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Analytical pyrolysis and FTIR spectroscopy of fossil *Sequoiadendron giganteum* (Lindl.) wood and MWLs isolated hereof

Abstract Recent and fossil woods from the genus of *Sequoiadendron*, as well as their milled wood lignins were investigated by means of FTIR spectroscopy and pyrolysis GC/MS technique. Though almost same in appearance the differences in band intensities of FTIR-spectra reveals the distinctly increased aromatic character and the oxidation in fossil specimens. More detailed information about the changes in old wood were obtained by analytical pyrolysis, which delivers degradation products with shortened side chains and more saturated units relating to fossil lignin.

Analytische Pyrolyse und FTIR-Spektroskopie von Holz und isoliertem MWL aus fossilem *Seqoiadendron giganteum*

Zusammenfassung Recentes und fossiles Holz der Gattung *Seqoiadendron giganteum*, sowie daraus isoliertes Björkman-Lignin wurden mittels FTIR Spektroskopie und GC/MS Pyrolyse-Technik untersucht. Obwohl sich die Holzarten äußerlich sehr ähneln, zeigen die Unterschiede der Bandenintensität in den FTIR Spektren einen deutlich erhöhten, aromatischen Charakter und Oxidationsgrad in den fossilen Proben. Detailliertere Information über Veränderungen in den alten Holzarten wurden durch pyrolytische Analyse gewonnen, welche Abbauprodukte mit kürzeren Seitenketten und gesättigtere Einheiten des fossilen Lignin aufweisen.

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1 Introduction

Two fossil trunks of sequoia tree were excavated in a coal mine located about 20 km west of Bosporus on the shore of Black sea. The wood was partly in such a good condition that it looked like as weathered recent wood. The ^{14}C-method of age determination revealed, however, that their age was beyond the detectable limit. Accordingly, the samples are older than 41,000 years. The previous two publications on this topic dealt with the chemical composition and ultrastructure of these woods and their ethanol extractives, respectively. (Uçar et al. 1996, 1998). The barks of the same fossil specimen were also investigated (Staccioli et al. 1998, 2002).

It has been firmly established that the fossilization is accompanied with selective removal of polysaccharides leaving behind residues enriched in lignin, which can easily be determined as acid insoluble matter (Klason lignin). The acid insoluble part of fossil woods in this study is about two thirds of the total material. Therefore, in this paper the lignin moiety has been described in greater detail.

Usually, lignin analysis comprises time consuming degradation experiments. Therefore, in the experimental design for the present study the more rapid analytical pyrolysis approach combined with gas chromatography and mass spectrometry (Py-GC/MS) was preferred. The literature contains a large body on Py-GC/MS analysis of lignocellulosic materials, which confirms that in screening experiments this technique leads to useful data (Obst 1983, Saiz-Jimenez et al. 1987, Bremer 1991, Faix 1992, Meier and Faix 1992, Faix et al. 1992, Kleen 1993, Marques et al. 1994).

Two specimens belonging to the same fossil trunk of *Sequoiadendron giganteum* found on the site were studied: one light reddish brown and a dark colored—apparently more degraded—sample. The fossil woods and a recent *S. giganteum* wood for comparison such as the MWLs isolated hereof were submitted to analytical pyrolysis. Their FTIR-spectra have also been recorded.

2 Materials and methods

The light reddish brown fossil wood looked like weathered recent red wood and will be designated here as **B** (brown) and the dark colored one as **D** (dark). In case of the recent *S. giganteum* wood, the sapwood and heartwood were submitted to separate analyses.

The lignin content was determined on the previously acetone extracted material (extraction time 4 days) according to Runkel and Wilke (1951) using 72% H_2SO_4 and 40% HBr for the primary hydrolysis.

2.1 Isolation of milled-wood lignins

A modified Björkman procedure was applied for MWL preparation. Two successive Soxhlet extractions were conducted: pure acetone followed by a mixture of acetone-water (90/10, v/v) were used as solvents (48 h extraction time). Then the samples were thoroughly dried over P_2O_5 for a week and ball milled in toluene using a Retsch mill equipped with steel vessels and balls during three days. The extraction was done with dioxane-water (100/4, v/v) in an ultrasonic bath during 14 h according to Wegener and Stoll (1976) and Wegener and Fengel (1979).

The crude lignin obtained by evaporating the solvent were purified according to the standard procedure. First, the crude preparation was dissolved in 90% acetic acid and reprecipitated into water. The insoluble part was seperated by centrifugation and the acetic acid removed under reduced pressure. The further purification was performed by dissolving the product in a dichloroethane-ethanol mixture (2/1, v/v) and by precipitation in ethyl ether. The MWLs were dried in a desiccator 2–3 days under vacuum over P_2O_5. The yields of MWL's were around 10% for fossil and between 6–7% for recent sapwood and heartwood based on wood extracted with acetone.

Carbohydrate contamination of MWLs was estimated by means of ion exchange chromatography of hydrolyzates obtained after TFA hydrolysis as described by Fengel and Wegener (1979).

2.2 FTIR spectroscopy

Spectroscopic measurements were performed in a Bio-Rad Excalibur series FTS 3000 spectrophotometer using the standard KBr method (300 mg KBr plus 1 mg lignin; resolution: 4 cm^{-1}; 64 scans). The spectra were base line corrected at 3,700, 1,850 and 700 cm^{-1} and normalized to the highest band at 1,510 cm^{-1}.

2.3 Pyrolysis GC/MS

Ball milled and acetone pre-extracted woods and MWLs were subjected to analytical pyrolysis in a CDS Pyroprobe 100 (coil filament) instrument. Before pyrolysis the samples (80–100 μg placed in an open quartz boat) remained for 30 s in the interface at 200°C. Each sample was pyrolysed in duplicate at 450°C for 10 s and from the results an average pyrogram was calculated. The temperature rising time was as short as possible (below 1 s). GC conditions: DB 1701 column (30 m×0.32 mm, 0.25 μm film, J&W Scientific); Injector and detector temperature: 250°C; Temperature program: 45°C, heating rate 4°C min, 280°C for 15 min, split 1/20; Carrier gas: helium; Product identification by quadrupol MS (HP 6890 Series, Mass Selective Detector). Product quantification by FID detector. The peak integrals are presented as %. The congruence indices were calculated according to Salo et al. (1989).

3 Results and discussions

It is documented in the literature that *S. giganteum* has a relative high Klason lignin contents (35,4% according to Leopold and Malmström 1952). Our results obtained by the Runkel-Wilke method confirm this yielding: 34% Klason residue after 6 h extraction with ethanol benzene and 35% residue after a 4 day extraction with acetone. Buried woods undergo selective removal of polysaccharides to leave lignin-enriched material. Thus the fossil woods gave rise to 66–72% Klason residues (dark sample) and 62–68% (light brown sample). The higher values are for the samples extracted with acetone. Obst et al. (1991) reported similar high lignin contents from Canadian Artic fossil softwoods. The lignin contents from woods of the Eocene and Paleocene were ranging from 66.5% to 85%, and those of Miocene (ca. 0.5 mill. yr-old) around 48%.

It is also well established that MWLs unavoidably contain polysaccharides, whose content rarely exceeds 2–3% when the lignin is properly prepared and carefully purified. The carbohydrate contents of the MWLs (Table 1) prepared both from recent and fossil woods are low.

As anhydroglucose occurs both in cellulose and glucomannane, it is not surprising that the yield of glucose (0.5%) is the highest. The absence of arabinose in fossil

Table 1 The sugar content of MWLs (based on lignin)
Tabelle 1 Zuckergehalt des MWL (bezogen auf Lignin)

Sugars	**MWL** from fossil wood		**MWL** from recent wood	
	Dark brown (**D**)	Light brown (**L**)	Sapwood	Heartwood
	%	%	%	%
Glucose	0.5	0.4	0.5	0.6
Xylose	<0.1	0.1	0.3	0.3
Galactose	0.1	0.1	0.3	0.3
Arabinose	nil	nil	0.3	0.3
Mannose	<0.1	0.1	0.3	0.3
Σ	≤ 0.8	0.7	1.7	1.8

MWLs is also self explanatory in view of the low arabinose content in arabionoxylans and its easy hydrolysation

Fig. 1 Normalized band intensities of MWLs isolated from *Sequoiadendron giganteum* recent and fossil woods. *Dotted box* Sapwood, ⊟ Heartwood, *grayed box* Fossil B, ■ Fossil D
Abb. 1 Normalisierte Bandenintensitäten von MWL aus rezentem und fossilem Holz der Gattung *Seqoiadendron giganteum. Gepunkteter Balken* Splintholz, ⊟ Kernholz, *grauer Balken* Fossil B, ■ Fossil D
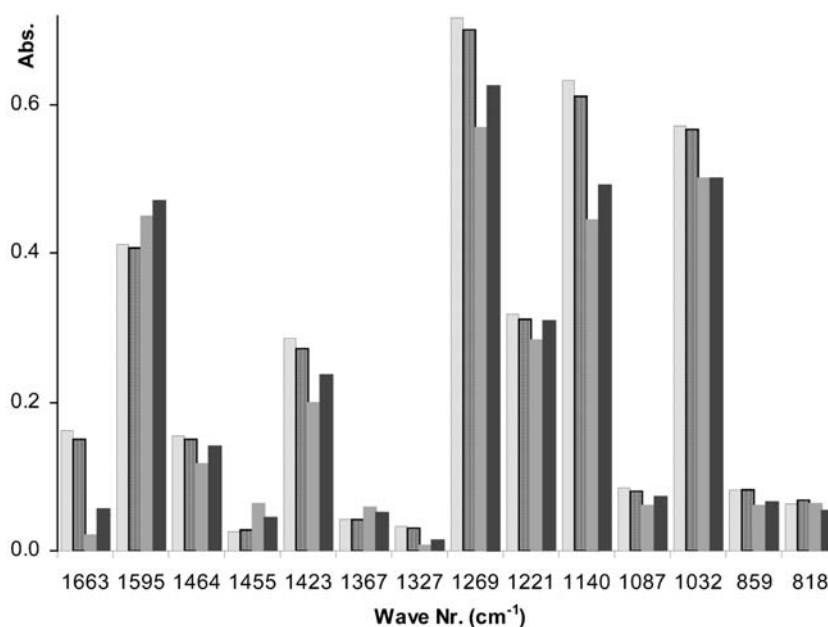
Table 2 Typical bands and their intensities of FTIR spectra of MWLs
Tabelle 2 Typische Banden und Intensitäten der FTIR Spektren von MWL

Peak No.	Sapwood		Heartwood		Fossil B		Fossil D	
	Wave No.	Norm.	Wave No.	Norm.	Wave No.	Norm.	Wave No.	Norm.
	cm^{-1}	Abs.	cm^{-1}	Abs.	cm^{-1}	Abs.	cm^{-1}	Abs.
1	1663.7	0.163	1663.1	0.151	1671.7[a]	0.021	1671.6[a]	0.057
2	1594.9	0.414	1595.4	0.407	1600.5	0.450	1596.5	0.472
3	**1510.0**	**1.000**	**1510.2**	**1.000**	**1510.7**	**1.000**	**1510.4**	**1.000**
4	1464.1	0.154	1464.0	0.150	1463.7	0.118	1463.9	0.140
5	1455.0	0.025	1454.9	0.028	1453.8	0.063	1454.6	0.045
6	1422.7	0.285	1422.9	0.272	1423.4	0.200	1423.4	0.237
7	1367.2	0.042	1367.2	0.042	1366.6	0.058	1365.4	0.050
8	1326.7	0.032	1326.7	0.030	1326.9	0.007	1326.9	0.014
9	1269.0	0.718	1269.1	0.701	1268.9	0.571	1269.1	0.626
10	1221.3	0.318	1221.5	0.312	1222.0	0.284	1222.4	0.309
11	1140.2	0.633	1140.2	0.612	1139.9	0.445	1140.1	0.491
12	1086.9	0.084	1086.8	0.079	1085.3	0.060	1086.1	0.074
13	1032.2	0.572	1032.2	0.568	1031.6	0.502	1032.4	0.501
14	859.1	0.081	859.2	0.083	858.0	0.061	858.0	0.066
15	818.5	0.063	817.8	0.068	819.0	0.063	819.8	0.054

[a] Shoulder

during the millennia. Uçar et al. (1996) could not detect arabinose in fossil woods, either. The content of other sugars is also less in fossil MWLs in comparison to recent MWLs. This observation is consistent with the lower polysaccharide content of the fossil material.

3.1 FTIR spectroscopy

The FTIR spectra of all MWLs seem to be very similar in appearance. Concerning the interpretation of lignin FTIR spectra one should keep in mind the hint of Hergert (1971) : "..., the most common error is to conclude that two or more lignin products are *identical* because their infrared spectra are *similar*. Rather, the opposite must be true, i.e., if the spectra are not precisely identical, it must

be concluded that products are not identical." Thus, for a better comparability of small differences we present the band intensities of the fingerprint region as a bar diagram (Fig. 1) and also in Table 2.

Both, the data in Table 2 and in Fig. 1 clearly display the typical features of a G lignin (1595 cm^{-1} <<1510 cm^{-1} dominant >>1463 cm^{-1}; absorbance max. at 1140 cm^{-1}; 1269 cm^{-1} second highest peak; 1032 cm^{-1} >1221 cm^{-1} two bands at 859 and 818 cm^{-1}, according to Faix 1991).

The recent MWLs do have almost exact band frequencies, whereas small shifts were observed in fossil MWLs but only for two bands. The band of aromatic skeletal vibrations at 1595 cm^{-1} tends very slightly to become higher, as being between 1597 and 1600 cm^{-1}

Table 3 Summarized results of analytical pyrolysis: **H** = phenol compounds with one OH, **G** = guaiacyl type compounds, **C** = mostly compounds of carbohydrate origin, **A** = benzene type compounds and phenols with two OH, **U** = unidentified compounds

Tabelle 3 Zusammengefasste Ergebnisse der Pyroyseberechnung: **H** = Phenolverbindungen mit einem OH, **G** = Guaiacylverbindungen, **C** = Verbindung überwiegend aus Kohlehydratursprung, **A** = Benzolartige Bestandteile und Phenole mit 2 OH, **U** = nicht identifizierte Zusammensetzungen

Chemical compounds	Milled wood lignins				Woods			
	Recent		Fossil		Recent		Fossil	
	Sapwood Area %	Heartwood Area %	Light brown Area %	Dark brown Area %	Sapwood Area %	Heartwood Area %	Light brown Area %	Dark brown Area %
Sum **H** sat.	1.3	1.9	8.0	6.3	0.2	0.4	4.5	4.7
Sum **H** un-sat.	0.0	1.5	6.5	3.1	0.8	1.2	3.4	2.7
Sum H total	**1.3**	**3.4**	**14.5**	**9.4**	**1.0**	**1.6**	**7.9**	**7.5**
Sum **G** sat.	48.2	40.8	52.1	56.8	11.4	10.8	26.7	22.5
Sum **G** un-sat.	46.2	46.9	26.0	27.8	12.6	11.3	24.4	16.1
Sum G total	**94.4**	**87.7**	**78.1**	**84.6**	**24.0**	**22.1**	**51.2**	**38.7**
Sum C	**2.9**	**6.2**	**3.5**	**3.5**	**74.9**	**75.9**	**39.8**	**51.9**
Sum A	**0.5**	**1.3**	**1.6**	**0.7**	**0.0**	**0.1**	**0.6**	**0.3**
Sum U	**0.9**	**1.4**	**2.3**	**1.8**	**0.1**	**0.2**	**0.5**	**1.6**
Sum Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

A far more extended table is available by the corresponding author

and the one at 1663 cm^{-1} changes to a shoulder at a bit higher wave number (1672 cm^{-1}).

As can be seen from both presentations, the differences between the spectra are indeed very small. During interpretation of these results for the lignins as a whole one should have the low yield of MWLs (around 10%) in mind and the fact that a MWL represents the less changed moiety of a (fossil) lignin.

Compared to the spectra of recent MWLs, the fossil ones exhibit lower intensities at the majority of bands. Especially, the following regions show a pronounced decrease in absorbance:

– **1672** cm^{-1}, shoulder instead of 1663 cm^{-1} (C=O stretch vibrations in conjugated para substituted aryl ketones). Coniferyl aldehyde alone absorbs at 1652 cm^{-1} and methylation increases the value to 1660 cm^{-1} (Hergert 1971).
– **1423** cm^{-1} (aromatic skeletal vibrations combined with C-H in plane deform.)
– **1327** cm^{-1} band appears in form of a shoulder but in higher intensities in fossil MWLs. As the interpretation of this band "syringyl ring breathing with CO stretching" does not apply for G lignins, it indicates condensation or substitution of aromatic ring at position 5 (Faix 1992). Obst et al. (1991) observed in the case of fossil white pine wood from the Miocene (Site "Resolute"; Klason residue 48%) still a distinct maximum in this region. In samples with Klason residues exceeding 65% the band also merged into the 1270 cm^{-1} band.
– **1269** cm^{-1} (G ring plus C=O stretch)
– The absorption maximum at **1140** cm^{-1} (C-H in plane deformations of guaiacyl units) instead of 1120 cm^{-1} is the indicator for the absence of syringyl units in lignins.

– **1032** cm^{-1} (C-H in plane deformations of guaiacyl rings assisted by C-O deformation in primary alcohols and unconjugated C=O stretch)

The decreased band intensities indicated above can be interpreted in general terms as a "loss" of guaiacyl units and secondary alcohols during fossilization. The splitting of aromatic methoxyl (or methyl) groups and terminal aliphatic CH$_2$OH groups could account for these observations.

There are only three following IR-bands of MWLs isolated from fossil woods showing somewhat higher absorptions:

– **1595** cm^{-1} band (aromatic skeletal vibrations and C=O stretch)
– **1455** cm^{-1} (C-H deformations: asym. in -CH$_3$ and -CH$_2$-)
– **1367** cm^{-1} (aliphatic C-H stretch in CH$_3$ but not OCH$_3$ groups with phenolic OH groups)

The higher intensities of the aromatic skeletal vibrations are a consequence of the splitting of aliphatic side chains and the lower carbohydrate contents in fossil MWLs. The increase in the intensities at 1455 and 1367 cm^{-1} allows the assumption that more saturated shortened side chains were then created.

3.2 Pyrolysis gas chromatography / mass spectrometry

A complete, very long table of pyrolysis products of woods and MWLs could not be provided here. However, it is available from the corresponding author with an off print. In this table, the peaks and their relative areas are listed as % values according to their origin: (1) Peaks of
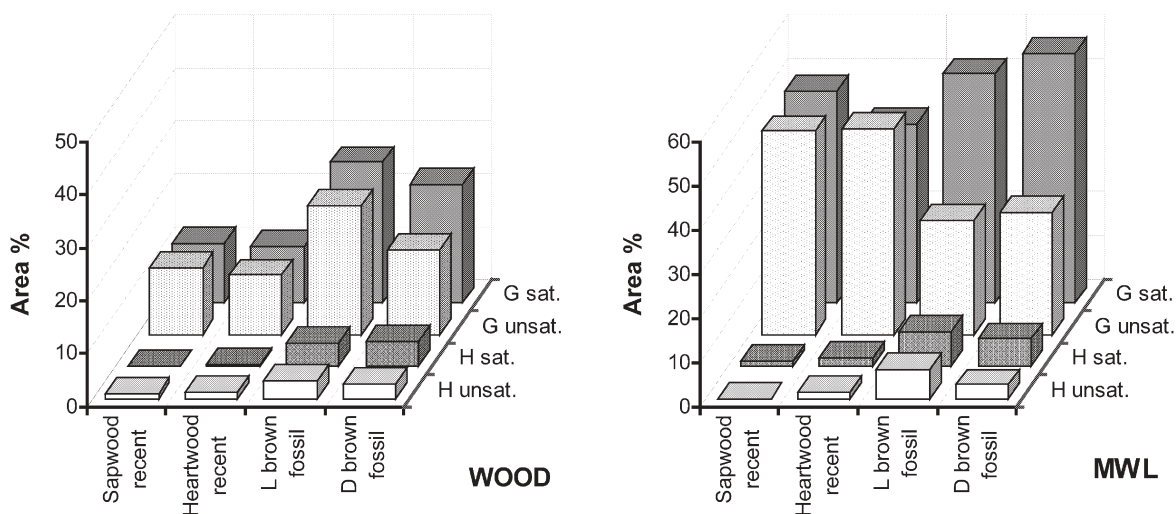
Fig. 2 The distribution of lignin related components in woods and MWLs
Abb. 2 Verteilung der ligninverwandten Bestandteile in den Holzarten und MWL

mostly carbohydrate origin, (2) Phenols with one OH group, (3) Guaiacyl type degradation products, (4) Benzenes and phenols with two OH groups, and (5) Unidentified compounds.

In Table 3 the results are summarized based on the above mentioned categories, where the phenols and guaicacols are additionally subdivided into substances with saturated and unsaturated side chains.

The full interpretation of the typical carbohydrate type degradation products is not intended here. Nevertheless it must be mentioned that the most abundant substances in this category are hydroxyacetaldehyde, methylglyoxal, acetol (partly results of the reverse aldol condensation, i.e. the less specific splitting of pyranose rings) and levoglucosan (as a results of glucan chain splitting and the subsequent dehydration of glucose units in cellulose), Shafizadeh and DeGroot (1976), Byrne et al. (1966).

The fossil specimens deliver 2–3 times more levoglucosan than the recent ones. This observation has two explanations: first, the degree of crystallization in fossil woods is probably higher as a result of the preferred hydrolysis of the amorphous regions (Fengel and Wegener 1988). Second, earth alkali metals are known to promote the reverse aldol condensation and thus lowering the levoglucosane yield (Kleen 1993). Clearly, the probability is high that the Na^+ and K^+ content in fossil woods became low due to ion exchange with Ca^{2+} in the course of fossilization. In view of this, it is understandable that the (supposedly more degraded) dark brown specimen yielded more levoglucosan than the other one.

It has to be recalled that listing of several unspecific degradation products such as methanol, formic acid, acetic acid, etc. among the carbohydrate type degradation product is not cogent. Moreover, one has to consider that no individual response factors were used for quantitative evaluation. For this reason the sum of carbohydrate and lignin type pyrolysis products cannot truly reflect the real carbohydrate/lignin ratio in the samples. Hence these data

should rather be interpreted as tendencies instead of absolute values.

As such, the data are consistent: all MWLs give rise mainly to guaicayl type phenols while the fossil ones also yield 9% (B sample) – 14% (D sample) phenols without methoxyl. This observation is undoubtedly the result of demethoxylation of G units during ageing. The sum of guiacyl units in pyrograms of recent woods (21–24%) and fossil woods (37–49%) also reflect properly the higher Klason residue of the fossil specimens.

The distribution of lignin related phenolics—subclassified as 4-hydroxy-phenyl, guaiacyl, saturated and non-saturated products—are presented in two different ways in Figs. 2 and 3. These Figures illustrate again well the demethoxylation and the relative increment of saturated product as far as the fossil samples are concerned. The latter finding can be rationalized in the following way:

Recent samples contain "native" lignins. This means that they contain a lot of β-O-4 linkages with OH groups in the neighboring α-position. From these units water is easily split as accompanying reaction of the thermal rupture of the β-O-4 linkages. As a consequence, unsaturated products such as coniferyl alcohol, coniferyl aldehyde but also isoeugenol, vinylguaicacol, etc. can be observed in the pyrograms. On the other hand, in aged lignins more "condensed" units can be expected, where the α-position is frequently substituted by C-C bonds. These units, however, are lowering the overall yield and lead to phenols having shorter side chains, which also contain less double bounds.

Generally, it can be stated that with the ageing of wood distinctly increased yields are observed for phenol, cresols, 4-vinyl phenol, guaiacol, 4-methyl guaiacol, 4-ethyl guaiacol, isoeugenol, while the amounts of vanillin, acetoguaiacone, coniferyl alcohol and coniferyl aldehyde decrease. The decrease of the latter two compound is especially pronounced, which also explain to a great ex-

Fig. 3 Normalized summative
composition of lignins and
woods
Abb. 3 Normierte sum-
marische Zusammensetzung der
untersuchten Hölzer und Lig-
nine
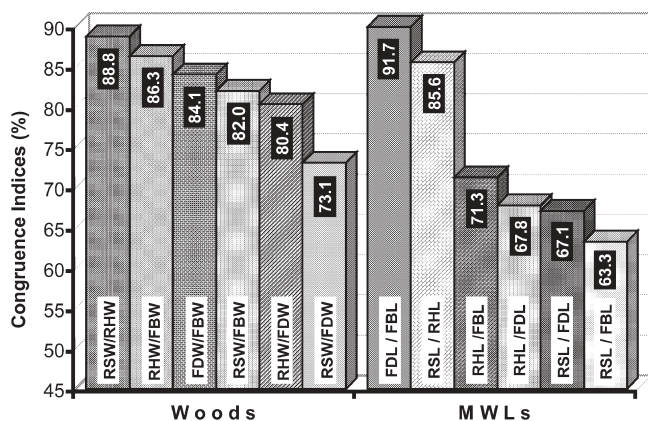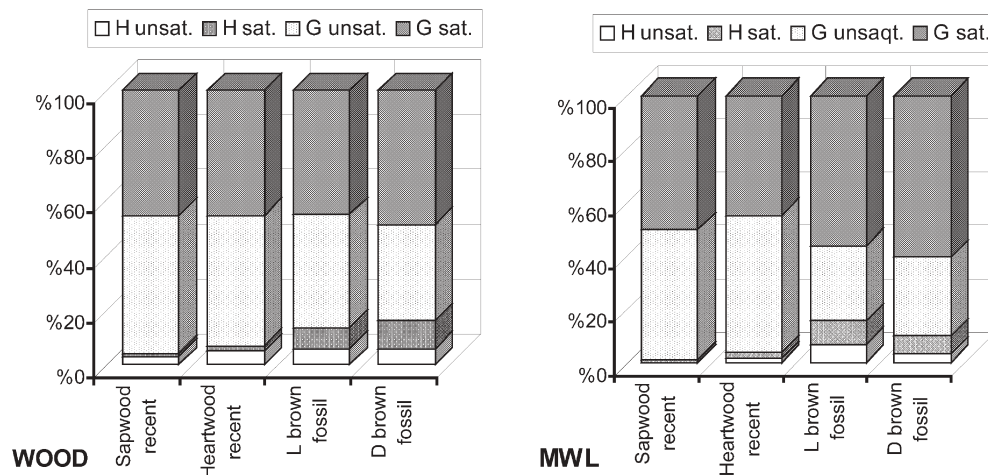
Fig. 4 Lignin related congruence indices between the relevant
substances: *R* recent, *F* fossil, *S* sap, *H* heart, *B* light brown, *D* dark
brown, *W* wood, *L*: lignin
Abb. 4 Ligninverwandte Übereinstimmungsindices zwischen den
betreffenden Substanzen. *R* jüngere, *F* fossile, *S* Saft, *H* Kernholz,
B hellbraun, *D* dunkelbraun, *W* Holz, *L* Lignin

tent the diminished yield of unsaturated substances in
fossil lignins.

3.3 Congruence indices

A pyrogram bears a lot of information which is not
completely described in a simple manner as represented
in Table 3 and Figs. 2 and 3. The approach of calculating
congruence indices is another possibility to account for
more complex similarities and differences between two or
several samples (Salo et al. 1989; Faix et al. 1991). The
reproducibility of pyrograms of identical samples is such
that one can obtain pyrograms with similarity indices
around 95%. In Fig. 4 the similarity indices are shown for
relevant pairs of pyrograms, where woods and MWLs are
compared.

Recent sapwood and heartwood pyrograms show 89%
similarity. The similarities between recent and fossil
brown woods are surprisingly high (86% heartwood vs.

fossil brown wood; 82% sapwood vs. fossil brown wood).
Thus the pyrograms confirm the visual impression con-
cerning the less degraded character of the light brown
sample. The two fossil woods are also similar on the 84%
level. On the other hand, the similarity indices between
the more degraded fossil wood (dark brown) and recent
woods are—as expected—lower (80–73%).

The pyrograms of the fossil MWLs are more similar
(92%) than those from recent MWLs (86%). The com-
parison between recent and fossil MWLs distinctly reveal
the differences caused by ageing, such as shortening of
the side chains, decrement of unsaturated pyrolysis
products and yield similarity indices between 71 and
64%.

4 Conclusions

A comparison of the FTIR spectra of MWLs obtained
from recent and fossil woods and the pyrograms of the
same specimens give a uniform picture of ageing of *S.
giganteum* in buried state in a geological time scale.
During a preferred hydrolytic removal of 50–60% of the
polysaccharides, the lignin moieties suffer relative little,
yet discernible structural changes, as far as the MWLs are
concerned. However, it should be noted that the MWLs
represent only 10% of the whole lignin content.

The darker fossil wood had changed more than the
light brown wood. Analytical pyrolysis gives evidence of
clear differences between the lignins in recent and fossil
samples, especially when the congruence indices were
taken for comparison. The pyrograms exhibit degradation
products with shortened side chains and less double
bonds. The FTIR spectra disclose more saturated groups,
a higher aromaticity, and the presence of more condensed
units in the case of fossil MWLs.

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