



A chromatographic investigation on ageing of natural dyes in silk under UV light

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Introduction

The poor light fastness of natural dyes is a major concern for textile conservators, curators, and scientists of archaeological chemistry. Artificially accelerated light experiments have been performed for several decades to investigate the fading of natural dyes under light ageing (Padfield and Landi 1966). The *Giles' diagrams* which were proposed to describe the fading rates of mainly synthetic dyes (Giles 1965) provided the basis for analogous interpretations of the ageing processes of natural dyes (Crews 1987). Interestingly, Giles (1965) noted that “in making practical suggestions for prolonging the life of museum specimens little can be added to the recommendations made by Russell & Abney 77 years ago”. The Russell and Abney report on the *Action of light on water colours* was published in 1888 and was presented in the open scientific literature by N.S. Brommelle in 1964 (Brommelle 1964). The Giles' statement indicates very accurately the complexity of the decay processes of natural dyes.

Colourimetry has been very often used as the main instrument to monitor the (i) artificially accelerated fading of natural dyes on textile fibres such as silk (Daniels 2006; Ishi et al. 2008; Padfield and Landi 1966; Tamburini and Dyer 2019), wool (Crews 1987), cotton (Cristea and Vilarem 2006; Daniels 2006; Kohara et al. 2000), and linen (Daniels 2006) and (ii) fading of textiles on display (Ford 1992). The

application of high-pressure liquid chromatography (HPLC) for the analysis of natural dyes (Wouters 1985) opened new avenues, as it became possible to investigate and monitor the ageing processes at the molecular level. HPLC was therefore employed to study the ageing of madder on wool (Clementi et al. 2007; Manhita et al. 2011) and silk (Degani et al. 2017; Vasileiadou et al. 2021), young fustic on silk (Valianou et al. 2009b; Vasileiadou et al. 2021), safflower on silk (Costantini et al. 2019; Wouters et al. 2010) and wool (Wouters et al. 2010), soluble redwood on wool (Manhita et al. 2013) and silk (Degani et al. 2017), cochineal on silk (Degani et al. 2017; Vasileiadou et al. 2021), weld, old fustic and logwood on silk (Degani et al. 2017), buckthorn and turmeric on silk (Vasileiadou et al. 2021), molluscan purple on silk and wool (Vasileiadou et al. 2019), tannins on wool (Degano et al. 2019), and carthamin on cotton (Laursen and Mouri 2013).

In this brief report, silk samples dyed with madder, soluble redwood (red dyes), buckthorn, weld, (yellow dyes), and indigo (blue dye) are exposed to a harsh environment of UV-C light to induce rapid and profound degradation of dye components. HPLC coupled to a diode-array detector (DAD) is used to monitor the degradation of dye molecules as a function of artificially accelerated ageing time. Several compounds of the aforementioned dyes are investigated. The goal of the study is to add to the existing literature more results relative to the complex decay phenomena of natural dyes. Attention focuses on light fastness which is studied using HPLC. Other fastness properties (e.g. wash, rub, perspiration) are not investigated in this brief study (Deveoglu et al. 2013, 2011, 2012; Shahid et al. 2012; Zarkogianni et al. 2010). Fourier-transform infrared (FTIR) spectroscopy is employed to reveal changes which are induced by the UV radiation to the silk composition, whereas structural changes were observed using scanning electron microscopy (SEM).

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Experimental

Materials

Dyeings of silk specimens with madder (*Rubia tinctorum* L.), soluble redwood (*Biancaea*, *Caesalpinia* trees), buckthorn (*Rhamnus* trees), and weld (*Reseda luteola* L.) were carried out in the past (Valianou 2009; Valianou et al. 2009a). Silk samples dyed with indigo (*Indigofera tinctoria* L.) were generously provided by R. Karadag (Istanbul Aydin University).

HPLC-grade dimethyl sulfoxide (DMSO) and trifluoroacetic acid (TFA) (assay > 99.0%) were obtained from Sigma-Aldrich. HPLC-grade acetonitrile (CH₃CN), methanol (MeOH), and water were purchased from ChemLab. Aqueous solution of hydrochloric acid (HCl, 37% m/m) was purchased from Riedel-de Haën.

Equipment

The HPLC–DAD system (Ultimate 3000, Dionex) was equipped with a LPG-3000 quaternary HPLC pump, a WPS-3000SL autosampler, a column compartment TCC-3000SD, and a UV–Vis Diode Array Detector (DAD 3000). Analyses were carried out by injecting 20 µL into an Alltima HP C18 (250 mm × 3 mm, i.d. 5 µm), Grace (Alltech Associates) column thermostated at 35 °C. HPLC was operated using a gradient elution programme, of two solvents containing (A) H₂O + 0.1% (v/v) TFA and (B) CH₃CN + 0.1% (v/v) TFA, which has been previously developed and validated (Vasileiadou et al. 2021). Monitoring wavelengths were 254 nm for the analysis of madder, soluble redwood and buckthorn, 288 nm for indigo and 360 nm for weld. HPLC peak areas were measured in triplicate, corresponding to three analyses for each prepared solution, and mean values and standard deviations were calculated. Moreover, three separate samples were analysed for each unaged, dyed silk specimen and relative standard deviations were calculated.

Artificially accelerated ageing conditions were developed in a homemade chamber (Vasileiadou et al. 2019, 2021) equipped with four UV lamps (25 W, λ = 254 nm). The distance between the specimens and the lamps was 30 cm. Dyed textiles were exposed to the UV-C radiation (254 nm) for short periods of time. UV-C radiation was used for the ageing treatment to accelerate and enhance the degradation of dye molecules. It is noted, however, that the reported results can be useful for the interpretation of effects induced on dyed silk after prolonged exposure to visible light which is typically used in heritage institutions that preserve and exhibit textiles of the cultural heritage.

FTIR measurements were obtained using a Spectrum Spotlight 400 Perkin Elmer spectrometer. Spectra were collected from the average of 32 scans from 4000 to 500 cm⁻¹ with a resolution of 4 cm⁻¹. The spectral data for each sample was subjected to baseline correction and to normalisation. SEM (JEOL, JSM-6510) was employed to study the surface structures of the dyed silk samples. The accelerating voltage was 20 kV and the working distance was set at 10 mm. The samples were carbon coated, using a Jeol JEE-4X vacuum evaporator.

Treatment in artificially accelerated ageing conditions

Large pieces of silk dyed with madder, soluble redwood, buckthorn, weld, and indigo were placed within the ageing chamber. Prior to exposure to the UV light, a small sample was taken from each piece. Thus, samples which were not exposed (t = 0) to the UV radiation were stored. The large dyed silk pieces were left under artificially accelerated ageing conditions for several days. The total exposure time to the UV radiation was slightly different for each of the dyed silk pieces and ranged within 22–26 days. During the treatment process and at regular intervals, a sample was removed from each of the five dyed silks and stored. Therefore, several individual samples were produced which were weighted and subjected to HPLC analysis to monitor the degradation of the studied dyes under UV-C radiation.

Dye extraction for HPLC analysis

Silk samples dyed with madder (0.2 mg), soluble redwood (1.0 mg), and buckthorn (0.3 mg) were treated with the HCl method (Wouters 1985). Weld was extracted from silk (1.0 mg) using the TFA method (Valianou et al. 2009a) to preserve the contained glycosides (Karapanagiotis et al. 2011; Mantzouris et al. 2011; Valianou et al. 2009a). Both methods are based on the same procedure: samples are immersed in hot (100 °C) methanolic solution of acid, either HCl (Wouters 1985) or TFA (Valianou et al. 2009a). The liquid phase is then evaporated under moderate temperature (~65 °C) and gentle nitrogen flow. The precipitated dye is dissolved in fresh solvent, which in the present study was DMSO. Finally, indigo was extracted from silk (0.3 mg) in a hot (80 °C) bath of DMSO.

Results and discussion

The UV–Vis absorbance maxima of the compounds which were studied are summarised in Table S1 of the Supplementary material. The reported results are in agreement with previously published studies, as briefly described next.

Alizarin (AL), lucidin (LUC), purpurin (PU), and rubiadin (RU) have been identified using HPLC–DAD in madder species in several studies (e.g. Boldizsár et al. 2006). The type B and type C compounds were chromatographically detected in soluble redwood first by Nowik (2001) and were subsequently used as markers for the identification of soluble redwood (*Caesalpinia* trees). The type C compound was recently identified as being urolithin C (Peggie et al. 2018) whereas the mass of the deprotonated molecular ion of the compound $[M-H]^-$ was reported more than a decade ago (Karapanagiotis et al. 2009). The structure of the type B compound is still pending. The UV–Vis absorbance maxima reported in Table S1 for colouring components of buckthorn, which are emodin (EM), isorhamnetin (ISORHM), kaempferol (KAM), kaempferide (KAD), quercetin (QUE), rhamnazin (RHZ), and rhamnetin (RHM), are in agreement with previously published data (Deveoglu et al. 2013; Mantzouris and Karapanagiotis 2013; Petrovicu et al. 2014). Apigenin (API), luteolin (LU), and their 7-O-glucosides and chrysoeriol (CHR) included in Table S1 are components of weld according to various previously published HPLC reports (e.g. Karapanagiotis et al. 2011). Finally, HPLC data for indigo components, indigotin (IND), and indirubin (INR) can be found in too many sources.

The aforementioned compounds were identified in the extracts of fresh and aged dyed silk samples, treated according to the methods which are described in the “Experimental” section (“Dye extraction for HPLC analysis”). The dye extraction methods are apparently of great importance as they can have enormous effects on the analytical results collected by HPLC. Moreover, the lack of standard materials (colouring compounds in pure form) is another reason which narrows the number of identified compounds in the dye extracts. As a result, other components which have been detected by other researchers in extracts of the studied dye sources were not identified herein. For example, some compounds which were not reported in the present study are munjistin, nordamnacanthal, pseudopurpurin, ruberythric acid, and xanthopurpurin, which are identified in madder extracts (Boldizsár et al. 2006; Derksen et al. 2003), brazilin and brazilein, detected in solutions of soluble redwood (Karapanagiotis et al. 2009) and various glycosides which are found in weld (Mantzouris et al. 2011) and buckthorn (Lech 2020) extracts.

Figure 1 shows three chromatograms of a silk sample dyed with buckthorn. The chromatogram at the bottom of the figure was taken before treating the dyed silk with UV light. The other two chromatograms were collected after leaving the same sample in the ageing chamber for $t=5$ and $t=26$ days. Figure 1 shows that the HPLC peak heights and areas of the detected compounds decrease with artificially accelerated ageing time, t . ISORHM is hardly detected after exposing the dyed silk to UV light for 26 days. A magnified

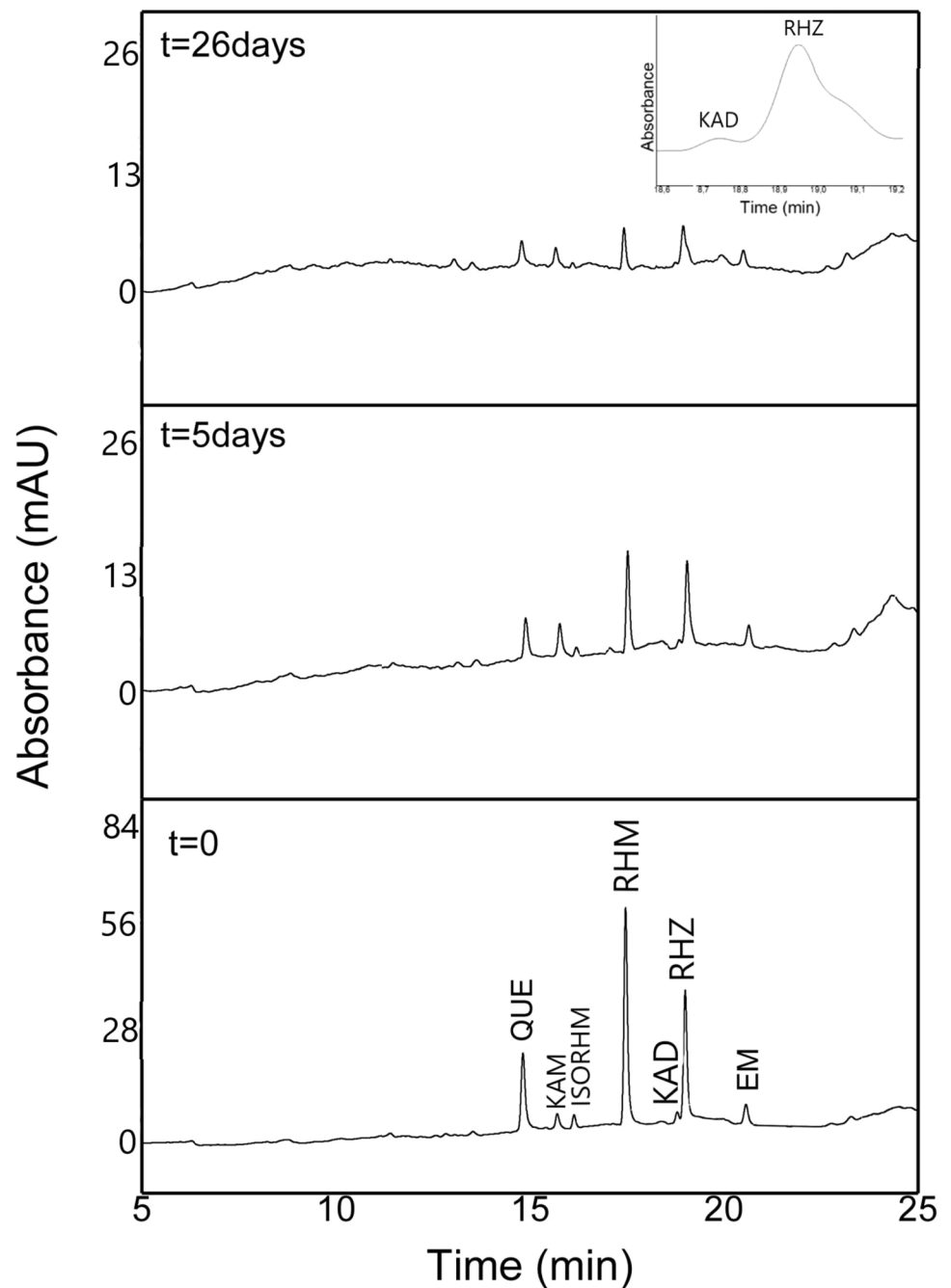
graph is provided in the chromatogram at the top to reveal the HPLC peak of KAD and to reveal the separation of KAD and RHZ.

The plots in Fig. 2 show the normalised areas of the HPLC peaks of the studied compounds as a function of t . For each compound, the HPLC peak areas were normalised to the highest value (taken as 100) corresponding apparently to the dyed silk which was not exposed to artificially accelerated ageing conditions. The raw HPLC data (i.e. actual HPLC peak areas) are included in Tables S2–S6 of the Supplementary material. The latter provides, furthermore, the standard deviations (SDs) of the measurements (Tables S2–S6). Moreover, for the unaged dyed silk specimens, the relative standard deviations (RSDs) calculated from the triplicate analyses of the dye solutions were compared with the corresponding RSDs which were obtained after analysing three different samples for each dyed silk specimen (Table S7). ISORHM, reported in Fig. 1, is excluded from Fig. 2 as it was impossible to measure the corresponding peak area with certainty after prolonged ageing. The five plots of Fig. 2 show the same tendency. Initially, the HPLC peak areas of the monitored compounds decrease rapidly with t . This dramatic UV-induced decay of the compounds is evidenced within roughly the first 5 days of treatment. For longer t , the effect of the ageing conditions on the monitored compounds becomes less significant, as the measured HPLC peak areas are only slightly affected by the UV radiation. These results correspond to the Type II fading-rate curve which was suggested by Giles (Giles 1965).

The trend of the results reported in Fig. 2 is in agreement with previously published HPLC data, concerning the degradation of natural dyes in harsh light conditions, as summarised next. Wool (Manhita et al. 2011) and silk (Vasileiadou et al. 2021) dyed with madder were exposed to UV-B (310 nm) and UV-C (254 nm) light, respectively. In both studies, it was reported that the AL and PU chromophores degradation rates were not constant, being more severe in the first days of light exposure (Manhita et al. 2011; Vasileiadou et al. 2021). A similar trend of the effects of light ageing on silk dyed with molluscan purple (Vasileiadou et al. 2019) and safflower (Costantini et al. 2019) was reported. In particular, it was shown that the amounts of indigoid compounds (Vasileiadou et al. 2019) and that of the Ct2 and Ct3 marker compounds of safflower (Costantini et al. 2019) drop initially rapidly and then slowly under UV light ageing.

Figure 3 shows the % relative integrated HPLC peak areas. For each dye (plot), the sum of the relative percentages of the monitored components equals to 100. Apparently, the given numbers are not actual mass compositions as for this purpose the HPLC instrument should have been calibrated using standard materials (Vasileiadou et al. 2016, 2021). However, potential changes in the actual mass compositions induced by the ageing process should be reflected

Fig. 1 Chromatograms (at 254 nm) of a silk sample dyed with buckthorn. The chromatogram at the bottom was collected before exposing the sample to artificially accelerated ageing conditions ($t=0$). The other two chromatograms were collected after exposing the sample to UV light for different periods, t , as indicated. The peaks for KAD and RHZ recorded in the top HPLC graph after treatment for $t=26$ days are magnified. Abbreviations are as follows: quercetin (QUE), kaempferol (KAM), isorhamnetin (ISORHM), rhamnetin (RHM), kaempferide (KAD), rhamnazin (RHZ) and emodin (EM)



on the reported HPLC peak areas of Fig. 3. Overall, the results of Fig. 3 suggest that the effects of the UV radiation do not cause any noticeable changes in the relative compositions of dyes. Minor effects can be noticed, primarily at the first stages of irradiation. For example, in the first day of treatment, AL degraded somewhat more extensively than PU. However, the AL/PU peak area ratio remained practically unaffected after this slight variation of the first day. A higher degradation rate of AL compared to PU was previously reported for wool dyed with madder and aged under a UV light of 310 nm (Manhita et al. 2011). However, natural

ageing led to an opposite effect as the extent of degradation of PU was greater than that of AL (Clementi et al. 2007). It should be stressed that ageing effects can be affected by several parameters such as, for instance, the type of the fibre (wool, silk, other), the mordanting materials and procedures, the amount of the dye attached to the fibres, the dyestuff source and the ageing (light, T and RH) conditions (Cristea and Vilarem 2006).

Similar observations can be reported for other dyes included in Fig. 3. For example, for the first 2 days of light ageing, it is observed that the type B compound exhibits

Fig. 2 HPLC peak areas, normalised to the highest value (taken as 100) vs accelerated ageing time for dyed silk samples. Peak areas were measured at 254 nm for madder, soluble redwood and buckthorn components, 360 nm for weld and 288 nm for indigo components. Abbreviations are as follows: purpurin (PU), lucidin (LUC), rubiadin (RU), alizarin (AL), apigenin (API), apigenin-7-O-glucoside (API-GLU), luteolin (LU), luteolin-7-O-glucoside (LU-GLU), chrysoeriol (CHRY), indigotin (IND), indirubin (INR). Abbreviations for buckthorn components were given in the caption of Fig. 1

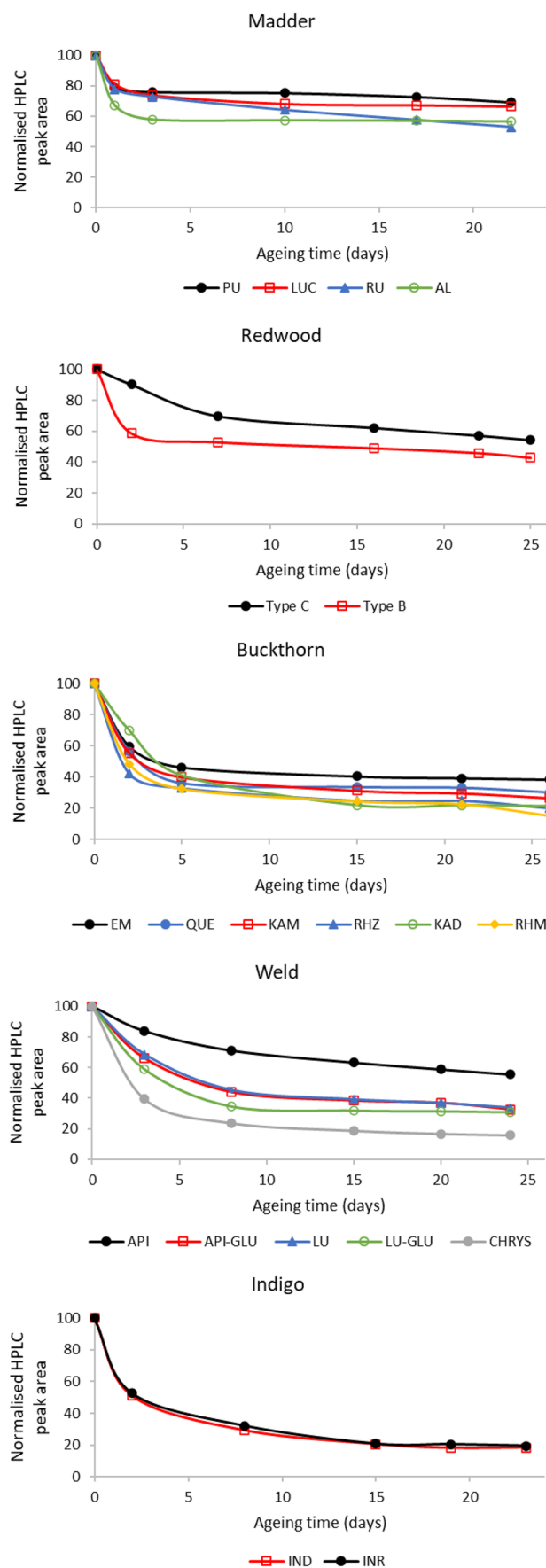
more light fastness than the type (urolithin) C compound. However, the relative ratio of the two compounds remains practically constant for longer ageing periods. Another noteworthy change with t is the slight increase/decrease of the relative percentage of QUE/RHM for silk dyed with buckthorn. Despite the aforementioned minor effects, the overall conclusion is that the % relative integrated HPLC peak areas of the investigated dyes remained practically unaffected by the UV radiation.

In this brief report, attention focuses on the degradation of natural dyes. However, a brief research on the effects of the UV-C radiation on silk fibres was carried out using FTIR and SEM. The results of these studies confirmed previously published data and are included in the Supplementary material, in Figure S1 (FTIR) and Figure S2 (SEM). In brief, FTIR spectra (Figure S1) showed that the UV-C radiation caused a decrease in amide I, II, and III intensities (Akyuz et al. 2014; Li et al. 2013; Ming et al. 2013; Sionkowska and Planecka 2011; Tsuboi et al. 2001; Vasileiadou et al. 2019). Structural damages and cracks were observed in the SEM images (Figure S2) of aged silk (Li et al 2013; Valianou et al. 2009b; Vasileiadou et al. 2019).

Conclusions

The decay of dye components of madder, soluble redwood (red dyes), buckthorn, weld, (yellow dyes), and indigo (blue dye) induced by artificial UV-C ($\lambda = 254$ nm) radiation was investigated, using silk dyed samples. Within the first 5 days of treatment, a rapid decrease in the amounts of the dye components in the silk fibres was recorded, according to HPLC results (peak area measurements). For longer treatment time, the effects of the ageing conditions on the monitored compounds became less significant and decay processes reached a saturation point. The % relative integrated HPLC peak areas of the investigated dyes remained practically unaffected by the UV-C radiation. Finally, as described in the Supplementary material, the ageing treatment caused a decrease in amide I, II, and III intensities of FTIR peaks and structural damages in silk, as revealed by SEM.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s12520-021-01492-0>.



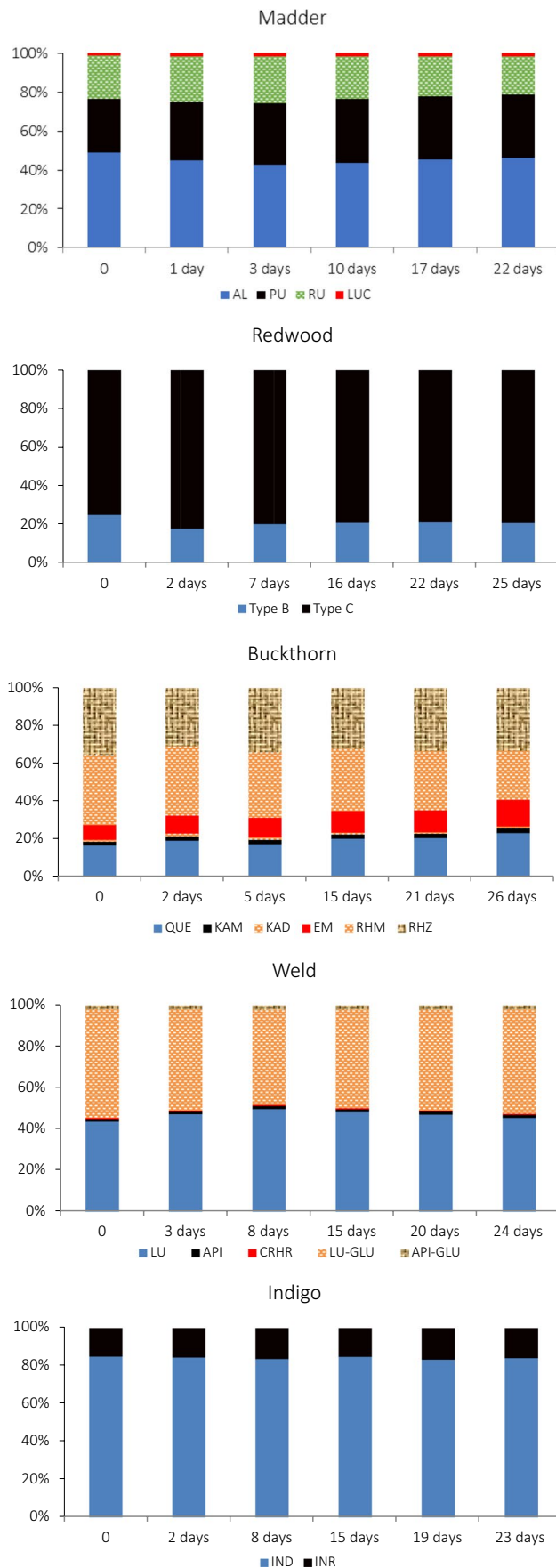


Fig. 3 Relative (%) HPLC peak areas (sum is taken as 100%) for various treatment periods which are indicated in the horizontal axis

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Declarations

Conflict of interest The authors declare no competing interests.

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