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The degradation of Burmese lacquer (thitsi) as observed in samples from two cultural artefacts

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ABSTRACT

Two cultural artefacts produced in Southeast Asia were analysed by Py-GC–MS with *in situ* silylation using HMDS. The page of a Burmese book (Kammavaca manuscript) from the early 20th century and a Cambodian wooden gilded sculpture representing a Buddha from the 16th century were investigated for diagnostic purposes.

Burmese lacquer (thitsi) and a drying oil were identified. Benzoic acid and alkylphenylketones were detected, indicating that oxidation at the benzylic position of thitsi monomers occurred. Alkylphenylketones resulted from the pyrolysis of the polymeric network, and we believe they were the result of the oxidising environment generated by the drying oil during the curing. In the case of the Cambodian Buddha, the detection of alkylphenylketones was crucial for identifying the lacquer, as the marker pyrolysis products of thitsi were present at the trace level. Alkylphenylcarboxylic acids, alkyl-oxo-phenylcarboxylic acids and alkylphenols with a carboxylic group on the side chain were also detected. These compounds were identified as trimethylsilyl derivatives on the basis of their mass spectra interpretation, and were present as free acids or esters. Although their molecular structure might be ascribed to the oxidation of the original components of thitsi, the length of the alkyl chains did not make the association straightforward. Therefore, we propose that the oxidative cleavage of the aromatic ring may be responsible for the formation of these compounds.

1. Introduction

Urushi (qi-lacquer in Chinese), Vietnamese lacquer and Burmese lacquer (sometimes referred to as thitsi) are the three natural lacquers used in East and Southeast Asia since ancient times to decorate and protect objects. They are produced from the sap of three lacquer trees belonging to the Anacardiaceae family growing in different regions of East and Southeast Asia: *Rhus vernicifera* (China, Japan and Korea), *Rhus succedanea* (Vietnam and Taiwan), and *Melanorrhoea (Gluta) usitata* (Laos, Burma, Thailand and Cambodia). The main component of the sap extracted from the trees is a mixture of alkyl-substituted catechols: urushiol from *R. vernicifera*; laccol from *R. succedanea* and thitsiol from *M. usitata* [1,2]. The main alkyl-substituents for urushiol and laccol are C15 and C17 alkenyl chains at the 3-position on the aromatic ring, respectively. In addition to these compounds, thitsiol contains catechol derivatives with an ω-phenylalkyl chain at the 3- and 4-positions with ten and twelve carbon atoms [3,4]. These features make the three lacquers chemically distinguishable.

The hardening of these lacquers occurs through a similar polymerisation process, leading 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 [5–7], and is catalysed by the enzyme laccase. All three coupling bonds are present in the polymeric network of urushi [8], nuclear–nuclear (C—C) and nuclear-side chain (C—C) bonds are formed in the Vietnamese lacquer [7], and only nuclear–nuclear (C—C) couplings have been observed in the polymerisation of ω-(phenylalkyl)catechols, the major components of thitsi [9]. It has recently been shown that when a drying oil is mixed with urushi, curing follows different pathways, and the lacquer components undergo autoxidative chain reactions as well [10].

The complexity of the resulting polymers and the chemical stability of the bonds involved in the polymeric network make

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pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC–MS) the most suitable analytical approach for the molecular analysis of Asian lacquers, their characterisation, and identification in samples of unknown composition [11–16]. The high number of polar phenolic moieties deriving from pyrolysis, as well as the presence of carboxylic moieties generated by ageing [17], make the use of a derivatising agent highly recommended. Tetramethylammonium hydroxide (TMAH) [18–23] and hexamethyldisilazane (HMDS) [17,24] have proven their suitability as derivatising agents for the analysis of oriental lacquers. Some recent works without derivatising agents have been performed, mainly using 100% methylsilicone as stationary phase of the capillary column [11,12,25]. Nevertheless, the amount of sample used (*ca.* 0.5 mg) is from five to ten times higher than the amount needed using HMDS [17,24], which represents a major disadvantage when dealing with the analysis of samples from cultural objects. The identification of the three lacquers by Py-GC–MS is based on the detection of specific molecular markers, *i.e.* 3-pentadec(en)ylcatechol for urushi, 3-heptadec(en)ylcatechol for Vietnamese lacquer, 3-(10-phenyldecyl)catechol and 3-(12-phenyldodecyl)catechol for thitsi, and on the recognition of pyrolytic profiles of alkylphenols, alkylcatechols, alkylbenzenes and aliphatic hydrocarbons [17,24].

Asian lacquers are known to be extremely resistant, inert to acids, alkalis and alcohols, stable up to 300 °C, and insoluble in most common solvents [1,4,5]. These are the main reasons why very ancient lacquered objects have survived for millennia [11,26,27]. Consequently, no particular attention has been paid to the study of degradation pathways undergone by the lacquers, although oxidation products have been recently detected in some archaeological samples containing urushi [17,28]. Recently, Schilling *et al.* [22] have listed a high number of marker molecules of Asian lacquers, some of which have been ascribed to the photo-oxidation of the lacquers' original constituents.

This work was undertaken to identify the materials used to decorate two historical cultural objects from Southeast Asia using Py-GC–MS with *in situ* silylation (HMDS), but it ended up giving new insights into the molecular composition of aged thitsi. Hypotheses for the chemical changes occurred in the lacquers were proposed, thus contributing to the development of knowledge in this field of research.

2. Materials and methods

2.1. Samples

The samples analysed were collected from two artistic/historic objects from Southeast Asia: a Burmese book (Kammavaca manuscript) from early 20th century and a gilded Buddha from Cambodia and dating back to the 16th century.

The Kammavaca manuscript is a selection of texts providing rules of conduct for monks. The pages have a foundation of cloth stiffened with many coats of lacquers. The surface of the page shows a red and gold decoration (*shwe zawa* technique) and some dark letters in Pali language are applied on the surface [29]. An image of the surface of the book page is shown in Fig. 1a. A sample from the black letters was analysed by Py(HMDS)-GC–MS.

The wooden gilded sculpture representing a Buddha showed remains of gilded decorations over a red background. The samples were received in small flakes, which naturally fell off the surface of the sculpture. The gold leaf was applied directly on the red base layer, which was analysed by both GC–MS and Py(HMDS)-GC–MS. An image of a sample is shown in Fig. 1b.

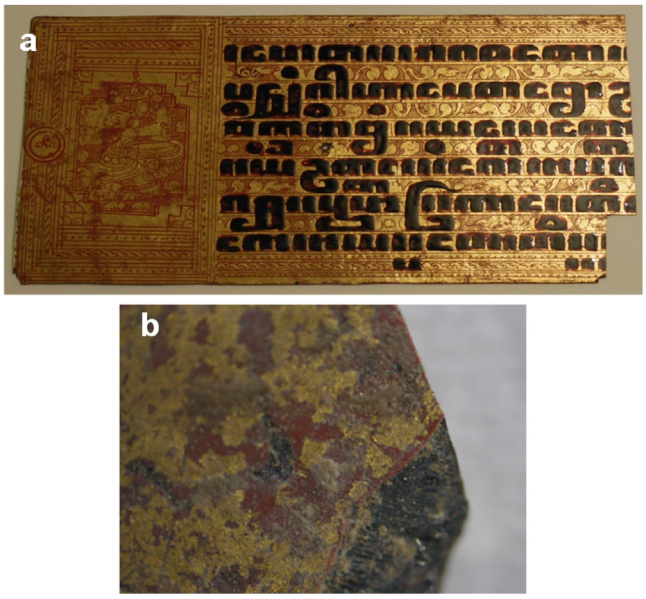

Fig. 1. Image of the cover page of the Burmese Kammavaca manuscript (a) and of a sample from the Cambodian Buddha wooden sculpture (b).

2.2. 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 silylating agent for the *in situ* derivatisation of pyrolysis products. The instrumentation consists of a micro-furnace Multi-Shot Pyrolyzer EGA/Py-3030D (Frontier Lab) coupled to a gas chromatograph 6890 Agilent Technologies (USA) equipped with an HP-5MS fused silica capillary column (stationary phase 5% diphenyl and 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 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 280 °C. The split/splitless injector was used with a 1:20 split ratio and kept at 280 °C. *Ca.* 100 μg of sample were admixed with 3 μL HMDS into a stainless steel cup and inserted into the micro-furnace. Chromatographic conditions were as follows: initial temperature 36 °C, 10 min isothermal; 10 °C min^{-1} up to 280 °C, 2 min isothermal; 20 °C min^{-1} up to 310 °C, 50 min isothermal. Carrier gas: He (purity 99.995%), constant flow 1.0 mL min^{-1}.

2.3. GC–MS

Given the small size of the samples analysed, GC–MS was only used for the characterisation of the sample collected from the Cambodian Buddha. An analytical procedure described in the literature was applied [30]. This methodology enables the identification of glycerolipids, natural waxes, terpenoid resins, proteinaceous and polysaccharide materials from a single microsample (less than 1 mg), by obtaining three different fractions from the same sample, *i.e.* the aminoacid fraction, the resinous-lipid fraction and the polysaccharide fraction. These fractions undergo a derivatisation step to obtain trimethylsilyl derivatives of the original compounds before GC/MS analysis. The same GC–MS apparatus described for Py(HMDS)-GC–MS was used. The injector was used in splitless mode. The temperature programs and conditions for the three runs are described in [30].