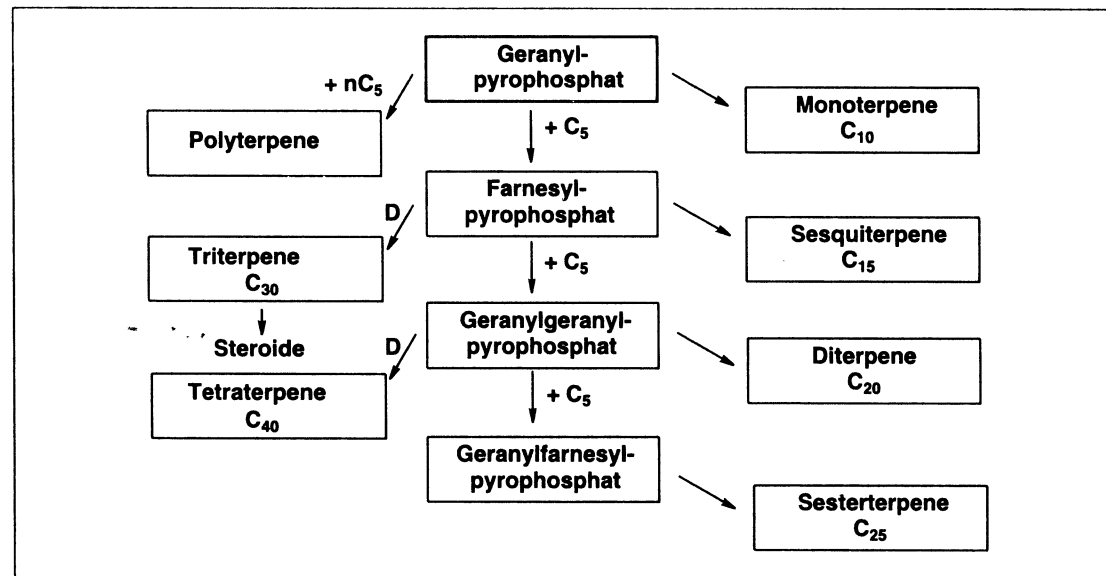
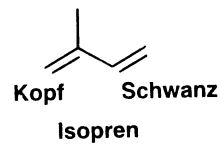
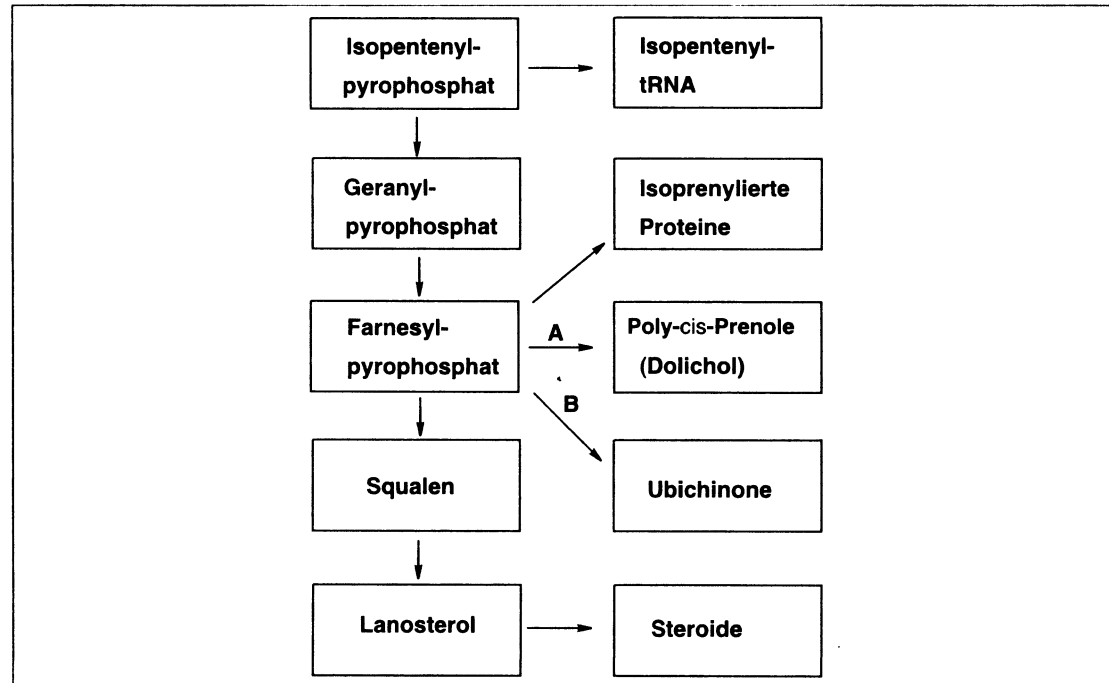


Isoprenoide Verbindungen: Terpene und Steroide

Allgemeine Einführung

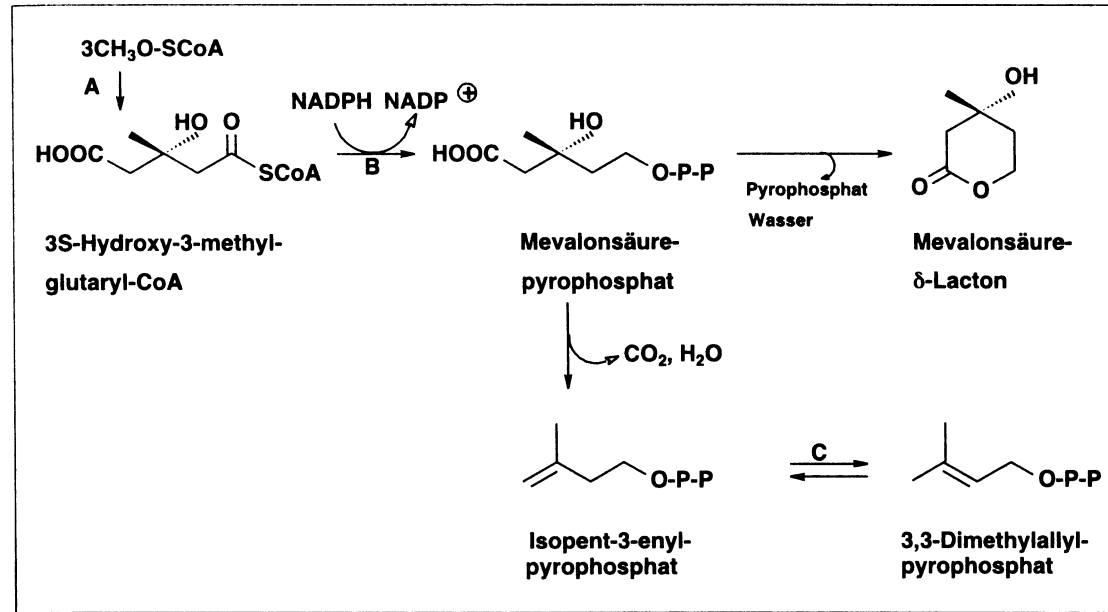


Schematische Darstellung der biosynthetischen Zusammenhänge bei den terpenoiden Verbindungen. D: Schwanz-Schwanz-Kondensation.

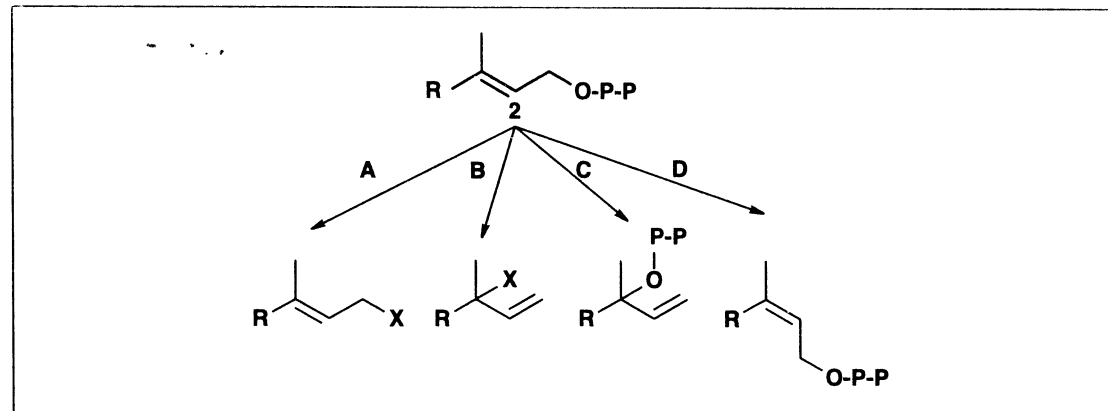


In Säugetieren vorkommende Isoprenoide. A: *cis*-Prenyl-Transferase; B: *trans*-Prenyl-Transferase.

Ausgangsstoffe der Biosynthese

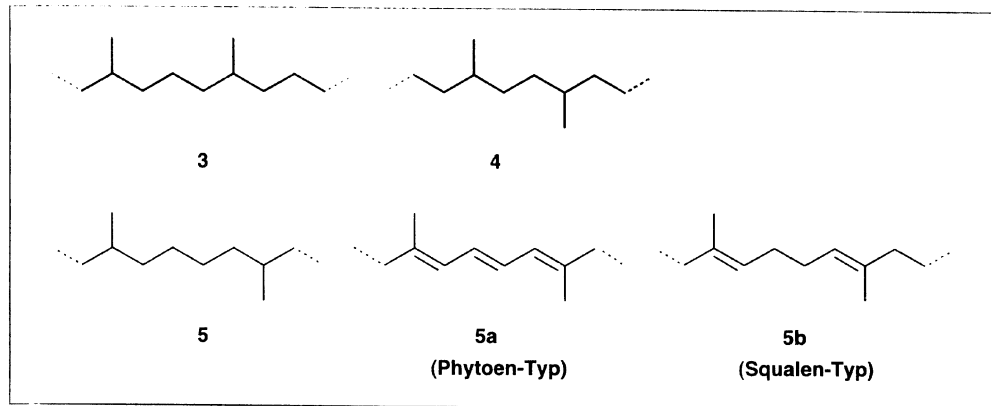
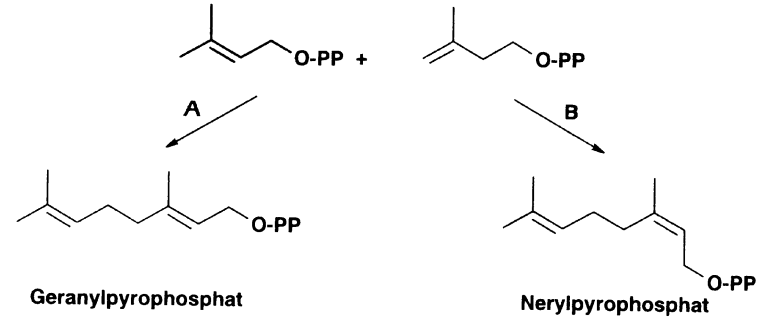


Biosynthese des „aktiven“ Isoprens. A: Hydroxymethylglutaryl-CoA-Synthase; B: Hydroxymethylglutaryl-CoA-Reduktase (HMG-CoA-Reduktase); C: Isopentenyl-diphosphat Δ^3 - Δ^2 -Isomerase.

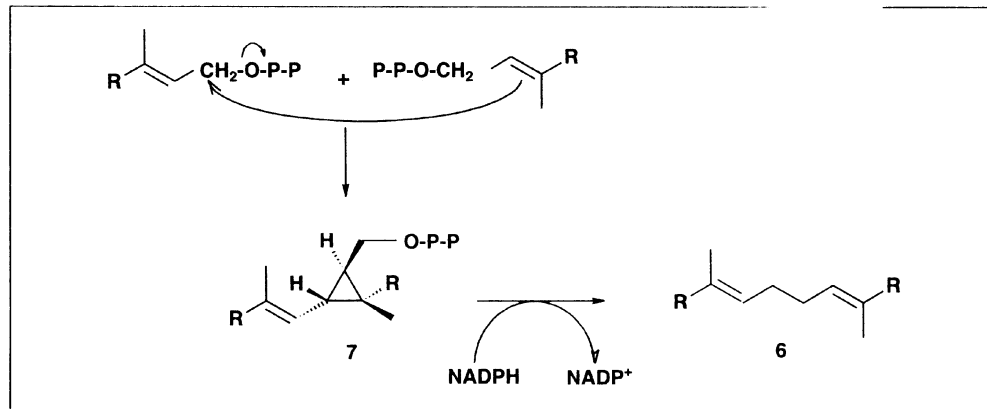


Reaktionstypen von Allylpyrophosphaten (2). A: Direkter nucleophiler Austausch der Pyrophosphatgruppe; B: Nucleophiler Austausch der Pyrophosphatgruppe, verbunden mit einer Allylumlagerung; C: Allylumlagerung; D: *cis-trans*-Isomerisierung.

Bildung acyclischer Precursoren

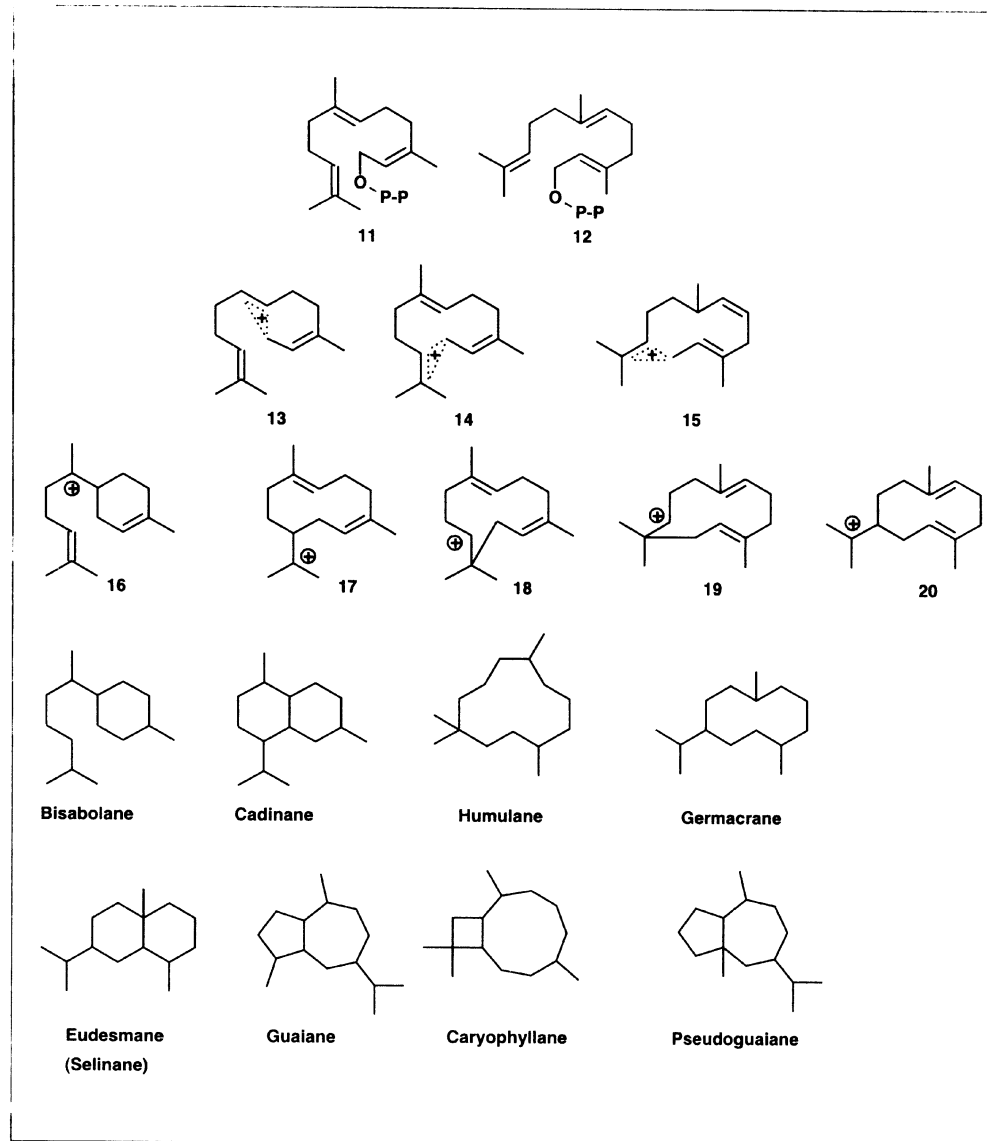
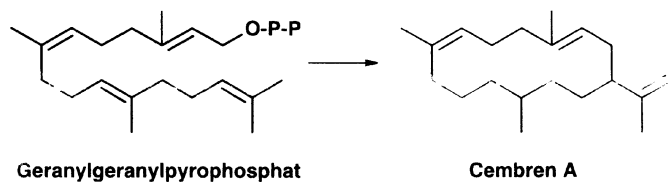
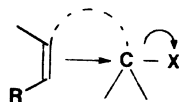


Dimerisierungen durch Kopf-Kopf- (4) und Schwanz-Schwanz-Kondensation (5).

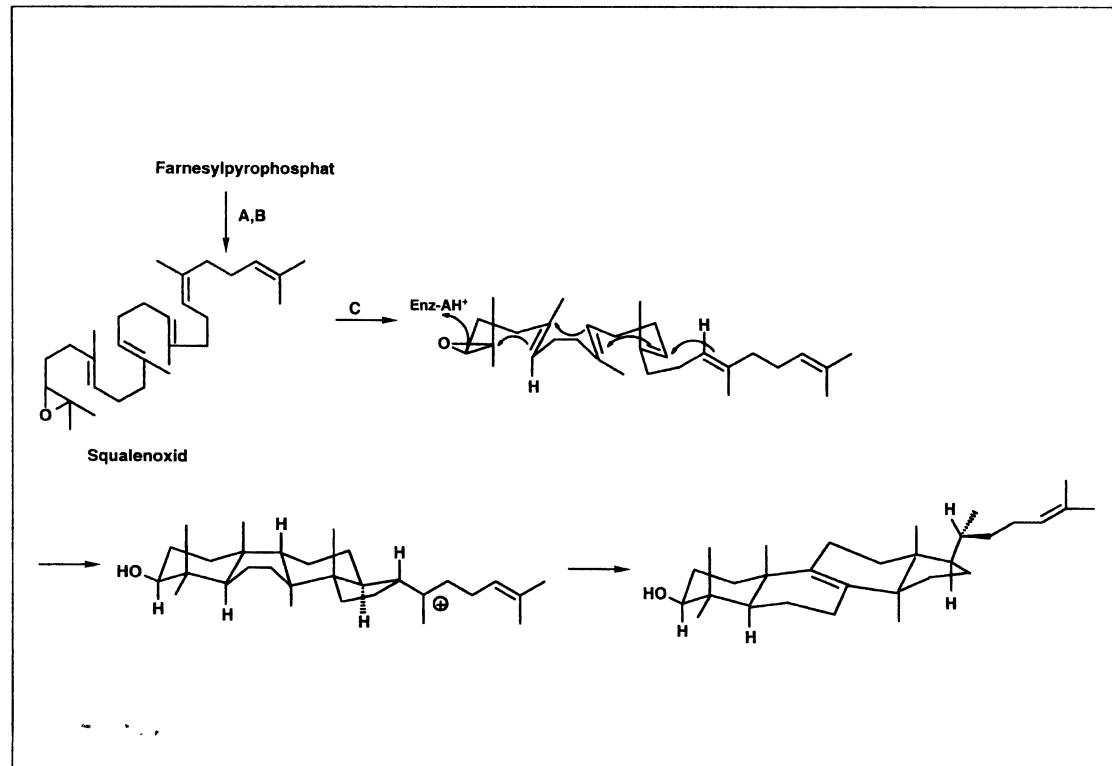


Dimerisierung von Farnesylpyrophosphat zum Triterpen Squalen. $R = C_{11}H_{19}$.

Intramolekulare Cycloadditionen

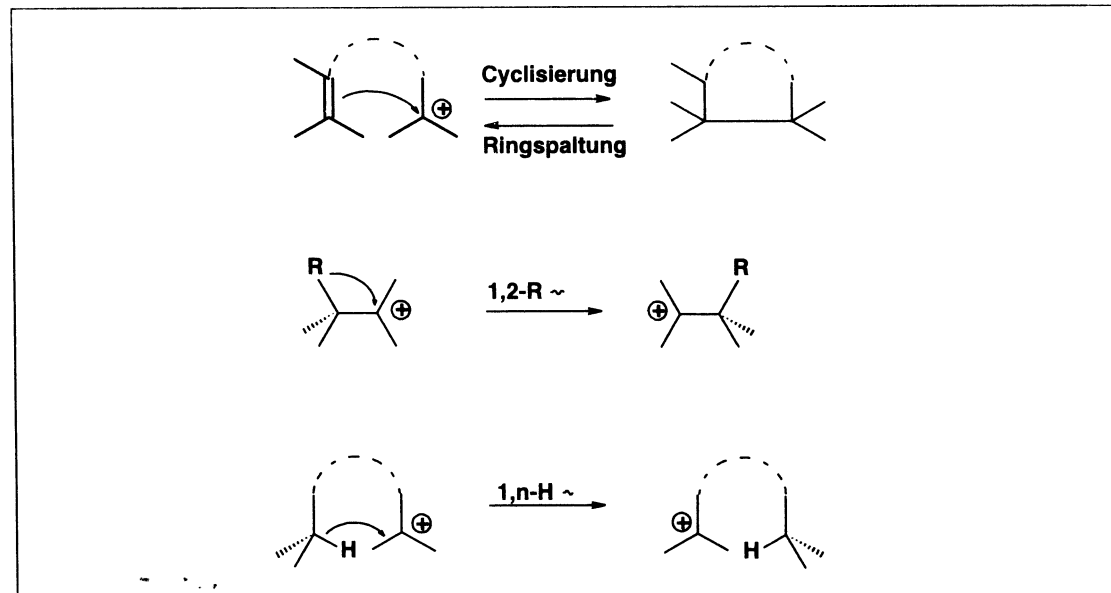
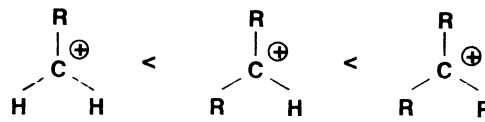


Angenommene Bildungsmöglichkeiten einiger Sesquiterpengrundgerüste.

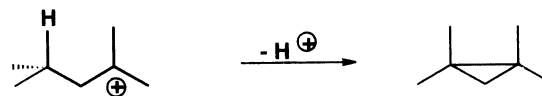


Cyclisierung des Squalens zum tetracyclischen Triterpen Lanosterol. A: Squalen-Synthase; B: Squalen-Epoxidase; C: Oxidosqualen-Cyclase.

Umlagerungen von Carbokationen

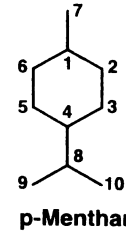


Umlagerungen von Carbeniumionen.

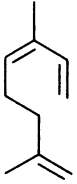


Terpene

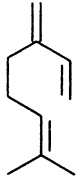
Monoterpene



Kohlenwasserstoffe

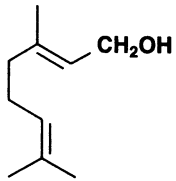


Ocimen

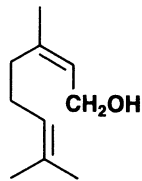


Myrcen

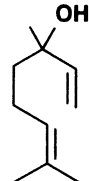
Alkohole:



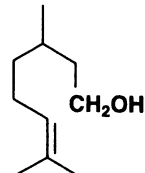
Geraniol



Nerol

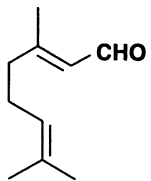


Linalool

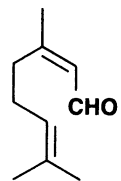


Citronellol

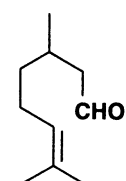
Aldehyde:



Geranial
(Citral a)

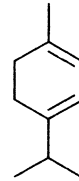


Neral
(Citral b)

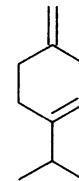


Citronellal

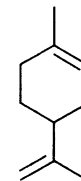
Kohlenwasserstoffe:



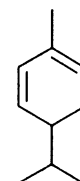
α -Terpinen



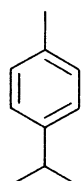
β -Terpinen



Dipenten

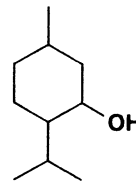


α -Phellandren

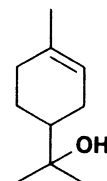


p-Cymen

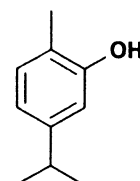
Alkohole und Phenole:



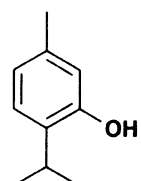
Menthol



α -Terpineol

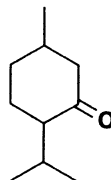


Carvacrol

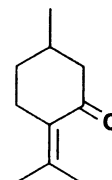


Thymol

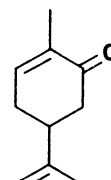
Ketone:



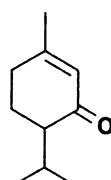
Menthon



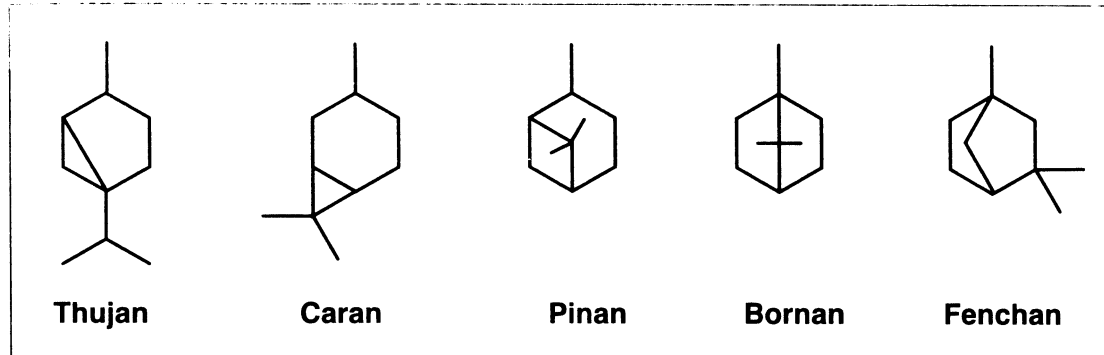
Pulegon



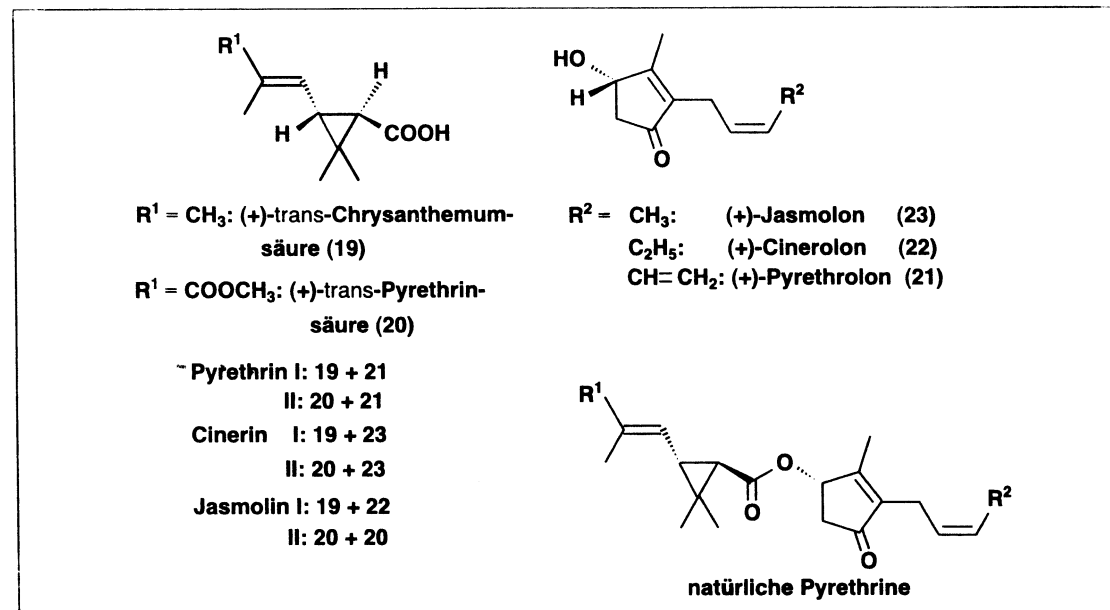
Carvon



Piperiton

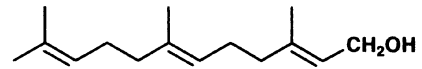


Grundkörper der bicyclischen Monoterpene.

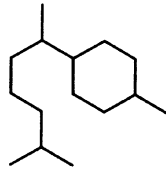


Natürliche Pyrethrine.

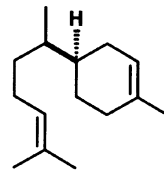
Sesquiterpene



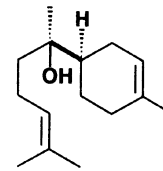
2-trans-6-trans-Farnesol



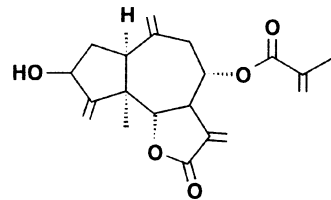
Bisabolon



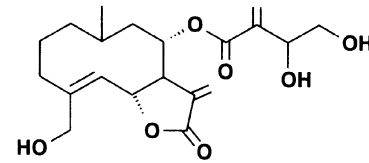
Bisabolen



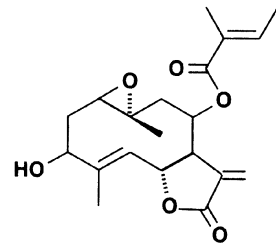
Bisabolol



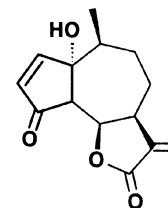
Cynaropikrin



Cnicin



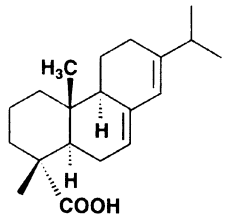
Helangin
(Eudesmanolid)



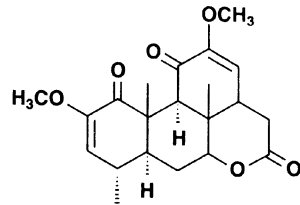
Parthenin
(Pseudoguaianolid)

Bitterstoffe aus der Gruppe der Sesquiterpenlactone.

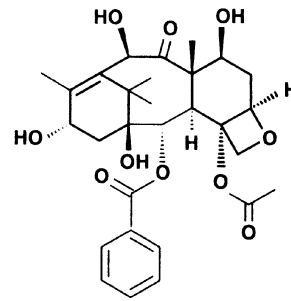
Diterpene



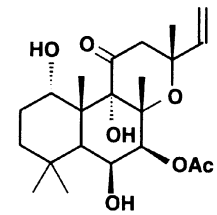
Abietinsäure



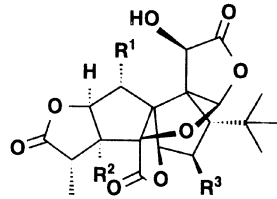
Quassin



10-Deacetylbaccatin III

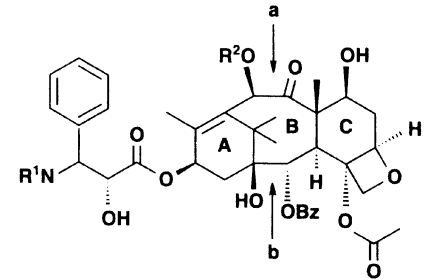


Forskolin



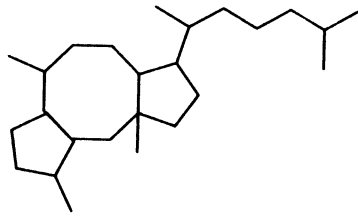
| | R ¹ | R ² | R ³ |
|-------------|----------------|----------------|----------------|
| Ginkgolid A | H | OH | H |
| Ginkgolid B | OH | OH | H |
| Ginkgolid C | OH | OH | OH |
| Ginkgolid J | H | OH | OH |
| Ginkgolid M | OH | H | OH |

Partialsynthese

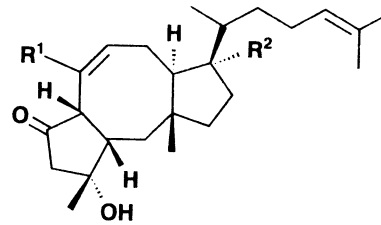


Docetaxel : R₁ = COOC(CH₃); R₂ = H;
 Paclitaxel : R₁ = COC₆H₅; R₂ = COCH₃

Sesterterpene



Ophiobolan

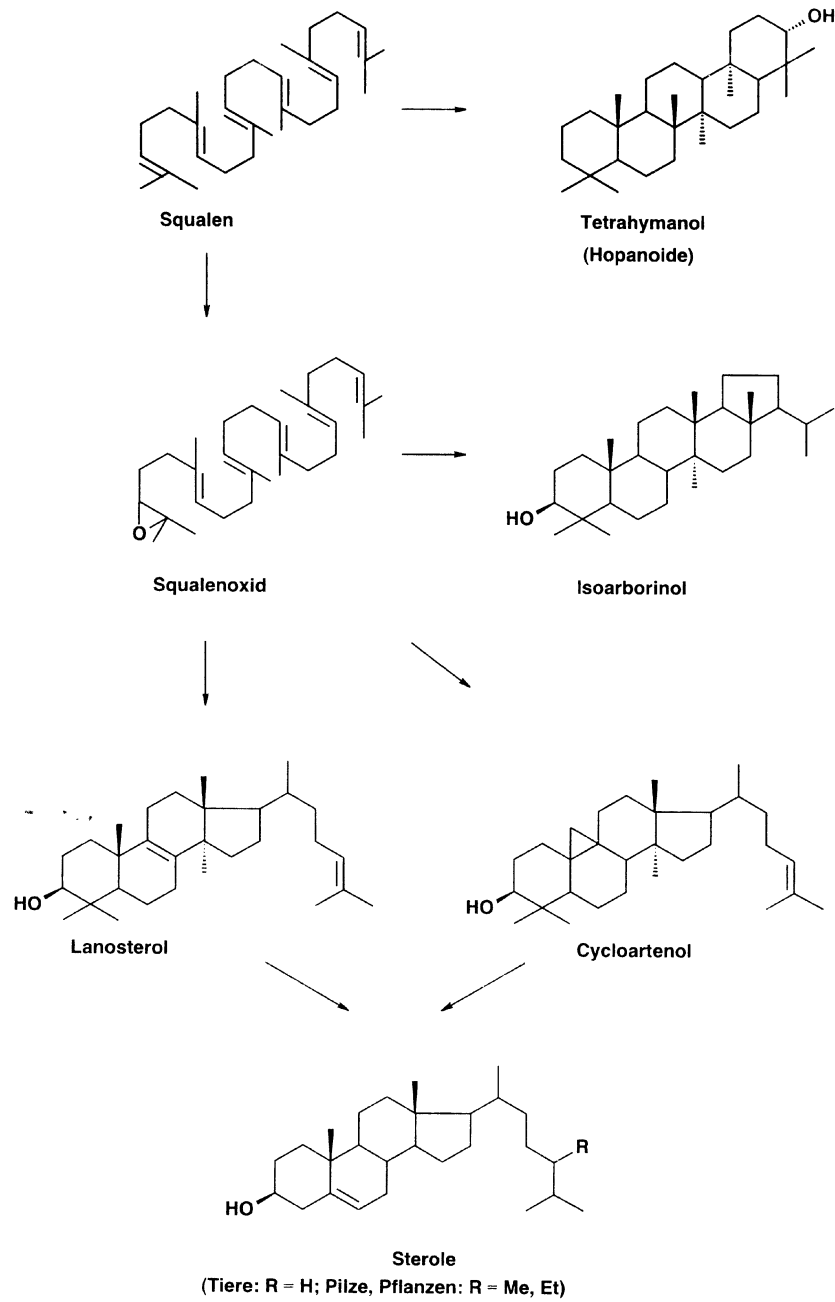


$R^1 = \text{CHO}$; $R^2 = \text{OH}$: Ophiobolin B

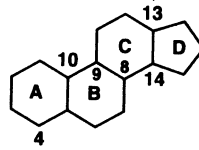
$R^1 = \text{CHO}$; $R^2 = \text{H}$: Ophiobolin C

$R^1 = \text{CH}_3$; $R^2 = \text{H}$: Ophiobolin F

Triterpene

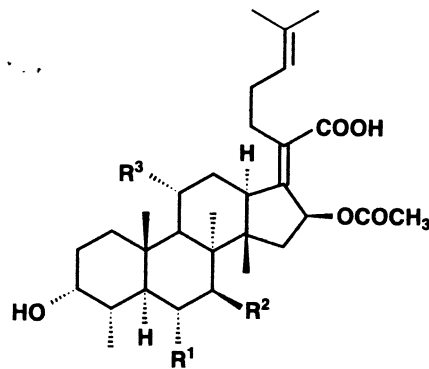


Stellung der Methylgruppen bei verschiedenen tetracyclischen Triterpenen und Steroiden.



| Verbindung | Stellung von Methylgruppen | | | | | | Verknüpfung der Ringe | | |
|----------------|----------------------------|---|---|----|----|----|-----------------------|------------|--------------|
| | 4 | 8 | 9 | 10 | 13 | 14 | A/B | B/C | C/D |
| ■ Protosterol | 2 | 1 | – | 1 | – | 1 | trans | trans | trans |
| ■ Damaradienol | 2 | 1 | – | 1 | – | 1 | trans | trans | trans |
| ■ Fusidinsäure | 1 | 1 | – | 1 | – | 1 | trans | trans | trans |
| ■ Lanosterol | 2 | – | – | 1 | 1 | 1 | trans | x | trans |
| ■ Cycloartenol | 2 | – | 1 | 1 | 1 | 1 | trans | cis | trans |
| ■ Cucurbitane | 2 | – | 1 | – | 1 | 1 | x | cis | trans |
| ■ Steroide | – | – | – | 1 | 1 | – | trans cis, x | trans x | trans cis |

x = sp²-hybridisierte C-Atome

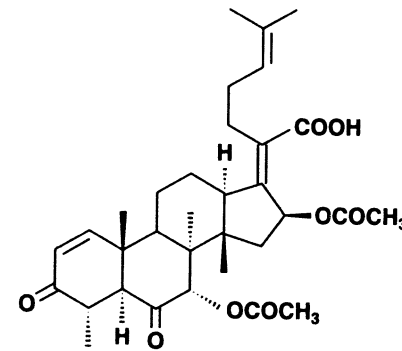


Fusidinsäure :

R¹, R² = H; R³ = OH

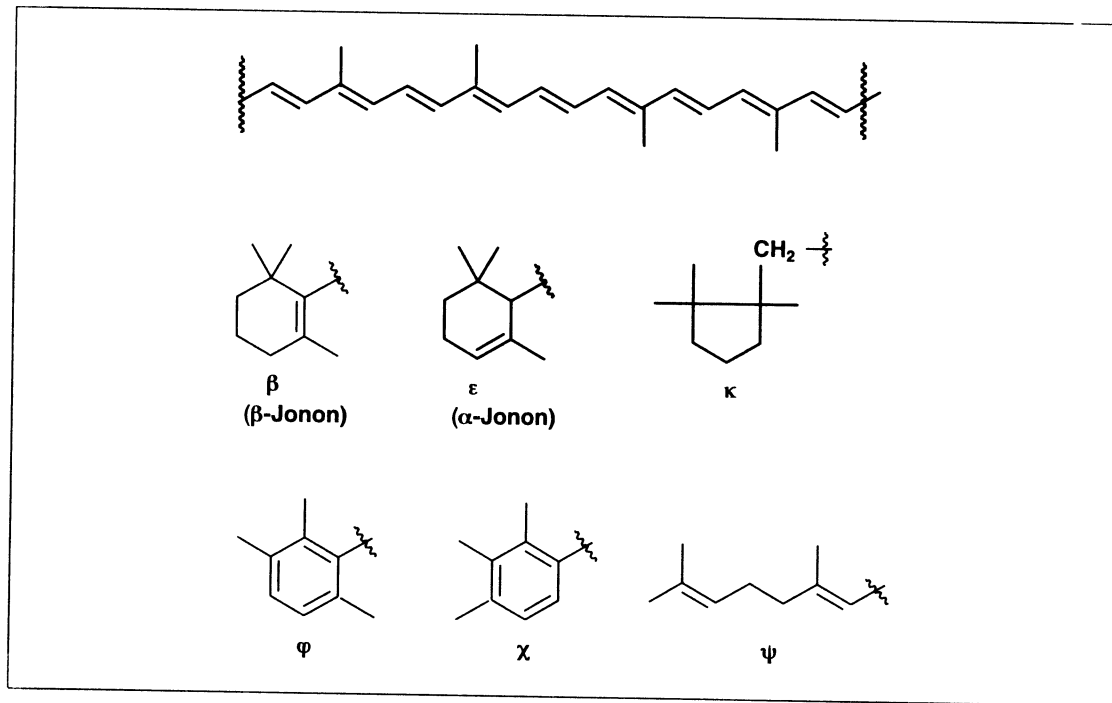
Cephalosporin P₁ :

R¹ = OCOCH₃; R² = OH; R³ = H

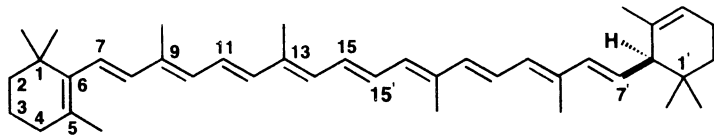


Helvolsäure

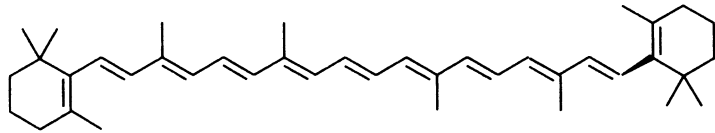
Tetraterpene



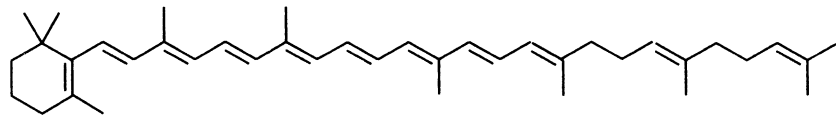
Grundtypen der Carotene.



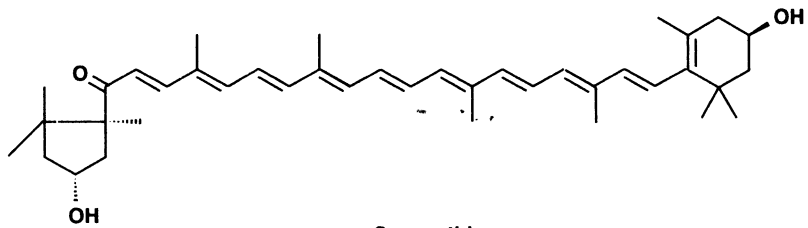
α -Caroten (β,ϵ -Caroten)



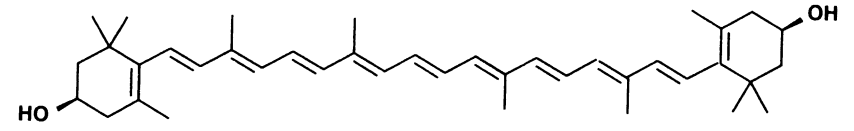
β -Caroten (β,β -Caroten)



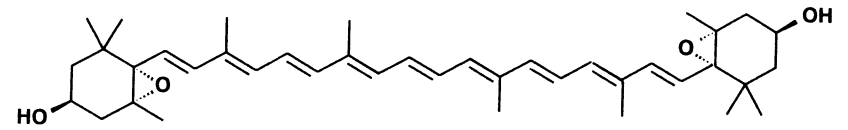
γ -Caroten (β,ψ -Caroten)



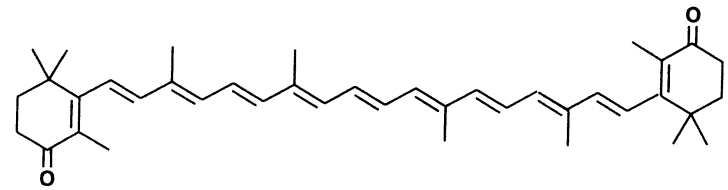
Capsanthin
(3R,3'S,5'R)-3,3'-Dihydroxy- β,χ -caroten-6'-on



Zeaxanthin
(3R,3'R)- β,β -Caroten-3,3'-diol

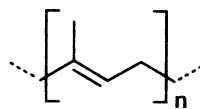


Violaxanthin

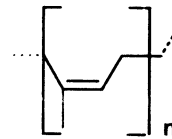


Canthaxanthin

Polyterpene

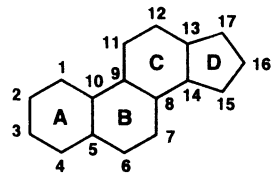


trans-Polypren

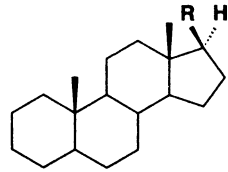


cis-Polypren

Steroide



Gonan



Androstan (Androgene): R = H

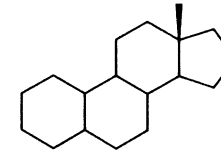
Pregnan (Gestagene, NNR-Hormone): R = C₂H₅

Cholan (Gallensäuren): R = CH(CH₃)CH₂CH₂CH₃

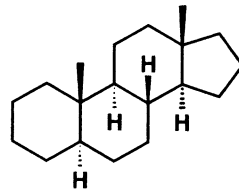
Cholestan (Zoosterole): R = CH(CH₃)CH₂CH₂CH₂CH(CH₃)₂

Ergostan (Mycosterole): R = CH(CH₃)CH₂CH₂CH(CH₃)CH(CH₃)₂

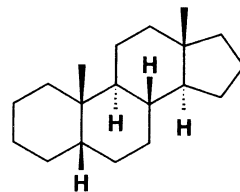
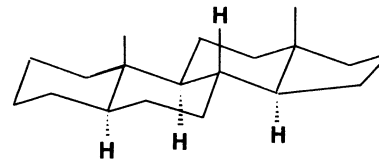
Stigmastan (Phyosterole): R = CH(CH₃)CH₂CH₂CH(C₂H₅)CH(CH₃)₂



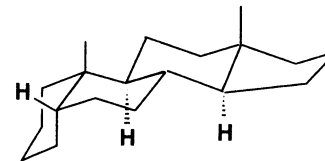
Estran (Estrogene)



5α-Reihe

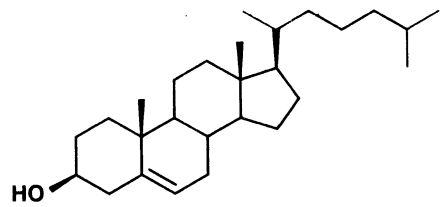


5β-Reihe

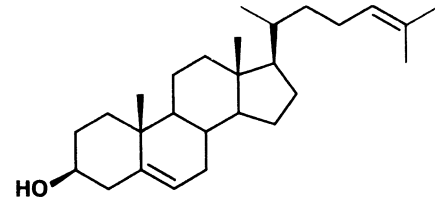


Stellung der Substituenten an den Verknüpfungsstellen der Ringe bei Steroiden und verschiedenen Triterpenen (X = Doppelbindungen).

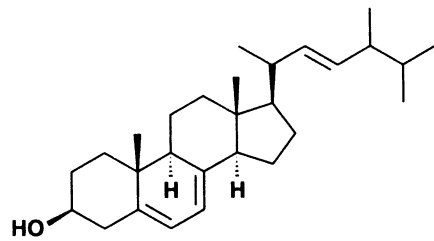
| Verbindung | 5/10 | 8/9 | 13/14 |
|---|---------------------------------------|----------------|----------------|
| ■ Protosterol, Fusidinsäure u. a. Steroidantibiotika | α/β | α/β | α/β |
| ■ Lanosterol | α/β | X | β/α |
| ■ pentacycl. Triterpene | α/β | β/α | X |
| ■ Sterole | X | β/α | |
| ■ Cholestanol | α/β | β/α | β/α |
| ■ Koprostanol | β/β | β/α | β/α |
| ■ Gallensäuren | β/β | β/α | β/α |
| ■ Steroidhormone | X | β/α | β/α |
| ■ Steroidsapogenine | β/α , β/β oder X | β/α | β/α |
| ■ Steroidalkaloide | β/α , β/β oder X | β/α | β/α |
| ■ Cardenolide, Bufadienolide | β/β | β/α | β/β |
| ■ Uzarigenin | β/α | β/α | β/β |
| ■ Digitanole | X | β/α | β/β |
| ■ Batrachotoxin | β/β | β/α | β/β |
| ■ Ecdysone | β/β | X | β/α |



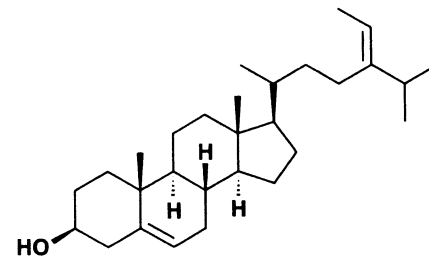
Cholesterol



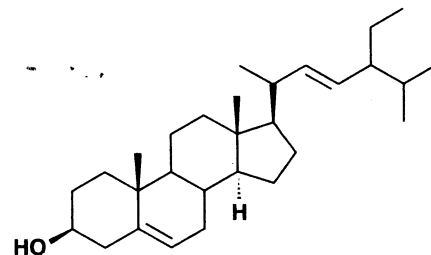
24-Dehydrocholesterol



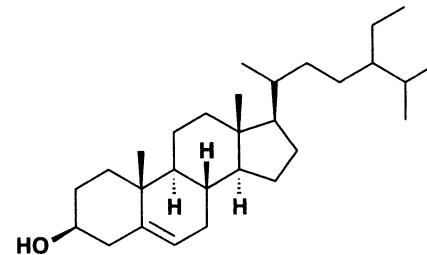
Ergosterol



Fucosterol



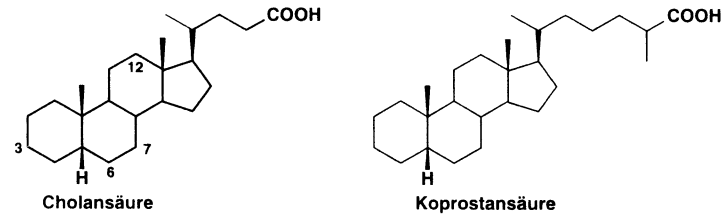
Stigmasterol



β -Sitosterol

Sterole.

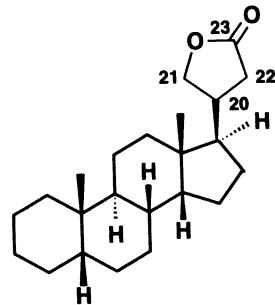
Gallensäuren



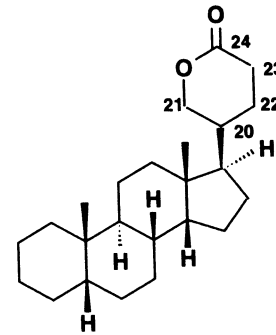
| Name | Grundkörper | Substituenten in Stellung | | | | Vorkommen | Konjugation* |
|----------------------------|----------------|---------------------------|------------|------------|-------------|------------------------|--------------|
| | | 3 α | 6 α | 7 α | 12 α | | |
| ■ Cholsäure | Cholansäure | OH | H | OH | OH | Säugetiere | Tau, Gly |
| ■ Desoxycholsäure | Cholansäure | OH | H | H | OH | Säugetiere | Tau, Gly |
| ■ Hyodesoxycholsäure | Cholansäure | OH | OH | H | H | Säugetiere (Schwein) | |
| ■ Chenodesoxycholsäure | Cholansäure | OH | H | OH | H | Säugetiere | Tau, Gly |
| ■ Lithocholsäure | Cholansäure | OH | H | H | H | Säugetiere (in Spuren) | Tau, Gly |
| ■ Trihydroxykoprostansäure | Koprostansäure | OH | H | OH | OH | Reptilien, Amphibien | Tau |

*Tau = Taurin, Gly = Glycin

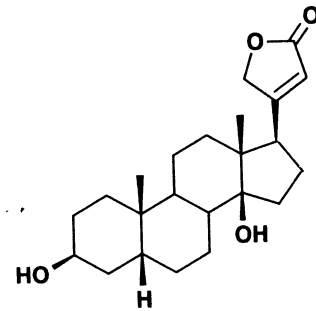
Cardenolide und Bufadienolide



5β,14β-Cardanolid



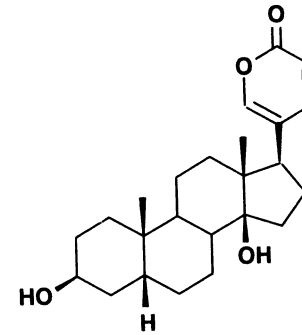
5β,14β-Bufanolid



Digitoxigenin

**3β,14-Dihydroxy-5β,14β-
card-20(22)-enolid**

Cardenolid-Typ

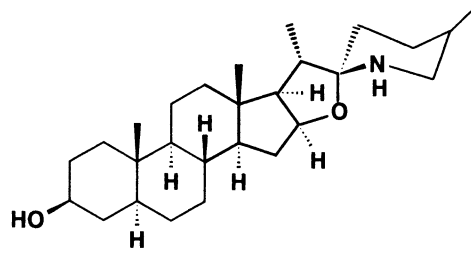


Bufalin

**3β,14-Dihydroxy-5β,14β-
bufa-20,22-dienolid**

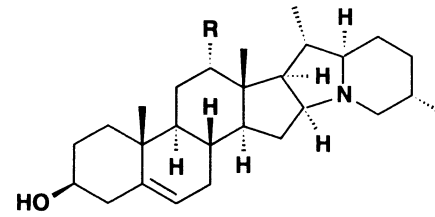
Bufadienolid-Typ

Steroidalkaloide



Tomatidin

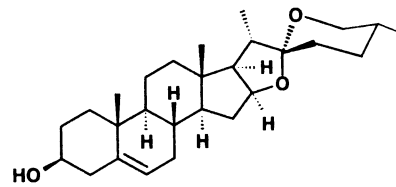
Spirosolan-Typ



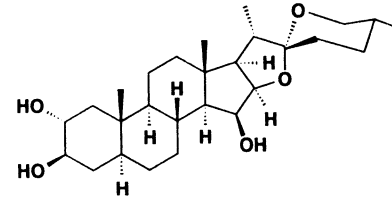
Solanidin (R = H)

Rubijervin (R = OH)

Solanidan-Typ

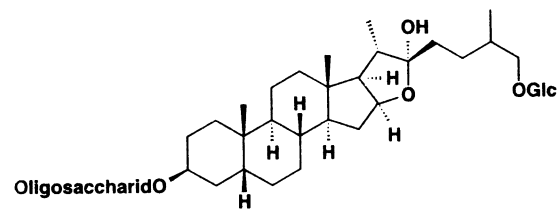


Diosgenin
(Δ-Reihe)

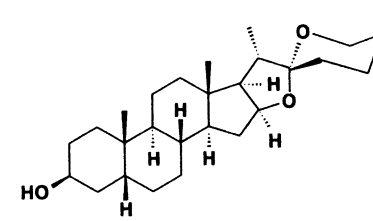


Digitogenin
(5α-Reihe)

Digitonin = Digitogenin + 2Glc + 2 Gal+ Xyl



Sarsaparillosid
(5β-Reihe)



Sarsapogenin
(25S)-5β-Spirostan-3β-ol

Steroidsaponine bzw. -sapogenine.