Session-2018-19

Organic Chemistry IV

Presented by:

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Properties

- Consistency: They are colorless, odorless and tasteless. Being lighter than water they have a specific gravity of 0.86.

- The consistency of lipids depends upon the presence of saturated and/or unsaturated fatty acids.

- Hydrolysis: It is brought about in presence of acids or alkalis under the activity of enzyme lipases.

- Acid hydrolysis results in the formation of glycerol and long chain of fatty acid whereas alkaline hydrolysis of fats results in the formation of sodium or potassium salts of fatty acids called as Soaps and the process is called as saponification.

Properties

- Hydrogenation: The conversion of liquid vegetable oil into solid vegetable ghee by reacting with hydrogen gas in the presence of catalyst (Ni) at 200º C.

- Emulsification: When fats or oils are rubbed with water , the large molecules of lipids breaked into smaller ones forming the emulsion and the process is called emulsification.

- Rancidity:
- When lipids are exposed to atmosphere (heat, light, air, moisture) for more than 30 days, an unusual and undesirable odour is developed.

- Such types of lipids are called rancid lipids and the phenomenon is termed as Rancidity.

Properties

- Rancidity is of two types
- (a) Hydrolytic and
- (b) Oxidativea.
- Hydrolytic Rancidity: This type of phenomenon occurs due to liberation of volatile acids during the hydrolysis of fats.
- Oxidative rancidity: When a part of unsaturated fatty acid oxidized to form aldehyde ketone, the phenomenon is termed as oxidative rancidity.

Properties

- Chemically, the acidic carboxyl group(COOH)of the fatty acid is the most reactive portion.
- It reacts with alcohols (R'OH) to yield esters(RCOOR') releasing water molecule.
- In complex lipids, the ester (principal covalent) bond link FA moieties to other groups.
- Ether (R'−O−R, second chemical) bond also links FAs and are chemically more stable as compared to ester bond

Properties

- In fatty acids, the hydrocarbon part is relatively defiant to chemical assail except C=C and different molecules respond with similar double bond.

- For instance, when platinum is present as a catalyst, hydrogen append to the double bond to bestow a SFA.

- Halogens (Iodine, Chlorine, Bromine) and their derivatives (hydroiodic acid)also retort with the double bond to structure the SFAs, but herein the halogen (one or two atoms) swap the hydrogen atoms (one or two) usually end owed in the saturated acyl chain

Properties

- C=C can also respond with oxygen in either enzymatically catalyzed oxidation reactions or non-enzymatic processes.

- The procedure engenders a range of products, several of which add to the stale smell in vegetable products and spoiled meat.

- Universally, it is known that highly unsaturated fatty acid is more easily oxidized.

Properties

- **Reactions of fatty acids:**

- Alike other carboxylic acids, fatty acids demonstrate some of the key reactions i.e. they undergo acid-base reactions and esterification.

- **20-100°C, H_2SO_4,HCl**

- $R\text{-}OH+R^1COOH = R^1COOR+H_2O$
- glycols, alditols + FA = emulsifiers
- Glycerol + FA(hydroxylacids) = emulsifiers(MAG and DAG)

Properties

interesterification

acidolysis

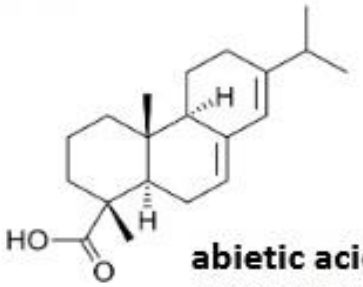
$R^1\text{-COOR} + R^2\text{-COOH} \rightarrow R^2\text{-COOR} + R^1\text{-COOH}$

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

Properties

alcoholysis

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

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)

Properties

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

hydrogenation

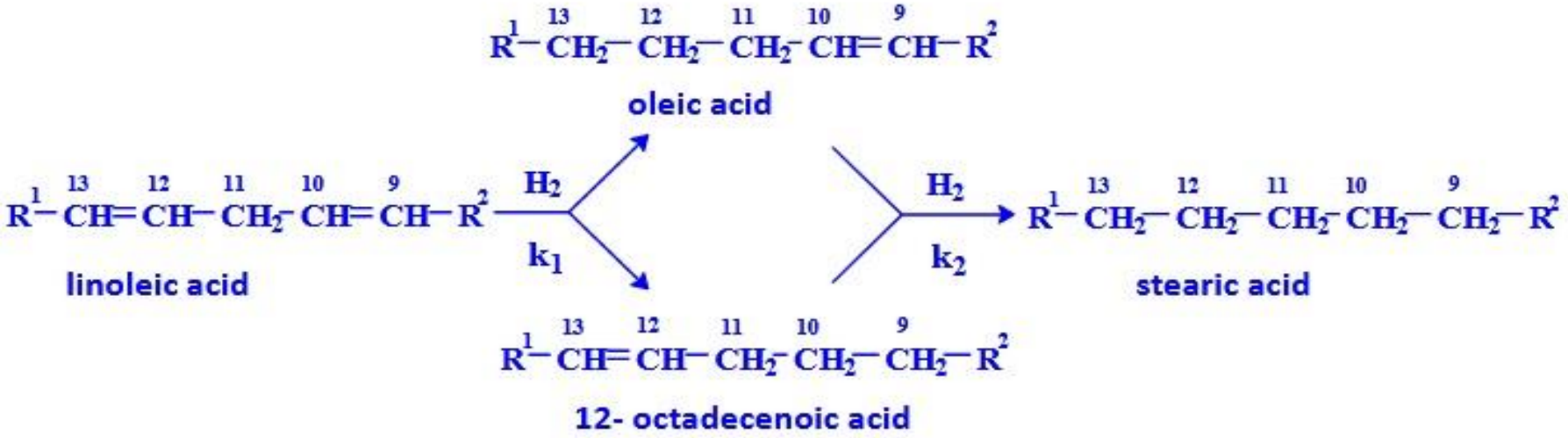
$-CH{=}CH- \rightarrow -CH_2\text{-}CH_2-$

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

hardened fats (hardening, hydrogenation)

stability against oxidation, consistency, absence of trans-acids

Properties



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

$k_1 < k_2$ nonselective

side-reactions

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

Properties

Rancidity of oils and fats

- hydrolytic rancidity
- scented rancidity
- reversion
- oxidation

hydrolytic rancidity

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

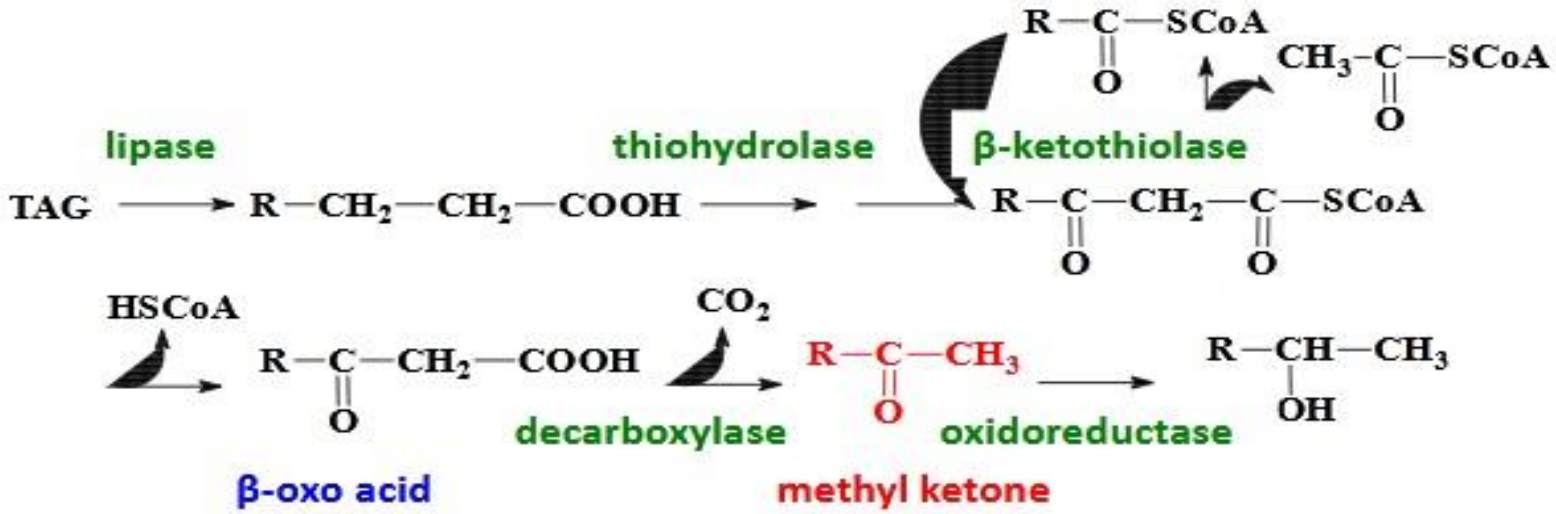
TAG → FA + DAG + MAG

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

Properties

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



Properties

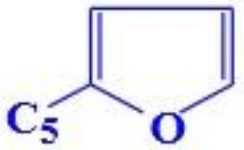
reversion

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

Properties

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)

Properties

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