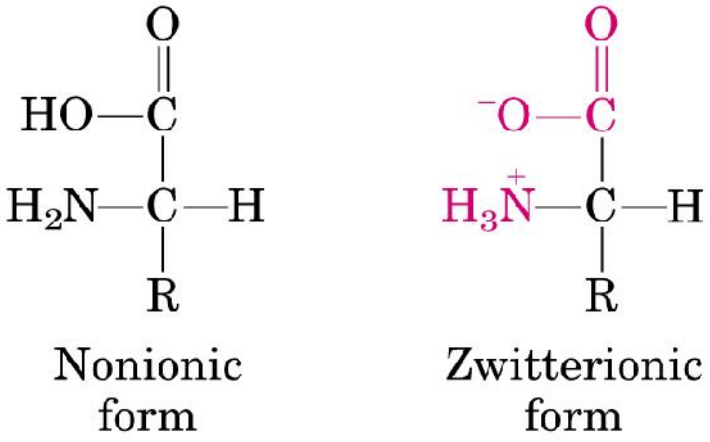
(b)

Ciclo da uréia



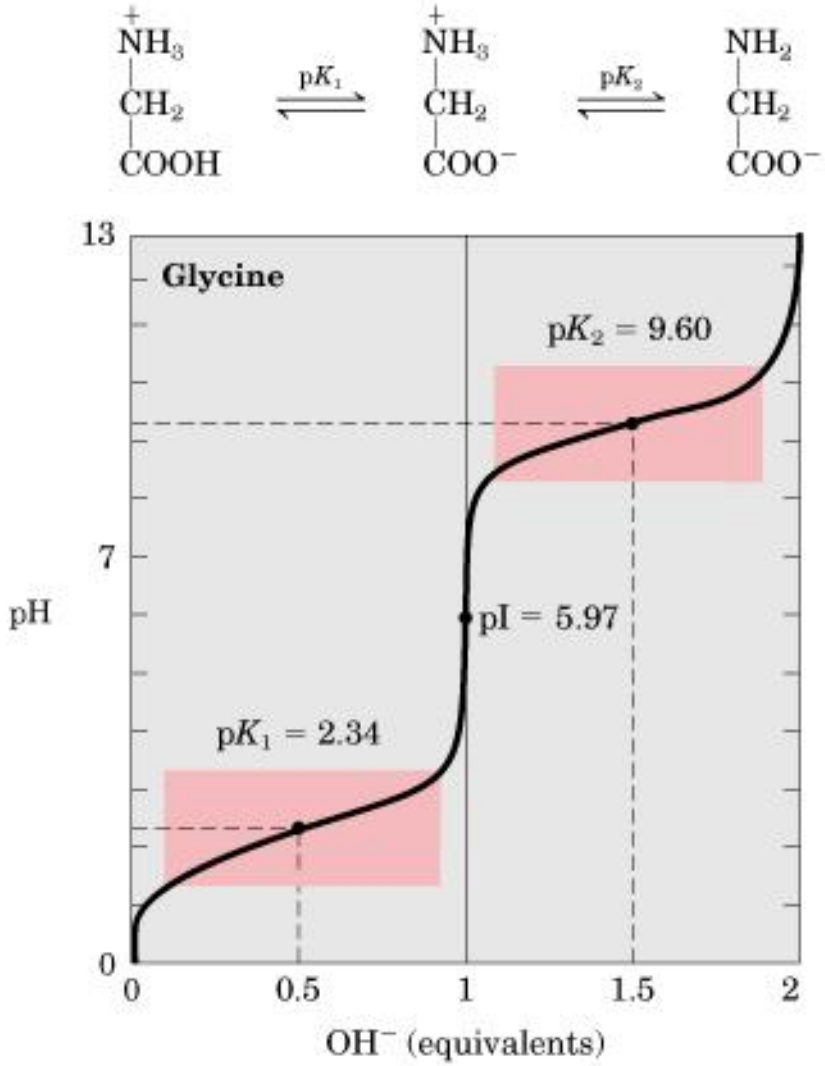
Caráter ácido-base

- Em solução aquosa, íon dipolar ou “zwitterion”
- Caráter anfótero



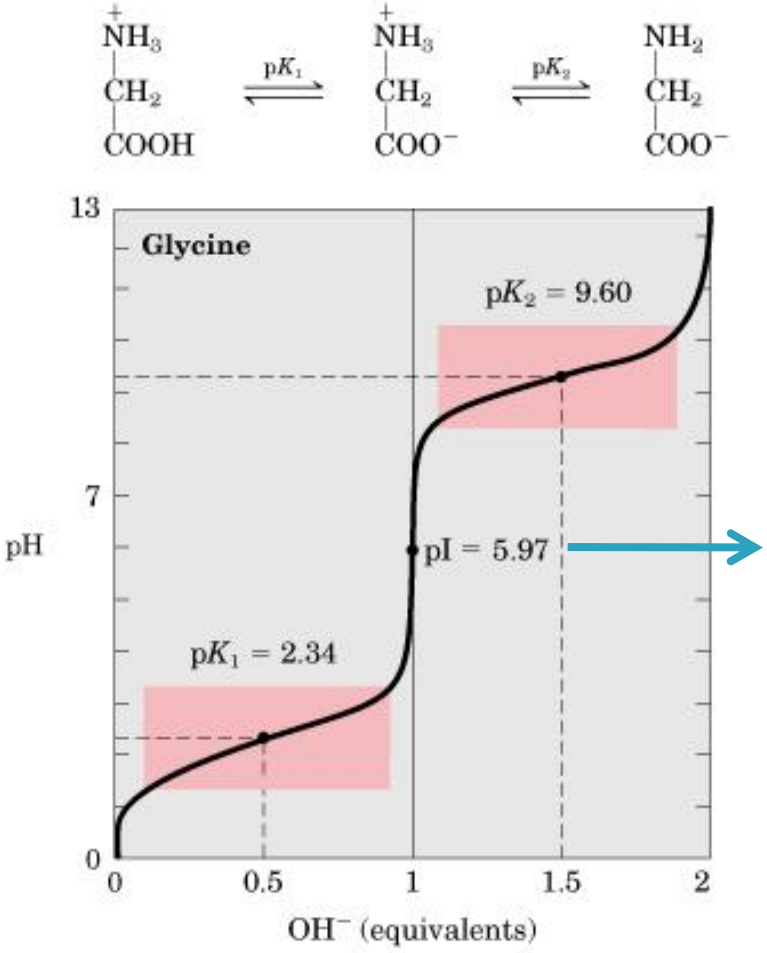
Curva de titulação da glicina

0,1M; 25°C



Carga elétrica de aminoácidos

- Curva de titulação – carga elétrica líquida e pH



Não tem grupos ionizáveis na cadeia lateral:

pI= ½ (pK1 +pK2) = ½ (2,34 + 9,60)

pI = 5,97

Ponto isoelétrico
pH isoelétrico

Separação por eletroforese

pH > pI: caminha para o eletrodo positivo

pH< pI: caminha para o eletrodo negativo

- Todos aa com único grupo α-amino, único α-carboxil e grupo R que não se ioniza, tem curva de titulação parecida com glicina

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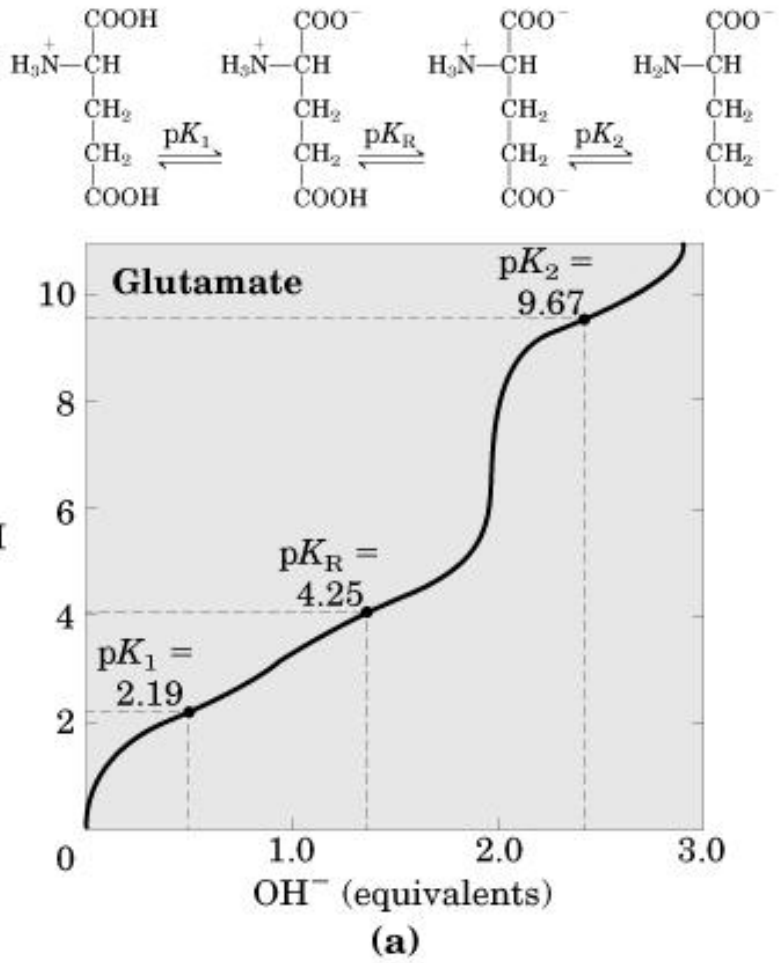
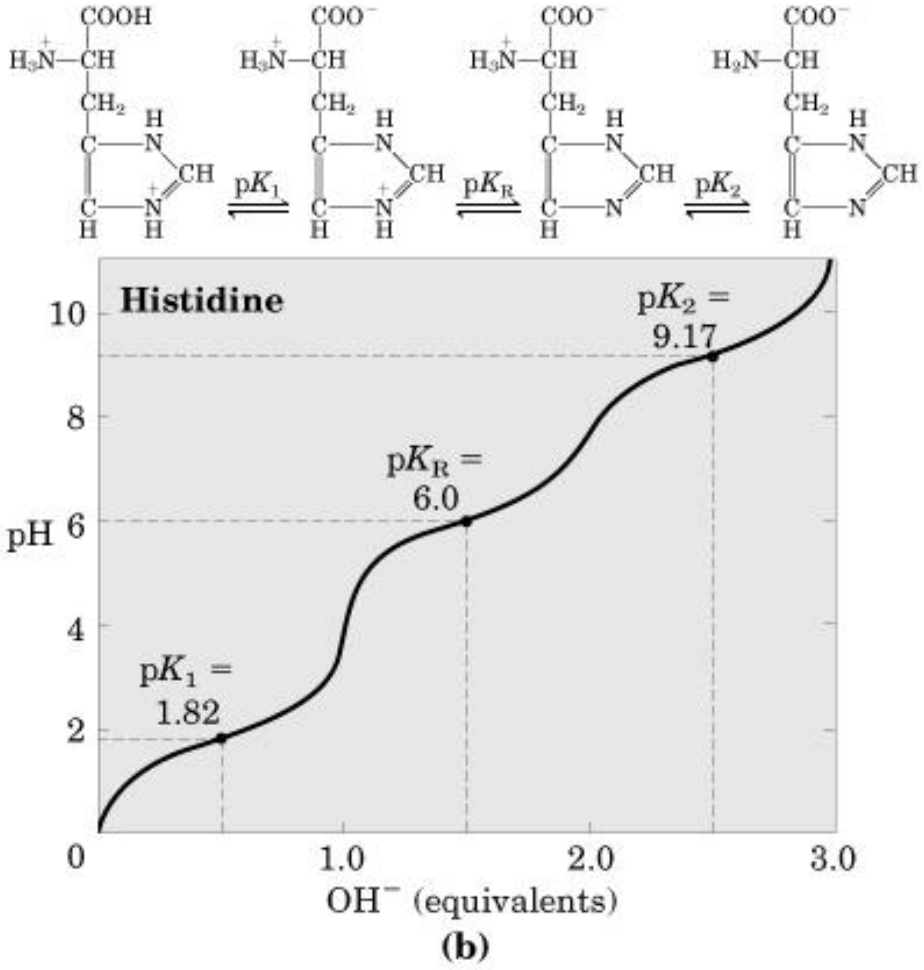
Aminoácidos com grupo R ionizável



- Curva de titulação com 3 estágios:
  - 3 possíveis ionizações
  - 3 pKa
  - pI reflete a natureza do grupo R ionizável
  - pI glutamato= 3,22
  - Presença de 2 grupos carboxil

Aminoácidos com grupo R ionizável



- pI = 7,59

Cálculo do pI

- Aminoácidos neutros: $pI = \frac{pk_{COOH} + pk_{NH2}}{2}$
- Aminoácidos ácidos: $pI = \frac{pk_{COOH} + pk_{R}}{2}$
- Aminoácidos básicos: $pI = \frac{pk_{NH2} + pk_{R}}{2}$

Determinação

- HPLC
  - Custo
  - Tratamento/processamento
- Reações características
  - cor
  - produção de gás
  - fluorescência

Aminoácidos essenciais

- Organismo animal não sintetiza ou o faz em quantidades insuficientes
- Valor biológico: proteínas que fornecem aa na proporção e em quantidades necessárias
- Exigência em aa essenciais depende da espécie e idade

Aminoácidos essenciais

Aminoácido	Cadeia
Arginina	Alifático
Fenilanalina	Aromático
Histidina	Heterocíclico
Isoleucina	Alifático
Leucina	Alifático
Lisina	Alifático
Metionina	Alifático
Treonina	Alifático
Triptofano	Heterocíclico
Valina	Alifático
Glicina*	Alifático

Table 1 Classification of amino acids (AA) in animal nutrition[a]

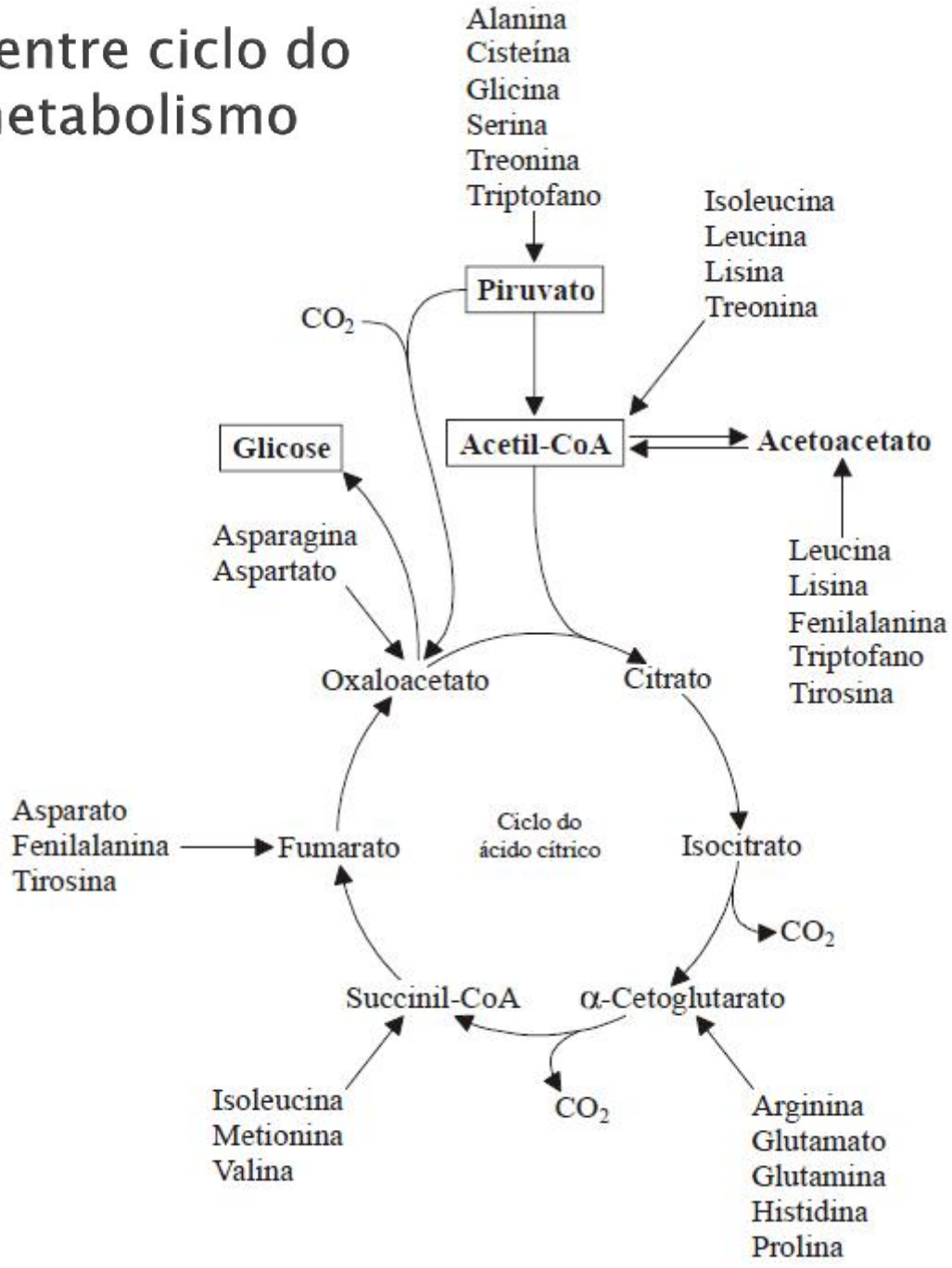
Mammals[b]			Poultry			Fish		
EAA	NEAA	CEAA[c]	EAA	NEAA	CEAA[c]	EAA	NEAA	CEAA[c]
Arg*	Ala	Gln*	Arg*	Ala	Gln*	Arg*	Ala	Gln*
Cys*	Asn	Glu*	Cys*	Asn	Glu*	Cys*	Asn	Glu*
His	Asp*	Gly*	Gly*	Asp*	Tau*	His	Asp*	Gly*
Ile	Ser	Pro*	His	Ser		Ile	Ser	Tau*
Leu*		Tau*	Ile			Leu*		
Lys			Leu*			Lys		
Met*			Lys			Met*		
Phe			Met*			Phe		
Thr			Phe			Pro*		
Trp*			Pro*			Thr		
Tyr*			Thr			Trp*		
Val			Trp*			Tyr*		
			Tyr*			Val		
			Val					

Wu et al., 2014

Destino no metabolismo

Glicogênicos	Cetogênicos	Glicogênicos e cetogênicos
Alanina	Leucina	Fenilalanina
Arginina	Lisina	Isoleucina
Asparagina		Tirosina
Aspartato		Treonina
Glicina		Triptofano
Cisteína		
Glutamato		
Glutamina		
Histidina		
Metionina		
Prolina		
Serina		
Valina		

Interrelações entre ciclo do ác. cítrico e metabolismo dos aa



Exigência de aminoácidos

Aminoácido	Rato	Cachorro	Pintainho	Homem
Arginina	+	–	+	–
Cistina*	–	–	(+)	–
Glutâmico*	–	–	(+)	–
Glicina*	–	–	(+)	–
Histidina	+	+	+	–
Isoleucina	+	+	+	+
Leucin	+	+	+	+
Lisina	+	+	+	+
Metionina	+	+	+	+
Fenilalanina	+	+	+	+
Treonina	+	+	+	+
Triptofano	+	+	+	+
Tirosina*	–	–	(+)	–
Valina	+	+	+	+

Composição em aminoácidos essenciais em amostras de tecido magro, leite, bactérias ruminais e alimentos

Item	Arginine	Histidine	Isoleucine	Leucine	Lysine	Methionine	Phenylalanine	Threonine	Tryptophan	Valine
					(% of CP)					
Lean tissue	6.6	**2.5**	2.8	6.7	**6.4**	**2.0**	3.5	3.9	0.6	4.0
Milk	3.4	**2.7**	5.8	9.2	**7.6**	**2.7**	4.8	3.7	1.5	5.9
Bacteria	5.1	**2.0**	5.7	8.1	**7.9**	**2.6**	5.1	5.8		6.2
Alfalfa silage	3.9	**1.7**	3.9	6.4	**4.4**	**1.4**	4.2	3.8	0.9	5.0
Corn silage	2.0	**1.8**	3.3	8.6	**2.5**	**1.5**	3.8	3.2	0.4	4.5
Grass silage	3.1	**1.7**	3.6	6.1	**3.3**	**1.2**	4.4	3.3	1.1	4.9
Barley	5.1	**2.3**	3.5	7.0	**3.6**	**1.7**	5.1	3.4	1.2	4.9
Corn	4.6	3.1	3.3	11.2	**2.8**	**2.1**	4.6	3.6	0.7	4.0
Oats	6.8	**2.4**	3.8	7.3	**4.2**	**2.9**	5.2	3.5	1.2	5.2
Wheat	4.7	**2.4**	3.3	6.6	**2.8**	**1.6**	4.6	2.9	1.2	4.2
Brewers grains	5.8	**2.0**	3.9	7.9	**4.1**	**1.7**	4.6	3.6	1.0	4.8
Canola meal	7.0	**2.8**	3.8	6.8	**5.6**	**1.9**	4.1	4.4	1.5	4.7
Corn DDG w/sol	4.1	**2.5**	3.7	9.6	**2.2**	**1.8**	4.9	3.4	0.9	4.7
Corn gluten meal	3.2	**2.1**	4.1	16.8	**1.7**	**2.4**	6.4	3.4	0.5	4.6
Cottonseed meal	11.1	**2.8**	3.1	5.9	**4.1**	**1.6**	5.3	3.2	1.2	4.2
Soybean meal	7.3	**2.8**	4.6	7.8	**6.3**	**1.4**	5.3	4.0	1.3	4.6
Sunflower meal	8.2	**2.6**	4.1	6.4	**3.6**	**2.3**	4.6	3.7	1.2	5.0
Blood meal	4.4	**6.4**	1.3	12.8	**9.0**	**1.2**	6.9	4.3	1.6	8.7
Feather meal	6.9	**1.2**	4.9	8.5	**2.6**	**0.8**	4.9	4.7	0.7	7.5
Fish meal	5.8	**2.8**	4.1	7.2	**7.7**	**2.8**	4.0	4.2	1.1	4.8
Meat meal	7.1	**2.1**	3.0	6.3	**5.4**	**1.4**	3.6	3.4	0.7	4.4

Schwab, O'Connor and NRC (2001)

Aminoácidos essenciais em proteínas animais (g/100g)

Aminoácido	Gelatina	Albumina ovo	Caseína	Carne bovina	Ovo integral	Leite bovino	Leite humano
Arginina	8,6	5,9	4,1	7,7	6,7	3,4	5,0
Histidina	0,7	2,6	3,1	3,3	2,4	2,7	2,7
Lisina	5,0	6,5	8,2	9,0	6,9	7,6	7,2
Triptofano	0,0	1,2	1,2	1,4	1,6	1,5	1,9
Fenilalanina	2,4	7,7	5,0	5,0	5,8	4,8	5,9
Metionina	0,9	5,3	3,4	3,2	3,3	2,7	2,0
Treonina	2,2	4,0	4,9	5,0	5,0	3,7	4,6
Leucina	3,2	9,9	9,2	8,0	9,4	9,2	15,0
Isoleucina	2,1	7,0	6,1	6,0	6,9	5,8	5,2
Valina	2,7	8,8	7,2	5,5	7,4	5,9	5,5

Deficiências

- Triptofano
  - catarata, degenerações, alterações nos dentes
  - Quando altera síntese de niacina (Vit. B3): Pelagra
- Lisina: náusea, vertigem
- Histidina: reduz hemoglogina circulante
- Arginina: reduz número de espermatozóides
- Metionina: danos hepáticos

Literatura sugerida

- LEHNINGER, A.L. Princípios de Bioquímica. São Paulo: Sarvier, 2002. 975 p.

- BERG, J. M.; TYMOCZKO, J.L.; STRYER, L. Bioquímica. Rio de janeiro: Editora guanabara Koogan S. A., 6a. ed., 2008. 1114 p.

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Meat or wheat for the next millennium?
Plenary Lecture

The nutritional value of plant-based diets in relation to human amino acid and protein requirements

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- Working with proteins. LEHNINGER, A.L. Princípios de Bioquímica. São Paulo: Sarvier, 2002. 975 p.