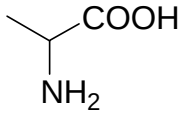
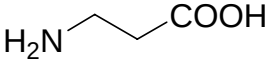
12 Naturstoffe

12.1 Aminosäuren, proteinogene Aminosäuren, Seitengruppen, Eigenschaften, Chiralität

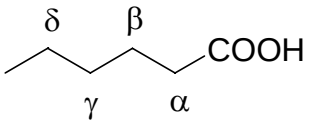
In der Natur, insbesondere in Peptiden und Proteinen, finden sich fast ausschließlich α-Aminosäuren. Es gibt jedoch auch entsprechende β–, γ–, δ–, etc. Aminosäuren.



α-Alanin (chiral)

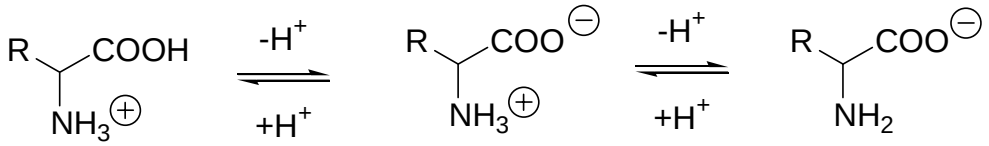


β-Alanin (achiral)



Chemische Eigenschaften von Aminosäuren:

Aminosäuren sind meist kristalline Feststoffe und liegen als Zwitterionen vor. Da Aminosäuren eine saure Carboxylatgruppe und eine basische Aminfunktion tragen, können sie pH-abhängig in drei Formen vorliegen. Den pH-Wert, bei dem eine Aminosäure in der (nach außen ungeladenen) zwitterionischen Form vorliegt wird Isoelektrischer Punkt (IP) genannt. Der IP ist für jede Aminosäure charakeristisch.



im Sauren

"neutral"
pH = IP

im Basischen

pK$_S$-Werte und IPs einiger Aminosäuren:

die α–Carboxylgruppe von Aminosäuren ist ungewöhnlich sauer. Weitere Carboxalgruppen sind weniger sauer je weiter entfernt sie von C$_\alpha$ sind.

allgemein: a-Carboxylgruppe: pK$_S$ = 1,7 – 2,6 (saurer als Ameisensäure!)
a-Aminofunktion: pK$_S$ = 8,9 – 10,6 (als Ammoniumion)

andere Grp.: β-Carboxylgruppe (Asp): pK$_S$ = 3,86 (ungefähr wie Ameisensäure)
γ-Carboxylgruppe (Glu): pK$_S$ = 4,24 (ungefähr wie Essigsäure)
Thiolgruppe –SH (Cys): pK$_S$ = 8,33
Hydroxylgrp. –OH (Tyr): pK$_S$ = 10,07
ε-Ammonium (Lys): pK$_S$ = 8,33
Guanidinogruppe (Arg): pK$_S$ = 12,48
Imidazolgruppe (His): pK$_S$ = 6,01 (als Imidazolium)

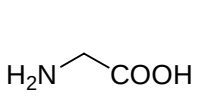
Einteilung der Aminosäuren:

Da fast alle Aminosäuren chiral sind (Ausnahme: Glycin) werden AS der L- bzw. D-Reihe zugeordnet. In der Natur kommen fast ausschließlich nur die L-Formen vor. Von allen möglichen Aminosäuren sind 20 besonders häufig. Sie werden als proteinogene (Protein-bildende) Aminosäuren bezeichnet.Aminosäuren können in „essentielle AS“ und „nicht-essentielle AS“ unterteilt werden. Essentielle AS sind solche, die der menschliche Organismus nicht produzieren kann und die deshalb mit der Nahrung aufgenommen werden müssen.

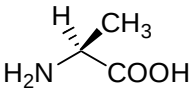
Essentielle Aminosäuren: L-Valin, L-Leucin, L-Isoleucin, L-Phenylalanin, L-Threonin, L-Methionin, L-Tryptophan, L-Lysin

AS warden “besser” nach ihren chemischen Eigenschaften unterteilt:

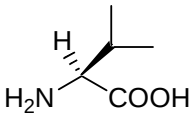
a) AS mit unpolarem Rest:



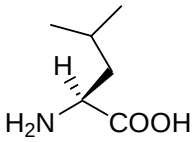
L-Glycin (Gly)



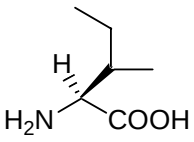
L-Alanin (Ala)



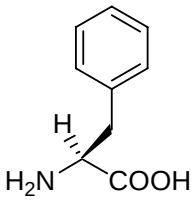
L-Valin (Val)



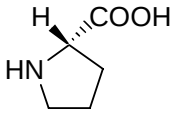
L-Leucin (Leu)



L-Isoleucin (Ile)

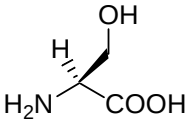


L-Phenylalanin (Phe)

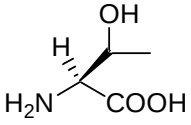


L-Prolin (Pro)

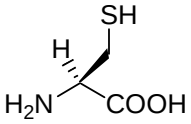
b) AS mit polarem, nicht ionisierbarem Rest:



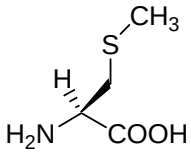
L-Serin (Ser)



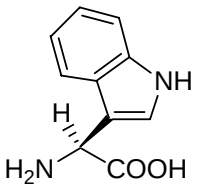
L-Threonin (Thr)



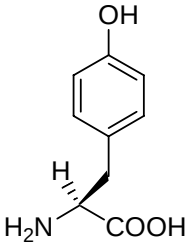
L-Cystein (Cys)



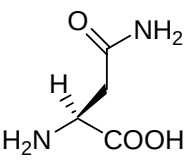
L-Methionin (Met)



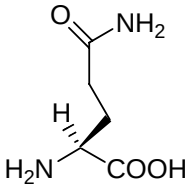
L-Tryptophan (Trp)



L-Tyrosin (Tyr)

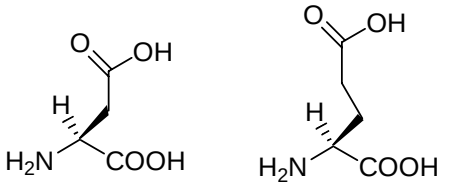


L-Asparagin (Asn)



L-Glutamin (Gln)

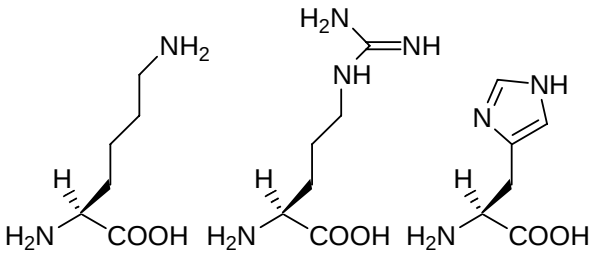
c) polare saure AS mit ionisierbarem Rest:



L-Asparaginsäure (Asp)

L-Glutaminsäure (Glu)

d) polare basische AS mit ionisierbarem Rest:



L-Lysin (Lys)

L-Arginin (Arg)

L-Histidin (His)

20 der proteinogenen Aminosäuren werden durch Codons des genetischen Materials kodiert. Sie werden daher als **kanonische Aminosäuren** oder auch als *Standardaminosäuren* bezeichnet. In Aminosäuresequenzen werden die Aminosäuren meist im **Einbuchstabencode** oder im **Dreibuchstabencode** dargestellt.

Die 20 kanonischen Aminosäuren

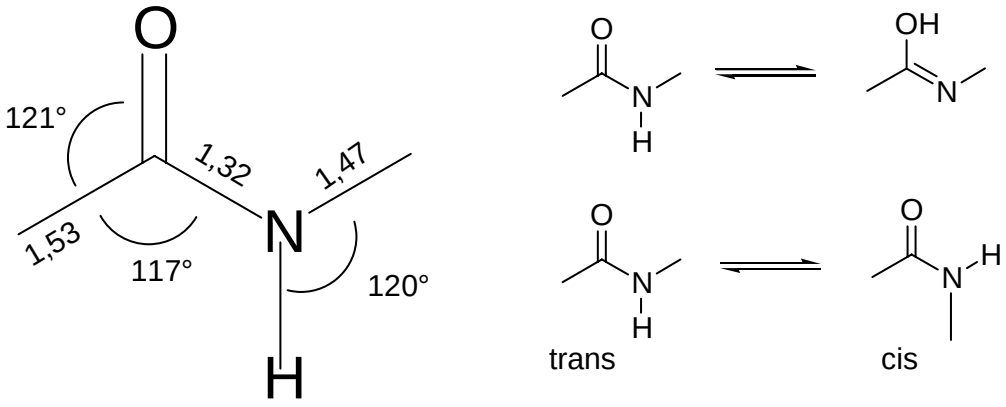
Aminosäure	**Dreibuchstabencode**	**Einbuchstabencode**	**Bemerkung**
Alanin	Ala	A	nicht-essentiell
Arginin	Arg	R	nicht-essentiell
Asparagin	Asn	N	nicht-essentiell
Asparaginsäure	Asp	D	nicht-essentiell
Cystein	Cys	C	nicht-essentiell
Glutamin	Gln	Q	nicht-essentiell
Glutaminsäure	Glu	E	nicht-essentiell
Glycin	Gly	G	nicht-essentiell
Histidin	His	H	semi-essentiell
Isoleucin	Ile	I	Essentiell
Leucin	Leu	L	Essentiell
Lysin	Lys	K	Essentiell
Methionin	Met	M	Essentiell
Phenylalanin	Phe	F	Essentiell
Prolin	Pro	P	nicht-essentiell
Serin	Ser	S	nicht-essentiell
Threonin	Thr	T	Essentiell
Tryptophan	Trp	W	Essentiell
Tyrosin	Tyr	Y	nicht-essentiell
Valin	Val	V	essentiell

12.2 Peptide, Proteine, Eigenschaften, Basizität, Konformation, Bildung und Hydrolyse

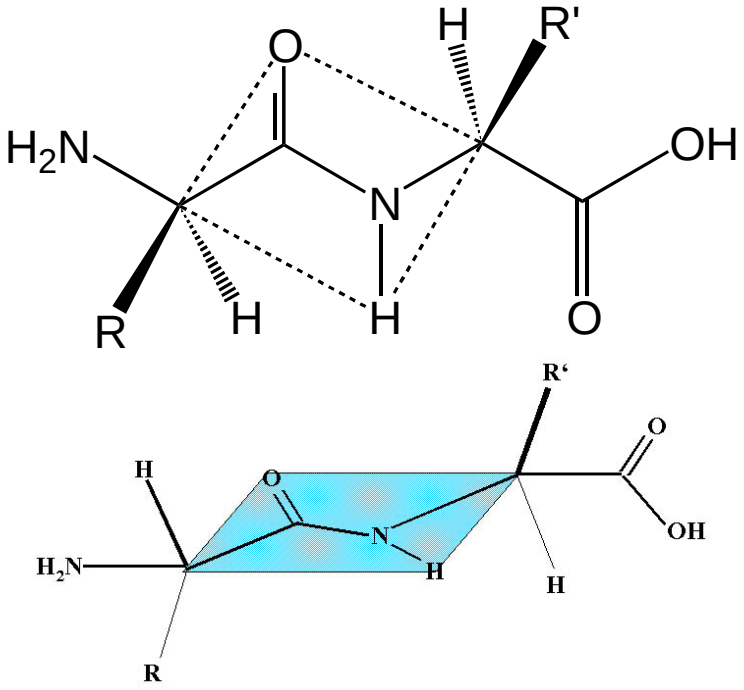
Peptidbindung: Peptide sind Amide aus zwei Aminosäuren:

Struktur der Amidbindung:

- Die C-N Bindung in Amiden besitzt Doppelbindungscharakter (ca. 40%)
- Rotation um die C-N Bindung ist gehindert (2 Konformere möglich)
- Das trans-Konformere ist thermodynamisch stabiler
- NH ist nicht protonierbar

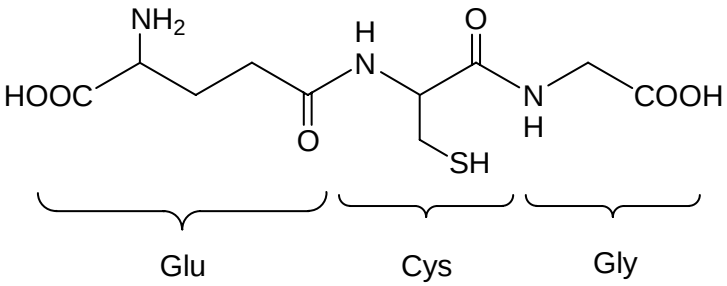


Die Peptidgruppe ist fast eben gebaut. In Peptiden stehen die Substituenten der Aminosäuren ober- bzw. unterhalb dieser Ebene

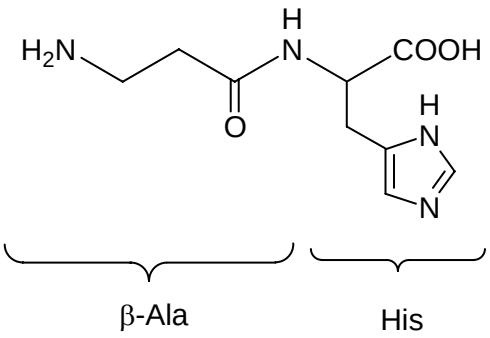


Einige natürlich vorkommende Peptide

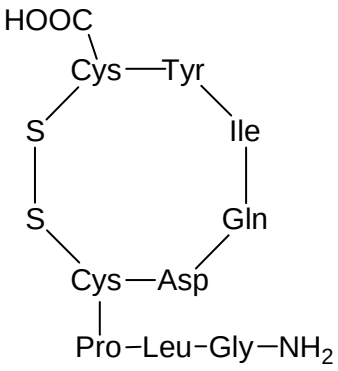
Glutathion
(biol. Redoxsystem)



Carnosin
(Neurotransmitter)



Ocytocin
(Hypophysenhormon)



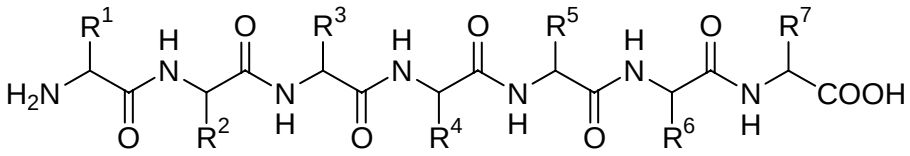
PROTEINE

Die Bezeichnung Protein kommt aus dem Griechischen: (proteuo) = „ich nehme den ersten Platz ein“

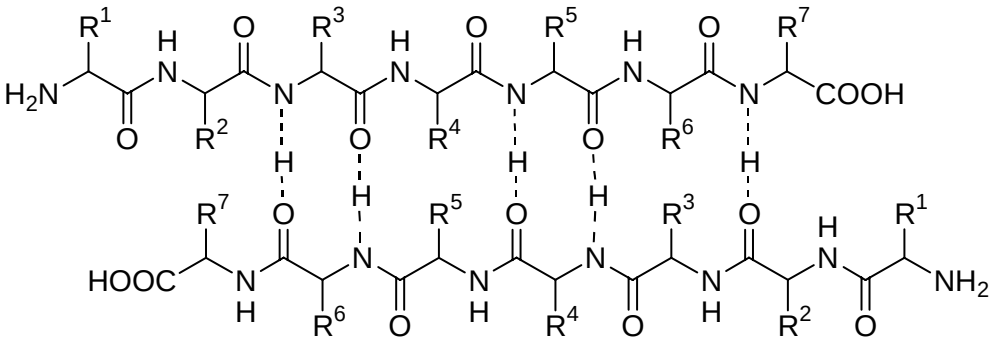
Einteilung: 1. Skleroproteine (faserartig, Stützstrukturen, wasserunlöslich) z.B.: Keratin (Fingernägel)

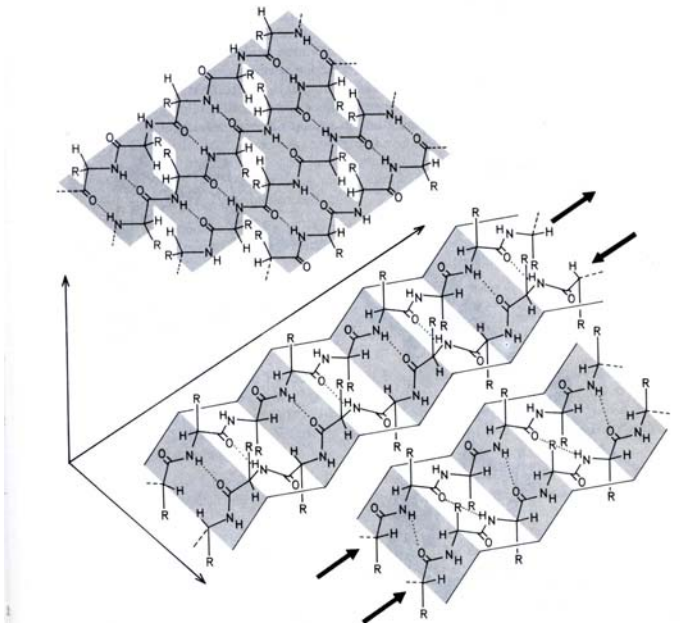
2. Sphäroproteine (sphärisch gebaut, wasserlöslich, denaturierbar) z.B.: Eiklarproteine

Chemische Struktur: aus einzelnen peptidisch gebundenen Aminosäuren

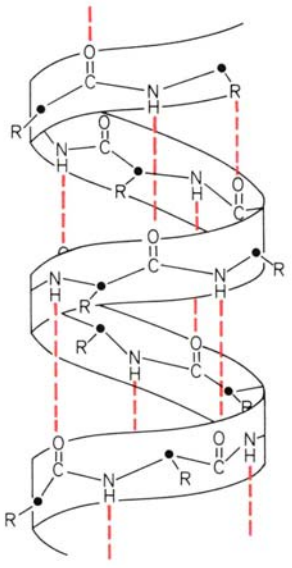


wegen der Planarität der peptidischen Einheiten und der Rotationsbarriere um die CN Bindung können sich leicht Wasserstoffbrücken zwischen zwei Proteinketten oder intramolekular ausbilden. → Faltblattstruktur oder Helix

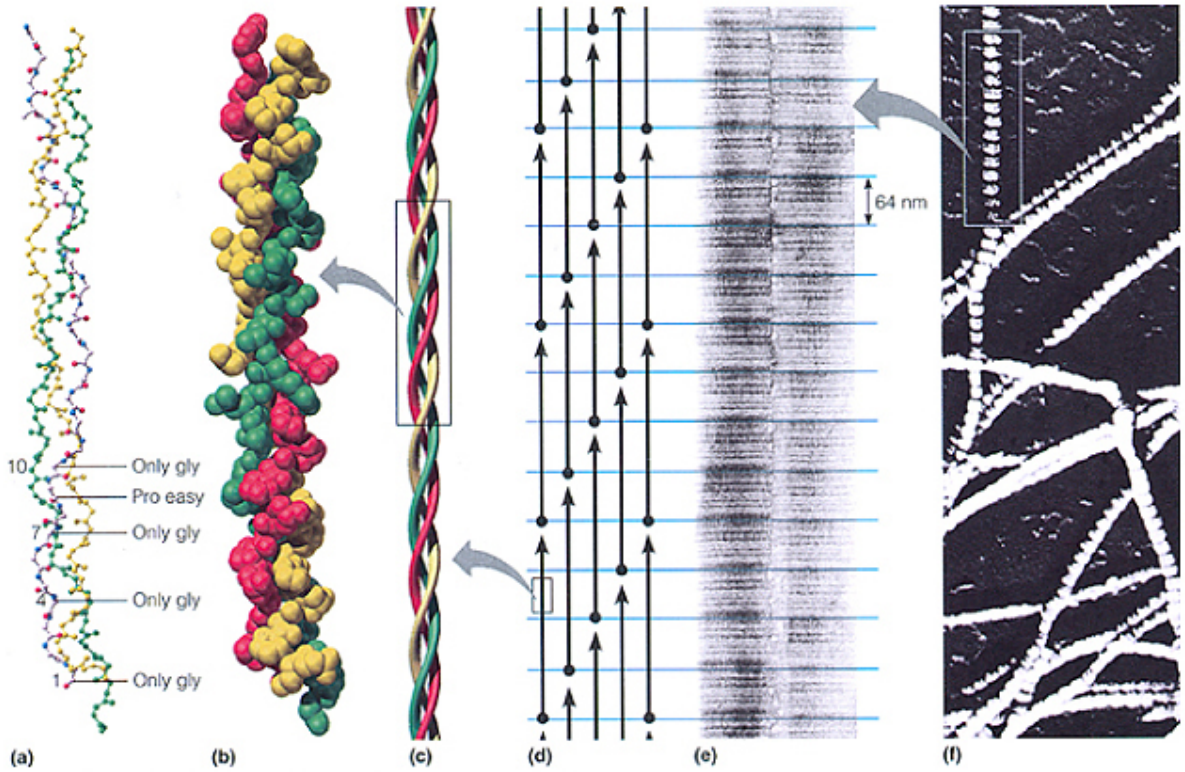




β-Faltblatt (antiparallel oder parallel)
Beispiel: Kollagenfasern



α-Helix



Strukturen von Proteinen:

1. Primärstruktur: Aminosäuresequenz

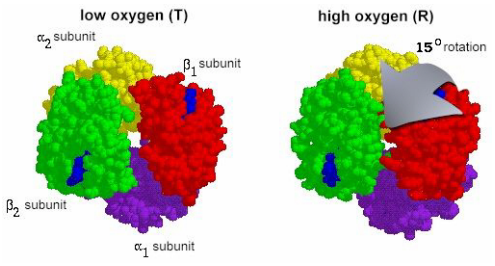
2. Sekundärstruktur: räumliche Anordnung der Kette (Flatblatt, Helix)
nur peptidisches Rückgrat, nicht räuml. Anordnung der AS Seitenketten

3. Tertiärstruktur: Gestalt des Proteins (räuml. Anordnung aller Atome)

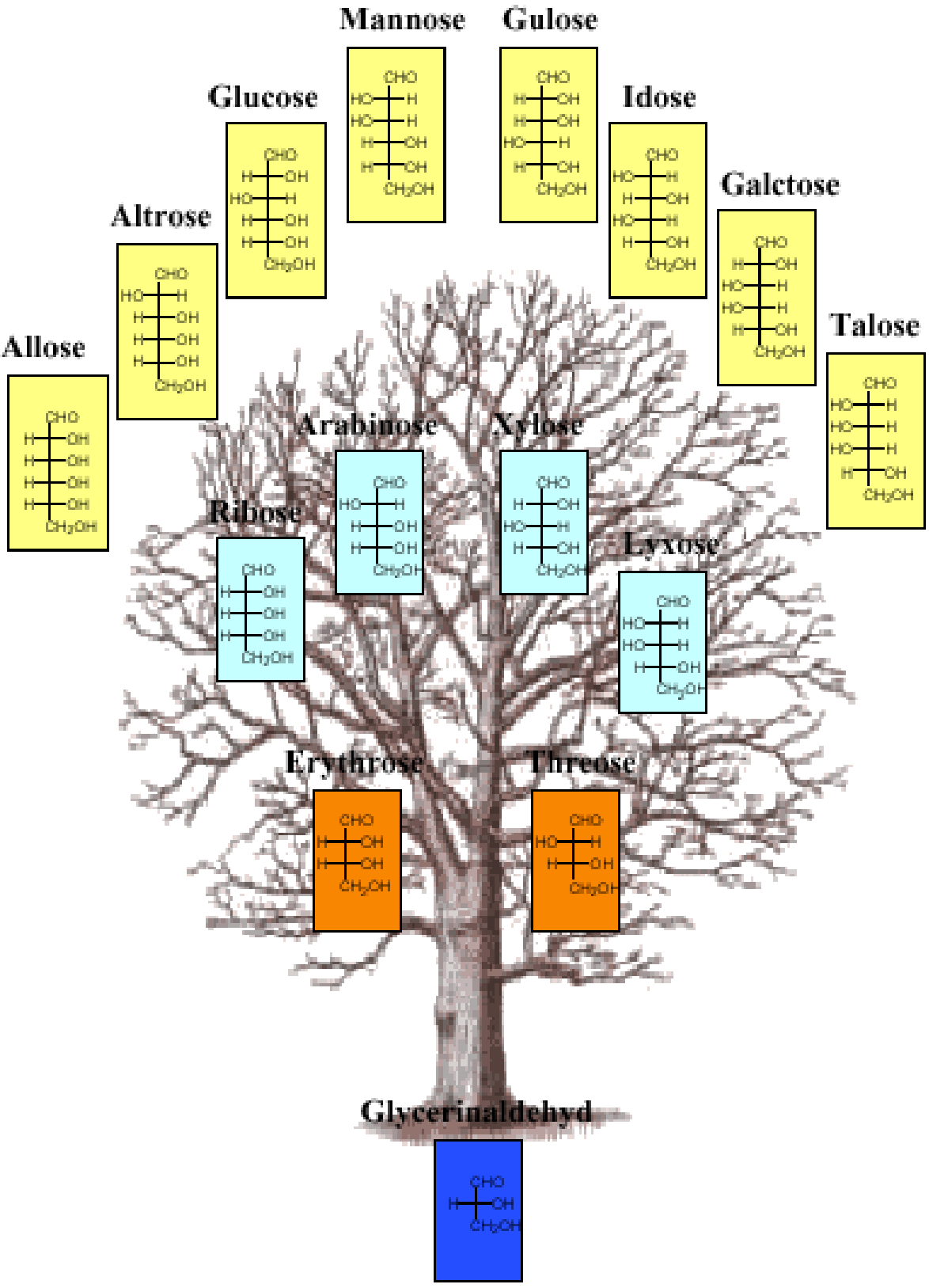
4. Quartärstruktur: Aggregate aus mehreren Proteinen (Dimere, Trimere, etc.)

Beispiel für Protein mit Quartärstruktur aus 4 Proteinketten (Untereinheiten):

Hämoglobulin

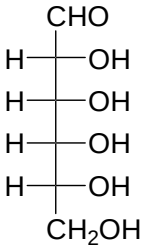


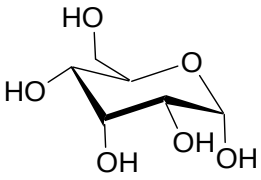
12.3 Kohlenhydrate, Triosen, Tetrosen, Pentosen, Hexosen, Aldosen, Ketosen, Pyranosen, Furanosen, Aminozucker, Anomere, Onsäuren, Uronsäuren, Schreibweisen: Fischer, Haworth, sterische Schreibweise, Konformation



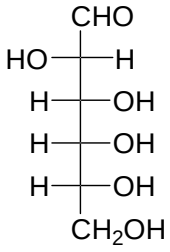
Hexosen

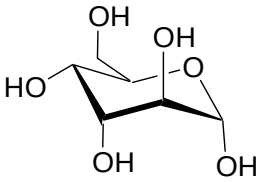
D-Allose



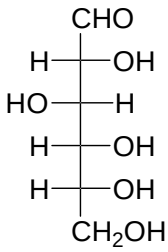


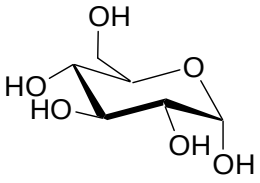
D-Altrose



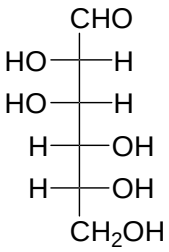


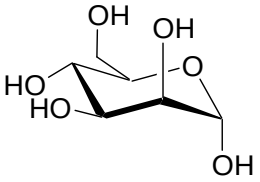
D-Glucose



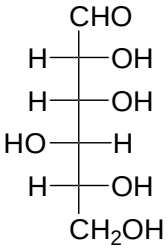


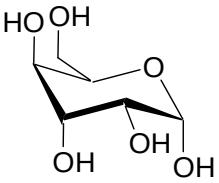
D-Mannose



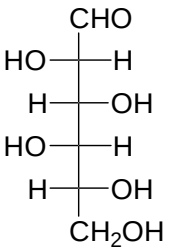


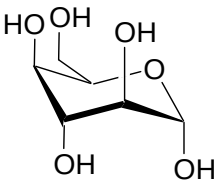
D-Gulose



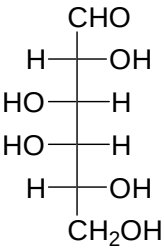


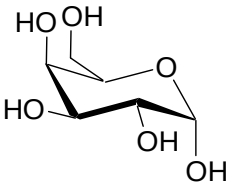
D-Idose



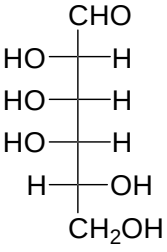


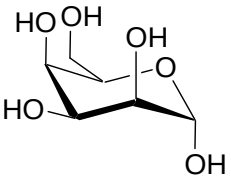
D-Galactose



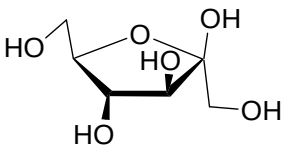


D-Talose

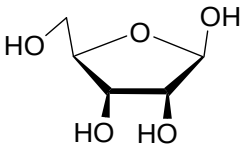




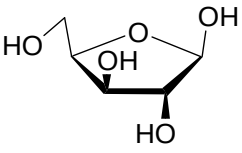
Furanosen



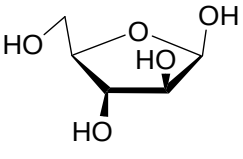
Fructose



Ribose



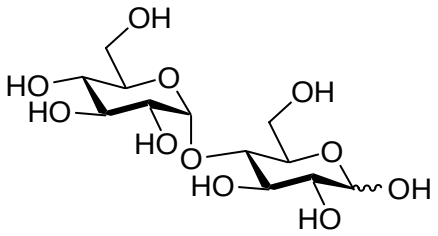
Xylose



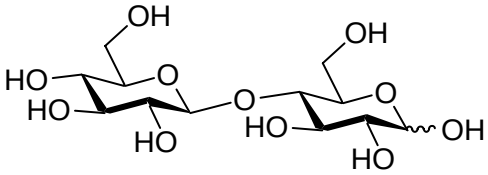
Arabinose

12.4 Saccharide, Glycoside, 1,4-, 1,6-Verknüpfung, Saccharose, Lactose, Maltose, Isomaltose, Cyclodextrine, Bildung und Hydrolyse von Sacchariden

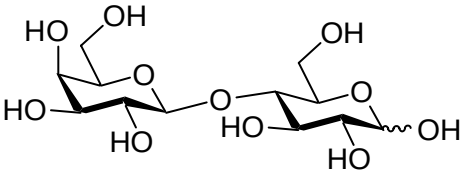
Maltose
4-O-(α-D-Glucopyranosyl)-D-glucopyranose



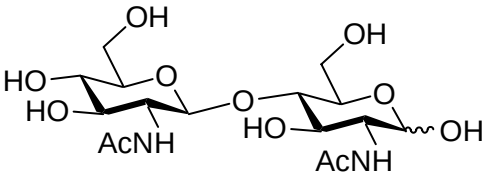
Cellobiose
4-O-(β-D-Glucopyranosyl)-D-glucopyranose



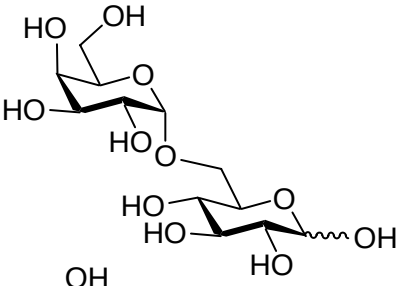
Lactose (Milchzucker)
4-O-(β-D-Galactopyranosyl)-D-glucopyranose



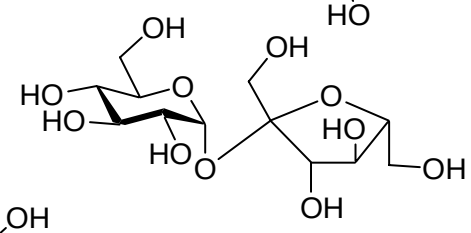
Chitobiose (Chitin)



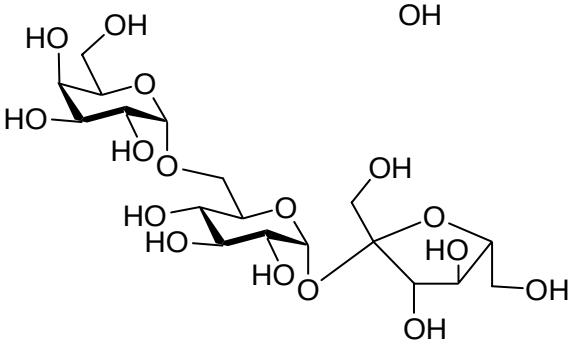
Melibiose



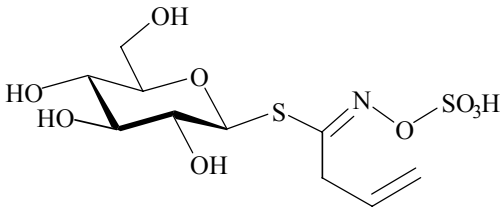
Saccharose (Rohrzucker)



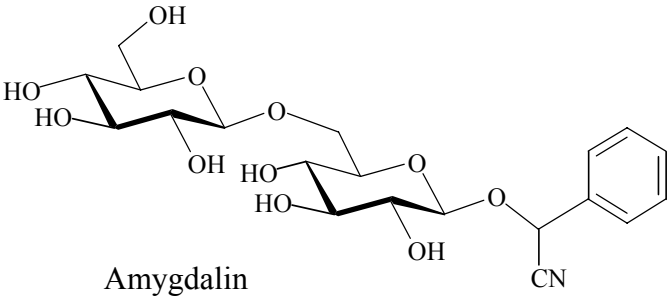
Raffinose (Rübenzucker)



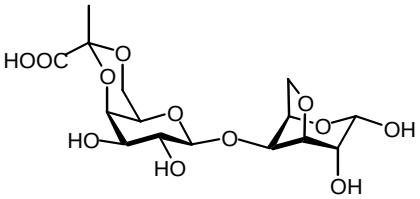
Einige Kohlenhydrate aus Nahrungsmitteln und anderen Quellen:



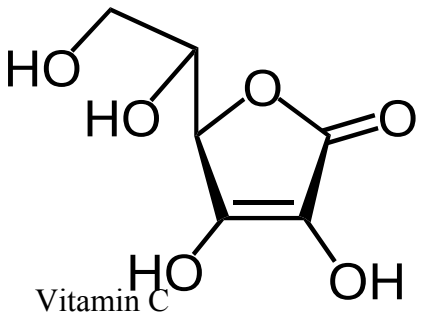
Sinigrin



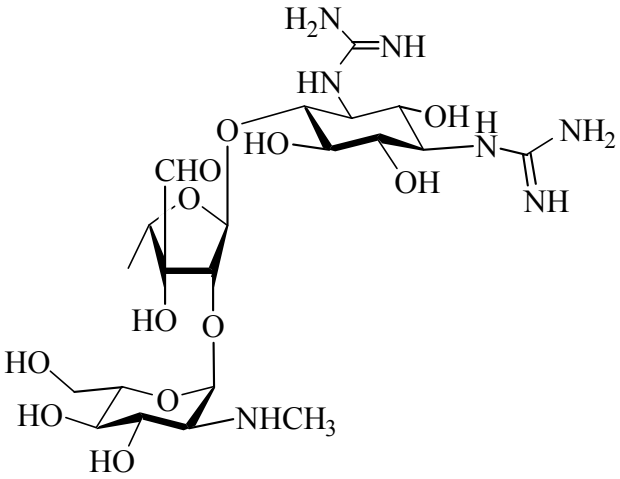
Amygdalin



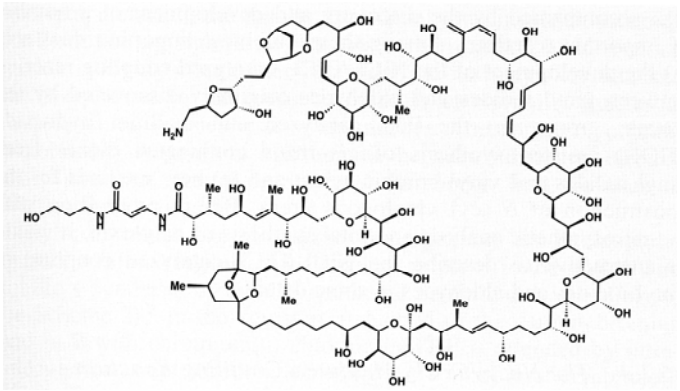
Agar-Agar



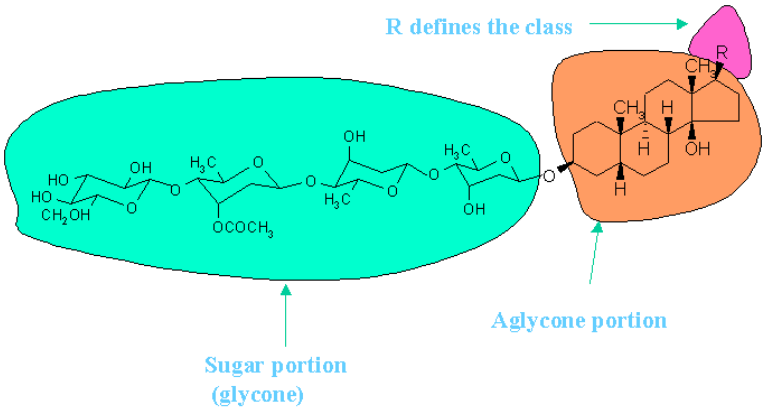
Vitamin C

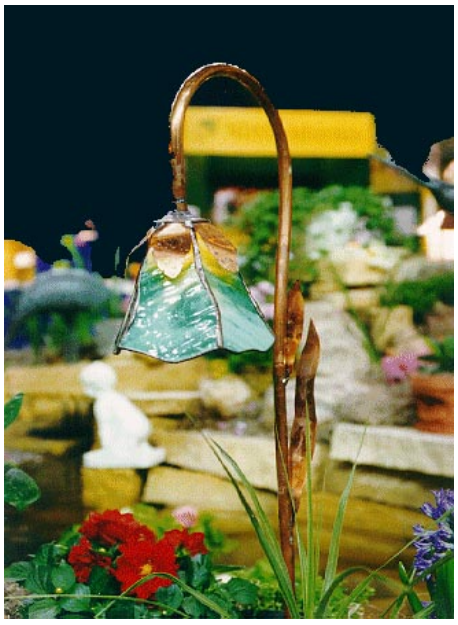


Streptomycin



Palytoxin





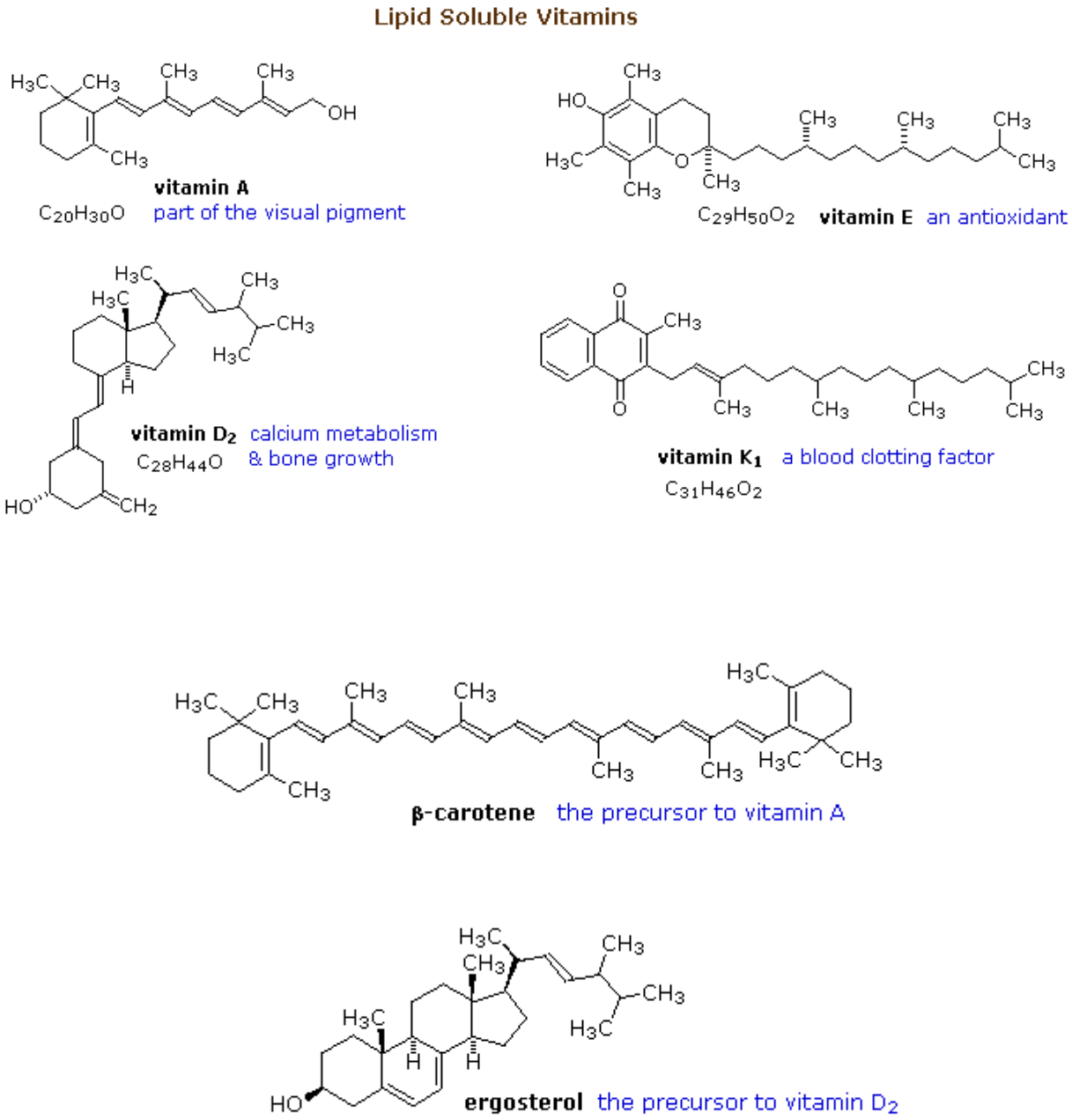
Herzglycoside

12.5 Fette und Lipide, Klassifizierung, Wachse, Sphingolipide, Terpene, Steroide

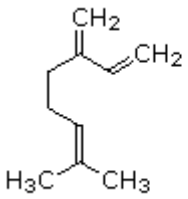
Stoffklassen

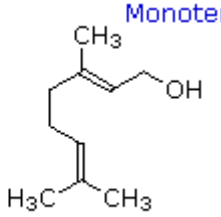
A. nicht hydrolysierbar

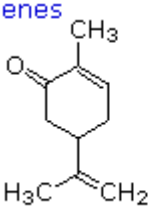
- Langkettige Alkane, Carotinoide, Vitamine
- Terpene, Steroide
- Fettalkohole >C10
- Fettsäuren >C10

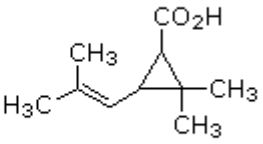


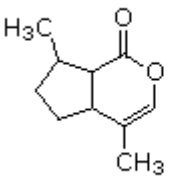
Monoterpenes

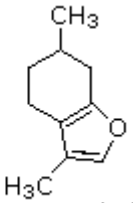

myrcene

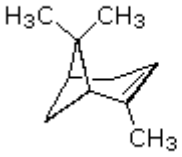

geraniol

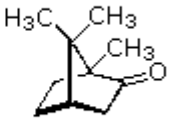

carvone


chrysanthemic acid

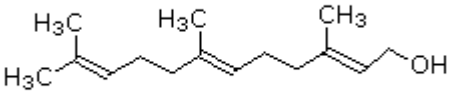

nepetalactone

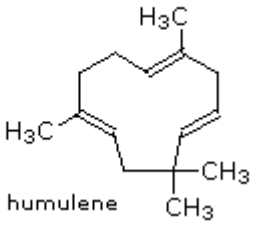

menthofuran

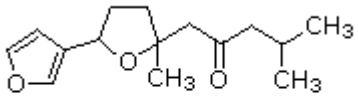

α-pinene

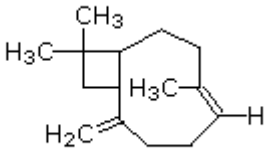

camphor

Sesquiterpenes

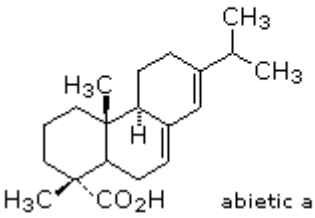

farnesol

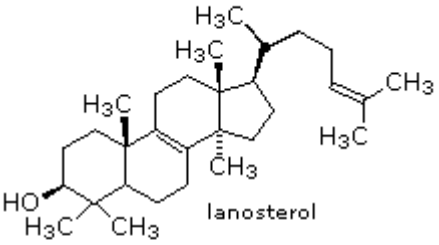

humulene

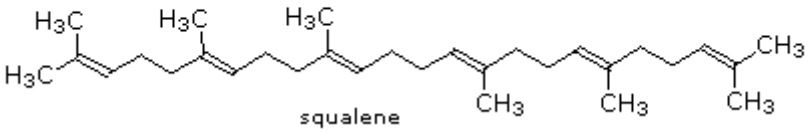

ngaione

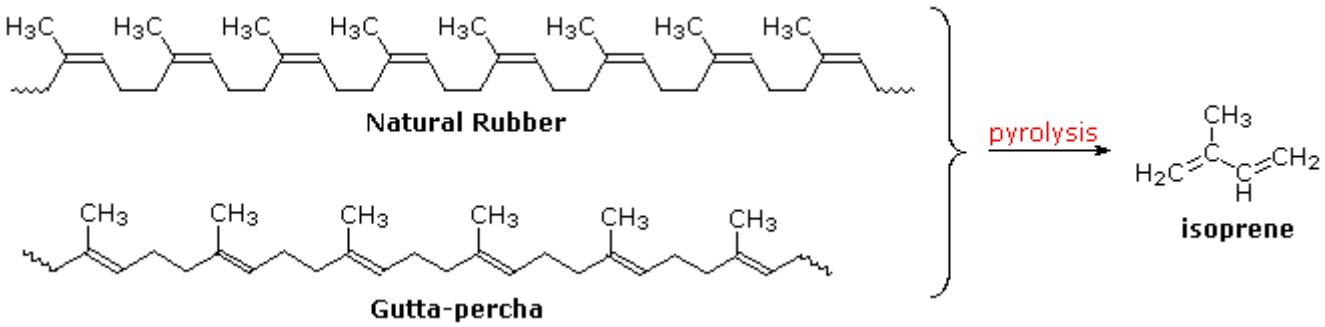

caryophyllene

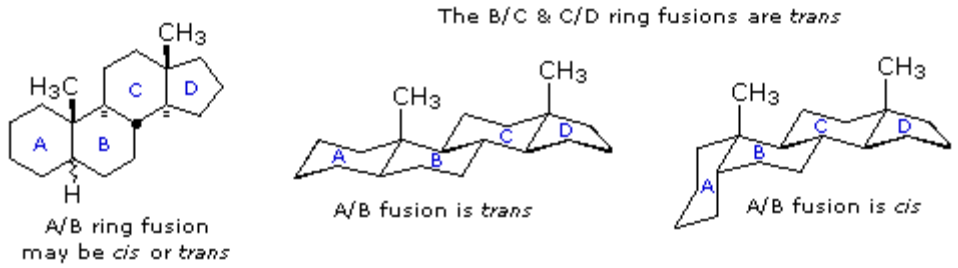
Diterpenes & Triterpenes


abietic acid

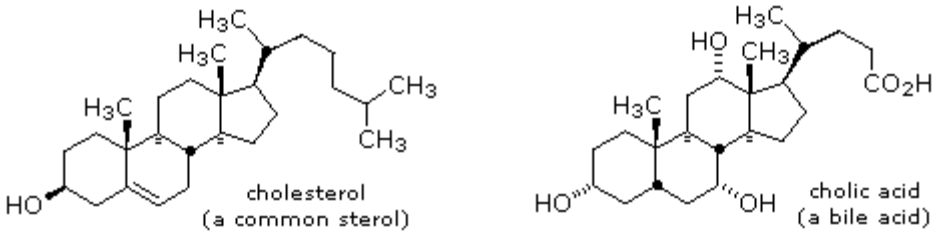

lanosterol


squalene

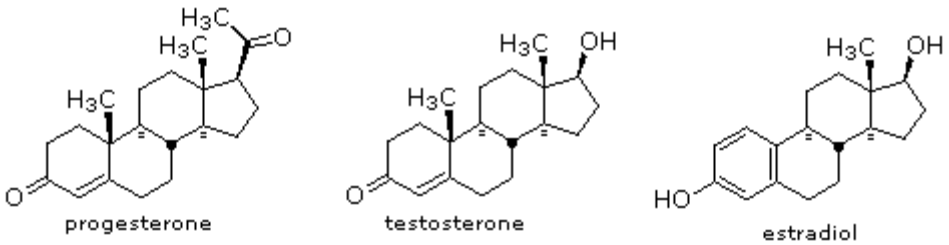




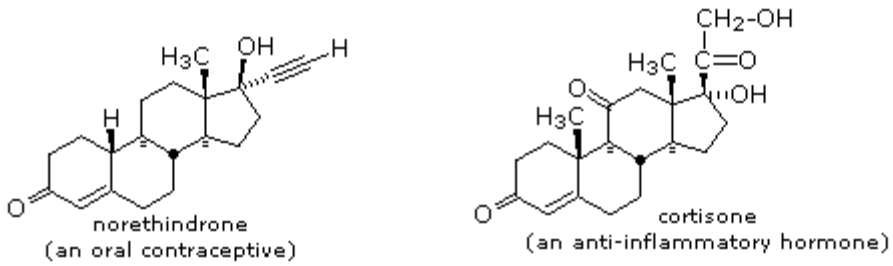
Common Steroid Conformations



Typical Animal Steroids



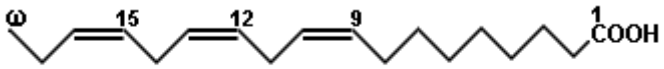
Steroid Sex Hormones



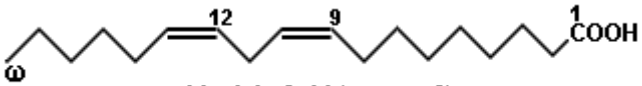
Medicinally Useful Steroids

Common Fatty Acids

Chemical Names and Descriptions of some Common Fatty Acids				
Common Name	Carbon Atoms	Double Bonds	Scientific Name	Sources
Butyric acid	4	0	butanoic acid	butterfat
Caproic Acid	6	0	hexanoic acid	butterfat
Caprylic Acid	8	0	octanoic acid	coconut oil
Capric Acid	10	0	decanoic acid	coconut oil
Lauric Acid	12	0	dodecanoic acid	coconut oil
Myristic Acid	14	0	tetradecanoic acid	palm kernel oil
Palmitic Acid	16	0	hexadecanoic acid	palm oil
Palmitoleic Acid	16	1	9-hexadecenoic acid	animal fats
Stearic Acid	18	0	octadecanoic acid	animal fats
Oleic Acid	18	1	9-octadecenoic acid	olive oil
Vaccenic Acid	18	1	11-octadecenoic acid	butterfat
Linoleic Acid	18	2	9,12-octadecadienoic acid	safflower oil
Alpha-Linolenic Acid (ALA)	18	3	9,12,15-octadecatrienoic acid	flaxseed (linseed) oil
Gamma-Linolenic Acid (GLA)	18	3	6,9,12-octadecatrienoic acid	borage oil
Arachidic Acid	20	0	eicosanoic acid	peanut oil, fish oil
Gadoleic Acid	20	1	9-eicosenoic acid	fish oil
Arachidonic Acid (AA)	20	4	5,8,11,14-eicosatetraenoic acid	liver fats
EPA	20	5	5,8,11,14,17-eicosapentaenoic acid	fish oil
Behenic acid	22	0	docosanoic acid	rapeseed oil
Erucic acid	22	1	13-docosenoic acid	rapeseed oil
DHA	22	6	4,7,10,13,16,19-docosahexaenoic acid	fish oil
Lignoceric acid	24	0	tetracosanoic acid	small amounts in most fats



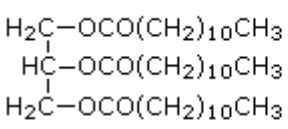
Alpha-Linolenic Acid (omega-3)



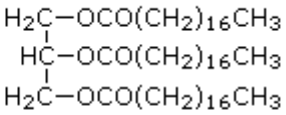
Linoleic Acid (omega-6)

B. hydrolysierbar

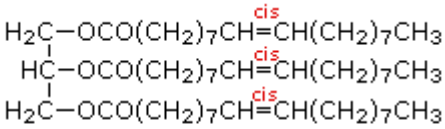
- Fette (Fettsäure + Glycerin)
- Waxe (Fettsäure + Fettalkohol)
- Sterolester (Fettsäure + Cholesterin s.o.)



trilaurin
mp 45° C



tristearin
mp 71° C



triolein
mp -4° C

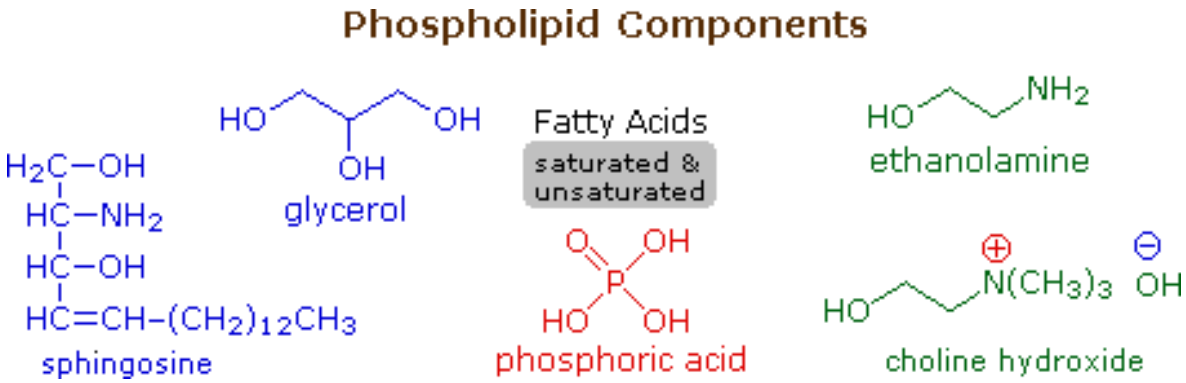
spermaceti: $CH_3(CH_2)_{14}CO_2$-$(CH_2)_{15}CH_3$

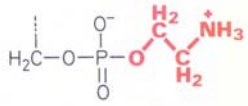
beeswax: $CH_3(CH_2)_{24}CO_2$-$(CH_2)_{29}CH_3$

carnuba wax: $CH_3(CH_2)_{30}CO_2$-$(CH_2)_{33}CH_3$

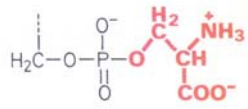
C. Phospholipide

- Phosphatidsäuren (Fettsäure + Glycerin + Phosphat)
- Phosphatide (Fettsäure + Glycerin + Cholin)

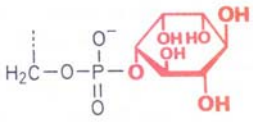




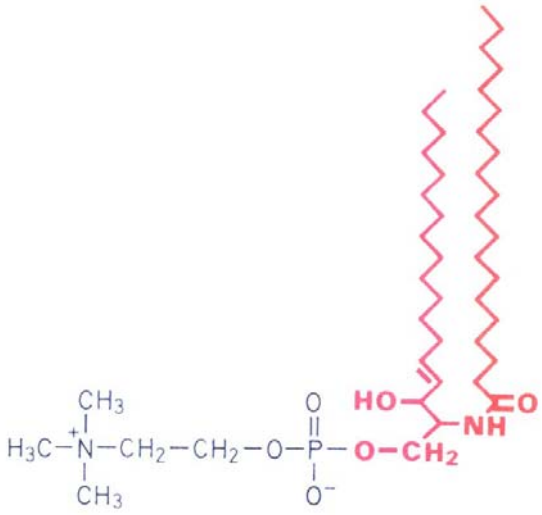
Phosphatidylethanolamin



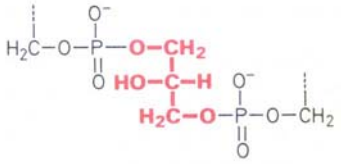
Phosphatidylserin



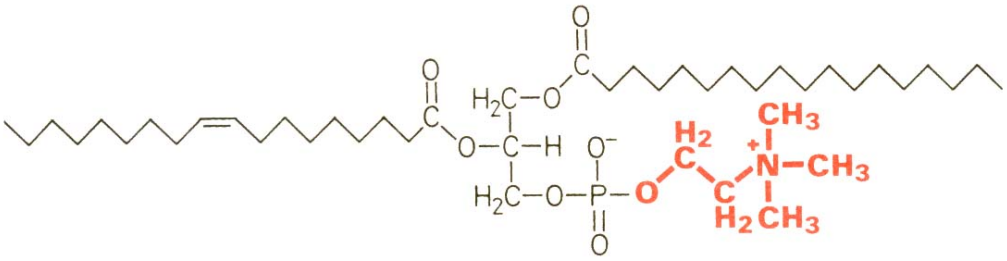
Phosphatidylinositol



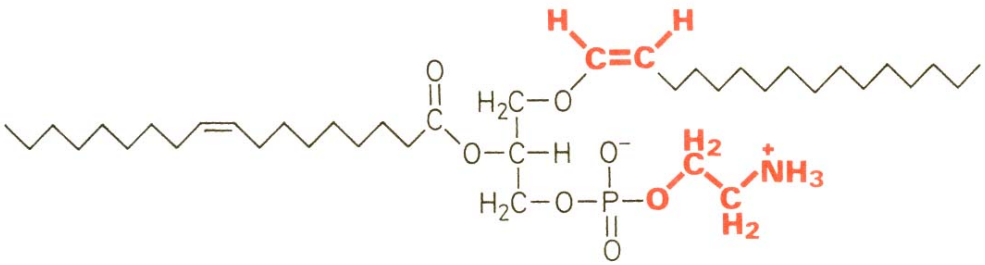
Sphingomyelin



Bisphosphatidylglycerol
(Cardiolipin)

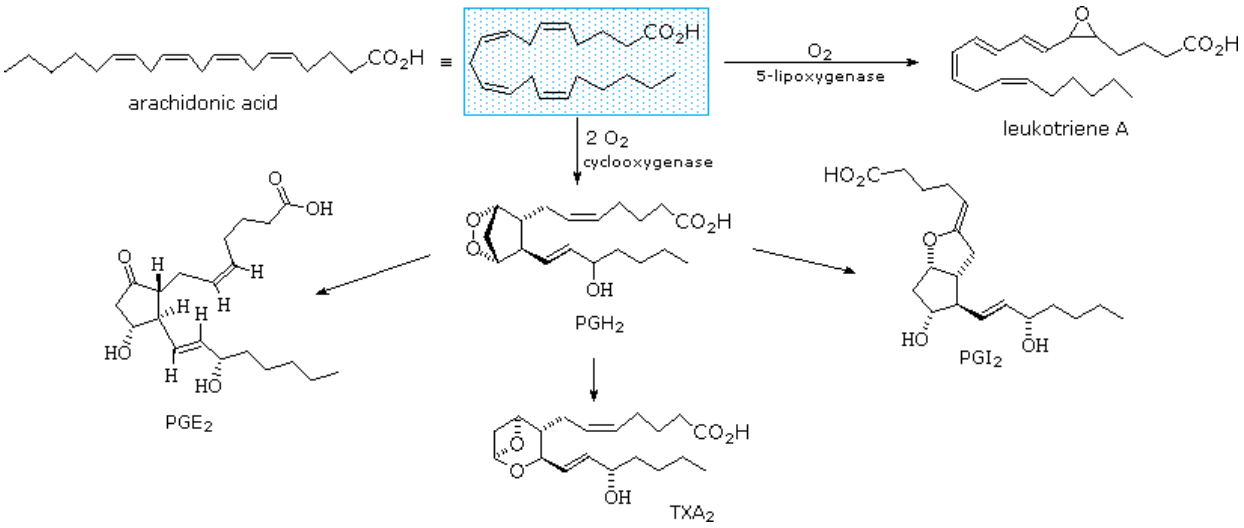


Phosphatidylcholin (Lecithin)



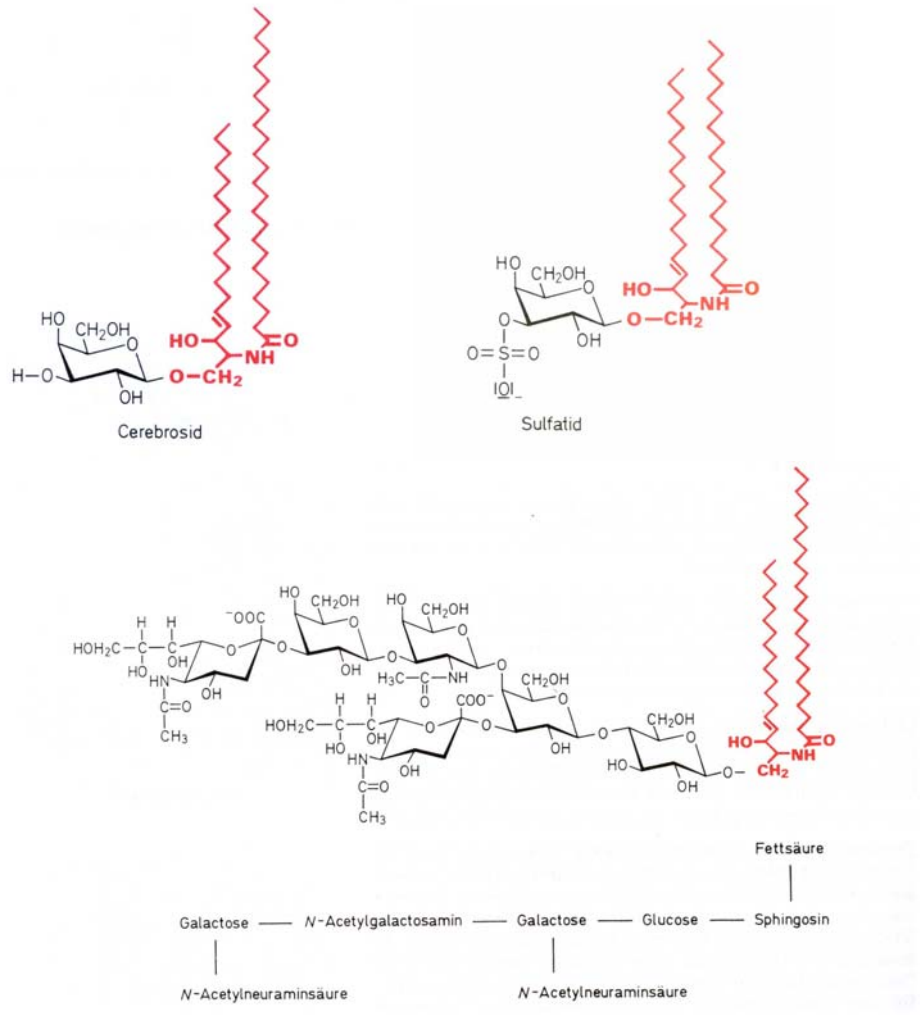
Plasmalogen, Plasmenylethanolamin
[1-(1-Alkenyl)-2-acyl-*sn*-glycerol-3-phospho-ethanolamin]

D. Prostaglandine, Tromboxane, Leukotriene



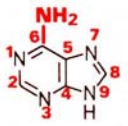
E. Glycolipide

- Cerebroside (Fettsäure + Sphingosin s.o. + Zucker)
- Ganglioside (Fettsäure + Sphingosin s.o. + Zucker + Neuraminsäure)

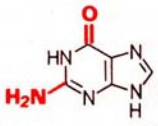


Purin-Derivate

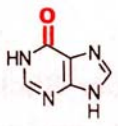
Basen:



Adenin (Ade)

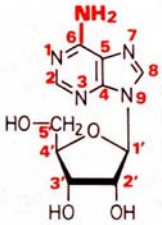


Guanin (Gua)

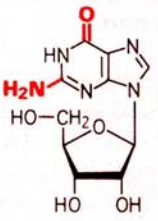


Hypoxanthin (Hyp)

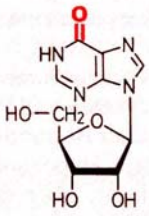
Nucleoside:



Adenosin (A)



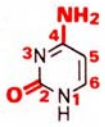
Guanosin (G)



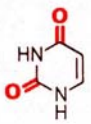
Inosin (I)

Pyrimidin-Derivate

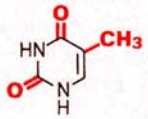
Basen:



Cytosin (Cyt)

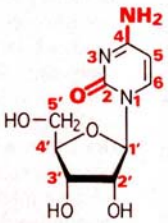


Uracil (Ura)

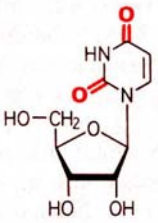


Thymin (Thy)

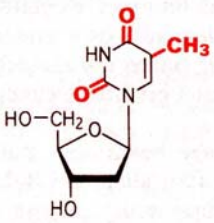
Nucleoside:



Cytidin (C)

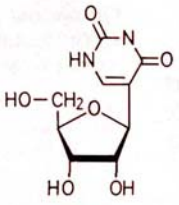


Uridin (U)

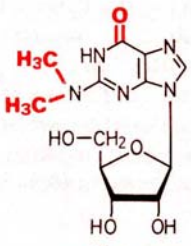


Thymidin (dT)

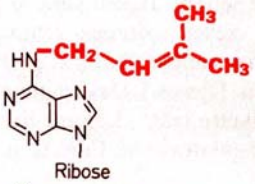
Seltene Nucleoside:



Pseudo-uridin (ψ)

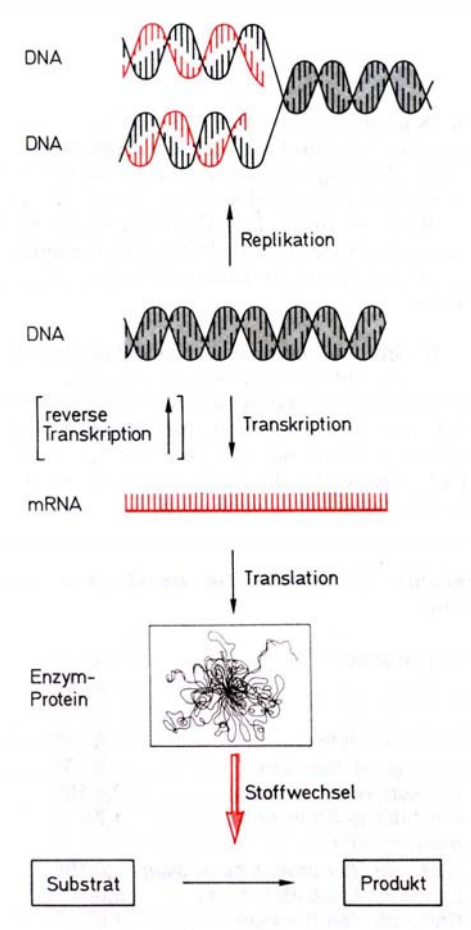


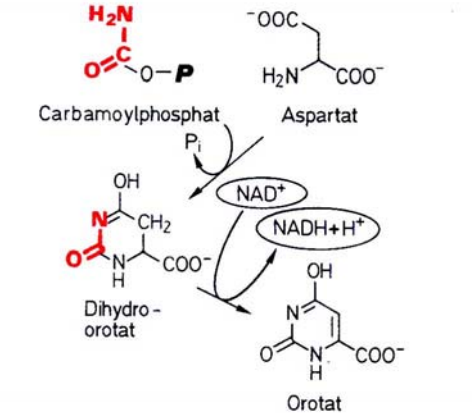
N^2-Dimethyl-guanosin (m^2_2G)

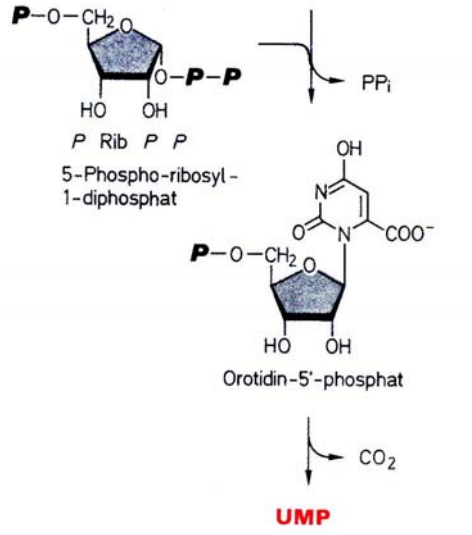


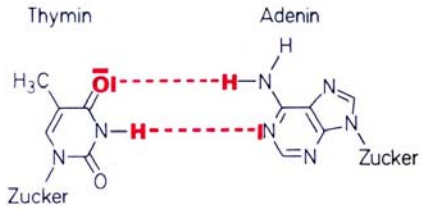
Ribose

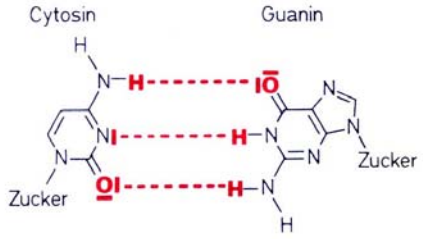
N^6-Isopentenyl-adenosin

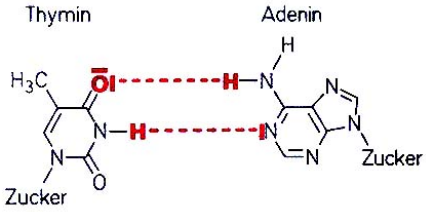

DNA
DNA
Replikation
DNA
reverse Transkription
Transkription
mRNA
Translation
Enzym-Protein
Stoffwechsel
Substrat
Produkt

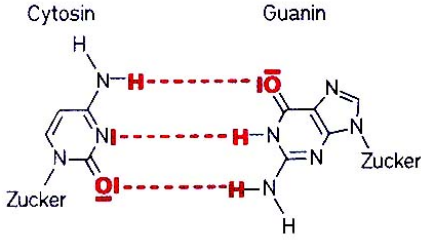

Carbamoylphosphat
Aspartat
Pi
NAD+
NADH+H+
Dihydro-orotat
Orotat

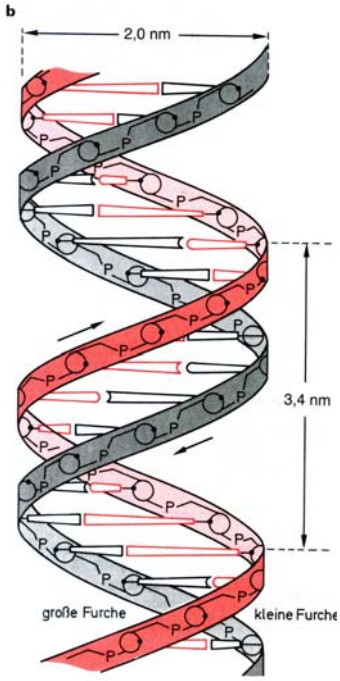

PPi
P Rib P P
5-Phospho-ribosyl-1-diphosphat
Orotidin-5'-phosphat
CO2
UMP


Thymin
Adenin
Zucker
Zucker


Cytosin
Guanin
Zucker
Zucker


Thymin
Adenin
Zucker
Zucker

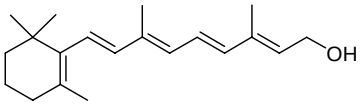

Cytosin
Guanin
Zucker
Zucker



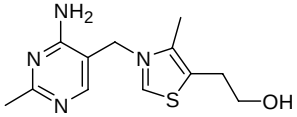
1. Base	2. Base				3. Base
	U	C	A	G	
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	„*Stop*“	„Stop“	A
	Leu	Ser	„*Stop*“	Trp	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gin	Arg	A
	Leu	Pro	Gin	Arg	G
A	lie	Thr	Asn	Ser	U
	lie	Thr	Asn	Ser	C
	lie	Thr	Lys	Arg	A
	Met (*Start*)	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

12.7 Weitere Naturstoffe: Vitamine, Alkaloide, Hormone, Antibiotika

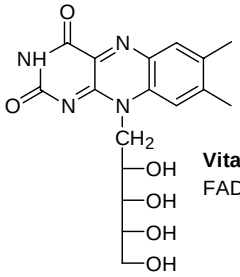
Vitamine



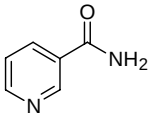
Vitamin A (Retinol)
Sehpigment, Immunsystem



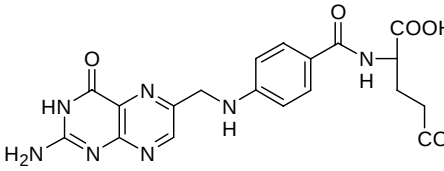
Vitamin B_1 (Thiamin)
Vorstufe für Coenzyme
Decarboxylasen



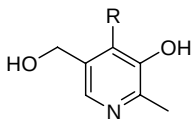
Vitamin B_2 (Riboflavin)
FAD für Oxidoreduktasen



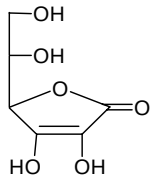
Vitamin B_3 (Nicotinamid)
NAD für Oxidoreductasen



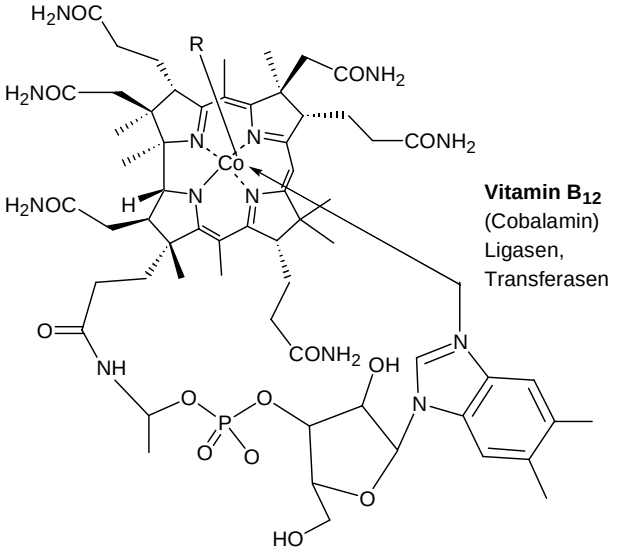
Vitamin B_4 (Folsäure)
C_1-Gruppentransfer



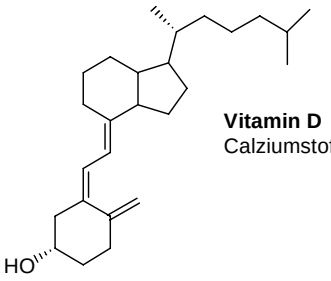
Vitamin B_6
Aminosäurestoffwechsel
R = CH_2OH Pyridoxol
R = CHO Pyridoxal
R = CH_2NH_2 Pyridoxamin



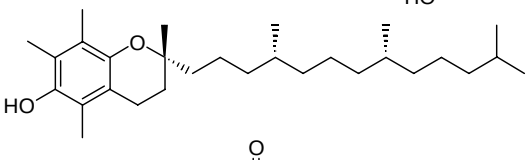
Vitamin C (Ascorbinsäure)
Radikalfänger
Immunsystem



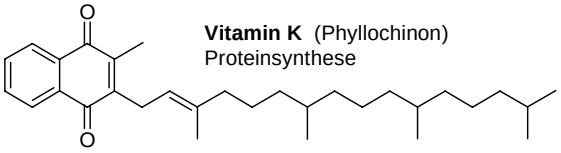
Vitamin B_{12}
(Cobalamin)
Ligasen,
Transferasen



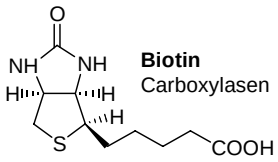
Vitamin D (Calciferol)
Calziumstoffwechsel



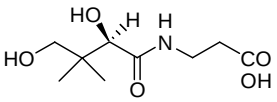
Vitamin E (Tocoferol)
Antioxidans



Vitamin K (Phyllochinon)
Proteinsynthese

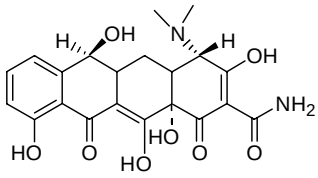


Biotin
Carboxylasen

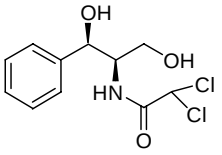


Pantothensäure
Coenzym A

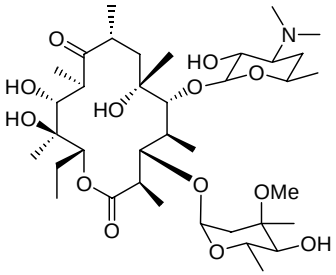
Antibiotika



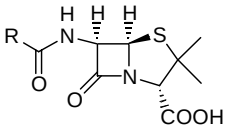
Tetracycline



Chloramphenicol



Erythromycin



Penicilline

Alkaloide (Wortbildung aus arabisch *al qualja*: „Pflanzenasche“ und griechisch *-oides*: „ähnlich“) sind natürlich vorkommende, chemisch heterogene, meist basische, stickstoffhaltige organische Verbindungen des Sekundärstoffwechsels, die auf den tierischen oder menschlichen Organismus wirken. Über 10000 verschiedene pflanzlichen, tierische oder von Mikroorganismen produzierte Substanzen werden dieser Stoffgruppe zugeordnet.

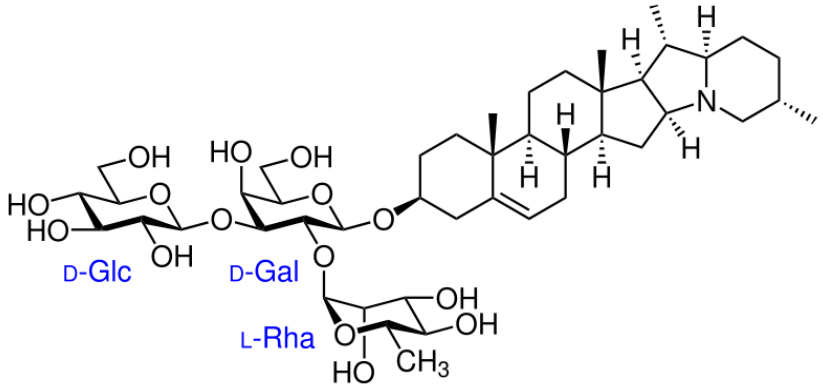
Einteilung nach chemischer Struktur

Die in der Literatur am häufigsten verwendete Einteilung der Alkaloide ist die Kategorisierung entsprechend ihrer chemischen Struktur. Namensgebend ist der Teil des Moleküls, der einen Stickstoff enthält.

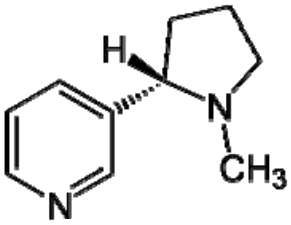
- Alkaloide mit heterocyclischem Stickstoff

- Pyrrolidin-Alkaloide: z. B. Hygrin
- Steroid-Alkaloide: z. B. Solanin
- Pyridin-Alkaloide: z. B. Nicotin, Anabasin
- Tropan-Alkaloide: z. B. Hyoscyamin, Scopolamin, Cocain
- Chinolin-Alkaloide: z. B. Chinin, Chinidin
- Isochinolin-Alkaloide: z. B. Morphin, Codein, Papaverin, Berberin, Tubocurarin
- Indol-Alkaloide: z. B. Ajmalin, Ergotamin, Yohimbin, Reserpin, Strychnin
- Purin-Alkaloide: z. B. Coffein, Theophyllin, Theobromin

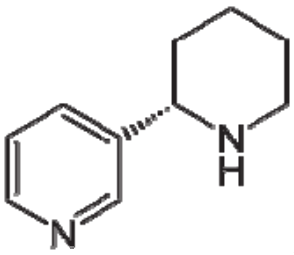
- Alkaloide mit acyclischem Stickstoff: z. B. Ephedrin, Mescalin



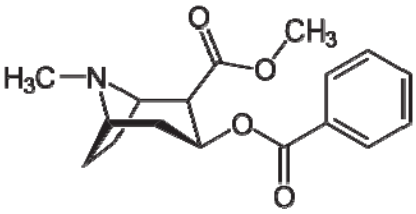
Solanin



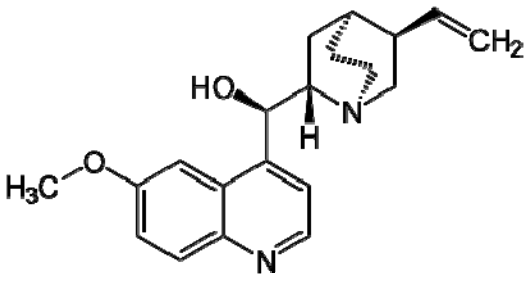
Nikotin



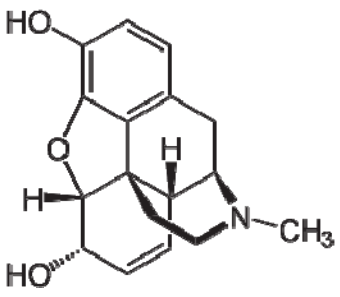
Anabasin



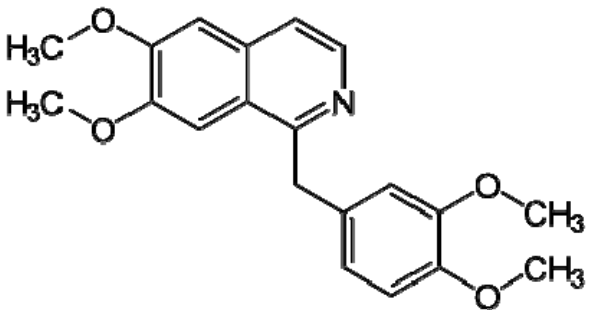
Cocain



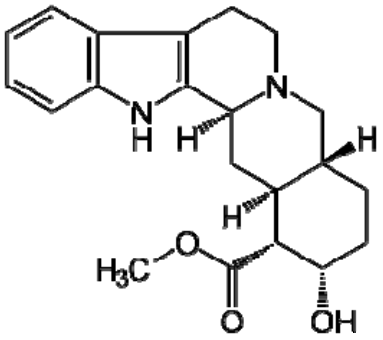
Chinin



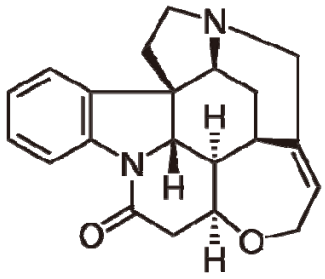
Morphin



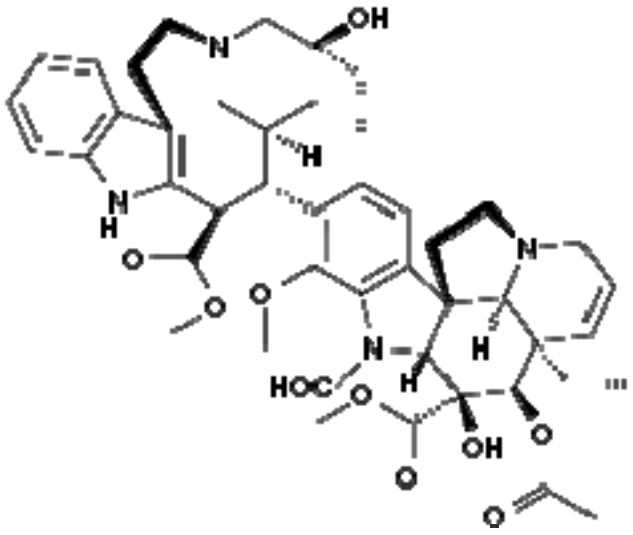
Papaverin



Yohimbin



Strychnin



Vincristin