

Systematic relationships of the Mesozoic wood genus *Xenoxylon*: an integrative biomolecular and palaeobotanical approach

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With 3 figures and 2 tables

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Abstract: *Xenoxylon* GOTHAN is one of the very few components of Mesozoic terrestrial biota which give clear palaeoecological signal. Unfortunately its systematic relationships are still unknown. This work analyzes the organic geochemistry of particularly well preserved samples of *Xenoxylon* from the Callovian of Łuków (eastern Poland) for comparison with the Bathonian of Gnaszyn (south-central Poland). The wood fragments from both Łuków and Gnaszyn contain phenolic abietanes like ferruginol, 6,7-dehydroferruginol, sugiol, hinokiol or 2-ketototarol. The presence of such biomolecules, with simultaneous absence or very small amount of tetracyclic diterpanes such as phyllocladanes, beyerane and/or kauranes, is characteristic for extant conifer families Cupressaceae s.l. and Podocarpaceae. Thus, the molecular composition of the wood genus *Xenoxylon* suggests systematic relationships with these extant families. This study presents the evidence that preserved biomarkers and biomolecules are not exceptional in fossil wood, and that their composition generally supports the anatomical data.

Key words: *Xenoxylon*, Jurassic, Callovian, wood, biomolecules, conifers, Poland.

1. Introduction

Among the about fifty wood morphogenera described for the Mesozoic softwoods, one stands out as having an amazing anatomy which has no modern equivalent. When first described by GOTHAN (1906), this Mesozoic wood genus was named *Xenoxylon*, from the Greek words “ξενος” [xenos] which means strange, alien, and “ξύλου” [xylon] which means wood, i. e. “the odd wood”.

A circumpolar Boreal genus ranging from the Late Triassic to the latest Cretaceous, *Xenoxylon* is of considerable palaeoecological interest. Indeed, PHILIPPE

& THÉVENARD (1996) demonstrated that the genus is an indicator of a relatively cool and wet climate, using the fact that the southern limit of *Xenoxylon* distribution range shifted southward during cooler/wetter periods, and that it is linked with sediments deposited in well watered environments under cool temperate climate. Even though this was demonstrated with independent palaeobiogeographical and taphonomical evidence, the uncertain botanical affinities of *Xenoxylon* are still puzzling (KHUDAIBERDYEV 1993; HALLAM 1998).

Since GOTHAN’s description, many hypotheses have been proposed. On the basis of its anatomy, *Xenoxylon*

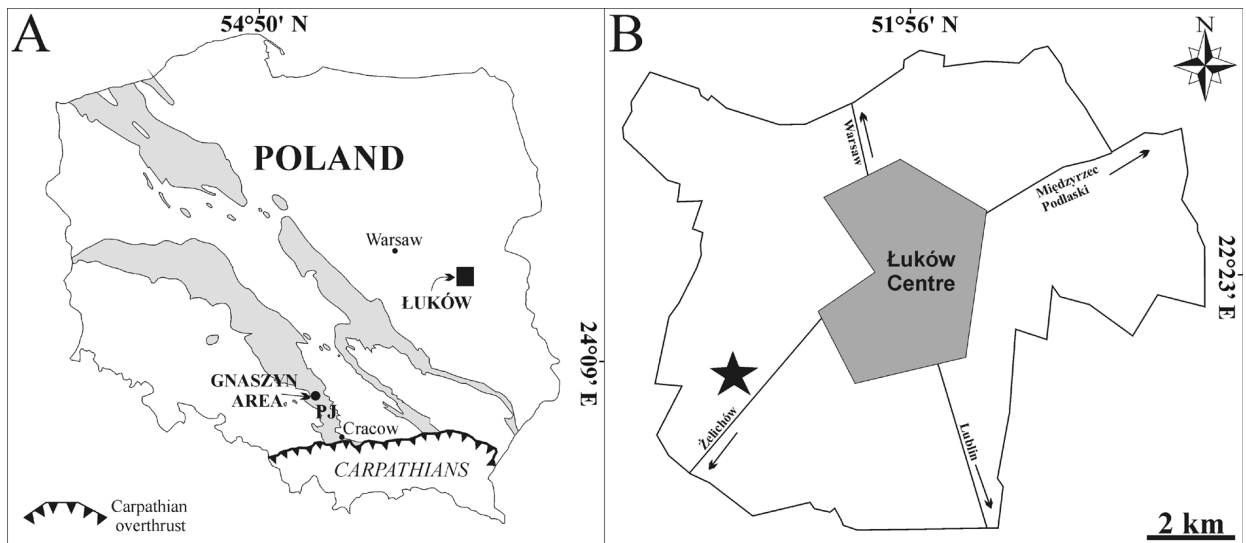


Fig. 1. **A** – Map of Poland with sampled areas of Łuków and Gnaszyn area indicated. PJ – Polish Jura; shaded areas indicate Jurassic deposits. **B** – Sketch map of Łuków locality with the abandoned clay-pit at Łapiguz indicated (asterisk).

has been suspected, but with no conclusive evidence, to be the wood of *Sciadopitys* (JARMOLENKO 1933; BAILEY 1953), a modern conifer, or that of *Podozamites* (NATHORST 1897) or *Baiera* (ARNOLD 1953), two fossil foliages, the former related to Conifers and the latter to Ginkgoales. OGURA (1954) found it associated with Conifer-type pith, but this is not conclusive either; MÜLLER-STOLL (1987) even thought it does not belong to Conifers. MÜLLER-STOLL & SCHULTZE-MOTEL (1988) saw similarities with a wood from the Indian Palaeozoic described by HOLDEN (1917), whereas other authors (BAILEY 1953; SHILKINA & KHUDAYBERDYEV 1971) consider *Xenoxylon* as belonging to the Podocarpaceae lineage.

PARICHIEV (1968) systematically joined *Xenoxylon* and *Sciadopitys* on the basis of their palaeogeographic distribution and the fact that the wood and *Sciadopitys*-like foliage are often associated in Early Cretaceous sediments all around the Arctic. It was subsequently demonstrated (BOSE & MANUM 1990, 1991) that these *Sciadopitys*-like foliages were not related to modern genus *Sciadopitys* (the umbrella-pine, which is endemic in Japan) but to different genera (*Mirovia*, *Oswaldheeria*, *Tritaenia*, etc.), grouped in a family named Miroviaceae. In turn, the systematic relationships of Miroviaceae are much discussed (GOMEZ 2002).

Moreover, there were also some controversies about how inclusive the morphogenus *Xenoxylon* should be. For example, KRÄUSEL (1949) as well as MEDLYN & TIDWELL (1975) included in *Xenoxylon* woods with some circopores per cross-field while all other species have a single large window-like oopore.

The latest research on the fossil wood genus *Protodopocarpoxyylon* occurring in the Middle Jurassic clays at Gnaszyn area near Częstochowa city (Polish Jura Chain, south-central Poland) showed that it has preserved relatively large amounts of unaltered natural products (bioterpenoids), some of which may be used as valuable molecular markers for (palaeo)taxonomy (MARYNOWSKI et al. 2007, see also OTTO et al. 2002, 2003).

While studying a small but interesting wood flora from Łuków, we chanced upon several well preserved samples of *Xenoxylon phyllocladoides* GOTHAN. We took this opportunity to perform an integrative xylological and biomolecular investigation in order to determine *Xenoxylon* systematic relationships. Here we analyzed the extractable organic matter of *Xenoxylon phyllocladoides* samples from the Callovian of Łuków (eastern Poland), as well as that from the samples of the same species from the Upper Bajocian and Bathonian of the Polish Jura Chain (PHILIPPE et al. 2006). Based on literature data, we compared this

biomolecular composition with that of other fossil wood genera and modern conifer families. Knowing the organic composition of the taxonomically well defined wood could help us better to circumscribe morphogenus *Xenoxylon*, and to reveal and discuss the botanical affinities of this enigmatic wood genus.

2. Material and methods

We analyzed two fossil wood sample sets. One is derived from a now abandoned and inaccessible clay-pit at Łapiguz near Łuków (see e. g., MAKOWSKI 1952; OLEMPKA & BŁASZYK 2001) where abundant Late Callovian palaeontological material was collected and is now in the archival collection of the Faculty of Earth Sciences, University of Silesia at Sosnowiec, Poland. The Callovian deposits at the Łuków locality (Fig. 1) are allochthonous to the region and were glacially-derived. Their most probable source, as was suggested by OLEMPKA & BŁASZYK (2001), is the bed of the Baltic Sea, north of Gdańsk in northernmost Poland. Thus they have been transported for ca. 200-300 km south to the present site.

The second sample set comes from the active 'Gnaszyn' and 'Alina' clay-pits located at Gnaszyn Dolny and Gnaszyn Górny respectively, near Częstochowa in south-central Poland (Fig. 1). Samples from the 'Gnaszyn' clay-pit come from the lower part of exposed clays (Middle Bathonian, Morrissi Zone; for stratigraphic details see ZATOŃ et al. 2006; MATYJA & WIERZBOWSKI 2006) and those from the 'Alina' clay-pit are of Late Bajocian age (Parkinsoni Chron, Parkinsoni Sub-chron; for stratigraphic details see MATYJA & WIERZBOWSKI 2000). Both sets include *Xenoxylon phyllocladoides* GOTHAN as well as other wood morphospecies. Among samples assigned to *Xenoxylon phyllocladoides*, samples Łuków W1, Gnaszyn W9 (from 'Gnaszyn' clay-pit) and MP1554 (from 'Alina' clay-pit) were selected for organic geochemistry.

All material is kept at the Faculty of Earth Sciences, University of Silesia at Sosnowiec, Poland; microscopic preparations are kept in the Laboratoire de Paléobotanique of the Université Lyon-1, France.

Microscopic wood analysis. – The samples were first sorted under a stereomicroscope in order to select a technique adapted to the nature of their preservation. Well mineralized samples were searched for a fresh fracture in radial plan, and if this was absent gently split with a disposable razor blade. On

the fracture plan, thick Collodion was applied and allowed to dry for a day. Collodion peel was then stripped off and studied with a normal transmitted light microscope. If not suitable for this technique, samples were mounted on aluminum stubs, with double-sided conducting adhesive tape, coated with gold/palladium at 25 kV for 5 minutes, and then observed under a 10 kV acceleration voltage with a Hitachi S-800 scanning electron microscope. Determination was performed following principles described in PHILIPPE (1995) and BAMFORD & PHILIPPE (2001).

Organic geochemistry, extraction and separation. – Three wood samples (Łuków W1 from Łapiguz clay-pit, GNW9 from 'Gnaszyn' clay-pit and MP1554 from 'Alina' clay-pit) were Soxhlet-extracted in pre-extracted cellulose thimbles with dichloromethane/methanol (90%/10%). Extracts were further separated using preparative pre-washed TLC plates coated with silica gel (Merck, 10 x 20 x 0.25 cm). Prior to separation, the TLC plates were activated at 120°C for 1 h. The plates were loaded with the *n*-hexane soluble fraction and developed with *n*-hexane. Bands comprising aliphatic (R_f 0.4-1.0), aromatic (R_f 0.05-0.4) and polar (R_f 0.0-0.05) fractions were collected.

Derivatization, silylation. – Aliquots of the total extract and polar fraction were converted to trimethylsilyl derivatives by reaction with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and anhydrous pyridine for 3 h at 70°C.

Gas chromatography - mass spectrometry (GC-MS). – The GC-MS analyses were performed with an Agilent 6890 Series Gas Chromatograph interfaced to an Agilent 5973 Network Mass Selective Detector and Agilent 7683 Series Injector (Agilent Technologies, Palo Alto, CA). A 0.5 µl sample was introduced into the cool on-column injector under electronic pressure control. Helium (6.0 Grade, Linde, Kraków) was used as the carrier gas at a constant flow rate of 2.6 ml/min. The GC separation was on either of fused-silica capillary column: J&W DB17-MS (60 m x 0.25 mm i. d., 0.25 µm film thickness) coated with a chemically bonded phase (50% phenyl-methylpolysiloxane). The GC oven temperature was programmed from 50°C (isothermal for 1 min) to 120°C at a rate of 20°C/min, then to 300°C at a rate of 3°C/min. The final temperature was held for 45 min.

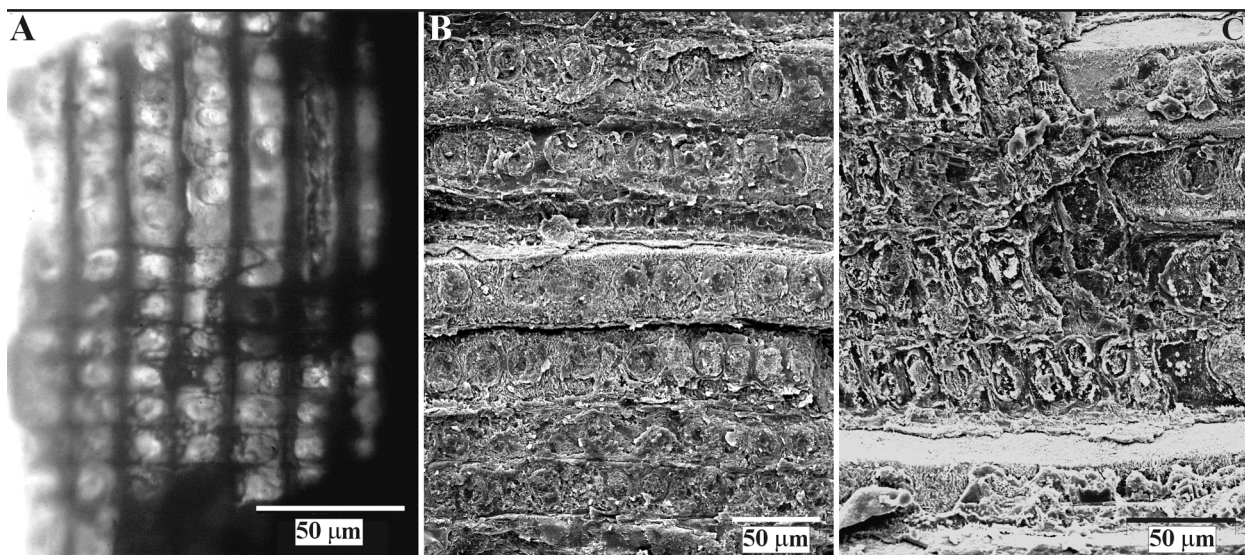


Fig. 2. *Xenoxylon phyllocladoides* GOTHAN. **A** – Sample Gnaszyn W9, Middle Bathonian of Gnaszyn, collodion peel, radial view. **B** – Sample Luków W1, Callovian of Luków, SEM, radial pitting on tracheids. **C** – Sample Luków W1, Callovian of Luków, SEM, ray in radial view. Sample MP1554, from the Upper Bajocian of Gnaszyn was already illustrated in Philippe et al. (2006, fig. 4 C, D).

The GC column outlet was connected directly to the ion source of a mass spectrometer. The GC-MS interface was kept at 280°C, while the ion source and the quadrupole analyzer were at 230 and 150°C, respectively. Mass spectra were recorded at m/z 45–550 (0–40 min) and m/z 50–700 (above 40 min). The mass spectrometer was operated in the electron impact mode (ionization energy: 70 eV).

Quantification and identification. – An Agilent Technologies Enhanced ChemStation (G1701 CA ver.C.00.00) and the Wiley Registry of Mass Spectral Data (7th Edition) software were used for data collection and mass spectra processing. The absolute abundances of the selected compounds were calculated by comparisons of peak areas for the internal standard (9-phenylindene) with the peak areas of the individual hydrocarbons obtained from the GC-MS ion chromatograms. Relative abundances are calculated by comparison with the major peak. Identification of individual compounds was aided by comparison with published mass spectra and by interpretation of mass fragmentation patterns.

3. Results

3.1. Wood identification and determination

Xylological results are given in Table 1. The generic diversity of the Gnaszyn Mid-Bathonian flora is higher than that from Luków. The Gnaszyn Late Bajocian flora is too poor to be compared. Within each genus, only one morphospecies is present, and it is the same when a genus occurs in both Luków and Gnaszyn floras. The *Protopodocarpoxylon* ECKHOLD wood is very similar to the *Protopodocarpoxylon* sp. mentioned from the Bathonian of Poland by PHILIPPE et al. (2006) and MARYNOWSKI et al. (2007). Six samples can safely be assigned to *Xenoxylon phyllocladoides* GOTHAN (Fig. 2), a wood which was originally described from the Upper Bajocian – Lower to Middle Bathonian of south-central Poland (GOTHAN 1906; PHILIPPE et al. 2006). These samples do not differ significantly from each other, and they are described collectively below.

The wood is a secondary xylem composed only of tracheids and parenchymatous rays. Late wood is little developed, limited to 1-3 tracheids layers. Tracheid cross-section is mostly quadrate. Parenchymatous rays

are homogenous, uniseriate, low, (1) 2-7 (12) cells in height. Tracheids radial walls have areolate pits. These are mostly uniseriate and contiguous. However, spaced pits are also frequent (about 42 %, $n = 352$). Biseriate pits have not been observed. At several places xenoxylloid radial pitting was observed, i.e. short rows of contiguous pits with strong flattening. Ray cell walls are all thin and smooth, only those in contact with tracheids being pitted. A single large window-like oopore covers the whole cross-field. Only very locally, when crossed by a terminal wall of ray cell, do cross-fields display two oopores. In the late wood, oopores are very slightly bordered. Axial parenchyma, resin canals and tangential tracheids pitting were not observed, neither traumatic tissues.

These xylological features are typical for *Xenoxylon* GOTHAN. From a wood anatomy point of view, the closest genus is *Protosciadopityoxylon* ZHANG, ZHENG & DING (ZHANG et al. 1999) which also has large window-like oopores in early wood cross-fields. But the latter never displays xenoxylloid pitting on tracheids radial walls (PHILIPPE & BAMFORD, in press). Among the species assigned to *Xenoxylon* in literature, several have mixed type of radial pitting like our specimens (so-called *phyllocladoides* – or *barberi* – group, DING et al. 2000): *X. ellipticum* MÜLLER-STOLL & SCHULTZE-MOTEL, *X. fuxinense* DING, ZHENG & ZHANG, *X. hopeiense* KHUDAIBERDYEV non CHANG, *X. liaoningense* DUAN & WANG, *X. nariwaense* YAMAZAKI, *X. phyllocladoides* GOTHAN, *X. pseudoellipticum* YAMAZAKI & TSUNADA. Several of these species differ from *X. phyllocladoides* only by features of questionable value (e.g. ray height or presence of tangential pitting). The description given by GOTHAN (1906) in the protologue of *Xenoxylon phyllocladoides* fits perfectly with Łuków material. This species is typified by material from Polish Bathonian, which we have not been yet able to locate, despite extensive search. We examined, however, topotypes from Częstochowa area (PHILIPPE et al. 2006), which are xylologically perfectly similar to our material. The material from Łuków and Gnaszyn Dolny can thus safely be assigned to *Xenoxylon phyllocladoides* GOTHAN.

3.2. Wood maturity range and molecular composition

The wood samples from Gnaszyn Dolny and Łuków are characterized by a very low range of maturity. The R_0 for the samples from Gnaszyn ranges from

0.25-0.30 % (MARYNOWSKI et al. 2007), and the vitrinite reflectance of the Łuków sample equals 0.33 % (MARYNOWSKI et al. 2008, this issue). These values correspond to those of the brown coal maturity level (e.g. TISSOT & WELTE 1984). Despite a slightly higher R_0 [%] value for the sample from Łuków, it is characterized by perfect state of preservation of organic compounds – a fact that has not been encountered in the Middle Jurassic samples so far.

The dichloromethan/methanol extract of the samples Łuków W1 and Gnaszyn W9 contains aliphatic lipids (*n*-alkanes, isoprenoids and *n*-fatty acids), sesquiterpenoids, diterpenoids, triterpenoids, steroids as well as aromatic hydrocarbons and polycyclic aromatic compounds. The molecular composition of the wood samples analyzed, and the relative abundances of individual compounds are given in Table 2.

Major constituents of Łuków and Gnaszyn W9 *Xenoxylon* extracts are diterpenoids of the abietane and totarane classes. Such polar diterpenoids as ferruginol, 2-ketototarol or sugiol are common components of recent conifer resins (OTTO & WILDE 2001) and Palaeogene and Neogene brown coals (OTTO & SIMONEIT 2001; STEFANOVA et al. 2002; OTTO et al. 2003), but their occurrence in Mesozoic wood and coals is rather sporadic (ALONSO et al. 2000; MARYNOWSKI et al. 2007). This is because they are unstable from the geological point of view and undergo further diagenetic transformations. The investigated *Xenoxylon* wood sample from Łuków is characterized by particularly rich composition of organic compounds of the diterpenoids group (Fig. 3). The main compound in the analyzed extract is ferruginol (Fig. 3), the concentration of which is 39.3 $\mu\text{g/gTOC}$. Quantitatively significant are also dehydroabietane (14.3 $\mu\text{g/gTOC}$), hinokiol (9.8 $\mu\text{g/gTOC}$), 2-ketototarol (7.6 $\mu\text{g/gTOC}$) and sugiol (4.3 $\mu\text{g/gTOC}$). Such diterpenoids as dehydroabietol, 18-norferruginol, 12-hydroxysimonellite and hinokiol (Fig. 3, Table 2) are described in the present paper for the first time in such an ancient material, as these Middle Jurassic *Xenoxylon* wood samples.

In comparison to the Łuków wood sample, the sample Gnaszyn W9 is characterized by a worse state of preservation of polar biomolecules. Nonetheless, in this sample, the same compounds occur as well, and sugiol is the main compound of the extract (Table 2). Similarly as in the case of the Middle Jurassic wood samples from the Polish Jura Chain investigated by MARYNOWSKI et al. (2007), the occurrence of long-

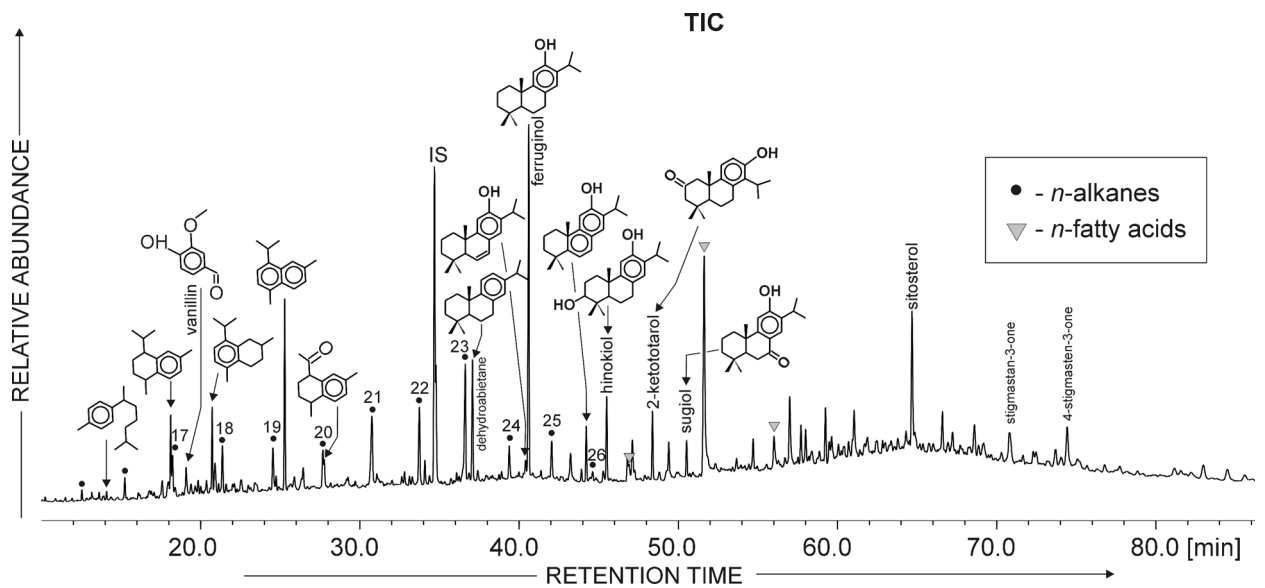


Fig. 3. GC-MS chromatogram (TIC) of total solvent extract (TMS derivatives) of the Middle Jurassic *Xenoxylon phyllocladoides* wood from Luków (Poland). Numbers indicate the number of carbons in the aliphatic lipid series.

chain fatty acids (Table 2), a characteristic of leaf waxes, is connected with early diagenetical contamination of wood fragments by clay sediments. This contamination may have occurred just after the wood fragments sank to the sea-bottom and were buried by clay sediments, but before the mineralization processes.

Middle Jurassic host clay sediments from the Częstochowa area are characterized by the presence of long-chain *n*-alkanes with an odd-over-even carbon number predominance (ZATOŃ & MARYNOWSKI 2004). The clays from the Luków area have not been investigated, because of our current inability to obtain unoxidized material, but the organic matter occurring in the calcitic concretions from the same area displays the presence of long-chain *n*-alkanes with slight odd carbon number predominance as well (MARYNOWSKI et al. 2008, this issue).

Among the sesquiterpenoids, cadalene (19.9 µg/g TOC) dominates. Slightly minor quantitative abundance of other sesquiterpenoids, as calamene (8.62 µg/g TOC), cadina-1(10),6,8-triene (8.64 µg/g TOC) and dihydro-*ar*-curcumene (1.01 µg/g TOC), are also noticed. Steroids are typical constituents of extant and fossil wood, and hopanes are the biomarkers attesting

to bacterial activity within the deposited wood fragments (Table 2) (e.g. OTTO & SIMONEIT 2001).

The sample MP1554 (from Alina brick pit) has the worse state of preservation of biological compounds. Its terpenoid composition shows many similarities with the previous samples and is mainly represented by simonellite as the major diterpenoid as well as retene. Other abietanes as norabietatrienes and dehydroabietane are detected in lower abundance than simonellite and retene in the aromatic fraction.

Sugiol is the unique detected bioditerpenoid and is present in much lower abundance than simonellite and retene. Sample MP1554 is different from the previous samples by the presence of 16(α)-phyllocladane in the aliphatic fraction. While this biomarker is the major diterpane, its relative abundance remains very low and its peak is not distinguishable in the chromatogram of the total organic extract. Furthermore, cadalene is the major sesquiterpenoid and its precursors (like calamene and cadina-1(10),6,8-triene) as well as dihydro-*ar*-curcumene remain below the detection limit.

Another difference is the lack or the very low abundance of *n*-acids which is certainly due to the absence of contamination of the fossil wood by leaf wax

compounds. This is also attested by the very low odd-over-even predominance of n-alkanes in the aliphatic fraction. C₂₉ steranes and hopanes are also detected in MP1554 *Xenoxylon* wood sample.

Among the aromatic hydrocarbons encountered by all our fossil wood samples, it is worth noting the presence of 4-hydroxybenzaldehyde and vanillin, those being lignin degradation products (OTTO & SIMONEIT 2001). Perylene is the most abundant polycyclic aromatic hydrocarbon (5.3 µg/gTOC). The other compounds from this group, however, occur in small and very small amounts in the investigated samples of the *Xenoxylon* wood with the exception of phenanthrene, which is quite abundant in the sample MP1554.

4. Discussion and conclusions

Containing about twenty species, *Xenoxylon* is one of the most homogeneous of all genera used for Mesozoic fossil woods (KRÄUSEL 1949). Both xenoxylid radial pitting (MÜLLER-STOLL 1951) and *Xenoxylon*-type of cross-field oopores are unknown outside the genus. Despite this homogeneity, some species show a mixed type of radial pitting (GOTHAN 1906) whereas others are typically araucarioid (PHILIPPE 1995). The occurrence of mixed type of radial pitting might be related to architectural variations (PHILIPPE 1992). The occurrence of clusters of much flattened pits is considered to be an apomorphic character (PHILIPPE 1995), and thus the genus can be regarded as monophyletic. The phylogeny of the genus is still very hypothetical, however (DING et al. 2000).

Up to now, *Xenoxylon* has never been found in anatomical connection with any foliage type. However, *Xenoxylon* is regularly associated with isolated foliages of the Miroviaceae family (PARICHIEV 1968; MANUM et al. 2000). At the Copenhagen Geological Museum, we examined the original material from Greenland studied by BOSE & MANUM (1990, 1991) and related by them to Miroviaceae. Unfortunately, we were unable to find any preserved woody structures in connection with the foliages. It is worth noting that Miroviaceae are represented in the Middle Jurassic of Poland (NOSOVA 2006).

As for the wood samples from Polish Middle Jurassic assigned to *Protopodocarpoxylon* sp. (MARYNOWSKI et al. 2007), the majority of diterpenoids encountered here in the *Xenoxylon phyllocladoides* wood samples are unaltered, preserved biomolecules, similar to those observed in extant plants (HEGNAUER

1962, 1986; OTTO & WILDE 2001), and some of them having a chemosystematical value. Some non-phenolic abietanes, such as dehydroabietane or abietic and dehydroabietic acids, are encountered among most conifer families and are therefore non-specific conifer markers (OTTO & WILDE 2001). On the other hand, phenolic abietanes like ferruginol, 6,7-dehydroferruginol, sugiol, hinokiol or 2-ketototarol are produced currently only by distinct conifer families (Cupressaceae s. l., Podocarpaceae and Araucariaceae) and are used as their characteristic biomarkers (HEGNAUER 1962, 1986; OTTO & WILDE 2001; OTTO & SIMONEIT 2001; MARYNOWSKI et al. 2007). As these phenolic abietanes are not synthesized by any extant Pinaceae representatives, it is thus highly probable that *Xenoxylon* is not related to this family. The CRAMER's hypothesis (1868), according which *Xenoxylon* belongs to *Pinaceae* based on the fact that by modern wood large window-like cross-field pits characterize Pinaceae, is thus invalidated.

Furthermore, an araucarian affinity of *Xenoxylon* may be also ruled out since Araucariaceae are characterized by the presence of tetracyclic diterpanes such as phyllocladanes, beyerane and/or kauranes as major compounds (HAUTEVELLE, unpublished data). The presence of totarane class biomarkers with relative high abundance in Łuków and Gnaszyn samples (Table 2) also attests that an Araucariaceae origin is unlikely because totaranes have never been reported in Araucariaceae (OTTO & WILDE 2001). Likewise, totaranes have never been reported in Cheirolepidiaceae, but this must be considered with care since the chemotaxonomy of this family is not presently well known. The organic extract of *Brachyoxylon trautii* wood, which belongs to the Cheirolepidiaceae family, is characterized by the presence of tetracyclic diterpanes (e.g. *ent*-beyerane) and ferruginol (HAUTEVELLE 2006) which is quite similar with those of *Frenelopsis alata*, which also belongs to the Cheirolepidiaceae (NGUYEN TU et al. 2000).

Thus, from a molecular point of view, *Xenoxylon phyllocladoides* seems to be closer to the Podocarpaceae and Cupressaceae s. l., and in a lesser extent to the Cheirolepidiaceae, than to the Pinaceae or Araucariaceae. Unfortunately, as the Miroviaceae family is yet to be studied from an organic geochemistry point of view, it cannot be compared.

The second interesting set of results is the great similarity we observed between the molecular composition of the wood species *Xenoxylon phyllocladoides* and that described for genus *Protopodo-*

carpoxylon (MARYNOWSKI et al. 2007). This is amazing, all the more since *Protopodocarpoxylon* is anatomically quite different from *Xenoxylon* (KRÄUSEL 1949). The genus *Protopodocarpoxylon* is sometimes put in relationships with the extinct conifer family Cheirolepidiaceae (AXSMITH & JACOBS 2005), but the molecular composition of this family is still not well known. Such chemical similarity between *Xenoxylon* and *Protopodocarpoxylon* may have phylogenetic relevance, but we do not think it is appropriate to justify a re-evaluation of the taxonomic circumscription of these genera. Indeed, these are form-genera, not natural ones.

Furthermore, the three wood samples here studied are characterized by various relative abundances of terpenoids compared to non-terpenoid products. Indeed, the Łuków sample shows the highest terpenoid concentration while the MP1554 sample presents the lowest one. Because terpenoids are the major components of resins and essential oils, this difference could be imputed to variable content of resin remaining within the fossil woods. On the other hand, the three samples also present different stages of molecular preservation. The Łuków sample presents the best preservation state as indicated by the abundance of biological compounds or compounds still bearing oxygenated functionalities which are generally removed during the first stages of the diagenesis. At the opposite, the sample MP1554 is characterized by the presence of only one biological terpenoid in low abundance while simonellite, retene and 2-methylretene, which are produced rather tardily during diagenesis, are much more abundant. Moreover, the higher relative abundance of phenanthrene in this sample is also characteristic of a more advanced diagenesis since this compound certainly originates from the late diagenesis of abietanes.

In conclusion, although comparisons are limited by available data, biomolecular study of *Xenoxylon phyllocladoides* clearly shows that *Xenoxylon* does not belong to the Pinaceae nor to the Araucariaceae. The wood *Xenoxylon* seems to be closer to the Podocarpaceae and Cupressaceae s.l., two modern families which are known to occur within the Jurassic (STEWART & ROTHWELL 1993), and in a lesser extend to the Cheirolepidiaceae, a Mesozoic extinct conifer family. Another extinct Mesozoic conifer family, the Miroviaceae, which is often associated with *Xenoxylon*, is unfortunately unknown from an organic geochemistry point of view and could not be compared. This study also shows evidence that preserved

biomarkers are not exceptional in fossil wood, and that they have a high potential for deciphering the systematic relationships of isolated vegetative organs of fossil plants.

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Table 1. Results for the analysis of Łuków and Gnaszyn (Poland) wood floras. The Łuków wood flora is Callovian, and that from the 'Gnaszyn' clay-pit is Middle Bathonian, and that from 'Alina' clay-pit is Late Bajocian in age (see text for details).

Localities	Gnaszyn area		
	Łuków	'Gnaszyn' clay-pit	'Alina' clay-pit
number of samples analyzed	15	25	2
undeterminable	5	6	0
<i>Agathoxylon</i> HARTIG	2	7	0
<i>Brachyoxylon</i> HOLLICK & HEFFREY	0	1	0
<i>Protopodocarpoxylon</i> ECKHOLD	2	8	1
<i>Protaxodioxylon</i> BAMFORD & PHILIPPE	0	1	0
<i>Xenoxylon</i> sp.	1	0	0
<i>Xenoxylon phyllocladoides</i> GOTHAN	3	2	1

Table 2. Biomarkers and PAHs identified in the Middle Jurassic *Xenoxylon phyllocladoides* GOTHAN wood from Luków (eastern Poland) and Gnaszyn (south-central Poland).

Compound	MW	Occurrence and relative abundance in the samples ¹			Source ²	Identification
		LUKÓW W1	GNW9	MP 1554		
ALIPHATIC LIPIDS						
<i>n</i> -Tetradecanoic acid	228	-	4.3	0.8	PI	MS
<i>n</i> -Hexadecanoic acid	256	1.3	34.9	2.6	PI	standard
<i>n</i> -Octadecanoic acid	284	3.6	24.6	-	PI	MS
<i>n</i> -Docosanoic acid	340	4.6	96.0	-	PI	MS
<i>n</i> -Tricosanoic acid	354	-	17.4	-	PI	MS
<i>n</i> -Tetracosanoic acid	368	66.7	95.2	-	PI	MS
<i>n</i> -Pentacosanoic acid	382	-	8.7	-	PI	MS
<i>n</i> -Hexacosanoic acid	396	9.2	23.9	-	PI	MS
SESQUITERPENOIDS						
Calamenene	202	-	0.2	-	C	SIMONEIT & MAZUREK 1982
Cadina-1(10),6,8-triene	202	2.71	0.9	-	C	SIMONEIT & MAZUREK 1982
Cadalene	198	54.2	4.2	23.7	C	standard
1,7-Dimethyl-4-isopropyl-naphthalene	198	-	0.6	0.6	C	ELIAS et al. 1997
Dihydro- <i>ar</i> -curcumene	204	2.7	0.6	-	C	ELLIS et al. 1995
DITERPENOIDS						
Phyllocladanes						
16(α)-Phyllocladane	274	-	-	0.9	C	
Abietanes						
Dehydroabietane ³	270	36.3	-	9.9	C	standard
16,17-Bisnordehydroabietane	242	6.1	0.3	-		MS
18,19-Bisnorsimonellite	224	-	0.1	-	C	MS
Simonellite	252	0.9	3.6	37.7	C	standard
Retene	234	0.5	0.4	19.7	C	PHILP 1985
1,2,3,4-Tetrahydroretene	238	-	0.2	-	C	PHILP 1985
2-Methylretene	248	-	0.2	-	C	BASTOW et al. 2001
Dehydroabietol ³	286	1.4	-	-	C	MS
Dehydroabietic acid	300	1.0	-	-	C	standard
18-Norferruginol	272	0.4	-	-	PCA	OTTO & SIMONEIT 2001
6,7-Dehydroferruginol	284	4.3	-	-	PCA	ENZELL & RYHAGE 1967
Ferruginol ³	286	100	3.0	-	PCA	standard
12-Hydroxysimonellite	268	17.1	-	-	C	OTTO & SIMONEIT 2001
Hinokiol ³	302	24.5	-	-	PCA	OTTO & SIMONEIT 2001
Sugiol ³	300	10.4	100	1.9	PCA	standard
Totaranes						
Diaromatic tricyclic totarane	252	0.5	-	-	C	OTTO et al. 1997
2-Ketototarol ³	300	20.0	25.0	-	PCA	MS
TRITERPENOIDS						
17 α 21 β (H)-norhopane	398	0.5	0.8	0.1	B	
17 α 21 β (H)-hopane	412	0.6	1.1	0.2	B	PHILP 1985
17 α 21 β (H)-homohopane 22S	426	0.3	0.7	0.1	B	PHILP 1985
C ₃₀ hop-17(21)-ene	410	0.5	-	-	B	MS

Table 2. (Cont.)

STEROIDS

Stigmast-4-ene	398	1.1	-	-	PI	MS
Stigmast-5-ene	398	1.2	-	-	PI	MS
1,9-Dimethyldiacholes-11(17)-ene (20S)	412	-	-	0.6	P1	MS
1,9-Dimethyldiacholes-11(17)-ene (20R)	412	-	-	0.6	P1	MS
Cholesterol	386	4.3	-	-	PI, F	standard
Campesterol	400	3.3	-	-	PI	MS
Cholesta-7,9(11)-dien-3-ol	414	8.3	-	-	P1	MS
β -Sitosterol ³	414	39.5	43.8	-	PI	standard
Stigmastanol	416	0.4	-	-	PI	standard
Stigmastan-3-one	414	10.5	3.1	-	PI	MS
Stigmasta-3,5-dien-7-one	410	1.3	2.4	1.1	PI	MS
Stigmast-4-en-3-one	412	12.0	-	-	PI	MS

AROMATIC HYDROCARBONS AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

4-Hydroxybenzaldehyde	122	-	53.8	-	PI	MS
Vanillin	152	12.9	-	0.8	P1	standard
Phenanthrene	178	2.5	1.8	25.8	-	standard
Anthracene	178	-	0.1	-	-	standard
3-Methylphenanthrene	192	0.1	0.8	2.7	-	RADKE et al. 1986
2-Methylphenanthrene	192	0.1	0.8	1.5	-	RADKE et al. 1986
9- + 4-Methylphenanthrene	192	0.1	1.2	3.9	-	RADKE et al. 1986
1-Methylphenanthrene	192	0.1	1.3	5.0	-	RADKE et al. 1986
Fluoranthene	202	0.3	2.1	5.5	-	standard
Pyrene	202	0.5	8.2	12.9	-	standard
Benzo[ghi]fluoranthene	226	0.4	1.6	2.8	-	MS
Benz[a]anthracene	228	0.1	1.1	1.5	-	standard
Chrysene/triphenylene	228	0.1	1.0	1.1	-	standard
Benzo[b]fluoranthene	252	0.5	7.6	4.0	-	WISE et. al. 2004
Benzo[k]fluoranthene	252	0.2	7.3	2.5	-	WISE et. al. 2004
Benzo[j]fluoranthene	252	0.3	6.9	1.0	-	WISE et. al. 2004
Benzo[e]pyrene	252	0.1	2.3	2.0	-	standard
Benzo[a]pyrene	252	0.1	2.0	1.5	-	standard
Perylene	252	6.2	59.7	100	-	standard
Benzo[ghi]perylene	276	1.8	6.8	1.6	-	WISE et. al. 2004
Indeno[1,2,3-cd]pyrene	276	1.9	2.9	2.9	-	WISE et. al. 2004

MS – Mass spectrum interpretation, GNW9 = Mid-Bathonian wood from ‘Gnaszyn’ clay-pit, Gnaszyn; MP1554 = Upper Bajocian wood from ‘Alina’ clay-pit, Gnaszyn.

¹ Abundance relative to major peak,

² C = conifers, PCA = Podocarpaceae, Cupressaceae + Araucariaceae, PI = plants, B = bacteria, F = fauna,

³ Unaltered natural products (biomolecules).