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EFFECT OF NATURAL AGING ON THE CHEMICAL COMPOSITION OF NORWAY SPRUCE, FIR, AND EUROPEAN OAK WOOD

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Abstract:
The chemical composition of a number of naturally aged construction wood samples of spruce, fir and oak was investigated. The content of lignin, polysaccharide, and extractives was determined using wet chemical and chromatographic methods. Differences to non-aged wood samples were found particularly found on oak wood samples with regard to lignin and polysaccharide content as well as to cellulose crystallinity. The composition of wood extractives of aged and non-aged wood samples revealed degradation processes due to oxidation and slight hydrolysis. The investigation showed that the relative content of the structural wood constituents depends on the sample age as well as the conditions they were aged under. The different degradation rates of those structural components may lead to contradictory results regarding their contents at certain degrees of aging. Cellulose crystallinity values are affected by extractives content.

Key words: *aged wood; chemical composition; cellulose; crystallinity; hemicellulose; lignin; non-aged wood.*

INTRODUCTION

Wood has played an important role in the human life since ancient times and has been widely used for various purposes. Although its importance decreased due to technological advancements and the discovery of new materials, it still belongs to the basic raw materials. However, the fact that it is an organic material means that it undergoes degradation in natural conditions. The biological degradation, caused by bacteria, insects or fungi, is especially fast when wood is in contact with liquid water or soil. When wood is taken out of the natural circle due to human activity and is stored in more favourable conditions, its longevity increases, but a slow degradation may still occur.

Although information about the degradation of wood is crucible for the conservation of wooden cultural heritage and for re-usage of wood as well, the aging process of wood and the properties of aged wood has been scarcely investigated so far. The literature on the chemical properties of aged wood is rather scarce as well. In addition, the measurements in the different studies were carried out with various methods, that makes direct comparison impossible. It has to be mentioned as well, that these methods were designed for the analysis of non-aged wood and may deliver false values when applied on aged wood with altered chemical structure (Hedges 1989). However, despite of the mentioned difficulties, conclusions of different studies mostly coincide with each other.

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Most studies considering the hemicelluloses in the aged samples report a decrease in their proportion (Chowdchury *et al.* 1967; Erhardt *et al.* 1996; Yonenobu and Tsuchikawa 2003) or some kind of modification (Ganne-Chédeville *et al.* 2011). Only one author found that the hemicellulose content of aged and non-aged spruce samples is similar (Holz 1981). However, it has to be mentioned that in this case only the pentosane content was investigated, not the whole hemicellulose fraction and the aged sample was only 60 years old. These may explain why the findings were different to those of other authors.

Investigations on softwood samples not older than 400 years show no changes in the cellulose content (Holz 1981; Erhardt *et al.* 1996). However, a decrease was found in older samples (Narayanamurti *et al.* 1961; Chowdchury *et al.* 1967; Tomassetti *et al.* 1990; Campanella *et al.* 1991). Considering the findings of Yonenobu and Tsuchikawa (2003), the decrease may primarily affect the amorphous regions of cellulose. To the best of the author's knowledge, the cellulose content of aged hardwoods has been investigated in only one study so far, that showed a decrease for an 2200 years old sample (Chowdchury *et al.* 1967). Kohara and Okamoto (1955) found reduced holocellulose content both in aged softwood and hardwood samples. They speculated that decrease occurs immediately at the beginning of aging in the case of hardwoods, but for softwoods, the holocellulose content may increase for about 100 years and decrease afterwards. As both hemicelluloses and/or cellulose degrade during aging, leading to mass loss of the component, a decrease in the holocellulose content seems to be reasonable. However, Van Zyl *et al.* (1973) report about an increase for wood samples over 4100 years.

Beside the proportion of cellulosic materials, the crystallinity of the cellulose may change as well. Investigations on samples older than 300 years state a decrease (Kohara and Okamoto 1955; van Zyl *et al.* 1973; Erhardt *et al.* 1996). Kohara and Okamoto (1955) suggest that in softwoods an increase occurs during the first hundred years of aging, followed by a decrease, but no period of increase may be present in hardwoods. However, there are studies which results do not fit in this theory: both Gawron *et al.* (2012) and Popescu *et al.* (2007) reported an increase in crystallinity for hardwood samples up to 180 and 260 years, respectively.

Increased lignin content was found for samples between 300 and 800 years of age (Narayanamurti et al. 1961; Tomassetti et al. 1990). Degradation and oxidation of the lignin structures was reported as well (Borgin *et al.* 1975; Ganne-Chédeville *et al.* 2011). For wood older than 4100 years, a decreased lignin content was observed (Van Zyl *et al.* 1973).

Beside the main component, content of extractives and ash were investigated as well. Kohara and Okamoto (1955) stated increased extractive content for samples over 240 years. Ash content may also increase with aging.

A comprehensive literature overview on the changes in chemical and physical properties of wood during its aging is given by Kránitz *et al.* (2015).

In a preceding study of naturally aged Norway spruce, silver fir and oak, Sonderegger *et al.* (2015) showed that, in comparison to non-aged wood samples, aging modifies wood colour and causes a reduction of impact bending strength, whereas sorption and swelling as well as bending and fracture toughness are not, or only partly, modified over extended time. The current study used the same aged wood samples and aims to clarify the remaining contradictories among different studies on the chemical properties of aged wood. In addition to the determination of the main components a qualitative analysis of the extractives was carried out that should deliver further information about the degradation processes.

MATERIAL AND METHODS

Material

The investigations were carried out on both aged and non-aged wood samples of the species Norway spruce (*Picea abies* L. Karst., Fig. 1) and European oak *(Quercus* sp.).

Information about the supposed origin and age of the specimens is given in Table 1. The aged materials came from demolished buildings, partly via wood trader. In the latter case, the closer growth place unfortunately remains unknown. The age of the specimen was determined by means of dendrochronology (cf. Günther 2013).

aged spruce (SA06) non-aged spruce (SR01)
Fig. 1.
Photographs of samples of aged and non-aged spruce.

Table 1

Wood samples used for chemical analysis

			Age in years	
ID	**species**	**origin**	**Estimated by provider**	**determined**
SA05	spruce	Appenzell, Switzerland	250 years	210-290
SA06	spruce	Chech Republic	150 years	150
SA07	spruce	Chech Republic	150 years	150
SA08	spruce	Switzerland	120 years	120
SR01	spruce	Appenzell, Switzerland	non-aged	
FA06	fir	Gstaad, Switzerland	120 years	120
FA07	fir	Gstaad, Switzerland	120 years	120
FR01	fir	Appenzell, Switzerland	non-aged	
OA04	oak	Appenzell, Switzerland	250 years	210-292
OR03	oak	Zürich, Switzerland	non-aged	

For the chemical analysis pieces from the sound, inner part of samples were used. In the first step, they were slivered with a router; subsequently the material was fractioned with 2mm and 1mm sieves. Chemicals used in the analysis were purchased from Sigma Aldrich.

Basic chemical analysis

The proportion of extractives, lignin, cellulose, hemicellulose and ash was determined using wet chemical methods, which are described below. For the determination of lignin and hemicellulose content, the sieve fraction <1mm was used, while for the cellulose content, the fraction of 1-2mm was taken. This sample size was chosen in order to obtain a cellulose which was not damaged additionally by mechanical means. The moisture content of the investigated samples is given in connection with the respective test methods below.

Ash content:

The ash content was determined according to the standard TAPPI-T-211-om-93 (2012). For each sample approx. 30g material of the 1-2mm sieve fraction was heated in a muffle furnace to constant weight at 525°C. The ash content was calculated according to Equation 1:

$$AC = m_a / m_{od} \times 100 \qquad (1)$$

where: AC ash content [%];
m_a weight of ash [g];
m_{od} oven dry weight of sample [g].

Content of extractives:

To determine the extractive content and for preparing material for further analysis, an ethanol-toluol extraction was carried out according to the standard TAPPI-T-204-cm-97 (1997).

For each material, two samples of ca. 5g were investigated; a sieve fraction of 1-2mm and a fraction <1mm. The material to be analysed was filled in an extraction thimble and extracted for 6 hours with an ethanol-toluol (1:1) solvent using a Soxhlet apparatus. After cooling down, most of the solvent was removed using a rotary evaporator and the extractives were dried at 60°C to constant weight. The extractive content was calculated according to Equation 2:

$$EC = m_e / m_{od} \times 100 \quad (2)$$

where: EC extractive content [%];
m_e weight of extractives [g];
m_{od} oven dry weight of sample [g].

Lignin content:

The acid-insoluble lignin content was determined according to the standard ASTM-D-1106-56 (1996). The determination was carried out twice for each sample using extracted material from the sieve fraction of <1mm.

Approximately 1g of the material was disintegrated with 20ml of 67% sulphuric acid cooled to 0°C. After 16 hours of storage at room climate, 630ml deionized water was added and the mixture was refluxed for 5 hours. The lignin was vacuum-filtrated over a G4 frit and washed until pH 7.0 was reached. The oven dried weight was subsequently determined.

The lignin content was calculated according to Equation 3:

$$LC = m_l / m_{od} \times 100 \quad (3)$$

where: LC lignin content [%];
m_l oven dry weight of lignin [g];
m_{od} oven dry weight of the sample before extraction [g].

Cellulose content:

The cellulose content was determined according to the Kürschner-Hoffer method (Kürschner and Hoffer 1931). The determination was carried out twice for each sample using extracted material from the sieve fraction of 1-2mm.

Approximately 1g of material was refluxed for 1 hour with 25ml nitration mixture (1 volume nitric acid, 4 volumes ethanol). After vacuum filtrating over a G3 frit, another 25ml of the nitration mixture was added. The material was cooked three times with the nitration mixture. After the third filtration, the material was washed with ethanol, and then subsequently with deionized water. The remaining cellulose was refluxed with deionized water for 30 minutes, filtrated with hot deionized water until acid free and then finally oven dried.

The cellulose content was calculated according to Equation 4:

$$CC = m_c / m_{od} \times 100 \quad (4)$$

where: *CC* cellulose content [%];
m_c oven dry weight of cellulose [g];
m_{od} oven dry weight of the sample before extraction [g].

Holocellulose content:

The holocellulose content was determined with peracetic-acid according to Poljak (Poljak 1948). The determination was carried out twice for each sample using extracted material from the sieve fraction of <1mm.

10ml of a 10% solution of sodium acetate in concentrated acetic acid was added to ca. 0.5g material. The mixture was disintegrated with 6ml 40% peracetic acid and refluxed at 70°C for 1 hour. After cooling down, 50ml of deionized water was added. The mixture was vacuum filtrated over a G2 frit and washed until acid free. Finally, the oven dry weight of the holocellulose was measured.

The holocellulose content was calculated according to Equation 5:

$$HOC = m_h / m_{od} \times 100 \quad (5)$$

where: HOC holocellulose content [%];
m_h oven dry weight of holocellulose [g];
m_{od} oven dry weight of the sample before extraction [g].

Hemicellulose content

The hemicellulose content was calculated as a difference of the holocellulose and cellulose content according to Equation 6:

$$HMC = HOC - CC \quad (6)$$

where: *HMC* hemicellulose content [%];
HOC holocellulose content [%] ;
CC cellulose content [%].

Cellulose crystallinity

The degree of crystallinity of the cellulose was determined by means of Raman spectroscopy. The measurements were carried out at the Institute of Wood and Plant Chemistry at Dresden University of Technology (Germany), with the FT-Raman-Spectrometer MultiRAM III (Bruker Optics GmbH). This Raman system is equipped with a standard diode-pumped, air-cooled Nd: YAG laser source (1064nm). For the measurements, a resolution of $4cm^{-1}$ was used with a laser power of 252mW. Data were collected and processed with the software Opus 7.0 (Bruker Optics GmbH). For each sample, wood dust from the sieve fraction of <1mm was analysed. As local differences due to wood inhomogeneity may occur, 5 measurements with 400 scans were performed. The average spectra of the samples were created after baseline correction and normalization (on the region of $1191.1\text{-}1079.2cm^{-1}$ – cellulose) to gain representative information about the samples.

The crystallinity was determined in agreement with Agarwal *et al.* (2010) as the ratio of the intensities of the peaks at 380 cm^{-1} and 1096 cm^{-1}, according to Equation, measured on the average spectra of the samples:

$$CR = \frac{I_{380}}{I_{1096}} \quad (7)$$

where: CR - crystallinity of cellulose [-];
I_{380} - Raman intensity of the peak at 380 cm^{-1} [-];
I_{1096} - Raman intensity of the peak at 1096 cm^{-1} [-].

Peak height was calculated by a baseline method that involved choosing a minimum intensity wavenumber near the peak and drawing a horizontal line under the peak.

Gas chromatography/mass spectrometry

GC/MS was used for the qualitative analysis of the components of extractives. The extraction was carried out on the basis of the standard TAPPI-T 204 cm-97 (1997) with an ethanol-toluol (1:1) solvent. After the extraction, the solvent was evaporated down with a rotary evaporator, dehydrated and filtered prior to the analysis.

GC/MS analyses were performed on an HP 6890 gas chromatograph (Agilent Technologies) equipped with a split/splitless injection port and an MSD 5973 (Agilent Technologies). Approximately 1μl of the concentrated solution of extracts was injected with split mode at a temperature of 260°C. The initial temperature of 80°C was increased to 280°C with a rate of 5°C/min. The substances were separated on a DB-1 capillary column (J&W Scientific, 100% dimethylpolysiloxane, 30m×0.25mm ID, 0.25μm film thickness). Helium, at a constant flow of 1ml/min, was used as the carrier gas. Electron impact mass spectra were recorded at 70eV in the m/z range of 10-550. The substances were identified by analysis of the individual mass spectra and comparison with the NIST 2.0 mass spectral library. Major substances not included in the NIST 2.0 mass spectral library were identified on the basis of mass spectra reference standards analysed at the same conditions as the sample material.

RESULTS AND DISCUSSION

Proportion of components

Proportions of the main chemical components of the investigated samples as determined by wet chemical analysis are presented in Table 2. It has to be noted that the total amount of components deviates

remarkably from 100% in some cases. This therefore has to be regarded as an error of the applied methods, for example, determination of the acid-soluble lignin content can cause errors up to 9% (Fengel and Wegener 1989). This has to be taken in account when evaluating the results. A considerable part of the errors is a consequence of imperfect separation due to similar chemical structure and/or strong chemical bonds between the main components.

Table 2

Content of wood components determined by wet chemical analysis

ID	species	age	ash	extracts	cellulose	hemicellulose	lignin
SA05	spruce	250 years	0.26%	1.29%	52.42%	19.88%	28.29%
SA06	spruce	150 years	0.33%	1.50%	52.95%	23.40%	29.48%
SA07	spruce	150 years	0.30%	1.84%	49.03%	27.11%	28.51%
SA08	spruce	120 years	0.32%	2.66%	49.03%	29.44%	30.50%
SR01	spruce	non-aged	0.26%	2.39%	53.01%	32.31%	29.00%
FA06	fir	120 years	0.39%	2.95%	51.83%	19.32%	31.27%
FA07	fir	120 years	0.40%	1.34%	56.43%	22.82%	29.90%
FR01	fir	non-aged	0.29%	1.38%	52.26%	20.98%	28.14%
OA04	oak	250 years	0.27%	5.24%	42.15%	17.37%	28.90%
OR03	oak	non-aged	0.30%	11.96%	35.34%	29.09%	31.62%

Differences between the ash content of aged and non-aged samples of spruce and oak wood are rather small and an age trend can be seen. In the case of fir, aged samples show an ash content increase of more than 30% compared to the non-aged wood sample. The presence of preservatives as a possible reason for this can be ruled out because: 1) preservatives are usually located only in the outer part, which was excluded in sample preparation and; 2) no evidence of preservatives was found by GC/MS investigations. As all the values are in agreement with earlier results reported in the literature (Wagenführ 1996), it is supposed that the observed differences are rather a result of natural variations than a consequence of aging or wood treatment. Thus, the influence of aging on the ash content can be considered negligible for the species investigated.

A decrease in the extractive content with age can be observed, but some exceptions occur. The most distinct difference is found in oak wood, where the amount of extractives is more than twice as high in the non-aged sample compared to the aged one.

The decrease probably results from a loss of liquid and volatile components. Moreover, it could be a consequence of biological degradation, although this is unlikely as no signs of considerable biological attack were apparent during microscopic investigations or during the analysis of the extractives' composition. The presence of wood preservatives in the wood of spruce and fir could be a reason for the outliers, but no evidence for their application was found. Furthermore, all values obtained are in the range given in the literature, only the results of samples SA08 and FA06 are comparatively high.

No significant changes in the cellulose content of fir and spruce samples can be stated, as the differences between the specimens do not exceed the accuracy of the determination. The difference is more pronounced in the case of oak, with the aged samples having higher cellulose content than the non-aged sample. The hemicellulose content of spruce and oak wood was found to diminish with age. In specimens older than 210 years about 30% of hemicelluloses are lost. Fir again shows a different behaviour: differences between aged and non-aged samples are not significant and no trend with age can be seen. Values determined for non-aged specimens agree well with those available in the literature.

Differences in the lignin content of various specimens are rather small. As the difference between the two values obtained for the same sample ranges up to 0.7% in some cases, no age trend regarding the apparent **lignin content can be stated.**

The Raman-spectra of aged and non-aged samples are rather similar, only small differences occur. The spectrum of the sample SA05 is shown in Fig. 2 as an example. In the case of oak, the fluorescence of the aged sample was obviously lower than that of the non-aged sample, probably as a consequence of the lower extractive content. As the vibrations of bonds in extractives may overlap with those of lignin structures, the spectra of extracted oak sawdust were recorded as well. By determining the spectral parameters (peak heights and areas) of these spectra, the influence of extractives could be filtered out, resulting in more reliable results regarding the amount of lignin. In the case of spruce and fir, the effect of extractives was

considered to be negligible and the evaluation was carried out based on the spectra of the unextracted materials.

Crystallinity of cellulose

The degree of cellulose crystallinity was determined with the help of Raman spectroscopy as the ratio of the cellulose peaks 1096 and 380 cm^{-1} (Fig. 3). The results for the various wood samples are presented in Table 3. Values of aged specimens are slightly lower than those of non-aged samples. Differences are rather small for spruce and fir samples and show no clear trend with age. In the case of oak, the value for the 250 year old sample OA04 is about 25% lower than that of the non-aged oak wood sample. However, values of un-extracted and extracted specimens differ remarkably. Looking at the results of the latter, the crystallinity of the aged sample is still lower, but the difference is less pronounced.

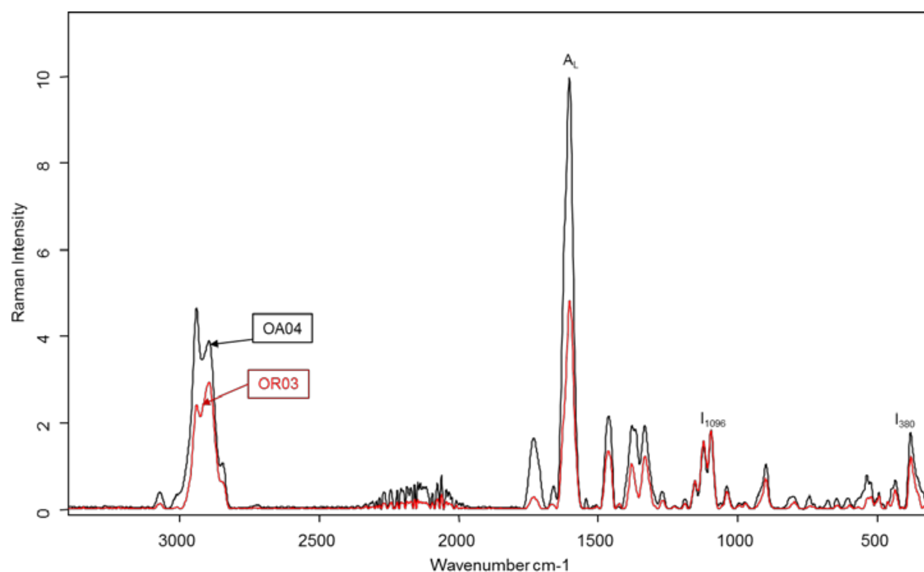

Fig. 2.
Raman-spectra of the aged oak sample OA04 compared to the non-aged oak sample OR03. A_L: area under the lignin peaks; I_{1096}: intensity of the peak at 1096cm^{-1} (cellulose I); I_{380}: intensity of the peak at 380cm^{-1} (crystalline cellulose).

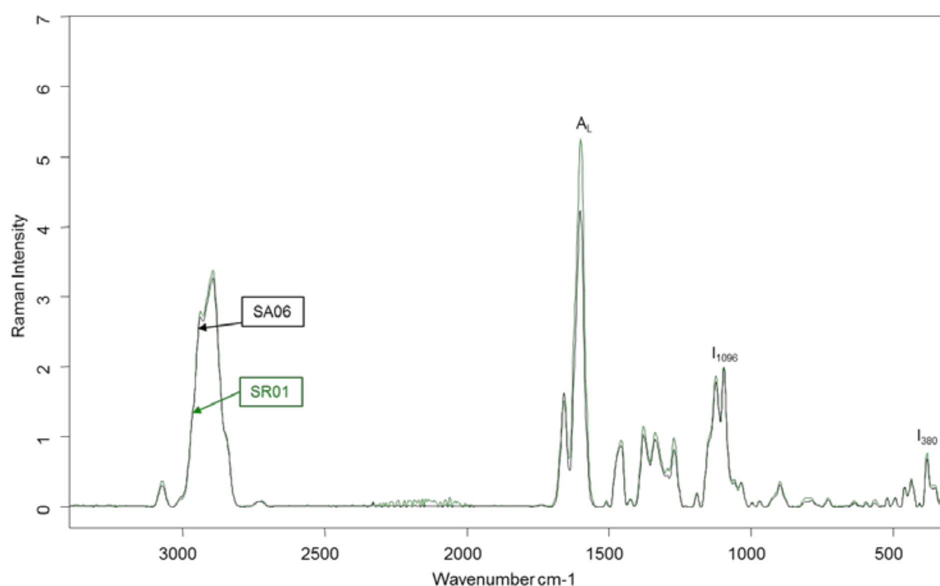

Fig. 3.
Raman-spectra of the aged spruce sample SA06 compared to the non-aged spruce sample SR01. AL: area under the lignin peaks; I1096: intensity of the peak at 1096cm^{-1} (cellulose I); I380: intensity of the peak at 380cm^{-1} (crystalline cellulose).

Table 3

Degree of cellulose crystallinity based on measurements by RAMAN spectroscopy

ID		species	age	cellulose 1096 cm^{-1}	cellulose 380 cm^{-1}	cell. crystallinity
SA05		spruce	250 years	1.87	0.77	0.41
SA06		spruce	150 years	1.92	0.72	0.37
SA07		spruce	150 years	1.74	0.71	0.40
SA08		spruce	120 years	1.75	0.75	0.43
SR01		spruce	non-aged	1.86	0.86	0.46
FA06		fir	120 years	1.79	0.73	0.41
FA07		fir	120 years	1.77	0.73	0.41
FR01		fir	non-aged	1.93	0.81	0.42
OA04	unextr.	oak	250 years	1.99	1.21	0.61
	extr.	oak		1.98	1.32	0.67
OR03	unextr.	oak	non-aged	1.99	1.58	0.79
	extr.	oak		2.00	1.46	0.73

Composition of extractives

The GC spectra of the wood extractives are presented in Figs. 4-6 and the main identified compounds are listed in Table 4. The phenolic compound vanillin was dominant and found in every sample. It is a common extractive that has already been isolated from various wood species, including both softwoods and hardwoods (Ekman 1976; Calimli and Olcay 1978; Flamini *et al.* 2007; Alanon *et al.* 2012a). However, it could be a degradation product of lignin as well (Ishikawa *et al.* 1963; Holmbom *et al.* 1992; Sjoholm *et al.* 1992). In the two samples SA07 and SR01, isovanillin was also detected. All of the spruce samples contained benzaldehyde, guaiacol and mequinol (p-guiaicaol), and the latter two were also found in one of the fir samples. Guaiacol and mequinol are well known substances related to lignin biosynthesis, while benzaldehyde is a characteristic volatile of *Quercus* species (Perez-Coello *et al.* 1998; Cadahia *et al.* 2003; Jordao *et al.* 2006). Its occurrence in spruce sapwood was reported by Wajs *et al.* (2006). Antiarol, found in both of the oak samples, was detected earlier in *Quercus* and other hardwood species as well (Flamini *et al.* 2007; De Rosso *et al.* 2009). Syringol, a well-known phenolic component of oak wood (Perez-Coello *et al.* 1998; Cadahia *et al.* 2003; Alanon *et al.* 2012b), could be identified only in the aged sample, suggesting that it may arise from lignin degradation. The non-aged oak sample OR04 contained pyrogallol, which may have been formed upon pyrolysis of gallic acid.

Together with vanillin, vanillic acid or its derivatives were present in most of the samples, except in the non-aged sample of spruce wood. In some cases, homovanillic acid and its methyl ester was detected as well. These phenolic acids are frequently reported as volatile compounds of the *Quercus* species (Perez-Coello *et al.* 1998; Cadahia *et al.* 2003; De Rosso *et al.* 2009; Alanon *et al.* 2012b) and were found in several tropical woods as well (Kilic and Niemz 2012).

Syringic acid and synapaldehyde were identified in the oak samples and syringaldehyde in the aged oak wood. Both aldehydes are known flavour compound components of *Quercus* species (Cadahia *et al.* 2003; De Rosso *et al.* 2009). However, aldehydes can be formed as oxidation products of lignin compounds as well. Ellagic acid was present in the samples of oak wood amongst the tannins group. Flavonoids were found in non-aged spruce and in all oak samples as well. 4-hydroxy-2-methoxycinnamaldehyde was detected in every sample. This substance was isolated from *Vanilla fragrans* (Sun *et al.* 2001), but no references about its occurrence in wood are known to the authors. Therefore, it is supposed that the peak identified represents rather its isomer, coniferaldehyde, a common extractive both in softwoods and hardwoods (Fengel and Wegener 1989; Cadahia *et al.* 2003).

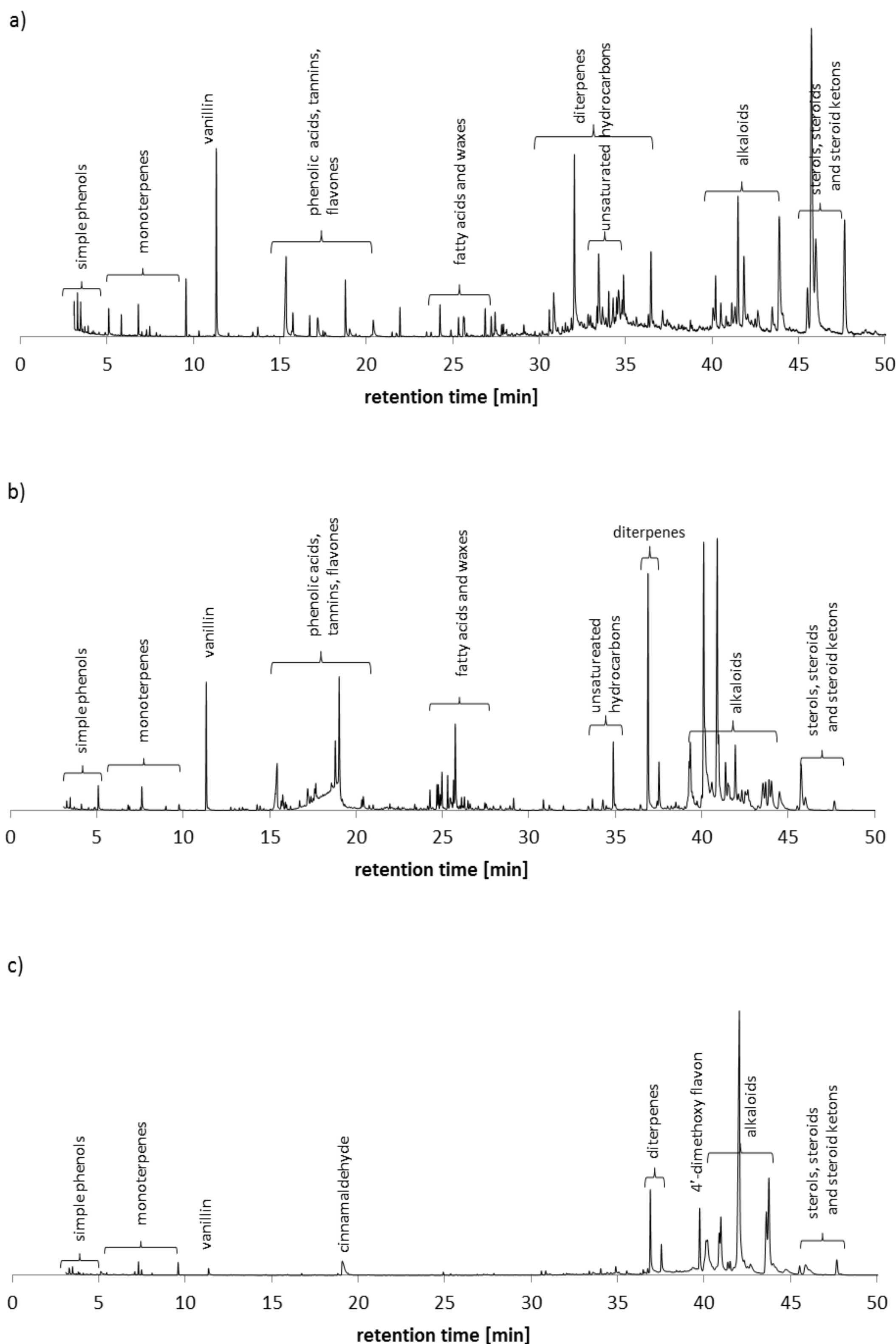

Fig. 4.
GC spectra of spruce samples:
a - SA05, 250 years; b - SA07, 150 years; c - SR01, non-aged.

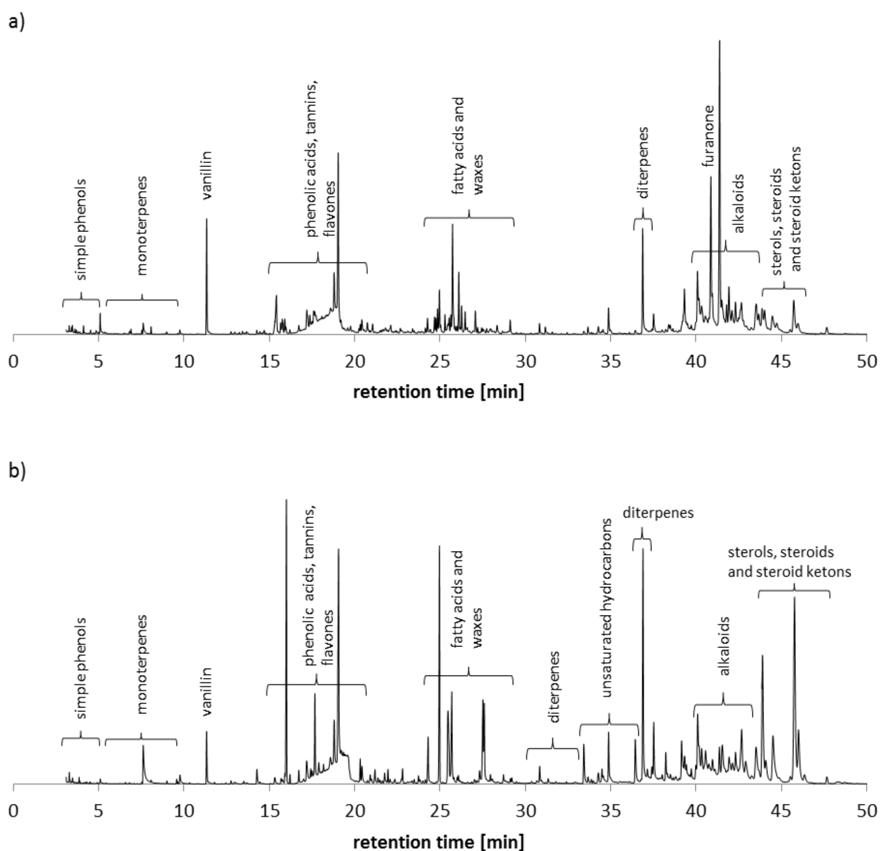

Fig. 5.
GC spectra of fir samples: a - FA06, 120 years; b - FR01, non-aged.

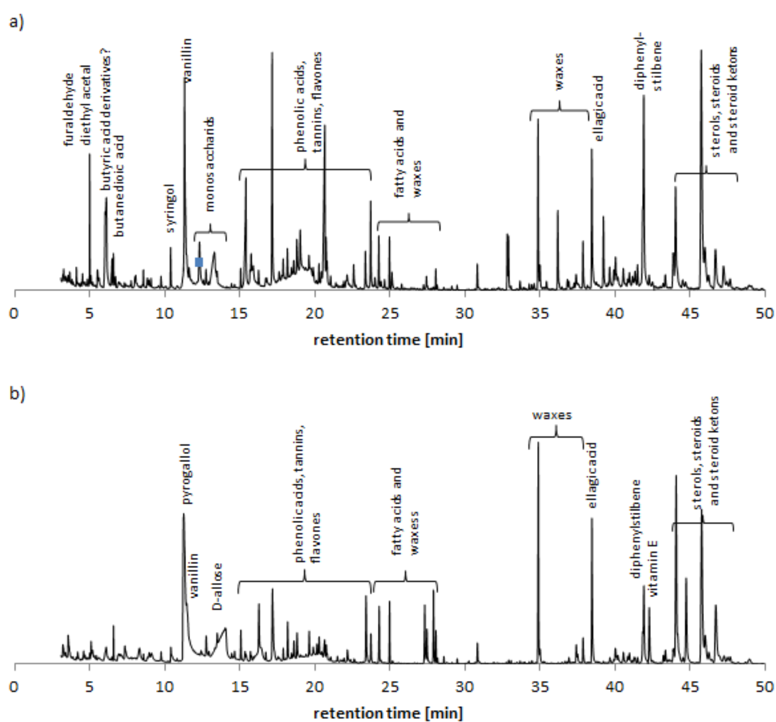

Fig. 6.
GC spectra of oak samples: a - OA04, 210 years; b - OR03, non-aged.

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Most terpenoids were detected in the spruce samples. The monoterpene alcohols α - terpineol, 4-terpineol and p-menthane-1,8-diol were isolated from the non-aged sample. The latter was found in the aged sample SA05 as well, together with borneol and fenchol. Furthermore, the diterpene alcohol epimanool was detected in this sample. The aged sample SA07 contained the monoterpene 3-carene. All of the mentioned components have been already identified in the *Pinaceae* family (Khan and Pentegova 1988; Barrero *et al*. 1994; Pichette *et al*. 1998; Ucar *et al*. 2003; Radulescu *et al*. 2011). The sesquiterpene alcohol, nerolidol, was present in fir samples that had been detected in the wood and sprouts of spruce in earlier investigations (Wajs *et al*. 2006; Radulescu *et al*. 2011).

In the spruce samples, resin acids were also found, in the form of methyl esters. The sample SA07 contained only dehydroabietic acid, while in the samples SA05 and SR01 its derivatives were detected as well. Dehydroabietic acid is one of the most abundant resin acids in softwoods (Fengel and Wegener 1989) and 7-oxodehydroabietic acid was proven to be present in the resin of *Pinus sylvestris* (Regert and Rolando 2002) and in the extracts of pine and spruce sawdust (Arshadi and Gref 2005). Colombini *et al*. (2005) identified both 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acid in archaeological resins of *Pinaceae*. According to the literature (Fengel and Wegener 1989), no mono- or diterpenoids were found in the oak samples. Fatty acids were absent in the spectrum of the non-aged spruce sample, while various compounds of this group could be identified in other samples. Hexadecanoid acid (palmitic acid) and 9-octadecenoic acid (oleic acid) were found in all three wood species investigated. Tetradecanoic acid (myristic acid) was detected in the aged oak sample, while the ethyl esters of tetradecanoic and/or hexadecanoic acid were present in fir and oak samples. The separation of the latter two was not possible with the analysis method applied. 9, 12-octadecadienoic acid was found only in non-aged samples of fir and oak. Further compounds identified in one of the softwood samples were octanoic acid, tridecanoic and octadecanoic (stearic) acid. Oak samples contained methyl and ethyl esters of fatty acid as well. Most of these fatty acids or their corresponding alcohols are well known wood extractives and, apart from pentacosanoic acid, have been previously described in the literature (Fengel and Wegener 1989; Ucar and Fengel 1995; Vikstrom *et al*. 2005; Moodley 2011).

In the aged spruce samples, unsaturated hydrocarbons C8-C10 were found, however, because of similar elution properties, the exact compounds could not be identified. Octadecene, nonadecene and docosene were detected earlier in *Eucalyptus* species (Moodley 2011), and docosene in *Betula* species as well (Lavoie and Stevanovic 2007). The presence of hydrocarbons with 14-28 carbon atoms was proven in the *Picea* genus, namely in *Picea orientalis* by Ucar (2005).

All of the samples contained steroid compounds. 3-methoxy-ergost-8(14)-ene and stigmastanol were present in every sample excluding non-aged spruce wood. Furthermore, various derivatives of colastanol and ergostanol were identified. Stigmastanol, colastanol and ergostanol are also often detected in the extractives of various wood species (Gutierrez *et al*. 1999; Ucar 2005; Vikstrom *et al*. 2005; Lavoie and Stevanovic 2006). β-sitosterol, the most common sterol compound of softwoods (Fengel and Wegener 1989) was only detected in sample SA05.

The most frequent compounds are listed in Table 3. Furthermore, furanones were detected, which are degradation products of the thermal decomposition of saccharides. As they are only present in small amounts in the samples, it is supposed that they were formed during the extraction or the GC/MS analysis and not because of the aging process. Butanedioic acid, found in the aged oak sample OA04 in the form of its ethyl ester, could be a product of microbial degradation. However, its amount is quite low and no other evidence for microbial attack was seen in the sample.

No compounds related to wood preservatives have been found. Thus, it can be stated that the wood samples used for the chemical investigations have not undergone any treatment that would influence the results.

Comparing the chromatograms of aged and non-aged woods, it can be stated that aged samples provided more peaks, especially at lower retention times. This indicates an increase in the number of bonds and low-molecular-weight substances in the material. These compounds could derive from microbial or thermal degradation, but also from alteration of extractives like oxidation, cross-linking or condensation.

Although quantification of the compounds is not possible with the method applied, a comparison of their relative amount within the sample can be made. The proportion of vanillin within the extractive compounds increases with aging in all wood species, indicating that oxidation has taken place. Benzaldehyde, found in the aged spruce samples, is an oxidation product as well. The relative amount of fatty acids in oak and fir samples is higher for non-aged wood. In the case of spruce, no fatty acids were found in the reference sample, and the same trend can be observed for the two aged samples. The amount of steroid compounds increases in spruce, but decreases in fir, while no clear trend can be seen for oak. Regarding the group of phenolic acids, a decreasing trend can be observed in both softwoods, when the non-aged sample is not considered. In contrast, their proportion is clearly higher in the aged oak sample than in the non-aged one. In spruce samples, an increase in the amount of unsaturated hydrocarbons can be

observed with increasing age. The amount of monoterpenoids in softwoods seems to increase with aging as well, probably as a result of decomposition of diterpenoids.

The results of the GC/MS analysis indicate that oxidation and degradation processes have taken place during the aging of wood. The comparison of individual compounds should be handled carefully, as the composition of extractives varies greatly according to the growing site, position of the tree and even within the tree. In addition, in the case of oak, it is not known whether it is *Q. robur* or *Q. petraea* which makes the comparison even more difficult.

As reported in the literature, the number of detectable and identifiable components greatly depends on the extraction method applied and on the temperature program of the GC/MS analysis (Perez-Coello *et al*. 1998; Wajs *et al*. 2006). The analysis carried out within this study allowed a broad range of extractives to be detected, from simple phenolic components to more complex substances like steroids. However, some peaks remain unidentified, probably due to the low resolution of the spectra. In order to obtain more precise information about the quality and quantity of extractives, further investigations are needed.

Chemical investigations reveal reduced hemicellulose and extractive content for oak and spruce samples, while ash and lignin content seem to be unaltered. The apparent cellulose content may increase for oak wood, but a conclusion can hardly be drawn because of differences in the total amount of compounds that originate from the uncertainties of the applied methods. Crystallinity of the aged oak samples was remarkably lower than in non-aged wood, while small differences among spruce samples prevented detecting any visible trend. In the case of fir, no chemical changes could be proven, which could be a consequence of species related properties. However, it has to be considered that the fir specimens investigated were only 120 years old. In addition, the spruce specimen of similar age shows only minor differences to its non-aged sample counterpart, therefore it is supposed that degradation processes are rather slow in the first 120 years and changes are too small to be detected by the wet chemical methods used in the present study. The observed trends related to the chemical compounds are in good agreement with the literature and the crystallinity results correspond to the theory of Kohara and Okamoto (1955) as well. GC/MS analysis of the compounds of extractives showed evidence that oxidation has taken place in all aged specimens. This is in accordance with statements by Fengel and Wegener (1989), who reported degradation for unsaturated compounds, fats and fatty acids during seasoning. The increased amount of vanillin and vanillic acid in aged samples, as well as the presence of aldehydes, confirms earlier studies reporting oxidation processes in lignin (Borgin *et al*. 1975).

Differences between spruce samples of the same age are most likely influenced by differing chemical processes due to different aging conditions.

Table 4

Main compounds of extractives identified by means of GC/MS "+": found; "-": not found

RT [min]	Compound	Sample						
	Phenols	SA05	SA07	SR01	FA06	FR01	OA04	OR04
3.28	Benzaldehyde	+	+	+	-	+	-	-
4.53	2-Methylphenol	-	-	-	-	-	+	-
5.09	Guaiacol	+	+	+	+	-	-	-
5.11	Mequinol	+	+	+	-	-	-	-
9.76	p-Vinylguaiacol	-	+	-	-	-	-	-
10.40	Syringol	-	-	-	-	-	+	-
11.28	Pyrogallol	-	-	-	-	-	-	+
11.33	Vanillin	+	+	+	+	+	+	+
11.35	Isovanillin	-	+	+	-	-	-	-
16.29	Antiarol	-	-	-	-	-	+	+
	phenolic acids, tannins and flavons	SA05	SA07	SR01	FA06	FR01	OA04	OR04
15.76	Vanillic acid and its methyl ester	+	+	-	+	+	+	+
15.76	2,4'-Dihydroxy-3'-methoxyacetophenone	-	+	-	+	-	-	-
15.91	Vanillic acid ethyl ester	-	+	-	+	-	-	-
17.17	Syringaldehyde	-	-	-	-	-	+	-
17.19	Homovanillic acid and its methyl ester	+	-	-	-	+	+	+
18.81	4-Hydroxy-2-methoxycinnamaldehyde	+	+	+	+	+	+	+
20.67	Syringic acid	-	-	-	-	-	+	+

RT [min]	Compound	Sample						
23.73	Synapaldehyde	-	-	-	-	-	+	+
37.43	Flavone 5,7-dihydroxy-8-methoxy-	-	+	-	-	-	+	-
38.46	Ellagic acid	-	-	-	-	-	+	+
38.47	3-Hydroxy-2-(3-hydroxy-4-methoxyphenyl)-7-methoxy-4H-chromen-4-one	-	-	-	-	-	-	+
39.76	7-Hydroxy-3',4'-dimethoxyflavone	-	-	+	-	-	-	-
	terpenoids, resin acids and their esters	SA05	SA07	SR01	FA06	FR01	OA04	OR04
6.82	Borneol	+	-	-	-	-	-	-
5.83	Fenchol	+	-	-	-	-	-	-
7.30	α -Terpineol	-	-	+	-	-	-	-
7.09	4-Terpineol	-	-	+	-	-	-	-
9.58	p-Menthane-1,8-diol	+	-	+	-	-	-	-
16.01	Nerolidol	-	-	-	+	+	-	-
23.40	3-Carene	-	+	-	-	-	-	-
25.34	Epimanool	+	-	-	-	-	-	-
32.04	Dehydroabietic acid methyl ester	+	+	+	-	-	-	-
33.36	15-Hydroxydehydroabietic acid, methyl ester	+	-	+	-	-	-	-
34.04	7-Oxodehydroabietic acid, methyl ester	+	-	+	-	-	-	-
36.49	15-Hydroxy-7-oxodehydroabietic acid, methyl ester	+	-	+	-	-	-	-
	fatty acids and waxes	SA05	SA07	SR01	FA06	FR01	OA04	OR04
6.82	Octanoic acid	-	+	-	-	-	-	-
24.27	Tetradecanoic acid	-	-	-	-	-	+	-
24.31	n-Hexadecanoic acid	+	+	-	+	+	-	+
24.99	Hexadecanoic acid, ethyl ester	-	-	-	+	+	+	+
25.70	Tridecanoic acid	-	-	-	-	+	-	-
27.33	9,12-Octadecadienoic acid and ethyl ester	-	-	-	-	+	-	+
27.45	9-Octadecenoic acid and ethyl ester	+	+	-	+	+	+	+
27.96	Octadecanoic acid	-	-	-	-	+	-	-
37.88	Tetracosanoic acid, ethyl ester	-	-	-	-	-	+	+
40.56	Pentacosanoic acid, 2,10-dimethyl-, methyl ester	-	-	-	-	-	+	-
40.57	Tetracosanoic acid, 2,4,6-trimethyl-, methyl ester	-	-	-	-	-	-	+
	hydrocarbons	SA05	SA07	SR01	FA06	FR01	OA04	OR04
33.45	1-Docosene / 1-nonadecene / Z-5-nonadecene	+	-	-	-	-	-	-
36.46	1-Docosene / 1-octadecene	-	+	-	-	-	-	-
	steroids	SA05	SA07	SR01	FA06	FR01	OA04	OR04
41.86	β -Sitosterol acetate / ergosta-4,6,22-trien-3.beta.-ol	+	-	-	-	-	-	+
43.88	Ergostenols	-	-	-	+	+	-	-
43.91	Cyclopropa[5,6]cholestan-3-ol,3',6-dihydro-, (3.alpha.,5.alpha.,6.beta.)-	-	-	-	-	+	-	-
44.04	Cholestane, 3-methoxy-, (3.beta.)-	-	-	-	-	-	+	+
44.09	Cholestan-3-ol, 5,6-epoxy-,	-	-	-	-	-	+	+
45.52	Cholesta-5,5-dien-7-one	+	-	+	-	-	-	-

RT [min]	Compound	Sample						
45.75	3-Methoxy-ergost-8(14)-ene	+	+	-	+	+	+	+
46.00	Stigmastanol	+	+	-	+	+	+	+
46.10	Stigmast-7-en-3-ol	-	-	+	-	-	-	-
47.23	Taraxasterol	-	-	-	-	-	+	-
	Further compounds	SA05	SA07	SR01	FA06	FR01	OA04	OR04
4.12	2(3H)-Furanone, 5-ethenyldihydro-5-methyl	-	+	-	-	-	-	-
5.01	2-Furaldehyde diethyl acetal	-	-	-	-	-	+	-
6.49	Butanedioic acid monoethyl ester	-	-	-	-	-	+	-
7.35	5-Hydroxymethylfurfural	-	-	-	-	-	-	+
7.61	2,3-Dihydrobenzofuran	-	+	-	+	+	-	-
8.59	Hydroxybutanedioic acid diethyl ester	-	-	-	-	-	+	-
22.60	2'-Methoxy-[1,1'-biphenyl]-2-carboxaldehyde	-	-	-	-	-	+	-
26.11	Dehydrojuvabione	-	+	-	+	+	-	-
34.89	10,11-Dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin	+	+	+	+	+	-	-
40.88 40.90	2(3H)-Furanone, dihydro-3,4-bis[(4-hydroxy-3-methoxyphenyl)methyl]-	-	+	+	+	-	-	-
41.93	α,β-Diphenylstilbene	-	-	-	-	-	+	+
43.48 43.54 43.69	Naphtho[2,3-c]furan-1(3H)-one, 3a, 4,9,9a-tetrahydro-6-hydroxy-4-(4-hydroxy-3-methoxyphenyl)-7-methoxy-,	+	+	+	+	-	-	-
43.53	(+)-Lariciresinol	-	-	-	-	+	-	-

CONCLUSIONS

The current investigations revealed a decrease in the hemicellulose, while its degradation products were detected by means of GC/MS investigations on the extractive compounds as well. These findings coincide well with the literature.

No considerable differences in the cellulose content of aged and non-aged samples were found for spruce, similarly to earlier investigations of different authors that were carried out on softwood specimens below 400 years of age. On the other hand, the oak sample investigated here showed a decrease even at the age of 250 years.as it was the case in an earlier study for an 2200 years old hardwood sample as well (Chowdchury *et al.* 1967). The results suggest that aging may affect the cellulose differently in hardwoods and softwoods. However, it cannot be excluded that the difference measured in the current study arises from the unusual high extractive content of the reference sample (12.0% for non-aged). No remarkable differences were detected in the crystallinity of cellulose either. In the case of spruce, it may coincide with the theory of Kohara and Okamoto (1955), namely that in softwoods an increase occurs during for about the first hundred years of aging, followed by a decrease. However, according to this theory the crystallinity of hardwoods should decrease even at the beginning of the aging that could not be stated here on the oak sample. The reason behind this discrepancy could lie in the accuracy of the applied methods or the differences between them (Thygesen *et al.* 2005; Agarwal *et al.* 2010). It has to be considered as well, that crystallinity can change due to different processes, which may be affected differently by the conditions of aging. Nevertheless, degradation of the amorphous parts of the cellulose lead to an increased crystallinity. On the other hand, due to high moisture content the crystalline structure of the cellulose may disintegrate, the transformation being partly irreversible and causing a decrease in the crystallinity. Such changes occur mostly at high moisture contents near to the fibre saturation point. Therefore, moisture content changes during the aging affect the crystallinity remarkably, and may also influence the relation of the two opposing processes. Thus, both increase and decrease in the crystallinity during aging may be possible, explaining the contradictory findings in this topic.

Similar to the cellulose, the proportion of lignin showed no considerable differences among the samples, including those of the reference material. However, degradation products of lignin were found by among the extractives by GC/MS analysis. Degradation and oxidation of the lignin structures due to aging was reported earlier in the literature (Borgin *et al.* 1975; Ganne-Chédeville *et al.* 2011). It is supposed that

the structure of lignin disintegrates on a long term resulting in soluble degradation products, and leading to a decrease of the lignin percentage as degradation of the crystalline cellulose is remarkably slower.

Most of the samples in the current investigation had lower extractive content than usual for the non-aged material. This can be explained by evaporation of the volatile components. Analysis of the composition of extractives by GC/MS confirms that suggestion. However, oxidation products of lignin and hemicelluloses were also found. With the passage of time, the decrease in the extractive content may turn into an increase as a result of increasing amount of these degradation products. This would explain the findings of Kohara and Okamoto (1955) as well, who stated increased extractive content for samples over 240 years. Ash content may also increase with aging (Van Zyl *et al*. 1973; Tomassetti *et al*. 1990), however, no significant changes were detected for the samples of the current study.

Summarizing the current results, it can be stated that the chemistry of wood undergoes remarkable changes during aging even at short time ranges and mild aging conditions. The first detectable change is a decrease in the extractive content due to evaporation of the volatile components. Among the main structural components, degradation of the hemicelluloses is the fastest, accompanied by some loss of the amorphous part of the cellulose. Oxidative crosslinking of lignin causes an increase in its percentage before its structure begins to disintegrate resulting in loss of this component. Degradation products of both the hemicelluloses and lignin appear among the extractable components increasing the extractive content over time. The crystalline part of the cellulose seems to be the most stable and may remain intact even through a very long time. The durability of the cellulose arises partly from its chemical structure, however, other compounds may also contribute to its resistance by reducing its accessibility (Schenzel *et al*. 2009).

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