A critical evaluation of the degradation state of dry archaeological wood from Egypt by SEM, FTIR, wet chemical analysis and Py(HMDS)-GC-MS

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Abstract

The degradation state of eleven wood samples from dry archaeological sites in Egypt was evaluated by combining the information obtained by scanning electron microscopy (SEM), wet chemical analysis (WCA), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and analytical pyrolysis gas chromatography mass spectrometry with *in situ* silylation (Py(HMDS)-GC-MS). The samples belonged to five different wood species (*Faidherbia albida*, *Ficus sycomorus*, *Taxus baccata*, *Pinus sylvestris* and *Tamarix* sp.) and came from three different archaeological sites corresponding to three different time periods (from *ca.* 1700 BC to *ca.* 1700 AD). The results were compared with reference sound woods of the same species. The main aim of this study was the in-depth investigation of wood chemical changes induced by degrading agents in dry burial environments. SEM enabled fungal attack to be identified in some of the samples. Wet chemical analysis highlighted the preferential loss of lignin or carbohydrates in these samples, but it also showed unusually high values of water-soluble substances in most of them. FTIR spectra acquired before and after the extraction of the samples permitted to shed light on the composition of this soluble fraction, which resulted to contain depolymerised carbohydrates and/or lignin units in most cases. Py(HMDS)-GC-MS, which was applied without any sample pre-treatment, enabled the alteration/depolymerisation of the single wood components to be evaluated, thus complementing the picture about chemical changes.

The results showed that, differently from waterlogged archaeological wood, the degraded wood components – depolymerised carbohydrates and/or lignin – are

mostly not leached away from the dry wood matrix, thus complicating the interpretation of data. The commonly used parameters, such as the H/L (holocellulose/lignin) ratio, failed to give a correct evaluation of wood degradation when both carbohydrates and lignin were degraded. The preservation conditions of the samples were very variable, from very good ones to high depletion of carbohydrates, to preferential depletion of lignin, or comparable levels of degradation of carbohydrates and lignin. This was sometimes observed within the same wood species and the same archaeological site.

This highlighted that a high interpretational effort needs to be undertaken in order to correctly evaluate the multiple causes of degradation affecting dry archaeological wood. An analytical approach using complementary techniques appears to be mandatory.

Keywords: SEM, wet chemical analysis, FTIR, Py(HMDS)-GC-MS, archaeological dry wood, Egypt

1. Introduction

A precise and straightforward definition of archaeological wood is very complicate to formulate. Florian defined it as "…dead wood, used by an extinct human culture, that may or may not have been modified for or by use, and that was discarded into a specific natural environment. […] The condition of archaeological wood could be near normal or extensively altered. Age alone is meaningless in terms of deterioration, which depends on the type of wood, the environment, and time." [1]. It

emerges from this definition that the preservation environment is among the most important factors to guarantee the survival of archaeological wood.

The burial environments suitable for wood preservation are waterlogged, extremely dry, or frozen ones, because microbial activity is drastically reduced in these conditions. In fact, biological degradation is the main threat for archaeological wood, as fungi, bacteria or insects can easily attack and metabolise wood, leading to important physical, chemical and morphological changes [2].

In the case of waterlogged burial environments, the low temperatures and reduced oxygen concentrations inhibit the action of many fungi and bacteria, although erosion and tunnelling bacteria and soft rot fungi can slowly metabolise the polysaccharide components of wood even underwater, leaving a porous and unstable structure [3-5]. Nevertheless, these species are considered slow wood degrader [6], thus it is not surprising that archaeological woods from waterlogged environments have survived hundreds or thousands of years, showing a certain degree of degradation in the external part, but keeping the internal part in better conditions [7-11]. Some famous shipwrecks, all excavated in waterlogged conditions, represent the most remarkable examples of archaeological wood findings [12-17].

Dry archaeological wood is rarer than waterlogged one. In fact, the completely dryness of wood can be reached only in particular sites, such as desert areas or places in which wood had been efficiently sheltered (houses, temples, tombs) [18-20]. As most of fungi and bacteria need water in their metabolism, wood with a water content much below the fibre saturation point is poorly degraded by microorganisms, whereas insects may still represent a significant threat [1]. Three main factors of decay have been previously highlighted for some wood objects from Egyptian tombs: soft rot, brown rot, and an abiotic form of degradation [19]. Brown rot fungi mainly

attack cellulose, causing depolymerisation and leaving a brown fragile residue rich in lignin [2]. Nevertheless, it has been shown that the action of some species of brown rot fungi can also demethoxylate and depolymerise lignin [21-23]. White rot fungi, active in aerobic conditions, are rarely responsible for wood decay in burial environments. Nevertheless, once the wood is removed from the burial, it can easily become a suitable substrate for the attack of these fungi [24], which can degrade the cell wall components [2], including lignin [25, 26].

Additional research in the field of wood long-term preserved in dry conditions has pointed out the degradation of hemicelluloses (especially xylans) and amorphous cellulose [27]. Lignin condensation (as a result of oxidation processes) has also been reported as a possible degradation effect in dry conditions using 2D-NMR analysis [28]. However, contrasting results are sometimes reported in the literature, showing relative decreases or relative increases in lignin content for wood preserved in dry conditions, depending on the cases [29-31]. This overview highlights that additional research is needed to broaden the range of scientific data available for dry archaeological wood.

A wide range of analytical techniques has been developed to assess the preservation state of archaeological wood [32]. The current trend in this research field is to find objective and easy-to-use parameters to describe the state of preservation of ancient wood samples, minimising the amount of sample needed. As an example, the H/L (holocellulose/lignin) ratio is considered a powerful parameter to highlight the decay of archaeological wood [32-34], as it easily estimates the preferential loss of holocellulose or lignin in an archaeological wood sample, by comparing the value with that obtained for a sound wood of the same species. This parameter can be obtained using different techniques, such as wet chemical analysis

(WCA), infrared spectroscopy (FTIR) and pyrolysis gas chromatography mass spectrometry (Py-GC-MS), but the absolute values can be only compared when the same technique is applied [32]. The H/L ratio and a few other approaches have been tested and are accepted in the analysis of waterlogged wood, but much less attention has been paid to their applicability to dry wood. It has also to be underlined that visual, physical (dimensional stability, density, *etc.*) and chemical evaluations of the preservation state of wood are not always in agreement [35], meaning that woods with acceptable dimensional stability could actually have undergone significant chemical changes. This makes the use of objective parameters even more important.

Our research focused on the integrated combination of the information obtained by scanning electron microscopy (SEM), wet chemical analysis (WCA), infrared spectroscopy (FTIR) and analytical pyrolysis gas chromatography mass spectrometry with *in situ* silylation (Py(HMDS)-GC-MS), to assess the degradation state of eleven wood samples from three dry archaeological sites in Egypt, namely the Khendjer Pyramid site (Saqqara), the Dakhla oasis (New Valley Governorate) and the El-Seiny mosque in the city of Jerja (Sohag governorate). Most of the objects and/or fragments from which the samples were taken were not considered to have a significant archaeological, artistic and historical importance, which was the main reason why the sampling was possible. However, these samples represent a significant variability in terms of geographical origin, chronology (from *ca.* 1700 BC to *ca.* 1700 AD) and wood species. In fact, five wood species were identified, which are representative of common Egyptian woods (*F. albida*, *F. sycomorus* and *Tamarix* sp.) and woods probably imported from Europe (*T. baccata* and *P. sylvestris*). Considering the compositional variability and the different behaviour towards decay

of different woods, all the results obtained for the archaeological samples were compared with those obtained for sound woods of the same species.

The main aim of this study was the in-depth investigation of wood chemical changes induced by degrading agents in dry burial environments, in order to test the applicability of common approaches used in the evaluation of the degradation state of archaeological waterlogged wood. In fact, this is the first application of Py(HMDS)-GC-MS to dry archaeological wood from various burial environments in Egypt.

In addition, the work turned out to show how delicate the interpretation of the results may be when dealing with multiple causes of degradation and how important is to complement the information obtained by a multi-analytical approach, in order to draw reliable conclusions.

2. Materials and methods

2.1. Samples

Eleven wooden samples were collected from storages and terrestrial sites, as parts of identified and unidentified objects, found during several excavations in Egypt. The objects were considered of no particular archaeological, artistic and historical significance, hence the possibility of sampling. However, from a scientific point of view, given their known provenance, dating and historical context, these objects represent a good variability of wood species, ages and environments, which makes them an excellent case study to understand the degradation processes occurred in archaeological woods from dry environments. The wood species were identified by optical microscopy.

Samples F1, F2, F3, F4, F5, F8 and F9 were collected from objects found in the Khendjer pyramid site (Saqqara), which is located 800 m south east of the step pyramid of Saqqara. The local weather is generally very dry and hot, and rainfall is rare. Summer temperatures range 36-18 °C (max/min). Winter temperatures range 22-10 °C (max/min). The location is 56 m higher above sea level and 33 m above the planted cultivated valley. The excavated pieces were found buried 2 m underground and mostly been reburied after previous excavations. It has not been ascertained whether the samples are contemporary with the pyramid (13th dynasty - *ca.* 1760 BC) or not. The wood species was *Faidherbia albida* for samples F1 and F8*, Ficus sycomorus* for samples F2, F3 F4 and F5 and *Taxus baccata* for sample F9.

Sample F6 was taken from an object found in the ancient excavation site of Dakhla oasis, New Valley Governorate. The local weather is almost always sunny, very hot in summer, very cold in winter nights and very dry during the year. Sample F6 dated back to the Greek-Roman period (332 BC – 395 AD) and was found in very dry conditions. The wood species was *Ficus sycomorus*.

Samples F11a, F11b and F11c were respectively taken from the crown, the body and the base of a painted column found in the El-Seiny mosque in the city of Jerja (south Egypt, Sohag governorate). This is one of the warmest places in Egypt with an annual mean temperature of 23.5 °C. The mosque was built in 1787 AD. The site is close to the Nile bank, thus water might be available under surface. The wood species was *Tamarix sp.* for sample F11a and *Pinus sylvestris* for samples F11b and F11c.

Reference sound woods of all these species were analysed in order to compare the results with those obtained for archaeological wood. In particular, one fragment of *Faidherbia albida* was kindly offered by Centro Studi Erbario Tropicale, University of

Florence, Italy (catalogue number FT-8461, collected on the 10th April 1909 by A. Pappi in Eritrea-Bogos and identified by E. Chiovenda). Because the amount of sample was very small, only Py(HMDS)-GC-MS was used to analyse the sample. *Ficus sycomorus, Taxus baccata, Pinus sylvestris* and *Tamarix sp.* were available at the CNR-IVALSA xylotheque (Florence, Italy).

2.2. Sampling

The archaeological samples were received in the form of small chunks (*ca.* 5 g). For each of them a sub-sample was taken and prepared for SEM observations. The rest of the material, generally weighing around 1.5 g, was homogenised by grinding it and oven-dried for 24 h at 40-50 °C to reduce the moisture content. The powder obtained was used to perform WCA (0.25-1 g), ATR-FTIR (0.1 g are usually enough to guarantee a good contact with the crystal) and Py(HDMS)-GC-MS (*ca.* 100 µg) analyses. In the latter case, analyses were performed in triplicate. In fact, although Py(HDMS)-GC-MS has the clear advantage of using very small amounts of sample, the representativeness of the results has to be guaranteed by repeating the analyses. All these measurements can therefore be considered representative of the average composition of the samples.

2.3. Scanning Electron Microscopy (SEM)

Transverse (TS), tangential longitudinal (TLS) and radial longitudinal (RLS) sections of the samples were prepared. The possibility to obtain good sections was strictly dependant on the structural integrity of the samples, which was very poor in some

cases (see Table 1). A PHILIPS (FEI) XL30 ESEM TMP scanning electron microscope was used. The electron source was a tungsten filament. The accelerating voltage of the beam was 15 kV. Images were acquired with the backscattered electrons (BSE) detector and water vapour around 0.5 Torr was used in the sample chamber to dissipate electron charging. This enabled uncoated samples to be observed. Images at different magnifications were obtained for most of the samples under investigation.

2.4. Gravimetric (wet) chemical analysis (WCA)

Wet chemical analysis (WCA) was used to measure the residual structural components of wood cell walls, in addition to ash and wood extractives. Before analyses, the material was sieved and the 40 to 120-mesh fraction was used. Laboratory operations were carried out by a stepwise approach: i) extraction of substances soluble in organic solvents; ii) extraction of water-soluble compounds; iii) assessment of acid lignin.

The substances soluble in organic solvents were assessed by extracting wood meal in a 1:2 mixture of ethanol and toluene (6 hours, 5 cycles per hour), by means of a Soxhlet extractor. The water-soluble compounds were extracted from the wood flour (8 hours, 2 cycles per hour) after extraction with organic solvents. The lignin content was then assessed following the procedure described in the TAPPI T222 standard method for acid (Klason) lignin [36]. The procedure provides for a treatment with concentrated sulphuric acid at room temperature, followed by a treatment with diluted sulphuric acid at the relevant boiling temperature. The holocellulose (cellulose and hemicelluloses) amount was calculated as a complement to 100 of the

sum of the results obtained from the other analyses. In fact, it has been shown that the direct extraction of holocellulose from degraded wood, although possible, gives unreliable results, because part of the polysaccharides is also extracted (together with lignin) during their isolation procedure [37].

The ash amount, measured on a separate sub-sample, was obtained by weighing the residue after wood flour calcination at 550°C for 2 hours in air. The results of WCA were referred to ash-free anhydrous weight of wood mass, which means that the values were calculated to exclude the ash amount. This series of values, which we indicated in this paper with the suffix “W”, was selected because it has been previously shown that the ash amount may influence quantitative determinations of wood components [38, 39]. Moreover, in sound wood the ash amount is usually negligible (< 1%), whereas it is normally appreciable in archaeological wood. Therefore, using an ash-free basis allows for a direct comparison between the values measured for archaeological and sound material.

2.5. ATR-FTIR analyses

Spectra were recorded on a Bruker FT-IR spectrometer (Alpha) with the following settings: 40 scans per sample, 4 cm^{-1} spectral resolution, 4000 to 400 cm^{-1} wavenumber range. A diamond single reflection attenuated total reflectance (ATR) accessory was used. Post spectroscopic manipulation was kept to a minimum: atmospheric compensation was applied and spectra were normalised in the range 700-1800 cm^{-1}, unless differently specified, by means of vector normalisation (Software OPUS 6.5 from Bruker). The vector normalisation calculates the average y-value of the spectrum. The average value is subtracted from the spectrum

decreasing the mid-spectrum to y = 0. The sum of the squares of all y-values is calculated and the spectrum is divided by the square root of this sum. The vector norm of the result spectrum is 1.

The spectra of the archaeological samples were acquired before and after the extraction procedure (with organic solvents and hot water).

2.6. 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 a silylation agent for the *in situ* thermally assisted derivatisation of pyrolysis products. The instrumentation was a micro-furnace Multi-Shot Pyrolyzer EGA/Py-3030D (Frontier Lab) coupled to a gas chromatograph 6890 Agilent Technologies (USA) equipped with a HP-5MS fused silica capillary column (stationary phase 5% diphenyl- 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 interface temperature was 250 °C. The samples were admixed with 5 µL of HMDS, put into a stainless steel cup and inserted in the micro-furnace. Chromatographic conditions were as follows: initial temperature 50 °C, 1 min isothermal, 10 °C min^{-1} to 100 °C, 2 min isothermal, 4 °C min^{-1} to 190 °C, 1 min isothermal, 30 °C min^{-1} to 280 °C, 30 min isothermal. The carrier gas was helium (purity 99.995%) used with constant flow 1.0 mL min^{-1}.

After instrumental analysis, the compounds were identified by comparing their mass spectra with spectra reported in the Wiley and NIST libraries and in the literature [40-

42]. The integration of identified peaks derived from lignin and holocellulose products was performed by AMDIS software. Semi-quantitative calculations were performed using chromatographic areas: peak areas were normalised with respect to the sum of the peak areas of all identified pyrolysis products, and the data were averaged and expressed as percentages. The percentage areas were used to calculate the relative abundances of wood pyrolysis products divided into categories. In this case, the calculations referred to the 100% of the wood component corresponding to the considered categories.

Samples were analysed in triplicate and the relative standard deviations associated with the calculated values were always below 10%.

3. Results

3.1. SEM

The presence of filamentous and spherical structures related to fungal hyphae and spores was highlighted in the cell lumens of most samples (Figure 1).

These observations revealed that wood decay fungi attacked the wood samples. The presence of fungi was clear in samples F2, F4, F6, F8 and F9. The attack of brown rot, white rot and soft rot fungi can be usually distinguished based on the morphological changes observed in the cell wall layers, especially in transverse sections [2, 43]. For our samples, this was not easy, as the samples tended to show features ascribable to multiple causes of degradation. Only in some cases the observations pointed towards the attack of a specific type of fungus. For sample F4 (Figure 1a) the cell walls appeared thin and slightly distorted, which can be

considered a sign of the attack by brown rot fungi [2]. For sample F6 (Figure 1b and 1c), voids were observed in both RLS and TS, indicating that all cell wall components were removed, as typical of simultaneous white rot fungi [43]. In fact, the intercellular pits appeared to join in some areas observed in RLS and entire parts of cell walls were missing in TS. For sample F8 (Figure 1d), in addition to various alterations observed, some horizontal “scratches” (not shown) were observed in RLS, suggesting the action of bacteria [2]. For sample F9 (Figure 1e and 1f), a detachment and separation of cell wall layers was clearly observed and the S_2 layer of the cell wall appeared the most affected, as it occurs with soft rot and/or white rot fungal attack [2, 43].

Samples F3 and F5 showed a relatively good preservation of the wood structure, although some thinning of cell walls was observed in some areas, which might indicate fungal activities. Nevertheless, fungal hyphae were not clearly observed in these samples.

For sample F11a, F11b and F11c well preserved wood structures were observed. Table 1 summarises the results about microbial attack and preservation of wood structure obtained by SEM observations.

3.2. Wet chemical analyses (WCA)

The WCA results obtained for archaeological and reference samples are shown in Table 2. A high variability among the data was observed. The holocellulose content of the archaeological samples ranged from 13.2% (sample F4) to 69.7% (sample F11b). The lignin content ranged from 14.2% (sample F5) to 49.6% (sample F4). When the H/L (holocellulose/lignin) ratio of an archaeological sample is lower than

the one of the sound wood of the same species, a preferential loss of holocellulose is usually indicated. In the opposite case, lignin is the preferentially removed wood component. A decrease in the H/L ratio is the common situation for waterlogged wood, as the polysaccharide components of wood are less stable than lignin underwater [44, 45]. On the contrary, the value here obtained for sample F5 (H/L 3.6) was much higher compared to the reference *F. sycomorus* (H/L 2.0). In fact, a limited decrease in holocellulose (compared to sound wood) was accompanied by a conspicuous decrease in lignin (14.2% for sample F5, 31.1% for reference *F. sycomorus*), thus indicating that lignin was preferentially removed. Similar results were obtained for samples F2 and F9.

Differently, for sample F4 the H/L ratio was 0.3, as result of a high relative decrease in holocellulose (13.2% for sample F4, 61.1% for reference *F. sycomorus*), indicating that carbohydrates were preferentially depleted from sample F4 during ageing.

A low content of holocellulose was detected in both samples F1 and F8 (21.6 % and 36.9 %, respectively). As the value for holocellulose in most woods is *ca.* 60-70% (Table 2 and [46]), the values obtained for samples F1 and F8 can be interpreted as a preferential loss of holocellulose, even if the analysis of the *F. albida* reference wood by WCA was not possible.

For sample F6 the relative contents of both holocellulose and lignin were lower than the corresponding sound wood, highlighting that both components were degraded at a similar extent in this sample. The resulting H/L ratio was 2.3, which was comparable to the one obtained for reference *F. sycomorus* (H/L 2.0). This highlighted that the H/L ratios often need to be integrated with additional information, otherwise the risk of misinterpretation is high.

As regards samples F3, F11a, F11b and F11c, the WCA results showed values very similar to the corresponding reference woods, except for a slight decrease in holocellulose observed for sample F3.

However, the most remarkable result obtained by WCA was related to the amount of the soluble substances, particularly from the hot water extraction. Six out of the eleven samples (F1, F3, F4, F5, F6 and F8) showed an amount of soluble substances above 20% and, among them, samples F1 and F6 reached *ca.* 40%. The values obtained for the aqueous extractives in the reference woods were < 4% (except for *Tamarix* sp., 8%), which are in agreement with the average values reported in the literature [46]. An increase in soluble substances has already been observed in 240- to 1300-years-old dry Japanese wood [47], although to a lower extent compared to our results. This highlighted the need to further investigate the nature of these soluble substances.

3.3. ATR-FTIR

FTIR wood spectra generally show a fingerprint region at 800–1800 cm^{-1}. By observing the relative changes in specific absorption bands, chemical modifications in archaeological wood components can generally be hypothesised. The assignment of the main infrared bands characteristic of wood and relevant for the discussion of our results is presented in Table 3.

In Figure 2 the FTIR spectra obtained for sample F4 and the reference *F. sycomorus* are shown. Absorption bands with maxima at 1736 cm^{-1}, 1030 cm^{-1} and 895 cm^{-1}, which are attributable to polysaccharides (Table 3), show high intensity in the sound wood and are drastically reduced (or absent) in sample F4. In contrast, bands with

maxima at 1595 cm^{-1}, 1505 cm^{-1}, 1330 cm^{-1} and 1217 cm^{-1}, attributable to aromatic skeletal vibrations in lignin, were more evident in sample F4 compared to reference wood. The band at 3330 cm^{-1}, related to the OH stretching, also decreases in sample F4 due to the depletion of polysaccharides. The FTIR spectrum obtained for sample F4 represents a typical spectrum of an archaeological wood highly depleted in polysaccharides, which is the most common situation in waterlogged environments [32, 38].

The comparison between the FTIR spectra obtained for the other archaeological and sound woods mainly confirmed the observations obtained by WCA analysis in terms of preferential loss/preservation of wood components. Nevertheless, the FTIR spectrum of sample F6 was similar to the reference one, with the exception of a strong decrease in the hemicelluloses bands at 1735 and 1230 cm^{-1}. This was actually the result of a comparable degradation of holocellulose and lignin.

On the other hand, the comparison between the results obtained before and after the extraction procedure (section 2.4) provided additional information and permitted to shed light on the nature of these soluble substances observed in WCA analysis (section 3.2). The spectra showed that in several cases the extraction procedure affected the composition of the samples, resulting in substantial differences in FTIR bands.

This was mostly evident for sample F1 (Figure 3a). After extraction, a strong relative decrease in the intensity of the absorption bands at *ca*. 1400 cm^{-1} and 1587 cm^{-1} was observed. The simultaneous occurrence of both these bands is associated with the vibration of carboxylates [48]. Sound wood does not usually show signals associated to these groups. The decrease in intensity suggests that these carboxylates are water-soluble (at least partially). It is reported that cellulose

degraded by brown rot fungi contains carboxylate groups [49]. Therefore, it can be suggested that these compounds containing carboxylate groups are constituted by modified oligo-sugars and therefore attributable to a partial alteration of cellulose. However, the band at 1370 cm^{-1} still showed a relatively high intensity in the spectrum obtained after extraction, the intensity of all signals in the region around 1030 cm^{-1} relatively increased, and the band at 896 cm^{-1} appeared. All these signals are associated with polysaccharides (Table 3). This highlighted that, although partial modifications occurred, the cellulose residual backbone was still preserved. Very similar results were obtained for sample F8.

For sample F4, in addition to the high depletion of polysaccharides already discussed, the spectra obtained before and after the extraction procedure gave additional information. In fact, the intensity of the absorption band at *ca.* 1030 cm^{-1} slightly increased, but the intensity of the band at 1120 cm^{-1} was almost unchanged (Figure 3b). This latter band is usually covered by the intensity of the C-O stretching vibration of carbohydrates. Thus, this occurrence actually evidenced a further decrease in the signals attributable to carbohydrates, which were partially extracted. Moreover, the two coupled signals at 1587 cm^{-1} and 1415 cm^{-1}, due to carboxylates and already observed for F1, were also detected in sample F4, although only a slight change was observed after extraction.

In the other samples, the extraction did not result in substantial changes in the FTIR spectra. However, in some cases interesting observations were obtained from the comparison between the spectra obtained after extraction and the reference woods. For sample F5 (Figure 4a) the two absorption bands at 1730 cm^{-1} and 1230 cm^{-1}, both attributable to hemicelluloses, disappeared after extraction, indicating degradation of this wood component. In addition, the absorption bands at 1505 cm^{-1},

1455 cm^{-1} and 1268 cm^{-1} significantly decreased with comparison to non-degraded wood, highlighting an alteration of the lignin structure.

For sample F9, significant differences were present in the region 1300-1800 cm^{-1} (Figure 4b). A broad band centred at 1578 cm^{-1} completely covered the other bands. This band is characteristic of metal chelates or salts of conjugated diketones [48]. Other associated vibrations should be present at 1500-1530, *ca.* 1450 and *ca.* 1250 cm^{-1} [48], but in our case they all overlap with other wood signals. It has been previously shown that the degradation by ligninase (a ligninolytic peroxidase secreted by white rot fungi) of the arylglycerol β-O-4 substructure of lignin produces decomposition to guaiacol and a diketone [50]. However, the relatively high intensity of the other bands in the spectrum suggested that the extent of lignin modification was relatively limited.

3.4. Py(HMDS)-GC-MS

The interpretation of Py(HMDS)-GC-MS analyses provided information on the material without any sample pre-treatment and was based on the comparison of pyrolytic profiles between archaeological and sound woods of the same species. The pyrolytic profiles of samples F1 and F8 (*F. albida*) were similar to each other, but very different from the sound wood, as shown in Figure 5 (the identification of pyrolysis products is reported in Table 4). In particular, the sample of sound *F. albida* showed the typical profile of a sound hardwood, with both holocellulose and lignin pyrolysis products present with comparable abundances. The most abundant holocellulose pyrolysis products were 2-hydroxy-1-cyclopenten-3-one (#12) and *E*-2,3-dihydroxy-cyclopent-2-enone (#47), whereas anhydrosugars were not detected

with high abundances, which is unusual in common hardwoods, such as oak wood [45]. Lignin monomers *E*-coniferyl and *E*-sinapyl alcohols (#97, 108) were the most abundant lignin pyrolysis products, in agreement with the pyrolytic pathways of lignin in other woods [41, 45, 51]. On the other hand, samples F1 and F8 showed holocellulose pyrolysis products with high relative abundances. In particular, 5-hydroxymethyl-2-furaldehyde (#34) and 1,6-anhydro-β-D-glucopyranose with different degrees of silylation (#54, 55, 71, 79). Among lignin pyrolysis products, only guaiacol (#26), syringol (#42) and a few other compounds were detected with significant abundances.

The *F. sycomorus* samples showed different pyrolytic profiles. Samples F2 (Figure 6b), F5 and F6 revealed holocellulose pyrolysis products with high relative abundance. Sample F4 (Figure 6c) mainly showed lignin pyrolysis products with guaiacol (#26) and syringol (#42) as the most abundant compounds, followed by 3-methoxy-1,2-benzenediol (#52), which is one of the main products of demethylation/demethoxylation reactions [52]. Significant relative abundances of syringaldehyde (#77) and acetosyringone (#86) were detected, whereas lignin monomers (#97, 108) showed very low abundances with respect to the sound *F. sycomorus*. Sample F3 showed a profile similar to what obtained for the corresponding sound wood.

The results for sample F9 (*T. baccata*) revealed high relative abundances of holocellulose pyrolysis products and a profile of lignin pyrolysis products similar to what obtained for sample F2 (Figure 6b).

For samples F11a (*Tamarix* sp), F11b (*P. sylvestris*) and F11c (*P. sylvestris*), the pyrolytic profiles showed the presence of both holocellulose and lignin pyrolysis products with minor differences with respect to the corresponding sound wood

samples, mainly regarding a slight relative decrease in holocellulose pyrolysis products. This was indicative of a good preservation state of all the wood components in these three samples. Figure 7 reports the pyrograms for the sound *P. sylvestris* and samples F11b and F11c.

In addition to the qualitative comparison of pyrolytic profiles, Py(HMDS)-GC-MS also enables additional information to be provided on the preservation state of the residual single wood components. In fact, the distribution of the percentage areas of the pyrolysis products divided into categories (Table 4) provides indications on specific degradation pathways undergone by the holocellulose or lignin [40, 41, 45]. Figure 8 shows the distribution of the categories of lignin pyrolysis products for the samples analysed. Generally, for the sound woods the monomers had the highest relative abundance (40-50%) [41, 45, 51], as they are produced by primary pyrolysis reactions, that have high yields when lignin structure has not undergone alterations [53-55]. The results for samples F11a, F11b and F11c showed only slight changes with respect to the corresponding sound woods, indicating that the residual lignin was not significantly affected by degradation. Sample F3 presented a slight reduction of the relative abundance of monomers and a relative slight increase in short chain pyrolysis products, indicative of a low alteration of the lignin structure affecting the side chain of the phenylpropane units. All the other archaeological samples showed that the lignin monomers were almost completely absent and the lignin pyrolysis products were mainly constituted by short chain compounds and demethylated/demethoxylated compounds. This unusual lignin profile indicated a significant alteration of the lignin structure for all these samples, mainly in terms of a drastic reduction of the length of the propanoid side chains and therefore depolymerisation.

The distribution of holocellulose pyrolysis products divided into categories was also investigated, as shown in Figure 9. The distribution varied significantly among the sound wood samples, mainly because hemicelluloses have different compositions depending on wood species [56, 57]. Although cellulose and hemicelluloses mostly result in the same pyrolysis products, the relative abundances of the categories are expected to vary reflecting the different composition of hemicelluloses in the various wood species. The two categories of pyrolysis products undergoing the most relative changes were anhydrosugars and cyclopentenones, as already observed in previous works [42, 45].

Also in this case, the results for sample F11a, F11b and F11c highlighted no significant differences in the distribution of holocellulose pyrolysis products with respect to the sound woods, indicating a good preservation of the residual holocellulose component. For all the other samples a significant relative increase in anhydrosugars and a relative decrease in cyclopentenones were detected with respect to the corresponding sound woods. Recent publications have shown that the relative abundance of anhydrosugars increases together with the depolymerisation degree of holocellulose [40, 42]. Samples F1, F2 and F8 showed the highest change in terms of increase in anhydrosugars, highlighting the highest level of depolymerisation of residual holocellulose.

4. Discussion

All the techniques evidenced a high variability in the state of preservation of the samples and the interpretation of the results was very complex. Complementary information was obtained by the various techniques and it was clear from the

549 comparisons that misleading information may be obtained if only one approach is
550 used to investigate such samples. In fact, it is here highlighted how the decay
551 patterns for some samples were very different from the ones usually encountered for
552 waterlogged wood. The loss of holocellulose was not the most common result in
553 these samples, thus suggesting that different mechanisms of degradation affected
554 them. This section aims at discussing the results in a more comprehensive way and
555 at highlighting some trends.
556
557 4.1. *Faidherbia albida* - samples F1 and F8 from the Khendjer pyramid site (*ca.* 1760
558 BC)
559
560 SEM analyses revealed an altered structure for these samples, with evident fungal
561 and bacterial activity in sample F8. The results obtained by WCA and Py(HMDS)-
562 GC-MS were not straightforwardly in agreement. In fact, an amount of lignin
563 comparable with the sound wood was obtained for both samples, but Py(HMDS)-
564 GC-MS highlighted that lignin was highly altered. In addition, a relative decrease in
565 holocellulose was observed by WCA analysis, but the relative abundances of
566 holocellulose pyrolysis products were higher than sound wood. However, WCA
567 analysis also revealed an extremely high content of substances soluble in water and
568 Py(HMDS)-GC-MS showed that the residual holocellulose was depolymerised. FTIR
569 spectra acquired before and after the extraction procedure finally explained the
570 reason of the disagreement between the results. In fact, a major fraction of these
571 soluble substances contained carboxylate groups and pointed to the presence of
572 oligo-sugars (perhaps given by the opening of the glucose ring). These were
573 produced during cellulose degradation and they were partially solubilised during the

extraction process in hot water accounting as extractable material in the WCA analysis. However, they accounted as holocellulose pyrolysis products using Py(HMDS)-GC-MS, as no pre-treatment of the sample was performed.

These high values of soluble substances are never encountered in the analysis of waterlogged archaeological wood [58], where the material is progressively leached during its long-time immersion in water. In contrast, when the material (like the one analysed here) is preserved in dry conditions, these depolymerisation products are not leached and thus they remain within the wood tissue.

The presence of carboxylate groups also hinted to the action of brown rot fungi [49].

4.2. *Ficus sycomorus* - samples F2, F3, F4 and F5 from the Khendjer pyramid site (*ca.* 1760 BC) and sample F6 from the Dakhla oasis (332 BC – 395 AD)

Despite the same wood species, four different degradation pathways were identified for these samples. For samples F2 and F5 a significant reduction in lignin was the main result. The phenomenon was present for sample F6 as well, but it was accompanied by a partial depletion of holocellulose. This was the only sample showing such a comparable degradation of lignin and holocellulose, probably reflecting its peculiar geographical/chronological origin. Sample F4 revealed a high depletion of holocellulose and sample F3 showed a relatively good preservation state of the wood components.

Generally, a good agreement was observed between FTIR and Py(HMDS)-GC-MS results. In fact, the residual lignin appeared to be highly altered in all samples (except for sample F3), whereas a minor extent of cellulose depolymerisation was observed. High amounts of soluble substances were obtained especially for sample

F6. However, the FTIR spectra highlighted minor differences before and after extraction and this was taken as an indication that both oligo-sugars from partially depolymerised holocellulose and water-soluble lignin aromatic units were present in the extracted material, confirming the comparable degradation of lignin and holocellulose. All this was also consistent with an attack by white rot fungi.

For sample F4 the detection of the demethylation product 3-methoxy-1,2-benzenediol (#52) with such relatively high abundance has to be underlined. In fact, this has been reported in the literature as a marker of the action of brown rot fungi [52].

4.3. *Taxus baccata* - sample F9 from the Khendjer pyramid site (*ca.* 1760 BC)

The results obtained for this sample fall under the category of a predominant depletion of lignin and alteration of the residual cellulose. In this case, the formation of conjugated diketones observed by FTIR was taken as a further indication of attack by white rot fungi.

4.4. *Tamarix* sp. - sample F11a - and *Pinus sylvestris* – samples F11b and F11c – from the city of Jerja (*ca.* 1787 AD)

The results obtained by all the techniques agreed with a good preservation of the wood components, which showed only slight changes with respect to the corresponding sound woods. These were also the most recent wood samples, probably the main reason why they showed the best preservation state.

4.5. Causes of degradation

Although fungal activity was clearly observed in most of the degraded samples, a definite cause of degradation is difficult to hypothesise. Some Py-GC-MS studies have demonstrated that the attack of white rot fungi results in an increase of lignin pyrolysis products with shortened side chain with respect to the original phenylpronane units [59-61], as well as a small increase in dihydroxybenzenes, because of demethylation reactions of the methoxy groups on the aromatic rings [62]. Consequently, the lignin degradation observed in most samples would suggest an attack by white rot fungi. However, this occurrence was not always clear in SEM images and could be suggested by WCA only when a decrease of lignin is evident. On the other hand, indications of an attack by brown rot fungi were obtained for samples F1, F4 and F8. Moreover, samples F1 and F8 appeared to show degradation features ascribable to a combined effect of both white and brown rot fungi. However, it is impossible to ascertain whether the attack started in the burial environment, or after excavation. Finally, the effects of time in terms of hydrolytic and oxidative degradation of wood components must be considered as well. In fact, if we consider the chronological line, the worst preserved samples were among the most ancient ones (F1, F4 and F8 from the Khendjer pyramid site - *ca.* 1760 BC). However, very different degradation pathways were observed within the same archaeological site and within the same wood species, which prevents from highlighting trends according to the geographical origin and the type of wood. Despite the speculative aspect of these hypotheses, these results highlighted how complex the evaluation of the preservation state of archaeological dry wood is with comparison to the waterlogged one.

649 Other techniques then the ones used here would be helpful in terms of providing
650 additional information on the extent and nature of degradation. In particular, gel
651 permeation chromatography (GPC) could give more precise results on the
652 depolymerisation of cellulose and lignin and on the preservation of the lignin-
653 carbohydrate complexes [63]. 2D-HSQC and ^{31}P NMR analyses also have the
654 potential to semi-quantitatively evaluate the different types of inter-monomeric bonds
655 present in lignin and quantify the amounts of the different types of phenolic, alcoholic
656 and acidic groups, respectively [64]. These techniques have been applied to
657 archaeological waterlogged wood, proving their suitability [65, 66], but only seldom to
658 dry archaeological wood [28], making this an interesting subject for future research.
659
660 **5. Conclusions**
661
662 The analyses of eleven samples of dry archaeological wood from Egyptian sites by
663 means of SEM, wet chemical analysis (WCA), FTIR and Py(HMDS)-GC-MS
664 highlighted that different degradation pathways had often simultaneously occurred
665 even in the same burial environment and within the same wood species. This
666 showed that a higher complexity of interpretation is required for dry archaeological
667 wood with respect to waterlogged archaeological wood, in order to correctly evaluate
668 the causes of decay and reliably assess the state of preservation of the samples.
669 In particular, preferential loss of lignin, preferential loss of holocellulose, comparable
670 loss of lignin and holocellulose and relatively good preservation of wood components
671 were all detected in this group of samples. Additionally, WCA analysis highlighted a
672 high content of water soluble substances, which is not usually present in
673 waterlogged wood, as water progressively solubilises the depolymerised wood

components. FTIR analyses performed before and after extraction with water and organic solvents allowed shedding light on the composition of the soluble substances. These were preferentially composed of oligo-sugars sometimes in combination with low molecular weight compounds derived from lignin. Carboxylates and diketone salts were observed as well and taken as an indication of fungal activity. Py(HMDS)-GC-MS revealed high degree of alteration of lignin and holocellulose in most samples.

These results represent new insights into the chemical processes taking place during the degradation of dry archaeological wood and show the limitations of the techniques used, when singularly applied. In fact, the simple estimation of the H/L ratio, one of the most common parameters to describe wood degradation, was not sufficient in most cases. The H/L ratio is a good indicator of the preservation state of archaeological wood if one component is preferentially degraded with respect to the other, as is usually the case for waterlogged wood, but fails when both components are involved in degradation at comparable level. In addition, the preferential loss of one wood component does not necessarily mean that the other component is not degraded. Chemical changes in the structure of residual wood components have to be considered by complementary approaches, such as FTIR strategies and/or the evaluation of the distribution of pyrolysis products.

Further research is also needed. Other complementary techniques (GPC, ^{31}P NMR, 2D-HSQC) should be applied to dry archaeological wood to explore their potentialities and limitations with such complex material. Standardised/objective parameters to assess the degradation state of degraded dry wood and establish the causes of degradation also seem far to be found.

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Figure 1. SEM images of samples **a)** F4 (*F. sycomorus* TS, 2000x), showing distortion of the cell walls; **b)** F6 (*F. sycomorus* RLS, 1000x), showing some voids in the structure (circles); **c)** F6 (*F. sycomorus* RLS, 1000x), showing entire wood cells missing (circle), **d)** F8 (*F. albida*, TS, 2000x), **e)** F9 (*T. baccata*, TS, 1500x) and **f)** F9 (*T. baccata*, TS, 2000x), showing degradation of the S2 layer of the cell wall. Arrows (full line) are used to indicate areas were fungal hyphae are particularly abundant. The dotted line arrow indicates a fungal spore.

Figure 2. Comparison between the spectra of reference *F. sycomorus* and the archaeological sample F4. Spectra were vector normalised in the range 400-4000 cm^{-1}.

Figure 3. FTIR spectra of sample F1 (**a**) and F4 (**b**) before and after extraction.

Figure 4. FTIR spectra of samples: **a)** F5 in comparison with reference *F. sycomorus*; **b)** F9 in comparison with reference *T. baccata*.

Figure 5. Py(HMDS)-GC-MS profiles for samples **a)** *F. albida* reference and **b)** F8. Peak labelling refers to Table 4. In Italic: lignin pyrolysis products.

Figure 6. Py(HMDS)-GC-MS profiles for samples **a)** *Ficus sycomorus* reference, **b)** F2, **c)** F4. Peak labelling refers to Table 4. In Italic: lignin pyrolysis products.

Figure 7. Py(HMDS)-GC-MS profiles for samples **a)** sound *Pinus sylvestris*, **b)** F11b, **c)** F11c. Peak labelling refers to Table 4. In Italic: lignin pyrolysis products.

Figure 8. Distribution of categories of lignin pyrolysis products expressed as percentages for all archaeological and the corresponding sound wood samples.

Figure 9. Distribution of categories of holocellulose pyrolysis products expressed as percentages for all the samples from Egypt and the corresponding sound wood samples.

Table 1. Information about microbial attack and preservation of wood structure obtained by SEM observations.

Sample	Species	Microbial decay	Typology	Structure preservation
F1	*Faidherbia albida*	Present	Not identified	Poor
F2	*Ficus sycomorus*	Present	Fungi	Poor
F3	*Ficus sycomorus*	Absent		Good
F4	*Ficus sycomorus*	Present	Fungi (possibly brown rot)	Poor
F5	*Ficus sycomorus*	Present	Not identified	Good
F6	*Ficus sycomorus*	Present	Fungi (white rot)	Poor
F8	*Faidherbia albida*	Present	Fungi and bacteria	Poor
F9	*Taxus baccata*	Present	Fungi (possibly white/soft rot	Poor
F11a	*Tamarix* sp.	Absent		Good
F11b	*Pinus sylvestris*	Absent		Good
F11c	*Pinus sylvestris*	Absent		Very good

Table 2. Results of wet chemical analyses for reference and archaeological woods, referring to an ash-free basis of calculation (series W). The values are expressed as a percentage of the total weight of the samples. The values of ash are reported in the last column, as an indication of the entity of corrections.

Sample	Species	Organic extractable fraction (W), %	Aqueous extractable fraction (W), %	Lignin (W), %	Holocellulose (W), %	H/L	Ash, %
Reference woods	*T. baccata*	11.0	2.3	27.2	59.2	2.2	0.3
	Tamarix sp.p.	4.1	8.1	20.2	62.3	3.1	5.4
	P. sylvestris	4.1	2.1	25.8	67.8	2.6	0.2
	F. sycomorus	1.1	4.4	31.1	61.1	2.0	2.3
F1	*F. albida*	2.7	45.4	30.3	21.6	0.7	19.7
F2	*F. sycomorus*	8.1	9.7	19.0	63.1	3.3	18.0
F3	*F. sycomorus*	5.9	20.2	30.8	43.0	1.4	11.7
F4	*F. sycomorus*	8.3	29.0	49.6	13.2	0.3	16.8
F5	*F. sycomorus*	6.1	28.8	14.2	50.9	3.6	11.0
F6	*F. sycomorus*	6.4	39.0	16.8	37.8	2.3	14.5
F8	*F. albida*	7.4	27.2	28.5	36.9	1.3	20.0
F9	*T. baccata*	3.5	11.3	20.4	64.8	3.2	11.1
F11a	*Tamarix* sp.	5.4	15.2	18.6	60.9	3.3	5.7
F11b	*P. sylvestris*	3.5	4.5	22.3	69.7	3.1	0.1
F11c	*P. sylvestris*	2.8	3.8	25.3	68.1	2.7	1.4

939 **Table 3.** Assignments of IR absorption bands for the analysed wood.

Band, cm^{-1}	**Assignment**
3330	OH stretching vibration
1736	ester groups in hemicelluloses
1587	C-O vibration in carboxylates (coupled with *ca*. 1400)
1578	C-O vibration in metal chelates or salts of conjugated diketones
1595	C=C in the aromatic skeleton
1505	C=C in the aromatic skeleton
1455	asymmetric C-H deformation and aromatic vibration in lignin
1400/1415	C-O vibration in carboxylates coupled (with *ca.* 1587)
1370	C-H symmetric deformation in carbohydrates
1330	C-O in syringyl ring
1317	CH_2 wagging in cellulose
1268	guaiacyl ring breathing
1230	C-O stretching in hemicelluloses
1217	C–O bond of the guaiacyl ring
1120	aromatic skeletal vibration and C-O stretching (in lignin)
1030	C-O-C deformations in polysaccharides
896	C-H deformation in cellulose

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Table 4. List of wood pyrolysis products identified by Py(HMDS)-GC-MS and divided into categories. The molecular weight (MW) of the derivatised compounds, the main *m/z* peaks in the mass spectra (base peak in bold), the attribution of the pyrolysis products to the corresponding wood component (H=Holocellulose, L=Lignin, G=Guaiacyl lignin, S=Syringyl lignin) and to the specific categories (dem=demthylated/demethoxylated compounds) are shown.

N°	Compound	MW	*m/z*	Origin	Category
1	1,2-dihydroxyethane (2TMS)	206	73,103,**147**,191	H/L	Small molecules
2	2-hydroxymethylfuran (TMS)	170	53, 73, **81**, 111, 125, 142, 155, 170	H	Furans
3	phenol (TMS)	166	75, **151**, 166	L	Others
4	2-hydroxypropanoic acid (2TMS)	234	73, 117, **147**, 190	H/L	Small molecules
5	2-hydroxyacetic acid (2TMS)	220	73, **147**, 177, 205	H/L	Small molecules
6	1-hydroxy-1-cyclopenten-3-one (TMS)	170	53, 73, 81, 101, 111, 127, **155**	H	Cyclopentenones
7	3-hydroxymethylfuran (TMS)	170	53, 75, **81**, 111, 125, 142, 155, 170	H	Furans
8	*o*-cresol (TMS)	180	73, **91**, 135, 149, 165, 180	L	Others
9	2-furancarboxylic acid (TMS)	184	73, 95, **125**, 169, 184	H	Furans
10	unknown holocellulose I		73, **152**, 167	H	Others
11	*m*-cresol (TMS)	180	73, 91, **165**, 180	L	Others
12	2-hydroxy-1-cyclopenten-3-one (TMS)	170	53, 73, 81, 101, 111, 127, **155**, 170	H	Cyclopentenones
13	*p*-cresol (TMS)	180	73, 91, **165**, 180	L	Others
14	3-hydroxy-(2H)-pyran-2-one (TMS)	184	75, 95, 125, 151, **169**, 184	H	Pyranones
15	unknown holocellulose II		59, 73, 85, 101, 115, **131**, 159	H	Others
16	unknown holocellulose III		**75**, 85, 103, 115, 129, 145, 173, 188	H	Others
17	*Z*-2,3-dihydroxycyclopent-2-enone (TMS)	186	59, **73**, 115, 143, 171, 186	H	Cyclopentenones
18	*E*-2,3-dihydroxycyclopent-2-enone (TMS)	186	**75**, 101, 143, 171, 186	H	Cyclopentenones
19	1,2-dihydroxybenzene (TMS)	182	75, 91, 136, **151**, 167, 182	H	Hydroxybenzenes
20	3-hydroxy-(4H)-pyran-4-one (TMS)	184	75, 95, 139, 151, **169**, 184	H	Pyranones
21	5-hydroxy-(2H)-pyran-4(3H)-one (TMS)	186	59, **75**, 101, 129, 143, 171, 186	H	Pyranones
22	2-hydroxymethyl-3-methy-2-cyclopentenone (TMS)	198	73, 103, 129, 173, **183**, 198	H	Cyclopentenones

23	1-hydroxy-2-methyl-1-cyclopenten-3-one (TMS)	184	73, 97, 125, 139, **169**, 184	H	Cyclopentenones
24	1-methy-2-hydroxy-1-cyclopenten-3-one (TMS)	184	73, 97, 125, 139, **169**, 184	H	Cyclopentenones
25	1,3-dihydroxyacetone (2TMS)	234	73, **103**, 147, 189, 219	H	Small molecules
26	guaiacol (TMS)	196	73, 151, **166**, 181, 196	G	Short chain
27	unknown holocellulose IV		**73**, 217, 232	H	Others
28	3-hydroxy-6-methyl-(2H)-pyran-2-one (TMS)	198	73, 109, 139, 168, **183**, 198	H	Pyranones
29	unknown holocellulose V		**73**, 101, 116, 131, 173	H	Others
30	2-methyl-3-hydroxy-(4H)-pyran-4-one (TMS)	198	73, 101, 153, **183**, 198	H	Pyranones
31	2-methyl-3-hydroxymethyl-2-cyclopentenone (TMS)	198	73, 103, 129, 173, **183**, 198	H	Cyclopentenones
32	2,3-dihydrofuran-2,3-diol (2TMS)	246	**73**, 147, 231, 246	H	Furans
33	2-furylhydroxymethylketone (TMS)	198	**73**, 81, 103, 125, 183, 198	H	Furans
34	5-hydroxymethyl-2-furaldehyde (TMS)	198	73, 81, 109, 111, 139, 169, **183**, 198	H	Furans
35	4-methylguaiacol (TMS)	210	73, 149, **180**, 195, 210	G	Short chain
36	1,2-dihydroxybenzene (2TMS)	254	**73**, 151, 239, 254	H	Hydroxybenzenes
37	2-hydroxymethyl-2,3-dihydropyran-4-one (TMS)	200	73, 142, 170, **185**, 200	H	Pyranones
38	1,4:3,6-dianhydro-α-D-glucopyranose (TMS)	186	**73**, 103, 129, 155, 170, 171, 186	H	Anhydrosugars
39	Z-2,3-dihydroxycyclopent-2-enone (2TMS)	258	**73**, 147, 230, 243, 258	H	Cyclopentenones
40	4-methylcatechol (2TMS)	268	**73**,180, 253, 268	G	Dem
41	4-ethylguaiacol (TMS)	224	73, 149, 179, **194**, 209, 224	G	Short chain
42	syringol (TMS)	226	73, 153, 181, **196**, 211, 226	S	Short chain
43	1,4-dihydroxybenzene (2TMS)	254	**73**, 112, 239, 254	H	Hydroxybenzenes
44	arabinofuranose (4TMS)	438	**73**, 147, 217, 230	H	Anhydrosugars
45	4-vinylguaiacol (TMS)	222	73, 162, 177, **192**, 207, 222	G	Short chain
46	3-hydroxy-2-hydroxymethyl-2-cyclopentenone (2TMS)	272	73, 147, **257**, 272	H	Cyclopentenones
47	*E*-2,3-dihydroxycyclopent-2-enone (2TMS)	258	73, 147, **243**, 258	H	Cyclopentenones
48	4-ethylcatechol (2TMS)	282	**73**, 147, 179, 231, 267, 282	G	Dem
49	3-hydroxy-2-(hydroxymethyl)cyclopenta-2,4-dienone (2TMS)	270	73, 147, **255**, 270	H	Cyclopentenones
50	eugenol (TMS)	236	73, 147, 179, **206**, 221, 236	G	Long chain
51	4-methylsyringol (TMS)	240	73, 167, **210**, 225, 240	S	Short chain

52	3-methoxy-1,2-benzenediol (2TMS)	284	73, 153, 254, 269, **284**	S	Dem
53	3,5-dihydroxy-2-methyl-(4H)-pyran-4-one (2TMS)	286	73, 128, 147, 183, **271**, 286	H	Pyranones
54	1,6-anhydro-β-D-glucopyranose (TMS at position 4)	234	**73**, 103, 117, 129, 145, 155, 171	H	Anhydrosugars
55	1,6-anhydro-β-D-glucopyranose (TMS at position 2)	234	**73**, 101, 116, 129, 132, 145, 155, 171	H	Anhydrosugars
56	*Z*-4-isoeugenol (TMS)	236	73, 179, **206**, 221, 236	G	Long chain
57	vanillin (TMS)	224	73, **194**, 209, 224	G	Carbonyl
58	1,2,3-trihydroxybenzene (3TMS)	342	**73**, 133, 147, 239, 327, 342	H	Hydroxybenzenes
59	5-methyl-3-methoxy-1,2-benzenediol (2TMS)	298	73, 151, 210, 253, 268, 283, **298**	S	Dem
60	4-ethylsyringol (TMS)	254	73, 191, 209, **224**, 239, 254	S	Short chain
61	*E*-4-isoeugenol (TMS)	236	73, 179, **206**, 221, 236	G	Long chain
62	1,4-anhydro-D-galactopyranose (2TMS)	306	**73**, 101, 116, 129, 145, 155, 171, 217	H	Anhydrosugars
63	1,6-anhydro-D-galactopyranose (2TMS)	306	**73**, 101, 116, 129, 145, 189, 204, 217	H	Anhydrosugars
64	2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one (2TMS)	288	**73**, 129, 147, 155, 183, 273, 288	H	Pyranones
65	4-vinylsyringol (TMS)	252	73, 179, **222**, 237, 252	S	Short chain
66	1,4-anhydro-D-glucopyranose (2TMS at position 2 and 4)	306	**73**, 101, 116, 129, 155, 191, 204, 217	H	Anhydrosugars
67	1,2,4-trihydroxybenzene (3TMS)	342	**73**, 133, 147, 239, 327, 342	H	Hydroxybenzenes
68	acetovanillone (TMS)	238	73, **193**, 208, 223, 238	G	Carbonyl
69	4-hydroxybenzoic acid (2TMS)	282	73, 147, 193, 223, **267**, 282	L	Acids
70	4-propenylsyringol (TMS)	266	73, 205, **236**, 251, 266	S	Long chain
71	1,6-anhydro-β-D-glucopyranose (2TMS at position 2 and 4)	306	**73**, 101, 116, 129, 155, 191, 204, 217	H	Anhydrosugars
72	vanillic acid methyl ester (TMS)	254	73, 193, **224**, 239, 254	G	Esters
73	5-vinyl-3-methoxy-1,2-benzenediol (2TMS)	310	**73**, 147, 179, 222, 280, 295, 310	S	Dem
74	*Z*-4-isopropenylsyringol	266	73, 205, **236**, 251, 266	S	Long chain
75	1,4-anydro-D-galactopyranose (3TMS)	378	**73**, 129, 147, 191, 204, 217, 243, 332	H	Anhydrosugars
76	unknown lignin I		**73**, 147, 193, 239, 313, 401, 416	L	Others
77	syringaldehyde (TMS)	254	73, **224**, 239, 254	S	Carbonyl
78	2,3,5-trihydroxy-4H-pyran-4-one (3TMS)	360	**73**, 147, 239, 255, 270, 330, 345, 360	H	Pyranones
79	1,6-anhydro-β-D-glucopyranose (3TMS)	378	**73**, 129, 147, 191, 204, 217, 243, 333	H	Anhydrosugars
80	1,4-anhydro-D-glucopyranose (3TMS)	378	**73**, 129, 147, 191, 204, 217, 243, 332	H	Anhydrosugars

81	*E*-4-isopropenylsyringol (TMS)	266	73, 205, **236**, 251, 266	S	Long chain
82	1,6-anhydro-β-D-glucofuranose (3TMS)	378	**73**, 129, 147, 191, 204, 217, 243, 319	H	Anhydrosugars
83	unknown lignin II		73, 179, 217,342, 358, 415, **430**	L	Others
84	unknown lignin III		**73**, 147, 193, 239, 313, 401, 416	L	Others
85	vanillic acid (2TMS)	312	73, 223, 253, 267, 282, **297**, 312	G	Acids
86	acetosyringone (TMS)	268	73, **223**, 238, 253, 268	S	Carbonyl
87	5-propyl-3-methoxy-1,2-benzenediol (2TMS)	326	**73**, 147, 179, 209, 296, 311, 326	S	Dem
88	coumaryl alcohol (2 TMS)	294	**73**, 189, 205, 267, 279, 294	G	Dem
89	syringic acid methyl ester (TMS)	284	73, 223, **254**, 269, 284	S	Esters
90	vanillylpropanol (2TMS)	326	73, 179, **206**, 221, 236, 311, 326	G	Long chain
91	*Z*-coniferyl alcohol (2 TMS)	324	**73**, 204, 252, 293, 309, 324	G	Monomers
92	4-hydroxy-3,5-dimethoxycinnamic acid methyl ester (TMS)	310	73, 147, 179, 222, **280**, 295, 310	S	Esters
93	coniferylaldehyde (TMS)	250	73, 192, **220**, 235, 250	G	Carbonyl
94	trihydroxycinnamyl alcohol (3TMS)	398	73, **147**, 210, 254, 368, 383, 398	S	Dem
95	syringic acid (2TMS)	342	**73**, 253, 297, 312, 327, 342	S	Acids
96	unknown lignin IV		73, 179, 209, 237, 280, **310**, 325, 340	L	Others
97	*E*-coniferyl alcohol(2 TMS)	324	73, 204, 235, 293, 309, **324**	G	Monomers
98	3,4-dihydroxy-5-methoxybenzoic acid (3TMS)	400	**73**, 137, 147, 223, 253, 297, 385, 400	S	Acids
99	syringylpropanol (2TMS)	356	73, 210, 240, 341, **356**	S	Long chain
100	*Z*-sinapyl alcohol (2TMS)	354	73, 234, 323, 339, **354**	S	Monomers
101	unknown lignin V		**73**, 179, 209, 237, 280, 310, 325, 340	L	Others
102	3,4-dihydroxycinnamyl alcohol (3TMS)	382	**73**, 205, 293, 355, 382	G	Dem
103	trihydroxycinnamyl alcohol I (3TMS)	398	**73**, 147, 210, 254, 368, 383, 398	S	Dem
104	sinapylaldehyde (TMS)	280	73, **222**, 250, 265, 280	S	Carbonyl
105	trihydroxycinnamyl alcohol II (3TMS)	398	**73**, 147, 210, 254, 368, 383, 398	S	Dem
106	*Z*-2-methoxy-3,4-dihydroxycinnamyl alcohol (3TMS)	412	**73**, 235, 323, 385, 412	S	Dem
107	sinapyl alcohol (TMS)	282	**73**, 234, 251, 267, 282	S	Monomers
108	*E*-sinapyl alcohol (2TMS)	354	73, 234, 323, 339, **354**	S	Monomers
109	*E*-2-methoxy-3,4-dihydroxycinnamyl alcohol (3TMS)	412	**73**, 235, 323, 385, 412	S	Dem

110	unknown lignin VI	**73**, 147, 196, 253, 355, 370	L	Others
111	unknown anhydrosugar I (dimer)	**73**, 103, 117, 147, 177, 189, 303, 347	H	Anhydrosugars
112	unknown anhydrosugar II (dimer)	**73**, 103, 117, 129, 147, 204, 217, 361	H	Anhydrosugars
113	unknown anhydrosugar III (dimer)	**73**, 117, 129, 147, 204, 217, 223, 361	H	Anhydrosugars
114	unknown anhydrosugar IV (dimer)	**73**, 117, 129, 147, 204, 217, 243, 273	H	Anhydrosugars
115	unknown anhydrosugar V (dimer)	**73**, 117, 129, 147, 190, 204, 347, 352	H	Anhydrosugars
116	unknown anhydrosugar VI (dimer)	**73**, 117, 129, 147, 204, 217, 289, 361	H	Anhydrosugars
117	unknown anhydrosugar VII (dimer)	**73**, 117, 129, 147, 204, 217, 289, 361	H	Anhydrosugars