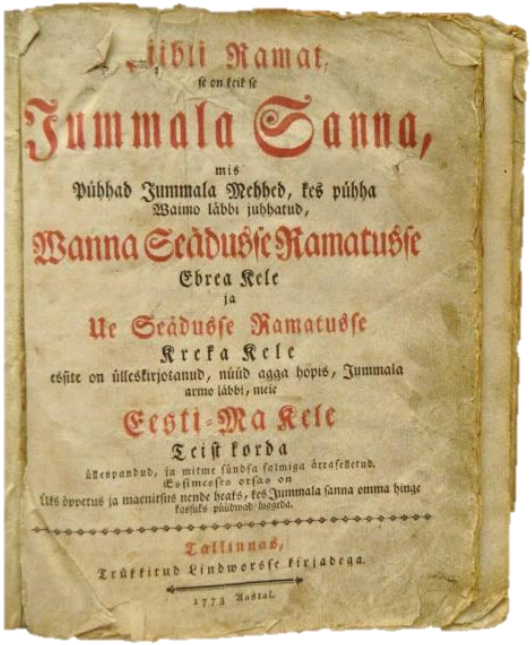
Chemistry of ageing:

I. INTRODUCTION

Prof. Ivo Leito

Aged materials

Chest (16th c.)



Jibli Ramat,
se on teine se
Jummala Sanna,
mis
Pühhad Jummala Mehhed, kes pühha
Waimo läbbi juhhatud,
Wanna Seäduse Ramatusse
Ebrea Kele
ja
Ue Seäduse Ramatusse
Kreka Kele
essite on ülleskirjotanud, nüüd agga hoppis, Jummala
arme läbbi, meie
Eesti-Ma Kele
Teist korda
ülespandud, ja mitme sündsa kaimiga öraseletud.
Essimesse otsas on
Ulle öpetus ja maenitsus nende peäle, kes Jummala sanna omma hinge
kasuks pühendab hoieda.
Tallinnas,
Trükkitud Lindworsse kirjadega.
1773 Aastal.

The Bible (Estonia, 1773)

Photo: Liisa Eero

Anna III (15th c.)

Photos: Conservation and Digitization Centre Kanut

Ageing process

- All materials age with time as a result of **physical-chemical-biological processes,** which lead to material **degradation**
  - The processes are e.g. **oxidation/corrosion**, **hydrolysis**, **polymerization**, formation of **mould**, etc
  - Ageing process is irreversible
- Ageing rate (speed) depends on:
  - nature of material
  - environmental factors

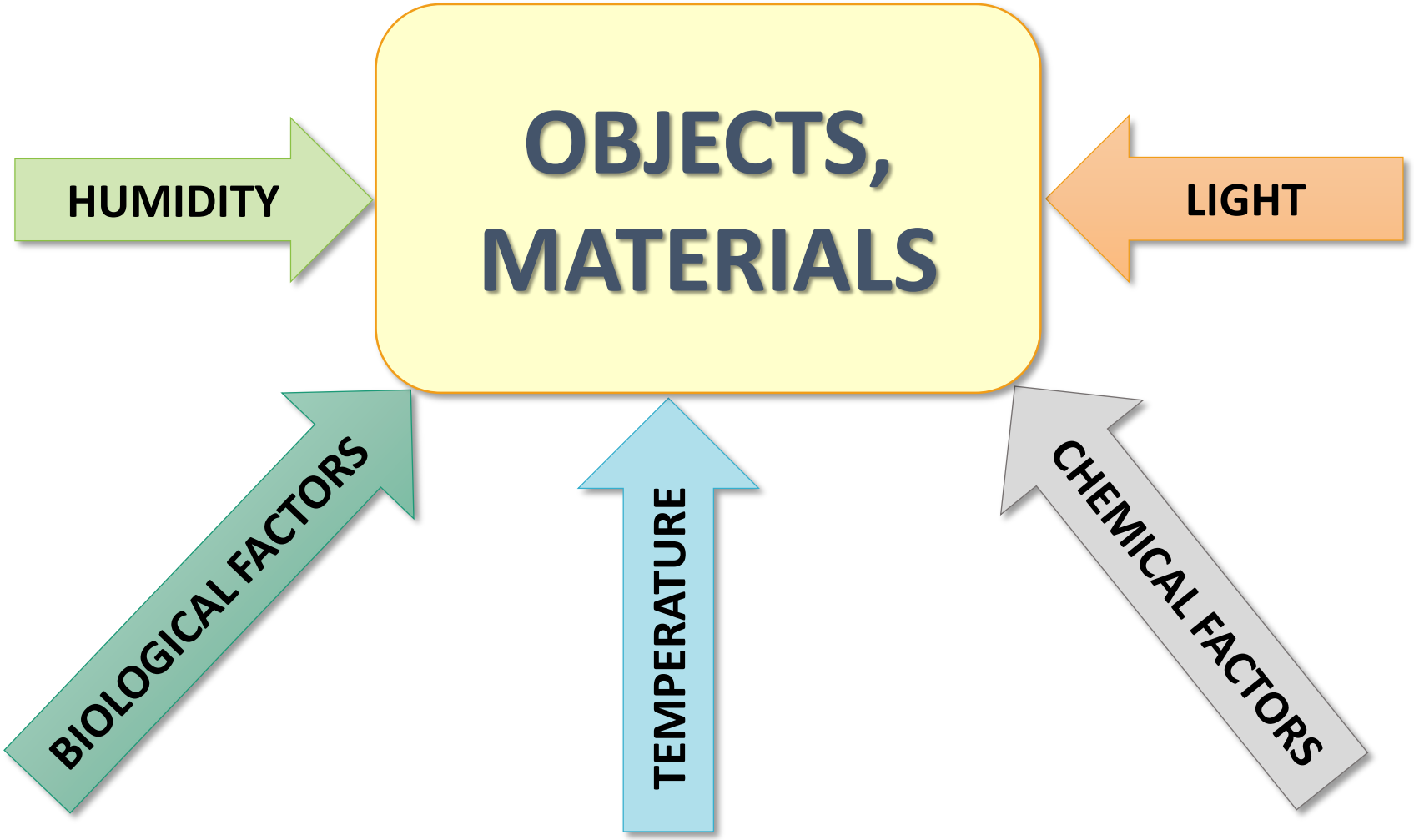
Cultural heritage objects chemistry ≈ chemistry of ageing

Chemistry of ageing:

II. ENVIRONMENTAL FACTORS

Prof. Ivo Leito

Factors that cause ageing



Temperature

- Increase of temperature accelerates ageing
- **Van't Hoff rule**:

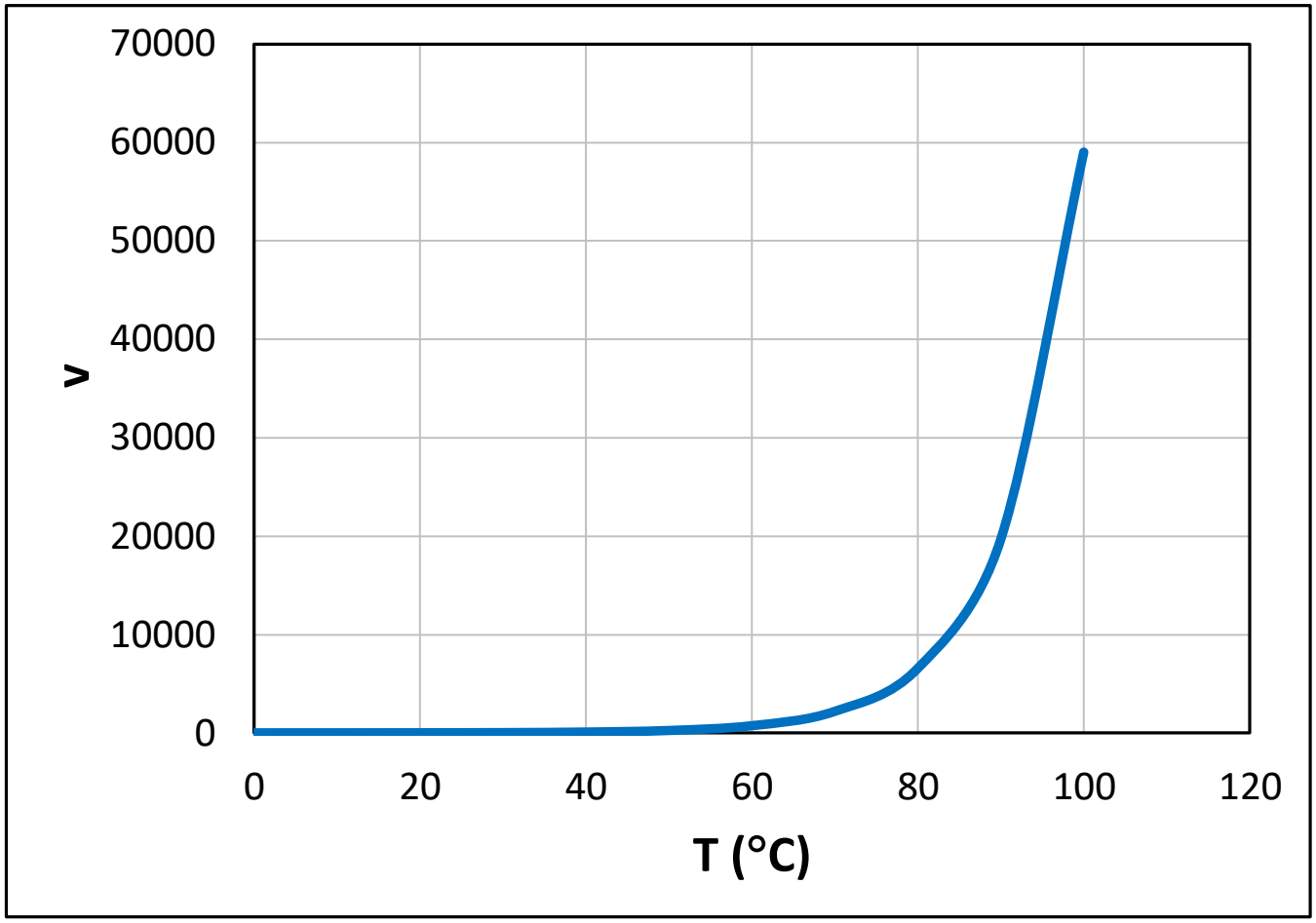
$$v_{t_2} = v_{t_1} \cdot \gamma^{\frac{t_2 - t_1}{10}}$$

$$\gamma = 2 \,..\, 4$$

- The rate (speed) of most of the chemical processes increases by 2 .. 4 times when the temperature increases by 10 degrees

*Temperature

- Reaction rate depends on temperature of exponentially



Humidity

ABSOLUTE HUMIDITY

The **amount of water** in a **volume unit** of air

RELATIVE HUMIDITY (RH)

The ratio of the **actual absolute humidity** to the **maximum possible absolute humidity** at the respective temperature (often expressed in %)

At 20 °C **a medium** absolute humidity of air can be e.g 7 g/m^3

At 20 °C **the maximum** absolute humidity of air is 17 g/m^3

The relative humidity is: $\frac{7\ \text{g/m}^3}{17\ \text{g/m}^3} \times 100\% \approx 40\%$

Relative humidity and temperature

- Relative humidity depends equally on

  Absolute humidity and **temperature**

At constant absolute humidity, the lower the temperature the higher the RH

- **Rule of thumb**: near room temperature, temperature decrease by 10 °C leads to RH increase of 2 times

Temperature	RH
20 °C	40 %
↓	↓
10 °C	80 %

Relative humidity for the CH materials

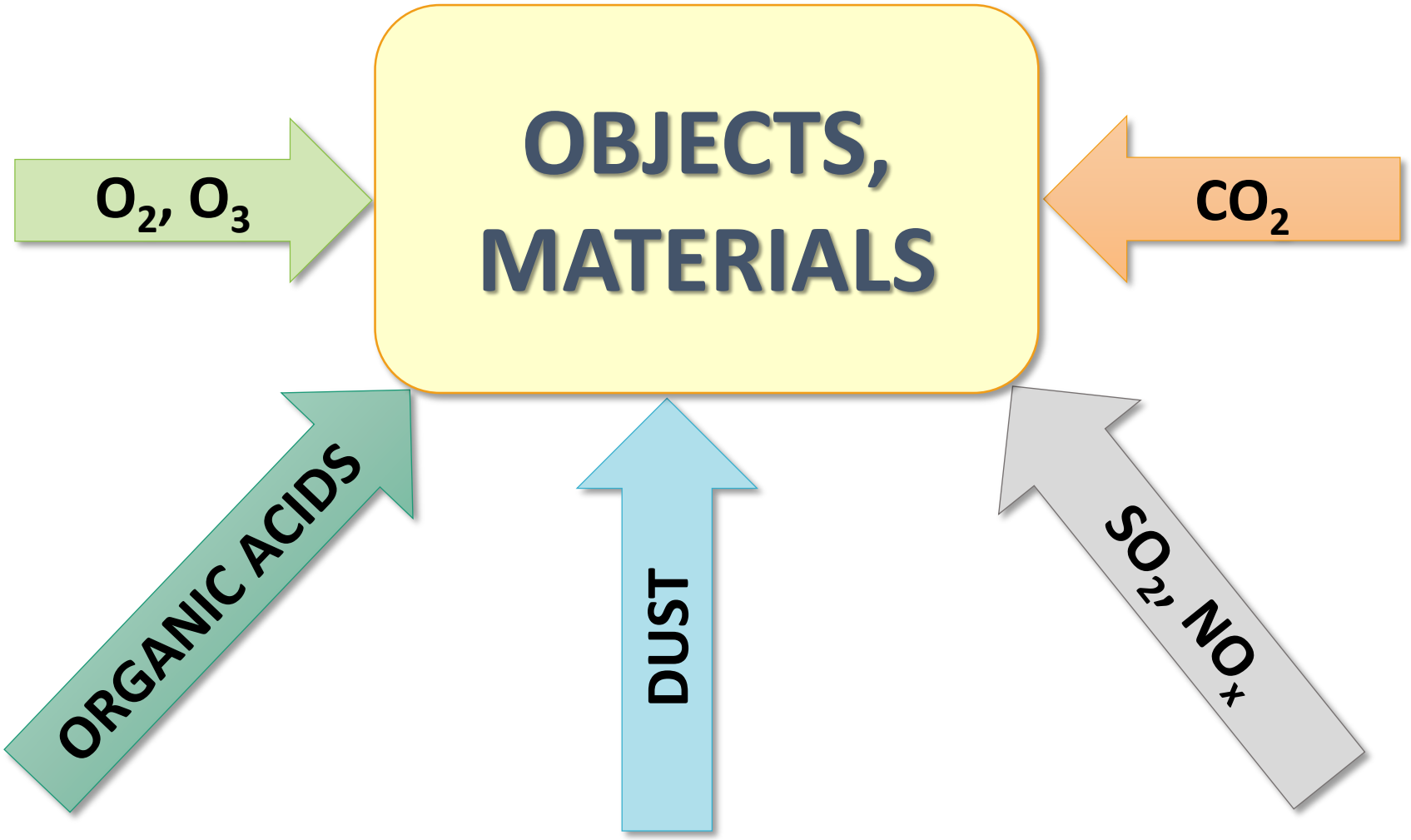
RH < 30 % (lower level)	**RH 30-60 %**	**RH > 60 %** (higher level)
Very dry air is **damaging for some materials**	**Suitable for most materials** (ensures stability of most materials)	At higher RH there is a **danger of mould growth**

Light

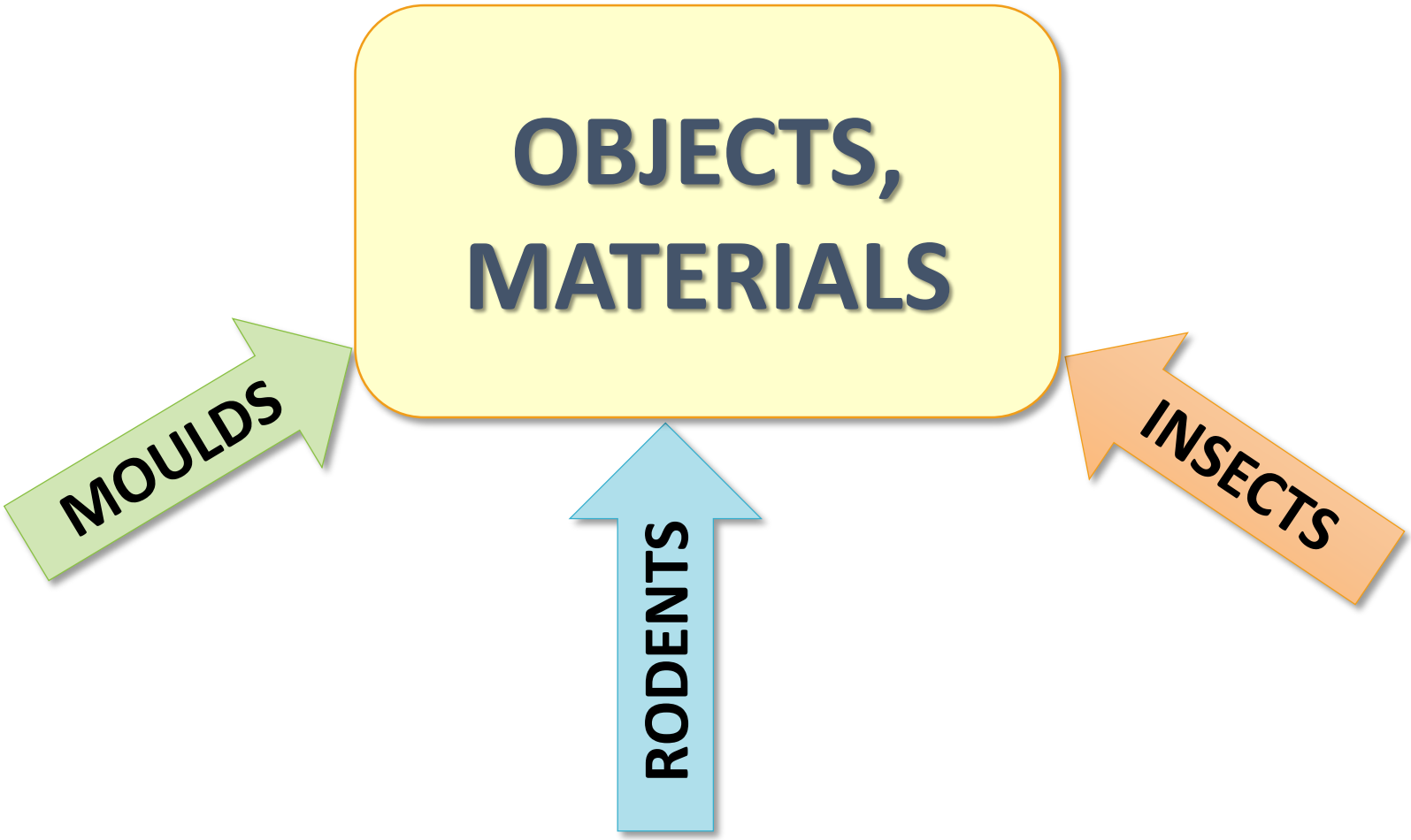
- Light: **visible light** and **UV radiation**
- Light mostly has damaging effect on materials via promoting **photochemical reactions**
    - Photochemical reactions cause **bleaching, yellowing/ browning** and **darkening** of materials

- **Organic materials** are most light affected
- **Inorganic materials** are usually stable to light

Chemical factors



Biological factors



Chemistry of ageing:

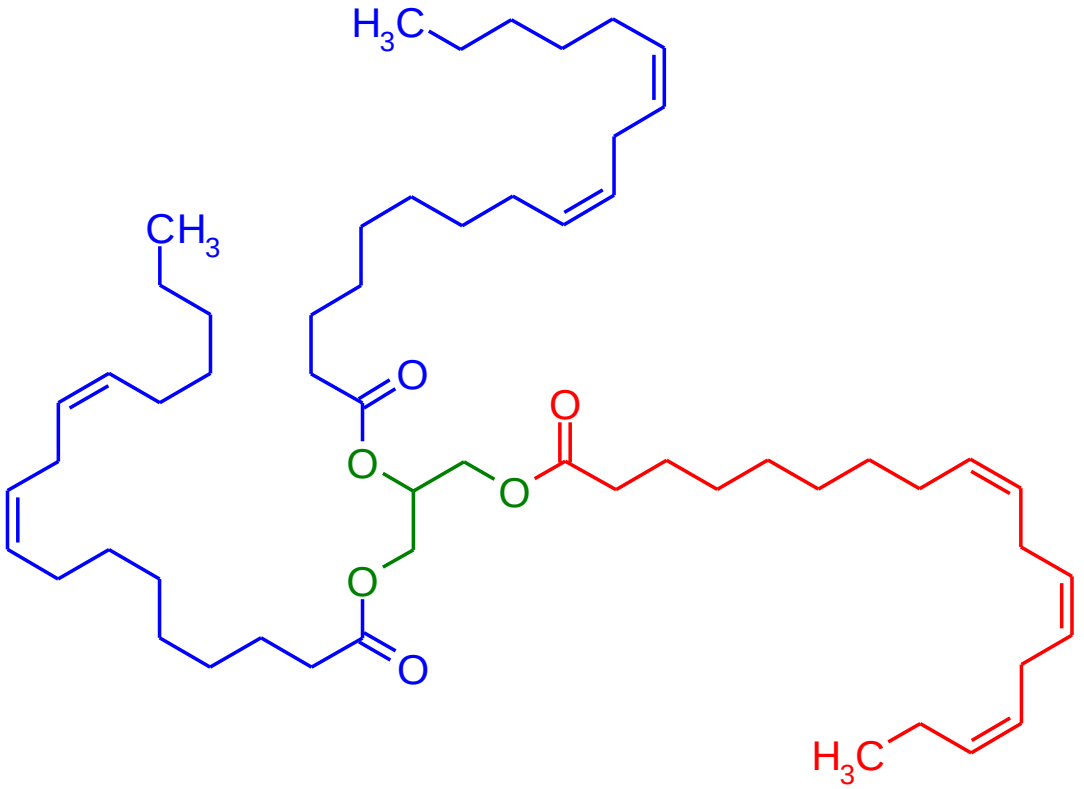
III. EXAMPLE: LINSEED OIL

Prof. Ivo Leito

Linseed oil

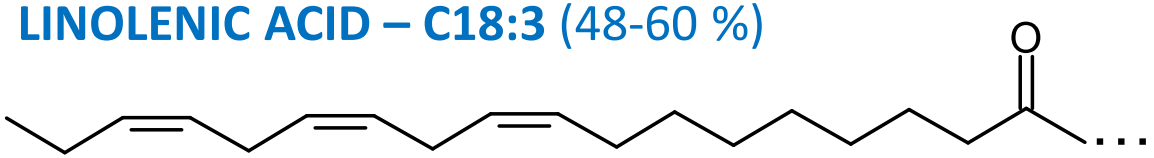
(http://www.seedguides.info/linseed-oil/)
(licence CC-by -SA 3.0)

- Obtained from the dried, ripened seeds of the flax plant *(Linum usitatissimum)*
- Consists of different **fatty acid triglycerides**

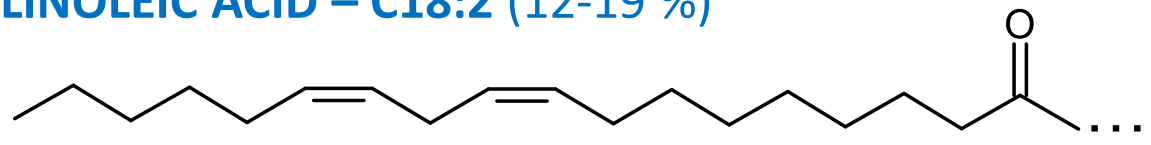


Composition of linseed oil

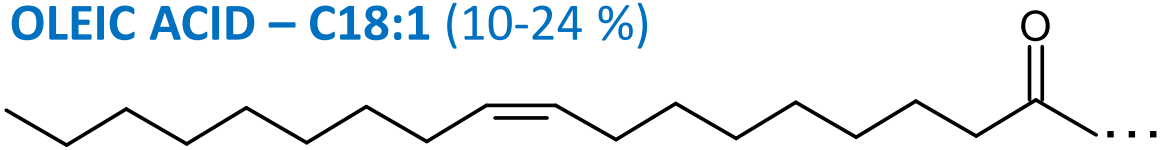
LINOLENIC ACID – C18:3 (48-60 %)



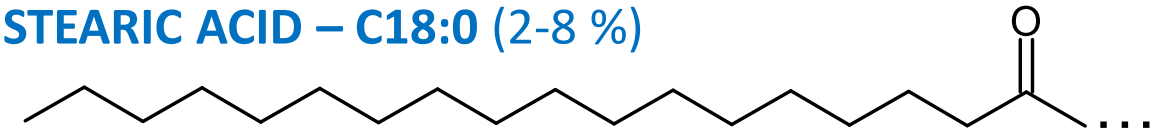
LINOLEIC ACID – C18:2 (12-19 %)



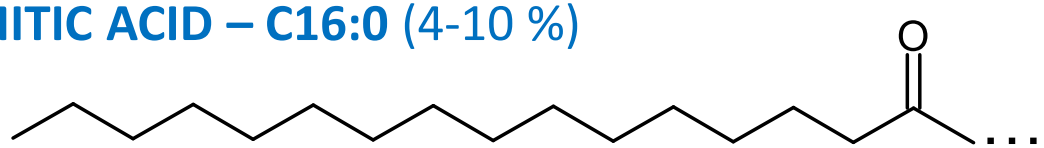
OLEIC ACID – C18:1 (10-24 %)

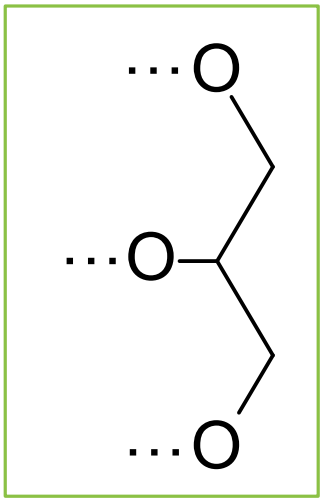


STEARIC ACID – C18:0 (2-8 %)

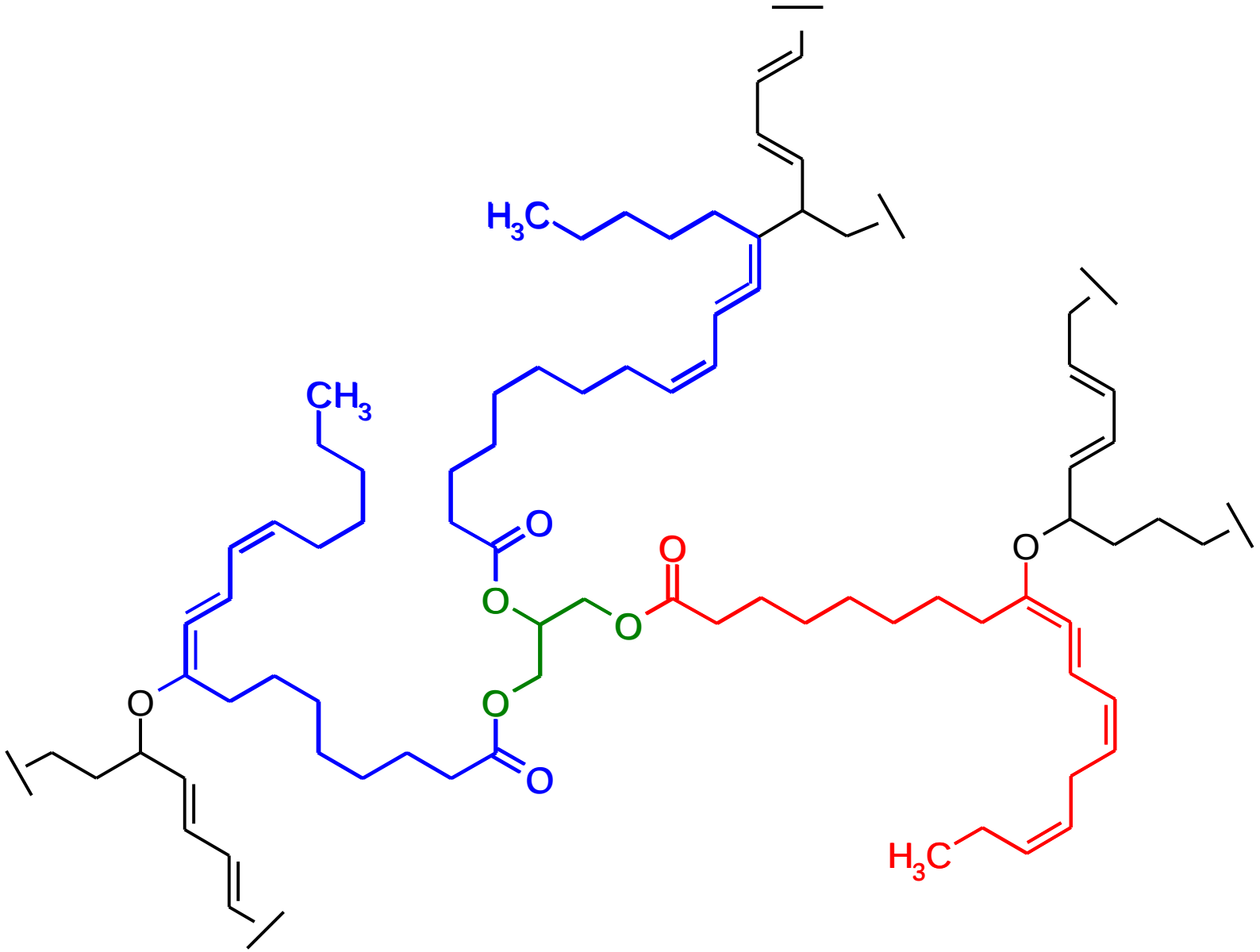


PALMITIC ACID – C16:0 (4-10 %)

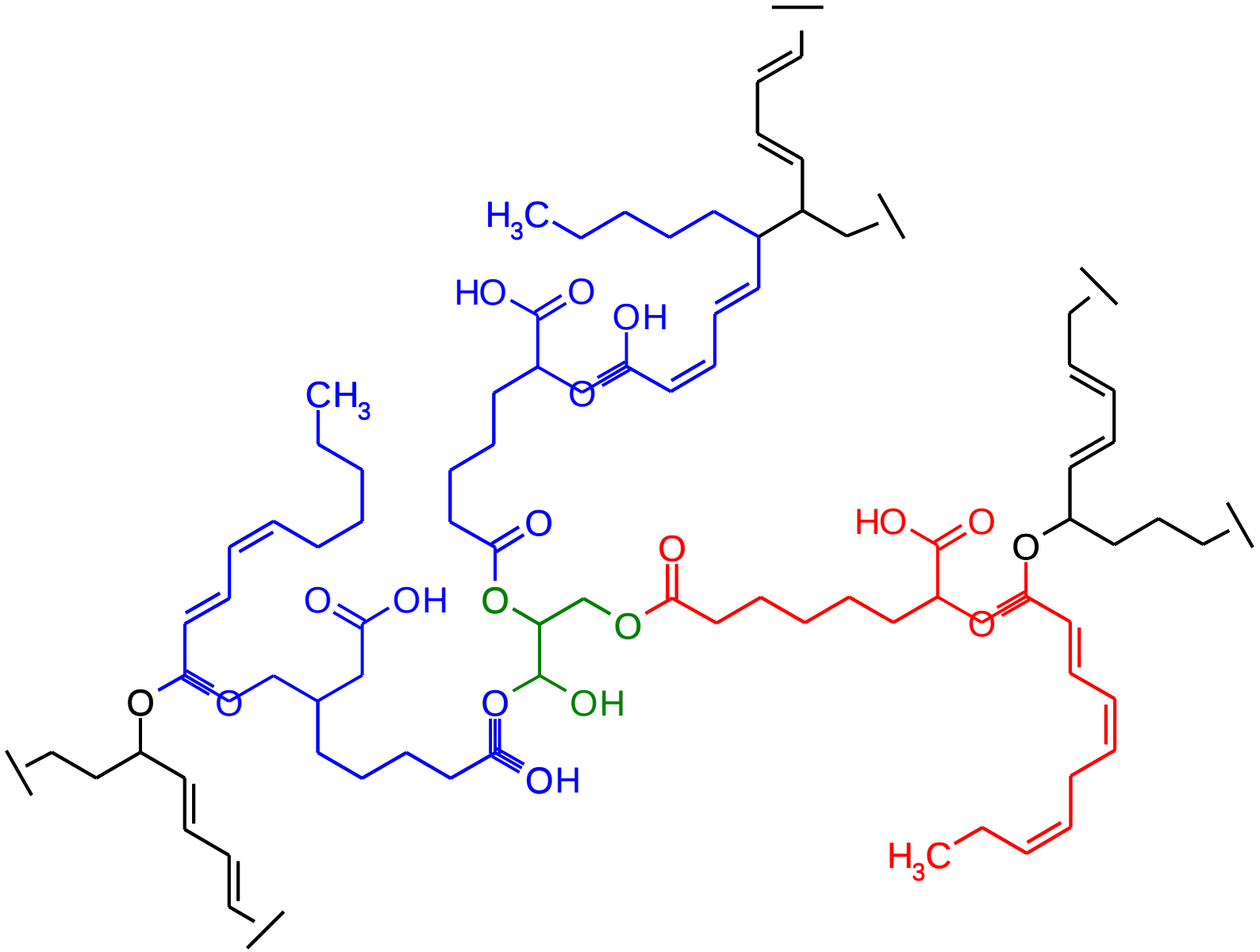




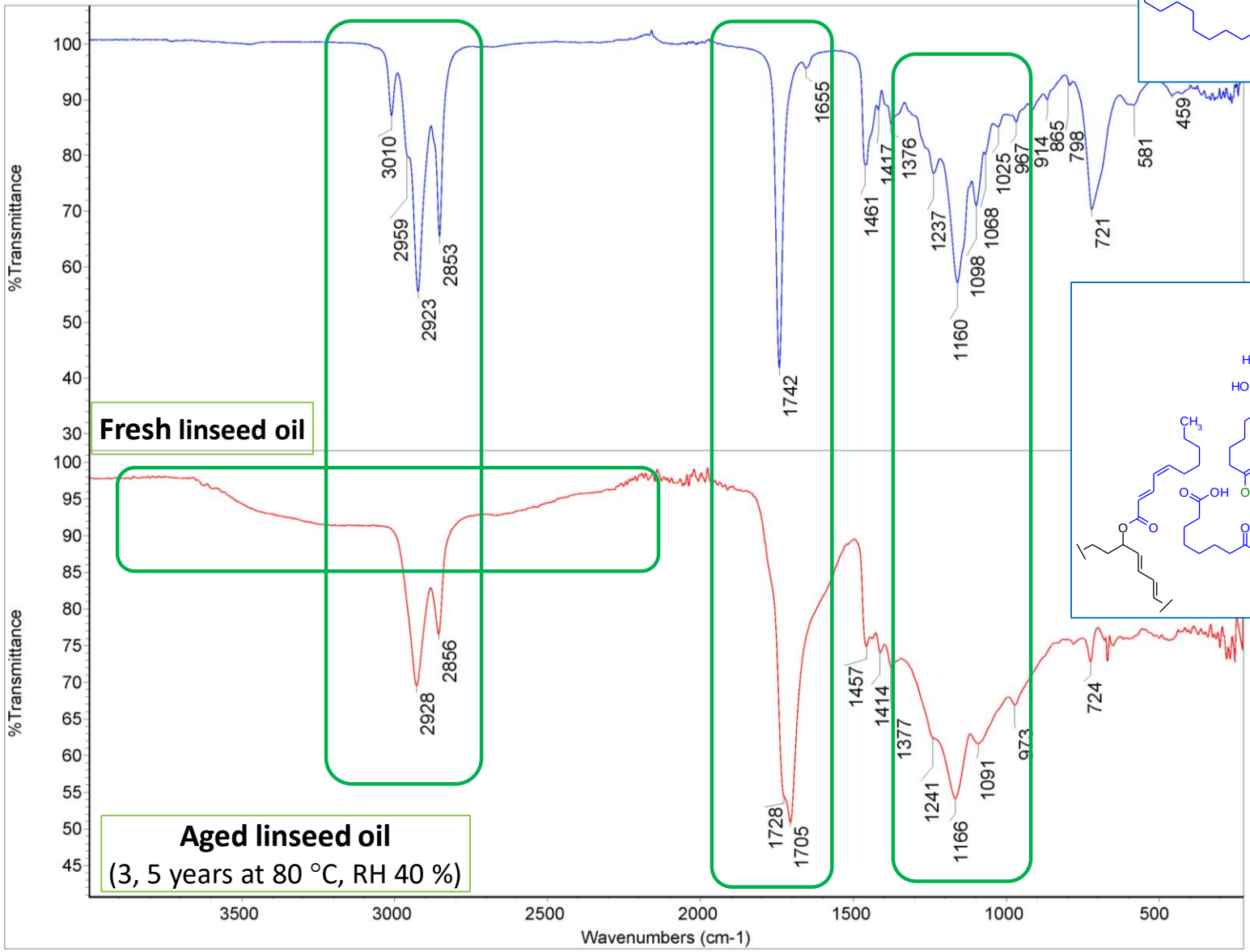
Drying (curing) of linseed oil

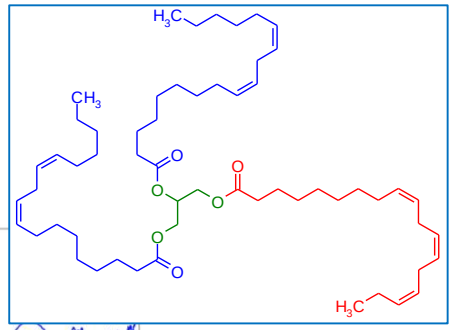


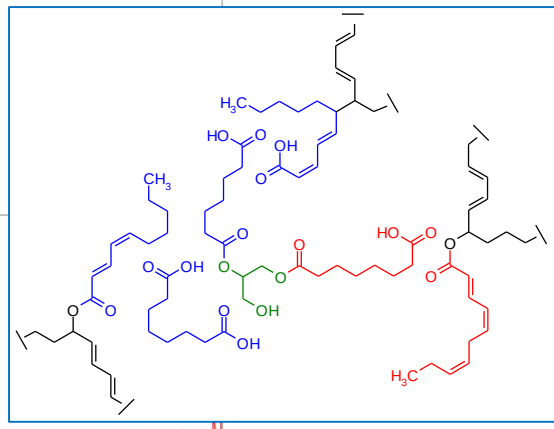
Maturing/degrading of the dried oil



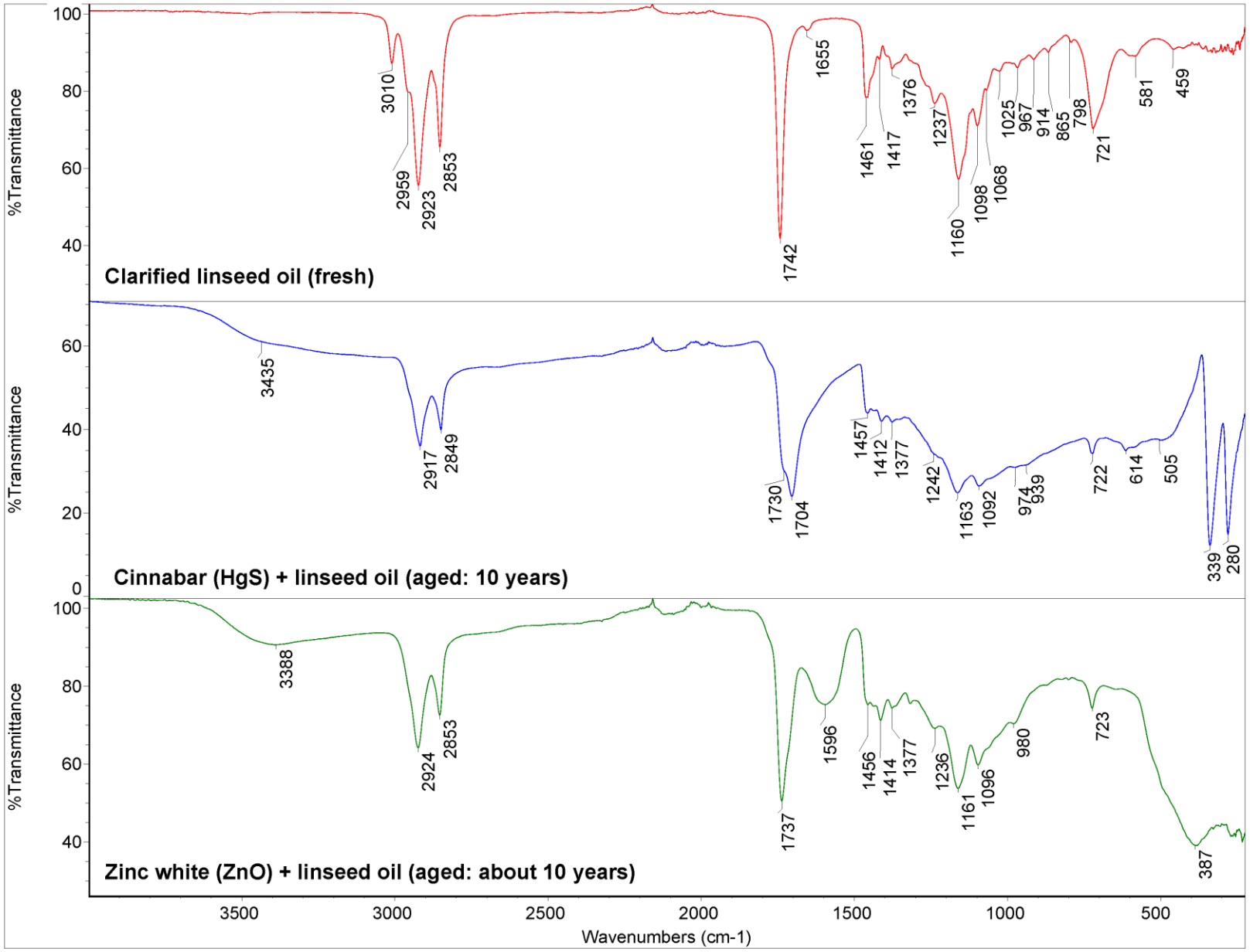
ATR-FT-IR spectra of fresh and aged linseed oil







ATR-FT-IR spectra of linseed oil + pigments



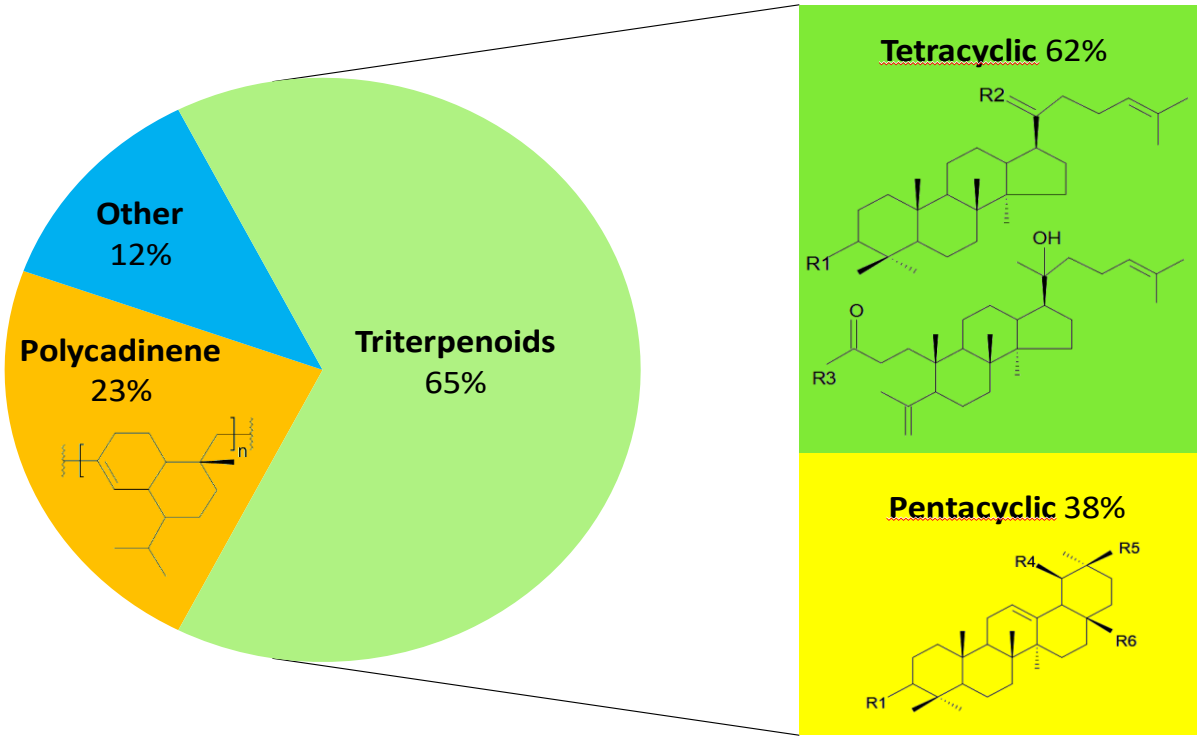
Chemistry of ageing:

IV. EXAMPLE: DAMMAR RESIN

Prof. Ivo Leito

Dammar resin

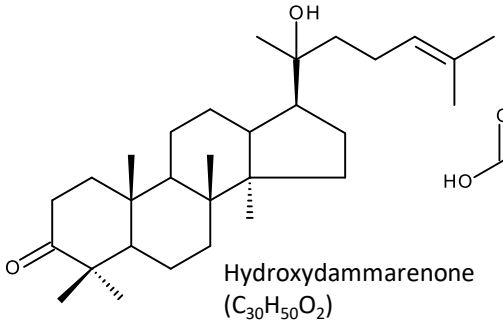
Is obtained from various species of trees belonging to the *Dipterocarpaceae* family



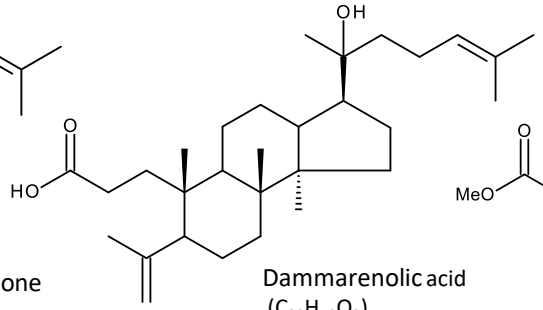
R1: O/ OH, H; **R2**: OH, H/ CH_2; **R3**: OH/ OMe;
R4 and R5: CH_3/ H; **R6**: COOH, H/ CHO, H

Vahur, S.; Teearu, A.; Haljasorg, T.; Burk, P.; Leito, I.; Kaljurand, I. *Journal of Mass Spectrometry*, **2012**, *47*(3), 392 - 409.

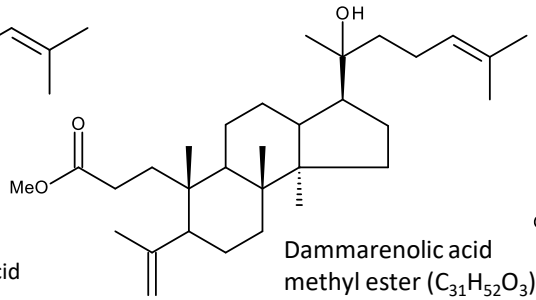
Components of dammar resin



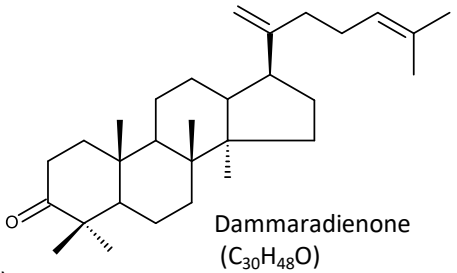
Hydroxydammarenone ($C_{30}H_{50}O_2$)



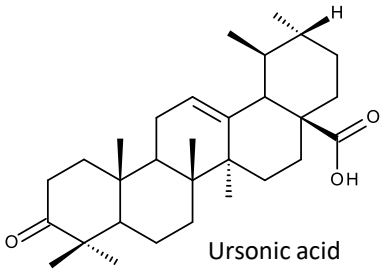
Dammarenolic acid ($C_{30}H_{50}O_3$)



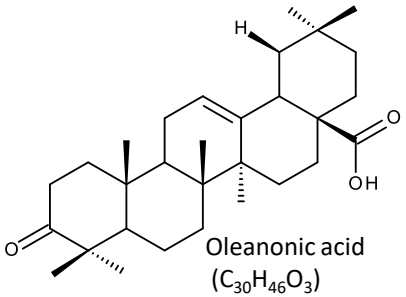
Dammarenolic acid methyl ester ($C_{31}H_{52}O_3$)



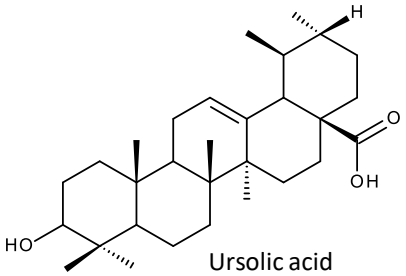
Dammaradienone ($C_{30}H_{48}O$)



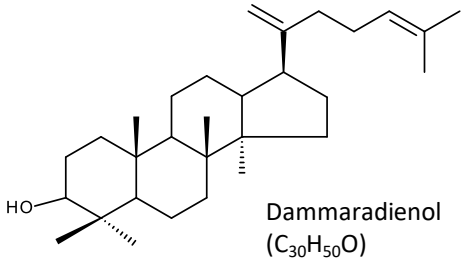
Ursonic acid ($C_{30}H_{46}O_3$)



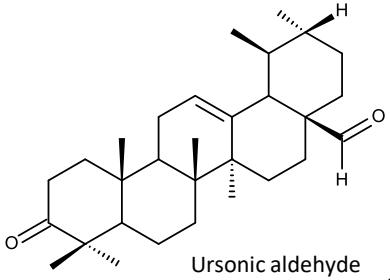
Oleanonic acid ($C_{30}H_{46}O_3$)



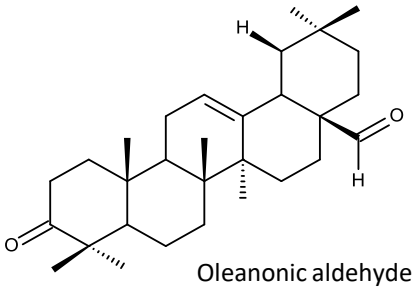
Ursolic acid ($C_{30}H_{48}O_3$)



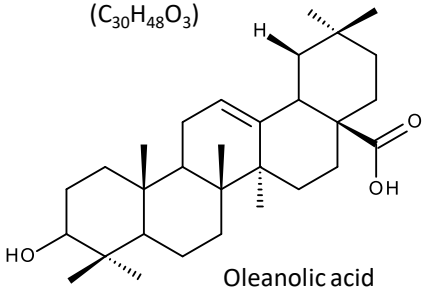
Dammaradienol ($C_{30}H_{50}O$)



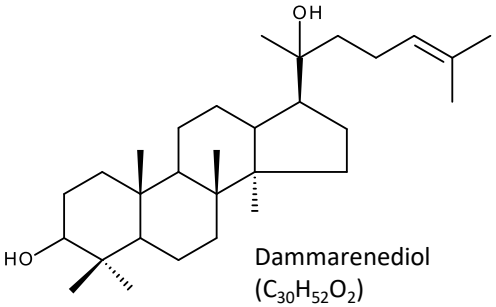
Ursonic aldehyde ($C_{30}H_{46}O_2$)



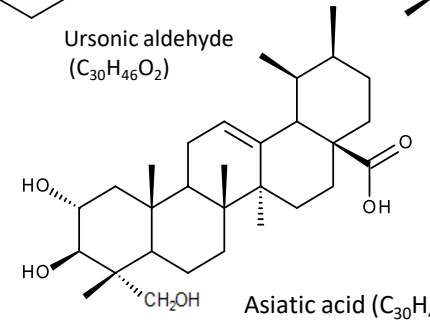
Oleanonic aldehyde ($C_{30}H_{46}O_2$)



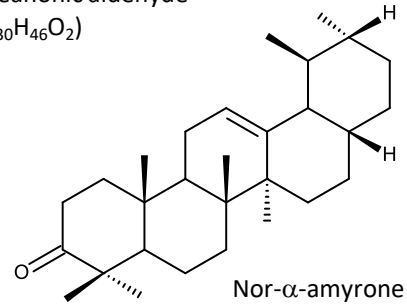
Oleanolic acid ($C_{30}H_{48}O_3$)



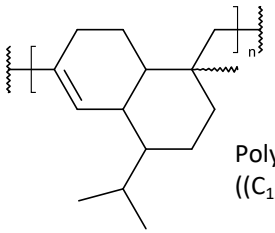
Dammarenediol ($C_{30}H_{52}O_2$)



Asiatic acid ($C_{30}H_{48}O_5$)

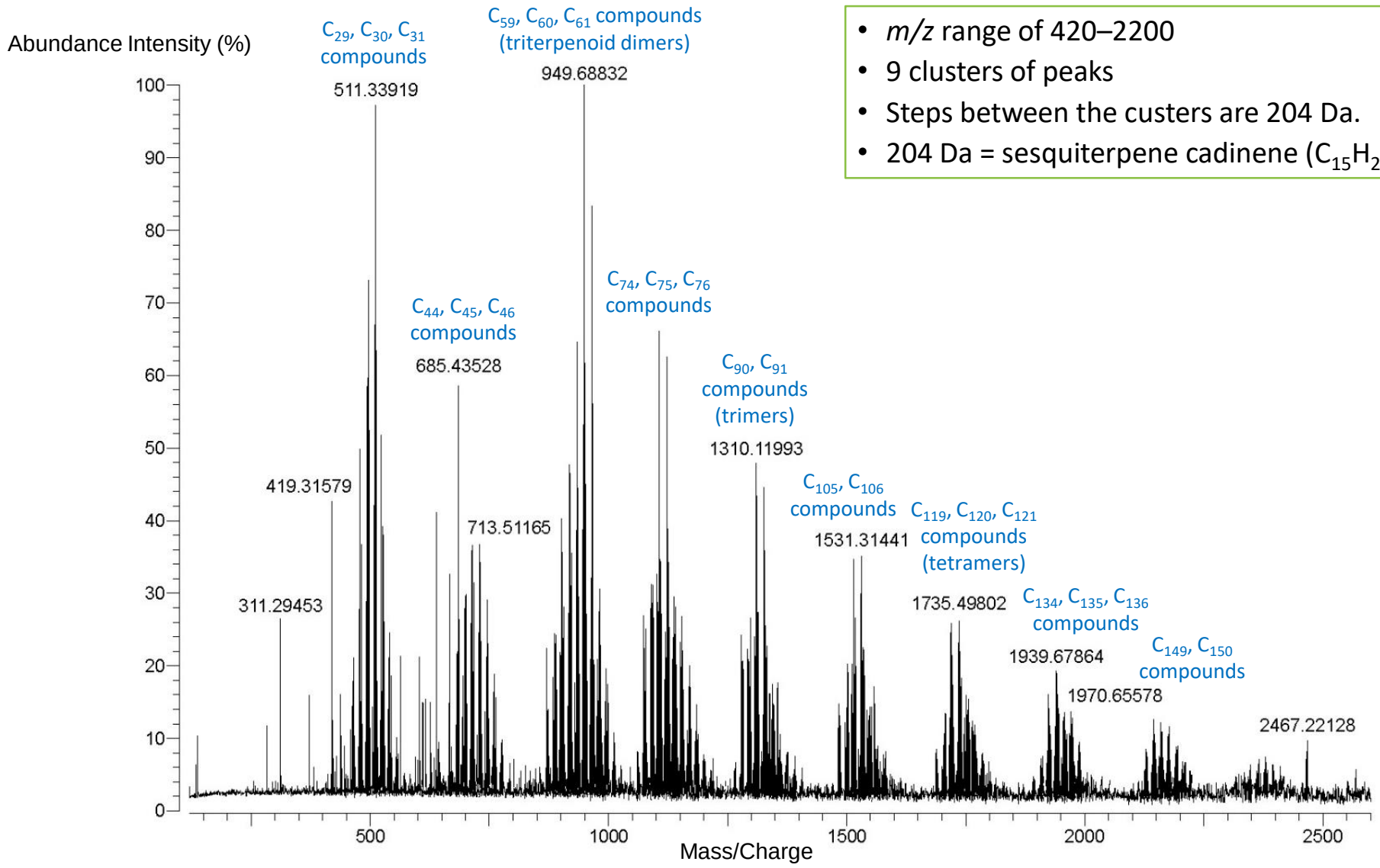


Nor-α-amyrone ($C_{29}H_{46}O$)



Polycadinene ($(C_{15}H_{24})_n$)

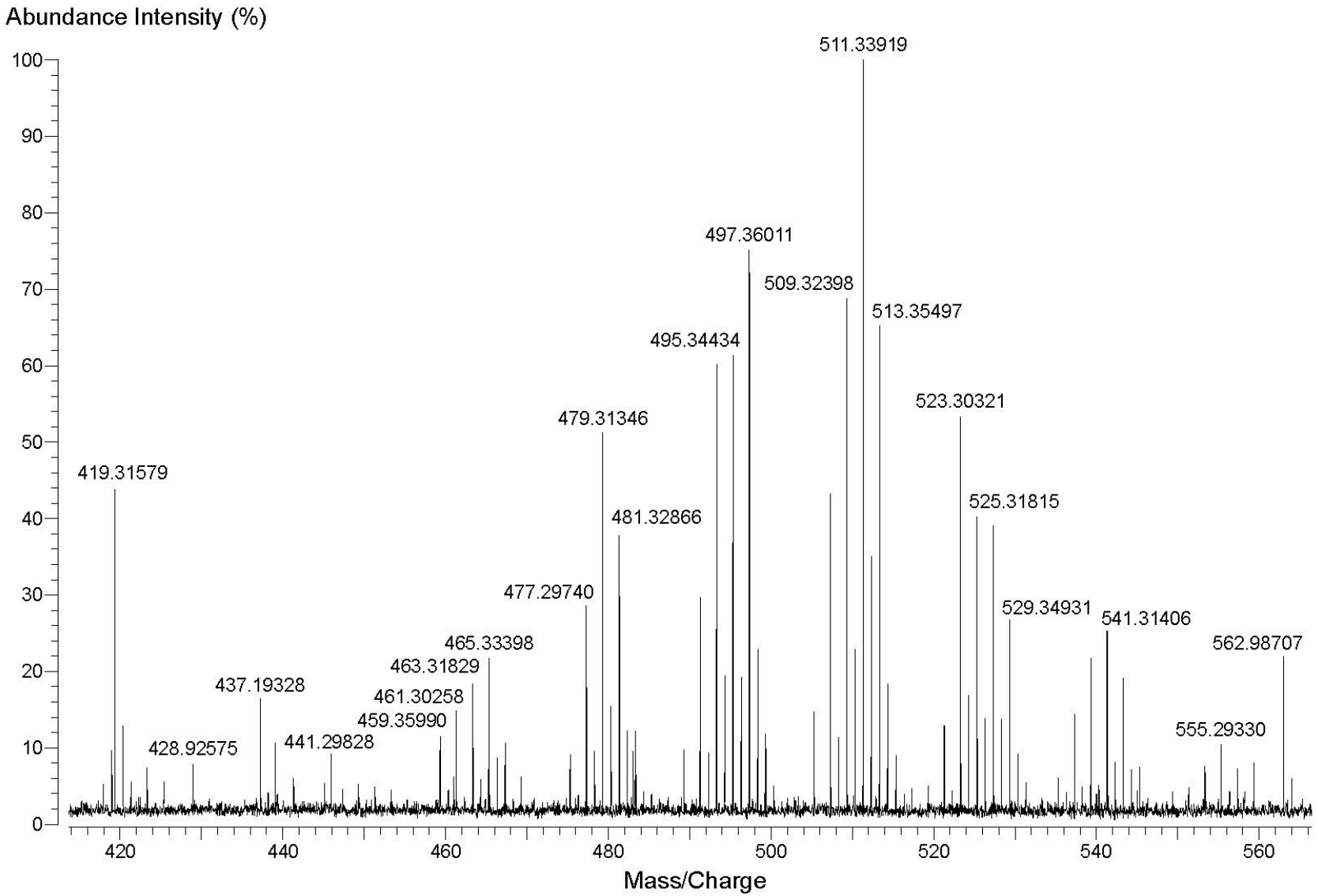
MALDI-FT-ICR-MS spectrum of dammar resin



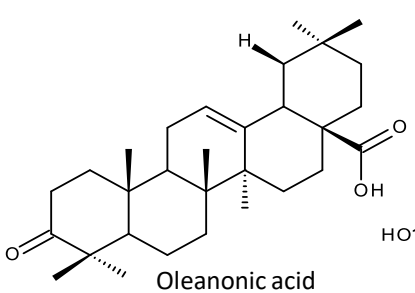
- *m/z* range of 420–2200
- 9 clusters of peaks
- Steps between the custers are 204 Da.
- 204 Da = sesquiterpene cadinene ($C_{15}H_{24}$)

Vahur, S.; Teearu, A.; Haljasorg, T.; Burk, P.; Leito, I.; Kaljurand, I. *J. Mass Spectrom*, **2012**, *47*(3), 392 - 409.

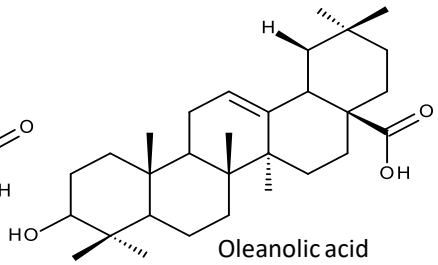
MALDI-FTMS spectrum of dammar resin (first cluster)



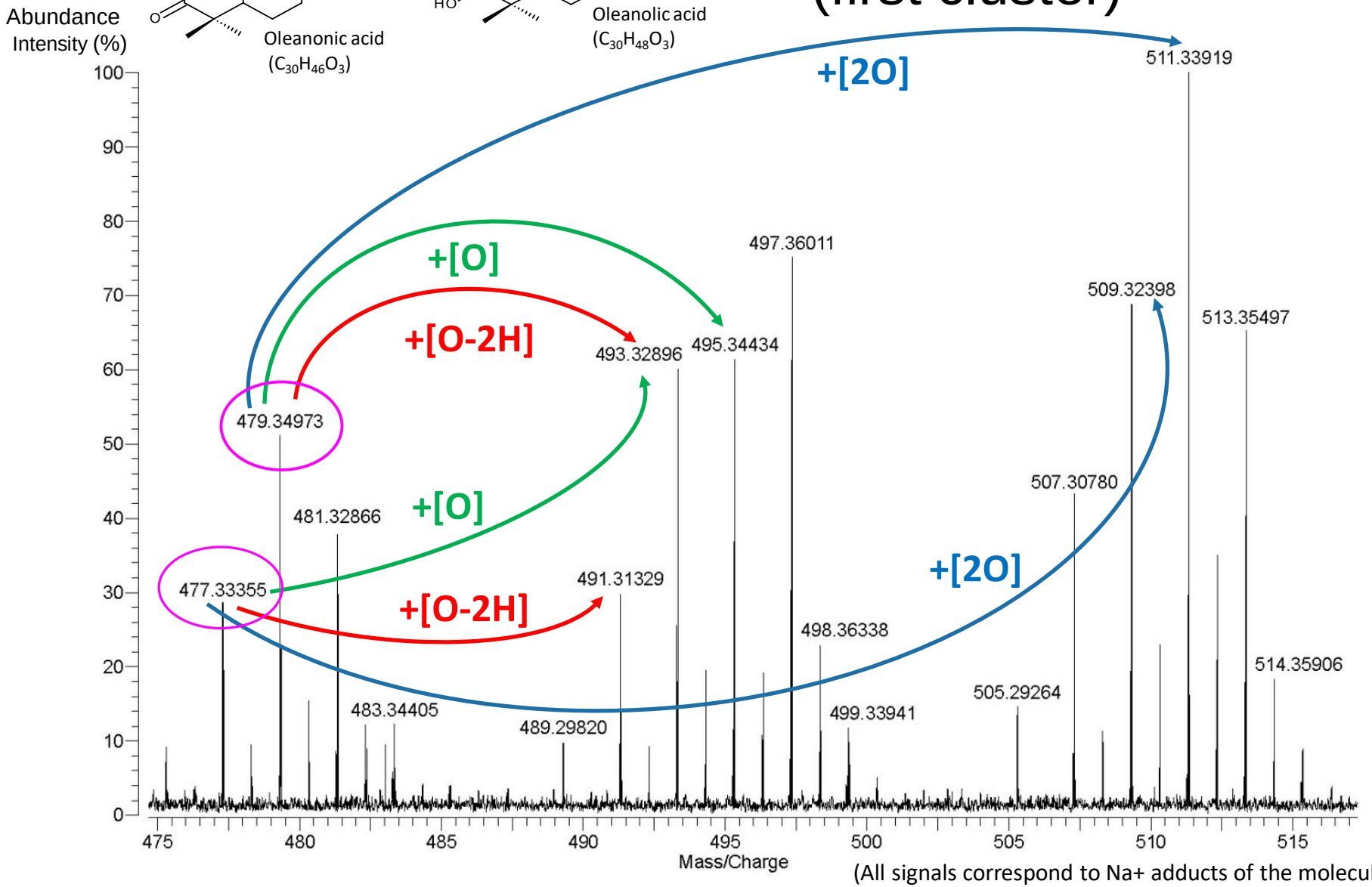
MALDI-FTMS spectrum of dammar resin (first cluster)



Oleanonic acid
($C_{30}H_{46}O_3$)



Oleanolic acid
($C_{30}H_{48}O_3$)



(All signals correspond to Na+ adducts of the molecules)

Summary

- Due ageing the composition of CH materials is usually very complex
- Analysis of the aged materials is challenging, both in terms of **knowledge** as well as **instrumentation**

- **More information is on the web:**

https://sisu.ut.ee/heritage-analysis/