LIPID REACTIONS

Technologically significant reactions (oleochemistry)

1. esterification

enzymatic (lipases)

nonenzymatic (acid and base catalysis)

<u>1.1.esterifications</u>

20-100 °C, H_2SO_4, HCl

$R\text{-}OH + R^1\text{-}COOH \rightarrow R^1\text{-}COOR + H_2O$

glycols, alditols + FA → emulsifiers

glycerol + FA (hydroxyl acids) → emulsifiers (MAG and DAG)

1.2. interesterification

acidolysis

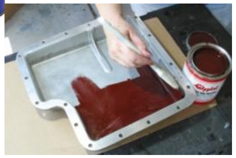
R^1-COOR + R^2-COOH → R^2-COOR + R^1-COOH

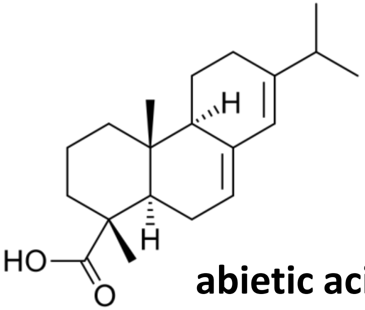
without catalyst, 250-300 °C; catalyst H_2SO_4, 150-170 °C

TAG + abietic acid → varnish

TAG + phthalic acid → glyptals

(drying oil – similar to natural resins)





abietic acid derived from lat. word *Abies* = fir; nonvolatile component of turpentine

exchange lower/higher FA   coconut oil, palm kernel fat

enzymatically using lipase - synthesis of "structured TAG“

CBE fat (Cocoa Butter Equivalent) = POSt + StOSt

alcoholysis

$R^1\text{-COOR} + R^2\text{-OH} \rightarrow R^1\text{-COOR}^2 + \text{R-OH}$

NaOH, NaOR 20 °C and more, H_2SO_4 ~ 100 °C, without catalyst 250 °C, enzymatically by lipases

methanolysis → Me-esters, biodiesel

butanolysis → Bu-esters (plasts softenings)

glycerolysis → parcial esters (emulsifiers)

transesterification

$R^1\text{-COOR} + R^2\text{-COOR}^3 \rightarrow R^1\text{-COOR}^3 + R^2\text{-COOR}$

without catalyst ~ 250 °C, acidic, basic catalyst < 100 °C, enz. lipases

in the resulting mixture the distribution of FA in TAG is accidental

– randomisation (melting point higher for about 20 °C)

2. molecule splitting - hydrolysis and saponification

$R^1\text{-COOR} \rightarrow R^1\text{-COOH} + R\text{-OH}$

autocatalysed hydrolysis at high temperatures over 200 °C

saponification by hydroxides soaps

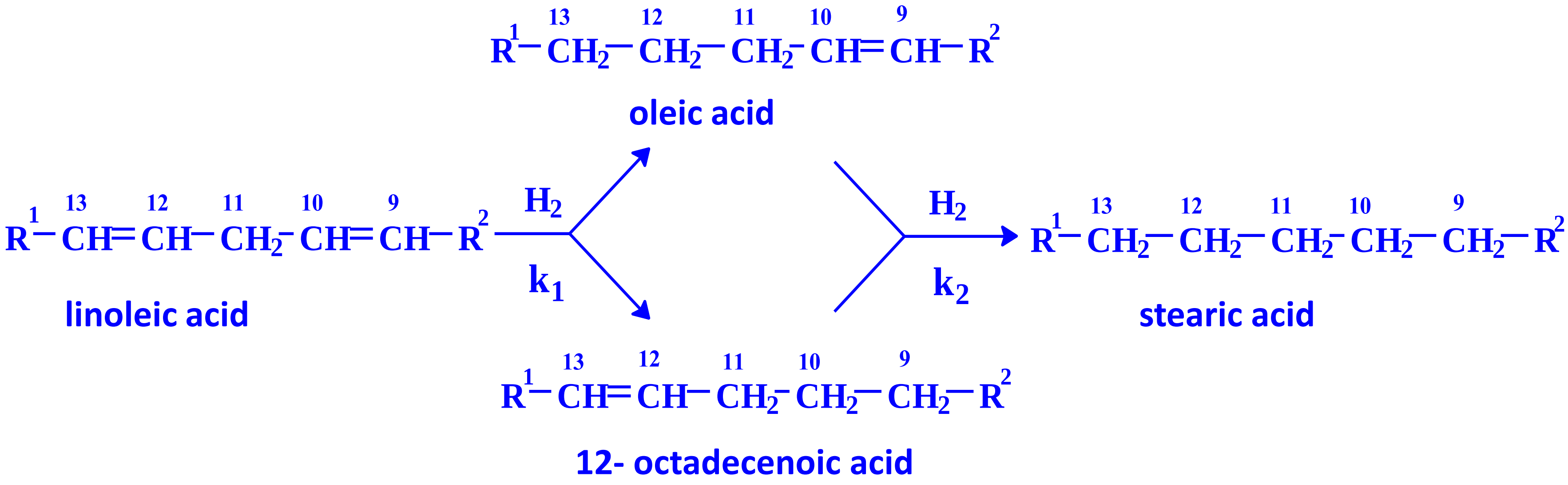
3. hydrogenation

$\text{-CH=CH-} \rightarrow \text{-CH}_2\text{-CH}_2\text{-}$

H_2, 150-200 °C, Ni-catalyst; 0,1-0,2 MPa

hardened fats (hardening, hydrogenation)

stability against oxidation, consistency, absence of trans-acids



$k_1 > k_2$ selective (dienic from trienic, rape oil)

$k_1 < k_2$ nonselective

side-reactions

- positional isomerisation (unusual isomers)
- *cis/trans* isomerisation (30-45% *trans*-isomers)

Rancidity of oils and fats

- hydrolytic rancidity
- scented rancidity
- reversion
- oxidation

hydrolytic rancidity

- enzymatic reactions: lipases (butter, coconut oil, palm oil)
- chemical reaction: frying

TAG → FA + DAG + MAG

• butter, milk, coconut oil, palm oil	undesirable
• chocolate	partly desirable
• cheese	desirable

threshold value (mg/kg) of free fatty acids

FA		cream		coconut fat	
		smell	taste	smell	taste
C4:0	rancid	50	60	35	160
C6:0	rancid	85	105	25	50
C8:0	moldy, rancid, soapy	200	120	> 1000	25
C10:0	soapy	> 400	90	> 1000	15
C12:0	soapy	> 400	130	> 1000	35
C14:0	soapy	> 400	> 400	> 1000	75

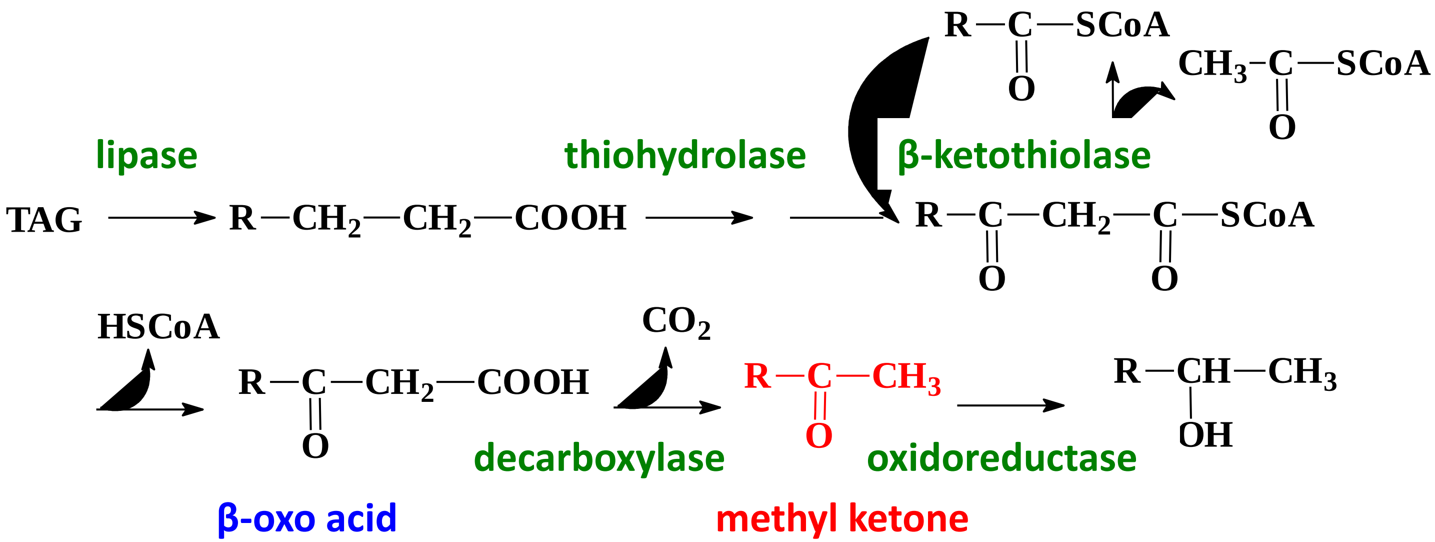
flavor of polyunsaturated fatty acids in emulsions

(taste of the corresponding TAG is neutral)

FA	threshold value μmol/l	taste
oleic	9-12	bitter, spicy
linoleic	4-6	bitter, spicy
elaidic	22	weakly spicy
α-linolenic	3-6	weakly spicy
γ-linolenic	0.6-1.2	weakly spicy
arachidonic	6-8	weakly spicy

scented rancidity

- enzymatic reaction: microorganisms and their enzymes
- FA with short and medium carbon chain
- milk fat, coconut oil, palm oil — undesirable
- mould cheeses — desirable



methylketon	smell	threshold value µg/kg (in water)
pentan-2-on	fruity (bananas)	2300
hexan-2-on	fruity (bananas)	930
heptan-2-on	flowery, herbal	650
octan-2-on	flowery	190
nonan-2-on	flowery, meaty	190

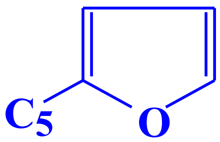
reversion

typical for soybean oil (or other oil containing linolenic acid)

chemical r. (autoxidation) →hydroperoxides→ derivatives of furan

off-flavour:

the smell of varnish, fish, grass, beans



refining can remove odor, but the defect returns ⇨ reversion

OXIDATIVE RANCIDITY

oxidation of the hydrocarbon chains

- nonenzymatic reactions

  atmospheric oxygen (triplet/ $^3O_2$) ⇨ autoxidation

  reactive oxygen species (singlet/$^1O_2$,radicals, H_2O_2)

  5 excited states $^1\Sigma$ (sigma) $^1\Delta$ (délta)

  157 kJ 93,8 kJ

  formation in food: photochemical reactions with the participation of photosensitizers from $^3O_2$

  pigments (riboflavin, chlorophyll, heme)

  free radicals

  •O_2^- (superoxide radical)

  •OH (hydroxyl radical)

- enzymatic reactions

  lipoxygenases (formerly lipoxidases)

consequences

negative

lowering of sensory quality

fats, oils, foods

cosmetics, gasoline

lowering of nutritive value

reaction of oxidised lipids with proteins

lowering of hygiene-toxicological quality

toxic products

aging, illness (*in vivo*)

positive

formation of aromatic compounds

nonenzymatic reactions
oxidation by triplet oxygen, autoxidation

general mechanism of hydrocarbon chain autoxidation
(radical reaction)

1. **induction stage**

   R-H → R• + •H   hydrocarbon radical

   iniciators, homolytic decomposition

1. **propagation stage**

   R• + O_2 → R-O-O•   hydroperoxyl radical

   R-O-O• + R-H → R-O-O-H + R•   hydroperoxide

   up to thousands of segments (influence temperature, pO_2 etc.)

   hydroperoxide= primary oxidation product

   decomposition of hydroperoxides

3. **terminal stage**

   mutual radical reactions, polymers of various types

   R• + R• → R-R   C-C bond

   R• + R-O-O• → R-O-O-R   C-O-O-C bond (peroxide)

   2 R-O-O• → R-O-O-R + O_2

initiation

mainly fotosensitized (photo-oxidation) and enzymatic reactions

singlet oxygen

hydroperoxide

„first radicals“ from hydroperoxide decomposition

hydroperoxide decomposition

monomolecular decomposition

R-O-O-H → R-O• + •OH **alkoxyl radical**

bimolecular decomposition (at higher concentrations of ROOH)

2 R-O-O-H → R-O-O• + R-O• + H_2O

reactivity of radicals

HO• > R-O• > R-O-O•

subsequent fate of alkoxyl radicals

decomposition → aromatic compounds

recombination in terminal stage

R• + R-O• → R-O-R **bond C-O-C**

R-O• + R-O-O• → R-O-R + O_2

oxidation of unsaturated acids (at ordinary temperature)

O : L : LL = 1 : 10 : 100

structure	dissociation energy (kJ / mol)
H-CH_2-	422
CH_3-CH-H-	410
-H-CH-CH=CH-	322
-CH=-CH-H-CH-CH=CH-	272

oxidation of unsaturated acids

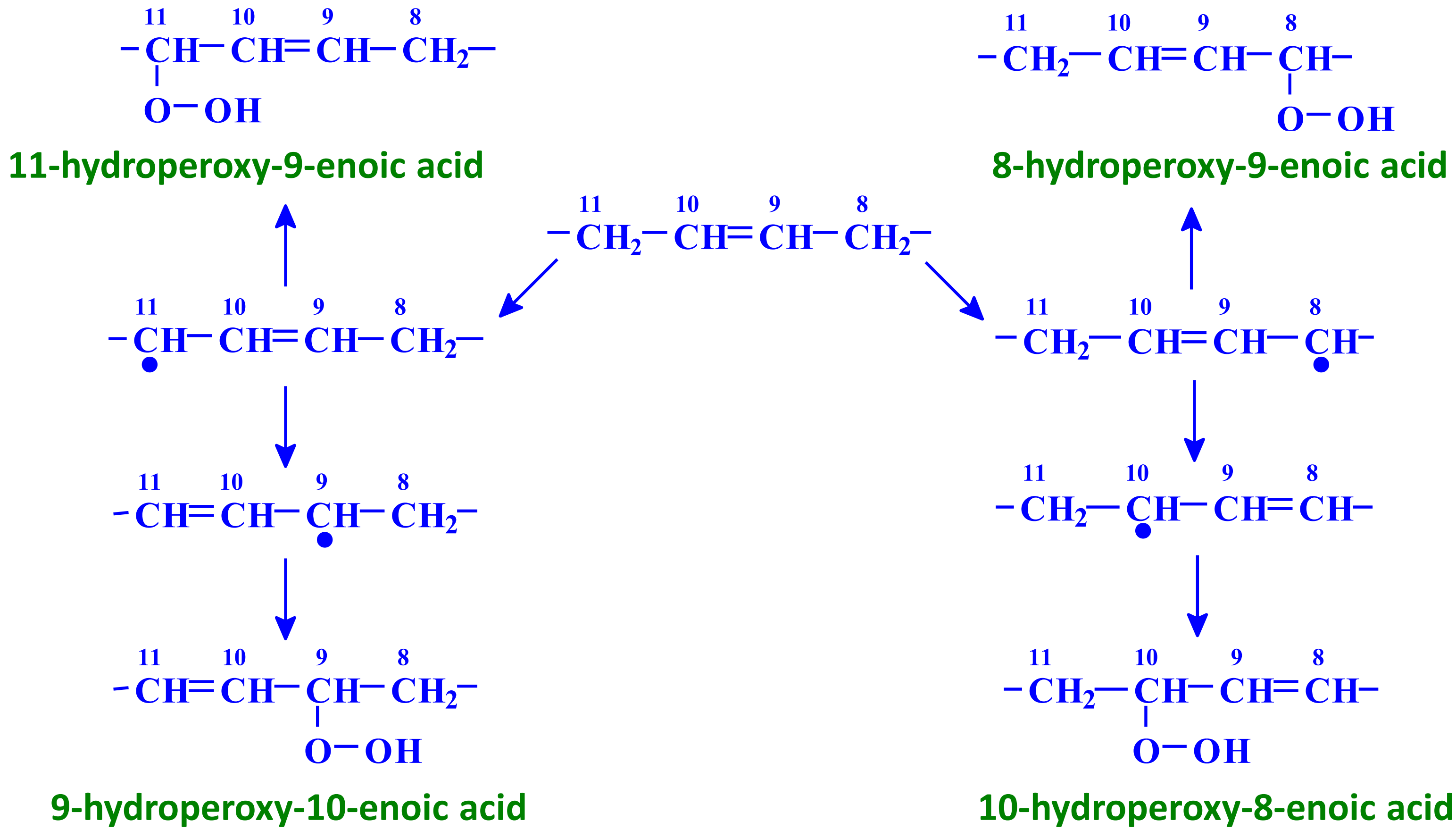
ambient temperature

oxidation of saturated acids

temperatures of frying and roasting

oxidation of oleic acid

→ mixture of 4 hydroperoxides in ratio of cca 1:1:1:1

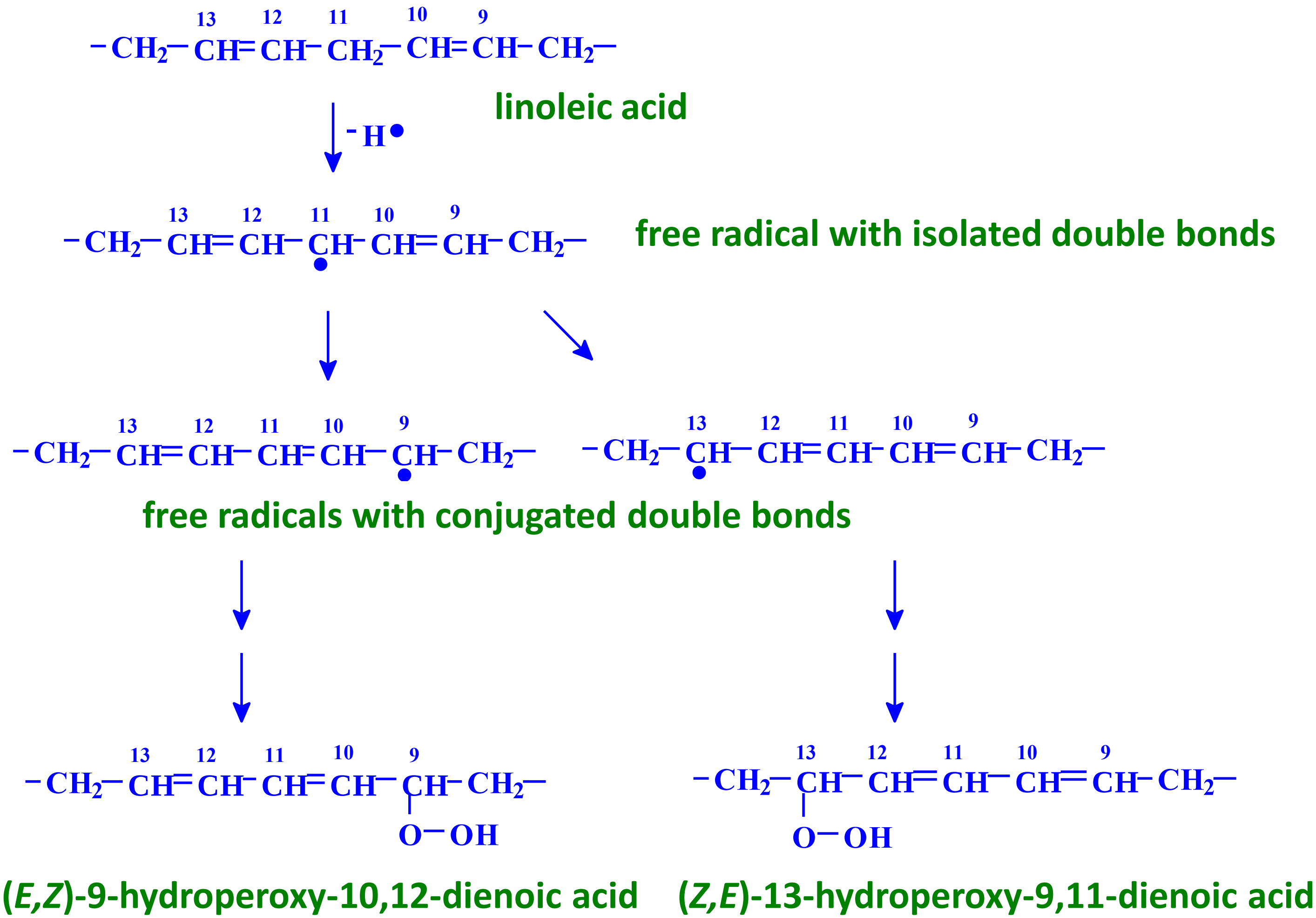


geometric isomers *cis* or *trans*

positional isomers - mainly *trans*

oxidation of linoleic acid

→ **mixture of 7 hydroperoxides, mostly 9- and 13-**



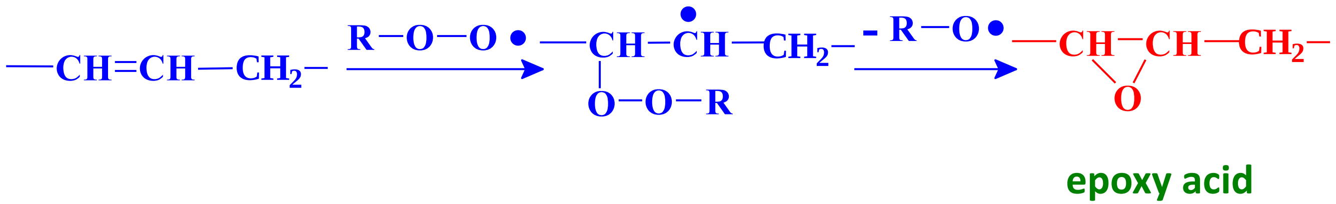
oxidation of linolenic acid

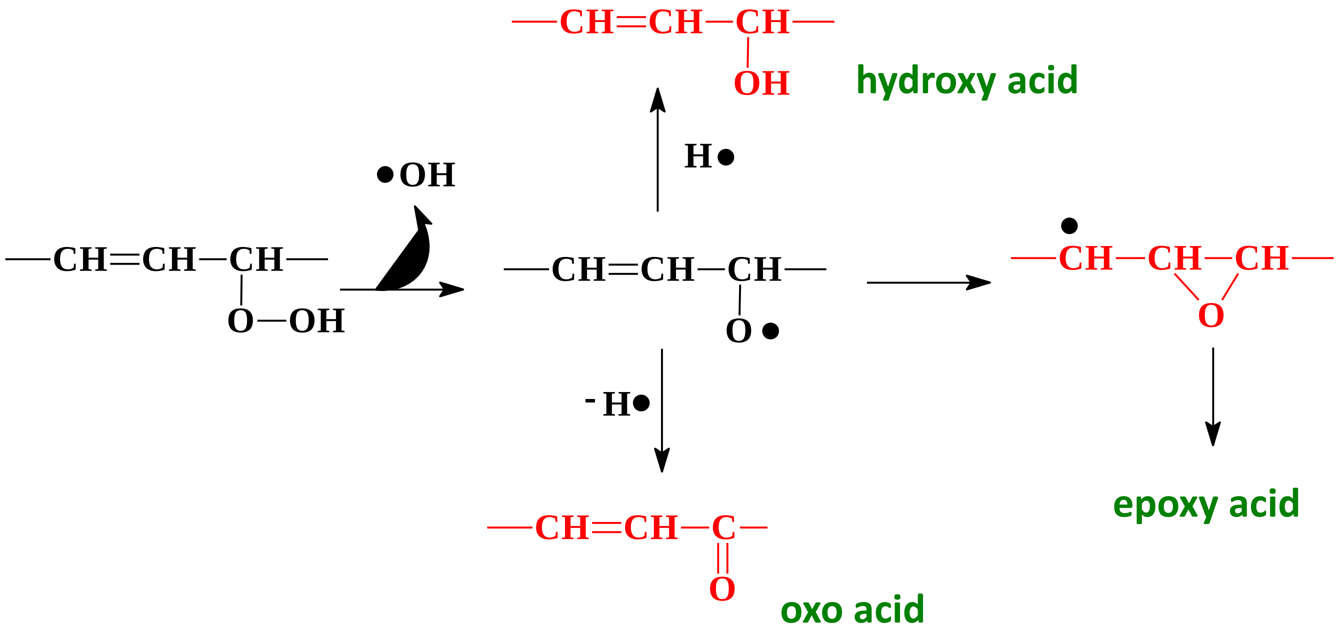
→**mixture of many hydroperoxides – mostly 9-, 12-, 13- and 16- with 2 conjugated double bonds and one isolated bond** subsequent reaction of hydroperoxides

→ secondary autooxidation products

• same number of C atoms	epoxy-, hydroxy-, oxo-acids
• lower number	aldehydes, hydrocarbons and others
• higher number	various polymers

formation of epoxy-, hydroxy- a oxo-compounds

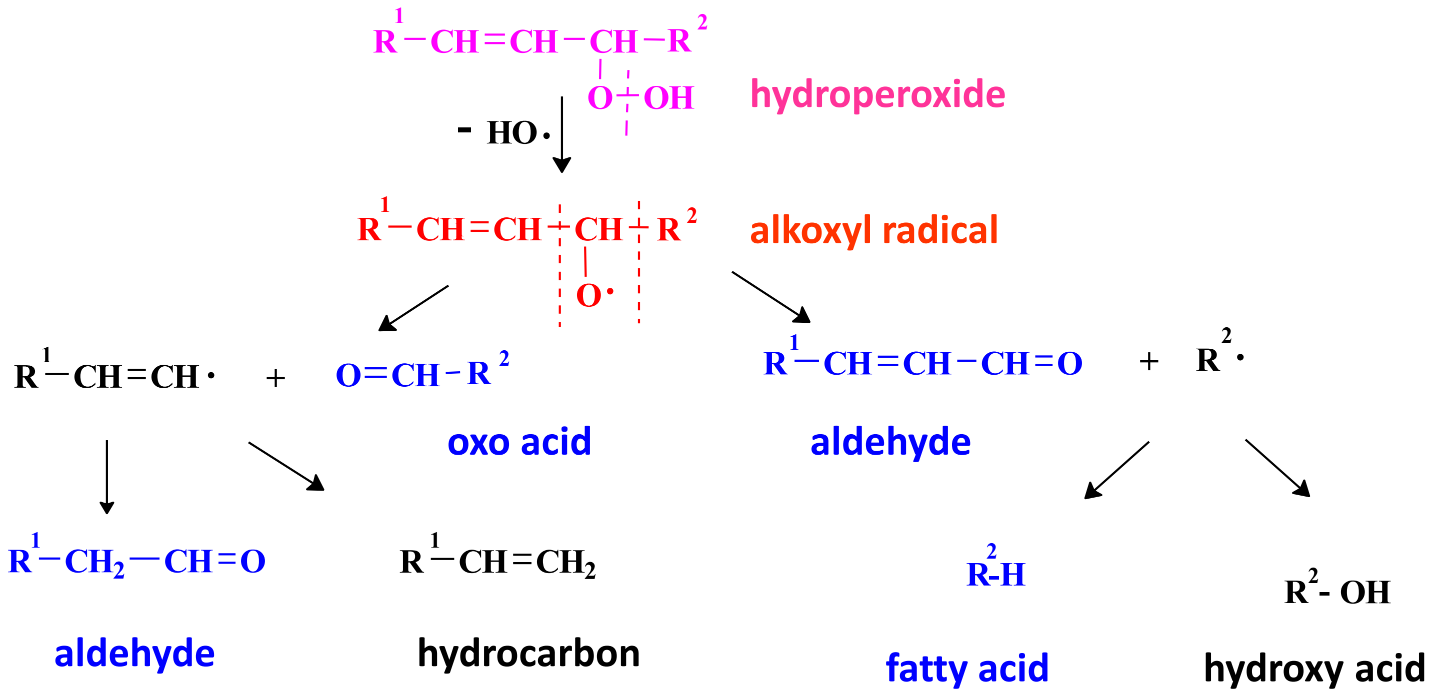




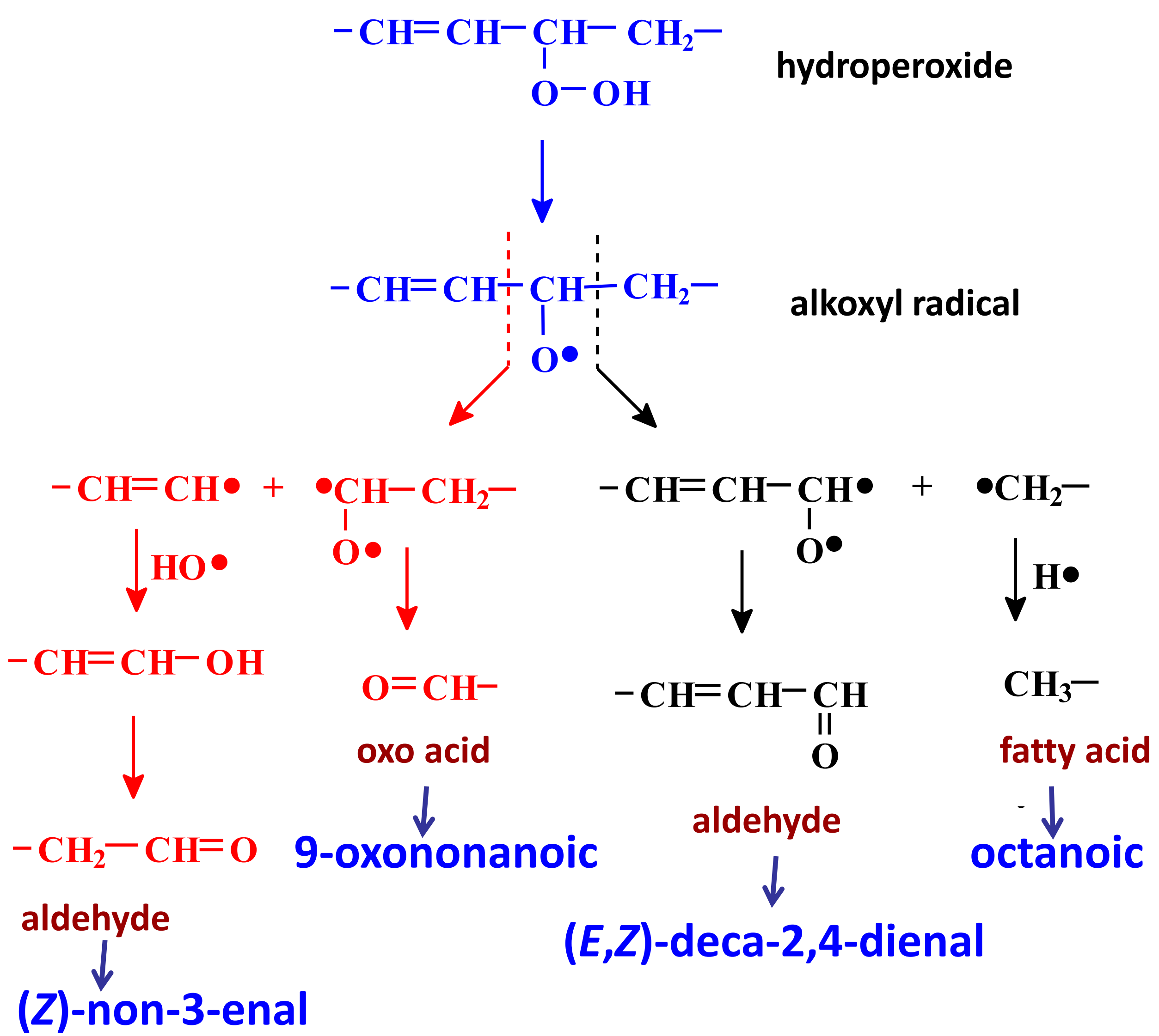
formation of aldehydes and hydrocarbons

volatile secondary products - flavour compounds

general mechanisms



for example 9-hydroperoxy-10,12-fatty acid from linoleic acid



subsequent reaction of aldehydes

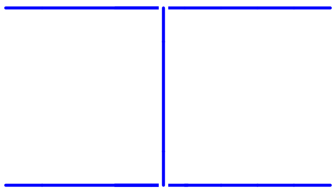
some of aldehydes arising by oxidation of unsaturated acids

primary aldehyde	aldehyde after isomeration	hydroperoxy acid
(*Z*)-undec-2-enal	(*E*)-2-undecenal	(*Z*)-8-hydroperoxyoctadec-9-enoic
(*E*)-dec-2-enal		(*E*)-9-hydroperoxyoctadec-10-enoic
nonanal		(*E*)-10-hydroperoxyoctadec-8-enoic
octanal		(*Z*)-11-hydroperoxyoctadec-9-enoic
(*Z,Z*)-undeca-2,5-dienal	(*E,E*)-undeca-2,4-dienal	(*Z,Z*)-8-hydroperoxyoctadeca-9,12-dienoic
(*E,Z*)-deca-2,4-dienal	(*E,E*)-deca-2,4-dienal	(*E,Z*)-9-hydroperoxyoctadeca-10,12-dienoic
(*Z*)-non-3-enal	(*E*)-non-2-enal	(*E,Z*)-10-hydroperoxyoctadeca-8,12-dienoic
(*Z*)-okte-2-nal	(*E*)-okt-2-enal	(*Z,Z*)-11-hydroperoxyoctadeca-9,12-dienoic
(*E*)-hept-2-enal		(*Z,E*)-12-hydroperoxyoctadeca-9,13-dienoic
hexanal		(*Z,E*)-13-hydroperoxyoctadeca-9,11-dienoic
pentanal		(*Z,Z*)-14-hydroperoxyoctadeca-9,12-dienoic
(*E,Z,Z*)-deca-2,4,7-trienal		(*E,Z,Z*)-9-hydroperoxyoctadeca-10,12,15-trienoic
(*Z,Z*)-nona-3,6-dienal	(*E,Z*)-nona-2,6-dienal	(*E,Z,Z*)-10-hydroperoxyoctadeca-8,12,15-trienoic
(*Z,Z*)-octa-2,5-dienal	(*E,E*)-octa-2,4-dienal	(*Z,Z,Z*)-11-hydroperoxyoctadeca-9,12,15-trienoic
(*E,Z*)-hepta-2,4-dienal	(*E,E*)-hepta-2,4-dienal	(*Z,E,Z*)-12-hydroperoxyoctadeca-9,13,15-trienoic
(*Z*)-hex-3-enal	(*E*)-hexe-2-nal	(*Z,E,Z*)-13-hydroperoxyoctadeca-9,11,15-trienoic
(*Z*)-pent-2-enal	(*E*)-pent-2-enal	(*Z,Z,Z*)-14-hydroperoxyoctadeca-9,12,15-trienoic
propanal		(*Z,Z,E*)-16-hydroperoxyoctadeca-9,12,14-trienoic

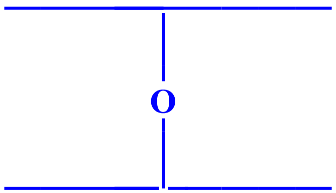
organoleptic properties of aldehydes

aldehyde	smell	precursor
propanal	pungent	linolenoic acid
pentanal	pungent	linoleic acid
hexanal	tallowish, grass	linoleic acid
heptanal	oily, greasy	oleic acid
nonanal	tallowish	linolenoic acid
(*E*)-pent-2-enal	oily, greasy, grass	linolenoic acid
(*Z*)-hex-3-enal	Grass	linolenoic acid
(*E*)-hex-2-enal	oily, greasy, grass	linolenoic acid
(*E*)-hept-2-enal	oily, greasy	linoleic acid
(*Z*)-okt-2-enal	after walnuts	linoleic acid
(*E*)-okt-2-enal	oily, greasy	linoleic acid
(*E*)-non-2-enal	oily, greasy	linoleic acid
(*E*,*Z*)-hepta-2,4-dienal	oily, greasy, after frying fats	linolenoic acid
(*E*,*E*)-hepta-2,4-dienal	oily, greasy	linolenoic acid
(*Z*,*Z*)-nona-3,6-dienal	after cucumber	linolenoic acid
(*E*,*Z*)-nona-2,6-dienal	after cucumber	linolenoic acid
(*E*,*Z*)-deca-2,4-dienal	after frying fats	linoleic acid
(*E*,*E*)-deca-2,4-dienal	after frying fats	linoleic acid
(*E*,*Z*,*Z*)-deca-2,4,7-trienal	after fish oil	linolenoic acid

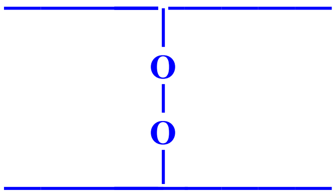
polymers formation usually by reaction of two radicals



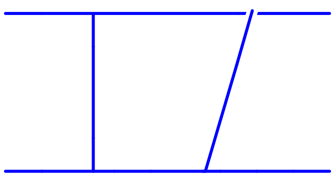
C-C bonds



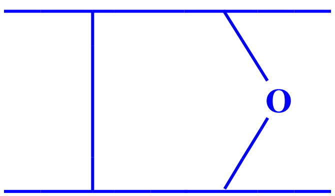
ether bonds



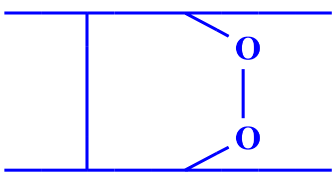
peroxide bonds



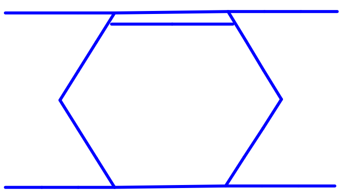
two-fold C-C bond cyclopentane cycle



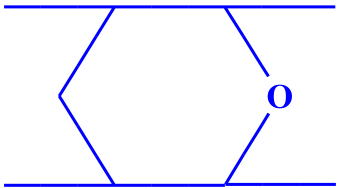
tetrahydrofurane bonds



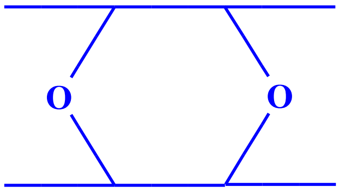
C-C and peroxide bonds



two-fold bond C-C cyclohexenic cycle



tetrahydropyrane bonds



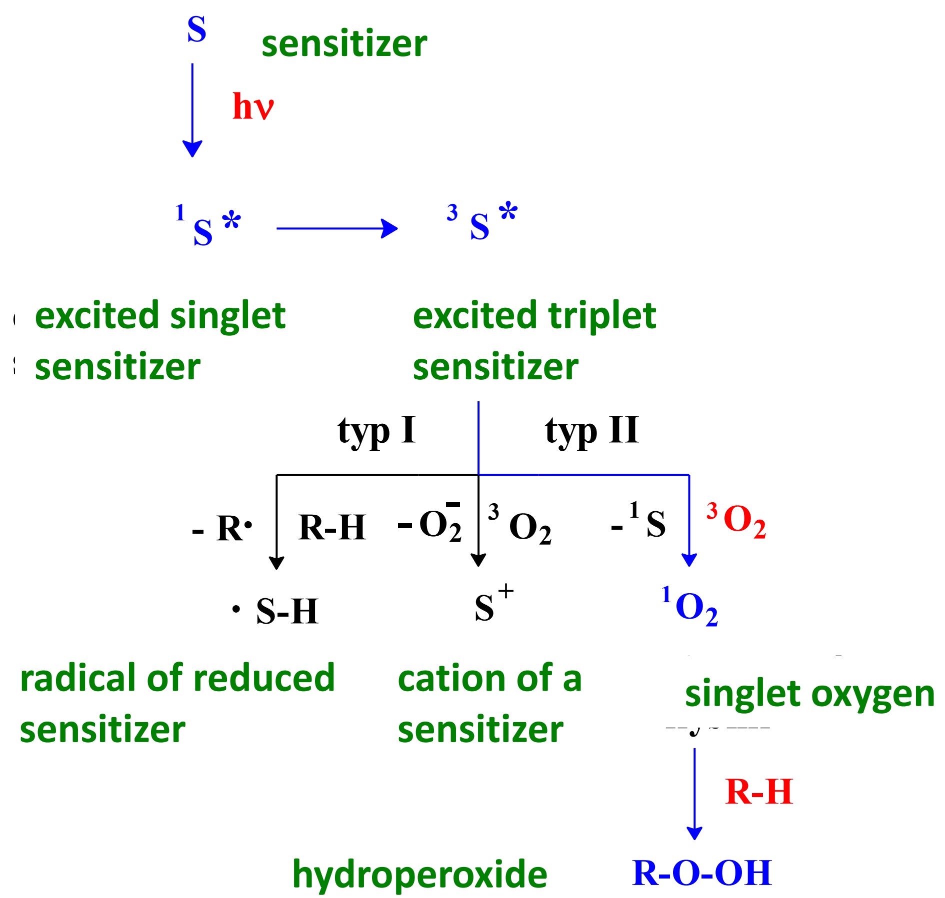
dioxane bonds

oxidation with singlet oxygen

formation

- photooxidation (photosensitizers)
- enzymatic reaction (photosynthesis)

addition to the double bond, ~ 1000 x faster than oxidation



scavengers of singlet oxygen and hydroxyl radicals

- can quench singlet oxygen

- **β-carotene and other carotenoides**
- **tocopherols**
- **ascorbic acid**

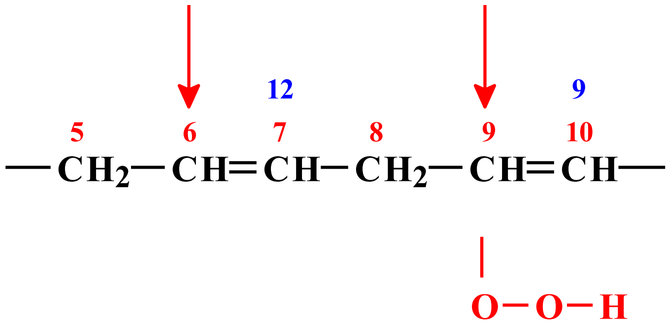
^{1}**carotenoid** + $^{1}O_2 \rightarrow$ ^{3}**carotenoid** + $^{3}O_2$

^{3}**carotenoid (excited triplet state)** $\rightarrow$ ^{1}**carotenoid** enzymatic oxidation

lipoxygenases (lipoxidases, linoleate: O_2 oxidoreductase)

$E_{18:2}$ = 17 kJ/mol

unsaturated FA → hydroperoxide of UFA (optically active)



$C_{18:2}$	9- a 13-hydroperoxides	10-hydroperoxides
$C_{18:3}$	9- a 13-hydroperoxides	10-hydroperoxides

specifity (regio-, stereo-)

example $C_{18:2}$

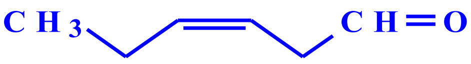
soya	→ (13*S*)-, 9-*cis*-, 11-*trans*-
tomatoes	→ (9*S*)-, 10-*trans*-, 12-*cis*
mushrooms	→(10*S*)-, 8-*trans*-, 12-*cis*-

negative, positive consequences

animals: decomposition by glutathionperoxidases

plants and mushrooms: splitting by lyases, isomerases, aroma compounds

13-OOH-9,11,15- ~

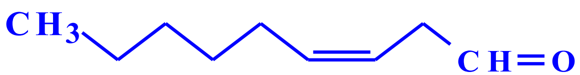


(*Z*)-hex-3-enal grass (green) flavour

(*Z*)-hex-3-enal —isomerace→ (*E*)-hex-2-enal leaf aldehyde

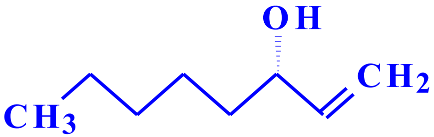
oily, greasy, green smell

9-OOH-10,12,15- ~ —lyasy→



(*Z*)-non-2-enal oily smell

10-OOH-8,12- ~ —lyasy→



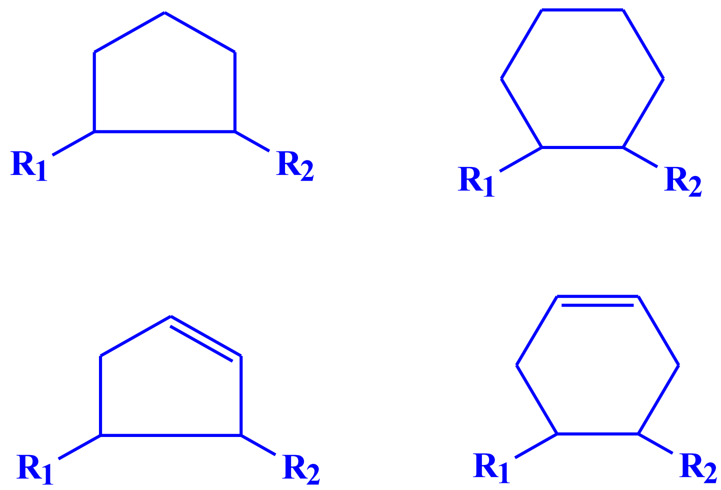
(*R*)-okt-1-en-3-ol mushroom-like smell

termic reactions

geometric isomerization *cis/trans*

positional isomerization

cyclization

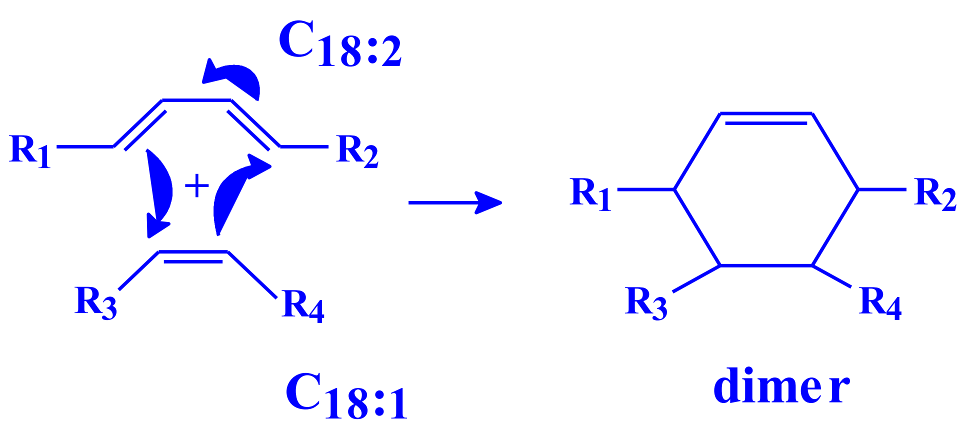


$C_{18:1}$

$C_{18:2}$

polymerization

Diels-Alder reaction



inhibition of autoxidation

- temperature
- air (oxygen)
- radiation (UV)
- composition of the fat (ratio of SFA/UFA)
- inhibitors (antioxidants, synergists)

antioxidants

classification according to origin

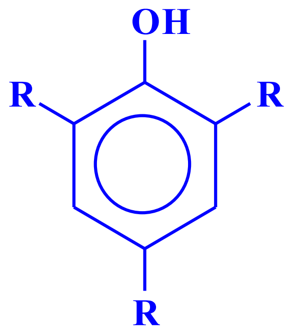
- natural (mostly tokopherols, phenols)
- synthetic (mostly phenols)

classification according to activity (mechanisms)

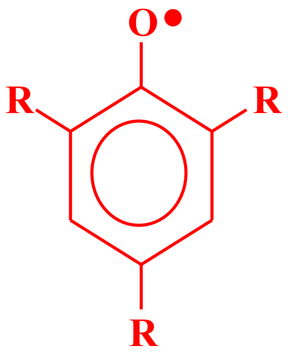
- primary (reaction with radicals)
- secondary (reduction of R-O-OH)

phenolic antioxidants (mechanism of action)

R-O-O• + H-A $\rightarrow$ R-O-O-H + A•



H-A (antioxidant)



A• (antioxidant radical)

main reactions

2A• $\rightarrow$ A-A

A• + R-O-O• $\rightarrow$ R-O-O-A

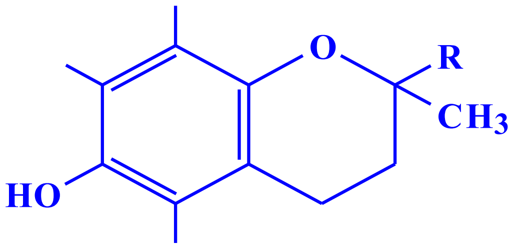
A• + R-O• $\rightarrow$ R-O-A

side reactions (> 0,01%)

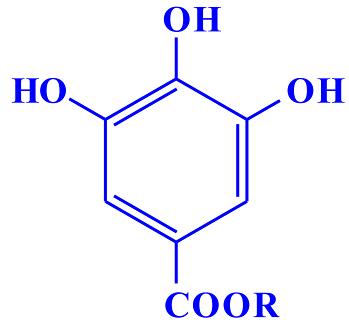
A• + O_2 $\rightarrow$ A-O-O•

A-O-O• + R-H $\rightarrow$ A-O-O-H + R•

main natural antioxidants

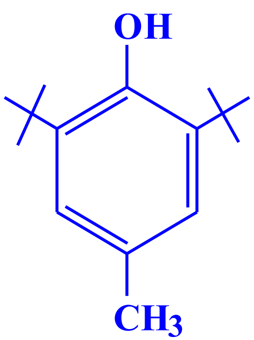


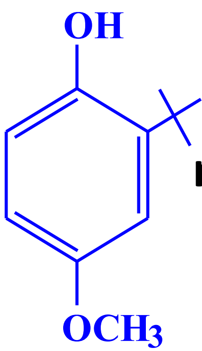
tocopherols



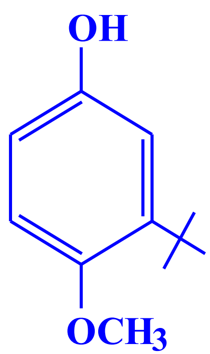
gallates

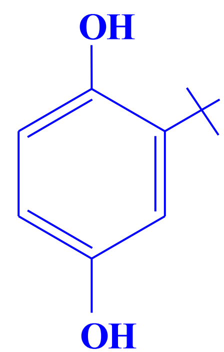
main synthetic antioxidants





nebo





BHT

BHA (cca 9 : 1)

TBHQ

applications

BHA, BHT, tocopherols, dodecylgallate — type of emulsion: oil/water

TBHQ, propygallate — pure fats (oils)

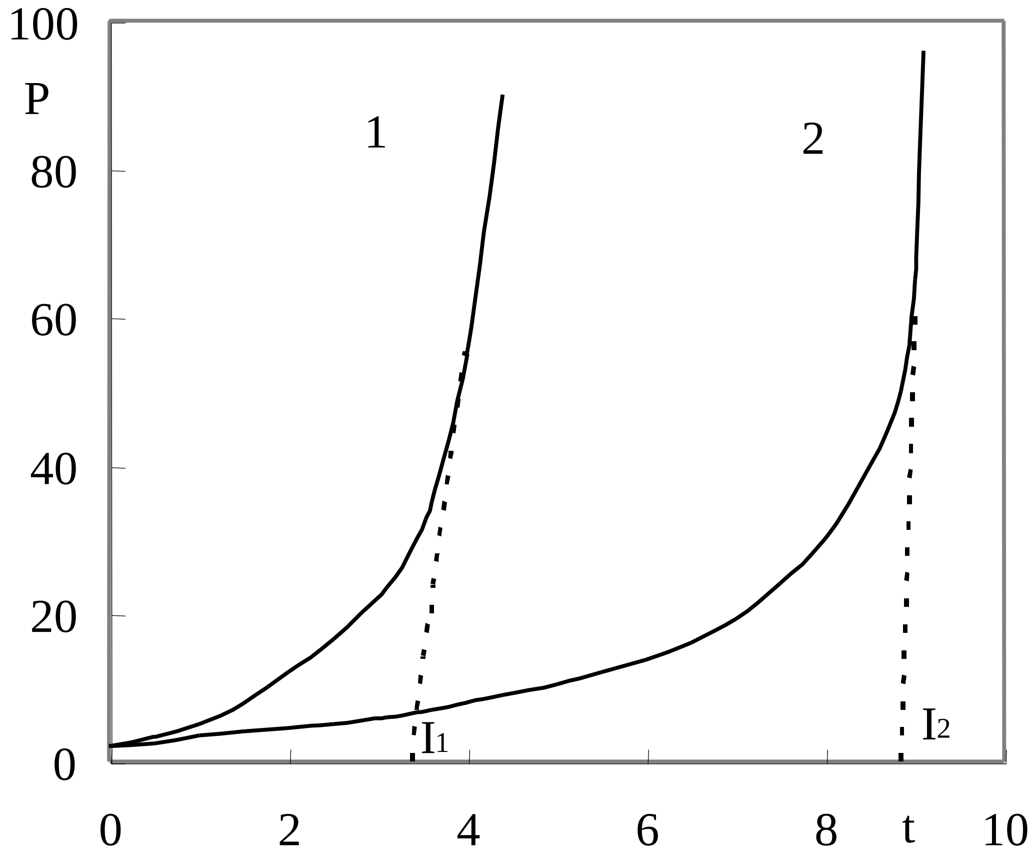
antioxidant effect on the process of autoxidation reactions

P - peroxide number

t – time of autoxidation at 60°C (days)

1 - antioxidant BHA = 0%   2 – BHA=0,02%

I_1 a I_2 = induction periods   **protective factor PF = $(I_2-I_1)/I_1$**



PF, lard, 0,02%	
α-tocopherol	5
BHT	6
γ-tocopherol	15
BHA + BHT	12
BHA	9.5
octylgallate	6