Alcohols, phenols, thiols, ethers, and sulfides

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Alcohols

- contain the hydroxyl **–OH** functional group
- primary / secondary / tertiary
- monofunctional / polyfunctional
- **naming**: -ol *(or alkyl alcohol)*
  -diol *(or alkyl glycol)*
  -triol,...
- -OH attached directly to the benzene ring
  → **phenols** *(= group name)*

If the hydroxyl group is not the principle one:

hydroxy-

Alcohols - properties

- low MW alcohols: colourless liquids, specific odour (unpleasant from C_4), narcotic effect, toxic
- *polyfunctional alcohols:* ***sweet taste***
- higher alcohols (from C_{12}): solid compounds
- **H-bonds** → solubility in water, higher boiling points than alkanes
- **structure**: polar functional group
  nonpolar hydrocarbon chain
  - ➢ hydrophobic properties increase with MW

Alcohols – important reactions

1. **with alkali metals** → alkoxide *(strong base!)*

   $2\ Na + 2\ CH_3OH \rightarrow H_2(g) + 2\ CH_3O^- + 2\ Na^+$

   (sodium methoxide)

2. **substitution**

   $CH_3CH_2CH_2OH + HCl \rightarrow CH_3CH_2CH_2Cl + H_2O$

3. **dehydration !**

   $CH_3\text{-}CH_2\text{-}OH \rightarrow CH_2{=}CH_2 + H_2O$

Alcohols – important reactions

4. **oxidation** (burning) !
   * primary alcohols → aldehydes
   * secondary alcohols → ketones
   * tertiary alcohols → no reaction

5. **esterification** !

   alcohol + acid → ester + H_2O

   * organic acid esters
   * inorganic acid esters (with H_2SO_4, H_3PO_4, HNO_3)

Alcohols – important examples

- **methanol** = methyl alcohol
- **ethanol** = ethyl alcohol
- ethane-1,2-diol = **ethylene glycol**
- propane-1,2,3-triol = **glycerol**
- **cyclohexanol, inositols**
- **cholesterol**

! add structure formulas !

Alcohols - toxicity

Ethylene glycol

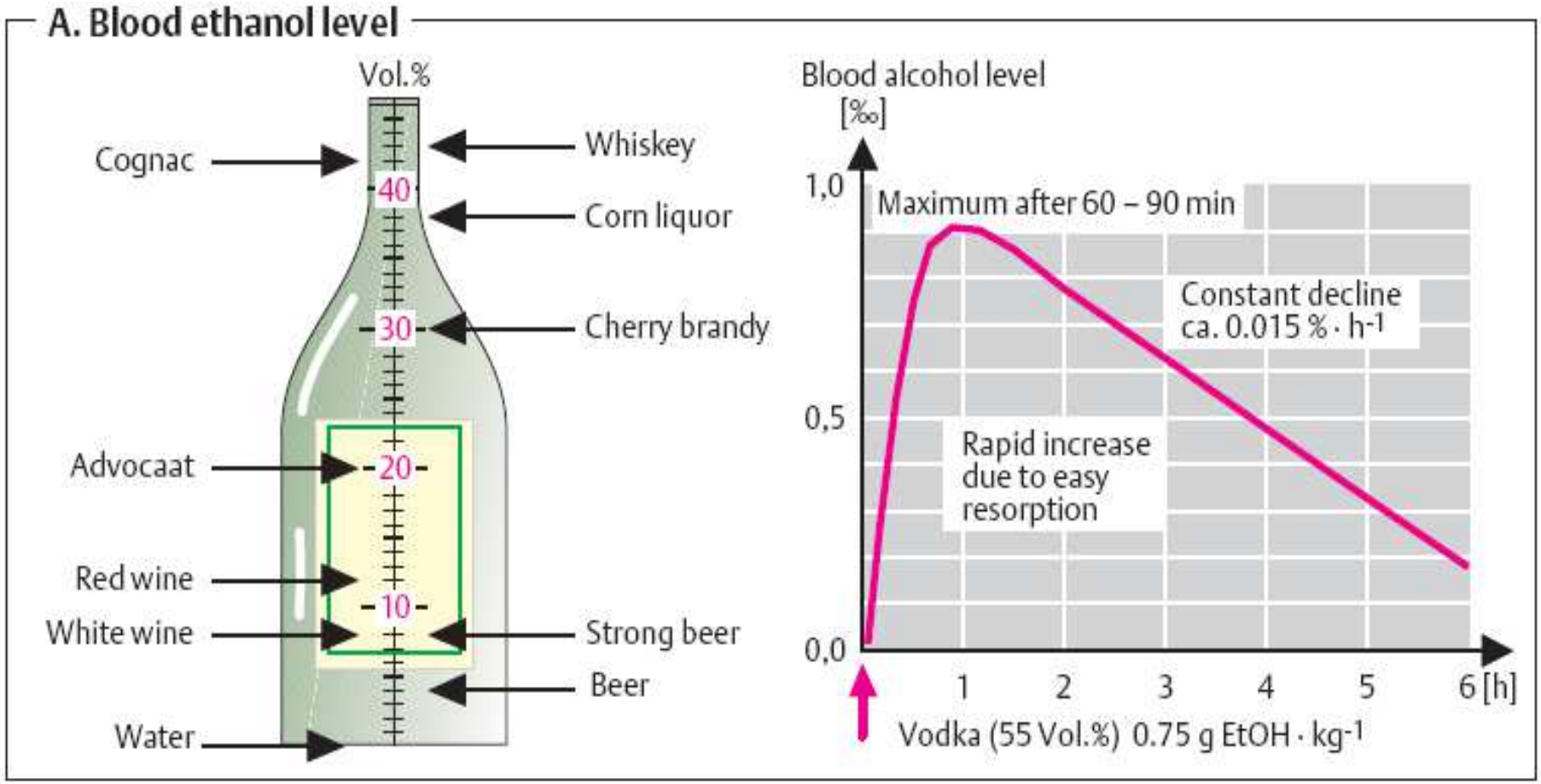
- toxic: 50 mL, lethal: 100 mL

Methanol

- 5-10 mL toxic, 30 mL lethal
- loss of eyesight, metabolic acidosis

Ethanol

- lethal: 6-8 g/kg (~ 1 L of vodka)
- degradation: oxidation of 0,15 g/kg/hour

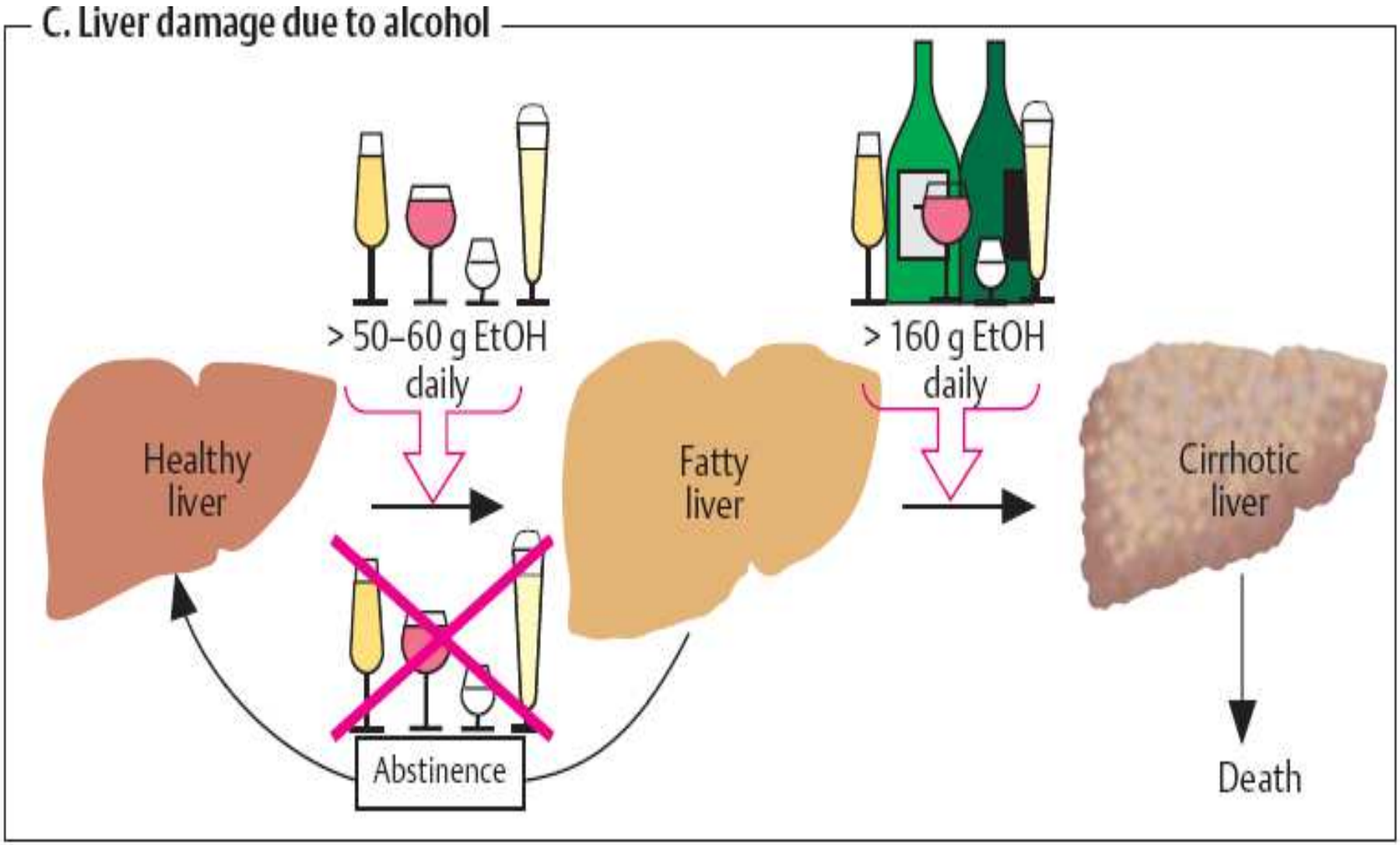


0,5 L of beer (4%) ~ 20 mL of ethanol = 16 g

70 kg man: 0,7 x 70 = 49 kg (L) water

i.e. 16 g etOH / 49 L = 0,33 g / L = 0,33 ‰

Color Atlas of Biochemistry / J. Koolman, K.H.Röhm. Thieme 1996. ISBN 0-86577-584-2



29,4 kJ/g of ethanol

Obrázek převzat z: Color Atlas of Biochemistry / J. Koolman, K.H.Röhm. Thieme 1996. ISBN 0-86577-584-2

Aromatic alcohols = PHENOLS

- **-OH group** is bound directly to the benzene ring (instead of 1 or more hydrogens)
- aromatic alcohols with –OH group attached to a side chain are not phenols! (benzyl alcohol)
- phenols are **stronger acids** than alcohols (but weaker than organic acids)
  - soluble in basic solutions

    K_a: acetic acid (10^{-5}), phenol (10^{-10}), ethanol (10^{-17})

- phenols also react with active metals

Aromatic alcohols = PHENOLS

- phenols are **effective germicides**
- C_6H_5-OH = „**phenol**" („carbolic acid")
  - 2-8% aq. solution (1867 Joseph Lister – desinfection)
- **Lysol** = mix of o-, m-, and p-cresols

- solid crystaline compounds
- little soluble in water
- characteristic odour
- toxic (CNS, liver, kidneys), caustic
- difunctional phenols are oxidized to **quinones**

Aromatic alcohols = PHENOLS

important trivial names:

- phenol
- pyrocatechol
- resorcinol
- hydroquinone
- o-, m-, p-cresols

! add structural formulas !

Sulfur alcohols = THIOLS

- **-SH group** instead of –OH group of alcohols
- **naming**: „hydrocarbon thiol" (or alkyl hydrosulfide)
- formerly called „**mercaptans**"

- **strong, disagreeable odour**
  (additional „marker" of natural gas)
- lower boiling point than alcohols
- weak acids (stronger than alcohols)
- **oxidation** $\Rightarrow$ disulfides $\rightarrow$ sulfonic acids

Sulfur alcohols = THIOLS

examples of thiols:

- methanethiol
- ethanethiol
- propane-1-thiol (in onion)
- prop-2-ene-1-thiol *= allyl mercaptan* (in garlic)
- benzenethiol *(= phenyl mercaptan)*
- cyclopentanethiol *(= cyclopentyl mercaptan)*

If the thiol group is not the principle one:
sulfanyl-

Ethers

- 2 alkyl or aryl groups bound to oxygen:
  - R_1-O-R_2 / R-O-Ar / Ar_1-O-Ar_2
- lower **boiling points** than alcohols (no H-bonds)
  - dimethyl ether is a gas, higher ethers: liquids
- not miscible with water
- soluble in organic solvents
- basic properties
- inflammable, volatile
- narcotic effect
  diethyl ether (l) = general anesthetics: depressant on the CNS

Ethers – naming:

radical functional names

CH_3-O-CH_2-CH_3 = ethyl methyl ether

(alphabetical order of alkyl names)

- **higher MW ethers**: alkoxy group (= the smaller alkyl)
  - *2-methoxypentane / 1,2-dimethoxyethane*
- **cyclic ethers = EPOXIDES**
  - oxygen is bound to neighbouring carbons
  - prefix: **epoxy-** (*2,3-epoxybutane*)
  - *epoxyethane* (= ethylene oxide = oxirane) is a toxic gas, used as a sterilant or in organic synthesis

Sulfur ethers - SULFIDES

- sulfur analogs of ethers
- more reactive than ethers
- **name:** alkyl alkyl sulfide or alkyl thioalkane

  - CH_3-S-CH_2-CH_3
    = **ethyl methyl sulfide** or methyl thioethane
  - CH_3-S-CH_3
    = **dimethyl sulfide** or methyl thiomethane

EXERCISE

- propan-1-ol
- 3-ethylpentan-3-ol
- benzyl alcohol
- methoxyethane
- butane-1-thiol
- propane-1,3-diol
- ethyl vinyl ether
- 3-sulfanylpropanoic acid
- cyclobutane thiol
- diethyl sulfide
- dimethyl disulfide