TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

Genuine Manuka Honey!?

Nicole Beitlich

Prof. Dr. K. Speer
Food Chemistry

Technische Universität Dresden, Germany

Manuka honey *(Leptospermum scoparium)*

'Healing honey'

- Antioxidant (Inoue et al. 2005)
- Antiinflammatory (Leong et al. 2011)
- Immunostimulatory (Tonks et al. 2003)
- Antitumor potential (Fernandez-Cabezudo et al. 2013)
- Antiulcer and wound healing (Doerler et al. 2012)
- Antibiotic, antiviral & antibacterial (Adams et al. 2008, Mavric et al. 2008)

Non-peroxide antibacterial activity (= NPA)

dihydroxyacetone → methylglyoxal (MGO)

Adams et al. (2008) *Carbohyd. Res.* 343, 651659; Doerler et al. (2012) *J. Dtsch. Dermatol. Ges.* 10, 624-632; Fernandez-Cabezudo (2013) *Plos One*. 8, e55993; Inoue et al. (2005) *J. Sci. Food Agric.* 85, 872-878; Leong et al. (2011) *J. L. Innate Immun.* 18, 459-466; Mavric et al. (2008) *Mol. Nutr. Food Res*. 52, 483-489; Tonks et al. (2003) *Cytokine*. 21, 242-247

Manuka honey *(Leptospermum scoparium)*

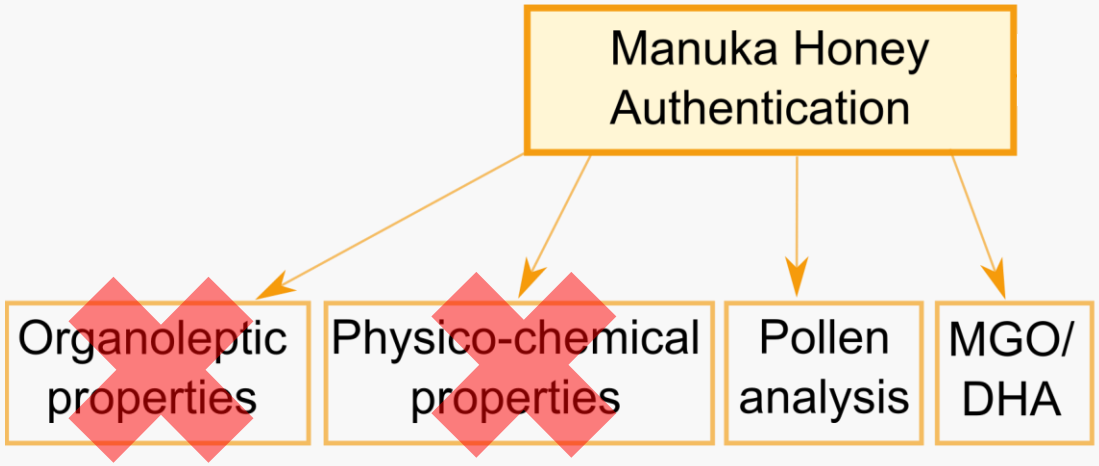
'Healing honey'

- Very expensive honey
- Production: 1.700 t
- Sale: 10.000 t

→ **Fraud ?!**

Adams et al. (2008) *Carbohyd. Res.* 343, 651659; Doerler et al. (2012) *J. Dtsch. Dermatol. Ges.* 10, 624-632; Fernandez-Cabezudo (2013) *Plos One*. 8, e55993; Inoue et al. (2005) *J. Sci. Food Agric.* 85, 872-878; Leong et al. (2011) *J. L. Innate Immun.* 18, 459-466; Mavric et al. (2008) *Mol. Nutr. Food Res*. 52, 483-489; Tonks et al. (2003) *Cytokine*. 21, 242-247

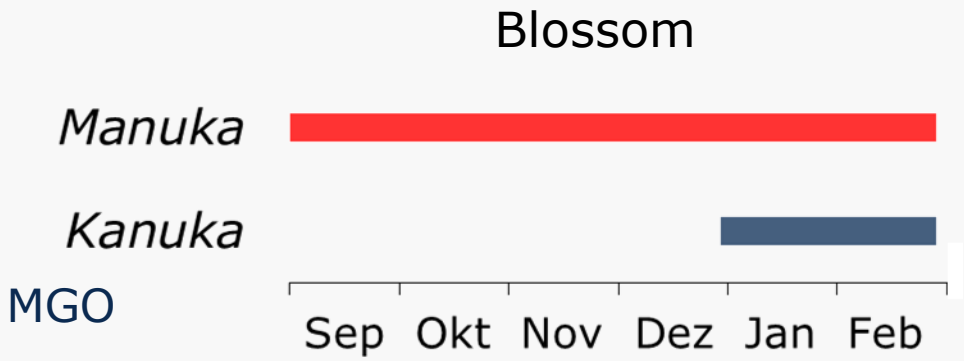
Authentication



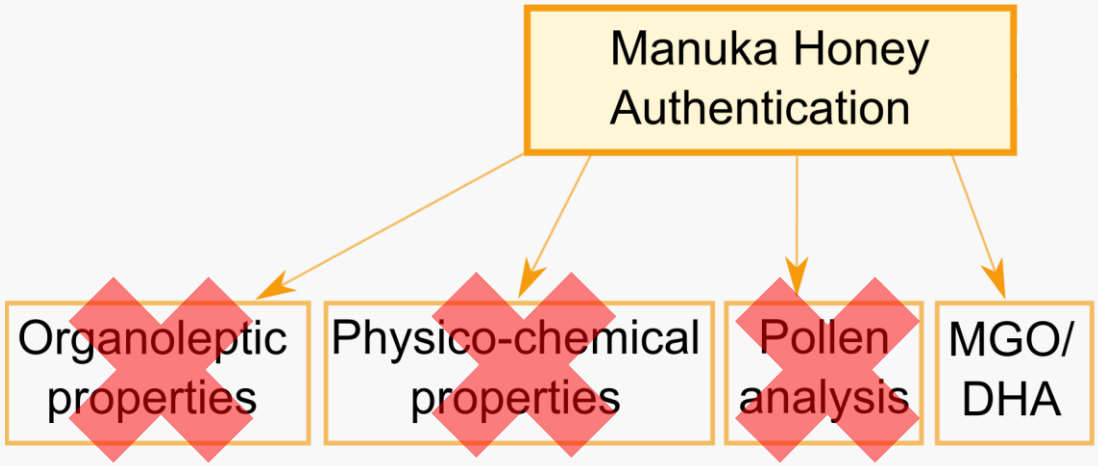
- Identical pollen
- No differentiation possible
- Natural mixing

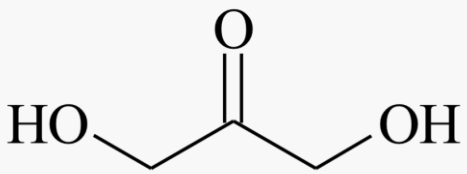
Manuka

Kanuka

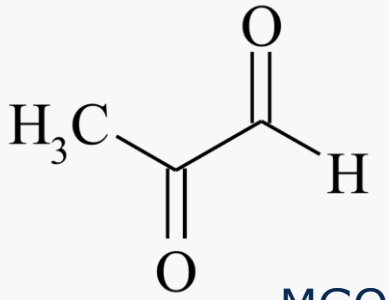


Authentication





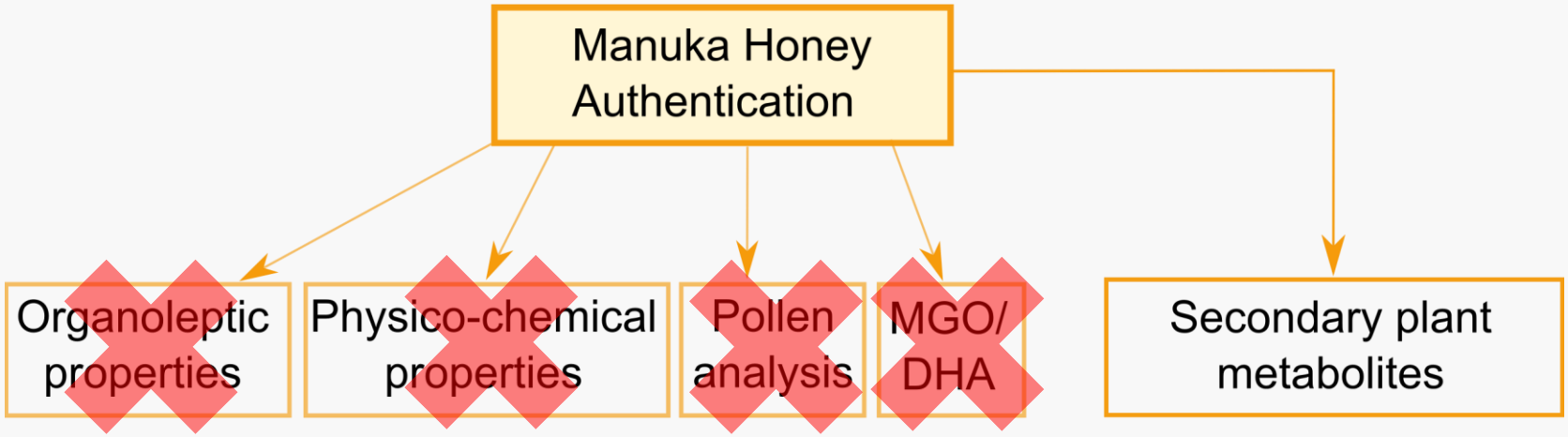
DHA



MGO

- Conversion MGO ⇔ DHA
- Adding MGO and/or DHA

Authentication

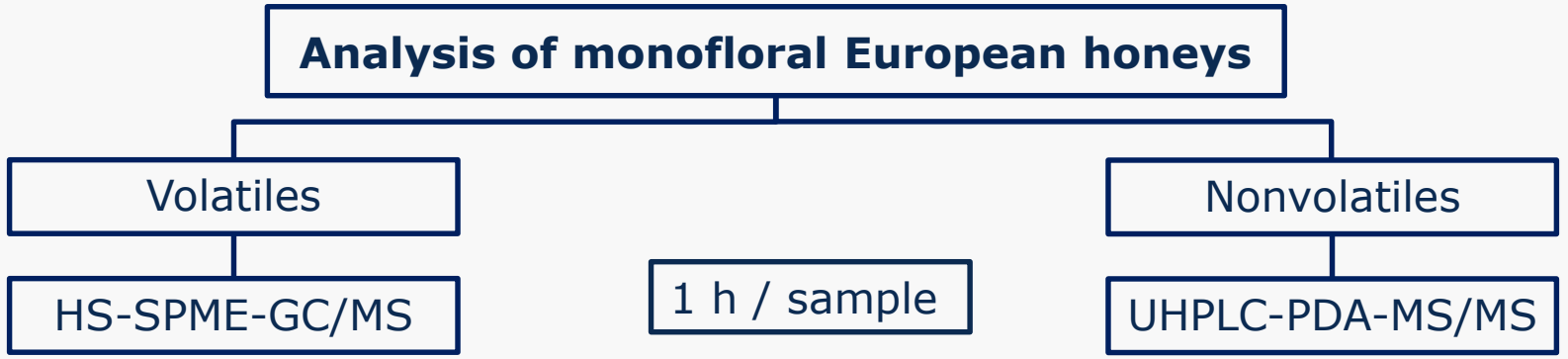


→ **Alternative methods are required**

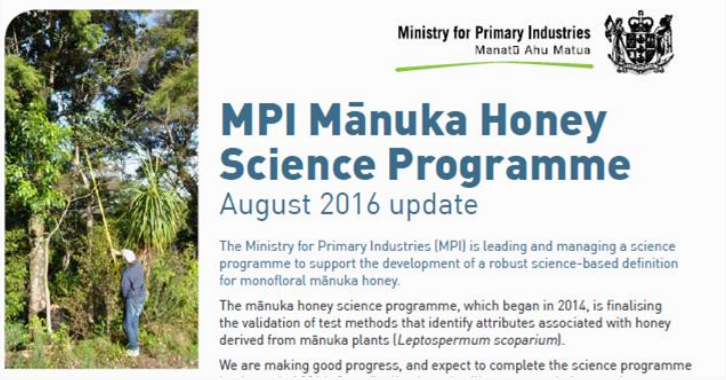
→ **Secondary plant metabolites are promising**

Our working group

- Authentication of 24 European monofloral honeys (sunflower, chestnut, cornflower, …) using secondary plant metabolites



MPI Manuka honey science programme



- Started in 2014
- Will be completed by the end of 2016
- Defined monofloral honeys of varying floral types

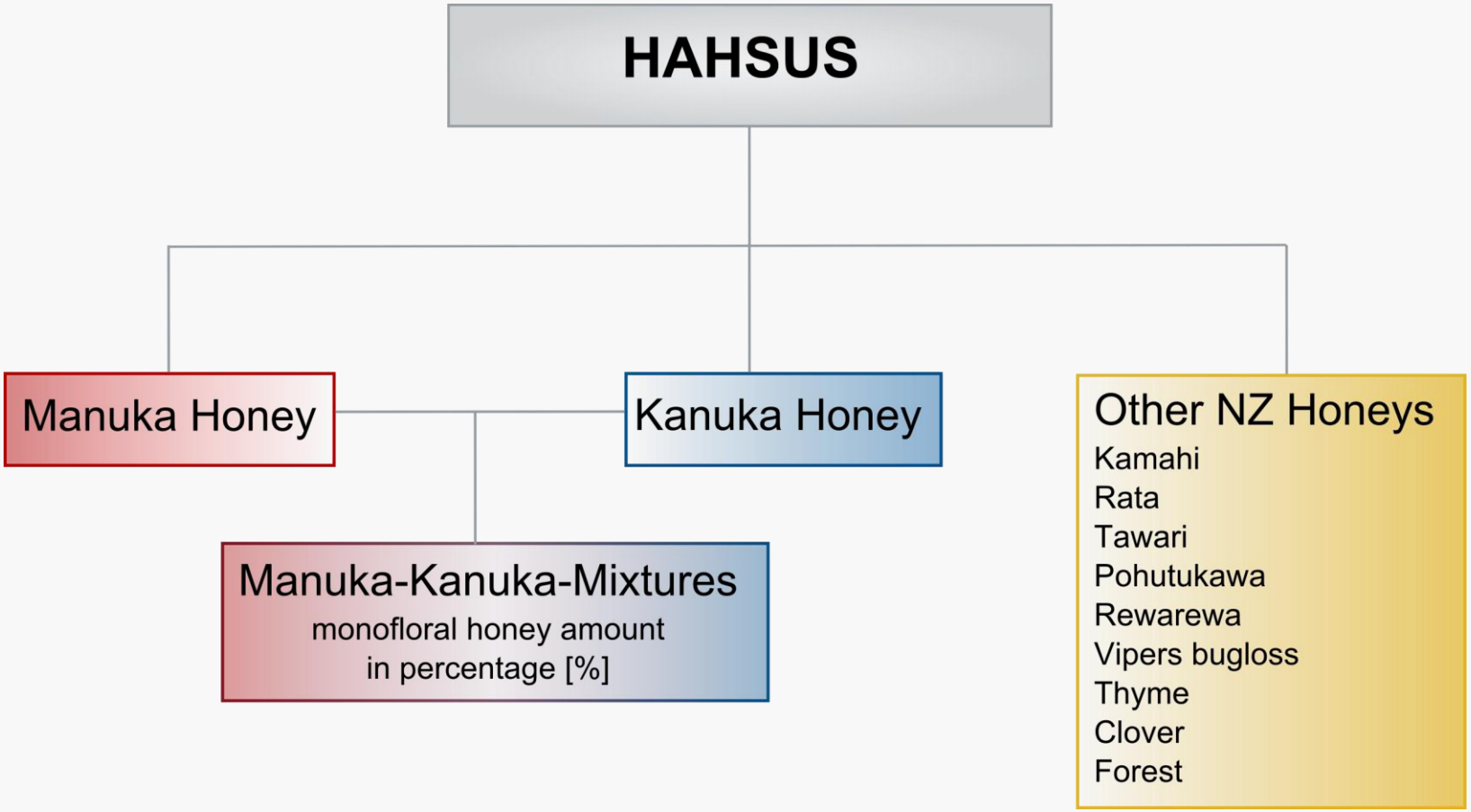
"The Ministry for Primary Industries (MPI) is leading and managing a science programme to support the development of a robust science-based definition for monofloral manuka honey."

"… attributes (chemical and/or DNA) …"

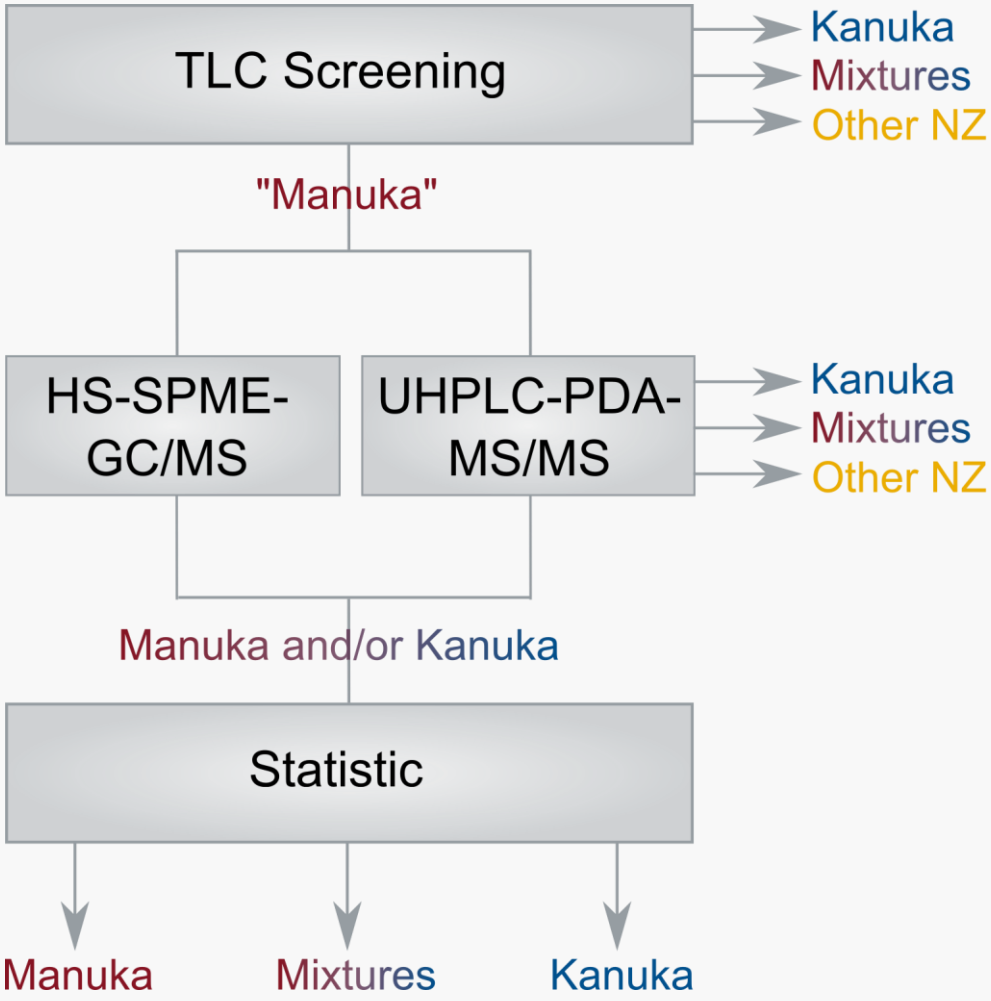
MPI (2016). Manuka honey science programme.

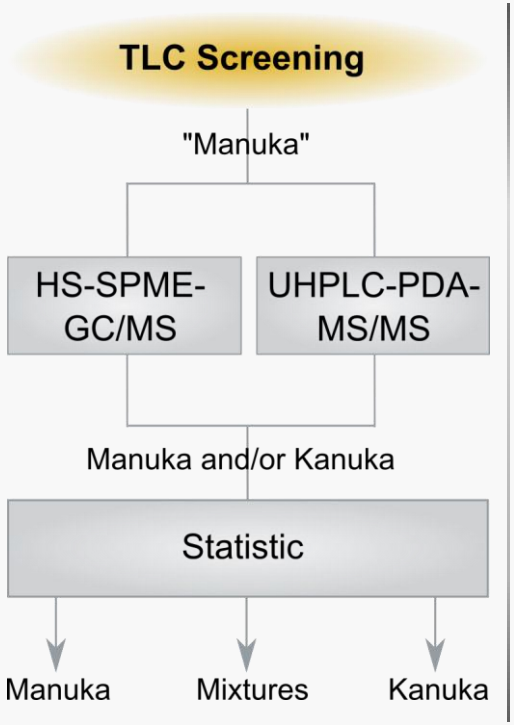
HAHSUS method

Honey **A**uthentication by **HS**-SPME-GC/MS and **S**PE-UHPLC-MS/MS combined with **S**tatistics

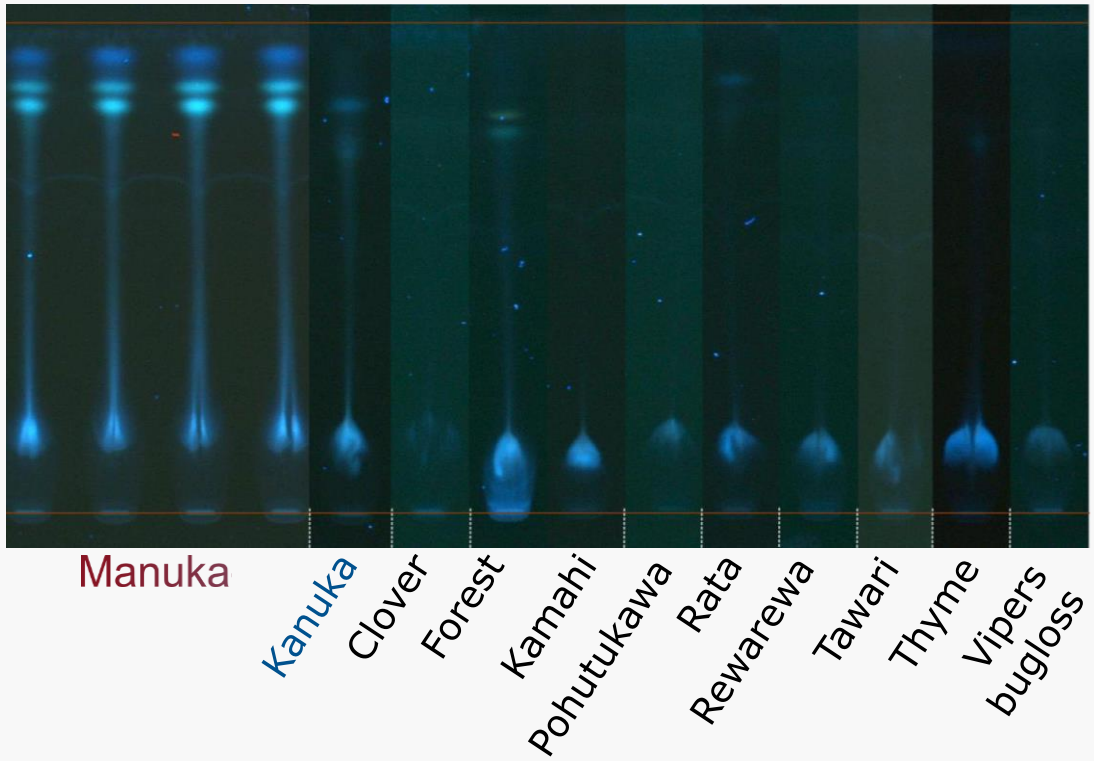


HAHSUS methods

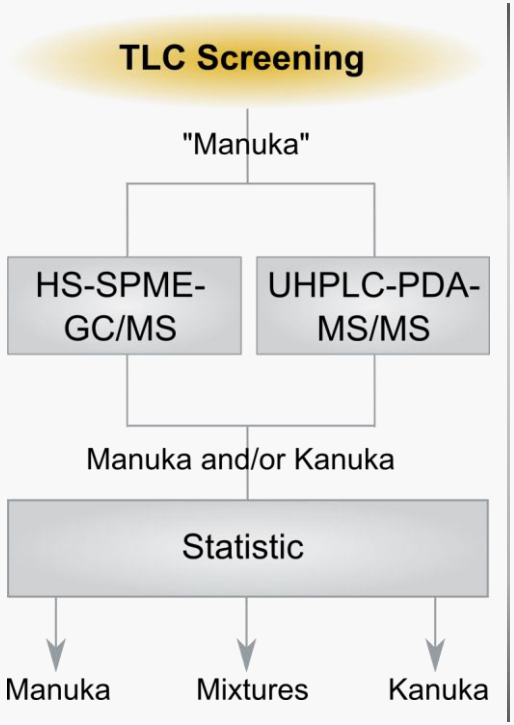




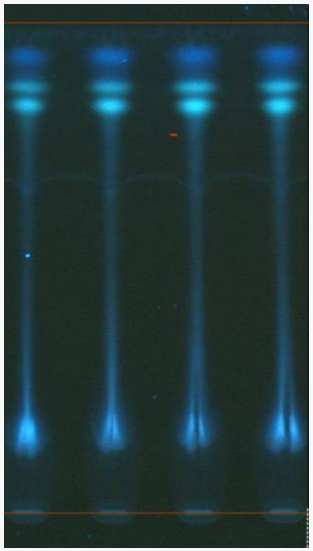
TLC Screening



Beitlich et al. (2016) Fluorescent Pteridine Derivatives as New Markers for the Characterization of Monofloral Genuine New Zealand Manuka (*Leptospermum scoparium*) Honey. *Journal of Agricultural and Food Chemistry.* DOI 0.1021/acs.jafc.6b03984



TLC Screening

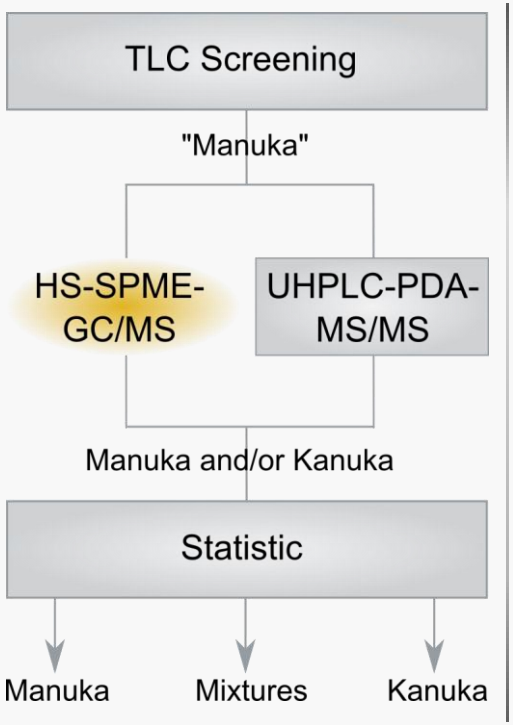


Manuka

1 **3,6,7-tri**methyl-2,4(1*H*,3*H*)-pteridinedione

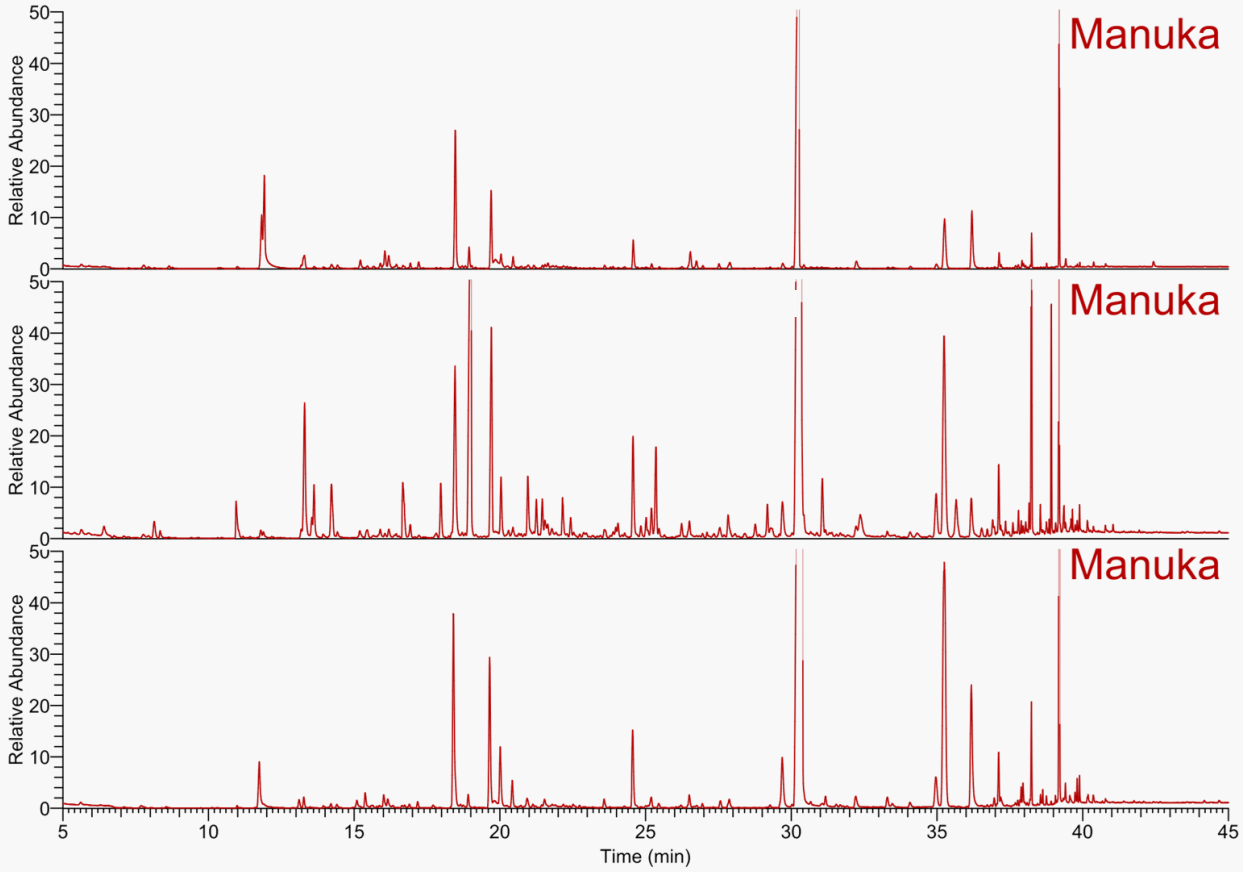
2 **6,7-di**methyl-2,4(1H,3H)-pteridinedione

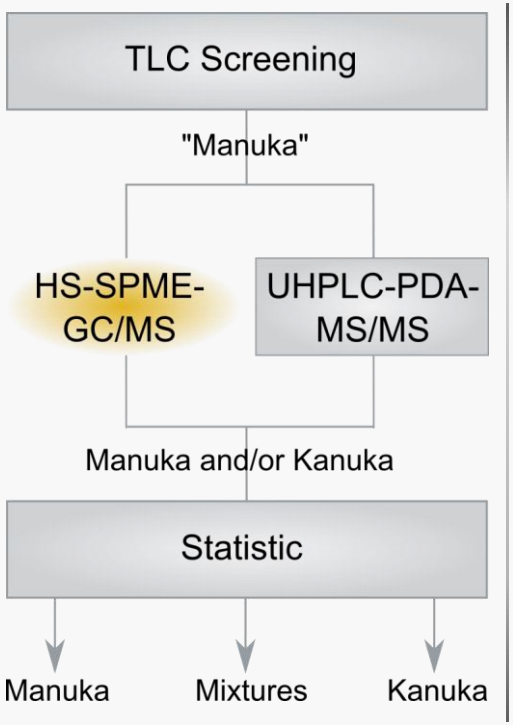
Beitlich et al. (2016) Fluorescent Pteridine Derivatives as New Markers for the Characterization of Monofloral Genuine New Zealand Manuka (*Leptospermum scoparium*) Honey. *Journal of Agricultural and Food Chemistry.* DOI 0.1021/acs.jafc.6b03984



HS-SPME-GC/MS

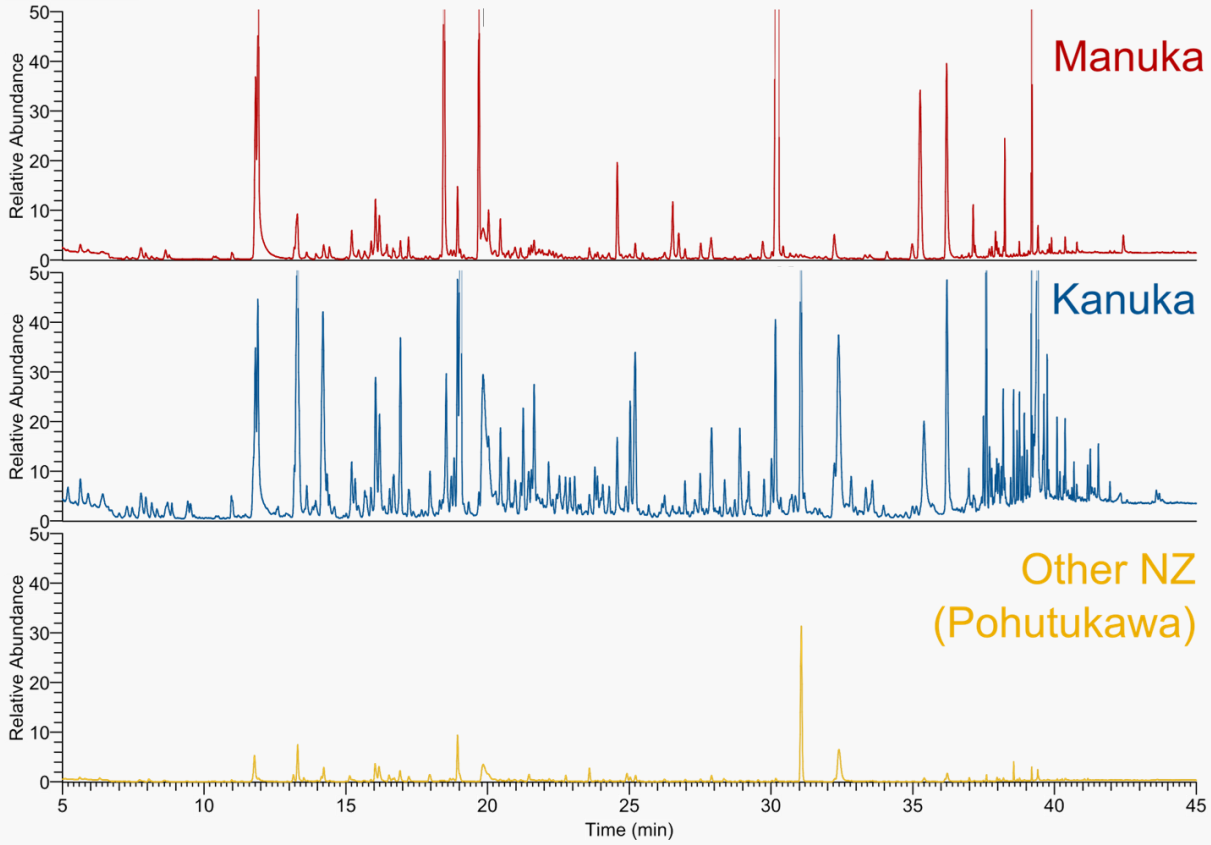
TIC profiles



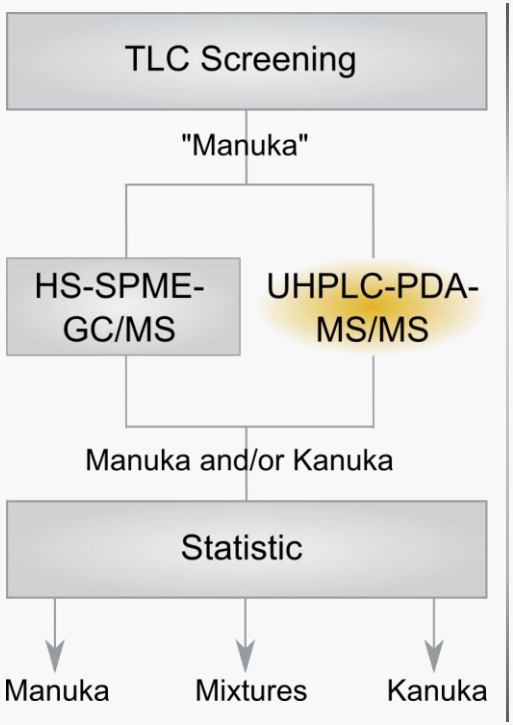


HS-SPME-GC/MS

TIC profiles

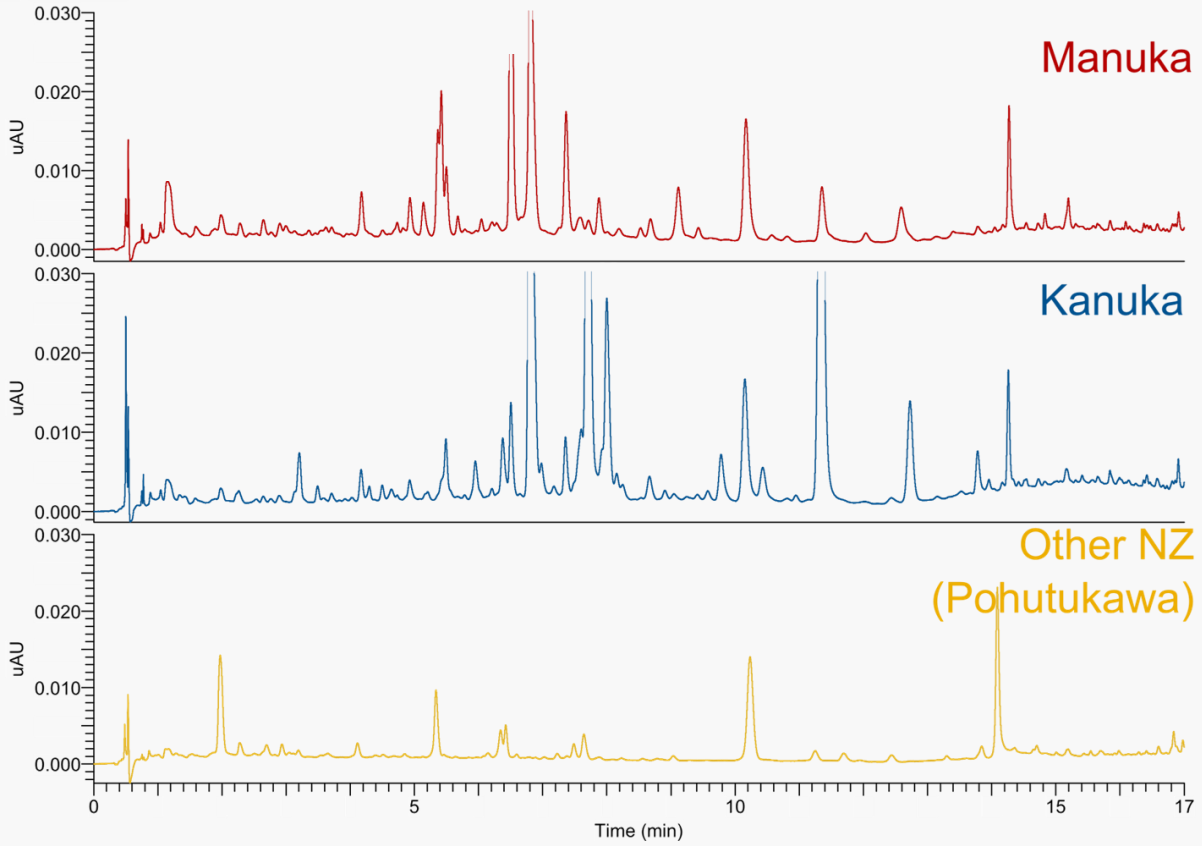


❖ Volatile marker compounds

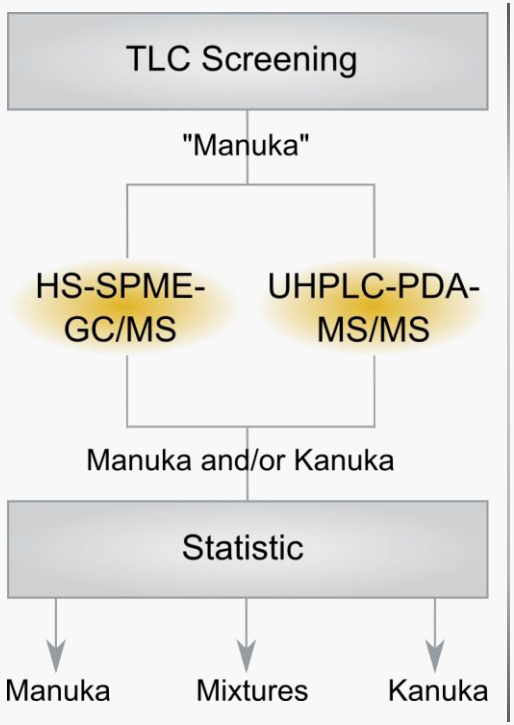


HS-SPME-GC/MS & **UHPLC-MS/MS**

PDA profiles, λ 254 nm



❖ Nonvolatile marker compounds

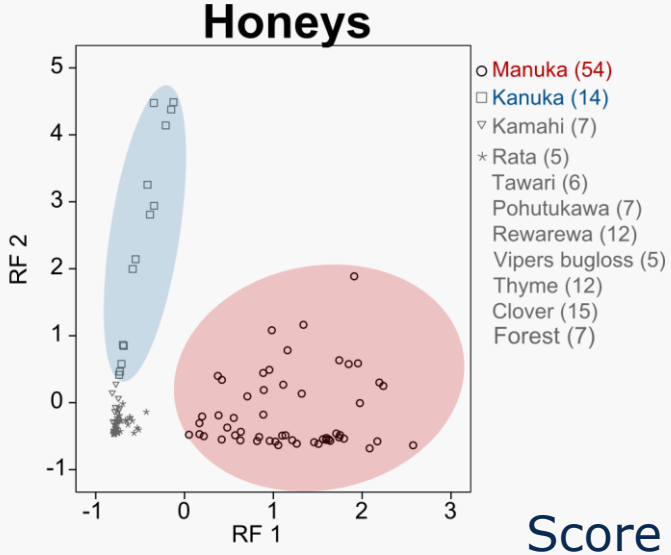


HS-SPME-GC/MS & UHPLC-MS/MS

Volatile markers

Nonvolatile markers

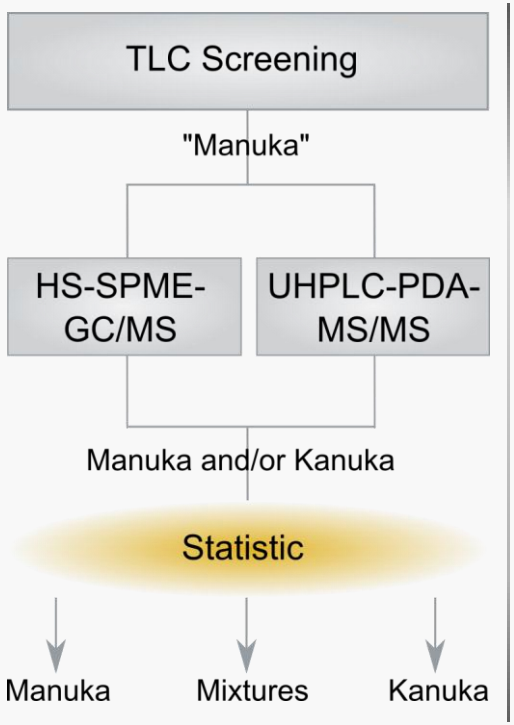
❖ Proved by significance test, boxplots, and PCA



Score plot

❖ Clear differentiation between manuka honey and kanuka honey

Beitlich et al. (2014) Differentiation of manuka honey and kanuka honey from jelly bush honey using HS-SPME-GC/MS and UHPLC-PDA-MS/MS. *Journal of Agricultural and Food Chemistry*. 62, 6435-6444.



Manuka-Kanuka-Mixtures

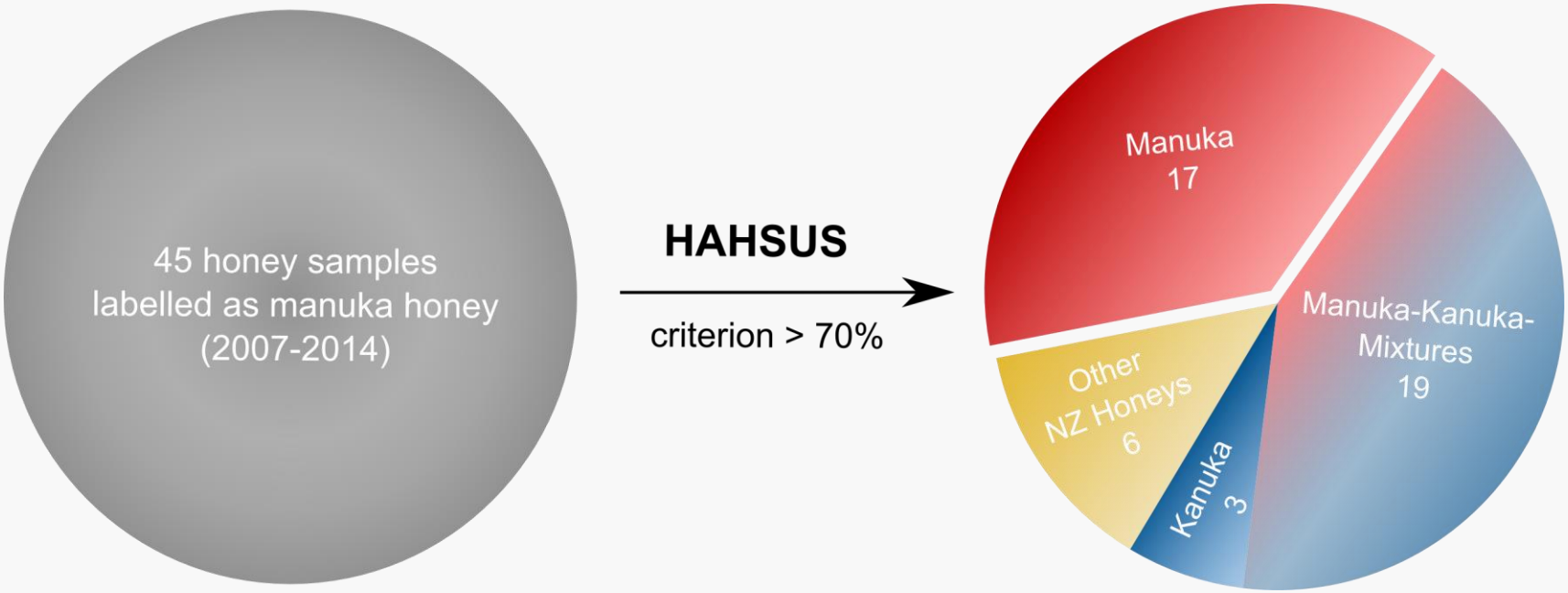
- Definition of monofloral honey:

  "…if it comes wholly or mainly from that particular source…" (Codex Stan 12-1981)

- Our definition: monofloral manuka honey >70%

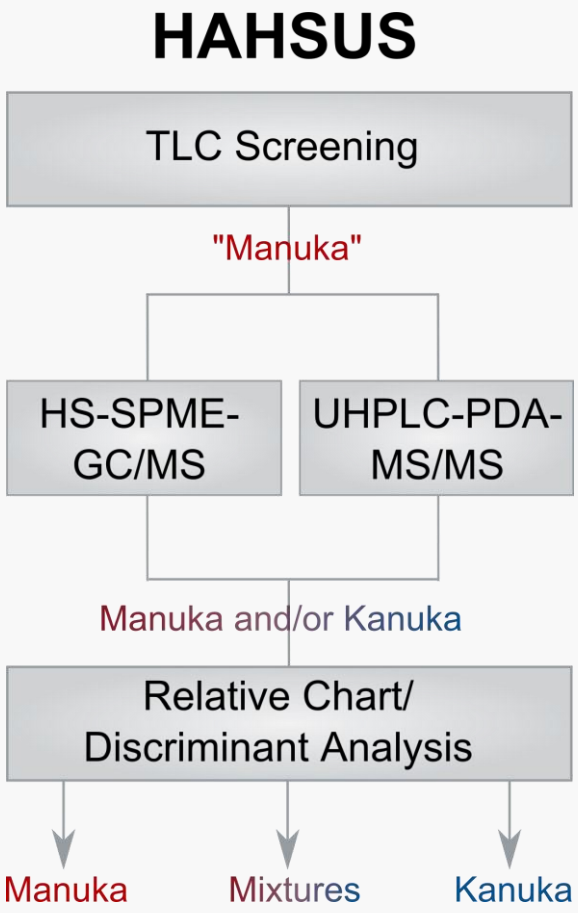
- Relative chart on the basis of special markers were developed

Classification of commercial manuka honeys

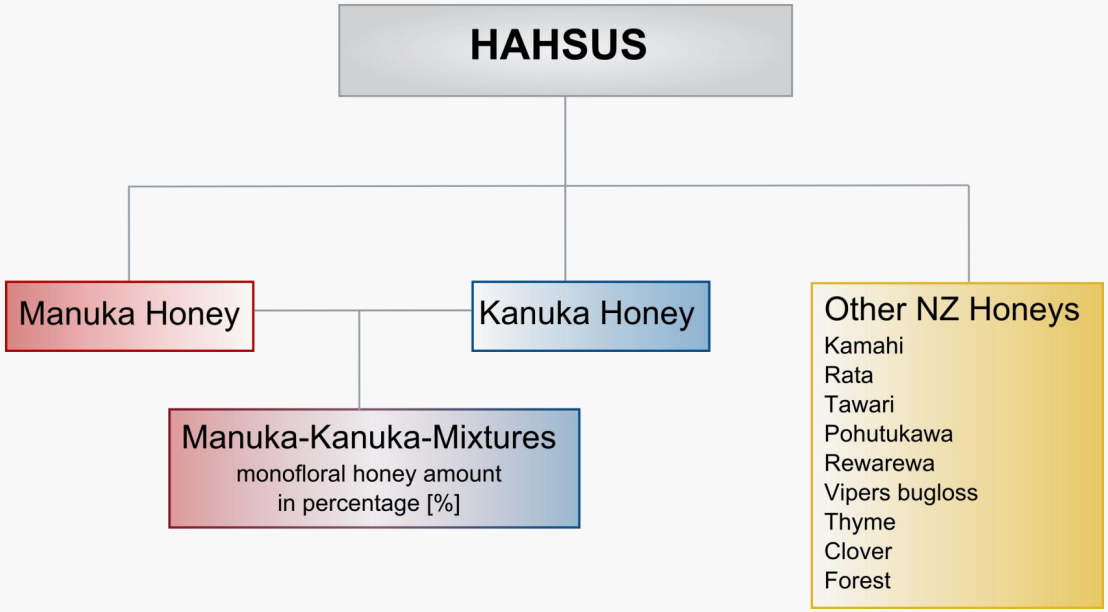


→ Summary

- Clear differentiation of manuka honey from kanuka honey and other NZ honeys
- Validated method for manuka honey authentication
- HAHSUS – **H**oney **A**uthentication by **HS**-SPME-GC/MS and **U**HPLC-PDA-MS/MS combined with **S**tatistics



Thank you for your attention!



Prof. Dr. Karl Speer

Phone: + 49 351-463 33132
e-mail: karl.speer@chemie.tu-dresden.de

Nicole Beitlich

phone: + 49 351 463 37868
e-mail: nicole.beitlich@chemie.tu-dresden.de