CHEMICAL CHANGES IN FIR WOOD FROM OLD BUILDINGS DUE TO AGEING

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Wood is a biological material and changes in its molecular structure during exposures usually have a negative influence on its strength and other mechanical and physical properties. In this work, wet chemical and physico-chemical methods have been used to determine the changes in the cellulose, hemicelluloses, lignin and extractives of the 108 to 390-year-old visually undamaged fir wood taken from beams situated in the Rychvald castle in Czech Republic. Natural ageing of the fir wood without activity of biological agents caused a significant increase of the extractives content (twofold, or for the oldest beam, even fourfold) and a decrease of the hemicelluloses (by maximum 24%), while the amounts of lignin and holocellulose were quite stable (decreased only by 4%). The molecular weights, respectively, degrees of polymerization, were stable in cellulose, decreased in hemicelluloses, while in lignin increased due to condensation reactions.

Keywords: historic wood, fir, ageing, lignin, cellulose, hemicelluloses, size exclusion chromatography

INTRODUCTION

Over centuries, due to its specific properties (strength, elasticity, thermal and sound insulation, colour, odour, durability etc.), wood has been used for production of various objects (structures, such as churches, steeples, trusses and ceilings in castles, altars, furniture, etc.), which are part of the cultural heritage nowadays. Wooden products are often damaged by natural weathering as a complex of sun light, water, oxygen, bacteria and other factors, and not seldom also by fire, fungi, insects and aggressive substances from preservatives. It is important to note that all damages of wood molecular (chemical), anatomical, morphological and geometric structure are reflected in its mechanical, physical and durability properties.

Wood ageing occurs already during the growth of trees and immediately after logging, as well, e.g. influencing the content and molecular composition of hemicelluloses, lignin and cellulose.[1,2] Variation in polysaccharides, lignin and extractives of cut wood is determined by the species, shape, machining and treatment. Another influencing factor is the environment, in which the wood is located during ageing.[3] In warm and dry environments, e.g. in deserts, wooden buildings persist over several thousand years.

On the contrary, in wetter conditions suitable for bacterial, fungal and insect activities, their degradation is quicker.[4,5] In dry truss and ceiling structures, the conditions for wood ageing are usually mild. However, the process of wood ageing is significantly accelerated if storm water penetrates into them or in the presence of condensed, absorbed or capillary water or under simultaneous influence of aggressive chemical substances released from fire retardants and other additives.[6-8] Ageing in the humid environment together with fungal decay is,

besides fire, one of the quickest and most dangerous processes of wood damaging.

Nowadays, ageing and other degradation processes in wood components – cellulose, hemicelluloses, lignin, extractives, are monitored by wet chemical, physical and physico-chemical analyses. Mainly, spectral analyses are used, e.g. FT-IR spectroscopy[9-13] or FT-NIR spectroscopy,[14] chromatographic analyses, e.g. high performance liquid chromatography (HPLC) and size exclusion chromatography (SEC) analyses,[15-16] radiation and other analyses of atoms, e.g. wide- and small angle X-ray scattering (WAXS or SAXS),[14,17] X-ray photoelectron spectroscopy (XPS),[18] one- or multidimensional nuclear magnetic resonance (NMR or M-NMR) spectroscopy,[19,20] ^{13}C-cross-polarized magic angle spinning NMR spectroscopy,[11]MALDI mass spectrometry (MALDI-MS),[21] direct exposure electron ionisation mass spectrometry (DE-MS),[22] pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS),[23] or chemiluminometry,[24] methods of thermal analysis, e.g. thermogravimetry (TG) or derivative thermogravimetry (DTG),[25] microscopic analyses, e.g. scanning electron microscopy (SEM),[26] UV microspectrophotometry[15] and others.

Natural ageing of wood under dry conditions can be accelerated by its thermal treatment, as reported by various authors. For example, Ters *et al.*,[11] found changes in polysaccharides, while lignin remained unchanged, in spruce wood subject to a 24-times 7-day cycle from -20 °C to 75 °C. Colom *et al.*,[27] using FT-IR, confirmed the well-known fact that lignin is the most sensitive structural component of wood under UV-radiation in Xenotest. Popescu *et al.*,[18,23] using Py-GC/MS and XPS analyses of lime-tree boards aged 6 to 250 years, pointed to subsequent degradation of hemicelluloses, as well as amorphous cellulose, under dry conditions of wood ageing. Crystalline cellulose and lignin appeared to be stable, only with a little condensation of lignin, without any significant changes in the proportional representation of its syringyl and guaiacyl units. Mainly acetyl groups degraded from hemicelluloses (especially xylan), and the ESP-spectroscopy showed cleaving of bonds between hemicelluloses and lignin. In the archaeological discovery of an Egyptian coffin, Crestini *et al.*[26] also found, using 2D-NMR analysis, significant changes in lignin, which was more condensed and contained a 2.5-fold proportion of carboxyl groups as a result of long-term oxidation processes. Lucejko *et al.*,[28] using Py-GC/MS analysis, reported a drop in polysaccharides

in archaeological fir wood used as a reinforcement of walls in a salt mine in Wieliczka, Poland (mining from the 13th to the 20th century), as well as a decrease in polysaccharides/lignin ratio (PS/L) from the value of 1.3 for sound fir to the value of 1.0. Using this analysis, they determined the decrease in polysaccharides and increase in lignin in oak wood, beech wood and alder wood from an archaeological site in Zólte, Poland.[29] In the archaeological oak wood (700-2700 years) found in soil and water, an increased proportion of lignin, decreased amount of polysaccharides and reduced degree of polymerization were observed.[14] Similar conclusions were reached for several sub-fossil oaks, e.g. for the ones aged 8150 years old found 16 meters below the ground level during the construction of the Gabčíkovo Dam, Slovakia,[30,31] 2700 years old from Biskupin, Poland[32] and 1200 years old from archaeological excavations in the area of Zelená Voda, Slovakia.[33] However, the lignin in the wood long laid in wet environment changes its structure; it usually de-polymerizes and the proportion of phenolic groups increases due to a decrease of the ether ones.[20] Fir wood and multiple other coniferous and deciduous woods used for the construction of two ships from the 2nd century BC and from the 1st century AD showed a threefold increase in lignin and a 2.6-fold decrease in polysaccharides.[9] Also, extractives change during wood ageing. It has been found that recent fir wood contains approximately 60 times more terpenes than 390-year old fir wood.[34]

From research works, it is well known that long term exposure of wood under dry conditions, i.e. only to the action of light, oxygen and water vapours, can partly change its molecular composition and also its strength, hygroscopicity and durability. In this work, the chemical structure of wood samples taken from six visually healthy (i.e. undamaged by fire, fungi or insects) fir beams built in the historic Rychvald castle, Czech Republic, was analysed with the aim to determine changes in their molecular level during natural ageing lasting from 1622 to 2011. The obtained results may be useful when using wood for repairing historical sites and in selecting appropriate remediation methods.

EXPERIMENTAL
Material
The samples for chemical analyses (Fig. 1) were taken from beams in historic buildings, which are part of the Rychvald castle in Czech Republic. Firstly, by microscopic and tree-ring dendrochronological analyses

of a number of wooden bores taken from several trusses and ceilings, six fir beams (*Abies alba* Mill.) were selected for chemical analyses, considering their age difference (A – year 1622, B – year 1725, C – year 1733, D – year 1866, E – year 1904, F – year 2011), and also good quality, without visually or microscopically determined fungal rot and insect galleries. Then, each sample (approx. 120×40×10 mm) taken from the fir beams was cut into 30 small specimens (10×10×10 mm)

and they were disintegrated into sawdust using the Polymix PX-MFC 90D mill (Kinematica AG, Switzerland). The sawdust was finally sieved into individual fractions (<0.355 mm, 0.355-0.50 mm, 0.50-1.00 mm, >1.00 mm) using the Analysette 3 device (Fritsch, Germany).
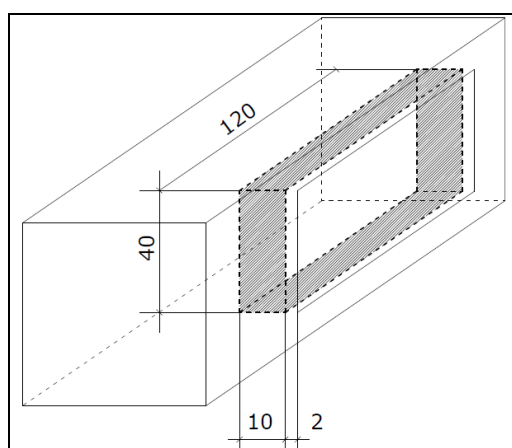
Figure 1: Sample (120×40×10 mm, length × height × width) taken from a visually undamaged part of the wooden beam near to its lateral surface

Chemical and physico-chemical analyses

The extractives were determined in the Soxhlet apparatus, using a mixture of ethanol and toluene, according to standard ASTM D 1107-96 (2007).[35] Lignin was determined according to standard ASTM D 1106-96 (2007),[36] cellulose according to Seifert,[37] holocellulose according to Wise *et al.*,[38] hemicelluloses by calculation of the difference between holocellulose and cellulose. All measurements were performed in three replicates per sample.

For isolation of dioxane lignin, extracted wood meal (fraction <0.355 mm) was used. The isolation was carried out in nitrogen atmosphere under the following conditions: 200 mL of 0.1 M HCl in dioxane-water (9:1) mixture was added to 10 g of wood meal. The working time was 5 h at a temperature of 80 °C. The molecular weight distribution (MWD) of the prepared dioxane lignins was determined using the method of the size exclusion chromatography (SEC) with the column Separon Hema S-300 (Tessek, Czech Republic), in the mobile phase 0.005 M LiBr in N,N-dimethylformamide.[39] The data were collected by the ChemStation software (Agilent Technologies, USA) and the calculations of molecular weights and polydispersity were carried out using the software "Clarity GPC module" (DataApex, Czech Republic). The system was calibrated by polystyrene standards with molecular weights ranging from 50 to 98,900 g·mol^{-1} (Tosoh,

Japan). Two samples of dioxane lignin were isolated and each sample was analysed twice by SEC.

In cellulose analysis, the determination of the degree of polymerization (DP), polydispersity (PD) and of the values of M_w, M_n, M_z, M_{z+1} was carried out using the SEC of cellulose tricarbanilates (CTC). The separation was performed at 35 °C with THF at a flow rate of 1 mL·min^{-1} PLgel 10 mm (7.5×300 mm) MIXED B column proceeded by PLgel 10 mm (7.5×50 mm) GUARD column (Polymer Laboratories, USA).[40] The data from the detector were collected by the ChemStation software (Agilent Technologies, USA). The values of molecular weights and DP were calculated after data conversion into the Clarity software (DataApex, Czech Republic). The column had been calibrated by polystyrene standards in the range of molecular weights from 162 to 6,035,000 (Polymer Laboratories, USA). A universal calibration with the coefficients for CTC: K = 2.01·10[-5] and α = 0.92 was used for determination of molecular weights.[41] Two samples of cellulose were derivatized into CTC and each derivate was analysed twice by SEC.

The SEC of hemicelluloses was carried out using the column TSK 3000 PW (Tosoh, Japan) in the mobile phase 0.1 M NaOH using the RI detector. The calibration was carried out with standard substances with known molecular weights – polyethylenglycols and dextrans in the range from 200 to 150,000.

Two samples of hemicelluloses were analysed by SEC in duplicate.

The qualitative and quantitative analyses of saccharides in the samples were carried out using the method of HPLC, according to standard ASTM E 1758-01.[42] The samples were hydrolysed in a two-stage process. In the first stage, 72% H_2SO_4 at a temperature of 30 °C was used for 1 hour, in the second one the formed oligomers were hydrolysed to monosaccharides after dilution to 4% H_2SO_4 at a temperature of 121 °C for 1 hour. The analysis was performed with the Agilent 1200 HPLC chromatograph with the column Aminex HPX-87P (BioRad, USA) at the temperature of 80 °C and the flow rate of the mobile phase of 0.6 ml·min^{-1}. Each hydrolysis was run in duplicate and each hydrolysate was analysed twice by HPLC.

RESULTS AND DISCUSSION
Changes in the amount of main wood components

Chemical analyses of the samples from the old fir wood beams showed that due to their 108 to 390-year natural ageing more significant changes occurred only in the amount of the extractives (increased twofold, or in 390-year-old wood even fourfold) and hemicelluloses (decrease by 24%) – see Table 1. It can be assumed that the high increase of extractives in the 390-year-old fir wood can be due to other factors as well, besides ageing, e.g. to the presence of some preservatives, which have not been analysed. Increases of extractives soluble in organic solvents (about 20 to 30%) were also found in other old fir beams, e.g. in 290 and 365-year-old wood by Fengel.[4] A significant decrease of the hemicelluloses (and the holocellulose) during wood ageing was mentioned as well as by more authors.[4,13,14,43,44,45]

During ageing of wood, cellulose is also subjected to decomposition, but more slowly than hemicelluloses and, under certain conditions, its amount in historic wood can also increase, as observed in this study. A relatively slight increase of the cellulose content due to quicker degradation of hemicelluloses was found for the tested samples of fir wood aged from 1 to 390 years (Table 1). A similar tendency was observed even in oak wood aged 8100 and 8500 years.[31,46] With respect to the high variability of contents of the main wood components, even in the same species, the degree and way of its degradation does not have to be accurately expressed by its amount. A more reliable indicator seems to be the cellulose to lignin ratio (C/L)[14] or the cellulose to hemicelluloses ratio (C/H). In the samples of fir wood, the C/L ratio increased with the ageing time (Table 1), which was

probably caused by higher stability of cellulose compared to lignin in the beams of historic buildings. This tendency is even more significant for the C/H ratio due to lower stability of hemicelluloses towards cellulose than lignin, which is also proved by the ratio of lignin to hemicelluloses, L/H (Table 1). The changes in cellulose depend on conditions and ageing time. For instance, the cellulose is degraded more in wet environment and its proportion in comparison with lignin is significantly decreased in the wood.[31,47] On the other hand, Fengel[4] did not observe any changes in the amount of cellulose in spruce and pine wood exposed to dry environment for 290 and 365 years. The cellulose values in oak wood were almost the same in the recent and in the 700-year-old wood. A higher amount of cellulose was contained in 1000-year-old wood, however in older samples cellulose dropped.[14]

Under certain conditions (dark and absence of the air), lignin is the most stable wood component in wood ageing. Light (mainly ultraviolet radiation) and air oxygen cause changes in the structure and amount of lignin. Fischer and Schmidt[48] found out oxidation changes in beech lignin as early as after several days of storing of chips, while Fengel and Stöcklhuber[49] in pine logs after 15 years of ageing. Similar photo-oxidation reactions could cause degradation of a part of lignin during ageing of fir beams in historic buildings (Table 1). In fir wood, a slight loss of lignin occurred after 290 and 390-year ageing (samples B and A), probably due to the oxidation changes, which had caused its higher solubility in sulphuric acid during determination. A similar phenomenon was observed by Borgin *et al.*,[50] who observed the oxidation reactions in lignin after 4100-4300 years of ageing of coniferous wood in dry air.

In the holocellulose of coniferous wood, hemicelluloses of arabino-4-*O*-methylglucurono-xylan and *O*-acetylgalactoglucomannan[51] types can be found in addition to cellulose. The main monosaccharide in the holocellulose of fir wood is glucose. Its amount relatively increased during ageing, which was caused by the higher stability of cellulose compared to hemicelluloses (Tables 1 and 2). During ageing of fir wood, xylan and galactan degradation occurred. On the contrary, mannan appeared to be more stable. The increase in the total amount of neutral saccharides in holocellulose could be caused by the deacetylation of hemicelluloses and degradation of acid components of polysaccharides, above all of uronic acids (Table 2).

Schwarz and Timell[52] found the following hemicelluloses in fir wood: arabino-4-*O*-methyl-glucuronoxylan (10:14:76), water-soluble galactoglucomannan (1:1:3) and alkali-soluble galactoglucomannan (0.1:1:3). Sun *et al.*[53] found out that the main saccharides in fir wood (Douglas fir) are glucose, mannose and xylose; galactose and arabinose occur less.

Mainly arabinoglucuronoxylan of fir wood hemicelluloses was dissolved in 5% KOH; galactoglucomannan was dissolved to a lesser extent (Fig. 2). During ageing, different changes in individual hemicelluloses occurred. A relative decrease in arabinose and xylose took place, whereas the amounts of galactose, glucose and mannose increased. It follows that arabinoglucuronoxylan is less resistant to ageing than galactoglucomannan and it degrades more quickly. In 24% KOH, hemicelluloses of the galactoglucomannan type were extracted from fir wood more than arabinoglucuronoxylan (Fig. 2). The results of this analysis do not show the resistance of individual hemicelluloses towards ageing as clearly as in the 5% KOH (decrease in mannose, xylose and galactose and increase in arabinose and glucose), which can be related to the different accessibility of more difficultly extractable hemicelluloses to external conditions (air, light etc.).

It should be noted that in these analyses there may be some differences in the amount of wood components caused by differences in the composition of the original material prior to ageing.

Table 1
Chemical characteristics of fir wood samples

Sample/ year	Extractives (%)	Lignin (%)	Cellulose (%)	Holo-cellulose (%)	Hemi-celluloses (%)	C/L	C/H	L/H
A/1622	3.54 (0.30)	28.24 (0.06)	45.81 (0.43)	72.59 (0.31)	26.78	1.62	1.71	1.05
B/1725	1.81 (0.23)	28.93 (0.04)	44.10 (0.21)	73.70 (0.17)	29.60	1.52	1.49	0.98
C/1733	1.54 (0.17)	29.61 (0.28)	44.35 (0.08)	74.51 (0.23)	30.16	1.50	1.47	0.98
D/1866	1.88 (0.15)	29.36 (0.09)	43.57 (0.34)	76.60 (0.23)	33.03	1.48	1.32	0.89
E/1904	1.65 (0.22)	29.66 (0.11)	43.51 (0.20)	76.61 (0.06)	33.10	1.47	1.31	0.90
F/2011	0.88 (0.13)	29.51 (0.49)	40.69 (0.32)	75.88 (0.08)	35.19	1.38	1.16	0.84

Note: C/L – cellulose to lignin ratio; C/H – cellulose to hemicelluloses ratio, L/H – lignin to hemicelluloses ratio; data in brackets show standard deviations (SD); the SD data miss for hemicelluloses and ratios C/L, C/H and L/H, if they were obtained using the calculation

Table 2
Amounts of neutral monosaccharides in the samples of fir wood holocellulose (%)

Sample/year	GLC	XYL	GAL	ARA	MAN	SUM
A/1622	60.58 (0.35)	3.10 (0.08)	0.60 (0.09)	0.97 (0.06)	13.07 (0.57)	78.32
B/1725	56.68 (0.20)	4.28 (0.05)	0.92 (0.11)	1.39 (0.08)	13.50 (0.64)	76.77
C/1733	57.82 (0.81)	3.61 (0.08)	0.54 (0.04)	1.52 (0.18)	14.11 (0.73)	77.59
D/1866	56.27 (0.51)	5.19 (0.38)	0.68 (0.06)	1.55 (0.10)	13.64 (1.04)	77.33
E/1904	51.49 (1.97)	4.30 (0.17)	0.67 (0.03)	1.76 (0.07)	12.66 (0.07)	70.88
F/2011	53.94 (0.45)	4.92 (0.11)	3.88 (0.07)	1.35 (0.07)	9.709 (0.07)	73.80

Note: GLC = D-glucose, XYL = D-xylose, GAL = D-galactose, ARA = L-arabinose, MAN = D-mannose. Data in brackets show standard deviations (SD)

Changes in degree of polymerization (DP) and molecular weight distribution (MWD) of main wood components

Significant characteristics affecting the strength properties of wood are the degree of polymerization (DP) and molecular weight distribution (MWD) of cellulose. During long ageing of oak wood (8150 years), a slight increase in the DP and cellulose crystallinity was found, which was caused by preferred degradation of cellulose in its amorphous part.[31] The increase in the crystallinity index (CI) of cellulose was also observed when pine wood was subjected to weathering.[54] During 390-year ageing of fir wood, no significant changes in the values of

DP or polydispersity (PD) (Table 3) were observed. The same applies to cellulose MWD (Fig. 3). These results are similar to the observations of other authors,[13,55] who, using the near infrared spectroscopy (NIR), found out that the amorphous part of cellulose is subject to slight changes, whereas the crystalline part is resistant. Cellulose in our work was, under the specific interior conditions, stable against the action of climatic agents and thus the strength properties of fir wood should not degrade due to its little changes. This assumption is supported by the research of Kúdela and Šmíra,[56] who investigated the mechanical properties of wood on similar samples as those used in this work. They found that natural ageing of wood does not have a negative impact on its strength properties.

Similarly, Yokoyama *et al.*[57] examined the mechanical characteristics of aged Hinoki wood from Japanese historical buildings in longitudinal (L) and radial (R) directions and no significant variation of L and R rigidity or L strength was observed. Recently, Froidevaux *et al.*[58,59] found that natural ageing of spruce wood (*Picea abies* (L.) Karst) during several centuries induces no significant changes of the wood properties along the radial direction, such as Young's modulus, the viscoelastic compliance and the mechano-sorptive behaviour. However, a significant reduction of about 20-25% of the radial strength has been determined.
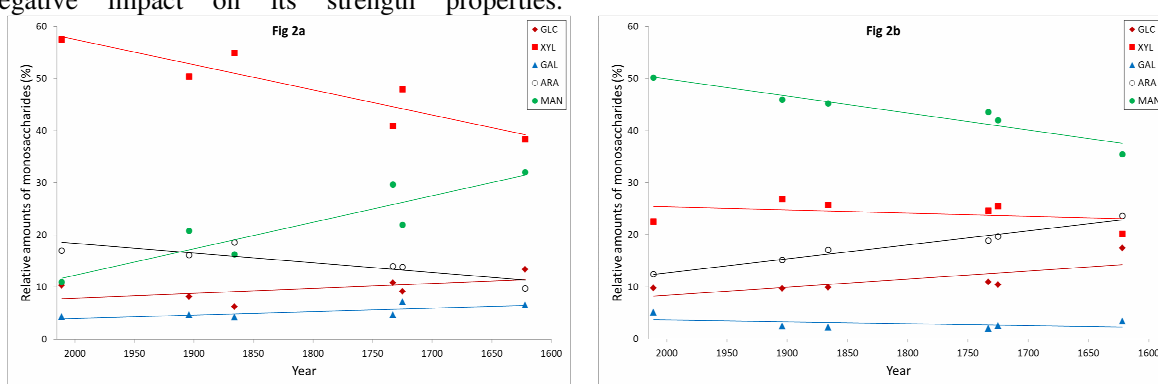
Figure 2: (a) Relative amounts of neutral monosaccharides in hemicelluloses soluble in 5% KOH;
(b) Relative amounts of neutral monosaccharides in hemicelluloses soluble in 24% KOH
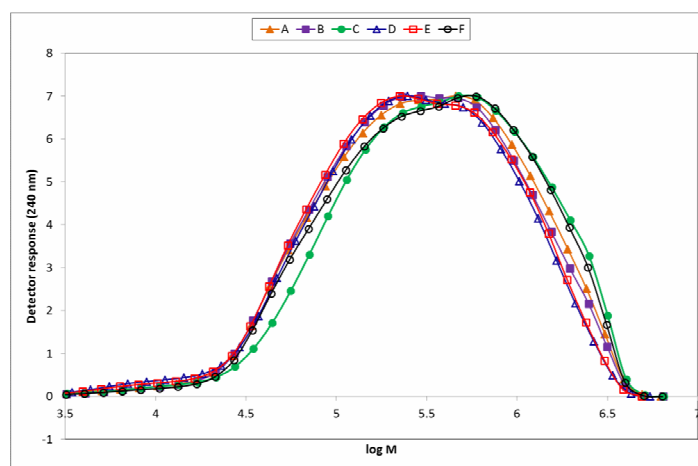
Figure 3: Molecular weight distribution of fir wood cellulose tricarbanilates

Hemicelluloses, which had been extracted from the holocellulose of fir wood by 5% and 24% solutions of KOH, were subjected to different changes during ageing. In the fraction soluble in 5% KOH, a decrease in molecular weights (M_w, DP_w)

occurred with age (Table 4). The changes in polydispersity do not show a clear tendency, which is probably caused by different cleavage of the glycoside bonds in this hemicelluloses fraction. It follows from the graphs of MWD (Fig. 4) that

degradation of high-molecular fractions depending on age occurs, which significantly influences the values of M_w and DP_w (Table 4). The fractions with

medium values of molecular weights increase and then cleave at various rates into shorter chains.

Table 3

Molecular weights (g.mol^{-1}) and polydispersity of fir wood cellulose samples

Sample/year	M_n	M_w	M_z	PD	DP_w
A/1622	42,615 (923)	195,132 (8,025)	438,223 (35,025)	4.58	1,205
B/1725	45,383 (989)	185,024 (7,892)	418,832 (34,587)	4.08	1,142
C/1733	50,566 (1,002)	225,604 (9,035)	478,157 (37,884)	4.46	1,393
D/1866	39,220 (828)	170,382 (7,758)	380,236 (33,689)	4.34	1,052
E/1904	40,220 (928)	170,767 (7,589)	379,704 (32,689)	4.25	1,054
F/2011	50,655 (1,105)	212,836 (8,987)	456,110 (37,587)	4.20	1,314

Note: Data in brackets show the standard deviation (SD). The PD and DP_w values were calculated; therefore the SD values are not mentioned; M_n = number average molecular weight (MW), M_w = weight average MW, M_z = z average MW, PD (polydispersity) = M_w/M_n), DP_w = $M_w/162$
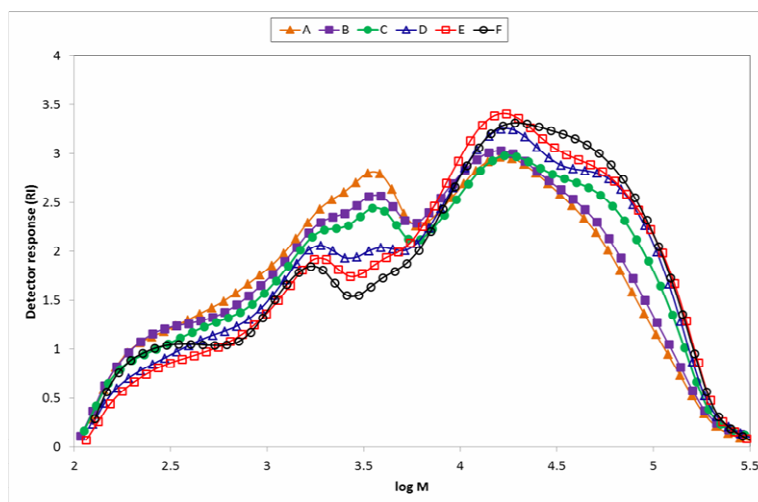
Table 4

Molecular weights (g.mol^{-1}) and polydispersity of hemicelluloses samples isolated from holocellulose of fir wood

Soluble in 5% KOH	M_n	M_w	M_z	PD	DP_w
A/1622	1,924 (131)	24,872 (679)	80,461 (4,273)	12.96	159
B/1725	2,056 (28)	26,595 (792)	82,749 (5,407)	12.94	172
C/1733	2,258 (53)	31,383 (622)	92,678 (3,642)	13.90	202
D/1866	2,745 (80)	34,285 (419)	91,101 (2,190)	12.50	224
E/1904	2,933 (60)	34,968 (616)	91,164 (1,733)	11.93	227
F/2011	2,743 (113)	35,376 (596)	90,031 (2,059)	12.92	231
Soluble in 24% KOH	M_n	M_w	M_z	PD	DP_w
A/1622	1,875 (27)	16,922 (386)	76,694 (2,223)	9.03	108
B/1725	2,468 (21)	28,677 (447)	87,756 (1,287)	11.62	183
C/1733	2,469 (52)	29,458 (444)	84,258 (3,024)	11.93	188
D/1866	3,031 (14)	34,553 (673)	92,004 (2,548)	12.50	220
E/1904	3,049 (28)	34,699 (653)	92,106 (2,704)	11.38	221
F/2011	2,256 (18)	29,020 (584)	97,244 (2,597)	12.86	184

Note: The DP_w values were obtained as a ratio of M_w and adequate molecular weight calculated from the relative ratio of pentoses and hexoses in individual samples. Data in brackets show the standard deviation (SD). The PD and DP_w values were calculated; therefore the SD values are not mentioned; M_n = number average molecular weight (MW), M_w = weight average MW, M_z = z average MW, PD (polydispersity) = M_w/M_n

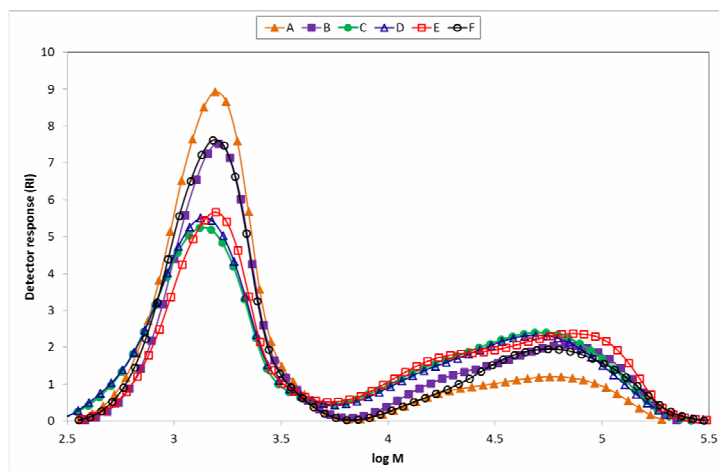Figure 4: Molecular weight distribution of fir wood hemicelluloses soluble in 5% KOH

In our samples, mainly condensation reactions occurred in lignin during wood ageing, which could be also observed in the curves of distribution of molecular weights (Fig. 6).
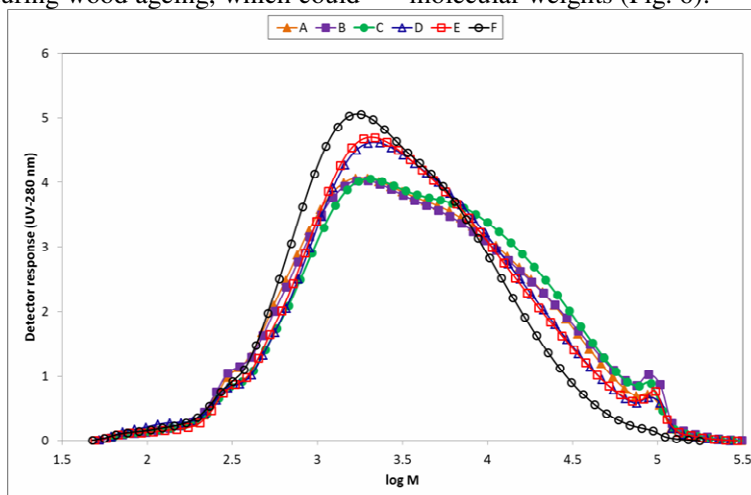

Figure 6: Molecular weight distribution of fir wood dioxane lignins

CONCLUSION

In the old fir wood beams, which were exposed in historic trusses and ceilings in the Rychvald castle in Czech Republic for 108 to 390 years, changes in the chemical composition occurred. Relatively to the recent fir wood, the cellulose in aged wood increased by 13%, both the lignin and holocellulose dropped by 4%, and the highest decrease by 24% for the hemicelluloses was observed. From hemicelluloses, arabinoglucuronoxylan appeared to be less resistant to ageing, compared to galactoglucomannan. No significant changes in the structure of cellulose were observed regarding the values of the degree of polymerization or polydispersity. The values of the hemicelluloses degree of polymerization dropped by up to 31-41%. Condensation was observed in lignin and the values of molecular weights almost doubled, compared to the recent fir wood.

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