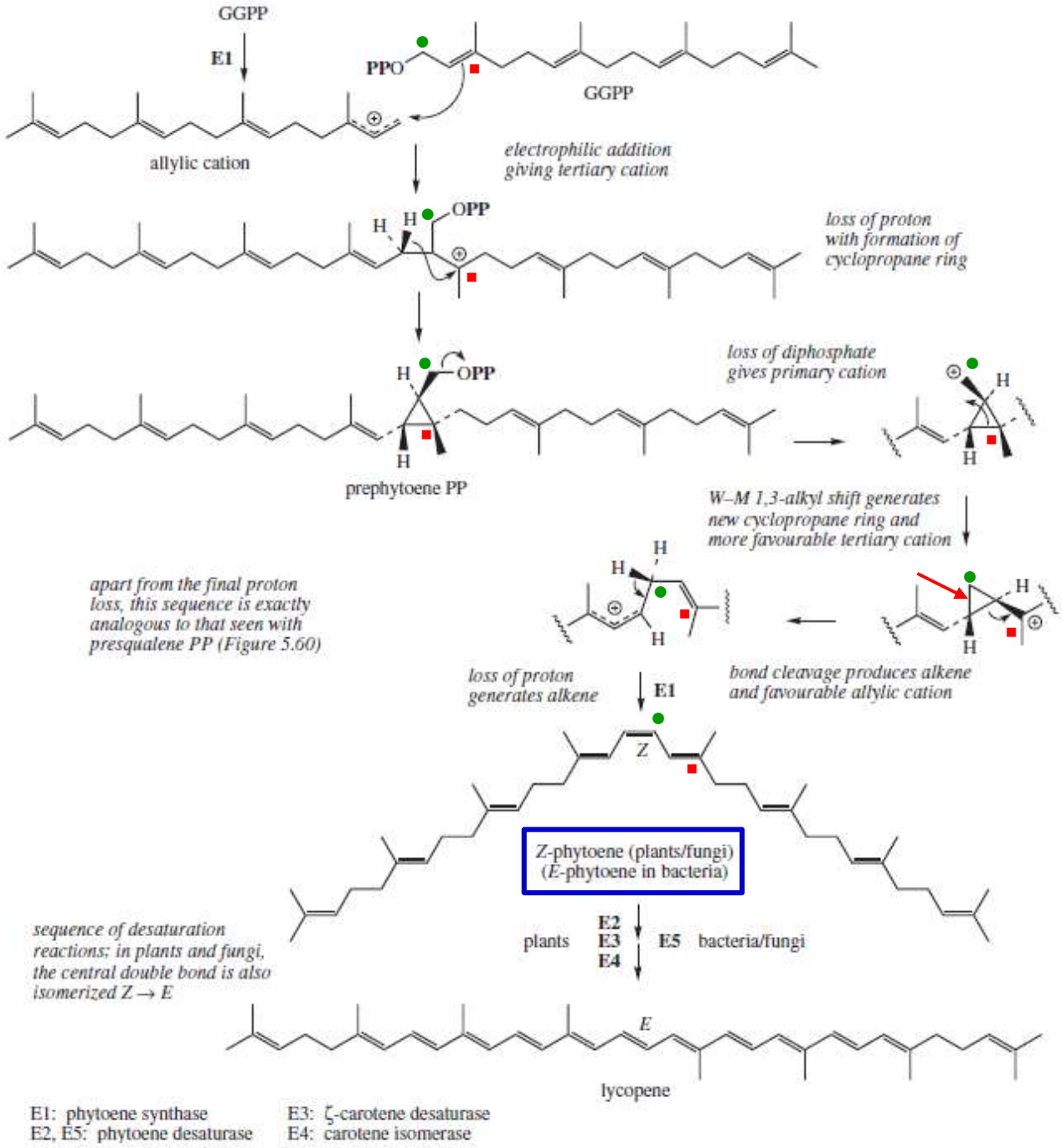
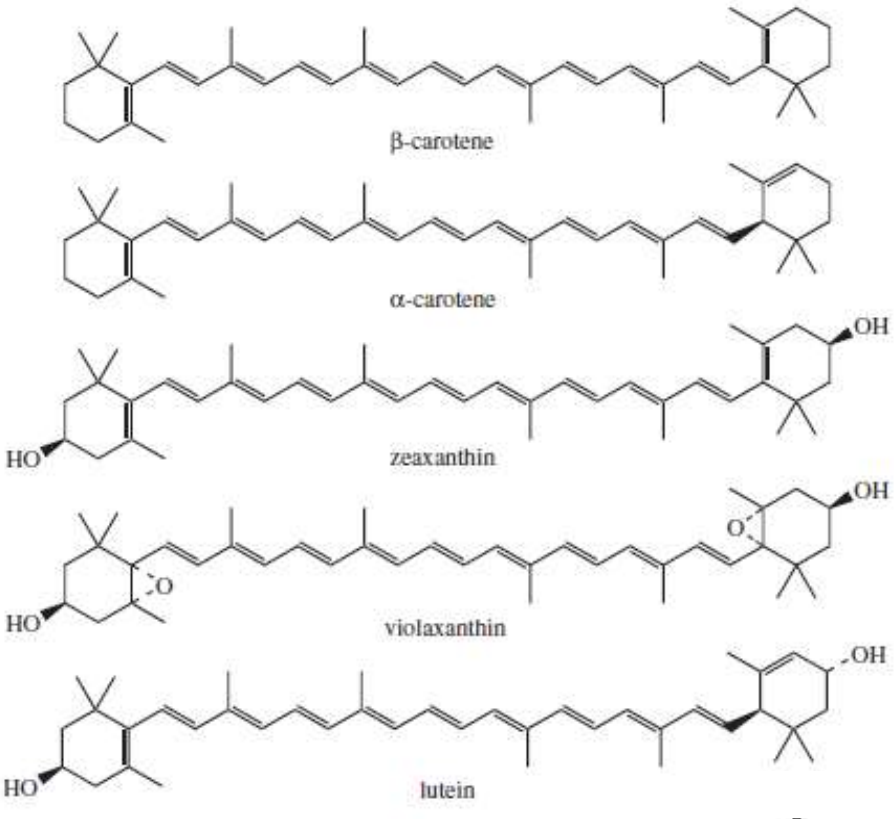
Dal geranilgeranil pirofosfato al fitene e ai carotenoidi

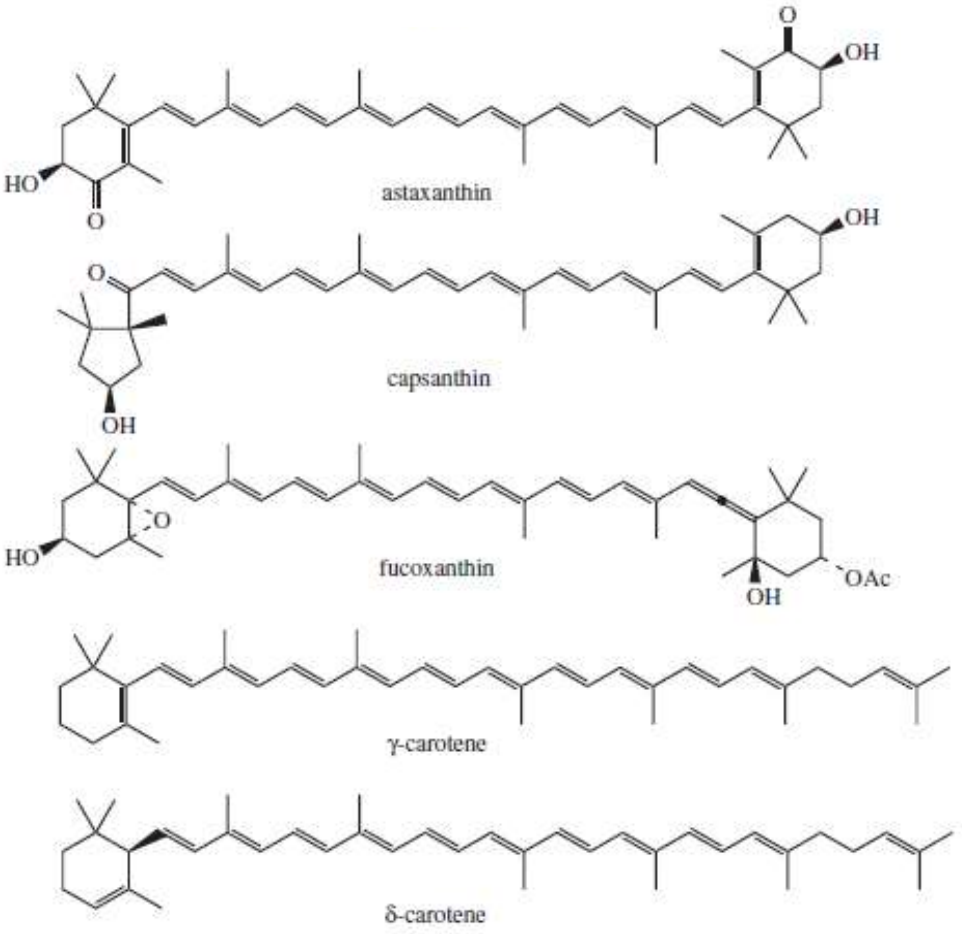

GGPP
E1
PPO
GGPP
allylic cation
electrophilic addition
giving tertiary cation
OPP
loss of proton
with formation of
cyclopropane ring
loss of diphosphate
gives primary cation
prephytoene PP
W–M 1,3-alkyl shift generates
new cyclopropane ring and
more favourable tertiary cation
apart from the final proton
loss, this sequence is exactly
analogous to that seen with
presqualene PP (Figure 5.60)
loss of proton
generates alkene
E1
bond cleavage produces alkene
and favourable allylic cation
Z
Z-phytoene (plants/fungi)
(E-phytoene in bacteria)
sequence of desaturation
reactions; in plants and fungi,
the central double bond is also
isomerized Z → E
plants
E2
E3
E4
E5
bacteria/fungi
E
lycopene
E1: phytoene synthase
E2, E5: phytoene desaturase
E3: ζ-carotene desaturase
E4: carotene isomerase

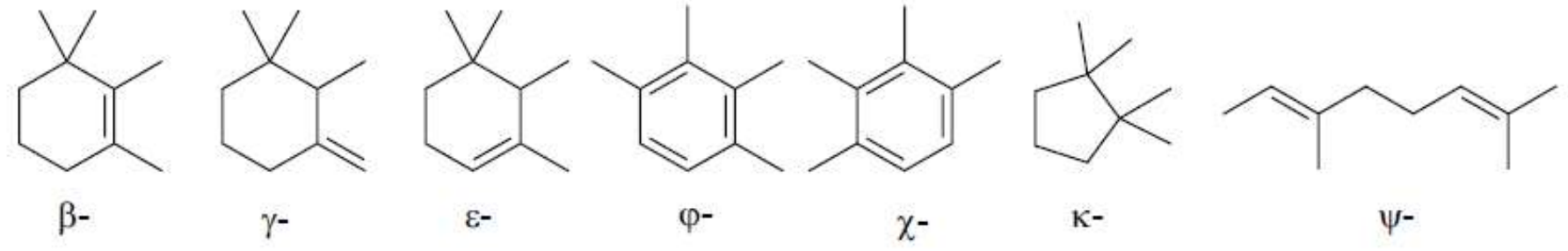
Carotenoidi

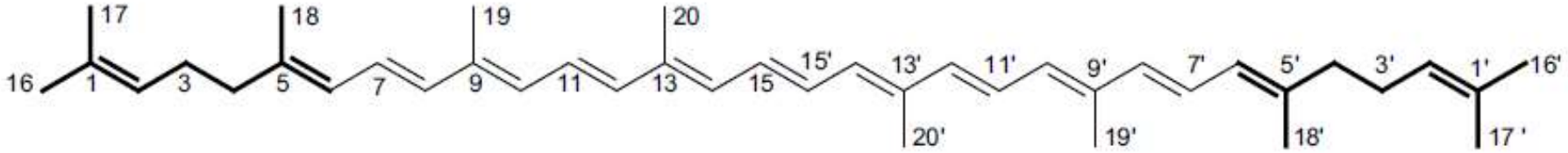


Riavvolgimento della parte terminale della catena

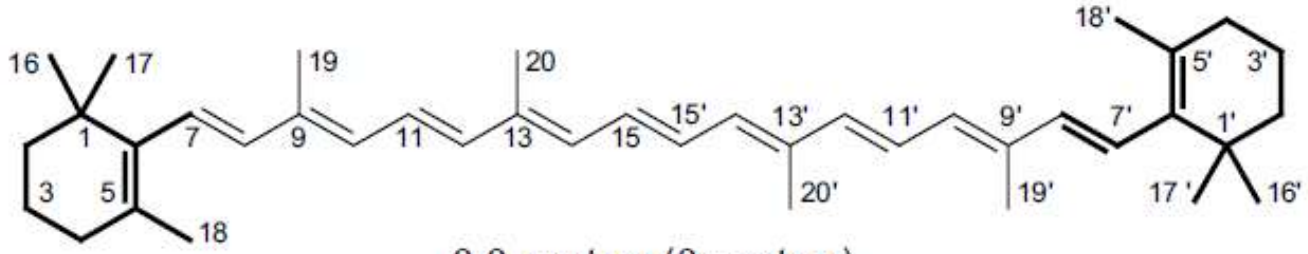
Introduzione di funzioni ossigenate



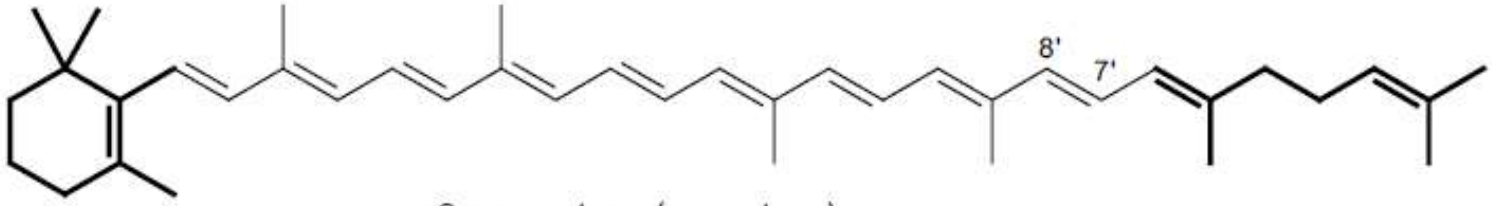




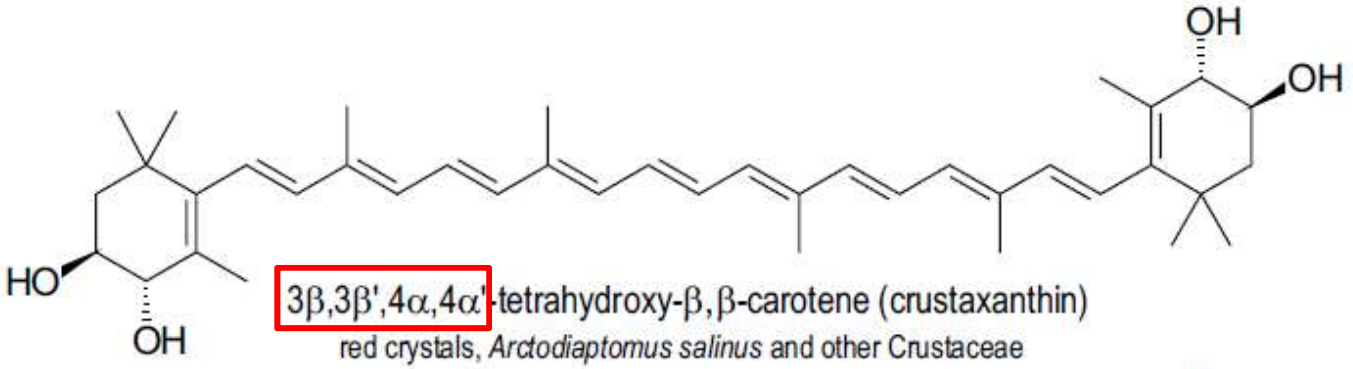
ψ,ψ-carotene (lycopene)



β,β-carotene (β-carotene)

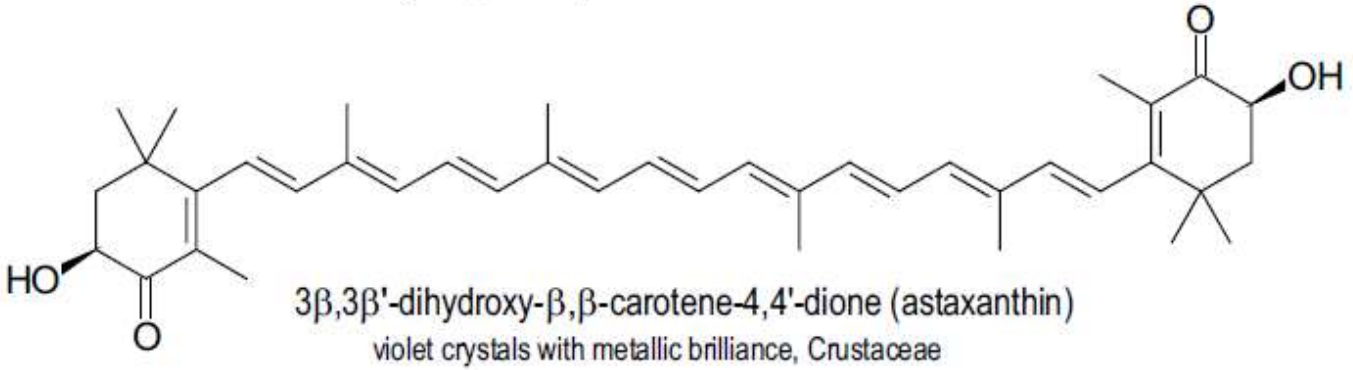


β,ψ-carotene (γ-carotene)



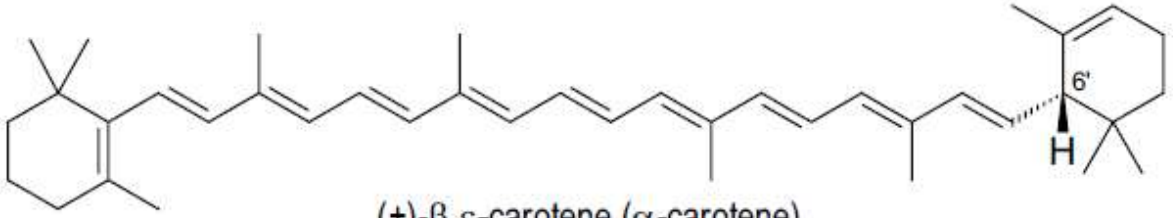
3β,3β',4α,4α'-tetrahydroxy-β,β-carotene (crustaxanthin)

red crystals, *Arctodiaptomus salinus* and other Crustaceae



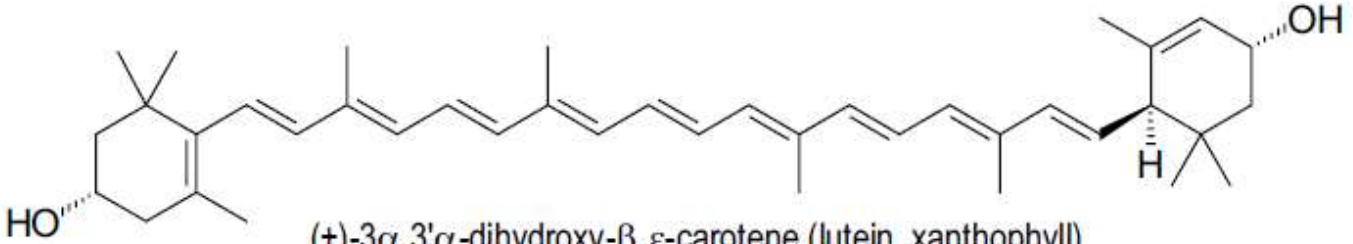
3β,3β'-dihydroxy-β,β-carotene-4,4'-dione (astaxanthin)

violet crystals with metallic brilliance, Crustaceae



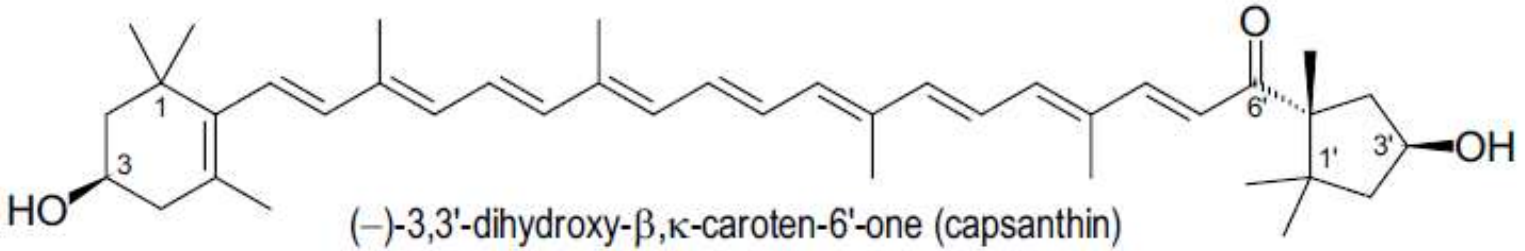
(+)-β,ε-carotene (α-carotene)

violet crystals, widely spread, vitamin A active



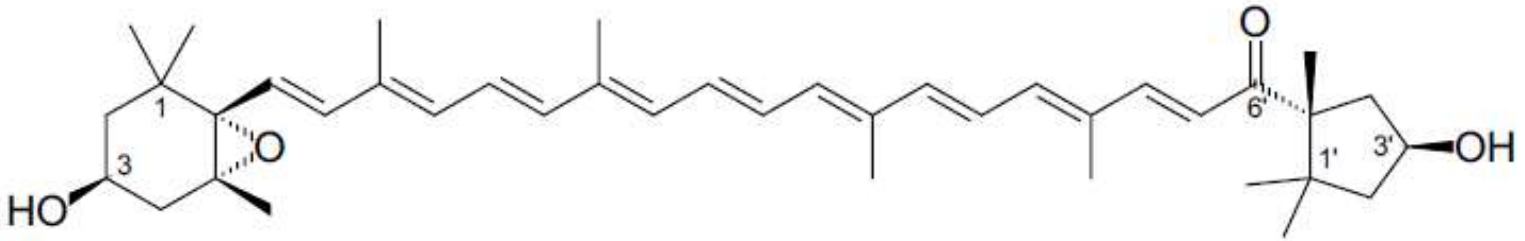
(+)-3α,3'α-dihydroxy-β,ε-carotene (lutein, xanthophyll)

copper red crystals, egg yolk, leaves of all higher plants, *Staphylococcus aureus*



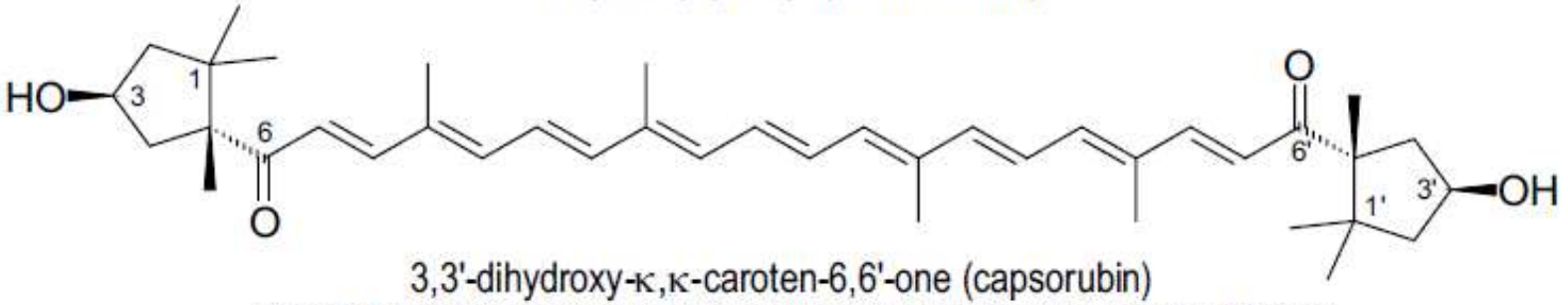
(–)-3,3'-dihydroxy-β,κ-caroten-6'-one (capsanthin)

red crystals, paprika (*Capsicum annuum*)



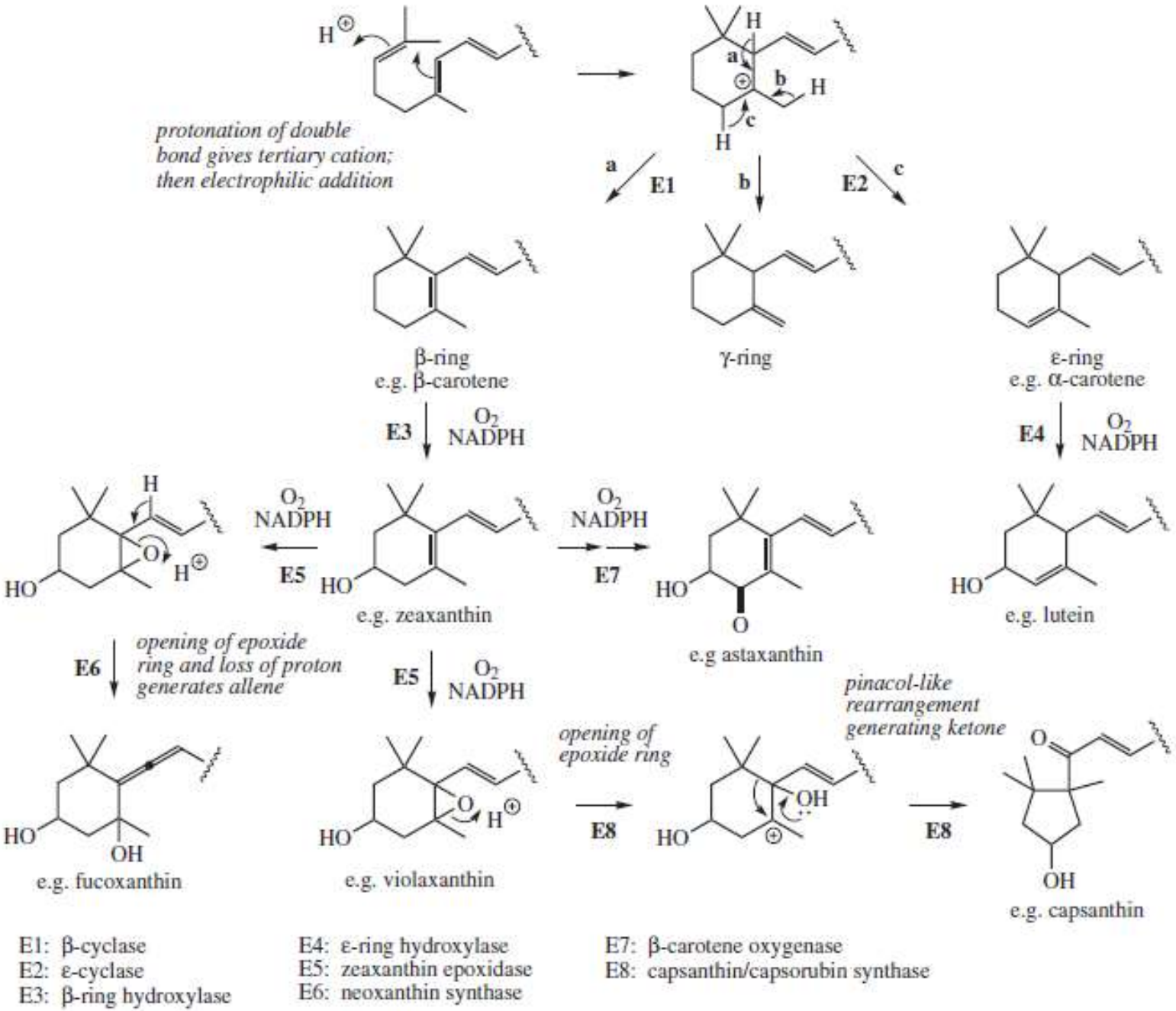
(+)-5α,6α-epoxy-3,3'-dihydroxy-β,κ-caroten-6'-one (capsanthin-5,6-epoxide)

red crystals, paprika (*Capsicum annuum*)

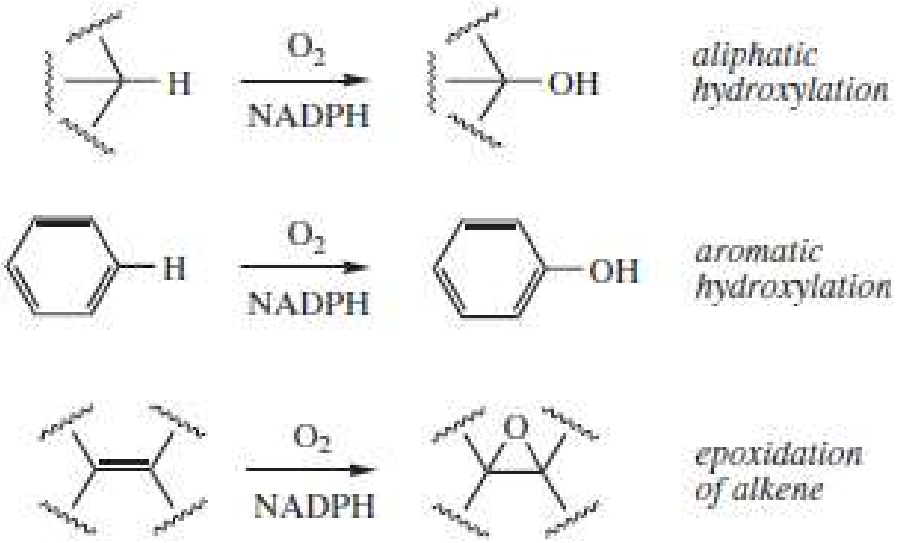


3,3'-dihydroxy-κ,κ-caroten-6,6'-one (capsorubin)

violet red crystals, paprika (*Capsicum annuum*), *Lilium bulbiferum* and other Liliaceae


protonation of double bond gives tertiary cation; then electrophilic addition
a
E1
b
E2
c
β-ring
e.g. β-carotene
γ-ring
ε-ring
e.g. α-carotene
E3
O2
NADPH
E4
O2
NADPH
O2
NADPH
E5
O2
NADPH
E7
e.g. zeaxanthin
e.g astaxanthin
e.g. lutein
E6
opening of epoxide ring and loss of proton generates allene
E5
O2
NADPH
opening of epoxide ring
E8
pinacol-like rearrangement generating ketone
E8
e.g. fucoxanthin
e.g. violaxanthin
e.g. capsanthin
E1: β-cyclase
E2: ε-cyclase
E3: β-ring hydroxylase
E4: ε-ring hydroxylase
E5: zeaxanthin epoxidase
E6: neoxanthin synthase
E7: β-carotene oxygenase
E8: capsanthin/capsorubin synthase

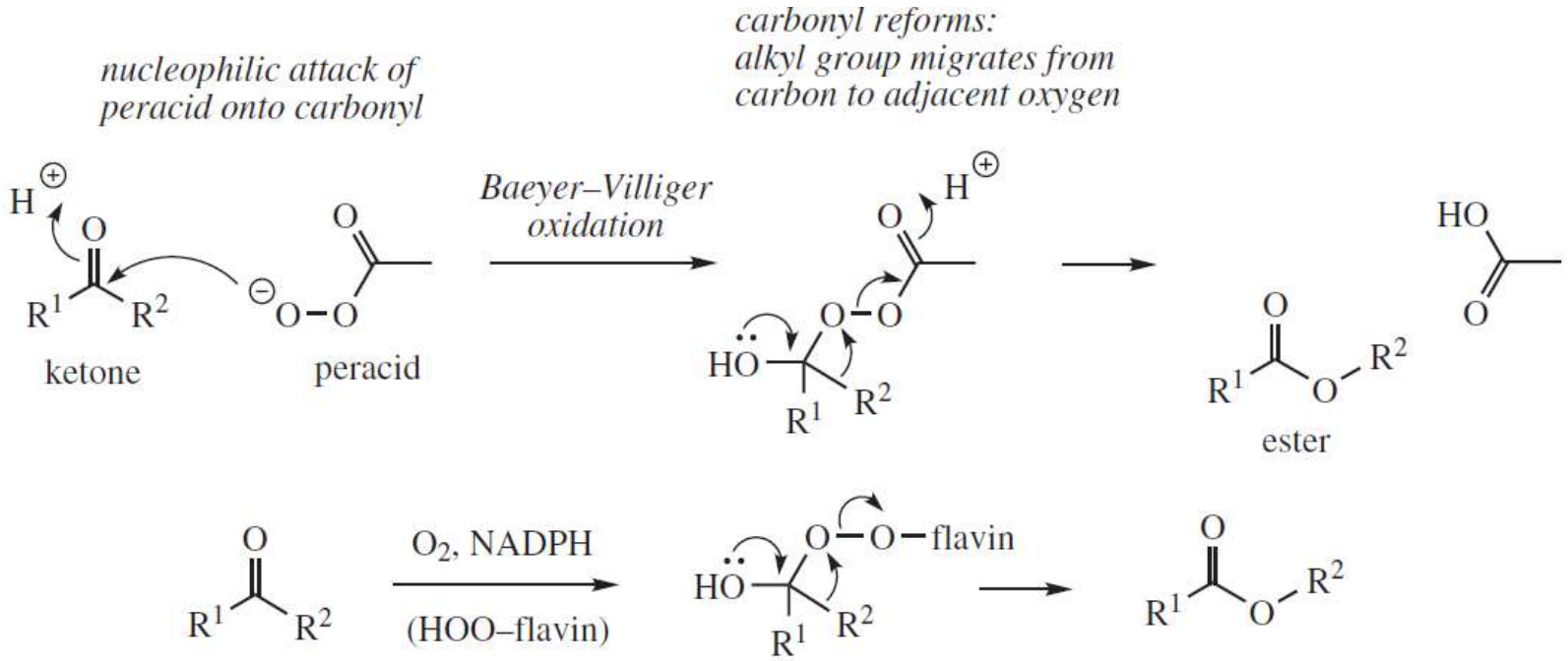
Monooxygenases



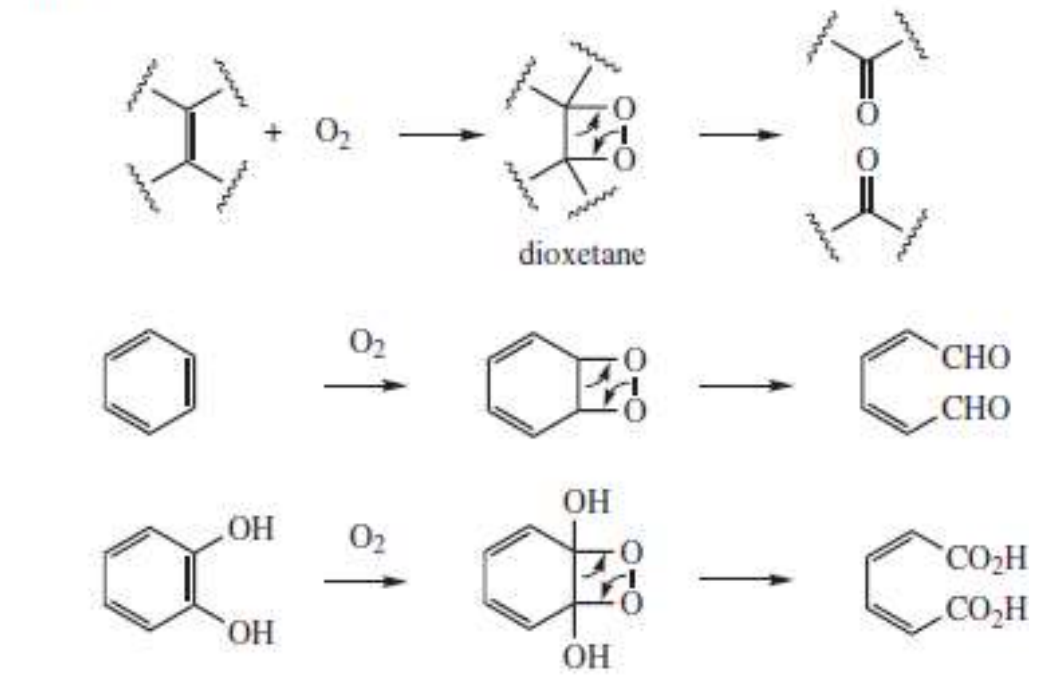
Solo un atomo di ossigeno viene inserito nel metabolita.

Il secondo atomo viene trasformato in acqua, e questa riduzione richiede l'intervento di un riducente!

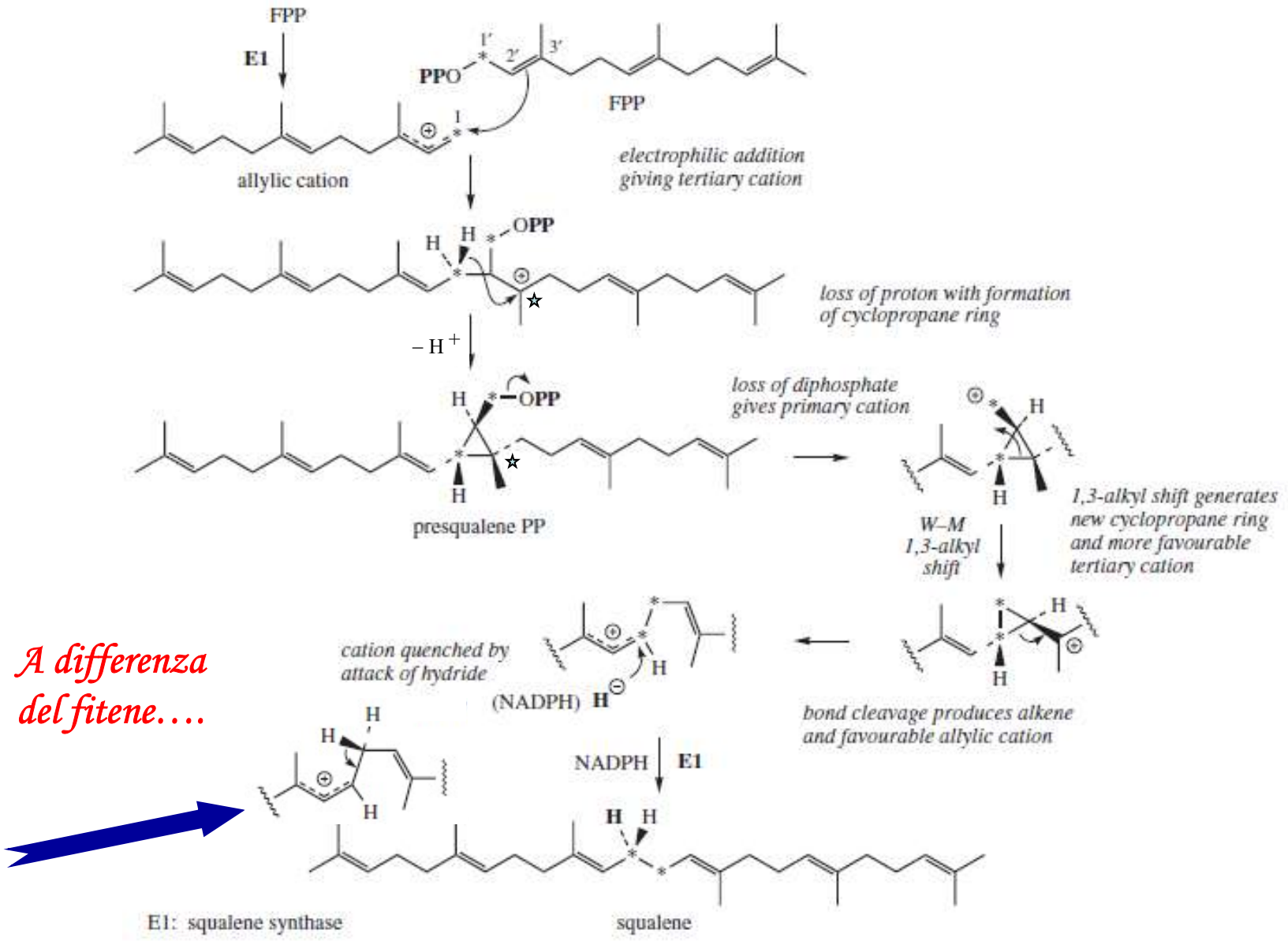
Baeyer–Villiger Monooxygenases



Dioxygenases

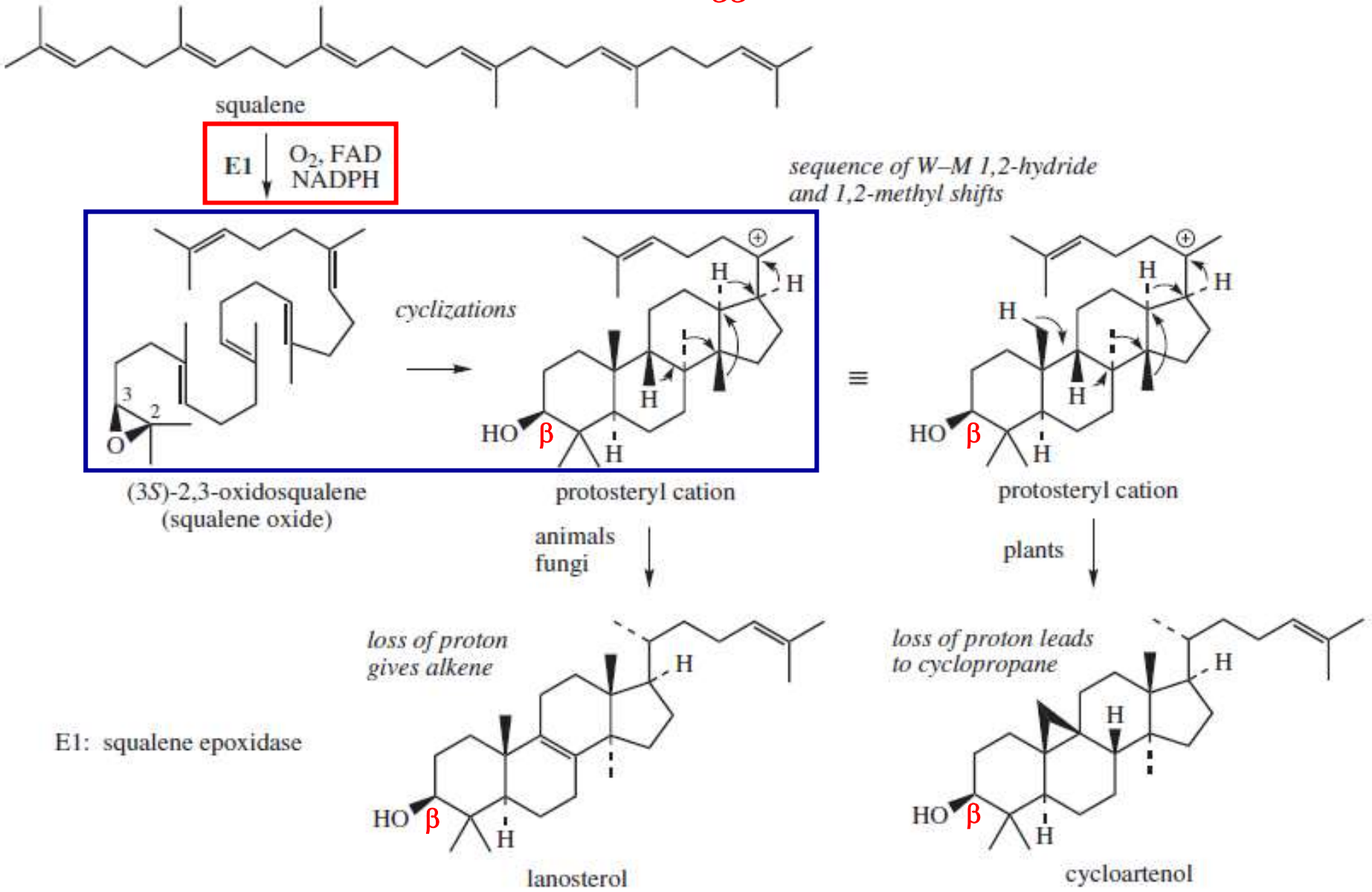


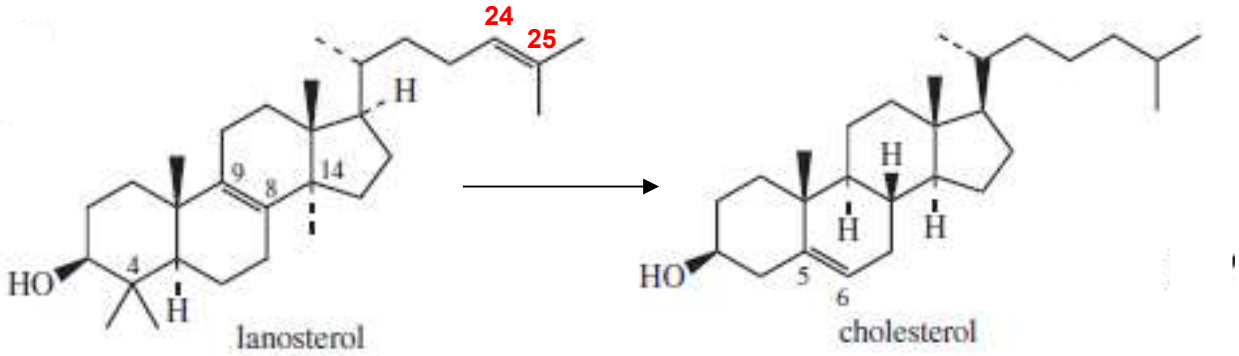
Dal farnesil pirofosfato allo squalene ed al colesterolo



A differenza del fitene….

…..in viaggio verso il colesterolo!



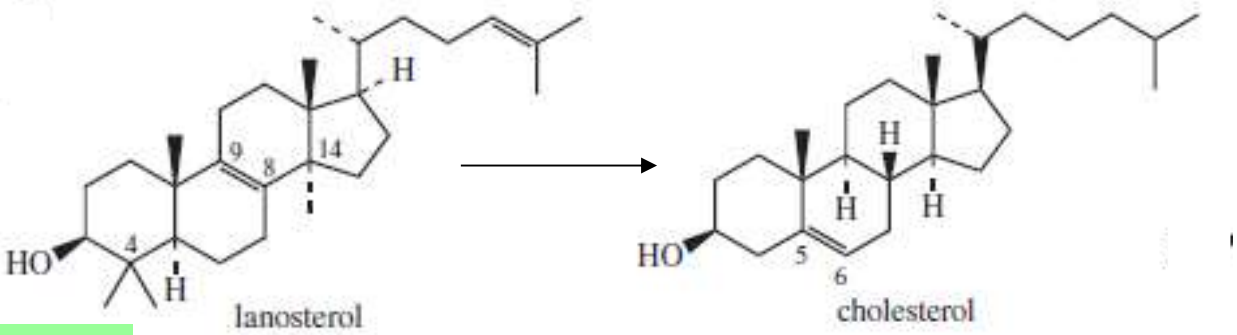


La trasformazione del lanosterolo in colesterolo richiede una ventina di passaggi, con una sequenza che può variare da specie a specie, ma che deve comunque comportare:

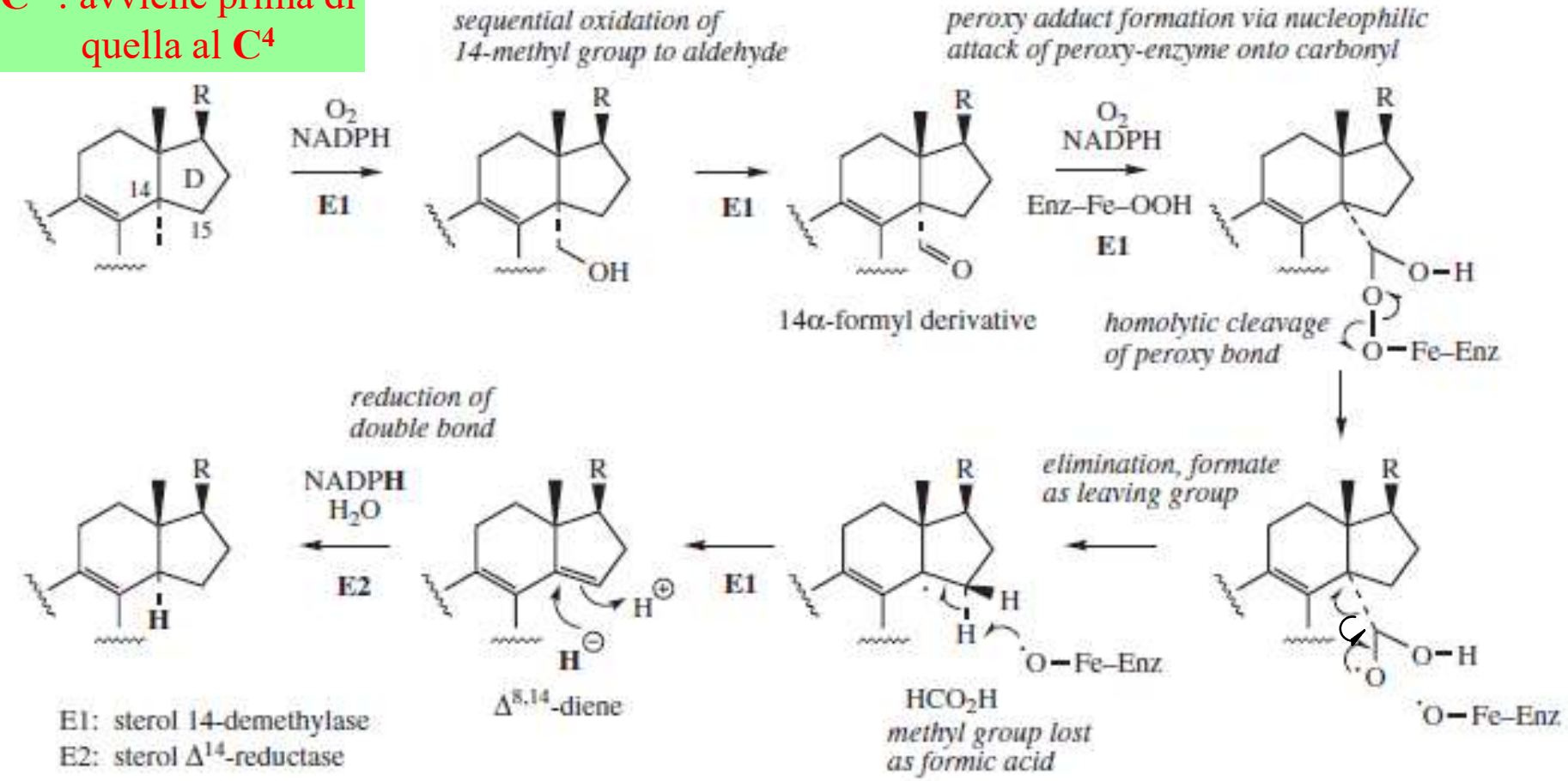
La riduzione del Δ^{24}

La isomerizzazione del Δ^{8} a Δ^{5}

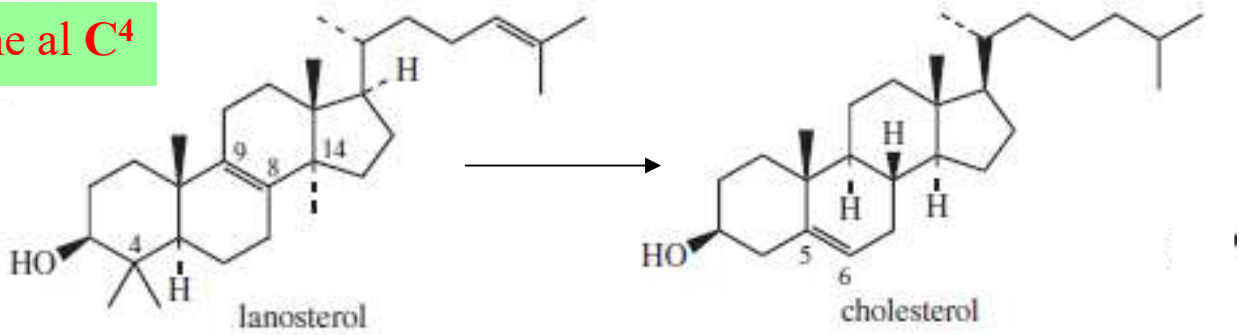
La demetilazione al C^{4} e al C^{14}

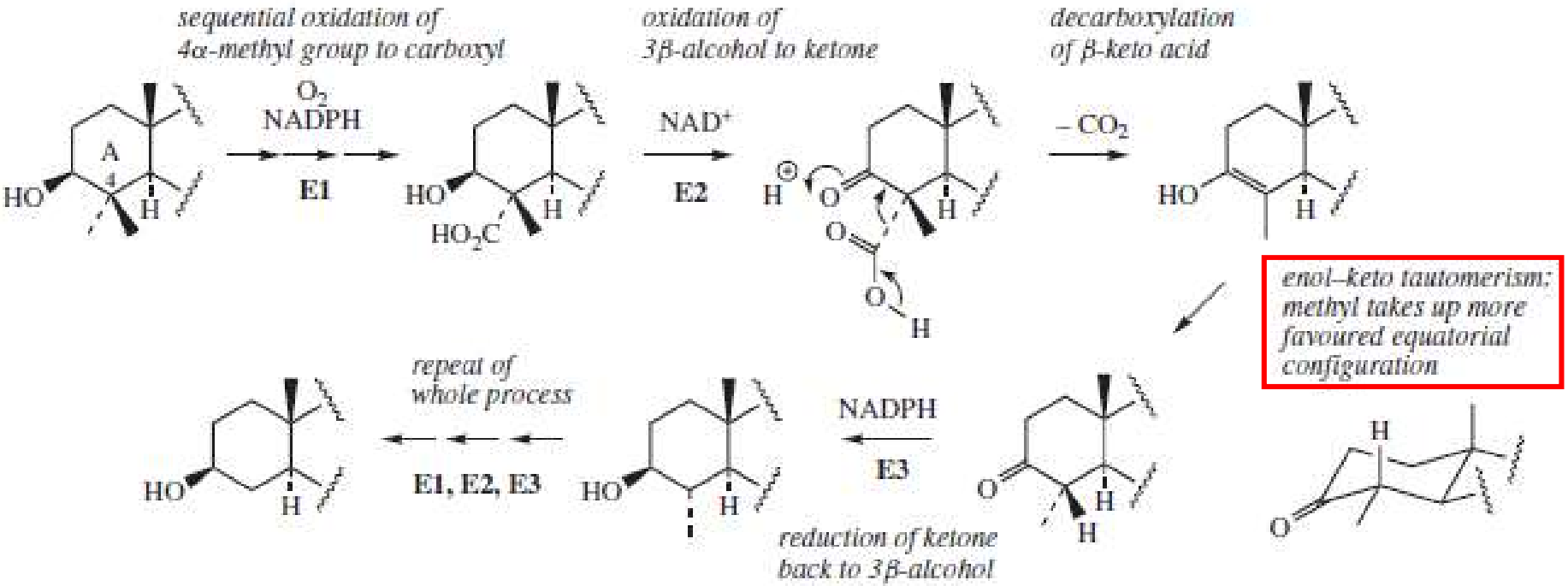


Demetilazione al C^{14}: avviene prima di quella al C^4



Demetilazione al C^4

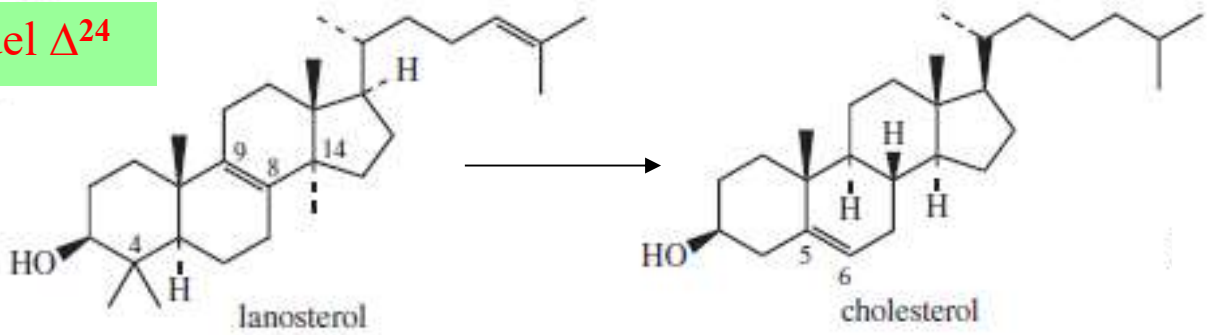


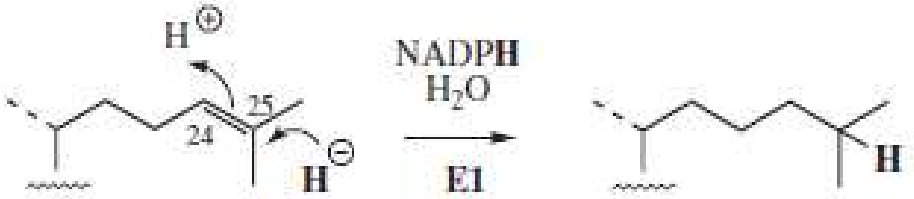


E1+E2+E3: sterol 4α-methyl oxidase (sterol C-4 demethylase)
E1: methylsterol monooxygenase

E2: sterol-4α-carboxylate 3-dehydrogenase (decarboxylating)
E3: 3-ketosteroid reductase

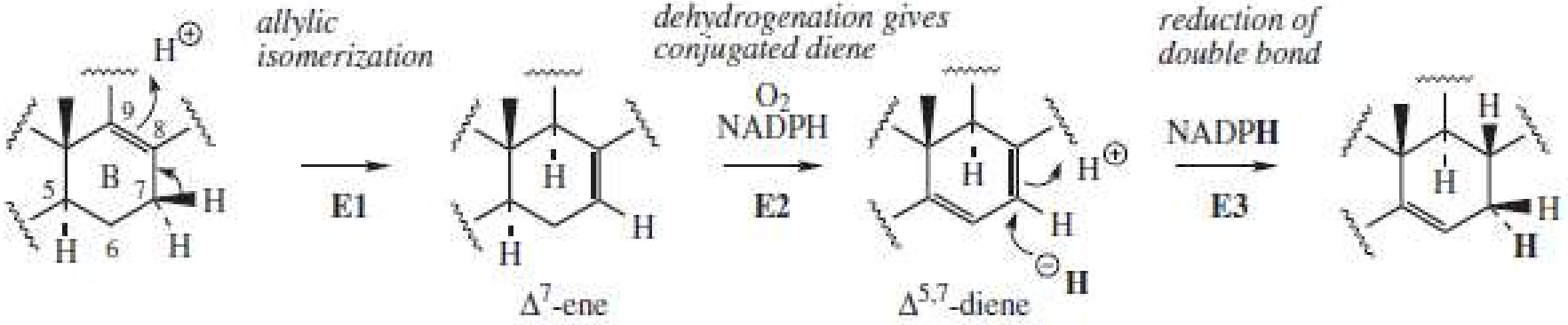
Riduzione del Δ^{24}



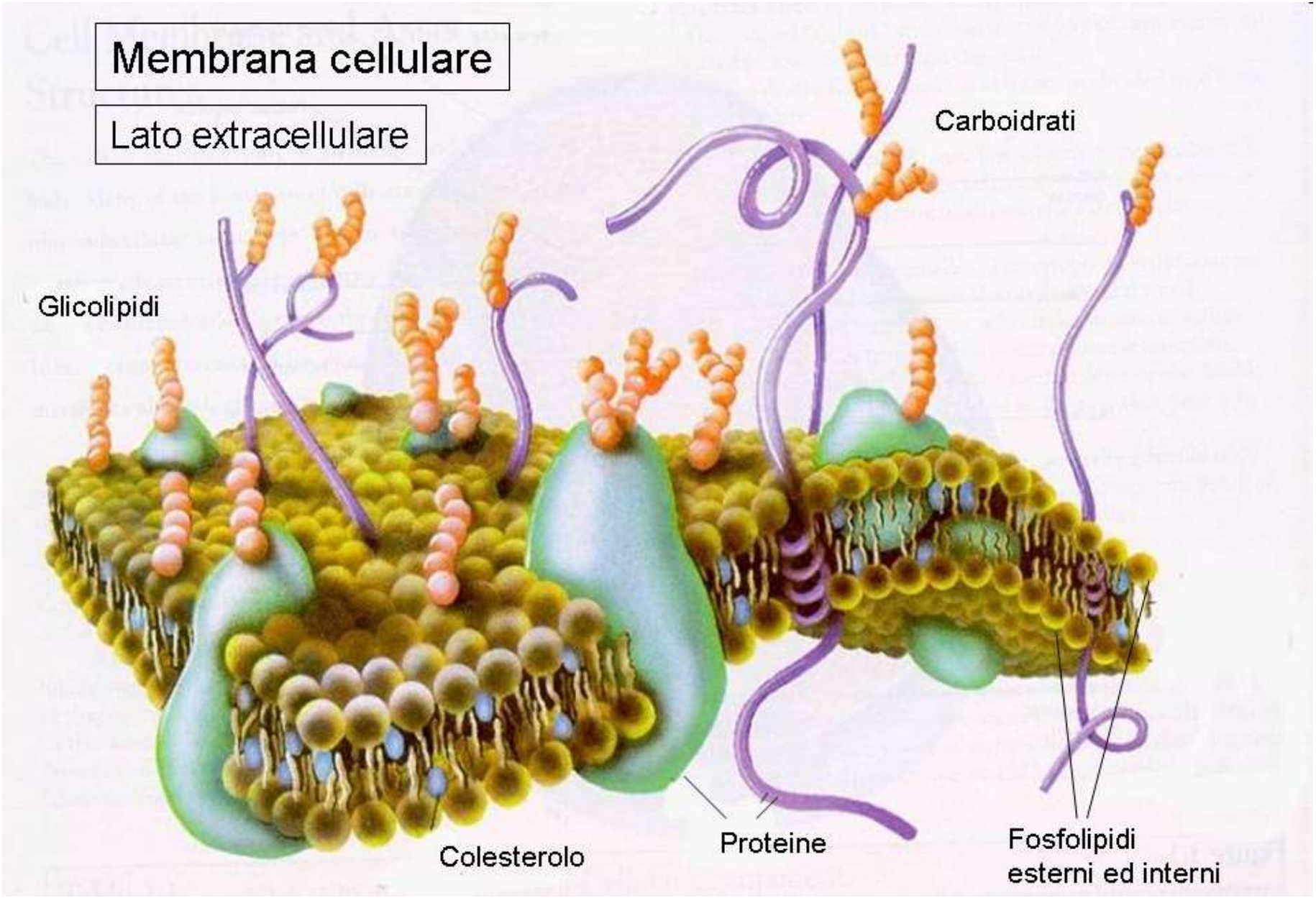


E1: sterol Δ^{24}-reductase

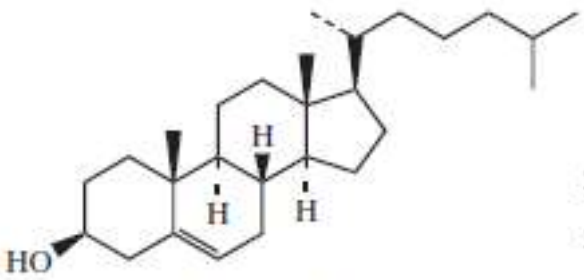
Isomerizzazione del Δ^{8} a Δ^{5}



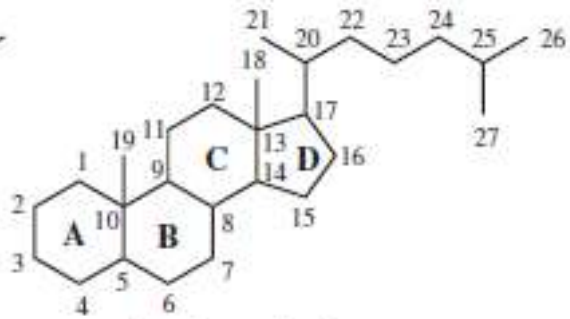
E1: sterol Δ^{8}-Δ^{7}-isomerase (cholestenol Δ-isomerase)
E2: Δ^{7}-sterol Δ^{5}-dehydrogenase (lathosterol oxidase)
E3: sterol Δ^{7}-reductase (7-dehydrocholesterol reductase)


Membrana cellulare
Lato extracellulare
Carboidrati
Glicolipidi
Colesterolo
Proteine
Fosfolipidi
esterni ed interni

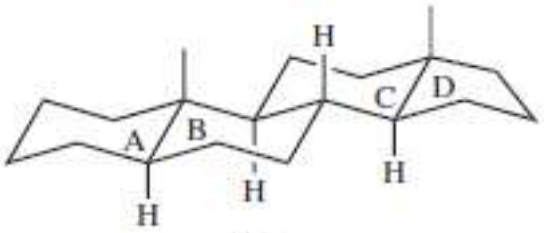
Cause della diversificazione strutturale nell'ambito degli steroidi



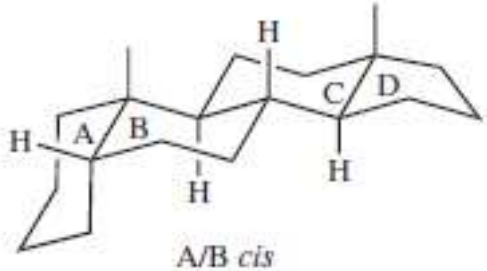
cholesterol



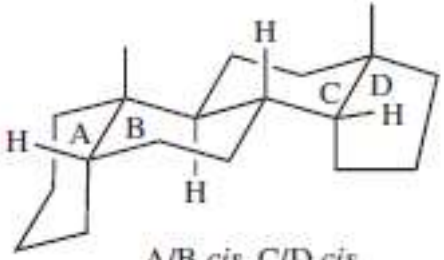
steroid numbering



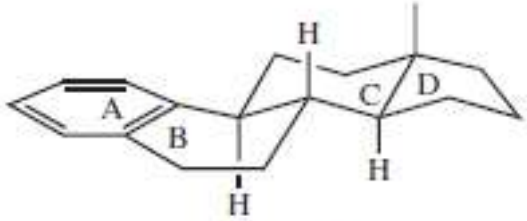
all-trans



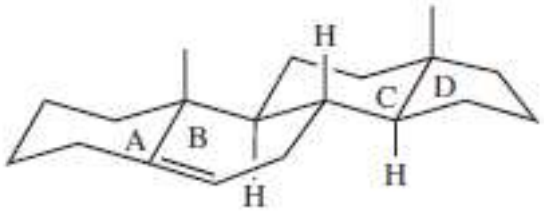
A/B *cis*



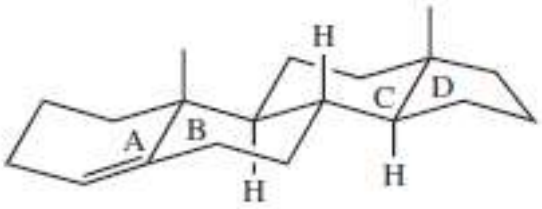
A/B *cis*, C/D *cis*



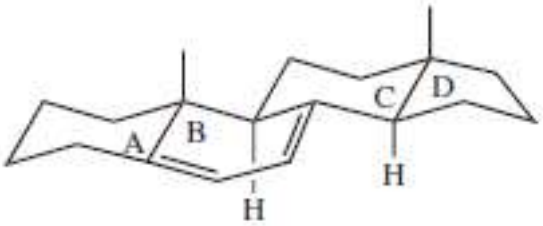
A ring aromatic



Δ^5-unsaturation

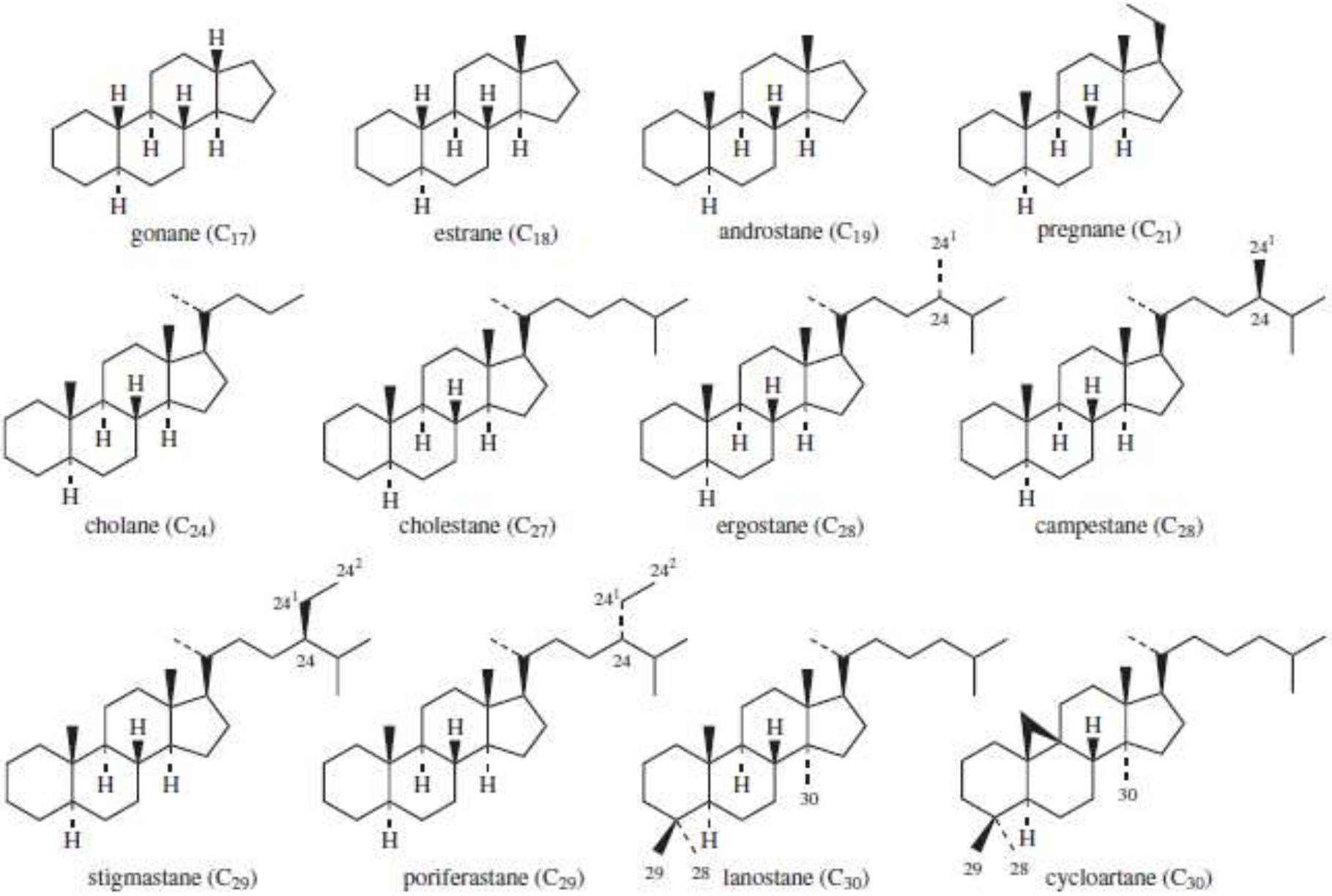


Δ^4-unsaturation



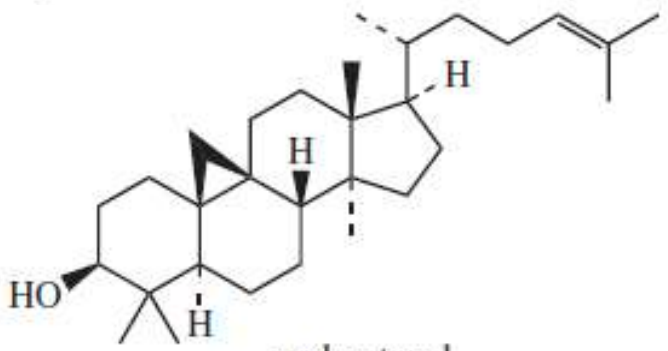
$\Delta^{5,7}$-unsaturation

Cause della diversificazione strutturale nell'ambito degli steroidi

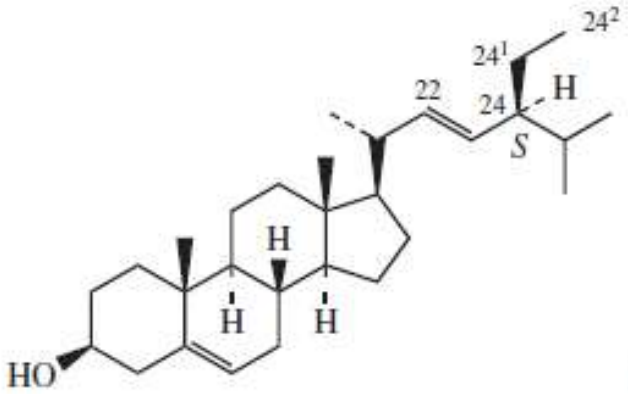


Fitosteroli

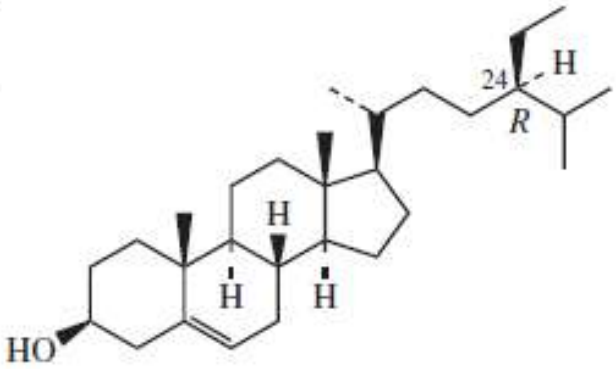
precursore



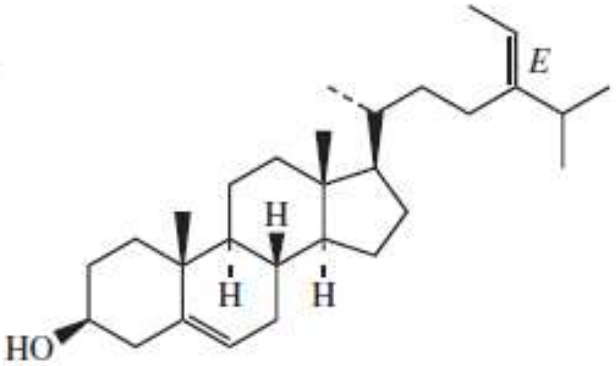
cicloartenol



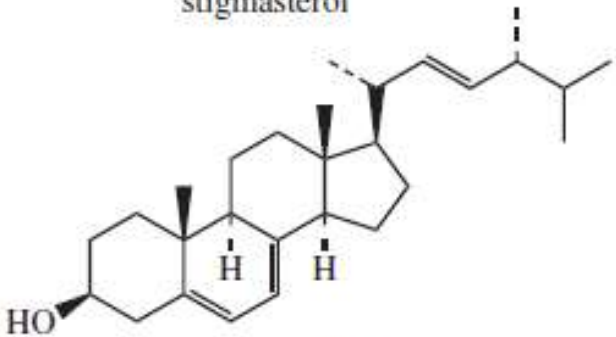
stigmasterol



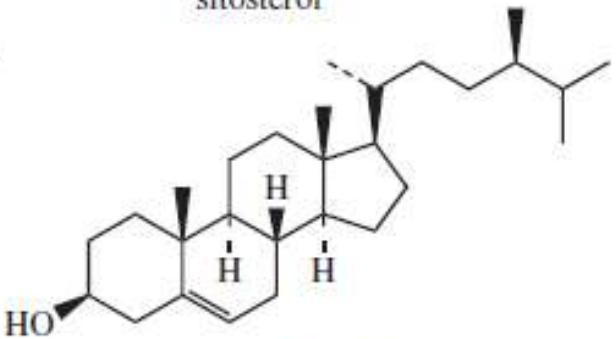
sitosterol



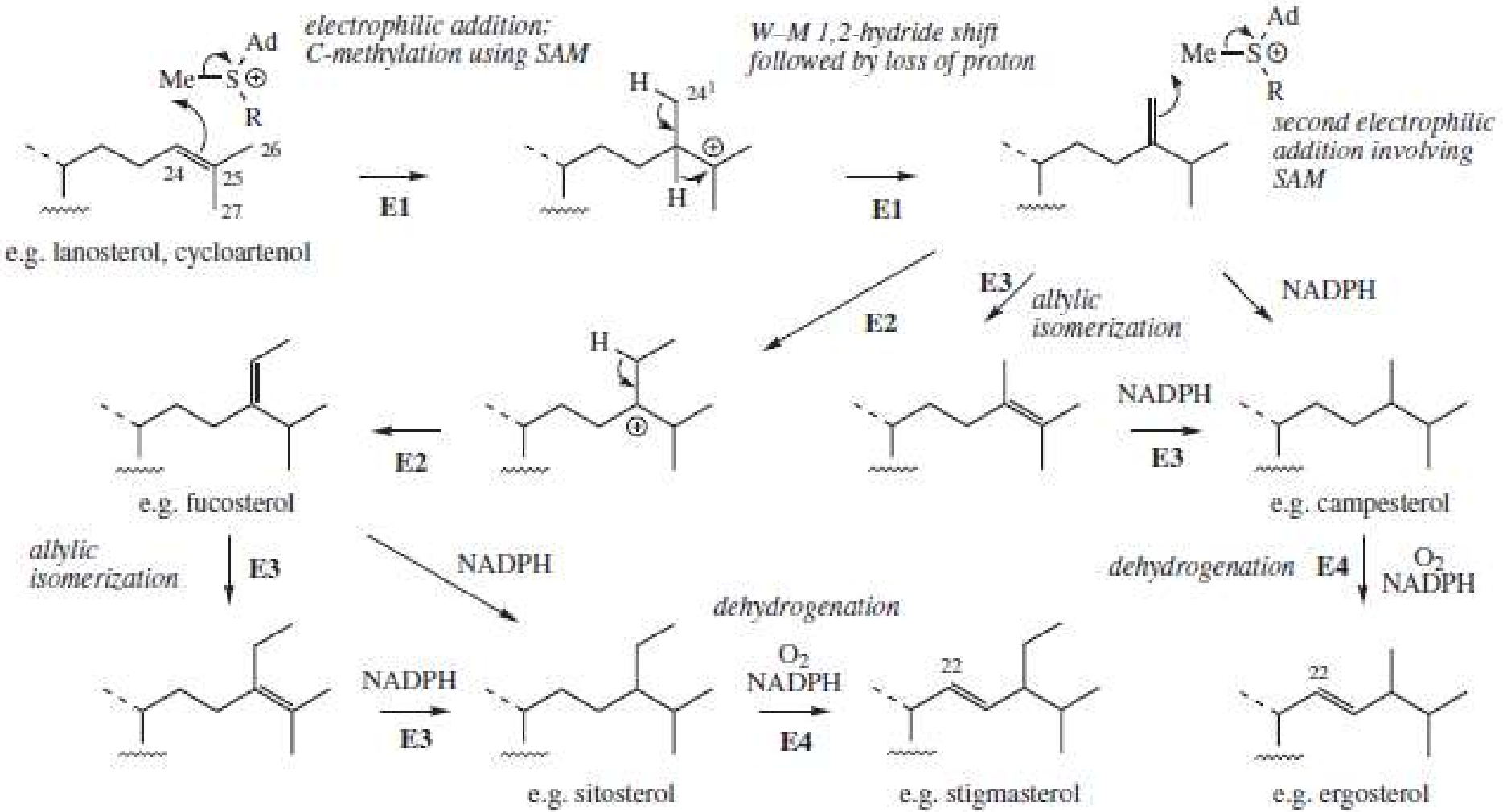
fucosterol



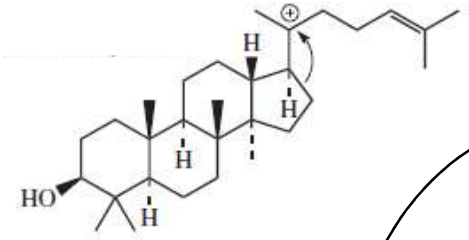
ergosterol

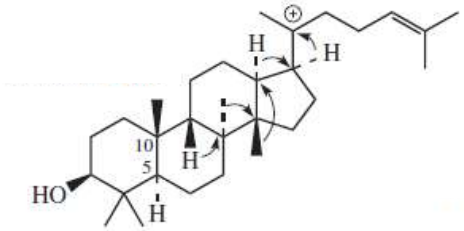


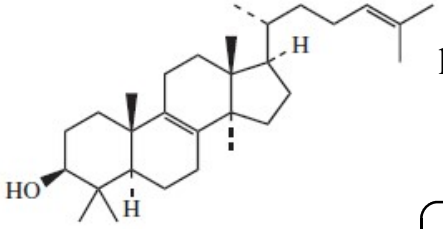
campesterol

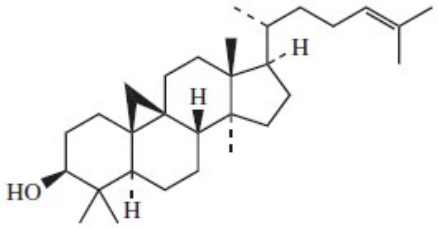


E1: sterol C-24 methyltransferase
E2: 24-methylenesterol *C*-methyltransferase
E3: Δ^{24} sterol reductase
E4 sterol C-22 desaturase









squalene

catione dammarenile

catione protosterile

lanosterolo

cicloartenolo

colesterolo

fitosteroli

vitamine D

saponine triterpenoidiche

saponine steroidee

pregnenolone

estrogeni androgeni

acidi biliari

progesterone

glicosidi cardioattivi

corticosteroidi

Steroidi