

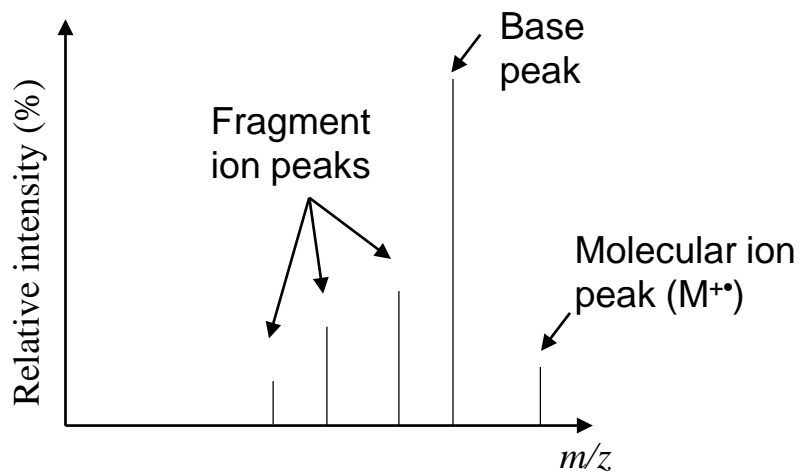
# A database of high-resolution MS/MS spectra for lichen metabolites

Damien Olivier-Jimenez, Marylène Chollet-Krugler, David Rondeau, Mehdi A. Beniddir, Solenn Ferron, Thomas Delhaye, Pierre-Marie Allard, Jean-Luc Wolfender, Harrie J. M. Sipman, Robert Lücking, Joël Boustie<sup>1</sup> & Pierre Le Pogam

(2019) 6:294 | <https://doi.org/10.1038/s41597-019-0305-1>

Eduardo Villicaña González  
04 July 2020

# Mass Spectrometry

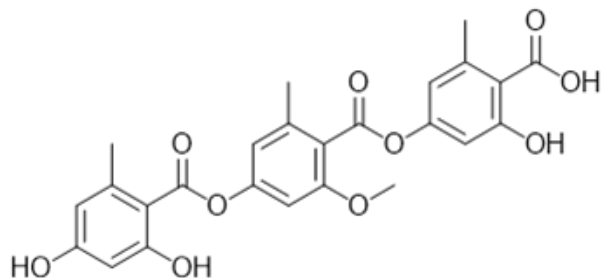


- ☞ Pure compound identification.
- ☞ Molecules structure elucidation.
- ☞ Molecular mass determination.
- ☞ Macromolecules sequence.
- ☞ Drug detection.
- ☞ Gas control during surgery.
- ☞ Quality control.

# Ionization

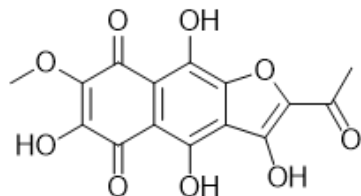
## NEG-ESI

- Acidic functions



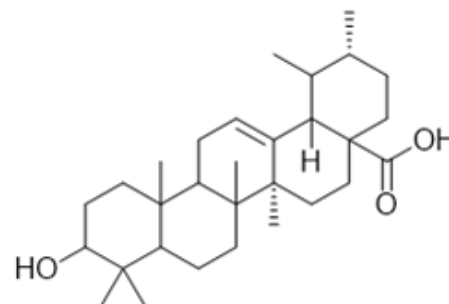
## POS-ESI

- Molecular environments where phenolic groups can instigate intramolecular H-H's
- $\gamma$ -pironone containing metabolites



## APCI

- Low to medium polarity
- Non-polar compounds





# Outline

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## Objectives

- Context
- Lichen Database

LDB Elaboration

LDB Validation

Relation with Natural Compounds in  
Ageing and Regeneration (NAR)

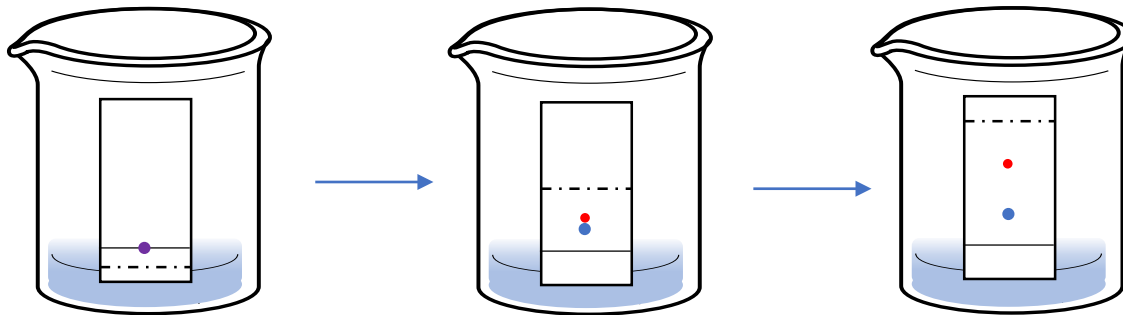
# Context

1996 ⇒ Huneck and Yoshimura: “Identification of Lichen Substances”

→ Chemical diversity (up to 1050 known metabolites)

→ Variety of bioactive properties

☞ Thin Layer Chromatography (TLC)



✓ Accessibility

✗ Sensitivity

✗ Resolution

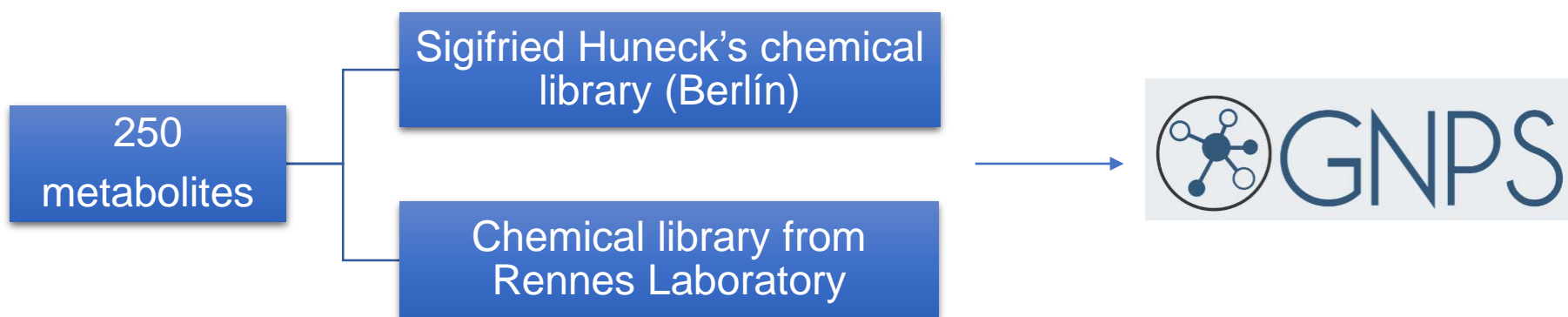
☞ Spot test



Chemical Tests | The British Lichen Society (accessed Jun 3, 2020).

# Lichen Database

☞ Meet modern metabolomics within lichen chemistry through an open access MS/MS library coined for a Lichen Data Base (LDB).



✓ Chemists      Dereplication

✓ Taxonomist      Chemical profiling



# Outline

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Objectives

LDB description

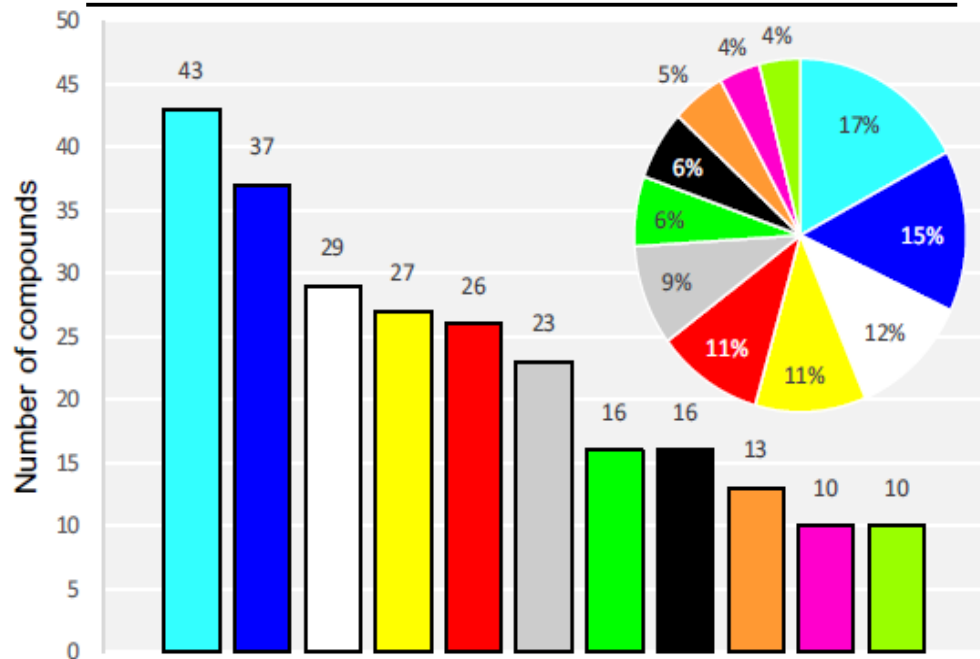
- Data acquisition
- Networking

LDB Validation

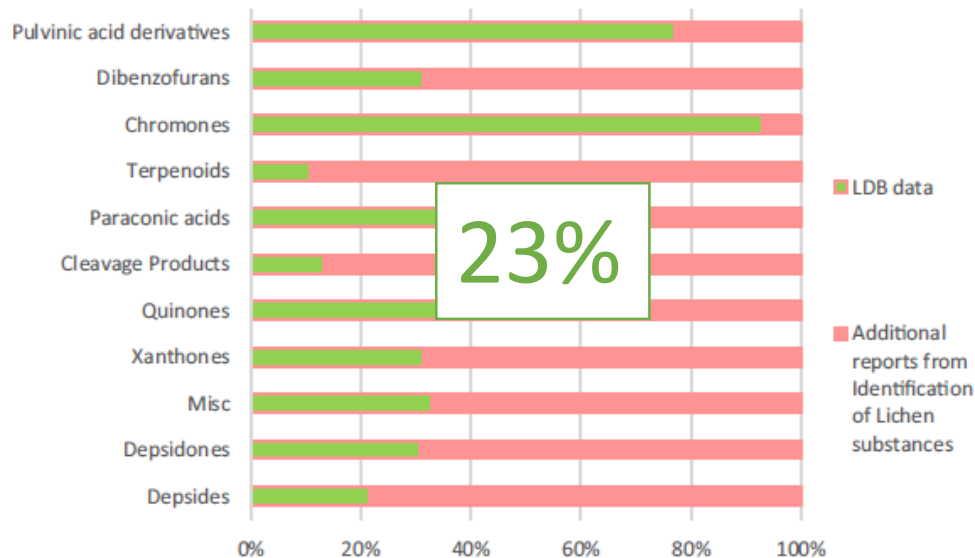
Relation with Natural Compounds in Ageing and Regeneration (NAR)

# Data acquisition

## Huneck and Yoshimura classification



- Depsides
- Depsidones
- Misc.
- Xanthones and bis-Xanthones
- Quinones
- Cleavage Products of Depsides and Depsidones
- Paraconic acids
- Terpenoids
- Chromanes and Chromones
- Dibenzofurans
- Pulvinic acid derivatives

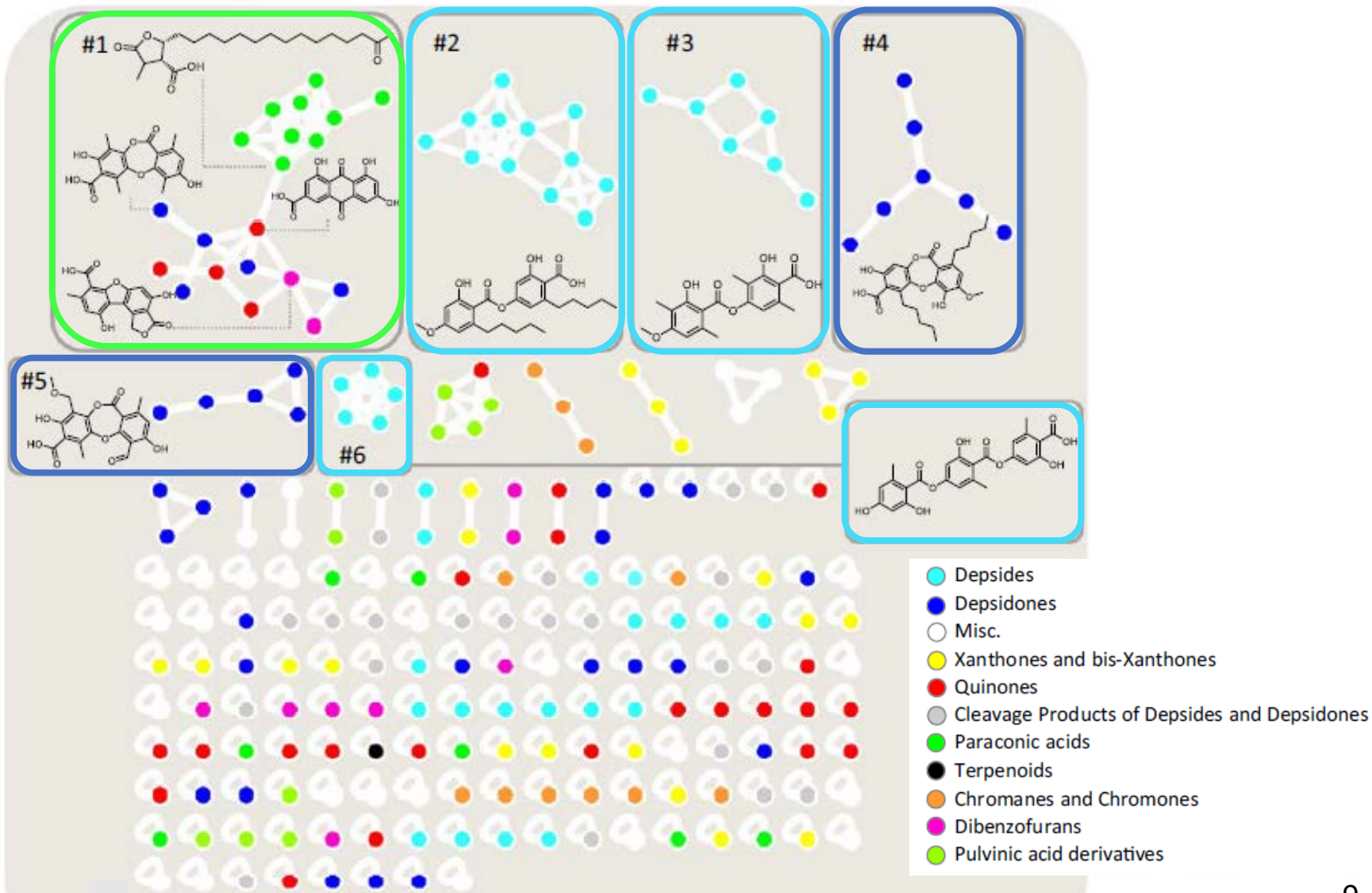


- ⇒ 309 MS/MS spectra from 250 metabolites:
- 226 ionized by NEG-ESI.
  - 68 ionized by POS-ESI.
  - 15 ionized by APCI.



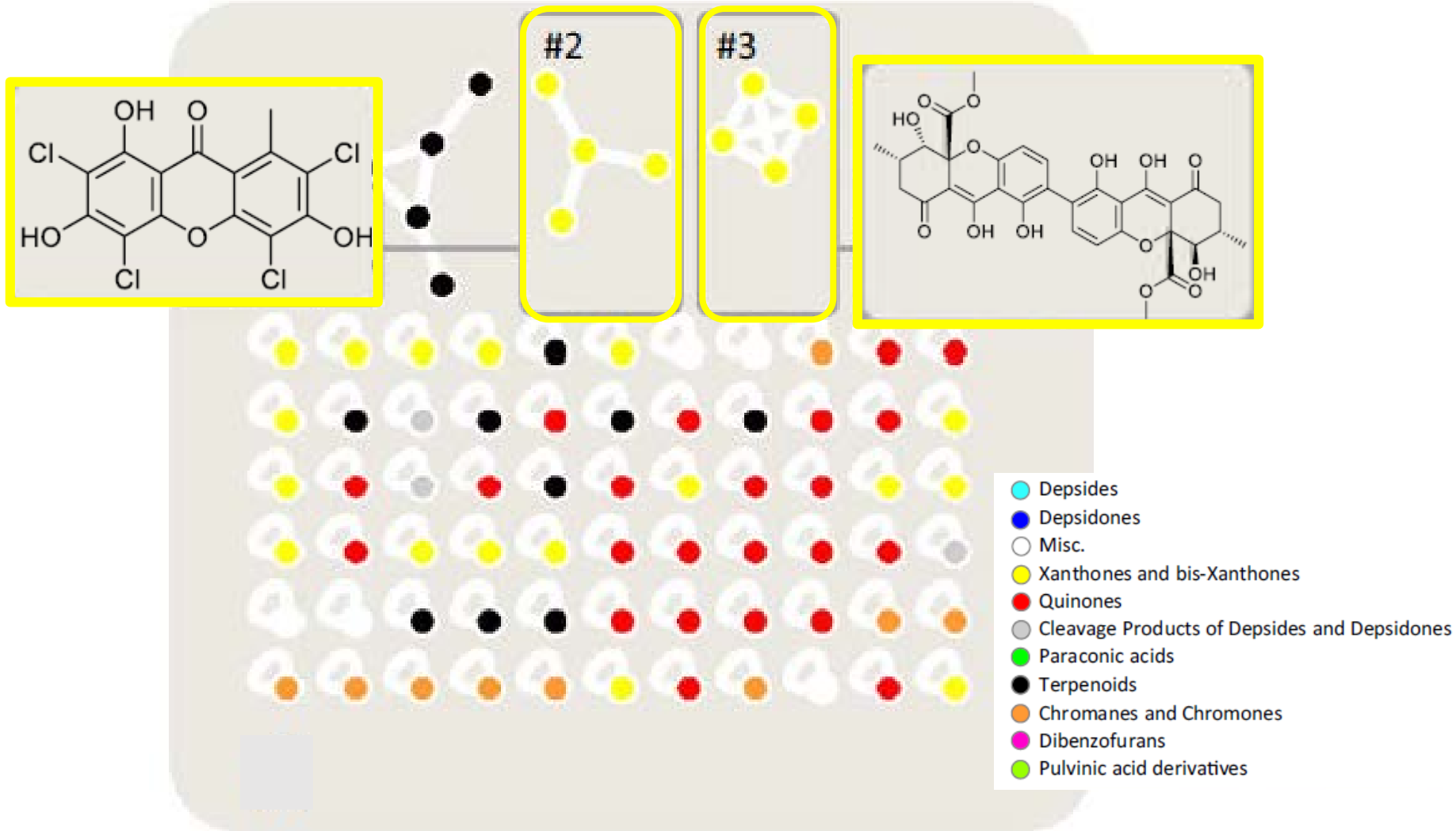
# Networking

Based on MS7MS similarity (NEG-ESI)



# Networking

Based on MS7MS similarity (POS-ESI)





# Outline

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Objectives

LDB Elaboration

LDB Validation

- Technical Validation
- *Ohiparma ventosa*
- *Evernia prunastri*
- *Hypogimnia physodes*

Relation with Natural Compounds in  
Ageing and Regeneration (NAR)

# Technical Validation

*Ophioparma ventosa*



*Ophioparma ventosa* (accessed May 18, 2020)

*Evernia prunastri*



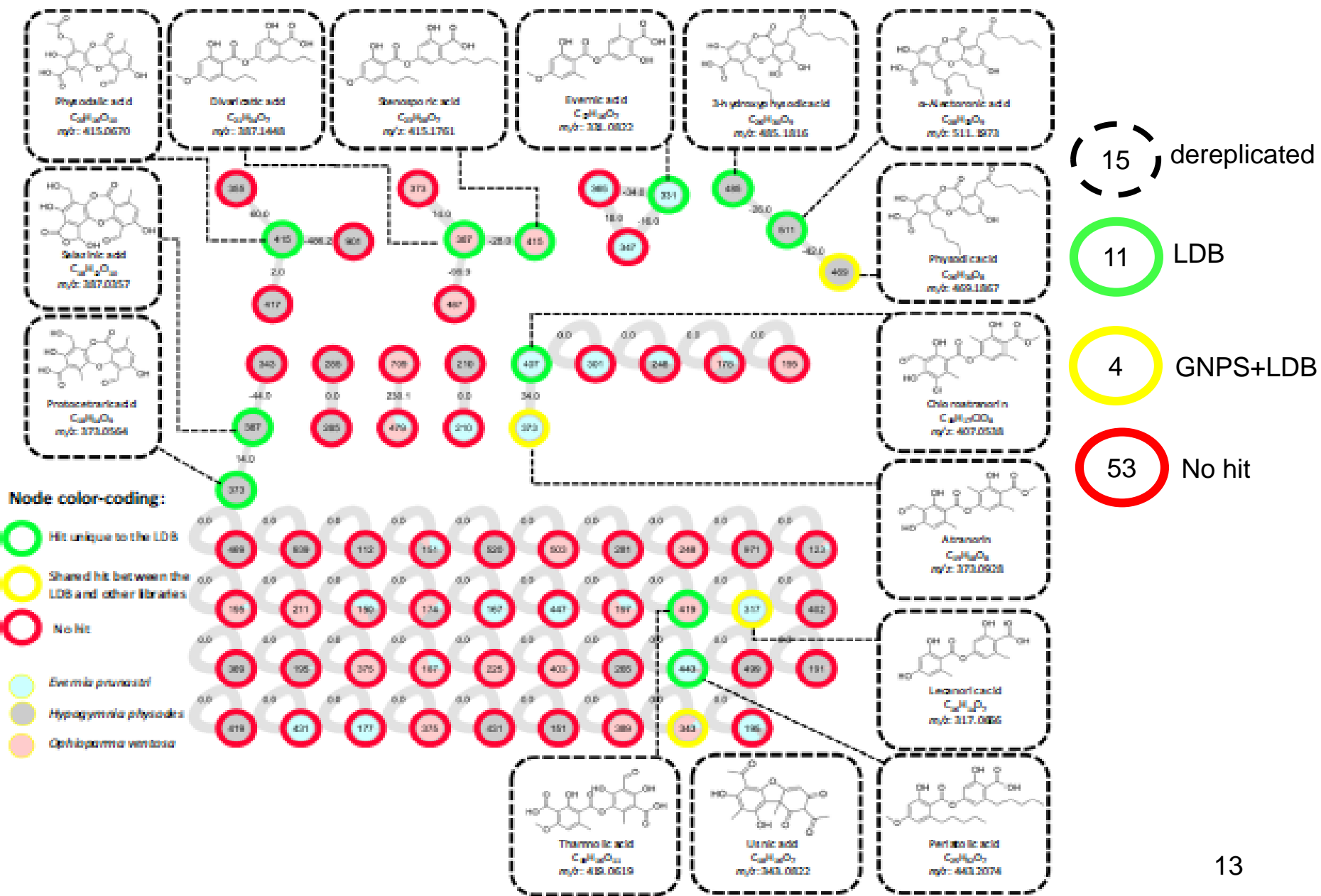
Kindrogan, Perthshire, March 2008

*Hypogymnia physodes*



*Hypogymnia physodes* - lichenology.info - species details (accessed May 18, 2020).

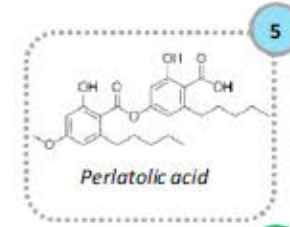
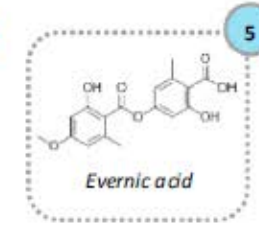
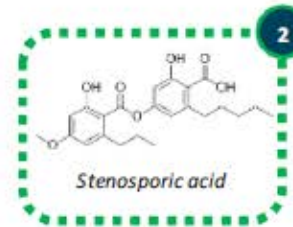
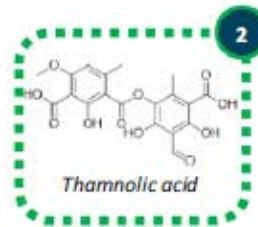
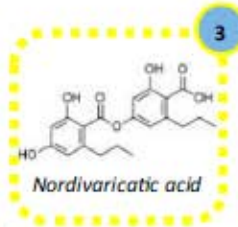
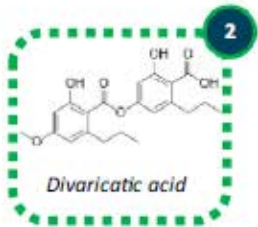
# Technical Validation



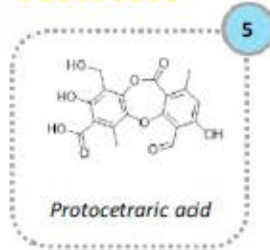
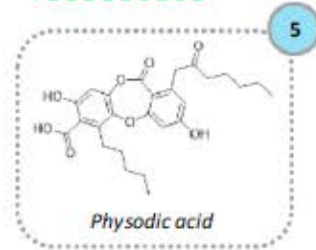
# Ophiparma ventosa



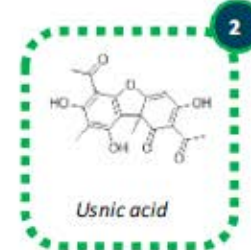
DEPSIDES



DEPSIDONES



DIBENZOFURANS



Metabolites dereplicated by MS/MS and reported in the literature

Metabolites that were either identified by MS/MS but not reported in the literature, or reported in the literature but only identified by gap-filling

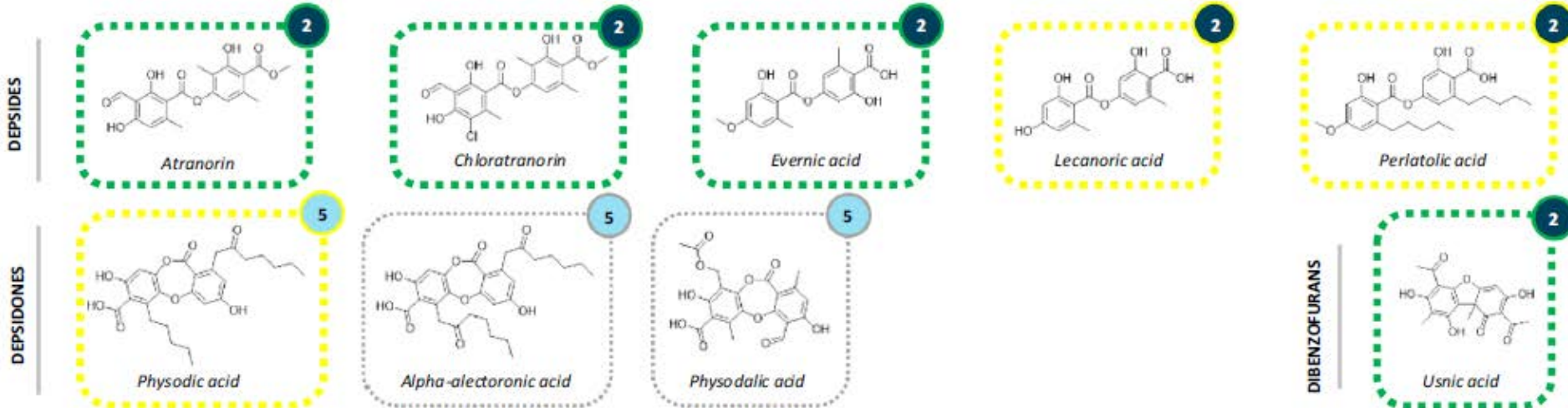
Metabolites not reported in the literature and only identified by gap-filing

Metabolites reported in the literature but not detected

2 3 5

Annotation confidence levels according to Schymanski et al.

# Evernia prunastri



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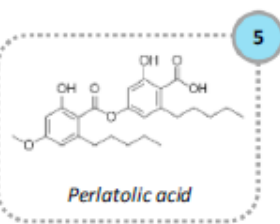
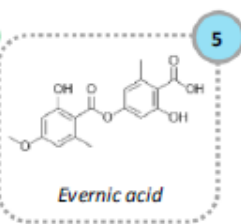
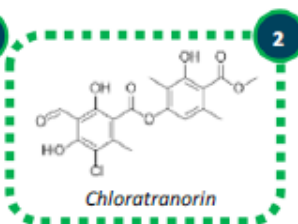
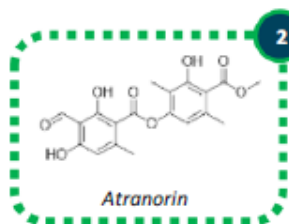
2 3 5

Annotation confidence levels according to Schymanski et al.

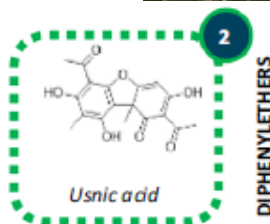
# Hypogymnia physodes



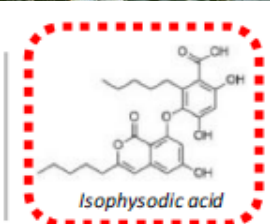
DEPSIDES



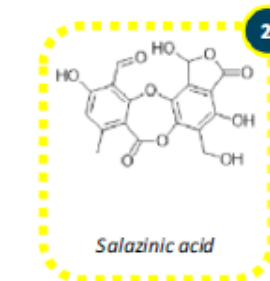
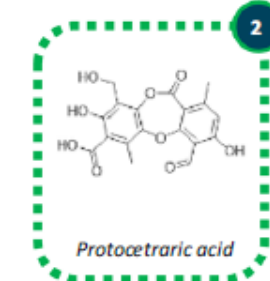
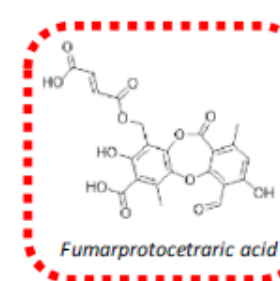
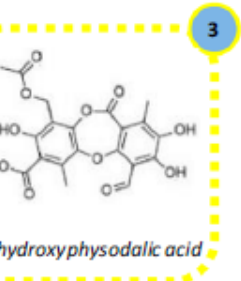
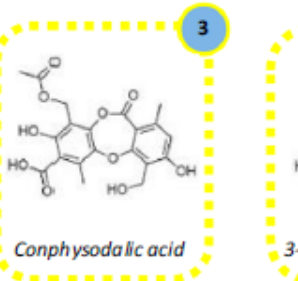
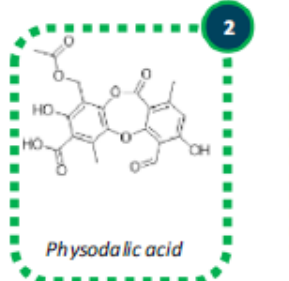
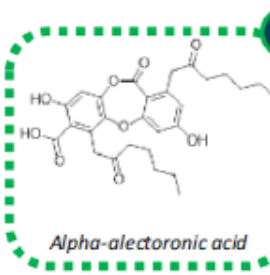
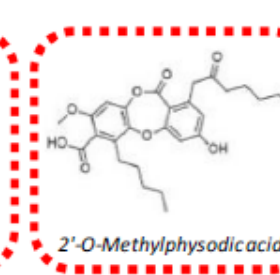
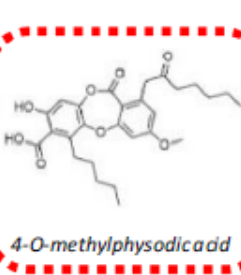
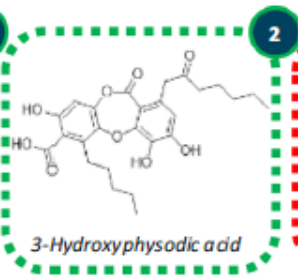
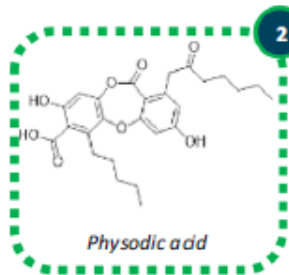
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# Outline

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Objectives

LDB Elaboration

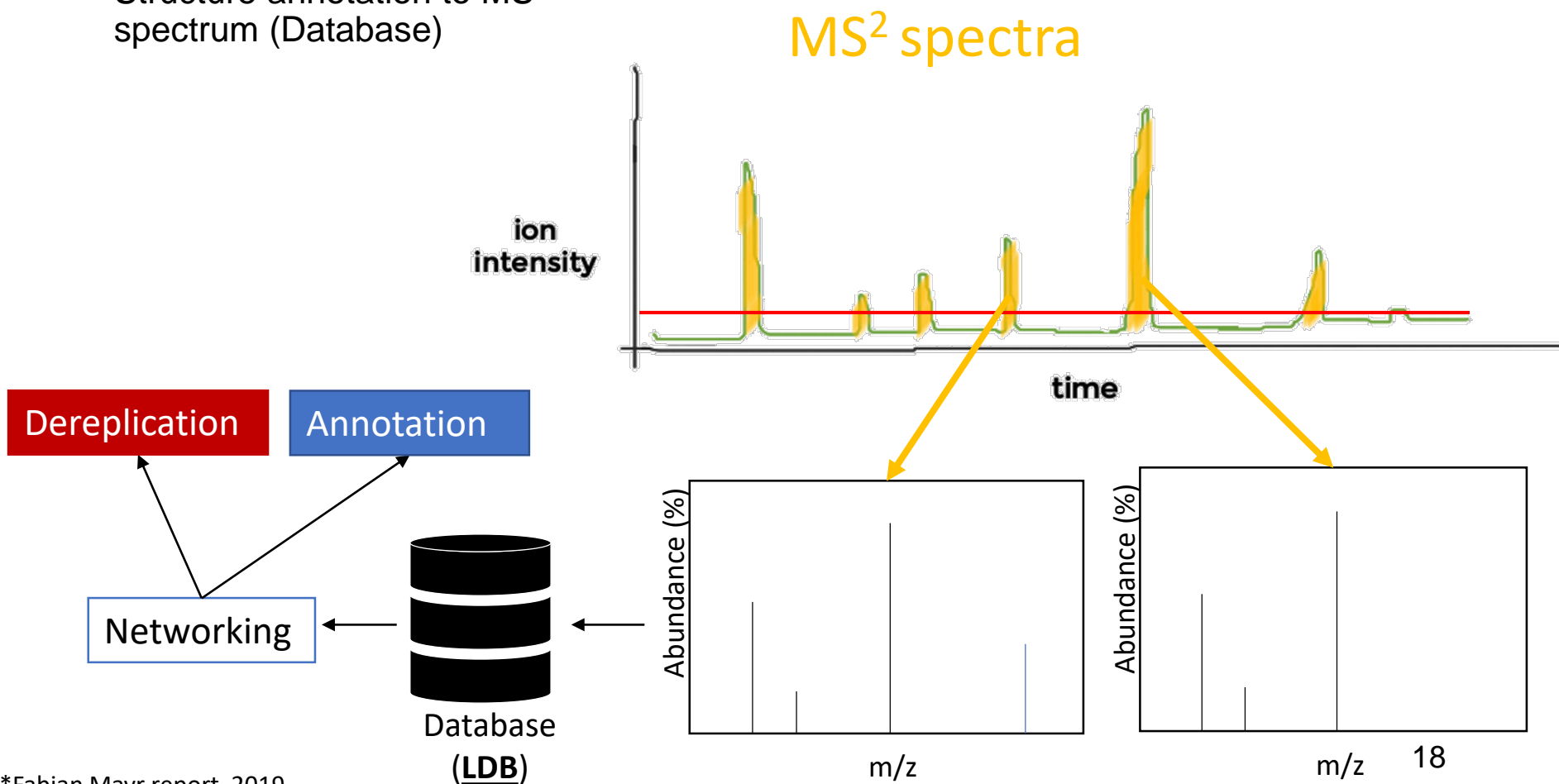
LDB Validation

**Relation with Natural Compounds in  
Ageing and Regeneration (NAR)**

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# LDB in ARDRE program – NAR project

- LC-MS (high resolution)
- Data dependent LC-MS<sup>2</sup>
- Comparison of MS<sup>2</sup> spectra
- Structure annotation to MS<sup>2</sup> spectrum (Database)





# LDB in ARDRE program – NAR project

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- ✓ Fast identification of known metabolites in complex mixtures
- ✓ Small crude extract quantities required
- ✓ Avoiding isolation procedures of non-interesting compounds

- ✗ Chirality and position isomers cannot be distinguished
- ✗ Minor peaks difficult
- ✗ Suitable ion source

Thank you for your attention



4<sup>th</sup> June 2020