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Methoxy-serratenes as discriminant biomarkers for soils developed under conifer forests

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INTRODUCTION

The evolution of landscapes through time constitutes a challenge for both archaeologists and paleoenvironmentalists. For example, human deforestation (for cultivation and building) strongly affected the shape of continental surfaces with supposed impacts on the global carbon cycle of which the timing and extent remains controversial.

Molecular biomarkers detected in soils can provide clue information on the past local vegetation, and thus on past land uses. In addition, if these biomarkers are transferred from soils to sedimentary archives, they can be used to reconstruct the evolution of ecosystems through time. Higher plant pentacyclic triterpenes are commonly associated with angiosperms and are increasingly used in environmental reconstructions. Due to their wide diversity of structures, functions and configurations, they constitute valuable chemotaxonomic targets, considering that a restricted number of organisms are able to synthesize specific structures. For example, pentacyclic triterpene methyl ethers can be related to Gramineae [1], [2] whereas triterpenyl acetates are mainly produced by Asteraceae [3]. Both reflect the development of open vegetation, either under the influence of climate or due to human activities.

MATERIALS AND METHODS

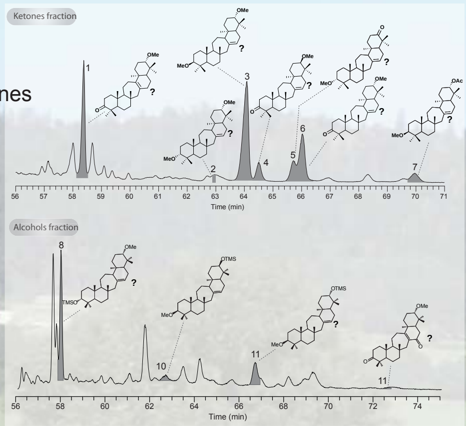
Soil samples were taken in the autumn of 2008 from Pessade forest, located on the north-eastern side of Sancy Massif (volcanic French Massif Central) in the Lake Aydat catchment, ca. 25 km SW Clermont Ferrand and mainly constituted by spruces and pines.

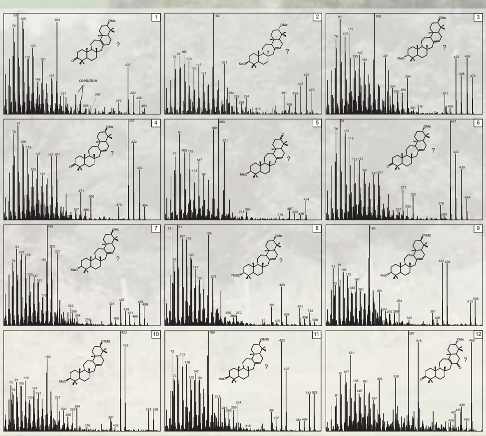
Samples were extracted using Accelerated Solvent Extraction (Dionex ASE 200) with DCM:MeOH (9:1) and separated into neutral, acidic and polar compounds by flash chromatography on aminopropyl-bonded silica. The neutral fraction was separated into five fractions (aliphatics, aromatics, ethers, ketones and alcohols) on silica gel column with solvent of increasing polarity before be analysed by GC-MS.

RESULTS

Neutral lipids are mainly composed by n-alkanes, sterols, stanones, stenones, diterpenes and diterpenols. A series of 11 original compounds were detected in the ketone and alcohol fractions.

Unsaturated pentacyclic triterpenes
Seven membered ring C
-> serratane structure
A methoxy group
Additional oxygenated groups
->methoxy,
->acetoxy,
-> ketone,
-> alcohol.





Concentrations range from 1 to 20 µg/g of soil.

DISTRIBUTION OF METHOXY-SERRATENES IN PLANTS

Bibliographic inventory of distribution of methoxy-serratenes in plants is summurized in the following tab :

	Pinaceae																	Taxodiaceae	Jungermanniaceae	Asteraceae	Neckeraceae
	Picea					Pinus											Cathaya	Taiwana	Nardia	Homogynes	Homalia
	abies	glehni	jezonensis (ajaensis)	obavata	sitchensis	armandii	banksiana	contorta	lambertiana	luchuensis	montelica	palustris	strobus	sylvestris	taeda	taiwanensis	argyrophylla	flousiana	scalaris	alpina	trichomanoides
21α-methoxyserrat-13-en-3-one (1)			x																		
3α,21α-dimethoxyserrat-14-ene (2)														x							
3β,21β-dimethoxyserrat-14-ene (3)									x	x	x			x							
21β-methoxyserrat-14-en-3-one (4)			x																		
3α-methoxyserrat-14-en-21-one (5)			x	x	x									x			x		x	x	
21α-methoxyserrat-14-en-3-one (6)	x																				
3β (or 3α)-methoxyserrat-14-en-21-yl acetate (7)																					
21α-methoxyserrat-14-en-3α-ol (8)																					
3α-methoxyserrat-14-en-21β-ol (9)	x	x	x	x																	
3β-methoxyserrat-14-en-21β-ol (10)	x	x	x	x	x						x										x
3β-methoxyserrat-14-en-21α-ol (11)									x	x	x					x					
21α-methoxyserrat-13-en-3,15-dione (12)			x																		
3α,21β-dimethoxyserrat-14-ene					x																
3β,21β-dimethoxyserrat-14-ene											x										
3α-methoxyserrat-14-en-21-yl formate		x																			
3β-methoxyserrat-13-en-21-one				x																	
3β-methoxyserrat-14-en-21-one			x	x	x	x			x	x	x		x	x							x
21β-methoxyserrat-14-en-3β-ol							x	x			x										
3α-methoxyserrat-14-en-21β-ol					x																x
3α-methoxyserrat-14-en-21α-ol					x																
21-acetoxy-3β-methoxyserrat-14-en-21α-ol										x								x			
3α-methoxy-21b-hydroxyserrat-14-en-16-one			x																		
3α-methoxyserrat-14-ene-21α,30-diol			x																		
3β-methoxyserrat-14-ene-21α,29-diol											x										
3β-methoxyserrat-14-ene-21β,29-diol											x										
29-hydroxy-3β-methoxyserrat-14-en-21-one						x															
3β-methoxyserrat-14-ene-21α,30-diol			x								x										
29-nor-3α-methoxyserrat-14-en-21-one			x																		
29-nor-3β-methoxyserrat-14-en-21-one			x			x					x										
21-oxo-3β-methoxyserrat-14-en-29-al						x															
21α-hydroxy-3β-methoxyserrat-14-en-29-al			x																		
21α-hydroxy-3β-methoxyserrat-14-en-30-al			x																		
Jezananal A and B			x																		
Piceanonol A		x	x																		
Piceanonol B			x																		
13α,14α-epoxy-3β-methoxyserratan-21β-ol			x																		
13α,14α-epoxy-21α-methoxyserratan-3-one			x																		
14β,15β-epoxy-3β-methoxyserratan-21-one			x																		
14β,15β-epoxy-3α-methoxyserratan-21β-ol			x																		
14β,15β-epoxy-3β-methoxyserratan-21β-ol			x																		

Serratane compounds are biosynthesized by many plants such as pines, spruces, ferns and club mosses.
Methoxy-serratenes are mainly biosynthesized by spruces and pines.

CONCLUSION

Methoxy-serratenes constitute novel tracers of conifers that are far more specific than classical diterpenoids. In addition, considering their lower volatility, they are likely to be preserved in lacustrine archives, although their resistance to early diagenetic processes remains to be documented. If resistant, there are likely to provide crucial information on the evolution of pine and spruce forests over decadal to millennial timescales.

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