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## Chemotaxonomic observations on some pliocenic woods from Arno Basin and fossil forest of Dunarobba (Italy)

### Abstract

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A new fossil wood from a lignite quarry in the Arno basin was examined for its terpene content. It was characterised by the lack of smell on comparison with two previous samples. Analysis has shown several components of diterpenes (abietane, abietatriene,  $\alpha$ -phyllocladane and simonellite) and only traces of sesquiterpenes in common with the previous samples. Comparison of all analysed samples with others from the fossil forest of Dunarobba shows the occurrence of many shared components especially diterpenes.

It is concluded that *Taxodioxyton gypsaceum*, the first species described from Dunarobba's forest, is probably the species which has given rise to the lignite of the Arno basin.

### Introduction

The first step in naming a living tree, as well as its geological remains, namely fossil woods, is given by botanical identification. This operation is carried out utilising several anatomical features characteristic for the species. However, in some cases these features are lacking, so that the use of chemotaxonomy is required. Chemical compounds of taxonomic value include secondary components of wood such as lignans, terpenes, phenols, etc. (Erdtman 1952).

Recently, some fossil softwoods were examined for their terpene components. The first fossil wood was from the fossil forest of Dunarobba and was identified as *Taxodioxyton gypsaceum* by Biondi & Brugiapaglia (1991). Other samples were from the lignite quarry of Castelnuovo dei Sabbioni (Arno basin), some of them identified as belonging to the genus *Sequoia*. Samples gathered at different times and in different sites in the quarry have been recognised as three distinct types apparently unlike in structure, smell and consistency. The first group (**A**) is characterized by an intense smell and the second one (**B**) by an imperceptible smell. Both were already been analysed and their terpene content discussed (Staccioli & al. 1993).

Analysis of last group (C), made up of scentless samples, constitutes the subject of the present study. Furthermore, comparisons with previously analyzed samples were made in order to make some botanical deductions from the chemical data.

### Material and Methods

The terpenoid fraction of the sample investigated was separated by steam distillation and recovered by extraction of the distillate with n-hexane (Browning 1967).

Gas chromatographic analysis was performed on a Shimadzu GC-14 instrument using a 2 m column FFAP 5% on chromosorb G AW DMCS kept at 50 °C for 10 min then heated up to 200 °C at a rate of 10 °C/min. Gas chromatography/ mass spectrometry was carried out on an INCOS 50 Finnigan MAT supported by the Wiley Database. The column used was of DB1 fused silica 30 m long, i.d. 0.32 mm, coating thickness 0.25 µm. The run data were: 80 °C for 5 min then to 280 °C at 3 °C/min. For the sake of comparison, the terpene fraction of previous analysed samples were re-examined by the same column.

### Results and Discussion

Figure 1 shows the total ion current of the components of the steam distillate of the fossil wood under investigation.

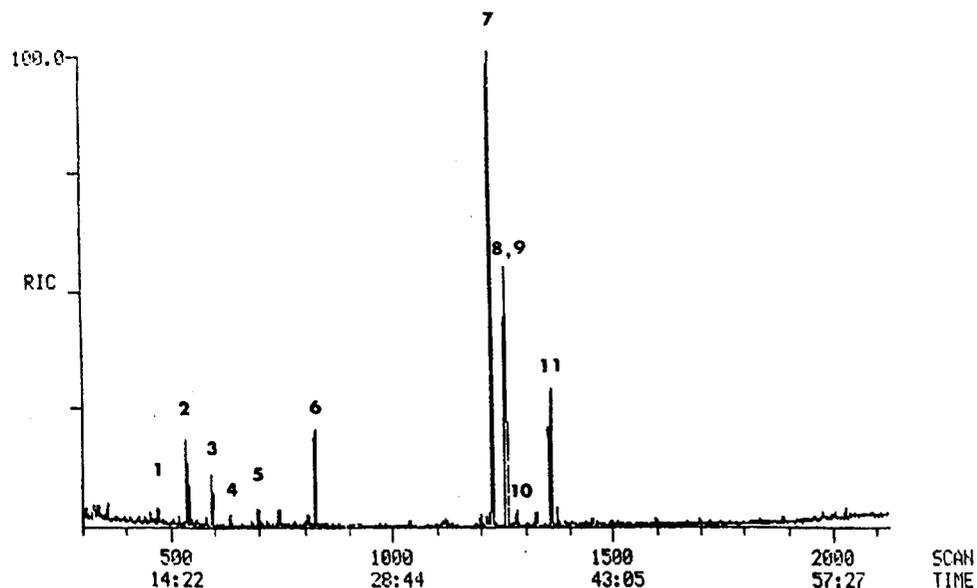


Fig. 1. Total ion current of the steam distillate of the scentless sample from the lignite quarry of the Arno Basin (C). Compound identity: 1 elemene; 2 & 3 selinane family sesquiterpanes; 4 208 MW sesquiterpene; 5 calamenene; 6 cadalene; 7 276 MW diterpene; 8  $\alpha$ -phyllocladane; 9 abietane; 10 abietatriene; 11 simonellite.

Table 1. Terpene components of three fossil woods from the Arno basin and one from the fossil forest of Dunarobba (Umbria).

Compound	MW	Arno basin			Dunarobba
		(A)	(B)	(C)	
sesquiterpene	194		tr		
sesquiterpene	208		x		
elemene	210	x	x	tr	tr
sesquiterpene	206	tr			
sesquiterpene	206	tr			
muurolane A	208	x		x	
sesquiterpene	206	x			
selinane-like s.	208				x
selinene-like s.	208				x
muurolane B	208	x			
sesquiterpene	206	tr			
sesquiterpene	206	tr			
sesquiterpene	206	tr			
$\alpha$ -cedrane	206	x	x		
selinane	208	xx	xx	x	
sesquiterpene	184			tr	
sesquiterpene	206	tr			
$\delta$ -selinene	204	x	x		
calamenene 1	202	x	x	tr	x
cadinatriene	202	x			
calamenene 2	202	x			
cadalene	198	x	x	x	x
diterpene	248				tr
diterpene	276	tr			
diterpene	274	tr			
norpimarane	276				x
sandoracopimarane	276	x		xx	
diterpene	276	tr			
isophyllocladene	272		xx		
abietane	276	x	x	x	x
$\alpha$ -phyllocladane	274	x	x	x	xx
abietatriene	276	x	x	tr	x
diterpene	276	tr			
simonellite	252	x	xx	x	x

tr means trace quantity, less than 1%

x means a quantity between 1% and 10%

xx means a quantity greater than 10%

Identification of the components was performed by a comparison with spectra reported in the literature, particularly those obtained from previous works on Dunarobba fossils (Staccioli & al. 1994) and on the other Arno basin lignites (Staccioli & al. 1993).

Likewise the previous samples, monoterpene compounds are totally lacking and sesquiterpenes are present in very low amounts in favour of diterpenes. The number of

compounds, however, is not large, the major component being a 276 MW diterpene (peak N° 7) already found by Livsey (1984) together with  $\alpha$ -phyllocladane and abietane (peaks N° 8 and 9) (Streibl & al. 1972), abietatriene (peak N° 10) and simonellite (peak N° 11) (Philp 1985). Other identified components were elemene which corresponds to the peak N° 1, first found in a fossil wood and proven by comparison with an authentic sample (Menchi & al. 1995). Further low amounts of sesquiterpenes of the selinene and cadinene families were shown from peak N° 2 to peak N° 6.

The results obtained allow us to reject the assumption that this specimen is different from the previously described perfumed ones (Staccioli & al. 1993) since its steam distillate shares several terpene compounds with them. Differences amongst the samples could be explained by the hypothesis that they represent the same species in different stages of degradation. Since Dunarobba fossils contain several terpenes in common with the Arno samples, the terpene components of four examined woods are compared in the Table 1.

The data show that the greatest number of components is present in the more perfumed sample (A) which previous analyses proved to possess the largest amount of terpenes. Moreover, the same mixture exhibits a balance between the lower molecular weight terpenes and the higher molecular weight diterpenes. The other samples contain, in fact, less sesquiterpenes and the portion of diterpenes becomes more important. There are several classes of compounds present in all four fossil samples examined: elemene, a monocyclic sesquiterpene; cadalene and calamenene which belong to bicyclic sesquiterpenes; several components of tricyclic and tetracyclic diterpenes, respectively abietane, abietatriene simonellite and  $\alpha$ -phyllocladane. It must be stressed that nearly all compounds appear in stable forms, with the exception of few terpenes which probably were not degraded from their original structures (for instance selinene and isophyllocladane). The occurrence of a high degree of similarity of terpenes in the four fossil samples suppose a sort of similarity of original species and a resemblance of terpene degradation paths. The selective terpene enrichment in some samples is surely due to an individual history of each sample after the first common degradation. From these data the occurrence of large forests made up of *Taxodioxylon gypsaceum*, or a closely related species, which covered areas near the fluvial lakes of central Italy can be deduced. Some trees were transformed into lignite and some survived as standing trunks on the shore of the old lake Tiberino near Dunarobba.

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