NEW INSIGHTS INTO THE FADING PROBLEMS OF SAFFLOWER RED DYED TEXTILES THROUGH A HPLC-PDA AND COLORIMETRIC STUDY

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Abstract

Safflower is well-known by conservators and restorers of textiles as the red dye source producing a nice though very delicate pink colour, extremely light-sensitive. Many historical silk fabrics from the most renowned museums are active witnesses of the degradation problems of this colourant, being a major challenge to textile conservators. However, the fading does not occur only because of light exposure, since fabrics stored for many years in museum deposits exhibit a gradual decolouration.
The aim of this study is to achieve a better knowledge on the environmental parameters involved in the degradation processes of carthamin, the main red dye constituent of safflower (*Carthamus tinctorius* L.). The newly gained information will contribute to a more realistic perspective on the problems of fading of safflower dyed textiles, possibly helping their conservation.
To evaluate the stability of safflower red, specific ageing tests were carried out on new silk samples, dyed with safflower through modern recipes deriving from traditional ones. For the artificial ageing, the effects of simulated sunlight, temperature, humidity and ozone were separately investigated through HPLC-PDA analysis and colorimetric examinations.
The results showed and confirmed that safflower red degrades most rapidly under light exposure. Besides that, the work revealed an important instability of the carthamin dye constituent in a dark environment, especially when subjected to high humidity conditions.
Moreover, the HPLC-PDA study was able to provide new insights on the different markers (e.g. Ct components) commonly revealed in historic objects dyed with safflower red but with still unclarified origins.

Keywords

Safflower red; dyes; HPLC-PDA; artificial ageing; preventive conservation

1. Introduction and research aim

Safflower (*Carthamus tinctorius* L.), also known as bastard or false saffron [1], is an annual or biannual thistle-like plant that belongs to the Compositae or Asteraceae botanic families [2-3], whose petals contain red and yellow dyes. The plant is native of Northern India and the Asiatic regions of the Middle East, although in the early ages it was cultivated also in Mediterranean areas and in central Europe [2].
Carthamin (NR 26, CI 75140) is the principal red dye contained in safflower petals: this compound is a C-glucosylquinochalcone whose chemical structure is depicted in figure 1 [1] produced by some enzymatic

processes from the yellow compound precarthamin [2, 4] during its late blooming state [5]. The yellow dyestuff of safflower (NY 5) is made up of several compounds, all of them classified within the quinochalcone family of flavonoids. Some of these dyeing matters are: hydroxysafflor yellow A, safflor yellow B, safflomin A, safflor yellow A, safflomin C, isosafflomic C, tinctormin. Depending on the different species, the yellow dyes represent between the 25% and 36% of the chemical composition of the petals and are water-soluble [2, 5]. Differently from the yellow compounds, carthamin is soluble in alkali and it makes up only 0.3-0.6% of the petals [2].

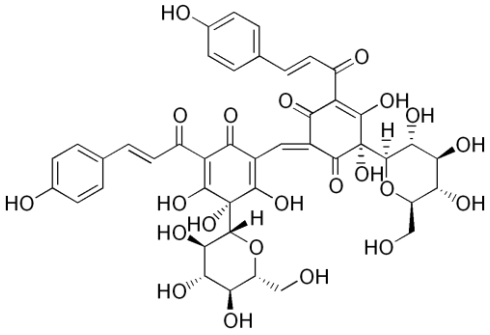

Figure 1. Chemical structure of carthamin.

Carthamin is notably unstable to light and has a low efficiency in dyeing since it is poorly contained within the petals. Historically, large quantities of flowers were needed and so the dyed textiles were extremely expensive. Despite this, safflower red had an important role in traditional dyeing, thanks to its ability to produce highly appreciated shades of pink [2]. In particular, safflower red was largely used in Oriental areas, notably in China [3], while its use in Europe is much rarely reported [3, 6, 7].

Sensitive safflower red has been recently identified by chromatographic analysis in some historical textiles belonging to the Victoria and Albert Museum of London and currently stored at Blythe House, London.[1] The fugitive colorant was detected in an 19th-century Russian pocket (object code 492-1907) and an 17th-century doublet from Italy (object code T. 59-1910), among others. Both the historical items show major problems of fading of the pink colour, which resulted to be obtained with safflower, as presented by the HPLC-PDA outcomes summarised in table 1. As deduced by the location of the faded areas, the degradation of the dyeing seems to be related, at least partially, to the overexposure to light. However, the doublet appears to be also discoloured in some parts not exposed to light, such as the inner lining. Therefore, this example can prove that other environmental parameters than light could have been involved in the degradation of the dye.

Table 1. Results from the HPLC-PDA analysis of historical samples.

Object	Colour	Sampling location	Extraction Method	Compounds detected	Sources of dye identified

[1] The analyses were carried out for the *Dye analysis and fading project (2015)* promoted by the Victoria and Albert Museum of London and involving both the Royal Institute for Cultural Heritage of Brussels (KIK-IRPA) and Ca' Foscari University of Venice.

492-1907 Russian pocket	Pink, taken from the inner part		DMSO	Carthamin	Safflower
	Beige (strongly faded pink)		DMSO	No compounds detected	-
T. 59-1910 Italian doublet	Pink, taken from mainly faded inner lining		DMSO	Ct1; Ct2; Ct3; Carthamin	Safflower

Artificial ageing is an important tool to evaluate the degradation processes of colourants and dyed textiles and to help their preventive conservation, assuring the optimal environmental conditions in museums and deposits. Previous studies have already stated the poor lightfastness of safflower red, showing that carthamin, within safflower-dyed wool, silk, and cotton, decreases during light exposure in both air and anoxic environment [3, 8]. However, it must be reminded that dyestuffs are actually sensitive to several indoor factors, such as temperature, humidity and ozone [9-18]. These parameters and their effects could be responsible for the degradation of dyes also in dark environments, thus during storage time.
As no in-depth studies on the interaction between safflower red within historic fabrics and these parameters have been published up to now, this research is the first in extending the knowledge on the degradation of this colourant to finally promote an effective preventive conservation of the dyed textiles.

2. Materials and methods

2.1 Preparation of the samples

Silk samples were dyed using different dyeing procedures and methods, which were modern recipes deriving from traditional ones, currently used for ageing tests with safflower dyeing [1, 2, 3, 5, 19, 20]. For the dyeing, safflower petals purchased from Kremer Pigmente (Germany) were employed following this proportion: 10 gr of petals for 1.2 gr of textile to dye (0.12 l of dye bath).
Two procedures, named procedure A and procedure B, were selected and for each procedure two different dyeing methods were employed (direct method and indirect method). The difference between the two

procedures is that procedure A involves a primary step where the yellow dyes are mainly removed through repeated washings in water. The two methods diverge since the indirect method involves safflower red being primarily precipitated into a cotton fabric through acidification and then dissolved with an alkaline solution to dye the silk; whilst with the direct method the dye is directly precipitated into the silk.
For the first step of procedure A, safflower petals were left in Milli-Q water for three weeks, rinsing them daily. Next, the two procedures followed the same steps: safflower petals were placed in an alkaline solution of sodium carbonate 1.5% (pH ≈ 12) and left to soak for an hour. Subsequently, the solution was filtered through a sieve: the resulting liquid represented the dye bath. The bath was divided in two equal parts: one used for the direct method and the other for the indirect method. For the direct method, silk was added to the alkaline dye bath and then a sufficient volume of a 10% solution of citric acid was employed to neutralise the solution (pH ≈ 5). The fabrics were left in the acidic bath overnight in the dark to allow a proper dyeing. For the indirect method, instead of silk, cotton was entered in the first alkaline dye bath. Then the solution was acidified, and the cotton fabric was left there for 24 hours. When the dyed cotton was ready, the dyestuff was dissolved through the alkaline solution and then precipitated on to the silk through the acidification of the bath. The dyed samples were eventually rinsed several times in water.
As two different procedures were followed (A and B) and for each procedure two dyeing methods were employed (direct and indirect), four types of dyed samples were obtained. The mock-ups and their specific codes are reported in table 2.

Table 2. Laboratory-prepared samples and their dyeing procedure.

Sample code	Procedure	Method
AD	A (without yellow dyes)	Direct
AI	A (without yellow dyes)	Indirect
BD	B (with yellow dyes)	Direct
BI	B (with yellow dyes)	Indirect

2.2 Artificial ageing

Artificial ageing was performed using specific and deliberately extreme conditions, in order to speed up the possible degradation processes of the dyes.

2.2.1 Light induced ageing

Two OSRAM Ultra-Vitalux® solar lamps (300 W, 230 V) were used for the ageing tests. The bulbs emitted a wavelength from 280 to 2000 nm (13.6 W in the range 315–400 nm, 3.0 W in the range 280–315). The lamps were placed at a distance of 30 cm from the samples and the illuminance upon their surface was around 2000 lux (40 times the limit admitted in international guidelines for museums exposition in the case of textiles [11]). In the ageing regime, the average temperature was 30 °C while the average relative humidity was 35%. The treatment lasted 1056 hours and the mock-ups were monitored after: 24 hours (t1); 48 hours (t2); 96 hours (t3); 192 hours (t4); 384 hours (t5); 720 hours (t6); 1056 hours (t7).

2.2.2 Ageing with ozone

The laboratory-prepared samples were aged for 12 hours in an atmosphere rich in ozone (≈ 650 ppb) and absence of light. For the treatment, a conventional industrial FISHER ozone generator (*Labor-und Verfahrenstechnik Ozon-Generator,* Germany), with water cooling system, was employed. The ozone is produced on demand in response to the amount of O_2 provided flue gas with a controlled ozone oxygen ratio (1:5). Samples were put in a glass chamber where the ozone flux was funnelled. The ozone concentration within the chamber was monitored through a portable ozone meter Aeroqual S500 Monitor® equipped with Aeroqual Monitor Software. The mock-ups were monitored after every 4 hours.

2.2.3 Ageing at different levels of RH%

The samples were exposed for 2400 hours at two levels of relative humidity: 60% and 90% at 20±2 °C, in a dark environment.
The two humidity treatments were obtained by inserting the samples into two sealed crystallization vessels where a saturated solution of NaBr (for the system at ≈ 60%) and of $(NH_4)_2SO_4$ (for the system at ≈ 90%) were previously added (as reported by European regulations [21]). The relative humidity within the systems was periodically checked thanks to digital thermo-hygrometers (precision 0.1°C, 2% RH). During the treatment, the mock-ups were investigated after: 720 hours (t1); 1440 hours (t2); 1920 hours (t4); 2400 hours (t5).

2.2.4 Ageing at low temperature
In order to investigate the potential effects of low temperature and humidity, the mock-ups were placed in a refrigerator at 4-7 °C and average relative humidity 50-60% for 1680 hours. The samples were studied at: 720 hours (t1); 1200 hours (t2); 1680 hours (t3).

2.2.5 Ageing at moderate temperature, dry environment
The textile samples were thermally treated in air through heating in a laboratory oven at a stable temperature of 50 °C (dry environment) for 1680 hours. The mock-ups were monitored at: 720 hours (t1); 1200 hours (t2); 1680 hours (t3).

2.3. Analytical techniques and instrumentation

2.3.1 HPLC-PDA

The dye composition and degradation were examined through High performance liquid chromatography and Photo Diode Array detection (HPLC-PDA).
All analyses were done after extracting the dye from the samples (0.5 mg average weight) by adding 150 µl of dimethylsulfoxide (DMSO) to the sample during 10 min at 80 °C without light exposure, after which the extract was immediately injected into the chromatographic system in order to minimise the loss of unstable constituents prior to the analysis.

The equipment consists of an Alliance E2695 XE Separations Module (Waters Chromatography BV USA) with online vacuum degasser and a temperature-controlled, end capped LiChrosorb RP-18 column (dimensions of 125 mm x 4 mm diameter, 5 µm particle size and 100 Å pore diameter) from Merck, VWR, Belgium. The mobile phase is composed out of pure methanol (grade: for HPLC > 99.8%, from Acros Organics), Milliq. water (ASTM Type I , resistivity: 18 MΩ.cm and TOC < 5ppb, Waters) and a 5 % solution of phosphoric acid (85 wt% pro analisi, Acros Organics). Details about the applied chromatographic protocol can be found elsewhere (Gleba 2016). The PDA detector (PDA model 996, Waters, USA) is made up of 512 diodes which scan the absorbance within the wavelength ranging between 200 and 800 nm, with a resolution of 1.2 nm with 1 scan/second.
Data treatment was done with the Empower 2 software system from Waters. The evaluation of the absorbance spectra and retention times of the detected constituents is achieved by comparison with a user-generated database of KIK-IRPA containing reference spectra obtained from commercial pure chemical compounds as well as organic constituents derived from extracts of textile references dyed with biological dye sources. In this research, peak areas of the selected compounds were all integrated at 255 nm as this wavelength was suitable for carthamin as well as for the dye degradation markers.
To obtain data to compare before and after the treatment allowing a semi-quantitative analysis, calculations were done according to the methods already developed by Wouters et al. [3] and also recently

presented [22]. All peak areas from HPLC-PDA chromatograms at 255 were normalized according to the weight of the sample analysed.

2.3.2 Colorimetry

To study the chromatic variations (in the CIEL*a*b* space) occurred during the ageing, a Konica Minolta CM 2600d/2500d spectrophotometer was employed. The measurements were performed in SCI (specular component included) modality. The spectrophotometer has an 8-degree viewing angle geometry, with a Xenon lamp diffusion light and a high-resolution monolithic polychromator. The instrument analysed circular areas with an average diameter of 3 mm; each acquired result was the average of three consecutive measurements made in the same point. The recorded data were elaborated by the software Spectra Magic NX.
The total colour difference, ΔE*, was calculated by the formula: $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. In the field of Heritage Science, it is assumed that when the ΔE values are higher than 3, the chromatic difference is visibly detectable. However, not all literature agrees with this threshold [23].

3. Results and discussion

3.1 Characterization of the laboratory-prepared samples

The four samples (BD, BI, AD, AI), right after the dyeing, were visibly different in colour. The hue of samples BD and BI appeared to be more orange, while the one of samples AD and AI were pinker. As depicted in figure 2, the colorimetric data confirmed the chromatic differences, showing that samples BD and BI had higher values of b* (yellow) compared to samples AD and AI, though sample AI had the highest value of a*(red).

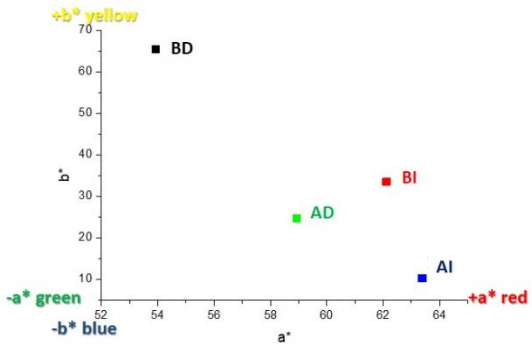

Figure 2. Colorimetric data (a* and b*) of the laboratory-prepared samples.

Considering the HPLC-PDA results, the four samples contained mainly the same principal markers: carthamin, Ct components, apigenin, Y1, Y2 and carthamin'. All these compounds, seen in the chromatograph of sample AI in figure 3, are related to the dyeing with safflower. Table 3 lists the main detected components together with their retention times and UV-Vis maximum absorption.

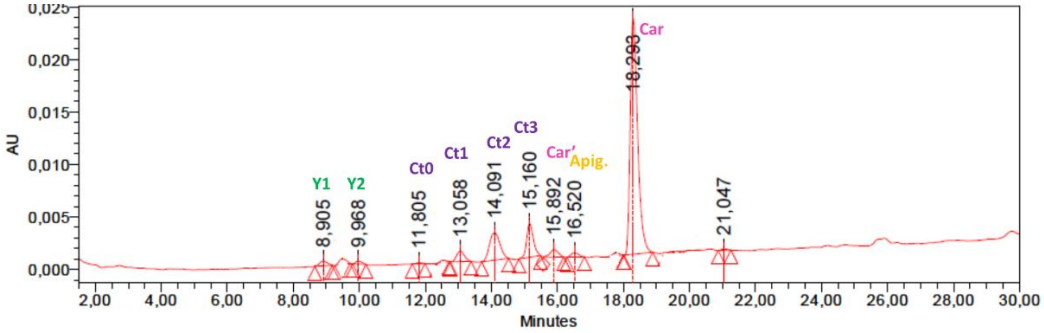

Figure 3. Chromatogram from sample AI (monitored at 255nm).

Table 3. Main compounds detected within the sample BD, BI, AD and AI at t0 (acquisition at 255 nm).

Retention time (min)	Main detected compounds	UV-Vis maximum absorption (nm)
9.6	Y1	400
10.7	Y2	400
12.4	Ct0	270
13.6	Ct1	280
14.6	Ct2	290
15.7	Ct3	305
16.5	Carthamin'	520
17.0	Apigenin	260/340
18.8	Carthamin	520

As previously stated, carthamin is the main red dye contained in *Carthamus tinctorius* L. while Ct components are uncoloured marker compounds for safflower often detected in historical and faded samples [3, 24, 25]. The chemical composition and the source of Ct compounds have not been defined yet although they have already been characterised by their retention times, UV-Vis spectra, mass spectra and fragmentations [3]. Apigenin (NY 1 and 2, CI 75580 [2]) is a yellow flavonoid component contained within several dyeing plants, including safflower (in the free form and sugar form) [3, 24, 26].

Besides, other compounds were detected in the newly prepared samples. They were named: Y1, Y2 and carthamin'. Carthamin', a marker with similar absorbance spectrum as carthamin, is a minor red dye contained within safflower [20], while Y1 and Y2 require some further explanations to be properly defined.

The presence of components with similar absorption spectra of those of Y1 and Y2 has already been reported in safflower red dyed samples and they are currently mainly described as decomposition products of carthamin [25, 27, 28]. The publication by Laursen and Mouri [8] was the first to state that carthamin deteriorates in aqueous solution by heating, probably via a reverse aldol condensation, leading to the formation of the two compounds, called A and B. However, as also suggested by Shybayama et al. [24], it might be difficult to discriminate the origin (yellow quinochalcones or decomposition products) of markers such as Y1 and Y2 when only HPLC-PDA is employed. This can be due to the great similarity between the absorption spectra of A and B and the many yellow quinochalcones dyes within safflower petals [29, 30].

To allow a better understanding of Y1 and Y2, two side tests were carried out:

I. HPLC-PDA analysis of the water extractions of yellow colourants obtained during the dyeing with procedure A (for the analysis the solutions were vacuum evaporated to dryness and the residue dissolved in MeOH/H_2O 1:1 v/v);

II. HPLC-PDA semi-quantitative evaluation of the of carthamin, Y1 and Y2 content (as described in paragraph 2.3.1) within the newly prepared samples treated with DMSO but at different temperatures and times, namely: 18 °C for 4 hours; 40 °C for 1 hour; 80 °C for 10 minutes.

The recalculated data presented in table 4, seem to suggest that temperature does play a role in the formation of Y1 and Y2, however, the content of carthamin does not appear to be affected by this; moreover, Y1 and Y2 were both revealed in the unheated yellow dyes water solutions. Because of the

contrasting results of the side tests it was not possible to define the origin of Y1 of Y2, though other interesting observations can be drawn from the accelerated ageing, as reported in the following section.

Table 4. Peak areas of the marker compounds Y1, Y2, carthamin extracted from the newly prepared sample AI with DMSO at different temperature and time (integration values recorded at 255 nm calculated per 0.5 mg of sample).

Compound	18 °C, 4 hours	40 °C, 1 hour	80 °C, 10 minutes
Y1	0.12	0.02	0.01
Y2	0.11	0.02	0.02
Carthamin	1.04	1.17	1.00

Considering the semi-quantitative data from the recalculation of the peaks areas, the amount of each compound varies from sample to sample, as depicted by the graphic of figure 4. Comparing the direct and indirect methods for the preparation of the mock-ups it was noted that the indirect dyeing lowers the amount of the Ct1, Ct2, Ct3. In fact, samples BD and AD had an overall higher amount of Ct components when compared to samples BI and AI. This indicates that, although the origin of Cts is not defined, these non-coloured components, are at least partially removed when safflower red is first precipitated on cotton and then removed to finally dye the silk, hence obtaining the more wanted pink shade. Further observations on the Ct markers are described in section 3.2.2.
Apart from that, it was observed that sample AI, made after the "purest" recipe, contains the lowest amount of carthamin. This might be the result of the loss of a certain quantity of carthamin during the elaborated preparation of sample. These findings were confirmed also by the HPLC-PDA analysis of the different dye baths (data not reported here).

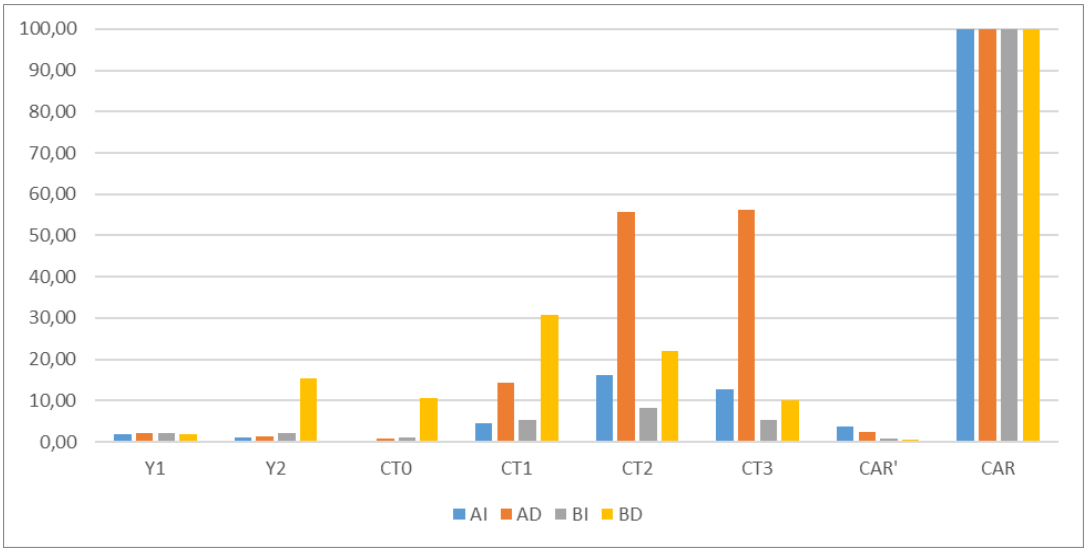

Figure 4. Peak areas of the marker compounds relative to carthamin (100%) (integration values recorded at 255 nm calculated per 0.5 mg of sample).

3.2 Accelerated Ageing

3.2.1 Colorimetric measurements

In table 5 are summarised the results from the colorimetric study of the aged samples. According to literature, the samples dyed with safflower red demonstrated to be extremely light-sensitive and so, non-surprisingly, light proved to cause the greatest change in colour [3, 8]. At the end of the light exposure the ΔE values were extremely high (> 65), mainly due to the increase of L* (because of the fading/whitening) and to the decrease of a* (less red hue). The b* parameter changed in a less predictable way, but

eventually it reached an average value of 20-25, possibly related to the yellowing of the silk fibres (as also reported by the data from the aged silk reference sample).
The most unexpected result was the visible colour change recorded during the ageing at 90% RH in dark environment: as shown by figure 5, the textiles appeared to turn yellow. The yellowing was clearly stated by the colorimetric measurements (table 5, ΔE > 9), that reported a significant increase of b* (shift towards yellow) and L* values, together with a decrease of a* values, the red colour component. It is interesting to notice the shift towards a yellowish hue mostly occurred in samples AD and AI prepared through procedure A (without yellow dyes), which indeed had lower b* values at t0.
The lowest colour shift (ΔE < 2) was detected after the 12-hours ozone ageing, followed by the one registered after treatment for 1680 hours at moderate temperature, dry environment (ΔE ≈ 2). Slightly higher variations were observed for mock-ups aged at 60% RH (ΔE between 2 and 3 after 2400 hours) and in the humid and cold environment (ΔE between 3 and 4 after 1680 hours). In both cases, the outcomes seem to be related to the increase of L*, a* and b*, the latter indicating a shift towards yellow, as also noticed for the ageing at 90% RH.

Table 5. Average values of the colorimetric parameters L*, a* and b* before and after the light ageing.

Accelerated ageing	Sample	ΔL*	Δa*	Δb*	ΔE
Light (1056 hours)	**Silk (reference)**	-1.2	-0.08	-9.19	9.27
	BD	-32.46	43.29	37.05	65.58
	BI	-38.79	57.93	9.7	70.39
	AD	-40.03	53.27	3.01	66.70
	AI	-37.80	61.40	-7.78	72.52
Ozone (12 hours)	**BD**	-1.05	-0.34	-0.49	1.21
	BI	-1.33	-0.57	-0.53	1.54
	AD	-1.42	-0.10	0.58	1.54
	AI	-1.28	0.97	0.51	1.69
90% RH (2400 hours)	**BD**	-6.89	6.09	-3.04	9.69
	BI	-8.00	3.60	-14.62	17.05
	AD	-11.09	5.15	-20.39	23.78
	AI	-9.90	7.05	-21	24.26
60% RH (2400 hours)	**BD**	-1.21	-1.01	-1.36	2.08
	BI	-0.68	-1.53	-1.72	2.40
	AD	-1.45	-1.05	-1.61	2.41
	AI	-2.03	-1.36	-1.96	3.13
Low temperature (1680 hours)	**BD**	-0.53	-1.36	-3.52	3.81
	BI	-1.61	-1.56	-1.74	2.84
	AD	-1.52	-1.35	-1.99	2.84
	AI	-1.62	-1.68	-2.28	3.26
Moderate temperature, dry environment (1680 hours)	**BD**	1.26	-1.25	0.87	1.98
	BI	-0.28	-1.13	1.04	1.56

AD	-0.01	-0.99	0.06	0.99
AI	-0.19	-1.02	-1.88	2.15

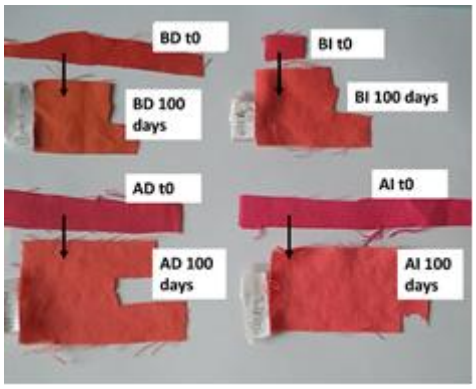

Figure 5. Samples before and after (2400 hours) of the ageing at 90% RH.

3.2.2 HPLC-PDA analysis

As reported in the previous section, it was not surprising that HPLC-PDA analyses performed on the light-aged samples shown no trace of carthamin or carthamin' after 44 days of treatment, confirming the complete discoloration of the textiles. However, more remarkably the semi-quantitative data obtained (table 6) illustrate that carthamin is greatly unstable in all the studied dark environments. A remarkable decrease of the red component was indeed reported at the end of all the ageing tests in dark.

Table 6. % decrease of carthamin at the end of the different accelerated ageing tests (recalculated peak areas, integration at 255 nm).

Accelerated ageing	Sample BD	Sample BI	Sample AD	Sample AI
Light (1056 hours)	> 99	> 99	> 99	> 99
Ozone (12 hours)	52	70	74	69
90% RH (2400 hours)	72	87	85	87
60% RH (2400 hours)	56	84	82	77
Low temperature (1680 hours)	74	85	78	74
Moderate temperature, dry environment (1680 hours)	59	77	81	75

Even though the approach of the current study is only semi-quantitative and it prevents the chemical characterization of unknown compounds, some interesting observations on the degradation path of safflower red can be here reported for the first time:

1. The overall content of Ct markers lowered at the end of every accelerated ageing, particularly because of the loss of Ct2 and Ct3. In general, only Ct0 appeared to increase during the different treatments, in accordance with Wouters et al. [3]. Nonetheless, the outcomes of the light ageing (figure 6) indicate that the growth of Ct0 took place only during the first stages as then, like all the other markers, also the content of Ct0 drastically dropped. The same observation is valid for Ct1, as illustrated in figure 6.
   Therefore, it can be said that all the Ct markers can be eventually greatly degraded by the continuous exposure to sunlight, making their detection in extremely faded historical samples challenging, as indeed often times noticed and also shown by the results in table 1. These new pieces of information on Ct markers, together with the one reported in paragraph 3.1, integrate the

data previously reported by Wouters et al., allowing a better understanding of the nature of these components.

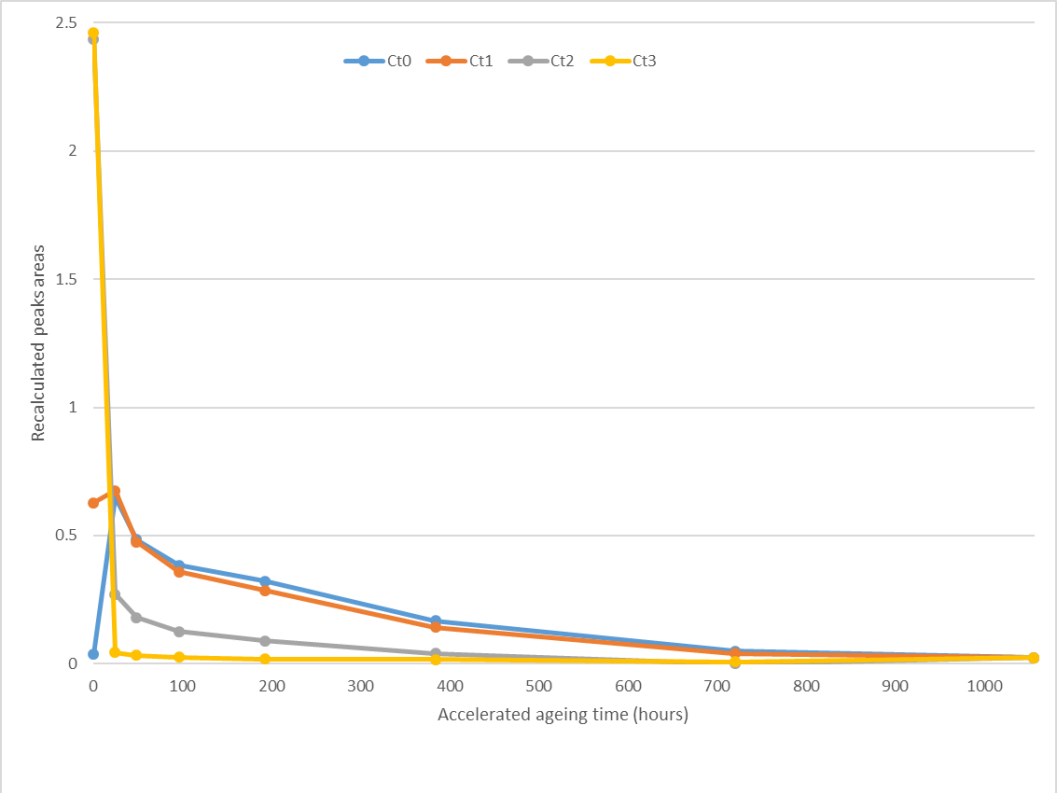

Figure 6. Peak areas of Cts markers at the different stages of the light ageing of sample AD (integration values recorded at 255 nm calculated per 0.5 mg of sample).

2. From the semi-quantitative data, it was observed that the content of both Y1 and Y2 at the end of all the ageing tests were lower than at t0. This suggests that, even if the two might be degradation products of carthamin caused by high temperature and water (see paragraph 3.1), the studied conditions did not promote their formation. In particular, it is interesting to underline that neither the exposure to 90% RH (high presence of water), nor to 50 °C (moderate temperature) were responsible for an increase of the Y1 and Y2. This might be due to the fact that the two factors (water and heating) were not simultaneously present in the ageing regimes [8], though it might also indicate that the markers are not the degradation products described by Laursen and Mouri.

3. A new yellow compound named Y3 was found within some samples at all the ageing regimes. This yellow component (retention time 11.10 min), not revealed within the mock-ups at t0, has an absorbance spectrum with maximum wavelength at around 400 nm (figure 7). The spectrum of Y3 is very similar to the ones of Y1 and Y2, though Y3 is necessarily a different component as the three of them were contemporary revealed in the same aged samples (figure 8). Besides, to see if the formation of Y3 was related to the degradation of carthamin by heating aqueous solutions (as A and B [8]), the extraction with DMSO on aged samples was repeated at different temperatures: 80 °C (10 minutes); 40 °C (1 hour); 18 °C (4 hours). It was observed that Y3 did not increase while rising the extraction temperature (differently from Y1 and Y2, see paragraph 3.1), proving that it cannot be the result of the degradation of carthamin caused by heat and water. At the same time, Y3 was not detected in undyed silk references, either aged or not, so it cannot be a contaminant from the fabric.

Y3 appeared to increase significantly especially in all the mock-ups conditioned at 90% RH, which indeed visibly yellowed during the treatment (section 3.2.1). Therefore, this yellowing could be due to the significant development of Y3 and the simultaneous decrease of carthamin and carthamin'.
The semi-quantitative analysis did not allow to estimate a clear relationship between the formation of Y3 and the decrease of Y1 and Y2, as Y3 was discontinuously detected during the different ageing tests, except the one at high relative humidity. Therefore, even though at 90% RH the growth of Y3 corresponded the lowering of Y1 and Y2 (figure 9), no reaction pathway can be surely proposed. Further analysis aimed to chemically characterize the different compounds are needed to clarify the kinetic.

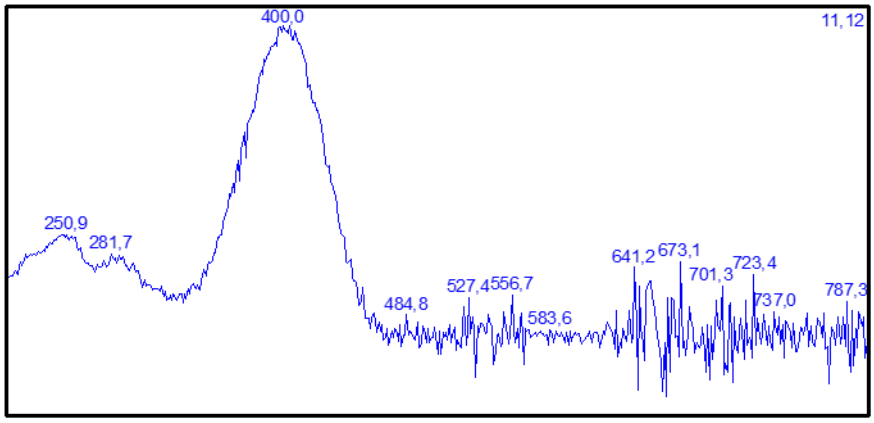

Figure 7. Absorption spectrum of Y3 formed temporarily during light ageing.

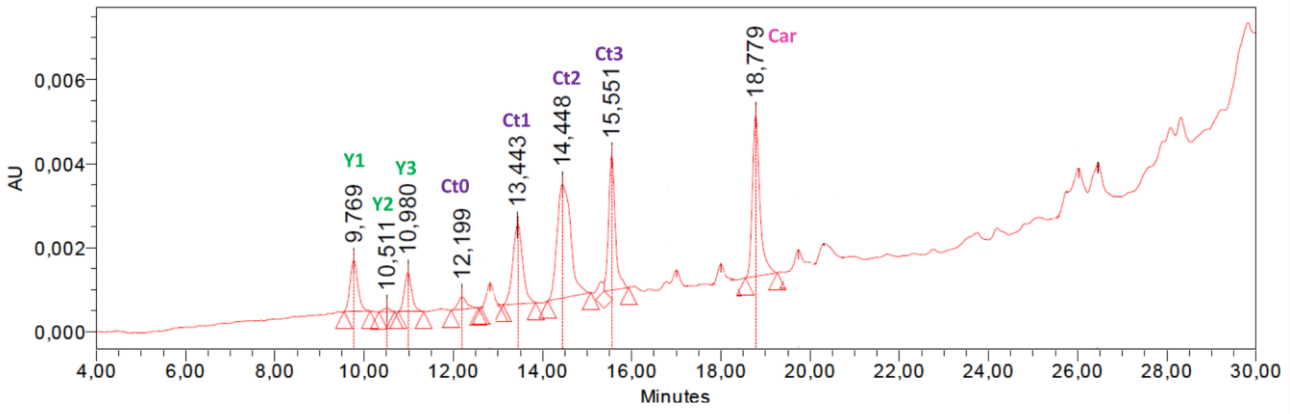

Figure 8. Chromatogram from sample AD aged at 90% RH for 2400 hours (monitored at 255nm).

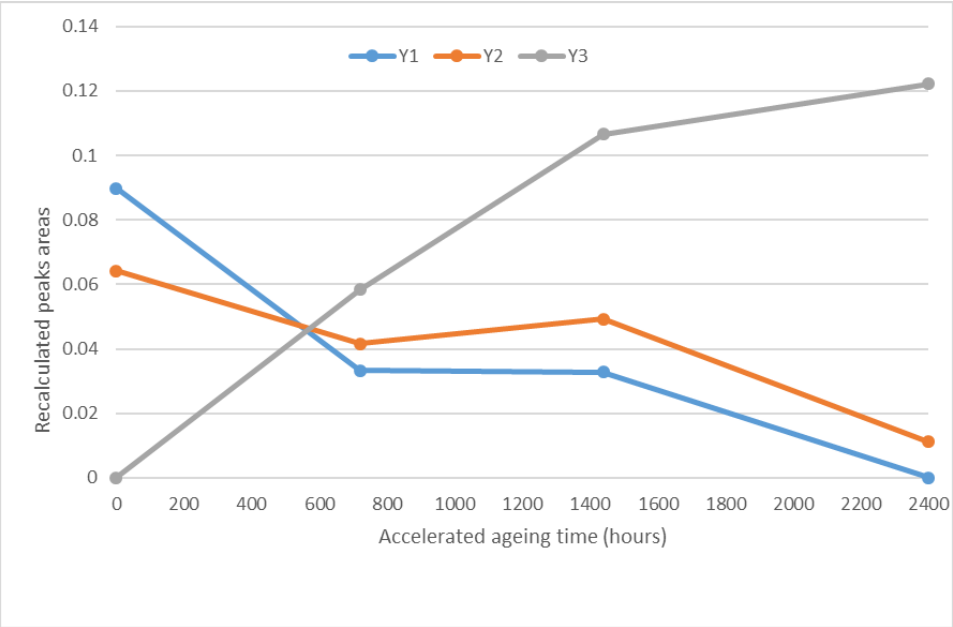

Figure 9. Peak areas of Cts markers at the different stages of the light ageing of sample AD (integration values recorded at 255 nm calculated per 0.5 mg of sample).

4. Conclusions and further perspectives

This study provides information on the stability of safflower red dyed textiles under the effect of different environmental parameters.

Both the colorimentric measurements and the HPLC-PDA outcomes, non-surprisingly, confirmed that light is highly dangerous for textiles dyed with safflower red. Indeed, no traces of carthamin were detected at the end of the treatment (1056 hours, 2000 lux). However, an important decrease of carthamin was revealed by HPLC-PDA for all the samples aged in dark environments (cold-humid; 60% RH; 90% RH; dry-moderate warm; ozone-rich), suggesting that the red dye is unstable within all the considered conditions.

The semi-quantitative approach of the research prevented to clearly define the degradation path of carthamin, nonetheless some interesting observations can be drawn for the first time on safflower red markers commonly detected in historic textiles. First of all, it was shown that the overall amount of Ct components (that on the newly prepared samples it seems to be influenced by the dyeing process employed) diminished at the end of all treatments, mainly because of the constant drop of Ct2 and Ct3. In particular, all the Ct markers were poorly revealed after the light ageing, as sometimes encountered in historical samples. Besides, two yellow compounds, named Y1 and Y2 (perhaps degradation components from carthamin [8] or yellow quinochalcones) were detected at t0 and at the end of the treatments, though at lower amounts. On the other hand, the HPLC-PDA analysis revealed the formation during the ageing tests of a new yellow component (named Y3, UV-Vis maximum absorption at ≈ 400 nm), not found on samples at t0 nor in the undyed aged silk reference. This yellow compound was identified within some of the textiles aged through all the conditions, but especially in the ones conditioned at 90% RH. The highly humid environment was also responsible for the greatest colour changes in the dark ($\Delta E > 9$ after 2400 hours), mainly due to a remarkable b* increase, that could be therefore linked to the relevant formation of Y3. The lowest colour changes ($\Delta E < 2$) were reported after the dry treatment at moderate temperature and the brief ageing with a high ozone concentration. A higher ΔE, even greater than 3, was observed at the end of the other tests in humid environments. This could indicate that humidity in dark, also if lower than 90% RH, can play a role in the degradation of the dyeing.

The results of this research can promote the preventive conservation of the highly sensitive textiles dyed with safflower red as it not only clearly confirmed the severe light sensitivity of this dye, but also revealed possible risks occurring in the absence of light. Especially the harmful influence of humidity in dark conditions, as possibly encountered during long-time storage, might provoke a colour shift, while degrading the major compound carthamin and increasing the formation of yellow compounds.

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