How chemical composition influences cocoa butter crystallization

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Overview

- Introduction and aim
- Materials and methods
- Chemical composition of different cocoa butters
- (What happens during isothermal crystallization), cf. next presentation of Koen Dewettinck
- Influence of chemical composition on different crystallization parameters
- Take home message

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Introduction

- CHEMICAL COMPOSITION of cocoa butter
- ~ growing conditions, plant age, cacao variety
- ~ production process, refining
- Influence on physical properties, e.g. crystallization kinetics
- => important e.g. for production of chocolate

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Aim

- Chemical characterization of twenty cocoa butters
- Quantitative investigation of influence on isothermal, static cocoa butter crystallization described by model of Foubert et al. (2002)
- All different chemical composition variables in one study
- Using biological variability, not by adding chemical substances

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Materials and methods

- 20 different cocoa butters (different countries of origin, also some with crystallization difficulties)
- Isothermal crystallization at 20°C followed by DSC
- Chemical analyses: fatty acid profile, triglyceride profile, free fatty acids, phosphorus (~phospholipids), iron, traces of soap, unsaponifiable matter, peroxide value, diglycerides
- Principal component analysis: reduce dimensionality of fatty acid and triglyceride profile data
- Multiple linear regression to investigate influence of chemical composition on crystallization properties

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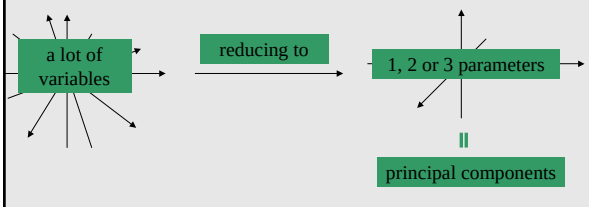
Analysis of fatty acid and triglyceride profile: principal component analysis



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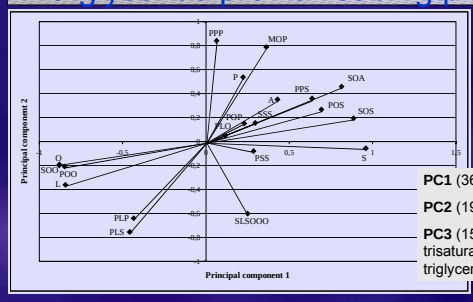
Analysis of fatty acid and triglyceride profile: loading plot

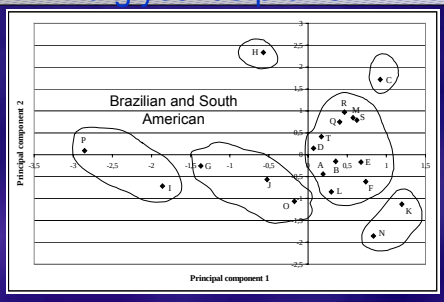


PC1 (36.5%)

PC2 (19.2%)

PC3 (15.2%) ~ trisaturated triglycerides (+)

Analysis of fatty acid and triglyceride profile



Minor components

- Free fatty acids: 1.16-2.77%
- Diglycerides: 0.59-2.22%
- Phospholipids: 0.006-0.16%: high in 'difficult' butters
- Peroxide value: 0-7.9 meq/1000g : high in 'difficult' butters
- Unsaponifiable matter: 0.31-0.53%
- Soap: 0-329ppm
- Iron: 0.140-5.71 ppm: high in 'difficult' butters

Minor components

- For all minor components: no link with country of origin => production and refining are more important than country of origin
- High correlation between
  - phospholipids – soap
  - iron - peroxide

Isothermal crystallization at 20°C

- Two-step process
- From research with time-resolved X-ray diffraction (synchrotron radiation, ESRF Grenoble)
  - First step: crystallization in α polymorph (kinetically favoured)
  - Second step: α mediated β' crystallization
  - No direct β' crystallization
- More details in next presentation (Koen Dewettinck, Phase behaviour of cocoa butter in a two-step isothermal crystallization)

Model of Foubert et al. (2002)

$$\frac{dh}{dt} = K \times (h^n - h)$$

$$h(t) = \frac{a_F - f(t)}{a_F}$$

f(t): amount of crystallization [%]

h: fraction remaining crystallizable fat (0<h<1) [-]

a_F: value of f as t approaches infinity [%]

K: rate constant [h^{-1}]

n: order of the reverse reaction [-]

Model of Foubert et al. (2002)

- f(0) related to induction time
- physical interpretation of 'induction time' more straightforward + easier to extract from curve
  ➡ represent as function of induction time
- t_ind_x: time needed to reach e.g. 1% crystallization (x=0.01)

$$f(t) = a_F\left[1-\left[1+\left((1-x)^{1-n}-1\right)\exp\left(-(1-n)\times K\times(t-t\_ind_x)\right)\right]^{\frac{1}{1-n}}\right]$$

Influence on a_F

a_F = amount of crystallization in second step
~ equilibrium amount of solid fat

a_F = 6.2*PC1-8.2*FFA-6.8*DG+91

- \+ PC1 (Sat, SatUSat versus U, SatUU)
  matches results found in literature <= lower percentage of triglycerides that are able to crystallize
- \- free fatty acids
- \- diacylglycerols
  matches results found in literature on palm oil

Influence on t_ind_x

= induction time of second step
~ induction time for polymorphic transition
BUT also growth rate (reverse influence as on K)

Influence on t_ind_x

t_ind_x = -0.2*PC1-0.06*PC3+0.006*P+0.17*FFA+0.17*DG-0.02

- \- PC1 (Sat, SatUSat versus U, SatUU)
- \+ phosphorus
- \+ free fatty acids
- \- PC3 (SatSatSat)
- \+ diacylglycerols
- P, FFA + DG are known to retard polymorphic transition

Influence on K

= rate constant

K = -1.3*FFA-2.2*DG-0.02*PO-3.8*UM-0.007*S-0.47*PC2+0.28*PC1+11

- \- diacylglycerols
  creation irregularities in packing
- \- soap
  influence known in chocolate industry

Influence on K

K = -1.3*FFA-2.2*DG-0.02*PO-3.8*UM-0.007*S-0.47*PC2+0.28*PC1+11

- free fatty acids
- \- PC2 (PPP, MOP, P versus PLP, PLS, SLS + OOO)
- \+ PC1 (Sat, SatUSat versus U, SatUU)
  only crystallization parameter for which not most important influence
  <= interference of extra oleate chain with molecular packing of mono-unsaturated triglycerides

Influence on n

= order of reverse reaction

reverse reaction ~ local remelting, redissolving of crystals or combination

order ~ how long reverse reaction effects crystallization process: higher n, shorter influence

Influence on n

n = 0.9*PC1+7.3*UM-0.4*Fe-0.39*DG+0.17*PO+0.02*P+1.9

- \+ PC1 (Sat, SatUSat versus U, SatUU)
  higher value => higher melting point => less effect of re-melting => higher n
- \- iron
- \+ unsaponifiable matter
- \+ peroxide value
- \+ phosphorus
- \- diacylglycerols
  promote nucleation => larger number of smaller crystals => redissolving promoted => lower n

Importance minor components

Not only triglyceride composition important for judging physical properties of cocoa butter

E.g. two butters A and B

a_F higher for butter A

Although

CB A higher amount di-unsaturated triacylglycerols

But

CB B higher amounts of diacylglycerols and free fatty acids; decreasing for final amount of solid fat

=> importance minor components

Take home message

- Most important chemical characteristic with influence in crystallization: ratio saturated versus unsaturated and mono-unsaturated versus di-unsaturated (except K)
- Physical properties cannot be judged only based on triacylglycerol composition
- most important minor components: free fatty acids and diacylglycerols: negative influence on equilibrium amount of solid fat, growth rate and polymorphic transition
- Other: phospholipids + traces of soap

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- FWO-Vlaanderen
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FRACTIONATION -
status and future prospects in a low-trans world

A two day conference (22-23 November) organised by the SCI Oils and Fats Group and Ghent University in Gent, Belgium

http://www.soci.org/SCI/events/details.jsp?eventID=EV672