



Two molecules newly identified by Mass Spectrometry in fermented cocoa beans have a strong impact on chocolate sensory quality.

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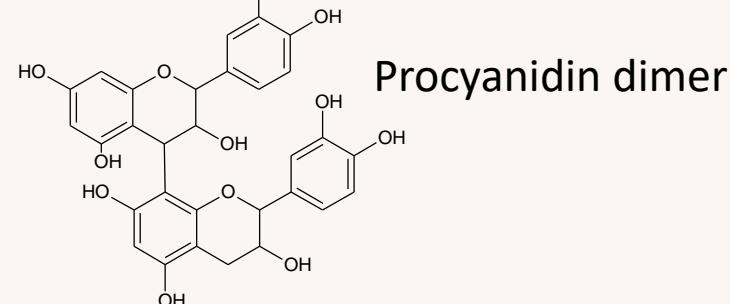
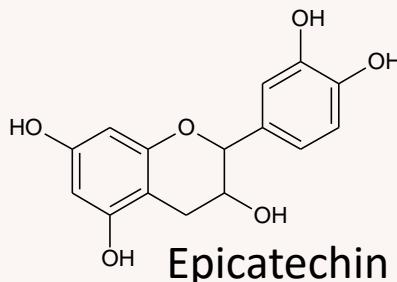
Polyphenols & Fermentation process

Polyphenols in plants

- Secondary metabolites produced by plants
 - Wide family of molecules
 - Defence, protection, colour



• Polyphenols in cocoa



Wide range of potentially new molecules



pH and T°C variations + metabolites



Raw Beans



Fermented Cocoa Beans

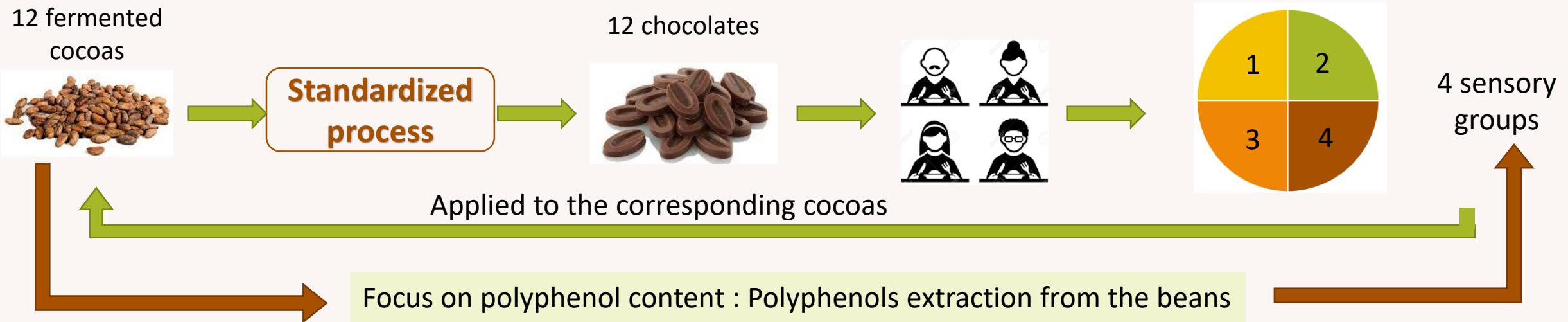


Drying



Fermentation

Impact on chocolate taste



Mass spectrometry

- widely used for polyphenols detection
- Fast and accurate
- Detection, identification and quantification after extraction

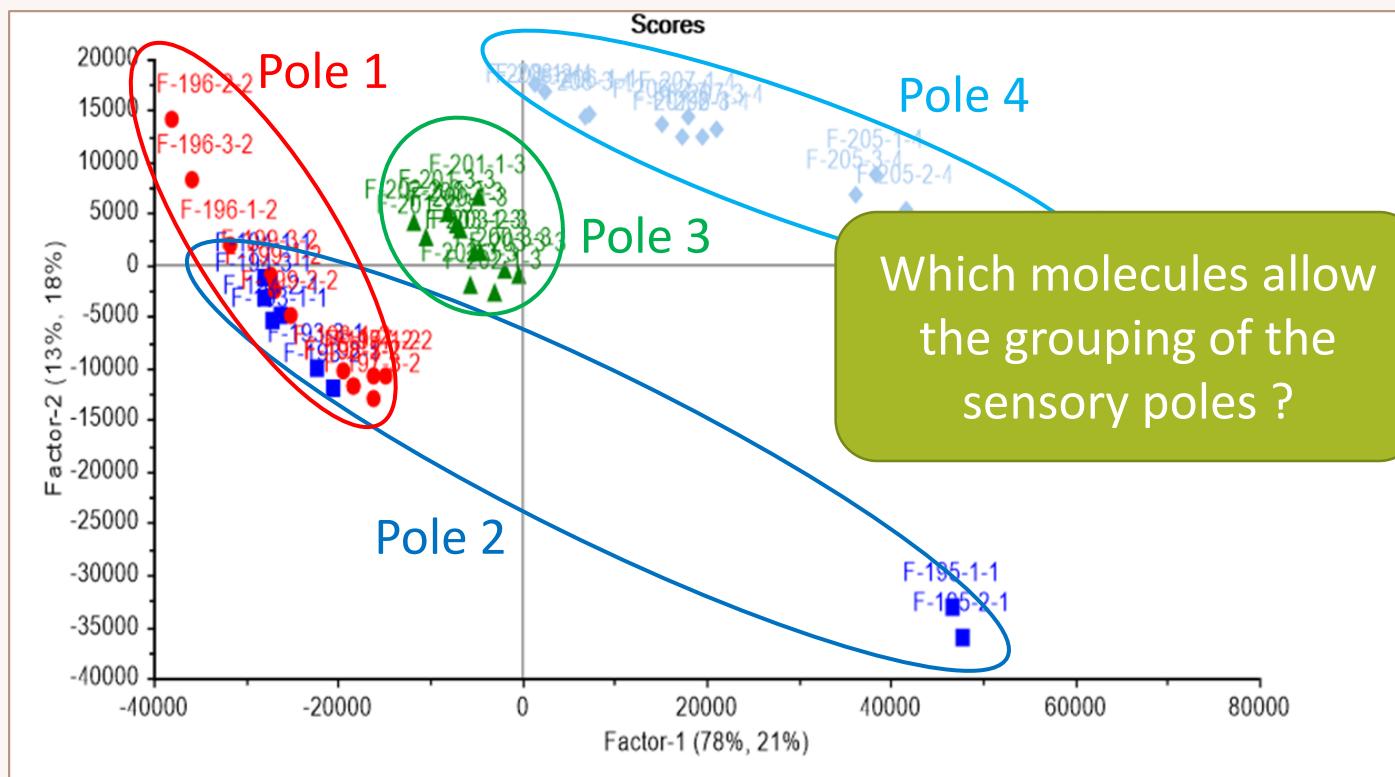
Liquid chromatography
(molecules separation)

Low resolution mass spectrometry
(mass signal (m/z) and relative quantity)

Use of the **polyphenols relative quantity** in fermented cocoas beans to **evaluate the sensory poles**

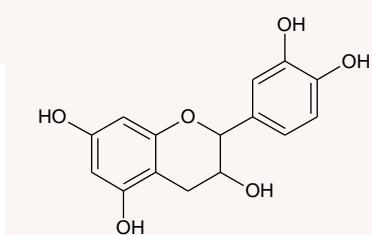
Problematic link between cocoa molecules and chocolate taste

Statistical treatment of the polyphenols relative quantity :



List of 32 mass signals
 (=type of molecules)

- Mainly flavan-3-ols
- Among them two signals with significant impact



$m/z = 605$

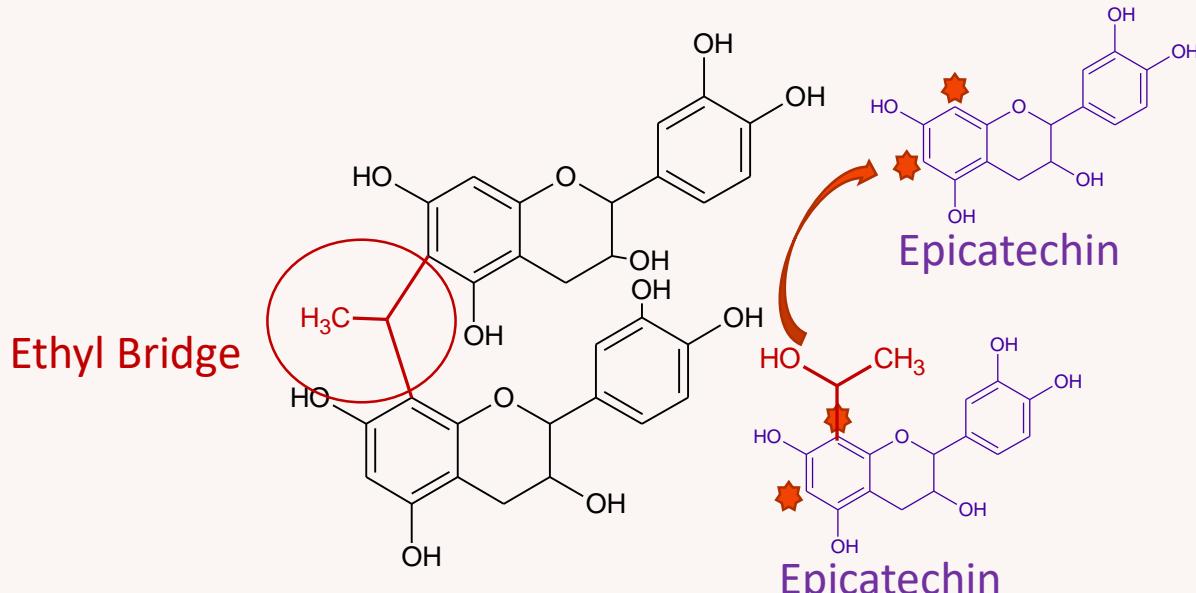
$m/z = 893$

Reported in cocoa not identified

Purpose of this work :
identify these two mass signals

Hypothesis: ethyl bridged flavanols

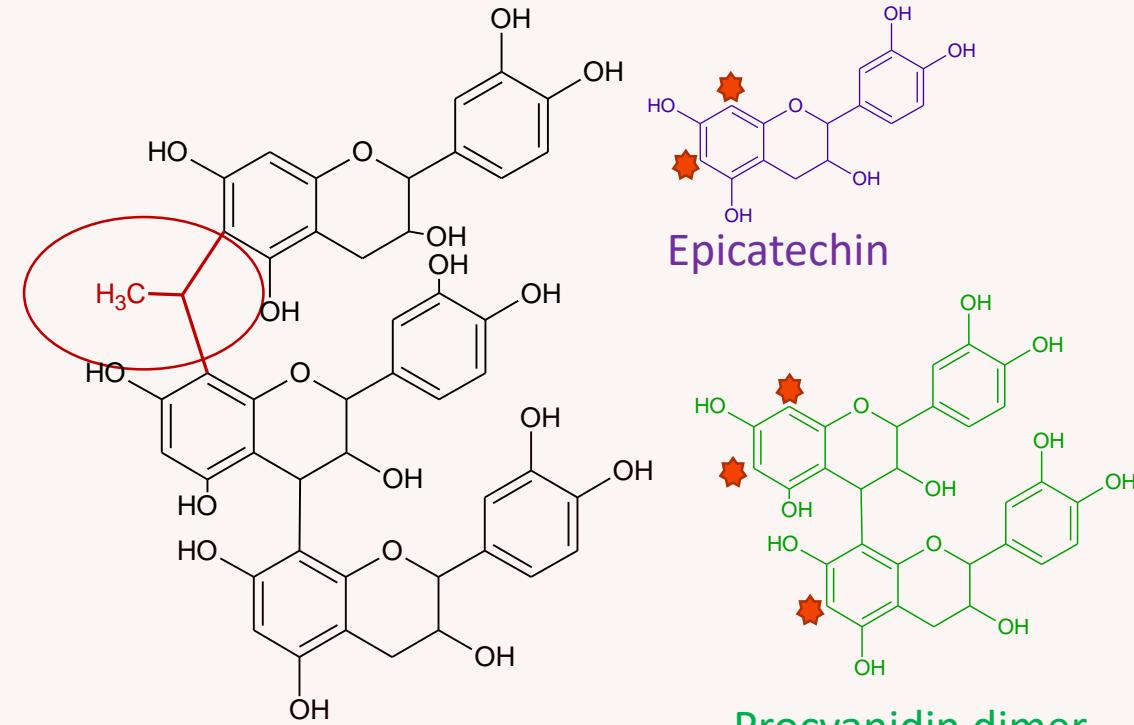
- Ethyl Bridged flavanols ?



Molecular Weight :
606.5734 g.mol

Ionized Molecular Weight :
605.1659 g.mol

Acetaldehyde + H⁺



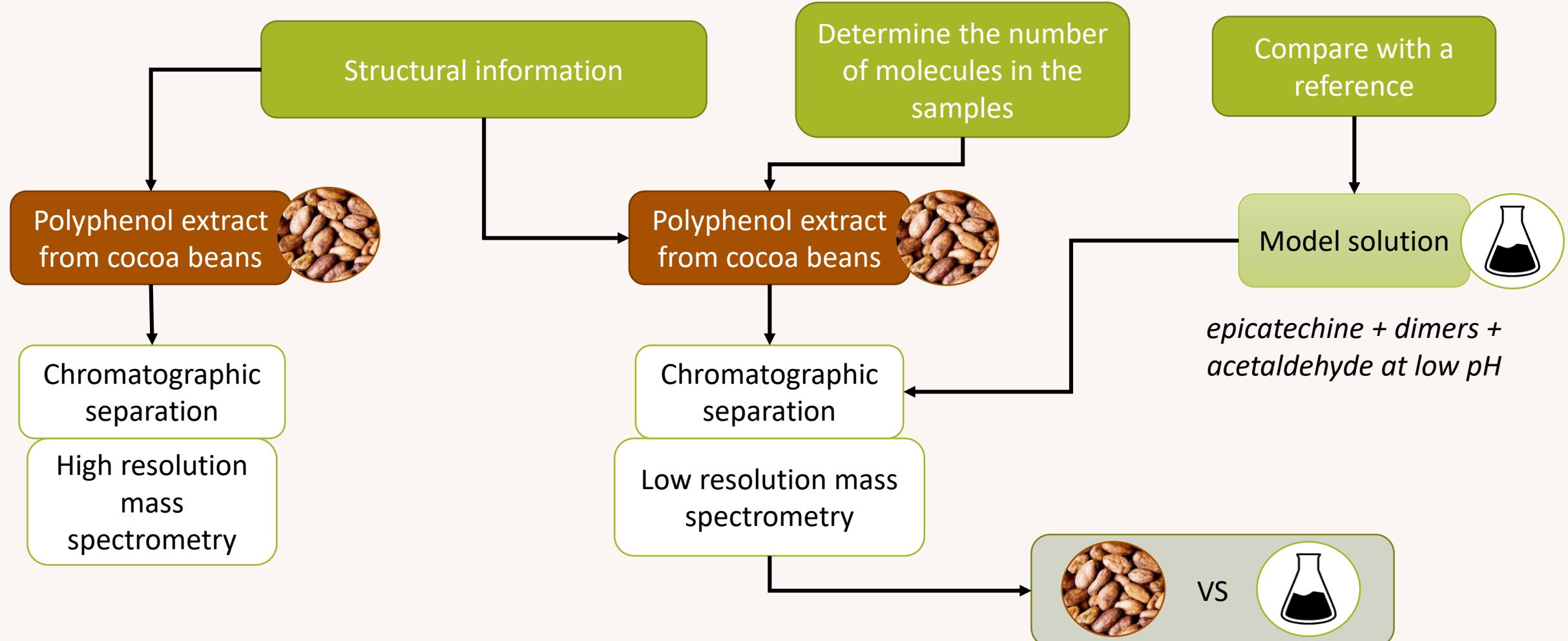
Molecular Weight :
894.8256 g.mol

Ionized Molecular Weight :
893.2292 g.mol

Acetaldehyde + H⁺



How to confirm this hypothesis ?



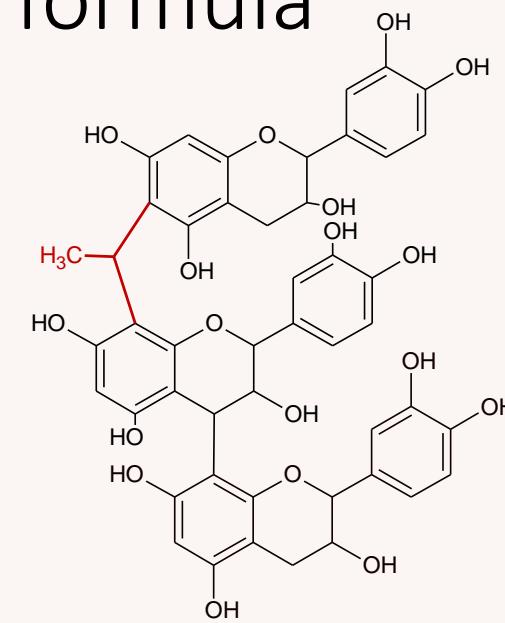
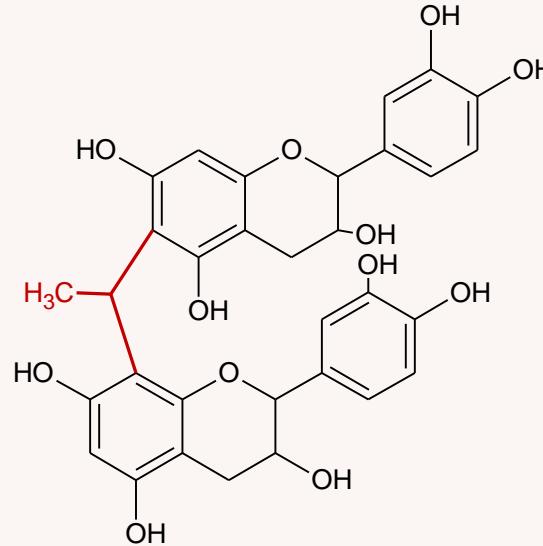
Structural information

Exact mass signal & chemical formula

High resolution mass signals



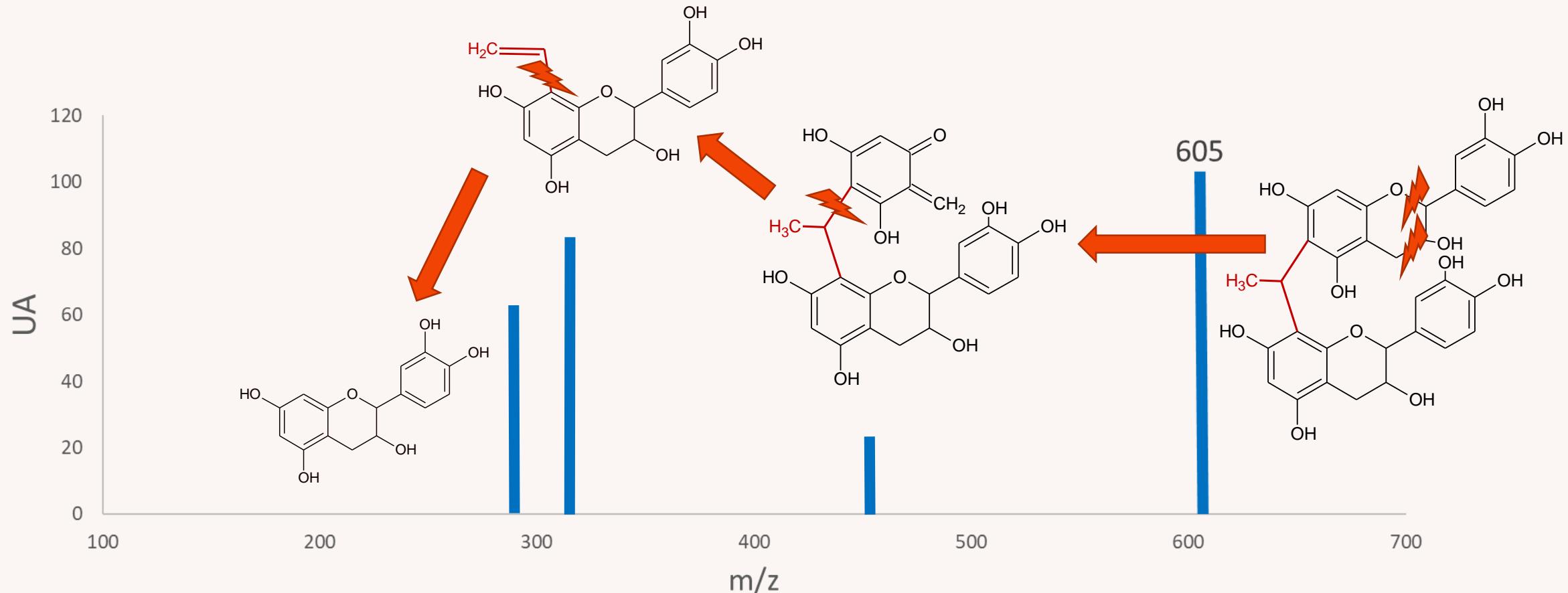
Exact chemical formula



Theoretical Ionized mass	605.1659	893.2292
Experimental Ionized mass	605.1641	893.2282
Mass defect (mDA)	1,8	1

Theoretical chemical formula	C ₃₂ H ₂₉ O ₁₂	C ₄₇ H ₄₁ O ₁₈
Experimental chemical formula	C ₃₂ H ₂₉ O ₁₂	C ₄₇ H ₄₁ O ₁₈

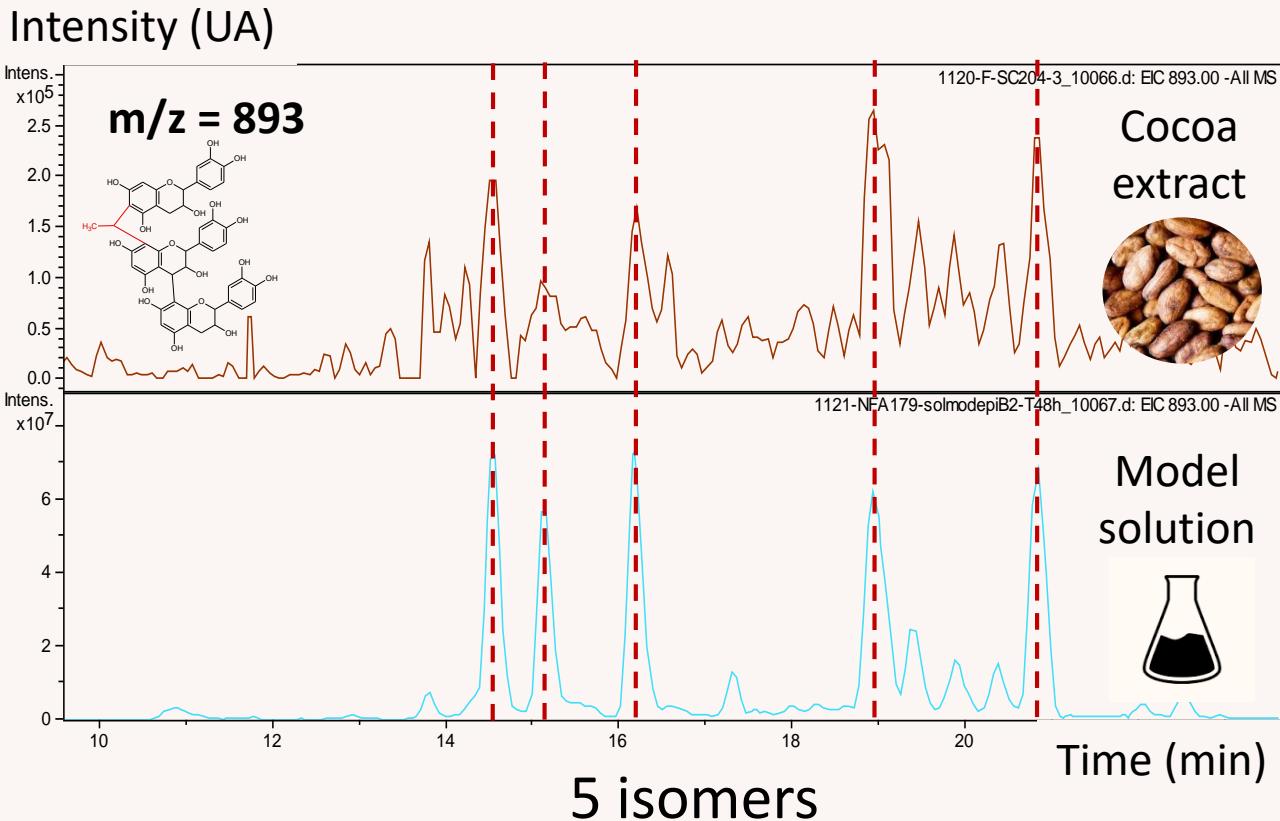
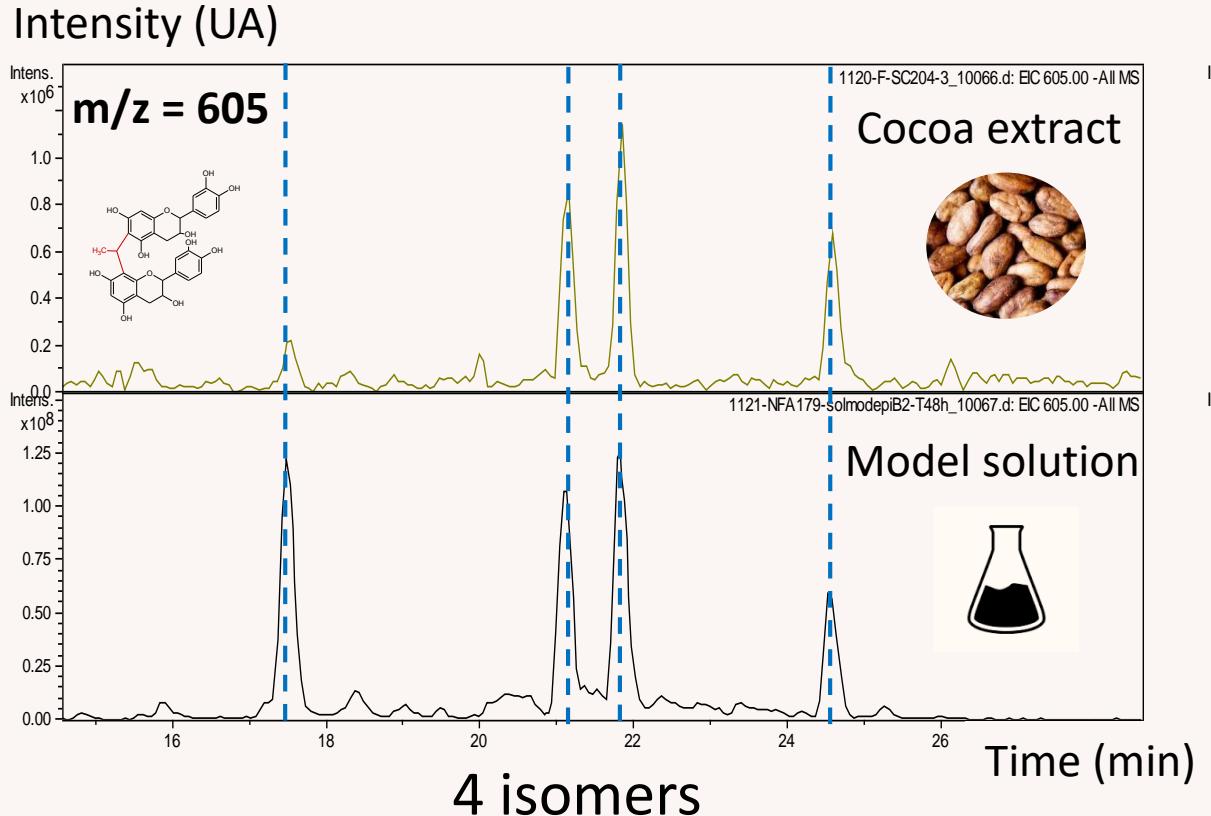
Structural information : fragmentation scheme



The fragmentation pattern is specific from ethyl bridged flavanols

The structure is confirmed for both signals at m/z = 605 and m/z = 893

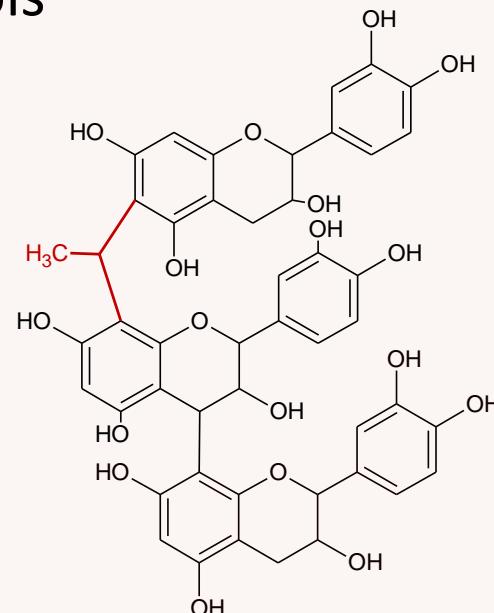
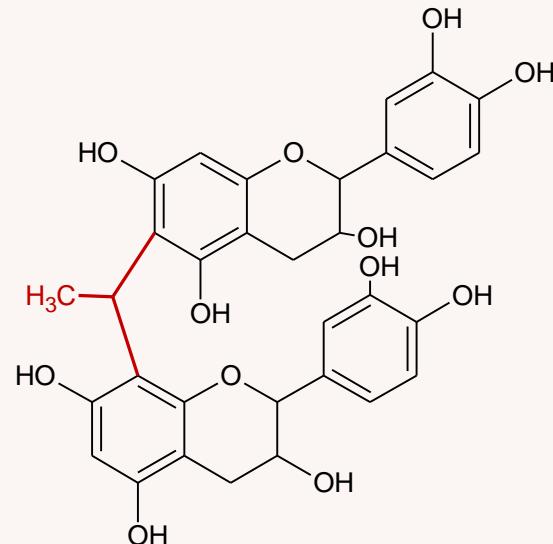
Low resolution mass spectrometry numbers of different molecules in samples



Conclusion

After statistical analysis, two unknown mass signals have been highlighted
These molecules discriminate the chocolate sensory poles

Mass spectrometry allowed to identify these two mass signals as
ethyl bridged flavanols



Thanks for your attention



Special thanks to

Anna Vallverdú-Queralt
Emmanuelle Meudec
Jean-Claude Boulet
Jean-Michel Roger
Clotilde Hue
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Véronique Cheynier
Nicolas Sommerer

