Mineral oil hydrocarbons in food

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Definitions

- MOSH = mineral oil saturated hydrocarbons
- MOAH = mineral oil aromatic hydrocarbons

- POSH = polymer oligomeric saturated hydrocarbons

Major sources in the past

- Jute- and sisal sacks for hazelnuts, cocoa beans, rice, oil seeds, copra, coffee…
- Release agents for bakeries, candies…
- Surface treatment agents for rice, fruits…
- Environment: diesel engines (diesel oil and lubricants), debris from tires and bitumen
- Feeds (binders for additives, waste oil admixed to used oils)
- Dust binders (wheat, rice, soy beans…)
- Recycled paperboard
- Pharmaceuticals, salad oil
- …

Most (known) sources stopped or strongly reduced

Chemical analysis

- The determination of MOSH and MOAH is demanding
  - commonly done by on-line coupling of HPLC with GC-FID
    - HPLC to isolate hydrocarbons and separate MOSH and MOAH
    - special instrument
    - introduction of 450 µl into GC is not standard technology
  - complex and variable mixtures, to be distinguished from other hydrocarbons
- Numerous auxiliary techniques
  - enrichment of samples
  - removal of interferences
  - confirmation/characterization: GCxGC, GC-MS

Present classification of mineral oil products

JECFA, EFSA, various legislations, from around 2000

- MOAH include genotoxic carcinogens → not acceptable (no limit)
  - acceptable mineral oil products must be “white”
- MOSH classified based on animal experiments with various products according to
  - viscosity
  - mean molecular mass
  - 5 % distillation point
- high reference values for some white oils and waxes (ADI or TDI)

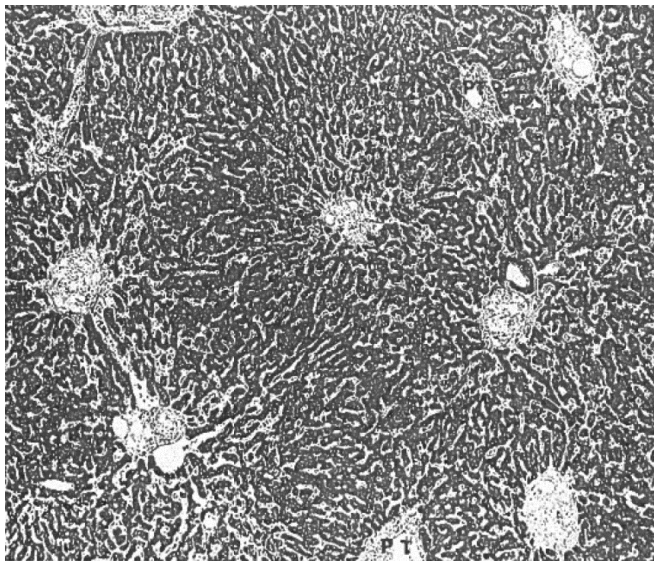
New data on MOSH toxicity

- A small part of the MOSH are strongly accumulated in human tissues (2014)
  - mean MOSH content per person: 2.3 g (maximum: 13 g)
- Extrapolation from animal experiments to humans under-estimates concentrations in human liver and spleen 100-1000 times
  - highest concentrations in human spleen exceeded the concentration in spleens of rats exposed to the highest dose
- strongest accumulation in humans in the mass range of the oils so far considered of least concern

Effects of MOSH

- 1950-1990 numerous reports of granulomas in human tissues (up to 80 % of population of industrialized countries)
  - inflammations?
  - probably far less today

Lipogranuloma in non-fatty human livers. A mineral oil induced environmental disease. Dincsoy et al., Am. Soc. of Clinical Pathol. 1981



- Increased organ weights in rats at concentrations reached or exceeded by some humans
  - from higher exposure in the past?

Tolerable MOSH concentrations

Legal limits derived from human data:

- Estimated human exposure 1998-2010: 0.03-0.3 mg/day/kg body weight (EFSA, 2012) = 1.8-18 mg/person/day
- Reduction to 0.01 mg/kg body weight?

- Standard assumptions for legal limit:
  - 1 kg food/day
  - 60 kg body weight
  - → 0.6 mg/kg food (average over all foods)

→ Limits of 1-5 mg/kg, depending on foods/feasibility

fits limits proposed by German BfR

- 12 mg/kg for C10-C16, 4 mg/kg for C17-C20

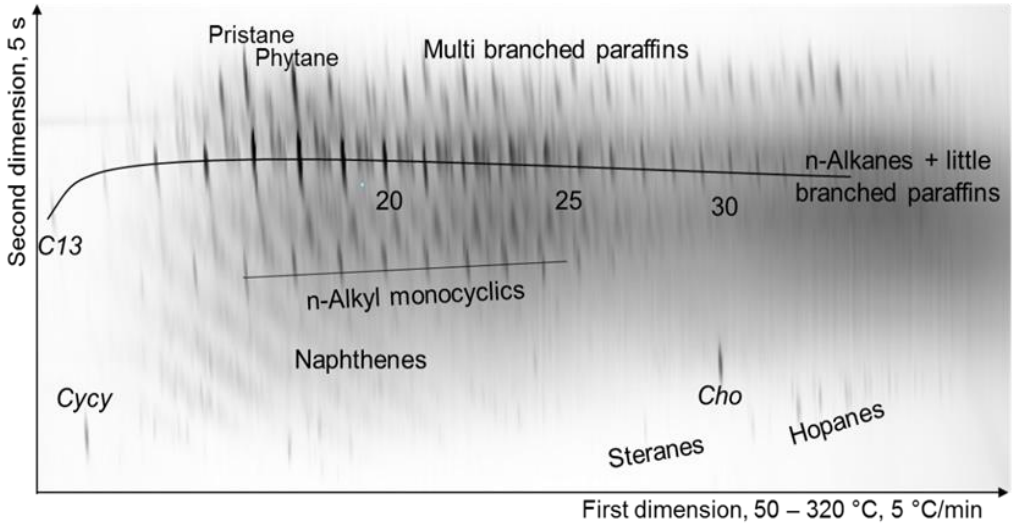
Most strongly accumulated MOSH

- Mass range: C20-C35
- Only few percent of these MOSH are accumulated
  = not metabolized = resist enzyme attack
  – structural elements hindering elimination are largely unknown
- Are disappearing MOSH completely eliminated…
  … or only, e.g., converted to non-degradable acids integrated into lipids?
- Relevant structural elements of interest also for the evaluation of POSH (oligomers from polyolefins etc.)

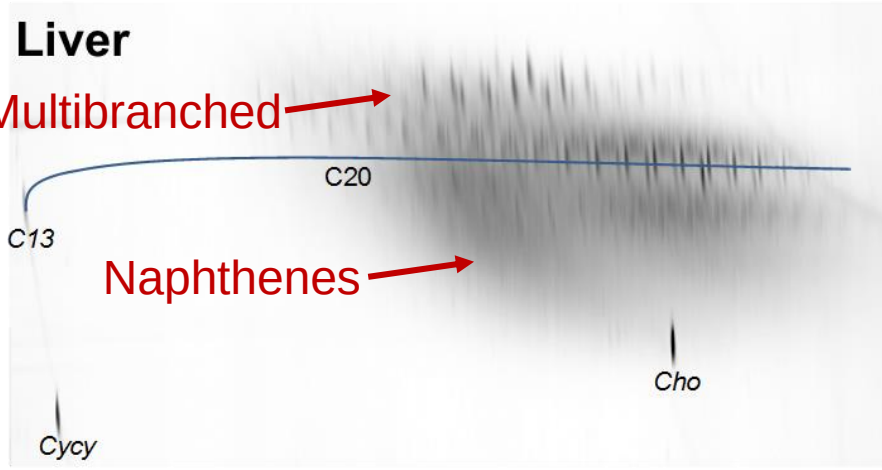
→ further research needed

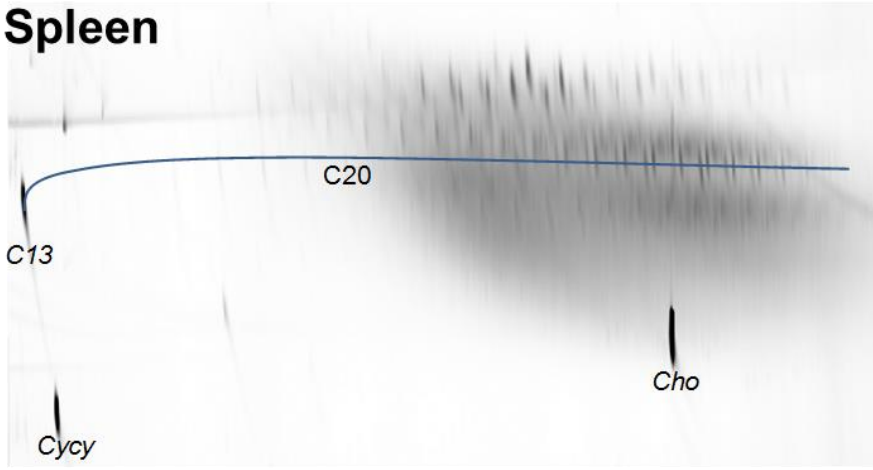
GCxGC of MOSH fed to rats isolated by HPLC

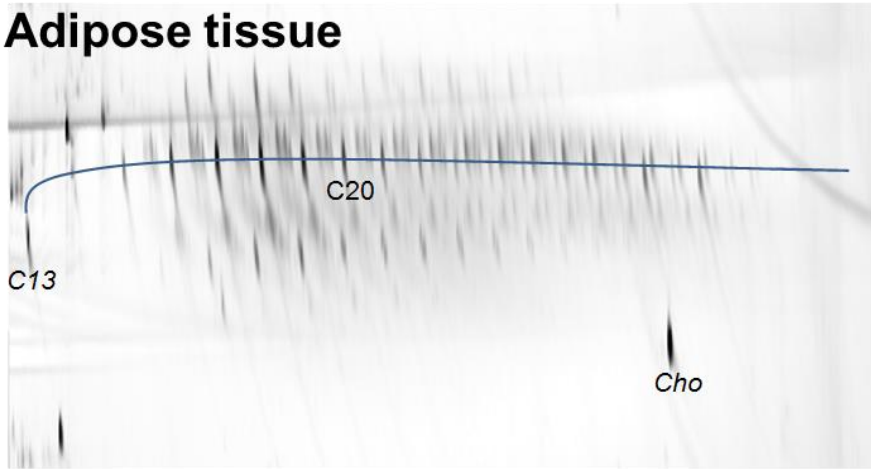
MOSH added to the feed



Accumulation of multibranched open chain hydrocarbons and some naphthenes (largely resulting from hydrogenation to remove MOAH!)







MOAH: composition depending on raffination

- Crude or little refined mineral oils are known to be carcinogenic
  - 35-50 % MOAH (e.g. batching oils for jute- and sisal bags)
- Technical mineral oil products on the market are refined to no longer produce tumors on mouse skin painting test
  - Extraction and/or partial hydrogenation of MOAH
  - 20-30 % MOAH
- Further reduction of MOAH content preferentially removes polyaromatic hydrocarbons
  - at a given level (10-20 % ?) only remain monoaromatic hydrocarbons
    - alkyl benzenes
    - monoaromatic polycyclic hydrocarbons
    - can they be shown to have no genotoxic potential?
- “White oils” contain <1 – 5 % MOAH

→ Limits depending on composition?

to do…

- Further investigation of sources of use/contamination
  - systematic analysis of food groups
- Estimation of the virtually non-avoidable contamination
  - e.g. from environment
- Re-classification of MOSH
  - MOSH below C17 are not accumulated: exhaled?
  - MOSH above C40 are not accumulated: not absorbed?
  - strongest accumulation: C20-C35
- Structural element rendering MOSH not degradable
  - evaluation of synthetic hydrocarbons
- Regulation of MOAH
  - Limits depending on the composition