DECOMPOSITION AND ANALYSIS OF CARTHAMIN IN SAFFLOWER-DYED TEXTILES

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Abstract

Carthamin from safflower petals has been used for centuries in Asia as a red colorant for dyes and cosmetics. Carthamin is unstable, however, both in hot, aqueous solutions, which causes difficulties in its analysis in textiles, and to light, which results in fading of dyed textiles. We have found, using HPLC and mass spectrometric analysis, that carthamin undergoes a reverse aldol condensation in hot, aqueous solutions. Carthamin can be detected by extracting textile fibers at low temperature using a good solvent, such as pyridine. It is well known that textiles dyed with carthamin fade if exposed to light. This fading appears to occur by photo-oxidation of carbon-carbon double bonds since exposure of both carthamin-dyed textile and of a model compound, 4-hydroxy-2',4'-dihydroxychalcone result in formation of 4-hydroxybenzaldehyde and 4-hydroxy benzoic acid. Assuming that the carthamin is not 100% decomposed by light, the residual carthamin may be detectable after extraction of the textile fibers at low temperature. The demonstration of intact carthamin in museum objects can inform decisions regarding lighting conditions, with the view of reducing photo-chemical fading.

1 Introduction

The petals of the safflower plant (Carthamus tinctorius L.) contain several yellow dyes, but most famous is its red dye, carthamin, which has been used as a red colorant for textiles and cosmetics, especially in Asia, for centuries. Carthamin is isolated by washing safflower petals extensively with water to remove the yellow dyes, extracting the insoluble red pigment into an alkaline solution and then precipitating the red dye itself by acidification with citric or acetic acid (e.g., from lemon juice, vinegar, etc.) Often the dye is further purified by adsorption onto cotton or other substances, from which it can be re-extracted and then used for dyeing.¹

Dyeing with carthamin is normally done at ambient temperature, and one needs to work relatively quickly as the dye in solution is not very stable. In 1997, Kim and Paik² studied the stability of solutions of carthamin and found that it has a half-life at 25 °C, at pH 5 (near the pH at which dyeing is done) of only 4 h. They also found that the stability decreases at higher temperatures, with the half-life decreasing to about 4 min at 80 °C.

Recently we obtained a number of red-dyed, Asian samples from the Peabody-Essex Museum (Salem, MA), among which was a specimen from a 19th C. red silk shawl from China. Although the shawl was clearly red, we were able to detect essentially no red color when extracting with pyridine-water (1:1) at 100 °C, conditions which work well for extracting anthraquinones from madder-dyed textiles.³ We did, however, detect the non-color red ‘ct’ compounds with M = 583 Da reported by Wouters et al.¹, which suggested that the shawl had been dyed with carthamin, in addition to the yellow dye, berberine, which is often found in red-dyed Asian textiles. Subsequent studies showed that solutions of carthamin, which are bright red at room temperature, decolorize irreversibly at high temperature. Fig. 1
shows an HPLC profile of the colorants extracted at low temperature.

A study of the heat-promoted decomposition of carthamin was carried out with the objective of understanding what is taking place and, possibly, of learning how to avoid decomposition. Since carthamin is known to be rather light-fugitive, we also sought to identify the products of light-catalyzed fading of carthamin.

2 Methods

Carthamin and various decomposition products were extracted from textile samples with our standard extraction solution pyridine/water/1.0 M oxalic acid (95:95:10) at various temperatures. [Note that the oxalic acid has no function in this case because carthamin does not require a mordant.] In addition, purified carthamin was heated with various reagents to study the effect of the reagent on stability.

Fading studies were carried out by exposing carthamin-dyed cotton fabric to sunlight in a south-facing window for up to two weeks, and then extracting the fabric and analyzing the products.

Extracts were analyzed by HPLC using a photodiode array detector and a mass spectrometer for detection (LC-DAD-MS); separations were accomplished using C-18 reversed phase columns and elution with acetonitrile-water gradients.

3 Results and Discussion

3.1 Decomposition of Carthamin by Heat

We found that heating of carthamin under a variety of conditions – in pyridine-water (weakly basic), in water (neutral) and in 2 M HCl (acidic) – resulted in discoloration (i.e., decomposition) of the carthamin. Most of our studies were done with pyridine-water mixtures because pyridine is a very good solvent for carthamin.

When a solution of carthamin (Fig. 2) was decolorized by heating and then analyzed by LC-DAD-MS, we discovered two new peaks (A and B) having molecular masses of 478 Da and 450 Da (Fig. 3) respectively. The sum of these masses is 928, which is equal to the molecular mass of carthamin (910 Da) and a molecule of water. We eventually deduced that a molecule of water is adding to carthamin to form a hydrate (Fig. 4) and undergoing a classical reverse aldol condensation to give the fragments A and B shown in Fig. 5.

These structures correspond to the peaks labeled A and B in Fig. 3. In confirmation of the proposed structure for A, we found that heating a solution of carthamin in CD3SOCD3-D2O resulted in the formation of a
product with a characteristic aldehyde proton at 9.6 ppm.

It can be estimated (based on the general rule that the rate of any reaction approximately doubles with each 10 °C that it is heated) from the results of Kim and Paik\(^2\), that the half-life of carthamin in water at 100 °C, at pH 7, would be about 1.5 min. Therefore heating carthamin at 100 °C in any aqueous solution for 10 min would be expected to result in complete decomposition. In our analytical work, we warmed samples at 40 °C for about 60 min in pyridine-water, and then cooled the extract to room temperature or lower. Under these conditions it can be calculated from the data of Kim and Paik\(^2\) that at least half of the original carthamin will survive extraction. One has to balance slow extraction at low temperature with decomposition of carthamin at high temperature. Nevertheless, because of its unique spectral properties, it is fairly easy to detect carthamin if it was there in the first place.

On the other hand, we found that heating of dry, carthamin-dyed silk at 120 °C for several days did not result in decolorization, although there was a slight change in color. This makes sense because (1) addition of water is required for the retro-aldol reaction to occur and (2) water is required so that the two products (A and B) can diffuse apart.

3.2 Decomposition of carthamin by light

When carthamin-dyed cotton cloth was exposed to sunlight, it eventually faded completely. Extraction of the cloth (e.g., as described in Section 2) and analysis of the products by LC-DAD-MS gave two peaks, C and D, with respective masses of 138 Da and 122 Da (Fig. 6). These were subsequently identified (Fig. 7) as 4-hydroxybenzoic acid and 4-hydroxybenzaldehyde, respectively, by HPLC analysis of the authentic compounds. Undoubtedly other products were also formed, but these were not identified in this study. The photo-oxidation of styryl compounds (in this case, carthamin) to aldehydes (e.g., D) is well-known as is air oxidation of aryl aldehydes to benzoic acids.

To confirm this idea, we exposed a model compound, 4-hydroxy-2',4'-dihydroxychalcone, also adsorbed on cotton cloth, to sunlight and identified the same decomposition products, C and D (Fig. 7).

4 Conclusions

Based on these observations, we conclude that:

Carthamin decomposes on heating in aqueous solutions via a reverse aldol condensation, resulting in loss of its red color.

Carthamin adsorbed on textile fibers fades on exposure to light, in the presence of air, as a result of photo-oxidation of carbon-carbon double bonds.

Carthamin can be extracted from textiles with minimal decomposition at low (40-50 °C) temperatures using a good solvent, such as pyridine-water (1:1), and working quickly.

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6 References