

4. AUTOXIDATION AND OTHER LIPID REACTIONS

A) Technologically significant reactions (oleochemistry)

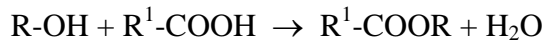
1. esterification

enzymatic (lipases)

nonenzymatic (acid and base catalysis)

1.1 esterifications

20-100 °C, H₂SO₄, HCl

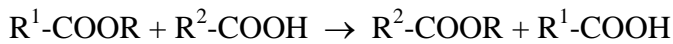


glycols, alditols + FA → emulsifiers

glycerol + FA (hydroxyl acid) → emulsifiers

1.2 interesterification

acidolysis



without catalyst, 250-300 °C; with catalyst H₂SO₄, 150-170 °C

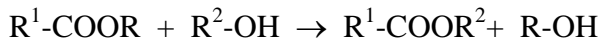
TAG + abietic acid. → varnish

TAG + phthalic acid → glyptals

(drying oil ~ natural resins)

exchange lower/higher FA → coconut oil, palm kernel fat

alcoholysis



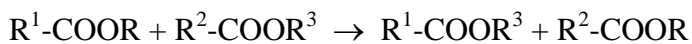
NaOH, NaOR 20 °C and more, H₂SO₄ ~ 100 °C, with catalyst at 250 °C

methanolysis → Me-esters, biofuels

butanolysis → Bu-esters (plasts softenings)

glycerolysis → parcial esters (emulsifiers)

transesterification



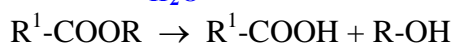
without catalyst ~ 250 °C, acidic, basic catalyst < 100 °C

cacao butter, randomisation (melting point higher for about 20 °C)

oil + tallow → digestability, consistence

2. molecule splitting

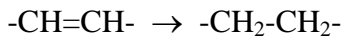
H₂O



saponification 1-2 MPa

hydroxides, soaps as products

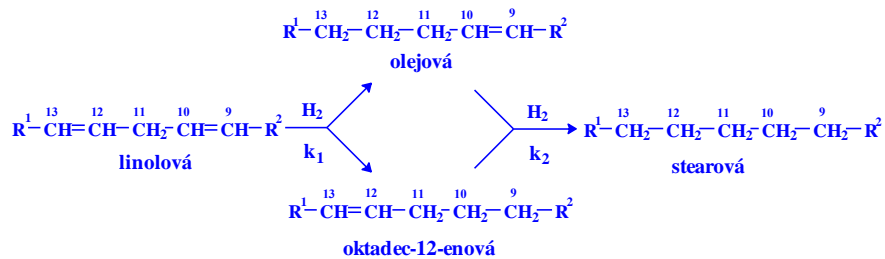
3. hydrogenation



H₂, 150-200 °C, Ni-catalyst; 0,1-0,2 MPa

hardened fats (hardening, hydrogenation)

composition of fatty acids (book 1, tab.3.43)



stability against oxidation, consistency, absence of *trans*-acids

side-reactions

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

hydrogenation smell: α -linolenic \rightarrow (*Z,E*)-oktadeca-9,15-dienoic \rightarrow (*E*)-non-6-enal

other products (fatty alcohols, ethers)

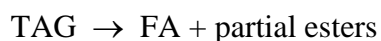
- FA \rightarrow R-OH (~ 20 MPa)
- esters \rightarrow ethers type R-O-R¹ (nonresorbate fats)

B. Rancidity of oils and fats

- hydrolytic rancidity
- scented rancidity
- reversion
- oxidation

hydrolytic rancidity

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



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

threshold value (mg/kg) free fatty acids, smell, taste (bitter)

scented rancidity

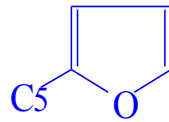
- enzymatic reaction: mikroorganisms and their enzymes
- FA with short and medium carbon chain

- milk fat, coconut oil, palm oil undesirable
- mould cheese desirable

reversion

chemical reaction (autooxidation)

wornish, fish and bean smell in oils containing C_{18:3} acids (soybean oil)



oxidative rancidity

- **consequences**

negative

lowering of sensory quality

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 reaction**

air oxygen (³O₂)

reactive forms of oxygen (singlet oxygen, radicals, H₂O₂)

singlet oxygen ¹O₂

formation: photosensitised reactions ³O₂

pigments (riboflavin, chlorophyll, hem)

free radicals

•O₂⁻ (superoxide radical)

•OH (hydroxyl radical)

- **enzymatic reactions**

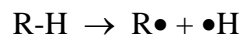
lipoxygenases (lipoxidases)

nonenzymatic reactions

oxidation by triplet oxygen, autoxidation

general mechanism of hydrocarbon chain autoxidation
(radical reaction)

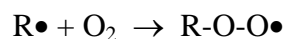
1. induction stage



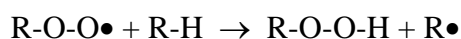
hydrocarbon radical

initiators, homolytic decomposition

2. propagation stage



hydroperoxyl radical



hydroperoxide

up to thousands of segments (influence temperature $p\text{O}_2$.)

hydroperoxide= primary oxidation product

hydroperoxides decomposition

3. terminal stage

mutual radical reactions, polymers of different type



bound C-C



bound C-O-O-C



induction

mostly photooxidation and enzymatic reaction

singlet oxygen

hydroperoxide, first radicals forming due to decomposition of hydroperoxides

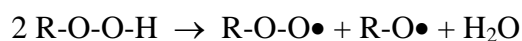
decomposition of hydroperoxides

monomolecular decomposition

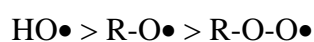


alkoxyl radical as a new species

bimolecular decomposition (at higher concentration ROOH)



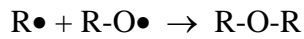
reactivity of radicals



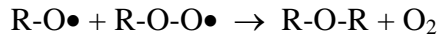
fate of alkoxy radicals

decomposition → aromatic compounds

recombination in terminal stage



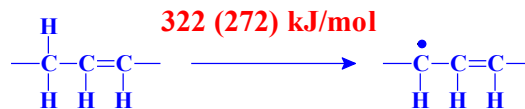
bound C-O-C



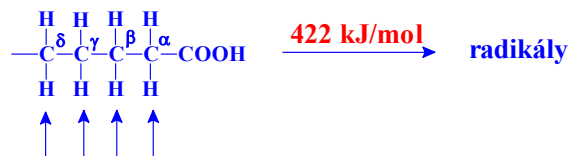
oxidation of unsaturated acids (at ordinary temperature)

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



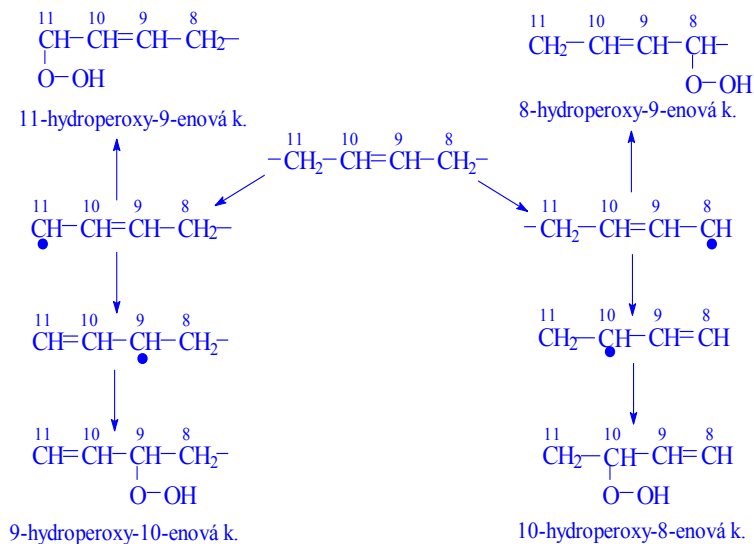
oxidation of saturated acids (at elevated temperature)



frying and roasting

mechanisms: oxidation of oleic acid

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



cis (or *trans*), *trans* -

geometric isomers

positional isomers

oxidation of linoleic acid

→ mixture 7 hydroperoxides, mostly 9- a 13-

oxidation of linolenic acid

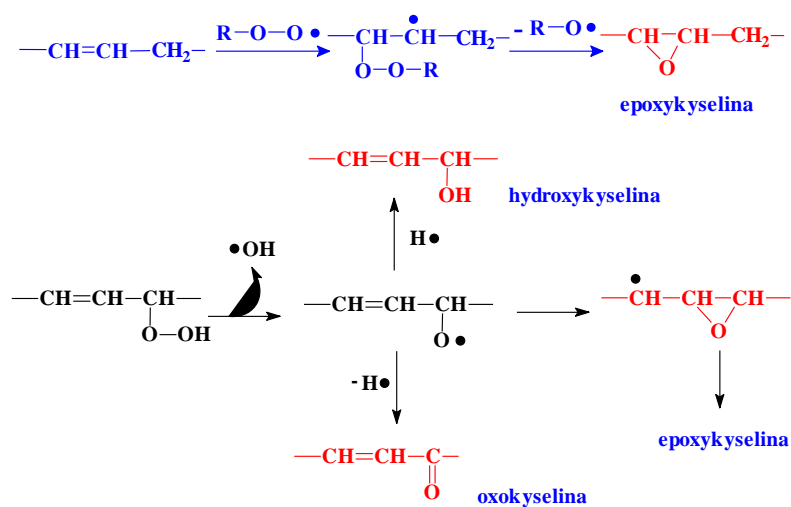
→ mixture of many hydroperoxides
 mostly 9-, 12-, 13- and 16- with 2 conjugated double bonds and one isolated bond

subsequent reaction of hydroperoxides

→ secondary autooxidation products

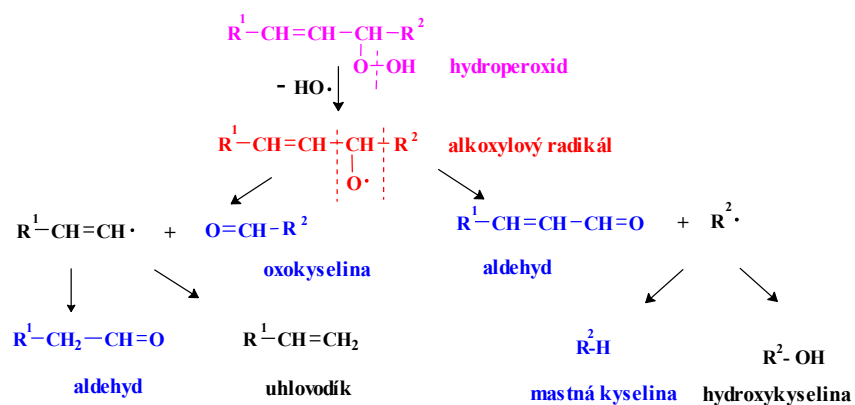
- same number C epoxy-, hydroxy-, oxo-acids
- lower number C aldehydes, hydrocarbons and others
- higher number C different polymers

formation of epoxy-, hydroxy- a oxo-compounds

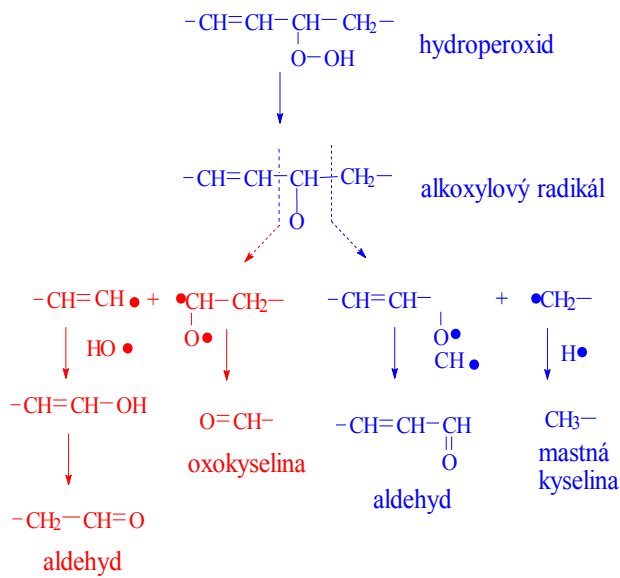


formation of aldehydes and hydrocarbons

general mechanisms

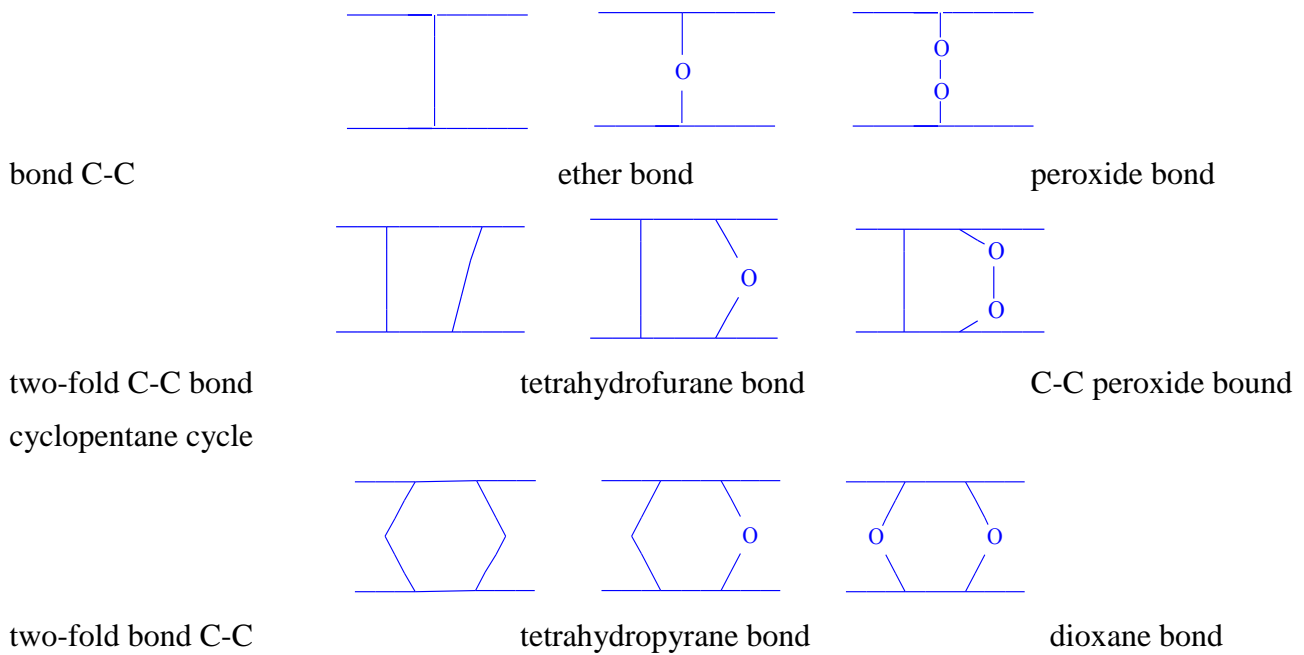


for example 9-hydroperoxy-10,12-fatty acid from linoleic acid



9-oxononanoic, octanoic, (E,Z)-deca-2,4-dienal, (Z)-non-3-enal,

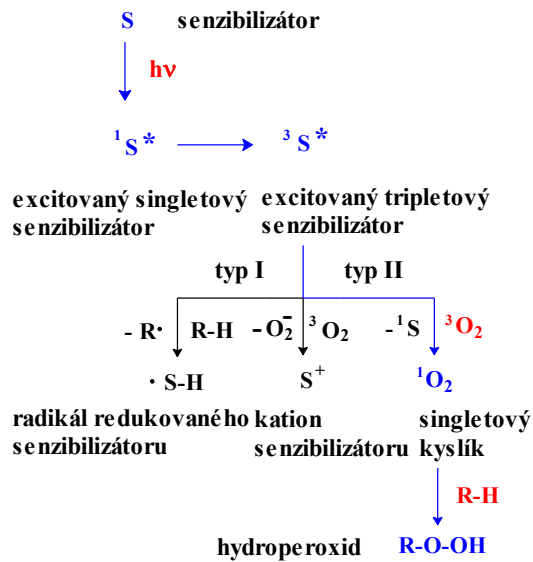
subsequent reaction of aldehydes polymers formation



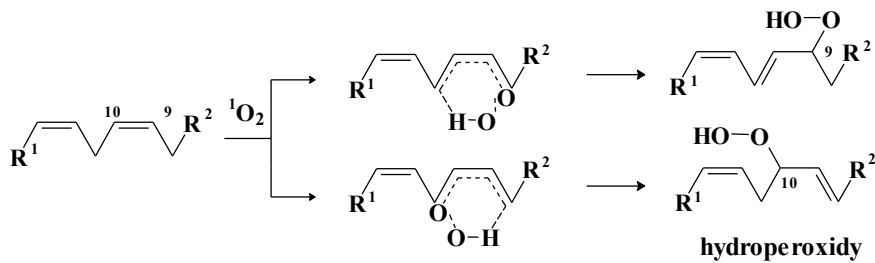
reaction of oxidised lipids with proteins

oxidation with singlet oxygen

- photooxidation (photosensitilisers)
- enzymatic reaction (photosynthesis)



addition on double bound, ~ 1000 times faster than autoxidation



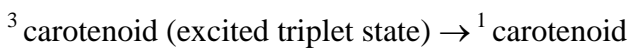
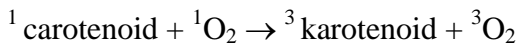
$C_{18:1} \rightarrow 9\text{- a } 10\text{-hydroperoxid}$

$C_{18:2} \rightarrow 9\text{- a } 13\text{-hydroperoxid}$

$C_{18:3} \rightarrow 9\text{-, } 12\text{-, } 13\text{-, } 16\text{- a } 10\text{-, } 15\text{-hydroperoxid}$

compoundss destroying singlet oxygen

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



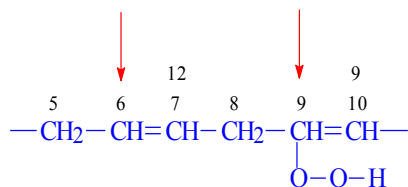
enzymatic oxidation

lipoxygenases (lipoxidases, linoleate: O_2 oxidoreductase), $E_{18:2} = 17 \text{ kJ/mol}$

En

unsaturated. lipid \rightarrow hydroperoxides of unsaturated lipids (optically active)

O_2



C_{18:2} 9- a 13-hydroperoxids 10-hydroperoxids

C_{18:3} 9- a 13-hydroperoxids 10-hydroperoxids

specificity (regio-, stereo-)

example C_{18:2}

soya → (13*S*)-, 9-*cis*-, 11-*trans*-

tomatoes → (9*S*)-, 10-*trans*-, 12-*cis*

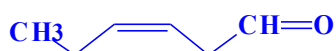
mushrooms → (10*S*)-, 8-*trans*-, 12-*cis*

negative, positive consequences

animals: decomposition by glutathionperoxidases

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

13-OOH-9,11,15- ~

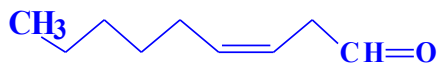


(*Z*)-hex-3-enal (green flavour)

(*E*)-hex-2-enal, leaf aldehyde, product of isomerisation of (*Z*)-hex-3-enal by isomerases

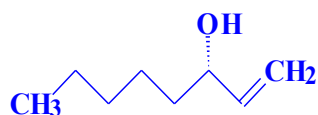
oily, greasy, green smell

9-OOH-10,12,15- ~



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

10-OOH-8,12- ~



(*R*)-1-octen-3-ol (mushroom-like smell)

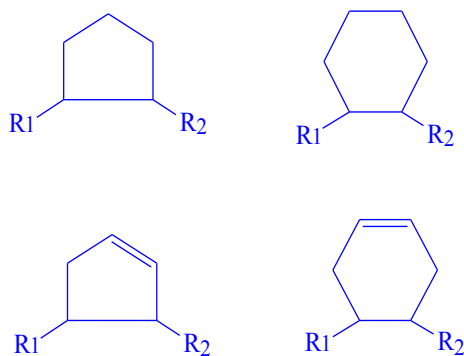
thermal reactions

geometrical isomerisation

cis/trans

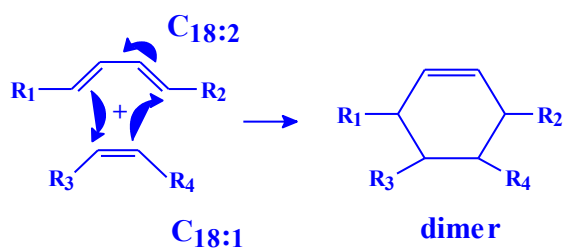
positional isomerisation

cyclisation

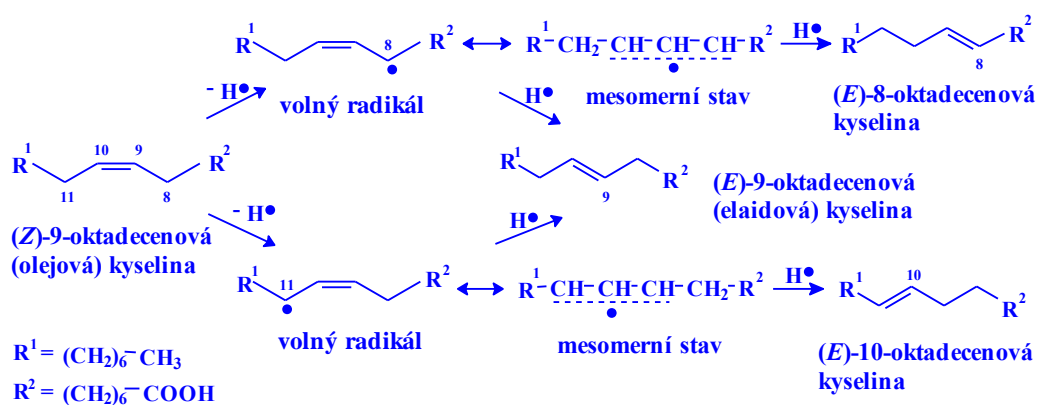


polymerisation

Diels-Alder reaction (monoene $C_{18:1}$ and diene $C_{18:2}$)



mechanisms of oleic acid isomers formation ($\sim 270^\circ\text{C}$)



inhibition of autooxidation

- temperature
- air
- radiation
- inhibitors (antioxidants, synergists)

antioxidants

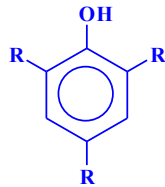
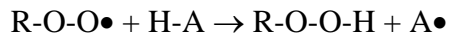
classification according to origin

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

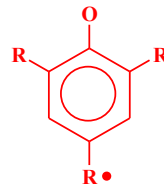
classification according to activity (mechanisms)

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

phenolic antioxidants (mechanism of action)

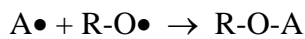
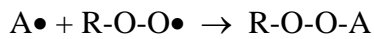
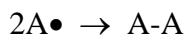


H-A (antioxidant)

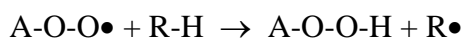
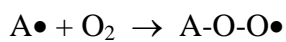


A• (radical antioxidant)

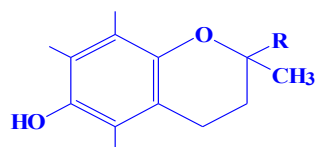
main reactions



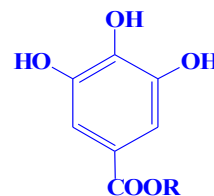
side reactions (> 0,01 %)



main natural antioxidants

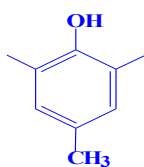


tocopherols

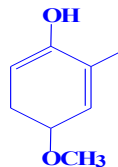


gallates

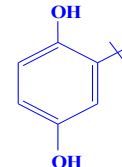
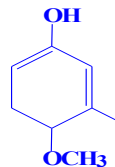
main synthetic antioxidants



BHT



BHA (isomers cca 9 : 1)



TBHQ

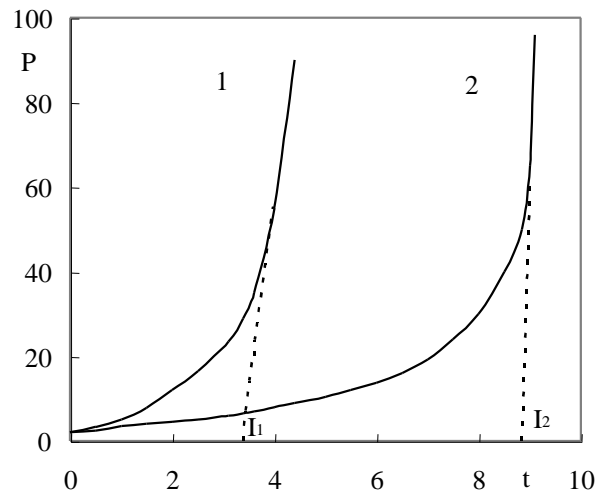
applications

BHA, BHT, tocopherols, dodecylgallate

TBHQ, propylgallate

type of emulsion: oil/water

pure fats (oils)



evaluation of fat oxidation

induction period

P - peroxide number, t – time of autoxidation at 60 °C (days), 1 - concentration of antioxidants (BHA) = 0 %, 2 - 0,02 %, I₁ a I₂ = induction periods, protective factor $PF = (I_2 - I_1) / I_1$