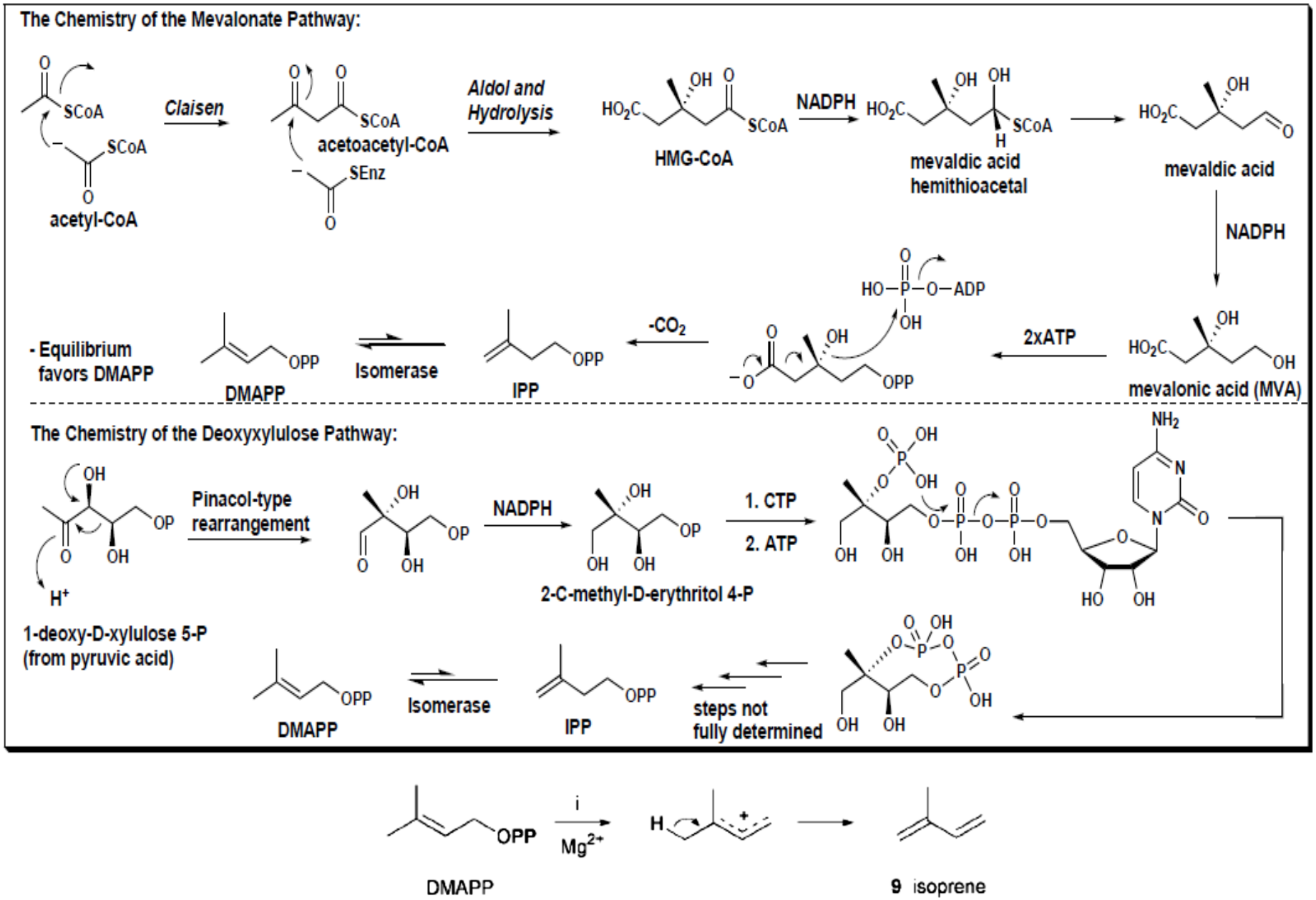
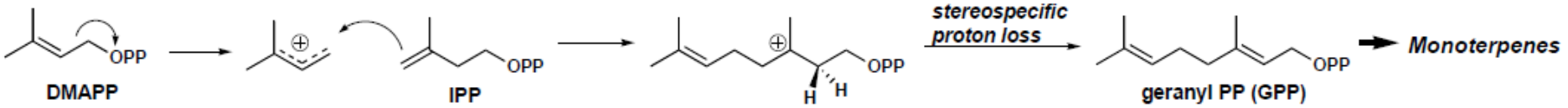
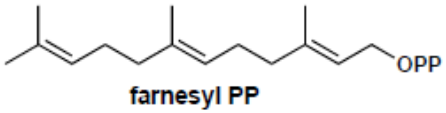



**Scheme 6** *Enzyme*: i, isoprene synthase.

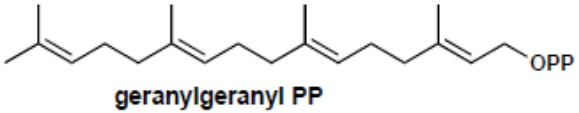
- All terpenes are formed through the reactions of IPP and DMAPP:



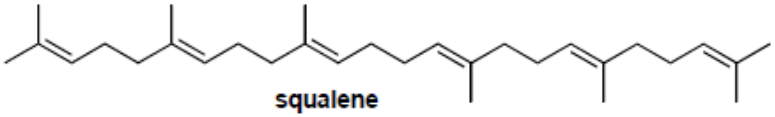

- repeat several times:




*Sesquiterpenes*



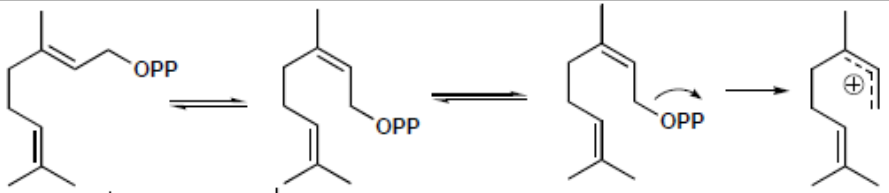

*Diterpenes*

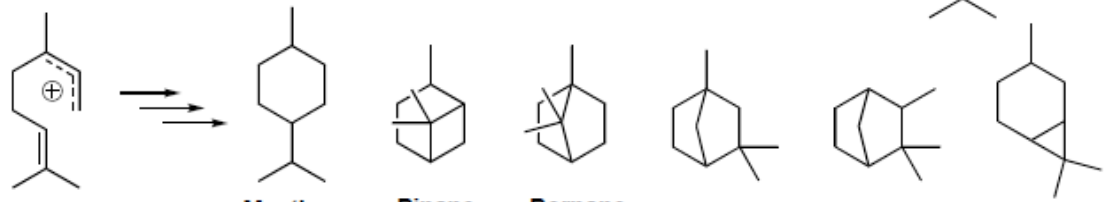



*Triterpenes (Steroids)*

| | |
|---|---|
| Hemiterpenes | $C_5$ |
| Monoterpenes | $C_{10}$ |
| Sesquiterpenes | $C_{15}$ |
| Diterpenes | $C_{20}$ |
| Sesterterpenes | $C_{25}$ |
| Triterpenes | $C_{30}$ |
| Tetraterpenes | $C_{40}$ |

- The interesting Chemistry involves the fate of the open-chain terpenes. A seemingly endless number of (enzyme-mediated) carbocation cyclizations leads to many different carbocyclic skeletons, which are often further oxidized and rearranged.

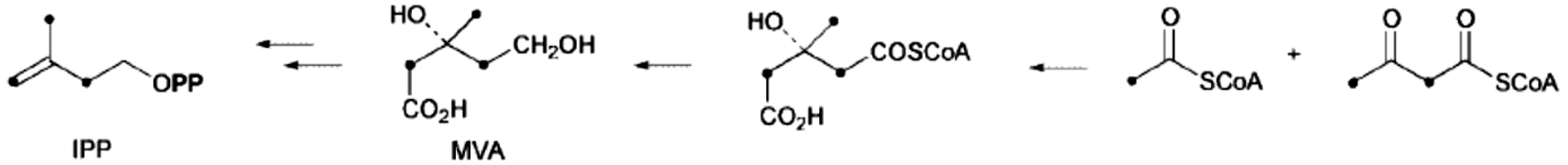


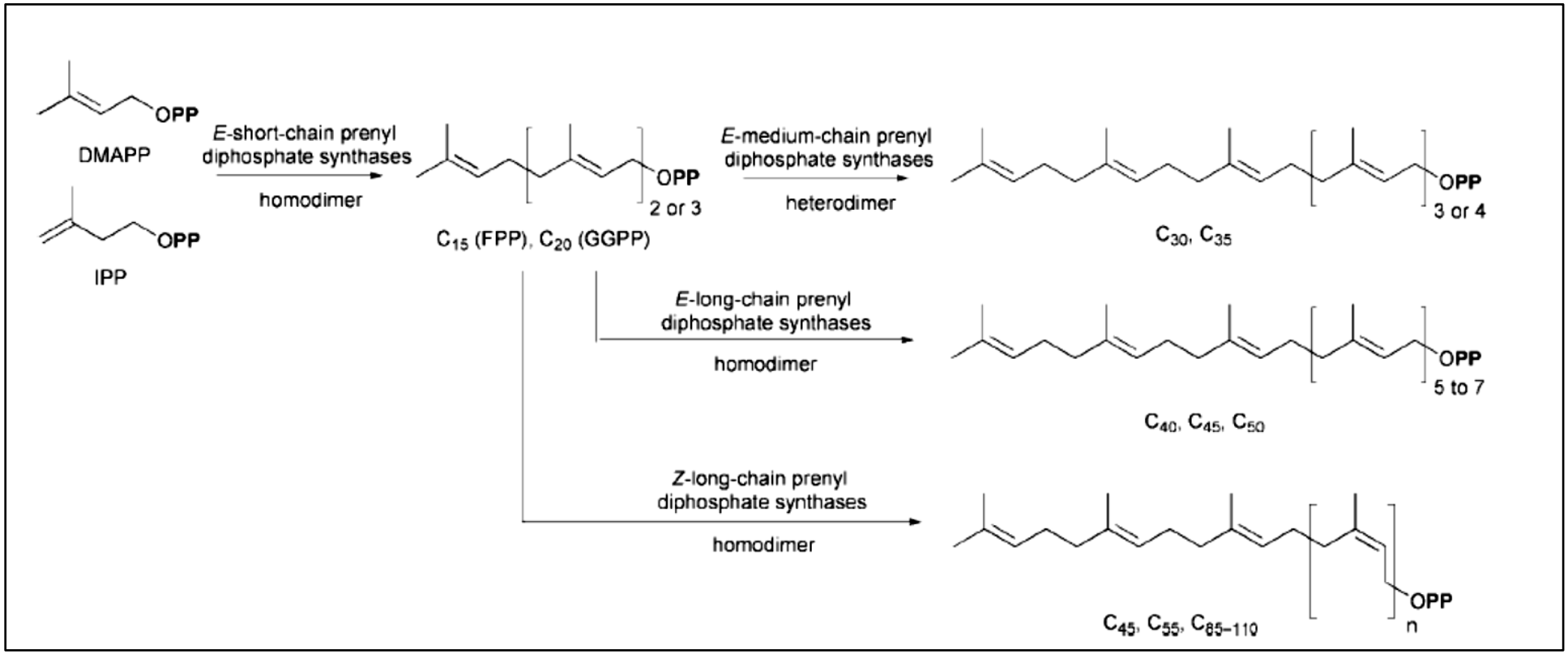



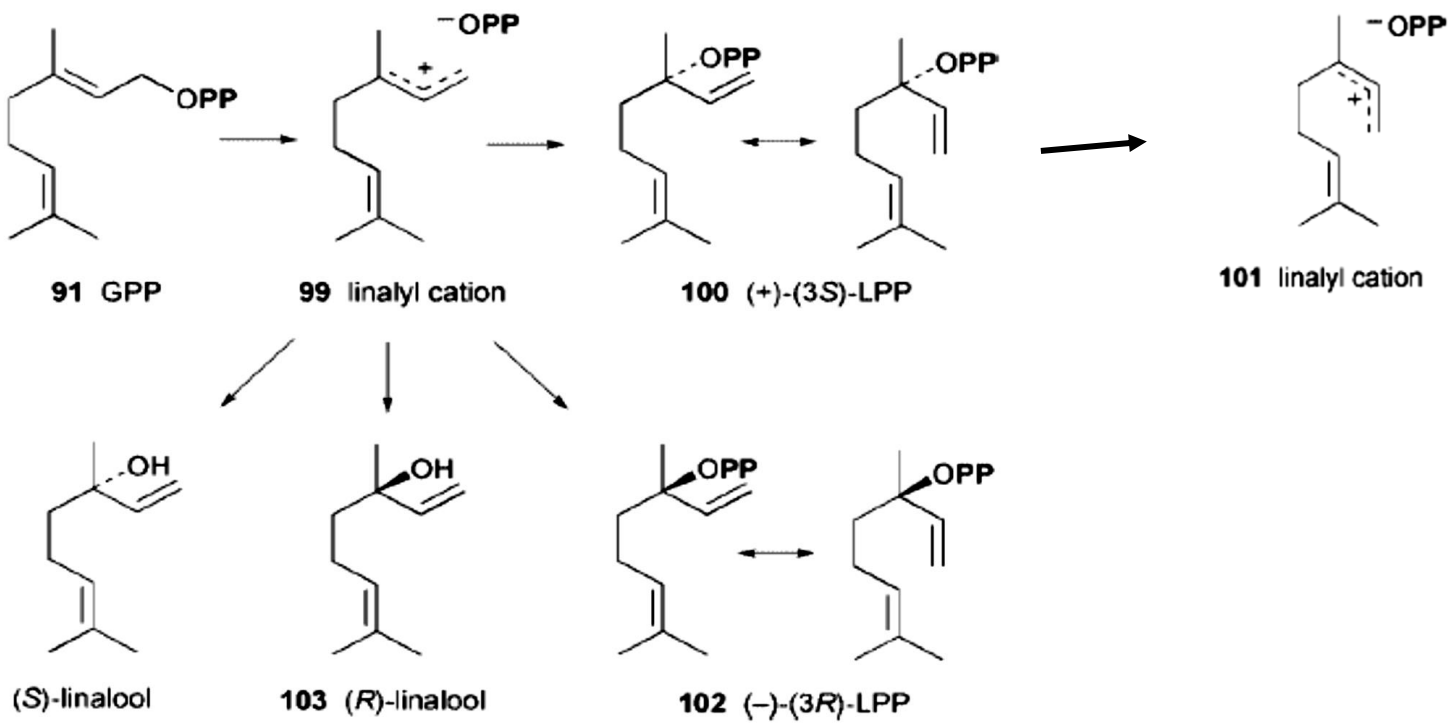
Menthane Type | Pinane Type | Bornane Type | Fenchane Type | Isocamphane type | Carane type | Thujane type

*with only 2 prenyl units:*
- *7 unique skeletons*
- *several sites of hydration or elimination to terminate carbocation*

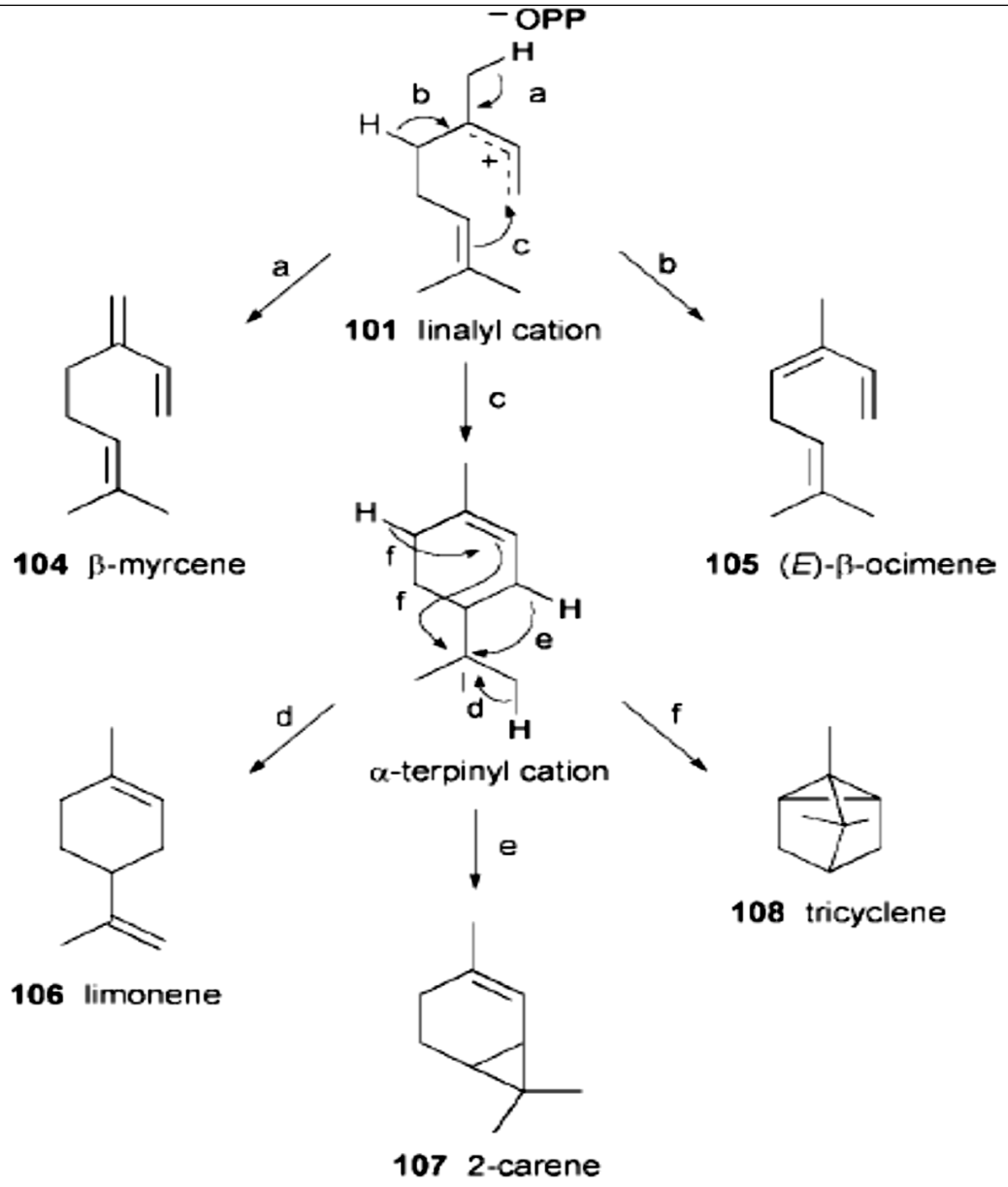
*Take Home Message*: Complexity increases extremely rapidly with each addition prenyl unit


OPP
IPP
HO
CH2OH
CO2H
MVA
HO
COSCoA
CO2H
O
SCoA
+
O
O
SCoA

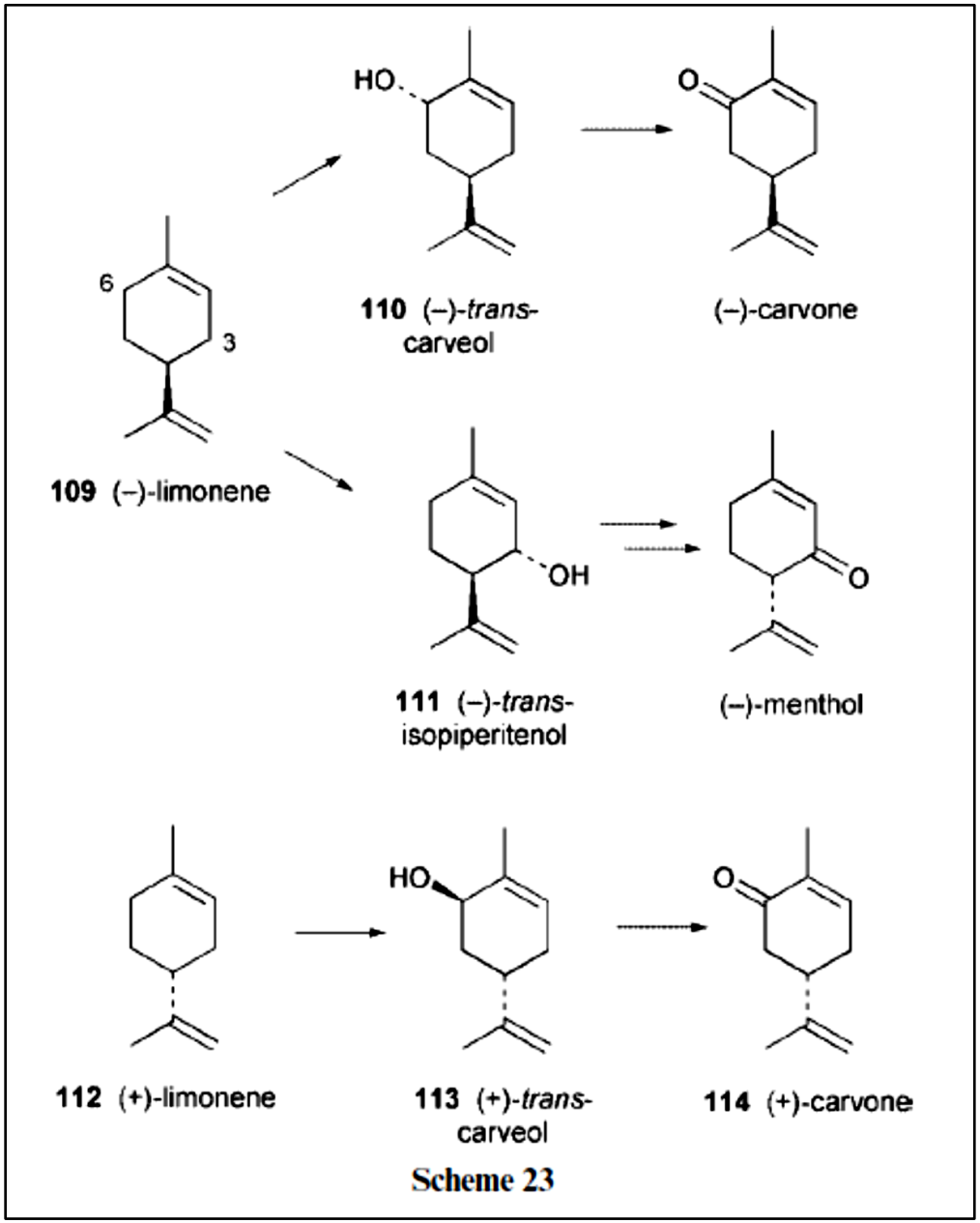

OPP
DMAPP
OPP
IPP
E-short-chain prenyl diphosphate synthases
homodimer
OPP
2 or 3
C15 (FPP), C20 (GGPP)
E-medium-chain prenyl diphosphate synthases
heterodimer
OPP
3 or 4
C30, C35
E-long-chain prenyl diphosphate synthases
homodimer
OPP
5 to 7
C40, C45, C50
Z-long-chain prenyl diphosphate synthases
homodimer
OPP
n
C45, C55, C65–110


OPP
−OPP
+
OPP
OPP
−OPP
+
91 GPP
99 linalyl cation
100 (+)-(3S)-LPP
101 linalyl cation
OH
OH
OPP
OPP
(S)-linalool
103 (R)-linalool
102 (–)-(3R)-LPP

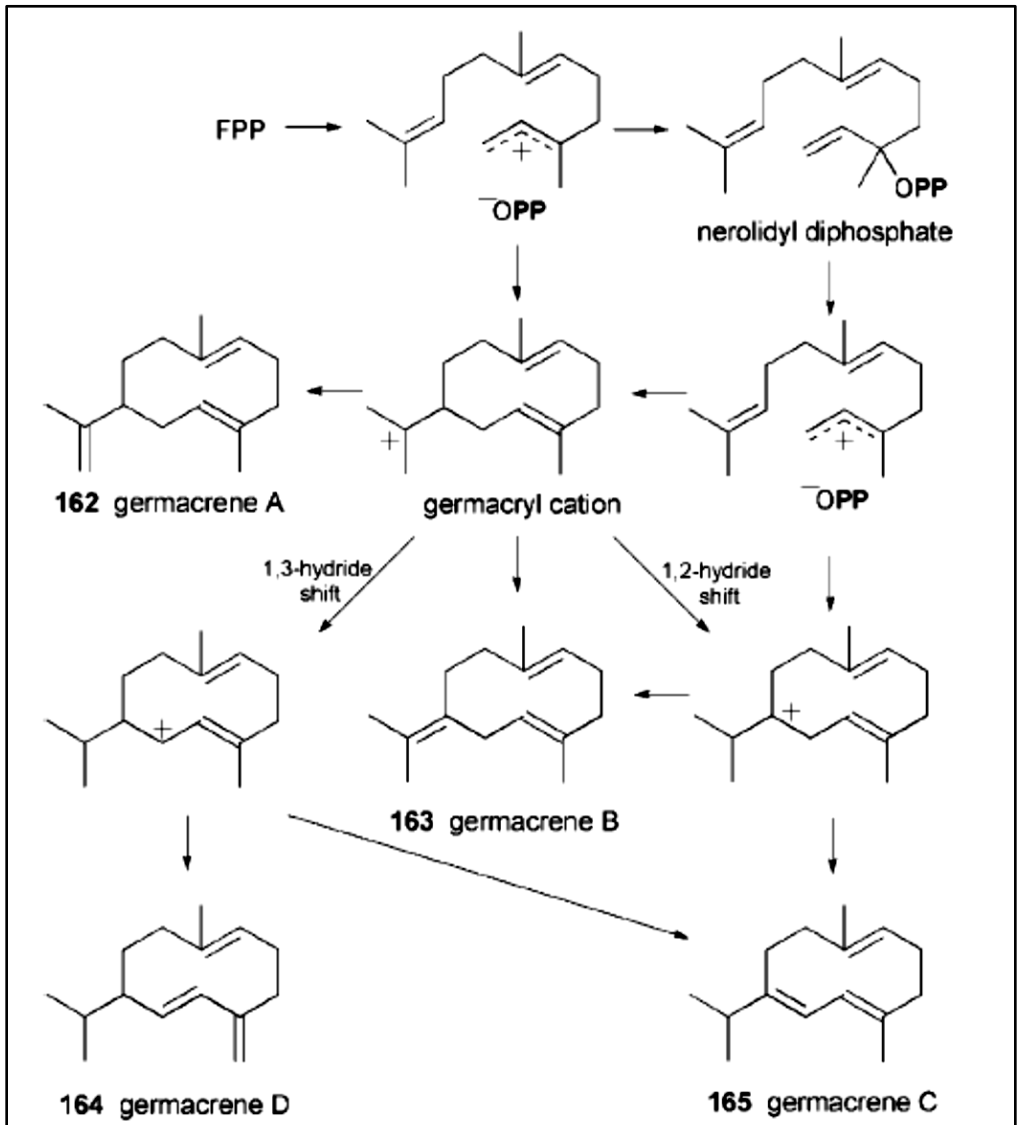
**Scheme 21**


−OPP
H
b
a
H
+
c
a
b
101 linalyl cation
c
104 β-myrcene
105 (E)-β-ocimene
H
f
f
H
e
d
H
d
f
α-terpinyl cation
e
106 limonene
108 tricyclene
107 2-carene

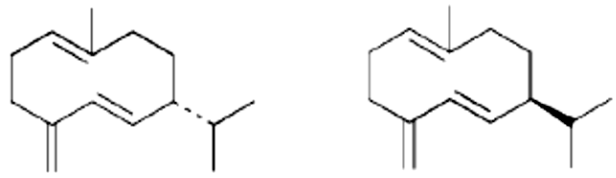
**Scheme 22**


HO
O
6
3
110 (–)-trans-carveol
(–)-carvone
109 (–)-limonene
OH
O
111 (–)-trans-isopiperitenol
(–)-menthol
HO
O
112 (+)-limonene
113 (+)-trans-carveol
114 (+)-carvone

Scheme 23

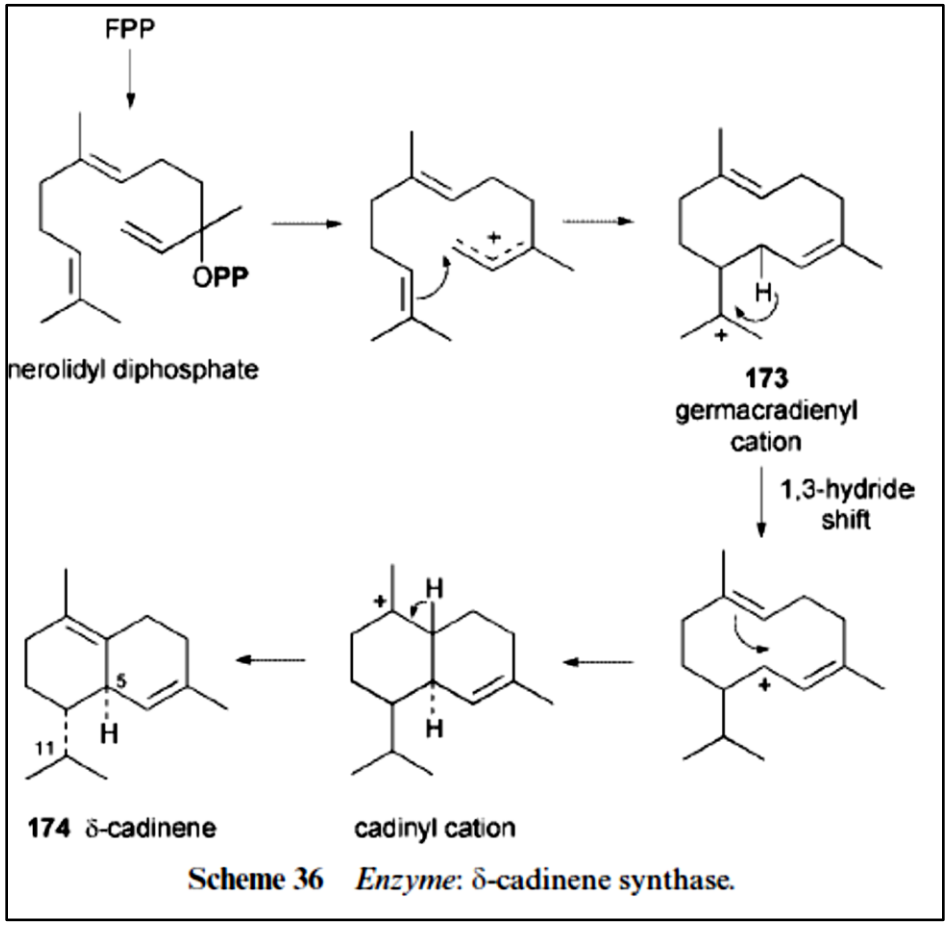



**Scheme 35**

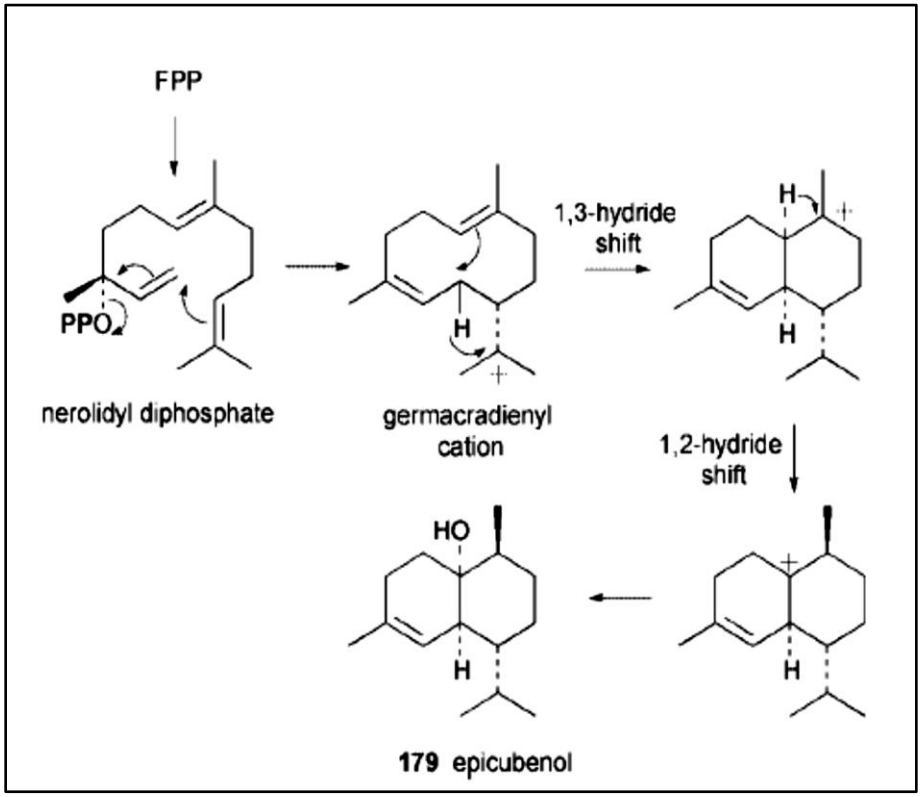


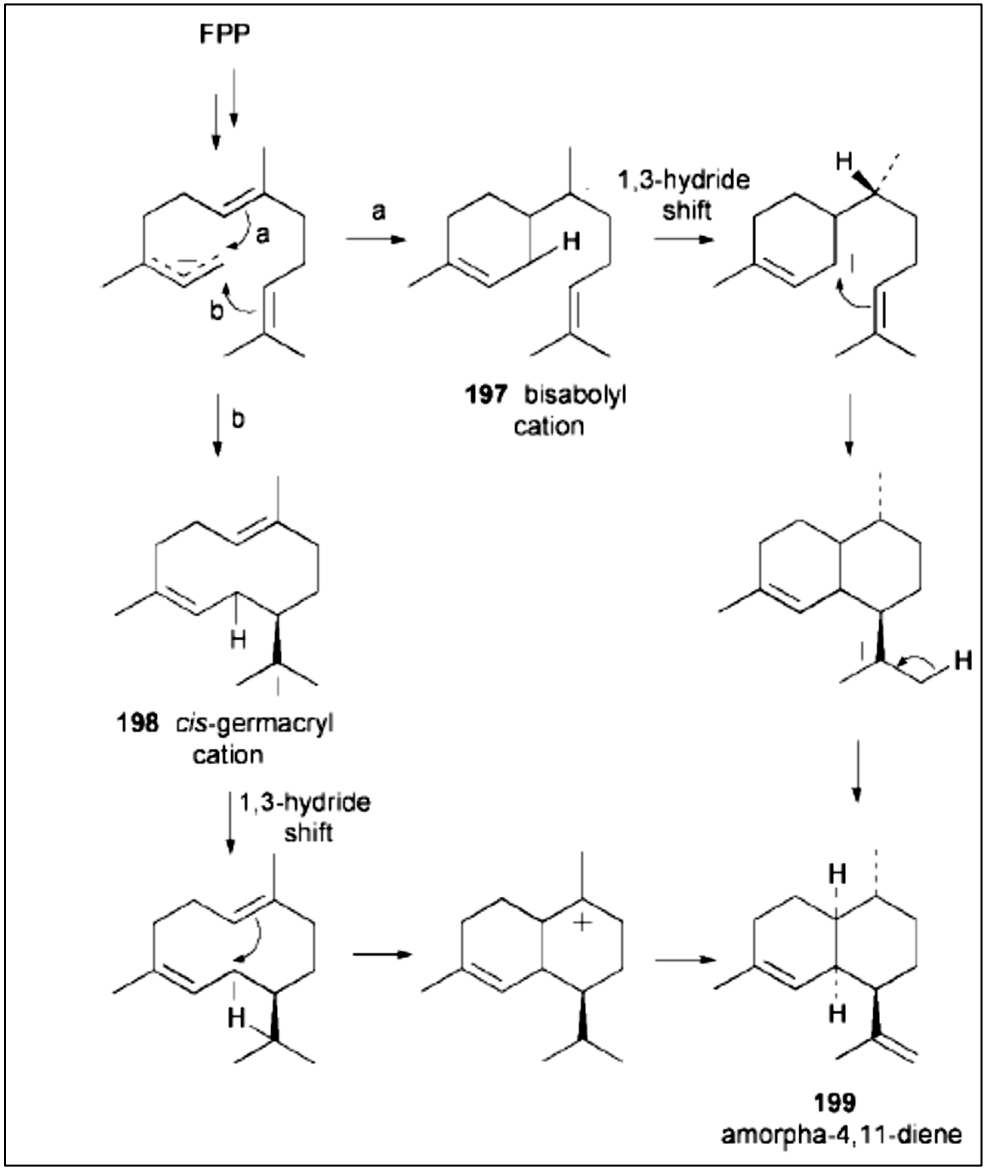
**166** (+)-germacrene D

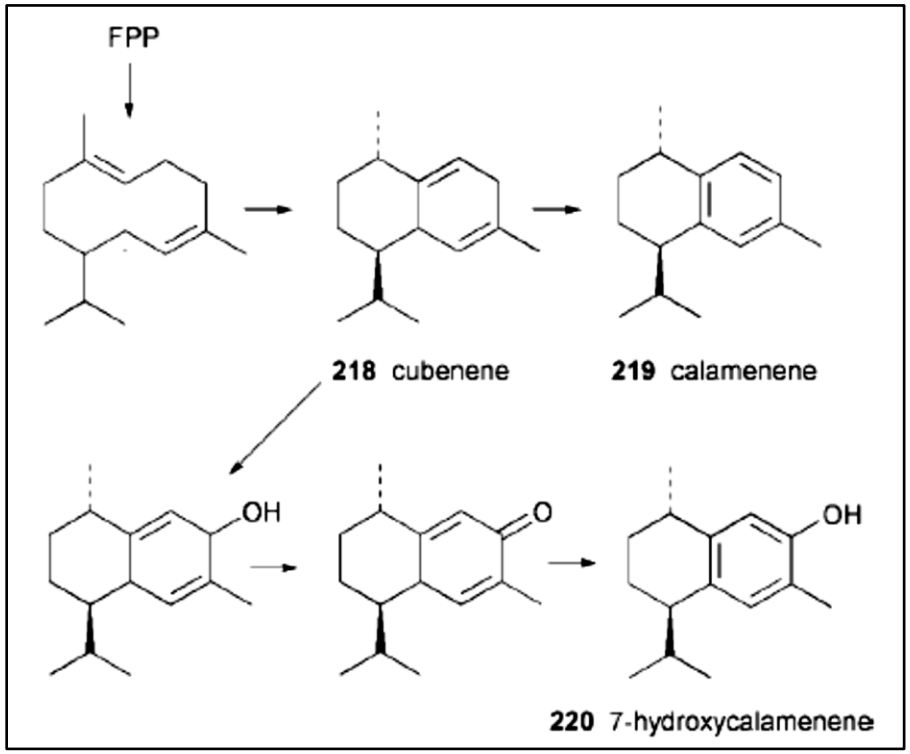
**167** (–)-germacrene D

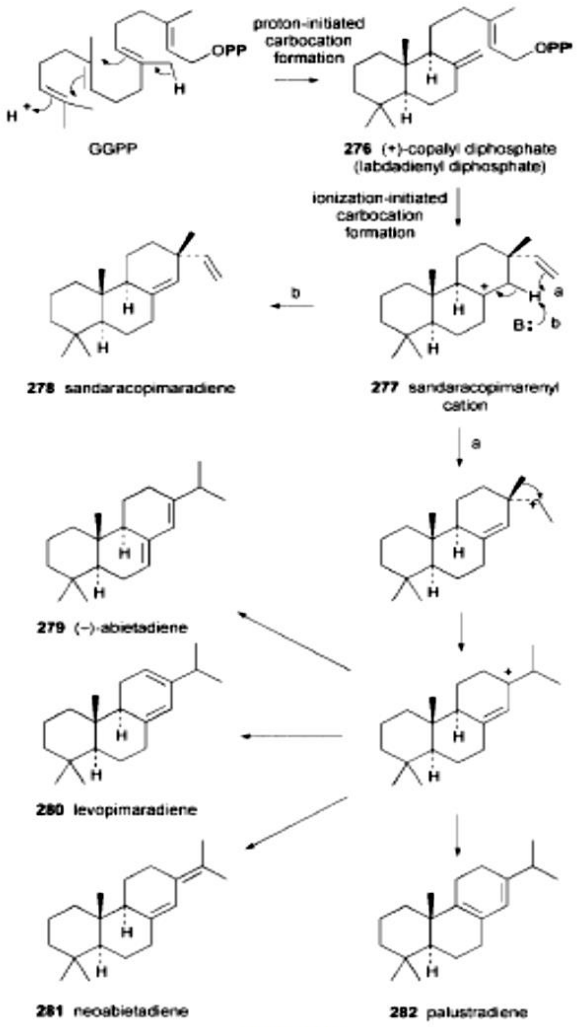



Scheme 36 *Enzyme*: δ-cadinene synthase.

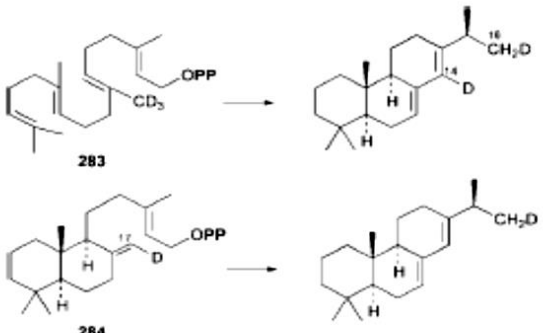


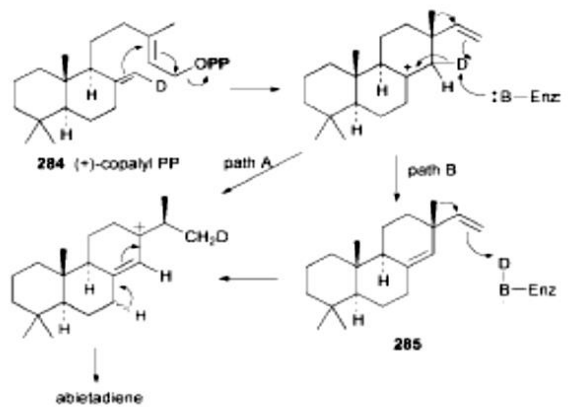

FPP
a
b
a
H
1,3-hydride shift
H
197 bisabolyl cation
b
H
198 cis-germacryl cation
H
1,3-hydride shift
H
H
H
199 amorpha-4,11-diene


FPP
218 cubenene
219 calamenene
OH
O
OH
220 7-hydroxycalamenene

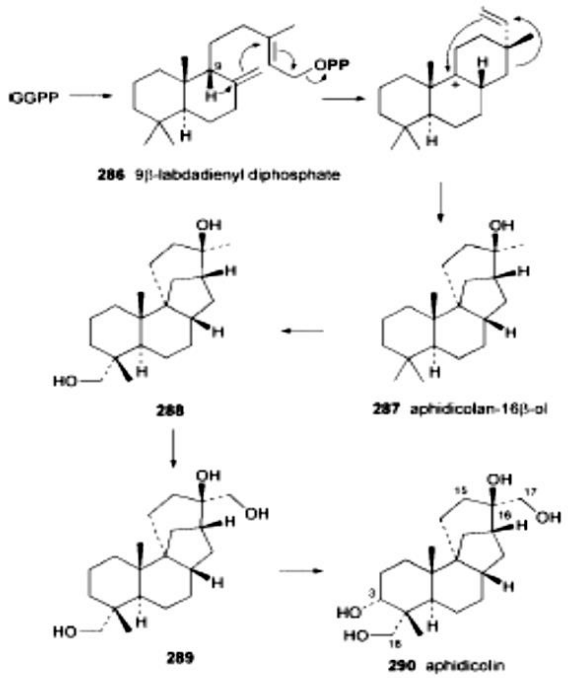



Scheme 65



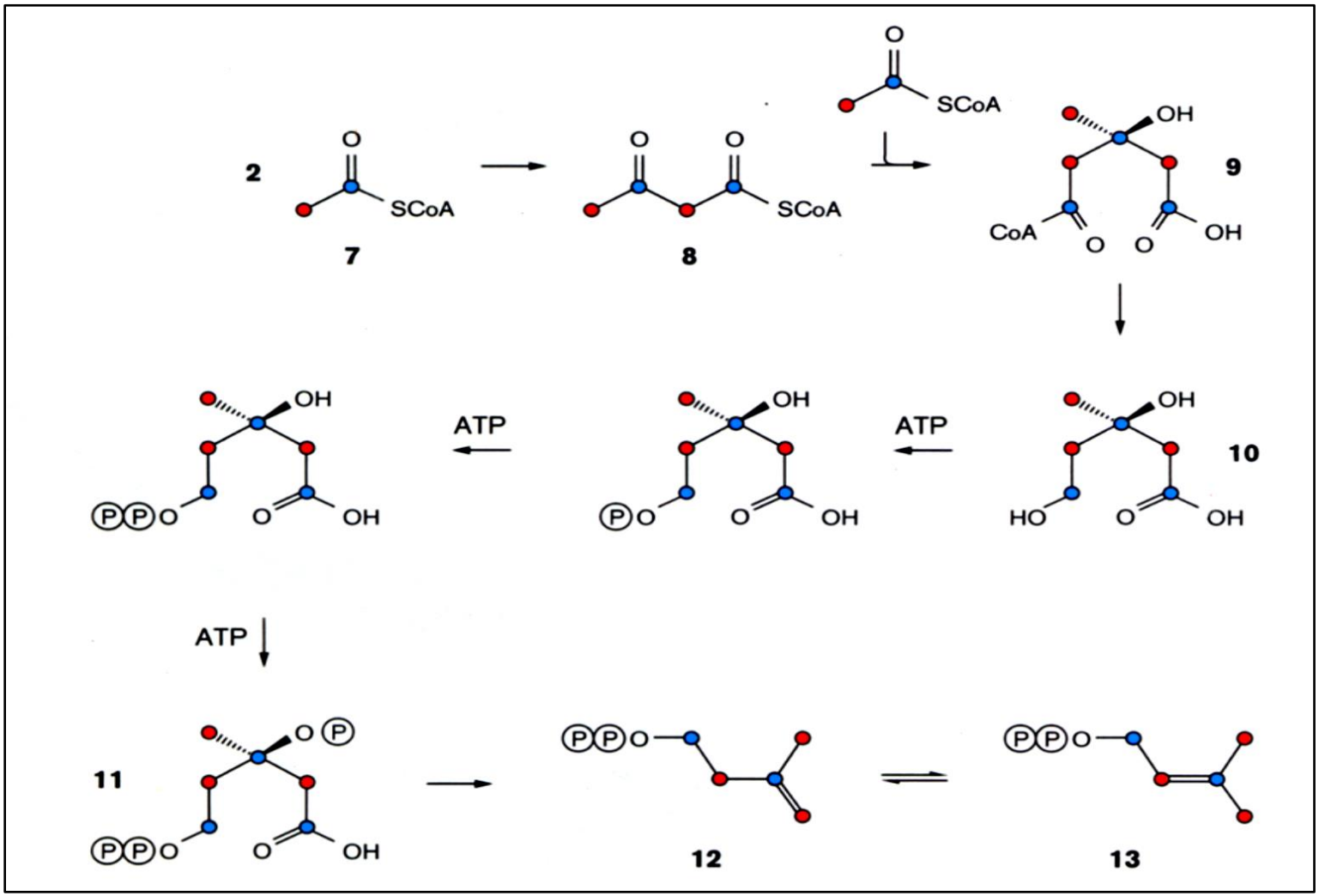

Scheme 67

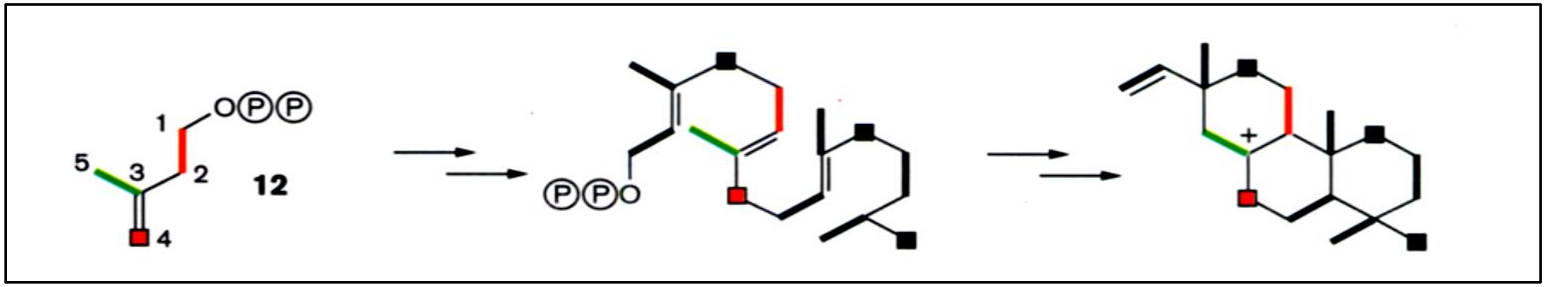


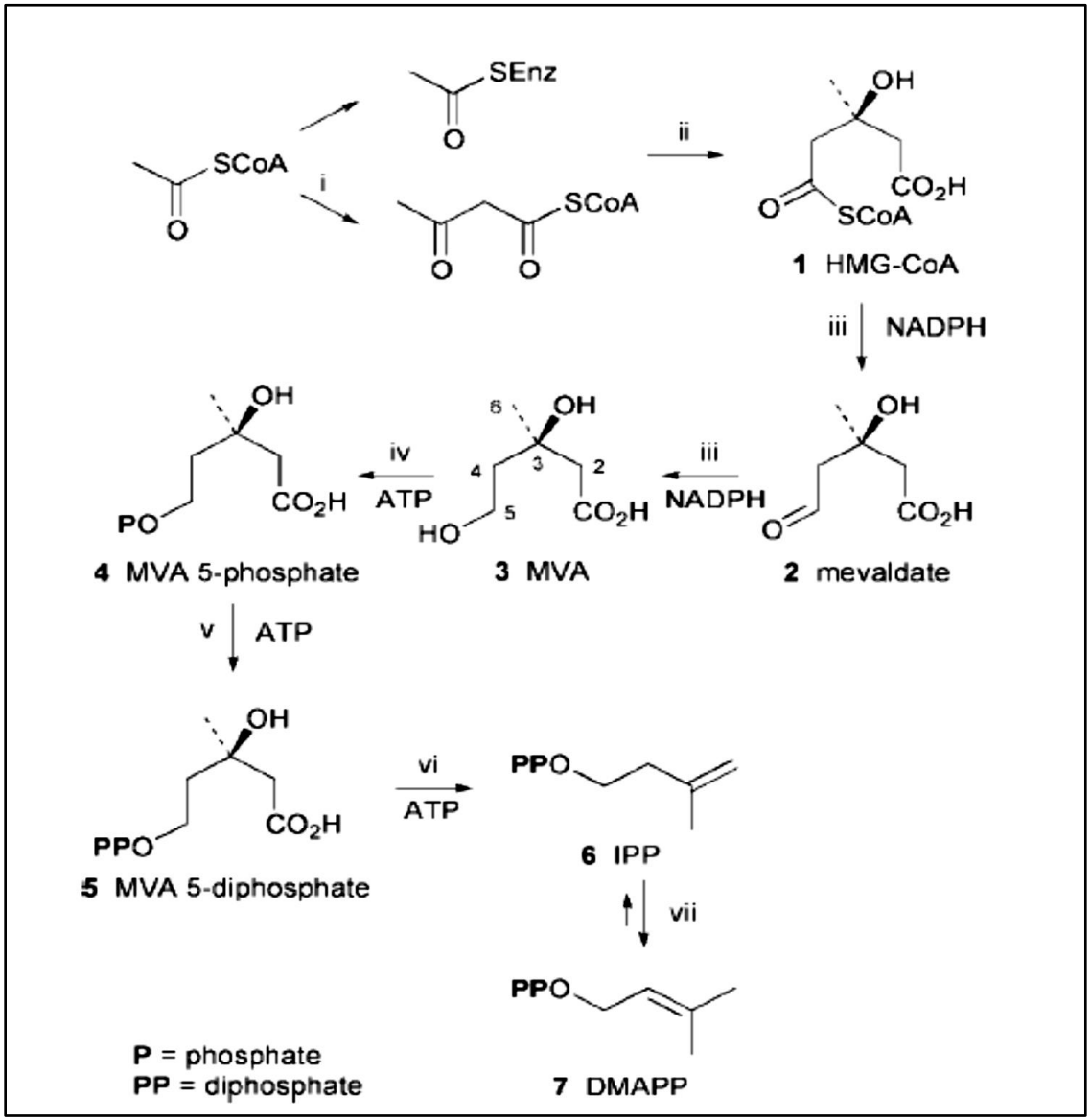

Scheme 68

samples of **287** were converted into aphidicolin by the cultures, or into **289** in the presence of a P-450 inhibitor.

Studies on the biosynthesis and metabolism of the gibberellins (GAs) always account for a considerable proportion of the diterpenoid research literature. These compounds, with over 120 different structures now known, play a significant role as plant growth hormones, and have their origins in *ent*-kaurene **292**. *ent*-Kaurene is produced from GGPP by the action of two enzymes, firstly copalyl PP synthase (*ent*-kaurene synthase A), which cyclizes the substrate to (−)-copalyl PP **291** in a protonation-initiated cyclization, and then kaurene synthase


2
7
SCoA
8
SCoA
SCoA
9
OH
CoA
O
O
OH
10
OH
HO
O
OH
ATP
OH
O
O
OH
ATP
OH
O
O
OH
ATP
11
O
P
O
O
OH
12
13


1
5
3
2
4
12
+


SEnz
SCoA
i
SCoA
ii
OH
CO2H
SCoA
1 HMG-CoA
iii NADPH
OH
CO2H
2 mevaldate
iii NADPH
6
OH
4
3
2
HO
5
CO2H
3 MVA
iv ATP
OH
PO
CO2H
4 MVA 5-phosphate
v ATP
OH
PPO
CO2H
5 MVA 5-diphosphate
vi ATP
PPO
6 IPP
vii
PPO
7 DMAPP
P = phosphate
PP = diphosphate