Characterization and identification of urushi using *in situ* Pyrolysis/silylation-Gas Chromatography-Mass Spectrometry

Diego Tamburini[1], Ilaria Bonaduce[1], Maria Perla Colombini[1,2]

[1] Department of Chemistry and Industrial Chemistry, University of Pisa, via Giuseppe Moruzzi 3, I-56124 Pisa, Italy
[2] Institute for the Conservation and Valorization of Cultural Heritage (ICVBC), National Research Council, Sesto Fiorentino, Florence, Italy

* Correspondence should be addressed to: Diego Tamburini, Department of Chemistry and Industrial Chemistry, University of Pisa, via Giuseppe Moruzzi 3, I-56124 Pisa, Italy email diego.tamburini@for.unipi.it tel. +39 050 2219258, fax +39 050 2219260

Abstract

Analytical pyrolysis coupled with gas chromatography and mass spectrometry is a very powerful tool to analyze polymers and macromolecules. In this paper this technique was applied to the characterization of the urushi oriental lacquer (qi-lacquer in Chinese) with the aim to set up an alternative analytical method to identify the lacquer.
Urushi is rich in mostly alcoholic polar moieties, thus a derivatization step is required, which is crucial for the detection and MS identification of all the compounds deriving from the thermal degradation. In this work hexamethyldisilazane (HMDS) was used for the first time as a derivatizing agent, thus proving to be a valid alternative to more common methylating agents.
Adopting this *in situ* Py/silylation-GC-MS procedure, we were able to characterize urushi lacquer and identify characteristic pyrolytic profiles of silylated alkylcatechols, silylated alkylphenols, aliphatic hydrocarbons, alkylbenzenes as well as characteristic molecular biomarkers.
The method was thus used to analyze six archaeological samples from Sichuan (China) dating back from the 2nd century BC to the 12th century AD, in which the presence of urushi was suspected, and the lacquer was identified in all of them through the identification of all the characteristic pyrolytic profiles and molecular biomarkers.
The method set up is promising to be used also for the characterization of the other oriental lacquers, such as laccol and thitsi.

Keywords: urushi, pyrolysis, *in situ* derivatization, silylating agents, hexamethyldisilazane

1. Introduction

Urushi (qi-lacquer in Chinese) is considered as the oldest and most precious lacquer in East Asia. It has been used for thousands of years as a coating material to decorate or protect objects, because of its capacity to lend the object great and lasting brightness, toughness and water resistance. It has been and is still used on several substrates, such as wood, ceramics, metals [1].
Objects of significant cultural value coated with urushi have maintained their beautiful surfaces for over two thousand years [2]. However, depending on the conservation conditions, there may be severe degradation, for example the Qin Shi Huang's

Terracotta Army. In fact, the priming layer of urushi, which is waterlogged due to the long period of time in humid soil, shrinks when the relative humidity decreases below 92%, thus causing the paint layer to become detached [3,4].

Oriental lacquers can be extracted from three species of the same tree, belonging to the *Anacardiaceae* family. These varieties are native to specific areas of East Asia: *Rhus vernicifera* from China, Japan and Korea, *Rhus succedanea* from North Vietnam and Taiwan, and *Melanorrhoea usitate* from Thailand and Burma [5,6]. Urushi is extracted from *Rhus vernicifera*. Although these plants are native to East Asia, in the mid-16th century, East Asian lacquered objects started to generate great interest and were imported to Europe. European craftsmen started to imitate East Asian lacquers with the use of other materials, such as plant terpenoid resins, oils, proteins and inorganic pigments [7]. Today, the only way to distinguish imitations from true oriental lacquer is chemical analysis [7,8].

In order to identify oriental lacquers in artistic and archaeological samples, a reliable analytical method is thus needed, which can also be used on small samples containing mixtures of organic and inorganic materials [9,10], as is the case with samples from works of art.

The sap from the three tree species is composed of water (30%), glycoproteins (2%), plant gum (7%), laccase enzyme (1%), and a mixture of catechol derivatives (60-65%), which varies depending on the plant of origin [5]. The mixture contained in the sap of *Rhus vernicifera* is called urushiol, laccol in *Rhus succedanea* and thitsiol in *Melanorrohoea usitate*. The principal component of urushiol is 3-pentadecylcatechol and the principal component of laccol is 3-heptadecylcatechol. The aliphatic chains may be saturated or have one, two or three double bonds. The composition of thitsiol is more complicated: in addition to the typical compounds of urushiol and laccol, it also contains alkylphenylphenols and alkylphenyl-1,2-dihydroxybenzenes (alkylphenylcatechols), such as 3-(10-phenyldecyl)phenol/catechol and 3-(12-phenyldodecyl)phenol/catechol [2,6,11,12].

The drying process of oriental lacquers is different from European lacquers, because of the phenolic fraction of the sap. During this process, polymerisation occurs, resulting in a very resistant film, which is inert to acids, alkalis and alcohols, is stable up to 300°C, and is insoluble in most common solvents. The structure and composition of the final polymer depends on the hardening process [12,13]. Polymerisation starts thanks to the laccase enzyme and leads to the formation of C-C aromatic nucleus-side chain coupling bonds, C-O phenolic oxygen-side chain coupling bonds and C-C bonds between side chains. The result is a cross-linked polymer, whose structure has not yet been completely clarified [2,12].

Several techniques have been used to analyze the lacquer, such as NMR [12,14,15], FTIR [2,12,13,15], XPS [16], thermal analysis (TG/DTA-MS) [13,15,17]. These studies mainly provide information on the structure and the chemical state of the polymer, however they are not useful for diagnostic purposes. GC-MS is used to characterize the monomeric fraction of the lacquer [11], but it cannot provide information on the polymerised fraction, which is the most abundant, and thus this method is unsatisfactory [18].

Pyrolysis techniques are the most suitable for the analysis of chemically untreatable polymeric materials, because they enable the polymeric network to be broken down into smaller molecules, which can then be more easily studied [19]: DIMS (direct inlet mass spectrometry) provides preliminary information on the type of lacquer [8]; EGA-IAMS (evolved gas analysis-ion attachment-mass spectrometry) has been used to characterize Japanese lacquers and to study the kinetics of water release during

heating [20]; direct probe Li^+ ion attachment mass spectrometry has been recently used and the results compared with those achieved with Py-GC-MS [21].
Py-GC-MS is currently the most common technique for characterizing and identifying oriental lacquers [5,8-10,13,18,22-25], and the most promising results have been achieved using thermally-assisted reactions with tetramethylammonium hydroxide (TMAH) as a derivatizing agent [18,22].
One of the main problems of the pyrolysis technique is, in fact, related to the low volatility of acidic, alcoholic and aminic pyrolysis products, which are not really suitable for gas chromatographic analysis, causing a rather low reproducibility of the resulting pyrograms, low sensitivity for specific compounds, and strong memory effects [19]. Moreover, the high fragmentation of natural macromolecules during pyrolysis leads to the formation of many unspecific compounds.
To overcome these problems, the sample can be pyrolyzed using a suitable reagent, which transforms polar functionalities into less polar moieties. Tetramethylammonium hydroxide (TMAH) is one of the most commonly used reagents for the online methylation of acidic and alcoholic moieties. Although the tetramethylammonium hydroxide thermochemolysis (TMH) method has been extensively applied to the characterization of materials used in the creation and restoration of works of art, the strong alkalinity of TMAH may cause problems in the interpretation of pyrograms. Consequently, other derivatizing agents have been proposed, mainly in the analysis of samples collected from artistic and archaeological objects, including methylating and silylating agents [26-31].
In this work we investigated into the Py/silylation-GC-MS characterization and identification of urushi, using hexamethyldisilazane (HMDS) as a silylating agent for use *in situ* during pyrolysis prior to GC-MS analysis.

2. Material and methods

2.1 Samples

A reference layer of urushi (from *Rhus Vernicifera*) was analyzed. The raw material was bought at a local producer in the northern slopes of the Qinling mountains near Xi'an (China) in 2007. The film was made in 2008. Six archaeological samples dating back to the Western Han dynasty (206 BC - 24 AD) and Southern Song dynasty (1127-1279 AD) were analyzed. The samples were collected from six different objects found in the Sichuan region of China. The description of the samples is presented in Table 1.

2.2 Instrumentation and method

Analytical pyrolysis with 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 derivatization of pyrolysis products was applied. The instrumentation consisted of a 5150 CDS Pyroprobe 5000 Series pyrolyzer connected to a gas chromatograph 6890 N (Agilent Technologies, Palo Alto, CA, USA) equipped with an HP-5MS fused silica capillary column (stationary phase 5% diphenyl – 95% dimethyl-polysiloxane, 30 m × 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m × 0.32 mm i.d., Agilent J&W, USA). The GC was coupled with a 5973 mass selective detector (Agilent Technologies, Palo Alto, CA, USA) single quadrupole mass spectrometer operating in electron ionization mode (EI) at 70 eV.

The pyrolysis temperature was 600° C, which was maintained for 20 s using a platinum coil probe and quartz sample tubes. Samples in the order of 100 μg and HMDS (5μL) were inserted into the centre of the pyrolysis quartz tube with glass wool, and then placed in the pyrolysis coil filament. The interface temperature was 200 °C. The GC-MS injector was used in split mode, at 280°C and 1:40 split ratio. Chromatographic oven conditions were as follows: initial temperature 32°C, 10 min isothermal, 10 °C min^{-1} to 280 °C, 2 min isothermal, 15°C min^{-1} to 300°C, 30 min isothermal. Carrier gas: He (purity 99.995%), constant flow 1.0 ml min^{-1}.

3. Results and discussion

3.1 Urushi reference sample

The urushi layer was analyzed in order to identify specific pyrolysis products and pyrolytic profiles to be used to diagnose the lacquer in a sample of unknown composition. Figure 1 shows the TIC profile of the reference sample. Numbers refer to Table 2, in which the identified compounds are listed.

The results showed a lipid fraction, in which hexadecanoic, octadecenoic and octadecanoic acids were the most abundant fatty acids. This fraction is present in urushi wax and can be extracted from the sap [32].

Mono-silylated 3-pentadecyl-1,2-dihydroxybenzene (3-pentadecylcatechol) (#33) and 3-pentadecenyl-1,2-dihydroxybenzene (3-pentadecenylcatechol[1]) (#32) were well evident in the pyrogram and were identified on the basis of the interpretation of their mass spectra (Figure 2) [2]. 3-pentadecylcatechol and 3-pentadecenylcatechol are the urushi monomers, and thus the molecular biomarkers of the lacquer. The corresponding bis-silylated compounds were also identified by extracting the *m/z* ratios corresponding to their molecular mass (Figure 2). In addition, 8-(2,3-dihydroxyphenyl)octanoic acid, derivatized both two and three times, was identified. The identification of this compound was not surprising: it is in fact not innately present in the lacquer, but it is known to derive from the oxidation of the lacquer [33]. As the lacquer investigated in this study was in the form of a reference layer which was prepared in 2008, it was reasonable to hypothesize that its components had undergone a certain degree of oxidation over time. Figure 2 shows the mass spectra of 8-(2,3-dihydroxyphenyl)octanoic acid (2TMS), 8-(2,3-dihydroxyphenyl)octanoic acid (3TMS), 3-pentadecenylcatechol (TMS), 3-pentadecylcatechol (TMS), 3-pentadecenylcatechol (2TMS), 3-pentadecylcatechol (2TMS). In our experimental conditions these compounds can all be considered the Py/silylation-GC-MS markers of urushi.

In addition to the Py/silylation-GC-MS markers cited above, the pyrolysis of urushi in the presence of HMDS resulted in a chromatogram with characteristic pyrolytic profiles of

---

[1] In Figure 2 3-pentadecenylcatechol was indicated with a double bond between C8 and C9, because it is known from the literature [13] that this is the most abundant monoalkenylcatechol in the composition of urushi. Nevertheless the identification of this compound is not completely certain and the double bond could actually occupy another position in the chain.

[2] The identification of these compounds was performed by assuming that for all of them the last *m/z* peak shown in the mass spectrum corresponded the molecular ion M^+. In addition, for all of them the base peak corresponded to the *m/z* ion 179, which is characteristic of alkylcatechols, as shown further in this section.

catechols (#13, #16, #24, #25, #32, #33), hydrocarbons (#22), and some alkylbenzenes (#1, #3), in accordance with the literature [5,12,22,25].

By extracting specific *m/z* values, we were able to identify the pyrolytic profiles of these characteristic pyrolysis products to be used for diagnostic purposes in a sample of unknown composition:

- mono-TMS alkylcatechols (*m/z* 179[3]; Figure 3);
- bis-TMS alkylcatechols (*m/z* 253[4]; Figure 4);
- TMS alkylphenols (*m/z* 180[5]; Figure 5);
- aliphatic hydrocarbons (*m/z* 57; Figure 6);
- alkylbenzenes (*m/z* 91; Figure 7).

The *m/z* ratios to be used to extract the pyrolytic profiles of these compounds were the base peaks (or the one of the most abundant peak) of the mass spectra for each category of compounds. In the insets of Figures 3, 4 and 5, the mass spectra of 3-heptylcatechol (TMS), 3-hexylcatechol (2TMS) and 3-heptylphenol (TMS) are shown, respectively. These compounds were the most abundant in the respective pyrolytic profiles.

During pyrolysis alkylcatechols (Figures 3 and 4) were formed from the thermal cleavage of C-C bonds between aromatic nuclei and side chains. The presence of both mono-derivatized and bis-derivatized compounds can be ascribed to steric hindrance in the polymeric network, which prevented HMDS from reacting with all the hydroxyl moieties. In addition the formation and transfer rates of pyrolysis products can affect the derivatization yield. This phenomenon has already been highlighted in the Py/silylation-GC-MS analysis of wood [34], whose polymeric network is as complex as that of urushi. In Figure 3 the most abundant peak was identified as 3-heptylcatechol (TMS). This can be explained by considering that the side chain of 15 carbon atoms of the urushi monomer has double bonds at different positions, however the double bond between C8 and C9 is the most abundant. The α position with respect to this double bond is the most susceptible to thermal cleavage and heptylcatechol was thus the product of this cleavage. The thermal energy of the pyrolysis process in our working conditions was in any case sufficient to break the side chain in other positions and the other alkylcatechols were obtained from these cleavages.

Alkyl-phenols (Figure 5) resulted from the cleavage of both C-C and C-O bonds between the aromatic ring and the phenolic oxygen in the lacquer catechols. Their abundance was low in comparison with alkylcatechols. Alkylphenols can also derive from secondary pyrolysis reactions of alkylcatechols, resulting in the loss of a hydroxyl group [22].

---

[3] The MS spectra of mono-TMS alkylcatechols (Figure 3) showed the molecular ion $M^{\cdot+}$ and the ion M-15$^+$, arising from the loss of a methyl group from the trimethylsilyl substituent; the base peak was at *m/z* 179, most likely ascribable to the fragment ion produced by the cleavage of the alkyl chain at the benzylic position and the loss of the underivatized hydroxyl group $(TMSO\text{-}Ph\text{-}CH_2)^{\cdot+}$.

[4] The MS spectra of bis-TMS alkylcatechols showed the molecular ion $M^{\cdot+}$, the ion M-15$^+$ and the base peak was at *m/z* 253, tentatively attributed to the radical fragment ion [se m-15 é + e non é punto +, allora anche questo che perde una catena alchilica dovrebbe essere solo +, no? $((TMSO)_2\text{-}Ph)^{\cdot+}$, corresponding to the loss of the alkyl chain. The *m/z* ion 179 was also present in these spectra.

[5] The MS spectra of TMS alkylphenols showed the $M^{\cdot+}$ and M-15$^+$ ions and the base peak was at *m/z* ratio 180, most likely ascribable to the fragment ion $(TMSO\text{-}Ph\text{-}CH_3)^+$, which is obtained after cleavage of the alkyl chain at the benzylic position.

Hydrocarbons (Figure 6) derived from the cleavage of C-C bonds between the side chains and C-O bonds between phenolic oxygen and side chains. The most abundant saturated hydrocarbon was identified as pentadecane, corresponding to the saturated side chain of the monomer, and the most abundant unsaturated hydrocarbon was tetradecene (#22), deriving from the cleavage of the side chain at the benzylic position. In Figure 6 the profile of alkanes was extracted, and thus from a quantitative point of view it cannot be considered as being representative of the chromatographic profiles of the whole hydrocarbon fraction produced in the pyrolysis process.
Alkylbenzenes (Figure 7) derived from the cleavage of C-O phenolic bonds and C-C bonds of the side chains and can also be considered as the final products of secondary pyrolysis reactions of catechols, resulting in the loss of both the hydroxyl groups [22].

3.2 Archaeological samples

In samples L2, L3, L8 and L9 all the molecular markers and the characteristic pyrolytic profiles of catechols, hydrocarbons, and alkylbenzenes were detected, as well as the fatty acids relative to the lipid fraction ascribable to the so called urushi wax. Figure 8 shows the extracted pyrolytic profiles for sample L8.
The main difference between these archaeological samples and the urushi reference sample was relative to the profiles of the mono-TMS alkylcatechols: for the reference sample 3-heptylcatechol was the most abundant, whereas for samples L8 and L9 3-pentadecylcatechol was the most abundant and for samples L2 and L3 these two compounds had almost the same abundance. This may be interpreted in terms of chemical changes undergone by the lacquer with time, which may have led to different pyrolytic profiles from the quantitative point of view. Differences in the composition of the original lacquer cannot be ruled out as well.
The pyrogram of sample L7 was dominated by the pyrolysis products of wood [35], due to an incomplete separation of the lacquer layer from the wooden support during sampling. Nevertheless, also in this case all the molecular markers and pyrolytic profiles of urushi were detected and mono-TMS 3-heptylcatechol and mono-TMS 3-pentadecylcatechol were the most abundant.
For sample L4 the most abundant pyrolysis products were identified as fatty and dicarboxylic acids, the trimethylsilyl diester of nonandioic acid being the most abundant, leading to the identification of a drying oil [19,30]. Urushi lacquer was identified also in this sample, thus the lacquer and the oil were probably mixed together. In the pyrolytic profile of mono-TMS alkylcatechols, mono-TMS 3-pentadecylcatechol was the most abundant (Figure 9). An important difference was observed with respect to the other samples: 8-(2,3-dihydroxyphenyl)octanoic acid, derivatized both two and three times, was detected with a significant higher abundance. In addition also the omologue 7-(2,3-dihydroxyphenyl)octanoic acid was detected, derivatized both two and three times. Figure 9 shows the pyrolytic profile obtained by the extraction of the ion *m/z* 179 for this sample. The inset shows the mass spectrum of bis-TMS 7-(2,3-dihydroxyphenyl)heptanoic acid. The presence of these compounds could be the result of a significant oxidation of the lacquer, possibly promoted by the presence of the drying oil. Drying oils age in fact through auto-oxidative pathways [30], and thus their simultaneous presence could have led to the presence of a high number of radicals, which might be responsible of the production of radicals among urushi components and a consequent increased reactivity of the lacquer towards oxygen.

4. Conclusions

Py-GC/MS with *in situ* derivatization using HMDS as silylating agent was used to characterize a reference sample of urushi (qi-lacquer in Chinese) from *Rhus Vernicifera* and to identify the oriental lacquer in six archaeological samples dating back to the 2nd century BC. The results led to the identification in the reference pyrogram of the silylated molecular biomarkers of the lacquer as well as characteristic pyrolytic profiles of silylated alkylcatechols and alkylphenols, aliphatic hydrocarbons, and alkylbenzenes. Silylated acid alkylcatechols were also identified in the pyrogram, which were the result of oxidative processes that have taken place over time in the analyzed lacquer reference layer. All the identified molecular biomarkers and characteristic pyrolytic profiles identified in the reference lacquer were detected in the pyrograms of all the archaeological samples. The pyrograms showed some differences in the relative abundances of alkylcatechols and acid alkylcatechols, most likely ascribable to degradation processes undergone by the lacquer with time. Most of the pyrolysis products were identified with varying degrees of derivatization, most likely due to steric hindrance phenomena. The results obtained proved that Py/silylation-GC-MS using HMDS as silylating agent is a suitable technique for the analysis of archaeological samples containing urushi also in presence of other materials. The technique is in fact suitable for the analysis of very small amounts of samples (ca. 50 µg) and can also be exploited to identify degradation products, such as oxidation markers.

Acknowledgments

We would like to thank Prof. Erwin Emmerling (Technische Universität, Munich, Germany), who bought the raw material in China; Dr. Catharina Blaensdorf (Technische Universität, Munich, Germany), who provided the sample to us; Mr. Zhou Tie and Mr. Zhang Zhijun (Laboratory of the Museum of the Terracotta Army of Qin Shihuang, Xi'an, China) for the selection of the samles; Prof. Christoph Herm (Hochschule der Bildenden Künste, Art Technology and Conservation of Works of Art, Dresden,Germay); Dr. Cristina Thieme (Technische Universität, Chair of Conservation, Art Technology and Conservation Science, Munich, Germany) members of the project team.

Bibliography

[1] J.S. Mills and R. White, *The Organic Chemistry of Museum Objects*, 1994, p.

[2] J. Kumanotani, *Progress in Organic Coatings*, 26, (1995) 163.

[3] I. Bonaduce, C. Blaensdorf, P. Dietemann and M.P. Colombini, *Journal of Cultural Heritage* 9, (2008) 103.

[4] E. Emmerling, C. Thieme, T. Zhou and Z. Zhang, *The Polychromy of Ancient Sculpture*, Karl M. Lipp Verlag, Munchen, 2001, p. 537.

[5] N. Niimura, T. Miyakoshi, J. Onodera and T. Higuchi, *Journal of Analytical and Applied Pyrolysis*, 37, (1996) 199.

[6] R. Lu, Y. Kamiya and T. Miyakoshi, *Talanta*, 71, (2007) 1536.

[7] J. Koller, K. Walch and U. Baumer, in M. Kühlenthal ⁀Ed.⁀, *Japanese and European Lacquerware: Adoption, Adaptation, Conservation*, Bayerisches Landesamt für Denkmalpflege, Munich, 2000, p. 537.

[8] N. Niimura, *International Journal of Mass Spectrometry*, 284, (2009) 93.

[9] S. Wei, V. Pintus, V. Pitthard, M. Schreiner and G. Guoding Song, *Journal of Archaeological Science*, 38, (2011) 2667.

[10] R. Lu, T. Honda, Y. Kamiya, K. Yoshida and T. Miyakoshi, *Journal of Analytical and Applied Pyrolysis*, In press., (2012).

[11] Y. Kamiya, W. Saiyo and T. Miyakoshi, *Journal of Oleo Science*, 7, (2002) 473.

[12] N. Niimura and T. Miyakoshi, *J. Mass Spectrom. Soc. Jpn.*, 51, (2003) 439.

[13] N. Niimura and T. Miyakoshi, *Talanta*, 70, (2006) 146.

[14] J.B. Lambert, J.S. Frye and G.W. Carriveau, *Archaeometry*, 33, (1991) 87.

[15] J. Xia, J. Lin, Y. Xu and Q. Chen, *Applied Materials and Interfaces* 3, (2011) 482.

[16] N. Niimura and T. Miyakoshi, *Surface and Interface Analysis*, 29, (2000) 381.

[17] N. Niimura, *Thermochimica Acta*, 532, (2012) 164.

[18] V. Pitthard, S. Wei, S. Miklin-Kniefacz, S. Stanek, M. Griesser and M. Schreiner, *Archaeometry*, 52, (2010) 1044.

[19] I. Bonaduce and A. Andreotti, in M.P. Colombini and F. Modugno (Eds.), *Organic Mass Spectrometry in Art and Archaeology*, Wiley&Sons Ltd, 2009, p. 303.

[20] M. Tsukagoshi, Y. Kitahara, S. Takahashi, T. Tsugoshi and T. Fujii, *Analytical methods*, 3, (2011) 1943.

[21] M. Tsukagoshi, Y. Kitahara, S. Takahashi and T. Fujii, *Journal of Analytical and Applied Pyrolysis*, 95, (2012) 156.

[22] A. Le Hô, M. Regert, O. Marescota, C. Duhamela, J. Langloisa, T. Miyakoshi, C. Gentyd and M. Sablierd, *Analytica Chimica Acta*, 710, (2012) 9.

[23] R. Lu, X. Ma, Y. Kamiya, T. Honda, Y. Kamiya, A. Okamoto and T. Miyakoshi, *Journal of Analytical and Applied Pyrolysis*, 80, (2007) 101.

[24] Lu R., Y. Kamiya and T. Miyakoshi, *Talanta*, 70, (2006) 370.

[25] N. Niimura, T. Miyakoshi, J. Onodera and T. Higuchi, *Archeometry*, 41, (1999) 137.

[26] A. Andreotti, I. Bonaduce, M.P. Colombini, C. Baracchini, A. Caleca and A. Paolucci, *Saving the medieval paintings by the master painter of The Triumph of Death in Pisa*, at: ICOM Committee for Conservation, New Delhi, 428.

[27] I. Bonaduce and M.P. Colombini, *Rapid Communications in Mass Spectrometry*, 17, (2003) 2523.

[28] I. Bonaduce and M.P. Colombini, *Journal of Chromatography A*, 1028, (2004) 297.

[29] M.P. Colombini, I. Bonaduce and G. Gautier, *Chromatographia*, 58, (200 3) 357.

[30] I. Bonaduce, L. Carlyle, M.P. Colombini, C. Duce, C. Ferrari, E. Ribechini, P. Selleri and M.R. Tiné, *PLoS One*, 7, (2012) e49333.

[31] G. Chiavari, D. Fabbri and S. Prati, *Journal of Analytical and Applied Pyrolysis*, 74, (2005) 39.

[32] Wang C., Dong Y., Cheng H., He Y., Ye J. and Z. H., *Advances in Biological Chemistry*, (2013) 329.

[33] A. Heginbotham, and Michael Schilling., in R.F.a.B.P. Shayne Rivers (Ed.), *East Asian Lacquer: Material Culture, Science and Conservation*, Archetype Publications, London, 2011, p. 92.

[34] M.P. Colombini, J.J. Lucejko, F. Modugno, M. Orlandi, E.-L. Tolppa and L. Zoia, *Talanta*, 80, (2009) 61.

[35] D. Tamburini, J.J. Łucejko, F. Modugno and M.P. Colombini, *International Biodeterioration & Biodegradation*, (2013).

Figure 1 TIC chromatographic profile obtained by analyzing the urushi reference sample.

Figure 2 Mass spectra and molecular structures for: **A)** 8-(2,3-dihydroxyphenyl)octanoic acid (2TMS); **B)** 8-(2,3-dihydroxyphenyl)octanoic acid(3TMS); **C)** 3-pentadecenylcatechol (TMS); **D)** 3-pentadecylcatechol (TMS); **E)** 3-pentadecenylcatechol (2TMS); **F)** 3-pentadecylcatechol (2TMS).

Figure 3 Extracted ion chromatogram of the ion with *m/z* 179: **CT4)** 3-butylcatechol (TMS); **CT5:1)** 3-pentenylcatechol (TMS); **CT5)** 3-pentylcatechol (TMS); **CT6:1)** 3-hexenylcatechol (TMS); **CT6)** 3-hexylcatechol (TMS) (#24); **CT7:1)** 3-heptenylcatechol (TMS); **CT7)** 3-heptylcatechol (TMS) (#25); **CT8:1)** 3-octenylcatechol (TMS); **CT8)** 3-octylcatechol (TMS); **C9:1)** 3-nonenylcatechol (TMS); **CT9)** 3-nonylcatechol (TMS); **CT10)** 3-decylcatechol (TMS); **CT15:1)** 3-pentadecenylcatechol (TMS) (#32); **CT15)** 3-pentadecylcatechol (TMS) (#33). **A)** mass spectrum for 3-heptylcatechol (TMS)(**CT7**).

Figure 4 Extracted ion chromatogram of the ion with *m/z* 253: **CT2)** 3-ethylcatechol (2TMS); **CT3)** 3-propylcatechol (2TMS); **CT4:1)** 3-butenylcatechol (2TMS) **CT4)** 3-butylcatechol (2TMS); **CT5:1)** 3-pentenylcatechol (2TMS); **CT5)** 3-pentylcatechol (2TMS); **CT6:1)** 3-hexenylcatechol (2TMS); **CT6)** 3-hexylcatechol (2TMS); **CT7:1)** 3-heptenylcatechol (2TMS); **CT7)** 3-heptylcatechol (2TMS). **B)** mass spectrum for 3-hexylcatechol (2TMS) (**CT6**).

Figure 5 Extracted ion chromatogram of the ion with *m/z* 180: **Ph6:1)** 3-hexenylphenol (TMS); **Ph6)** 3-hexylphenol (TMS); **Ph7:1)** 3-heptenylphenol (TMS); **Ph7)** 3-heptylphenol (TMS); **Ph8)** 3-octylphenol (TMS). **C)** mass spectrum for 3-heptylphenol (TMS) (**Ph7**).

Figure 6 Extracted ion chromatogram of the ion with *m/z* 57: **C9)** nonane; **C10)** decane; **C11:1)** undecene; **C11)** undecane; **C12:1)** dodecene; **C12)** dodecane; **C13:1)** tridecene; **C13)** tridecane; **C14:1)** tetradecene (#18); **C14)** tetradecane; **C15:1)** pentadecene; **C15)** pentadecane.

Figure 7 Extracted ion chromatogram of the ion with *m/z* 91: **B2)** ethylbenzene (#1); **o-B1,1)** o-xylene; **m-B1,1)** m-xylene; **p-B1,1)** p-xylene; **B3)** propylbenzene (#3); **B3:1)** propenylbenzene; **B4)** butylbenzene; **B5)** pentylbenzene; **B6)** hexylbenzene; **B7)** heptylbenzene; **B8)** octylbenzene; **B9)** nonylbenzene.

Figure 8 Extracted ion chromatograms of the ions with *m/z* 179, 253, 91 and 57 for sample L8. Abbreviations are coherent with those presented in the other figures.

Figure 9 Extracted ion chromatogram of the ion with *m/z* 179 for the sample L4. The attributions are the same as Figure 3, except for: **CT7 acid)** 7-(2,3-dihydroxyphenyl)octanoic acid (2TMS); **CT8 acid)** 8-(2,3-dihydroxyphenyl)octanoic acid (2TMS). **Inset:** mass spectrum for 7-(2,3-dihydroxyphenyl)heptanoic acid (2TMS) (**CT7 acid**).