International Symposium on Cocoa Research

2022 International Symposium on Cocoa,

Decoding the Fine Flavour Properties of Dark Chocolates

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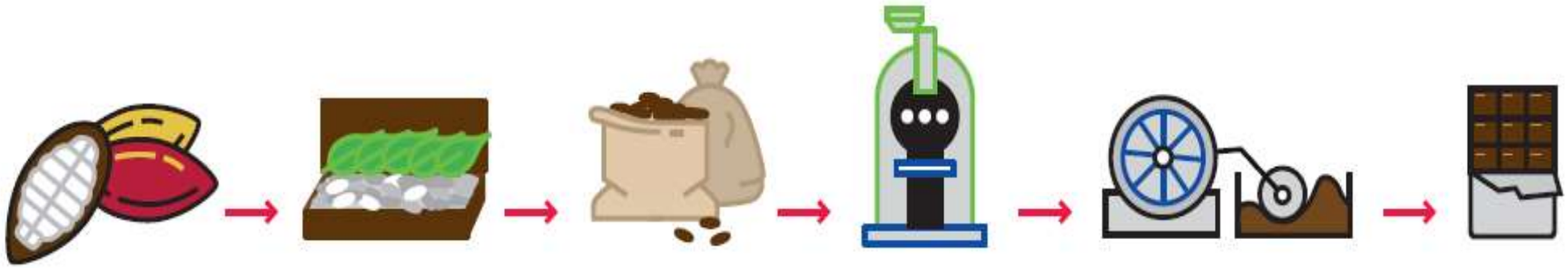
Leibniz-Institute for Food Systems Biology at the Technical University of Munich

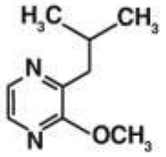
Cocoa and chocolate key odorants

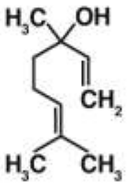
Aroma development along the processing chain

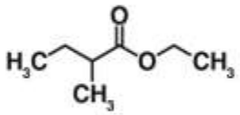


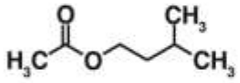
Harvest → Fermentation → Drying/ Transportation → Roasting → Conching → Final Product

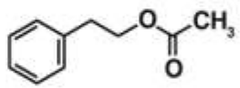
Cocoa and chocolate key odorants

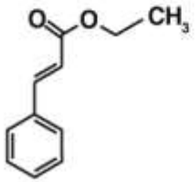

bell pepper-like

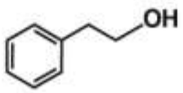

bergamot-like

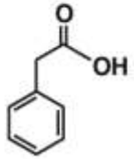

fruity

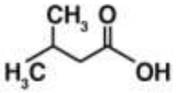

banana-like

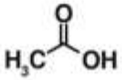

dried fruits, flowery

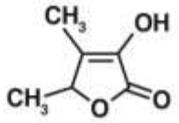

cinnamon-like

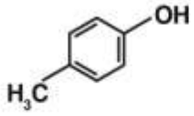

flowery, rose-like

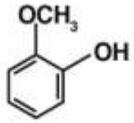

honey, beeswax-like

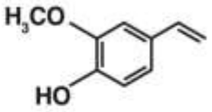

sweaty, cheesy

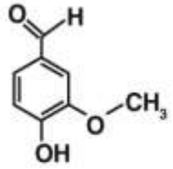

pungent

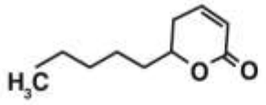

seasoning

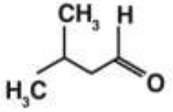

phenolic, horse-like

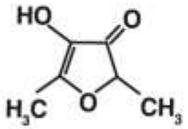

smoky

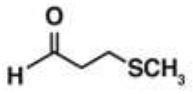

spicy, clove-like

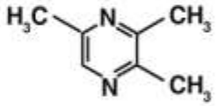

vanilla-like

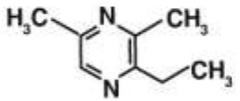

coconut-like


malty, cocoa-like


caramel-like


cooked potato-like


earthy, roasty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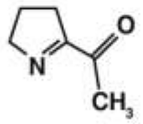
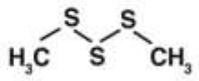
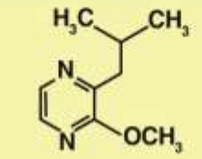
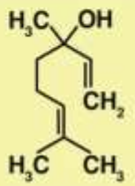

popcorn-like


cabbage-like

Cocoa and chocolate key odorants


bell pepper-like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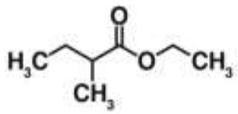
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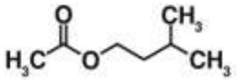
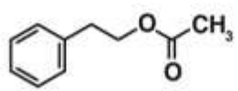
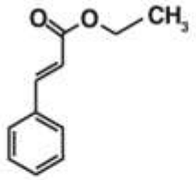
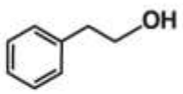
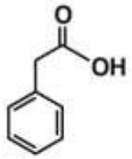

banana-like


dried fruits, flowery


cinnamon-like


flowery, rose-like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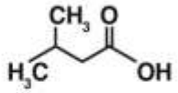
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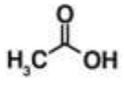
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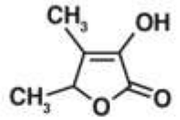
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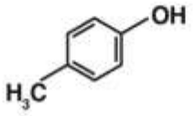
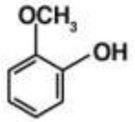
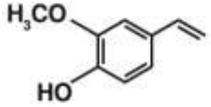

phenolic, horse-like


smoky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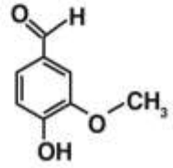
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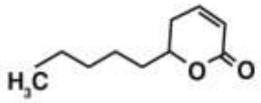
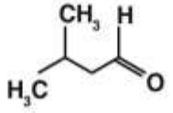
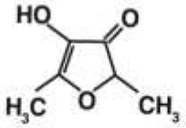
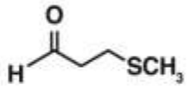
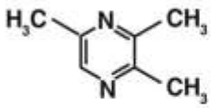
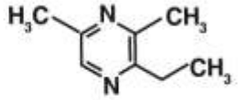

coconut-like

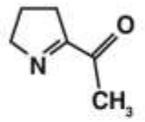

malty, cocoa-like

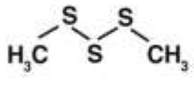

caramel-like


cooked potato-like

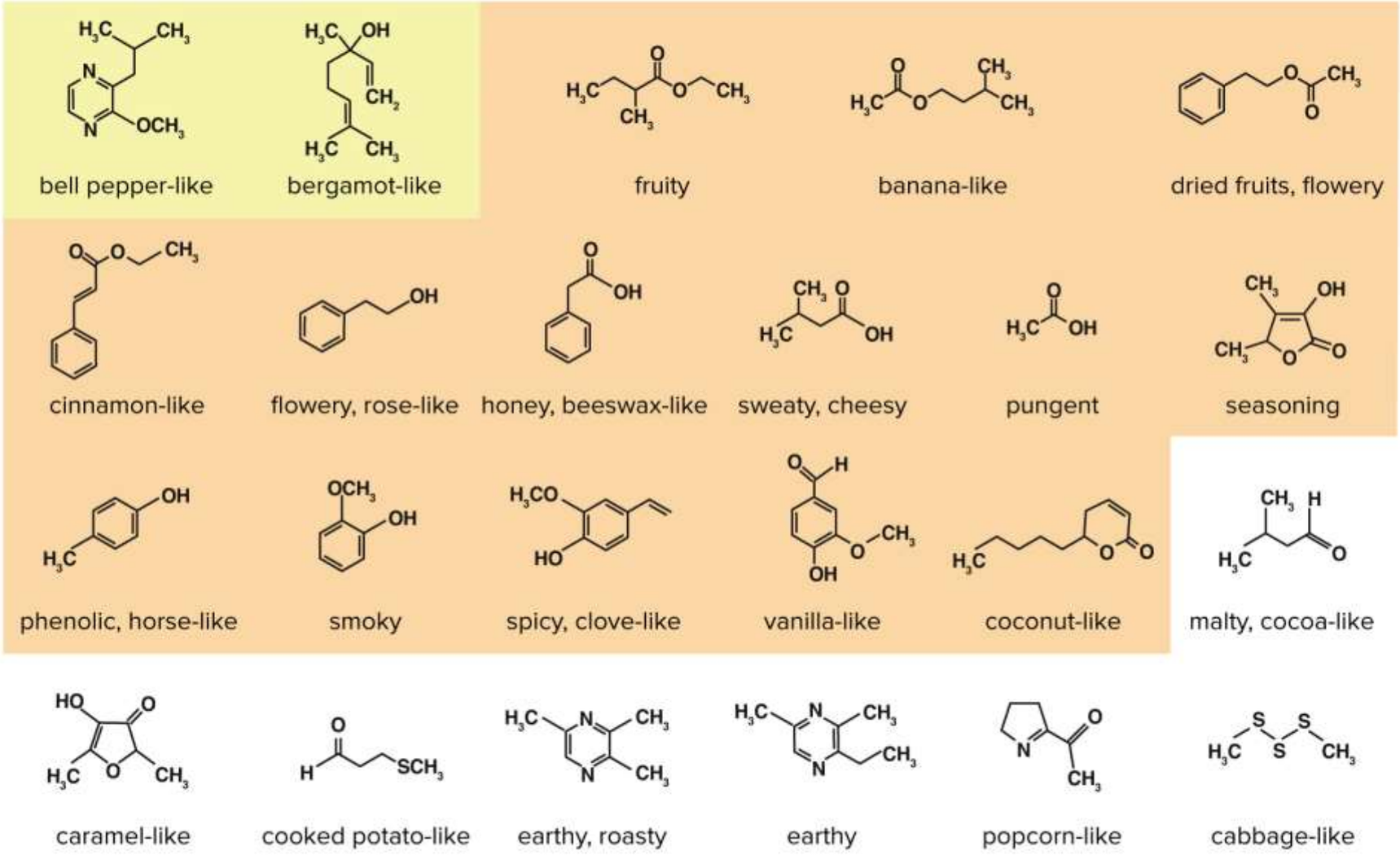

earthy, roasty


earthy

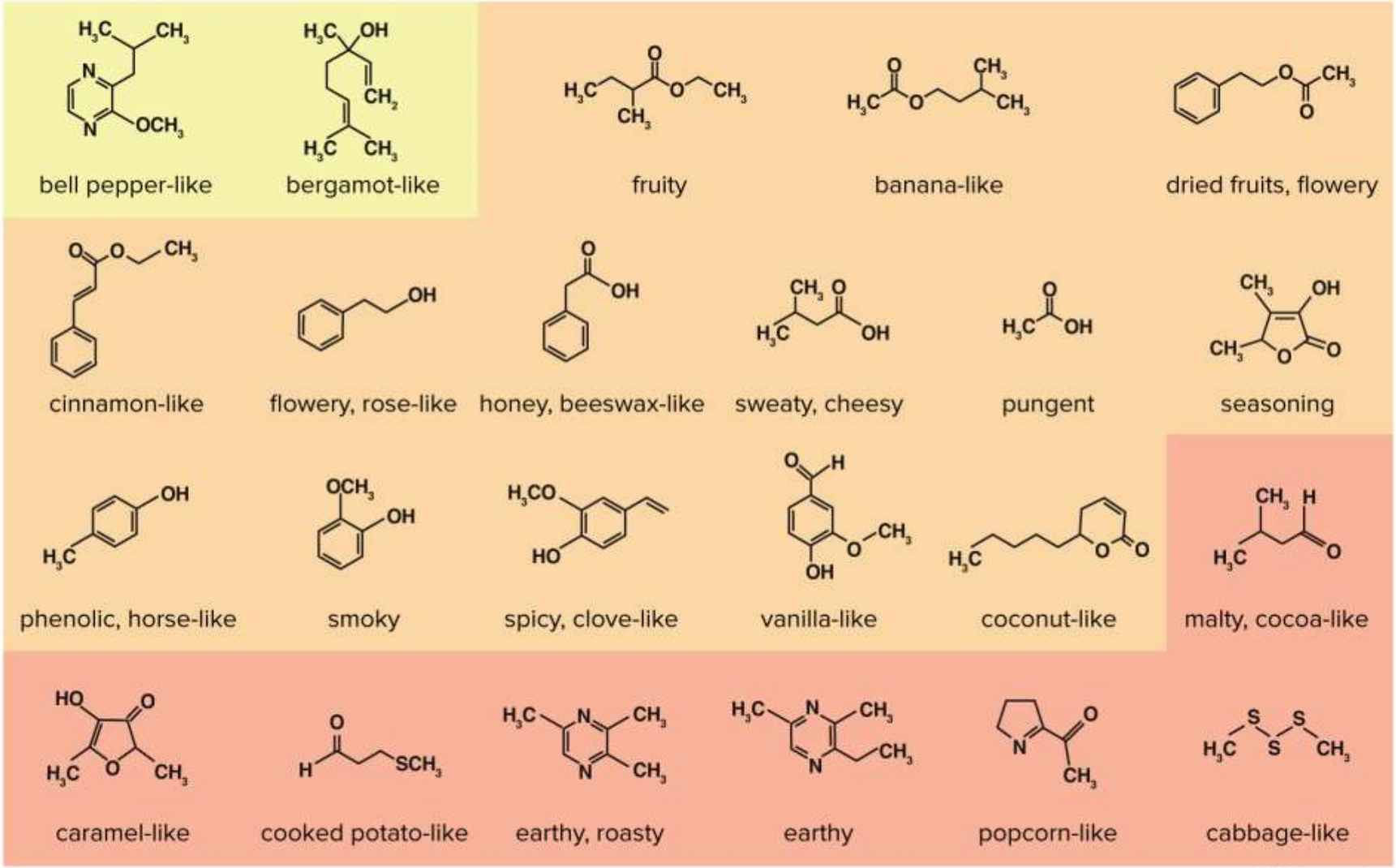

popcorn-like


cabbage-like

Cocoa and chocolate key odorants



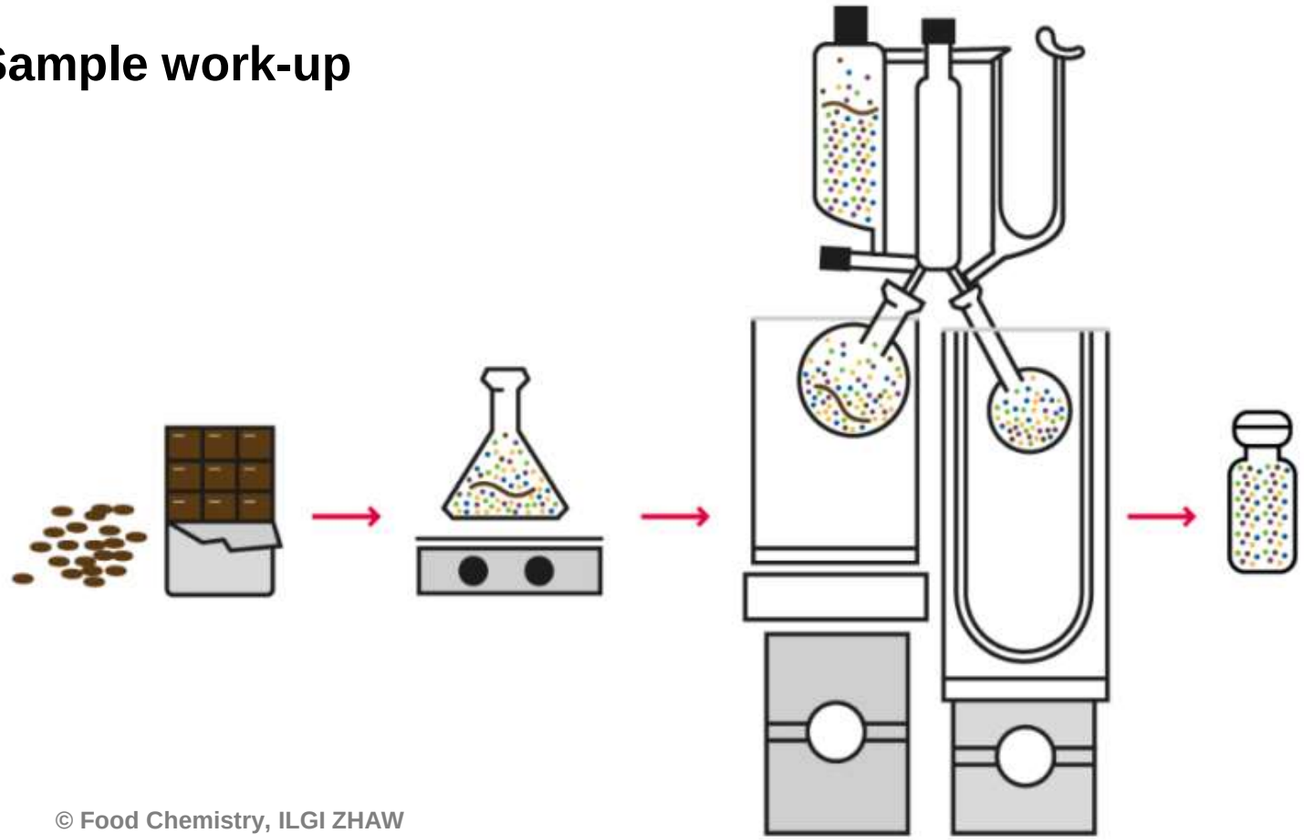
Cocoa and chocolate key odorants



compounds present in unfermented fresh cocoa beans
compounds mostly formed during fermentation
compounds mostly formed during thermal processing

Chocolate Aroma Analysis

Sample work-up

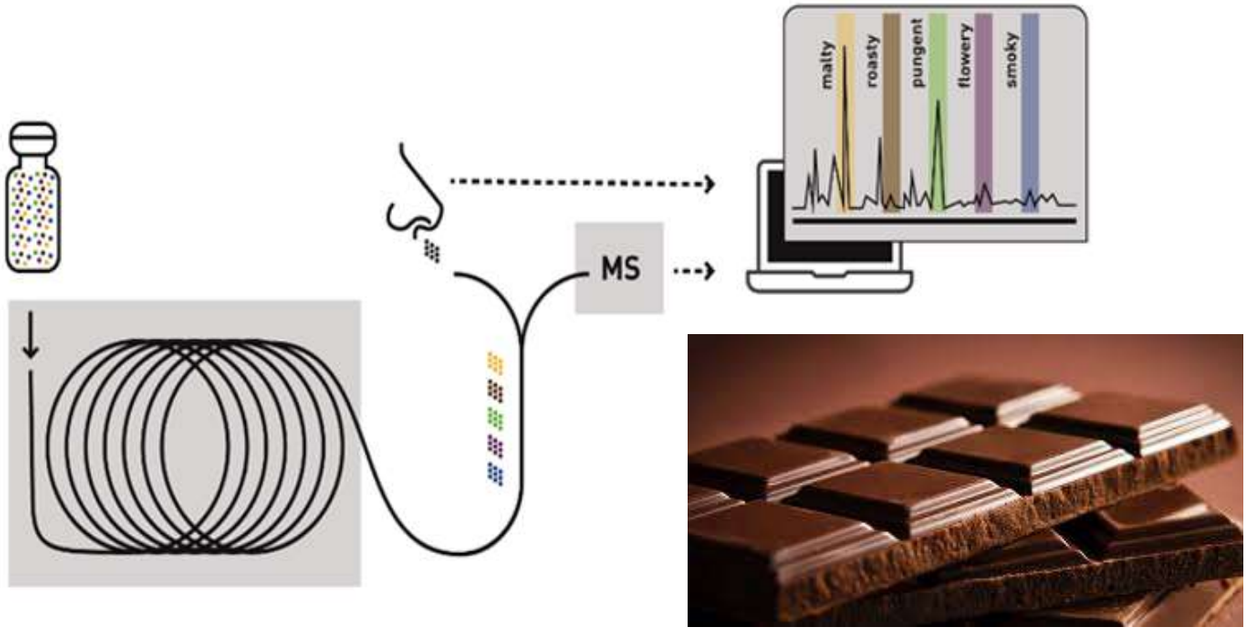


SAFE*

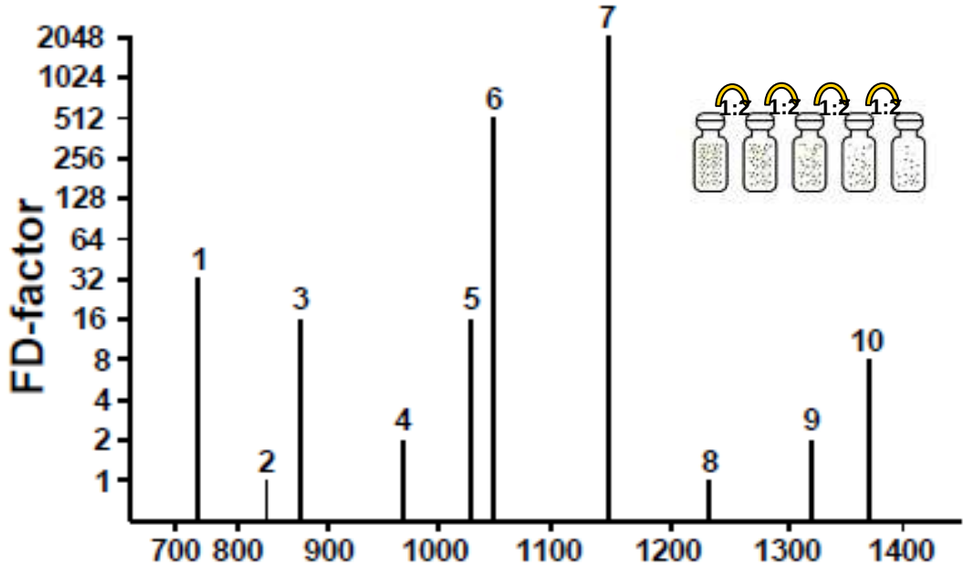
* Engel, W., Bahr, W., & Schieberle, P. Solvent assisted flavour evaporation – a new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices. *European Food Research and Technology* **1999**, *209(3),* 237–241.

Chocolate Aroma Analysis

Identification of odor-active compounds with gas chromatography-olfactometry (GC-O)



Chetschik, I. Key Odorants of Cocoa. *Chimia* **2021**, *75*, 981.

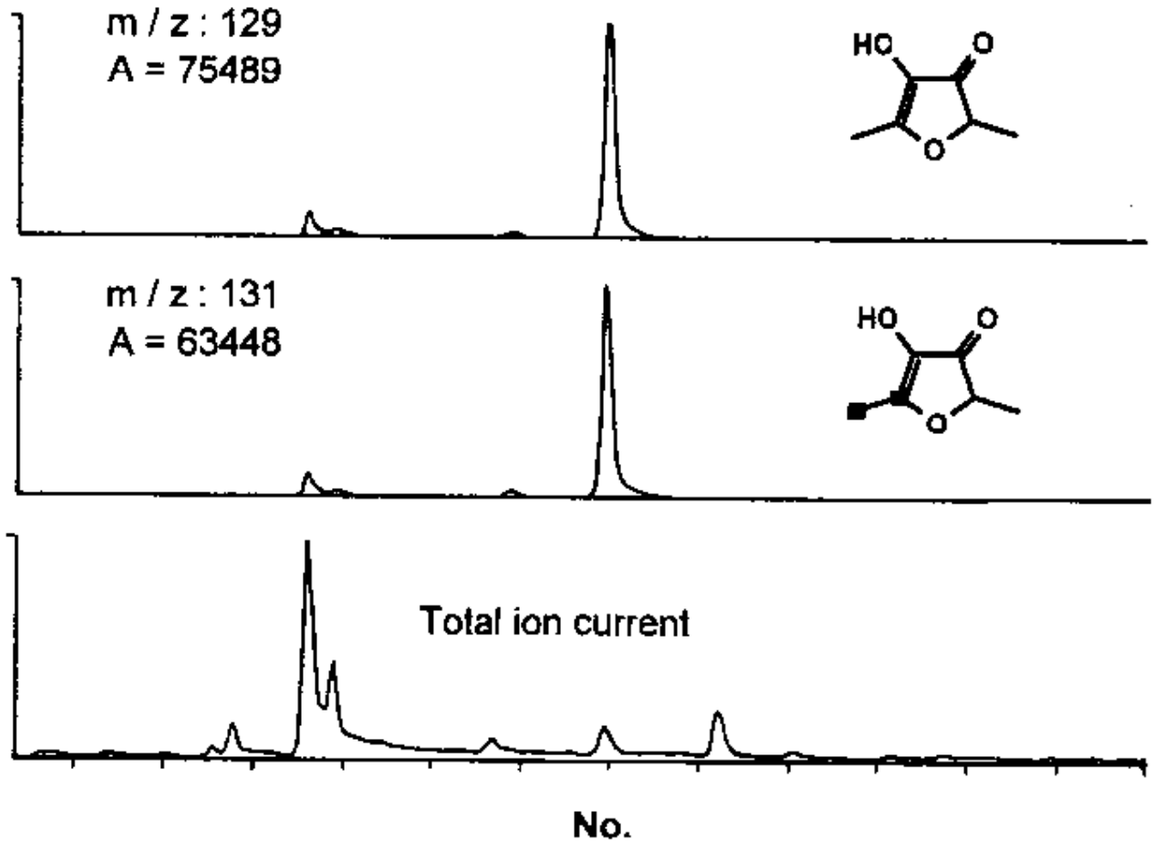


Aroma Extract Dilution Analysis (AEDA)

Source: Steinhaus, PhD-Thesis 2001

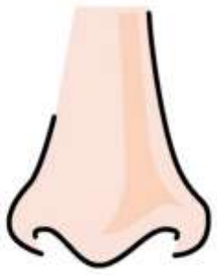
Chocolate Aroma Analysis

Quantification by gas chromatography-mass spectrometry using isotopically substituted odorants



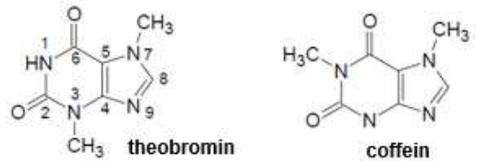
Odor activity value (OAV)/
Dose over threshold factor (DoT factor)
=

$$\frac{\text{concentration}}{\text{odor threshold}}$$



Chocolate Taste

Alkaloids - bitter

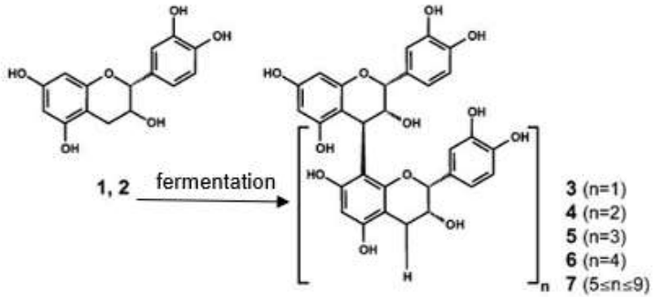


- stimulating compounds
- no significant changes during fermentation & processing
- ratio theobromine/coffeine for differentiation between Forastero/Criollo varieties

Organic acids - sour

- citric acid is already present in unfermented cocoa beans
- lactic acid and acetic acids as fermentation products
- acetic acid can be removed by thermal processing

Polyphenols – bitter/adstringent



epicatechin
«bitter, rough adstrigent»

proanthocyanidine
«adstringent»

- antioxidative properties → health beneficial effects

Diketopiperazines (DKPs) - bitter

27-34

R: residue of Gly, L-Ala, L-Val, L-Ile, L-Leu, L-Phe, L-Tyr, L-Thr

35-50

R_1: residue of L-Ala, L-Val, L-Leu, L-Phe
R_2: residue of Gly, L-Val, L-Ile, L-Leu, L-Phe, L-Tyr, L-Ser, L-Asn, L-Asp

- formed mostly during roasting
- synergistical effect on bitterness with coffein

Dose over threshold factor (DoT factor)

=

$$\frac{\text{concentration}}{\text{taste threshold}}$$

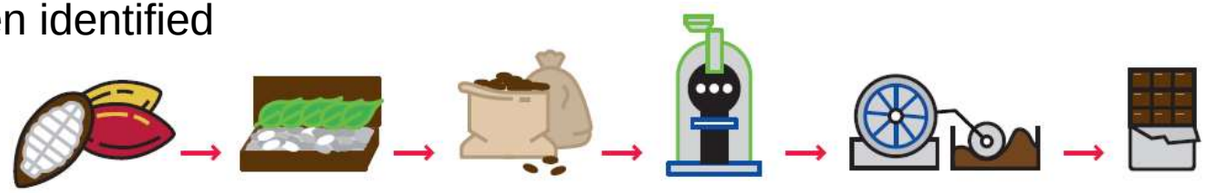
Cocoa key tastants according Stark et al, 2005 *(figure ZHAW Research Group Food Chemistry)*

Perspectives of Cocoa Flavour Research

In the past:

Flavour research mostly done on intermediates/products produced in big industrial scale (no defined origin/variety)

- Key compounds of cocoa/chocolate flavour have been identified
- Focus: Effect of technological processing on flavour



Today:

- More and more consumers demand flavourful, fairly traded, sustainable and traceable products
- The scene of small batch producers is growing

  → awareness for a broad range of different cocoa flavours

Perspectives of Cocoa Flavour Research

Today:

Flavour diversity of cocoa and chocolate described on sensory level

- products of defined variety/origin show different flavour properties than products produced in an industrial scale

- Such products have not been studied comprehensively with the methods of the molecular science
- **The molecular background of fine flavour properties like fruity, cocoa-like and floral is not fully understood yet**

Origin	Cocoa type	Duration (days)	Special flavor character
Ecuador	Nacional (Arriba)	2 Short	Aromatic, floral, spicy, green
Ecuador	Criollo (CCN51)	2	Acidic, harsh, low cocoa
Ceylon	Trinitario	1.5	Floral, fruity, acidic
Venezuela	Trinitario	2	Low cocoa, acidic
Venezuela	Criollo	2	fruity, nutty
Zanzibar	Criollo	6 Medium	Floral, fruity
Venezuela	Forastero	5	Fruity, raisin, caramel
Ghana	Forastero	5	Strong basic cocoa, fruity notes
Malaysia	Forastero/Trinitario	6	Acidic, phenolic
Trinidad	Trinitario	7–8 Long	Winy, raisin, molasses
Grenada	Trinitario	8–10	Acidic, fruity, molasses
Congo	Criollo/Forastero	7–10	Acidic, strong cocoa
Papua New Guinea	Trinitario	7–8	Fruity, acidic

Afoakwa et al, Flavor Formation and Character in Cocoa and Chocolate: A Critical Review, Critical Reviews in Food Science and Nutrition, **2008**, *48:9*, 840-857

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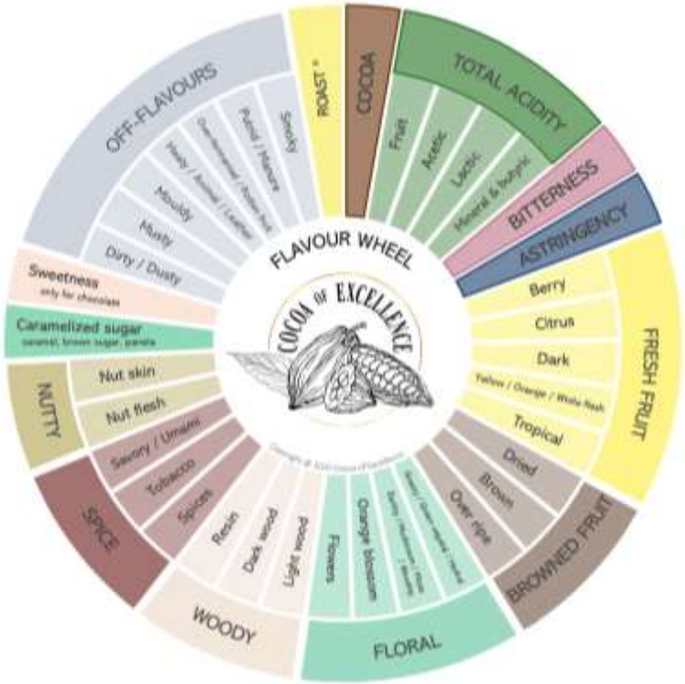
Sensory References

sensory reference samples

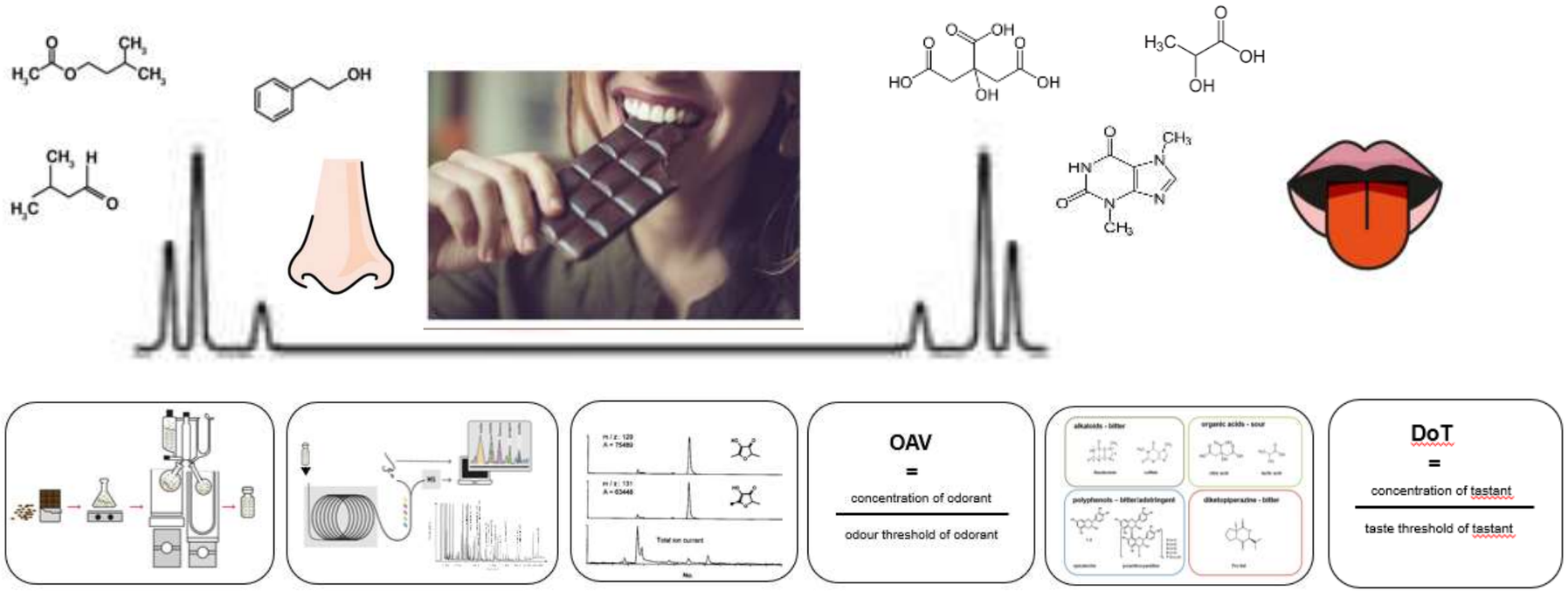
- samples with distinct flavour attributes
- essential for the global standardisation of sensory assessments of cocoa and chocolate
- from *Cocoa of Excellence*
- chocolates produced out of reference liquors (75% cocoa mass, 25% sugar)



sample code	cocoa variety	cocoa bean origin	reference attributes
Ref1	Forastero	Ghana	cocoa, roast degree
Ref2	Criollo	Mexico	fruity (fresh fruit, browned fruit), acidic
Ref3	Trinitario	Dominican Republic	fruity (fresh fruit, browned fruit), acidic
Ref4	Trinitario	Madagascar	fruity (fresh fruit), acidic
Ref5	Nacional	Ecuador	floral, bitter, astringent
Ref6	Forastero	Ivory Coast	cocoa, roast degree

Aim of the Investigation

- Decoding the fine flavour properties of chocolates produced of reference liquors deriving from the *Cocoa of Excellence* Program
- Better understanding the fine flavour attributes for the future development of standardised training samples for sensory panels

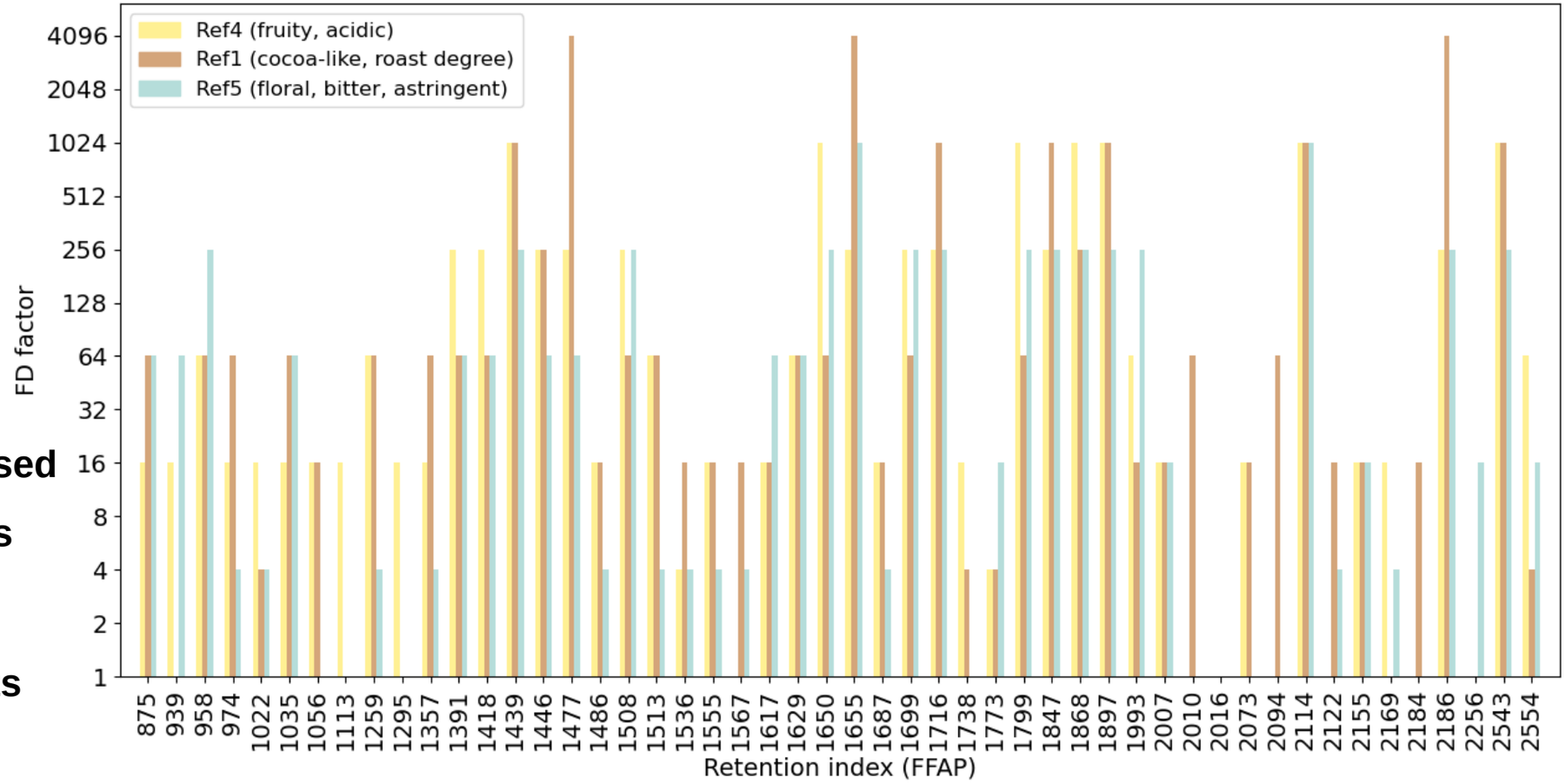


Results – GC-O Analysis

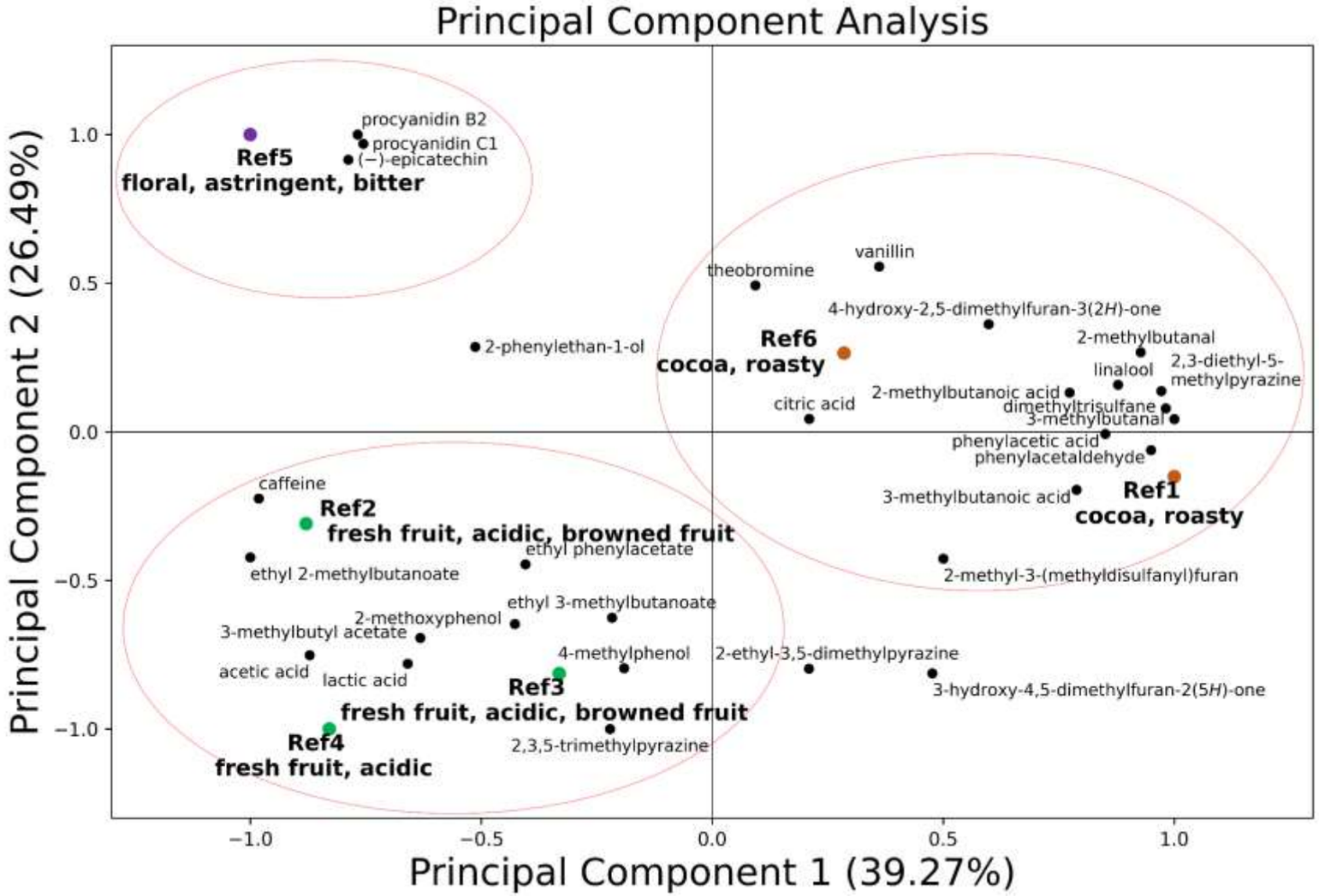
GC-O analysis (AEDA)

- 47 odor-active compounds were identified
- all were known cocoa and chocolate odorants

- **the distinct fine flavour properties have to be caused by quantitative differences of known key odorants**
- **quantitation of 27 odorants and 8 tastants**



Results - PCA



Dose over threshold factor (DoT factor)

$$= \frac{\text{concentration}}{\text{odor/taste threshold}}$$

Ullrich, L.; Casty, B.; André, A.; Hühn, T.; Steinhaus, M.; Chetschik, I. Decoding the Fine Flavor Properties of Dark Chocolates. J. Agric. Food Chem. **2022**, *70*, 13730–13740.

Results - Decoding the Fine Flavor Properties of Dark Chocolates

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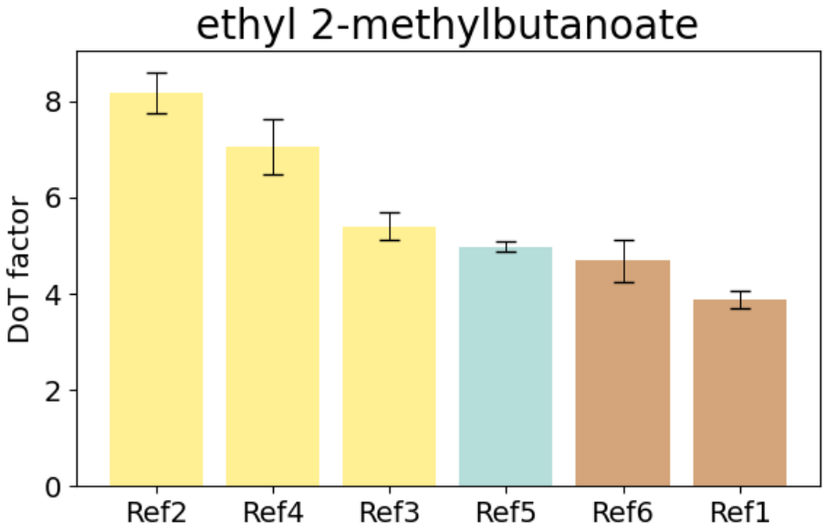

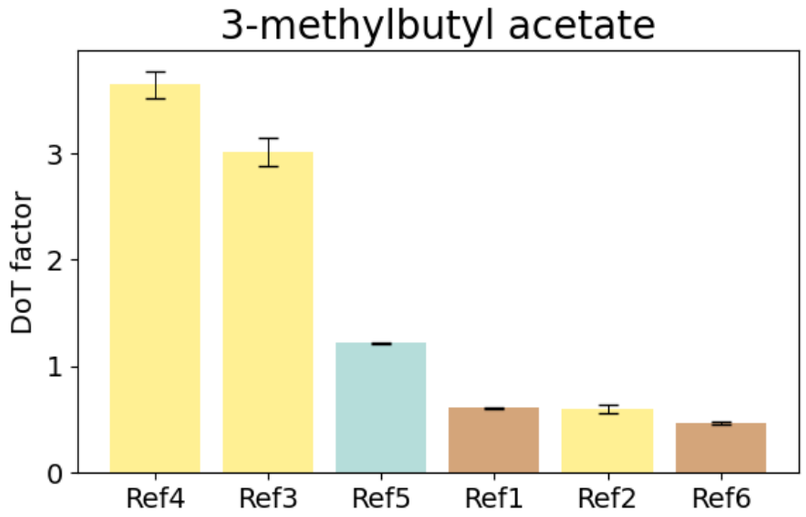

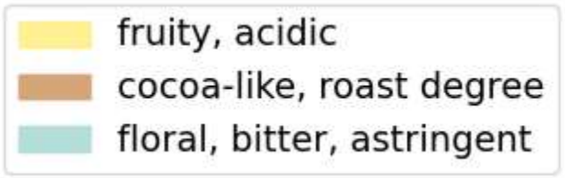

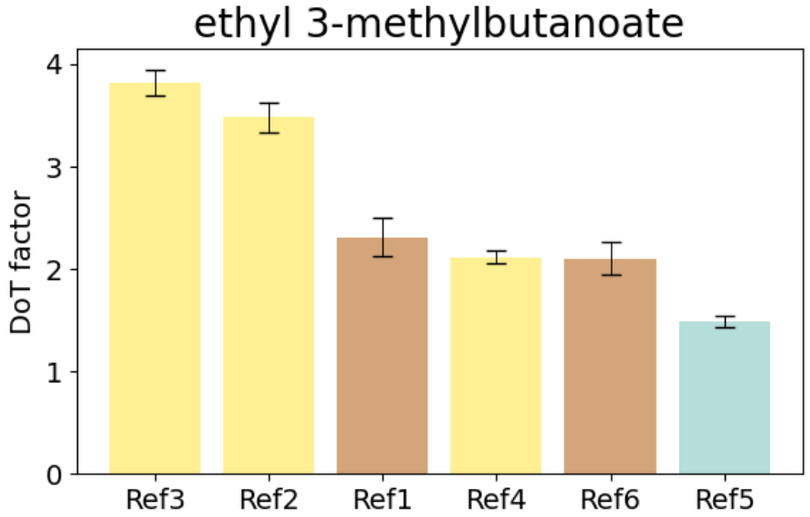

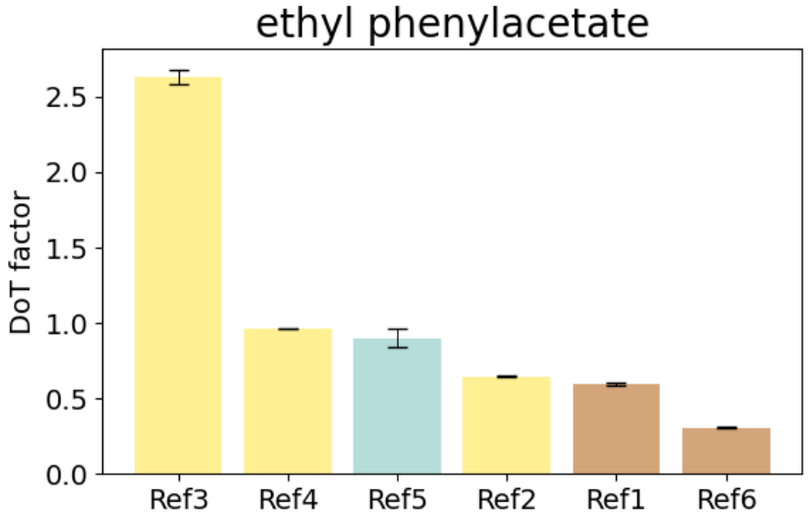

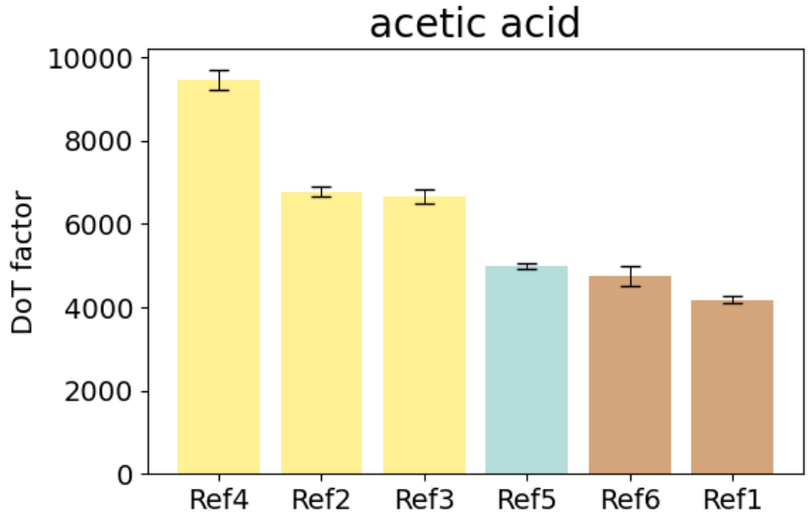

Results - Decoding the Fine Flavor Properties of Dark Chocolates

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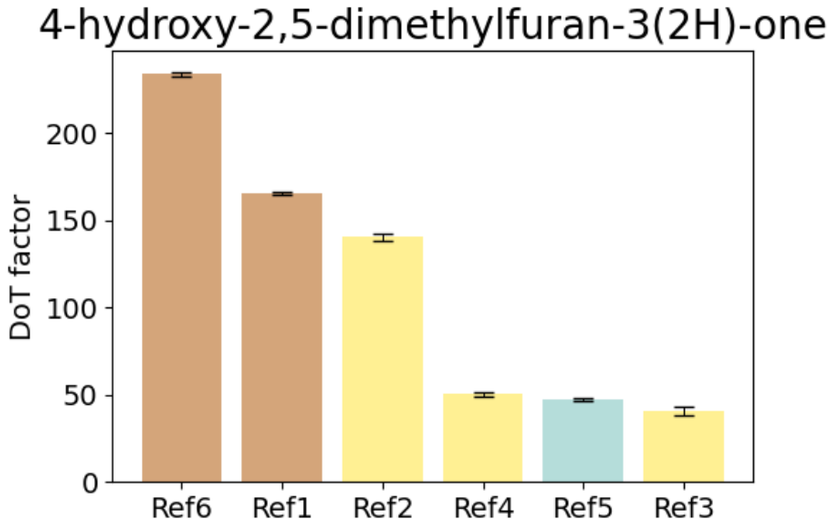
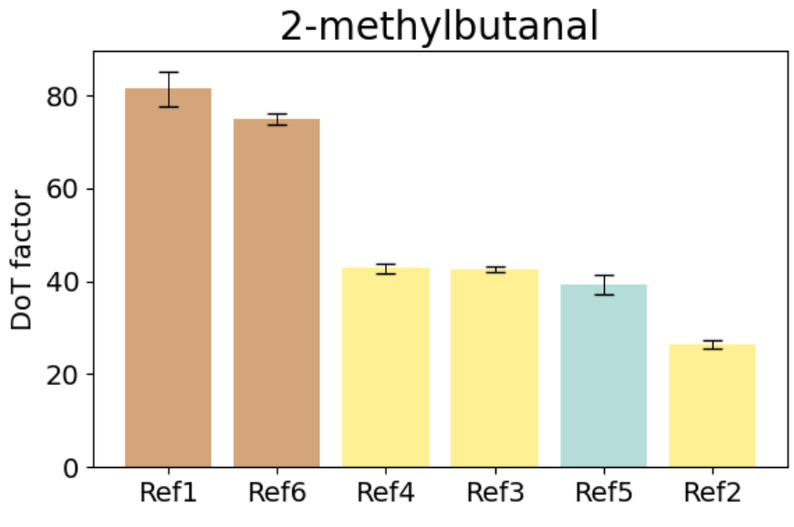
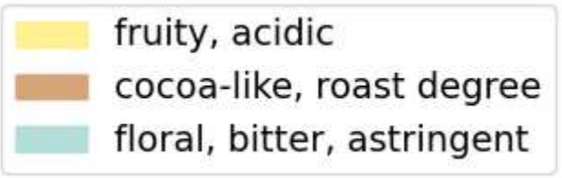
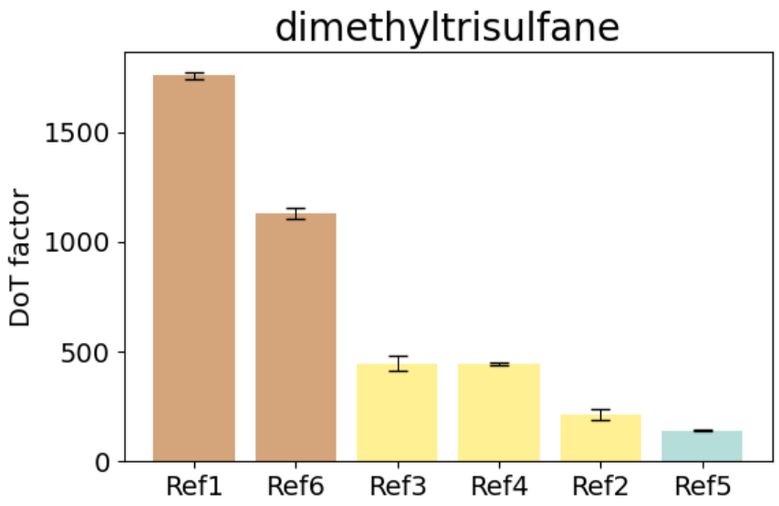
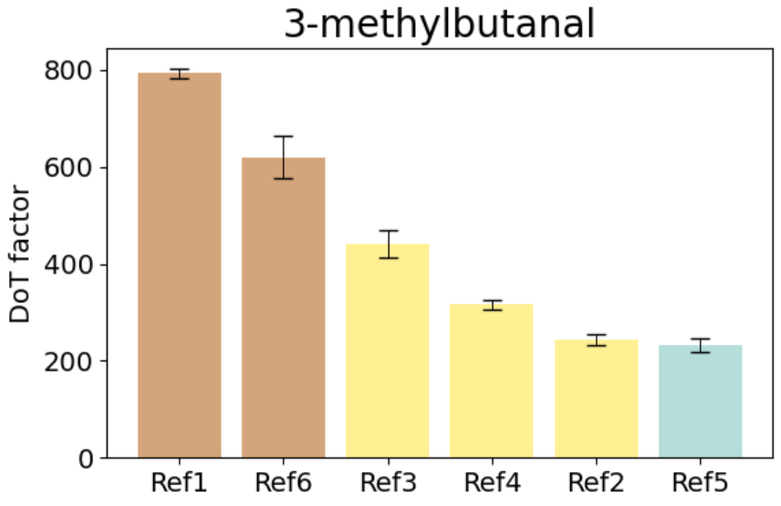
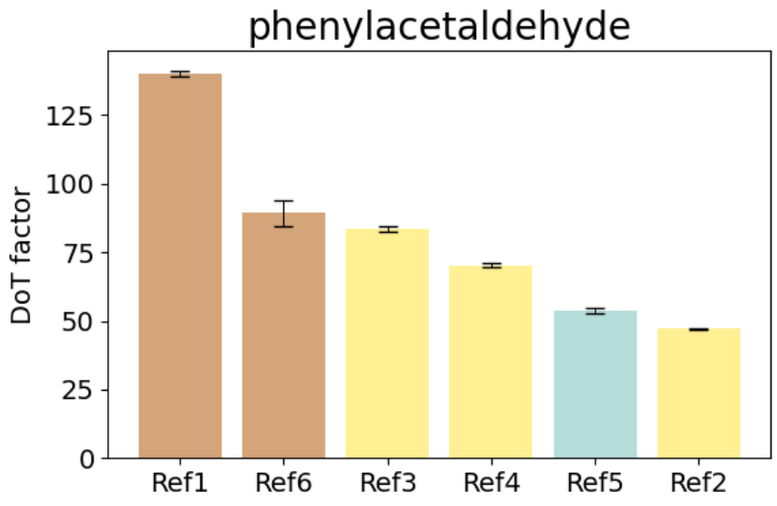




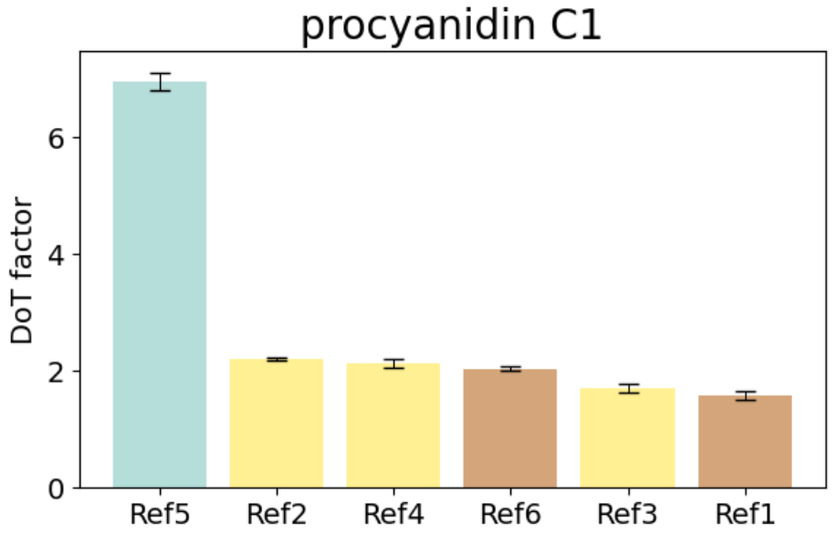


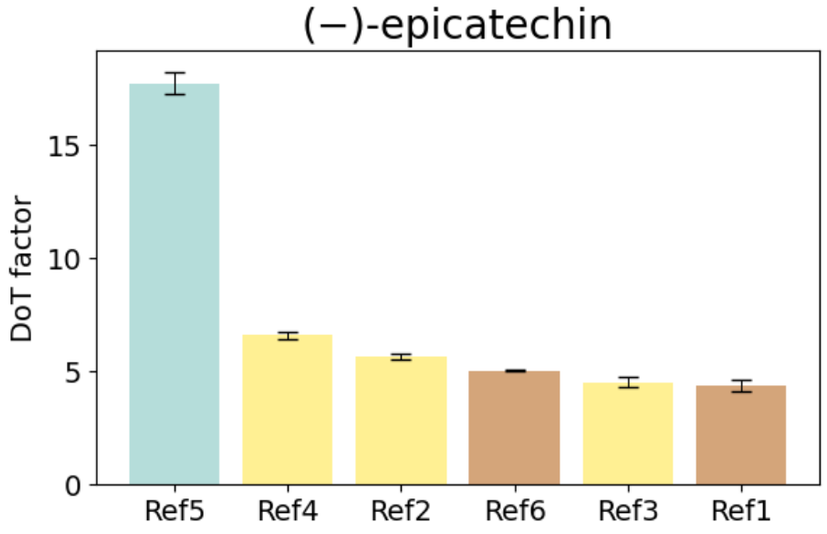


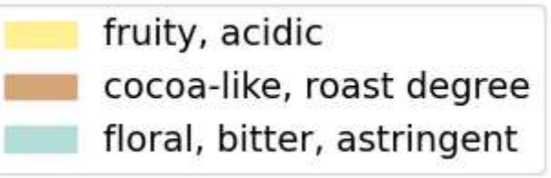


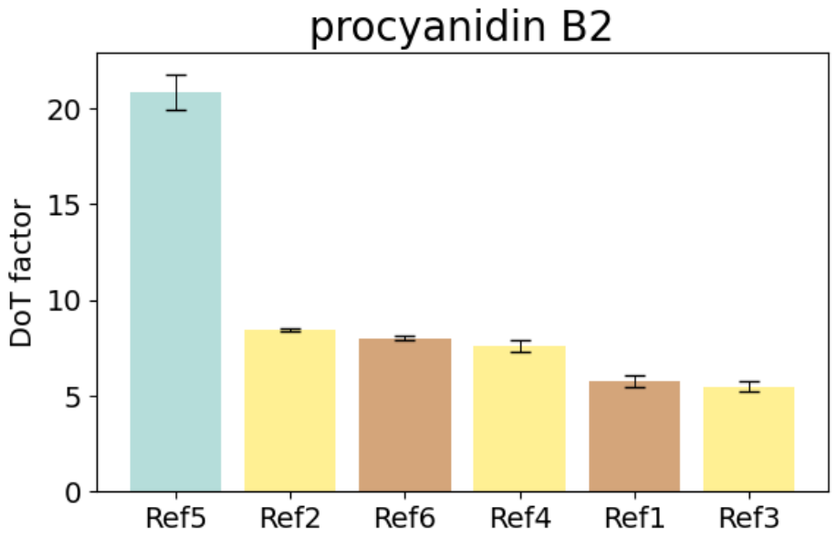


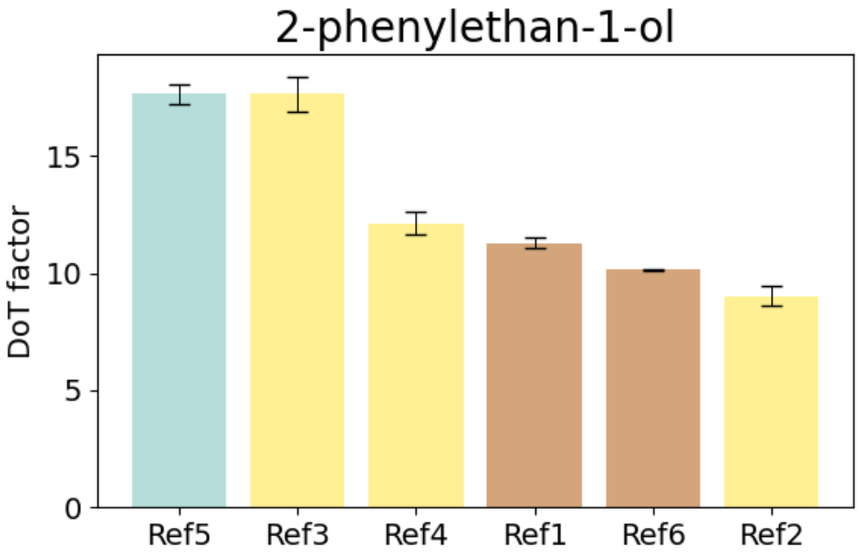
Results - Decoding the Fine Flavor Properties of Dark Chocolates











Results - Decoding the Fine Flavor Properties of Dark Chocolates – Summary

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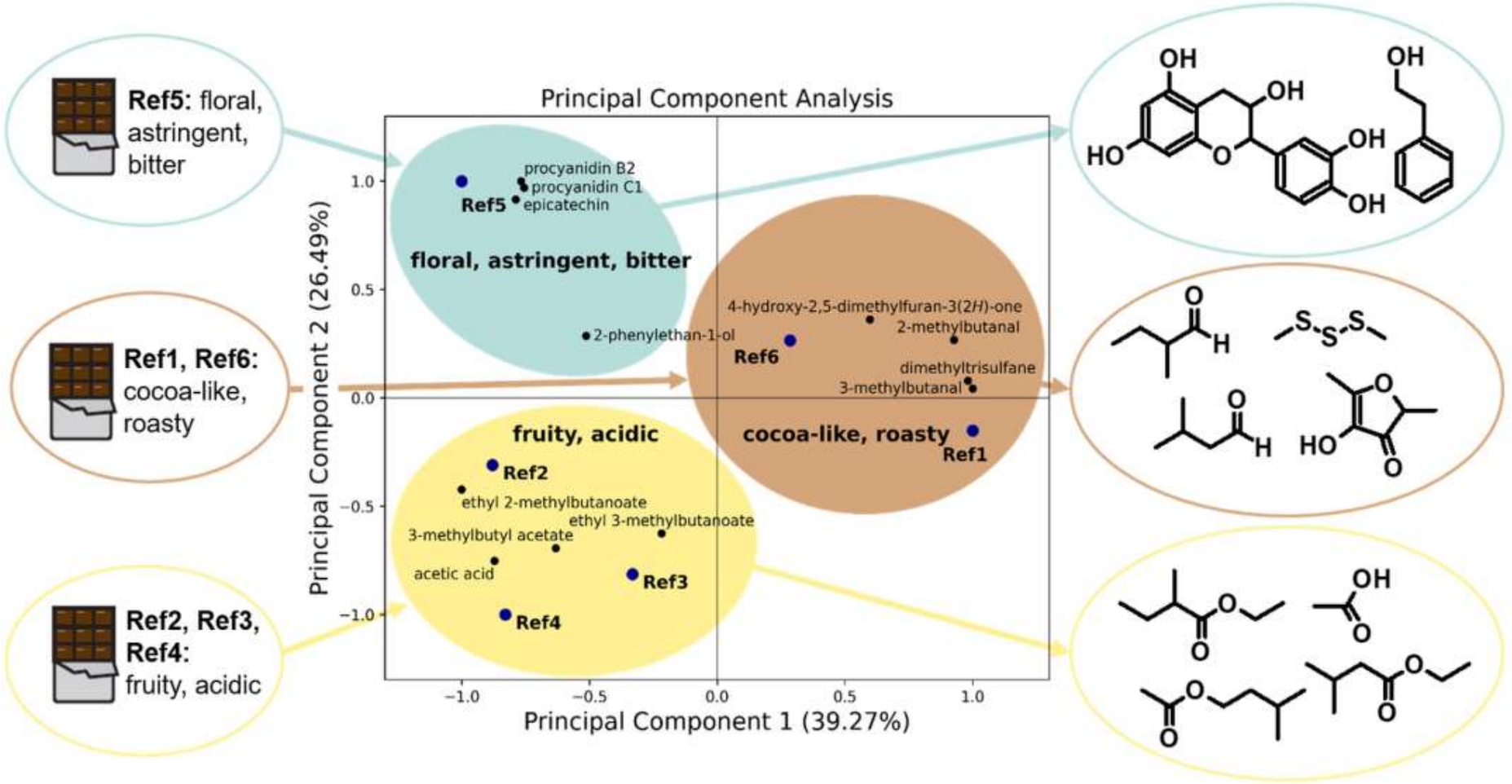

2-phenylethan-1-ol

polyphenols

2- & 3-methylbutanal

4-hydroxy-2,5-dimethylfuran-3(2*H*)-one

dimethyltrisulfane

ethyl 2-methylbutanoate

ethyl 3-methylbutanoate

3-methylbutyl acetate

acetic acid

Results - Decoding the Fine Flavor Properties of Dark Chocolates – Outlook

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Understanding the fine flavour attributes is important for

- the development of standardised training samples for sensory evaluation of cocoa products and the future quality assessment of cocoa and chocolate
- understand the diversity of chocolate flavours and further research of fine flavour cocoa products e.g. single-variety small batch chocolates
- finding objective indicators for fine or flavour cocoa
- the biodiversity of cocoa, fair cocoa farming and sustainability of cocoa




Thank you for listening!

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