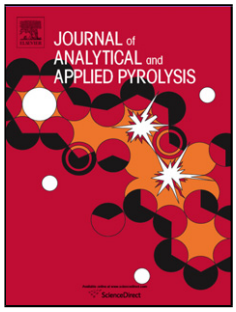

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Archaeological wood degradation at the site of Biskupin (Poland): wet chemical analysis and evaluation of specific Py-GC/MS profiles

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Abstract

Eight samples of ca. 3000 year old oak wood from the Biskupin site and a piece of sound oak (*Quercus* sp.) wood were analysed. The degradation state of archaeological oak wood was investigated using two analytical approaches: classical wet chemical analysis and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) with *in situ* silylation. The results were compared with those obtained for sound oak wood.
Chemical analysis provided information on the amount of wood components. Their alteration at a molecular level was investigated by Py-GC/MS, highlighting how degradation can affect the formation of primary and secondary wood pyrolysis products.
The results showed that the chemical changes in the wood material in the eight samples examined had different entities and extents with comparison to sound oak wood. Samples taken from the external parts of the fragments had undergone a significant loss in polysaccharide components, whereas the internal parts were in a relatively good state of preservation. Evaluation of the relative amounts of pyrolysis products deriving from holocellulose and lignin highlighted that specific categories of compounds, such as lignin monomers and anhydrosugars, can be taken as an index for good preservation of wood components.
These results will be used to evaluate the effectiveness of the *in situ* conservation strategy by repeating the analyses on these samples after some years and comparing the results.

Keywords: archaeological wood, degradation, Py-GC/MS, silylation, wet chemical analysis

1. Introduction

In 1933 a fortified settlement dating back to the Bronze and early Iron Ages (around mid 8th century BC) was found in Biskupin (Poland). The site was situated on a marshy island, occupying an area of about 2 ha. Several excavation campaigns were conducted between 1934 and 1974 [1] which highlighted that the village was abandoned after around 150 years of occupation, probably due to gradual flooding caused by violent climate change and the subsequent rising of the lake-water level [2]. The settlement was surrounded by a breakwater, consisting of several rows of oak and pine wood piles. Behind the breakwater, there was a fortified embankment, made of wooden boxes filled with earth and sand. The inner part of the settlement was composed of a total of 104-106 houses in thirteen rows. The streets were also made of wood. At the end of the archaeological campaign in 1974, the findings included a considerable amount of oak- and pine-wood, as well as troughs made of lime-wood, a birch-wood ladle, an ash-wood disk wheel, a canoe hollowed out of a spruce tree trunk, and an alder-wood structural element from one of the houses. It has been estimated that about 8000 m^3 of wood were used to build the settlement.

After excavation, some of the timber construction elements were exposed in the trenches for a long time, undergoing quick decomposition. Thus in the 1970s, an attempt was made to conserve the wood with phenol resin, leading to the total destruction of considerable amount of the archaeological wood [1].

After this attempt, it was decided to adopt an *in situ* conservation strategy by leaving the wood remains in the environment in which they had been found, either in the ground or water. Today Biskupin is an open-air museum, where it is possible to visit a reconstruction of the ancient village, whereas the archaeological wood is still kept underground.

It is known that waterlogged conditions are ideal for the long term preservation of archaeological wood. Important archaeological wood findings such as the Vasa ship [3], the Oseberg ship [4], the Roman ships of San Rossore [5], etc. were found underwater in a good state of preservation. Anaerobic conditions and low temperatures prevent the biodegradation of wood by white rot fungi, brown rot fungi and insects. However soft rot fungi and bacteria are still active in waterlogged conditions and can slowly degrade wood, resulting in alterations in the physical, chemical and mechanical properties [6-8]. In addition, since excavations started in Biskupin, and because of climate changes, there have also been changes in the burial environment, such as the lowering of the ground water and aeration of the soil. These phenomena could have contributed to accelerate the decay of the wood and it is therefore necessary to understand the dynamics of degradation.

Wood is a very complex material from a chemical point of view and its complexity is enhanced due to degradation [9]. Degradation has not a univocal meaning and the causes can be different (biological, chemical, mechanical, etc) [10,11]. For instance, a wood can be considered degraded from a chemical point of view when chemical changes involve its components, but this does not necessarily imply a decrease in its mechanical properties [12]. This is why complementary approaches need to be used in order to assess the preservation state of wood from different points of view. Physical and mechanical properties are very important, because they are related to the usability and the general strength of wood [13]. Studying the wood morphology is also important, because it

provides information on biological attacks and the structural integrity [7]. Finally, the assessment of the state of degradation from a chemical point of view provides information on the components of the wood at the molecular level and offers the possibility to understand the causes of decay, in order to establish preventive conservation conditions [14-16]. In this work degradation from a chemical point of view is considered with attention to the chemical changes undergone by archaeological wood components with respect to sound wood.

Many analytical techniques have been used to evaluate wood deterioration, starting with microscopic techniques, such as SEM and TEM, which are essential to investigate wood morphology [17]. Analytical methods have been applied to archaeological and historical wood [16,18-20]. They are widely used in the pulp and paper industry, and are based on the determination of wood components by isolating and quantifying them using gravimetric techniques [21,22].

To investigate the functionalities and the chemical bonds, various instrumental techniques have also been applied, such as NMR [23,24], FT-IR [25-27] and thermal analysis [28]. Analytical pyrolysis is also a very powerful approach [29-31] coupled with GC, MS or GC/MS. Py-GC/MS enables complex macromolecules to be studied by observing smaller and simpler molecules [32]. It only requires very small amount of sample, and provides semi-quantitative results and information at a molecular level [31].

The pyrolysis of cellulose and hemicelluloses involves chain scission and water elimination as primary reactions, leading to the formation of anhydrosugars as the most abundant pyrolysis products. Secondary pyrolysis reactions involve further decomposition and the rearrangement of anhydrosugars, which produce smaller molecules, such as furans, pyrans and cyclopentenones [33-35]. During the pyrolysis of lignin, the formation of the monomers (coniferyl and sinapyl alcohols) is the first pyrolytic reaction, due to the predominant initial cleavage of the β-ether bonds between phenylpropane units. Reactions involving conversion/alteration of the side-chain and the methoxy substituents on the aromatic ring on the other hand, are secondary reactions, which lead to the formation of guaiacyl and syringyl units with shorter side chains and different functionalities [36-39]. The use of *in situ* silylation enhances the detection of non-volatile compounds and protects alcoholic functionalities, particularly primary alcohol [40], which can easily undergo radical oxidation reactions. For example, the pyrolysis of lignin without derivatisation, produces coniferylaldehyde and sinapylaldehyde as major products [36], whereas the *in situ* derivatisation allows the TMS derivatives of coniferyl and sinapyl alcohols to be detected.

Some studies on Biskupin wood have already been carried out. An archaeological wood fragment of an oak trunk was investigated. The degree of degradation of sapwood and heartwood was determined on the basis of selected wood physical properties, the concentration of major chemical constituents (TAPPI methods) and microscopic observations, concluding that the wooden constructions deposited in the soil of the Biskupin site are generally in a good state of preservation [19]. In addition, within the framework of a monitoring program, results were obtained for sound oak wood deposited in the water of the lake and underground, and recovered after two years of deposition. The results showed that the wood had been colonized by aerobic and anaerobic bacterial and fungal microflora [41]. FT-IR was used to analyse pine and oak wood after 2, 4, 6 and 8

years of deposition [26]. Some selected water and soil parameters, such as groundwater level, pH and water conductivity, as well as redox potential and soil temperature, were measured, finding periodic fluctuations. Archaeological material situated in the layer of wet peat, where the samples investigated in this work were taken, lied in reducing conditions, which were proven not to favor degradation processes of wood [1].

In a previous work the different potentials of wet chemical analysis and Py(HMDS)-GC/MS analysis of archaeological wood were tested and compared [20]. In this paper we exploited the information given by the two approaches in a complementary way, using classical analysis to quantitatively determine the amounts of lignin and holocellulose, and Py(HMDS)-GC/MS to evaluate the chemical changes occurred at molecular level in the two components of archaeological oak wood from the Biskupin site. Wood pyrolysis products were grouped into categories. Changes in their relative abundances were evaluated and related to wood degradation, highlighting differences in the yields of primary and secondary pyrolysis reactions of archaeological wood. The analyses will be repeated after some years in order to evaluate the effectiveness of the *in situ* conservation strategy.

2. Materials and methods

2.1 Samples

A piece of wood was taken from a 68-year old oak (*Quercus* sp.) growing in the Gołąbki Forest District in the neighbourhood of Biskupin (Kujawsko-Pomorskie Voivodeship) in Poland. The experimental material, of approximately 240 mm diameter cut out from the log, came from the outer part of the heartwood zone extending across the annual increments from 29 to 59 (the last heartwood annual increment). Two main tissues can be found in wood: sapwood is the living tissue, involved in water conduction and rich in parenchyma cells; heartwood is more internal dead tissue rich in other types of cells, such as tracheids and fibres and darker in colour. Higher concentration of extractives in heartwood makes this tissue more resistant to fungal and bacterial degradation than sapwood [42]. Nevertheless the chemical composition (lignin and holocellulose) are very similar in heartwood and sapwood and the two tissues show similar behaviour under pyrolytic condition [43,44]. For these reason we decided to use a reference sample taken from the heartwood even if one of the archaeological sample was taken from the sapwood.

Eight archaeological oak wood samples were analyzed, taken from five different fragments of archaeological wood and believed to originally belong to the pavement of the ancient settlement. In the Biskupin site six measuring stations were created in order to monitor the environmental parameters [1]. The investigated fragments were taken from four of these stations, thus significantly representing the variability of conditions in the site. The fragments were extracted from the peat, the samples were taken and the fragments were put again in the burial environment. For some fragments different wood tissues were identified, thus three samples were taken from the same fragment (Oak 4): one corresponding to the sapwood (sample 4A), directly exposed to the site environment, one to the external part of the heartwood (sample 4B), and the third to the internal part of the heartwood (sample 4C). Two samples were taken from the fragment called Oak 199,

corresponding to the external (sample 199B) and internal (sample 199C) parts of the heartwood, respectively, the former being directly exposed to the site environment. Three additional samples were taken from three different wood fragments (Oak 5, Oak 6, Oak 106) respectively, which seemed to show only one degradation zone, corresponding to the heartwood and directly exposed to the site environment. Table 1 reports the description of the samples.

2.2 Classical wet chemical analysis

The classical wet chemical analysis of wood components was performed using three different standard methods. The determination of acid-insoluble lignin was assessed according to T 222 om-06 standard TAPPI method [45], using 72% sulphuric acid to hydrolyse and solubilise carbohydrates. The analysis of the holocellulose content was conducted according to the chlorite method [46], using $NaClO_2$ as a reagent. Cellulose content was determined according to the Seifert method [47], using a mixture of acetylacetone, 1,4-dioxane and hydrochloric acid to isolate cellulose. The amount of sample necessary for each analysis was about 150-200 g and each determination was repeated for three replicates. The amount of hemicelluloses was calculated as the difference between the amount of holocellulose and cellulose.

2.3 Py(HMDS)-GC/MS

Analytical pyrolysis was performed using 1,1,1,3,3,3-hexamethyldisilazane (HMDS, chemical purity 99.9%, Sigma Aldrich Inc., USA) as silylating agent for the *in situ* derivatisation of pyrolysis products. The instrumentation consisted of a 5150 CDS Pyroprobe 5000 Series pyrolyser with a platinum filament coil connected to a gas chromatograph 6890 Agilent (USA) equipped with an HP-5MS fused silica capillary column (stationary phase 5% diphenyl and 95% dimethyl-polysiloxane, 30 m x 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m x 0.32 mm i.d., Agilent J&W, USA). The GC was coupled with an Agilent 5973 Mass Selective Detector operating in electron impact mode (EI) at 70 eV. The pyrolysis temperature was 550°C and was carried out for 20 s. Similar amounts (ca. 100 µg) of sample were inserted into the centre of the pyrolysis quartz tube with quartz wool and 7 µL of HMDS.
Chromatographic conditions were as follows: initial temperature 60°C, 2 min isothermal, 15°C min^{-1} to 100°C, 3 min isothermal, 4°C min^{-1} to 200°C, 5 min isothermal, 15°C min^{-1} to 280°C, 5 min isothermal. Carrier gas: He (purity 99.995%), constant flow 1.0 mL min^{-1}. Before being analysed, all the samples were oven-dried for 24 h at 40-50°C to remove the residual water content. After instrumental analysis, the compounds were identified by comparing their mass spectra with spectra reported in the Wiley and NIST libraries or in the literature [30,33,34,48-51]. Semi-quantitative analysis of pyrolysis products was performed by measuring the peak areas of 88 peaks, corresponding to the main identified pyrolysis products. The areas were normalized for each chromatogram, and the data from three replicated analyses were averaged and expressed as percentages.

3. Results and discussion

3.1 Classical wet chemical analysis

The reference oak wood samples showed the following content of wood components: holocellulose 66.4 ± 0.4%, cellulose 38.5 ± 0.2%, and lignin 25.5 ± 0.2%. The amount of hemicelluloses was also calculated as the difference between holocellulose and cellulose, obtaining 27.9%. The results were calculated for three replicates. The data were in agreement with those reported in the literature for the analysis of oak wood by similar methods [41,52,53]. The results obtained for the archaeological and reference samples are presented in Table 2.

For the archaeological samples, the amount of holocellulose varied from 22.7 to 57.0%. Extreme values were obtained for samples 199B and 199C from the same fragment, highlighting significant degradation differences between separate zones of the same wood piece. This is often observed for archaeological wood and this is why sampling plays a key role to obtain significant results on wood preservation state [7,13,31]. Substantial differences in holocellulose content were also observed between samples from fragment Oak 4: sample 4A (external sapwood) showed 26.1% carbohydrates, while sample 4C (internal heartwood) showed 48.4%. For samples 5, 6 and 106, which were characterised by one zone of degradation, holocellulose content was 42.1%, 47.1% and 50.9% respectively. The percentage of polysaccharides in the reference oak was 66.4%, thus a degradation of the polysaccharide component had occurred in all the archaeological samples analysed. The effects of degradation from a chemical point of view were the most destructive in the external zones.

The loss of holocellulose was accompanied by variations in the relative amounts of the two polysaccharidic components (cellulose and hemicelluloses). In the archaeological samples, the depletion of hemicelluloses generally appeared to be more significant than the depletion of cellulose, suggesting that hemicelluloses was less resistant in the burial conditions than cellulose, as already described in the literature [54,55]. The investigated archaeological oak wood samples included from 4.7% to 18.3% of this component, and the most advanced degradation occurred in the sapwood of samples 4A and 6. Sample 199B was the best preserved, also in terms of hemicelluloses content. On the other hand, the amount of cellulose in the archaeological samples varied between 11.0% and 42.5%. As for holocellulose, the lowest concentration of cellulose was detected in samples 4A and 199B. The highest value was obtained in sample 6, which also showed the lowest amount of hemicelluloses, thus representing a good example of how degradation pathways can differ from sample to sample.

The relative percentage of lignin, as an effect of holocellulose decrease, was generally higher than in the reference sample. In the archaeological samples, the percentage of lignin fluctuated from 32.5% to 64.1%. Unlike with the holocellulose, the highest amount of lignin was found in samples with the lowest amount of polysaccharides.

In order to understand changes in wood composition, two parameters were calculated: the ratio between the content of holocellulose and lignin (H/L ratio), and the ratio between the content of cellulose and lignin (C/L ratio). A comparison of the values obtained for the

reference wood with those obtained for the archaeological samples gives information on the degradation in terms of relative changes in the chemical composition of wood, highlighting the preferential loss of cellulose or hemicelluloses.

For the reference sample, the average H/L ratio was 2.6 and the average C/L ratio was 1.5. For the archaeological samples, the values of H/L ratios ranged from 0.4 to 1.8. The C/L ratios ranged from 0.2 to 1.2. The lowest values of these ratios were obtained for samples 4A and 199B, confirming advanced degradation of both cellulose and hemicelluloses in the most external zones of the wood fragments, in agreement with other works present in the literature [13,56]. The highest values of the ratios (H/L = 1.8; C/L = 1.2) were found for sample 199B, highlighting it as the best-preserved sample. The other samples showed H/L ratio and C/L ratio values of around 1.0.

3.2 Py(HMDS)-GC/MS analysis

In order to identify the pyrolysis products and estimate the uncertainty in the measurement, five replicate samples of reference sound oak-wood were analysed by Py(HMDS)-GC/MS. A total of 91 pyrolysis products were identified and attributed to wood components (holocellulose, guaiacyl-lignin and syringyl-lignin). Figure 1 shows the obtained chromatographic profile. The peak identification is reported in Table 3.

The peaks corresponding to 88 pyrolysis products were used to perform semi-quantitative analyses, by integrating the peak areas and calculating the percentage amount of each pyrolysis product with respect to the sum of the areas of each pyrolysis product in the chromatogram.

Table 3 lists the pyrolysis products identified together with the *m/z* (mass/charge ratio) of their main fragments in the mass spectra, their attribution to holocellulose (H), guaiacyl-lignin (G) or syringyl-lignin (S) components, their attribution to specific categories, the percentage areas and the calculated parameters.

The pyrolysis products 1, 4 and 5 were not used to perform semi-quantitative evaluations, because they derive from the pyrolysis of both lignin and holocellulose. On the other hand, some unidentified compounds (marked as “unknown”) were included in the calculations because it is known that they derive from the pyrolysis of holocellulose [30,33,34,48-50]

The pyrolytic H/L ratio was calculated (ratio between the sum of the peak areas of holocellulose pyrolysis products - ΣH - and of lignin pyrolysis products - ΣL). The C/L ratio cannot be calculated by this technique, because both cellulose and hemicelluloses produce many of the same pyrolysis products. It is thus impossible to distinguish between them, and only the percentage of holocellulose content can be estimated. It is also important to note that the H/L ratio is characteristic for the technique and conditions adopted: the absolute values obtained by different techniques cannot be compared, because they are calculated by measuring different physical units. In this case the amounts of wood components were obtained by classical wet chemical analysis, while chromatographic peak areas of pyrolysis products were obtained by Py-GC/MS. Thus the importance the H/L ratio is not related to the comparison of absolute values obtained by different techniques, but to the identification of changes between sound and archaeological wood and by comparing trends among the results.

Oak wood lignin has a guaiacyl-syringyl composition and pyrolysis coupled with GC/MS enables the two components of hardwood lignin to be identified, thanks to the identification of their specific pyrolysis products [57]. It was therefore possible to calculate another significant parameter, i.e. the ratio between syringyl-lignin (ΣS) and guaiacyl-lignin (ΣG) pyrolysis products (S/G). This enables alterations in lignin involving the methoxy groups to be assessed [58].

For the reference sample, the pyrolytic H/L ratio was 3.4 ± 0.2, and the pyrolytic S/G ratio was 1.3 ± 0.1. The pyrolytic H/L and S/G ratios were also calculated for all the archaeological samples (Figure 2).

The trend observed for the pyrolytic H/L ratio was generally in agreement with that obtained by classical wet chemical analysis, with slight differences for samples 5, 6 and 106. Also in the case of Py-GC/MS, the extreme H/L values were obtained for the two samples 199B and 199C, and similar differences were detected for fragment 4, thus confirming that the external part was more degraded in terms of loss of carbohydrates. An interesting result was that the pyrolytic H/L and S/G ratio showed a positive correlation (Fig. 2), and in particular the correlation index between the two parameters for the examined samples was 0.8. The decrease in the H/L ratio corresponded to a decrease in the S/G ratio, indicating that also lignin had undergone chemical changes, which would not have been detectable if the analysis had been limited to the determination of the lignin content. In more degraded samples, the syringyl component of lignin showed higher alteration with respect to the guaiacyl component, the former being less resistant to chemical changes than the latter [59,60].

In order to investigate changes in wood components in more detail and to understand how wood degradation can affect the formation of primary and secondary pyrolysis products, we divided the pyrolysis products of holocellulose and lignin into categories according to their molecular structure. Five categories were selected for holocellulose pyrolysis products (Table 3): furans, cyclopentenones, pyranones, hydroxybenzenes and anhydrosugars. Six categories were selected for lignin pyrolysis products: short side chain aromatic compounds (guaiacyl and syringyl units with up to C2 alkyl substituent on the aromatic ring), long side chain compounds (guaiacyl and syringyl units with C3 alkyl substituent on the aromatic ring), monomers (coniferyl and sinapyl alcohols, which show an unaltered side chain), carbonyl compounds (guaiacyl and syringyl units containing aldehyde and ketone functionalities), carboxyl compounds (guaiacyl and syringyl units containing acid and ester functionalities), demethylated compounds (guaiacyl and syringyl units in which one or more methyl groups were removed from the methoxy substituents).

The sum of the peak areas of the pyrolysis products assigned to each category was calculated and expressed as a percentage with respect to the total abundance of the respective wood component (holocellulose or lignin), in order to evaluate differences in the relative abundances unaffected by the total amount of the wood components in the samples.

Of the holocellulose pyrolysis products, the relative abundances of cyclopentenones and anhydrosugars showed the highest differences among the samples. Figure 3 shows the distribution of holocellulose pyrolysis products for all the samples analysed.

In the reference oak, similar relative amounts of cyclopentenones and anhydrosugars were found. All the archaeological samples generally showed a higher relative amount of cyclopentenones and a lower relative amount of anhydrosugars. In addition, samples 4A, 4B and 4C showed a progressive decrease in cyclopentenones, and a progressive increase in anhydrosugars. Considering that these samples were affected by a progressive depletion of carbohydrates from C (internal part) to A (external part), it was possible to assume that more degraded samples produced higher relative amounts of cyclopentenones and lower relative amounts of anhydrosugars during pyrolysis, if compared to less degraded wood. Since anhydrosugars are mainly formed during primary pyrolysis reactions, it was possible to conclude that the decrease in the pyrolysis yield for anhydrosugars was related to the degradation state of carbohydrates. Partial depolymerisation and hydrolysis reactions easily result in a more open and reactive structure for degraded polysaccharides, in which the chains are shorter and the number of side chains is enhanced. As a consequence, when pyrolysis reactions occur, secondary reactions forming five-member ring compounds, such as cyclopentenones, are favoured because of the increased availability of sugars not linked in the polymer network.

The same trend was also observed for samples 199B and 199C. Sample 199C, in which the holocellulose component was well preserved, showed a higher relative amount of anhydrosugars and a lower relative amount of cyclopentenones than the more degraded sample 199B. A high relative amount of cyclopentenones was also found for sample 5, which showed a high depletion of carbohydrates.

In addition among the pyrolysis products of holocellulose, monosilylated, disilylated and trisilylated (persilylated) anhydrosugars were identified. The effectiveness of the derivatisation reaction with HMDS can be affected by steric hindrance, thus preventing the molecules of HMDS from achieving all the functionalities [40,61]. This phenomenon can be correlated with the degree of degradation: more degraded polymer networks, which present a more open and incoherent structure, are more reactive towards HMDS because steric hindrance is reduced. Thus the relative amount of persilylated anhydrosugars was higher for those samples that showed a higher degradation of carbohydrates. The percentages of monosilylated, disilylated and persilylated anhydrosugars were calculated in terms of the total content of anhydrosugars, and Figure 4 shows the distribution observed.

For the reference oak sample, the percentage of persilylated anhydrosugars was ca. 20%. This percentage was higher for all the archaeological samples, except for sample 199C. This sample, in fact, showed a very good preservation of the carbohydrate component. For samples 4A, 4B and 4C, the percentage of persilylated anhydrosugars decreased along the series, given the better preservation of the wood, and the same was found for samples 199B and 199C. Sample 5, which showed a high degradation in terms of carbohydrates, had the highest percentage of persilylated anhydrosugars. The opposite trend was found for monosilylated anhydrosugars, which were more abundant in the preserved samples.

For the pyrolysis products of lignin, other notable observations were obtained in the data evaluation. Figure 5 shows the distribution of lignin pyrolysis products for all the samples analysed.

Coniferyl alcohol and sinapyl alcohol, referred to as lignin monomers because they are the only pyrolysis products with the same structure as the main constituent monomers of the lignin network, were the most abundant pyrolysis products for the reference sample, while their abundance was considerably reduced for all the archaeological samples. In contrast the opposite trend was observed for the short side chain aromatic molecules, produced in secondary pyrolysis reactions. The abundance of short side chain aromatic molecules, such as guaiacol or syringol, in the pyrolysis profile was considered as an index of the degradation of lignin. The increase in the yield for secondary reactions may be related to a less coherent and less reticulated structure, which is relatively more suitable to undergo further pyrolysis degradation. This cannot be linked directly to lignin degradation, which is known to be quite stable in waterlogged conditions [9], however it is probably the result of the cleavage of carbohydrate-lignin bonds. The partial cleavage of these bonds allowed thermal energy to break not only the inter-monomeric bonds, but also other bonds, resulting in the increase in lignin pyrolysis products with a short side chain.

Another class of pyrolysis lignin products whose abundance can be interpreted as an index of degradation are phenols containing a carbonyl or carboxylic groups in the side chain, such as vanillin, syringaldehyde, vanillic acid or syringic acid. These pyrolysis products are present in sound lignin in very small relative amounts and cannot be formed during pyrolysis due to the absence of oxygen. Thus, the increase in carbonyl or carboxylic functionalities in pyrolysis products highlighted that these functionalities were included in the lignin after oxygen inclusion due to oxidative processes. With respect to the reference sample, all the archaeological samples showed higher relative amounts of carbonyl and carboxyl compounds, thus indicating a slight degree of oxidation for lignin.

Finally samples 199B and 199C showed a slightly higher relative amount of demethylated compounds (catechols) with respect to all the other samples. Demethylation of syringyl groups, with formation of dihydroxybenzenes, has been reported in literature as an index of lignin alteration [62].

4. Conclusions

Classical wet chemical analysis was confirmed to be a valuable tool to establish the state of preservation of archaeological wood, and to quantitatively compare differences in degradation among different artefacts and samples. The best preserved and the most degraded samples were identified in terms of loss of hemicelluloses and cellulose with respect to sound oak wood, proving that the samples directly exposed to the burial environment had undergone the highest loss of the carbohydrates component.

Py(HMDS)-GC/MS data were interpreted grouping the pyrolysis products into categories, according to their chemical and structural features. Among holocellulose pyrolysis products, anhydrosugars (mainly levoglucosan) were observed to have relative high abundance in samples showing good preservation of carbohydrates, whereas cyclopentenones showed relative high abundance in more degraded samples in terms of loss of carbohydrates. Consequently, the prevalence of cyclopentenones over anhydrosugars is a pyrolysis index of the degradation of polysaccharides. Among lignin pyrolysis products, lignin monomers (sinapyl and coniferyl alcohols) were relatively more abundant in better preserved samples. On the other hand, relative high abundances of guaiacyl and syringyl units with short side chain were observed in more degraded

samples. Thus, these two categories of pyrolysis products can be used as indexes to highlight the state of preservation/alteration of lignin in archaeological wood.
In addition, the silylation yield for anhydrosugars, observed in pyrograms in the monosilylated, disilylated and trisilylated (persilylated) forms, can also be exploited as an index for wood preservation, because steric hindrance is reduced when the polymeric network is damaged, thus increasing the derivatisation yield of sugars.
The described analytical approach and the obtained data represent a starting point to evaluate the effectiveness of the in situ conservation strategy, that is carried out at present in Biskupin site. The results here reported will be used to compare the results that will be obtained monitoring the same artefacts in the next years.

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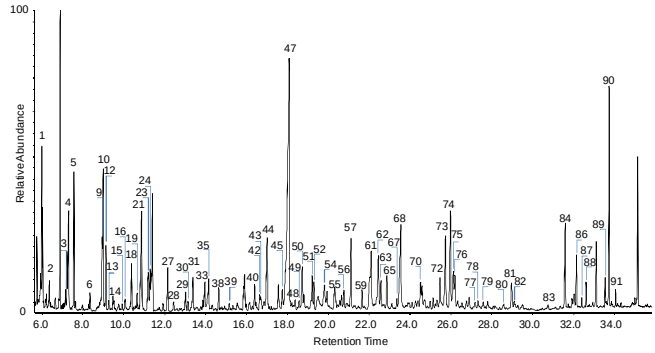
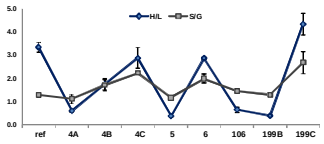
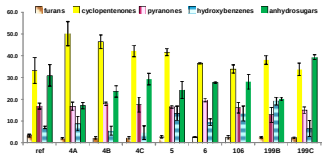
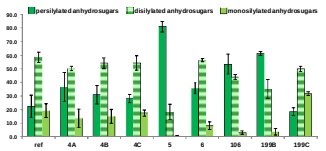
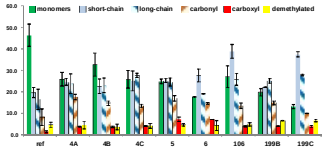








571 

Wood fragment	Samples	Description of the fragment	Condition of deposition
Oak 4	- 4A: sapwood (A) - 4B: external part of heartwood (B) - 4C: internal part of heartwood(C)	Transverse section 7 x 8 cm, length 50 cm	Vertical position in bottom mule
Oak 5	- 5: heartwood	Transverse section 12 x 16 cm, length 25 cm	Horizontal position in peat at a depth of 100 cm
Oak 6	- 6: heartwood	Transverse section 6 x 8 cm, length 30 cm	Horizontal position in peat at a depth of 100 cm
Oak 106	- 106: heartwood	Transverse section 17 x 17 cm, length 4 cm	Vertical position in peat at a depth of 100 cm
Oak 199	- 199B: external part of heartwood (B) - 199C: internal part of heartwood (C)	Transverse section 7 x 10 cm, length 5 cm	Vertical position in peat at a depth of 100 cm

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Sample name	Holocellulose % (w/w)	Cellulose % (w/w)	Hemicelluloses % (w/w)	Lignin % (w/w)	H/L	C/L
Reference	66.4 ± 0.4	38.5 ± 0.2	27.9	25.5 ± 0.2	2.6	1.5
4 A	26.1 ± 0.5	21.4 ± 0.6	4.7	59.0 ± 0.4	0.4	0.4
4 B	40.3 ± 0.5	30.2 ± 0.5	10.1	44.2 ± 0.5	0.9	0.7
4 C	48.4 ± 0.4	36.8 ± 0.3	11.6	38.5 ± 0.3	1.3	0.9
5	42.1 ± 0.4	30.4 ± 0.3	11.7	42.3 ± 0.1	1.0	0.7
6	47.1 ± 0.3	42.5 ± 0.4	4.6	43.7 ± 0.5	1.1	1.0
106	50.9 ± 0.4	32.5 ± 0.3	18.4	37.3 ± 0.1	1.4	0.9
199 B	22.7 ± 0.6	11.0 ± 0.8	11.7	64.1 ± 0.7	0.3	0.2
199 C	57.0 ± 0.3	38.7 ± 0.4	18.3	32.5 ± 0.3	1.7	1.2

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N°	Compound[a]	Most abundant *m/z*[b]	Origin	Category	A %
1	1,2-dihydroxyethane (2TMS)	73,103,**147**,191	H-L		
2	2-hydroxymethylfuran (TMS)	53, 73, **81**, 111, 125, 142, 155, 170	H	Furans	0.3
3	phenol (TMS)	75, **151**, 166	H	Hydroxybenzenes	0.5
4	2-hydroxypropanoic acid (2TMS)	73, 117, **147**, 191, 219	H-L		

5	2-hydroxyacetic acid (2TMS)	73, **147**, 177, 205	H-L		
6	1-hydroxy-1-cyclopenten-3-one (TMS)	53, 73, 81, 101, 111, 127, **155**, 169	H	Cyclopentenones	0.7
7	3-hydroxymethylfuran (TMS)	53, 75, **81**, 111, 125, 142, 155, 170	H	Furans	0.1
8	o-cresol (TMS)	73, 91, 135, 149, **165**, 180	G-S		0.2
9	2-furancarboxylic acid (TMS)	73, 95, **125**, 169, 184	H	Furans	0.2
10	holocellulose unknown I	73, **152**, 167	H		3.2
11	m-cresol (TMS)	73, 91, **165,** 180	G-S		0.5
12	2-hydroxy-1-cyclopenten-3-one (TMS)	53, 73, 81, 101, 111, 127, **155**, 170	H	Cyclopentenones	1.6
13	p-cresol (TMS)	73, 91, **165,** 180	G-S		0.1
14	3-hydroxy-(2H)-pyran-2-one (TMS)	75, 95, 125, 151, **169**, 184	H	Pyranones	0.0
15	holocellulose unknown II	59, 73, 85, 101, 115, **131**, 159	H		0.2
16	holocellulose unknown III	59, **73**, 85, 103, 115, 129, 145, 173, 188	H		0.2
17	*Z*-2,3-dihydroxy-cyclopent-2-enone (TMS)	59, **73**, 115, 143, 171, 186	H	Cyclopentenones	0.4
18	*E*-2,3-dihydroxy-cyclopent-2-enone (TMS)	75, 101, **143**, 171, 186	H	Cyclopentenones	1.2
19	3-hydroxy-(4H)-pyran-4-one (TMS)	75, 95, 139, 151, **169**, 184	H	Pyranones	0.5
20	1,2-dihydroxybenzene (TMS)	**75**, 91, 136, 151, 167, 182	H	Hydroxybenzenes	0.1
21	5-hydroxy-2H-pyran-4(3H)-one (TMS)	59, 75, 101, 129, 143, **171**, 186	H	Pyranones	7.5
22	2-hydroxymethyl-3-methy-2-cyclopentenone (TMS)	**73**, 103, 129, 173, 183, 198	H	Cyclopentenones	0.0
23	1-hydroxy-2-methyl-1- cyclopenten-3-one (TMS)	73, 97, 125, 139, **169**, 184	H	Cyclopentenones	0.9
24	1-methy-2-hydroxy-1-cyclopenten-3-one (TMS)	73, 97, 125, 139, **169**, 184	H	Cyclopentenones	0.9
25	1,3-dihydroxyacetone (2TMS)	**73**, 103, 147, 189, 219	H		1.1
26	guaiacol (TMS)	73, 151, **166,** 181, 196	G	Short-Chain	0.3
27	holocellulose unknown IV	**73**, 217, 232	H		1.3
28	3-hydroxy-6-methyl-(2H)-pyran-2-one (TMS)	73, 109, 139, 168, **183**, 198	H	Pyranones	0.0
29	holocellulose unknown V	**73**, 101, 116, 131, 173	H		0.4
30	2-methyl-3-hydroxy-(4H)-pyran-4-one (TMS)	73, 101, 153, **183**, 198	H	Pyranones	0.2
31	2,3-dihydrofuran-2,3-diol (2TMS)	73, 147, **231**, 246	H	Furans	0.8
32	2-furyl-hydroxymethylketone (TMS)	73, 81, 103, 125, **183**, 198	H	Furans	0.0
33	5-hydroxymethyl-2-furaldehyde (TMS)	73, 81, 109, 111, 139, 169, **183**, 198	H	Furans	1.1
34	4-methylguaiacol (TMS)	73, 149, **180,** 195, 210	G	Short-Chain	0.6
35	1,2-dihydroxybenzene (2TMS)	**73**, 151, 239, 254	H	Hydroxybenzenes	1.4
36	2-methyl-3-hydroxymethyl-2-cyclopentenone (TMS)	**73**, 103, 129, 173, 183, 198	H	Cyclopentenones	0.1
37	2-hydroxymethyl-2,3-dihydropyran-4-one (TMS)	73, 142, 170, **185**, 200	H	Pyranones	0.1
38	*Z*-2,3-dihydroxy-cyclopent-2-enone (2TMS)	73, 147, 230, **243**, 258	H	Cyclopentenones	0.7
39	1,4:3,6-dianhydro-α-D-glucopyranose (TMS)	**73**, 103, 129, 155, 170, 171, 186	H	Anhydrosugars	0.2
40	4-methylcatechol (2TMS)	**73**,180, 253, 268	G-S	Demethylated	1.1
41	4-ethylguaiacol (TMS)	73, 149, 179, **194,** 209, 224	G	Short-Chain	0.0
42	syringol (TMS)	73, 153, 181, 196, 211, 226	S	Short-Chain	0.7
43	1,4-dihydroxybenzene (2TMS)	73, **239,** 254	H	Hydroxybenzenes	0.2
44	arabinofuranose (4TMS)	**73,** 129, 147, 217, 230	H	Anhydrosugars	3.6
45	4-vinylguaiacol (TMS)	73, 162, 177, **192,** 207, 222	G	Short-Chain	0.9
46	3-hydroxy-2-hydroxymethyl-2-cyclopentenone (2TMS)	73, 147, **257**, 272	H	Cyclopentenones	1.0
47	*E*-2,3-dihydroxy-cyclopent-2-enone (2TMS)	73, 147, **243**, 258	H	Cyclopentenones	17.2

48	4-ethylcatechol (2TMS)	**73**,180, 253, 267, 282	G-S	Demethylated	0.2
49	3-hydroxy-2-(hydroxymethyl)cyclopenta-2,4-dienone (2TMS)	73, 147, **255**, 270	H	Cyclopentenones	0.9
50	eugenol (TMS)	73, 147, 179, **206,** 221, 236	G	Long-Chain	0.3
51	4-methylsyringol (TMS)	73, 167, **210**, 225, 240	S	Short-Chain	0.8
52	3,5-dihydroxy-2-methyl-(4H)-pyran-4-one (2TMS)	73, 128, 147, 183, **271**, 286	H	Pyranones	0.8
53	1,6-anydro-β-D-glucopyranose (TMS at position 4)	73, 103, 117, **129**, 145, 155, 171	H	Anhydrosugars	1.1
54	1,6-anydro-β-D-glucopyranose (TMS at position 2)	**73**, 101, 116, 129, 132, 145, 155, 171	H	Anhydrosugars	1.1
55	*Z*-isoeugenol (TMS)	73, 179, **206,** 221, 236	G	Long-Chain	0.1
56	vanillin (TMS)	73, **194,** 209, 224	G	Carbonyl	0.3
57	1,2,3-trihydroxybenzene (3TMS)	73, 133, 147, **239**, 327, 342	H	Hydroxybenzenes	2.5
58	4-ethylsyringol (TMS)	73, 191, 209, **224**, 239, 254	S	Short-Chain	0.1
59	*E*-isoeugenol (TMS)	73, 179, **206,** 221, 236	G	Long-Chain	0.7
60	1,4-anydro-D-galactopyranose (2TMS)	**73**, 101, 116, 129, 145, 155, 171, 217	H	Anhydrosugars	1.7
61	1,6-anydro-D-galactopyranose (2TMS)	**73**, 101, 116, 129, 145, 161, 189, 204, 217	H	Anhydrosugars	3.3
62	2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one (2TMS)	**73**, 129, 147, 155, 183, 273, 288	H	Pyranones	1.7
63	4-vinylsiringol (TMS)	73, 179, 222, **237**, 252	S	Short-Chain	0.9
64	1,4-anydro-D-glucopyranose (2TMS at position 2 and 4)	**73**, 101, 116, 129, 155, 191, 204, 217	H	Anhydrosugars	0.1
65	1,2,4-trihydroxybenzene (3TMS)	73, 133, 147, 239, 327, **342**	H	Hydroxybenzenes	0.9
66	acetovanillone (TMS)	73, **193,** 208, 223, 238	G	Carbonyl	0.1
67	4-propenyl-syringol (TMS)	73, 205, **236**, 251, 266	S	Long-Chain	0.3
68	1,6-anydro-β-D-glucopyranose (2TMS at position 2 and 4)	73, 101, 116, 129, 155, 191, 204, **217**	H	Anhydrosugars	6.5
69	4-hydroxy-3,5-dimethoxy cinnamic acid methyl ester (TMS)	**73**, 133, 147, 280, 292, 310	S	Carboxyl	0.1
70	*Z*-4-isopropenylsyringol (TMS)	73, 205, **236**, 251, 266	S	Long-Chain	0.1
71	1,4-anydro-D-galactopyranose (3TMS)	**73**, 129, 147, 157, 191, 204, 217, 243, 332	H	Anhydrosugars	0.3
72	syringaldehyde (TMS)	73, **224**, 239, 254	S	Carbonyl	0.8
73	2,3,5-trihydroxy-4H-pyran-4-one (3TMS)	**73**, 133, 147, 239, 255, 270, 330, 345, 360	H	Pyranones	2.0
74	1,6-anydro-β-D-glucopyranose (3TMS)	**73**, 103, 129, 147, 191, 204, 217, 243, 333	H	Anhydrosugars	5.1
75	1,4-anhydro-D-glucopyranose (3TMS)	**73**, 103, 129, 147, 191, 204, 217, 243, 332	H	Anhydrosugars	1.0
76	*E*-4-isopropenylsyringol (TMS)	73, 205, **236**, 251, 266	S	Long-Chain	1.1
77	vanillic acid (2TMS)	73, 253, 282, **297,** 312	G	Carboxyl	0.1
78	acetosyringone (TMS)	73, **223**, 238, 253, 268	S	Carbonyl	0.2
79	coumaryl alcohol (2 TMS)	**73,** 189, 205, 267, 279, 294	G-S	Demethylated	0.1
80	vanillylpropanol (2TMS)	73, 179, **206,** 221, 236, 311, 326	G	Long-Chain	0.1
81	*Z*-coniferyl alcohol (2 TMS)	73, 204, 252, 293, 309, **324**	G	Monomers	0.8
82	coniferylaldehyde (TMS)	73, 192, **220**, 235, 250	G	Carbonyl	0.1
83	syringic acid (2TMS)	73, 253, 297, 312, **327**, 342	S	Carboxyl	0.1
84	*E*-coniferyl alcohol(2 TMS)	73, 204, 235, 293, 309, **324**	G	Monomers	3.0
85	syringylpropanol (2TMS)	**73**, 210, 240, 341, 356	S	Long-Chain	0.3
86	*Z*-sinapyl alcohol (2TMS)	73, 234, 323, 339, **354**	S	Monomers	0.6
87	3,4-dihydroxycinnamyl alcohol (3TMS)	**73**, 205, 293, 355, 382	G-S	Demethylated	0.2
88	sinapylaldehyde (TMS)	73, **222**, 250, 265, 280	S	Carbonyl	0.4

89	sinapyl alcohol (TMS)	**73**, 234, 251, 267, **282**	S	Monomers	0.7
90	*E*-sinapyl alcohol (2TMS)	**73**, 234, 323, 339, 354	S	Monomers	5.6
91	3-methoxy-4,5-dihydroxycinnamyl alcohol (3TMS)	73, 235, 323, 385, **412**	G-S	Demethylated	0.2
ΣH	Sum of holocellulose pyrolysis products				77.1
ΣL	Sum of lignin pyrolysis products				22.9
ΣS	Sum of syringyl-lignin pyrolysis products				13.0
ΣG	Sum of guaiacyl-lignin pyrolysis products				10.0
ΣH/ΣL	H/L ratio				3.4
ΣS/ΣG	S/G ratio				1.3

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