CHEMICAL CHARACTERISATION OF THE ORGANIC MATERIALS USED FOR THE CONSTRUCTION OF THE TEMPLES AND BUILDINGS IN MỸ SƠN (VIETNAM) FROM THE CHAMPA KINGDOM

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Introduction

The archaeological site of Mỹ Sơn hosts a series of abandoned and partially ruined temples related to the Champa civilisation (4th-14th centuries AD). The site is situated in the Quảng Nam Province (Duy Xuyên district) in Central Vietnam and represents a unique example of interchange between Indian and South-Asian cultures. The temples show the typical Hindu architecture and were dedicated to the worship of the god Shiva. In 1997 the Mỹ Sơn Conservation Project started with the aim to safeguard the archaeological site and in 1999 UNESCO recognised Mỹ Sơn as a world heritage site. In the framework of this project, research focused on understanding the engineering principles and technological skills used for the buildings, the original materials used and their compatibility with modern materials to be chosen for conservation. The Mỹ Sơn temples are classified into ten principal groups, each consisting of multiple temples. For purposes of identification, letters were assigned to the groups: A, A', B, C, D, E, F, G, H, K. Within each group, numbers were assigned to the edifices (Hardy *et al.* 2009). Figure 1 shows a schematic map of the site and an image of one of the temples. Most of the temples were made of red bricks, generally fired at low temperatures (less than 850°C). However, the mortar/binder used to join the bricks has almost completely degraded and is mostly not visible today, although remains of the mortar are found as greyish/dark residues (Table 1). Nevertheless, the towers and the temples have remained stable, creating one of the most fascinating "mysteries" of the site. Among the hypotheses around the materials used as binding agents in the mortar of the bricks, a vegetable resin probably from

Figure 1. A schematic map of the Mỹ Sơn site and an image of one of the temples.

an autochthonous plant of the Dipterocarpaceae family (*Dipterocarpus alatus*) seemed to be the most reasonable option. This kind of resin is still used today and it is called dầu rái. Its main modern uses are wood lacquering, water-proofing of boats and traditional medicine. Some chemical analyses, mainly FTIR, seemed to support the hypothesis that dầu rái resin was used in the bricks' mortar, most likely to increase the adhesive properties of the material (Hardy *et al.* 2009). Dark residues are sometimes present on the surface of the bricks as well, suggesting that a coating material was applied.

Natural resins are produced by many varieties of plants. From a chemical point of view, plant resins are a complex mixture of mono-, sesqui-, di- and triterpenes, which have respectively 10, 15, 20, and 30 carbon atoms per molecule. The mono- and sesquiterpenes are both present in most resins. The di- and triterpenes are rarely found together in the same resin, thus terpenic resins are divided into diterpenoid and triterpenoid resins (Scalarone and Chiantore 2009). The mono- and sesquiterpenoids are rarely found in ancient samples because of their high volatility, except when they have been conserved in very particular conditions (Hamm *et al.* 2004). On the other hand, diterpenes and triterpenes are useful to identify the resins and sometimes assess their botanical origin (Evershed *et al.* 1997). Plant resins and resinous materials played a prominent role in ancient times, as their intrinsic properties meant that they were used as adhesives, hydro-repellents, coating and sealing agents (Charters *et al.* 1993; Pollard and Heron 1996; Ribechini *et al.* 2009; Robinson *et al.* 1987; Serpico and White 2000).

The Dipterocarpaceae family consists of 17 genera and nearly 500 species. All Dipterocarpaceae species produce the so-called triterpenoid resin "dammar" that has been traded for centuries and therefore had, and has nowadays, an important economic role in Southeast Asian countries (Burger *et al.* 2011; Burger *et al.* 2009; Lampert *et al.* 2002). Because of the chemical complexity of resinous materials especially in archaeological findings, analytical procedures for chemical analysis are normally based on chromatographic and mass spectrometric techniques (GC-MS, DE-MS, Py-GC-MS) (Burger *et al.* 2009; Evershed 2008; Lampert *et al.* 2003; Lluveras *et al.* 2009; Ribechini 2009).

In this work, microscopic observations of cross sections and GC-MS analyses were performed to investigate some samples of the organic materials used in the construction of the temples and buildings in the archaeological site of Mỹ Sơn (Vietnam). In particular, attention was focused on the possible presence of organic residues in the mortar used to join the bricks and in the plaster used to caulk them. The results of this investigation are presented in this article.

Materials and methods

Samples

A sample of dầu rái resin, supposed to be produced from *Dipterocarpus alatus* and used in conservation practices of the temples, was used as reference material and prepared as fresh resin produced locally from the plant.

Three fragments of mortar (samples G, G1 and G1a), four fragments of plaster (samples G1b, A1, A1a and E7) and a whole brick were collected from various Mỹ Son temples and samples taken from these were analysed for possible organic residues. The fragments were *ca.* 2 cm in length. The dimensions of the brick were *ca.* 25 cm length, *ca.* 10 cm width and *ca.* 8 cm height (Table 1). The samples are named with the same identification letters that are assigned to the Temple groups, thus corresponding to the building they were taken from (A, E and G). Table 1 contains the sample descriptions. All of the samples showed some greyish/dark residues on the surfaces.

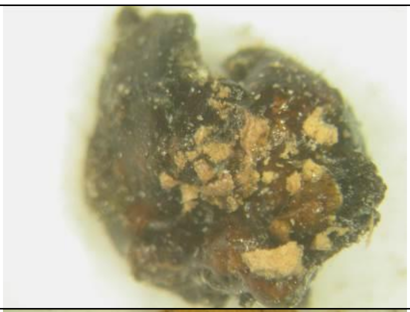
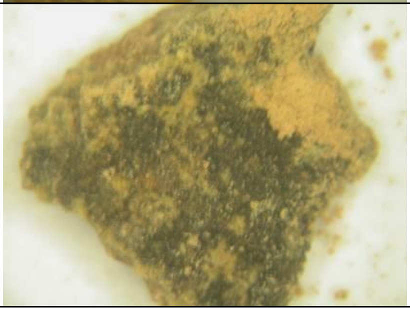
Microscopic investigations

Cross sections were prepared by embedding fragments of samples A1, A1a, G1a, G1b and E7 in an epoxy resin. The polished cross sections were observed using an Olympus System Metallurgical Microscope BX51M coupled with an Olympus Reflected Fluorescence System U-RFL-T.

Analytical GC-MS procedure and instrumentation

From all samples, *ca.* 2 mg of the superficial layers (dark or greyish areas) were sampled and subjected to an analytical procedure for the analysis of lipids, waxes and resinous materials by GC-MS (Lluveras *et al.* 2009). Samples were subjected to saponification by adding 400 µL KOH/MeOH (10% w/w) and 600 µL H_2O and putting them in a water bath at 60°C for 3 h. Neutral organic components were extracted with n-hexane (3 × 200 µL) and, after acidification with trifluoroacetic acid, the acidic organic components were extracted from the residual solution with diethyl ether (3 × 200 µL). The extracts were combined and an aliquot for each sample was derivatised with N,O-Bis(trimethyl)-silyl-trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS), using isooctane as a solvent. 2µl were analysed by GC-MS using hexadecane and tridecanoic acid as internal standards.

The analyses were performed using a gas chromatograph 6890N GC System (Agilent Technologies, Palo Alto, CA, USA) coupled on-line with a 5975 Mass Selective Detector (Agilent Technologies, Palo Alto, CA, USA) single quadrupole mass spectrometer equipped with PTV injector (split/splitless mode, 280°C). The MS transfer line temperature was 280°C; the MS ion source temperature was kept at 230°C and the MS quadrupole temperature was 150°C. For the gas chromatographic separation, a HP-5MS fused silica capillary column (5% diphenyl/95% dimethyl-polysiloxane, 30 m x 0.25 mm i.d., 0.25 mm film thickness (J&W Scientific, Agilent Technologies, Palo Alto, CA)) with a deactivated silica precolumn (2 m x 0.32 mm i.d. (J&W Scientific Agilent Technologies, Palo Alto, CA)) was used. The carrier gas was used in the constant flow mode (He, purity 99.995%) at 1.2 mL/min. The chromatographic oven was programmed as follows: initial temperature 80°C, isothermal for 2 min; 10°C/min up to 200°C, and

Sample name	**Brief description**	**Image**
R	*Ca.* 5 g of fresh natural resin used for restoration (dầu rái resin from *Dipterocarpus alatus*)	
G	Sample taken on 22.01.2011 from the G Group: it is from the mortar between two bricks	
G1	Sample taken on 21.04.2011 from the G Group: it is from the mortar of G1 *cella*	
G1a	Sample taken on 21.04.2011 from the G Group: it is from the mortar of the entrance of G1 *cella*	
G1b	Sample taken in June 2013 from the G group: it is the plaster of G1 *cella*	
A1	Sample taken on 21.04.2011 from the A1 *cella*: it is the plaster on the bricks	

A1a	Sample taken on 22.04.2011 from the A1 architectural stone block: plaster	
E7	Sample taken in June 2013: plaster	
Brick	Whole brick dated back to 12th century. A sample was taken from the surface, corresponding to the plaster.	

Table 1. List of the samples analysed.

isothermal for 3 min; 10°C/min up to 280°C, and isothermal for 30 min.

Results

Microscopy

The making of the cross sections was sometimes difficult, as the bricks and mortar had porous and fragile structures. Figure 2 shows some images obtained from sample G1a, corresponding to a mortar sample. Some very faint fluorescence was observed under the UV light at the edge of the sample, but the material mostly appeared relatively homogeneous.

Figure 3 shows some images at different magnifications obtained from the cross section of sample A1, corresponding to a plaster sample. In this case, multiple layers were applied on the brick.

The exact number is difficult to ascertain from these images, but at least three layers were visible on the left hand side of the cross section. Under UV illumination, the middle layer produced an intense yellow fluorescence, which was a clear indication of the presence of organic material. Nevertheless, natural resins usually produce a yellow-greenish fluorescence, thus the results suggested that some other organic material was likely to be present.

Figure 4 shows some images obtained for sample G1b. This sample also had multiple layers and at least three were noticed. The whitish top layer on the surface revealed a greenish fluorescence when exposed to UV light. Another slightly fluorescent layer seemed to be present under the surface, showing that the organic material might have been applied in more than one step.

Figure 5 shows the images of the cross section of sample E7. Although the quality of the cross section was not as good as the previous three, due to the porosity of the structure, also in this case a slightly fluorescent superficial layer was visible under UV light.

The remaining four polished samples did not show specific stratigraphy or fluorescence. However, these results suggested that the mortar and plaster were applied differently on the surface of the bricks, the former as a relatively homogeneous paste and the latter in layers.

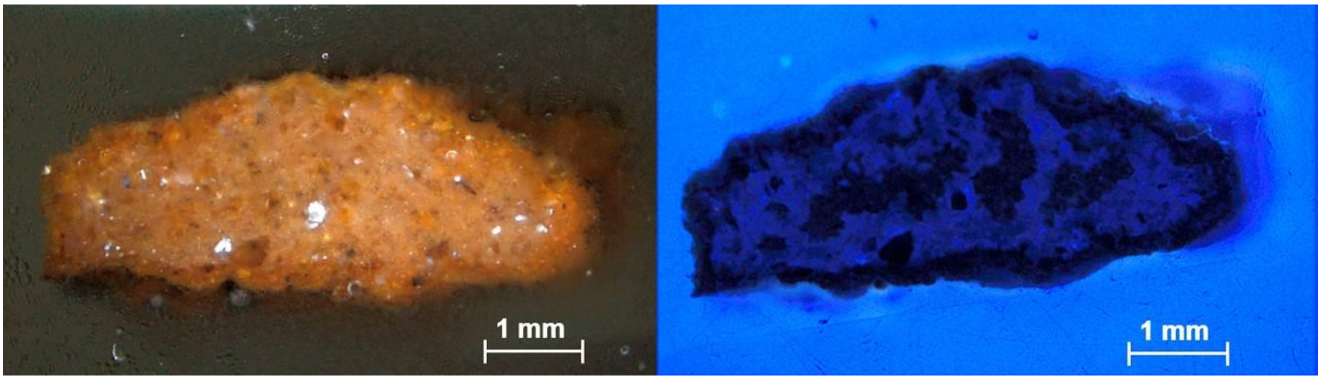


Figure 2. Cross section images of sample G1a. Left: dark field, magnification 5x; right: UV light showing very faint fluorescence, magnification x5.

GC-MS analysis

GC-MS analysis of the fresh resin sample used as a reference material showed a chromatographic profile typical of a dammar-like triterpenoid resin (Figure 6). The freshness of the resin was evident as sesquiterpenes were present with high relative abundances at low retention times. Triterpenes with dammarane, ursane and oleanane structures were identified at high retention times. The occurrence of dammarane, oleanane and ursane derivatives is a typical feature of dammar. In addition, the absence of monoterpenoids is described in the literature as a feature common to all Asian Dipterocarpaceae resins, thus in agreement with the provenance of the material (Burger *et al.* 2011).

The samples from group G (samples G, G1, G1a and G1b) were three mortars and one plaster sample. Figure 7 reports the chromatogram obtained for sample G, corresponding to a mortar sample. The results showed a high abundance of carboxylic acids, in particular monocarboxylic acids, dicarboxylic acids and hydroxycarboxylic acids. Triterpenoid compounds were also present in the chromatogram, in particular dammaradienone, 20, 24-epoxy-25-

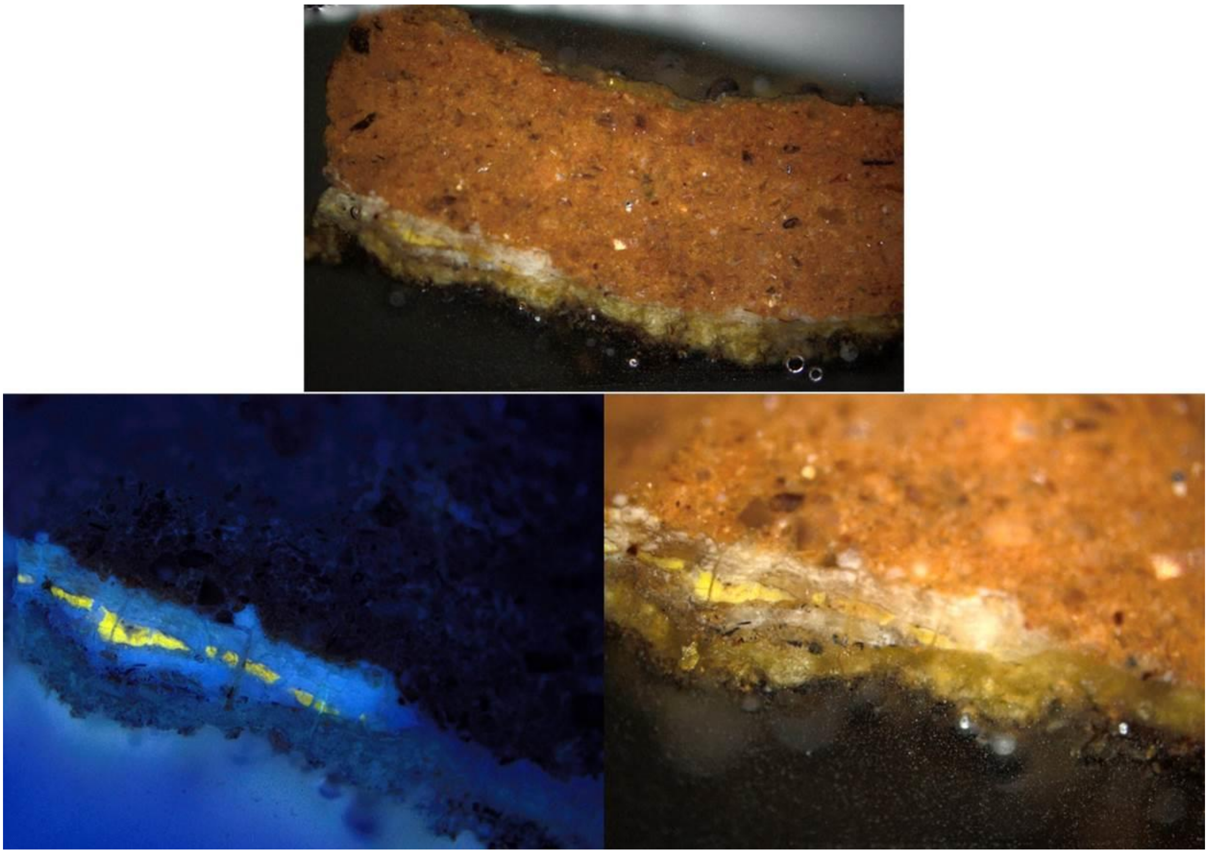


Figure 3. Cross section images of sample A1. At the top: dark field, magnification x5; bottom left: UV light showing yellow fluorescence of organic material in the surface layer, magnification x10; bottom right: same area, dark field, magnification x10.

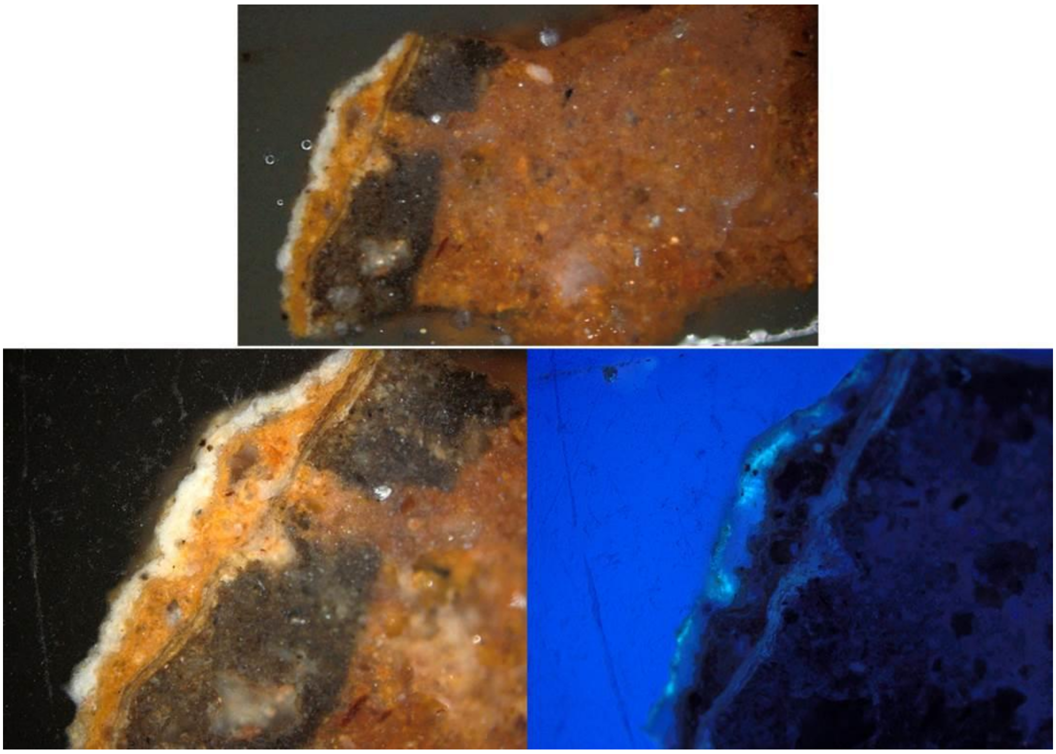


Figure 4. Cross section images of sample G1b. At the top: dark field, magnification x5; bottom right: UV light showing light-coloured fluorescence in the surface layer, magnification x10; bottom right: dark field, magnification x10.

hydroxy-dammaren-3-one, hydroxydammarenone and two unidentified triterpenoid compounds, which were also present in the reference resin sample.

Therefore, the results showed that a triterpenoid resin was present in this sample. It was not possible to ascertain if the resin was exactly the same as the reference, due to the degradation phenomena that has occurred, which resulted in a different profile of triterpenes. Nevertheless, the resinous material was definitely obtained from a tree belonging to the Dipterocarpaceae family. Furthermore, the results also highlighted that a lipid fraction was predominant in the sample. In addition to palmitic and stearic acid, aliphatic long-chain α,ω-dicarboxylic acids and ω-hydroxycarboxylic acids with dominant chain-lengths 16, 18, and 22 carbon atoms were present with significant relative abundance. These compounds are typically present in the bark of trees (Orsini *et al.* 2015; Ribechini *et al.* 2015), thus indicating that the resin was not the only organic material added to the mortar mixture. Identical results were obtained for sample G1a, also corresponding to a mortar sample

Sample G1, on the contrary, showed some differences in the chromatographic profile. Figure 8 shows the chromatographic profile of sample G1. Despite some qualitative differences in the relative abundances of the compounds, a similar lipid fraction was present in this sample compared to sample G and G1a, but no other compounds were identified. Therefore, the triterpenoid resin was not present in this sample. Very similar results were obtained for sample G1b, which corresponded to a plaster sample.

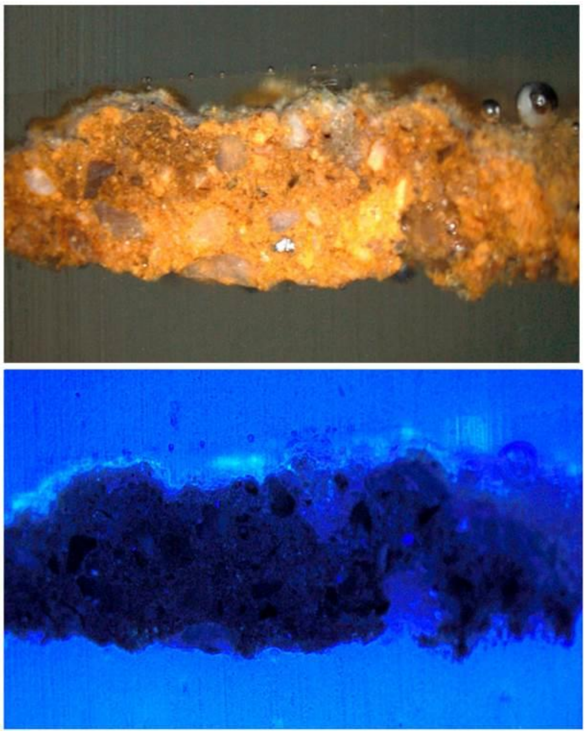


Figure 5. Cross section images for sample E7. Top: dark field, magnification x5; bottom: UV light showing faint fluorescence in the surface layer, magnification x5.

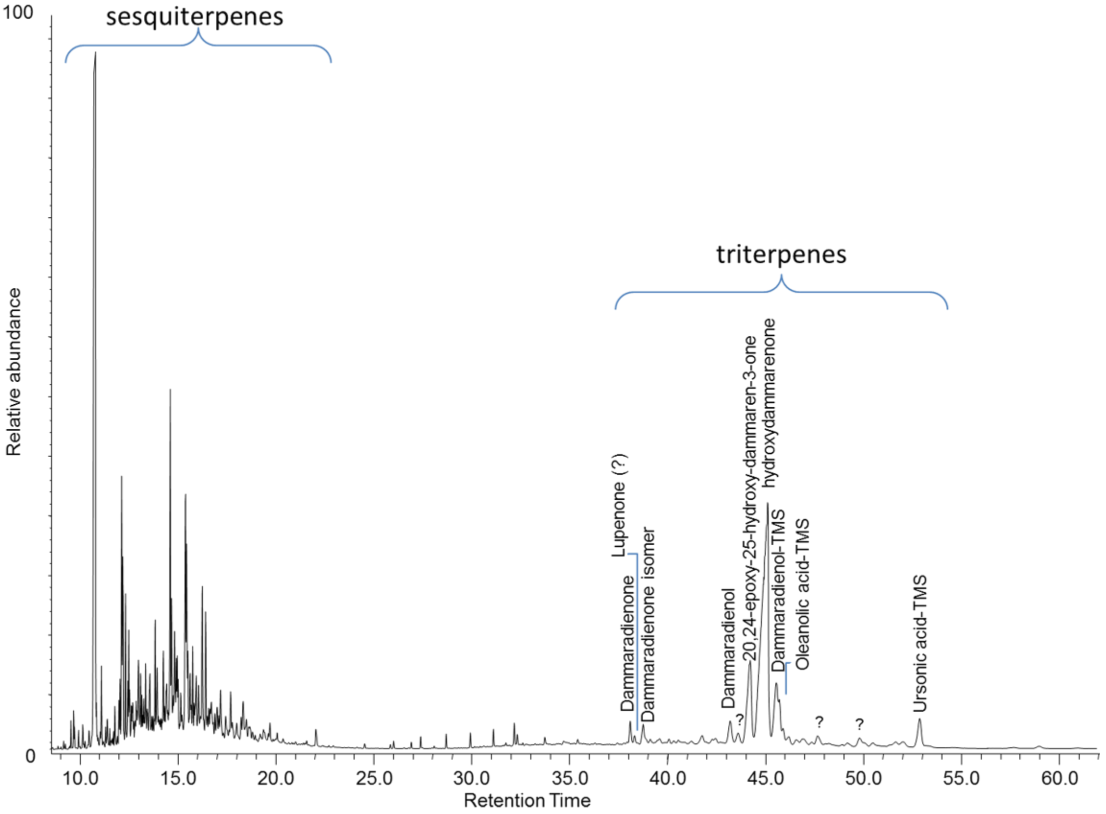


Figure 6. Total ion chromatogram (TIC) obtained by GC/MS analysis of the fresh resin showing characteristic compounds of Dipterocarpus alatus resin.

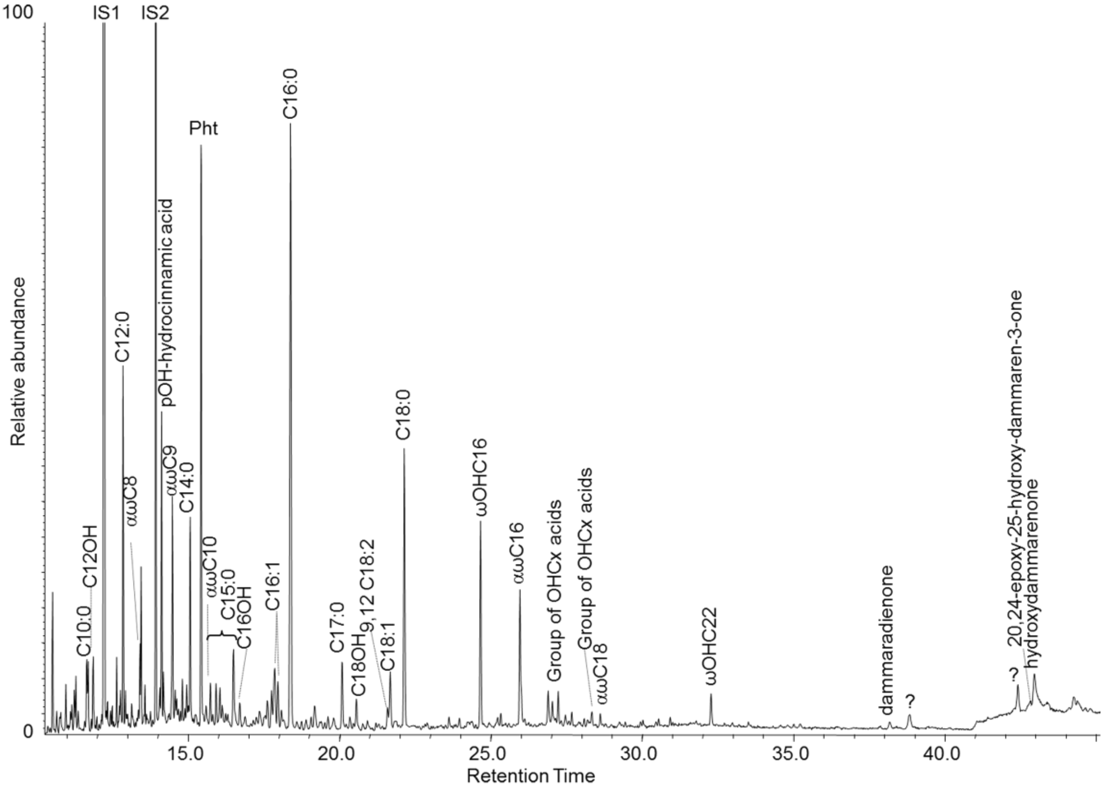


Figure 7. TIC obtained by GC-MS analysis of sample G (Internal standards: IS_1 = hexadecane, IS_2 = tridecanoic acid; Pht = phthalate present as contamination). The acidic and alcoholic moieties are present as TMS-derivatives. Cx:y: linear monocarboxylic acid with x carbon atoms and y unsaturations; CxOH: linear alcohol with x carbon atoms; aωCx: dicarboxylic acid with x carbon atoms; ωOHCx: ω-hydroxyacid with x carbon atoms.

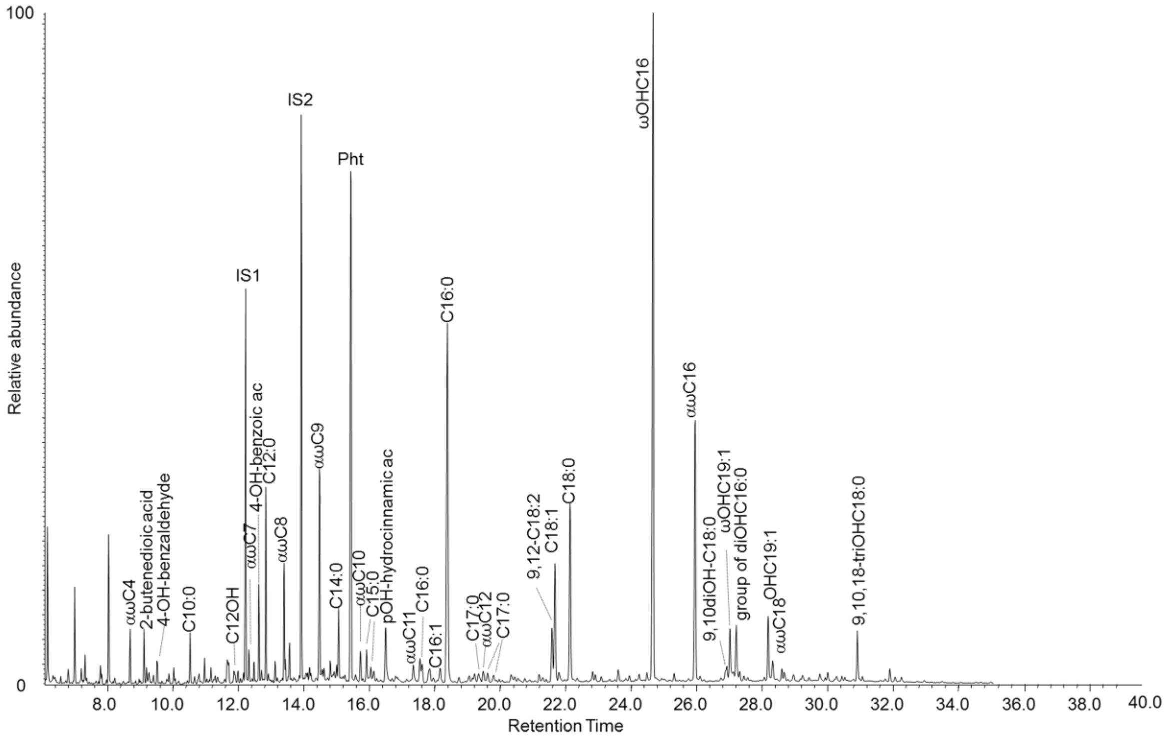


Figure 8. TIC obtained by GC-MS analysis of sample G1 (Internal standards: IS_1 = hexadecane, IS_2 = tridecanoic acid; Pht = phthalate present as contamination). The absence of triterpenoid compounds is highlighted. For the legend, see Figure 7.

The samples from the A group (samples A1 and A1a) were both taken from plasters. They showed a similar composition to each other and the chromatographic profiles revealed high abundances of saturated and unsaturated monocarboxylic acids, dicarboxylic acids and hydroxycarboxylic acids, as shown in Figure 9. With respect to the samples from the G group, a higher abundance of unsaturated and isomerised compounds was highlighted. The formation of unsaturations and isomerisation are sometimes indications of thermal treatments, thus the tree bark might have been exposed to high temperatures in these cases. Also for these samples, no traces of resin were found.

A general lower amount of organic material was detected in sample E7 (plaster) compared to the other samples, but the composition of the lipid fraction was again very similar (Figure 10). Triterpenes derived from the resin were not found. On the other hand, 4-hydroxybenzoic acid, 4-hydroxyhydrocinnamic acid, cinnamic acid, vanillic acid and ferulic acid were all detected with significant relative abundance. These aromatic compounds were generally detected in all samples and are commonly found in tree extracts. Therefore, they confirmed again the vegetable origin of the material. Nevertheless, monocarboxylic acids with odd-number carbon atoms were generally detected in all the samples. In particular, pentadecanoic, heptadecanoic and nonadecanoic acids were present, as well as their ramified and unsaturated forms in some cases. These compounds are generally ascribed to the presence of fats of animal origin (Evershed *et al.* 2002), but they can easily be the result of contamination from the burial site or the environment. In addition, minor amounts of moieties with odd-number carbon atoms have been identified in suberin from various species of plants (Ribechini *et al.* 2015). Therefore, the results concerning the possible presence of some animal-derived material in the samples are not conclusive

Finally, a further confirmation of the results was also obtained for the material found on the brick surface (Figure 11), which showed again a similar composition to the other plaster samples.

Conclusions

The microscopic observations and GC-MS analyses performed on the samples from Mỹ Sơn temples confirmed that organic materials were used in the formulation of the plaster and mortar of the bricks during the Champa kingdom.

The observation of the polished cross sections highlighted that the plaster was usually applied in thin layers, whereas the mortar was composed of a relatively homogeneous mixture of materials. The UV light produced fluorescence in most samples, ranging from bright yellow colours to faint green

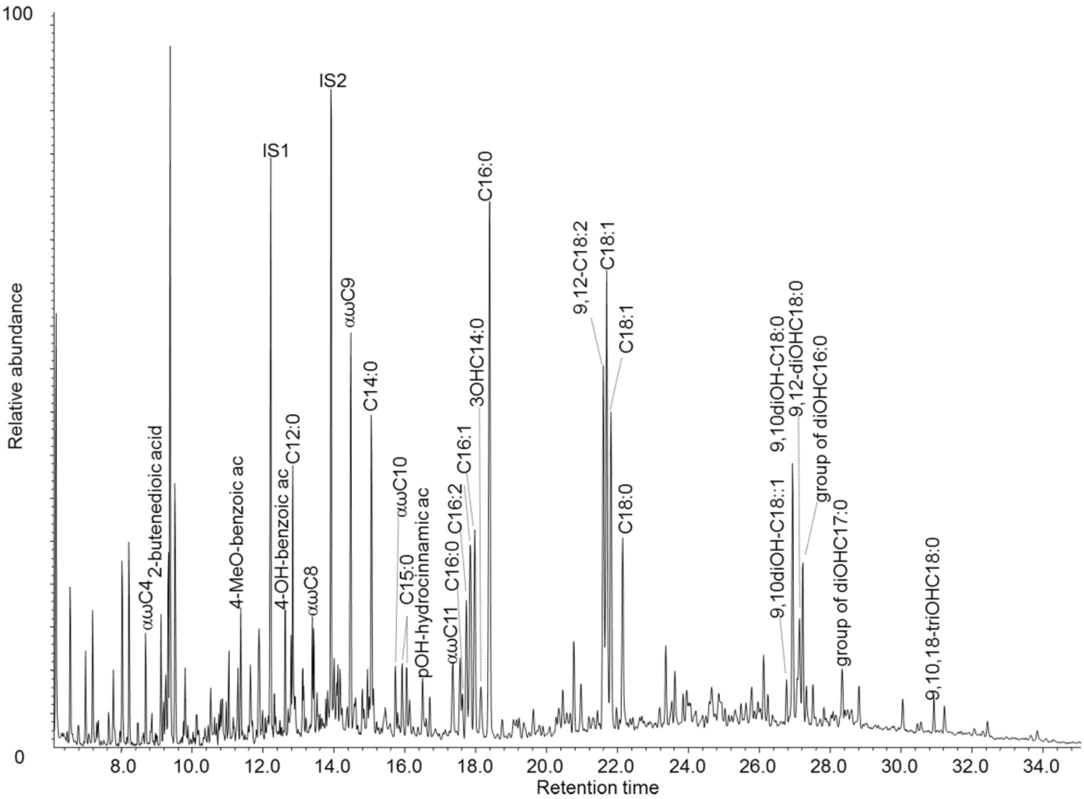


Figure 9. TIC obtained by GC-MS analysis of sample A1 (Internal standards: IS_1 = hexadecane, IS_2 = tridecanoic acid; Pht = phthalate present as contamination). In addition to the compounds detected for all the samples, a high abundance of unsaturated and isomeric compounds is highlighted. For the legend, see Figure 7.

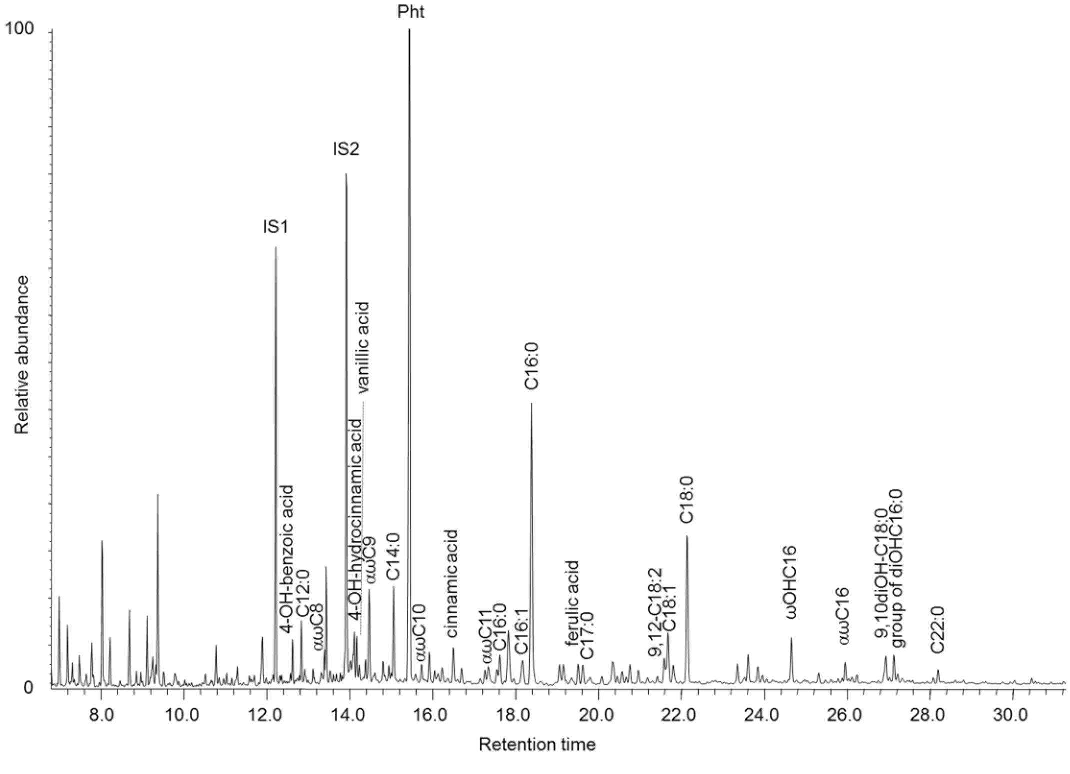


Figure 10. TIC obtained by GC-MS analysis of sample E7 (Internal standards: IS_1 = hexadecane, IS_2 = tridecanoic acid; Pht = phthalate present as contamination). A general low abundance of organic material is noticed. For the legend, see Figure 7.

shadows, indicating the presence of organic materials.

Some indications for the use of a dammar-like resin produced from a tree belonging to the Dipterocarpaceae family were obtained for two out of the three mortar samples (G and G1a). The comparison between the results obtained for the archaeological samples and those obtained for a fresh local resin produced from the plant *Dipterocarpus Alatus* did not allow us to ascertain the botanical source of the resin, mainly because of the degradation of the archaeological resin. Nevertheless, the same triterpenoid compounds, such as dammaradienone, 20,24-epoxy-25-hydroxy-dammaren-3-one and hydroxydammarenone, were detected in both the archaeological and the fresh resin, suggesting that the origin might be the same or closely related.

More interestingly, none of the plaster samples showed the presence of the resin, but all of them revealed a lipid fraction consisting of long-chain aliphatic monocarboxylic acids (saturated and unsaturated), dicarboxylic acids, and highly oxidised carboxylic acids, such as hydroxy- and dihydroxycarboxylic acids. Although some differences in the relative abundances, the distribution and nature of these molecules indicated the presence of suberin, which is a major component of tree bark. The presence of isomeric and unsaturated carboxylic acids with high relative abundances suggested that the material might have been submitted to vigorous thermal treatments (pyrolysis regime). In addition to the lipid fraction, most samples also contained aromatic acids such as ferulic, hydroxybenzoic, vanillic, cinnamic, caffeic acids, thus confirming the hypothesis of a plant origin for the organic material.

Considering the different functions of a plaster and a mortar – coating and adhesive material, respectively – it may be hypothesised that a tree bark-derived material was used in both the construction elements, whereas the resin was added only to the mortar, probably to increase its adhesive properties. The addition of thermally-processed bark might have increased the waterproofing and isolating properties of the plaster, in a similar way to the use of pitch on wood surfaces. The quantitative differences observed among the various samples might be due both to different production parameters (temperature and duration of the thermal treatments) used to process the bark, and to different plant sources possibly employed. Moreover, the possibility that several plants could be used at the same time should not be excluded. There is also evidence that resin extraction from some trees in South-East Asia is performed by firing the trunks of the trees. A similar process might

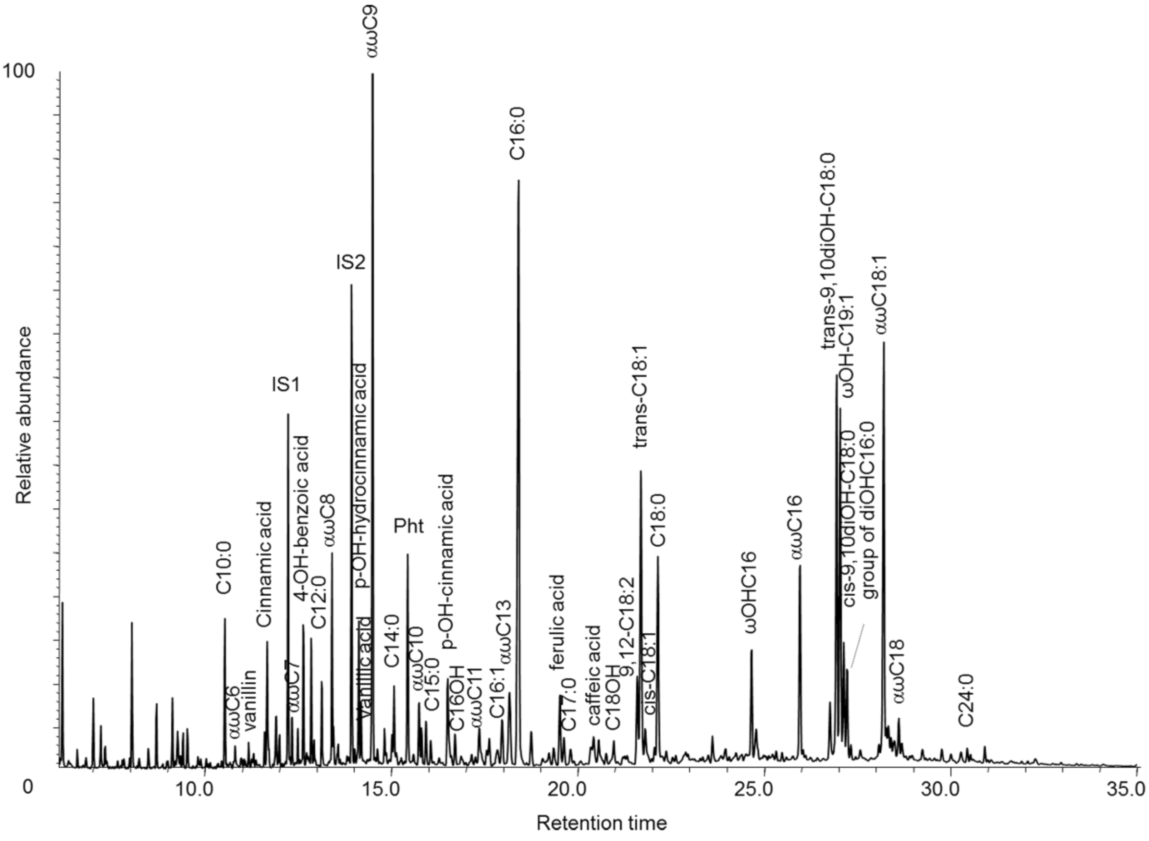


Figure 11. TIC obtained by GC-MS analysis of the surface of the brick (Internal standards: IS_1 = hexadecane, IS_2 = tridecanoic acid; Pht = phthalate present as contamination). For the legend, see Figure 7.

have been used by Champa people to produce a sticky material to apply on the bricks used in the construction of the Mỹ Sơn temples.

At the moment it is not possible to state the botanical source from which the "glue" was obtained and the transformations deliberately induced by man before the use of the material, but these results shed light on the actual composition of the organic adhesive, which was not just made of resin but in many cases of a composite mixture of ingredients including tree bark compounds in many cases.

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