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Chemical characterisation of lignites from Montebamboli and Ribolla (South Tuscany, Italy) and botanical suggestions of their plant source material

Abstract

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Lignite samples from the mines of Montebamboli and Ribolla (southern Tuscany) are chemically investigated to assess whether they are made up of the fossil species *Taxodioxylon gypsaceum*, the same morphotaxon of the famous and monospecific Pliocene forest of Dunarobba (Umbria, central Italy). All the samples contain aromatic hydrocarbons as well as linear and branched alkanes. In addition, Montebamboli contains traces of cadalene and α-phyllocladane while Ribolla contains sesquiterpenes, diterpenes, and de-A-lupane. The presence of aromatic hydrocarbons and alkanes contrasts with the composition of materials of Dunarobba and Santa Barbara (Arno valley) as they contain, almost exclusively, terpenes. The residual terpenes of Montebamboli can only point to a generic conifer species while those of Ribolla suggest a blend of conifers and angiosperms since its terpenes do not agree in number and proportion with those of Dunarobba and Santa Barbara. Owing to the great degradation of the materials, shown by pyrolysis gas chromatography mass spectrometry analysis, cation exchange capacity values and indirect palaeobotany, the original plant material of the two lignites cannot be defined monospecific.

Introduction

A few decades ago, in a clay quarry near Dunarobba (Umbria, central Italy), a Pliocene fossil forest made up of numerous, huge, monospecific, still standing trunks was discovered. Based on anatomical characteristics the trunks were assigned to the fossil species *Taxodioxylon gypsaceum* (Biondi & Brugiapaglia 1991). Samples of two lignites from close to Dunarobba, examined to identify the original botanical species by means of residual terpenes, were tentatively assigned to the same fossil species constituting the fossil forest of Dunarobba (Staccioli & al. 1996a). In addition, the important lignite quarry of Santa Barbara (Arno valley), about 100 km north of Dunarobba, was shown to contain the same residual terpenes as those of Dunarobba trunks (Staccioli & al. 1996b). Only subsequently, based on anatomical examination of less degraded specimens, the characteristic structures of the morphotaxon *Taxodioxylon gyspaceum* were recognised in the Santa Barbara lignites (Biondi & al. 1998). Owing to the widespread distribution of the taxon *Taxodioxylon gypsaceum* during and before the Pliocene epoch in Central Italy (Biondi & al. 1998) and the similarity in geological history of the Umbria and Tuscany regions (Martini & Sagri 1993) the possibility that the original plant source could have been *Taxodioxylon gypsaceum* was investigated in other Tuscany lignite mines. In particular, the investigation was performed on the lignites of Montebamboli and Ribolla located in southern Tuscany about 100 km west of Dunarobba (Fig. 1).

The materials were examined by cation exchange capacity (CEC), residual terpene analysis (RTA) and pyrolysis gas chromatography mass spectrometry (Py GC MS). The CEC method is based on the property of unaffected lignocellulosic materials, for instance wood, bark, or leaves, to exhibit characteristic ranges of cation exchange values which arise from the presence of carboxyl groups (in acid, salt and ester forms) bound to their polyoses. Normally, the loss of polyoses causes the decrease or loss of CEC of fossils as previously shown by the analyses of several woods from Canadian arctic regions which, being 25-65 million years old, exhibited no or negligible CEC values (Staccioli & al. 1997).

Identification of residual terpenes as biomarkers of the original species in coals, fossil wood, and fuels (Hagemann & Hollerbach 1987 ; Grimalt & al. 1988; Dehmer 1989; Li & al. 1990; Hoppenheimer & al. 1992; Simoneit & al. 1986; Philp 1985) is also carried out on Montebamboli and Ribolla samples and the results compared with those of Dunarobba and Santa Barbara. During diagenesis terpenes are subjected to processes of simplification of their structures to form carbon skeleta (Dehmer 1989; Schultze & Michaelis 1990;

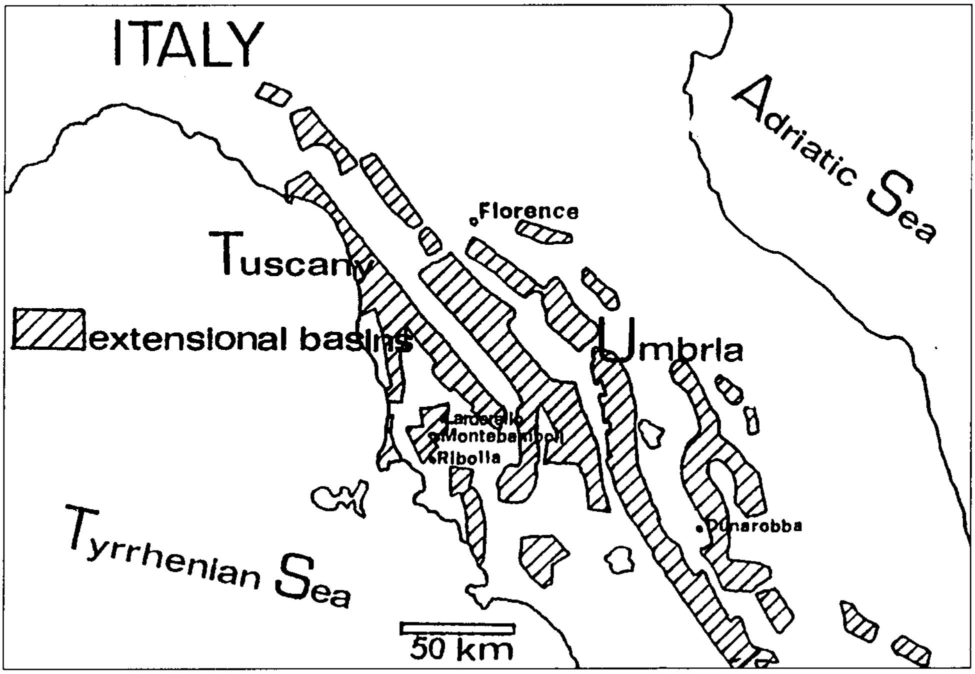

Fig. 1. Location of Montebamboli and Ribolla lignite pit mines and the geothermal fields of Larderello.

Staccioli & al.1994) , however, particular diterpenes such as phenol-diterpenes, distinctive of some species of geological ages, are less affected by diagenesis, owing to their stable aromatic structure (Otto & al. 1997; Staccioli & Bartolini 1997).

To assess the presence of polysaccharides and lignin and the extent of degradation of lignites, PyGCMS was also used. According to Hedges (1990), Allen & al. (1996), and Kuroda & Yamaguchi (1995) PyGCMS together with the main wood components enables the distinction between softwood and hardwood species and makes an evaluation of the effects of environmental influences possible.

Experimental

Materials and methods

Materials derived from the Miocene mines of Montebamboli and Ribolla (southern Tuscany), also famous for important recoveries of hominoid fossils (Huerzeler 1958). Lignite samples were collected from the entire main fields in areas which were well apart from each other. Geological evidence assigns to them an age of about 7 million years, corresponding to the Upper Messinian (Trevisan 1952). The site of deposition can be described as a lacustrine-marine environment (Martini & Sagri 1993). Their appearance and structure show that they are black lignites rather than xyloid lignites (Abbolito 1943). The interior parts of the samples were milled in a Wiley mill and the 40-60 mesh fraction (the standard particle size for chemical analysis of wood between 0.42 and 0.25 mm) was retained. The samples had a rather large inorganic content (from 10 to 25%), in particular sulphides, in agreement with the occurrence of pyrite mines in the same region and the development of hydrogen sulphide during incineration.

CEC measurements were carried out using 1 g of material, whose carboxyls were previously changed to acid form by means of treatment with a 1N HCl solution and with distilled water for elimination of excess acidity, as previously described elsewhere (Staccioli & al. 1997). To the modified sample, placed in a Gooch funnel, 200 ml of 3% sodium chloride solution was added for 1 h and the amount of acidity in the filtrate was assessed by titration and expressed as milliequivalents per 100 g of oven-dry material. Saponification of esters was achieved by treatment of the organic matter with a mild alkaline solution (3% sodium carbonate) for 3 days at room temperature. Holocellulose was prepared according to the Norman and Jenkins (N & J) method as reported by Browning (1967). Lignin was obtained according to the method described by Fengel & al. (1981).

While previously analysed lignites (Staccioli & al. 1994; Staccioli & al. 1996) were extracted by steam distillation, these lignites, because of the small amount of collected material, were extracted with dichloromethane (CH_2Cl_2). Equivalence of the two methods was proven in the case of the Dunarobba forest and lignites from nearby mines with unpublished results.

Five portions (1 g) of each lignite were individually extracted with 1 ml of HPLC grade CH_2Cl_2 for 15 min under ultrasonic vibration. The combined extracts of each sample were then gently evaporated to small volume under nitrogen and submitted to GC-MS analysis without any further manipulation.

Gc-ms apparatus and conditions

All measurements were carried out with a Hewlett-Packard GC-MS system consisting of a 5890 II Gas Chromatograph equipped with an HP Ultra-1 fused silica capillary column (25 m x 0.21 mm i.d., 0.33 μm) and a 5971A quadrupole mass analyser. A Hewlett-Packard Vectra 486 DX data system was used for data acquisition and editing. Gas chromatography of the dichloromethane extracts was carried out under the following operative conditions: isothermal at 130°C for 1 min, followed by a temperature increase of 3.5°C/min up to a final temperature of 250°C maintained for 15 min. The carrier gas flow in the chromatographic column was programmed at a constant value of 0.4 ml/min corresponding to a head pressure of 69 kPa at 130°C. The transfer line and injection temperatures were 280°C and 260°C, respectively. The injection volume was 1μl in the splitless mode (0.2 min) for all the samples. The mass spectrometer conditions were: electron energy, 70eV; emission current, 300 μA; ion source temperature,175°C. Electron impact mass chromatograms were obtained in the positive ion mode by repetitive scanning in the 50-450 mass range (cycle time 0.43 s).

Prolysis gas chromatography–mass spectrometry

The pyrolysis measurements were performed using a Curie-point pyrolyser (Horizon Instrument-England) device coupled with a GC/MS system (GC 8000/MD 800-Fison Instrument). The pyrolysis occurred at 610 °C for 5 sec and the related compounds were gas chromatographically separated using a capillary column (J & W DB-17, 15 m x 0.25 mm, film thickness: 0.5 μm) under the following operative conditions: 50 °C then at 290 °C at the rate 5 °C/min and hold at the final temperature for 10 min. Positive ions generated from analytes by electron ionisation were recorded in the 50-450 amu mass range at 200 °C ion source temperature.

Results and Discussion

Assessment of cation exchange capacity

Table 1 reports the CEC values of lignite samples from Montebamboli, Ribolla and Dunarobba as well of their derivatives N & J holocellulose and the Fengel lignin.

The Dunarobba values depict a situation where the hypothetical original carboxyl forms are transformed but not completely lost. In fact, the acid carboxyl fraction, present as a rule in conifer species, is totally salified and most of the original ester carboxyls are transformed into salt carboxyls. Moreover, the N & J holocellulose value, although lower than the sum of salt and ester carboxyls, shows that the holocellulose structure is preserved and contains most of the original carboxyl groups.

The Montebamboli values do not show any, or exhibit very low amounts of salt and ester carboxyls while the Ribolla samples give inhomogeneous results ranging from zero to values larger than those of Dunarobba. This large variability for Ribolla samples indicates that its source materials are more heterogeneous than those of Montebamboli and degraded to a different extent.

Table 1. Cation exchange capacities of Montebamboli, Ribolla, Dunarobba and of their N.& J. holocellulose and Fengel lignin.

	salt carboxyls	**esters**	**h**	
M.Bamboli 1	nil	0.5	traces	traces
M.Bamboli 2	nil	0.4	traces	traces
M.Bamboli 3	traces	0.6	traces	traces
Ribolla	nil	traces	traces	traces
Ribolla 2	2.8	2.7	traces	5.5
Ribolla 3	0.2	4.6	3.8	5.1
Ribolla 4	1.4	2.3	3.1	3.8
Dunarobba	6.2	2.5	5.6	1.2

All values are expressed as milliequivalents in 100g of oven dry material.

CH_2Cl_2 soluble components in Montebamboli lignite

Table 2 lists the components of the CH_2Cl_2 extract of the Montebamboli lignite samples. Their identification was carried out by GC/MS with the aid of a library search of mass spectra NIST data base or by direct comparison with authentic samples. The first eluting compounds were aromatic hydrocarbons (benzene, toluene, xylenes, naphthalenes, anthracenes, phenanthrenes) followed by n-alkanes. Benzofuran and dibenzothiophene (this latter probably related to the occurrence of sulfides) were minor constituents. Cadalene and α-phyllocladane were present in trace amounts. These latter compounds can be classified as biological markers because their relationship to precursor compounds present in the original plant is known (Philp 1985). Aliphatic hydrocarbons were largely composed of members of the n-alkane series from C18 to C31; the branched hydrocarbon pristane and phytane were also present in small amounts.

From a quantitative point of view, the principal compounds were naphthalene and the isomers of methylnaphthalene. These classes of compounds are greatly different from those of the Dunarobba fossil forest and the Santa Barbara lignites, showing almost exclusively residual terpenes.

Table 2. Components of CH_2Cl_2 extracts of Montebamboli and Ribolla lignite samples vs. *Taxodioxylon gypsaceum* of the Dunarobba fossil forest.

No	Compound	Samples							
		MB1	MB2	MB3	RB1	RB2	RB3	RB4	TG
1	naphthalene	xx	xx	xx	x	x	x	x	
2	hydrocarbon	tr	—	—	tr	—	—	tr	
3	methylnaphthalene	xx	xx	xx	x	x	x	x	

Table 2. (continued).

4	methylnaphthalene	xx	xx	xx	x	x	x	tr	
5	ionene	—	—	—	-	tr	-	tr	
6	hydrocarbon	—	—	—	tr	-	-	tr	
7	elemane	—	—	—	—	tr	—	tr	m
8	dimethylnaphthalene	x	x	x	x	x	tr	x	
9	206 MW sesquiterpene	-	-	—	-	-	-	-	tr
10	dimethylnaphthalene	x	l	x	tr	tr	tr	tr	
11	dimethylnaphthalene	x	x	x	tr	tr	tr	tr	
12	muurolane	—	—	—	—	tr	—	tr	
13	dimethylnaphthalene	tr	tr	—	tr	tr	tr	tr	
14	hydrocarbon	l	l	—	l	—	tr	—	
15	naphthalene derivative	tr	tr	—	tr	tr	tr	tr	
16	selinane	—	—	—	—	tr	—	tr	
17	unknown	—	—	—	tr	tr	tr	—	
18	dibenzofuran	l	l	tr	tr	—	—	—	
19	calamenene 1	-	-	—	-	-	-	—	m
20	hydrocarbon	—	—	—	tr	—	—	—	
21	methylionene	—	—	—	—	tr	—	tr	
22	trimethylnaphthalene	l	l	tr	tr	tr	tr	tr	
23	trimethylnaphthalene	l	l	tr	l	tr	tr	tr	
24	cadinatriene	—	—	—	—	tr	—	tr	
25	norcadalene	tr	—	—	—	-	—	—	
26	trimethylnaphthalene	l	l	tr	tr	tr	tr	tr	
27	calamenene	—	—	—	—	tr	—.	tr	
28	trimethylnaphthalene	l	l	tr	-	-	-	tr	
29	methyldibenzofuran	l	tr	tr	l	tr	tr	tr	
30	hydrocarbon	x	l	—	l	tr	tr	tr	
31	cadalene	tr	tr	tr	-	x	x	x	
32	hydrocarbon	x	l	—	l	tr	tr	tr	
33	pristane	xx	xx	x	xx	x	x	x	
34	heptadecane	tr	tr	tr	l	l	l	tr	
35	196 MW compound	tr	tr	—	-	-	-	tr	
36	dibezothiophene	tr	tr	—	.	-	-	—	
37	anthracene	l	l	tr	l	l	l	l	
38	phenanthrene	tr	tr	tr	l	l	tr	tr	
39	phytane	l	l	tr	tr	-	-	tr	
40	octadecane	x	x	tr	l	l	tr	tr	
41	tetrahydroretene	-	-	—	-	-	-	—	tr
42	methyldibenzothiophene	tr	tr	tr	tr	—	—	—	
43	210 MW compound	tr	tr	tr	-	-	-	—	

Table 2. (continued).

44	metylphenanthrene	tr	tr	—	-	-	-	—	
45	nonadecane	x	x	tr	tr	tr	tr	—	
46	276 MW diterpane	-	-	—	-	-	-	—	tr
47	274 MW diterpane	-	-	—	-	-	-	—	tr
48	276 MW diterpane	-	-	—	-	-	-	—	l
49	276 MW diterpane	-	-	—	-	-	-	—	l
50	4,9dimethylnaphthothiophene		tr	tr	—	-	-	-	—
51	2,8dimethylbenzothiophene		tr	tr	—	-	-	-	—
52	eicosane	x	x	tr	l	l	l	l	
53	dimethylphenanthre	x	x	tr	x	tr	tr	tr	
54	abietane	-	-	—	-	-	-	—	m
45	α-phyllocladane	tr	tr	tr	tr	l	l	l	m
56	abietatriene	-	-	—	-	-	-	—	m
57	simonellite	-	-	—	-	-	-	—	m
58	heneicosane	x	l	tr	l	l	l	l	
59	docosane	l	x	l	tr	tr	tr	tr	
60	phenolditerpene	-	-	—	-	-	-	tr	tr
61	tricosane	x	l	tr	l	l	l	l	
62	306 MW compound	tr	tr	tr	tr	tr	—	tr	
63	330 Mw compound	-	-	—	tr	tr	—	tr	
64	310 MW compound	tr	tr	tr	tr	—	—	tr	
65	342 MW compound	-	-	—	x	—	—	—	
66	tetracosane	x	x	tr	tr	tr	tr	tr	
67	de-A-lupane	-	-	—		xx	tr	l	l
68	342 MW compound	-	-	—	l	—	—	tr	
69	pentacosane	x	l	tr	l	l	l	l	
70	squalene	-	-	—	-	-	-	—	l
71	324 MW compound	-	-	—	tr	tr	—	—	
72	hexacosane	l	l	tr	tr	tr	tr	tr	
73	338 MW compound	-	-	—	tr	tr	—	—	
74	heptacosane	l	l	tr	l	l	tr	tr	
75	hydrocarbon	-	-	—	tr	tr	—	—	
76	octacosane	l	-	—	tr	tr	tr	tr	
77	nonacosane	l	l	tr	l	l	l	tr	
78	tricosane	l	l	tr	tr	tr	tr	tr	
79	henatricosane	l	l	tr	l	tr	tr	tr	

Notes

xx	means an amount larger than 10%
x	means an amount between 5 and 10%
l	means an amount between 1 and 5%
tr	means an amount less than 1%

n-alkanes from octadecane to henatricosane were identified from chromatograms not reported in this paper.

CH_2Cl_2 soluble components in Ribolla lignite

The components of the CH_2Cl_2 extract of Ribolla samples are reported in Table 2. Similar to the case of Montebamboli samples, the first components were aromatic compounds with essentially the same structures exhibited by the Montebamboli extract. In order, linear alkanes from C18 to C31 as well as pristane and traces of phytane were eluted analogously to the Montebamboli extract. Among terpene-related compounds, the terpenes elemane, muurolane, selinane, cadalene, calamenene, cadinatriene, ionene and methylionene were detected. In addition, two compounds of 342 MW as well as de-A-lupane were found. According to Philp (1985), ionene and methylionene are typical carotenoid degradation products of spores and were proposed as markers of sporopollenin from both gymnosperm and angiosperm species. De-A-lupane derives from triterpenoid constituents of higher terrestrial plants (Philp 1985) and indicates plant material predominantly derived from land plants belonging to angiosperms. The mass spectra of two unidentified compounds close to de-A-lupane's Rf do show some similarities with those of de-A-lupane, but they are insufficient to suggest that they are related to each other.

Comparison of the twoF lignites

As shown in Figure 2, the CH_2Cl_2 extract components of the two lignites exhibit similarities to the extent that a relationship must link the samples from the two mines since they both contain aromatic hydrocarbons, linear alkanes, pristane and phytane together with variable traces of terpenoids. The common geological history and the two extensional basins close to each other can explain the apparent similar composition of the two lignites. The Montebamboli lignites are, however, much richer in aromatic compounds than the Ribolla ones. This may point to some thermal influence which is different for the two lignite sites. The presence of the thermal source of Larderello about 4 km from Montebamboli and 25 km from Ribolla could explain this difference in aromatic hydrocarbon content. With reference to the origin of n-alkanes, their occurrence has been well established in the range from C7 to C20 in various plants and micro-organisms; alkanes with a carbon number of more than 20 probably derive from plant waxes (Eglinton & Hamilton 1963).

The predominance of odd- or even-numbered carbon alkanes (Caldicott & Eglinton 1973) may be taken into consideration in order to obtain information about the relative maturity of a fuel. From this point of view, the Ribolla sample has even-numbered carbon n-alkanes with a lower concentration of odd-numbered ones suggesting that material from this site was more recent (or immature). This is confirmed by common evaluation and studies carried out some years ago when the mines were exploited (Abbolito 1943 ; Cipriani & Tanelli 1983).

The branched hydrocarbon pristane is useful for gaining information about the environmental conditions of deposits. Powell & Mc Kirdy (1973) and Brooks & al. (1969) pointed out that pristane is formed in coals before phytane. Lignite samples contain the phytane hydrocarbon in traces; the occurrence of pristane in amounts larger than phytane seems to indicate an oxidising environment during diagenesis of the two lignites (Philp 1985).

According to Goossens & al.(1963), another possible source of pristane is tocopherols which can be degraded under rather severe conditions. Since tocopherols are relatively

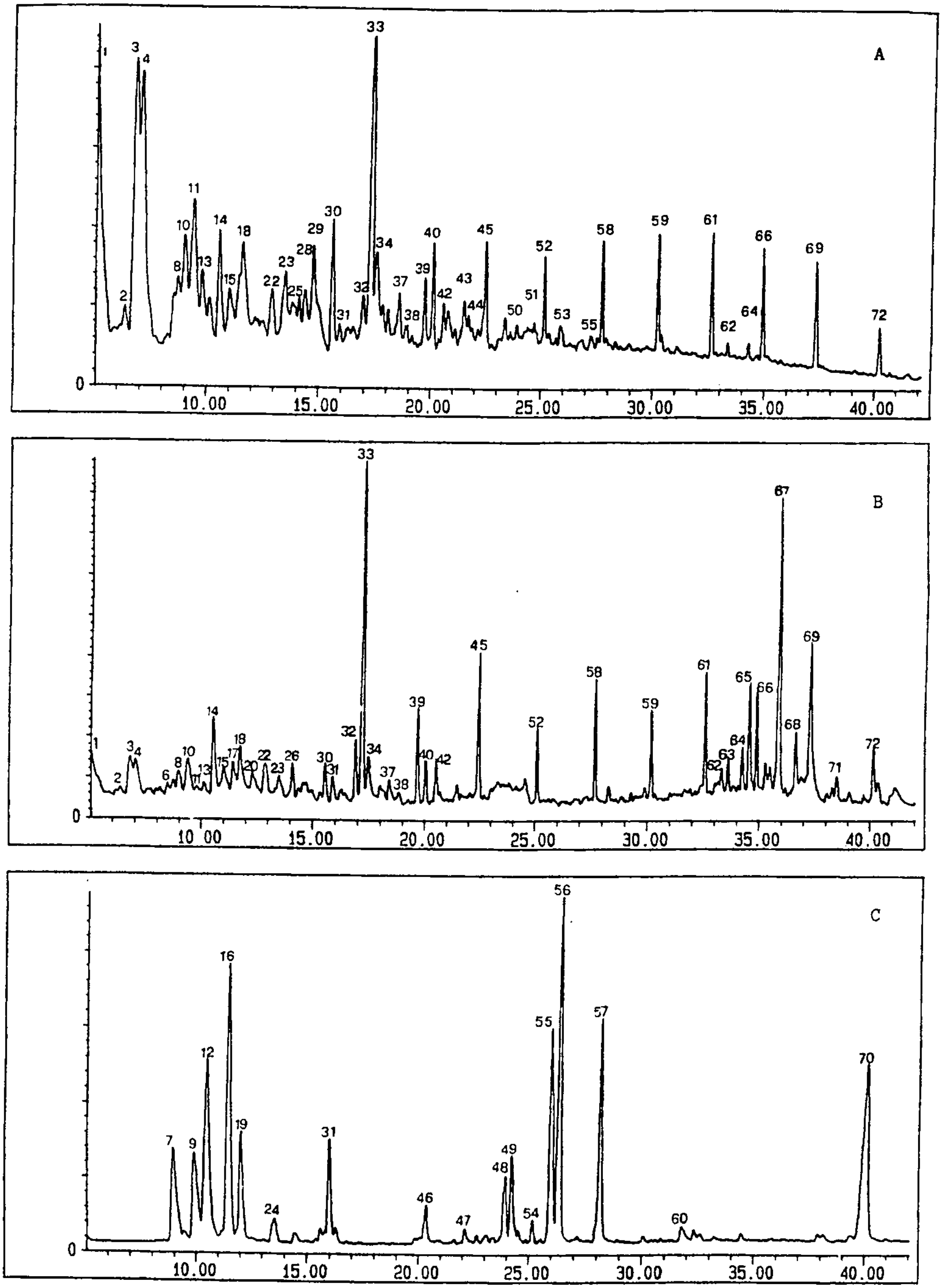

Fig. 2. Gas Chromatogram Mass Spectrometry (GC-MS) of the lignite dichloromethane extracts. Total ion current (TIC) traces of Montebamboli (A), Ribolla (B) and of the *Taxodioxylon gypsaceum* from the Dunarobba fossil forest (C).

abundant in algae, cyanobacteria and higher plants (Newton & al.1977), the suggested pathway could support the predominance of pristane with respect to phytane in the examined lignites. However, recent analyses on CH_2Cl_2 extracts from a 24 million-year-old white pine from the Canadian arctic have shown the presence of this compound among other degraded terpenoids (Staccioli & al. 1998).

Pyrolysis gas chromatography-mass spectrometry analysis

In Figure 3 the total ion current (TIC) traces from Py-GC-MS of samples of Dunarobba, Montebamboli and Ribolla are reported. A list of all identified pyrolysis components is given in Table 3.

Table 3. Compounds identified in the pyrolysate of *Taxodioxylon gyspaceum* and in the lignites of Montebamboli and Ribolla.

No.	Compound	No.	Compound
1	phenol	23	cadinatriene
2	cresol	24	eugenol
3	cresol	25	dodecanoic acid
4	guaiacol	26	phytane
5	xylenol	27	sesquiterpane
6	ethylphenol	28	tetradecanoic acid
7	naphthalene	29	cadalene
8	methylguaiacol	30	diterpane
9	elemane	31	sesquiterpane
10	methylfuraldehyde	32	pentadecanoic acid
11	dihydrobenzofuran	33	238 MW compound
12	muurolane	34	hexadecanoic acid
13	ethylguaiacol	35	abietane
14	cadinane	36	α-phyllocladane
15	methylnaphthalene	37	octadecanoic acid
16	methylpyrocatecol	38	abietatriene
17	methylnaphthalene	39	simonellite
18	vinylguaiacol	40	308 MW compound
19	selinane	41	306 MW compound
20	sesquiterpane	42	plasticiser
21	dimethylnaphthalene	43	squalene
22	pristane		

Since the Dunarobba sample is a fossil the pyrolysis does not supply the products exhibited by a modern conifer species (Saiz-Jimenez 1987). The only product ascribable to polysaccharides is methylfuraldehyde which derives from pyrolysis of hexoses which excludes the presence of a large amount of pentosans, for instance xylans. The compounds derived from lignin are similar to those reported by Saiz-Jimenez (1987) for a fossil spruce, as both derive from softwood species.

Neither Montebamboli nor Ribolla samples present compounds related to polysaccha-

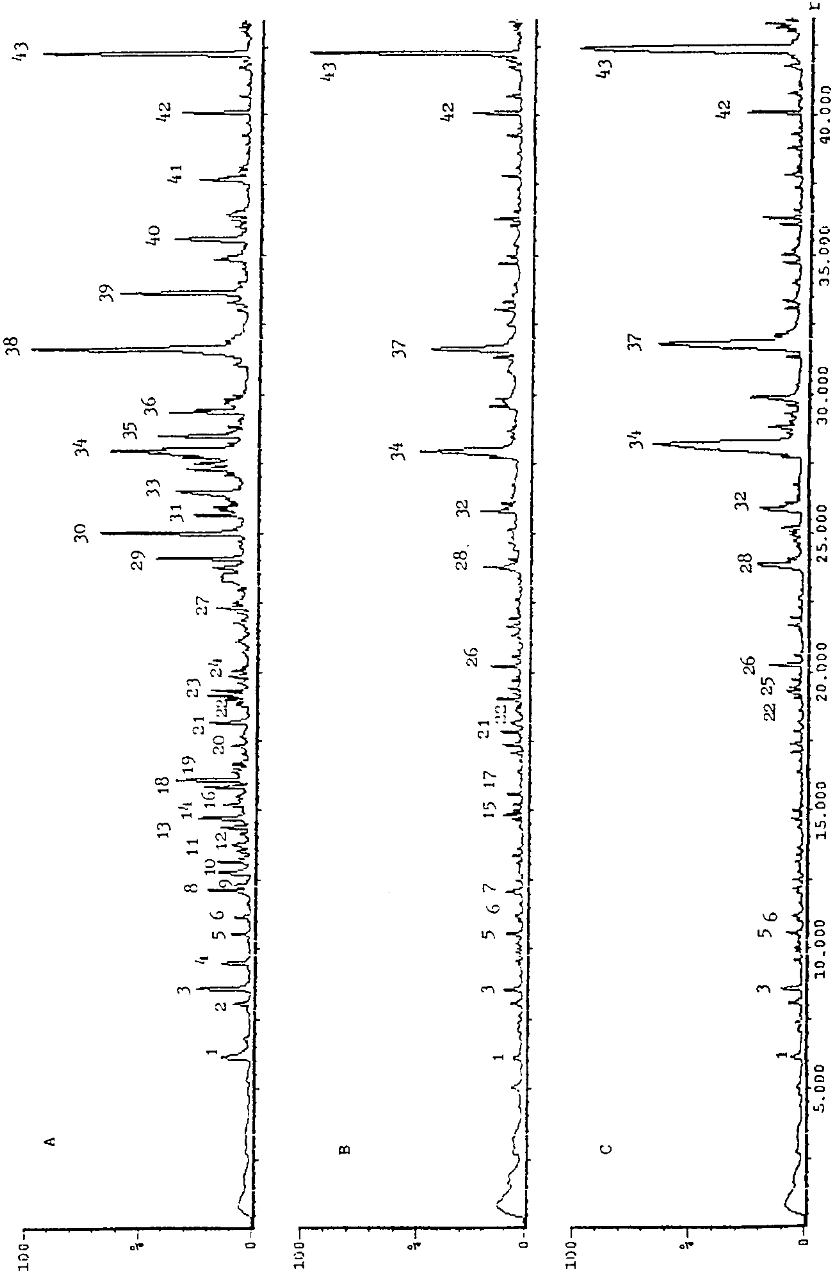

Fig. 3. Pyrolysis-gas chromatography-mass spectrometry of the sample of *Taxodioxylon gypsaceum* from the fossil forest of Dunarobba (1) and the lignites of Ribolla (2) and Montebamboli (3).

rides and those expected from lignin are limited to traces of less complex structures such as phenol and cresols. It can be inferred that the structure of lignins from Montebamboli and Ribolla is quite simplified since most of the methoxyl groups, characteristic of lignin, were lost. Since the complex structures of guaiacyl and syringyl type (characteristic of conifer and broadleaf species, respectively) are lacking nothing can be suggested about the presence of broadleaf species. In fact, due to the loss of methoxyl groups during diagenesis, the simplified structures can be derived from either possible structures. Both lignites also show some fatty acids together with compounds of naphthalene and phenanthrene series with the proportion already determined in the CH_2Cl_2 analyses: the content is greater for Montebamboli than for Ribolla. Other compounds include n-alkanes, pristane, phytane and some terpenoids.

Botanical inferences

The analysis of residual terpenes of the fossil species Dunarobba have indicated several compounds characterising the morphotaxon *Taxodioxylon gypsaceum*. In particular, elemane, cadinanes, muurolanes, selinane, cadalene, calamenene and cadinatriene derive from degradation of original sesquiterpenes while abietatriene, abietane, sandaracopimarane, α-phyllocladane and simonellite result from degradation of diterpenes (Staccioli & al. 1994). Moreover, the amount of residual diterpenes and sesquiterpenes should be taken into consideration. In fact, the diterpene content is always larger than that of sesquiterpenes and this was also confirmed from a recent analysis of a mineralised sample of *Taxodioxylon gypsaceum* from the same fossil forest of Dunarobba (Staccioli & al. in press).

On the contrary, the residual terpenes of the Montebamboli lignites (namely cadalene and a-phyllocladane) are not specific to any particular fossil conifer and cannot supply the identification of the exact plant species from which they were derived.

The components of Ribolla lignite are rather different from that of Montebamboli in this respect. The number of terpenes is much higher but they do not meet all the requirements of *Taxodioxylon gypsaceum* composition. In particular, the residual sesquiterpene amount is larger than that of residual diterpenes. Since sesquiterpenes are, as a rule, lost more easily than diterpenes greater quantities of the former cannot derive from an homogeneous material. The identified sesquiterpenes could be then related to parts of trees richer in sesquiterpenes than in diterpenes, for instance conifer needles or barks (Fengel & Wegener 1984). The other biomarkers identified in the lignites are generically related to the degradation of pollens (ionene and methylionene) so that the botanical species cannot be identified (Philp 1985). Analogously, the compound de-A-lupane, referring to triterpene compounds of hardwood species, cannot be used to indicate specific angiosperms.

Indirect palaeobotanical information

Unfortunately, the Montebamboli and Ribolla sites, as well as other sites in the mine district of southern Tuscany have not been investigated from a palaeobotanical point of view. However, some palynological investigations were recently carried out on the lignite mine of Baccinello located about 40 km and 60 km southwest of Ribolla and

Montebamboli, respectively (Harrison & Harrison 1989). The three mines are connected by geological history and by the recovery in their lignite layers of complete skeletons (Baccinello and Montebamboli) and relative parts (Ribolla) of the hominoid *Oreopithecus bambolii*. According to Harrison and Harrison (1989), pollen and spore analysis of the *Oreopithecus*-bearing lignite provides evidence of a lowland mixed mesophytic forest. Trees were gymnosperms and angiosperms but aquatic trees, shrubs and algae were also present. The most important gymnosperm families were *Taxodiaceae*, *Taxaceae* and *Pinaceae*, whereas angiosperms were represented by the genera *Alnus*, *Quercus* and *Tilia*.

Conclusions

The lignites of Montebamboli and Ribolla show rather similar CH_2Cl_2 extracts consisting of aromatic hydrocarbons from benzene to phenanthrene, some of their homologues, several linear alkanes, the isoprenoid hydrocarbons pristane and phytane together with small amounts of residual terpenes. The presence of greater amounts of aromatic hydrocarbons in Montebamboli than in Ribolla suggests a thermal degradation of the two lignites that could be imputed to the geothermal field of Larderello with high temperature steam sources much closer to Montebamboli.

While the residual terpenes of Montebamboli can only suggest that its lignite is derived from conifer species, the Ribolla ones do not completely match in amount and composition with the biomarkers of *Taxodioxylon gypsaceum*. Ribolla's large amount of residual sesquiterpenes can be imputed to other tree parts like bark and leaves (Fengel and Wegener 1984)· while the presence of ionene, methylionene and de-A-lupane, not strictly specific to conifers (Philp 1985), suggests the presence of hardwood inputs.

The low CEC values of Montebamboli suggest a strong influence of the environment on the original material while samples with high CEC values point to remains of not completely degraded lignocellulosic material, probably the source of sesquiterpenes and diterpenes.

Pyr GC MS data demonstrate that both lignites contain small amounts of polysaccharides and that their lignin was degraded to such an extent to possess only traces of methoxyl groups making any hypotheses on the original plants (whether conifer or broadleaf alone or a blend of both) possible .

Palaeobotanical clues from palynological studies on another mine in the southern Tuscany district, coherent with the previous ones, indicate that the most abundant families were *Taxodiaceae*; followed by *Taxaceae*, *Pinaceae* as well as the broadleaf genera *Alnus*, *Quercus* and *Tilia*. These results indicate that the materials of Montebamboli and Ribolla are botanically different from those of Dunarobba and Santa Barbara and the monospecific community found in Dunarobba and Santa Barbara represent an exceptional event which did not occur in sites with similar geological history.

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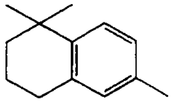
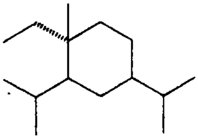
Appendix. Structures of some biomarkers occurring in Montebamboli, Ribolla and *Taxodioxylon gypsaceum* samples.



I. ionene



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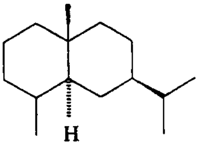
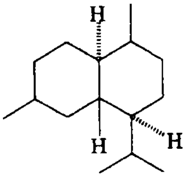
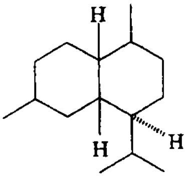


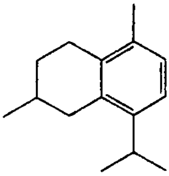
III. selinane



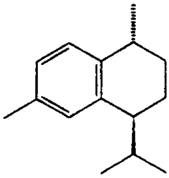
IV. cadinane



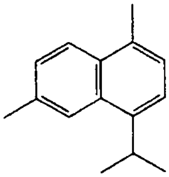
V. muurolane



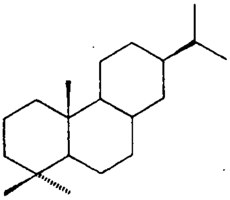
VI. cadinatriene



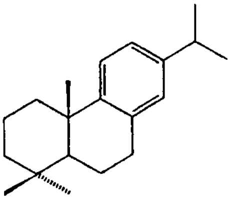
VII. calamenene



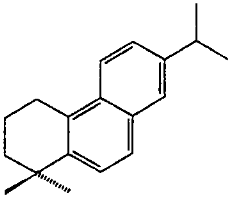
VIII. cadalene



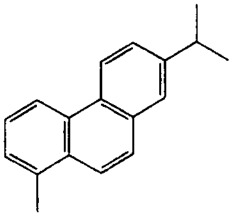
IX. abietane



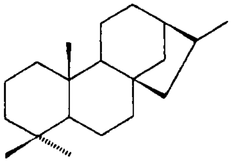
X. abietatriene



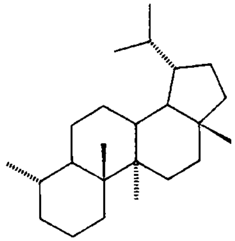
XI. simonellite



XII. retene



XIII.α -phyllocladane



XIV. de-A-lupane