Naturwissenschaften (2007) 94:228–236
DOI 10.1007/s00114-006-0179-x

SHORT COMMUNICATION

Biomolecules preserved in ca. 168 million year old fossil conifer wood

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Received: 27 June 2006 / Revised: 18 September 2006 / Accepted: 10 October 2006 / Published online: 1 December 2006

Abstract Biomarkers are widely known to occur in the fossil record, but the unaltered biomolecules are rarely reported from sediments older than Paleogene. Polar terpenoids, the natural products most resistant to degradation processes, were reported mainly from the Tertiary conifers, and the oldest known are Cretaceous in age. In this paper, we report the occurrence of relatively high concentrations of ferruginol derivatives and other polar diterpenoids, as well as their diagenetic products, in a conifer wood *Protopodocarpoxylon* from the Middle Jurassic of Poland. Thus, the natural product terpenoids reported in this paper are definitely the oldest polar biomolecules detected in geological samples. The extracted phenolic abietanes like ferruginol and its derivatives (6,7-dehydroferruginol, sugiol, 11,14-dioxopisiferic acid) are produced only by distinct conifer families (Cupressaceae s. l., Podocarpaceae and Araucariaceae), to which *Protopodocarpoxylon* could belong based on anatomical characteristics. Therefore, the natural product terpenoids are of great advantage in systematics of fossil plant remains older than Paleogene and lacking suitable anatomical preservation.

Keywords Biomolecules · Fossil conifer wood · Middle Jurassic

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Introduction

Organic compounds derived from formerly living organisms are ubiquitous in sedimentary organic matter. Despite various biological and abiotic alterations of the biomolecules in the sediments, some compounds retain their basic skeletal structures and can be used as characteristic molecular markers (biomarkers; Peters et al. 2005). The presence of sedimentary biomarkers have been reported in rocks back to the Precambrian (Jackson et al. 1986; Brocks et al. 1999, 2005), but unaltered biomolecules are rarely preserved in sediments older than Paleogene (Briggs et al. 2000). Taking into account the current knowledge, it appears that the natural products most resistant against degradation processes, apart from *n*-alkanes and fatty acids derived from leaf waxes, are cyclic natural products, the terpenoids (Otto et al. 2002a,b). Triterpenoids of the fernane class were isolated from Triassic sediments with embedded remains of the seed fern *Dicroidium* (Paull et al. 1998). However, the terpenoids included only fernane-type hydrocarbons, and polar bioterpenoids were not found. Polar terpenoids such as ferruginol, sugiol, and other phenolic diterpenoids were reported predominantly from Tertiary conifers, sediments, resinites, and lignites from

different locations (e.g., Grimalt et al. 1988; Stefanova et al. 2002; Otto and Simoneit 2001; Otto et al. 2002a, 2003, 2005). The oldest polar terpenoids are known from Cretaceous resinites (Alonso et al. 2000) and a few Cretaceous gymnosperm remains, such as *Sphenolepis* (Otto et al. 1999) and *Tritaenia* (Otto et al. 2002b). In all these cases only minor amounts of ferruginol and other unaltered terpenoids were detected.

In this paper, we report the occurrence of relatively high concentrations of ferruginol derivatives and other polar diterpenoids, as well as their diagenetic products, in a fossil wood sample identified as a species of *Protopodocarpoxylon* Eckhold (Philippe et al. 2002) from the Middle Jurassic (Bathonian) of the Polish Jura, south-central Poland. Taking into account only the most significant occurrence of such biological compounds in Eocene and Miocene conifers (Otto et al. 2002a), the natural product terpenoids reported in this paper are definitely the oldest polar biomolecules detected in geological samples.

Materials and methods

Sampling and samples pre-treatment

The fossil woods were collected in two active clay-pits ('Gnaszyn' and 'Anna') located in Gnaszyn Dolny and Kawodrza Dolna near Częstochowa, south-central Poland (Fig. 1), where the Middle Jurassic (Middle Bathonian to Upper Bathonian) clays are exposed, being a part of the Polish Jura monoclinal structure (Kopik 1998; Matyja and Wierzbowski 2000; Zatoń and Marynowski 2006). The wood samples consist of the following conifer taxa: *Protopodocarpoxylon* Eckhold (Philippe et al. 2002), *Agathoxylon* sp., *Xenoxylon phyllocladoides* Gothan, and *Protaxodioxylon* sp. (see Fig. 2; Table 1). Generally, the wood remains in the Polish Jura area occur abundantly in uppermost Bajocian through Bathonian sediments. They occur either as scattered fragments in the host clays or are embedded in carbonate concretions.

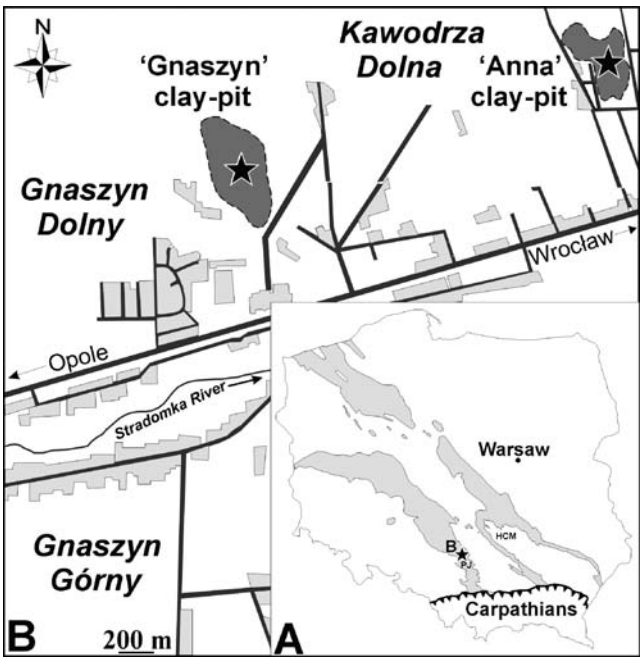

Fig. 1 **a** Map of Poland indicating Jurassic sediments (*shaded*) and study area (*asterisk*). *PJ* Polish Jura, *HCM* Holy Cross Mountains. **b** The investigated Gnaszyn/Kawodrza area with sampled clay-pits (*asterisks*)

For the present investigation, all samples were derived from the Middle (Morrisi Zone–'Gnaszyn' clay-pit) and Upper Bathonian (lower part of the Hodsoni Zone=Bremeri Zone–'Anna' clay-pit) interval, as was dated using ammonites [see Matyja and Wierzbowski (2003); Zatoń et al. (2006)]. According to the time-scale of Gradstein et al. (2004), the sediments containing the wood investigated are about 168 millions year old. All the samples were collected from within the clays and carbonate concretions. The wood remains occurring in the surface and sub-surface of the exposures were omitted due to their possible weathering.

In the laboratory, the wood samples were treated with methanol/acetone mixture to remove any potential contaminants. For further analyses, subsamples were taken from within larger wood pieces to obtain as unweathered material as possible.

Analytical methods

For anatomical investigations, all samples were studied as Parlodion® casts. A radial fresh fracture was prepared, and then liquid Parlodion® (purified pyroxylin) was applied. After 1 day of drying, the Parlodion® cast was peeled off, mounted on a glass slide, and observed under a normal transmitted light microscope. Freshly polished wood fragments were used in the reflectance analysis. The analyses were carried out using the Axioplan II microscope adapted for reflected white light in oil immersion and a total magnification of 500×. The standard used was 0.42%.

For organic geochemistry analyses, the fossil wood was pulverized and Soxhlet-extracted in pre-extracted thimbles with organic solvent (dichloromethane/methanol, 90:10 v/v). An aliquot of the total extract was converted to the trimethylsilyl derivatives by reaction with *N*,*O*-bis-(trimethylsilyl)trifluoroacetamide and pyridine for 3 h at 70°C. Gas chromatography–mass spectrometry (GC–MS) analysis of the derivatized total extract was performed on a Hewlett–Packard model 6890 GC coupled to a Hewlett–Packard model 5973 quadrupole MSD. Separation was achieved on fused silica capillary columns coated with DB5 (30 m× 0.25 mm i.d., 0.25 μm film thickness) and DB35 (60 m×

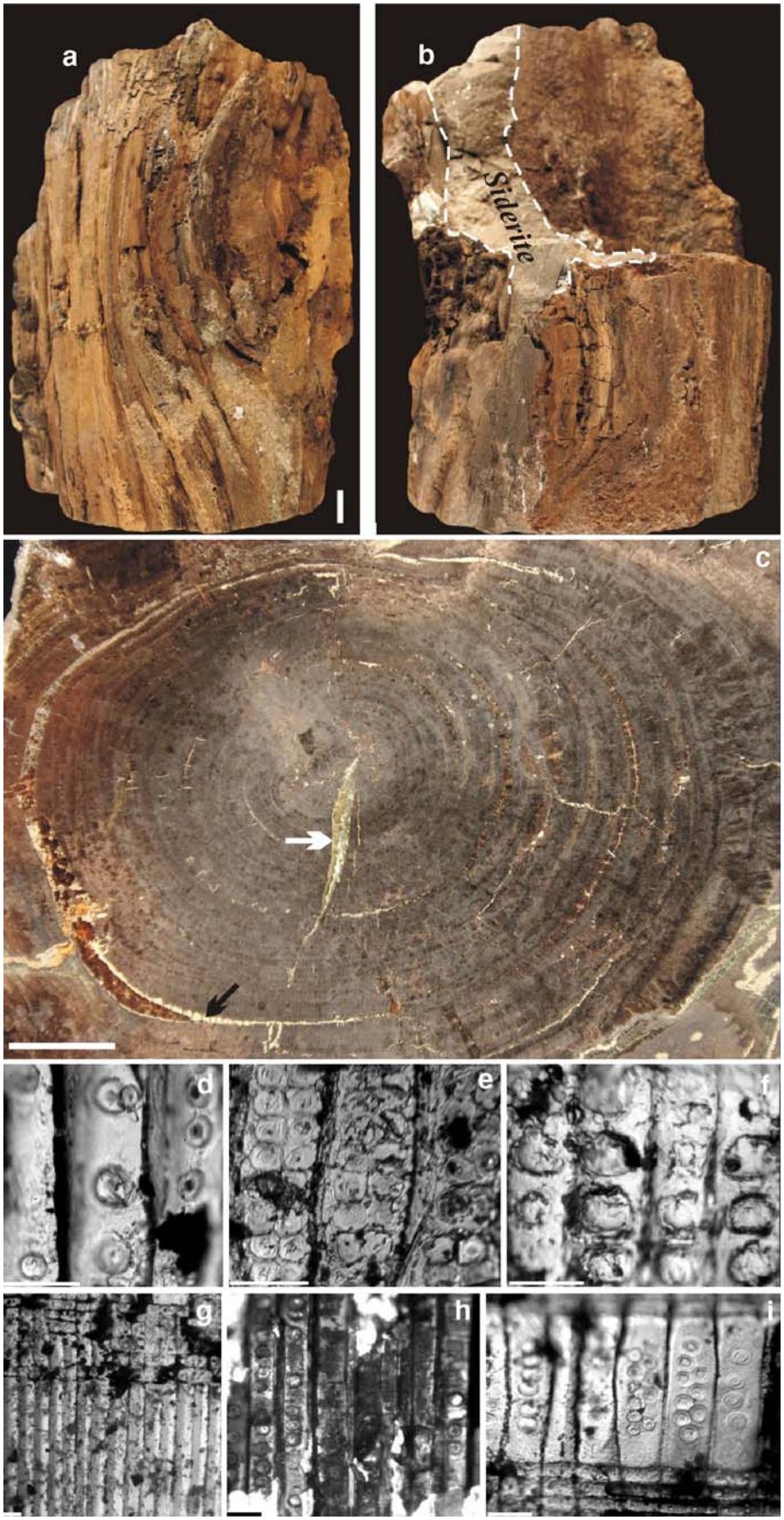
a
b
Siderite
c
d
e
f
g
h
i

Table 1 General characteristics of the analyzed samples

Sample	Composition	Anatomical preservation[a]	Species	R_0 (%)
Gnaszyn W1	siderite and calcite	relatively good	*Protopodocarpoxylon* sp.	–
Gnaszyn W2	calcite and siderite	average	*Protopodocarpoxylon* sp.	–
Gnaszyn W3	calcite and siderite	poor	*Protopodocarpoxylon* sp.	0.25–0.30
Gnaszyn W4	calcite and siderite plus very little pyrite	average to excellent (pyrite)	*Protopodocarpoxylon* sp.	0.25–0.30
Ganszyn W5	siderite	relatively good	*Protopodocarpoxylon* sp.	0.45–0.50
Ganszyn W7	siderite	good	*Protaxodioxylon* sp.	–
Gnaszyn W8	siderite	average	*Agathoxylon* sp.	–
Gnaszyn W9	siderite and calcite	good	*X. phyllocladoides*	–
Anna W5	lignite	poor	*Agathoxylon* sp.	–
Anna W6	lignite and siderite	poor to average	*Protopodocarpoxylon* sp.	0.25–0.30
Anna W7	lignite	poor	*Agathoxylon* sp.	–

[a] Anatomical preservation quantified as the percentage of tracheids with preserved radial pitting: poor, <50%; average, 50 to 70%; relatively good, 70 to 80%; good, 80 to 90%; excellent, >90%

0.25 mm i.d., 0.25 μm film thickness). The GC operating conditions were as follows: temperature hold at 65°C for 2 min, increase from 65 to 300°C at a rate of 6°C min^{-1} with final isothermal hold at 300°C for 20 min. Helium was used as carrier gas. The sample was injected with a 1:2 split. The mass spectrometer was operated in the electron impact mode at 70 eV ionization energy and scanned from 50 to 650 Da. Data were acquired and processed with the Chemstation software. Individual compounds were identified by comparison of their mass spectra with those of authentic standards, with published data, and by interpretation of mass spectrometric fragmentation patterns.

Results

The state of preservation of the wood fragments differs among specimens (Fig. 2; Table 1). Generally, they are either coalified and/or permineralized (Fig. 2a–c). The quality of preservation of the wood structure depends mainly on the time of permineralization after burial. Most of the wood samples display some bacterial attack on the cell walls, although the specimens studied as prepared peels have all the diagnostic xylological features and sometimes details as delicate as fibrilla on tori (less than a micron in diameter). Thus, it can be hypothesized that, after a short drift and residence in salt-water, the woody fragments sank to an oxygen-poor (anoxic/dysoxic) sea-bottom, where they were rapidly buried in sediment. Mineralization processes began immediately after deposition.

The molecular composition of selected wood samples and relative abundance of individual compounds in each of the samples are given in Table 2.

Discussion

All of the investigated samples are tracheidoxyls (i.e., isolated secondary xylem fragments composed of tracheids only, with a minor proportion of other types of cells; Fig. 2d–i). Growth rings are asymmetrical but faint, with a limited amount of late wood and a sharp transition from early to late wood.

The vitrinite reflectance (R_0) measurements, conducted on the wood samples Gnaszyn W3, Gnaszyn W4, and Anna W6, gave values of 0.25–0.30%. The exception is the sample Gnaszyn W5, the R_0 value of which is 0.45–0.50% (see Table 1).

Among the different wood samples from the Polish Jura, a negative correlation is observed between the anatomical and chemical wood preservation. This phenomenon was also reported for the preservation of fossil leaves preservation [see Collinson et al. (2005)]. For example, sample Anna W6 in which radial pitting is evident only locally, has some of the best-preserved biomarkers (Fig. 3) of all samples analyzed. In this regard, early diagenetic mineralization processes in a marine clay matrix are essential for good preservation of tissues by carbonates (e.g., siderite and calcite) and pyrite (Fig. 2c). Indeed, these are triggered by bacterial activity, which in turn depends on destruction of organic matter. The paradoxical negative correlation we

◀ **Fig. 2** Appearance of the wood samples analyzed. **a**, **b** *Protopodocarpoxylon* sp. (sample Gnaszyn W4), partially filled with siderite (**b**); **c** *Protopodocarpoxylon* sp. (sample Gnaszyn W3) showing distinct growth rings affected by calcite (*white arrow*) and pyrite (*black arrow*) mineralization. Scale bars for **a**–**c** equal 1 cm. **d**–**f** Photomicrographs showing tracheids of the analyzed woods: **d** *Protopodocarpoxylon* sp., **e** *Protaxodioxylon* sp., and **f** *X. phyllocladoides* Gothan. **g**–**i** Different state of micromorphological preservation of the woods: **g** *Protopodocarpoxylon* sp. (poor preservation), **h** *Protopodocarpoxylon* sp. (average preservation), **i** *Protaxodioxylon* sp. (good preservation), see Table 1 for further explanation. Scale bars for **d**–**i** equal 50 μm

Table 2 Biomarkers identifed in the Jurassic *Protopodocarpoxylon* Eckhold wood from south-central Poland

Compound	Relative abundance in the samples[a]				Source[b]	Identification
	ANNA W6	GNW2	GNW4	GNW5		
ALIPHATIC LIPIDS						
n-Octacosan-10-ol	–	–	1.3	11.3	Pl	MS
n-Nonacosan-10-ol[c]	100	–	–	–	Pl	Franich et al. (1979)
n-Nonacosanediols (4 isomers)[c]	27.8	–	–	–	Pl	Franich et al. (1979)
n-Hexadecanoic acid	–	52.0	12.4	9.5	Pl	standard
n-Octadecanoic acid	–	23.8	12.1	6.6	Pl	MS
n-Docosanoic acid	1.0	9.2	26.7	2.6	Pl	MS
n-Tricosanoic acid	0.9	–	4.8	0.6	Pl	MS
n-Tetracosanoic acid	13.7	8.4	100	2.1	Pl	MS
n-Pentacosanoic acid	0.7	–	5.4	0.5	Pl	MS
n-Hexacosanoic acid	5.4	–	80	0.7	Pl	MS
DITERPENOIDS						
Abietanes						
Dehydroabietane	0.8	35.8	0.9	1.1	C	standard
Simonellite	0.8	100	1.2	1.4	C	standard
Dehydroabietic acid	0.6	–	0.7	0.9	C	standard
6,7-Dehydroferruginol	4.3	–	–	–	PCA	Enzell and Ryhage (1967)
Ferruginol[c]	5.8	3.5	5.4	0.7	PCA	standard
Sugiol[c]	1.4	29.7	20	6.4	PCA	standard
7-Acetoxy-6,7-dehydroroyleanone[c]	3.6	–	–	–	PCA	Otto et al. (2002a)
11,14-Dioxopisiferic acid[c]	7.4	–	–	–	PCA	Otto et al. (2002a)
Labdanes						
Labdanoic acid	1.5	–	–	–	C	Otto and Simoneit (2001)
Communic acid[c]	3.7	–	0.6	–	C	standard
Lambertianic acid[c]	10.4	–	1.1	–	C	standard
Totaranes						
2-Ketototarol[c]	5.8	–	3.8	0.6	PCA	MS
TRITERPENOIDS						
24,25-Dinorlupatriene	10.1	–	–	–	Pl	Wolff et al. (1989)
Homohopane	4.2	–	1.3	1.5	B	Philp (1985)
C_{30} hop-17(21)-ene	1.2	–	0.8	–	B, Pl	MS
STEROIDS						
Campesterol	–	–	1.2	7.2	Pl	MS
Cholesterol	–	–	9.5	11.9	Pl, F	standard
Stigmastene	6.8	–	–	–	Pl	Philp (1985)
Stigmastanone	3.3	–	–	–	Pl	Wiley MS library
Sitosterol[c]	7.3	12.0	6.2	100	Pl	standard
Stigmastanol	1.3	–	–	–	Pl	standard
Stigmasta-3,5-dien-7-one	–	–	–	6.4	Pl	MS
POLYCYCLIC AROMATIC HYDORCARBONS						
Perylene	–	–	27.3	14.2	–	standard

[a] Abundance relative to major peak
[b] *C* Conifers, *PCA* Podocarpaceae, Cupressaceae, Araucariaceae, *Pl* plants, *B* bacteria, *F* fauna
[c] Unaltered natural products (biomolecules); MS—Mass spectrum interpretation

observed could be explained by hyperblastic mineralization (one calcite crystal encompassing several tracheids) being favored during early diagenesis. The biomarkers are either trapped in the mineral matrix, or they were extracted by the mineral waters before mineralization.

The second process causing changes in the molecular composition of the wood is diagenetic oxidation. Petrographic analyses of the woods in the context of vitrinite reflectance (R_0) measurements revealed that two different wood samples from the same locality could differ significantly in R_0 values. A wood sample (Gnaszyn W5), with features characteristic of oxidation processes, displayed R_0 values between 0.45–0.50%, whereas other samples, (Gnaszyn W3, W4, and Anna W6) without any signs of oxidation, had R_0 values of 0.25–0.30%, a characteristic for typical brown coals (see Table 1; Fig. 4). It is well known

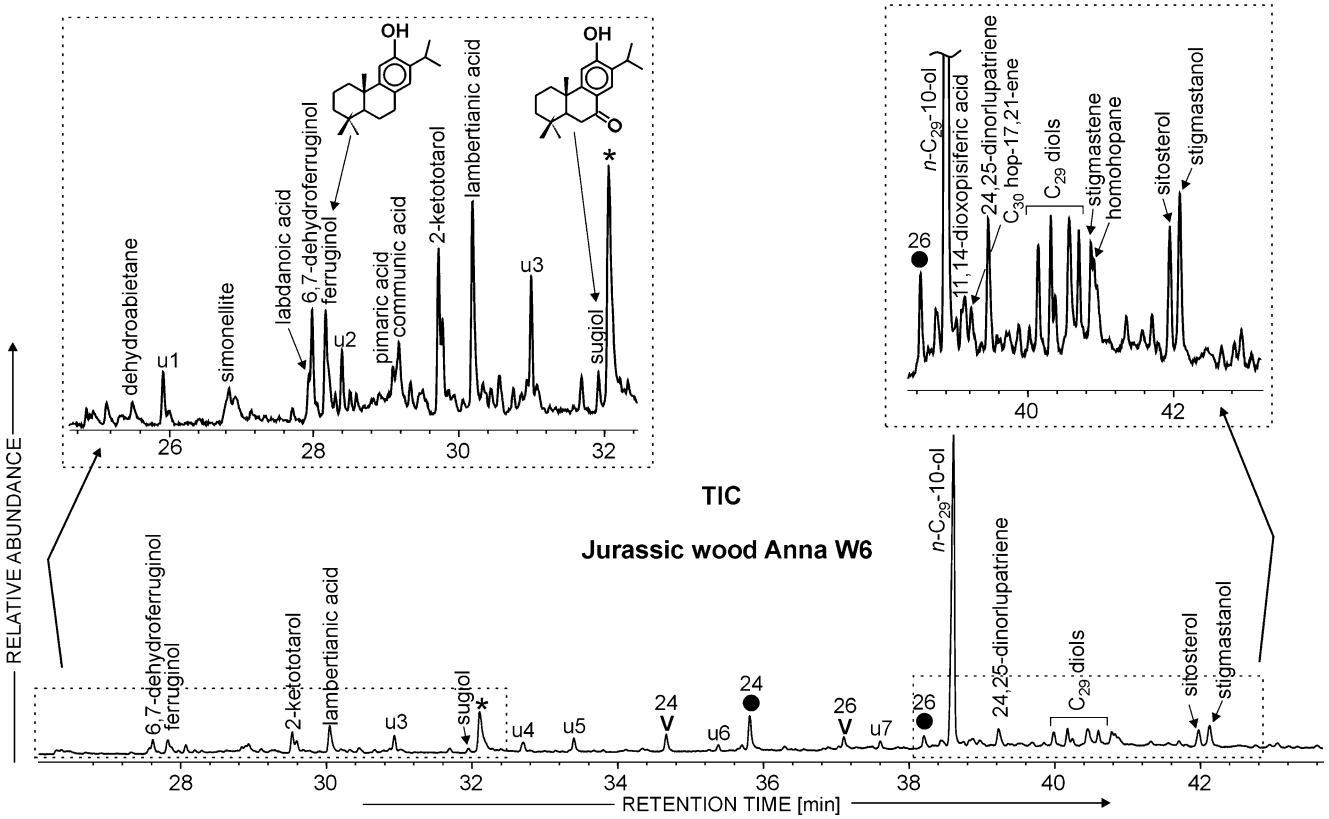

Fig. 3 GC–MS chromatogram (*TIC*) of the total solvent extract of the Jurassic *Protopodocarpoxylon* wood from Poland. *Asterisks* indicate contamination, *inverted carets* indicate *n*-alkanols, filled circles indicate *n*-alkanoic acids, *u1–u7* indicate unknown compounds. Scale expansions shown as *inserts*. *Numbers* indicate the number of carbons in the aliphatic lipid series

that oxidation processes are the cause of gradual chemical changes of organic matter similar to that characteristic for natural maturation (Elie et al. 2000).

For the wood samples with the best preserved molecular compositions, the clay sediments have protected them from oxidation by meteoric waters. Wood biomolecule preservation has probably also been favored by the very low degree of thermal maturity (at the brown coal level) and the presence of the antimicrobial resin phenols such as ferruginol and its derivatives (e.g., Cambie et al. 1983).

The solvent extract of the best chemically preserved sample (Anna W6-*Protopodocarpoxylon*) contains aliphatic lipids, diterpenoids, triterpenoids, and steroids (Table 2, Fig. 3). The aliphatic lipids are composed of long-chain (C_{24}–C_{29}) *n*-alkanols and *n*-alkanoic acids. The predominant compound is the secondary alcohol *n*-nonacosan-10-ol (relative abundance = 100%) accompanied by four *n*-nonacosanediols (10,13-diol; 7,13-diol; 5,10-diol; and 7,10-diol). These alcohols and acids are typical constituents of higher plant waxes (Baker 1982; Barthlott et al. 1998). Nonacosan-10-ol and the C_{29} diols are constituents of higher plant waxes and are especially common in conifer waxes (Bianchi 1995). Major constituents of the extract are diterpenoids of the abietane, labdane, and totarane classes, which are known as common constituents of conifer resins (Hegnauer 1962, 1986; Otto and Wilde 2001).

The triterpenoids are represented by one lupane and one hopane derivative. Hopanes are common constituents of bacterial membranes, and lupane type triterpenoids have been described from flowering plants but occur also in microorganisms (Simoneit 1986; Peters et al. 2005). The occurrence of long-chain fatty acids, a characteristic for leaf waxes, in the fossil wood investigated is related with contamination of some of the wood fragments by the host Middle Jurassic clay sediments. This process may have occurred at the early stages of diagenesis when the fresh wood was porous and fractured enough to allow the host sediment to enter inside. This is obvious from the partial mineralization (sideritization) of the inner part of the wood (Fig. 2b). This is important to note that the host clay sediments contain high concentrations of long-chain *n*-alkanes with an odd over even carbon number predominance (Zatoń and Marynowski 2004). Hopanes present in the wood samples may have been derived from the similar source or from bacterial degradation processes occurring at the early stages of diagenesis.

With the exception of simonellite and labdanoic acid, most of the diterpenoids are unaltered, preserved biomole-

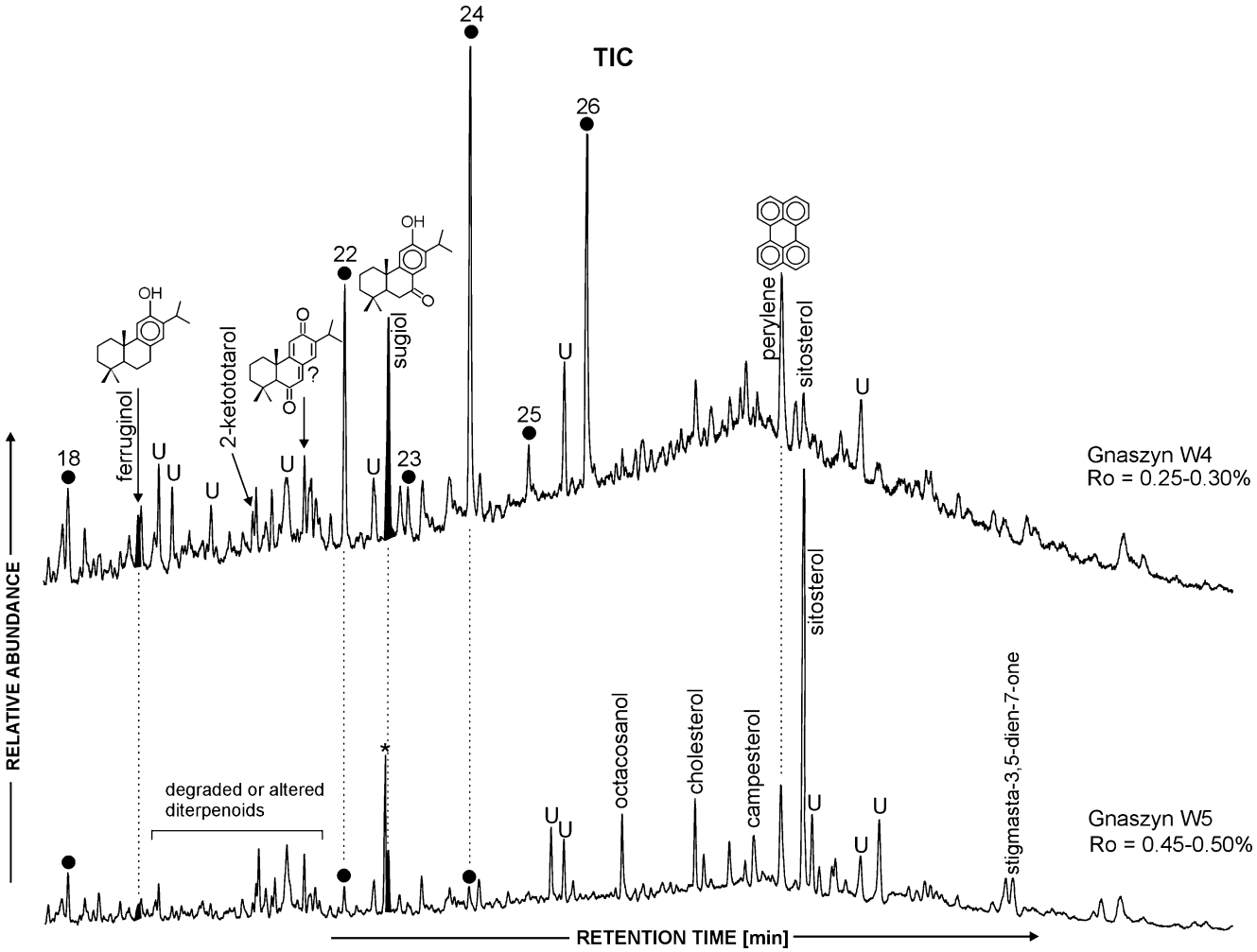

Fig. 4 GC–MS (*TIC*) traces of the silylated total extracts (TMS derivatives) of the two *Protopodocarpoxylon* sp. wood samples. Note the significant concentration differences of ferruginol and sugiol caused by maturity differences. *Filled circles* indicate *n*-alcanoic acids, *asterisk* indicates contamination, *U* unknown compounds. DB-35MS column was used

cules, as observed in extant plants especially conifers (Hegnauer 1962, 1986; Otto and Wilde 2001). Although the polar terpenoids (such as ferruginol and sugiol) are still preserved in the more oxidized samples (Gnaszyn W5), their concentration is lower in comparison to the samples Anna W6 and Gnaszyn W4 (Figs. 3 and 4). Simonellite is interpreted as the diagenetic product of dehydroabietane and other abietane type biomolecules, and labdanoic acid was generated from the reduction of bicyclic acids such as communic acid (Simoneit 1986; Otto and Simoneit 2001). The aliphatic alcohols and acids identified in the Jurassic wood are also preserved as they are found in extant plants (e.g., Franich et al. 1979). Many of bioterpenoids and aliphatic lipids detected in the *Protopodocarpoxylon* (conifer supra) wood are unaltered in comparison to their degradation products (see Table 2; Figs. 3 and 4). Comparable compositions of polar biomarkers were hitherto reported only from much younger geological samples, namely, fossil plants, resins, and coals of Tertiary or Cretaceous ages (e.g., Grimalt et al. 1988; Alonso et al. 2000; Otto and Simoneit 2001; Otto et al. 2002a,b, 2003, 2005; Stefanova et al. 2002). Polar diterpenoids under discussion are surely derived from the fossil wood analyzed. The nature of the host clays, namely, their impermeability as well as the wood sample location for the present study (the samples were collected from within the clays, not from the surface of the exposures), have not allowed meteoric waters to migrate and contaminate the woods with post-Jurassic or even recent polar terpenoids. This is supported by the fact that the compounds have not been detected in the host clays.

Due to the excellent preservation of the organic compounds in the wood, the constituents of the solvent extract can be used as chemosystematic markers. The composition of diterpenoids is similar to patterns observed in extant conifers (Hegnauer 1962, 1986; Otto and Wilde 2001). The identified labdane derivatives and non-phenolic abietanes such as dehydroabietane or abietic acid occur in

most conifer families and are therefore non-specific conifer markers (Otto and Wilde 2001). In contrast, phenolic abietanes like ferruginol and its derivatives (6,7-dehydroferruginol, sugiol, 11,14-dioxopisiferic acid) are produced only by distinct conifer families (Cupressaceae s. l., Podocarpaceae, and Araucariaceae) and can be used as their characteristic biomarkers (Hegnauer 1962, 1986; Otto and Wilde 2001). Thus, the chemosystematic characteristics are in accordance with the botanical assignment to the Podocarpaceae based on morphological and anatomical characteristics.

Conclusions

The biomolecular preservation of the Jurassic wood taxa of Poland is exceptionally good. The major solvent extractable components are unaltered biomolecules or their slightly degraded alteration products. The preservation of polar diterpenoids is caused by the limited biodegradation of natural product compounds in the resin due to the presence of antimicrobial phenols and/or the rapid burial of the wood in anaerobic sediments. The combined analysis of chemical and anatomical characteristics of fossil plant remains is a great advantage for the botanical assignment of fossil plants. The detection of characteristic biomarkers in fossil plant material without suitable anatomical preservation allows the determination of systematic relationships.

Acknowledgment This research has been financed in part by the University of Silesia grants BW33/2003, BW34/2004, and BW19/2005. Warm thanks are due to Dr. Slawomir Kurkiewicz (Medical University of Silesia) for technical assistance. M.Z. thanks the Foundation for Polish Science (Grants for Young Scientist' 2006) for financial support.

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