LIPID BIOMARKERS IN TREE RINGS: CHEMOTAXONOMY, DIAGENESIS AND POTENTIAL FOR PALAEOENVIRONMENTAL RECONSTRUCTIONS

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Introduction

Tree rings are reputed paleoenvironmental and palaeoclimate archives. In addition to an annually-resolved absolute chronology, they afford crucial palaeoclimate information from tree-rings thickness, and carbon and oxygen isotopes of cellulose. To our knowledge, lipid biomarkers preserved in tree rings have received little attention. We here report lipid biomarkers found in tree rings from different species, location and age to address the following questions: Are there specific distributions or biomarkers related to taxonomy? How are biomarkers preserved depending on the age of the sample? Are there differences in molecular imprints related to provenance/climate or type of wood (initial/final)? Do biomarker amounts allow further studies (such as compound-specific isotope analyses) at the annual/seasonal scale?

What?

Where?

Sample name	Species	Angio/ Gymno	Location	Age
REM19	*Araucaria araucana*	G	Patagonia	
TRA20-1&4	*Austrocedrus chilensis*	G	Patagonia	2009-2018
Villars-A	*Cedrus sp.*	G	France	1997-1999
Villars-D	*Cedrus sp.*	G	France	1930
FRO#18	*Sequoia sp.*	G	France	Modern
PBL-1	*Fitzroya cupressoides*	G	Patagonia	before 2008
Bomi	*Picea linzhiensis*	G	Himalaya	1789-1798
LT109	*Pinus sylvestris*	G	Sweden	-1300
COUT203	*Pinus sylvestris*	G	France	-4200
PAZ20-05	*Nothofagus pumilio*	A	Patagonia	before 2008
AMS-PHYL	*Phylica arborea*	A	French Southern Lands	post 1950
FRREU12-Phyl	*Phylica nitida*	A	Indian Ocean	Modern
FRREU12-Psi	*Psidium guajava*	A	Indian Ocean	Modern
ANG HV-63	*Quercus sp.*	A	France	
ANG	*Quercus sp.*	A	France	1903 - 1908
Preuilly26-BI	*Quercus sp.*	A	France (initial wood)	XII e
Preuilly26-BF	*Quercus sp.*	A	France (final wood)	XII e

How?

Preparation

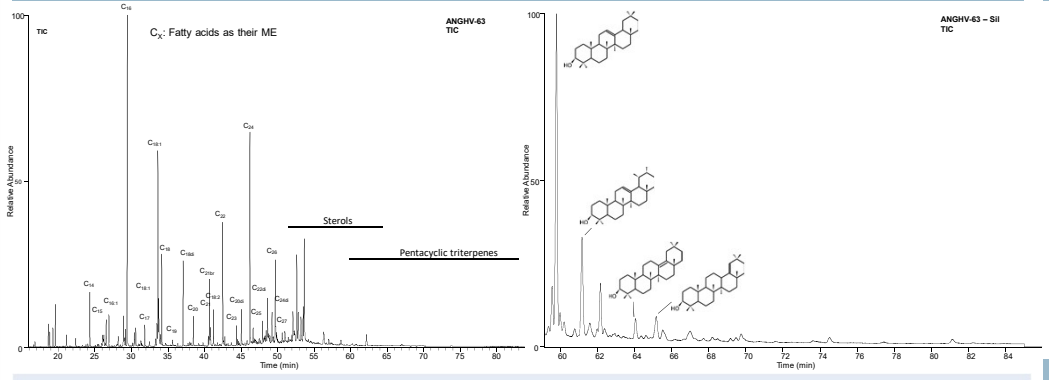
Test 1: Extraction/esterification (H_2SO_4) -> liquid-liquid extraction
Test 2: Extraction (DCM:isoprop) -> Separation Neutrals/Acidic (NH_2-silica)
-> esterification of acids (acetyl chloride+anhydrous methanol)
-> silylation was performed on some sample to ascertain identification

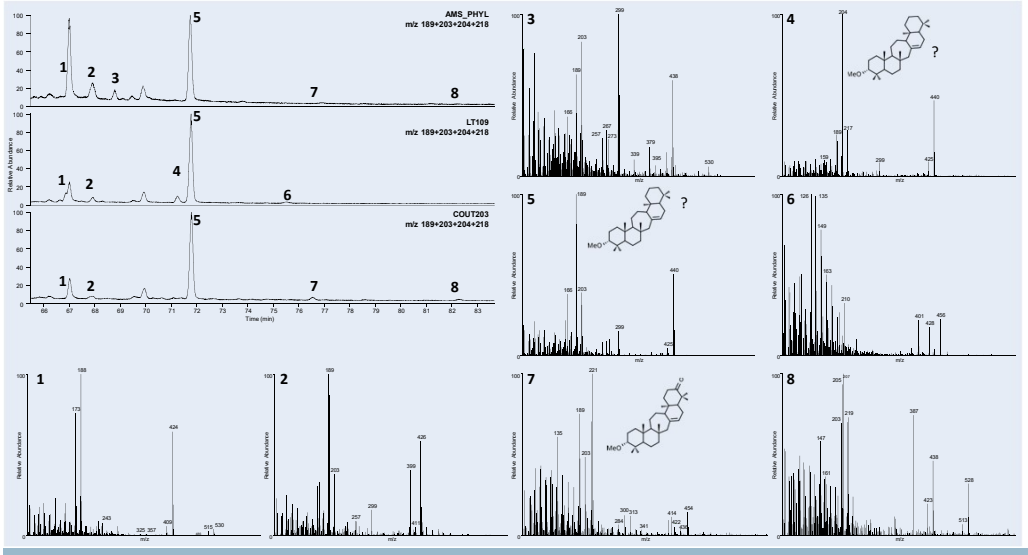
-> Test 1: better yields

Identification/quantitation

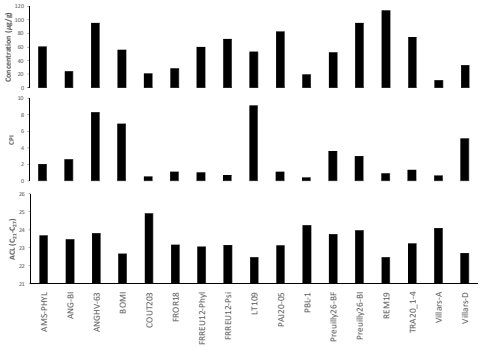
- GC: Trace 1300
  - Column: BPX5 60 m, 0.32 mm id, 0.25 µm
- MS: ISQ QD
- Identification with available standards

Biomarker distributions





Quantitations



Synthesis

Species	Division	Familly	C3-oxygenated pentacyclic triterpenes	Tricyclic diterpenes	Serratenes	Tetracyclic triterpenes
Austrocedrus chilensis	Gymno	Cupressaceae				
Fitzroya cupressoides	Gymno	Cupressaceae				
Sequoia	Gymno	Cupressaceae				
Araucaria Araucana	Gymno	Araucariaceae				
Cedrus sp.	Gymno	Pinaceae				
Picea linzhiensis	Gymno	Pinaceae				
Pinus sylvestris	Gymno	Pinaceae				
Nothofagus pumilio	Angio	Fagaceae				
Phylica arborea	Angio	Rhamnaceae				
Phylica nitida	Angio	Rhamnaceae				
Psidium guajava	Angio	Myrtaceae				
Quercus sp.	Angio	Fagaceae				

- Different preservation depending on age/conditions
- Sufficient amounts to get information at the tree ring scale
- Strong taxonomic relevance
- No difference
  - between initial and final wood
  - related to provenance/climate

Conclusions

This preliminary study indicates that lipids in tree rings, although not abundant, have the potential to retain environmental information. Future work will focus on a more detailed examination of quantitative differences related to provenance, climate and age of the samples and seasonal/annual variations through a tree ring core.

Le Milbeau et al. (2013). Methoxy-serratenes in a soil under conifers and their potential use as biomarkers of Pinaceae. Organic Geochemistry 55, 45-54.
Xu et al. (2004). On the origins of triterpenoid skeletal diversity. Phytochemistry 65, 261-291.

FROG French Researchers in Organic Geochemistry