University of Ghent,
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Influence of processing on minor components in vegetable oils

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General introduction

Oils and fats

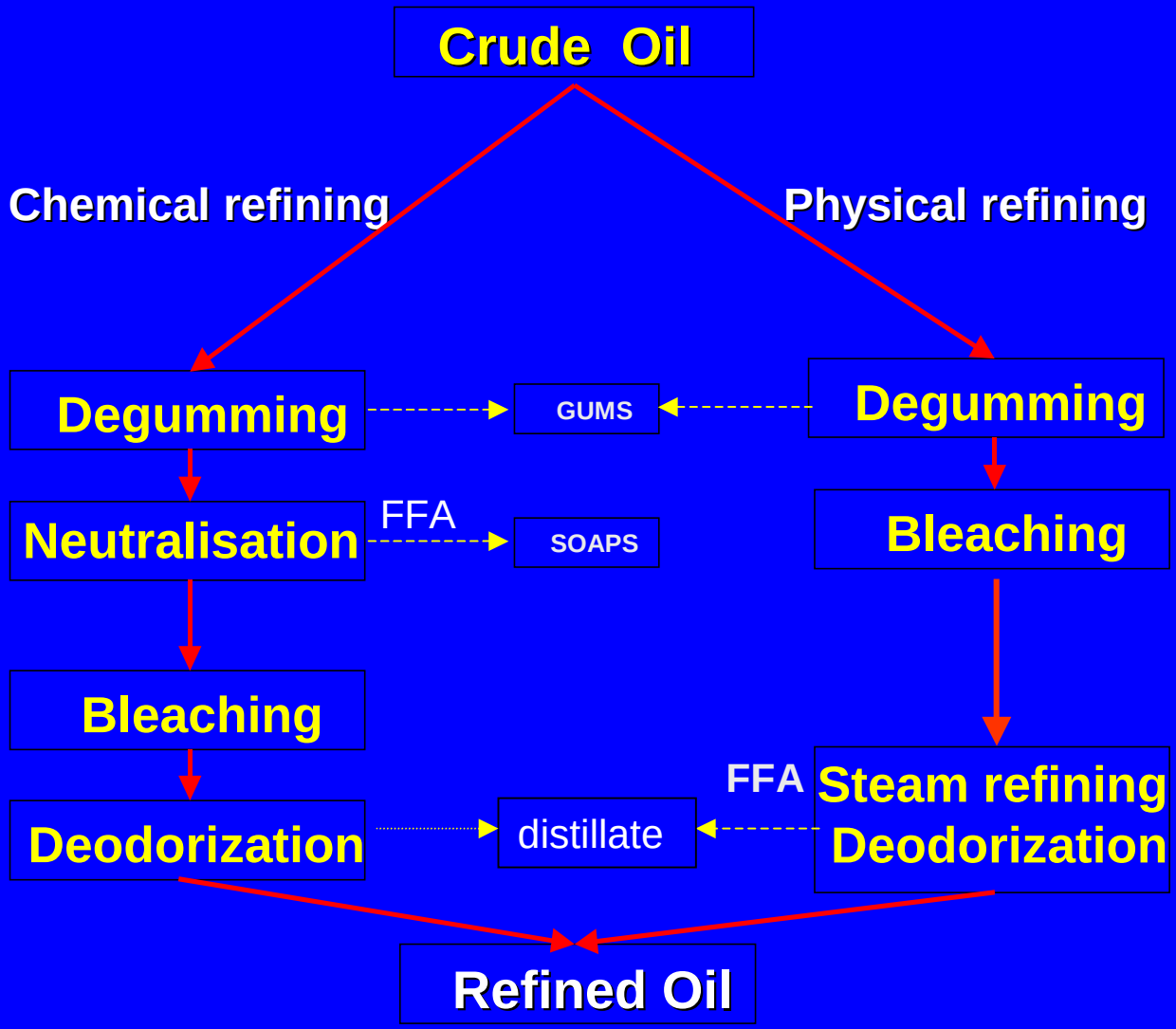
Nutritional importance

- delivering energy (9 kcal/g)
- essential fatty acids (ω3, ω6)
- fat soluble vitamins
  (Vitamine A, D, E, K)
- sensorial and rheological appreciation of foods

Composition crude oil

- Triglycerides (>98%) and partial acylglycerides, free fatty acids
- Tocopherols, phytosterols, phospholipids, waxes, metals, colouring pigments
- Odour, flavour components

Overview vegetable oil refining



Vegetable oil quality characteristics

Traditional parameters

bland taste

light colour

good oxidative stability

Currently : minor components

+ : Functional minor components

tocopherols, phytosterols,

oryzanol, coenzyme Q10

→ application in functional foods

- : Harmful contaminants

pesticides, PAH's, PCB's

Tocopherols

Chemical structure

Name	R1	R2	R3
α-toco	CH_3	CH_3	CH_3
γ-toco	H	CH_3	CH_3
δ-toco	H	H	CH_3

Non-polar and polar oxidation products

Natural source : vegetable oils, corn oil 1100 ppm, soya oil 900 ppm

Nutritional importance : → Vitamin E, prevention of free radical damage *in vivo* e.g. cardiovascular diseases, cancers, neurological disorders (Alzheimer,...)

Application : dietary supplements

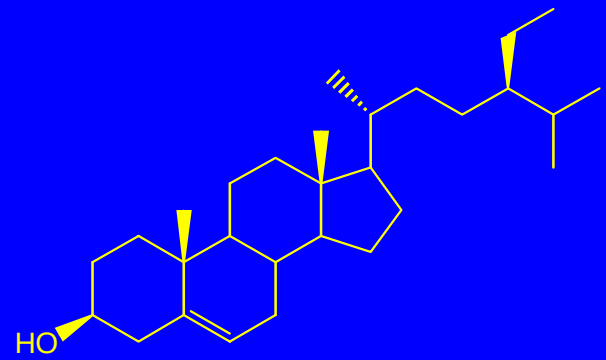
Phytosterols

Chemical structure :

- flexible side chain at C17

  (sitosterol, campesterol, stigmasterol,…)

- sterols versus stanols



β-sitosterol

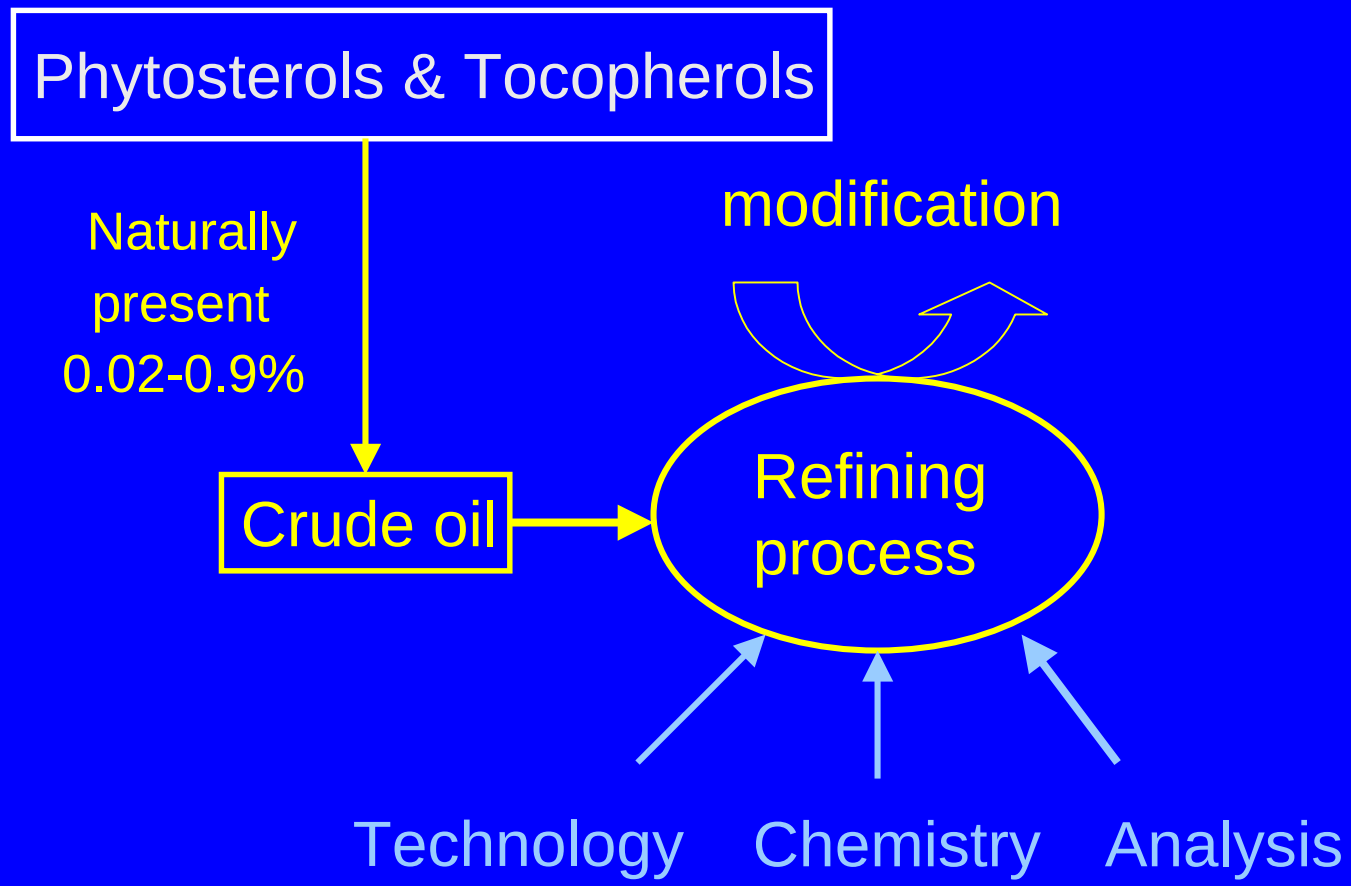
Function : Essential component of the membranes

Natural source : vegetable oils and cereals

Nutritional importance : phytosterols lower plasma cholesterol and LDL cholesterol

Application : in functional foods (e.g. margarine's,…)

Objective study



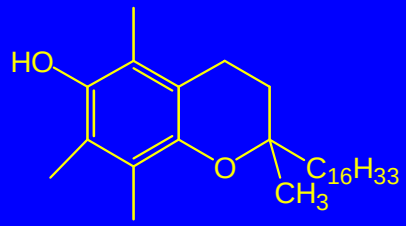
Observations → chemical modification → explanations

Occurrence of tocopherols and phytosterols in vegetable oils : free or bounded

Natural occurrence

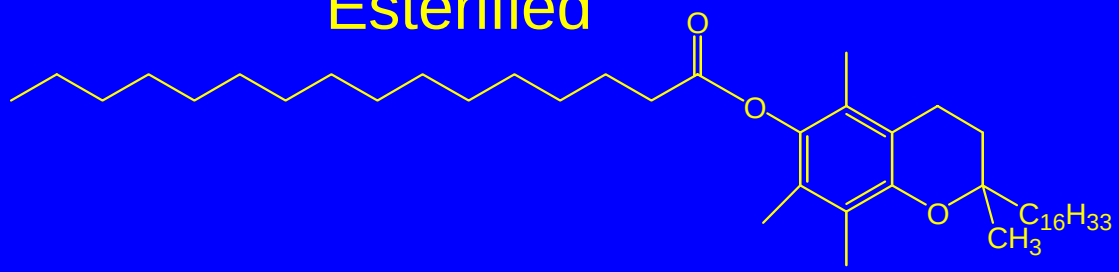
Tocopherols

Free



→ Data available

Esterified



→ Confuse data

→ synthesis of tocopheryl esters

→ development of analytical procedure (HPLC - UV)

→ tocopheryl esters are absent in crude vegetable oils

Natural occurrence

- Tocopherols

$\rightarrow$ only free tocopherols occur naturally in vegetable oil

- Phytosterols occur
  - free

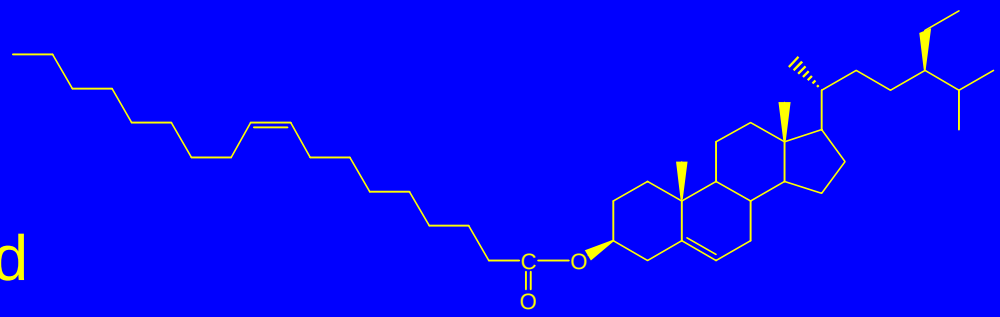
β-sitosterol

Natural occurrence

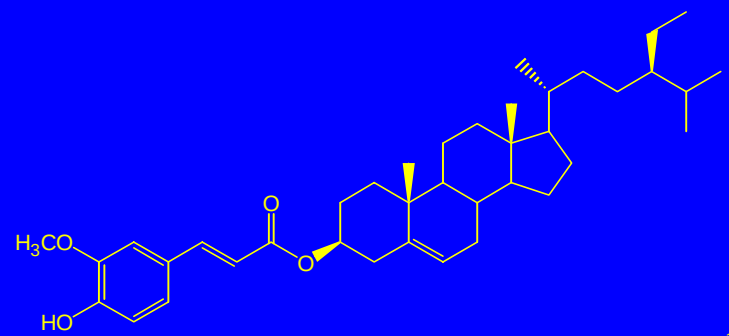
- Tocopherols

→ only free tocopherols occur naturally in vegetable oil

- Phytosterols occur
  - free
  - esterified to fatty acid
  - esterified to phenolic acids
    - e.g. rice bran oil



β-sitosteryl-oleate



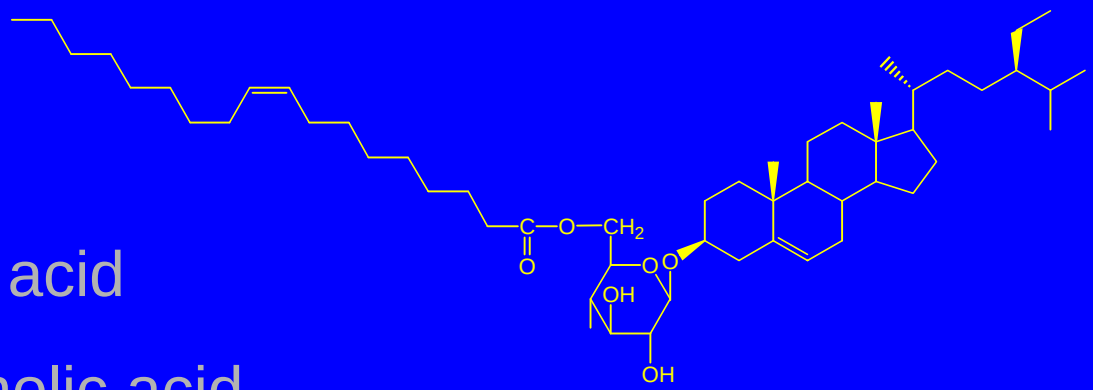
β-sitosteryl ferulate (γ-oryzanol)

Natural occurrence

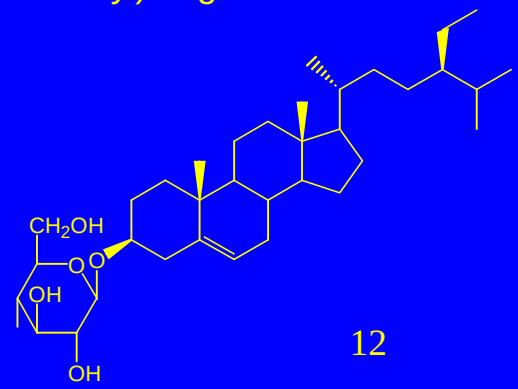
- Tocopherols

$\rightarrow$ only free tocopherols occur naturally in vegetable oil

- Phytosterols occur
  - free
  - esterified to fatty acid
  - esterified to phenolic acid
  - linked to sugar



β-sitosteryl-(6'O-oleoyl)-D-glucoside



β-sitosteryl-D-glucoside

Total sterol analysis

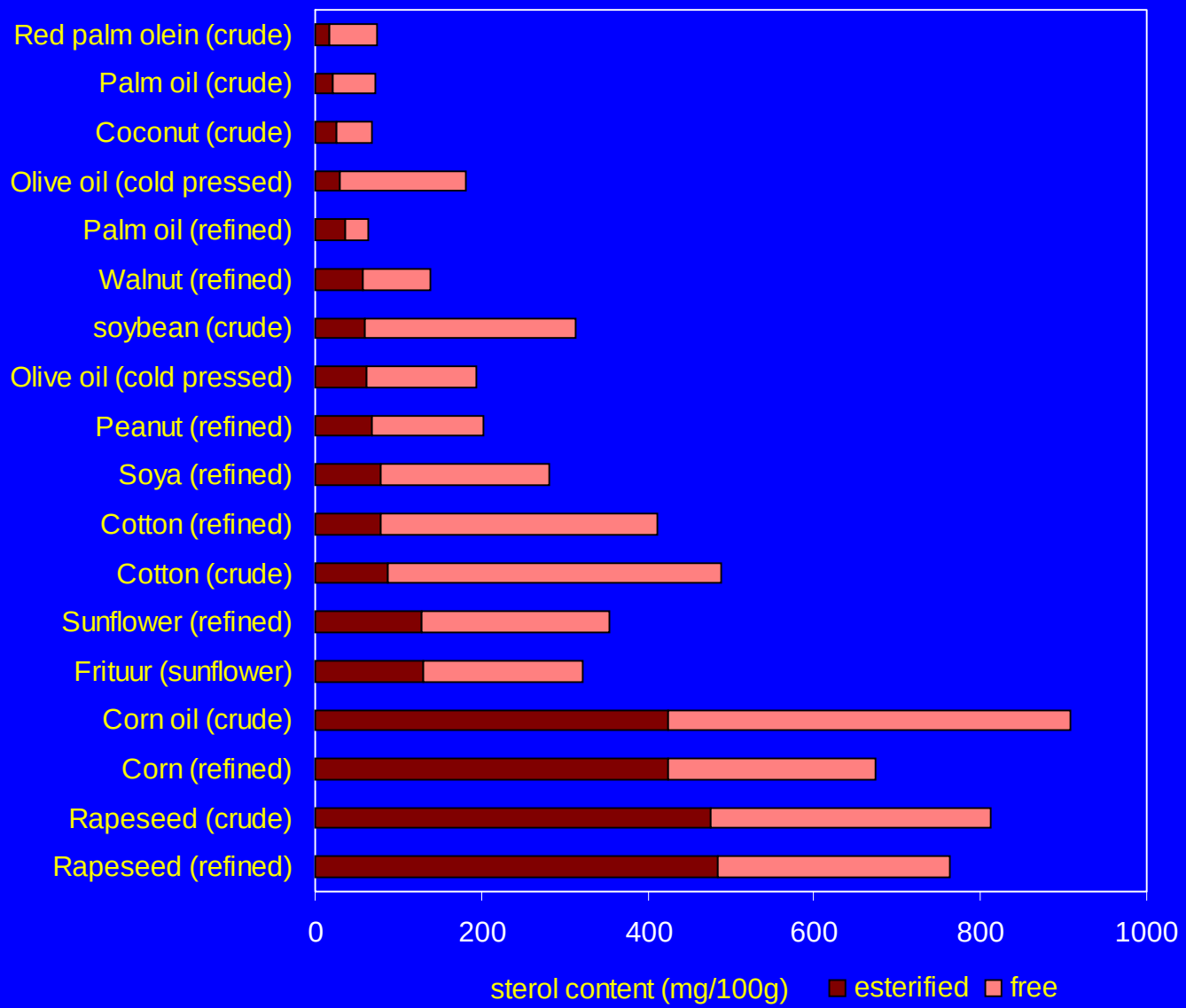
- Has been widely studied
- Involves a saponification Steryl esters $\rightarrow$ free sterols
- Little data is available on level of free and esterified phytosterols

Analysis free - esterified sterols

• Free and esterified sterols were separated on polarity by silica gel chromatography, followed saponification and GC quantification

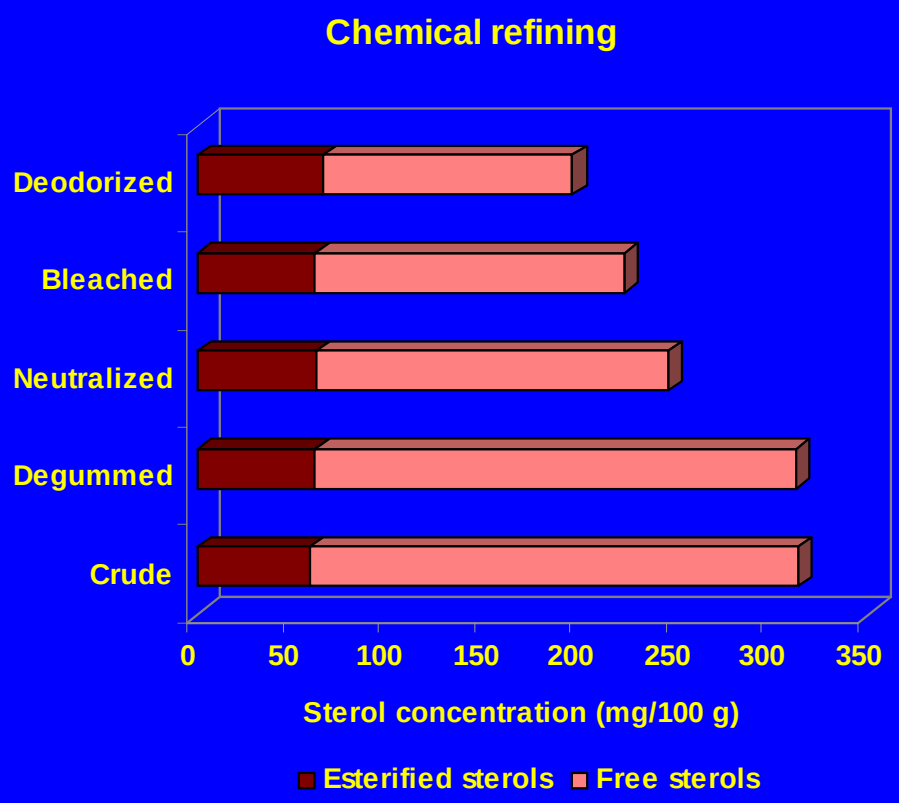
•Development and validation of analytical method

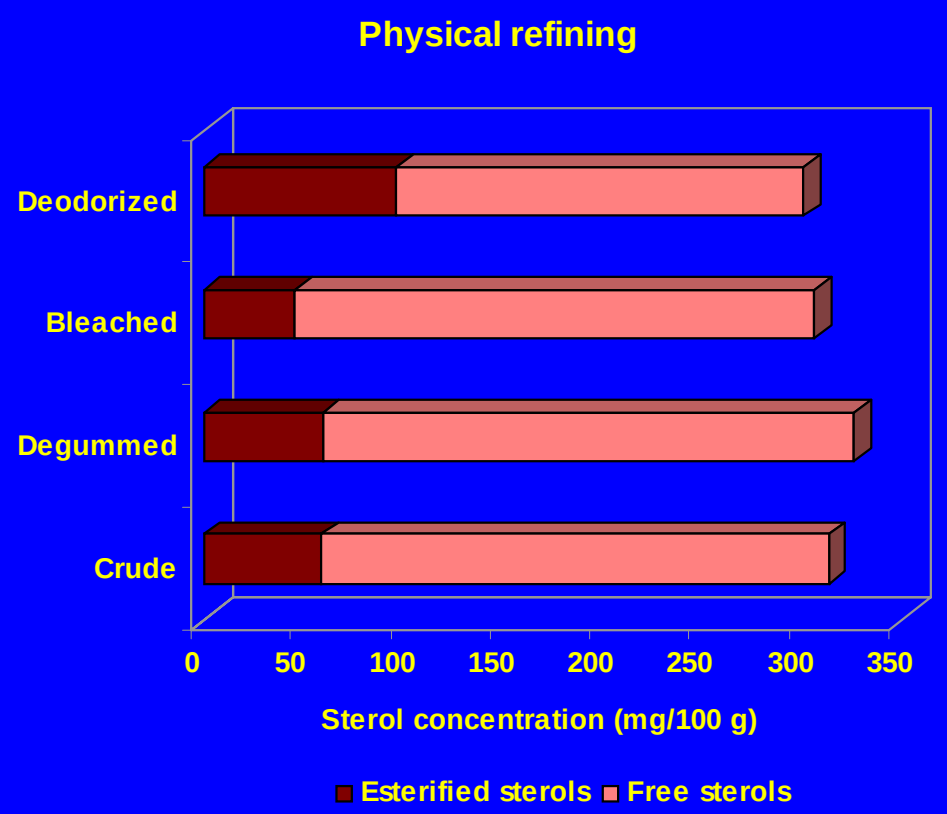
Free and esterified phytosterols



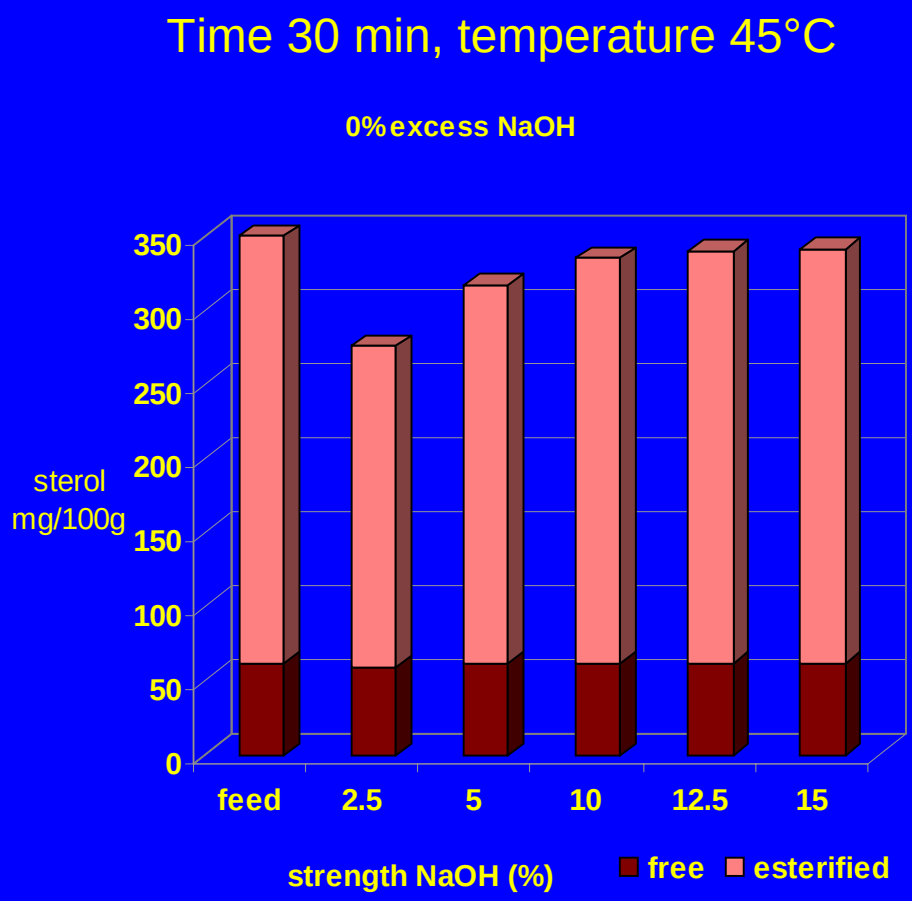
Influence of refining on free and esterified phytosterols in soybean oil

Influence of refining on soybean

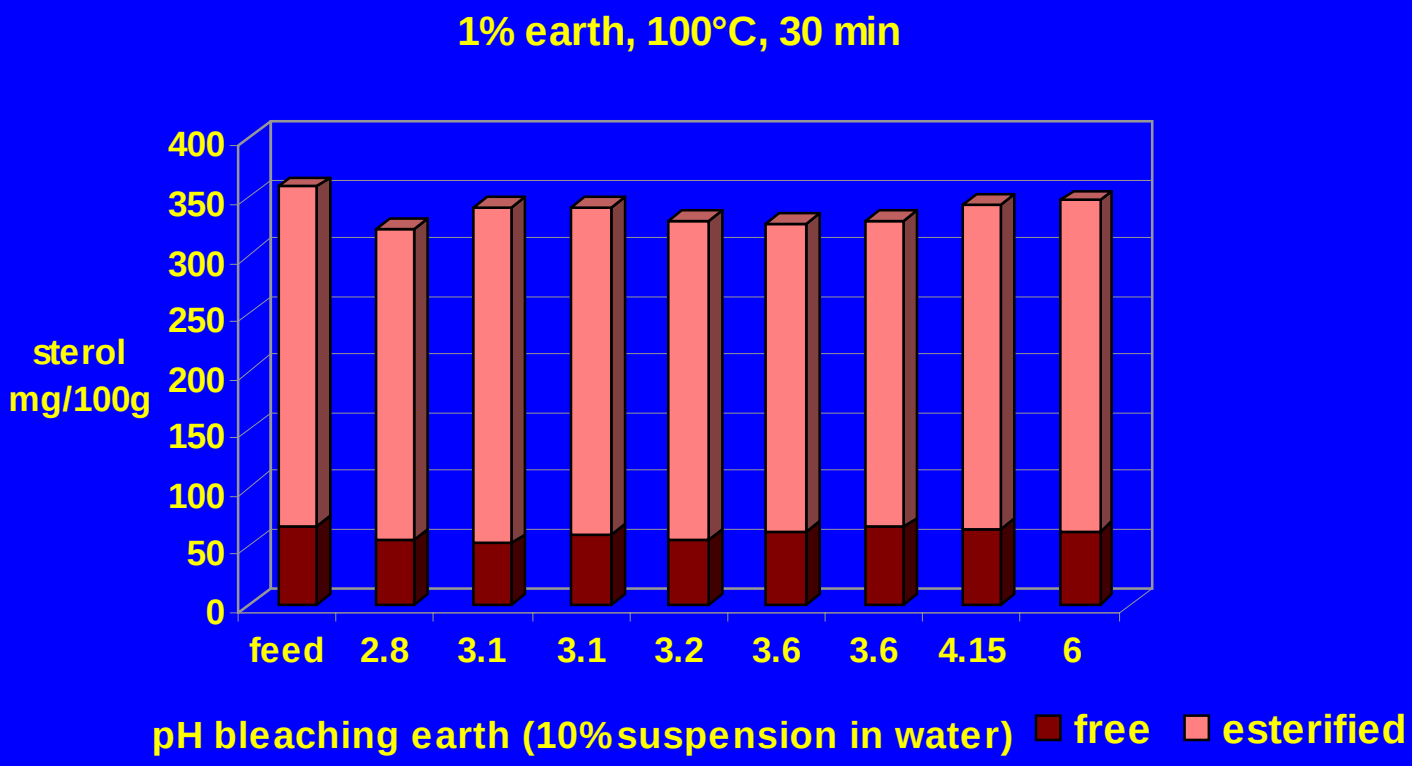




Chemical neutralisation of soybean

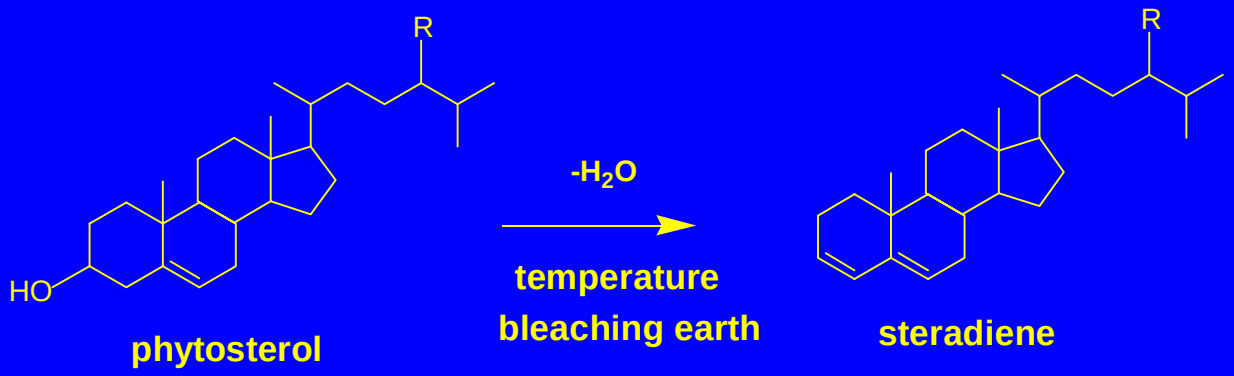


Bleaching of soybean oil



Steradienes - disteryl ethers

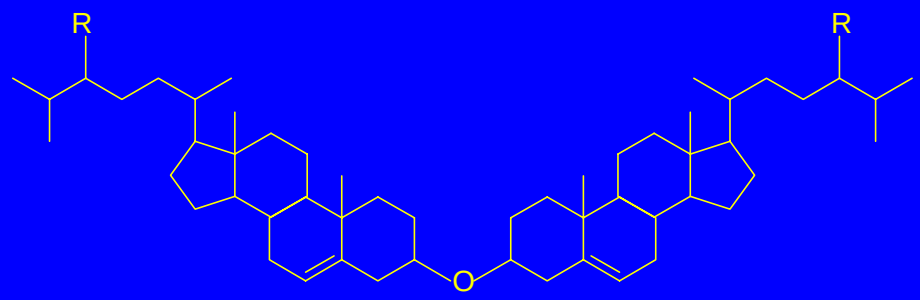
- Steradienes : sterol dehydration products



phytosterol

steradiene

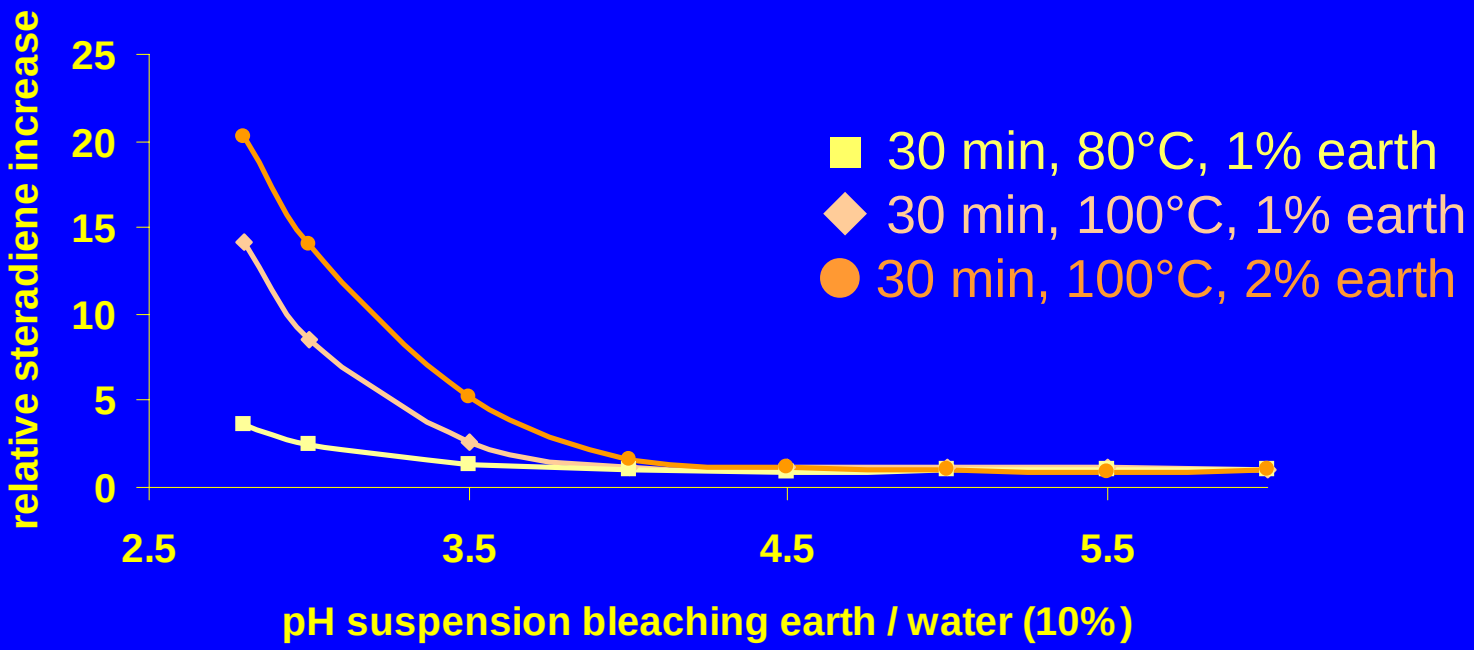
- Disteryl ethers : sterol condensation products



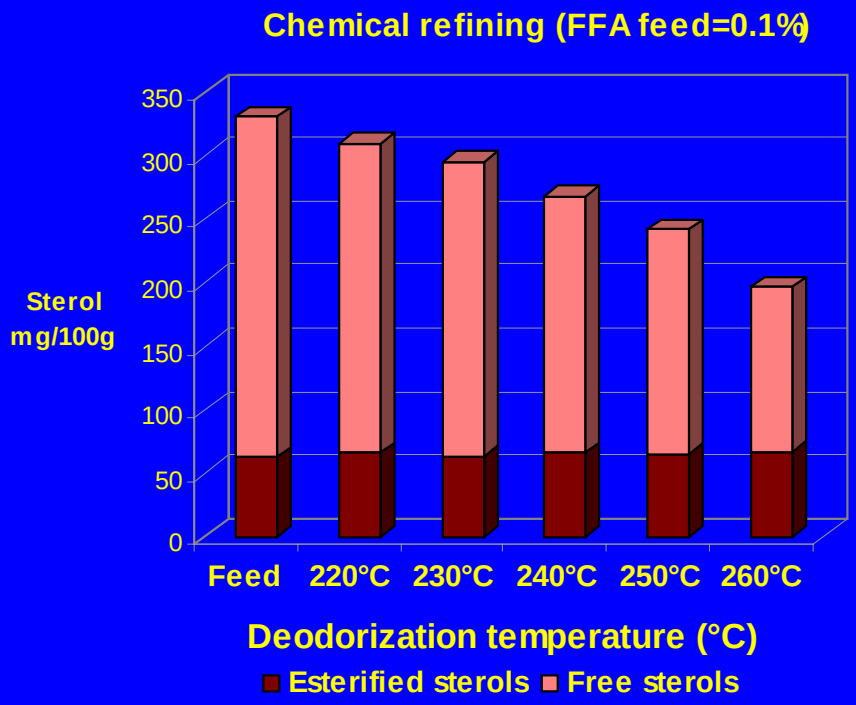
→ ratio dehydration / condensation : 10/1

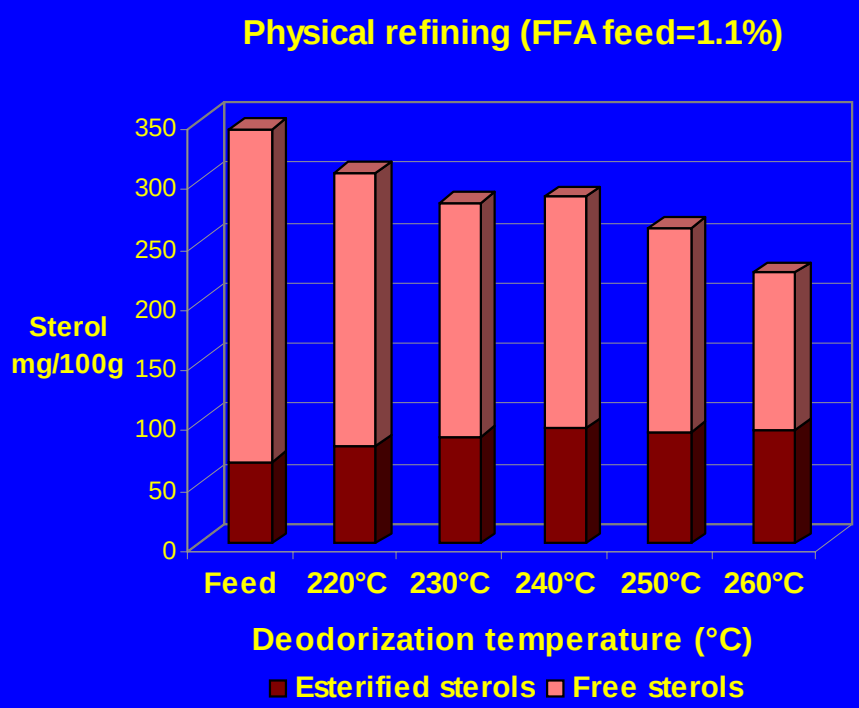
Steradienes - bleaching

- Steradiene formation is mainly influence by
  - bleaching temperature
  - degree of acid activation of the bleaching earth



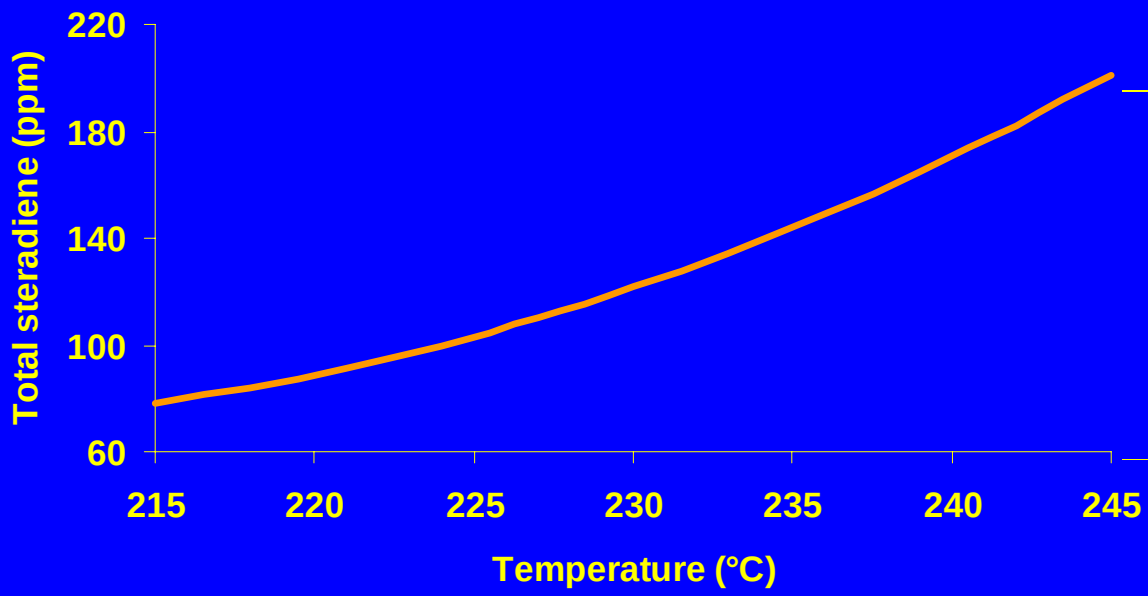
Deodorization of soybean oil





Steradiene - deodorization

- Degree of sterol dehydration is mainly influenced by deodorization temperature
- Steradienes are distillated and condensed in the deodoriser distillate (90 - 600 ppm steradienes in soya distillate)



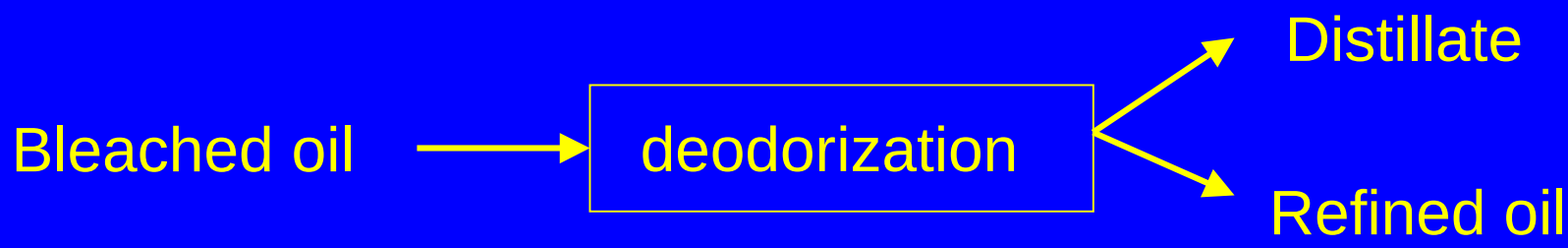
Temperature (°C)	Free sterol Dehydration (%)
220	0.05
230	0.1
240	0.23
250	0.4
260	1.06

Influence of processing on tocopherols

Stability of tocopherols

Objective : assess the stability of tocopherols at high temperature

Tocopherol mass balance during deodorization



$Toco_{\text{bleached oil}} = toco_{\text{refined oil}} + toco_{\text{distillate}} + ??$

Observation :

Tocopherol loss of 20-30% in the tocopherol mass balance

Explanation : analytical - incomplete condensation - thermal breakdown - oxidative degradation

Stability of tocopherols

- Fundamental study

α-tocopherol (2000ppm)
dissolved in triolein and
heated to 245°C, 5-6 mbar
for 80 min, **no steam injection**

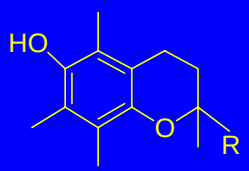
Tocopherol loss (%)	
Reference :	**9**
With TBHQ : (1500ppm)	3
N_2 flush :	0

Conclusion : thermal stability, probably oxidative degradation

⇒ major tocopherol oxidation products?

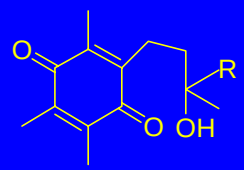
Tocopherol oxidation

- Previous tocopherol oxidation studies :
  - oxidation of α-tocopherol dissolved in a solvent
  - oxidation initiators : K_3FeCN_6, $FeCl_3$, tBOOH, AIBN
  - oxidation at room temperature
  - formation of several known oxidation products

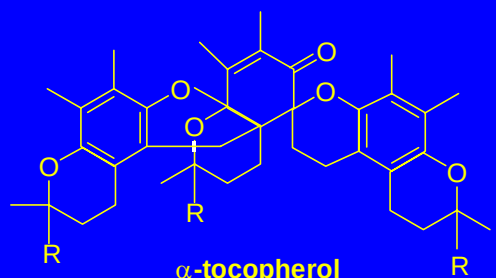


α-tocopherol

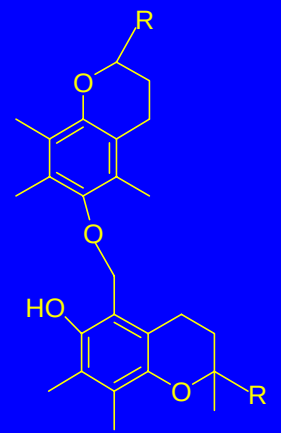
α-tocopheroldimer quinone



α-tocopherolquinone



α-tocopherol spirotrimeer

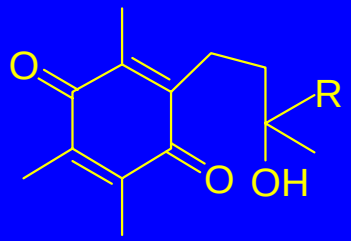


Tocopherols

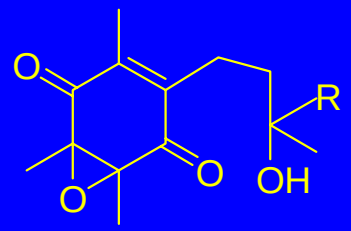
- Identification of oxidation products in triglycerides

  - synthesis of most important tocopherol oxidation products

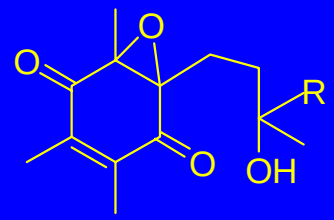
  - used as standards for the identification of tocopherol oxidation products formed in triolein



α-Tocopherolquinone



7,8-epoxy-
α-tocopherolquinone



4a,5-Epoxy-
α-tocopherolquinone

Tocopherols are antioxidants → prone to oxidation

Concentration of tocopherol oxidation products?

Stability of tocopherol during thermoxidation stress

- Objective :

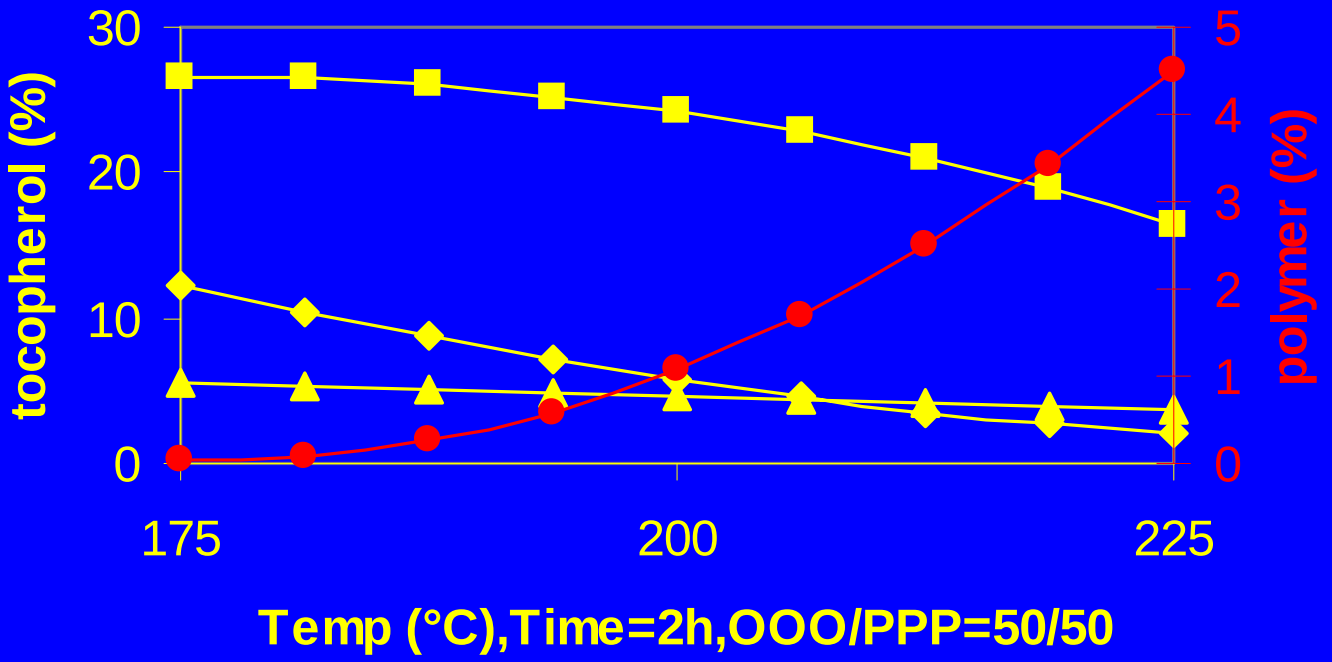
  - Modeling of α-tocopherol degradation in function of heating time, temperature and triacylglycerol unsaturation

  - Quantification of α-tocopherol oxidation products formed

- Experimental :

  - Statistical central composite design
  - Addition of α-tocopherol standard (1000 ppm) to technical grade triolein and tripalmitin
  - Heating : 5g of oil in OSI tubes, no air bubbling

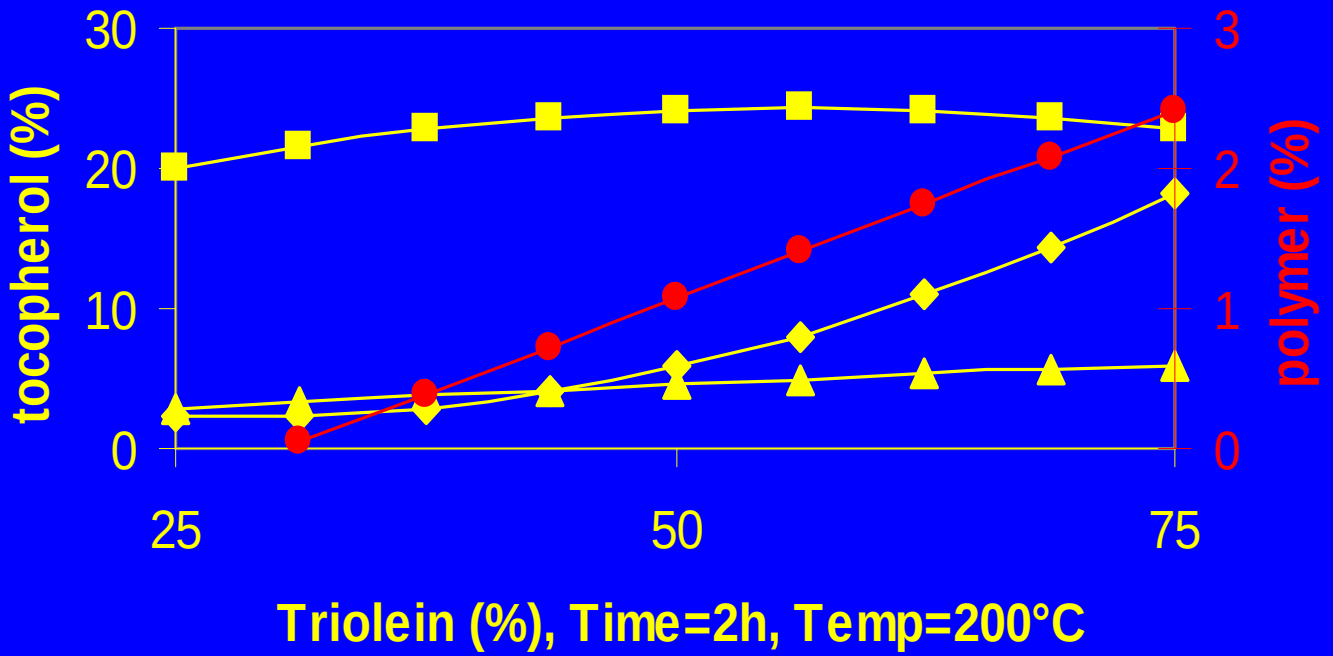
Modeling of α-tocopherol oxidation products during thermoxidation in triolein and tripalmitin



α-tocopherol (◆), epoxy-α-tocopherolquinone (■);

α-tocopherolquinone (▲), total triacylglycerol, polymer (●)

Modeling of α-tocopherol oxidation products during thermoxidation in triolein and tripalmitin



α-tocopherol (◆), epoxy-α-tocopherolquinone (■);

α-tocopherolquinone (▲), total triacylglycerol, polymer (●)

Deodoriser distillate : characterisation and technology to improve quality

Characterisation of deodoriser distillate

Analytical characterisation

major components

free free fatty acids

physical refining : > 70%

chemical refining : < 60%

monoglycerides

diglycerides

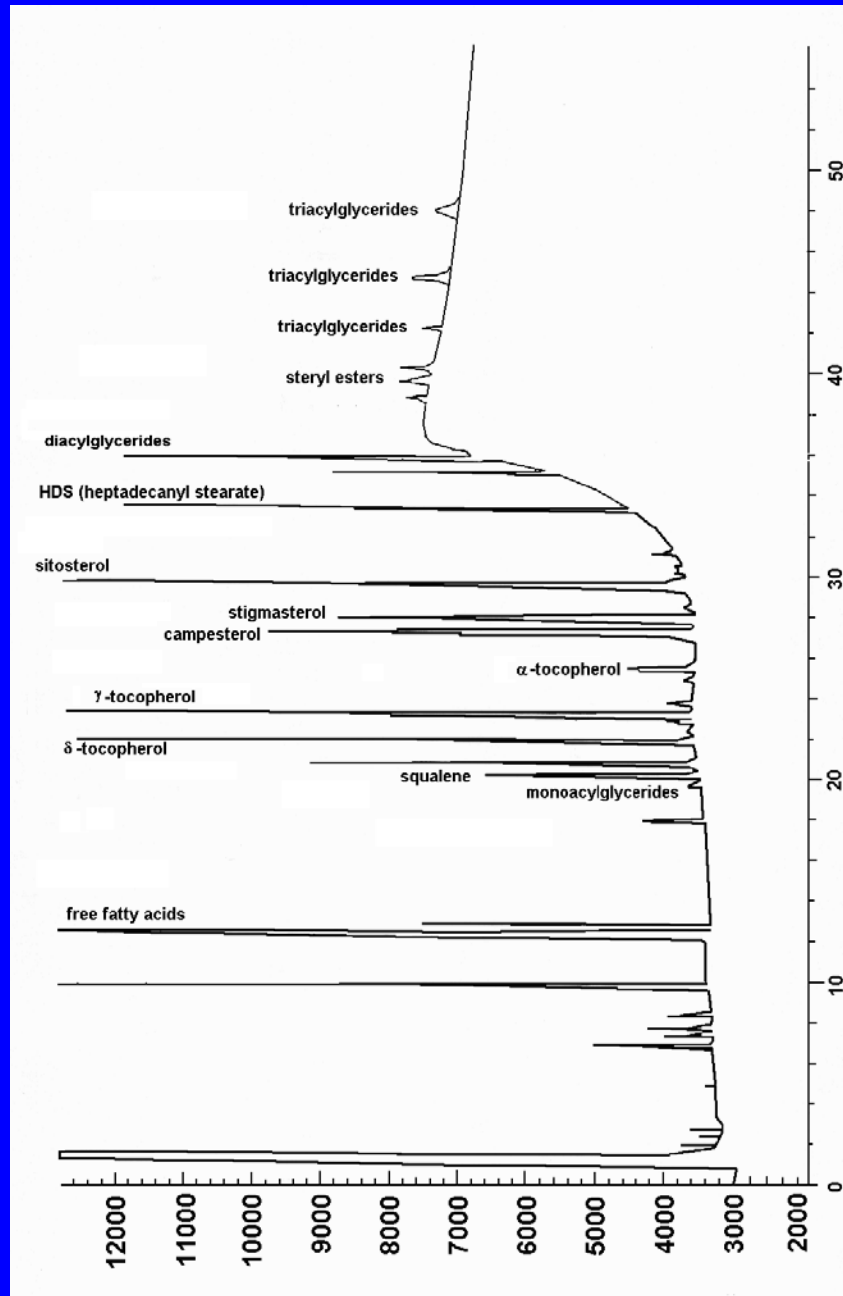
triglycerides

squalene

tocopherols and phytosterols

physical refining : 2-5%

chemical refining : 10-25%



Deodorization technology

- Observation :
  - chemical distillate : high tocopherol and phytosterol content
    $\rightarrow$ high economic value
  - physical distillate : high free fatty acid content
    $\rightarrow$ low economic value

- Objective :
  - develop new deodorization technology to improve the quality of physical deodoriser distillate

Deodorization technology

- Methodology :
  - condensation of free fatty acids in a first distillate fraction
  - condensation of tocopherols and phytosterols in a second distillate fraction

$\rightarrow$ by optimisation of the temperature profile

Improved deodorization technology : conclusion

	Free fatty acids	tocopherols	phytosterols
Chemical	10-24	10-15	10-17
Physical	76-87	2-5	2-7
Distillate 1	90-96	1-2	1-2
Distillate 2	37-67	8-10	10-15

General conclusion

The new and fundamental view followed in this research indicates that tocopherols and phytosterols are stable components, however several transformation reactions can take place of which the ratio is influenced by the technological conditions

Acknowledgement

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Revilija Mozuraityte

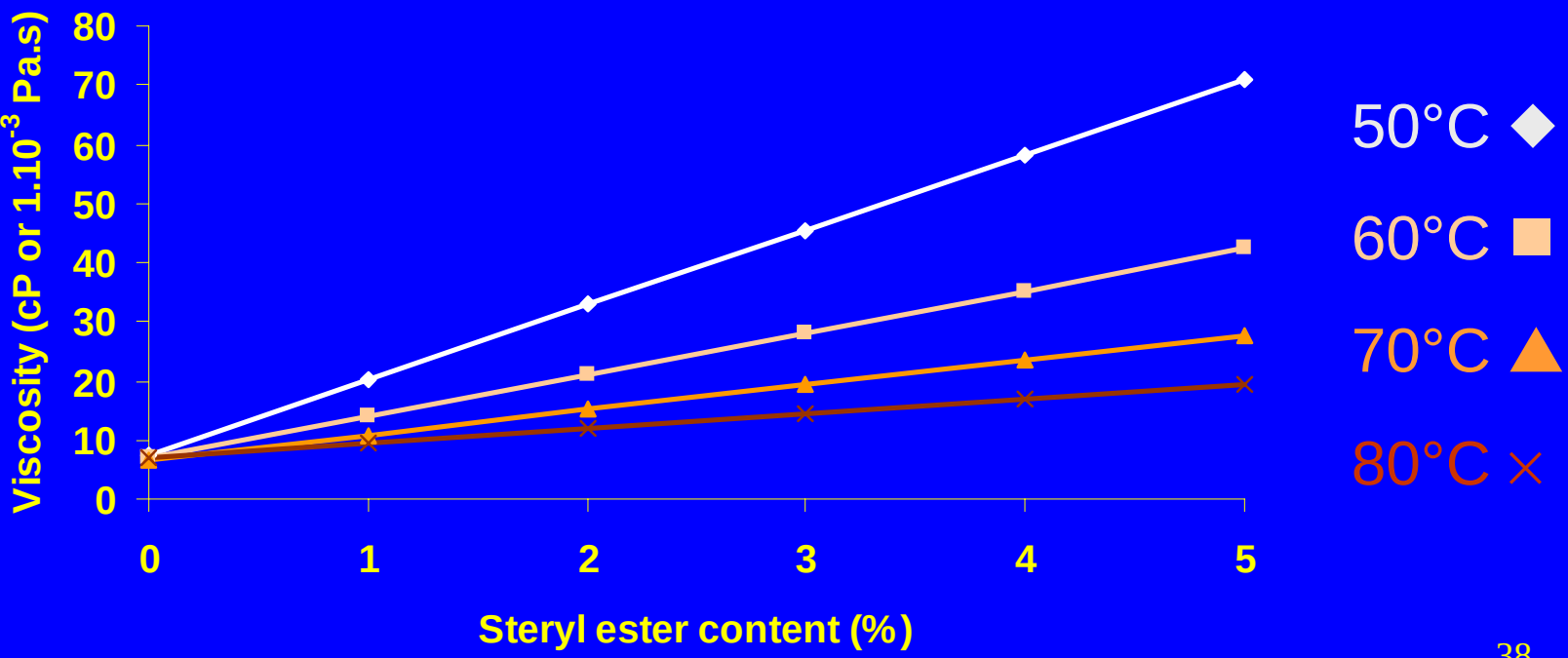
Jose Ayala Vila

Characterisation of deodorizer distillate

2. Rheological characterisation

viscosity is determined by

- Chemical distillate : phytosterols
- Physical distillate : free fatty acids



Characterisation of deodorizer distillate

2. Rheological characterisation

viscosity is determined by

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