

Osnove kemije prirodnih organskih spojeva

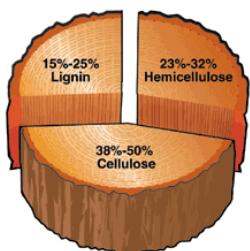
6. Polifenoli

Polifenoli. Strukturni tipovi. Nalaženje u prirodi. Izolacija i određivanje strukture. Biosinteza. Laboratorijska sinteza.

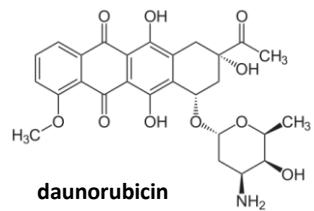
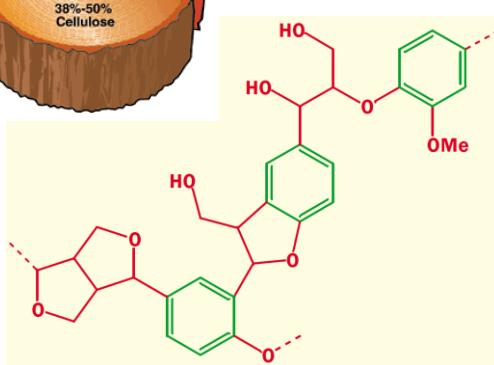
doc. dr. sc. Đani Škalamera

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Aromatski spojevi u prirodi



Dio strukture lignina

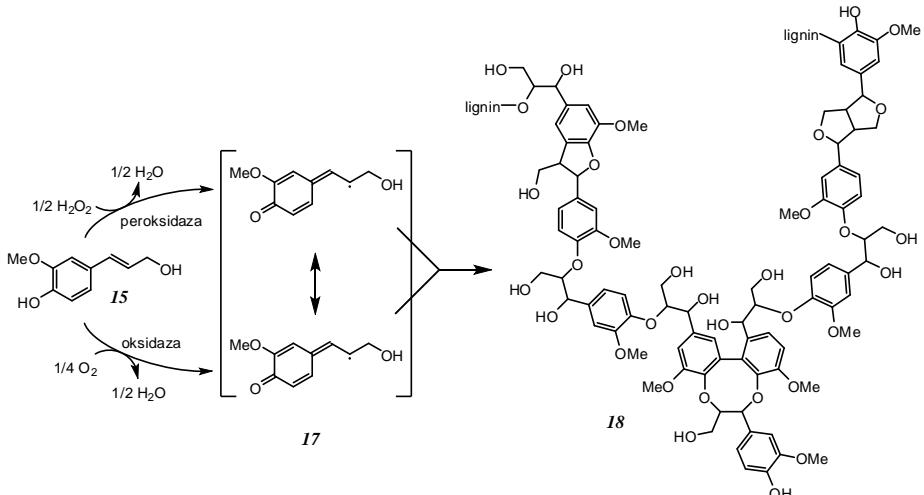


Iz *Streptomyces peucetius*



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Biosinteza lignina



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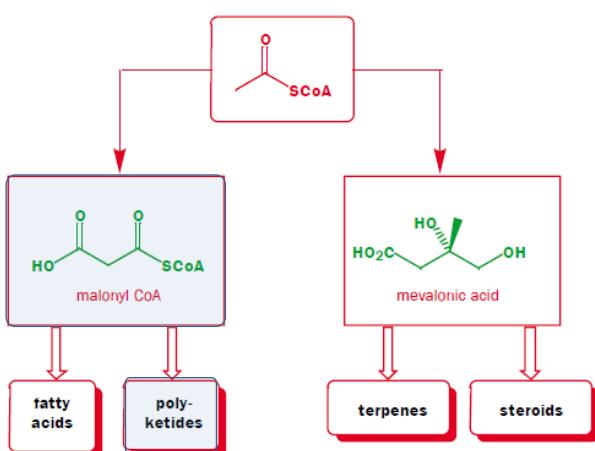
Biosinteza aromatskih prirodnih spojeva

Dva biosintetska puta: preko šikiminske kiseline i iz acetata

Biosinteze preko šikiminske kiseline

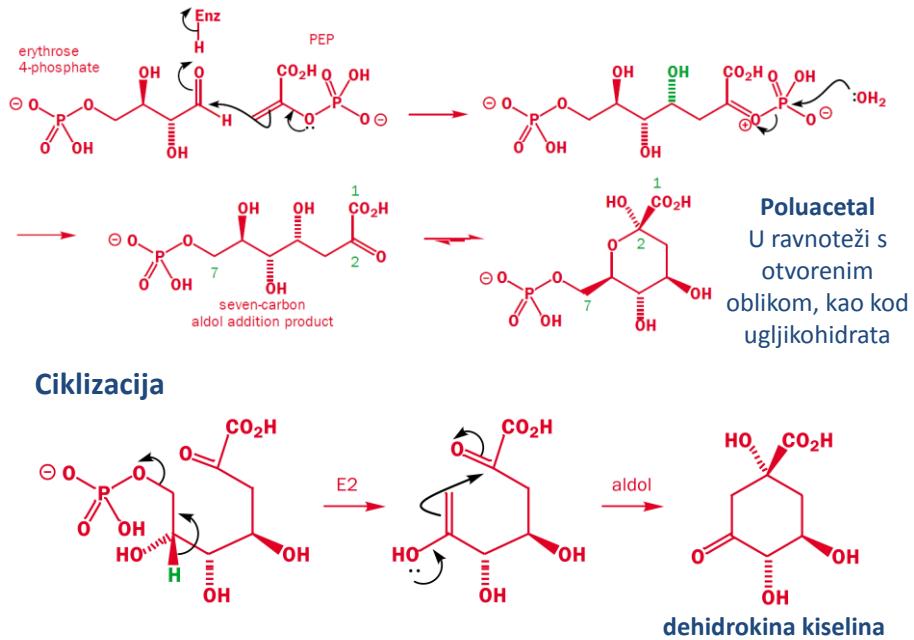


Acetatni put



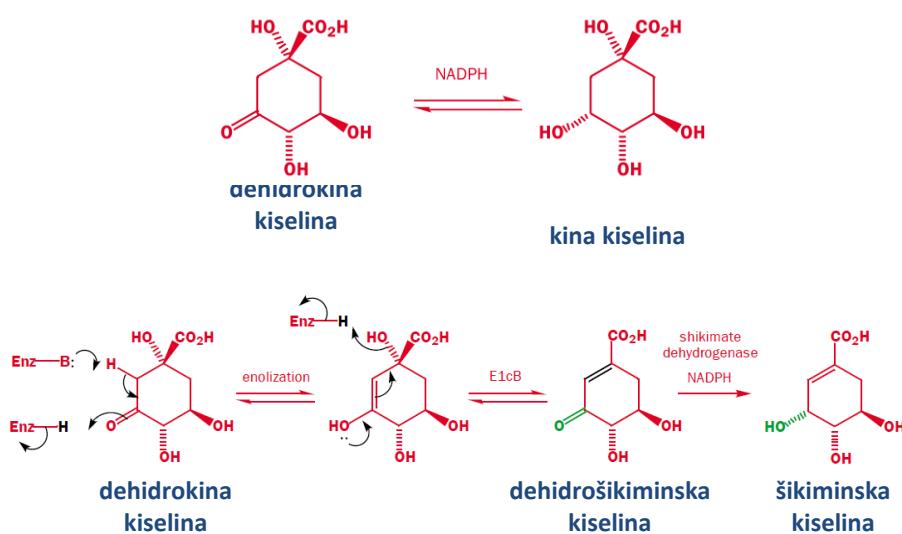
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Biosinteza šikiminske kiseline



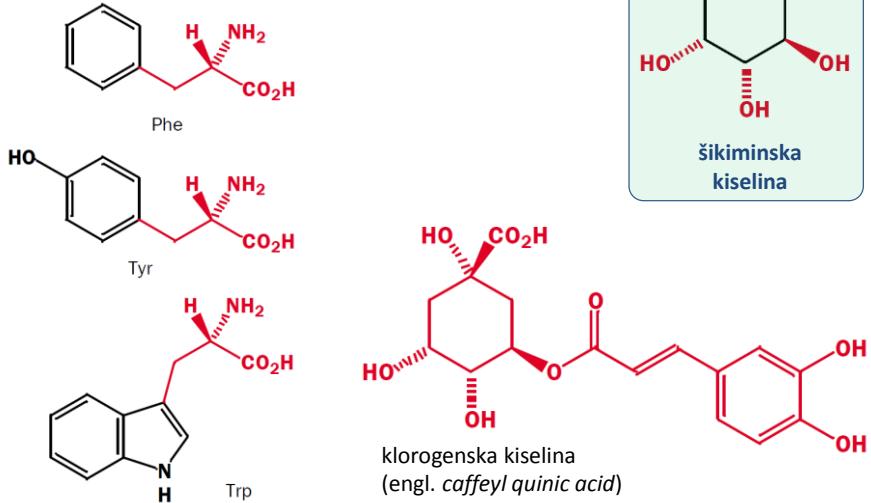
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Biosinteza šikiminske kiseline



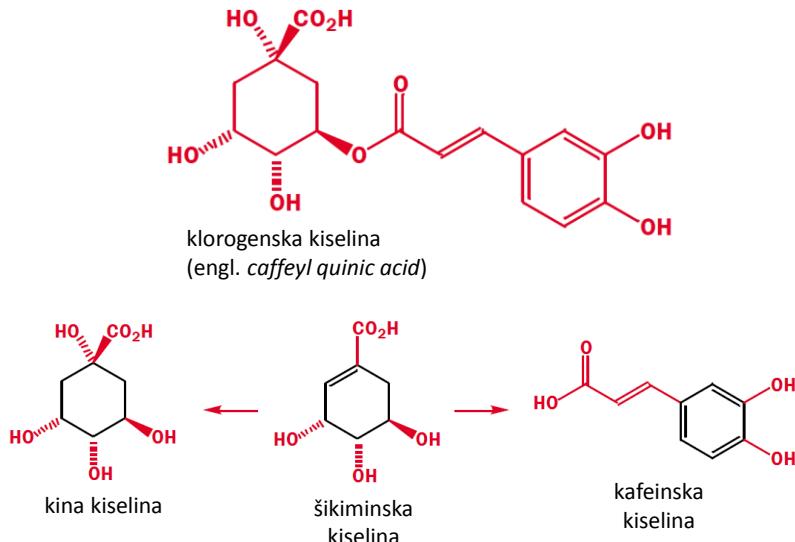
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Biosinteze preko šikiminske kiselina



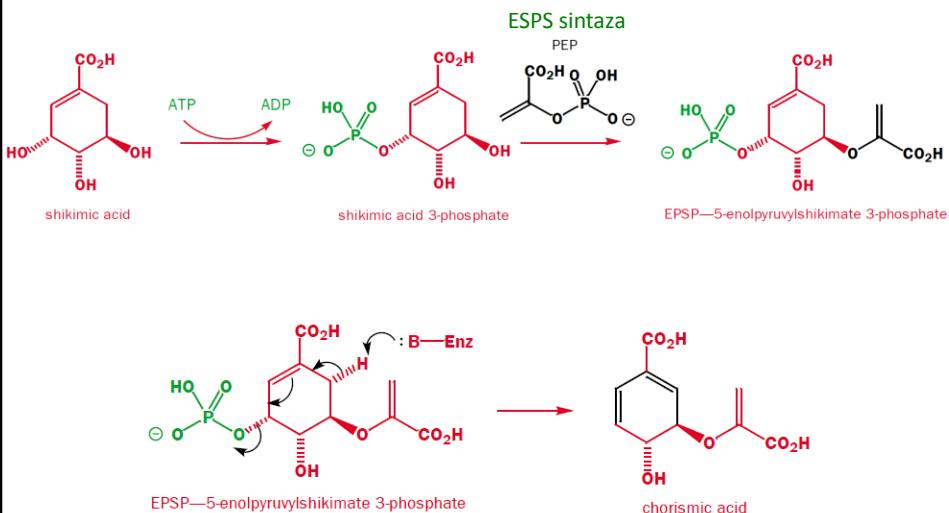
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Biosinteze preko šikiminske kiselina



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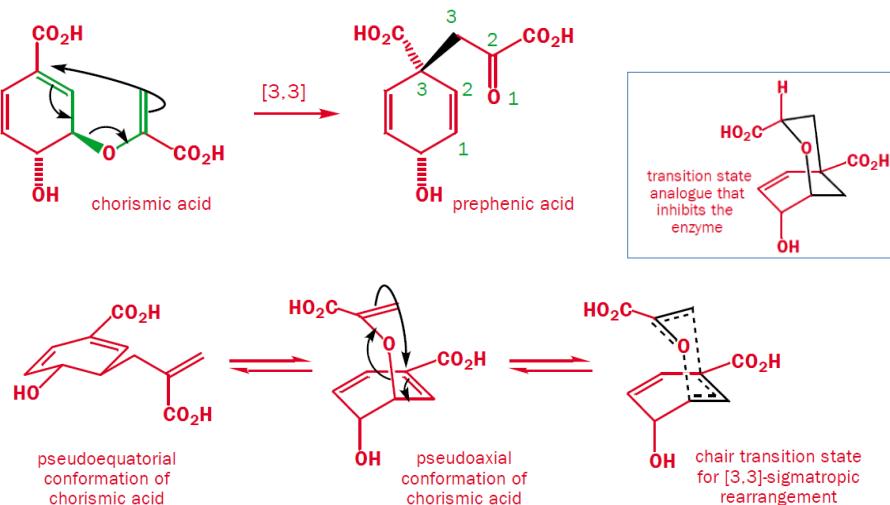
Biosinteza fenilalanina i tirozina



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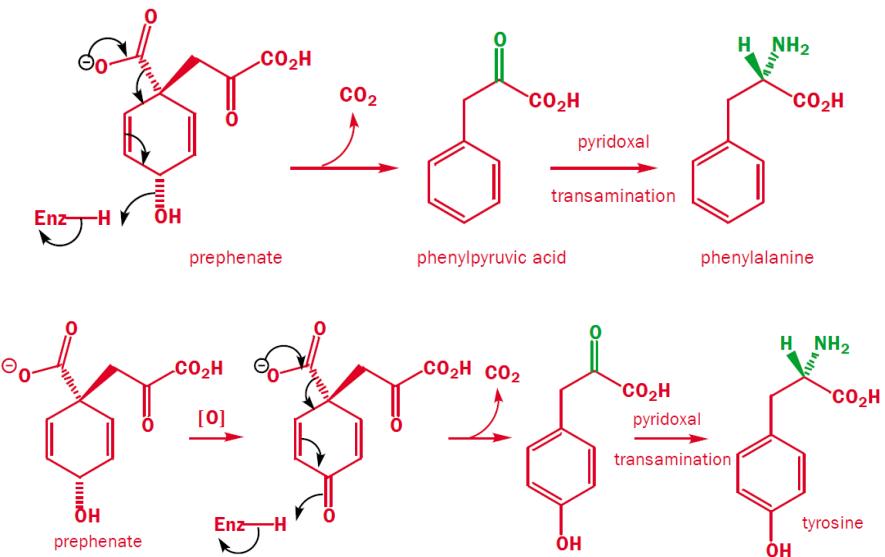
Biosinteza fenilalanina i tirozina

Sigmatropno pregrađivanje



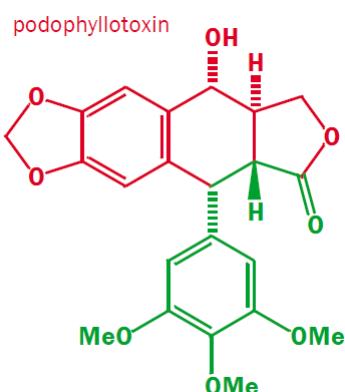
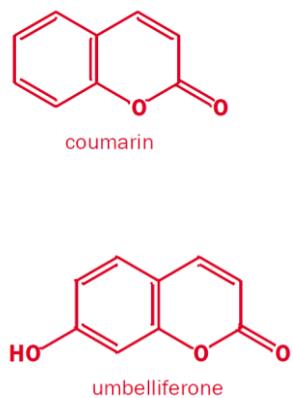
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Biosinteza fenilalanina i tirozina



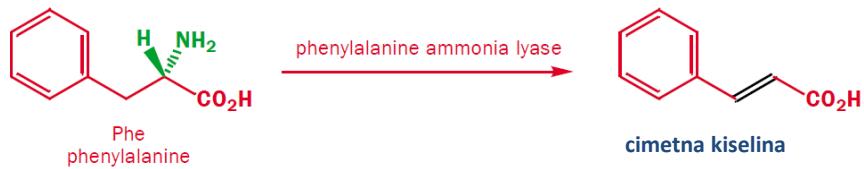
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Ostali spojevi nastali šikimatnim putem

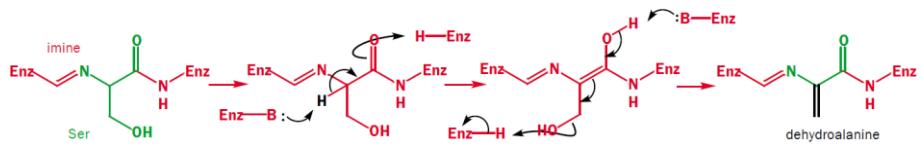


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Alkeni nastali eliminacijom amonijaka



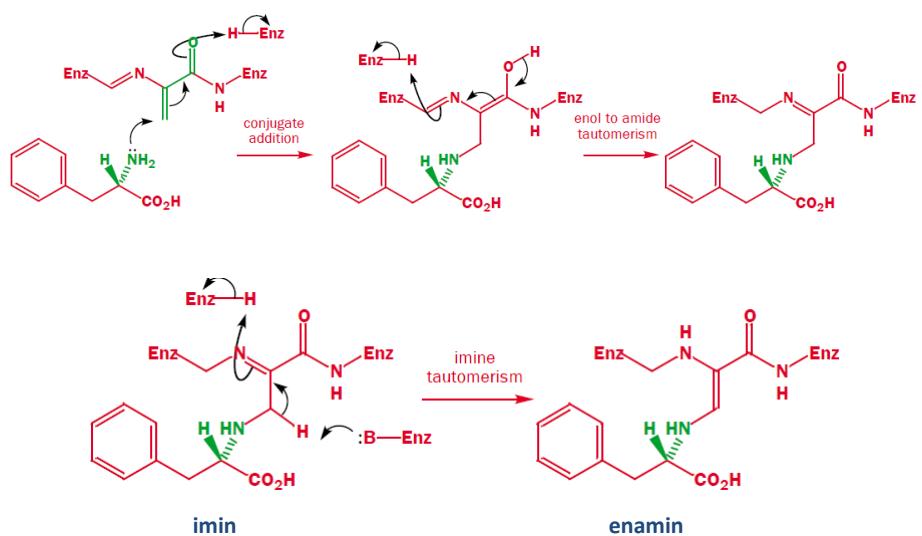
Mehanizam reakcije



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Alkeni nastali eliminacijom amonijaka

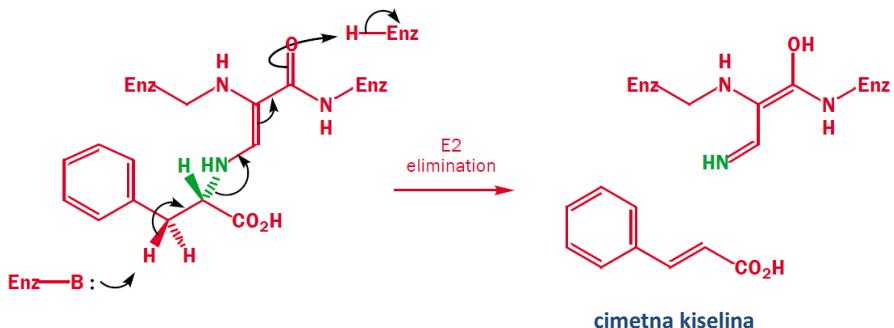
Mehanizam reakcije



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Alkeni nastali eliminacijom amonijaka

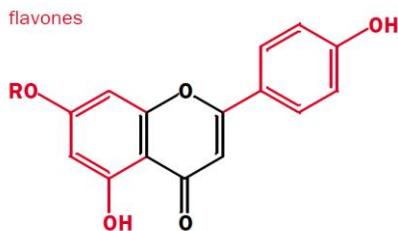
Mehanizam reakcije



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Flavononidi i antocijani

flavones



R = H; naringenin, R = glucose; naringin
—a bitter substance from grapefruit peel

anthocyanidins

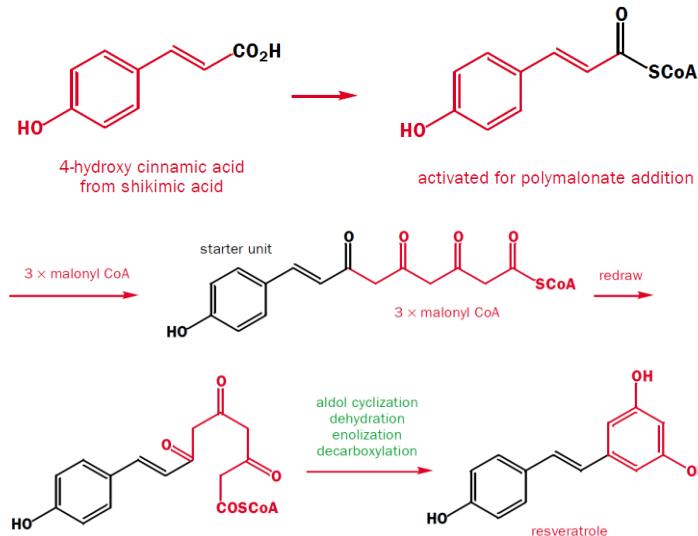


pelargonidin, pigment of raspberries,
geraniums, and red grape skins

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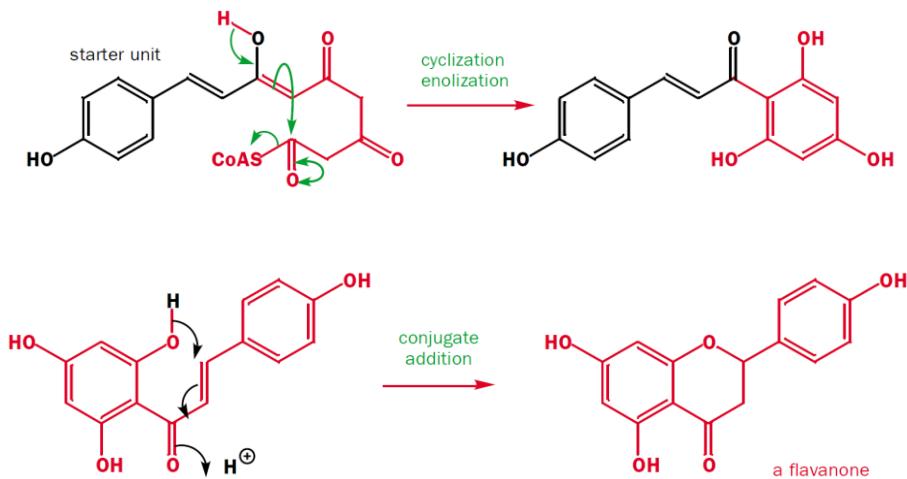
Biosinteze flavononida i antocijana

Acetatni put biosinteze



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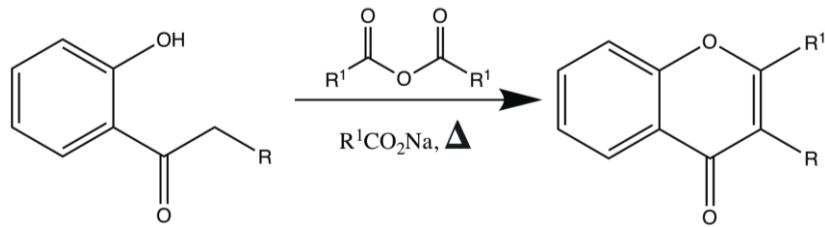
Biosinteze flavononida i antocijana



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Kemijske sinteze flavononida i antocijana

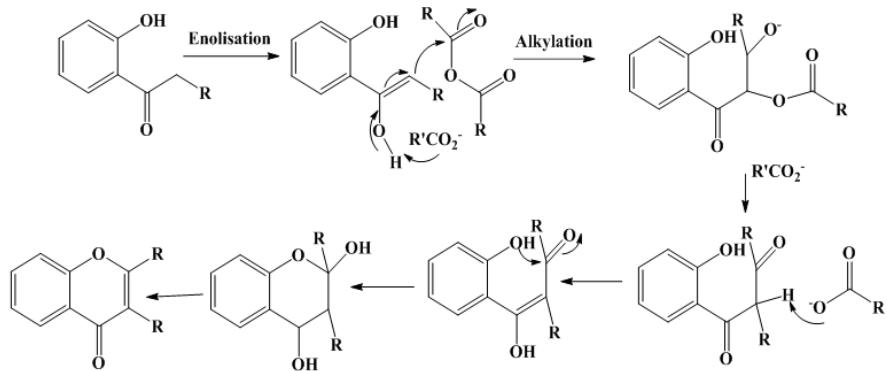
Robinsonova sinteza



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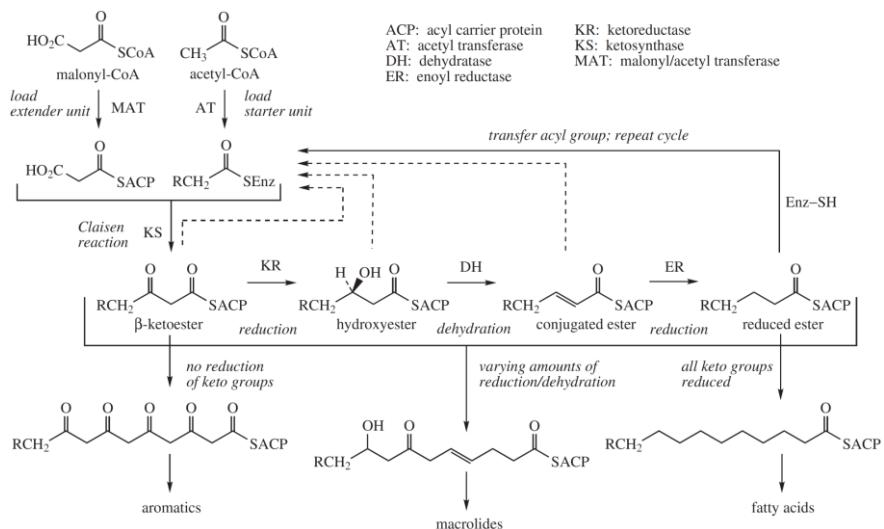
Kemijske sinteze flavononida i antocijana

Robinsonova sinteza - mehanizam



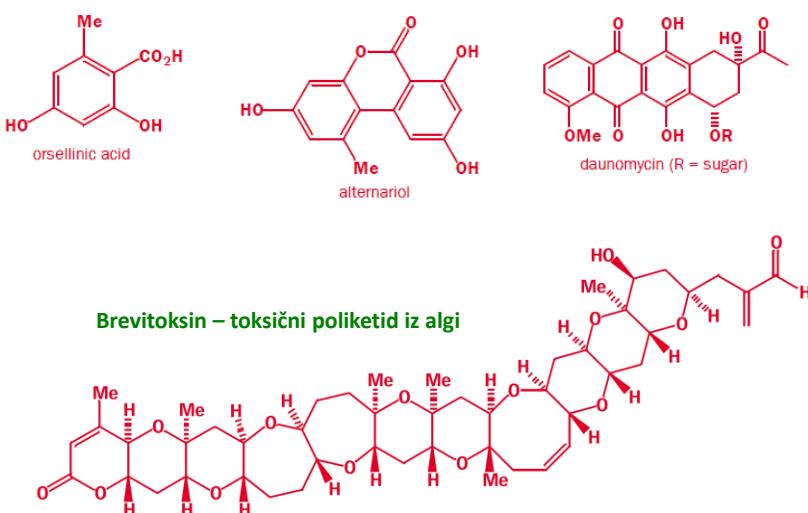
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Biosinteze preko acetata - poliketidi



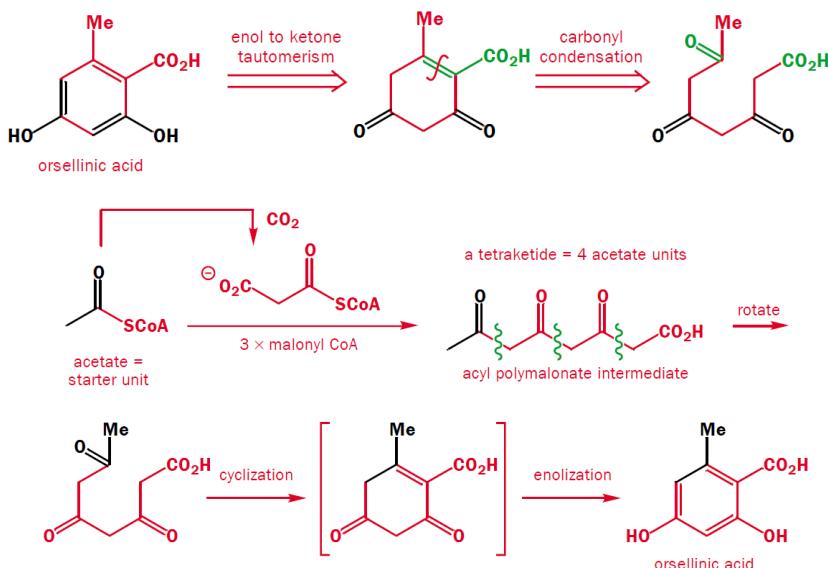
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Biosinteze preko acetata - poliketidi



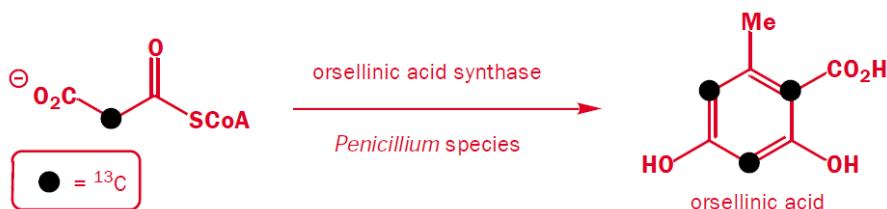
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Biosinteze preko acetata - poliketidi

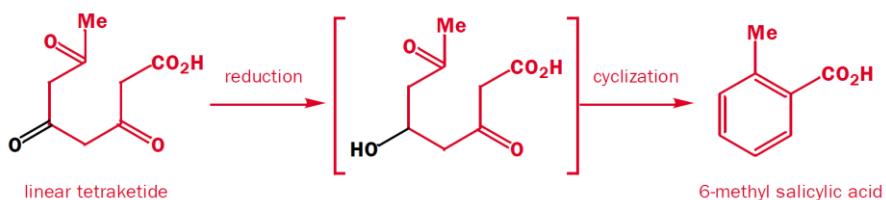


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Biosinteze preko acetata - poliketidi

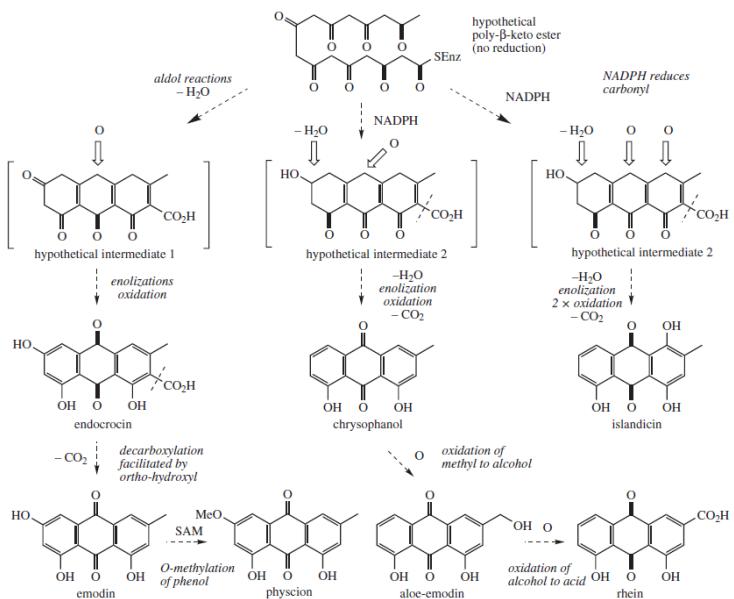


Preko istog međuproducta mogu nastati i drugi spojevi:



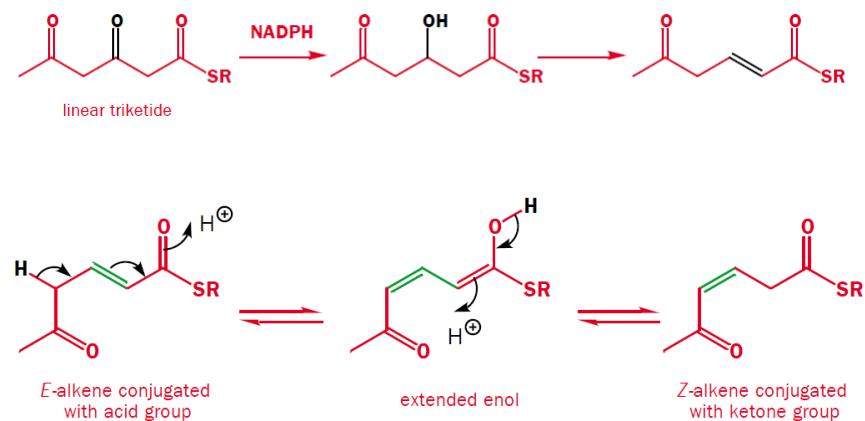
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Biosinteze preko acetata - poliketidi



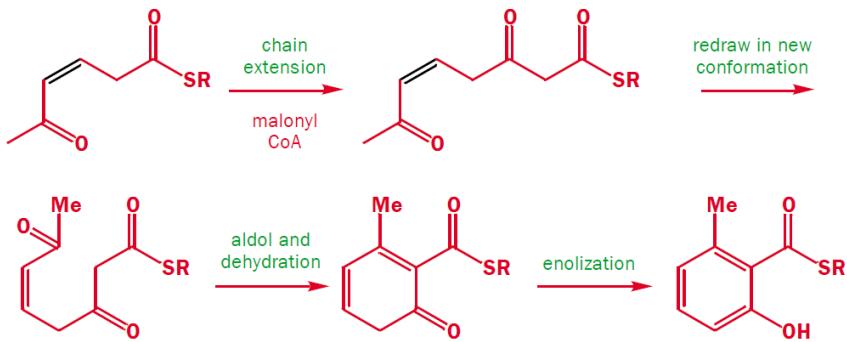
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Biosinteze preko acetata - poliketidi



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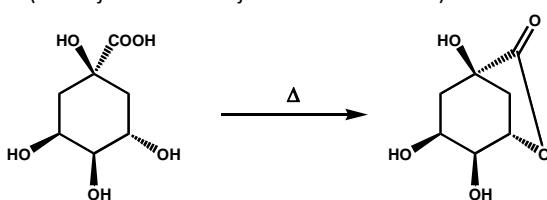
Biosinteze preko acetata - poliketidi



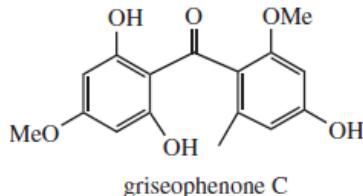
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ZADACI

- 1.) Kina kiselina zagrijavanjem vrlo lako prelazi u lakton. Objasnite to na temelju njezine strukture (nacrtajte konformacije stolca te molekule).



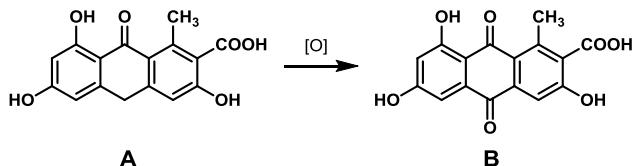
- 2.) Griseofenon C, međuproduct u biosintezi griseofulvina, kojeg proizvodi gljivica *Penicillium griseofulvum*, poliketidni je spoj koji nastaje acetatnim putem. Prikažite ravni poli- β -keto lanac čijom ciklizacijom nastaje ovaj spoj. (Metilne skupine su na kisik dodane u zadnjem stupnju iz S-adenozilmisionina)



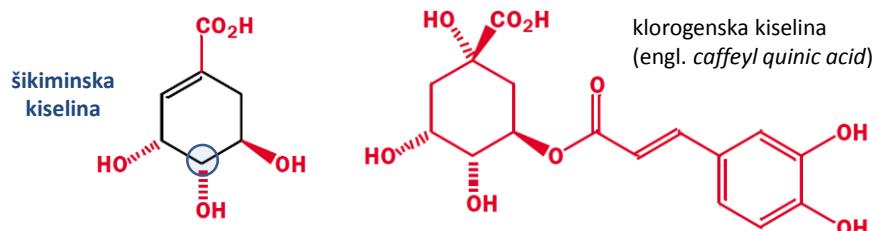
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ZADACI

3.) Antrakinon **B** nastaje iz antrona **A** reakcijom oksidacije. Prikažite ravn poli- β -ketonski lanac iz kojeg nastaje spoj **A**.



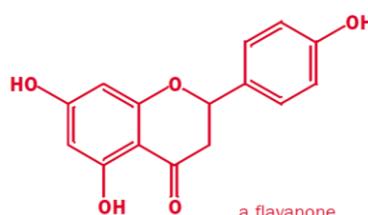
4.) Označite gdje će se naći radioaktivni biljeg ako je biosinteza započeta iz šikiminske kiseline označene na C-atomu kako je prikazano:



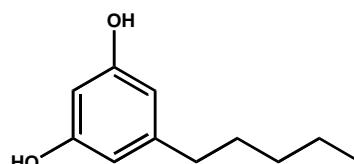
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DOMAĆA ZADAĆA

1.) Biosinteza flavonoida koristi oba puta sinteze aromatskog prstena. Tako jedan prsten nastaje acetatnim putem, a drugi šikimatnim. Prikažite korake u biosintези flavona.



2.) Predložite biosintezu olivetola. Poli- β -ketonski lanac iz kojeg kreće biosinteza mora sadržavati i $-C(O)SCoA$ skupinu na početku lanca. (Mala pomoć: u sintezi dolazi do reakcije dekarboksilacije, tj. gubitka $COOH$ skupine kao CO_2)



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