



NMR spectroscopy and micro-analytical techniques for studying the constitutive materials and the state of conservation of an ancient Tapa barkcloth from Polynesia, is. Wallis

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NMR spectroscopy and micro-analytical techniques for studying the constitutive materials and the state of conservation of an ancient Tapa barkcloth from Polynesia, *is. Wallis*

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ABSTRACT

In this study a multi-analytical approach has been performed to characterise the constitutive materials of an ancient painted barkcloth or Tapa. Originating from Wallis Island, Polynesia, this cloth likely served utilitarian or ceremonial purposes and is part of the Felice Junck collection at the Pigorini, Muciv museum of Rome. During a recent conservation project, some micro-samples were taken from the support, brown and black painted areas and were investigated using the complementarity of SEM-EDX, FT-IR, Raman/SERS and solid-state ¹³C NMR and ¹H HR-MAS spectroscopy. The combination of these techniques allowed the chemical characterization of the constitutive materials, from distinguishing the lignin and cellulose content of the support to the use of organic materials including condensed tannins (catechin, anthocyanidins, alkaloids), phlobaphene and vegetal anthraquinone based *Morinda* genus dyes for the decorations. A primary focus was placed on an understanding of its state of conservation where data of alteration products collected, namely metal carboxylates and oxalates can serve to formulate apt restoration efforts for this specific artefact.

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Introduction

The historical manufacture of decorated barkcloth, called *Tapa* or *Kappa*, is based on ancient technologies and traditions typically developed in tropical island regions of the Pacific Ocean such as Tonga, Tahiti, Fiji and Hawaii. Barkcloth is made of fibrous materials from the inner bark of trees according to the available sources in the specific island of provenance namely, paper mulberry (*Broussonetia papyrifera*, BP), candlenut (*Aleurites moluccana*) breadfruit (*Artocarpus altilis*, AA), banyan (*Ficus prolixa*, FP) and mamaki (*Pipturus albidus*, PA) [1]. Pieces of bark were extracted and while wet, beaten with mallets intermixing the fibres. The mechanical action promotes the formation of strong paper-like sheets which are characterized by a network of fibres markedly more flattened, twisted

and directionless than that observable in paper and papyrus. Barkcloth sheets are folded and pressed several times and traditionally decorated with stamped or painted symmetric patterns using dyes from local plants, trees and earth pigments. The barkcloth production across the islands involved undoubtedly similar methods of manufacturing, however the decorative methods and designs of the individual islands permitted them to be distinguished for trade purposes. In the 19th century, the manufacture of barkcloth was eventually affected by the direct use of imported textiles and dyes, given to the growing trade with the West. Fortunately, the historical cloths held nowadays in museum collections were collected and conserved by early missionaries and explorers together with raw local materials and letters concerning their production providing a key insight to the traditional practices which could well have been lost.

In recent years, there have been a few analytical investigations on historical barkcloths such as those in collections from the Bishop Museum, Hawaii [2], The Hunterian and Centre for Tex-

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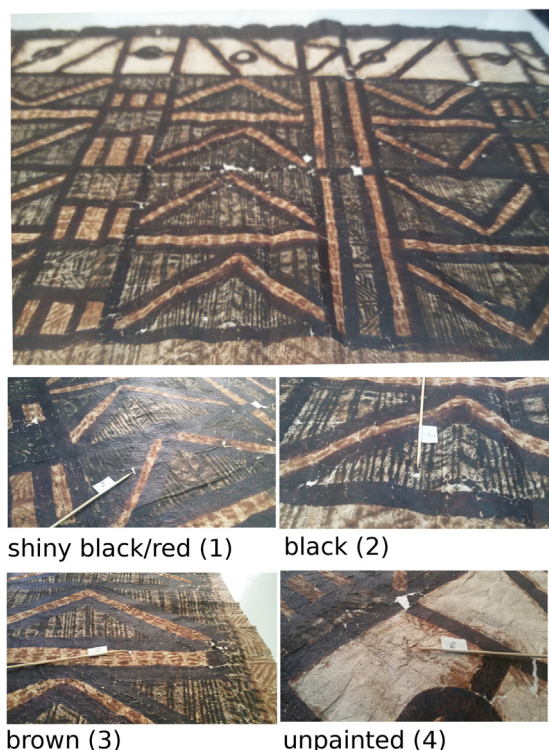


Fig. 1. Polynesian Tapa Barkcloth, Pignorini Museum.

tile Conservation and Technical Art History, University of Glasgow and Economic Botany Collection, London [3,4], on an archaeological barkcloth originating from the Gambier archipelago [5] and more recently from the British Museum and the National Gallery [6]. Therein, dedicated authors utilised spectroscopic (XRF, Raman, FTIR), microscopic (SEM and SEM-EDX), chromatographic (HPLC) and genetic sequencing techniques to provide a knowledge of the material bark sources, red, yellow and brown dyes and execution techniques synergic with surviving texts for a continuation and preservation of the traditional cultural practice.

In this work, a multi-analytical approach was carried out to analyse a historic barkcloth (Fig. 1) coming from Wallis island, one of the two island groups known as Uvéa together with Futuna and forming one French Overseas Territory. This barkcloth was acquired in 1927, exhibited at the Pignorini museum (Muciv, the Felice Junck collection, Rome), and it was investigated with a multi-analytical approach after a recent restoration work. Specifically, micro-samples from the support, brown and black decorative areas were examined by SEM-EDX, FT-IR, Raman/SERS and NMR spectroscopy to elucidate information regarding its actual state of conservation and to characterize the original materials.

Scanning electron microscopy (SEM) with EDX was used to observe the morphology of the barkcloth fibres and to analyse the metal elements content such as iron. In particular, iron could be a strong catalyst for the oxidation of cellulosic materials and its presence especially in brown and black area, is an important factor to be evaluated [7]. The use of vibrational spectroscopy, such as ATR-FTIR and surface-enhanced Raman spectroscopy, was focused towards understanding the presence of constituent fibres, natural dyes, binders and possibly products coming from degradation processes [8].

High-resolution NMR spectroscopy is a powerful technique to study complex materials both in solid and liquid state. In this frame, solid-state NMR spectroscopy was used to characterize cellulose and its degradation derivatives, and other organic compounds present in artworks. The ^{13}C CPMAS spectrum of the barkcloth

may be actually considered as the “fingerprint” of cellulose-based materials, allowing the recognition of the type of cellulose, the determination of the crystalline/amorphous ratio, the detection of the possible presence of hemicellulose, cellulose oligomers, and non-cellulosic compounds such as binders and dyes [9–11]. By NMR spectroscopy vegetable tannins extracts [12,13] and tanned leathers [14] were extensively studied, in these studies the ^{13}C CPMAS NMR spectral region between 70 ppm–165 ppm has been successfully analysed because it contains few signals from leather collagen but numerous signals from tannins. On the contrary, few studies have been reported to characterise vegetable tannins on paper and papyrus. In this study ^{13}C solid state NMR was used to characterise condensed tannins and anthraquinone on a cellulose-based material and to perform a comparison between the model samples and the Polynesian barkcloth. In addition, ^1H high-resolution magic angle spinning (HR-MAS) NMR spectroscopy was used to characterise the presence of low-molecular mass compounds that could be derived by degradation process of cellulose and other additives compounds present in the barkcloth. Recently, this technique is causing a lot of interest in medicine, biology, materials and food science because of its versatility, allowing the investigation of semi-solid micro samples without pre-treatment processes. In particular, the most important advantage of HRMAS instead of solid-state NMR technique is the possibility to obtain a well-resolved ^1H NMR spectra on very small samples [15,16]. Because of strong dipolar interactions the proton nuclei produce very large resonances and proton spectra cannot be used for a microscopic chemical characterization of solid samples [17]. On the contrary, by HR-MAS NMR spectroscopy, samples are analysed directly in contact with deuterated solvents or water in order to increase the local mobility and thereby reducing the magnitude of the strong dipolar interactions. Furthermore, MAS control permits to produce high-resolution NMR spectra even in dynamically averaged or susceptibility broadened heterogeneous systems. In cellulose-based materials, HR-MAS permits to analyse the low molecular components that show a greater mobility at the interface between water and the cellulose fibres, such as carboxylic acids, more complex dicarboxylic and hydroxy-carboxylic acids, and amino acids residues of additives used during the manufacturing [18]. Because these products can trigger further degradation processes, their characterization is important in order to develop novel and suitable ways of conservation.

Research aim

The main aim of the project was to investigate the unique prospective provided by solid state NMR spectroscopy to characterise natural dyes and other plant-based materials used in the manufacturing of ancient tropical barkcloths. A multi-analytical approach was carried out to analyse tannins and anthraquinone dyes applied on a Polynesian ancient barkcloth. A wide database of ^{13}C CPMAS NMR spectra was also collected by comparing different polyflavonoid extracts and hydroxyanthraquinones, and on specifically cellulose-base model samples. A further strength of this approach lies in combining the NMR methodologies (solid state NMR and HRMAS NMR) with ATR/FT-IR and Raman/SERS spectroscopies to provide for the characterization of dyes, binders and surface products of deterioration in order to assess its current state of conservation.

Materials and methods

The Polynesian Tapa barkcloth, analysed in this study, is dated back at early 1800 and is part of Felice Junck collection at the Pignorini Museum (Muciv) in Rome. The barkcloth was decorated with

black/red, black and brown areas. The black/red area was covered by transparent shiny layer Fig. 7 following the pattern decoration. Four micro-samples were collected from uniform colour areas of the barkcloth. Sample (1) was collected from the shiny black/red area; sample (2) was collected from a matte black area; samples (3) and (4) from a brown and an unpainted area respectively, see Fig. 1.

Four colorants model/samples made of *quebracho*, *mimosa*, *gambier* tannins and pure alizarin (Carlo Erba reagents), were prepared using woodpulp paper (WP) strips immersed in a solution of distilled water and colorant (6% w/w) mixed for 4 h at room temperature (25 °C). In the case of alizarin, the immersion and mixing were performed at 70 °C. The samples were then dried in an oven at 40 °C for three days.

SEM-EDX

Scanning Electron Microscopy images of the samples were recorded with a FEDSEM LEO Supra 55 VP microscope, combined with a Carl Zeiss GEMINI column, and an Oxford EDX (Energy Dispersive X-ray spectroscopy) analytical instrument with a Peltier cooler. The samples were not pre-treated or modified, and graphite tape between the sample and the support was just used. All the images were acquired at 5 and 15 keV, both in secondary electrons and in-lens mode.

NMR spectroscopy

^{13}C CPMAS NMR spectra were carried out on a Bruker Advance III spectrometer operating at the carbon frequency of 100 MHz on samples (1), and (4). Because of the low amount, samples (2) and (3) were not analysed. Samples, 1 mg, were packed into 4 mm zirconia rotors with an available volume reduced to 12 μl and sealed with Kel-F caps. The spin rate was 12 kHz. The contact time for the cross-polarization was 1.5 ms, the recycle delay was 3 s, and the ^1H $\pi/2$ pulse width was 3.5 μs . The cross-polarization was achieved applying the variable spin-lock sequence RAMP-CPMAS [19,20], the RAMP was applied on the ^1H channel, and during the contact time the amplitude of the RAMP was increased from 50 to 100% of the maximum value. Spectra were acquired with 1024 data points in time domain, zero-filled and Fourier transformed with a size of 4096 data points applying an exponential multiplication with a line broadening of 8 Hz.

High Resolution Magic Angle Spinning (HR-MAS) proton spectra were recorded using a Bruker AVIII 600 MHz NMR spectrometer, operated at proton frequency of 600.13 MHz. The spectrometer was equipped with a high-resolution magic angle spinning (HR-MAS) and triple-resonance 4-mm with built-in z-gradient probe head from Bruker Biospin, which included a ^2H lock channel. All measurements were carried out at 300 K. Samples (1) and (4) were held with D_2O in a zirconia rotor with a reduced volume of 12 μL , spinning at 7 kHz to increase the spectral resolution.

Micro FT-IR and attenuated total reflection (ATR-FTIR)

FTIR analyses were carried out with a JASCO FTIR 470-plus spectrophotometer. Measurements were performed in reflection mode.

The ATR analyses were performed employing a monolithic crystal diamond, fitted into a Nicolet iS50 FTIR spectrometer that has a mercuric cadmium telluride (MCT) detector. The scan used a resolution of 4 cm^{-1} over 64 scans. The interpretation of the ATR spectra was based on comparison with the internal spectral library in Thermo ScientificTM OMNICTM Spectra, software and published data [21,22].

Surface-enhanced Raman spectroscopy (SERS)

SERS spectra were recorded using a laboratory Jasco Ventuno spectrophotometer equipped with a confocal set-up and a CCD cooled to -50°C . Measurements were performed with an argon laser emitting at 785 nm over the range 150–1800 cm^{-1} with exposure times from 2 to 10 seconds and up to 10 accumulations. 20% and 50% objective lens were utilized with a power of max 5 mW with an overall spectral resolution of 4–8 cm^{-1} . Polystyrene was used for instrument calibration.

Colloidal SERS was carried out utilizing citrate-reduced colloids prepared according to a modified Lee and Meisel procedure [23]. The colloid showed an absorption maximum at 426 nm and FWHM of 110 nm, as measured with a Hewlett Packard 8453 photodiode array UV-vis spectrometer (following a 1:9 dilution with ultrapure water to observe maximum absorbance within the instrumental range). SERS measurements were carried out by adding a 10- μl drop of colloid aggregated with magnesium sulphate directly onto the Tapa samples, where spectra could be obtained after some minutes with laser excitation at 785 nm that remained constant in quality until the evaporation of the liquid.

Results and discussion

SEM-EDX

Painted samples (1), (2), and (3) were examined by SEM-EDX to study the structure of the support and the nature of pigments. The support morphology shows a paper-like dense weave with different layers of fibres indicates the manufacturing technique, Fig. 2a–c. As shown in Fig. 2d, a relative thick layer of painting covers the upper layers of the sample. Many different particles in the painting layer and the elemental analysis can be examined as reported in Table 1, showing further traceable elements namely, silicon, aluminium, iron and copper, materials which could also indicate the presence of inorganic substrates for the preparation of pigments by precipitation or adsorption of an organic dyestuff [24].

ATR-FTIR spectroscopy

The high spatial resolution afforded by ATR-FTIR has been exploited in the investigation of these samples. The cellulose matrix, with main characteristic bands of vibration described elsewhere [25], roughly dominates the spectrum collected from all the samples, where main features are distinctive in the overall trace observable in the unpainted sample (4) (Fig. 3). In the same spectrum, the presence of silicate materials is observed and the calcite CO_3^{2-} stretching at 873 cm^{-1} can be appreciated. The spectrum collected on shiny black sample (1), provides ulterior information regarding the use of a combination of proteinaceous and lipidic materials although whole egg may be suspected as containing both protein and lipid, given by the broad shoulder at 3065 cm^{-1} due to the N–H stretching component of the protein and the weak shoulder at 1744 cm^{-1} (C=O stretching) of lipidic materials [26]. The sharp C–H stretchings at 2800–3000 cm^{-1} are highly indicative of an egg together with the main amides I and II at $\sim 1640 \text{ cm}^{-1}$ and $\sim 1540 \text{ cm}^{-1}$. Historical data to this regard provides information of oil possibly used as a varnish/binder as reported by Bisulca et al. [2] where oil extracts from Kukui nuts were used in “oiled Tapa” to protect fibres from water damage. Ulteriorly annotations, collected in the B. P. Bishop Museum of Honolulu museum’s archive, can be read that beaten egg was applied by feather’s brush on barkcloth surface by the Polynesians’ who were the first to introduce this practice in the Hawaiian Islands [27]. Beyond such, the band at 1538 cm^{-1} , as well as at 1411 cm^{-1} , are also indicative of the formation of metal

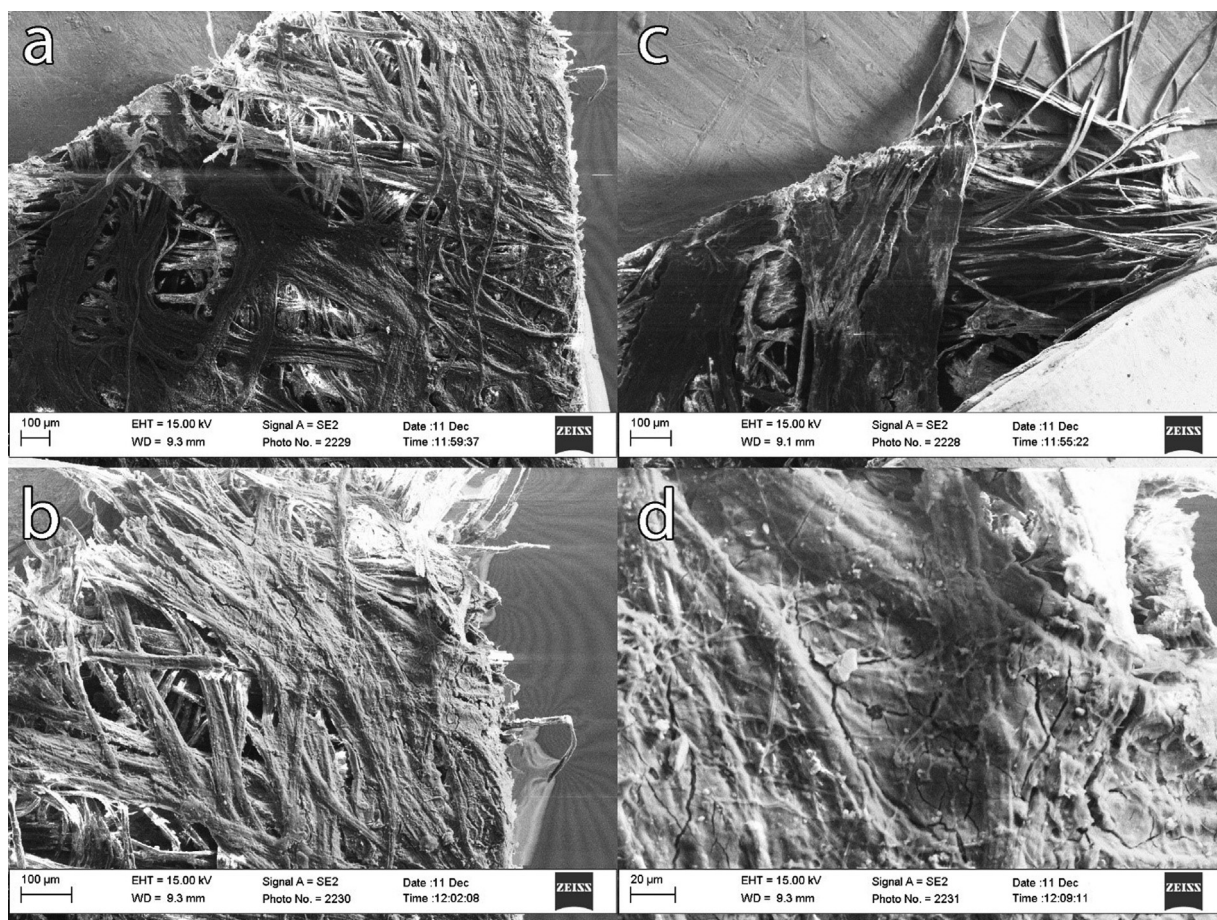


Fig. 2. Fibres structure of sample (2) (a, b) and (3) (c) using secondary electrons view by SEM-EDX. In the image (d) is possible to see the thick painted layer on the fibres of sample (2).

Table 1
Summarized results

Sample	Image/color	SEM/EDX	FTIR	Raman/SERS	NMR
1	Black + red	Main: C, Ca, O, Secondary: S, K, Na, Mg	Oxalates Cellulose Lipidic- material No lignin No hemicellulose	Black-Tannin (possible condensed), anthraquinone Red-Morinda citrifolia, phlobaphene Alkaloids?	Polycondensed Tannins (possible prorobinetidin) Cellulose, no lignin, no hemicellulose.
2	Black	Main: C, Ca, O, Secondary: Fe, Al, Si, Mg.	Cellulose No lignin No hemicellulose	Black-Tannin (possible condensed), anthraquinone, alkaloid	–
3	Brown	Main: C, Ca, O, Secondary: Cu, Al, Si, S	Cellulose No lignin No hemicellulose	Anthraquinone possible Morinda genus, alkaloid	–
4	Unpainted	–	Cellulose No lignin No hemicellulose		Cellulose, no lignin, no hemicellulose, carboxylic acids and di-carboxylic acid, pyruvic, hexanoic acid.

carboxylates (stearate/palmitate), attributed to the ν_{as} and ν_s modes of the COO^- . Literature in the Heritage science field [28,29] has highlighted that such a saponification process, can take place dur-

ing the aging of a lipidic constituent through the reaction of free fatty acids and available metal cations (possibly Ca, Na in this case as suggested by SEM-EDX) leading to the formation of metal carboxy-

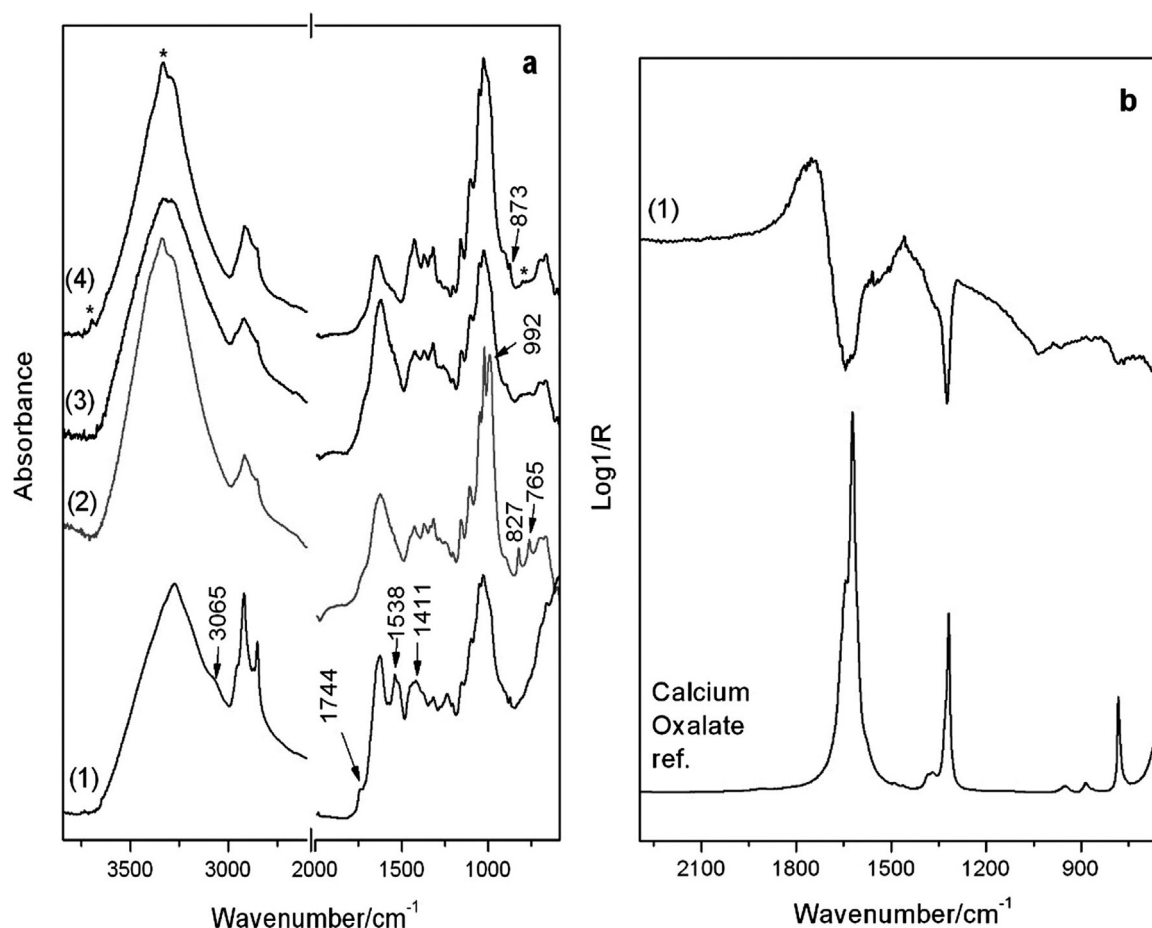


Fig. 3. a) ATR IR spectra of samples (1), (2), (3), (4) collected from painted and unpainted area of Polynesian barkcloth; b) b) Reflection mode spectrum obtained by micro-FTIR on crystallized particles in sample (1) with relative calcium oxalates monohydrate reference.

lates. The occurrence of metal soaps as products of degradation, is given to affect both the aesthetical and mechanical properties of an artefact and is of important current interest to scientists and conservators alike. The surface of sample (1) by external reflectance FTIR could also be investigated, where it was possible to further observe the presence of calcium oxalates crystals, a further common alteration product as given in Fig. 3b, in comparison with its reference. It has also been of interest, to investigate the presence of vegetable tannin materials considering their complex and heterogeneous polyphenolic nature. In sample (2), undeniably hampered by the matrix, the characteristic tannin fingerprint is barely distinguishable, although the bands at 992 cm^{-1} and those at 827 cm^{-1} and 765 cm^{-1} are observed possibly related to generic tannins [30]. These bands are not noticed in any other sample. In all samples, no bands due to lignin or hemicelluloses were observed (1730 cm^{-1} or 810 cm^{-1}). Usually, the intensity of these bands may decrease due to degradation by sunlight or UV rays. Furthermore, the treatment with alkali probably used in the manufacturing of Tapa in combination with the retting process, could cause the elimination of most of the lignin content [2].

SERS

All samples were firstly investigated by Raman spectroscopy leading to a high fluorescence output. Thus, the added sensitivity of colloidal SERS conditions were required, to simultaneously quench the fluorescence and amplify signals relating to lowly concentrated organic constituent. In this way, a small piece of sample was necessarily examined micro-destructively. Spectra collected

from the black samples (1) and (2), and brown sample (3) can be observed in Fig. 4a. Polyphenolic constituents dominate by observing the overall profile, that on a first glance are seemingly anthraquinone related, although many of the characteristic bands result particularly shifted. Given such, for black samples (1) and (2) the especially pronounced 1501 cm^{-1} band provides instead for spectral similarities to epicatechin/catechin and anthocyanidins materials. This together with the presence of a tentative $\nu(\text{C}=\text{C})$ aromatic mode at 1631 cm^{-1} , a shifted $\nu(\text{C}-\text{O})$ at 1587 cm^{-1} , the and a inter-ring $\nu(\text{C}-\text{C})$ which is sensitive to changes in delocalized π -electron density falling at a higher wavenumber $\sim 1360\text{ cm}^{-1}$ and the $\gamma(\text{CH})$ at 660 cm^{-1} , support this hypothesis, see Fig. 4ai-ii. This heterogeneity of materials could actually suggest the presence or indeed the co-presence of tannin-based materials therein [31–33]. Tannin polyphenolic metabolites may be classified loosely as hydrolysable (gallic/ellagic acid containing), condensed or complex tannins, although these have up until now been scarcely studied through SERS.

In these black samples, the presence of condensed tannins is possibly suspected as those containing catechol, proanthocyanidins, related to flavonoid dyes and having polymeric flavan-3-ol structures [34].

In brown sample (3), a more evident anthraquinone presence was observed see Fig. 4aiii, with the location of bands relatively characteristic suggesting at least a greater interaction of this main constituent with the silver particles. In comparison with standard anthraquinone references, a tentative identification of the genus *Morinda* was provided by comparing the main bands highlighted with those as reported in the recent literature [35].

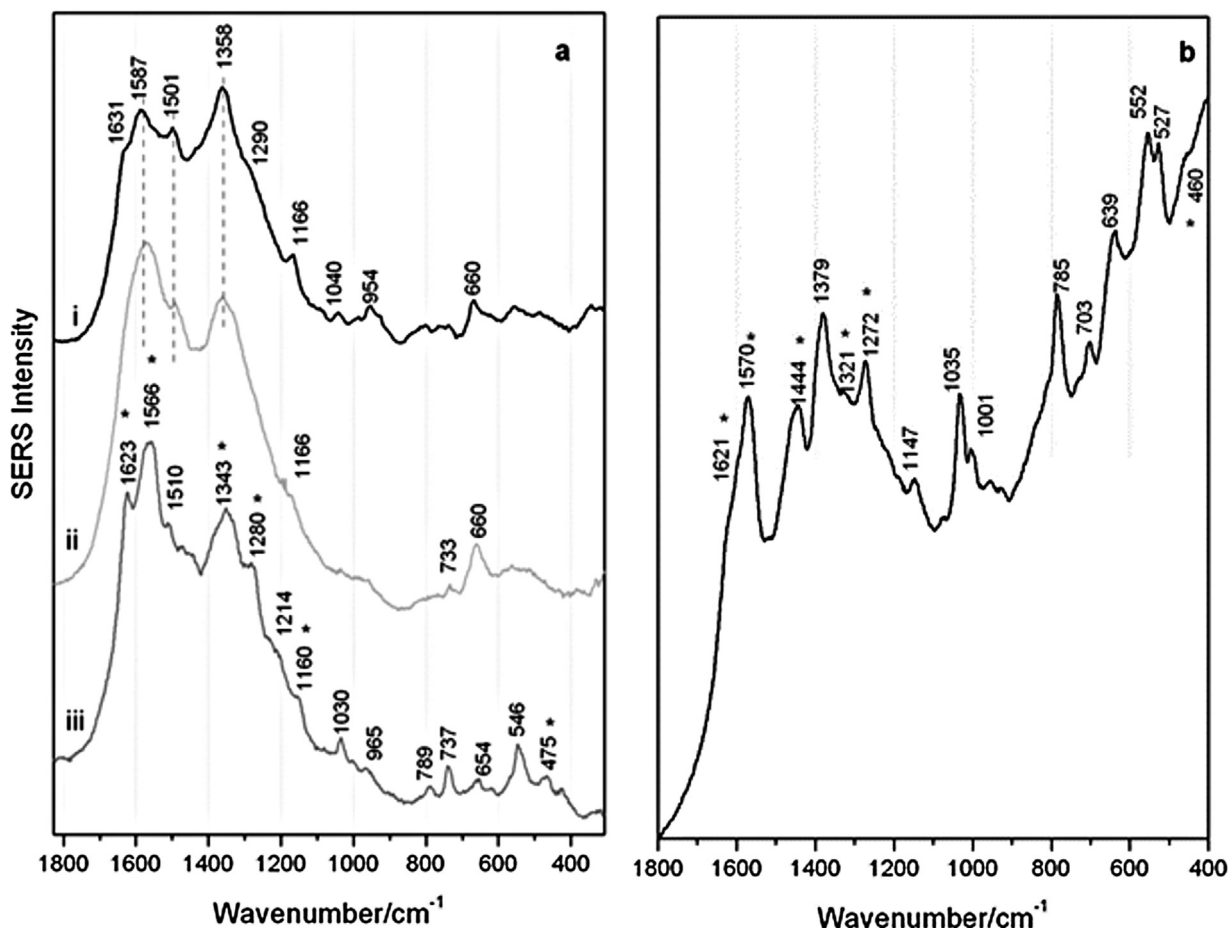


Fig. 4. SERS spectra of samples a) i. Black sample 1, ii. Black sample (2) and iii. Brown sample 3; b) i. red sample (1).

This dye has been characteristically associated with the manufacturing of barkcloth in the Pacific region [1–3]. However, to add a further challenge, is the significance of the band at $733\text{--}737\text{ cm}^{-1}$, observed in samples (2) and (3), which is characteristically found in the SERS of alkaloid materials and attributed to the out of plane CH deformations due to a suspected flat orientation of the component to the metal surface [36].

Interestingly, in sample (1) in correspondence to red particles, a further SER spectrum resulted which is given in Fig. 4b. Bands of *Morinda*, are more apparent- and correspond to those from *Morinda citrifolia* given by the further highly noticeable 1440 cm^{-1} amongst the others highlighted [30].

Furthermore, the pyridine nature of another component is evident due to the presence of marker bands at 1001 cm^{-1} and 1035 cm^{-1} . The 1379 cm^{-1} band too is rather intense suggesting a direct interaction with the silver surface.

It is here that we note from literature, that condensed tannins on treatment with acids or enzymes may be converted into red phlobaphenes, also known as “tanner red” indicating this man-made process utilized in tanning. The natural analogue used in dyeing, are tannins for example cinchotannic acid contained in cinchona barks, through oxidation rapidly yields a dark-coloured phlobaphene called cinchona red [37]. It is possible that here we have some type of natural phlobaphene, whose alkaloids have not yet been analysed through SERS, although we do seem to have some positive correspondence with cinchona alkaloids bands vibrationally analysed in aqueous solutions [38]. Given the wealth of materials located here and qualitatively assigned, further accurate investigations by chromatographic methods should be performed to confirm the aforementioned hypotheses.

NMR spectroscopy

Samples (1) and (4) were investigated by ^{13}C CPMAS NMR spectroscopy. The spectrum collected from the unpainted area (4), showed the characteristic bands of the cellulose structure, observed in Fig. 5. The resonance at 106.3 ppm is due to the anomeric carbon C1, resonances at 90.3 and 66.8 ppm are respectively from C4c and C6c in the crystalline domain, while resonances at 85.4 and 64.5 ppm are due to C4a and C6a in the amorphous domain. Because resonance C1 gives information about the presence of microcrystalline polymorphous forms I_α and I_β of the cellulose [39,40], this band can provide important information about the degree of crystallinity in a paper material. In Fig. 5, the spectral region of C1 ($102\text{--}110\text{ ppm}$) obtained in a pure cellulose sample was compared with that found in samples (1) and (4). In both samples the band resonances of the anomeric carbon C1 is poorly resolved indicating that the cellulose in the barkcloth shows a weak degree of crystallinity, caused by both the manufacture and the state of conservation.

The weak signal of resonances in the range of $110\text{--}220\text{ ppm}$ and $20\text{--}40\text{ ppm}$ are due to non-cellulosic components. No resonance at 53 ppm due to $-\text{OCH}_3$ of lignin was found. In both samples, resonances due to methyl groups of saturated aliphatic chains (35 ppm) and carbonyl groups (170 ppm) were found. These resonances are usually found in degraded papers due to photo-oxidation processes. In the sample (4) no resonances of phenolic groups of lignin ($120\text{--}160\text{ ppm}$) were found, indicating a complete loss of lignin content. The lack of lignin peaks might be caused by the retting method used to produce the barkcloth [2].

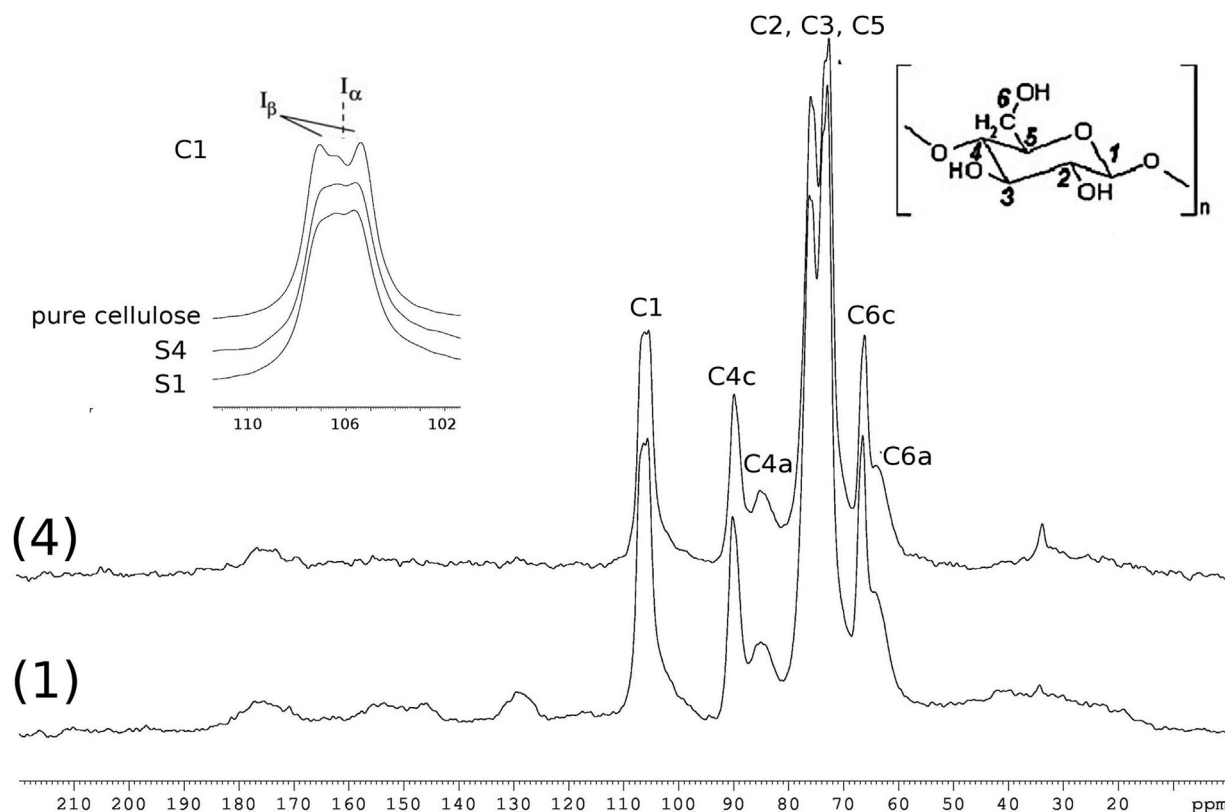


Fig. 5. ^{13}C CPMAS NMR spectra at 400 MHz along with resonance assignment, a) of sample (4) unpainted area and of sample (1), of black-red area. b) expanded spectra.

In sample (1), the same band of resonances of cellulose were found, in addition bands in the range of 130–150 ppm can be also observed, see Fig. 5b. Considering that sample (1) was collected in a painted area and the lignin content in this barkcloth seems to be negligible, the contribution of other aromatic compounds should be considered (i.e. colorants). It is well known that natural dyes have been used to decorate modern and ancient barkcloth, consequently, the presence of natural colorants have to be taken into account in particular of those able to give resonances in the region of 130–180 ppm. Two types of colorants were considered: vegetable tannins from three different sources such as *quebracho*, *mimosa* and *gambier* and pure alizarin as anthraquinone-based colorants. Polyflavonoids extract from *mimosa* and *quebracho* are mostly composed of robinetinidin (resorcinol A-ring; pyrogallol B-ring) and fisetinidin (resorcinol A-ring; catechol B-ring) repeating units linked each other C4–C6. *Gambier*, instead, is mostly composed of catechin (phloroglucinol A-ring; catechol B-ring) and gallo catechin (phloroglucinol A-ring, pyrogallol B-ring) C4–C8 linked units. Liquid state ^{13}C NMR spectra, collected on tannins extracts in solution, have showed characteristic fingerprints and chemical shift that can be used to distinguish between different sources, structural features and properties of phenolic polycondensates [14]. In this study, on the contrary, solid-state ^{13}C CP-MAS NMR spectroscopy was used for the first time to analyse tannins colorants in an ancient painted backcloth.

It is well known that the resonance bands between 70 ppm and 165 ppm are usually used to characterise the tannins in leather and differentiate between their sources. In the case of tannins on cellulose-based materials the diagnostic spectral region must be reduced between 110 ppm and 165 ppm, due to the overlapping between cellulose and tannins signals, see Fig. 6. *Quebracho*, *mimosa* and *gambier* in woodpulp paper (WP) model/samples showed the same fingerprinting – (bands at 154 ppm, 145 ppm, 132 ppm) with some differences in signal intensity, furthermore the C7 and C8a

carbon resonances at 154 ppm of the flavonoid A-ring can be observed in all samples, see Fig. 6a–c. The resonance at 117 ppm is indicative of C2', C5' and C6' carbon atoms of B-ring that is a diagnostic band for *quebracho* and *gambier*, whereas the diagnostic band of *mimosa* tannin centred at 105 ppm (B-ring C2' and C6') cannot be observed in these samples due to their overlap with the cellulose signals. ^{13}C NMR spectrum of alizarin showed a very different fingerprint compared to those found in vegetable tannins, see Fig. 6d. ^{13}C CPMAS NMR spectrum of pure alizarin (1,2 dihydroxy anthraquinone), shows two distinct region of resonances: one from carbon in the anthraquinone structure and the second one from carbon in hydroxylic groups, see Fig. 6d.

^{13}C CPMAS NMR spectrum acquired in alizarin on woodpulp paper (WP) shows the same characteristics bands found in pure alizarin, with some differences in chemical shift and intensity signal. The bands corresponding to C9 and C10 with a chemical shift of 189 ppm and 180 ppm shift to not well-defined peak at approximately 174 ppm (see the starred peak in Fig. 5d). As well known, alizarin act as di-anionic tridentate ligand, involving the quinoid 9-oxygen and its neighbored deprotonated 1,2-oxygen atoms in co-ordination with metals, that in case of cellulose-based materials, can be found in the wooden pulp (i.e. iron, manganese, copper, aluminium, calcium and magnesium [41,42]). The formation of alizarin complex and its effect on the chemical shift is quite difficult to be evaluated, however several studies have reported that the interaction between the anthraquinone and metal cations can influence the chemical shift of the nearby atoms moving it towards upfield region of the NMR spectrum [43].

In Fig. 6e, ^{13}C CPMAS NMR spectra of tannins and alizarin in model/samples with those obtained in Polynesian barkcloth were reported (spectral region 100–200 ppm). The presence of well-known diagnostic bands, centred at 154 ppm and 145 ppm, and the absence of a strong resonance at 117 ppm, suggests the presence of condensed polyflavonoid tannins mostly composed of prorobi-

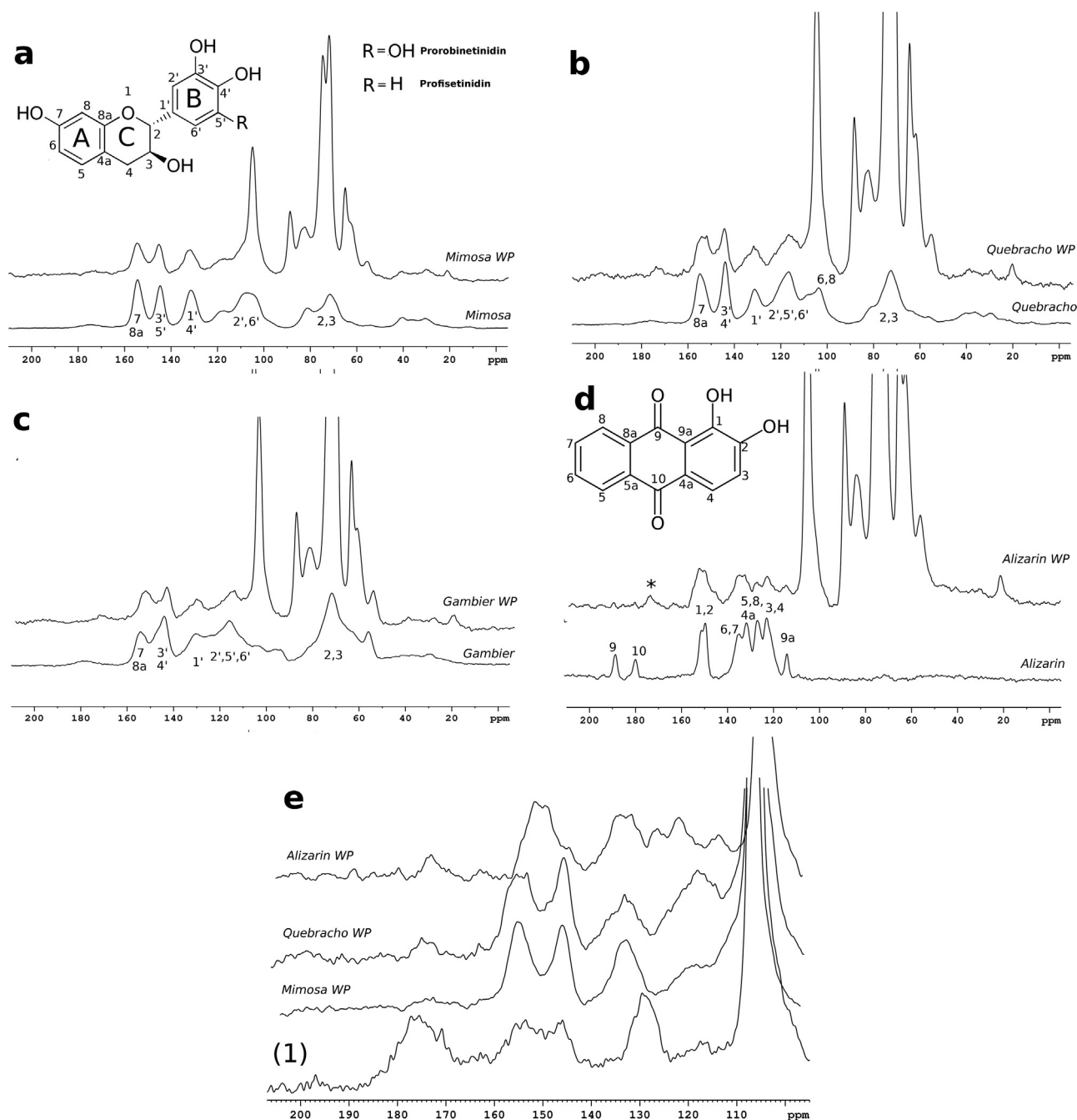


Fig. 6. ^{13}C CPMAS spectra of a) *Mimosa* in power and on woodpulp paper (WP); b) *Quebracho* in power and on woodpulp paper (WP); c) *Gambier* in power and on woodpulp paper (WP); d) Alizarin pure in power and on woodpulp paper (WP), e) Enlarged view of spectral region from 105 ppm to 205 ppm in *Mimosa* WP, *Quebracho* WP, and *Gambier* WP model samples and barkcloth sample (1).

netinidin. However, the band at 130 ppm shows a higher intensity and a shifting forwards upfield region of NMR spectrum than that found in tannins model/ samples. These results seem to imply the presence of a sort of altered tannin-based compound, see Fig. 6e. Unfortunately, as the amount of material collected from the artwork was inadequate to obtain well-resolved NMR spectra and to perform a semi-quantitative analysis, the presence of other colorants in minor concentration, that may cause a shifting of the band at 130 ppm, cannot be neglected.

To evaluate the state of conservation of Polynesian barkcloth, samples (1) and (4) were also analysed by ^1H HR-MAS NMR spectroscopy in order to characterise low molecular mass degradation products of cellulose, see Fig. 7.

^1H HRMAS spectra show the characteristic resonances of compounds arising from the hydrolytic and oxidative reactions of cellulose. In sample (1), it can be observed the presence of sharp peaks of pyruvic acid (resonances band centred at 2.4 ppm) and hexanoic acid and other carboxylic acids of lower molecular mass that can also occur with similar resonances at about 0.86, 1.30, and 1.54 ppm and 2.16 ppm. In the spectral region between 3 and 4 ppm, the resonance bands of cellobiose are well evident. The fact that the bands of carboxylic acids are sharper and more intense than those found in a young cellulose [17] is due to the higher sensitivity of ^1H HR-MAS NMR to amorphous region in comparison to the crystalline region of cellulose. Furthermore, more sharp and stronger intense peaks were observed in sample (1) as compared

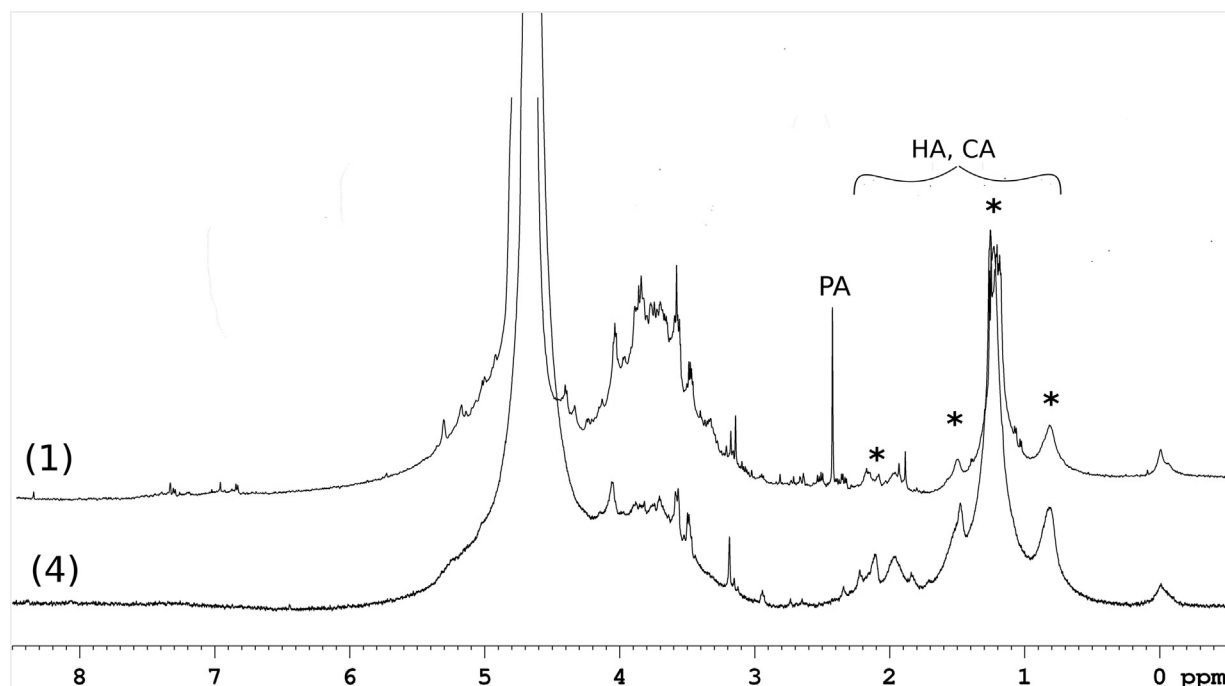


Fig. 7. ^1H HR-MAS NMR spectra of samples (1) and (4), in D_2O . (HDO resonance at 4.7 ppm) Labelling: pyruvic acid (PA); hexanoic acid (HA) and carboxylic acids (CA).

to sample (4), indicating that the painted area showed a higher degree of degradation. In this sample, the large resonance centred at 1.99 ppm was reduced to sharp peaks but less intense, this could be explained by the consumption of cellulose fibres of amorphous region, depolymerization of cellulose and the formation of carboxylic and dicarboxylic acids. These results are in accordance with the findings reported in Ref. [17].

Discussion and conclusions

The Polynesian barkcloth (Wallis Island), at the Pigorini Museum, is characterized by a geometric decoration coloured in black-red and brown. In these areas, the results showed the presence of organic colorants, summarized in Table 1. The vibrational spectroscopic examination has led to the qualitative identifications of bark material-based tannins, evidencing also to the presence of alkaloids in the samples. In addition, FT-IR data suggested the presence of a lipidic material, possibly an oil, or egg, that might be applied as varnish to make some black/red area shinier than other area of the artwork.

The various coloured plant extracts, used for dyeing and painting barkcloths, come from barks, roots, fruits and leaves. Tannins-based dyes mixed to coloured earths, and different plant-colorant extracts were the most used materials in the objects from Fiji Islands, Tonga and Samoa. Furthermore, the use of noni, *Morinda citrifolia*, was found in red areas of the barkcloth together with phlobaphene probably coming from the alteration of tannin compounds. The noni (*Morinda citrifolia*) is a small tree better known for its super-food fruits; the aerial bark and root of noni was used in several Polynesian islands groups to produce yellow and red pigments [44]. These dyes were mixed with iron and clay-based materials. The presence of poly-condensed tannins was also confirmed by NMR spectroscopy by comparing various type of tannins and anthraquinone to those collected from the artwork NMR analyses also showed that the barkcloth support is mostly constituted by cellulose, with a severe depletion of lignin and hemicellulose. The presence of calcium oxalates, characterized by FT-IR analysis, might originate either from raw materials or from degradation

process. Oxalic acid is mainly formed as product of oxidative reaction of lignin and hemicellulose, whereas calcium oxalate crystals can be also readily found in the inner bark and in the sapwood of trees [45,46]. Furthermore, the related presence of metal carboxylates and oxalates might be due to the saponification of the fatty chains possibly coming from lipidic compounds used as varnish/binder. However, several compounds could have been produced by chemical-mechanical processes of manufacturing and could result barely discernible from other compounds produced by aging processes [47,48]. However, HR-MAS NMR examination has led to identify degradation products coming from the amorphous region of cellulose, such as hexanoic acid, pyruvic and dicarboxylic acids, suggesting that photo-oxidation and hydrolytic mechanisms occurred.

These findings enabled to improve the knowledge of the Tapa constitutive materials, and the manufacturing of backcloths made in Polynesia islands, and could be useful for further investigation performed on similar artworks. Finally, for the first time, a set of solid-state NMR spectra of dyes applied on cellulose-based materials were collected and analysed, these results could be useful for further researches aimed at the analysis to other types of artworks by NMR spectroscopy.

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References

- [1] V. Daniels, The characteristics of modern and old barkcloth (tapa), *The Conservator* 29 (1) (2005) 95–104.
- [2] C. Bisulca, L. Schattenburg-Raymond, K. du Preez, Hawaiian Barkcloth from the Bishop Museum Collections: A Characterization of Materials and Techniques, *Mater Res Soc Symp Proc* 1656 © (2014), <http://dx.doi.org/10.1557/opl.2014.811>.
- [3] T.H. Flowers, M.J. Smith, J. Brunton, Colouring of Pacific barkcloths: Identification of the brown, red and yellow colourants used in the

- decoration of historic Pacific barkcloths, *J Heritage Sci* 7.2 (2019), <http://dx.doi.org/10.1186/s40494-018-0243-9>.
- [4] M.J. Smith, A.S. Holmes-Smith, F. Lennard, Development of non-destructive methodology using ATR-FTIR with PCA to differentiate between historical Pacific barkcloth, *J Cult Herit* 39 (2019) 32–41, <http://dx.doi.org/10.1016/j.culher.2019.03.006>, in press.
 - [5] A. Seelenfreund, M. Sepúlveda, F. Petchey, B.P. Ahumada, C. Payacan, S. Gutierrez, J. Carcamo, O. Kardailsky, X. Moncada, A.M. Rojas, M. Moraga, E. Matisoo-Smith, D. Seelenfreund, Characterization of an archaeological decorated bark cloth from Agakauitai Island, Gambier archipelago, French Polynesia, *J Archaeol Sci* 76 (2016) 56–69.
 - [6] D. Tamburini, C.R. Cartwright, M. Melchiorre Di Crescenzo, G. Rayner, Scientific characterisation of the dyes, pigments, fibres and wood used in the production of barkcloth from Pacific islands, *Archeol Anthropol Sci* 11 (2019) 3121–3141.
 - [7] V. Daniels, Factors affecting the deterioration of the cellulosic fibres in black-dyed New Zealand flax (*Phormium tenax*), *Stud Conserv* 44 (1999) 77–85.
 - [8] F. Pozzi, M. Leona, Surface-enhanced Raman spectroscopy in art and archaeology, *J Raman Spectrosc* 47 (2016) 67–77.
 - [9] D. Capitani, A. Segre, M. Pentimalli, M. Bicchieri, P.F. Minafò, Ancient deteriorated paper: Washing and restoring processes as studied by ¹³C CP-MAS NMR spectroscopy, *Quinio* 2 (2000) 37–43.
 - [10] K. Castro, E. Princi, N. Proietti, M. Manso, D. Capitani, S. Vicini, J.M. Madariaga, M.L. De Carvalho, Assessment of the weathering effects on cellulose based materials through a multianalytical approach, *Nucl Instrum Methods Phys Res B* 269 (2011) 1401–1410.
 - [11] H. Kono, S. Yunoki, T. Shikano, M. Fujiwara, T. Erata, M. Takai, CP/MAS ¹³C NMR Study of Cellulose and Cellulose Derivatives. 1. Complete Assignment of the CP/MAS ¹³C NMR Spectrum of the Native Cellulose, *J Am Chem Soc* 124 (2002) 7506–7511.
 - [12] A. Pizzi, A. Stephanou, A comparative ¹³C NMR study of polyflavonoid tannin extracts for phenolic polycondensates, *J Appl Polym Sci* 50 (1993) 2105–2113.
 - [13] S.J. Hill, C.D. McIntosh, W.J. Grigsby, Esterification of Condensed Tannins and Their Impact on the Properties of Poly(Lactic Acid), *J Wood Chem Technol* 23 (2003) 179–195.
 - [14] F.H. Romer, A.P. Underwood, N.D. Senekal, S.L. Bonnet, M.J. Duer, D.G. Reid, J.H. van der Westhuizen, Tannin Fingerprinting in Vegetable Tanned Leather by Solid State NMR Spectroscopy and Comparison with Leathers Tanned by Other Processes, *Molecules* 16 (2011) 1240–1252.
 - [15] T.M. Alam, J.E. Jenkins, HR-MAS NMR Spectroscopy in Material Science, in: *Advanced Aspect of Spectroscopy*, IntechOpen, Rijeka, Croatia, 2012, pp. 279–306.
 - [16] S. Viel, F. Ziarelli, G. Pagès, C. Carrara, S. Caldarelli, Pulsed field gradient magic angle spinning NMR self-diffusion measurements in liquids, *J Magn Reson* 190 (2008) 113–123.
 - [17] D. Topgard, O. Soderman, Diffusion of Water Absorbed in Cellulose Fibers Studied with ¹H-NMR, *Lagmuir* 17 (2001) 26.
 - [18] C. Corsaro, D. Mallamace, J. Łojewska, F. Mallamace, L. Pietronero, M. Missori, Molecular degradation of ancient documents revealed by ¹H HR-MAS NMR spectroscopy, *Sci Report* 3 (2013) 2896.
 - [19] G. Metz, X. Wu, S.O. Smith, Ramped-Amplitude Cross Polarization in Magic-Angle-Spinning NMR, *J Magn Reson A* 110 (2) (1994) 219–227.
 - [20] R.L. Cook, C.H. Langford, R. Yamdagni, C.M. Preston, A Modified Cross-Polarization Magic Angle Spinning ¹³C NMR Procedure for the Study of Humic Materials, *Anal Chem* 68 (22) (1996) 3979–3986.
 - [21] P. Calvini, A. Gorassini, FTIR: Deconvolution spectra of paper documents, *Restaurator* 23 (1) (2002) 48–66, ISSN 0034-5806.
 - [22] L. Monico, F. Rosi, C. Miliani, A. Daveri, B.G. Brunetti, Non-invasive identification of metal-oxalate complexes on polychrome artwork surfaces by reflection mid-infrared spectroscopy, *Spectrochim Acta A* 116 (2013) 270–280.
 - [23] P.C. Lee, D. Meisel, Adsorption and surface-enhanced Raman of dyes on silver and gold sols, *J Phys Chem* 86 (1982) 3391–3395.
 - [24] C. Clementi, B. Doherty, P.L. Gentili, C. Miliani, A. Romani, B.G. Brunetti, A. Sgamellotti, Vibrational and electronic properties of painting lakes, *Appl Phys A* 92 (2008) 25–33.
 - [25] P. Garside, P. Wyeth, Identification of Cellulosic Fibres by FTIR Spectroscopy - Thread and Single Fibre Analysis by Attenuated Total Reflectance, *Stud Conserv* 48 (2003) 269–275.
 - [26] L. Nodari, P. Ricciardi, Non-invasive identification of paint binders in illuminated manuscripts by ER-FTIR spectroscopy: A systematic study of the influence of different pigments on the binders' characteristic spectral features, *Herit Sci* 7 (2019) 7.
 - [27] P.M. Vitousek, L.L. Loope, C.P. Stone, Introduced species in Hawaii. biological effects and opportunities for ecological research, *Trends Ecol Evol (Amst.)* 2 (1987) 224.
 - [28] F. Gabrieli, F. Rosi, A. Vichi, L. Cartechini, L. Pensabene Buemi, S.G. Kazarian, C. Miliani, Revealing the Nature and Distribution of Metal Carboxylates in Jackson Pollock's *Alchemy* (1947) by Micro-Attenuated Total Reflection FT-IR Spectroscopic Imaging, *Anal Chem* 89 (2017) 1283–1289.
 - [29] Y. Maor, P. Shor, Z. Aizenshtat, White halos surrounding the Dead Sea scrolls, *J Cult Herit* 28 (2017) 90–98.
 - [30] L. Falcão, M.E.M. Araújo, Application of ATR-FTIR spectroscopy to the analysis of tannins in historic leathers: The case study of the upholstery from the 19th century Portuguese Royal Train, *Vib Spectrosc* 74 (2014) 98–103.
 - [31] C. Zaffino, B. Russo, S. Bruni, Exploiting external reflection FTIR spectroscopy for the in-situ identification of pigments and binders in illuminated manuscripts. Brochantite and posnjakite as a case study, *Spectrochimica Acta A* 149 (2015) 41–47.
 - [32] M. Bicchieri, M. Monti, G. Piantanida, A. Sodo, Non-destructive spectroscopic investigation on historic Yemenite scriptorial fragments: Evidence of different degradation and recipes for iron tannic inks, *Anal Bioanal Chem* 405 (2013) 2713–2721.
 - [33] S. Bruni, V. Gugliemi, F. Pozzi, Historical organic dyes: A surface-enhanced Raman scattering (SERS) spectral database on Ag Lee-Meisel colloids aggregated by NaClO₄, *J Raman Spectrosc* 42 (2011) 1267–1268.
 - [34] K. Khanbabaee, T. van Ree, Tannins: Classification and Definition, *Nat Prod Rep* 18 (2001) 641–649.
 - [35] E. De Luca, M. Redaelli, C. Zaffino, S. Bruni, *Vib Spectrosc* 95 (2018) 62–67.
 - [36] M. Leona, J. Lombardi, Identification of berberine in ancient and historical textiles by surface-enhanced Raman scattering, *J Raman Spectrosc* 38 (2007) 853–858.
 - [37] M. Roman, K. Chruszcz-Lipska, M. Baranska, Vibrational analysis of cinchona alkaloids in the solid state and aqueous solutions, *J Raman Spectrosc* 46 (2015) 1041–1052.
 - [38] A. Solovchenko, E.M. Yahia, C. Chen, Chapter 11 – Pigments, in: Elhadi M. Yahia (Ed.), *Postharvest Physiology and Biochemistry of Fruits and Vegetables*, Woodhead publishing, 2019, pp. 225–252, ISBN 978-0-12-813278-4.
 - [39] R.H. Atalla, D.L. Vanderhart, Native cellulose: A composite of two distinct crystalline forms, *Science* 223 (Jan 20(4633)) (1984) 283–285.
 - [40] J.J. Sugiyama, R. Vuong, H. Chanzy, Electron diffraction study on the two crystalline phases occurring in native cellulose from an algal cell wall, *Macromolecules* 24 (1991) 4168.
 - [41] P. Tucker, P. Douglas, A. Durrant, A.S. Hursthouse, Heavy metal content of newspapers: Longitudinal trends, *Environ Monit Health* 11 (1) (2000) 47–66.
 - [42] U. Hamm, A. Geller, L. Gottsching, Heavy metals in wood, virgin pulps, waste paper and paper (in German), *Das Papier* 40 (10A) (1986) 37–46.
 - [43] M. Doskocz, K. Kubas, A. Frąckowiak, R. Gancarz, NMR and ab initio studies of Mg²⁺, Ca²⁺, Zn²⁺, Cu²⁺ alizarin complexes, *Polyhedron* 28 (2009) 2201–2205.
 - [44] A.W. Larsen, Evolution of Polynesian bark cloth and factors influencing cultural change, *J Anthropol Archaeol* 30 (2) (2011) 116–134.
 - [45] M. Häärä, A. Sundberg, S. Willför, Paper chemistry: Calcium oxalate - a source of "hickey" problems - A literature review on oxalate formation, analysis and scale control, *Nord Pulp Pap Res J* 26 (3) (2018) 263–282, <http://dx.doi.org/10.3183/npprj-2011-26-03-p263-282>.
 - [46] H. Terelius, M. Nilsson, T. Blomberg, Calcium oxalate in mechanical pulp, in: *Proceedings of the IMP Conference*, 2001, pp. 125–132.
 - [47] L.L. Zhang, R.Y. Zhu, J.Y. Chen, J.M. Chen, X. Feng, Seawater-retting treatment of hemp and characterization of bacterial strains involved in the retting process, *Proc Biochem* 43 (2008) 1195–1201.
 - [48] L. Qu, M. Tian, X. Guo, N. Pan, X. Zhang, S. Zhu, Preparation and Properties of Natural Cellulose Fibres from *Broussonetia papyrifera* (L.) Vent. Bast, *Bast Fibres Textiles Eastern Eur* 22 (2014) 24–28.